A Thesis

CRYSTAL-STRUCTURE STUDIES BY NEUTRON AND X-RAY DIFFRACTION

Submitted to the University of Glasgow for
the Degree of Doctor of Philosophy in the
Faculty of Science

by

Murdoch Currie, B.Sc.

Chemistry Department. May 1969.

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SUMMARY

The theme of this thesis is the study of hydrogen bonding, mainly in acid salts, by neutron and X-ray diffraction.

In Part I some aspects of the theory and practice of neutron diffraction and its application to the study of crystal structure are discussed and comparisons made with X-ray diffraction. Part II contains a short review of hydrogen bonding.

The crystal-structure analyses by neutron diffraction of the acid salts potassium tetroxalate and potassium hydrogen malonate and of the Tutton salt ammonium nickel sulphate hexahydrate are described in Part III. The structure of each compound is discussed.

In Part IV the X-ray crystal-structure analysis of the acid salt 1-methyl-2-quinolonium dihydrogen arsenate is described and its structure discussed. Also described is the structure analysis of a material which was thought to be potassium deuterium di-aspirinate, but which was recently found not to be deuterated.

A reprint of a published paper (Currie, Curry and Speakman, 1967) on the crystal-structure analysis by neutron diffraction of ammonium tetroxalate, which is isomorphous with potassium tetroxalate, is included as Appendix I, and a note on the setting-up of crystals on a four-circle neutron diffractometer as Appendix II.

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PART I

SOME ASPECTS OF NEUTRON DIFFRACTION

1. INTRODUCTION

Just as Rontgen's discovery of X-rays in 1895 was followed by the discovery of X-ray diffraction by crystals (Friedrich, Knipping and Laue, 1912) so also was the discovery of neutrons in 1932 followed by that of neutron diffraction in 1936.

The neutron itself was discovered by Chadwick in 1932, and Elsasser (1936) made the suggestion that wave-mechanical considerations would determine the motion of neutrons, which should, therefore, be diffracted by crystals in the same way as X-rays. The diffraction of neutrons was duly demonstrated first of all by Halban and Preiswerk (1936), whose experiments were carried out with polycrystalline samples, and then by Mitchell and Powers (1936), who showed that diffraction by single crystals took place. In both cases radium-beryllium neutron sources were used, which, whilst sufficient to prove that diffraction did occur, were too weak to provide any quantitative data.

It was thus not until after 1945, with the construction of nuclear reactors, from which neutrons were available in relative abundance, that the application of neutron diffraction to the serious study of crystal structure became practicable. Since then it has become a technique of considerable importance for supplementing and amplifying the results obtainable by X-ray diffraction.

2. NEUTRON SCATTERING BY A NUCLEUS

If a plane wave of neutrons described by a wave-function,

$$\psi = \exp(iKz) ,$$

where $K = 2\pi/\lambda$ is the wave-number, is incident on a nucleus, the scattered wave will be spherically symmetrical and of the form,

$$\psi = -(b/r) \exp(iKr) ,$$

where r is the distance from the nucleus to the point at which the scattered wave is measured. The quantity b, which has the dimensions of a length, is known as the nuclear scattering length, or neutron scattering amplitude, of the nucleus (Bacon, 1962, 1963).

With the exception of certain nuclei which have high absorption coefficients b is real, and may be positive or negative. If b is positive there is a change of phase of 180° between the incident and scattered beams, whilst if b is negative no change of phase occurs. In the case of nuclei with high absorption coefficients b is a complex number, indicating that the change of phase is appreciably different from either 0° or 180°.

The scattering cross-section of the nucleus is defined as

$$\sigma = \frac{\text{outgoing current of scattered neutrons}}{\text{incident neutron flux}}$$

$$= 4\pi r^2 v \frac{|(b/r) \exp(iKr)|^2}{v|\exp(iKz)|^2}$$

$$= 4\pi b^2 ,$$

where v is the neutron velocity.

The actual value of the scattering length of any nucleus depends on the boundary conditions at the nuclear surface, which cannot at the present time be determined directly. It is, however, possible to express them in terms of certain quantities relating to the compound nucleus formed by combination of the incident neutron and the nucleus. On this basis the scattering length is composed of two terms, viz. the "potential" term, which is equal to the nuclear radius, and hence is always positive, and the "resonance" term, which is a function of the energy of the incident neutron itself and the energy it should have if it is to produce resonance in the compound nucleus. The resonance term may be either positive or negative, and in a few cases it is negative and sufficiently large numerically to outweigh the potential term, thus giving a resultant scattering length which is negative.

So far we have considered neutron scattering by a nucleus with zero spin. Such scattering is entirely "coherent", i.e. it is coherent with that by other nuclei and can therefore produce interference. If, however, the scattering nucleus has a non-zero spin I, combination may take place with a neutron, of spin $\frac{1}{2}$, to form one of two alternative compound nuclei, having spins of $I + \frac{1}{2}$ and $I - \frac{1}{2}$ respectively. Different scattering lengths, b_+ and b_-, are associated with these two possible compound nuclear systems, and the resultant scattering is of two different types, the total scattering cross-section σ being the sum of two terms, one of which is the cross-section for "coherent" scattering, and the other that for "incoherent" scattering, i.e. scattering which does not give diffraction. It is noteworthy that the major component of the scattering cross-section is not always coherent and that in certain cases, e.g. hydrogen, practically all the scattering is incoherent.

As the nuclear scattering length cannot be calculated directly from theoretical considerations it is in practice determined experimentally. There are three main methods for doing this : the determination of the refractive index for slow neutrons, the measurement of the total scattering cross-section by transmission experiments, and the measurement of the intensities of coherent Bragg peaks in diffraction patterns. These methods are discussed at length by Bacon (1962).

3. NEUTRON SCATTERING BY AN ASSEMBLY OF NUCLEI

If a plane wave of neutrons described, as before, by a wave-function,

$$\psi = \exp(iKz) ,$$

is incident on an assembly of nuclei in a crystal, the resultant wave after scattering by the set of planes having Miller indices $(hk\ell)$ is given by

$$\psi = \exp(iKz) - \sum_j (b_j/r) \exp(iKr) \exp 2\pi i (hx_j + ky_j + \ell z_j)$$

in which the summation is over all the nuclei in the unit cell of the crystal and x_j , y_j and z_j are the fractional coordinates of the j th nucleus, whose scattering length is b_j .

At unit distance from the nuclei this becomes

$$\psi = \exp(iK) \left\{1 - \sum_j b_j \exp 2\pi i \left(hx_j + ky_j + \ell z_j \right)\right\},$$

and the structure factor for the set of planes $(hk\ell)$ is defined as

$$F(hk\ell) = \sum_j b_j \exp 2\pi i \left(hx_j + ky_j + \ell z_j \right) ,$$

which is analogous to the similar expression in X-ray crystallography,

$$F(hk\ell) = \sum_j f_j \exp 2\pi i \left(hx_j + ky_j + \ell z_j \right) ,$$

where f_j is the X-ray scattering factor of the j th atom.

The close resemblance of the expressions for the structure factor in neutron and X-ray crystallography is not only immediately apparent, but is also indicative of the ready applicability to the former of principles originally derived for the latter. These are dealt with at length in the many text-books on the subject, e.g. Lipson and Cochran (1966), and it is not therefore proposed to mention them further here.

4. COMPARISON OF X-RAY AND NEUTRON SCATTERING AMPLITUDES

The nuclear scattering length, or neutron scattering amplitude, b , in neutron diffraction is analogous to the scattering factor f_x in X-ray diffraction, but differs from it in several ways, thus giving rise to the differences between X-ray and neutron diffraction.

The X-ray scattering factor of an element (at $\sin\theta = 0$) is directly proportional to its atomic number, the X-rays being scattered by the extra-nuclear electrons. Neutrons, however, are scattered by the nucleus, and, whilst there is a slight overall increase in scattering length with increasing atomic weight as a result of potential scattering, resonance scattering causes marked differences from nucleide to nucleide, and in certain cases b has a negative value. The X-ray and neutron cases are compared in Figure 1. It should also be remarked that, as a result of the differing masses of their nuclei, different isotopes of the same element have different values of b, cf. hydrogen and deuterium, -0.378 and 0.65×10^{-12} cm. respectively.

Another striking difference is that, unlike f_x, b does not vary with the Bragg angle θ (Figure 2). This is because the dimensions of the nucleus are small in comparison with a neutron wavelength in the region of 1 Å. The cloud of electrons, however, by which X-rays are scattered, has dimensions which are comparable to the wavelength of the X-rays, and hence f_x diminishes as the Bragg angle θ increases.

5. FACTORS AFFECTING INTENSITY

The intensity $I(hk\ell)$ of a beam of neutrons diffracted by the set of planes having Miller indices $(hk\ell)$ of an ideally

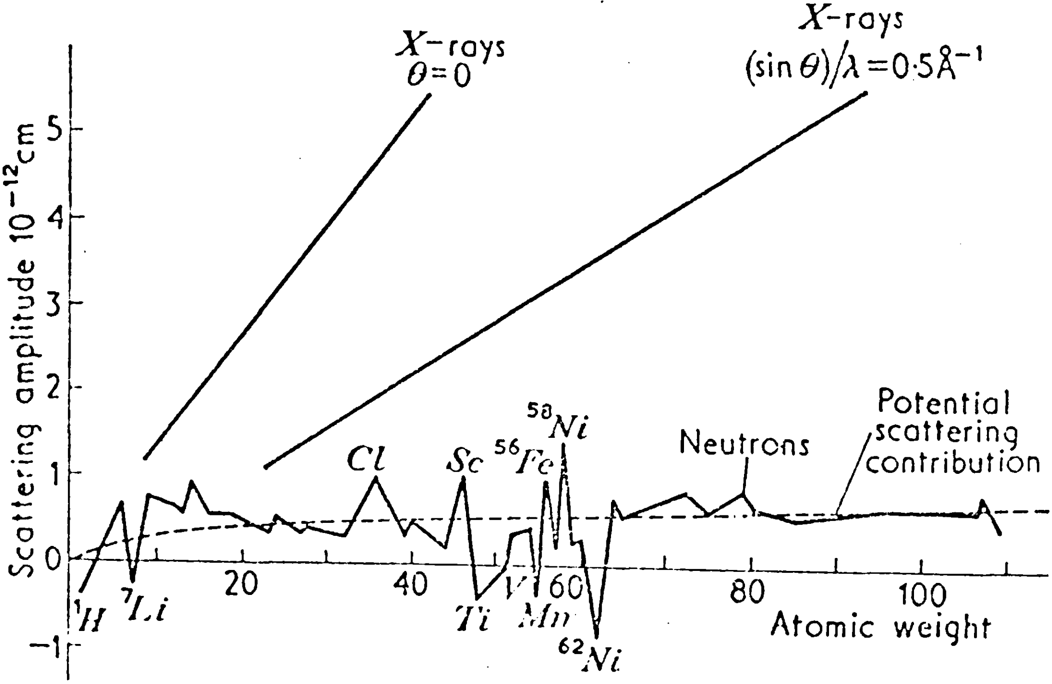


Figure 1 The irregular variation of neutron scattering amplitude with atomic weight due to the superposition of "resonance scattering' on the slowly increasing "potential scattering"; for comparison, the regular increase for X-rays is shown. (G.E. Bacon, "Neutron Diffraction", 2nd edition, Oxford University Press, 1962, p.34.)

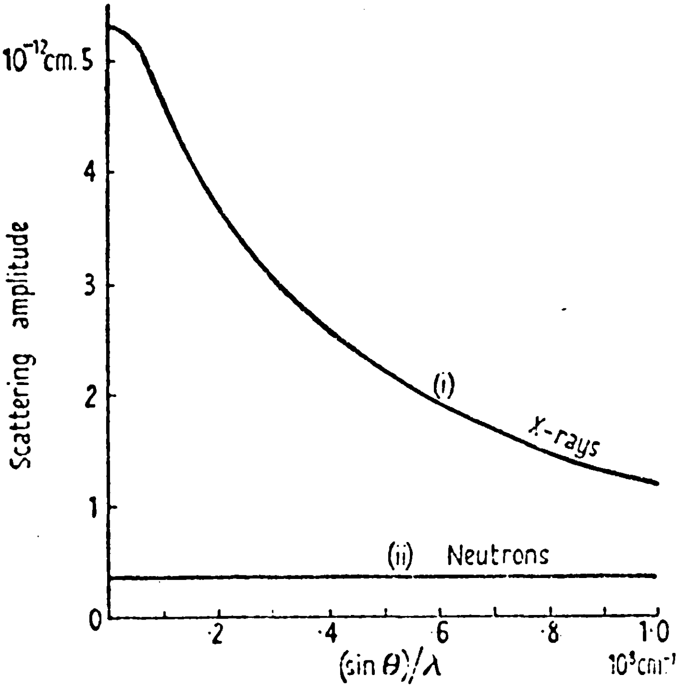


Figure 2 X-ray and neutron scattering amplitudes for a potassium atom. (G.E. Bacon, "Neutron Diffraction", 2nd edition, Oxford University Press, 1962, p.19.)

imperfect crystal which is rotating with uniform velocity through the position of the Bragg reflexion may be expressed as

$$I(hk\ell) = K \, . \, L(hk\ell) \, . \, |F(hk\ell)|^2$$

where K = constant for the experiment,

$L(hk\ell)$ = Lorentz factor,

and $|F(hk\ell)|$ = structure amplitude.

The Lorentz factor depends on the velocity with which a particular set of planes pass through the reflecting position, and is given by

$$L(hk\ell) = \frac{1}{\sin 2\theta} \quad .$$

Unlike the X-ray case no polarisation correction is required.

True absorption of neutrons, i.e. attenuation of the incident neutron beam through nuclear capture processes, is negligible for most elements, though there are a few notable exceptions, e.g. lithium, boron and cadmium. Incoherent scattering processes, however, may contribute to the effective absorption coefficient μ more than true absorption; this is particularly so in the case of compounds containing hydrogen, which has a large incoherent scattering cross-section. It is therefore preferable to determine μ experimentally by measuring the attenuation of a narrow monochromatic beam in passing through a sample of known thickness. Nonetheless, absorption is not a serious problem in neutron diffraction, and in any case a correction for it may be applied relatively easily, e.g. Busing and Levy (1957).

More serious in neutron diffraction, owing to the size of the crystals generally used, is the problem of extinction, i.e. attenuation of the incident beam through Bragg reflexion. There are two types, viz. primary extinction, by which the incident beam is attenuated in a perfect crystal, and secondary extinction, by which the incident beam is attenuated by reflexion in two or more mosaic blocks with identical orientations. Fundamental corrections for extinction, particularly for secondary extinction, are very difficult to make, but nevertheless are now possible on the basis of a theoretical treatment developed by Zachariasen (1967).

6. THE COLLECTION OF NEUTRON-DIFFRACTION DATA

The layout of a typical neutron diffractometer is shown in Figure 3. Essentially the collection of neutron-diffraction data is similar to that of X-ray diffraction data although there are necessarily differences in the techniques employed in the two cases.

Useful quantitative diffraction measurements usually require a beam of monochromatic radiation, so that Bragg's Law,

$$n\lambda = 2d \sin \theta ,$$

may be satisfied. With X-rays, which have a characteristic spectrum (Figure 4a), this is easily achieved by using a sufficiently high voltage and the appropriate filter, e.g. for radiation from a copper target a nickel filter drastically curtails the unwanted

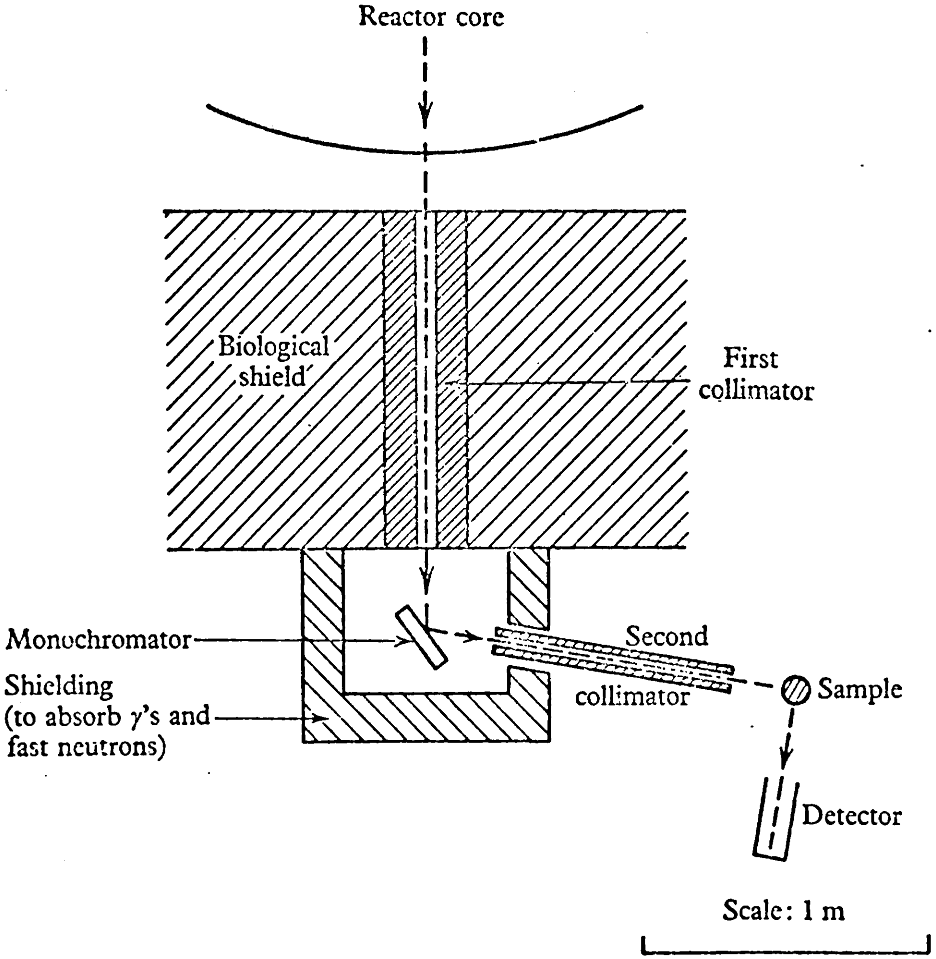

Reactor core
Biological shield
First collimator
Monochromator
Shielding (to absorb γ's and fast neutrons)
Second collimator
Sample
Detector
Scale: 1 m

Figure 3 Schematic diagram of a neutron-diffraction assembly. A second collimator is used after the monochromator in case the degree of primary collimation is insufficient. (U.W. Arndt and B.T.M. Willis, "Single Crystal Diffractometry", Cambridge University Press, 1966, p.200.)

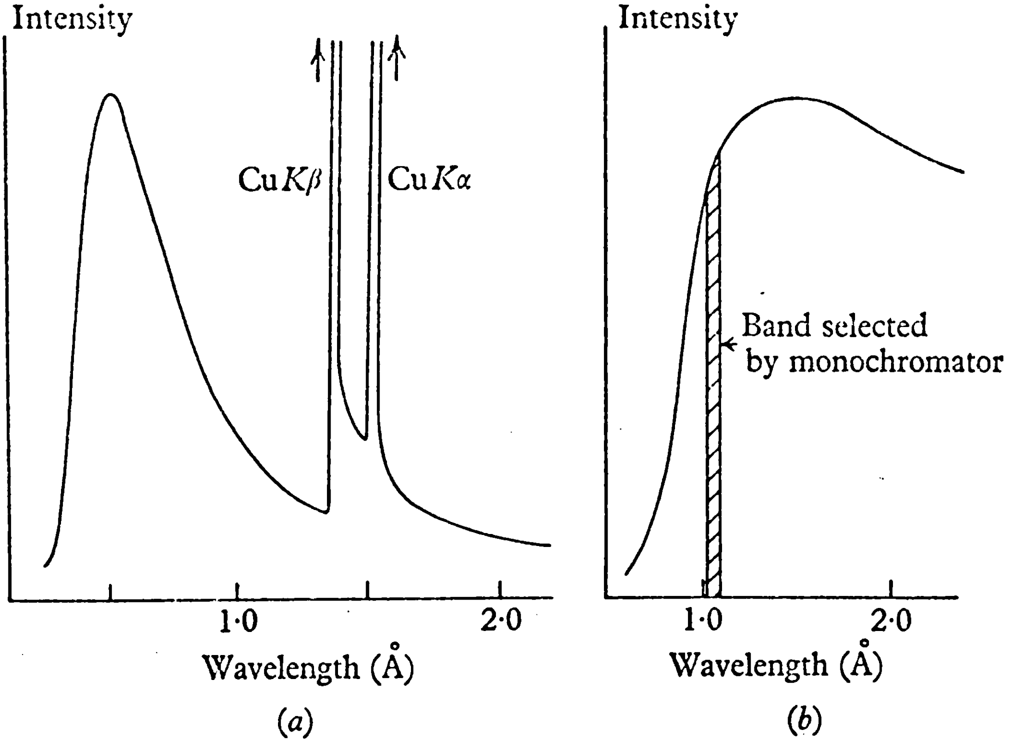


Figure 4 Intensity curves : (a) for X-rays from a copper target which gives intense lines of characteristic K radiation; (b) for a beam of slow neutrons emerging from a reactor. (U.W. Arndt and B.T.M. Willis, "Single Crystal Diffractometry", Cambridge University Press, 1966, p.4.)

wavelengths.

The thermal neutron spectrum, however, is "white" (Figure 4b), and monochromatisation is achieved by diffracting the collimated beam off a large single crystal of a suitable material, e.g. calcium fluoride, copper, zinc or lead. The position of this crystal is adjusted so that, in accordance with Bragg's Law, radiation of a narrow range of wavelength is diffracted from a particular set of planes. The resultant beam is not, therefore, strictly monochromatic, and the range of wavelength obtained may be varied by adjusting the cadmium slits at the end of a second collimator placed between the monochromator and the specimen.

The obvious choice for the Bragg angle θ is that which would give a beam of maximum intensity. However, if this is done there would be a fairly strong component of radiation of wavelength one-half of that desired, as a result of second-order reflexion satisfying the condition,

$$n\frac{\lambda}{2} = 2\frac{d}{2}\sin\theta \ .$$

To overcome this difficulty, θ is usually chosen so as to give a wavelength on the short wavelength side of the peak intensity (Figure 4b) and hence the intensity of the second-order reflexion is very low.

As the energy of thermal neutrons is of the order of 0.1 eV. compared with 10 eV. for X-ray quanta, the neutrons diffracted from the specimen cannot be detected directly, but only through their reactions with atomic nuclei which give rise to particles of much greater energy. In the neutron work to be described later in this thesis boron-trifluoride proportional counters were used. These are filled with BF_3 gas which has been enriched to 96 % in the reactive ^{10}B isotope. The nuclear reaction,

$$^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{4}_{2}\alpha + {}^{7}_{3}Li ,$$

takes place, and the energetic particles produced, viz. $^{4}_{2}\alpha$ and $^{7}_{3}Li$ are then detected (Arndt and Willis, 1966). Such counters, and indeed most counters used to detect neutrons, are large in comparison with those used to detect X-rays.

Owing to the comparative weakness of the beam of thermal neutrons there are certain problems peculiar to the collection of neutron data which do not arise to any significant extent in the collection of X-ray data. Not least of these is the necessity of using a much larger crystal, of minimum volume $3\,mm^3$, which is several times that of a crystal from which X-ray data would be collected. In practice even larger crystals are often used in order that sufficient neutrons may be diffracted for detection without excessive counting times. The production of crystals both of a suitable size and of good quality is often difficult, and the use of a large crystal may in itself cause serious extinction problems. To overcome these difficulties to some extent, more efficient monochromators have recently been developed at A.E.R.E., Harwell in order to increase the intensity of the monochromatised neutron beam incident on the specimen so enabling data to be collected from smaller crystals and hence reducing the effects of extinction.

7. THE APPLICATIONS OF NEUTRON DIFFRACTION

Neutron diffraction is by no means as widely used a technique as X-ray diffraction and seems unlikely to become so owing to the very high cost of providing the neutrons. Indeed, Arndt and Willis (1966) have estimated that it costs in the region of £1 per reflexion to collect neutron data on a fully automatic diffractometer, whilst the cost of similarly collected X-ray data is approximately 8d per reflexion. (These costs assume intensive utilisation of the equipment.) Neutron diffraction is not, therefore, to be used lightly, and hence its application is generally limited to problems which cannot be solved in a fully satisfactory way by X-ray methods.

The advantages of using neutron diffraction in preference to X-ray diffraction nearly all arise from the differences between the nuclear scattering length b and the X-ray scattering factor f_x which have already been briefly discussed.

Its first application, which is of particular interest to the chemist, is for the location of light atoms, in particular, hydrogen. The accuracy of the determination of an atomic position depends on the contribution of the atom to the intensity data, and the average contribution of an atom i to the intensity of a Bragg reflexion may be written

$$P(i) = \frac{f_i^{\,2}}{\sum_{i=1}^{n} f_i^{\,2}} ,$$

where f_i is the scattering amplitude of the atom i and n is the number of atoms in the asymmetric unit of the unit cell of the crystal.

Thus in the structure analysis by neutron diffraction of ammonium tetroxalate, $C_4H_7NO_8.2H_2O$ (Appendix I), the contribution of the hydrogen atoms to the total scattering was approximately 20% and their positions were determined to within 0.01 Å. If, however, this analysis had been carried out by X-ray diffraction the contribution of the hydrogen atoms to the total scattering would have been in the region of 1 % at low sin θ and zero at high sin θ, with the result that their positions could not have been determined with any degree of accuracy, if indeed they could have been located at all.

A complementary use of neutron diffraction is in distinguishing between atoms of neighbouring atomic number; such a distinction is difficult using X-ray diffraction owing to the similarity of their scattering factors. Neutron diffraction, in which the scattering length has no regular dependence on atomic number, can often provide a solution to this problem, and has been used successfully in the structure determinations of alloys of transition elements, e.g. an iron-cobalt alloy (Shull and Siegel, 1949), and of spinels, e.g. magnesium aluminium oxide (Bacon, 1952).

A third, and very important, application of neutron diffraction is in studies of magnetic materials, e.g. the oxides of the transition metals. The object of such studies, which have to be carried out at low temperatures, is to ascertain the particular form of magnetic coupling between the magnetic atoms, and hence to relate this to the electronic structure. A comprehensive account of this aspect of neutron diffraction is given by Bacon (1962).

A very recently developed application involves a combination of very accurate X-ray and neutron-diffraction studies of relatively simple structures. Parameters derived from the refinement of neutron-diffraction data are used with observed structure amplitudes from the X-ray analysis to compute electron-density difference syntheses in which atomic charge distributions and bonding electrons may be detected (e.g. Coppens, 1967). Such details of chemical bonding were hitherto inaccessible experimentally.

PART II

THE HYDROGEN BOND

1. INTRODUCTION

The concept of the hydrogen bond originated towards the end of the last century when it was established not only that association was more likely among molecules containing certain functional groups than among others, but also that the presence of hydroxyl groups was especially significant, viz. alcohols and phenols formed association complexes whereas hydrocarbons did not (Nernst, 1891). Hydrogen bonding in ammonium salts was postulated by Werner in 1903 and in 1912 Moore and Winmill proposed a hydrogen-bonded structure for trimethyl ammonium hydroxide. Intra-molecular hydrogen bonding in some azo derivatives of eugenol was proposed by Oddo and Puxeddu in 1906 and in 1-hydroxy-anthraquinone by Pfieffer in 1913.

An important development came when it was recognised by Latimer and Rodebush (1920) that hydrogen bonding was the cause of the association of water, which results in its unusual chemical and physical properties, e.g. high melting point, high boiling point, expansion on solidification, etc.

Since then hydrogen bonding has been found in many different environments, from inorganic salt hydrates to proteins and nucleic acids. Of particular importance is its role in biological systems, of which there is no better example than de-oxyribonucleic acid (DNA), in which bases attached to two sugar-phosphate chains are linked through hydrogen bonds to form a double helix (Watson and Crick, 1953).

2. THE CHARACTERISTICS OF HYDROGEN BONDS

A hydrogen bond exists between a functional group X—H and an atom or group of atoms Y in the same or in a different molecule when (1) there is evidence of bond formation (association or chelation) or (2) there is evidence that this new bond linking X—H and Y specifically involves the hydrogen atom linked to X (Pimentel and McClellan, 1960).

Strong hydrogen bonds are usually formed only when X and Y are electronegative, e.g. fluorine, oxygen or nitrogen, which have electronegativity values of 4.0 , 3.5 and 3.0 respectively (Pauling, 1960). Weaker bonds may, however, occur in certain favourable circumstances, e.g. in o-chlorobenzoyl acetylene there is a C—H···O bond between the ≡C—H ethynyl group and a neighbouring carbonyl oxygen atom (Ferguson and Islam, 1966).

Typical hydrogen bonds normally have energies in the range 6—12 Kcal.mole^{-1} and are hence about ten times weaker than covalent bonds. In the bifluoride ion, however, the energy of the F··H··F bond may be in the region of 40 Kcal.mole^{-1} — a remarkably high value.

3. THE DETECTION OF HYDROGEN BONDS

Until the advent of spectroscopic and diffraction techniques only the classical methods of physical chemistry, such as measurements of solubility, molecular weight, dielectric constant and conductivity, were available for the detection of hydrogen bonds. By these methods their presence is usually implied indirectly, e.g. when association of solute molecules is taking place through hydrogen bonding cryoscopic measurements indicate increasing values of the apparent molecular weight as the concentration of solute goes up.

Hydrogen bonding may also be studied by various spectroscopic techniques. Of these, the most useful at the present time is the infra-red spectrum, in which a characteristic lowering of the X—H stretching frequency is observed if a bond X—H···Y is formed. For "straight" hydrogen bonds there is an approximately linear relationship between the X—H stretching frequency and the X···Y distance (Nakamoto, Margoshes and Rundle, 1955; Bellamy and Pace, 1969), and hence it is possible not only to detect the bond from the spectrum, but also to make an estimate of its length.

It is, however, from X-ray and, more recently, neutron diffraction that most of the quantitative information about the dimensions of hydrogen bonds available at the present time has come. Although hydrogen atoms are not easily detected by X-ray diffraction it is nonetheless one of the few ways by which the X···Y distance may be determined directly. Using neutron diffraction even the hydrogen atoms may be located with considerable precision.

This subject has been reviewed by Hamilton (1962), Ibers (1965) and Hamilton and Ibers (1968).

4. O—H···O BONDS

The hydrogen bonds most commonly found in crystals are formed between oxygen atoms. On general grounds it is to be expected that, as the O···O distance diminishes the O—H distance will increase, but it is only since the advent of neutron diffraction that there has been any direct evidence that this is so.

A graph to show the relationship between O···O and O—H distances in hydrogen bonds was first drawn by Nakamoto, Margoshes and Rundle (1955). A similar graph by Pimentel and McClellan (1960) makes use of the information available in 1959 and is shown in Figure 1.4 of Part III of this thesis. While the use of even later data might change the position of the curve slightly, the trend is obvious: as the O···O distance diminishes the O—H distance increases, and, hypothetically, a point should be reached at which the bond is truly symmetrical, with the proton mid-way between the two oxygen atoms.

The study of crystals containing O—H···O bonds, and, in particular, short O—H···O bonds, is therefore of special interest, and has provided the main theme of this thesis.

PART III

CRYSTAL-STRUCTURE ANALYSES BY NEUTRON DIFFRACTION

CHAPTER 1

POTASSIUM TETROXALATE

1.1 INTRODUCTION

The crystal-structure analysis of ammonium tetroxalate (ATO) was one of the first in this country to be carried out using full three-dimensional neutron-diffraction data. These data were collected at A.E.R.E., Harwell by Mr. N.A. Curry and Dr. J.C. Speakman in the summer of 1965; the subsequent structure analysis and least-squares refinement were undertaken by the present writer. A comprehensive account of the ATO work, written mainly by Dr. Speakman, has already been published (Currie, Curry and Speakman, 1967); a reprint of this paper and a table of observed structure amplitudes and final calculated structure factors are presented as Appendix I.

Also mentioned briefly in the paper is the crystal-structure analysis by neutron diffraction of potassium tetroxalate (KTO), which was previously studied by Haas (1964) using X-ray methods. In this case the data were collected at Harwell by the writer, who also carried out the subsequent work. The structure analysis of potassium tetroxalate is now described in more detail.

1.2 EXPERIMENTAL

Crystal Data

The unit cell used in this analysis differs from that of Haas. The alternative cells are symmetrically related by the transformation matrix $00\bar{1}/010/\bar{1}00$.

The following parameters were established by Cu-Kα X-rays, for which λ was taken as 1.5418 Å for $\tilde{\alpha}$ and 1.5405 Å for α_1, by use of a least-squares treatment of high-order reflexions whose positions on Weissenberg photographs were compared with lines due to aluminium wire.

Potassium tetroxalate, $C_4H_3KO_8.2H_2O$, F.W. = 254.09.
Triclinic, $\underline{a} = 6.354$ (±5), $\underline{b} = 10.605$ (±7), $\underline{c} = 7.021$ (±5) Å,
$\alpha = 86.13^\circ$, $\beta = 100.16^\circ$, $\gamma = 78.10^\circ$ (each ± 0.08°), $\underline{U} = 453.92$ Å^3.
$\underline{D}_m = 1.79$, $\underline{Z} = 2$, $\underline{D}_x = 1.859$.
Space group $P\bar{1}$ (C_i^1, No.2).
Linear absorption coefficient for neutrons ($\lambda \approx 1$ Å), $\mu = 1.35$ cm^{-1}.

Preparation of Crystals

One of the main problems facing the neutron crystallographer is that of preparing suitably large and at the same time well-formed crystals. The method used to prepare such crystals of KTO was as follows:

A saturated solution of KTO in water was prepared and filtered into a beaker immersed in a thermostat at 20°C. A small volume of this solution was transferred to a 5 ml. beaker placed on a glass stand in a wide glass tube. This tube, which contained a small amount of concentrated sulphuric acid, was stoppered and immersed in the thermostat so that the 5 ml. beaker was below the level of the water in the tank. A small, well-formed crystal selected from KTO freshly recrystallised from water was dropped into the 5 ml. beaker. The tube was then corked and left standing for two or three days to allow crystal growth to take place as the water vapour distilled from the solution into the sulphuric acid.

This procedure was carried out many times with varying degrees of success. On some occasions a large number of small crystals formed and no growth took place. On others growth did take place, but the crystal produced was of obvious poor quality. However, a number of reasonable crystals were eventually produced and the most suitable of these, of approximate dimensions $5 \times 3 \times 2$ mm^3, was selected for the data collection.

Data Collection

Neutron-diffraction data were collected in the spring of 1966 in the DIDO reactor at A.E.R.E., Harwell, from which a neutron beam, monochromatised to $\lambda = 1.103$ Å, was derived.

Intensity measurements were made with a Ferranti Mark II automatic diffractometer (Bunce and Wheeler, 1965; Dyer, 1966; Arndt and Willis, 1966). This instrument permits rotation of the crystal through three Eulerian angles, Φ, χ and ω, and rotation of the counter through 2θ about an axis coincident with that of ω. The diffractometer is controlled by punched paper tape which contains instructions for rotating the shafts to bring each set of planes close to the reflecting position, followed by instructions for advancing the crystal by small angular steps through the reflexion. The number of neutrons detected at each step, during a fixed monitor count, is recorded both on paper tape and teleprinter paper. The tape which controls the diffractometer is prepared in two stages: first, the four angular positions corresponding to each reflexion, out to a specified value of θ, are computed and output on punched cards, using a program due to M.J.D. Powell (1965); secondly, this deck of cards is used to prepare a tape containing instructions, in appropriate form, to find and measure each reflexion (Curry, 1966). A further program (Curry, 1967) is used to "process" the tape output from the diffractometer to yield a set of relative intensities and structure amplitudes.

Neutron-scattering structure amplitudes were measured for 743 independent reflexions, partially covering the reciprocal sphere to $\theta = 45^\circ$. Of these 372 had values significantly above the background, 242, whose integrated intensities were lower than a certain threshold value (chosen to be three times their standard deviations, σ, based on counting statistics), were assigned intensities equal to one-half of that threshold value, and a further 129 had intensities of zero. All were included in the subsequent refinement.

I am grateful to Mr. N.A. Curry and Dr. J.B. Forsyth for their helpful advice and guidance during the collection of these data.

Structure Analysis and Refinement

The starting point for the structure analysis was the set of fractional coordinates found by Haas for the non-hydrogen atoms. The seven hydrogen atoms were located in their expected positions in neutron-scattering density and difference syntheses.

Refinement by least-squares analysis was then commenced. After two cycles of isotropic full-matrix refinement with unit weights the R-value was 0.354 and R' ($= \Sigma w\Delta^2/\Sigma w F_o^2$) 0.114. At this point a weighting scheme (McGregor, 1967) of the same form as that used in the refinement of ATO was introduced. In this scheme all values of Δ^2 are grouped into a two-dimensional array, according to ranges of $\sin\theta/\lambda$ and of $|F_o|$. In each group $\langle\overline{\Delta^2}\rangle$ is calculated. Any group in which the number of terms is inadequate is rejected. The values of $\langle\Delta^2\rangle$ in all other groups are then fitted, by least squares, to a surface. In the KTO analysis the function obtained was

$$f = -0.28 - 0.11\ |F_o| + 0.063|F_o|^2 - 0.175\ \left(\frac{\lambda}{\sin\theta}\right)^2 + 3.09 \times 10^{-3}\ \left(\frac{\lambda}{\sin\theta}\right)^4 - 3.77\ \left(\frac{\sin\theta}{\lambda}\right)^2$$

Then $w\ [= \exp(-f)]$ was calculated for each reflexion. Using this scheme, whose adequacy was demonstrated by the uniformity of the average values of $w\Delta^2$ over various ranges of $\sin\theta$ and $|F_o|$, six cycles of anisotropic, block-diagonal least-squares refinement were carried out, the final values of R and R' being, respectively, 0.206 and 0.052. By this time parameter shifts were all less than one-third of their standard deviations and the refinement was therefore considered complete.

Final positional parameters are given in Table 1.1, and in Table 1.2 are the final anisotropic vibrational parameters, which are values of U_{ij} in the expression :

$$\exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell\, b^*c^* + 2U_{31}\,\ell h\, c^*a^* + 2U_{12}hk\, a^*b^*)\right].$$

In these tables estimated standard deviations, derived from the inverse of the least-squares matrix, are given in parentheses. Observed structure amplitudes and final calculated structure factors are given in Table 1.3 and their agreement analysed in Table 1.4. Nuclear scattering lengths used in the structure-factor calculations were : K, 0.35; O, 0.577; C, 0.661; and H, -0.378×10^{-12} cm.

The group of atoms whose parameters appear in these tables constitutes the crystal chemical unit (CCU) of the structure; the CCU is shown in Figure 1.1. Other symmetry-related units are denoted as follows:

CCU	x,	y,	z;				
I	1 - x,	- y,	- z;	IV	2 - x,	- y,	1 - z;
II	1 + x,	y,	1 + z;	V	1 - x,	1 - y,	1 - z;
III	1 - x,	- y,	1 - z;	VI	x,	y,	1 + z.

TABLES AND DIAGRAMS

Table 1.1

KTO : fractional (*x*,*y*,*z*, x 10^4) and orthogonal (*X*',*Y*',*Z*' in Å, x 10^3) coordinates. (*X*' and *Z*' are, respectively, parallel to *a** and *c*, *Y*' is perpendicular to them both.)

	x	*y*	*z*	*X*'	*Y*'	*Z*'
K^+	8372	2747	8407	5116 (22)	4024 (19)	5161 (29)
C(1)	5077	635	5377	3102 (9)	1349 (7)	3181 (13)
C(2)	4123	650	-238	2519 (8)	1238 (8)	-583 (12)
C(3)	7542	4182	3365	4609 (9)	5432 (8)	1816 (13)
C(4)	7198	5384	4448	4398 (10)	6657 (8)	2702 (14)
O(1)	6764	673	6676	4133 (11)	1615 (10)	3977 (16)
O(2)	4910	1526	731	3000 (11)	2270 (10)	72 (19)
O(3)	3491	1561	4865	2133 (12)	2118 (10)	3136 (19)
O(4)	2306	757	-1068	1409 (12)	1109 (11)	-954 (18)
O(5)	8246	3074	4454	5039 (15)	4353 (11)	2423 (19)
O(6)	7254	4321	1563	4432 (15)	5540 (10)	594 (17)
O(7)	6475	6428	3452	3957 (14)	7666 (11)	2158 (20)
O(8)	7704	5159	6281	4707 (16)	6487 (12)	3916 (17)
O(9)	2177	3564	493	1330 (12)	4062 (10)	358 (19)
O(10)	9444	1317	2430	5771 (12)	2454 (12)	742 (21)
H(1)	2227	3932	1960	1361 (20	4458 (18)	1408 (23)
H(2)	2571	4254	-185	1571 (24)	4845 (23)	-113 (39)
H(3)	8603	699	2097	5257 (20)	1887 (17)	558 (30)
H(4)	10866	780	3100	6640 (20)	2275 (23)	1014 (34)
H(5)	8681	2328	3520	5304 (24)	3621 (18)	1665 (30)
H(6)	3717	2425	533	2271 (19)	3062 (20)	131 (41)
H(7)	3508	2445	5457	2143 (24)	3055 (19)	3613 (33)

Table 1.2

KTO : anisotropic vibrational parameters ($\text{Å}^2 \times 10^3$).

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{23}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
K^+	49 (9)	20 (8)	58 (15)	-8 (17)	12 (23)	22 (15)
C(1)	34 (4)	7 (3)	56 (7)	-24 (7)	13 (9)	15 (6)
C(2)	27 (3)	13 (4)	50 (6)	-17 (8)	14 (9)	16 (6)
C(3)	32 (3)	10 (3)	50 (7)	2 (7)	3 (9)	27 (6)
C(4)	40 (4)	8 (3)	59 (7)	-4 (7)	28 (10)	3 (6)
O(1)	36 (4)	11 (4)	56 (8)	31 (9)	-15 (12)	16 (8)
O(2)	32 (4)	15 (4)	87 (11)	-20 (11)	-6 (13)	4 (8)
O(3)	37 (5)	10 (4)	78 (10)	36 (10)	-13 (13)	26 (8)
O(4)	39 (5)	14 (4)	77 (11)	-18 (11)	17 (13)	28 (8)
O(5)	59 (7)	10 (4)	68 (11)	23 (10)	7 (17)	27 (9)
O(6)	65 (7)	7 (4)	57 (9)	-7 (9)	23 (16)	26 (9)
O(7)	52 (6)	10 (4)	84 (12)	4 (11)	26 (16)	33 (9)
O(8)	64 (7)	21 (5)	49 (9)	-2 (10)	2 (16)	6 (11)
O(9)	39 (5)	12 (4)	85 (11)	-36 (11)	15 (13)	21 (8)
O(10)	37 (5)	20 (5)	91 (14)	-14 (13)	2 (14)	24 (9)
H(1)	53 (9)	35 (8)	42 (12)	-27 (15)	45 (20)	-23 (16)
H(2)	51 (10)	42 (10)	73 (20)	43 (22)	-20 (26)	27 (19)
H(3)	49 (9)	25 (7)	78 (18)	-17 (18)	27 (23)	-32 (15)
H(4)	39 (8)	36 (9)	81 (22)	-42 (23)	-10 (23)	63 (17)
H(5)	66 (11)	17 (7)	82 (18)	22 (17)	65 (27)	1 (16)
H(6)	36 (8)	22 (8)	140 (30)	31 (24)	-21 (27)	11 (15)
H(7)	59 (11)	25 (8)	79 (21)	14 (19)	23 (28)	12 (17)

Table 1.3

KTO: Observed structure amplitudes and final calculated structure factors.

h	k	l	Fo	Fc
0	1	0	0.00	-0.22
0	2	0	4.35	4.63
0	2	5	0.67	-0.45
0	2	6	0.73	0.31
0	2	7	0.74	1.11
0	2	8	0.72	0.36
0	3	-5	1.50	-2.33
0	3	0	1.06	-0.76
0	4	-2	2.38	-2.05
0	4	-1	6.43	-6.13
0	4	0	4.65	-4.52
0	4	1	4.72	4.45
0	4	2	0.63	-0.53
0	4	3	1.31	-0.78
0	4	4	2.04	1.62
0	4	5	0.38	0.27
0	4	6	0.00	0.24
0	4	7	2.37	1.91
0	5	-7	1.21	-1.23
0	5	-6	1.42	0.91
0	5	-5	3.99	-4.25
0	5	-4	0.72	-0.80
0	5	-3	1.70	-2.08
0	5	0	4.72	-4.33
0	5	2	0.66	-0.48
0	5	3	4.11	3.77
0	5	4	0.69	0.34
0	5	5	4.10	2.82
0	5	6	0.00	0.05
0	5	7	0.73	1.04
0	5	8	0.00	-0.37
0	6	-7	1.56	-1.45
0	6	-6	1.90	-1.67
0	6	-5	1.01	1.24
0	6	-4	1.01	1.09
0	6	-3	0.71	-0.32
0	6	-2	4.49	3.28
0	6	0	3.19	2.69
0	6	1	3.72	2.99
0	6	2	0.35	0.23
0	6	3	0.72	0.49
0	6	4	1.33	1.52
0	6	5	0.38	0.43
0	6	7	0.77	-0.64
0	6	8	0.00	-0.79
0	7	-7	0.00	-0.24
0	7	-6	0.77	0.55
0	7	-5	1.84	-1.42
0	7	-4	0.25	0.53
0	7	-3	3.55	-3.40
0	7	-1	0.35	-0.60
0	7	0	0.31	0.26
0	7	2	5.09	-5.15
0	7	3	0.76	-3.72
0	7	4	0.38	-0.68
0	7	5	1.07	0.86
0	7	6	1.26	-0.97
0	7	7	1.15	0.56
0	8	-6	2.43	-1.91
0	8	-5	1.29	1.27
0	8	-4	1.76	1.45
0	8	-3	3.21	2.82
0	8	-2	5.67	-5.02
0	8	-1	5.26	4.69
0	8	0	4.98	-4.54
0	8	1	1.61	-1.34
0	8	2	1.93	-1.61
0	8	3	0.38	0.20
0	8	4	0.38	-1.03
0	8	5	0.76	0.23
0	8	7	0.40	-1.25
0	9	-5	2.22	1.88
0	9	-4	0.50	0.57
0	9	-3	2.32	-1.99
0	9	-2	1.13	-0.99
0	9	-1	0.50	1.09
0	9	0	3.43	-3.21
0	9	1	0.50	-0.32
0	9	2	5.77	-5.95
0	9	3	1.81	-1.47
0	9	4	1.58	-1.69
0	9	5	0.50	-0.92
0	9	6	2.32	-1.40
0	9	7	0.25	0.42
0	10	-5	0.76	0.75
0	10	-4	1.94	-1.52
0	10	-3	0.76	1.32
0	10	-2	1.86	-1.28
0	10	-1	4.26	4.16
0	10	0	4.12	-4.13
0	10	1	5.86	-6.01
0	10	2	2.73	-2.02
0	10	3	0.74	-0.36
0	10	4	0.00	-0.35
0	11	-4	0.76	0.30
0	11	-3	0.76	0.46
0	11	-2	1.49	-1.38
0	11	-1	2.96	2.45
0	11	0	0.71	0.69
0	11	1	0.00	0.07
0	11	3	0.73	-0.66
0	11	4	1.50	-1.50
0	12	-2	0.77	0.91
0	12	0	0.00	-0.05
0	13	0	1.17	1.09
1	-12	0	2.03	-2.26
1	-11	0	0.00	-0.09
1	-10	0	2.52	-2.34
1	-9	0	7.94	9.13
1	-8	0	1.73	-1.54
1	-7	0	6.74	7.06
1	-6	0	2.94	3.00
1	-5	0	3.15	-2.98
1	-5	5	0.74	-0.23
1	-5	6	0.74	-0.52
1	-4	0	3.88	3.47
1	-3	0	0.77	0.71
1	-2	0	1.00	-0.72
1	-1	0	4.01	-4.56
1	0	0	3.28	-3.05
1	1	0	2.41	-2.43
1	2	-1	3.09	-2.48
1	2	0	4.25	-5.75
1	2	1	0.57	0.25
1	2	3	4.98	5.30
1	2	4	1.16	-1.01
1	2	6	2.10	-2.49
1	2	7	0.74	-0.16
1	2	8	0.00	0.21
1	3	-7	0.00	0.35
1	3	-6	0.73	1.00
1	3	-5	0.67	0.47
1	3	-4	1.26	-1.31
1	3	-3	1.46	1.56
1	3	-2	1.98	-1.47
1	3	-1	0.58	0.30
1	3	0	0.76	-0.70
1	3	1	0.54	-0.44
1	3	2	2.85	-2.48
1	3	3	1.46	0.65
1	3	4	0.69	-0.35
1	3	5	3.40	-2.49
1	3	6	2.33	1.99
1	3	7	1.81	-1.58
1	3	8	0.00	-0.71
1	4	-8	0.78	-0.99
1	4	-7	0.74	0.85
1	4	-6	0.74	0.32
1	4	-5	2.46	-2.63
1	4	-4	0.35	0.22
1	4	-3	0.68	0.57
1	4	-2	0.00	0.24
1	4	-1	2.49	-2.02
1	4	0	0.88	0.48
1	4	1	6.63	-8.84
1	4	2	5.29	4.70
1	4	3	3.50	-2.51
1	4	4	0.00	-0.12
1	4	5	1.55	-0.05
1	4	6	0.73	-0.64
1	4	7	1.27	-0.81
1	4	8	0.00	0.14
1	5	-8	0.00	-0.04
1	5	-7	0.74	0.14
1	5	-6	0.00	0.73
1	5	-5	3.02	2.87
1	5	-4	0.35	0.62
1	5	-3	5.61	5.29
1	5	-2	2.31	2.33
1	5	-1	2.67	-2.45
1	5	0	3.00	2.64
1	5	1	4.06	3.89
1	5	2	0.64	-0.23
1	5	3	2.52	-1.94
1	5	4	0.69	-0.25
1	5	5	6.80	-5.52
1	5	6	3.67	3.37
1	5	7	0.74	-0.61
1	5	8	0.76	-0.43
1	6	-7	0.00	0.31
1	6	-6	0.00	0.64
1	6	-5	0.74	0.01
1	6	-4	3.72	2.57
1	6	-3	2.90	2.73
1	6	-2	2.42	1.85
1	6	-1	2.65	-2.47
1	6	0	0.00	-0.30
1	6	1	4.93	-4.83
1	6	2	3.46	-2.82
1	6	3	3.36	-3.01
1	6	4	1.99	-1.32
1	6	5	2.09	1.31
1	6	6	1.10	-0.15
1	6	7	0.74	-0.80
1	6	8	0.00	-0.40
1	7	-7	0.00	0.27
1	7	-6	0.00	-0.12
1	7	-5	1.11	1.31
1	7	-4	0.37	-0.62
1	7	-3	2.63	2.30
1	7	-2	0.72	-1.20
1	7	-1	3.23	-2.69
1	7	0	0.00	-0.04
1	7	1	1.63	1.35
1	7	3	0.72	0.43
1	7	4	1.74	1.48
1	7	5	0.73	-0.69
1	7	6	2.08	1.67
1	7	7	0.77	0.57
1	8	-5	0.77	1.31
1	8	-4	1.98	-1.69
1	8	-3	2.86	2.53
1	8	-2	0.72	-0.26
1	8	-1	1.70	1.19
1	8	0	7.50	8.81
1	8	1	0.72	-0.02
1	8	2	1.85	1.38
1	8	3	0.73	-0.75
1	8	4	1.41	0.84
1	8	5	1.92	1.23
1	8	6	1.60	1.44
1	9	-6	0.00	-0.14
1	9	-5	0.00	-0.16
1	9	-4	4.54	3.75
1	9	-3	4.41	-4.03
1	9	-2	3.04	2.43
1	9	0	1.99	-1.73
1	9	2	0.00	0.15
1	9	3	0.00	0.02
1	9	4	1.83	1.43
1	9	6	2.66	-1.95
1	9	7	0.81	0.57
1	10	-4	0.00	-0.00
1	10	0	6.74	7.51
1	10	1	0.76	-0.63
1	10	2	2.22	2.50
1	10	3	2.21	1.50
1	11	-4	1.16	0.74
1	11	-3	2.15	-2.60
1	11	-2	3.50	3.45
1	11	0	0.37	-0.55
1	11	1	1.51	1.50
1	11	2	0.00	0.03
1	11	4	0.78	0.41
1	11	5	0.76	0.42
1	12	-3	0.77	-0.36
1	12	-2	0.77	-0.86
1	12	-1	0.77	0.79
1	12	0	1.10	-0.71
1	12	1	0.77	0.80
1	12	2	1.32	1.52
1	12	3	1.35	-0.92
1	12	4	0.77	-0.81
1	13	-1	0.77	0.58
1	13	0	1.92	-2.11
1	13	1	1.27	1.16
1	13	2	0.00	0.49
2	-12	-2	7.61	9.00
2	-12	0	1.08	-1.08
2	-11	-4	1.23	0.55
2	-11	-3	3.30	3.12
2	-11	-2	0.76	-0.55
2	-11	0	3.23	-3.67
2	-10	0	0.66	0.59
2	-10	3	0.78	-0.55
2	-9	-4	1.90	1.02
2	-9	-3	3.34	3.16
2	-9	-2	0.73	0.56
2	-9	0	2.18	-2.01
2	-9	1	1.78	1.73
2	-9	3	1.39	1.67
2	-8	-4	1.32	-1.40
2	-8	-3	2.34	1.73
2	-8	0	0.00	-0.14
2	-8	1	2.15	-1.77
2	-8	2	1.05	0.12
2	-8	5	0.78	0.96
2	-7	-3	1.93	1.68
2	-7	-1	5.14	4.43
2	-7	0	1.26	-1.36
2	-7	1	5.25	4.78
2	-7	3	3.83	4.27
2	-7	4	0.74	-0.64
2	-6	-6	0.79	-1.66
2	-6	-5	0.74	-0.20
2	-6	-4	0.73	-1.14
2	-6	-3	1.47	-0.52
2	-6	-2	5.37	-4.81
2	-6	0	2.77	2.68
2	-6	3	1.61	-1.10
2	-5	-5	0.67	-0.75
2	-5	-2	1.74	-2.16
2	-5	-1	0.00	-0.15
2	-5	0	5.61	5.14
2	-4	-3	0.00	0.35
2	-4	0	2.43	-2.02
2	-4	4	1.95	1.88
2	-3	-6	0.00	1.15
2	-3	-1	2.07	-1.60
2	-3	0	2.87	-2.67
2	-2	-6	0.00	-0.33
2	-2	-4	2.66	-4.27
2	-2	-2	2.13	-1.91
2	-2	-1	4.32	-4.39
2	-2	0	2.49	-2.08
2	-2	1	3.41	3.21
2	-2	3	0.00	-0.16
2	-2	5	0.69	-1.70
2	-1	-4	1.12	-1.66
2	-1	-2	2.08	2.09
2	-1	0	3.78	3.64
2	-1	1	1.81	1.72
2	-1	3	0.62	0.47
2	0	-2	2.49	2.08
2	0	0	3.34	-3.39
2	0	1	2.43	2.08
2	0	2	0.59	-0.95
2	1	-6	2.00	1.74
2	1	-4	0.00	0.00
2	1	-2	4.27	4.81
2	1	0	4.55	6.13
2	1	1	1.83	-2.34
2	1	2	2.23	-1.74
2	2	-6	0.00	-0.05
2	2	-4	5.22	4.99
2	2	-2	4.07	4.39
2	2	0	2.31	-2.25
2	2	1	0.00	0.69
2	2	2	1.34	1.31
2	3	-6	0.69	0.56
2	3	-4	0.67	0.73
2	3	-2	3.35	3.20
2	3	-1	3.06	-2.52
2	3	0	1.41	1.22
2	3	1	3.49	-3.71
2	3	2	0.00	0.05
2	4	-3	0.66	0.92
2	4	0	1.03	-0.95
2	4	3	3.70	3.44
2	5	-5	1.51	1.67
2	5	-3	0.64	0.57
2	5	0	2.77	-2.41
2	5	5	0.00	1.06
2	6	-2	5.34	-4.96
2	6	-1	3.44	3.13
2	6	0	2.49	-2.29
2	6	1	2.63	2.69
2	6	2	0.64	-0.68
2	7	-4	1.03	0.32
2	7	0	2.33	2.75
2	7	4	0.74	-0.71
2	8	-3	1.22	-1.16
2	8	0	3.31	3.36
2	8	3	3.21	-2.36
2	9	-1	0.00	0.32
2	9	0	1.68	-1.60
2	9	2	1.13	-1.04
2	10	0	1.69	-1.41
2	11	0	1.01	-1.02
2	12	0	0.34	-0.37
2	13	0	0.00	0.03
3	-11	0	1.39	-1.36
3	-10	0	1.61	1.80
3	-9	0	2.58	-2.84
3	-8	0	4.42	4.67
3	-7	-2	0.00	0.21
3	-7	-1	4.61	4.31
3	-7	0	0.63	-0.31
3	-6	-4	3.91	4.05
3	-6	0	2.27	1.36
3	-6	2	0.00	0.22
3	-5	0	2.33	2.44
3	-4	-5	1.89	1.75
3	-4	-1	1.78	1.57
3	-4	0	3.91	-4.26
3	-4	3	2.55	1.73
3	-3	-2	3.91	-3.75
3	-3	0	0.00	0.09
3	-3	1	3.20	3.27
3	-3	4	2.39	-2.31
3	-2	-3	0.98	-0.94
3	-2	0	0.25	-0.14
3	-2	1	1.95	1.67
3	-2	4	0.00	0.04
3	-1	0	0.00	0.15
3	-1	2	2.27	-1.79
3	0	-6	0.00	-0.36
3	0	0	0.31	-0.32
3	0	2	3.57	-3.95
3	1	-1	0.58	-0.77
3	1	0	0.00	-0.38
3	2	-6	1.22	-1.29
3	2	0	4.11	4.04
3	2	5	1.76	-1.61
3	3	-3	0.62	-0.44
3	3	0	2.58	-2.66
3	3	2	3.68	-3.18
3	4	-3	0.64	0.95
3	4	0	0.30	-0.47
3	4	2	1.95	-1.38
3	5	-5	2.13	-1.91
3	5	-2	1.40	1.29
3	5	-1	0.62	-0.20
3	5	0	0.68	0.39
3	5	1	5.33	-6.56
3	6	0	2.09	-1.88
3	7	-4	2.46	2.52
3	7	0	0.00	0.14
3	8	-3	0.72	-0.92
3	8	0	3.78	-3.46
3	8	2	0.00	0.49
3	9	-1	0.00	-0.21
3	9	0	4.47	4.16
3	9	1	0.69	0.79
3	10	0	2.71	-2.23
3	11	0	2.65	2.74
3	12	0	0.57	-0.39
3	13	0	0.68	0.86
4	-10	0	0.73	-0.54
4	-9	0	1.13	1.47
4	-8	0	0.57	0.61
4	-7	0	0.23	0.28
4	-6	0	4.42	-4.92
4	-5	-3	0.74	0.73
4	-5	-2	0.72	-0.69
4	-5	0	2.48	-2.29
4	-5	1	0.00	0.93
4	-4	0	0.66	-0.75
4	-4	2	0.63	0.21
4	-4	4	0.00	-1.10
4	-3	0	4.80	-5.13
4	-3	2	1.11	0.95
4	-2	-5	2.17	-2.64
4	-2	0	1.20	-1.42
4	-2	3	3.50	-3.32
4	-1	-5	0.66	0.63
4	-1	-1	2.34	-2.46
4	-1	0	1.01	-0.83
4	-1	3	4.13	-3.97
4	0	-5	1.40	-0.85
4	0	-2	0.00	0.32
4	0	-1	2.44	-1.93
4	0	0	4.79	4.76
4	1	-5	1.80	-1.89
4	1	-2	0.64	-0.77
4	1	-1	5.03	5.40
4	1	0	0.76	0.77
4	1	5	0.00	0.61
4	1	6	0.76	-2.06
4	2	-5	0.00	0.24
4	2	-2	0.00	0.28
4	2	-1	3.58	-3.07
4	2	0	4.28	4.66
4	2	4	2.03	-2.00
4	2	6	1.03	-0.69
4	3	-6	0.77	1.11
4	3	-5	0.68	-0.67
4	3	-1	4.01	3.96
4	3	0	1.11	0.74
4	4	-5	1.98	1.86
4	4	0	2.85	2.37
4	4	5	0.74	-0.57
4	4	6	0.00	0.21
4	5	-6	2.85	3.12
4	5	-4	0.67	-0.94
4	5	0	0.33	0.53
4	5	3	3.89	3.99
4	5	5	1.30	1.16
4	5	6	0.76	0.45
4	6	-4	0.64	-0.10
4	6	0	1.07	-0.72
4	7	-3	2.36	1.95
4	7	0	2.02	-1.59
4	7	2	1.69	-1.81
4	8	-2	2.56	2.52
4	8	-1	0.00	-0.31
4	8	0	2.27	-1.63
4	9	0	0.00	0.11
4	10	-5	0.00	0.17
4	10	-3	0.77	0.73
4	10	-2	1.69	-1.33
4	10	0	1.26	-1.94
4	11	0	2.39	-2.62
4	11	3	0.00	-0.20
4	12	-1	0.75	0.34
4	12	0	0.24	0.52
4	12	1	0.00	-0.49
5	-8	0	[illegible]	-2.70
5	-7	-5	0.00	0.35
5	-7	-4	2.02	1.33
5	-7	0	1.21	-1.06
5	-6	0	0.00	-0.07
5	-5	0	1.26	1.02
5	-4	0	3.05	2.33
5	-3	-2	3.72	3.30
5	-3	-1	2.37	2.45
5	-3	0	0.42	-0.45
5	-2	-3	5.09	4.96
5	-2	0	0.42	0.06
5	-1	-4	0.66	-0.75
5	-1	0	0.34	-0.37
5	-1	1	3.89	3.59
5	0	-4	0.78	0.76
5	0	0	0.00	-0.16
5	1	-4	0.68	-0.93
5	1	0	0.00	0.44
5	1	2	0.00	0.09
5	2	-4	0.00	0.14
5	2	0	1.39	-0.91
5	2	2	1.70	1.75
5	3	0	3.78	3.74
5	3	2	2.83	2.66
5	4	-3	1.92	-1.76
5	4	0	2.52	-1.97
5	4	2	1.22	-0.86
5	5	0	3.09	-2.44
5	5	1	1.21	-0.80
5	6	-2	0.67	-0.36
5	6	-1	0.00	0.26
5	6	0	0.34	0.44
5	6	1	4.38	-5.00
5	7	0	2.39	-2.29
5	8	0	2.14	1.67
5	9	0	0.00	-0.44
5	10	0	3.15	2.68
5	11	0	0.00	-0.40
5	12	0	0.57	0.66
6	-7	-2	2.47	2.30
6	-6	-4	0.76	0.22
6	-6	-3	2.86	2.63
6	-6	-2	0.74	0.59
6	-6	0	3.46	3.23
6	-6	1	0.74	-0.39
6	-5	-5	0.76	0.37
6	-5	-4	0.73	-0.55
6	-5	-3	0.00	-0.56
6	-5	-2	0.00	-0.02
6	-5	0	1.44	-1.48
6	-5	1	1.16	1.68
6	-5	2	0.77	-0.80
6	-4	-4	2.57	-2.38
6	-4	-3	0.00	0.08
6	-4	-2	0.00	-1.13
6	-4	0	0.69	0.65
6	-4	1	0.76	0.60
6	-4	2	0.74	0.26
6	-3	-4	0.74	-0.79
6	-3	-3	0.00	-0.12
6	-3	-2	1.18	-0.86
6	-3	0	1.92	1.86
6	-3	1	1.98	-1.61
6	-3	2	0.77	0.81
6	-3	3	1.31	1.20
6	-2	-4	2.28	-1.88
6	-2	-3	1.21	-1.49
6	-2	-2	0.74	-0.96
6	-2	0	1.83	-1.77
6	-2	2	0.00	1.28
6	-2	3	0.00	0.15
6	-1	-4	0.00	-0.40
6	-1	-3	1.88	-1.73
6	-1	-2	0.74	-0.56
6	-1	0	1.27	1.06
6	-1	1	2.49	-1.96
6	-1	2	0.77	0.94
6	-1	3	1.81	1.67
6	-1	4	1.44	-1.20
6	0	-4	0.74	-0.39
6	0	-3	0.00	-0.23
6	0	-2	0.00	0.01
6	0	0	0.24	0.37
6	0	1	0.00	-0.09
6	0	2	0.73	0.98
6	0	3	1.29	-1.23
6	0	4	1.21	0.93
6	1	-4	0.74	-0.51
6	1	-3	0.74	-0.50
6	1	-2	0.00	-0.36
6	1	0	1.79	1.56
6	1	1	0.00	-0.66
6	1	3	0.00	0.13
6	1	4	0.76	-0.53
6	2	-4	1.99	1.94
6	2	-3	2.46	2.32
6	2	-2	0.74	-0.33
6	2	0	0.69	-0.91
6	2	1	0.00	-0.56
6	2	2	0.76	-1.30
6	2	3	0.00	-0.80
6	2	4	0.74	-0.89
6	3	-4	1.35	1.36
6	3	-3	1.26	-1.14
6	3	-2	0.77	0.84
6	3	0	1.01	-0.55
6	3	1	0.74	-0.93
6	3	2	3.99	-4.36
6	3	3	0.00	-0.40
6	3	4	0.76	-0.92
6	4	-4	0.00	0.25
6	4	-3	0.00	-0.79
6	4	-2	0.74	-1.47
6	4	0	1.79	-1.96
6	4	1	0.73	-0.25
6	4	2	0.76	-0.93
6	4	3	0.74	-0.13
6	4	4	0.00	-0.11
6	5	-4	0.74	0.38
6	5	-3	0.74	0.04
6	5	-2	0.73	1.95
6	5	0	0.50	0.52
6	5	1	0.77	1.10
6	5	2	0.00	0.53
6	5	3	0.77	0.53
6	5	4	0.77	0.44
6	6	-4	0.00	0.05
6	6	-3	0.76	-0.33
6	6	-2	1.39	0.37
6	6	0	0.00	0.23
6	6	1	0.77	0.36
6	6	2	0.78	-0.89
6	6	4	0.00	-0.54
6	7	-4	0.00	0.48
6	7	-3	0.00	-0.15
6	7	-2	1.66	1.65
6	7	0	0.00	0.06
6	7	1	1.49	1.13
6	7	2	1.79	1.64
6	7	3	0.82	-0.69
6	7	4	0.76	0.34
6	8	-5	0.00	0.79
6	8	-4	0.00	-0.09
6	8	-3	0.00	1.06
6	8	-2	0.00	-0.71
6	8	0	0.00	0.12
6	8	2	0.74	-0.54
6	8	3	0.00	0.07
6	9	0	0.35	-0.49
6	9	1	0.00	0.11
6	9	2	0.73	-0.04
6	9	3	0.74	0.04
6	10	-3	0.00	0.21
6	10	-2	0.00	-0.41
6	10	-1	0.76	0.49
6	10	0	0.25	0.20
6	10	1	0.74	0.41
6	10	2	0.74	0.52
7	-4	-3	2.15	-1.80
7	-4	-2	2.37	2.08
7	-3	-4	0.00	0.44
7	-3	-3	0.76	-0.70
7	-3	-2	0.76	-0.57
7	-3	-1	0.74	-0.61
7	-3	0	0.25	0.10
7	-3	-1	0.74	-0.61
7	-2	-5	0.73	-0.07
7	-2	-4	0.76	0.58
7	-2	-3	0.77	-0.62
7	-2	-2	0.76	0.42
7	-2	-1	1.26	1.18
7	-2	0	1.26	-1.23
7	-2	1	1.26	-1.40
7	-1	-5	1.45	1.20
7	-1	-4	0.33	0.51
7	-1	-3	3.91	3.92
7	-1	-2	0.00	0.17
7	-1	-1	1.75	1.50
7	-1	0	2.14	-1.47
7	-1	1	0.38	0.58
7	-1	2	0.33	-0.47
7	0	-4	1.13	0.99
7	0	-3	0.76	0.35
7	0	-2	0.38	0.15
7	0	-1	1.65	1.56
7	0	0	1.89	-1.32
7	0	1	0.76	-0.72
7	0	2	0.74	-0.09
7	1	-4	0.38	0.19
7	1	-3	2.08	2.34
7	1	-2	0.38	-0.12
7	1	-1	0.76	0.46
7	1	0	1.26	-0.80
7	1	1	1.25	0.67
7	1	2	0.00	0.01
7	2	-4	0.38	0.33
7	2	-3	2.08	2.20
7	2	-2	1.39	-1.22
7	2	-1	0.76	0.39
7	2	0	1.89	1.35
7	2	1	0.76	0.34
7	2	2	1.26	0.79
7	2	3	0.74	0.57
7	3	-4	0.00	0.27
7	3	-3	0.00	-0.24
7	3	-2	0.00	0.16
7	3	-1	1.40	1.29
7	3	0	0.63	0.54
7	3	1	0.38	0.24
7	3	2	0.77	0.62
7	3	3	0.37	0.36
7	4	-4	0.76	-0.11
7	4	-3	1.20	1.01
7	4	-2	0.76	0.62
7	4	-1	0.76	0.61
7	4	0	3.78	3.63
7	4	1	0.38	0.33
7	4	2	1.51	1.76
7	4	3	0.38	-0.07
7	5	-5	0.38	0.38
7	5	-4	0.00	0.11
7	5	-3	0.74	-0.54
7	5	-2	0.76	0.67
7	5	-1	0.00	0.10
7	5	0	1.39	1.02
7	5	1	0.00	-0.42
7	5	2	0.77	-0.35
7	6	-4	1.34	-1.20
7	6	-3	0.00	0.15
7	6	-2	0.00	-0.43
7	6	-1	0.78	-0.79
7	6	0	1.16	-0.37
7	6	1	0.00	-0.07
7	6	2	0.00	-0.25
7	7	-4	0.00	-0.39
7	7	-3	0.35	-0.71
7	7	-2	0.74	-0.42
7	7	-1	0.73	-0.96
7	7	0	1.08	0.95
7	7	1	0.74	-0.30
7	7	2	0.76	0.11
7	8	0	0.76	-0.79
8	1	-2	1.39	1.29
8	1	-1	0.00	0.35
8	2	-3	0.91	-1.14
8	2	-2	0.00	0.45
8	2	-1	1.59	-1.13
8	2	0	0.19	[illegible]
8	3	-3	0.74	0.10
8	3	-2	1.42	-1.16
8	3	-1	0.76	0.70
8	3	0	1.26	-0.93
8	4	-2	0.00	-0.05
8	4	-1	1.36	[illegible]
8	5	-1	0.77	0.54

Table 1.4

KTO : Analysis of the agreement of $|F_o|$ and $|F_c|$ at the end of the refinement. N is the number of reflexions. Structure factors are on the absolute scale.

(a) As a function of sin θ/λ

	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
0·0 - 0·3	195·21	193·74	26·61	83	0·136	0·23
0·3 - 0·4	223·10	218·92	36·48	109	0·164	0·24
0·4 - 0·5	330·72	324·64	60·57	194	0·183	0·19
0·5 - 0·6	236·90	230·94	66·27	232	0·280	0·14
0·6 - 0·7	99·05	96·93	33·31	125	0·336	0·12

(b) As a function of $|F_o|$

	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
0·0 - 0·4	13·88	56·63	47·52	171	3·423	0·28
0·4 - 1·0	151·12	136·91	54·44	211	0·360	0·26
1·0 - 2·0	239·19	210·20	44·27	161	0·185	0·28
2·0 - 3·0	225·29	206·99	29·71	93	0·132	0·32
3·0 - 4·0	192·65	185·48	17·77	55	0·092	0·32
4·0 - 5·5	179·44	179·90	17·98	39	0·100	0·46
5·5 - 8·0	83·42	89·03	11·54	13	0·138	0·89
All	1084·98	1065·14	223·23	743	0·206	0·30

Table 1.5

Bond lengths (Å) and angles (°) found by neutron diffraction in the H_2Ox and HOx^- residues of KTO. Those found by X-ray diffraction in KTO and by neutron diffraction in ATO are also shown.

	KTO		ATO
	Neutron	X-ray	Neutron
Residue A			
C(1) - O(1)	1·288 (16)	1·211 (5)	1·211 (4)
C(1) - O(3)	1·242 (14)	1·298 (5)	1·288 (4)
$C(1) - C(1^{III})$	1·494 (12)	1·553 (9)	1·549 (5)
O(1) - C(1) - O(3)	123·3 (1·1)	126·4 (0·6)	126·3 (0·3)
$O(1) - C(1) - C(1^{III})$	117·8 (0·8)	120·8 (0·5)	120·6 (0·2)
$O(3) - C(1) - C(1^{III})$	118·6 (1·0)	112·6 (0·5)	113·0 (0·2)
Residue B			
C(2) - O(2)	1·313 (16)	1·289 (6)	1·296 (4)
C(2) - O(4)	1·178 (15)	1·209 (6)	1·206 (4)
$C(2) - C(2^{I})$	1·566 (11)	1·554 (9)	1·544 (5)
O(2) - C(2) - O(4)	126·1 (1·0)	126·1 (0·6)	126·5 (0·3)
$O(2) - C(2) - C(2^{I})$	107·9 (0·8)	112·0 (0·5)	112·0 (0·2)
$O(4) - C(2) - C(2^{I})$	125·1 (0·9)	121·7 (0·6)	121·6 (0·2)
Residue C			
C(3) - O(5)	1·310 (16)	1·307 (6)	1·291 (4)
C(3) - O(6)	1·240 (21)	1·211 (6)	1·212 (4)
C(3) - C(4)	1·526 (14)	1·551 (9)	1·549 (3)
C(4) - O(7)	1·228 (16)	1·272 (6)	1·247 (4)
C(4) - O(8)	1·264 (21)	1·223 (6)	1·230 (4)
O(5) - C(3) - O(6)	125·1 (1·2)	124·4 (0·6)	124·8 (0·3)
O(5) - C(3) - C(4)	116·0 (1·2)	113·2 (0·5)	113·3 (0·2)
O(6) - C(3) - C(4)	118·8 (0·9)	122·1 (0·5)	121·8 (0·2)
O(7) - C(4) - O(8)	128·6 (1·3)	127·3 (0·6)	127·5 (0·3)
O(7) - C(4) - C(3)	116·9 (1·3)	114·5 (0·4)	115·0 (0·2)
O(8) - C(4) - C(3)	114·5 (0·9)	117·9 (0·4)	117·5 (0·2)

Table 1.6

$K^+\cdots O$ distances (Å) in KTO.

	Neutron	X-ray
$K^+\cdots O(1)$	2·858 (24)	2·870 (4)
$O(2^{VI})$	3·359 (28)	3·250 (4)
$O(4^{II})$	2·885 (24)	2·931 (4)
$O(5)$	2·759 (34)	2·879 (4)
$O(6^{VI})$	2·964 (31)	2·915 (4)
$O(7^{V})$	3·053 (26)	3·044 (4)
$O(8)$	2·790 (25)	2·870 (4)
$O(9^{II})$	2·914 (26)	2·893 (4)
$O(10^{VI})$	3·013 (33)	2·924 (4)

Table 1.7

Details of the water molecules and 0 – H···0 hydrogen bonds in KTO. (Distances in Å, angles in degrees).

	Neutron			X-ray
Bond	0 – H	H···0	0···0	0···0
0(9) – H(1)···0(8^{V})	1·123(29)	1·617(26)	2·713(23)	2·714(5)
0(9^{VI})–H(2^{VI})···0(6^{V})	0·945(31)	1·771(30)	2·704(11)	2·733(5)
0(10) – H(3)···0(4^{I})	0·941(23)	1·896(23)	2·804(18)	2·780(5)
0(10) – H(4)···0(1^{IV})	0·986(25)	1·906(24)	2·816(16)	2·859(5)
0(5) – H(5)···0(10)	1·086(29)	1·417(30)	2·500(23)	2·537(5)
0(2) – H(6)···0(9)	1·078(22)	1·392(23)	2·466(15)	2·503(5)
0(3) – H(7)···0(7^{V})	1·052(26)	1·463(29)	2·508(19)	2·505(5)

H(1) – 0(9) – H(2)	99·6(2·6)	H(3) – 0(10) – H(4)	102·9(2·1)
0(9) – H(1)···0(8^{V})	163·7(1·8)	0(5) – H(5)···0(10)	174·4(2·0)
0(9^{VI})–H(2^{VI})···0(6^{V})	168·7(2·4)	0(2) – H(6)···0(9)	173·8(4·1)
0(10) – H(3)···0(4^{I})	161·6(2·4)	0(3) – H(7)···0(7^{V})	171·7(3·1)
0(10) – H(4)···0(1^{IV})	152·2(2·8)		

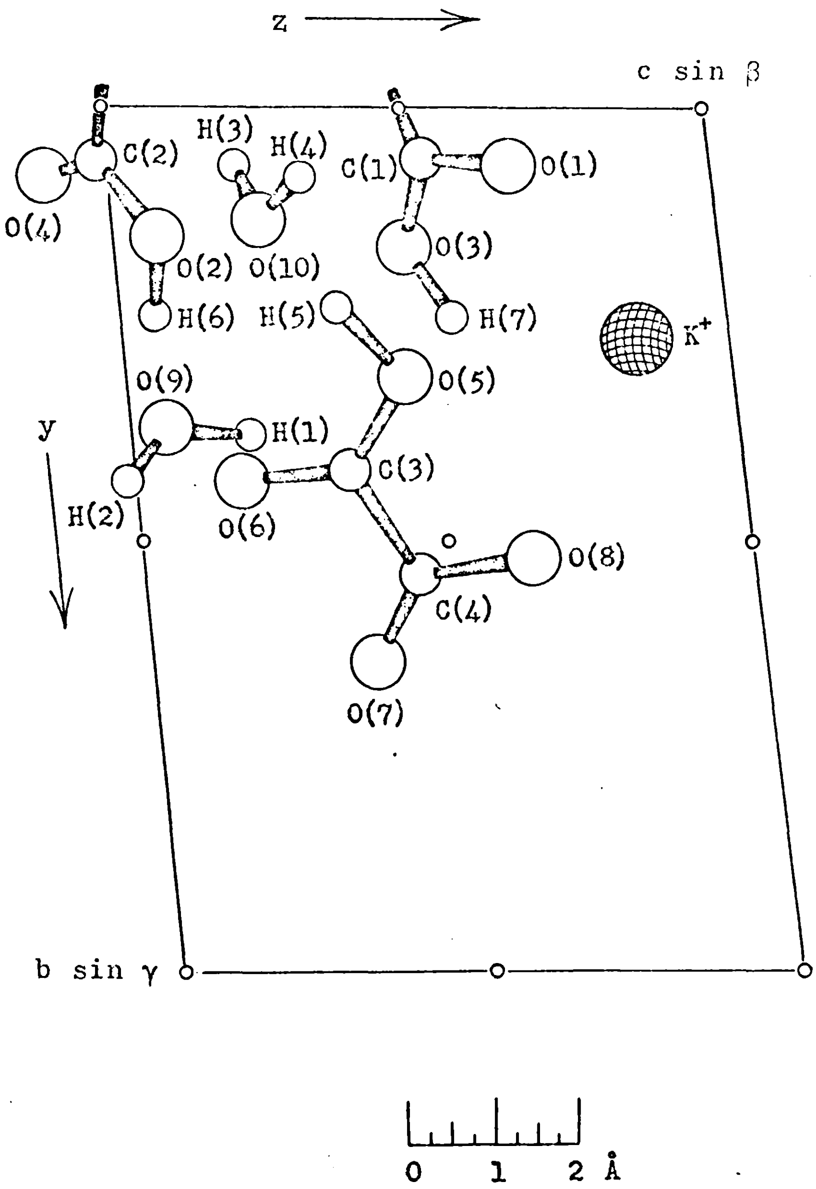

z
c sin β
H(3)
H(4)
C(2)
C(1)
O(1)
O(4)
O(2)
O(10)
O(3)
H(6)
H(5)
H(7)
K⁺
O(9)
O(5)
y
H(1)
C(3)
H(2)
O(6)
O(8)
C(4)
O(7)
b sin γ
0
1
2 Å

Figure 1.1 The crystal chemical unit (CCU) of KTO.

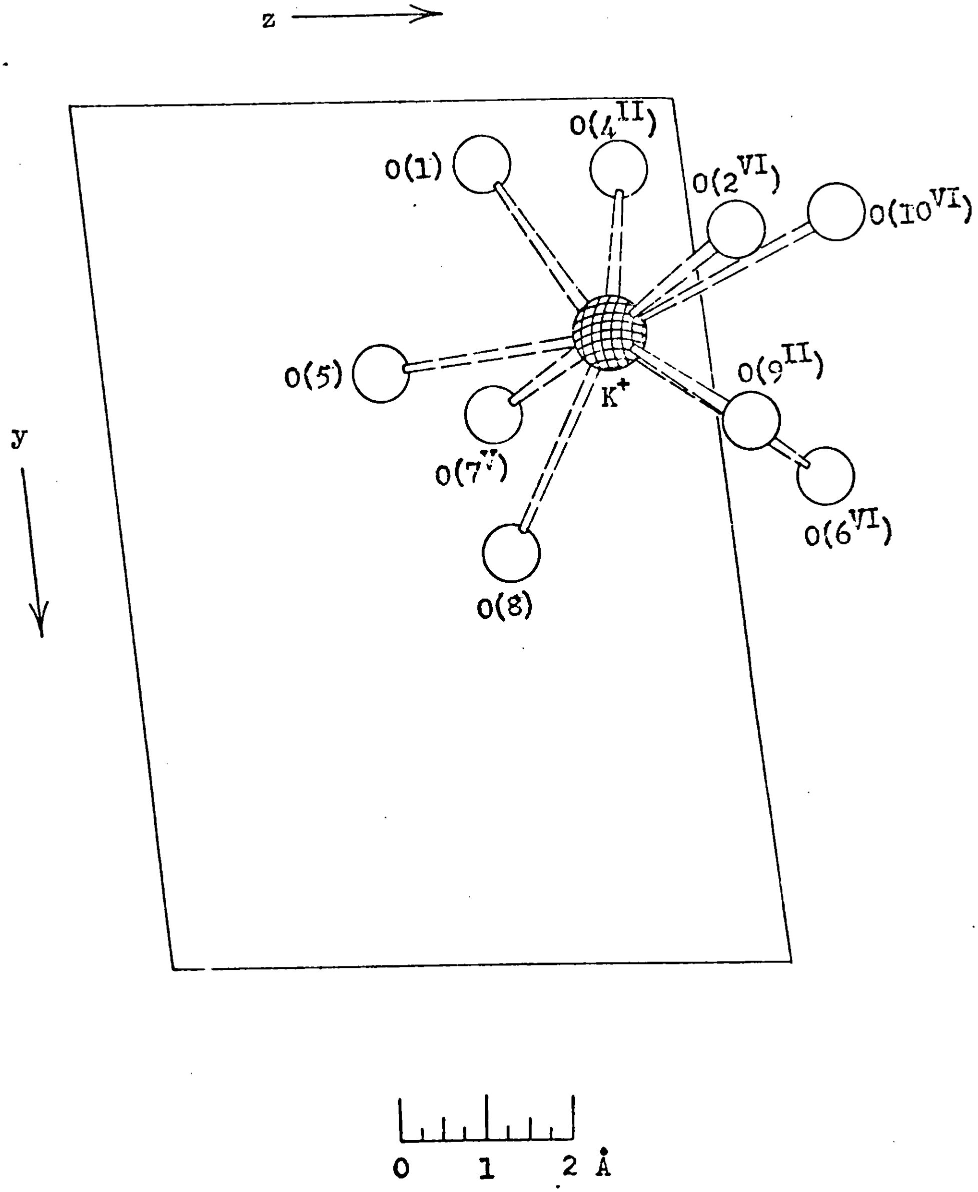

z
y
O(1)
O(4^II)
O(2^VI)
O(10^VI)
O(5)
K+
O(9^II)
O(7^V)
O(6^VI)
O(8)
0
1
2 Å

Figure 1.2 The environment of the potassium ion in KTO.

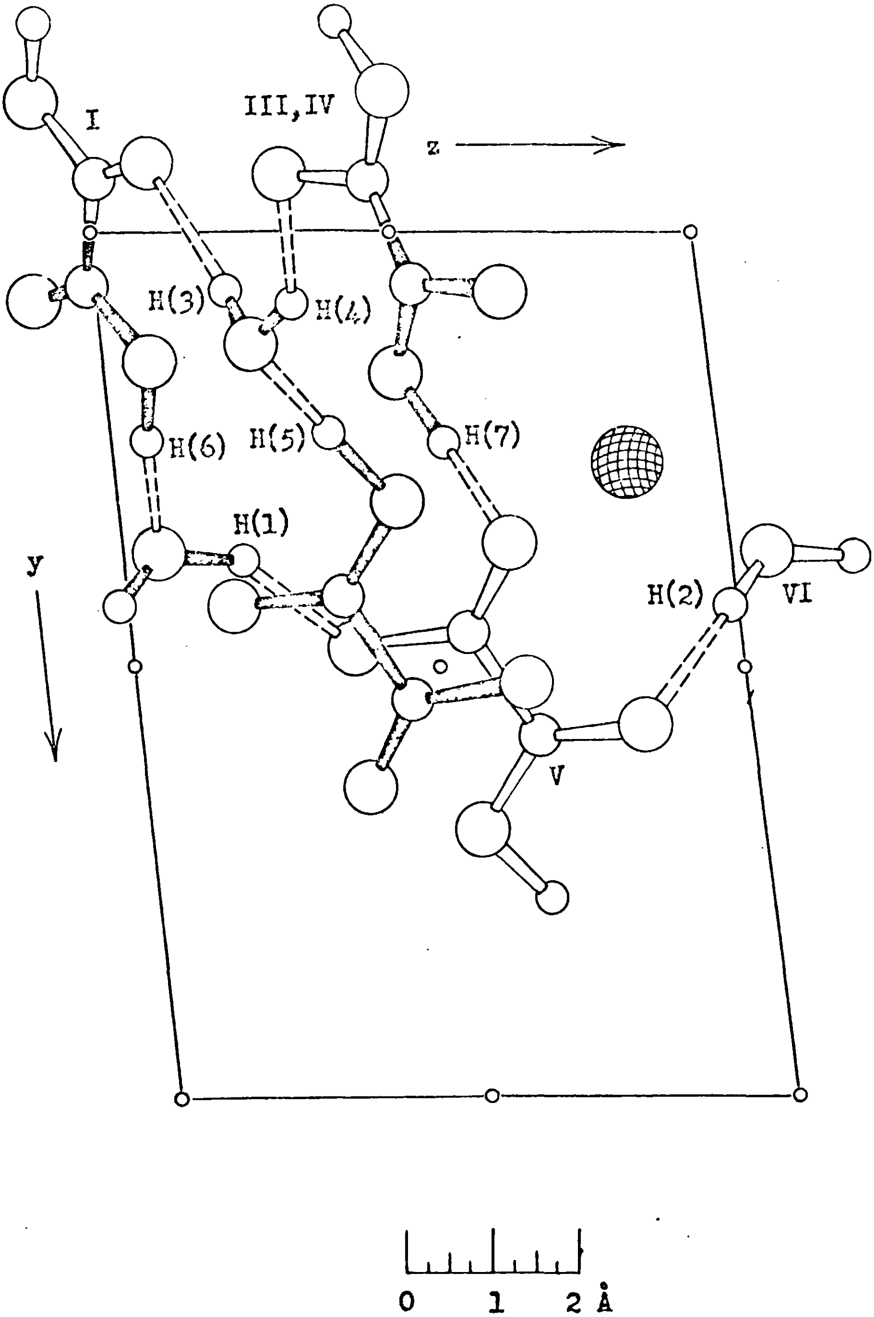

I
III,IV
z
H(3)
H(4)
H(6)
H(5)
H(7)
H(1)
y
H(2)
VI
V
0
1
2 Å

Figure 1.3 Hydrogen bonding in KTO.

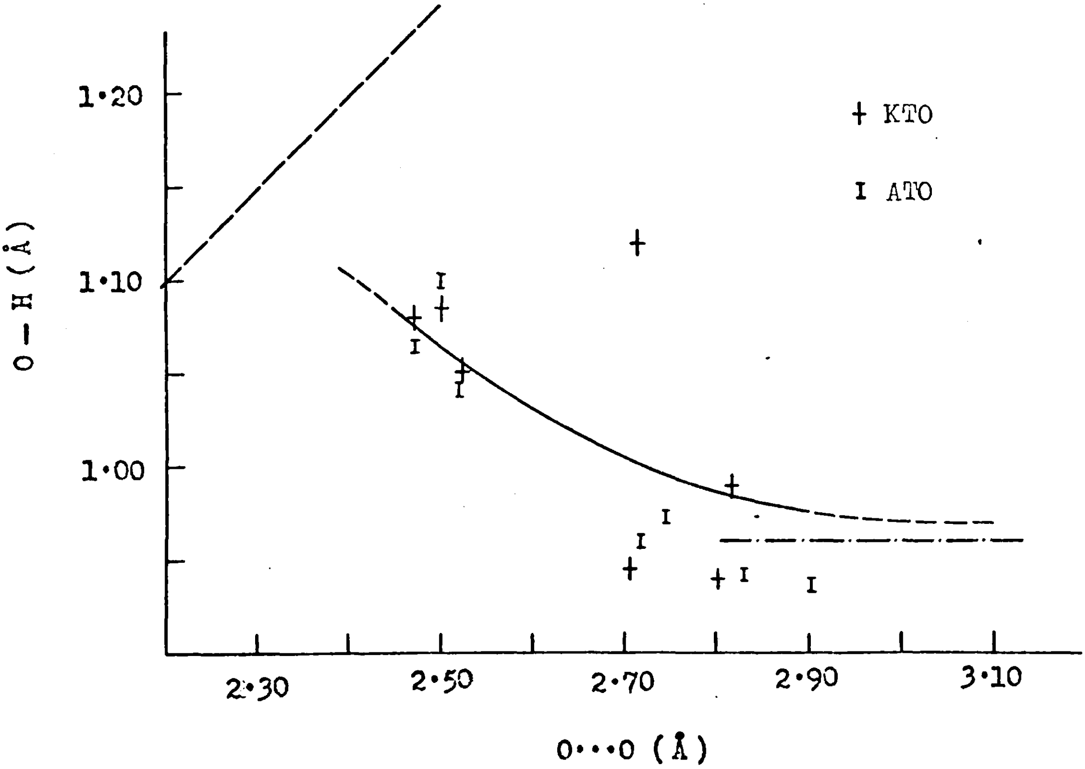


Figure 1.4 Graph showing the Nakamoto-Margoshes-Rundle relationship between O···O and O—H distances in hydrogen bonds. The curve is that of Pimentel and McClellan (1960). The diagonal broken line corresponds to hypothetical centrosymmetric bonds. The horizontal broken line indicates the O—H distance in gaseous water. The values derived from the analyses of ATO and KTO are shown.

1.3 DISCUSSION

The formula of potassium tetroxalate (KTO), KHOx . H_2Ox . $2H_2O$, suggests that the asymmetric unit in the crystal will consist of the potassium ion, one unsymmetrical half-oxalate ion, HOx^- , one symmetrical unionised oxalic acid molecule, H_2Ox, and two molecules of water. As we can see from Figure 1.1, however, the expected H_2Ox molecule is made up of two crystallographically independent half-H_2Ox molecules, each of which is duplicated by a different centre of symmetry.

In Table 1.5 the dimensions of the H_2Ox molecules (residues A and B) and the HOx^- ion (residue C) found in KTO by the present neutron-diffraction analysis are compared with those found in KTO by X-ray diffraction (Haas, 1964) and in ammonium tetroxalate (ATO) by neutron diffraction (Appendix I); estimated standard deviations are given in parentheses.

In the H_2Ox molecules and in one carboxyl group of the HOx^- ion the C—O distances should differ in the sense that C—O (H) > C=O , and in the other carboxyl group of the HOx^- ion the C—O distances should be nearly equal owing to ionisation and charge delocalisation. Haas, however, found that in the HOx^- ion the C(4)—O(7) and C(4)—O(8) distances, 1.272 (±6) Å and 1.223 (±6) Å respectively, apparently differed to a significant degree, thus indicating that most of the negative charge was localised on O(7) , whilst in ATO the corresponding distances, 1.247 (±4) Å and 1.230 (±4) Å respectively, differed to a much lesser extent, so implying the expected charge delocalisation. Unfortunately, the distances found in KTO by neutron diffraction, 1.228 (±16) Å and 1.264 (±21) Å respectively, are not of sufficient accuracy to enable any further conclusion to be reached regarding this.

The environment of the potassium ion is shown in Figure 1.2 and $K^{+}\cdots O$ distances are listed in Table 1.6, where, for comparison, those found by Haas are given too.

The extensive system of hydrogen bonding is shown in Figure 1.3 and details are given in Table 1.7, in which the $O\cdots O$ distances found by Haas are also given. [Haas erroneously states that there is a hydrogen bond, of length 3.098 Å, between O(9) and O(8).]

Data from Table 1.7 and from Table 4 of the ATO paper have been used to plot fourteen points in Figure 1.4 which shows the Nakamoto-Margoshes-Rundle relationship between O—H and $O\cdots O$ distances in hydrogen bonds (Part II). The curve drawn by Pimentel and McClellan (1960) to represent the trend of information available in 1959 is also shown. Our points suggest that the curve ought to rise more steeply, particularly in the region of 2.5 Å, and that the limiting O—H distance should be lower than the 0.96 Å of gaseous water.

CHAPTER 2

POTASSIUM HYDROGEN MALONATE

2.1 INTRODUCTION

Some of the crystalline acid salts (MHX_2) of monobasic acids (HX) have "very short" hydrogen bonds lying across a crystallographic element of symmetry (Speakman, 1967). In such salts, which have anomalous infra-red spectra and are of Type A (Blinc, Hadzi and Novak, 1960; Shrivastava and Speakman, 1961), the two anion residues are crystallographically equivalent and the hydrogen bonds have symmetrical potential functions. These may have a single minimum, corresponding to the proton lying mid-way between the two oxygen atoms, cf. the bifluoride ion, HF_2^- (Levy and Peterson, 1952), or a double minimum, corresponding to an equal distribution of O—H···O and O···H—O in the crystal at any one time.

A similar situation exists in the acid salts (MHY) of some dibasic acids (H_2Y) in which the two terminal carboxyl groups are crystallographically equivalent rather than being, respectively, ionised and unionised, as the conventional formulation (M^+HY^-) would imply. These salts also have the anomalous infra-red spectra characteristic of Type A.

Typical of the Type A acid salts of dibasic acids is potassium hydrogen malonate, of which a very accurate structure analysis by X-ray diffraction has been carried out by Dr. Speakman and others; a preliminary note on this work has already been published (Ferguson et al., 1968).

The present structure analysis by neutron diffraction was undertaken in order to supplement the X-ray analysis. One of the main objects was to study the symmetrical hydrogen bond, which lies across a centre of inversion, and, whilst the refinement is not yet complete, it appears that the potential function has a double minimum, thus indicating that the proton is either statistically disordered or is undergoing vibrational motion in the potential well between the oxygen atoms; these possibilities cannot be distinguished crystallographically (Ibers, 1965).

2.2 EXPERIMENTAL

Crystal Data

Potassium hydrogen malonate, $KHC_3H_2O_4$, F.W. = 142.2.
Monoclinic, $\underline{a} = 9.473\ (\pm 6)$, $\underline{b} = 11.559\ (\pm 7)$, $\underline{c} = 4.726\ (\pm 5)$ Å,
$\beta = 91.6^\circ\ (\pm 0.1^\circ)$, $\underline{U} = 517.3$ Å^3. $\underline{D}_m = 1.75$, $Z = 4$, $\underline{D}_x = 1.825$.
Space group C 2/m (C^3_{2h}, No.12).
Linear absorption coefficient for neutrons ($\lambda \approx 1$ Å), $\mu = 1.07$ cm^{-1}.

Preparation of Crystals

Potassium hydrogen malonate is easily prepared by mixing equimolar solutions of potassium hydroxide (in water) and malonic acid (in methanol).

A number of large crystals suitable for neutron diffraction were grown in the summer of 1967 by a method similar to that described in Chapter 1 for potassium tetroxalate, except that a methanol-water solvent was used rather than water alone. Limited data were collected from one of these crystals in the autumn of 1967 and spring of 1968.

The crystal used for the final, successful data collection in the winter of 1968 was prepared by the simpler procedure of introducing a seed crystal into a saturated solution of potassium hydrogen malonate in a small beaker which was left standing in a warm atmosphere for two or three days to allow crystal growth to take place.

Data Collection

Neutron-diffraction data were collected in the DIDO reactor at A.E.R.E., Harwell using a Ferranti Mark II automatic diffractometer similar to that described in the previous chapter.

Unfortunately, no fewer than three visits to Harwell were necessary before full three-dimensional data were successfully collected.

On the first visit, in the autumn of 1967, almost continuous instrumental faults were encountered with the result that only two-dimensional, *c*-axial data, in all 85 independent reflexions, could be collected. The crystal used on this occasion, of approximate dimensions $8 \times 5 \times 3$ mm^3, was taken to Harwell again in the spring of 1968. This time difficulties concerning the orientation of the crystal with respect to the diffractometer, as well as some computing problems, resulted in the only useful data collected again being two-dimensional; some three-dimensional data were also collected, but proved useless owing to the crystal not being properly set. On both these visits the neutron beam was monochromatised to $\lambda = 1.042$ Å.

The second crystal, of dimensions $10.5 \times 3.9 \times 1.3$ mm^3, was taken to Harwell in the winter of 1968. After some initial difficulties, which, together with those previously experienced, moved the writer to prepare a short note, "The Setting-up of Crystals on a Four-circle Neutron Diffractometer" (Appendix II), three-dimensional data were, at last, successfully collected.

In all, neutron-scattering structure amplitudes were measured for 454 independent reflexions, covering the reciprocal sphere to $\theta = 45^\circ$, and including some additional reflexions to $\theta = 55^\circ$. Of these, 354 had values significantly above the background, 86, whose integrated intensities were lower than a certain threshold value (chosen to be three times their standard deviations, σ) were assigned intensities equal to one-half of that threshold value, and a further 14 had intensities of zero.

I should like to thank Dr. J.B. Forsyth and Mr. S.A. Wilson for helpful advice during these visits to Harwell.

Structure Refinement

So far only the 415 neutron-diffraction data out to $\theta = 45^\circ$, not yet corrected for absorption, have been included in the refinement, the starting point for which was the set of parameters obtained by refinement of 1092 X-ray diffraction data to $R = 0.112$ (Sime and Speakman, 1969). After four cycles of full-matrix least-squares refinement, with anisotropic vibrational parameters for the non-hydrogen atoms and unit weights, the values of R and R' were, respectively, 0.139 and 0.021. A further six cycles of full-matrix refinement, with anisotropic vibrational parameters for all the atoms and unit weights, reduced R to 0.090 and R' to 0.011.

By this time parameter shifts were all less than one-third of their standard deviations and the refinement was therefore considered to be complete for the present. It is intended to apply absorption corrections and to carry out further least-squares refinement using all 454 data; at the same time a suitable weighting scheme will be introduced.

The final positional parameters are given in Table 2.1 and the final vibrational parameters in Table 2.2. For comparison, those found from the X-ray analysis are also shown. Standard deviations derived from the inverse of the least-squares matrix are given in parentheses. Observed structure amplitudes and final calculated structure factors are given in Table 2.3 and their agreement analysed in Table 2.4. Nuclear scattering lengths used in the structure-factor calculations were : K, 0.35; O, 0.577; C, 0.661; and H, -0.378×10^{-12} cm.

The group of atoms whose parameters appear in these tables constitutes the crystal chemical unit (CCU) of the structure; the CCU is shown in Figure 2.1. Other symmetry-related units are denoted as follows :

CCU	x	y	z
I	$\frac{1}{2} - x$	$\frac{1}{2} - y$	$1 - z$
II	x	y	$-1 + z$
III	$-x$	y	$2 - z$
IV	x	$-y$	z
V	x	$-y$	$-1 + z$
VI	$\frac{1}{2} - x$	$-\frac{1}{2} + y$	$1 - z$
VII	$\frac{1}{2} - x$	$\frac{1}{2} - y$	z

TABLES AND DIAGRAMS

Table 2.1

Fractional ($x,y,z \times 10^5$) and orthogonal ($X',Y,Z' \times 10^4$) coordinates. ($X' = ax \sin\beta$; $Y = by$; $Z' = ax \cos\beta + cz$.)

(a) Neutron structure analysis.

	x	y	z	X'	Y	Z'
K^+	15448	0	28062	14628(94)	0	12861(110)
O(1)	17705	30473	66783	16766(45)	35224(42)	31102(54)
O(2)	9481	13206	77401	8978(48)	15265(44)	36334(54)
C(1)	0	30297	100000	0	35020(47)	47260
C(2)	9534	23789	80495	9028(31)	27498(31)	37794(37)
H(1)	25000	25000	50000	23674	28900	23630
H(2)	6432	36134	112519	6091(117)	41767(111)	53010(124)

(b) X-ray structure analysis.

	x	y	z	X'	Y	Z'
K^+	15435	0	27730	14616(12)	0	12697(13)
O(1)	17748	30462	66548	16806(29)	35211(27)	30981(29)
O(2)	9449	13217	77703	8948(30)	15278(27)	36473(29)
C(1)	0	30355	100000	0	35087(52)	47260
C(2)	9532	23733	80472	9026(34)	27433(35)	37779(33)
H(1)	25000	25000	50000	23674	28900	23630
H(2)	6132	35800	112636	5807(476)	41381(497)	53394(483)

Table 2.2

Vibrational parameters ($\mathring{A}^2$ x 10^4).

(a) Neutron structure analysis.

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{33}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
K^+	211(44)	75(38)	175(61)	0	71(80)	0
O(1)	287(22)	132(19)	304(33)	-37(39)	478(44)	-200(33)
O(2)	378(25)	111(19)	349(34)	-151(40)	400(44)	-60(35)
C(1)	228(25)	107(24)	115(33)	0	242(46)	0
C(2)	135(16)	85(15)	71(22)	-62(28)	59(27)	-33(23)
H(1)	397(58)	229(48)	230(67)	12(94)	-26(106)	-330(91)
H(2)	770(66)	510(58)	713(84)	-922(121)	923(118)	-888(108)

(b) X-ray structure analysis.

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{33}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
K^+	324(6)	234(5)	332(6)	0	120(9)	0
O(1)	436(16)	279(12)	428(15)	-65(23)	491(25)	-137(23)
O(2)	509(17)	246(12)	416(15)	-78(22)	477(26)	-88(23)
C(1)	397(29)	234(21)	310(23)	0	339(41)	0
C(2)	261(17)	242(14)	266(15)	-29(24)	149(25)	-93(25)

	$\underline{U}_{iso}$
H(2)	190(119)

Table 2.3

Observed structure amplitudes and final calculated structure factors.

h	k	l	Fo	Fc
-11	-3	0	0.77	0.68
-11	-3	1	0.75	0.82
-11	-1	0	0.78	-0.18
-11	-1	1	1.69	-1.65
-10	-6	0	4.05	-3.98
-10	-6	1	1.34	1.13
-10	-4	0	1.82	1.79
-10	-4	1	0.76	0.43
-10	-4	2	0.75	0.36
-10	-2	0	6.31	-6.85
-10	-2	1	5.29	-5.16
-10	-2	2	3.40	3.39
-10	0	0	7.40	7.71
-10	0	1	7.51	7.66
-10	0	2	3.20	-3.26
-9	-7	0	2.06	-1.85
-9	-7	1	3.55	3.41
-9	-7	2	0.75	-0.39
-9	-5	0	0.76	0.63
-9	-5	1	3.85	-3.66
-9	-5	2	0.75	-0.77
-9	-3	0	2.62	-2.61
-9	-3	1	3.39	3.00
-9	-3	2	3.31	3.43
-9	-3	3	1.74	1.03
-9	-1	0	0.78	0.26
-9	-1	1	0.00	0.41
-9	-1	2	1.16	-1.18
-9	-1	3	2.80	-2.37
-8	-8	0	0.79	1.08
-8	-8	1	6.30	6.43
-8	-8	2	3.07	-3.45
-8	-6	0	0.77	0.77
-8	-6	1	1.56	-1.63
-8	-6	2	1.29	1.28
-8	-6	3	0.77	-0.59
-8	-4	0	1.88	-1.80
-8	-4	1	3.18	2.94
-8	-4	2	1.36	1.37
-8	-4	3	0.78	0.85
-8	-2	0	1.23	1.10
-8	-2	1	6.58	-6.34
-8	-2	2	6.73	-6.70
-8	0	0	0.75	-0.01
-8	0	1	11.07	12.20
-8	0	2	7.74	7.79
-7	-11	0	2.92	3.13
-7	-9	0	0.77	-0.34
-7	-9	1	3.74	3.41
-7	-9	2	1.79	1.69
-7	-7	0	0.76	0.75
-7	-7	1	0.00	-0.42
-7	-7	2	3.93	3.44
-7	-7	3	0.78	0.70
-7	-5	0	1.33	-1.15
-7	-5	1	1.26	1.19
-7	-5	2	7.04	-6.94
-7	-3	0	6.47	5.99
-7	-3	1	3.04	-2.84
-7	-3	2	0.75	0.37
-7	-3	3	2.46	2.58
-7	-1	0	2.23	-1.88
-7	-1	1	2.88	2.46
-7	-1	2	0.73	-0.45
-7	-1	3	0.79	-1.08
-6	-10	0	7.65	7.58
-6	-10	1	1.54	-1.67
-6	-10	2	3.81	-3.68
-6	-8	0	8.31	-8.21
-6	-8	1	0.00	-0.02
-6	-8	2	4.74	4.76
-6	-8	3	3.62	-4.02
-6	-6	0	6.76	6.39
-6	-6	1	0.74	0.38
-6	-6	2	4.82	-4.80
-6	-6	3	1.35	1.45
-6	-4	0	1.14	1.12
-6	-4	1	2.54	-2.47
-6	-4	2	2.99	2.95
-6	-4	3	5.30	5.19
-6	-2	0	0.69	-0.24
-6	-2	1	0.63	0.20
-6	-2	2	7.93	-8.02
-6	-2	3	5.13	-5.23
-6	0	0	2.01	1.63
-6	0	1	1.22	-1.00
-6	0	2	8.91	9.00
-6	0	3	7.21	7.14
-5	-11	0	4.07	4.21
-5	-11	1	0.76	-0.71
-5	-11	2	4.93	-4.59
-5	-9	0	3.85	-3.65
-5	-9	1	2.61	-2.40
-5	-9	2	3.68	3.21
-5	-9	3	3.74	3.60
-5	-7	0	2.30	2.05
-5	-7	1	1.44	1.41
-5	-7	2	2.32	2.10
-5	-7	3	6.09	5.76
-5	-5	0	5.29	-4.88
-5	-5	1	5.57	-5.29
-5	-5	2	0.73	0.70
-5	-5	3	4.74	-4.73
-5	-3	0	9.23	9.33
-5	-3	1	3.05	2.73
-5	-3	2	6.86	-6.46
-5	-3	3	1.11	1.57
-5	-3	4	3.61	3.57
-5	-1	0	5.45	-4.31
-5	-1	1	3.42	-2.87
-5	-1	2	5.16	4.89
-5	-1	3	2.70	2.24
-5	-1	4	2.89	-2.75
-4	-12	0	1.74	-2.15
-4	-12	1	2.35	-2.27
-4	-12	2	0.75	0.08
-4	-10	0	4.21	4.20
-4	-10	1	8.38	8.45
-4	-10	2	0.77	1.01
-4	-10	3	3.14	-3.18
-4	-8	0	8.64	-8.59
-4	-8	1	11.37	-12.39
-4	-8	2	1.83	1.50
-4	-8	3	5.85	5.83
-4	-6	0	3.91	3.58
-4	-6	1	3.86	3.77
-4	-6	2	1.34	1.11
-4	-6	3	3.92	-4.27
-4	-4	0	2.63	-2.16
-4	-4	1	2.62	2.39
-4	-4	2	1.03	0.68
-4	-4	3	3.88	4.22
-4	-4	4	2.33	2.42
-4	-2	0	3.12	2.77
-4	-2	1	2.53	-2.29
-4	-2	2	2.76	2.30
-4	-2	3	6.63	-6.95
-4	-2	4	6.76	-7.38
-4	0	0	7.55	-7.45
-4	0	1	2.77	-2.12
-4	0	2	0.67	-0.36
-4	0	3	9.26	9.40
-4	0	4	6.09	5.93
-3	-13	0	2.86	-3.40
-3	-13	1	1.64	1.88
-3	-11	0	0.76	1.08
-3	-11	1	3.76	3.73
-3	-11	2	0.76	-0.17
-3	-11	3	5.37	-5.52
-3	-9	0	2.52	-2.11
-3	-9	1	4.35	-4.30
-3	-9	2	0.77	-0.97
-3	-7	0	1.67	-1.53
-3	-7	1	4.88	4.62
-3	-7	2	6.19	6.22
-3	-7	3	0.75	0.37
-3	-5	0	0.65	-0.43
-3	-5	1	5.40	-5.02
-3	-5	2	4.14	-4.27
-3	-5	3	0.72	-0.68
-3	-5	4	4.60	-4.73
-3	-3	0	2.73	-2.35
-3	-3	1	7.62	7.61
-3	-3	2	3.93	3.41
-3	-3	3	6.40	-6.47
-3	-3	4	2.04	2.19
-3	-1	0	1.21	-0.76
-3	-1	1	3.48	-2.95
-3	-1	2	1.05	0.75
-3	-1	3	3.36	3.06
-3	-1	4	1.15	-1.22
-2	-12	0	1.31	1.00
-2	-12	1	0.75	0.51
-2	-12	2	1.92	-2.05
-2	-10	0	2.98	-2.94
-2	-10	1	7.89	8.11
-2	-10	2	8.56	8.72
-2	-8	0	2.53	2.48
-2	-8	1	8.02	-8.10
-2	-8	2	10.53	-11.41
-2	-8	3	0.77	0.10
-2	-6	0	3.97	-3.52
-2	-6	1	4.51	3.97
-2	-6	2	4.72	4.61
-2	-6	3	0.72	0.55
-2	-6	4	2.36	-2.98
-2	-4	0	3.08	2.81
-2	-4	1	3.13	2.75
-2	-4	2	3.23	2.69
-2	-4	3	3.86	-3.63
-2	-4	4	5.94	2.87
-2	0	0	2.83	2.42
-2	0	1	8.15	-9.93
-2	0	2	1.17	-0.75
-2	0	3	1.51	1.05
-2	0	4	9.60	10.80
-1	-13	0	6.27	6.59
-1	-13	1	1.18	-1.11
-1	-13	2	0.74	-0.43
-1	-11	0	8.13	-8.38
-1	-11	1	3.35	3.25
-1	-11	2	2.75	2.70
-1	-11	3	0.76	-0.92
-1	-9	0	4.45	4.29
-1	-9	1	0.74	-0.44
-1	-9	2	5.22	-5.14
-1	-9	3	1.92	-1.72
-1	-7	0	7.08	6.53
-1	-7	1	0.69	0.73
-1	-7	2	1.85	1.86
-1	-7	3	3.24	3.42
-1	-5	0	5.24	-4.85
-1	-5	1	2.83	2.30
-1	-5	2	6.60	-6.18
-1	-5	3	5.98	-5.84
-1	-5	4	1.85	1.63
-1	-3	0	1.34	-1.45
-1	-3	1	1.19	-1.00
-1	-3	2	7.08	6.62
-1	-3	3	4.41	3.96
-1	-3	4	2.18	-1.70
-1	-1	0	3.97	3.83
-1	-1	1	2.24	1.98
-1	-1	2	5.07	-5.10
-1	-1	3	2.44	-2.11
-1	-1	4	3.11	2.96
0	-12	0	2.73	-2.97
0	-12	1	1.27	1.06
0	-12	2	1.27	-1.20
0	-10	0	4.43	4.20
0	-10	1	1.47	-1.41
0	-10	2	4.24	3.98
0	-8	0	0.71	0.65
0	-8	1	1.59	1.40
0	-8	2	9.19	-9.44
0	-8	3	7.95	-7.52
0	-6	0	1.77	1.22
0	-6	1	3.99	-3.51
0	-6	2	3.38	3.21
0	-6	3	6.93	6.67
0	-6	4	2.03	2.34
0	-4	0	5.33	4.47
0	-4	1	4.56	4.11
0	-4	2	2.79	-2.19
0	-4	3	0.69	-0.36
0	-4	4	2.44	-2.33
0	-2	0	7.62	-7.83
0	-2	1	4.11	-3.63
0	-2	2	4.46	3.80
0	-2	3	1.68	-1.43
0	-2	4	0.72	-0.18
0	0	1	2.72	2.06
0	0	2	9.46	-10.07
0	0	3	3.77	3.35
0	0	4	5.37	4.84
1	-13	1	4.19	4.31
1	-11	1	8.60	-8.71
1	-11	2	3.70	3.69
1	-11	3	5.24	5.65
1	-9	1	2.42	2.46
1	-9	2	0.78	-0.72
1	-9	3	2.60	-2.73
1	-7	1	3.84	3.07
1	-7	2	3.95	-3.44
1	-7	3	2.19	2.24
1	-5	1	7.51	-6.87
1	-5	2	1.62	1.43
1	-5	3	2.39	-2.39
1	-5	4	4.15	-4.29
1	-3	1	1.19	-0.93
1	-3	2	1.88	1.53
1	-3	3	9.75	8.93
1	-3	4	3.61	3.26
1	-1	1	0.49	0.16
1	-1	2	2.52	-1.87
1	-1	3	4.14	-3.23
2	-12	1	4.40	-4.47
2	-12	2	0.73	1.34
2	-10	1	0.00	0.11
2	-10	2	0.78	-0.75
2	-8	1	1.31	-0.77
2	-8	2	2.95	2.59
2	-8	3	5.15	-5.21
2	-6	1	0.63	0.24
2	-6	2	0.71	-0.69
2	-6	3	5.24	5.06
2	-6	4	3.66	3.39
2	-4	1	0.62	-0.07
2	-4	2	3.25	3.18
2	-4	3	2.35	-2.35
2	-4	4	2.72	-2.74
2	-2	1	10.66	-10.60
2	-2	2	3.74	-3.21
2	-2	3	5.94	5.53
2	-2	4	1.64	-1.58
2	0	1	10.05	13.39
2	0	2	6.27	5.83
2	0	3	5.90	-5.38
2	0	4	0.72	0.65
3	-13	1	4.47	4.42
3	-11	1	7.23	-7.34
3	-11	2	3.83	-3.35
3	-11	3	3.64	3.60
3	-9	1	4.55	4.45
3	-9	2	4.33	3.90
3	-7	1	2.57	2.21
3	-7	2	2.74	2.27
3	-7	3	3.17	-3.03
3	-5	1	4.83	-4.12
3	-5	2	2.88	-2.59
3	-5	4	3.40	-3.45
3	-3	1	0.62	0.17
3	-3	2	5.13	4.24
3	-3	3	1.68	1.66
3	-3	4	3.69	3.55
3	-1	1	0.90	1.05
3	-1	2	0.64	0.29
3	-1	3	2.43	-2.27
3	-1	4	3.63	-3.35
4	-12	1	1.74	1.89
4	-12	2	2.58	-2.94
4	-10	1	3.55	-3.83
4	-10	2	0.78	0.74
4	-10	3	0.77	-0.49
4	-8	1	6.03	5.91
4	-8	2	2.67	2.28
4	-6	1	0.00	-0.17
4	-6	2	1.48	0.91
4	-6	3	3.45	-3.37
4	-4	1	0.69	0.88
4	-4	2	1.29	0.93
4	-4	3	1.53	1.73
4	-4	4	1.91	-2.58
4	-2	1	3.07	-2.60
4	-2	2	7.97	-7.42
4	-2	3	4.29	-4.30
4	-2	4	4.19	4.44
4	0	1	7.51	7.34
4	0	2	11.55	13.37
4	0	3	2.24	2.52
4	0	4	6.09	-6.06
5	-11	1	3.76	3.75
5	-11	2	5.62	-5.86
5	-9	1	0.76	-0.16
5	-9	2	2.80	2.43
5	-9	3	0.00	0.47
5	-7	1	0.00	0.24
5	-7	2	0.76	0.23
5	-5	1	2.28	1.85
5	-5	2	2.51	-2.20
5	-5	3	3.10	-2.88
5	-3	1	2.19	1.75
5	-3	2	1.13	-0.75
5	-3	3	0.74	1.00
5	-1	1	0.67	0.54
5	-1	2	0.00	0.07
5	-1	3	0.77	-1.41
5	-1	4	0.76	-0.21
6	-10	1	4.21	4.26
6	-10	2	3.88	-4.25
6	-8	1	5.01	-4.71
6	-8	2	3.78	3.89
6	-8	3	1.47	1.34
6	-6	1	5.08	4.66
6	-6	2	3.37	-3.19
6	-4	1	2.95	-2.72
6	-4	2	0.77	-0.75
6	-4	3	2.32	2.35
6	-2	1	3.58	3.16
6	-2	2	3.82	-3.88
6	-2	3	5.77	-5.72
6	0	1	3.12	-2.90
6	0	2	3.60	3.96
6	0	3	7.74	8.34
7	-9	1	4.99	-4.37
7	-9	2	2.63	-2.58
7	-7	1	1.63	1.39
7	-7	2	0.77	0.64
7	-7	3	1.57	1.43
7	-5	1	4.56	-4.33
7	-5	2	0.79	-0.55
7	-3	1	6.60	6.24
7	-3	2	1.41	-1.02
7	-3	3	0.76	-0.13
7	-1	1	5.04	-4.60
7	-1	2	0.00	-0.48
7	-1	3	1.99	1.65
8	-8	1	7.54	-7.64
8	-8	2	4.31	-3.89
8	-6	1	3.55	2.73
8	-6	2	3.06	3.30
8	-6	3	1.15	-1.38
8	-4	1	1.77	-1.54
8	-4	2	1.52	-1.98
8	-2	1	0.78	-0.71
8	-2	2	2.95	2.71
8	0	1	2.33	-1.88
8	0	2	2.84	-2.48
9	-7	1	0.00	0.02
9	-5	1	1.22	-1.51
9	-5	2	2.32	-2.37
9	-3	1	2.36	2.47
9	-3	2	4.50	4.71
9	-3	3	0.75	-0.07
9	-1	1	2.12	-2.20
9	-1	2	0.79	-1.19
9	-1	3	0.00	0.34
10	-6	1	0.75	0.18
10	-4	1	0.77	0.01
10	-4	2	0.75	-0.26
10	-2	1	1.23	1.33
10	-2	2	1.59	1.71
10	0	1	0.77	-0.73
10	0	2	1.58	-1.17
11	-1	1	1.23	1.45

Table 2.4

Analysis of the agreement of $|F_o|$ and $|F_c|$ at the end of the refinement. N is the number of reflexions. Structure factors are on the absolute scale.

(a) As a function of sin θ/λ.

	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
0·0 - 0·3	244·71	227·73	29·82	64	0·122	0·47
0·3 - 0·4	293·58	276·52	24·27	82	0·083	0·30
0·4 - 0·5	481·18	470·12	37·17	139	0·077	0·27
0·5 - 0·7	337·40	332·17	30·72	130	0·091	0·24

(b) As a function of $|F_o|$.

	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
0·0 - 0·4	0·00	2·77	2·77	11	-	0·25
0·4 - 1·0	55·68	40·77	22·70	75	0·408	0·30
1·0 - 2·5	166·37	156·29	22·06	97	0·133	0·23
2·5 - 4·0	350·33	328·77	30·91	108	0·088	0·29
4·0 - 6·0	306·83	291·80	19·45	63	0·063	0·31
6·0 - 8·5	321·28	319·79	12·28	45	0·038	0·27
8·5 - 14·0	156·39	166·34	11·81	16	0·075	0·74
All	1356·88	1306·53	121·98	415	0·090	0·29

Table 2.5

$K^+\cdots O$ distances (Å) and $O\cdot\cdot K^+\cdot\cdot O$ angles (°).

	Neutron	X-ray
$K^+\cdots O(1^{I})$	2·771 (7)	2·773 (3)
$K^+\cdots O(2)$	2·856 (10)	2·859 (3)
$K^+\cdots O(2^{II})$	2·882 (10)	2·882 (3)
$O(1^{I})\cdot\cdot K^+\cdot\cdot O(1^{VI})$	109·1 (0·3)	109·1 (0·1)
$O(1^{I})\cdot\cdot K^+\cdot\cdot O(2)$	67·6 (0·2)	67·3 (0·1)
$O(1^{I})\cdot\cdot K^+\cdot\cdot O(2^{II})$	75·0 (0·2)	75·3 (0·1)
$O(1^{I})\cdot\cdot K^+\cdot\cdot O(2^{IV})$	119·3 (0·4)	118·5 (0·1)
$O(1^{I})\cdot\cdot K^+\cdot\cdot O(2^{V})$	127·1 (0·4)	128·0 (0·1)
$O(2)\cdot\cdot K^+\cdot\cdot O(2^{II})$	110·9 (0·2)	110·8 (0·1)
$O(2)\cdot\cdot K^+\cdot\cdot O(2^{IV})$	64·6 (0·3)	64·0 (0·1)
$O(2)\cdot\cdot K^+\cdot\cdot O(2^{V})$	157·3 (0·3)	157·2 (0·1)

Table 2.6

Bond lengths (Å) and angles (°).

	Neutron	X-ray
C(1) - H(2)	1·076 (12)	1·035 (49)
C(1) - C(2)	1·509 (4)	1·516 (4)
C(2) - O(2)	1·232 (5)	1·223 (4)
C(2) - O(1)	1·282 (6)	1·293 (4)
O(1)···O(1^{I})	2·479 (10)	2·459 (5)
C(2) - C(1) - H(2)	108·0 (0·6)	108·9 (2·6)
C(2) - C(1) - H(2^{III})	108·4 (0·7)	106·9 (2·7)
C(2) - C(1) - C(2^{III})	120·2 (0·4)	119·4 (0·4)
H(2) - C(1) - H(2^{III})	102·3 (1·0)	105·1 (3·8)
C(1) - C(2) - O(1)	112·8 (0·3)	112·5 (0·3)
C(1) - C(2) - O(2)	124·5 (0·4)	124·4 (0·3)
O(1) - C(2) - O(2)	122·6 (0·4)	123·1 (0·3)
C(2) - O(1)···O(1^{I})	111·8 (0·3)	111·7 (0·2)

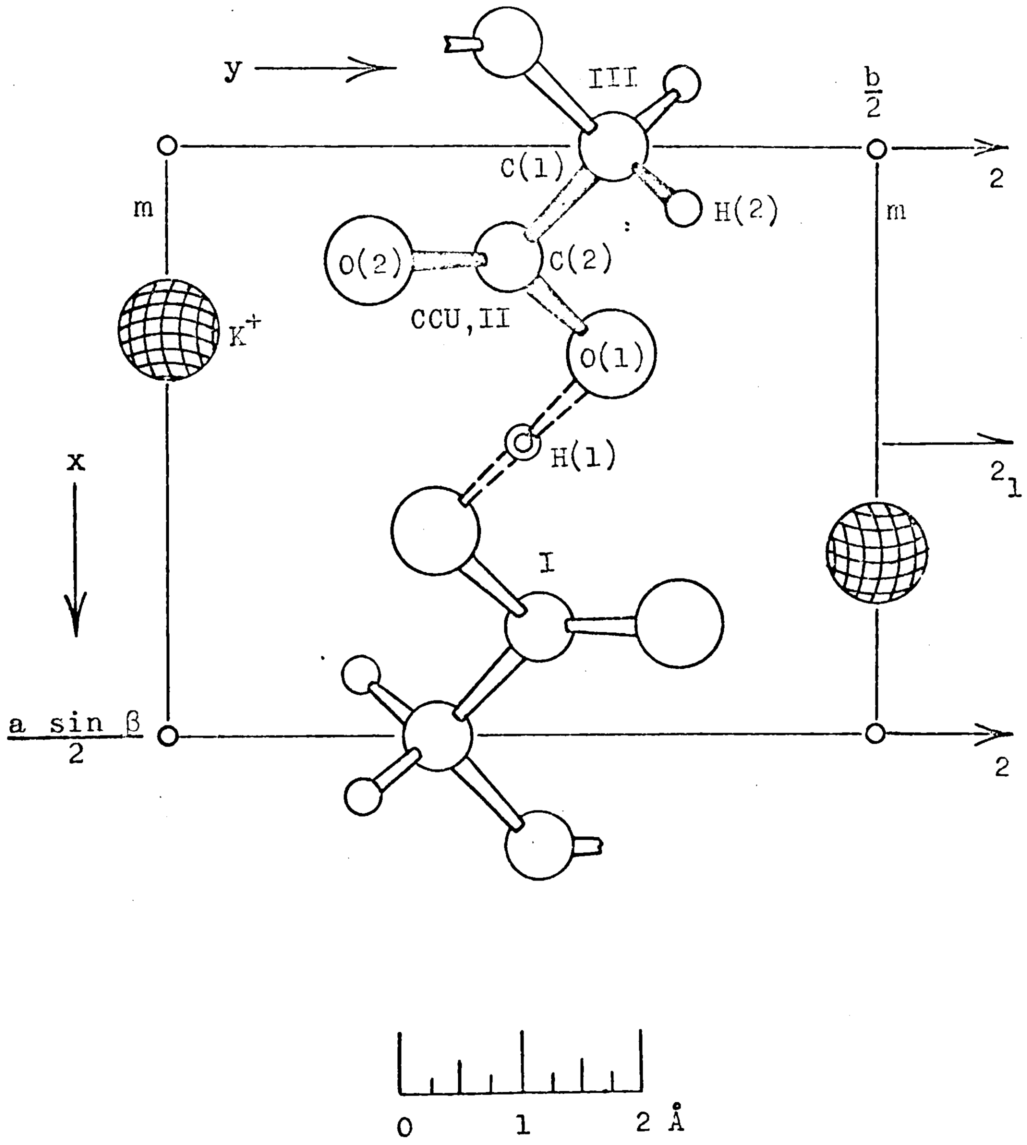

y
III
b/2
C(1)
2
m
H(2)
m
O(2)
C(2)
CCU,II
K+
O(1)
H(1)
x
2_1
I
a sin β/2
2
0
1
2 Å

Figure 2.1 The crystal structure of potassium hydrogen malonate as seen in its c-axial projection.

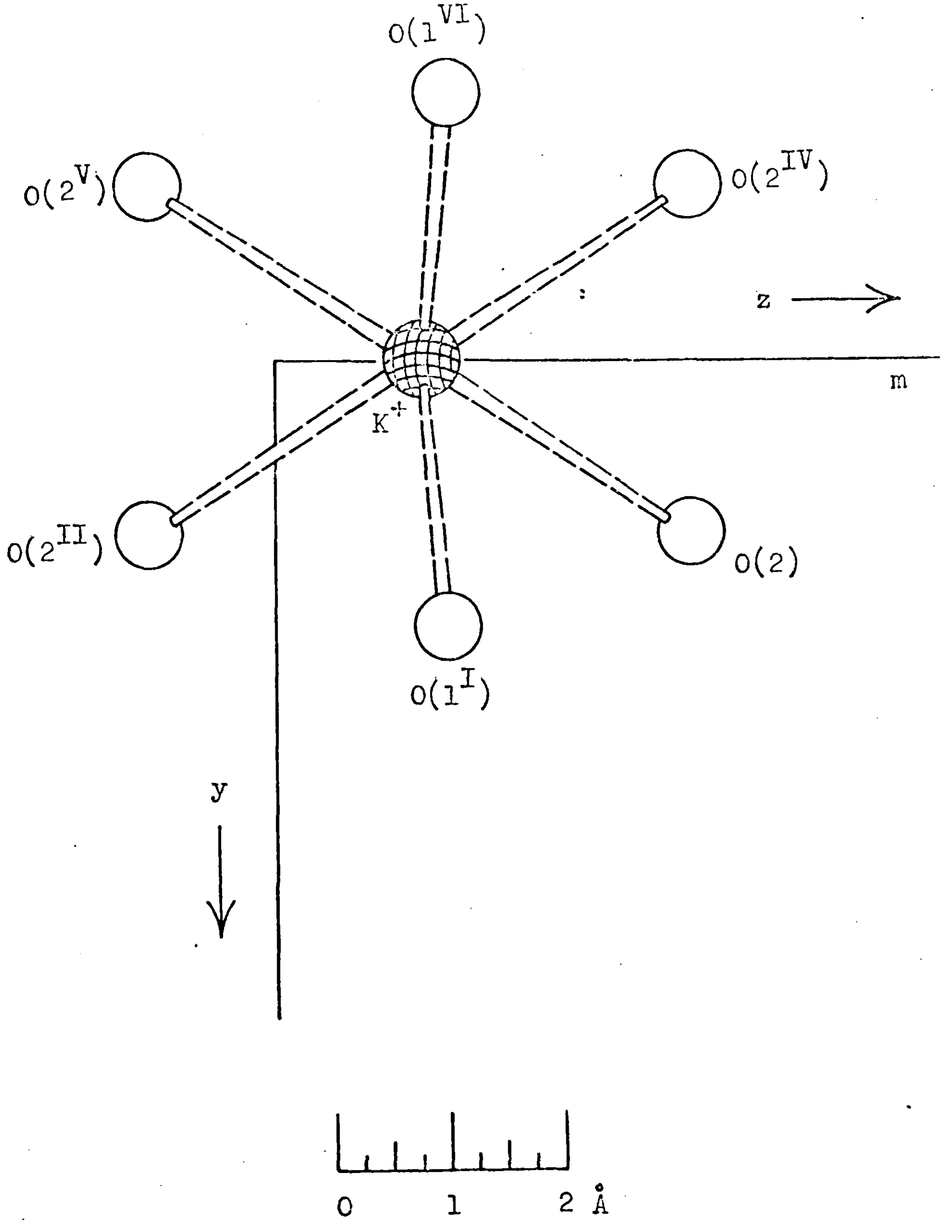

O(1^VI)
O(2^V)
O(2^IV)
z
m
K+
O(2^II)
O(2)
O(1^I)
y
0
1
2 Å

Figure 2.2 The environment of the potassium ion in potassium hydrogen malonate.

2.3 DISCUSSION

In the crystal structure of potassium hydrogen malonate, which is shown in Figure 2.1, the malonate residues, each of which has a two-fold axis of symmetry, are linked into infinite chains through hydrogen bonds lying across centres of inversion, whilst the potassium ion lies on a plane of symmetry.

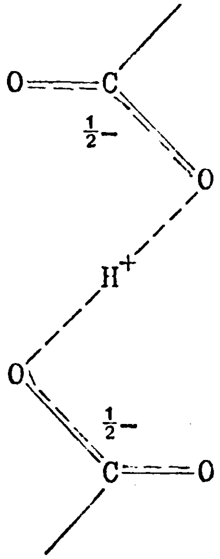
The environment of the potassium ion, which is coordinated to eight oxygen atoms, is shown in Figure 2.2, and in Table 2.5 the $K^+\cdots O$ distances and $O\cdots K^+\cdots O$ angles found by neutron diffraction are compared with those found by X-ray diffraction (Sime and Speakman, 1969); standard deviations are given in parentheses.

Bond lengths and angles in the malonate residue found by neutron diffraction are given in Table 2.6; those found by X-ray diffraction are also given. C(1), C(2), O(1) and O(2) are approximately coplanar, the equation of the plane through them being, in orthogonal coordinates,

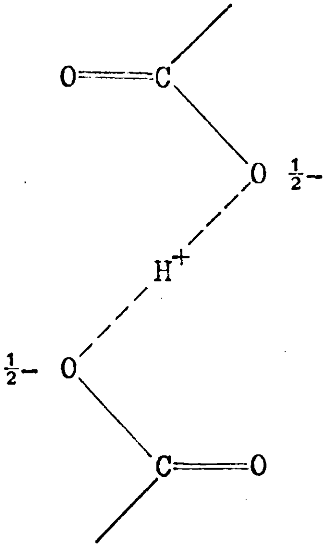
$$-0.692\,X' + 0.082\,Y - 0.717\,Z' = -3.104\ \text{Å}\ .$$

The dihedral angle between this plane and that through C(1), $C(2^{III})$, $O(1^{III})$ and $O(2^{III})$ is 9.4°.

In the carboxyl group the C(2)—O(1) and C(2)—O(2) bond lengths are, respectively, 1.282 (±6) Å and 1.232 (±5) Å. Their difference, 0.050 Å, implies some degree of charge delocalisation, viz.



rather than



The C(1)—H(2) distance found by neutron diffraction, viz. 1.076 (±12) Å, is greater than that found by X-ray diffraction, viz. 1.035 (±49) Å. Whilst their difference of 0.041 Å is not statistically significant it is nonetheless of interest to note that these results follow the general trend that C—H distances found by X-ray diffraction are consistently shorter than those found by neutron diffraction (Hamilton, 1962).

The O···O distance of the hydrogen bond, 2.479 (±10) Å by neutron diffraction and 2.459 (±5) Å by X-ray diffraction, is similar to those found in the Type A acid salts of monobasic acids (Speakman, 1967), and agrees well with that of the symmetrical hydrogen bond in potassium hydrogen succinate, viz. 2.446 (±4) Å (McAdam, 1969).

Neutron-scattering density and difference syntheses computed with limited two-dimensional data indicate that the potential function of the hydrogen bond has a double minimum, and this is also implied by the similarity of the $O \cdots O$ distance to those of some unsymmetrical hydrogen bonds, e.g. $O(2) \cdots O(9) = 2.472$ (±4) Å in ammonium tetroxalate (Appendix I). The acidic proton is therefore either statistically disordered or is undergoing vibrational motion in the potential well between the oxygen atoms; these possibilities are, however, indistinguishable crystallographically (Ibers, 1965). Similar results have been obtained from the structure analysis by neutron diffraction of the Type A acid salt potassium hydrogen di-aspirinate (Sequeira, Berkebile and Hamilton, 1967).

The shortest non-bonded intermolecular contacts in the structure are : $O(2) \cdots O(2^{IV}) = 3.053$ Å ; $O(1) \cdots O(2^{I}) = 3.132$ Å ; $O(1) \cdots C(2^{I}) = 3.186$ Å ; $O(1) \cdots C(1^{II}) = 3.533$ Å ; and $O(1) \cdots C(1^{VII}) = 3.621$ Å .

Whilst the results obtained by neutron diffraction are in excellent agreement with those obtained by X-ray diffraction, it is noteworthy that the U_{ij}'s derived from the neutron-diffraction analysis are consistently lower than those from the X-ray analysis (Table 2.2). This may be accounted for by the fact that no absorption corrections have yet been applied to the X-ray data (e.g. Hamilton, 1969), but could nevertheless be indicative of the inadequacy, when high accuracy is required, of using spherically symmetrical X-ray scattering factors calculated on the basis of free, non-bonded atoms (Coppens, 1969)

2.4 FUTURE WORK

Once all the neutron-diffraction data have been corrected for absorption, and further least-squares refinement carried out, an electron-density difference synthesis will be computed using the observed structure amplitudes from the X-ray analysis, also, if possible, corrected for absorption, and structure factors calculated from the neutron-diffraction parameters and spherically symmetrical X-ray scattering factors. In such a synthesis it should be possible to locate the bonding electrons; this was successfully done in a similar study of s-triazine, $C_3H_3N_3$, by Coppens (1967).

CHAPTER 3

AMMONIUM NICKEL SULPHATE HEXAHYDRATE

3.1 INTRODUCTION

The crystal structure of ammonium nickel sulphate hexahydrate, a member of the isomorphous series of Tutton salts (Tutton, 1916), was determined by Grimes, Kay and Webb (1963) from an X-ray analysis of the three axial projections.

As half the atoms in this structure are hydrogen atoms it was considered that a neutron-diffraction study would be of interest. Accordingly, neutron-diffraction data for the three axial projections were collected by Mr. N.A. Curry at A.E.R.E., Harwell in 1965. Using these data, very kindly supplied by Mr. Curry, it has been shown that the hydrogen atoms appear in their expected positions and that those of the ammonium ion are not disordered.

A useful supplement to this work would be the collection and refinement of full three-dimensional X-ray diffractometer data as the data used in the original X-ray analysis were limited in number.

3.2 EXPERIMENTAL

Crystal Data

The unit cell used in this analysis differs from that of Grimes et al. in that $\underline{a}$ and $\underline{c}$ have been interchanged. The space group is therefore $P\,2_1/c$ instead of $P\,2_1/a$, the alternative cells being symmetrically related by the transformation matrix $001/010/\bar{1}00$.

The following parameters were established by Grimes et al. :

Ammonium nickel sulphate hexahydrate, $(NH_4)_2Ni(SO_4)_2.6H_2O$,
F.W. = 395.0. Monoclinic, $\underline{a}$ = 6.239 (±1), $\underline{b}$ = 12.459 (±1),
$\underline{c}$ = 9.181 (±1) Å, β = 106.95° (±0.04°), $\underline{U}$ = 682.6 $Å^3$.
$\underline{D}_m$ = 1.923 (Tutton, 1916), $\underline{Z}$ = 2, $\underline{D}_x \doteq$ 1.922.
Space group $P\ 2_1/c$ (C^5_{2h}, No.14).
Linear absorption coefficient for neutrons ($\lambda \approx 1$Å), μ = 2.35 cm^{-1}.

Data Collection

Neutron-scattering structure amplitudes were measured on a spectrometer in the DIDO reactor at A.E.R.E., Harwell by Mr. N.A. Curry. These comprised 190 $0k\ell$, 96 $h0\ell$ and 149 $hk0$ reflexions, of which, respectively, 55, 18 and 25 were recorded as having zero intensity. Absorption corrections were applied to the $hk0$ data only.

Structure Analysis and Refinement

The starting point for the analysis was the set of fractional coordinates found by Grimes et al. for the non-hydrogen atoms. Regions of negative scattering density appeared in neutron-scattering density and difference syntheses of the three projections in positions where hydrogen atoms would be expected, and coordinates were obtained accordingly.

The number of data with non-zero structure amplitudes did not permit refinement of the parameters of all the atoms, and this being so only the hydrogen parameters were refined, the ratio of non-zero data to parameters then being approximately eight to one. The parameters of the non-hydrogen atoms used in the structure-factor calculations were those of Grimes et al. Nuclear scattering lengths used were : Ni, 1.03; S, 0.31; O, 0.577; N, 0.94; and H, -0.378×10^{-12} cm.

Three cycles of full-matrix least-squares refinement with unit weights reduced the R-value from 0.266 to 0.232, the corresponding values of R' being, respectively, 0.102 and 0.070. By this time parameter shifts were all less than one-third of their standard deviations and the refinement was therefore considered complete.

The data with observed structure amplitudes of zero were not included in the structure-factor calculations during the refinement, but when they were included in the final structure-factor calculation the values of R and R' obtained were, respectively, 0.320 and 0.114.

Final positional parameters are given for all the atoms in Table 3.1 and their final isotropic vibrational parameters in Table 3.2; estimated standard deviations are given in parentheses. Observed structure amplitudes and final calculated structure factors are given in Table 3.3 and their agreement analysed in Table 3.4.

The group of atoms whose parameters appear in these tables constitutes the crystal chemical unit (CCU) of the structure; the CCU is shown in Figure 3.1. Other symmetry-related units are denoted as follows :

CCU	x,	y,	z;				
I	$-1 + x$,	y,	z;	III	x,	$\frac{1}{2} - y$,	$-\frac{1}{2} + z$;
II	$1 - x$,	$\frac{1}{2} + y$,	$\frac{1}{2} - z$;	IV	$-1 + x$,	$\frac{1}{2} - y$,	$-\frac{1}{2} + z$.

TABLES AND DIAGRAMS

Table 3.1

Fractional ($x, y, z \times 10^3$) and orthogonal (X', Y, Z' in Å, $\times 10^2$) coordinates ($X' = ax \sin\beta$, $Y = by$, $Z' = ax \cos\beta + cz$).

(a) X-ray structure analysis (Grimes, Kay and Webb, 1963).

	x	y	z	X'	Y	Z'
Ni	0	0	0	0	0	0
S	741	136	409	442 (1)	169 (1)	241 (1)
N	348	347	133	208 (2)	432 (2)	59 (4)
O(1)	581	229	411	347 (2)	285 (2)	272 (4)
O(2)	951	179	383	568 (2)	223 (2)	179 (4)
O(3)	623	70	280	372 (2)	87 (2)	144 (4)
O(4)	780	73	549	466 (2)	91 (2)	362 (6)
O(10)	1020	394	333	609 (2)	491 (2)	120 (4)
O(20)	149	110	161	89 (1)	137 (2)	121 (4)
O(30)	700	65	-6	418 (2)	81 (2)	-133 (3)

(b) Neutron structure analysis.

	x	y	z	X'	Y	Z'
H(1)	418	305	235	249 (6)	380 (6)	140 (7)
H(2)	371	418	175	221 (4)	521 (4)	93 (4)
H(3)	208	339	63	124 (9)	422 (10	20 (10)
H(4)	440	334	81	263 (11)	416 (12)	-6 (12)
H(11)	990	313	361	591 (4)	390 (4)	151 (4)
H(12)	942	400	236	562 (4)	498 (4)	45 (5)
H(21)	92	115	247	55 (5)	143 (5)	210 (6)
H(22)	326	93	220	195 (8)	116 (7)	143 (8)
H(31)	679	143	-33	405 (5)	178 (5)	-154 (5)
H(32)	653	61	88	390 (7)	76 (6)	-38 (7)

Table 3.2

Isotropic vibrational parameters ($\text{Å}^2 \times 10^3$)

(a) X-ray structure analysis (Grimes, Kay and Webb, 1963).

	$\underline{U}_{iso}$		$\underline{U}_{iso}$
Ni	13	O(3)	25
S	13	O(4)	25
N	25	O(10)	25
O(1)	25	O(20)	25
O(2)	25	O(30)	25

(b) Neutron structure analysis.

	$\underline{U}_{iso}$		$\underline{U}_{iso}$
H(1)	59 (12)	H(12)	33 (8)
H(2)	31 (7)	H(21)	46 (10)
H(3)	82 (21)	H(22)	69 (18)
H(4)	99 (29)	H(31)	44 (9)
H(11)	34 (7)	H(32)	57 (14)

Table 3.3

Observed structure amplitudes and final calculated structure factors.

h	k	l	Fo	Fc
0	1	1	0.00	-0.06
0	2	1	2.90	-3.02
0	3	1	5.14	5.95
0	4	1	1.94	2.68
0	5	1	1.46	-1.29
0	6	1	5.09	-4.32
0	7	1	0.00	1.24
0	8	1	3.11	2.63
0	9	1	4.11	4.16
0	10	1	2.60	2.08
0	11	1	4.42	4.06
0	12	1	0.00	-1.24
0	13	1	1.84	-1.93
0	14	1	0.00	0.84
0	15	1	1.53	0.73
0	16	1	0.00	-0.00
0	17	1	2.20	1.99
0	18	1	2.29	-2.57
0	19	1	2.96	3.20
0	1	2	3.64	3.45
0	2	2	2.71	2.77
0	3	2	0.00	0.32
0	4	2	2.70	2.72
0	5	2	4.05	3.84
0	6	2	3.19	-2.75
0	7	2	0.84	-1.10
0	8	2	0.00	-0.32
0	9	2	1.78	-2.37
0	10	2	4.09	3.77
0	11	2	0.52	0.46
0	12	2	2.51	2.18
0	13	2	0.00	0.66
0	14	2	2.01	2.34
0	15	2	2.24	-1.28
0	16	2	1.73	2.12
0	17	2	0.00	0.63
0	18	2	0.00	0.65
0	19	2	2.26	1.07
0	1	3	1.88	1.98
0	2	3	0.82	-0.83
0	3	3	0.00	0.13
0	4	3	6.98	7.73
0	5	3	7.12	8.11
0	6	3	2.18	2.25
0	7	3	2.34	2.21
0	8	3	1.41	-0.86
0	9	3	6.19	-5.53
0	10	3	3.83	-4.58
0	11	3	1.47	0.24
0	12	3	1.51	-1.92
0	13	3	4.85	4.38
0	14	3	0.00	0.18
0	15	3	3.25	3.19
0	16	3	2.05	2.39
0	17	3	2.07	1.54
0	18	3	0.00	-1.13
0	19	3	0.00	0.42
0	1	4	2.03	1.73
0	2	4	6.54	7.76
0	3	4	5.16	-5.87
0	4	4	7.83	8.51
0	5	4	3.73	-3.39
0	6	4	2.95	-2.51
0	7	4	2.65	2.37
0	8	4	5.80	-5.23
0	9	4	3.65	4.44
0	10	4	1.05	0.33
0	11	4	1.12	0.97
0	12	4	2.87	2.22
0	13	4	0.00	-0.62
0	14	4	4.45	4.39
0	15	4	2.04	-1.27
0	16	4	0.00	4.43
0	17	4	1.97	-1.15
0	1	5	6.56	6.87
0	2	5	2.45	-1.40
0	3	5	2.02	-2.23
0	4	5	3.80	4.21
0	5	5	2.21	2.19
0	6	5	1.53	2.22
0	7	5	0.00	0.32
0	8	5	2.71	-3.29
0	9	5	1.42	1.91
0	10	5	2.24	-2.10
0	11	5	1.64	0.87
0	12	5	2.77	2.65
0	13	5	0.00	1.99
0	14	5	1.69	-2.02
0	15	5	0.00	0.46
0	16	5	0.00	-0.32
0	17	5	2.60	2.32
0	1	6	2.72	2.42
0	2	6	4.88	4.89
0	3	6	0.00	2.43
0	4	6	3.17	-3.60
0	5	6	1.42	-1.25
0	6	6	0.00	0.35
0	7	6	1.68	-0.10
0	8	6	2.51	2.45
0	9	6	0.00	-0.11
0	10	6	4.11	3.93
0	11	6	1.12	-0.86
0	12	6	0.00	0.58
0	13	6	0.00	0.01
0	14	6	1.91	-1.48
0	15	6	1.53	1.18
0	16	6	1.60	0.93
0	1	7	5.67	5.70
0	2	7	1.06	1.42
0	3	7	6.19	6.28
0	4	7	0.00	-0.59
0	5	7	4.93	-4.29
0	6	7	2.33	2.97
0	7	7	4.66	-4.35
0	8	7	2.00	-2.13
0	9	7	3.99	3.70
0	10	7	1.43	-1.19
0	11	7	0.00	0.11
0	12	7	0.00	0.32
0	13	7	2.31	2.34
0	14	7	0.00	-0.17
0	15	7	3.25	2.95
0	16	7	0.00	-0.48
0	17	7	3.84	2.99
0	1	8	6.62	-6.85
0	2	8	0.00	1.15
0	3	8	3.65	-2.29
0	4	8	2.08	1.12
0	5	8	0.00	0.58
0	6	8	4.80	5.00
0	7	8	0.00	0.05
0	8	8	0.00	-0.80
0	9	8	1.15	-0.19
0	10	8	2.57	-2.26
0	11	8	2.90	1.63
0	12	8	3.60	3.18
0	13	8	1.74	1.21
0	14	8	2.38	2.64
0	15	8	1.62	-0.60
0	16	8	0.00	0.84
0	1	9	0.00	-1.26
0	2	9	2.77	2.21
0	3	9	4.91	5.17
0	4	9	0.00	-0.17
0	5	9	3.27	2.84
0	6	9	1.42	-0.86
0	7	9	0.00	0.23
0	8	9	1.43	0.82
0	9	9	0.00	-0.15
0	10	9	1.99	0.94
0	11	9	0.00	0.36
0	12	9	2.80	-3.75
0	13	9	2.18	2.07
0	14	9	1.06	1.40
0	15	9	2.76	2.69
0	1	10	0.00	-1.71
0	2	10	0.00	-0.18
0	3	10	2.07	0.62
0	4	10	2.87	2.67
0	5	10	2.57	2.11
0	6	10	2.60	1.87
0	7	10	1.24	0.55
0	8	10	0.00	0.72
0	9	10	3.34	-2.61
0	10	10	0.00	0.71
0	11	10	0.00	0.56
0	12	10	1.19	0.59
0	1	11	5.30	5.25
0	2	11	0.00	-0.32
0	3	11	3.43	0.56
0	4	11	0.00	0.44
0	5	11	1.42	-0.63
0	6	11	0.00	-0.36
0	7	11	0.00	0.07
0	8	11	0.00	-0.34
0	9	11	1.73	-2.02
0	10	11	0.00	0.77
0	11	11	2.78	2.87
0	1	12	2.08	2.00
0	2	12	1.30	0.86
0	3	12	1.47	0.18
0	4	12	0.00	1.44
0	5	12	0.00	-0.84
0	6	12	0.00	-0.19
0	7	12	0.00	0.60
0	8	12	3.50	3.68
0	9	12	1.50	0.28
0	10	12	3.32	1.98
0	1	13	3.37	2.97
0	2	13	2.14	-1.51
-9	0	2	3.63	2.46
-8	0	2	1.43	-0.17
-7	0	2	2.31	1.35
-6	0	2	0.00	-2.58
-5	0	2	4.76	-3.13
-4	0	2	4.99	6.34
-3	0	2	5.73	6.40
-2	0	2	2.96	-1.48
-1	0	2	5.28	7.01
0	0	2	4.19	6.30
1	0	2	0.83	-1.56
2	0	2	3.81	3.52
3	0	2	0.00	-1.53
4	0	2	3.02	1.95
5	0	2	0.60	2.34
6	0	2	3.20	-1.50
7	0	2	0.00	1.51
8	0	2	2.48	-1.16
9	0	2	0.00	0.44
-9	0	4	0.00	1.29
-8	0	4	5.13	4.89
-7	0	4	4.26	2.67
-6	0	4	3.54	1.88
-5	0	4	4.37	5.11
-4	0	4	7.44	7.56
-3	0	4	2.50	2.76
-2	0	4	4.98	-4.76
-1	0	4	4.85	-2.84
0	0	4	4.70	-5.95
1	0	4	1.87	1.44
2	0	4	3.06	2.30
3	0	4	3.29	-1.79
4	0	4	0.00	1.73
5	0	4	1.39	-0.40
6	0	4	1.80	2.11
7	0	4	4.34	2.15
8	0	4	1.80	0.16
-9	0	6	0.00	0.94
-8	0	6	1.97	2.09
-7	0	6	1.83	0.74
-6	0	6	4.38	3.71
-5	0	6	1.63	-1.07
-3	0	6	3.11	3.07
-2	0	6	4.52	3.73
-1	0	6	1.66	-0.88
0	0	6	6.33	6.51
1	0	6	8.16	11.23
2	0	6	0.00	0.85
3	0	6	0.00	1.91
4	0	6	3.41	2.16
5	0	6	1.55	-0.97
6	0	6	5.67	5.54
7	0	6	1.94	2.92
-8	0	8	1.77	-0.50
-7	0	8	1.29	0.92
-6	0	8	1.37	-0.45
-5	0	8	5.39	-4.83
-4	0	8	2.70	-2.09
-3	0	8	4.51	4.22
-2	0	8	2.71	1.77
-1	0	8	5.28	-4.69
0	0	8	2.87	3.15
1	0	8	1.52	0.80
2	0	8	0.00	-2.53
3	0	8	6.51	5.95
4	0	8	2.47	-0.25
5	0	8	4.01	2.47
6	0	8	5.34	4.71
-8	0	10	0.00	-0.78
-7	0	10	4.16	4.35
-6	0	10	2.82	2.84
-5	0	10	1.55	-0.55
-4	0	10	5.26	6.05
-3	0	10	6.21	6.09
-2	0	10	1.99	1.28
-1	0	10	2.23	2.45
0	0	10	2.73	3.11
1	0	10	1.74	-0.36
2	0	10	4.17	4.00
3	0	10	0.00	1.09
4	0	10	0.00	-0.63
-7	0	12	0.00	6.41
-6	0	12	0.00	0.72
-5	0	12	4.30	3.75
-4	0	12	3.01	3.03
-2	0	12	3.92	2.46
-1	0	12	3.37	2.09
0	0	12	2.63	1.37
1	0	12	0.00	1.96
2	0	12	0.00	0.31
3	0	12	2.93	1.57
-5	0	14	0.00	0.86
-3	0	14	2.94	1.41
-2	0	14	1.81	0.23
-1	0	14	1.89	0.71
0	0	14	3.00	2.17
1	0	0	2.31	3.01
2	0	0	0.89	-1.05
3	0	0	3.32	3.53
4	0	0	0.00	2.35
5	0	0	5.66	4.31
6	0	0	0.00	2.13
7	0	0	3.02	2.29
9	0	0	3.68	0.70
1	1	0	3.01	3.53
2	1	0	1.60	-1.90
3	1	0	1.95	1.89
4	1	0	2.91	-3.95
5	1	0	5.03	5.79
6	1	0	0.00	0.25
7	1	0	2.79	-2.96
8	1	0	1.67	1.27
9	1	0	2.87	-1.84
0	2	0	2.50	3.14
1	2	0	2.82	3.10
2	2	0	0.00	-0.15
3	2	0	1.04	0.34
4	2	0	4.45	4.78
5	2	0	2.78	2.46
6	2	0	3.61	2.84
7	2	0	3.15	2.48
8	2	0	2.23	2.38
9	2	0	1.54	1.54
1	3	0	2.52	3.18
2	3	0	2.94	-2.61
3	3	0	3.91	-5.66
4	3	0	1.71	1.04
5	3	0	0.77	-0.63
6	3	0	2.92	0.52
7	3	0	2.76	-2.02
8	3	0	2.48	-2.28
9	3	0	1.48	-0.43
0	4	0	0.00	0.89
1	4	0	0.00	-0.63
2	4	0	3.51	3.71
3	4	0	1.79	0.86
4	4	0	1.30	0.58
5	4	0	1.49	0.51
6	4	0	1.45	-1.82
7	4	0	1.98	1.16
8	4	0	0.00	-1.26
9	4	0	3.07	1.04
1	5	0	4.30	6.43
2	5	0	6.89	-7.47
3	5	0	2.07	1.02
4	5	0	1.63	1.04
5	5	0	1.46	-4.67
6	5	0	2.02	1.28
7	5	0	0.00	0.75
8	5	0	0.00	-0.99
9	5	0	0.00	-0.27
0	6	0	1.89	-1.64
1	6	0	4.35	2.69
2	6	0	3.40	2.72
3	6	0	5.52	5.75
4	6	0	1.03	-1.25
5	6	0	2.45	-2.07
6	6	0	2.11	2.01
7	6	0	2.54	-2.58
8	6	0	1.52	0.57
9	6	0	2.34	0.43
1	7	0	1.27	0.36
2	7	0	5.04	5.55
3	7	0	2.48	1.63
4	7	0	0.00	0.45
5	7	0	3.36	2.42
6	7	0	2.35	0.77
7	7	0	4.27	2.43
8	7	0	2.91	2.50
0	8	0	2.81	1.97
1	8	0	1.90	0.85
2	8	0	3.15	4.25
3	8	0	1.51	0.88
4	8	0	2.51	1.40
5	8	0	4.65	3.96
6	8	0	3.58	2.79
7	8	0	3.59	4.23
8	8	0	3.05	3.09
1	9	0	4.81	-5.36
2	9	0	5.10	5.23
3	9	0	4.07	-1.00
4	9	0	2.48	-1.66
5	9	0	3.02	3.22
6	9	0	2.13	-2.37
7	9	0	1.52	-0.84
8	9	0	0.00	1.78
0	10	0	1.83	-2.24
1	10	0	4.87	5.40
2	10	0	2.56	3.02
3	10	0	2.96	-2.04
4	10	0	3.10	3.16
5	10	0	1.67	2.19
6	10	0	2.75	2.51
7	10	0	2.66	3.11
8	10	0	0.00	1.04
1	11	0	3.38	-3.24
2	11	0	3.13	-2.36
3	11	0	0.00	0.43
4	11	0	1.10	1.35
5	11	0	2.22	-1.67
6	11	0	1.56	-0.33
7	11	0	1.91	-0.15
0	12	0	3.51	3.25
1	12	0	1.14	1.45
2	12	0	1.34	1.57
3	12	0	2.29	2.85
4	12	0	0.00	0.91
5	12	0	1.72	1.54
6	12	0	0.93	1.36
7	12	0	0.00	-0.49
1	13	0	2.32	-1.93
2	13	0	0.00	-0.42
3	13	0	0.00	1.05
4	13	0	1.45	0.26
5	13	0	0.00	-0.98
6	13	0	0.00	0.58
7	13	0	1.61	0.70
0	14	0	3.32	4.10
1	14	0	2.46	-1.81
2	14	0	1.37	-1.74
3	14	0	2.70	2.58
4	14	0	1.94	1.36
5	14	0	1.93	1.20
6	14	0	0.00	-0.36
2	15	0	1.35	0.88
3	15	0	1.15	-0.58
4	15	0	2.66	-2.71
5	15	0	0.00	0.29
6	15	0	0.00	-0.10
0	16	0	2.16	2.18
2	16	0	0.96	-0.20
3	16	0	1.79	0.83
4	16	0	2.27	2.22
5	16	0	0.82	0.35
1	17	0	3.80	3.93
2	17	0	0.00	-0.35
3	17	0	0.74	-0.22
4	17	0	1.72	1.16
0	18	0	5.21	3.34
1	18	0	1.89	1.40
2	18	0	3.24	2.64
3	18	0	3.42	1.99
4	18	0	0.00	0.11
1	19	0	2.63	1.92
2	19	0	2.11	-1.54

Table 3.4

Analysis of the agreement of $|F_o|$ and $|F_c|$ at the end of the refinement. N is the number of reflexions. Structure factors are on the absolute scale.

	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
(a) For each projection.						
$0k\ell$	386·61	391·89	103·31	190	0·267	0·54
$h0\ell$	265·12	254·81	100·91	96	0·381	1·05
hk0	322·57	301·10	105·68	149	0·328	0·71
(b) As a function of sin θ/λ.						
0·00 - 0·30	176·52	192·11	38·63	59	0·219	0·65
0·30 - 0·45	233·66	238·36	55·57	79	0·238	0·70
0·45 - 0·50	230·14	232·86	80·31	115	0·349	0·70
0·60 - 0·80	307·51	284·50	131·05	182	0·426	0·72
(c) As a function of $\|F_o\|$.						
0·0	0·00	83·06	83·06	98	-	0·85
0·1 - 1·2	21·29	20·62	11·00	23	0·517	0·48
1·2 - 2·4	246·27	196·48	87·28	136	0·354	0·64
2·4 - 3·6	279·41	245·17	61·39	96	0·220	0·64
3·6 - 4·8	192·32	186·47	39·90	46	0·208	0·87
4·8 - 6·5	151·30	151·41	15·54	28	0·103	0·55
6·5 - 8·0	57·23	64·62	7·39	8	0·129	0·92
All	974·30	947·80	309·90	435	0·318	0·71

Table 3.5

Bond lengths (Å) and angles (°) involving the hydrogen atoms.

Bond	N - H	H···O	N···O	N - H···O
N - H(1)···O(1)	1·05(7)	1·89(7)	2·94(6)	172(6)
N - H(2)···O(3^{II})	0·96(5)	1·93(5)	2·88(4)	168(4)
N - H(3)···O(2^{IV})	0·93(9)	1·95(10)	2·86(4)	167(9)
N - H(4)···O(1^{III})	0·86(12)	2·15(12)	2·98(5)	162(11)

N(1) - N - H(2)	97(5)	H(2) - N - H(3)	112(7)
H(1) - N - H(3)	129(9)	H(2) - N - H(4)	111(9)
H(1) - N - H(4)	104(9)	H(2) - N - H(4)	104(10)

Bond	O - H	H···O	O···O	O - H···O
O(10) - H(11)···O(2)	1·07(5)	1·71(5)	2·77(4)	172(4)
O(10) - H(12)···O(4^{III})	0·88(6)	1·75(6)	2·63(6)	173(4)
O(20) - H(21)···O(2^{I})	0·96(7)	1·90(6)	2·81(3)	157(5)
O(20) - H(22)···O(3)	1·10(8)	1·80(9)	2·88(3)	149(7)
O(30) - H(31)···O(1^{III})	1·00(6)	1·73(6)	2·72(4)	168(5)
O(30) - H(32)···O(3)	0·99(7)	1·83(8)	2·80(5)	167(6)

H(11) - O(10) - H(12)	104(4)	H(31) - O(30) - H(32)	102(5)
H(21) - O(20) - H(22)	100(6)		

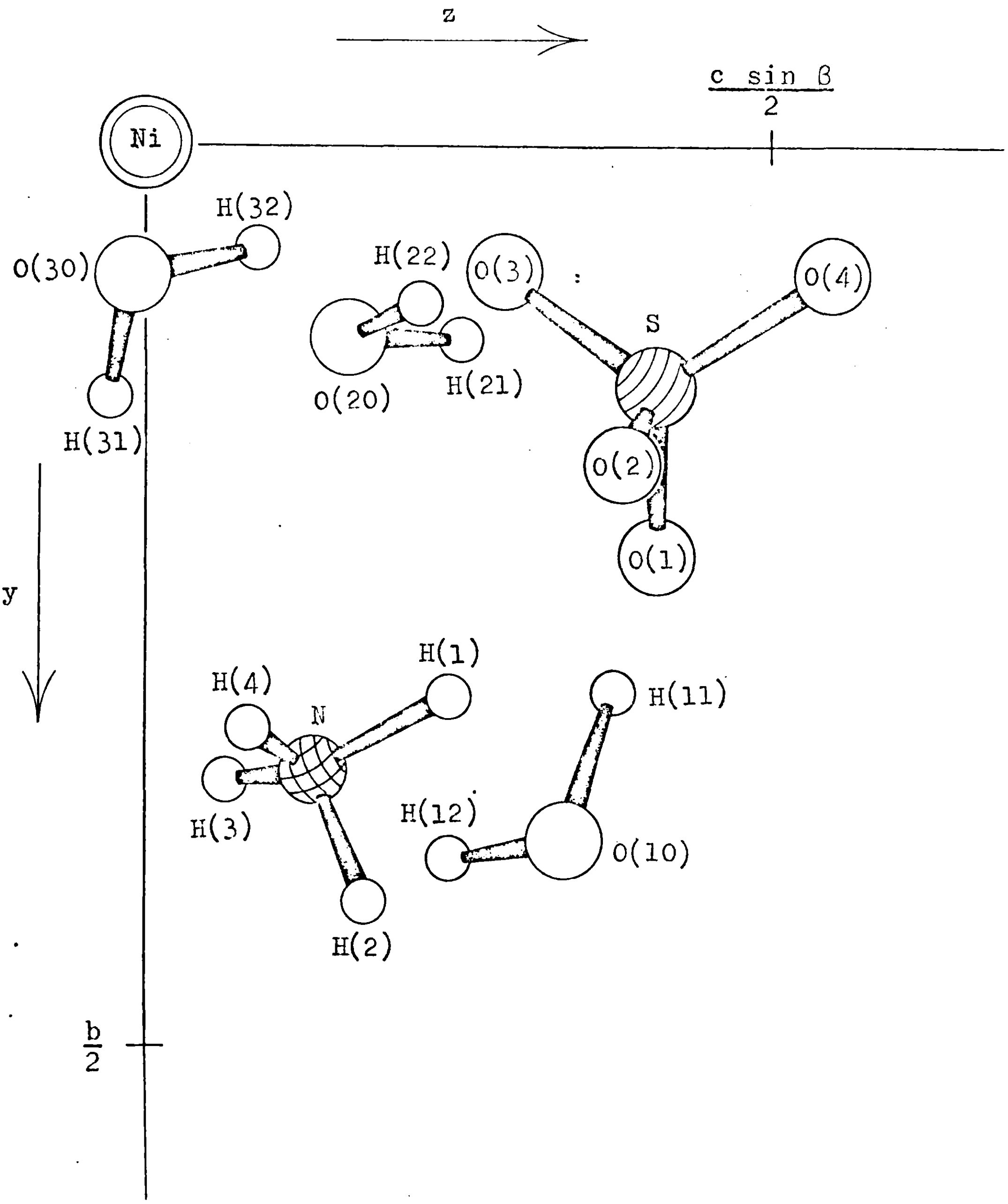

z
c sin β / 2
Ni
H(32)
O(30)
H(22)
O(3)
O(4)
S
O(20)
H(21)
H(31)
O(2)
O(1)
y
H(1)
H(4)
N
H(11)
H(12)
H(3)
O(10)
H(2)
b/2

Figure 3.1 The crystal chemical unit (CCU) of ammonium nickel sulphate hexahydrate.

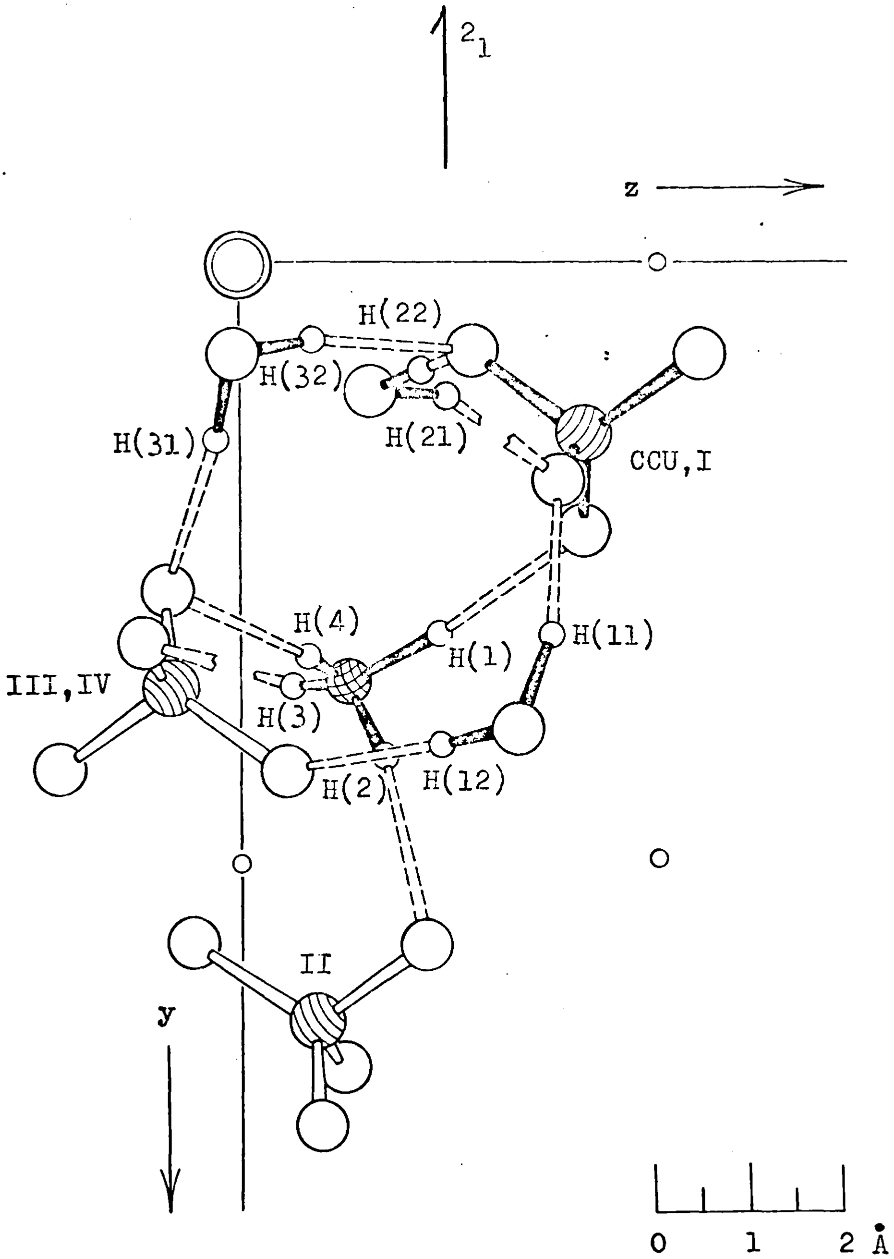

2_1
z
H(22)
H(32)
H(21)
H(31)
CCU,I
H(4)
H(1)
H(11)
III,IV
H(3)
H(2)
H(12)
II
y
0
1
2 Å

Figure 3.2 Hydrogen bonding in ammonium nickel sulphate hexahydrate.

3.3 DISCUSSION

The crystal structure of ammonium nickel sulphate hexahydrate is fully described by Grimes, Kay and Webb (1963). Its most striking feature, the intricate system of N—H···O and O—H···O hydrogen bonds, is shown in Figure 3.2 and details are listed in Table 3.5 (standard deviations are given in parentheses).

The structure analysis by neutron diffraction has shown that, in common with ammonium oxamate (Beagley and Small, 1963), ammonium acetate (Nahringbauer, 1967), and ammonium tetroxalate (Appendix I), there is no disorder of the hydrogen atoms of the ammonium ion, which is approximately tetrahedral, and there are four N—H···O hydrogen bonds, with N···O distances between 2.86 and 2.98 (each ± 10) Å to oxygen atoms of different sulphate groups.

Hydrogen bonding also takes place between the oxygen atoms of the water molecules and oxygen atoms of different sulphate groups, the O···O distances ranging from 2.63 to 2.88 (each ± 6) Å.

It is noteworthy that there are no hydrogen bonds between the ammonium ion and the water molecules, nor between the two water molecules, and that, of the four sulphate oxygen atoms, O(1), O(2) and O(3) are each involved in three hydrogen bonds, whilst the fourth, O(4), is involved in only one.

PART IV

CRYSTAL-STRUCTURE ANALYSES BY X-RAY DIFFRACTION

CHAPTER 1

1-METHYL-2-QUINOLONIUM DIHYDROGEN ARSENATE

1.1 INTRODUCTION

The crystalline basic salts (BHB^+X^-) of certain organic bases (B) contain short and apparently symmetrical hydrogen bonds (Mills and Speakman, 1963a). Such compounds have anomalous infra-red spectra, similar to those of Type A acid salts (Hadzi, 1962). On this basis, Cook (1963) recorded the spectra of a number of basic salts of $HAsF_6$ and other similar acids. Dr. Cook kindly provided specimens of these compounds for crystallographic studies in this department.

When the specimen supposed to be Q_2HAsF_6 (Q = 1-methyl-2-quinolone) was examined it was found to consist of a mixture of crystals of different habit, the major component of which could be described as "blocks" and the minor as "needles" (Plate). The latter were studied first as they seemed the more suitable for X-ray work.

Initially, in 1965, it was thought that both types of crystal were of the same compound, viz. the basic salt Q_2HAsF_6 ; however, before the structure analysis of the "needles" had proceeded very far, it was realised that they were of a different compound, which was eventually concluded to be an acid salt of the form $QH^+H_2AsO_4^-$. This was confirmed beyond doubt early in 1968 by the direct preparation of identical crystals from ortho-arsenic acid and 1-methyl-2-quinolone.

The crystal-structure analysis of the "blocks" has now also been carried out, and they have proved to be indeed the basic salt Q_2HAsF_6 (Calleri and Speakman, 1969).

Plate

Crystals of Q_2HAsF_6 ("blocks")
and QH_3AsO_4 ("needles").

1.2 EXPERIMENTAL

Preparation

1-Methyl-2-quinolone was prepared from quinoline and methyl iodide according to a method given by Decker (1893). I am very grateful to Professor J.D. Loudon for much helpful advice during the course of this preparation.

The acid salt (QH_3AsO_4) was easily prepared by adding an aqueous solution of ortho-arsenic acid ($H_3AsO_4 . \frac{1}{2}H_2O$) to solid 1-methyl-2-quinolone (Q) in an approximately 1:1 mole ratio. The crystals so obtained were identical, both morphologically and crystallographically, with the minor component of the material prepared by Dr. Cook.

Crystal Data

1-Methyl-2-quinolonium dihydrogen arsenate, $C_{10}H_{12}NO_5As$, F.W. = 301.1. M.p. = 132 - 136°C. Orthorhombic, $\underline{a}$ = 18.928 (±9), $\underline{b}$ = 12.717 (±6), $\underline{c}$ = 4.875 (±2) Å, $\underline{U}$ = 1173.5 $Å^3$. $\underline{D}_m$ = 1.72 (by flotation), $\underline{Z}$ = 4, $\underline{D}_x$ = 1.707. F(000) = 608.
Space group $P\,na2_1$ (C_{2v}^9, No.33), from systematic absences.
Linear absorption coefficient for CuKα radiation, $\mu = 44\ cm^{-1}$.

Crystallographic Measurements

Cell dimensions were derived by means of a least-squares treatment of high-order reflexions whose positions on hk0 and $0k\ell$ Weissenberg photographs, taken with CuKα ($\lambda = 1.5418$ Å) and CuKα_1 ($\lambda = 1.5405$ Å) radiation, were compared with those for lines due to Al wire ($a = 4.04907$ Å).

All the intensity data used in this analysis were estimated from series of multiple-film equatorial and equi-inclination Weissenberg photographs, taken with CuKα radiation, by visual comparison with a calibrated intensity strip. The intensities were corrected for Lorentz, polarisation and rotation factors, but no corrections for absorption were applied.

Initially 578 intensities were obtained from photographs of the reciprocal nets hk0 to hk3. At this stage no account was taken of "unobserved" reflexions.

At a later date hk4 data were collected from another crystal and at the same time the original photographs of the hk0 to hk3 reciprocal nets were re-estimated. The "unobserved" reflexions, of which there were 315, were each assigned a value equal to one-half of the minimum observable intensity. A total of 1227 independent structure amplitudes were obtained in this way.

Finally, once the salt had been prepared directly and a plentiful supply of crystals was available, a crystal was mounted to rotate about the a-axis and data collected from the reciprocal nets $0k\ell$ to $3k\ell$. This enabled all the data to be placed on a common scale, as well as providing additional data, mainly from the hk5 and hk6 reciprocal nets. A total of 1281 independent reflexions, of which 321 were "unobserved", were thus made available for the final stages of the refinement.

Preliminary Work

Prior to the collection of three-dimensional data this structure was studied in the centrosymmetric c-axial projection (Currie, 1965). The x- and y-coordinates of the arsenic atom were determined from a Patterson synthesis, and in the subsequent electron-density synthesis all the atoms of one quinolone ring were located. The environment of the arsenic atom was, however, less well-defined.

At this point it was concluded that the crystals were not of the basic salt Q_2HAsF_6 (Q = 1-methyl-2-quinolone), but of a compound of the form $QAsF_5$ or $QHAsF_6$.

Initial Postulated Structures and their Refinement

A three-dimensional electron-density synthesis was computed from limited hk0 to hk3 data. With only the arsenic atom, in position $(x, y, \frac{1}{4})$, contributing in the structure-factor calculation, pseudo-symmetry was encountered, each atom (other than arsenic) being accompanied by a "ghost" due to the effect of a mirror at $z = \frac{1}{4}$. Nevertheless, a consistent set of z-coordinates for the atoms of the quinolone ring was easily obtained from the synthesis.

As a result of the pseudo-symmetry the environment of the arsenic atom was somewhat confused, and it was not possible to reach a definite conclusion regarding either the number or positions of the atoms concerned, although the source of the crystals implied that there should be six fluorine atoms octahedrally coordinated to the arsenic atom. If this were so the compound would have been a salt of the form $QH^{+}AsF_{6}^{-}$, which was chemically reasonable.

However, from electron-density and difference syntheses calculated on the basis of all the atoms whose positions had been determined, it appeared that there were only four, rather than six, atoms coordinated to the arsenic atom. Pseudo-symmetry was still present in this region and "real" and "pseudo" atoms could not be distinguished until further syntheses were computed from more complete hk0 to hk4 data.

From the heights of the peaks in these syntheses it was concluded that the four atoms, which were tetrahedrally coordinated to arsenic, could be fluorines. Nevertheless, this was eventually rejected as unlikely, since $As^{V}F_{4}^{+}$ would require a negatively charged quinolone system, whilst a trigonal pyramidal, rather than tetrahedral, arrangement would be expected for $As^{III}F_{4}^{-}$.

It was still expected from the origin of the crystals that at least some of the atoms were fluorines, and after further deliberation it was concluded that three of the atoms coordinated to arsenic were fluorines and the fourth oxygen. The compound would thus be a neutral adduct of 1-methyl-2-quinolone and arsenyl trifluoride. Owing to the very similar scattering properties of oxygen and fluorine it was difficult to decide from electron-density and difference syntheses which atoms were oxygen and which fluorine. Indeed, a disordered structure, with one oxygen and three fluorine atoms randomly distributed among the four positions, was considered. However, as one As—X (X = O or F) distance was shorter than the others, it was concluded that this atom was oxygen and refinement was subsequently carried out on this basis.

After refinement by electron-density syntheses the value of R was 0.177 , and this was reduced to 0.118 by three cycles of full-matrix least-squares refinement with isotropic vibrational parameters and unit weights. A further five cycles of block-diagonal least-squares refinement with anisotropic vibrational parameters and a weighting scheme reduced R to 0.105. By this time the shifts in positional parameters were all less than one-sixth of their standard deviations, and those in vibrational parameters less than one-third of their standard deviations; the refinement was therefore considered complete.

Calculations of molecular geometry, however, revealed some remarkably short intermolecular contacts involving the atoms attached to arsenic and the quinolone oxygen, and also some other apparently anomalous bond lengths in the quinolone system, which implied that the model, viz. $QAsOF_3$, was incorrect.

At this point the possibility that only one, or two, of the atoms coordinated to arsenic were fluorines, the remainder being oxygens, was considered, but it was finally concluded that all four were most likely to be oxygen atoms. The compound would thus almost certainly be an acid salt of the form $QH^+H_2AsO_4^-$, and this was confirmed absolutely by the preparation of crystals identical to the original material from ortho-arsenic acid and 1-methyl-2-quinolone.

Refinement of the True Structure

Scarcity of the original crystals had prevented not only an analysis for fluorine being carried out, but also the collection of other than c-axial data. The latter was now remedied by the collection of $0k\ell$ to $3k\ell$ data which were used to place all the data on a common scale, as well as providing some additional data. Subsequent refinement was carried out with 1281 independent $|F_o|$ values.

The refinement was restarted from the parameters obtained from the final cycle carried out on the basis that the structure was $QAsOF_3$. Three cycles of block-diagonal least-squares refinement, with anisotropic vibrational parameters and a simple weighting scheme, of the form,

$$\sqrt{w} = 1 \text{ for } |F_o| < p, \ \sqrt{w} = \frac{p}{|F_o|} \text{ for } |F_o| > p$$

with p set at 20, reduced the value of R from 0.147 to 0.121. Further refinement was carried out with the weighting scheme which had been used originally, viz.

$$\sqrt{w} = \left\{[1 - \exp(-p_1(\frac{\sin\theta}{\lambda})^2)]/[1 + p_2|F_o| + p_3|F_o|^2 + p_4|F_o|^3]\right\}^{\frac{1}{2}}$$

in which $p_1 = 500$, $p_2 = 0.0125$, $p_3 = 0.0003$ and $p_4 = 0.00003$, but this did not reduce R significantly. The adequacy of this weighting scheme was demonstrated by the uniformity of the average value of $w\Delta^2$ over various ranges of $\sin\theta$ and $|F_o|$.

The positions of the six hydrogen atoms attached to the carbon atoms of the quinolone cyclic system were derived from geometrical considerations and were included in the structure-factor calculations of the final three cycles of refinement. Each hydrogen atom was assumed to have an isotropic vibrational parameter equal to the average of the U_{ii}'s of the carbon atom to which it was attached. The hydrogen parameters were not refined. The value of R was reduced to 0.119, the corresponding value of R' being 0.022.

By this time shifts in positional and vibrational parameters were all less than one-eighth of their standard deviations, and the refinement was therefore considered complete.

The course of the analysis is summarised in Table 1.1. Final positional parameters are given in Table 1.2 and final vibrational parameters in Table 1.3. Estimated standard deviations derived from the inverse of the least-squares matrix are given in parentheses. Observed and final calculated structure amplitudes are given in Table 1.4 and their agreement analysed in Table 1.5. For the structure-factor calculations the atomic scattering factors used were from International Tables, Volume III (1962).

The group of atoms whose parameters appear in these tables constitutes the crystal chemical unit (CCU) of the structure; the CCU is shown in Figure 1.1. Other symmetry-related units are denoted as follows :

CCU	x,	y,	z;				
I	x,	y,	-1 + z;	V	1 - x,	- y,	$-\frac{1}{2}$ + z;
II	x,	y,	1 + z;	VI	1 - x,	- y,	$\frac{1}{2}$ + z;
III	- x,	- y,	$-\frac{1}{2}$ + z;	VII	$-\frac{1}{2}$ + x,	$\frac{1}{2}$ - y,	z;
IV	- x,	- y,	$\frac{1}{2}$ + z;	VIII	$\frac{1}{2}$ - x,	$\frac{1}{2}$ + y,	$\frac{1}{2}$ + z;
IX	$\frac{1}{2}$ - x,	$-\frac{1}{2}$ + y,	$-\frac{1}{2}$ + z.				

TABLES AND DIAGRAMS

Table 1.1

Course of the analysis.

(1) Fourier refinement.

Cycle	Atoms in structure-factor calculation	Number of data	R
1	As	578	0·32
2	As + O + N + 10C	578	0·22
3	As + 4F + O + N + 10C	578	0·17
4	As + F + 4O + N + 10C	1227	0·18

(2) Least-squares refinement.

(a) Atoms: As + F + 4O + N + 10C

Number of data: 1227

Cycles	Final R	Final R'	Notes
1 - 3	0·118	0·018	Isotropic, unit weights.
4 - 8	0·105	0·018	Anisotropic, weighting scheme.

(b) Atoms: As + 5O + N + 10C

Number of data: 1281

Cycles	Final R	Final R'	Notes
1 - 4	0·121	0·021	Anisotropic, simpler weighting scheme.
5 - 8	0·121	0·022	Anisotropic, original weighting scheme.
9 - 11	0·119	0·022	Anisotropic, original weighting scheme, six quinolone hydrogen atoms included in structure-factor calculations.

Table 1.2

Fractional ($x,y,z \times 10^5$) and orthogonal ($X,Y,Z \times 10^3$) coordinates.

	x	y	z	X	Y	Z
As	6986	12111	125000	1322(1·5)	1540(1·5)	6094
O(1)	2855	19523	100753	540(14)	2483(12)	4912(17)
O(2)	15012	17400	132882	2842(12)	2213(14)	6478(12)
O(3)	8592	204	111371	1626(12)	26(11)	5429(16)
O(4)	1889	11960	152432	358(13)	1521(14)	7431(17)
O(11)	23898	19819	95621	4523(12)	2520(11)	4662(15)
N	31870	16072	62704	6032(13)	2044(14)	3057(18)
C(2)	26753	13136	78415	5064(16)	1671(16)	3823(32)
C(3)	24398	2400	79240	4618(15)	305(15)	3863(18)
C(4)	27596	-4546	61628	5223(18)	-578(19)	3004(24)
C(5)	36342	-8750	25846	6879(17)	-1113(17)	1260(32)
C(6)	41616	-4900	7861	7877(15)	-623(22)	383(26)
C(7)	43644	5629	8497	8261(18)	716(24)	414(25)
C(8)	40531	12330	24494	7672(20)	1568(18)	1194(36)
C(9)	35398	9198	44891	6700(15)	1170(17)	2188(22)
C(10)	33098	-1417	43949	6265(15)	-180(16)	2143(17)
C(11)	34032	27354	63198	6442(20)	3479(18)	3081(28)
H(3)	20337	13	92729	3849	2	4521
H(4)	25916	-12449	61253	4905	-1583	2986
H(5)	34943	-16757	26197	6614	2131	1277
H(6)	43939	-10066	-6572	8317	1280	-3204
H(7)	47907	8210	-4165	9068	1044	-2030
H(8)	41845	20381	22630	7920	2592	11032

Table 1.3

Vibrational parameters ($\mathring{A}^2 \times 10^3$).

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{23}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
As	58(1)	58(1)	37(1)	0(2)	3(2)	7(1)
O(1)	95(9)	53(6)	61(9)	18(14)	-41(18)	45(13)
O(2)	66(7)	83(8)	28(7)	-5(11)	-6(11)	-49(13)
O(3)	61(6)	47(6)	60(8)	-18(12)	-7(14)	24(10)
O(4)	57(7)	104(11)	48(9)	-29(15)	39(14)	-2(12)
O(11)	69(7)	48(6)	60(9)	-14(12)	34(13)	-7(10)
N	56(7)	54(7)	52(9)	-2(14)	30(15)	5(12)
C(2)	55(8)	64(9)	59(15)	19(20)	18(21)	50(13)
C(3)	58(7)	56(7)	28(9)	13(13)	5(15)	-6(13)
C(4)	63(9)	62(10)	61(12)	-12(19)	19(20)	-9(15)
C(5)	61(8)	62(9)	80(14)	-43(28)	59(25)	20(14)
C(6)	38(7)	99(14)	70(14)	-41(25)	-19(18)	49(16)
C(7)	59(10)	99(15)	51(13)	-4(24)	36(19)	-10(18)
C(8)	63(9)	85(12)	74(16)	4(26)	-100(29)	-8(17)
C(9)	47(7)	55(8)	65(14)	-1(18)	33(17)	-11(13)
C(10)	57(8)	55(8)	31(9)	-17(14)	12(14)	11(13)
C(11)	74(11)	50(9)	88(17)	-6(20)	-14(24)	-29(16)

	$\underline{U}_{iso}$		$\underline{U}_{iso}$
H(3)	46	H(6)	69
H(4)	62	H(7)	69
H(5)	67	H(8)	77

Table 1.4

Observed and final calculated structure amplitudes.

h	k	l	Fo	Fc
3	16	0	6.3	5.4
2	16	0	7.2	8.6
1	16	0	3.0	1.1
0	16	0	9.6	9.1
6	15	0	5.3	6.3
5	15	0	3.9	2.0
4	15	0	8.6	8.6
3	15	0	4.2	2.3
2	15	0	9.0	8.9
1	15	0	6.1	7.8
10	14	0	10.5	2.2
9	14	0	4.0	2.9
8	14	0	4.3	0.6
7	14	0	4.5	2.0
6	14	0	4.7	2.2
5	14	0	14.5	13.7
4	14	0	4.9	1.1
3	14	0	16.7	15.2
2	14	0	5.1	2.3
1	14	0	9.6	8.5
0	14	0	6.3	3.8
12	13	0	4.0	3.6
11	13	0	4.3	1.7
10	13	0	4.6	4.3
9	13	0	9.8	7.8
8	13	0	5.1	2.1
7	13	0	9.8	9.5
6	13	0	5.4	6.3
5	13	0	5.5	2.8
4	13	0	10.4	10.0
3	13	0	5.6	5.5
2	13	0	5.6	3.7
1	13	0	19.1	17.4
14	12	0	4.0	7.5
13	12	0	10.8	2.7
12	12	0	4.8	5.8
11	12	0	5.1	5.3
10	12	0	7.5	6.0
9	12	0	5.5	4.2
8	12	0	13.1	13.6
7	12	0	5.7	5.0
6	12	0	29.2	28.1
5	12	0	10.1	8.8
4	12	0	11.7	12.0
3	12	0	7.2	6.0
2	12	0	15.0	14.2
1	12	0	10.2	10.2
0	12	0	28.8	25.0
15	11	0	12.0	8.7
14	11	0	4.8	0.4
13	11	0	5.1	2.1
12	11	0	12.0	10.9
11	11	0	5.6	1.5
10	11	0	17.9	15.0
9	11	0	20.4	17.6
8	11	0	5.9	4.8
7	11	0	5.9	3.1
6	11	0	24.9	21.5
5	11	0	5.9	4.9
4	11	0	27.0	23.6
3	11	0	5.9	3.1
2	11	0	27.2	26.5
1	11	0	10.1	8.5
18	10	0	7.0	6.2
17	10	0	13.7	11.6
16	10	0	4.6	0.2
15	10	0	4.9	1.6
14	10	0	5.3	2.4
13	10	0	11.0	8.4
12	10	0	5.7	6.7
11	10	0	18.7	15.9
10	10	0	9.3	7.2
9	10	0	19.0	17.6
8	10	0	5.9	2.9
7	10	0	15.5	13.4
6	10	0	11.6	8.5
5	10	0	45.7	43.3
4	10	0	5.7	2.7
3	10	0	34.6	33.4
2	10	0	13.2	11.3
1	10	0	13.8	11.0
0	10	0	25.3	26.3
19	9	0	10.2	7.8
18	9	0	4.2	5.6
17	9	0	4.7	4.2
16	9	0	9.6	5.8
15	9	0	15.3	13.5
14	9	0	5.7	2.5
13	9	0	18.9	17.1
12	9	0	11.8	10.8
11	9	0	11.8	9.9
10	9	0	26.1	24.9
9	9	0	20.1	17.4
8	9	0	5.7	6.1
7	9	0	49.4	47.9
6	9	0	11.1	8.2
5	9	0	19.3	19.3
4	9	0	19.4	21.3
3	9	0	15.1	12.7
2	9	0	14.9	13.5
1	9	0	54.4	50.3
20	8	0	8.8	7.6
19	8	0	4.1	1.6
18	8	0	4.7	0.7
17	8	0	5.1	3.4
16	8	0	12.2	10.6
15	8	0	5.7	6.8
14	8	0	21.4	19.7
13	8	0	5.9	3.3
12	8	0	27.6	24.3
11	8	0	5.8	2.9
10	8	0	5.7	1.9
9	8	0	5.6	4.7
8	8	0	43.5	42.0
7	8	0	5.4	3.7
6	8	0	47.5	45.0
5	8	0	22.6	22.4
4	8	0	18.0	16.6
3	8	0	13.9	12.5
2	8	0	41.2	38.4
1	8	0	4.8	3.1
0	8	0	55.2	52.6
21	7	0	4.6	4.6
20	7	0	9.0	9.2
19	7	0	4.6	3.1
18	7	0	18.8	16.4
17	7	0	5.5	3.6
16	7	0	16.2	14.4
15	7	0	25.6	24.8
14	7	0	18.6	13.7
13	7	0	20.6	19.1
12	7	0	13.6	10.4
11	7	0	5.7	4.0
10	7	0	42.5	39.4
9	7	0	16.8	14.7
8	7	0	12.7	12.0
7	7	0	31.5	32.4
6	7	0	29.9	24.4
5	7	0	47.2	45.0
4	7	0	63.4	58.5
3	7	0	23.0	20.4
2	7	0	15.9	15.6
1	7	0	48.2	44.7
22	6	0	3.1	1.0
21	6	0	4.0	1.3
20	6	0	4.6	0.9
19	6	0	18.1	17.6
18	6	0	5.4	1.3
17	6	0	13.9	14.2
16	6	0	5.9	2.3
15	6	0	20.4	19.4
14	6	0	16.6	15.2
13	6	0	14.1	11.8
12	6	0	14.9	11.3
11	6	0	38.4	38.0
10	6	0	5.3	5.3
9	6	0	52.7	53.8
8	6	0	4.8	2.7
7	6	0	12.3	11.0
6	6	0	4.5	5.4
5	6	0	33.4	34.5
4	6	0	16.2	14.6
3	6	0	79.9	77.8
2	6	0	29.2	24.0
1	6	0	44.4	41.8
0	6	0	30.1	26.0
22	5	0	3.6	2.3
21	5	0	20.7	18.1
20	5	0	16.2	14.2
19	5	0	5.3	2.7
18	5	0	8.0	8.1
17	5	0	14.8	14.5
16	5	0	20.7	18.7
15	5	0	30.5	27.6
14	5	0	10.0	8.4
13	5	0	8.0	8.9
12	5	0	30.3	28.0
11	5	0	25.7	23.6
10	5	0	29.5	29.6
9	5	0	41.2	39.3
8	5	0	26.3	26.7
7	5	0	46.1	50.1
6	5	0	12.9	11.9
5	5	0	14.0	13.0
4	5	0	61.2	63.9
3	5	0	45.3	41.7
2	5	0	34.5	31.6
1	5	0	6.5	10.5
23	4	0	3.1	2.0
22	4	0	10.5	8.6
21	4	0	6.4	7.3
20	4	0	13.8	10.9
19	4	0	5.4	1.8
18	4	0	5.7	2.5
17	4	0	5.9	2.5
16	4	0	22.5	21.0
15	4	0	5.8	3.4
14	4	0	43.3	39.0
13	4	0	7.7	8.2
12	4	0	12.3	13.3
11	4	0	7.9	3.5
10	4	0	15.8	13.5
9	4	0	19.6	16.4
8	4	0	46.2	45.8
7	4	0	4.0	2.7
6	4	0	38.0	38.0
5	4	0	3.6	1.6
4	4	0	11.9	13.6
3	4	0	19.1	20.9
2	4	0	73.1	76.5
1	4	0	56.4	55.6
0	4	0	89.9	104.0
23	3	0	7.6	7.1
22	3	0	8.2	7.0
21	3	0	16.6	15.1
20	3	0	9.9	9.0
19	3	0	5.6	2.7
18	3	0	20.3	18.2
17	3	0	5.9	5.3
16	3	0	21.1	20.8
15	3	0	23.2	19.7
14	3	0	5.6	2.6
13	3	0	34.4	32.5
12	3	0	25.5	24.4
11	3	0	20.1	17.5
10	3	0	43.2	45.0
9	3	0	46.2	44.0
8	3	0	15.5	16.4
7	3	0	12.5	15.4
6	3	0	24.3	25.5
5	3	0	9.3	3.2
4	3	0	50.7	57.6
3	3	0	29.0	35.4
2	3	0	64.2	70.2
1	3	0	102.9	93.7
23	2	0	3.7	2.5
22	2	0	4.4	1.4
21	2	0	8.6	7.3
20	2	0	5.4	3.7
19	2	0	18.0	17.5
18	2	0	5.9	3.7
17	2	0	30.9	29.7
16	2	0	5.8	1.6
15	2	0	16.1	15.2
14	2	0	12.2	11.8
13	2	0	5.2	6.1
12	2	0	16.7	15.4
11	2	0	63.5	60.8
10	2	0	14.5	13.6
9	2	0	21.3	23.0
8	2	0	21.6	18.4
7	2	0	28.0	26.2
6	2	0	61.0	59.8
5	2	0	111.9	113.3
4	2	0	17.8	20.7
3	2	0	101.8	115.9
2	2	0	14.9	10.6
1	2	0	105.5	128.6
0	2	0	43.9	52.7
23	1	0	8.9	9.3
22	1	0	4.5	1.9
21	1	0	12.3	11.8
20	1	0	7.7	6.4
19	1	0	8.1	7.0
18	1	0	19.6	18.4
17	1	0	5.9	2.6
16	1	0	25.4	22.8
15	1	0	25.0	22.8
14	1	0	5.4	4.7
13	1	0	21.7	23.6
12	1	0	39.3	35.3
11	1	0	12.9	13.6
10	1	0	4.3	5.7
9	1	0	23.0	23.0
8	1	0	3.7	2.4
7	1	0	43.5	43.9
6	1	0	49.6	48.3
5	1	0	30.0	34.5
4	1	0	93.6	102.7
3	1	0	86.4	96.8
2	1	0	54.5	61.8
24	0	0	5.8	6.0
22	0	0	10.3	9.1
20	0	0	16.6	17.5
18	0	0	13.1	12.3
16	0	0	13.6	11.5
14	0	0	42.2	46.2
12	0	0	66.6	72.3
10	0	0	55.2	57.1
8	0	0	51.0	56.6
6	0	0	73.3	98.7
4	0	0	17.7	16.8
1	16	1	3.9	2.6
3	15	1	7.8	5.9
2	15	1	7.4	4.2
1	15	1	7.2	4.7
3	14	1	6.7	5.8
2	14	1	6.7	3.9
1	14	1	15.4	11.1
14	13	1	1.9	3.3
13	13	1	2.5	5.3
12	13	1	2.9	2.7
11	13	1	7.8	7.5
10	13	1	3.4	4.4
9	13	1	9.5	12.3
8	13	1	3.8	6.7
7	13	1	3.9	3.6
6	13	1	5.7	6.9
5	13	1	10.0	11.6
4	13	1	4.2	1.3
3	13	1	14.4	16.8
2	13	1	4.2	5.9
1	13	1	4.3	3.5
0	13	1	10.4	10.8
15	12	1	2.5	3.8
14	12	1	2.9	3.0
13	12	1	3.3	4.3
12	12	1	12.3	14.1
11	12	1	3.5	3.8
10	12	1	5.8	10.4
9	12	1	4.1	5.8
8	12	1	4.2	4.2
7	12	1	4.3	1.7
6	12	1	9.2	10.2
5	12	1	4.4	5.6
4	12	1	18.8	18.0
3	12	1	4.5	2.2
2	12	1	13.8	15.5
1	12	1	4.5	8.5
17	11	1	2.2	3.5
16	11	1	4.9	5.1
15	11	1	3.2	2.3
14	11	1	12.1	13.1
13	11	1	3.8	3.9
12	11	1	7.5	6.0
11	11	1	10.2	9.9
10	11	1	4.3	3.7
9	11	1	9.8	10.5
8	11	1	19.9	21.7
7	11	1	4.5	6.5
6	11	1	16.1	17.1
5	11	1	13.8	16.8
4	11	1	11.3	11.9
3	11	1	14.9	15.0
2	11	1	20.2	22.8
1	11	1	4.5	2.4
0	11	1	25.4	27.4
18	10	1	2.5	2.0
17	10	1	6.0	6.2
16	10	1	3.4	5.5
15	10	1	13.1	13.9
14	10	1	3.9	5.5
13	10	1	13.1	13.1
12	10	1	4.3	2.9
11	10	1	4.4	2.6
10	10	1	9.5	10.5
9	10	1	16.1	15.8
8	10	1	4.5	7.1
7	10	1	35.0	34.8
6	10	1	4.5	1.8
5	10	1	17.0	19.6
4	10	1	19.3	22.4
3	10	1	17.8	18.1
2	10	1	10.7	12.9
1	10	1	24.9	26.2
19	9	1	6.2	7.9
18	9	1	3.1	2.3
17	9	1	8.5	8.5
16	9	1	5.4	5.8
15	9	1	5.7	6.9
14	9	1	11.7	11.0
13	9	1	4.4	6.4
12	9	1	4.5	1.9
11	9	1	20.2	20.8
10	9	1	4.5	1.1
9	9	1	26.6	28.3
8	9	1	18.4	17.8
7	9	1	4.4	4.7
6	9	1	18.2	18.5
5	9	1	22.7	22.8
4	9	1	15.0	17.4
3	9	1	38.2	40.4
2	9	1	21.5	23.3
1	9	1	21.2	24.3
0	9	1	18.3	20.1
20	8	1	2.5	3.7
19	8	1	3.1	3.9
18	8	1	15.6	16.0
17	8	1	3.8	0.7
16	8	1	10.5	11.3
15	8	1	4.3	7.6
14	8	1	4.4	2.9
13	8	1	4.5	4.6
12	8	1	26.4	28.0
11	8	1	11.0	12.2
10	8	1	34.1	37.3
9	8	1	4.4	4.8
8	8	1	19.1	22.0
7	8	1	11.8	10.8
6	8	1	27.4	28.7
5	8	1	10.6	12.4
4	8	1	54.2	56.8
3	8	1	12.2	13.6
2	8	1	39.4	42.6
1	8	1	3.8	4.2
21	7	1	2.4	2.5
20	7	1	6.0	8.1
19	7	1	6.9	6.3
18	7	1	3.8	2.6
17	7	1	6.5	6.1
16	7	1	12.2	14.7
15	7	1	7.7	6.9
14	7	1	11.1	13.8
13	7	1	10.1	11.1
12	7	1	20.0	20.7
11	7	1	16.8	18.8
10	7	1	6.8	7.0
9	7	1	28.1	25.8
8	7	1	44.6	42.8
7	7	1	16.8	16.6
6	7	1	45.3	43.3
5	7	1	29.5	31.1
4	7	1	19.5	20.6
3	7	1	38.8	42.3
2	7	1	27.8	30.9
1	7	1	14.6	15.7
0	7	1	53.7	57.0
22	6	1	2.1	2.2
21	6	1	9.0	9.7
20	6	1	3.3	3.7
19	6	1	9.2	10.3
18	6	1	4.1	5.8
17	6	1	14.1	16.3
16	6	1	4.4	3.3
15	6	1	19.9	21.9
14	6	1	4.5	5.5
13	6	1	30.9	34.2
12	6	1	12.3	12.5
11	6	1	8.5	7.7
10	6	1	7.7	9.2
9	6	1	32.2	34.5
8	6	1	11.4	11.0
7	6	1	63.0	65.8
6	6	1	23.4	21.9
5	6	1	18.3	19.6
4	6	1	14.7	15.4
3	6	1	31.4	30.9
2	6	1	25.0	24.4
1	6	1	56.5	62.0
22	5	1	6.0	7.8
21	5	1	3.2	1.9
20	5	1	3.6	2.5
19	5	1	8.9	9.4
18	5	1	4.2	6.2
17	5	1	17.8	18.7
16	5	1	9.0	9.7
15	5	1	8.5	7.7
14	5	1	19.7	20.8
13	5	1	18.5	19.8
12	5	1	18.4	20.8
11	5	1	31.5	32.6
10	5	1	13.9	16.4
9	5	1	29.6	34.2
8	5	1	23.8	25.9
7	5	1	9.0	10.2
6	5	1	33.9	35.3
5	5	1	58.4	58.6
4	5	1	33.7	31.4
3	5	1	45.1	49.6
2	5	1	35.5	38.6
1	5	1	37.5	38.9
0	5	1	60.1	63.0
23	4	1	2.1	2.2
22	4	1	2.9	1.9
21	4	1	3.4	2.9
20	4	1	9.3	9.2
19	4	1	4.1	4.7
18	4	1	24.8	27.8
17	4	1	9.5	10.3
16	4	1	10.6	9.5
15	4	1	7.1	6.3
14	4	1	14.2	18.1
13	4	1	6.0	6.4
12	4	1	40.5	44.0
11	4	1	9.6	8.5
10	4	1	43.3	49.8
9	4	1	3.5	6.5
8	4	1	20.5	20.7
7	4	1	21.3	18.9
6	4	1	54.3	58.2
5	4	1	37.2	39.9
4	4	1	50.2	57.3
3	4	1	28.5	27.1
2	4	1	50.7	54.9
1	4	1	20.5	17.3
23	3	1	4.2	4.2
22	3	1	8.4	9.6
21	3	1	6.6	7.8
20	3	1	7.9	7.9
19	3	1	8.4	7.2
18	3	1	8.2	10.0
17	3	1	14.3	15.0
16	3	1	11.9	11.8
15	3	1	10.9	11.6
14	3	1	28.1	29.5
13	3	1	20.4	19.9
12	3	1	22.4	22.3
11	3	1	35.0	33.6
10	3	1	7.1	9.6
9	3	1	26.6	24.2
8	3	1	56.8	65.4
7	3	1	2.9	3.1
6	3	1	55.6	56.3
5	3	1	27.9	30.5
4	3	1	22.1	21.8
3	3	1	70.3	71.4
2	3	1	53.4	56.5
1	3	1	35.7	32.4
0	3	1	82.4	79.2
23	2	1	6.4	6.7
22	2	1	3.2	1.9
21	2	1	11.9	13.0
20	2	1	4.0	0.7
19	2	1	12.8	13.3
18	2	1	4.4	3.9
17	2	1	11.1	11.3
16	2	1	4.5	1.7
15	2	1	34.3	36.5
14	2	1	4.3	1.6
13	2	1	37.5	42.0
12	2	1	4.7	4.8
11	2	1	3.7	1.2
10	2	1	3.4	5.7
9	2	1	49.2	54.9
8	2	1	31.5	32.9
7	2	1	56.2	59.4
6	2	1	26.9	25.9
5	2	1	36.9	40.3
4	2	1	40.7	40.1
3	2	1	27.6	23.8
2	2	1	34.6	25.9
1	2	1	87.3	103.0
24	1	1	1.6	3.2
23	1	1	2.7	4.9
22	1	1	8.7	9.6
21	1	1	3.7	2.5
20	1	1	5.8	5.1
19	1	1	8.6	9.4
18	1	1	4.5	1.6
17	1	1	16.1	16.8
16	1	1	11.0	12.1
15	1	1	19.6	20.1
14	1	1	33.2	35.5
13	1	1	21.1	21.4
12	1	1	17.1	18.0
11	1	1	43.1	50.4
10	1	1	11.8	12.5
9	1	1	53.6	60.2
8	1	1	49.7	50.9
7	1	1	33.4	32.4
6	1	1	76.2	76.2
5	1	1	56.3	58.0
4	1	1	75.7	63.1
3	1	1	107.5	174.6
2	1	1	78.0	81.7
1	1	1	35.0	38.9
0	1	1	43.2	61.6
24	0	1	1.7	8.2
22	0	1	3.3	3.8
20	0	1	10.0	13.1
18	0	1	20.9	24.2
16	0	1	20.0	22.9
14	0	1	9.4	6.8
12	0	1	43.9	49.8
10	0	1	57.1	67.0
8	0	1	22.0	22.0
6	0	1	57.0	59.3
4	0	1	84.4	84.8
2	0	1	80.4	99.6
2	15	2	3.6	6.4
1	15	2	4.4	1.9
6	14	2	2.8	4.2
5	14	2	5.2	5.2
4	14	2	4.4	3.5
3	14	2	14.0	14.4
2	14	2	3.9	2.4
1	14	2	5.1	4.8
0	14	2	5.2	5.2
12	13	2	2.1	1.0
11	13	2	2.5	1.9
10	13	2	6.8	8.4
9	13	2	7.4	7.6
8	13	2	3.2	1.6
7	13	2	12.2	13.3
6	13	2	3.5	4.0
5	13	2	10.2	11.1
4	13	2	7.4	8.2
3	13	2	3.7	2.3
2	13	2	5.4	3.4
1	13	2	9.3	11.2
14	12	2	8.7	9.1
13	12	2	2.6	1.6
12	12	2	8.3	7.2
11	12	2	6.4	6.4
10	12	2	4.8	3.7
9	12	2	5.7	6.3
8	12	2	16.0	15.2
7	12	2	3.9	1.4
6	12	2	19.9	17.3
5	12	2	4.0	3.5
4	12	2	5.8	5.1
3	12	2	5.8	5.2
2	12	2	11.7	10.8
1	12	2	4.2	2.5
0	12	2	19.9	17.6
16	11	2	6.0	6.1
15	11	2	7.1	6.4
14	11	2	2.9	3.6
13	11	2	3.2	4.3
12	11	2	12.4	11.8
11	11	2	3.7	3.0
10	11	2	16.9	15.9
9	11	2	4.9	6.8
8	11	2	10.0	9.3
7	11	2	13.9	13.0
6	11	2	6.0	6.0
5	11	2	9.1	7.8
4	11	2	21.1	18.5
3	11	2	6.1	7.3
2	11	2	12.2	11.2
1	11	2	13.3	13.7
17	10	2	8.6	10.2
16	10	2	2.8	4.0
15	10	2	3.1	3.6
14	10	2	6.9	6.0
13	10	2	6.4	6.8
12	10	2	3.9	2.7
11	10	2	22.7	21.8
10	10	2	4.2	5.0
9	10	2	15.1	13.0
8	10	2	8.0	7.5
7	10	2	6.1	4.4

h	k	l	|Fo|	|Fc|
6	10	2	9.2	8.9
5	10	2	26.2	26.5
4	10	2	9.7	8.7
3	10	2	28.4	26.5
2	10	2	10.1	10.9
1	10	2	22.7	23.2
0	10	2	11.4	8.7
18	9	2	6.2	6.0
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16	9	2	3.3	1.7
15	9	2	14.0	13.2
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13	9	2	14.2	13.0
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11	9	2	4.2	4.3
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9	9	2	18.5	19.0
8	9	2	10.9	9.0
7	9	2	25.5	23.3
6	9	2	19.8	18.3
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3	9	2	15.9	14.2
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14	8	2	16.4	14.9
13	8	2	4.2	4.0
12	8	2	15.7	15.5
11	8	2	4.3	3.0
10	8	2	12.8	11.8
9	8	2	18.1	17.2
8	8	2	27.5	28.0
7	8	2	8.4	8.2
6	8	2	49.7	49.3
5	8	2	10.7	12.4
4	8	2	5.6	6.8
3	8	2	11.1	10.9
2	8	2	23.9	24.0
1	8	2	15.0	15.1
0	8	2	53.6	56.2
20	7	2	2.3	3.3
19	7	2	2.9	3.2
18	7	2	10.9	10.4
17	7	2	3.6	5.7
16	7	2	12.0	11.8
15	7	2	11.6	10.6
14	7	2	4.2	2.7
13	7	2	10.1	10.2
12	7	2	20.5	20.9
11	7	2	4.3	3.5
10	7	2	27.6	26.7
9	7	2	24.4	21.4
8	7	2	15.8	14.5
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6	7	2	17.4	17.6
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3	7	2	8.9	7.4
2	7	2	37.9	38.2
1	7	2	29.4	28.1
21	6	2	2.0	3.0
20	6	2	2.7	3.9
19	6	2	11.5	10.6
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17	6	2	13.1	12.3
16	6	2	4.1	4.3
15	6	2	4.2	4.7
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12	6	2	4.3	2.5
11	6	2	35.7	34.6
10	6	2	13.0	12.4
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7	6	2	7.5	5.7
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2	6	2	11.6	11.1
1	6	2	38.2	36.1
0	6	2	11.1	11.7
21	5	2	8.2	8.2
20	5	2	6.8	6.9
19	5	2	3.4	5.3
18	5	2	7.6	6.6
17	5	2	4.0	4.6
16	5	2	9.4	9.1
15	5	2	18.3	18.9
14	5	2	4.3	7.2
13	5	2	20.5	17.7
12	5	2	19.1	19.6
11	5	2	15.1	16.4
10	5	2	36.8	36.5
9	5	2	29.9	26.9
8	5	2	9.0	7.9
7	5	2	53.4	50.9
6	5	2	13.2	12.3
5	5	2	31.3	29.0
4	5	2	34.5	33.6
3	5	2	28.2	25.4
2	5	2	33.7	31.5
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22	4	2	4.1	5.9
21	4	2	2.8	3.5
20	4	2	13.0	11.2
19	4	2	3.6	1.8
18	4	2	3.9	1.9
17	4	2	4.1	3.0
16	4	2	16.0	14.9
15	4	2	4.3	4.1
14	4	2	31.5	30.9
13	4	2	13.9	13.9
12	4	2	25.3	24.2
11	4	2	7.4	7.0
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8	4	2	59.9	59.9
7	4	2	6.6	4.4
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4	4	2	39.8	35.0
3	4	2	14.8	13.6
2	4	2	39.6	35.1
1	4	2	9.3	9.2
0	4	2	103.7	91.5
22	3	2	2.3	1.7
21	3	2	8.9	7.4
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19	3	2	3.8	2.2
18	3	2	14.2	14.7
17	3	2	4.2	2.7
16	3	2	13.8	14.8
15	3	2	29.1	29.3
14	3	2	14.0	15.5
13	3	2	16.9	14.4
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7	3	2	36.3	34.1
6	3	2	19.9	19.4
5	3	2	49.0	43.4
4	3	2	57.2	51.4
3	3	2	32.6	26.9
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1	3	2	26.8	23.3
22	2	2	2.5	2.8
21	2	2	4.4	1.7
20	2	2	3.5	1.7
19	2	2	14.1	14.5
18	2	2	4.1	5.2
17	2	2	15.3	13.8
16	2	2	5.3	6.9
15	2	2	12.0	10.9
14	2	2	11.8	13.6
13	2	2	21.4	18.7
12	2	2	3.9	3.3
11	2	2	63.2	59.4
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9	2	2	67.9	67.2
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7	2	2	10.8	24.6
6	2	2	54.8	42.5
5	2	2	60.6	56.9
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3	2	2	83.4	72.2
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1	2	2	53.0	43.4
0	2	2	28.5	23.5
23	1	2	3.9	5.2
22	1	2	2.6	1.6
21	1	2	10.8	10.3
20	1	2	8.0	7.2
19	1	2	5.5	4.7
18	1	2	10.1	10.1
17	1	2	10.0	8.8
16	1	2	16.8	18.0
15	1	2	24.2	24.5
14	1	2	15.2	16.5
13	1	2	28.9	30.7
12	1	2	36.1	39.1
11	1	2	11.1	8.7
10	1	2	49.1	51.1
9	1	2	51.5	49.4
8	1	2	15.8	15.0
7	1	2	63.8	56.9
6	1	2	8.7	5.9
5	1	2	43.8	40.8
4	1	2	46.0	41.8
3	1	2	10.1	7.6
2	1	2	66.4	53.7
1	1	2	48.1	48.2
22	0	2	8.0	7.4
20	0	2	8.8	9.2
18	0	2	4.1	3.2
16	0	2	21.5	21.3
14	0	2	42.3	36.7
12	0	2	23.4	23.1
10	0	2	31.8	29.9
8	0	2	59.7	63.1
6	0	2	100.2	84.2
4	0	2	69.6	49.9
2	0	2	39.9	37.0
2	14	3	4.8	4.1
1	14	3	10.3	8.7
3	13	3	10.1	12.2
2	13	3	4.8	3.4
1	13	3	6.9	7.8
0	13	3	6.9	7.2
4	12	3	15.6	17.0
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2	12	3	12.7	13.9
1	12	3	4.1	4.3
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8	11	3	11.1	13.9
7	11	3	4.1	1.9
6	11	3	13.3	13.4
5	11	3	4.3	7.0
4	11	3	4.3	5.2
3	11	3	7.6	10.6
2	11	3	11.7	12.7
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0	11	3	15.4	19.3
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7	10	3	20.3	21.7
6	10	3	4.5	4.9
5	10	3	7.2	9.1
4	10	3	4.6	4.1
3	10	3	4.6	6.0
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14	9	3	7.7	9.4
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8	9	3	15.8	16.7
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6	9	3	4.7	5.8
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8	8	3	6.6	7.4
7	8	3	4.7	2.4
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15	7	3	3.9	2.9
14	7	3	11.9	13.7
13	7	3	7.6	7.9
12	7	3	9.1	8.4
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16	6	3	3.9	4.8
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13	6	3	17.6	19.3
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11	6	3	4.7	5.5
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3	6	3	16.8	15.7
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17	5	3	9.3	12.4
16	5	3	11.7	10.6
15	5	3	6.2	9.0
14	5	3	12.8	12.2
13	5	3	4.6	3.8
12	5	3	5.7	5.2
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5	5	3	33.8	27.9
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18	4	3	13.2	14.9
17	4	3	4.0	2.7
16	4	3	12.1	14.0
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19	3	3	5.4	6.4
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17	3	3	11.4	12.7
16	3	3	4.4	7.2
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7	3	3	3.8	2.8
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16	2	3	4.5	3.6
15	2	3	22.7	24.2
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12	2	3	4.6	4.7
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12	1	3	18.9	17.5
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4	11	4	13.3	14.0
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2	11	4	9.1	9.6
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9	10	4	8.0	7.8
8	10	4	3.3	2.3
7	10	4	3.5	1.5
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2	8	4	14.3	13.7
1	8	4	8.6	9.7
0	8	4	27.0	26.7
15	7	4	9.0	9.7
14	7	4	3.0	1.4
13	7	4	6.8	5.2
12	7	4	13.0	13.8
11	7	4	3.9	3.2
10	7	4	14.0	13.6
9	7	4	10.2	10.9
8	7	4	7.3	6.8
7	7	4	7.4	7.3
6	7	4	8.6	7.5
5	7	4	4.3	3.9
4	7	4	19.9	20.6
3	7	4	4.3	2.6
2	7	4	17.9	17.9
1	7	4	11.8	13.0
16	6	4	2.4	2.4
15	6	4	6.0	4.6
14	6	4	3.4	5.3
13	6	4	10.5	8.7
12	6	4	3.9	2.6
11	6	4	18.7	18.1
10	6	4	4.2	3.8
9	6	4	20.5	18.6
8	6	4	4.3	6.9
7	6	4	4.3	3.3
6	6	4	4.3	1.1
5	6	4	23.4	23.2
4	6	4	8.4	10.1
3	6	4	32.5	36.0
2	6	4	4.1	4.1
1	6	4	11.1	10.7
0	6	4	10.4	10.0
17	5	4	2.2	3.3
16	5	4	5.8	6.6
15	5	4	13.1	12.6
14	5	4	3.7	1.3
13	5	4	15.4	15.0
12	5	4	5.8	5.8
11	5	4	6.0	7.4
10	5	4	15.7	14.1
9	5	4	16.7	15.5
8	5	4	10.5	10.3
7	5	4	23.6	24.4
6	5	4	16.5	15.1
5	5	4	19.0	18.7
4	5	4	18.8	19.2
3	5	4	11.0	9.6
2	5	4	16.4	16.1
1	5	4	25.9	27.4
17	4	4	2.7	1.2
16	4	4	7.1	6.6
15	4	4	5.1	5.6
14	4	4	24.0	20.9
13	4	4	4.1	2.9
12	4	4	16.0	14.1
11	4	4	4.3	3.3
10	4	4	4.3	4.3
9	4	4	10.5	7.7
8	4	4	25.7	25.2
7	4	4	4.1	3.4
6	4	4	36.7	34.4
5	4	4	11.9	11.3
4	4	4	10.7	8.8
3	4	4	6.3	6.3
2	4	4	29.5	32.0
1	4	4	3.5	4.9
0	4	4	51.5	51.5
18	3	4	10.0	11.2
17	3	4	5.9	6.6
16	3	4	12.7	10.4
15	3	4	13.7	12.2
14	3	4	8.0	6.7
13	3	4	7.2	7.7
12	3	4	16.8	15.1
11	3	4	8.6	8.7
10	3	4	20.7	21.0
9	3	4	17.7	16.5
8	3	4	4.1	4.2
7	3	4	22.0	22.6
6	3	4	13.9	12.8
5	3	4	12.4	11.9
4	3	4	31.7	31.0
3	3	4	16.3	14.4
2	3	4	23.7	22.9
1	3	4	32.3	33.3
18	2	4	2.5	2.1
17	2	4	12.9	12.1
16	2	4	3.5	4.4
15	2	4	12.1	9.4
14	2	4	4.1	1.9
13	2	4	4.2	5.6
12	2	4	4.3	3.1
11	2	4	26.0	22.3
10	2	4	4.3	3.7
9	2	4	13.8	19.2
8	2	4	4.0	3.3
7	2	4	3.9	5.6
6	2	4	21.1	20.9
5	2	4	41.6	47.0
4	2	4	12.1	12.2
3	2	4	41.0	41.8
2	2	4	7.3	6.6
1	2	4	20.3	22.1
0	2	4	6.5	5.1
18	1	4	12.1	11.7
17	1	4	9.5	8.9
16	1	4	14.1	9.6
15	1	4	14.8	12.5
14	1	4	4.1	4.0
13	1	4	17.0	12.1
12	1	4	12.8	10.6
11	1	4	4.3	2.3
10	1	4	21.9	19.7
9	1	4	21.3	17.0
8	1	4	13.0	10.1
7	1	4	37.6	31.9
6	1	4	23.9	21.8
5	1	4	10.3	7.3
4	1	4	31.5	29.5
3	1	4	15.9	16.9
2	1	4	26.6	29.0
1	1	4	22.9	31.4
18	0	4	6.5	5.7
16	0	4	15.5	12.3
14	0	4	21.6	17.1
12	0	4	15.8	12.3
10	0	4	16.1	12.1
8	0	4	23.4	18.2
6	0	4	43.3	37.2
4	0	4	7.0	5.8
2	0	4	32.1	37.1
0	0	4	45.0	51.7
3	9	5	9.2	12.8
2	9	5	5.9	6.2
1	9	5	2.5	4.5
3	8	5	2.9	1.0
2	8	5	10.7	12.9
1	8	5	3.2	2.9
3	7	5	7.8	9.1
2	7	5	6.1	6.6
1	7	5	7.1	6.1
3	6	5	5.0	6.0
2	6	5	4.7	8.1
1	6	5	15.9	16.5
3	5	5	15.4	18.7
2	5	5	7.0	8.0
1	5	5	13.1	12.4
3	4	5	6.8	7.8
2	4	5	15.8	19.7
1	4	5	5.9	4.2
3	3	5	16.4	18.8
2	3	5	12.5	13.2
1	3	5	6.1	3.3
3	2	5	8.2	10.5
2	2	5	5.4	2.0
1	2	5	20.9	21.7
3	1	5	22.5	26.6
2	1	5	15.4	16.2
1	1	5	15.7	13.5
2	0	5	10.9	8.2
2	4	6	7.1	10.3
2	3	6	8.3	10.3
1	3	6	7.5	7.9
3	2	6	12.3	16.7
2	2	6	3.2	1.9
1	2	6	7.4	6.5
3	1	6	4.8	5.7
2	1	6	6.7	6.6
1	1	6	6.7	7.6
2	0	6	10.1	14.3

Table 1.5

Analysis of the agreement of $|F_o|$ and $|F_c|$ at the end of the refinement. N is the number of reflexions. Structure factors are on the absolute scale.

(a) As a function of the layer line index.

ℓ	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
0	5844	5589	683	292	0.117	2.3
1	5457	5815	629	287	0.115	2.2
2	4951	4650	492	273	0.099	1.8
3	3498	3280	526	204	0.151	2.6
4	2291	2226	266	187	0.116	1.4
5	279	298	52	28	0.187	1.9
6	74	88	18	10	0.249	1.8

(b) As a function of $|F_o|$.

0 - 5	1148	1073	419	299	0.365	1.4
5 - 10	1958	1873	356	272	0.182	1.3
10 - 15	2611	2572	313	213	0.120	1.5
15 - 22	3261	3180	289	179	0.089	1.6
22 - 32	3165	3102	227	119	0.072	1.9
32 - 44	3225	3175	298	85	0.093	3.5
44 - 58	3297	3269	287	65	0.087	4.4
58 - 72	1531	1423	154	24	0.101	6.4
72 - 115	2197	2279	323	25	0.147	12.9
All	22393	21945	2667	1281	0.119	2.1

Table 1.6

Dimensions of the arsenate ions.
(Bond lengths in Å, angles in degrees).

As-0(1)	1·702(15)	0(1)···0(2)	2·797(19)
As-0(2)	1·705(12)	0(1)···0(3)	2·736(17)
As-0(3)	1·681(12)	0(1)···0(4)	2·703(23)
As-0(4)	1·649(16)	0(2)···0(3)	2·713(18)
		0(2)···0(4)	2·749(18)
		0(3)···0(4)	2·802(21)

0(1)-As-0(2)	110·3(0·6)
0(1)-As-0(3)	107·9(0·7)
0(1)-As-0(4)	107·5(0·7)
0(2)-As-0(3)	106·5(0·6)
0(2)-As-0(4)	110·1(0·7)
0(3)-As-0(4)	114·5(0·7)

Table 1.7

Bond lengths (Å) and angles (°) within the quinolone molecule of QH_3AsO_4; for comparison the mean values for the two quinolone molecules in Q_2HAsF_6 are also given.

	QH_3AsO_4	Q_2HAsF_6
N-C(2)	1·290(28)	1·326
C(2)-O(11)	1·311(27)	1·277
C(2)-C(3)	1·437(22)	1·480
C(3)-C(4)	1·373(26)	1·335
C(4)-C(10)	1·409(26)	1·423
C(10)-C(5)	1·423(29)	1·410
C(5)-C(6)	1·416(31)	1·332
C(6)-C(7)	1·393(32)	1·445
C(7)-C(8)	1·297(35)	1·354
C(8)-C(9)	1·446(34)	1·397
C(9)-C(10)	1·419(23)	1·359
C(9)-N	1·402(24)	1·440
N-C(11)	1·492(23)	1·507

	QH_3AsO_4	Q_2HAsF_6
N-C(2)-O(11)	120·1(1·5)	119·7
O(11)-C(2)-C(3)	118·1(1·9)	121·3
N-C(2)-C(3)	121·6(1·9)	119·9
C(2)-C(3)-C(4)	117·2(1·7)	118·1
C(3)-C(4)-C(10)	121·8(1·6)	121·6
C(4)-C(10)-C(9)	118·4(1·6)	120·8
C(4)-C(10)-C(5)	120·9(1·6)	120·2
C(9)-C(10)-C(5)	120·7(1·6)	118·8
C(10)-C(5)-C(6)	117·6(1·6)	119·4
C(5)-C(6)-C(7)	120·9(2·0)	121·9
C(6)-C(7)-C(8)	121·3(2·0)	118·0
C(7)-C(8)-C(9)	122·5(1·9)	119·1
C(8)-C(9)-C(10)	116·5(1·7)	122·5
C(8)-C(9)-N	125·1(1·6)	119·8
C(10)-C(9)-N	117·9(1·5)	117·7
C(9)-N-C(2)	123·0(1·5)	122·2
C(9)-N-C(11)	118·6(1·6)	119·3
C(11)-N-C(2)	118·3(1·7)	118·6

Table 1.8

Intermolecular contents (<3·8 Å).

C(1)···C(8^{II})	3·754 Å	N···C(7^{II})	3·423 Å
C(2)···C(7^{II})	3·645	N···C(8^{II})	3·462
C(2)···C(8^{II})	3·444		
C(2)···C(9^{II})	3·665	0(1)···C(7^{VII})	3·629
C(3)···C(5^{II})	3·505	0(1)···C(8^{VII})	3·480
C(3)···C(6^{II})	3·665	0(2)···C(5^{VIII})	3·695
C(3)···C(10^{II})	3·592	0(3)···C(1^{IX})	3·225
C(4)···C(5^{II})	3·582	0(4)···C(1^{VII})	3·681
C(4)···C(6^{II})	3·482	0(11)···C(4^{VIII})	3·364
C(6)···C(7^{V})	3·686	0(11)···C(5^{VIII})	3·481
C(6)···C(7^{VI})	3·726	0(11)···C(8^{II})	3·578
C(6)···C(9^{I})	3·745	0(11)···C(9^{II})	3·512
C(7)···C(7^{VI})	3·712		
C(7)···C(9^{I})	3·501		

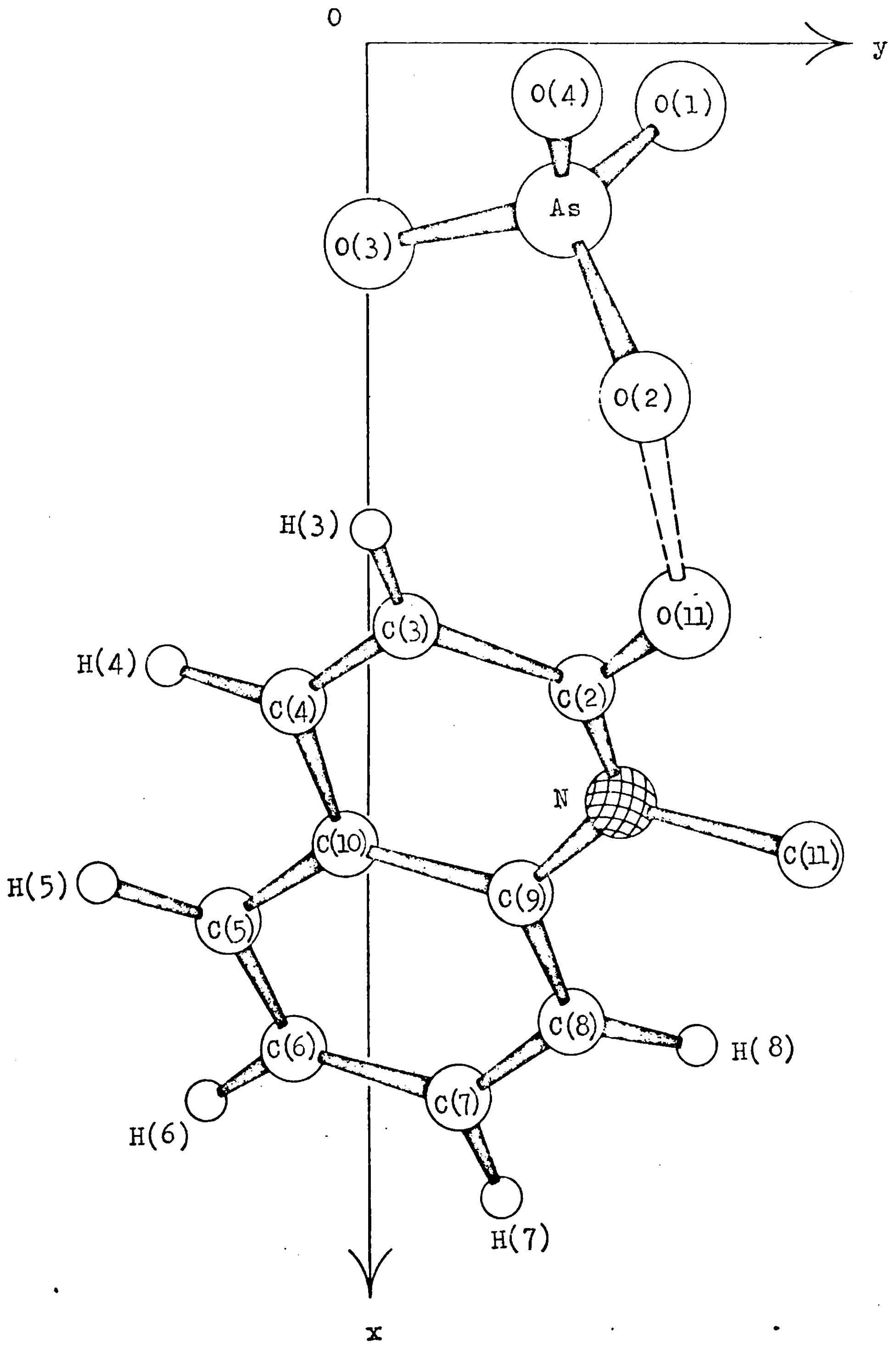
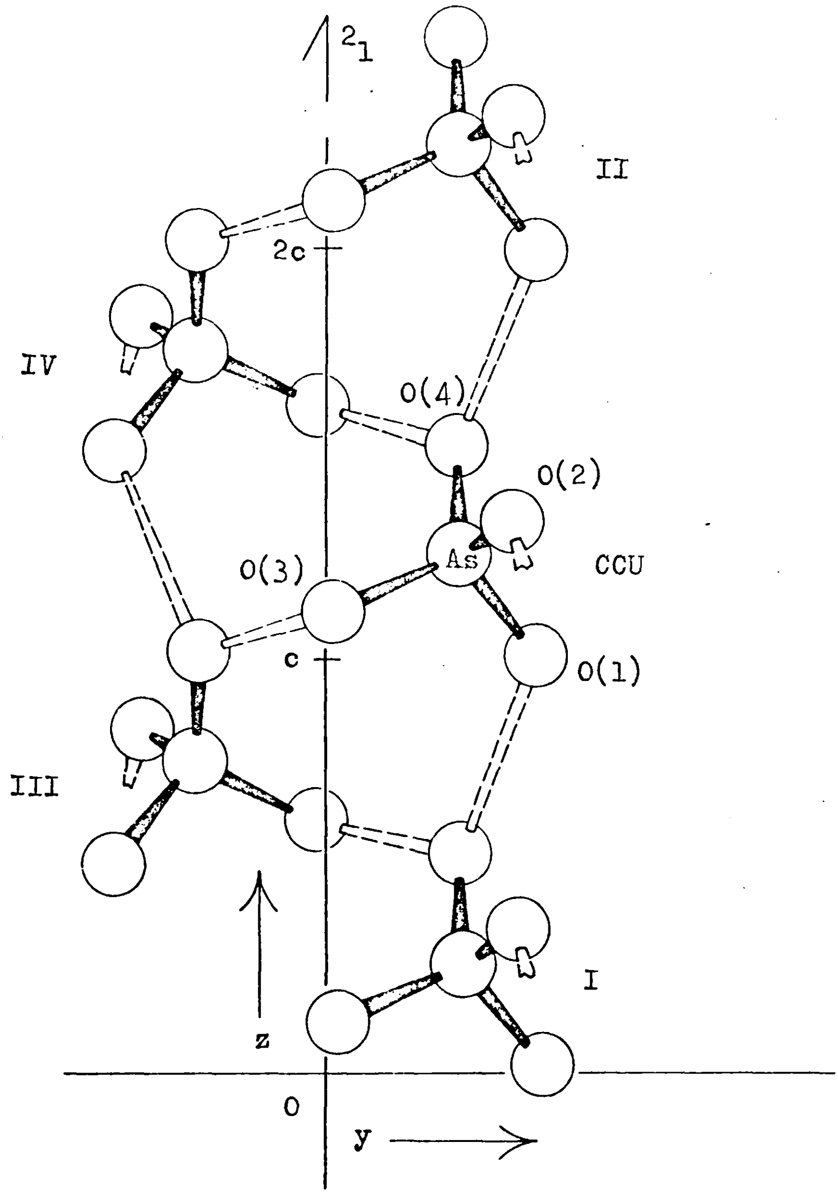

O
y
x
O(4)
O(1)
As
O(3)
O(2)
H(3)
O(11)
C(3)
H(4)
C(4)
C(2)
N
C(10)
C(11)
H(5)
C(9)
C(5)
C(8)
H(8)
C(6)
C(7)
H(6)
H(7)

Figure 1.1 The crystal chemical unit (CCU) of 1-methyl-2-quinolonium dihydrogen arsenate.



2_1
II
2c
IV
O(4)
O(2)
As
CCU
O(3)
c
O(1)
III
I
z
O
y

Figure 1.2 · The helix of arsenate ions as seen in the a-axial projection.

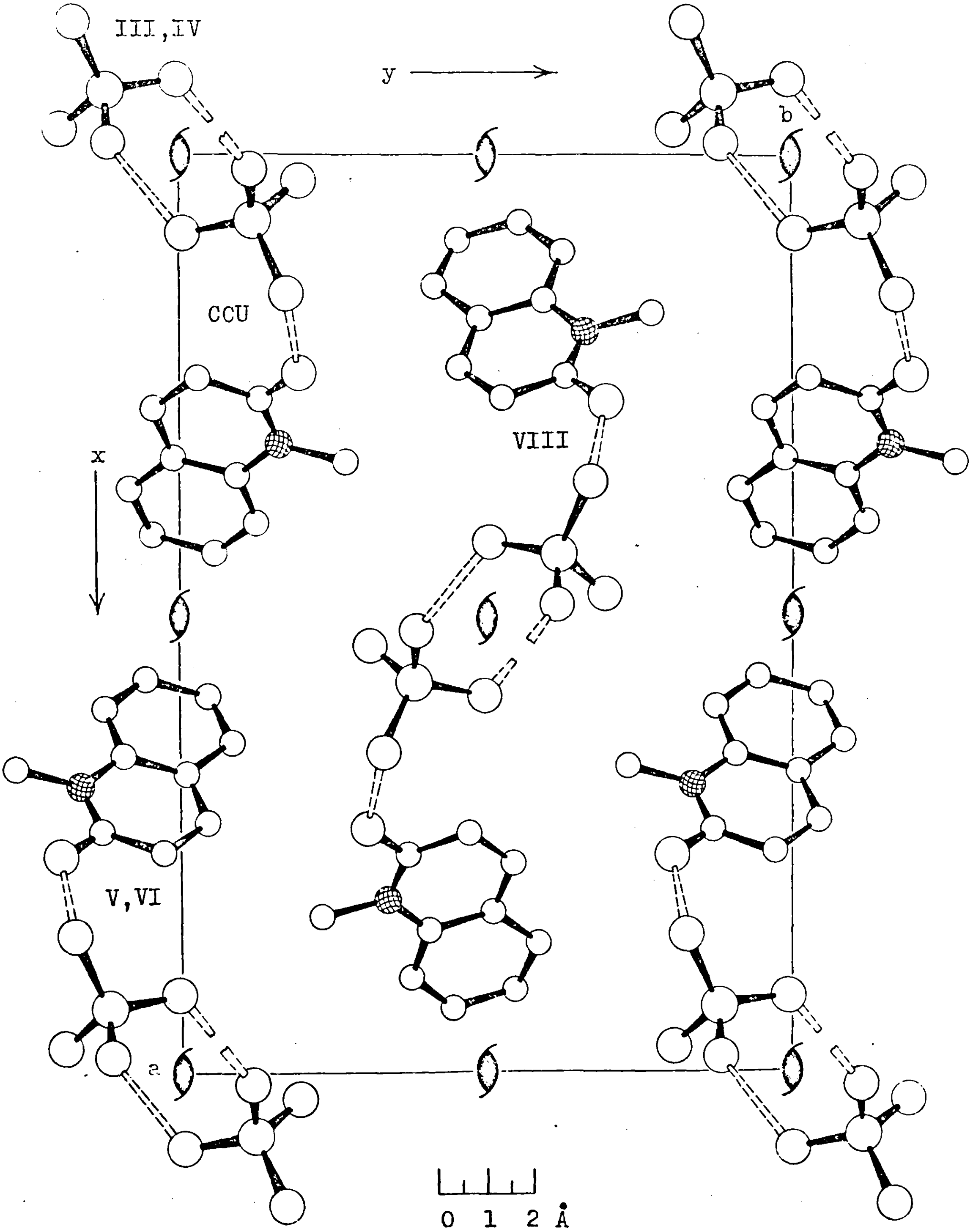

III,IV
y
b
CCU
VIII
x
V,VI
a
0 1 2 Å

Figure 1.3 The crystal structure as seen in its c-axial projection.

1.3 DISCUSSION

The crystal structure of 1-methyl-2-quinolonium dihydrogen arsenate (QH_3AsO_4), which is shown in Figures 1.2 and 1.3, may be described in terms of a helix of AsO_4 tetrahedra elongated in the z-direction. Each tetrahedron is linked through hydrogen bonds to those directly above and below it in the z-direction, $O(1)\cdots O(4^I) = 2.551$ (±23) Å, and to those related to it by the 2_1 axis parallel to z, $O(3)\cdots O(4^{III}) = 2.553$ (±18) Å. Hydrogen bonding also takes place between one oxygen atom of each tetrahedron and the quinolone oxygen atom, $O(2)\cdots O(11) = 2.495$ (±18) Å.

The arsenate group, whose dimensions are given in Table 1.6, in which standard deviations are given in parentheses, differs little from a regular tetrahedron, and is consistent with a bonding system involving the formation of four σ bonds using sp^3 hybrid orbitals of arsenic. The As—O(4) bond length, 1.649 (±16) Å, indicates that this bond has a considerable degree of double-bond character, due to overlap between filled $p-\pi$ orbitals of oxygen and unfilled $d-\pi$ orbitals of arsenic. It is comparable with, for example, those found by Calleri and Ferraris (1967) in haidingerite, $CaHAsO_4.H_2O$, where the mean As=O distance is 1.653 (±6) Å, and by Ferguson and Macaulay (1969) in triphenylarsine oxide monohydrate, $Ph_3AsO.H_2O$, in which the As=O distance is 1.644 (±7) Å. The other, longer As—O bonds, whose average length is 1.696 (±14) Å, are in good agreement with, for example, those found by Ferguson and Macaulay (1968) in triphenylarsine "hydroxychloride", $Ph_3AsOHCl$, where the mean As—O distance is 1.700 (±14) Å, and in triphenylarsine "hydroxybromide", $Ph_3AsOHBr$, in which the As—O bond distance is 1.712 (±12) Å.

The crystal structure of the parent acid, ortho-arsenic acid, $H_3AsO_4.\frac{1}{2}H_2O$, has recently been studied by Worzala (1968). The As—O bond distances in two crystallographically independent AsO_4 tetrahedra vary from 1.594 to 1.714 Å, but these values may be modified once least-squares refinement has been carried out (Stephens, 1968).

The average As—O bond distance in QH_3AsO_4 is 1.684 (+14) Å, which is similar to that found in most structures containing AsO_4 tetrahedra. In most cases the average As—O bond distance differs little from 1.68 Å, although the individual As—O bond lengths may vary considerably from the mean, depending on the environment. This is consistent with the theoretical treatment by Cruickshank (1961) of the distribution of bonds in XO_4^{n-} ions.

The dimensions of the quinolone molecule are given in Table 1.7; for comparison the mean values for the two quinolone molecules in Q_2HAsF_6 (Calleri and Speakman, 1969) are also given. The twelve non-hydrogen atoms of the molecule are nearly coplanar, the equation of the mean plane through them being, in orthogonal coordinates :

$$-0.685X + 0.213Y - 0.696Z = -5.808\ \text{Å}.$$

The root mean square distance of the atoms from the plane is 0.028 Å, and only C(8), +0.052 Å, and C(9), -0.059 Å, lie significantly out of the plane.

Protonation of the quinolone oxygen atom is evident in the lengthening of the C(2)--O(11) bond to 1.311 (±27) Å, and the shortening of the N--C(2) bond to 1.290 (±28) Å. No reason is immediately apparent for the shortening of the C(7)--C(8) bond to 1.297 (±35) Å. The dimensions of the quinolone residues in Q_2HAsF_6 are similar. Comparison with the molecular dimensions of 1-methyl-2-quinolone itself would be of interest, and it is hoped to study this some time in the future.

Intermolecular contacts of less than 3.7 Å are given in Table 1.8. The shortest C···C contact is $C(2)\cdots C(8^{II}) = 3.444$ Å, the shortest O···C contact $O(3)\cdots C(1^{IX}) = 3.225$ Å, the shortest N···C contact $N\cdots C(7^{II}) = 3.423$ Å, and the shortest N···O contact $N\cdots O(2^{I}) = 3.511$ Å.

CHAPTER 2

POTASSIUM HYDROGEN DI-ASPIRINATE

2.1 INTRODUCTION

The present X-ray crystal-structure analysis was undertaken in order to study the effect of isotopic substitution on the hydrogen bond in the acid salt potassium hydrogen di-aspirinate (KHDA), of which very accurate structure analyses by both X-ray diffraction (Manojlovic and Speakman, 1967) and neutron diffraction (Sequeira, Berkebile and Hamilton, 1967) have been carried out. Accordingly, data were collected from a crystal believed to be potassium deuterium di-aspirinate; very recently, however, mass-spectrometric analyses of some crystals of the same batch established that no deuterium was present. Nevertheless, as considerable effort went into the collection of the data and the refinement of the structure, the results of this analysis, which are in excellent agreement with those of the previous analyses, are reported here in full.

2.2 EXPERIMENTAL

Crystal Data

Potassium hydrogen di-aspirinate [bisacetylsalicylate], $KH(C_9H_7O_4)_2$, F.W. = 398.4. Monoclinic, a = 26.578 (±18), b = 7.181 (±4), c = 10.673 (±11) Å, $\beta = 116.36^\circ$ (±0.01°), U = 1825.4 $Å^3$. D_m = 1.45 (by flotation), Z = 4, D_x = 1.453. F(000) = 824. Space group C 2/c (C_{2h}^6, No.15).

Linear absorption coefficient for MoKα radiation, $\mu = 3.6\ cm^{-1}$.

The "Deuterated" Crystals

In November 1967 Dr. Armin Wilson of the Bristol-Meyers Co., Hillside, New Jersey, prepared crystals of the acid potassium salt of aspirin which he thought to be deuterated at the acidic hydrogen atom, viz. $KD(C_9H_7O_4)_2$.

These crystals were sealed into two tubes, one of which was sent to Dr. W.C. Hamilton at Brookhaven, and the other to Dr. J.C. Speakman in this department. From the latter batch a suitable crystal was selected and mounted for the collection of X-ray diffractometer data; at the same time it was coated with collodion to prevent loss of deuterium to the atmosphere. The remaining crystals were put into a stoppered tube, successively within two other stoppered tubes, and protected by blue silica-gel air-drier.

Data were duly collected in June 1968. By August 1968, an analysis of some of the crystals sent to Brookhaven had been carried out, and from this Dr. Hamilton thought it likely that the deuteration was more than 100 %, i.e. more deuterium was present than could be accounted for by deuteration of only the acidic hydrogen, so that other hydrogens too must have been replaced by deuterium.

In December 1968 the infra-red spectrum of one of the crystals sent to Glasgow was run by Professor D. Hadzi of the University of Ljubljana, Yugoslavia, who reported that there was no significant deuteration, and this seemed to be confirmed in February 1969 when ordinary mass-spectrometric analyses were carried out in this department by Mr. W.A. Lawrie and Miss A. Tennant; one, of the high-mass region, showed that no hydrogen atoms of the aspirinate residue were substituted by deuterium, whilst another, of the low-mass region, proved inconclusive regarding the acidic ion.

In March 1969 Dr. R.I. Reed and Mr. D.H. Robertson carried out a deuterium analysis as follows : a crystal was reacted with a Grignard reagent in ether,

$$KD(C_9H_7O_4)_2 \ + \ CH_3MgI \ \rightarrow \ CH_3D \ ,$$

the methane produced was separated (condensed) and submitted to mass-spectrometry. No significant amount of CH_3D was found; the methane was substantially pure CH_4 . This method could pick out only the acidic hydrogen atom, and the result, which was repeated, suggests that the sample is, at the present time, potassium hydrogen di-aspirinate (KHDA) .

I am very grateful to all those who carried out analyses of these crystals.

Data Collection

A crystal of dimensions $0.39 \times 0.36 \times 0.36$ mm^3 was mounted on a Hilger and Watts Y290 computer-controlled four-circle diffractometer.

Prior to the data collection the positions in reciprocal space of a number of high-order reflexions were determined precisely, using molybdenum radiation, and cell dimensions derived by a least-squares treatment.

Intensity data were collected, using molybdenum radiation with balanced filters of zirconium and yttrium, in three batches, for which the ranges of θ were

$0.50^\circ < \theta < 22.80^\circ$, $22.75^\circ < \theta < 29.20^\circ$ and $29.15^\circ < \theta < 34.60^\circ$

All the reflexions in the first batch were scanned fully, whilst for the second and third batches a rapid scan of each reflexion was carried out, and a longer counting time spent scanning only those reflexions whose intensity was significantly above the background. However, the latter method tended to be less convenient in several respects and we reverted to the original mode of operation towards the end of the data collection.

Equivalent reflexions were averaged, and a set of 2364 independent reflexions obtained. Of these, 191 had an integrated intensity which was either less than or equal to that of the background, and a further 337 had an integrated intensity which was not significantly above the background. Structure amplitudes were derived by applying Lorentz and polarisation corrections to the intensities. No corrections for absorption were made.

I should like to thank Mr. A. McAdam for collaborating with me in the collection of these data.

Structure Refinement

The starting point for the refinement was the set of atomic parameters found for KHDA by Manojlovic and Speakman (1967). Three cycles of block-diagonal least-squares refinement, with anisotropic vibrational parameters (for the non-hydrogen atoms) and unit weights, reduced the value of R to 0.101, the corresponding value of R' being 0.013.

At this point a weighting scheme identical to that used by Manojlovic and Speakman in the refinement of their KHDA linear-diffractometer data was introduced, viz.

$$w = w_1 w_2$$

where $w_1 = 1$ for $|F_o| < p_1$, $w_1 = \frac{p_1}{|F_o|}$ for $|F_o| > p_1$

and $w_2 = 1$ for $(\frac{\sin\theta}{\lambda})^2 > p_2$, $w_2 = (\frac{\sin\theta}{\lambda})^2 / p_2$ for $|F_o| < p_2$, with p_1 taken as 20.0 and p_2 as 0.16

However, this scheme, which had been devised by Dr. K.W. Muir, did not prove satisfactory for our data until it was modified so as to down-weight substantially terms of low $|F_o|$ by incorporating an additional factor w_3 such that

$$w = w_1 w_2 w_3$$

where $w_3 = 0.25$ for $|F_o| < |F_o|_{min}$, $|F_o|_{min}$ being the structure amplitude of the minimum observable reflexion; $|F_o|_{min}$ was taken as 9.0.

Four cycles of block-diagonal least-squares refinement using this weighting scheme led to final values of $R = 0.095$ and $R' = 0.012$;

the weighting scheme was justified by the uniformity of the average value of $w\Delta^2$ over various ranges of $\sin\theta$ and $|F_o|$.

The final positional parameters are given in Table 2.1 and the final vibrational parameters in Table 2.2; estimated standard deviations, derived from the inverse of the least-squares matrix, are given in parentheses. Observed structure amplitudes and final calculated structure factors are given in Table 2.3 and their agreement analysed in Table 2.4. For the structure-factor calculations the atomic scattering factors used were from International Tables, Volume III (1962).

The group of atoms whose parameters appear in these tables constitutes the crystal chemical unit (CCU) of the structure; the CCU is shown in Figure 2.1. Other symmetry-related units are denoted as follows:

CCU	x,	y,	z;
I	$-x$,	$1-y$,	$-z$;
II	$-x$,	y,	$\frac{1}{2}-z$;
III	x,	$-y$,	$\frac{1}{2}+z$;
IV	$\frac{1}{2}-x$,	$\frac{3}{2}-y$,	$-z$;
V	$\frac{1}{2}-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$;
VI	x,	$-1+y$,	z;
VII	$-x$,	$-1+y$,	$\frac{1}{2}-z$;
VIII	x,	$1-y$,	$\frac{1}{2}+z$;
IX	$-x$,	$2-y$,	$-z$.

TABLES AND DIAGRAMS

Table 2.1

Fractional (*x*,*y*,*z*, x 10^5 for K^+,O,C; *x*,*y*,*z*, x 10^4 for H) and orthogonal (*X*',*Y*,*Z*' x 10^4 for K^+,O,C; *X*',*Y*,*Z*' x 10^3 for H) coordinates. (*X*' = *ax* sin β; *Y* = *by*; *Z*' = *ax* cos β + *cz*.)

	x	*y*	*z*	*X*'	*Y*	*Z*'
K^+	0	24362	25000	0	17492 (13)	26675
O(1)	3891	89605	1793	9267 (26)	64336 (31)	-2679 (26)
O(2)	7328	98852	23824	17453 (31)	70976 (37)	16772 (29)
O(3)	15171	72101	40611	36132 (31)	51769 (30)	25427 (27)
O(4)	7939	52841	29277	18908 (36)	37940 (38)	21869 (34)
C(1)	16540	72129	29340	39392 (36)	51789 (36)	11786 (37)
C(2)	21481	63727	31469	51160 (38)	45756 (45)	8226 (48)
C(3)	23140	63725	20828	55111 (43)	45755 (50)	-5086 (57)
C(4)	19758	72065	8187	47056 (40)	51743 (44)	-14582 (43)
C(5)	14799	80583	6171	35246 (36)	57859 (39)	-10881 (38)
C(6)	13105	80732	16854	31211 (31)	57966 (35)	2517 (34)
C(7)	7772	90465	14445	18510 (33)	64954 (35)	6240 (32)
C(8)	10561	62656	39162	25152 (43)	44987 (42)	29322 (40)
C(9)	9283	65833	51069	22109 (71)	47268 (59)	43535 (48)
H(1)	0	10000	0	0	7181	0
H(2)	2354	5825	4082	5606 (68)	4182 (72)	1577 (67)
H(3)	2661	5717	2138	6338 (79)	4105 (82)	-860 (78)
H(4)	2052	7102	89	4888 (51)	5099 (51)	-2327 (50)
H(5)	1250	8729	-305	2978 (48)	6268 (50)	-1801 (47)
H(7)	633	5548	5149	1507 (114)	3984 (118)	4747 (114)
H(8)	917	7765	5336	2183 (94)	5575 (97)	4612 (89)
H(9)	1256	6434	6093	2991 (112)	4620 (119)	5019 (109)

Table 2.2

Vibrational parameters : anisotropic ($\mathring{A}^2 \times 10^4$) for K^+, O and C atoms and isotropic ($\mathring{A}^2 \times 10^3$) for H atoms.

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{23}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
K^+	367(5)	346(5)	352(5)	-	376	-
O(1)	314(12)	504(16)	311(12)	-58(23)	167(19)	153(23)
O(2)	513(17)	627(20)	299(12)	-110(25)	232(23)	432(30)
O(3)	451(14)	443(16)	288(11)	49(21)	212(21)	75(24)
O(4)	607(19)	555(20)	570(18)	-90(30)	691(31)	-315(32)
C(1)	297(14)	330(18)	348(15)	-45(26)	233(25)	-21(25)
C(2)	300(16)	418(22)	533(23)	159(36)	218(32)	168(31)
C(3)	359(19)	463(24)	793(32)	48(45)	553(42)	118(35)
C(4)	370(17)	452(24)	579(23)	-96(36)	607(35)	-3(31)
C(5)	310(15)	348(17)	404(18)	-31(28)	339(28)	-12(26)
C(6)	239(13)	287(14)	326(14)	-40(24)	201(23)	-11(23)
C(7)	277(13)	315(16)	279(14)	51(24)	229(23)	96(25)
C(8)	482(21)	370(19)	426(19)	216(31)	456(34)	206(33)
C(9)	1002(42)	543(29)	603(28)	140(47)	1105(61)	295(58)

	$\underline{U}_{iso}$		$\underline{U}_{iso}$
H(1)	87 (62)	H(5)	14 (11)
H(2)	44 (17)	H(7)	96 (33)
H(3)	56 (20)	H(8)	73 (26)
H(4)	16 (11)	H(9)	95 (33)

Table 2.3

KHDA: Observed structure amplitudes and final calculated structure factors.

h	k	l	|Fo|	Fc
35	3	0	1.0	0.7
34	0	0	3.4	-3.4
33	5	1	1.0	-0.2
33	3	1	7.5	0.5
33	1	1	9.7	-10.7
32	4	0	8.0	6.3
32	2	0	10.0	-11.7
32	0	2	8.8	-8.4
32	0	0	5.7	-0.2
31	3	0	0.9	-0.6
31	1	0	1.3	-0.2
30	6	0	5.0	-5.9
30	4	2	10.3	-9.7
30	4	0	0.9	7.3
30	2	2	13.7	11.4
30	2	0	15.1	-14.2
30	0	2	12.0	-11.0
30	0	0	10.7	14.7
29	3	1	17.5	15.3
29	3	0	4.0	-0.6
29	1	3	9.3	10.6
29	1	2	9.4	-9.0
29	1	1	5.3	-7.0
29	1	0	7.1	5.3
28	4	0	3.6	-2.7
28	2	1	5.9	6.1
28	2	0	3.5	2.3
28	0	0	17.9	18.1
27	5	3	6.6	8.9
27	3	3	14.3	-14.0
27	3	1	26.7	25.9
27	1	0	6.5	10.5
26	8	0	6.0	7.0
26	6	3	7.2	-6.9
26	6	1	1.0	-7.7
26	6	0	11.0	-12.1
26	4	1	14.6	12.8
26	4	0	11.3	9.6
26	0	4	9.5	10.1
26	0	0	27.2	38.0
25	7	3	12.5	-11.6
25	5	4	7.5	9.5
25	5	3	6.0	7.4
25	5	0	14.6	-17.0
25	3	4	14.0	-13.8
25	3	1	7.5	6.3
25	1	5	12.5	-11.2
25	1	1	9.7	-9.2
25	1	0	11.4	12.8
24	8	0	5.9	5.6
24	6	4	9.1	-6.3
24	6	1	7.8	-5.8
24	6	0	8.9	-13.4
24	4	4	12.4	11.7
24	4	3	10.4	9.9
24	4	2	27.7	-28.0
24	4	0	12.7	13.0
24	2	4	14.1	-13.3
24	2	2	24.0	23.7
24	2	0	7.0	-5.5
24	0	6	10.7	11.2
24	0	4	16.2	16.0
24	0	2	16.1	-16.0
24	0	0	27.6	28.3
23	7	1	11.4	12.5
23	7	0	8.6	-9.7
23	5	3	8.1	8.3
23	5	2	12.5	-11.7
23	5	1	12.2	-12.1
23	5	0	0.9	0.2
23	3	1	5.6	4.6
23	3	0	14.1	-14.4
23	1	6	4.4	6.5
23	1	5	12.6	-11.3
23	1	3	13.2	-11.6
23	1	2	17.4	18.1
23	1	1	17.5	-16.7
23	1	0	6.0	6.7
22	6	4	6.7	-9.2
22	6	1	9.4	9.4
22	4	5	7.3	8.5
22	4	3	10.3	-8.9
22	4	1	15.8	-14.6
22	4	0	3.0	-1.6
22	2	6	6.9	9.0
22	2	5	16.7	-15.9
22	2	4	9.8	-9.8
22	2	3	16.5	17.7
22	2	2	26.3	24.0
22	2	1	8.5	-8.7
22	2	0	13.3	-12.5
22	0	2	0.8	-3.6
22	0	0	13.8	13.0
21	7	1	16.9	15.0
21	7	0	6.6	-6.7
21	5	3	11.9	12.5
21	5	1	15.9	-12.3
21	3	7	7.2	-9.0
21	3	5	9.1	9.0
21	3	3	22.4	-22.1
21	3	2	10.0	11.3
21	3	1	4.3	-4.0
21	3	0	9.7	-10.5
21	1	3	38.5	39.1
21	1	2	10.5	10.6
21	1	1	40.5	-38.9
21	1	0	3.8	-3.1
20	8	1	12.3	10.7
20	6	4	11.9	-10.6
20	6	3	11.2	10.4
20	6	2	12.4	12.3
20	6	0	13.3	-16.3
20	4	4	3.7	2.7
20	4	2	13.4	-12.5
20	4	1	3.7	-0.9
20	4	0	20.6	20.0
20	2	6	15.8	16.0
20	2	3	25.4	-24.3
20	2	2	0.8	-0.8
20	2	1	13.9	-14.5
20	2	0	53.6	-52.0
20	0	6	11.7	-13.3
20	0	4	6.6	-5.2
20	0	2	55.1	55.4
20	0	0	12.0	11.5
19	9	0	1.0	-6.2
19	7	4	9.5	-7.7
19	5	3	9.3	9.2
19	5	1	15.0	-14.7
19	5	0	0.8	0.5
19	3	7	9.1	-10.7
19	3	6	6.7	8.0
19	3	5	4.5	6.7
19	3	4	20.7	-20.6
19	3	3	20.0	-24.4
19	3	2	[illegible]	[illegible]
19	3	1	5.3	3.4
19	3	0	27.4	19.6
19	1	9	7.3	-10.1
19	1	5	10.3	-9.7
19	1	4	15.6	15.3
19	1	3	20.2	20.1
19	1	2	5.4	5.0
19	1	1	34.5	-34.0
19	1	0	20.7	-20.2
18	8	2	12.9	-11.4
18	8	1	10.1	9.8
18	8	0	12.5	13.5
18	6	5	8.4	5.6
18	6	4	11.3	-9.1
18	6	2	17.5	15.3
18	6	1	5.4	5.4
18	6	0	12.5	-13.3
18	4	8	7.7	7.9
18	4	3	13.2	-11.9
18	4	2	5.6	-1.6
18	4	1	21.4	20.4
18	4	0	2.5	2.9
18	2	4	26.9	-26.8
18	2	3	14.7	-13.4
18	2	2	49.4	45.5
18	2	1	48.0	-47.3
18	2	0	34.7	-33.2
18	0	8	9.8	10.4
18	0	4	39.7	39.2
18	0	2	55.5	-55.6
18	0	0	6.2	-3.5
17	9	3	8.7	11.6
17	9	0	1.0	2.7
17	7	5	9.7	9.1
17	7	1	12.0	10.8
17	5	5	11.2	-9.4
17	5	2	0.8	-0.0
17	5	1	20.0	-19.8
17	5	0	14.0	14.2
17	3	7	9.5	-8.9
17	3	4	0.8	3.3
17	3	3	14.5	-11.6
17	3	2	12.8	-12.2
17	3	1	8.7	8.2
17	3	0	8.0	8.4
17	1	5	21.0	-20.5
17	1	4	12.9	14.0
17	1	3	36.6	-37.8
17	1	2	11.5	-11.9
17	1	1	6.5	-7.5
17	1	0	4.6	-3.3
16	10	2	5.8	-3.5
16	8	5	10.7	9.2
16	6	5	4.5	-6.2
16	6	4	14.1	-15.3
16	6	3	5.3	4.0
16	6	2	13.7	13.5
16	6	0	10.2	-10.2
16	4	7	7.4	-6.4
16	4	6	18.0	-16.8
16	4	5	13.0	11.3
16	4	4	25.9	24.3
16	4	3	7.0	-9.5
16	4	2	11.5	-12.1
16	4	1	9.8	-11.7
16	4	0	30.9	34.3
16	2	9	11.1	-12.7
16	2	6	10.2	10.3
16	2	5	9.3	-9.0
16	2	4	14.1	-14.8
16	2	3	30.9	-30.8
16	2	2	30.4	31.9
16	2	1	19.9	20.6
16	2	0	5.5	-6.0
16	0	10	13.2	-13.1
16	0	8	7.8	10.8
16	0	4	9.0	10.0
16	0	2	65.5	-65.7
16	0	0	23.0	-21.9
15	9	2	12.8	-12.2
15	9	1	14.8	-14.2
15	7	6	6.2	-8.0
15	7	5	7.8	8.1
15	7	4	8.7	8.1
15	7	2	11.5	12.9
15	7	1	22.6	22.3
15	5	5	0.9	1.7
15	5	3	12.7	11.9
15	5	2	16.8	-16.0
15	5	1	12.1	-12.2
15	5	0	15.8	13.5
15	3	7	10.6	-9.9
15	3	6	6.7	-7.4
15	3	5	7.0	-5.5
15	3	4	14.6	16.1
15	3	3	50.0	-49.1
15	3	2	20.8	20.3
15	3	1	30.4	30.7
15	3	0	20.8	-22.9
15	1	9	7.5	-9.8
15	1	8	4.9	5.0
15	1	7	14.6	15.4
15	1	6	9.4	-11.2
15	1	5	30.0	-29.2
15	1	4	9.9	9.0
15	1	3	35.0	34.4
15	1	2	47.7	-47.8
15	1	1	46.2	-45.2
15	1	0	27.1	25.1
14	8	5	10.6	10.5
14	8	4	13.6	14.5
14	8	2	13.9	-15.7
14	6	4	5.1	-7.5
14	6	2	9.9	8.5
14	6	1	9.0	8.3
14	6	0	4.7	-4.0
14	4	8	8.0	8.9
14	4	6	16.5	-16.3
14	4	4	18.2	17.1
14	4	3	13.6	-15.3
14	4	2	13.7	13.8
14	4	1	10.7	-11.5
14	4	0	44.2	50.4
14	2	7	7.7	-9.7
14	2	6	13.0	12.1
14	2	5	20.0	[illegible]
14	2	4	0.7	1.4
14	2	3	15.6	14.0
14	2	2	35.2	-35.1
14	2	1	13.2	12.0
14	2	0	23.9	-24.9
14	0	10	15.6	-17.6
14	0	6	20.4	-19.3
14	0	4	7.2	7.3
14	0	2	46.6	-44.9
14	0	0	97.1	103.8
13	9	2	7.7	-8.6
13	7	3	9.1	-6.7
13	7	1	7.5	8.8
13	5	7	7.5	8.3
13	5	6	13.3	-12.0
13	5	5	13.5	-13.2
13	5	4	23.9	25.5
13	5	3	24.9	24.3
13	5	2	17.4	19.7
13	5	1	6.4	-7.1
13	5	0	4.6	8.5
13	3	11	3.2	-9.7
13	3	10	3.2	0.6
13	3	7	12.7	-14.7
13	3	6	2.6	-0.8
13	3	5	13.4	13.4
13	3	4	22.9	23.4
13	3	3	49.6	-47.9
13	3	2	24.1	-25.6
13	3	1	41.7	42.6
13	3	0	11.7	14.3
13	1	10	14.7	-12.9
13	1	9	14.2	-14.1
13	1	7	12.6	10.7
13	1	6	9.5	-9.1
13	1	5	20.9	-21.3
13	1	4	21.2	-21.8
13	1	3	27.6	26.7
13	1	2	12.8	-12.8
13	1	1	26.4	-26.5
13	1	0	13.7	-13.8
12	8	6	3.1	-8.3
12	8	2	14.7	-13.2
12	8	1	10.6	12.6
12	8	0	11.5	12.7
12	6	10	5.0	4.2
12	6	5	11.3	11.7
12	6	4	6.4	9.1
12	6	3	10.9	15.1
12	6	2	27.5	26.8
12	6	1	48.7	-46.9
12	6	0	15.2	-15.2
12	4	8	12.1	13.3
12	4	5	21.8	-20.2
12	4	4	31.6	30.2
12	4	3	5.6	-7.7
12	4	2	57.3	-57.0
12	4	1	31.6	32.3
12	4	0	66.5	65.9
12	2	8	16.5	-17.5
12	2	7	0.8	-0.5
12	2	6	9.2	9.8
12	2	5	8.5	-9.0
12	2	4	14.3	-14.5
12	2	3	15.4	15.7
12	2	2	13.5	13.1
12	2	1	7.3	-8.3
12	2	0	0.5	-3.0
12	0	8	19.4	20.9
12	0	6	35.5	-36.2
12	0	4	13.3	14.6
12	0	2	84.2	-81.2
12	0	0	71.4	71.4
11	9	3	14.9	12.2
11	9	1	9.1	-6.1
11	7	5	15.3	13.8
11	7	3	27.6	-27.5
11	7	2	25.0	-23.8
11	7	1	3.0	3.6
11	7	0	2.9	6.6
11	5	7	6.7	7.6
11	5	5	11.9	-13.5
11	5	4	20.4	20.2
11	5	3	2.5	-5.2
11	5	2	31.3	31.4
11	5	1	16.5	16.4
11	5	0	11.0	-11.2
11	3	11	13.3	-12.1
11	3	7	14.7	-13.8
11	3	6	9.7	8.8
11	3	5	16.0	15.2
11	3	4	19.5	-13.3
11	3	3	17.5	19.2
11	3	2	31.3	29.9
11	3	1	13.1	13.1
11	3	0	15.0	14.0
11	1	11	11.7	12.9
11	1	7	10.3	-7.8
11	1	6	4.3	-4.3
11	1	5	25.0	-25.7
11	1	4	21.0	-19.9
11	1	3	23.4	22.7
11	1	2	21.7	-20.8
11	1	1	43.8	-44.4
11	1	0	30.1	-27.9
10	10	0	9.8	-11.5
10	8	3	0.9	-7.0
10	8	0	20.5	20.7
10	6	10	9.9	11.3
10	6	9	11.3	-8.9
10	6	6	20.7	17.7
10	6	5	12.8	-13.3
10	6	4	0.5	-1.1
10	6	3	6.2	4.4
10	6	2	12.8	12.8
10	6	1	5.6	-3.1
10	6	0	8.9	-8.8
10	4	9	5.8	7.4
10	4	8	10.3	10.3
10	4	6	6.1	-3.0
10	4	5	0.7	0.7
10	4	4	48.4	47.3
10	4	3	27.0	28.1
10	4	2	35.6	-36.5
10	4	1	6.3	-6.4
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10	2	12	5.1	-8.5
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9	7	3	21.9	-21.3
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9	5	6	14.0	15.1
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9	5	4	9.1	-8.1
9	5	3	23.3	23.7
9	5	2	39.9	-40.1
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9	3	7	28.7	-29.4
9	3	6	22.3	22.4
9	3	5	24.7	23.0
9	3	4	0.7	-0.2
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9	3	0	22.1	24.5
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9	1	5	2.8	-4.5
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9	1	3	30.4	31.1
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8	8	6	9.7	-6.9
8	8	5	4.0	-5.8
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8	4	12	12.6	11.6
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7	1	0	34.9	32.5
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h	k	l	|Fo|	Fc
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-23	5	6	5.6	-7.2
-23	5	5	19.1	-18.8
-23	5	4	3.5	-3.3
-23	5	3	8.9	9.9
-23	5	2	0.8	-0.1
-23	5	1	11.2	-15.9
-23	3	16	10.6	6.4
-23	3	14	5.4	5.7
-23	3	13	13.4	12.4
-23	3	12	3.0	1.1
-23	3	11	17.3	-17.4
-23	3	10	0.8	-1.2
-23	3	8	3.0	3.0
-23	3	7	3.0	-2.5
-23	3	6	9.7	9.0
-23	3	5	26.8	24.9
-23	3	4	5.1	-2.3
-23	3	3	0.7	2.0
-23	3	2	6.2	6.3
-23	3	1	25.2	27.0
-23	1	16	7.4	-7.0
-23	1	15	5.3	3.2
-23	1	14	0.9	-6.4
-23	1	13	7.1	-5.9
-23	1	12	0.9	6.1
-23	1	11	17.5	18.0
-23	1	10	7.1	-11.3
-23	1	9	0.8	-1.5
-23	1	8	12.2	11.2
-23	1	7	73.2	72.2
-23	1	6	15.9	-15.5
-23	1	5	57.5	-57.0
-23	1	4	15.4	14.8
-23	1	3	7.8	6.0
-23	1	2	0.7	-0.6
-23	1	1	13.2	-13.4
-24	8	5	11.4	-10.8
-24	8	4	17.0	16.6
-24	6	10	9.8	8.2
-24	6	9	0.9	1.8
-24	6	8	3.5	-3.0
-24	6	7	1.5	-4.3
-24	6	6	2.9	2.5
-24	6	5	5.8	-7.0
-24	6	4	8.7	-9.7
-24	6	3	0.9	2.7
-24	6	2	5.5	7.7
-24	6	1	10.5	-13.1
-24	4	14	8.1	-9.4
-24	4	9	3.8	4.7
-24	4	8	13.9	13.9
-24	4	7	5.6	7.3
-24	4	6	21.5	-20.9
-24	4	5	18.4	17.8
-24	4	4	2.6	5.7
-24	4	3	4.2	-5.7
-24	4	2	23.2	-21.7
-24	2	15	9.6	5.2
-24	2	12	11.3	-11.3
-24	2	10	7.9	5.1
-24	2	9	10.1	10.7
-24	2	8	24.0	-22.2
-24	2	7	2.7	1.2
-24	2	6	14.4	13.5
-24	2	5	19.2	-18.5
-24	2	4	7.0	-10.5
-24	2	3	13.9	15.1
-24	2	2	21.9	22.7
-24	2	1	9.2	9.3
-24	0	10	12.8	-12.9
-24	0	8	19.7	18.7
-24	0	6	13.1	12.5
-24	0	4	33.1	32.0
-24	0	2	34.3	-35.2
-25	7	8	4.2	-7.3
-25	7	7	11.5	-12.8
-25	5	13	9.4	-8.3
-25	5	12	7.3	6.2
-25	5	11	2.7	7.0
-25	5	10	5.1	-6.4
-25	5	9	17.3	-19.2
-25	5	8	9.4	12.7
-25	5	7	8.3	12.4
-25	5	6	3.3	-11.7
-25	5	5	20.5	-19.6
-25	5	3	12.0	13.2
-25	3	13	8.2	9.3
-25	3	12	6.9	5.6
-25	3	11	0.9	-7.0
-25	3	9	27.7	27.3
-25	3	7	3.4	3.6
-25	3	6	21.1	-19.9
-25	3	5	13.7	13.7
-25	3	4	23.9	24.1
-25	3	3	23.0	-22.3
-25	3	2	4.5	-1.3
-25	3	1	13.4	13.7
-25	1	15	1.0	25.5
-25	1	14	3.7	-4.9
-25	1	13	6.3	-7.2
-25	1	12	6.4	7.7
-25	1	11	9.4	9.7
-25	1	10	15.0	-14.9
-25	1	9	15.4	-15.7
-25	1	8	20.2	17.9
-25	1	7	5.7	4.5
-25	1	6	15.6	15.0
-25	1	5	2.1	6.4
-25	1	4	11.1	-13.3
-25	1	3	26.2	26.3
-25	1	2	5.7	5.7
-25	1	1	1.7	-3.8
-26	8	5	8.9	8.7
-26	8	4	11.6	12.4
-26	6	8	10.7	-9.6
-26	6	4	11.3	-8.9
-26	4	14	5.2	-6.5
-26	4	13	10.6	6.4
-26	4	12	12.3	10.9
-26	4	10	10.8	-13.0
-26	4	9	8.4	10.1
-26	4	8	12.9	12.3
-26	4	6	30.9	-31.2
-26	4	4	20.3	19.9
-26	4	2	20.4	-20.6
-26	2	13	9.1	-5.6
-26	2	12	15.1	-15.2
-26	2	10	13.2	14.0
-26	2	9	13.7	13.3
-26	2	8	2.6	-4.6
-26	2	7	3.4	-0.6
-26	2	6	38.6	37.6
-26	2	5	13.5	-15.0
-26	2	4	3.9	-2.6
-26	2	3	6.9	8.0
-26	2	2	6.7	-6.0
-26	2	1	2.5	5.0
-26	0	14	8.2	6.5
-26	0	10	16.9	-15.4
-26	0	8	22.5	23.5
-26	0	6	55.7	-55.2
-26	0	4	29.5	27.4
-26	0	2	7.8	2.1
-27	7	11	2.3	-6.6
-27	7	7	7.8	-9.6
-27	7	5	17.2	16.2
-27	7	3	11.7	-12.4
-27	5	13	10.1	-9.1
-27	5	8	11.6	-10.1
-27	5	6	15.0	-15.5
-27	5	1	7.4	-7.7
-27	3	14	9.5	-9.2
-27	3	13	13.1	10.7
-27	3	12	11.7	7.7
-27	3	9	14.1	13.9
-27	3	7	11.6	-11.3
-27	3	6	5.4	9.8
-27	3	5	1.8	4.3
-27	3	4	16.0	-17.8
-27	3	3	8.5	-8.8
-27	3	1	16.3	17.1
-27	1	15	6.6	6.6
-27	1	13	7.1	-8.2
-27	1	11	9.4	12.5
-27	1	10	5.6	-4.5
-27	1	9	6.7	-6.5
-27	1	8	16.9	16.3
-27	1	7	16.0	15.6
-27	1	6	0.8	-0.3
-27	1	5	6.0	-8.3
-27	1	4	11.2	12.1
-27	1	3	35.3	36.1
-27	1	2	1.6	2.4
-27	1	1	17.9	-21.4
-28	8	8	10.3	8.9
-28	6	8	17.7	-15.9
-28	6	5	6.1	8.7
-28	4	14	8.8	-7.1
-28	4	13	7.3	6.4
-28	4	12	6.6	6.5
-28	4	11	3.5	-2.5
-28	4	10	15.0	-15.0
-28	4	9	9.9	10.7
-28	4	8	14.1	13.1
-28	4	7	11.0	-9.4
-28	4	6	12.8	-11.3
-28	4	5	10.7	-15.6
-28	4	4	17.8	17.8
-28	4	3	0.9	3.7
-28	4	2	22.6	-22.4
-28	4	1	0.9	0.3
-28	2	14	17.4	17.9
-28	2	13	7.9	-7.1
-28	2	12	4.7	-1.5
-28	2	11	6.9	3.2
-28	2	10	12.0	12.1
-28	2	9	6.7	4.5
-28	2	7	3.0	-5.1
-28	2	6	0.6	1.5
-28	2	5	1.0	-2.3
-28	2	4	7.4	-6.5
-28	2	3	0.6	-2.3
-28	2	2	10.5	11.2
-28	2	1	6.0	-6.7
-28	0	16	10.7	1.0
-28	0	14	13.7	-17.5
-28	0	12	2.7	-1.7
-28	0	10	13.6	-14.7
-28	0	8	33.0	-34.0
-28	0	6	11.1	[illegible]
-28	0	4	21.9	20.5
-28	0	2	0.6	-0.4
-29	7	11	7.5	-9.1
-29	7	6	11.1	9.6
-29	7	5	13.2	10.9
-29	7	4	8.9	-9.5
-29	7	3	14.4	-14.4
-29	5	14	1.0	-3.5
-29	5	9	6.8	-6.9
-29	5	8	6.2	-9.4
-29	5	7	7.5	8.3
-29	5	6	3.0	-4.4
-29	5	5	15.5	-13.8
-29	5	4	13.6	11.9
-29	5	3	10.4	9.9
-29	5	2	9.4	-10.5
-29	5	1	7.0	-8.0
-29	3	12	5.2	-6.0
-29	3	11	7.3	-10.5
-29	3	10	3.9	3.2
-29	3	9	15.8	16.5
-29	3	8	3.4	0.6
-29	3	7	32.3	-31.0
-29	3	6	8.9	-5.5
-29	3	5	26.8	27.4
-29	3	4	11.9	-11.7
-29	3	3	5.2	-7.6
-29	3	2	3.2	-9.6
-29	3	1	4.9	5.0
-29	1	13	8.1	-6.4
-29	1	12	6.1	1.6
-29	1	11	27.2	26.7
-29	1	10	1.7	7.1
-29	1	9	7.8	-8.4
-29	1	8	4.2	-0.5
-29	1	7	9.6	10.0
-29	1	6	10.2	11.5
-29	1	5	20.5	-19.6
-29	1	4	7.1	5.0
-29	1	3	4.7	-4.4
-29	1	2	10.9	11.6
-29	1	1	5.9	-6.8
-30	8	6	9.7	-7.9
-30	6	8	9.9	-7.8
-30	6	6	12.3	12.7
-30	6	4	8.3	-8.2
-30	4	12	11.6	11.9
-30	4	10	10.6	-11.1
-30	4	9	0.9	-6.2
-30	4	8	0.9	-2.6
-30	4	7	10.8	-10.3
-30	4	6	3.5	-6.1
-30	4	5	6.7	7.6
-30	4	4	4.9	4.0
-30	4	3	3.4	1.5
-30	4	2	10.5	-11.7
-30	4	1	0.9	-2.4
-30	2	14	7.3	8.2
-30	2	13	11.7	8.6
-30	2	12	7.8	-8.5
-30	2	11	4.8	3.7
-30	2	10	3.1	5.0
-30	2	9	0.9	-0.9
-30	2	8	5.7	-2.1
-30	2	7	6.4	6.7
-30	2	6	3.2	1.9
-30	2	5	7.8	-6.3
-30	2	4	9.1	-11.9
-30	2	3	1.9	0.9
-30	2	2	18.4	21.2
-30	2	1	9.7	-11.2
-30	0	14	9.0	-7.2
-30	0	12	4.3	5.0
-30	0	10	0.9	1.9
-30	0	8	24.8	24.4
-30	0	6	11.9	-10.2
-30	0	4	24.3	24.5
-30	0	2	16.2	-16.9
-31	7	9	2.5	7.2
-31	7	1	10.0	8.7
-31	5	9	9.7	-8.2
-31	5	7	4.2	4.1
-31	5	6	10.8	11.0
-31	5	5	8.4	7.4
-31	5	4	13.4	-15.1
-31	5	2	11.8	-11.1
-31	3	15	12.1	-11.7
-31	3	14	8.8	7.0
-31	3	13	9.0	8.0
-31	3	12	8.1	-9.9
-31	3	11	5.0	-2.4
-31	3	10	6.5	0.5
-31	3	9	15.2	12.3
-31	3	8	14.4	-12.6
-31	3	7	15.6	-17.9
-31	3	6	6.7	0.2
-31	3	5	0.9	3.3
-31	3	4	0.9	1.7
-31	3	3	9.5	-9.9
-31	3	1	0.9	-1.9
-31	1	15	8.6	8.8
-31	1	13	6.1	-9.8
-31	1	12	0.9	0.1
-31	1	11	0.9	2.5
-31	1	10	12.8	14.1
-31	1	9	17.1	-16.8
-31	1	8	0.9	0.9
-31	1	7	7.4	10.9
-31	1	6	0.8	-0.3
-31	1	5	16.1	-15.5
-31	1	4	3.9	5.6
-31	1	3	0.0	7.7
-31	1	2	0.0	0.2
-31	1	1	11.6	-12.1
-32	6	6	12.8	-12.5
-32	6	5	15.4	-14.7
-32	6	4	15.6	-16.5
-32	6	3	6.7	7.6
-32	6	1	13.3	-12.3
-32	4	10	6.2	-3.6
-32	4	8	4.6	6.0
-32	4	7	3.7	2.8
-32	4	6	15.1	-15.8
-32	4	5	[illegible]	12.2
-32	4	4	[illegible]	7.7
-32	4	3	11.4	-11.7
-32	4	2	0.4	-6.1
-32	2	12	12.6	-11.5
-32	2	11	3.4	7.1
-32	2	10	10.2	17.6
-32	2	9	9.0	-9.7
-32	2	8	15.7	-13.6
-32	2	7	11.0	-12.0
-32	2	6	16.0	16.7
-32	2	5	4.7	1.3
-32	2	4	12.8	-12.0
-32	2	3	0.9	-3.9
-32	2	2	9.5	6.2
-32	2	1	5.3	-7.1
-32	0	12	20.3	20.3
-32	0	10	11.6	-13.4
-32	0	8	11.5	11.5
-32	0	6	0.9	-3.2
-32	0	4	4.8	5.7
-32	0	2	0.9	5.0
-33	5	11	1.0	7.1
-33	5	10	3.3	-6.0
-33	5	7	7.5	6.6
-33	5	5	11.2	-11.3
-33	5	3	9.3	9.3
-33	5	1	8.4	-6.8
-33	3	13	0.7	6.7
-33	3	11	10.8	-9.4
-33	3	9	3.0	-2.2
-33	3	8	6.5	-0.8
-33	3	7	5.6	-3.9
-33	3	6	3.4	6.8
-33	3	5	9.8	9.0
-33	3	4	7.4	6.3
-33	3	3	19.3	-20.4
-33	3	2	5.9	-5.4
-33	1	11	3.4	1.9
-33	1	10	6.5	6.0
-33	1	9	7.3	-6.3
-33	1	8	7.8	-3.4
-33	1	7	0.9	1.5
-33	1	6	4.7	-3.1
-33	1	5	8.0	-8.4
-33	1	4	0.9	-0.9
-33	1	3	7.6	9.1
-33	1	2	6.5	2.8
-33	1	1	8.9	-14.0
-34	6	8	6.5	-5.1
-34	6	5	12.4	12.4
-34	6	2	9.7	9.6
-34	4	8	8.1	9.1
-34	4	5	6.3	-7.1
-34	4	4	12.3	-12.3
-34	4	3	6.4	-7.5
-34	2	14	4.3	6.6
-34	2	10	10.5	7.7
-34	2	9	7.2	-6.2
-34	2	8	15.9	-19.1
-34	2	7	3.2	1.5
-34	2	6	16.8	16.3
-34	2	5	7.5	-2.2
-34	2	4	0.9	-4.9
-34	2	3	0.9	1.1
-34	2	1	1.0	-5.1
-34	0	12	11.7	10.7
-34	0	10	0.9	0.1
-34	0	8	6.3	8.5
-34	0	6	10.5	-12.2
-34	0	4	4.9	10.3
-34	0	2	3.5	-5.8
-35	5	9	6.4	-3.3
-35	5	7	8.0	8.0
-35	5	5	11.8	-12.2
-35	5	4	12.7	12.4
-35	3	11	12.0	-13.1
-35	3	4	12.2	-11.3
-35	3	3	15.2	-13.1
-35	1	11	12.5	11.1
-35	1	9	15.3	-17.0
-35	1	8	0.9	-0.0
-35	1	7	11.2	11.4
-35	1	6	0.9	0.1
-35	1	5	9.0	-7.8
-35	1	4	1.3	4.5
-35	1	3	8.1	6.5
-35	1	1	10.2	-10.2
-36	4	11	10.9	-7.6
-36	4	10	5.5	-4.4
-36	4	6	6.4	-8.1
-36	4	4	12.5	12.2
-36	2	10	4.9	5.8
-36	2	4	14.9	-14.5
-36	2	3	16.0	-15.5
-36	0	14	1.0	-5.2
-36	0	12	8.6	2.7
-36	0	8	5.4	-6.7
-36	0	6	0.9	2.4
-36	0	4	8.7	8.3
-36	0	2	8.9	-7.7
-37	5	7	8.8	8.5
-37	3	11	10.9	-7.5
-37	3	10	6.7	-6.5
-37	3	6	1.0	-5.3
-37	1	7	15.2	14.2
-37	1	5	7.4	-2.4
-38	4	8	6.5	7.0
-38	4	5	6.7	5.3
-38	4	4	7.8	8.3
-38	4	3	1.0	-1.7
-38	2	12	0.8	-7.6
-38	2	11	9.7	-7.9
-38	2	8	8.0	-8.9
-38	2	5	14.3	-13.7
-38	2	4	7.9	-8.1
-38	0	10	7.3	-9.1
-38	0	8	12.1	-11.0
-38	0	6	8.9	-7.3
-38	0	4	7.3	8.7
-38	0	2	22.1	-21.4
-39	3	9	8.3	5.4
-39	3	3	3.1	-7.2
-39	1	11	1.0	4.0
-39	1	10	9.4	-6.9
-39	1	5	13.1	-13.0
-39	1	3	6.1	5.7
-40	0	12	6.1	6.6
-40	0	10	15.0	-11.0
-40	0	8	[illegible]	9.1
-40	0	6	10.3	-11.1
-41	1	7	13.5	-14.9
-41	0	[illegible]	15.0	-6.1
-42	1	[illegible]	3.3	-3.0
-42	0	8	6.8	4.3
-42	0	6	7.3	-6.5

Table 2.4

KHDA : analysis of the agreement of $|F_o|$ and $|F_c|$ at the end of the refinement. N is the number of reflexions. Structure factors are on the absolute scale.

(a) As a function of sin θ/λ.

	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
0·0 - 0·1	562	582	39	8	0·069	4·9
0·1 - 0·2	3309	3355	134	52	0·040	2·6
0·2 - 0·3	6094	5975	260	148	0·043	1·8
0·3 - 0·4	6691	6806	486	280	0·073	1·7
0·4 - 0·5	8269	8465	650	463	0·079	1·4
0·5 - 0·6	7154	7310	746	573	0·104	1·3
0·6 - 0·7	4714	4862	864	510	0·183	1·7
0·7 - 0·8	2815	2914	548	330	0·195	1·7

(b) As a function of $|F_o|$.

	$\Sigma\|F_o\|$	$\Sigma\|F_c\|$	$\Sigma\|\Delta\|$	N	R	$\Sigma\|\Delta\|/N$
0 - 3	321	1264	1020	268	3·183	3·8
3 - 6	1197	1315	467	260	0·390	1·8
6 - 9	2802	2793	549	371	0·196	1·5
9 - 12	3866	3793	431	372	0·112	1·2
12 - 15	3662	3588	264	274	0·072	1·0
15 - 20	4291	4258	228	249	0·053	0·9
20 - 30	6223	6145	245	257	0·039	1·0
30 - 45	5849	5788	189	161	0·032	1·2
45 - 70	4823	4767	126	87	0·026	1·4
70 - 140	5189	5132	142	57	0·027	2·5
140 - 250	1386	1427	67	8	0·048	8·4
All	39608	40270	3728	2364	0·094	1·6

Table 2.5

$K^{+}\cdots O$ distances (Å) and $O\cdots K^{+}\cdots O$ angles (°) in KHDA: (a) present work, (b) Manojlovic and Speakman (1967).

	(a)	(b)
$K^{+}\cdots O(2^{VII})$	2·717 (4)	2·720 (3)
$K^{+}\cdots O(1^{I})$	2·761 (3)	2·766 (2)
$K^{+}\cdots O(4)$	2·826 (4)	2·832 (3)
$O(2^{VII})\cdots K^{+}\cdots O(2^{VI})$	95·22 (11)	94·93 (9)
$O(2^{VII})\cdots K^{+}\cdots O(1^{VIII})$	69·75 (9)	69·83 (7)
$O(2^{VII})\cdots K^{+}\cdots O(1^{I})$	81·74 (9)	81·79 (8)
$O(2^{VII})\cdots K^{+}\cdots O(4^{II})$	89·77 (10)	90·19 (8)
$O(2^{VI})\cdots K^{+}\cdots O(4^{II})$	168·38 (9)	168·19 (8)
$O(1^{VIII})\cdots K^{+}\cdots O(1^{I})$	137·40 (10)	137·72 (8)
$O(1^{VIII})\cdots K^{+}\cdots O(4^{II})$	109·85 (9)	109·99 (8)
$O(1^{I})\cdots K^{+}\cdots O(4^{II})$	100·72 (9)	100·49 (8)
$O(4)\cdots K^{+}\cdots O(4^{II})$	87·31 (11)	86·84 (9)

Table 2.6

Bond lengths (Å) in KHDA: (a) present work, (b) Manojlovic and Speakman (1967), (c) Sequeira, Berkebile and Hamilton (1967).

	(a)	(b)	(c)
Benzene Ring:			
C(1) - C(2)	1·370 (5)	1·390 (4)	1·392 (3)
C(2) - C(3)	1·389 (7)	1·372 (6)	1·394 (4)
C(3) - C(4)	1·382 (7)	1·390 (5)	1·399 (4)
C(4) - C(5)	1·381 (6)	1·387 (4)	1·382 (3)
C(5) - C(6)	1·399 (5)	1·393 (5)	1·395 (3)
C(6) - C(1)	1·382 (5)	1·394 (4)	1·393 (3)
C(2) - H(2)	0·98 (7)	0·93 (5)	1·081 (6)
C(3) - H(3)	1·01 (8)	1·03 (6)	1·083 (6)
C(4) - H(4)	0·89 (5)	0·85 (4)	1·080 (7)
C(5) - H(5)	1·02 (5)	1·01 (4)	1·088 (5)
Carboxyl Group:			
C(6) - C(7)	1·497 (5)	1·504 (4)	1·501 (3)
C(7) - O(2)	1·218 (5)	1·221 (4)	1·217 (4)
C(7) - O(1)	1·286 (4)	1·284 (4)	1·284 (3)
Acetyl Group:			
C(1) - O(3)	1·403 (5)	1·392 (4)	1·390 (4)
O(3) - C(8)	1·348 (5)	1·360 (4)	1·356 (4)
C(8) - C(9)	1·471 (6)	1·477 (6)	1·491 (4)
C(8) - O(4)	1·201 (6)	1·199 (4)	1·204 (4)
C(9) - H(7)	1·10 (12)	0·93 (7)	0·98 (2)
C(9) - H(8)	0·89 (10)	0·83 (10)	1·01 (2)
C(9) - H(9)	1·03 (11)	1·13 (12)	0·99 (2)
Hydrogen Bond:			
$O(1)\cdots O(1^{IX})$	2·439 (4)	2·455 (5)	2·448 (4)

Table 2.7

Bond angles (°) in KHDA: (a) present work,
(b) Manojlovic and Speakman (1967),
(c) Sequeira, Berkebile and Hamilton (1967).
Estimated standard deviations are approximately 0·3°.

	(a)	(b)	(c)
C(1) - C(2) - C(3)	119·6	119·8	119·5
C(2) - C(3) - C(4)	119·5	120·2	119·6
C(3) - C(4) - C(5)	120·4	120·0	120·0
C(4) - C(5) - C(6)	120·5	120·6	121·3
C(5) - C(6) - C(1)	117·9	118·3	118·2
C(6) - C(1) - C(2)	122·1	121·3	121·5
C(1) - C(6) - C(7)	123·0	122·6	122·5
C(5) - C(6) - C(7)	119·1	119·1	119·3
C(6) - C(7) - O(1)	114·5	114·5	114·4
C(6) - C(7) - O(2)	121·3	121·4	121·1
O(1) - C(7) - O(2)	124·1	124·1	124·4
C(2) - C(1) - O(3)	116·9	117·4	116·6
C(6) - C(1) - O(3)	121·0	121·4	121·9
C(1) - O(3) - C(8)	118·1	118·1	118·0
O(3) - C(8) - C(9)	111·7	111·4	111·4
O(3) - C(8) - O(4)	122·7	122·6	122·7
O(4) - C(8) - C(9)	125·7	125·8	125·9

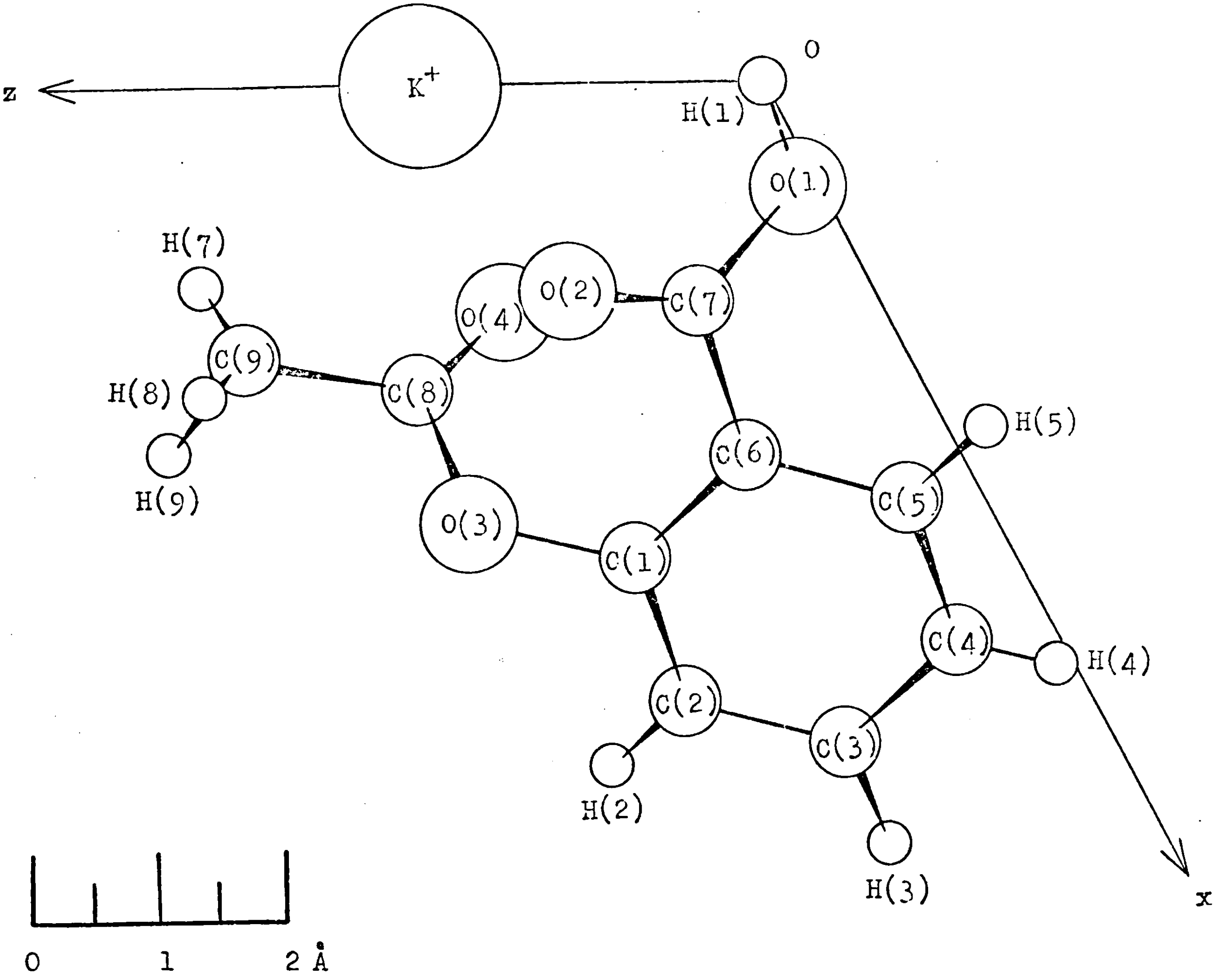
z
K$^+$
O
H(1)
O(1)
H(7)
O(2)
C(7)
O(4)
C(9)
H(8)
C(8)
H(5)
C(6)
H(9)
C(5)
O(3)
C(1)
C(4)
H(4)
C(2)
C(3)
H(2)
H(3)
x
0
1
2 Å

Figure 2.1 The crystal chemical unit (CCU) of KHDA.

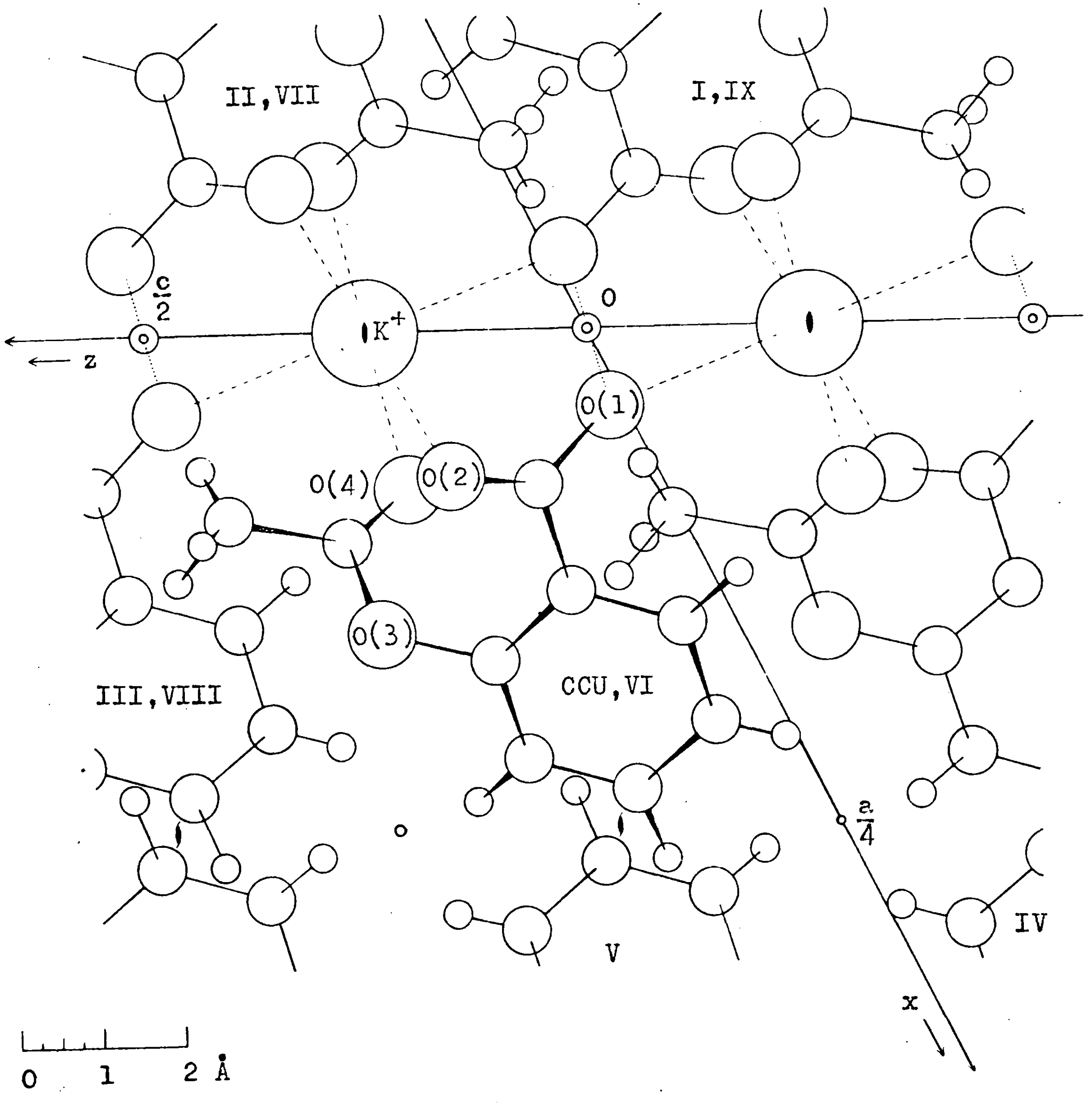
II,VII
I,IX
c
2
z
K+
0
O(1)
O(4)
O(2)
O(3)
III,VIII
CCU,VI
a
4
V
IV
x
0
1
2 Å

Figure 2.2 The crystal structure as seen in its b-axial projection.

2.3 DISCUSSION

A general view of the crystal structure of potassium hydrogen di-aspirinate (KHDA) is shown in Figure 2.2. With the cation lying on a 2-fold axis and the two aspirinate residues related by a crystallographic centre of inversion, it is typical of that found in the acid salts of several other aromatic acids, e.g. p-chlorobenzoic acid (Mills and Speakman, 1963b), and in common with them is of Type A (Shrivastava and Speakman, 1961).

$K^{+} \cdots O$ distances and $O \cdots K^{+} \cdots O$ angles are given in Table 2.5, and bond lengths and angles in the aspirinate residues in Tables 2.6 and 2.7 respectively; standard deviations are given in parentheses. For comparison, the values found from the other analyses (Manojlovic and Speakman, 1967; Sequeira, Berkebile and Hamilton, 1967) are also given in these tables. No significant differences are apparent.

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APPENDIX I

The Crystal Structures of the Acid Salts of Some Dibasic Acids. Part I. A Neutron-diffraction Study of Ammonium (and Potassium) Tetroxalate

By **M. Currie** and **J. C. Speakman,*** Chemistry Department, The University, Glasgow W.2
N. A. Curry, Solid State Physics Division, A.E.R.E., Harwell

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The Crystal Structures of the Acid Salts of Some Dibasic Acids. Part I. A Neutron-diffraction Study of Ammonium (and Potassium) Tetroxalate

By **M. Currie** and **J. C. Speakman**,* Chemistry Department, The University, Glasgow W.2
N. A. Curry, Solid State Physics Division, A.E.R.E., Harwell

Potassium and ammonium tetroxalates ($MHOx,H_2Ox,2H_2O$, where M = K,NH_4 and H_2Ox = oxalic acid) are isomorphous, and the structure of the former has been accurately determined by Haas, using *X*-ray diffraction. The structure of the latter has now been determined by neutron-diffraction analysis, based on 1731 independent reflexions and refined by anisotropic least-squares to *R* = 8·85%. In general, and where comparable, the results confirm those of Haas.

The positions of the hydrogen-atoms attached to oxygen have been fixed with estimated standard deviations of ±0·007 Å, and for those attached to N, ±0·010 Å. The structure involves seven distinct hydrogen bonds between O atoms: they range in length (O $\cdots$ O) from 2·899 to 2·472 Å, and the corresponding O–H distances tend to increase inversely from 0·945 to 1·102 Å. The four H atoms of the ammonium ion form four, nearly linear, N–H $\cdots$ O bonds with N $\cdots$ O lengths = 2·927, 2·938, 2·950, 2·974 (each ±0·004) Å and N–H = 1·004, 1·022, 1·015, 0·995 (each ±0·010) Å. There is a fifth N $\cdots$ O contact of 2·973 Å, without any intervening proton.

The oxalate residues have their C and O atoms coplanar, and C–C = 1·544, 1·549 (each ±0·005), and 1·549 (±0·003) Å. In the three un-ionised carboxyl groups C=O = 1·206, 1·211, 1·212 (each ±0·004) Å and C–O(H) =1·296, 1·288, 1·291 (each ±0·004) Å. The remaining ionised carboxyl group has C$\overline{\cdots}$O = 1·230, 1·247 (each ±0·004) Å.

According to Groth's *Chemische Krystallographie*, ammonium, potassium, and rubidium tetroxalates ($MH_3Ox_2,2H_2O$, where H_2Ox = oxalic acid and M = NH_4, K, or Rb) are isomorphous. Some years ago one of us confirmed this isomorphism by preliminary *X*-ray study, with the intention of determining the crystal structure, using the isomorphism to solve the phase problem. Before this plan had been put into effect however, Haas[1] published an account of an accurate structure analysis of potassium tetroxalate (KTO). In 1965 we decided to supplement Haas's *X*-ray work with a three-dimensional neutron-diffraction study. This seemed useful for two reasons: first, the tetroxalate structure includes an interesting variety of hydrogen bonds, and Haas's location of the hydrogen atoms in them was necessarily of limited accuracy, which should be improved by neutron diffraction; secondly, the dimensions found by Haas for one carboxyl group are anomalous.

Though the tetroxalates crystallise beautifully, we were more successful in growing the large crystals needed for neutron diffraction in the case of ammonium tetroxalate (ATO). Our main effort therefore went into collecting intensity measurements for ATO, and this information has been used in a detailed refinement of the structure. ATO offers the additional interest of the role played by the four hydrogen atoms of the ammonium ion when this replaces potassium which, according to Haas, has seven oxygen atoms within 2·95 Å.

The crystal of KTO available proved of poor quality, and we collected only partial data. This Paper describes our study of ATO in some detail, with a brief note on KTO.

Crystal Data.—For both ATO and KTO we chose unit cells to accord with the goniometric data collected by Groth. Our cell therefore differs from that used by Haas for KTO. The alternative cells are symmetrically related by the transformation matrix, $00\bar{1}/010/\bar{1}00$. Thus transformed our results agree well with those of Haas.

The following parameters were established by Cu-$K\alpha$ *X*-rays, for which λ was taken as 1·5418 Å for $\tilde{\alpha}$ and 1·5405 Å for α_1, by use of a least-squares treatment of high-order reflexions whose positions on Weissenberg photographs were compared with lines due to aluminium wire.

Ammonium Tetroxalate.—$C_4H_7NO_8,2H_2O$, M = 233·18; Triclinic, a = 6·329 (±5), b = 10·551 (±6), c = 7·226 (±5) Å, α = 85·75°, β = 97·62°, γ = 79·73° (each ± 0·07°), U = 468·34 Å^3, D_m = 1·64, Z = 2, D_c = 1·654. The axial ratios derived from these cell dimensions are: $a:b:c$ = 0·5998 : 1 : 0·6849, which agree fairly well with the parameters recorded by Groth (Vol. III, p. 142), *viz.*, $a:b:c$ = 0·6053 : 1 : 0·6835; α = 86° 44′, β = 94° 32′, γ = 79° 14′. The angles also agree except for β; in citing these results, due to Rammelsberg, Groth comments that the value for β is 'unmöglich.'

Potassium Tetroxalate.—$C_4H_3KO_8,2H_2O$, M = 254·09; a = 6·354 (±5), b = 10·605 (±7), c = 7·021 (±5) Å, α = 86·13°, β = 100·16°, γ = 78·10° (each ± 0·08°), U = 453·92 Å^3, D_m = 1·79 (Groth cites 1·76—1·85), Z = 2, D_c = 1·859. Derived axial ratios are $a:b:c$ = 0·5992 : 1 : 0·6620, which agree with the parameters given by Groth (p. 140), *viz.*, $a:b:c$ = 0·6001 : 1 : 0·6649; α= 86° 33′, β = 100° 14′, γ = 78° 37′. The holohedry reported by Groth implies that the *space group* is $P\bar{1}$ (No. 2), and this is borne out by Haas's analysis as well as by our own.

Structure Analysis and Refinement.—Neutron-scattering structure amplitudes were measured for 1731 independent reflexions, covering the reciprocal sphere to θ = 45°. Of these 1226 had values significantly above background. All 1731 terms were included in the refinement however; 411 whose integrated intensities were less than a certain threshold value (chosen to be three times their standard deviations, σ) went in with their intensities put equal to half that threshold value (the formal error in these weak intensities can therefore never exceed 1·5σ); whilst 94 which gave zero intensity went in as zero.

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[1] D. J. Haas, *Acta Cryst.*, 1964, **17**, 1511.

The starting point for the analysis was the set of fractional co-ordinates found by Haas in KTO for the C and O atoms, and co-ordinates for the N atom assumed to occupy the same position as K^+. Three cycles of neutron-scattering-density synthesis and structure-factor calculations enabled us to allocate signs to all terms, and to find positions (of negative scattering-density) for all H atoms. Further refinement was then by one cycle of isotropic full-matrix, least-squares analysis, followed by seven cycles of anisotropic, block-diagonal analysis. Nuclear scattering-lengths used were: C, 0·661; O, 0·577; N, 0·940; and H, $-0{\cdot}378 \times 10^{-12}$ cm. In the last cycle parameter shifts were all less than one-third of their standard deviations (σ) and in a great majority of cases were less than one-fifth. The least-squares weighting scheme, which is explained in the Experimental section, was judged satisfactory from the uniformity of $\Sigma(w\Delta^2)$ over ranges of $\sin\theta$ and $|F_o|$. A final difference-synthesis was computed, with use of $(F_o - F_c')$ as coefficients, where F_c' is the structure factor calculated for all atoms except H. The three-dimensional function showed negative regions at the positions of the H atoms, but no other significant density. The final R-value was 8·85%, with $R' = 0{\cdot}90\%$.

Our final co-ordinates are listed in Table 1, and vibrational parameters in Table 2; standard deviations, derived from the least-squares residuals, are given in parentheses.

The crystal structure of the tetroxalates is too complex for simple verbal or pictorial description. Rapid comprehension may be expedited by the pair of stereoscopic views in Figure 1.* The asymmetric unit consists of one complete oxalate residue, two half-residues, two water molecules, and the cation. The best choice of a crystal chemical unit (CCU) is not self-evident. Our choice, represented by the atoms numbered in Table 1, is specified in Figure 2(*a*). After allowance for the change of axes, our CCU corresponds closely with the atoms listed by Haas in his Table 1.† Our O(9) and O(10) are his $H_2O(1)$ and $H_2O(2)$.

In subsequent description of the structure, we need other symmetry-related units: they are as follows:

CCU $x\ y\ z$

I	$1 - x, -y, -z$	IV	$2 - x, -y, 1 - z$
II	$1 + x, y, 1 + z$	V	$1 - x, 1 - y, 1 - z$
III	$1 - x, -y, 1 - z$	VI	$x, y, 1 + z$

Relevant parts of these are denoted in Figure 2(*b*). The oxalate residue based on C(1), O(1), and O(3), and corresponding to Haas's I, we designate *A*. Oxalate *B* (Haas's II) is based on C(2), O(2), and O(4). Oxalate *C* (Haas's III) consists of C(3), C(4), and O(5)—O(8).

Correction of atomic co-ordinates for the effects of rigid-body libration of the oxalate residues was considered; inspection of the vibrational parameters, in Table 2, suggested that such effects might be present. The usual computational procedures for dealing with these corrections fail when the librating unit has high symmetry; the oxalate groups have nearly *mmm* symmetry in ATO. We therefore used a method due to Beagley and Small.[2] Preliminary results indicated that the libration principally took the form of torsion about the C–C axis; corrections were then evaluated on the assumption that other modes of libration were negligible. Corrections thus apply only to the eight O atoms, O(1)—O(8), and the amended co-ordinates are appended in the lower part of Table 1. The effects on interatomic distances exceed standard deviations, though never by more than three-fold. We therefore give precedence to the uncorrected values, but, where appropriate, we add the corrected distances or angles in square brackets. We assume that the attached H atoms " ride " on their O atoms, and that therefore the O–H distances need no significant correction.

DISCUSSION

The Oxalate Residues.—Figure 3 shows the dimensions of the oxalate residues. The formula $NH_4HOx,H_2Ox,2H_2O$ suggests that one residue will be the half-ion, HOx^-, and hence chemically unsymmetrical; that the other will be an un-ionised molecule, H_2Ox, and hence symmetrical. Identification is aided by the consideration that the crystallographically distinct half-oxalates, each duplicated by a centre of inversion, must correspond to H_2Ox. The dimensions of *A* and *B* accord with this deduction. In particular the C–O distances differ in the sense $C{-}O(H) > C{=}O$. Our location of H atoms confirms the assignment of double and single bonds. Residue *C* must then represent HOx^-, and we expect one of its carboxyl groups to have $C{-}O(H) > C{=}O$, and the other, being ionised, to have the C–O distances nearly equal. In KTO Haas's findings were anomalous in this detail: his dimensions for the carboxyl groups do not differ significantly. Our results for *C* in ATO, shown in Figure 3, reveal the expected difference. This is supported by the absence of any proton covalently attached to O(7).

Our knowledge of the dimensions of the carboxyl group in crystals is less definitive than one might expect after 30 years of *X*-ray study. Carboxylic acids normally crystallise as centrosymmetric, hydrogen-bonded dimers (VII). Amongst the structures that have been accurately determined, the O(H) · · · O distances do not differ greatly from a mean of 2·65 Å; the hydrogen bonds are all of moderate strength. But, while the sum of

---

* Such a picture is best seen with a stereoscopic viewer. After a little practice, however, many people can achieve stereopsis without instrumental aid. The picture should be viewed in a good, even light; it helps if a piece of card is held between the eyes, and normal to the picture, so that each eye can see only its appropriate half of the diagram.

† Haas's co-ordinates are stated to be in Å. They are in fact fractional, though their standard deviations are in Å. The positions of atoms in his Figure 1 do not always correspond directly with his co-ordinates.

[2] B. Beagley and R. W. H. Small, *Proc. Roy. Soc.*, 1963, *A*, **275**, 469; B. Beagley, Ph.D. Thesis, Birmingham, 1962.

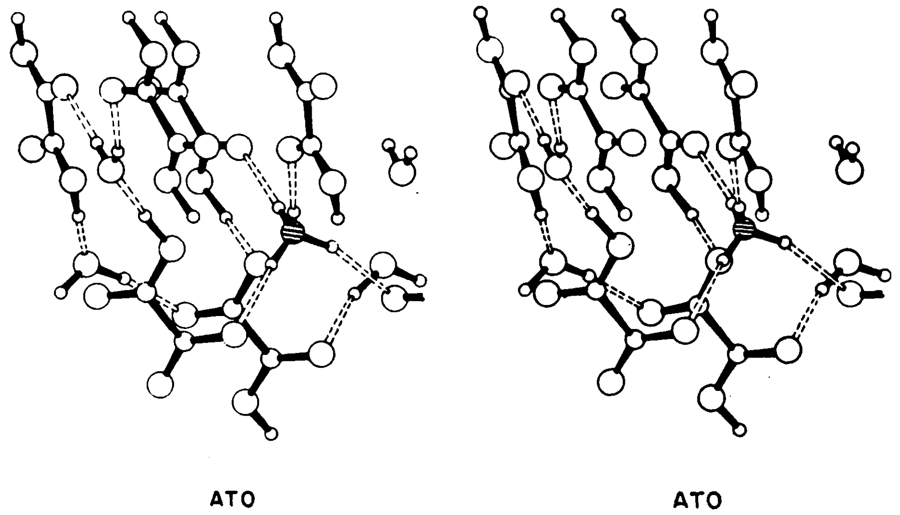


FIGURE 1 Stereoscopic views to show the crystal structure of ATO. The largest circles represent O atoms, the smallest H atoms, the intermediate C atoms, and the N atom of the ammonium ion is hatched

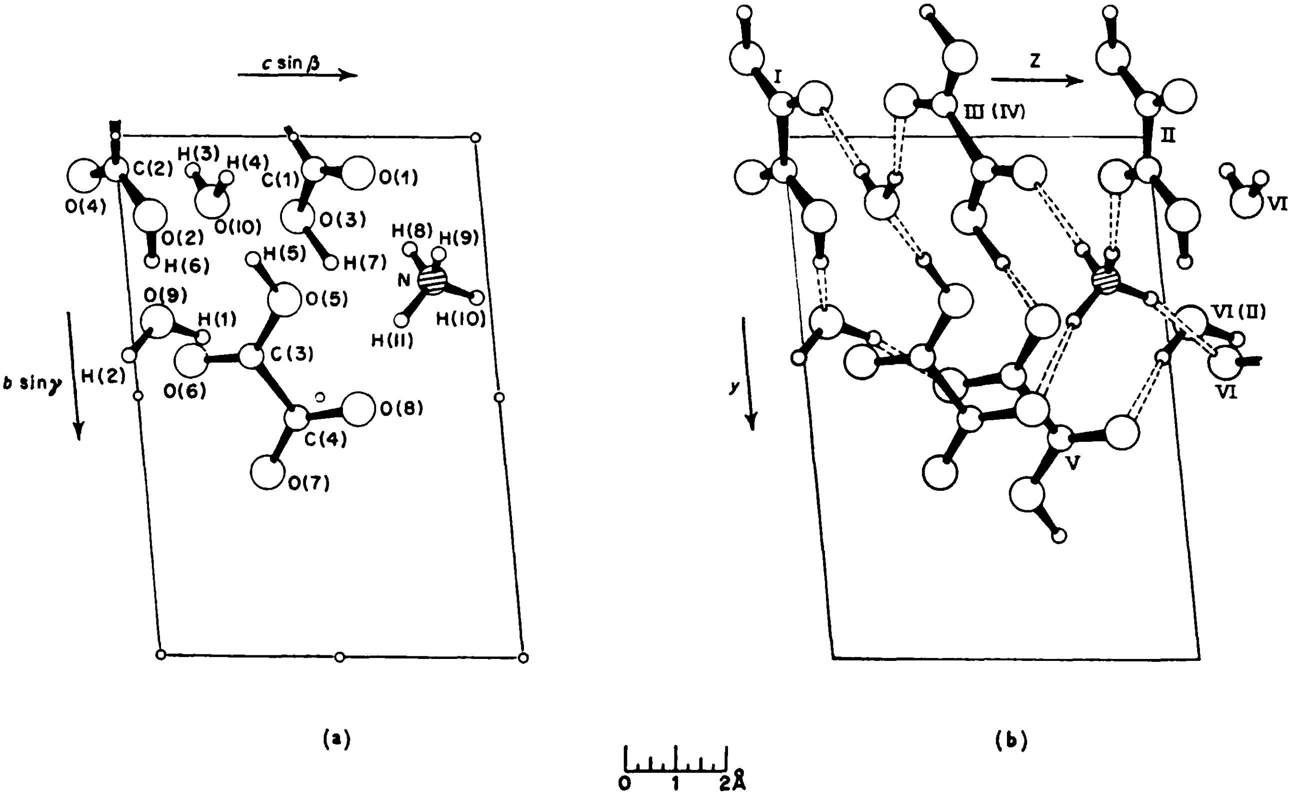

c sin β
C(2)
H(3)
H(4)
C(1)
O(1)
O(4)
O(2)
O(10)
O(3)
H(6)
H(5)
H(7)
H(8)
H(9)
N
O(9)
O(5)
H(10)
H(1)
H(11)
C(3)
b sin γ
H(2)
O(6)
O(8)
C(4)
O(7)
I
III (IV)
Z
II
VI
VI (II)
y
VI
V
(a)
0 1 2Å
(b)

FIGURE 2 (*a*) The crystal chemical unit (CCU) of ATO. This consists of one entire oxalate residue, two half-residues, two water molecules, and the ammonium ion

(*b*) The CCU of ATO together with the additional units needed in a description of the structure. These are denoted by roman numerals corresponding to the point-positions specified in the text. [Note that only the necessary parts of these additional units are shown. Thus (I) involves only the half-oxalate, related by a centre of symmetry at (½,0,0), needed to complete oxalate *B*.]

TABLE 1

Ammonium tetroxalate: fractional ($x, y, z \times 10^5$) and orthogonal (X', Y', Z' in Å, $\times 10^4$) co-ordinates (X' and Z' are, respectively, parallel to a^* and c, Y' is perpendicular to them both). Numbering of atoms is shown in Figure 2(*a*). Standard deviations of X', Y', and Z' are given in parentheses

	x	y	z	X'	Y'	Z'
N	84,200	27,511	84,431	51,854 (20)	38,999 (18)	56,095 (18)
C(1)	50,682	6290	54,740	31,212 (25)	12,669 (21)	35,794 (22)
C(2)	41,799	6460	−999	25,742 (25)	11,787 (22)	−3725 (23)
C(3)	75,571	42,206	32,401	46,540 (26)	53,431 (22)	20,371 (22)
C(4)	72,516	54,193	43,618	44,659 (26)	65,679 (23)	29,670 (23)
O(1)	66,000	6819	66,445	40,646 (33)	15,054 (29)	43,007 (33)
O(2)	49,813	15,254	7663	30,677 (32)	21,997 (30)	2550 (34)
O(3)	34,182	15,421	48,999	21,051 (35)	20,307 (30)	33,744 (32)
O(4)	23,872	7708	−9816	14,701 (32)	10,960 (30)	−8494 (34)
O(5)	81,555	31,392	42,951	50,225 (42)	42,767 (27)	26,647 (30)
O(6)	72,574	43,218	15,392	44,694 (39)	54,138 (30)	8411 (29)
O(7)	66,639	64,804	33,860	41,039 (38)	76,142 (28)	23,942 (28)
O(8)	76,174	52,283	60,835	46,911 (41)	64,106 (28)	41,655 (28)
O(9)	23,249	35,566	7232	14,318 (34)	40,198 (28)	6056 (30)
O(10)	94,408	12,536	25,177	58,141 (38)	24,461 (35)	11,250 (41)
H(1)	23,636	38,879	19,355	14,556 (71)	43,730 (60)	15,042 (61)
H(2)	26,017	42,217	−1706	16,022 (70)	47,527 (55)	−115 (58)
H(3)	85,952	6540	20,607	52,933 (74)	17,143 (66)	8189 (70)
H(4)	108,493	7830	29,870	66,815 (73)	21,191 (73)	13,091 (78)
H(5)	85,761	23,521	35,430	52,816 (70)	34,987 (57)	20,243 (61)
H(6)	38,177	24,007	7244	23,511 (59)	29,818 (56)	3908 (59)
H(7)	34,333	24,100	56,583	21,144 (67)	29,457 (58)	39,890 (60)
H(8)	74,658	21,459	79,141	45,978 (102)	31,492 (89)	52,600 (98)
H(9)	99,406	22,361	87,046	61,219 (93)	35,396 (97)	56,305 (105)
H(10)	80,029	30,823	96,226	49,286 (116)	41,986 (95)	65,227 (78)
H(11)	83,007	35,206	74,629	51,120 (95)	46,954 (72)	49,713 (69)

Co-ordinates of eight oxygen atoms, corrected for the effects of torsional oscillation, are given below

	x	y	z	X'	Y'	Z'
O(1)	66,163	6775	66,533	40,746	15,028	43,054
O(2)	49,933	15,292	7747	30,751	22,052	2603
O(3)	34,016	15,467	48,909	20,949	20,335	33,696
O(4)	23,756	7673	−9893	14,630	10,910	−8542
O(5)	81,613	31,316	43,123	50,261	42,694	26,760
O(6)	72,518	43,295	15,232	44,660	54,213	8306
O(7)	66,572	64,884	33,694	40,998	76,219	23,834
O(8)	76,233	52,209	61,002	46,948	64,035	41,765

TABLE 2

Ammonium tetroxalate: vibrational parameters ($Å^2 \times 10^4$). Standard deviations are given in parentheses

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
N	352 (10)	235 (8)	288 (8)	−109 (13)	36 (15)	−32 (14)
C(1)	286 (12)	140 (10)	226 (10)	−98 (16)	37 (18)	−10 (18)
C(2)	255 (11)	163 (10)	257 (10)	−113 (16)	92 (18)	30 (18)
C(3)	318 (12)	143 (9)	231 (10)	−101 (15)	101 (18)	0 (17)
C(4)	288 (11)	157 (9)	244 (10)	−158 (16)	49 (17)	−5 (17)
O(1)	319 (15)	189 (12)	401 (15)	−217 (22)	−106 (25)	−21 (22)
O(2)	287 (14)	213 (12)	455 (17)	−285 (23)	26 (25)	−11 (23)
O(3)	375 (16)	181 (12)	354 (15)	−185 (21)	−139 (25)	135 (23)
O(4)	280(14)	223 (13)	432 (16)	−261 (23)	9 (24)	34 (22)
O(5)	655 (23)	132 (11)	263 (13)	−7 (19)	139 (28)	−24 (26)
O(6)	547 (20)	193 (12)	238 (13)	−120 (20)	112 (26)	2 (25)
O(7)	565 (20)	150 (11)	239 (12)	−79 (19)	111 (26)	65 (25)
O(8)	626 (22)	171 (12)	225 (12)	−126 (19)	171 (27)	−15 (26)
O(9)	376 (16)	178 (12)	329 (14)	−95 (20)	171 (24)	−5 (23)
O(10)	358 (17)	277 (15)	608 (21)	−462 (30)	2 (31)	38 (27)
H(1)	577 (36)	357 (26)	456 (29)	−215 (44)	250 (54)	−67 (50)
H(2)	601 (37)	308 (25)	420 (27)	19 (41)	215 (52)	−162 (49)
H(3)	555 (37)	423 (31)	616 (37)	−483 (55)	192 (61)	−219 (55)
H(4)	447 (34)	488 (34)	665 (40)	−181 (59)	82 (60)	−6 (56)
H(5)	588 (37)	303 (24)	468 (29)	−149 (42)	158 (53)	−120 (49)
H(6)	373 (27)	329 (24)	490 (29)	−205 (42)	121 (45)	−12 (43)
H(7)	491 (32)	317 (25)	442 (28)	2 (41)	−40 (49)	55 (46)
H(8)	763 (55)	618 (46)	799 (53)	−361 (79)	17 (87)	−472 (83)
H(9)	571 (43)	622 (45)	886 (58)	39 (81)	−25 (81)	191 (75)
H(10)	1079 (74)	657 (47)	494 (38)	−212 (67)	393 (86)	27 (94)
H(11)	865 (56)	454 (33)	444 (32)	76 (51)	155 (67)	−247 (70)

C=O and C–O(H) distances is roughly constant at 2·50 Å, the difference ranges widely from 0·04 to 0·12 Å. Perhaps this very significant variation, in otherwise similar situations, is due to partial disorder of the H atoms: that is to say, the dimers occur randomly as (VII) or (VIII) in unequal proportions.* By X-ray methods some randomness in the positions of the H atoms would be hard to detect.

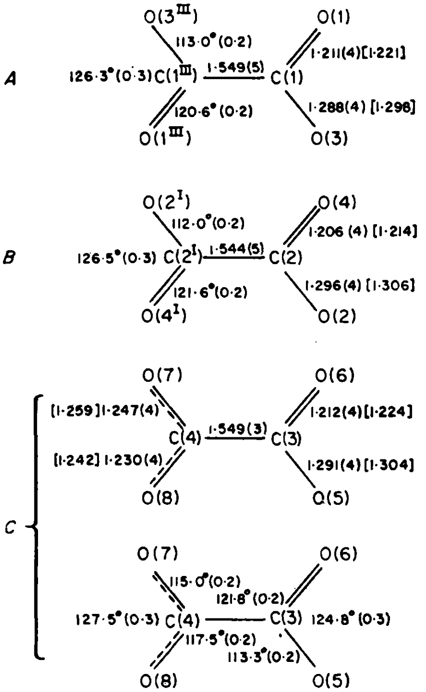
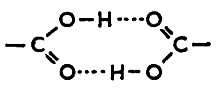
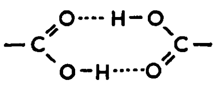


FIGURE 3 Bond-lengths and bond-angles in the crystallographically distinct oxalate residues (the lengths shown in square brackets have been corrected for libration)


(VII)


(VIII)

In ATO we have three carboxyl groups (not dimerised) whose dimensions are known with some precision, and whose protons have been definitely located. Their dimensions do not differ significantly: the average C–O(H) and C=O distances are 1·292 and 1·210; their average sum is 2·501; and their difference 0·082 (±0·004) Å.

The C–C bonds all exceed the notional length of 1·54 Å, and greatly exceed that expected between sp^2-hybridised C atoms. This supports the conclusion reached by several authors, and notably by Beagley and Small,[2,3] that the bond in the oxalate residue is anomalous. These two workers have plotted electron-density difference syntheses and found significant residual density at the mid-point of the C–C bond. This they have tentatively ascribed to the bonding electrons. A possible objection is that errors tend to accumulate at special (or quasi-special) positions; so that the density found at the centre of the oxalate group might be a Fourier-artefact. A similar error could occur in a neutron-diffraction synthesis. On the other hand, since neutrons are not scattered by (paired) electrons, electron density should not be detectable in a difference synthesis. Our neutron-diffraction difference map showed only a trace of negative scattering power at the mid-points of the C–C bonds. So far as it goes, therefore, this evidence favours the contention of Beagley and Small that their effect is not a Fourier-artefact.

Each oxalate residue is planar in its C and O atoms. The mean planes are:

$$\text{oxalate } A\text{: } 0{\cdot}4774X' + 0{\cdot}4209Y' - 0{\cdot}7713Z' = -0{\cdot}7419$$
$$\text{oxalate } B\text{: } 0{\cdot}3443X' + 0{\cdot}3665Y' - 0{\cdot}8644Z' = 1{\cdot}6416$$
$$\text{oxalate } C\text{: } 0{\cdot}9575X' + 0{\cdot}2524Y' - 0{\cdot}1394Z' = 5{\cdot}5222$$

The deviations of C and O atoms from these respective planes are not significant. The H atoms are however displaced from the planes of their oxalate residues as follows: H(7) by 0·086 Å from plane A; H(6) by 0·077 Å from plane B; and H(5) by 0·136 Å from plane C.

Environment of the Cation.—A potassium ion in a crystal is usually co-ordinated to 6, 7, or 8 O atoms When isomorphous substitution of K^+ by NH_4^+ occurs, either the four H atoms must occupy the 6—8 positions randomly, or the structure must undergo subtle changes so as to achieve a co-ordination based on four N–H ··· O hydrogen bonds. Neutron diffraction helps us to make a detailed study of such changes in the tetroxalate system.

TABLE 3

Details of the structure around the cation in ATO. (Distances in Å: standard deviations in parentheses). $K^+ \cdots O$ distances in KTO are given for comparison; N ··· O contacts involving a hydrogen bond are asterisked. Certain distances have been roughly corrected for the effects of torsional oscillation of the oxalate residues; these are given in square brackets

	ATO	KTO
$N/K^+ \cdots O(1)$	2·950 (4) * [2·946]	2·870 (4)
$O(2^{VI})$	3·298 (4) [3·294]	3·250 (4)
$O(4^{II})$	2·927 (4) * [2·924]	2·931 (4)
O(5)	2·973 (4) [2·961]	2·879 (4)
$O(6^{VI})$	2·974 (4) * [2·970]	2·915 (4)
$O(7^{V})$	3·247 (4) [3·239]	3·044 (4)
O(8)	2·938 (3) * [2·926]	2·870 (4)
$O(9^{II})$	3·069 (4)	2·893 (4)
$O(10^{VI})$	3·166 (4)	2·924 (4)

N–H(8)	1·015 (10)	H(8) ···· O(1)	1·977 (10) [1·974]
H(9)	1·004 (10)	$H(9) \cdots O(4^{II})$	1·960 (10) [1·958]
H(10)	0·995 (9)	$H(10) \cdots O(6^{VI})$	2·018 (9) [2·015]
H(11)	1·022 (7)	H(11) ··· O(8)	1·941 (8) [1·930]

H(8)–N–H(9)	106·4 (0·8)°	N–H(8) ···· O(1)	159·7 (0·9)°
H(8)–N–H(10)	112·9 (0·9)	$N–H(9) \cdots O(4^{II})$	161·0 (0·8)
H(8)–N–H(11)	108·6 (0·7)	$N–H(10) \cdots O(6^{VI})$	160·4 (0·8)
H(9)–N–H(10)	109·2 (0·9)	N–H(11) ··· O(8)	164·2 (0·7)
H(9)–N–H(11)	111·1 (0·8)		
H(10)–N–H(11)	108·7 (0·7)		

Haas lists nine $K^+ \cdots O$ contacts in KTO. Seven of these have distances less than 2·95 Å and so may qualify as direct K$^+$ · · · O contacts, and they are included in Table 3. An ionic radius for NH$^+$ is difficult$_4$ to designate, but Pauling has suggested a value similar to that of Rb$^+$, *viz.*, *ca.* 1·48 Å, which is 0·15 Å greater than the accepted radius of K$^+$. As Table 3 shows, there are five notably short NH$_4$$^+$ · · · O contacts in ATO. They do not generally correspond to the shortest K$^+$ · · · O contacts; and they are significantly shorter than we should predict were we to increase the K$^+$ · · · O distances by 0·15 Å.

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* Because of the environment (VII) and (VIII) are not equivalent in a crystal.

[3] B. Beagley and R. W. H. Small, *Acta Cryst.*, 1964, **17**, 783.

The H atoms appear to be entirely localised along four of these NH$_4$$^+$ · · · O contacts. An almost regularly tetrahedral co-ordination of the H atoms round the N is achieved, with the N–H · · · O angles never less than 160°. This favourable arrangement causes the bonding to be concentrated into these directions.

One other contact, to O(5), remains short, though no proton is evident. The other cation · · · O distances are considerably increased as compared with KTO. Table 3 also includes details of the structure of the NH$_4$ ion.

The Hydrogen Bonding.—Apart from the N–H · · · O bonds, ATO includes seven hydrogen bonds between O atoms. Details of these are given in Table 4. The O · · · O distances range from 2·90 to 2·47 Å, and our results enable us to add well-authenticated points to the Nakamato–Margoshes–Rundle graph which shows how the O–H distance tends to increase as the overall O · · · O distance diminishes. In Figure 4 we plot our seven points and we also show the curve drawn by Pimentel and McClellan [4] to represent the trend of the information available in 1959.

Unfortunately, we cannot directly observe the change in the position of the proton as the O · · · O distance is reduced in an isolated hydrogen bond. Figure 4 is based on the bonds in a large number of different crystalline compounds. Only insofar as these different bonds are deemed to be " comparable " may we draw a curve to represent the relationship between the O–H and O · · · O distances in the idealised hydrogen bond. Our seven points suggest that the Pimentel–McClellan curve, if it has any general significance, ought to rise more steeply, especially in the region of 2·5 Å.

A chief interest in this diagram (and a chief reason for studying " very short " hydrogen bonds [5]) lies in how this curve, which is respectably observational though not-too-well defined, behaves as it approaches the straight line, of slope 0·5, which represents the mathematical relationship between O–H and O · · · O in a bond of postulated symmetry. (We show this as a broken line in Figure 4.) Does the curve bend over to the left so as ultimately to converge on to the diagonal line? Or does it rise more and more steeply until it cuts the line? The special interest attaching to this region of the graph is matched by its special obscurity. On the experimental side, accurate information is scarce and

TABLE 4

Details of the water molecules and O–H · · · O hydrogen bonds in ATO. (Distances in Å: standard deviations in parentheses). Certain distances have been roughly corrected for the effects of torsional oscillation of the oxalate residues; these are given in square brackets

O(9)–H(1)	0·966 (7)	H(1) · · · · O(8^{V})	1·765 (7)	O(9) · · · · O(8^{V})	2·721 (4) [2·714]
O(9^{VI})–H(2^{VI})	0·973 (6)	H(2^{VI}) · · · O(6^{V})	1·787 (6)	O(9^{IV}) · · · O(6^{V})	2·745 (4) [2·734]
O(10)–H(3)	0·949 (8)	H(3) · · · · O(4^{I})	1·906 (7)	O(10) · · · O(4^{I})	2·833 (5) [2·824]
O(10)–H(4)	0·945 (8)	H(4) · · · · O(1^{IV})	2·000 (8)	O(10) · · · O(1^{IV})	2·899 (5) [2·889]
O(5)–H(5)	1·040 (7)	H(5) · · · · O(10)	1·483 (7)	O(5) · · · · O(10)	2·520 (5) [2·520]
O(2)–H(6)	1·069 (7)	H(6) · · · · O(9)	1·403 (7)	O(2) · · · · O(9)	2·472 (4) [2·472]
O(3)–H(7)	1·102 (7)	H(7) · · · · O(7^{V})	1·399 (7)	O(3) · · · · O(7^{V})	2·500 (4) [2·500]

H(1)–O(9)–H(2)	108·1 (0·6)°	H(3)–O(10)–H(4)	107·4 (0·7)°
O(9)–H(1) · · · · · O(8^{V})	169·5 (0·6)	C(4^{V})–O(8^{V}) · · · · O(9)	143·2 (0·2)
O(9^{VI})–H(2^{VI}) · · O(6^{V})	167·4 (0·6)	C(3^{V})–O(6^{V}) · · · · O(9^{VI})	125·1 (0·2)
O(10)–H(3) · · · · O(4^{I})	164·8 (0·7)	C(2^{I})–O(4^{I}) · · · · O(10)	125·2 (0·2)
O(10)–H(4) · · · · O(1^{IV})	158·2 (0·7)	C(1^{IV})–O(1^{IV}) · · · O(10)	125·0 (0·2)
O(5)–H(5) · · · · · O(10)	173·3 (0·7)	C(3)–O(5) · · · · · O(10)	113·1 (0·2)
O(2)–H(6) · · · · · O(9)	178·2 (0·6)	C(2)–O(2) · · · · · O(9)	113·4 (0·2)
O(3)–H(7) · · · · · O(7^{V})	177·1 (0·7)	C(1)–O(3) · · · · · O(7^{V})	114·7 (0·2)

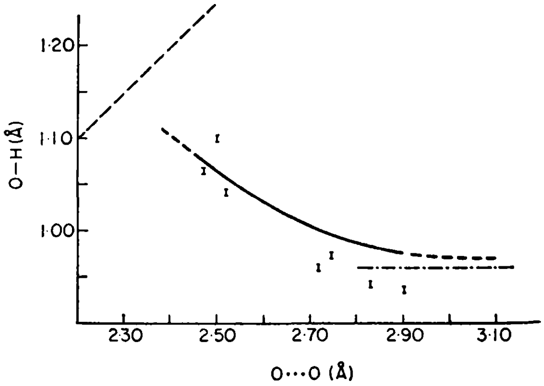

FIGURE 4 Graph showing the Nakamoto–Margoshes–Rundle relationship between O · · · O and O–H distances in hydrogen bonds. The curve is that given by Pimentel and McClellan (1960). The diagonal broken line corresponds to hypothetical centrosymmetric bonds. The values derived from the analysis of ATO are indicated by vertical lines whose lengths give their standard deviations

hard to obtain. There is one well-authenticated bond with $O \cdots O = 2{\cdot}411$ Å and the proton not significantly displaced from the mid-point; but, as the uncertainties of O–H and $O \cdots O$ are each at least 0·005 Å, unambiguous symmetry of the bond is not proved.[6] On the theoretical side we face an indeterminacy problem: a moderately short $O \cdot\cdot H \cdot\cdot O$ bond may have its proton moving in a situation of double potential-energy minimum; as the bond becomes still shorter, the minima come closer together and the energy barrier between them lower, and ultimately only a single minimum remains; when the top of the barrier lies near to, or below, the zero-point energy level, the location of the proton becomes abnormally uncertain.

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[4] G. C. Pimentel and A. L. McClellan, " The Hydrogen Bond," W. H. Freeman and Co., San Francisco and London, 1960, p. 259.

[5] J. C. Speakman, *Chem. Comm.*, 1967, 32.

Though some of the bonds in ATO are " very short " the protons in them are well away from the mid-point. Bonds in which genuine symmetry had been suspected (chiefly on spectroscopic grounds) are not much shorter than $O(2){-}H \cdots O(9)$.[5] But they have the difference of lying across an element of crystallographic symmetry. The consequent symmetry of total environment may favour the establishment of internal symmetry in such bonds.[7]

Very short hydrogen bonds seem to be formed only when the proton donor is an acid of adequate strength. The three short bonds in ATO all have carboxyl groups as donors, whereas the four longer bonds have water molecules as donors. More surprisingly, the shortest bond $O(2)H \cdots O(9)$ has a water molecule as acceptor.

Potassium Tetroxalate.—A limited number of data were collected from a crystal of KTO. They proved to be of inferior quality, but were used in a partial refinement to $R = 20\%$ for 700 reflexions. We do not consider the co-ordinates and molecular dimensions thus derived to be worth reporting. However, seven H atoms were duly revealed, in a Fourier synthesis, in positions in good general agreement with those found in ATO.

EXPERIMENTAL

The crystal of ATO used had dimensions $0{\cdot}5 \times 0{\cdot}4 \times 0{\cdot}2$ cm. The neutron beam, monochromatised to $\lambda = 1{\cdot}103$ Å and with an intensity of $4{\cdot}3 \times 10^5$ neutrons cm.$^{-2}$ sec.$^{-1}$, was derived from the DIDO reactor at A.E.R.E., Harwell. Intensity measurements were made with a Ferranti Mark II automatic diffractometer.[8] This instrument permits rotation of the crystal through thee Eulerian angles, ψ, χ, and ω, and rotation of the counter through 2θ about an axis coincident with that for ω. The diffractometer is controlled by punched paper tape which contains instructions for rotating the shafts to bring each set of planes close to the reflecting position, followed by instructions for advancing the crystal by small angular steps through the reflexion. The number of neutrons detected at each step, during a fixed monitor count, is recorded both on paper tape and on teleprinter paper. The tape which controls the diffractometer is prepared in two stages: first, the four angular positions corresponding to each reflexion, out to a specified value of θ, are computed and output on punched cards, using a programme due to M. J. D. Powell of Theoretical Physics Division, A.E.R.E., for the IBM 7030 computer; secondly, this deck of cards is used to prepare a tape containing instructions, in appropriate form, to find and measure each reflexion. ATLAS programmes (written by N. A. C.) are used for the second stage above and also to " process " the diffractometer output to yield a set of relative intensities and structure amplitudes. The intensities were corrected for absorption (with $\mu = 1{\cdot}4$ cm.$^{-1}$) by the programme ORABS due to Wehe, Busing, and Levy, and adapted for ATLAS. No correction was made for secondary extinction, and examination of the final list of structure factors suggests that no serious error arose from this cause.

TABLE 5

Ammonium tetroxalate: analysis of the agreement of observed and calculated structure factors at the end of the refinement. N is the number of reflexions. Structure factors are on the absolute scale

(*a*) As a function of the magnitude of the observed structure factors.

Range of $\lvert F_o\rvert$	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	N	R	$\Sigma\lvert\Delta\rvert/N$
0·0—0·4	3·33	59·15	62·88	108	18·883	0·58
0·4—0·8	245·63	202·86	80·95	428	0·330	0·19
0·8—1·2	230·58	218·56	29·69	230	0·129	0·13
1·2—1·7	383·25	374·12	31·62	269	0·083	0·12
1·7—2·4	522·52	517·86	27·32	256	0·052	0·11
2·4—3·1	412·06	408·73	20·31	151	0·049	0·13
3·1—4·0	538·59	534·95	22·12	155	0·041	0·14
4·0—5·2	366·27	370·42	14·57	81	0·040	0·18
5·2—6·5	210·25	215·15	11·34	36	0·054	0·32
6·5—8·0	120·37	126·03	6·62	17	0·055	0·39

(*b*) As a function of the layer line index.

h	$\Sigma\lvert F_o\rvert$	$\Sigma\lvert F_c\rvert$	$\Sigma\lvert\Delta\rvert$	N	R	$\Sigma\lvert\Delta\rvert/N$
−8	6·15	5·61	0·53	4	0·087	0·13
−7	51·33	45·46	7·43	47	0·145	0·16
−6	98·01	95·15	11·32	79	0·116	0·14
−5	99·04	96·21	9·99	65	0·101	0·15
−4	225·69	223·92	16·29	125	0·072	0·13
−3	111·29	110·10	10·89	68	0·098	0·16
−2	304·94	304·95	23·70	159	0·078	0·15
−1	340·13	343·56	30·60	175	0·090	0·17
0	372·93	359·88	28·29	184	0·076	0·15
1	366·27	363·96	31·82	179	0·087	0·18
2	343·21	339·92	26·64	172	0·078	0·15
3	297·93	296·20	27·58	157	0·093	0·18
4	212·80	207·03	17·36	130	0·082	0·13
5	140·50	143·10	15·54	99	0·111	0·16
6	65·74	64·75	10·03	60	0·153	0·17
7	32·59	32·74	3·70	28	0·114	0·13
All	3068·55	3032·54	271·71	1731	0·089	0·16

The least-squares analysis was done at Glasgow, with the programme developed by D. W. J. Cruickshank and his co-workers. The weighting scheme is due to D. R. McGregor,[9] and is as follows: All values of Δ^2, where $\Delta = \lvert F_o\rvert - \lvert F_c\rvert$, are grouped into a two-dimensional array, according to ranges of $(\sin\theta)/\lambda$ and of $\lvert F_o\rvert$. In each group $\langle\overline{\Delta^2}\rangle$ is calculated. Any group in which the number of terms is inadequate is rejected. The values of $\langle\Delta^2\rangle$ in all other groups are then fitted, by least squares, to a surface. In this particular analysis the function obtained was

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[6] R. D. Ellison and H. A. Levy, *Acta Cryst.*, 1965, **19**, 260 (the difficulties of locating the proton precisely are fully discussed in this Paper).

[7] Lj. Manojlović and J. C. Speakman, *J. Chem. Soc.* (*A*), 1967, 971.

[8] R. F. Dyer, U.K.A.E.A. document AERE-R5259, Part 1, 1966; B. T. M. Willis and U. W. Arndt, " Single Crystal Diffractometry," Cambridge University Press, 1966.

[9] D. R. McGregor, Ph.D. Thesis, Glasgow, 1967.

$$f = -1{\cdot}99 - 0{\cdot}75\,|F_o| + 0{\cdot}166\,|F_o|^2 - 0{\cdot}0164\left(\frac{\lambda}{\sin\theta}\right)^2 + 8{\cdot}69 \times 10^{-5}\left(\frac{\lambda}{\sin\theta}\right)^4 - 4{\cdot}89 \times 10^{-11}(\sin\theta/\lambda)^2$$

Then w [$= \exp(-f)$] was calculated for each reflexion. The adequacy of this weighting scheme and of the analysis generally is supported by Table 5.

Observed structure amplitudes and final calculated structure factors are stored on magnetic tape at Glasgow (and, we hope, in due course elsewhere). A copy of these data can be had from Dr. J. G. Sime (at The Chemistry Department, University of Glasgow, Glasgow W.2) by quoting reference GL/1967/4. The copy will normally take the form of a print-out, though out-put on paper tape or on cards may be available on request.

We are indebted to the Solid State Physics Division, A.E.R.E., Harwell, and particularly to Dr. G. Low for making neutron-diffraction facilities available (to J. C. S. and M. C.), and to J. B. Forsyth, S. A. Wilson, and N. Povall for their guidance. We have made extensive use of the KDF9 crystallographic programmes developed at Glasgow by D. W. J. Cruickshank, J. G. Sime, K. W. Muir, and others. One of us (M. C.) acknowledges a maintenance grant from the S.R.C.

[7/534 *Received, May 3rd*, 1967]

ATO: Observed structure amplitudes and final calculated structure factors.

h	k	l	Fo	Fc
-8	-3	0	1.68	-1.53
-8	-2	0	0.52	0.42
-8	-2	1	3.04	-2.86
-8	-1	1	0.90	0.80
-7	-8	-1	1.26	1.07
-7	-8	0	1.21	-1.11
-7	-7	-2	0.00	-0.01
-7	-7	-1	1.67	-1.34
-7	-7	0	1.81	1.48
-7	-6	-2	0.53	0.08
-7	-6	0	1.24	-1.16
-7	-5	-3	0.90	-0.69
-7	-5	-2	0.52	0.26
-7	-5	-1	1.91	-1.78
-7	-5	0	1.14	[illegible]
-7	-4	[illegible]	[illegible]	[illegible]
-7	-4	[illegible]	[illegible]	[illegible]
-7	[illegible]	-1	[illegible]	[illegible]
-7	-4	0	4.31	[illegible]
-7	-3	-3	0.52	[illegible]
-7	-3	-2	1.02	0.97
-7	-3	-1	1.03	0.65
-7	-3	0	0.56	0.66
-7	-2	-3	0.91	0.65
-7	-2	-2	1.28	1.26
-7	-2	-1	0.00	0.18
-7	-2	0	1.27	1.18
-7	-2	1	1.12	0.99
-7	-1	-3	0.80	0.65
-7	-1	-2	0.48	0.31
-7	-1	-1	2.04	2.02
-7	-1	0	1.03	-1.04
-7	-1	1	1.06	0.88
-7	0	-3	0.91	-1.06
-7	0	-2	0.48	-0.32
-7	0	-1	0.53	-0.52
-7	0	0	1.36	-1.23
-7	0	1	2.16	2.18
-7	1	-2	0.77	-0.79
-7	1	-1	0.52	0.05
-7	1	0	2.31	-2.31
-7	1	1	1.73	1.70
-7	2	-2	1.65	1.46
-7	2	-1	0.53	-0.42
-7	2	0	1.34	-1.28
-7	2	1	0.53	0.27
-7	3	-1	0.87	0.98
-7	3	0	0.54	0.24
-7	3	1	0.60	-0.41
-7	4	0	0.00	-0.17
-7	4	1	0.58	-0.47
-6	-10	-2	0.51	-0.11
-6	-10	-1	1.09	0.97
-6	-10	0	0.55	0.63
-6	-9	-3	0.64	0.63
-6	-9	-2	0.43	0.40
-6	-9	-1	0.41	0.67
-6	-9	0	1.78	-1.69
-6	-8	-3	0.52	-0.13
-6	-8	-2	0.52	0.15
-6	-8	-1	3.84	3.46
-6	-8	0	0.60	-0.50
-6	-7	-4	0.42	0.54
-6	-7	-3	2.08	-1.97
-6	-7	-2	2.37	2.27
-6	-7	-1	2.74	2.57
-6	-7	0	1.11	0.81
-6	-6	-4	0.90	-0.70
-6	-6	-3	0.97	0.90
-6	-6	-2	1.42	-1.29
-6	-6	-1	0.54	0.39
-6	-6	0	0.60	0.61
-6	-5	-5	0.51	-0.51
-6	-5	-4	0.96	0.83
-6	-5	-3	0.80	0.73
-6	-5	-2	0.70	0.66
-6	-5	-1	1.59	1.44
-6	-5	0	0.51	0.09
-6	-4	-3	0.92	1.03
-6	-4	-2	1.22	-1.23
-6	-4	-1	1.49	1.61
-6	-4	0	0.91	-0.95
-6	-3	-5	1.40	1.46
-6	-3	-4	1.49	-1.44
-6	-3	-3	0.91	0.66
-6	-3	-2	4.82	-5.05
-6	-3	-1	1.72	-1.84
-6	-3	0	0.56	0.43
-6	-2	-5	0.58	0.52
-6	-2	-4	1.24	-1.21
-6	-2	-3	1.39	-1.25
-6	-2	0	1.28	-1.45
-6	-1	-5	1.65	-1.80
-6	-1	-4	1.32	-1.13
-6	-1	-3	0.00	0.37
-6	-1	-2	0.00	-0.36
-6	-1	-1	1.54	-1.43
-6	-1	0	2.03	2.16
-6	0	-4	0.55	0.50
-6	0	-3	2.29	-2.09
-6	0	-2	0.83	0.67
-6	0	-1	0.56	-0.41
-6	0	0	0.00	0.26
-6	0	1	2.25	-2.31
-6	1	-4	1.41	-1.49
-6	1	-3	1.10	0.90
-6	1	-2	1.01	0.99
-6	1	-1	2.23	-2.26
-6	1	0	1.14	1.24
-6	2	-4	2.55	2.71
-6	2	-3	0.83	0.58
-6	2	-2	2.40	2.21
-6	2	-1	2.11	-2.16
-6	2	0	2.45	-2.50
-6	2	1	2.53	-2.64
-6	3	-3	0.57	0.57
-6	3	-2	1.25	1.30
-6	3	0	0.90	0.57
-6	3	1	0.90	-0.86
-6	4	-3	0.56	-0.62
-6	4	-2	0.55	0.34
-6	4	-1	0.83	0.98
-6	4	0	0.00	-0.01
-6	4	1	1.83	2.10
-6	5	-2	0.56	-0.38
-6	5	1	2.82	3.02
-6	6	-1	0.54	-0.31
-6	6	0	1.88	2.00
-6	6	1	0.00	-0.00
-6	7	1	3.00	3.13
-5	-11	-2	0.58	-0.22
-5	-11	-1	2.44	2.41
-5	-11	0	0.62	-0.68
-5	-10	-4	1.07	-1.17
-5	-10	-3	0.60	0.29
-5	-10	-2	0.60	0.41
-5	-10	-1	0.59	0.14
-5	-10	0	4.94	5.06
-5	-9	-4	0.58	0.38
-5	-9	-3	0.58	-0.48
-5	-9	-2	1.63	-1.52
-5	-9	-1	1.88	-1.68
-5	-8	-5	0.60	0.66
-5	-8	-4	7.00	-7.03
-5	-8	0	0.78	-0.41
-5	-6	1	1.94	1.89
-5	-5	-6	0.75	0.77
-5	-5	-5	1.38	-1.45
-5	-5	-4	0.60	0.50
-5	-5	-3	0.00	0.23
-5	-5	-2	0.60	-0.57
-5	-5	-1	0.82	-0.66
-5	-5	0	3.58	-3.88
-5	-5	1	0.85	0.84
-5	-5	2	0.00	-0.01
-5	-4	-6	1.40	-1.50
-5	-4	-5	0.56	0.20
-5	-4	-4	0.57	0.16
-5	-4	-3	0.00	-0.41
-5	-4	[illegible]	[illegible]	[illegible]
-5	-4	[illegible]	[illegible]	[illegible]
-5	-4	[illegible]	[illegible]	[illegible]
-5	-4	1	[illegible]	[illegible]
-5	-4	[illegible]	[illegible]	-1.32
-5	-3	-6	1.35	1.73
-5	-3	-5	2.17	-2.14
-5	-3	-4	0.87	1.00
-5	-3	-3	3.00	-3.02
-5	-3	-2	1.72	1.68
-5	-3	-1	0.49	-0.24
-5	-3	0	3.99	3.99
-5	-3	1	2.91	2.76
-5	-2	-4	5.02	4.76
-5	-2	-3	0.58	0.66
-5	-2	-2	0.65	0.84
-5	-2	1	0.57	0.55
-5	-1	-5	0.57	0.51
-5	-1	-4	4.06	4.00
-5	0	-6	0.58	-0.69
-5	0	-5	0.56	-0.24
-5	0	-4	0.91	-0.66
-5	0	-3	1.09	1.17
-5	0	-1	4.81	5.12
-5	1	-6	0.55	0.26
-5	1	-5	1.88	1.91
-5	1	-4	0.00	-0.29
-5	1	-3	0.55	-0.32
-5	1	-2	0.96	-1.06
-5	1	-1	4.01	4.43
-5	1	0	0.97	0.91
-5	1	1	1.32	1.45
-5	2	-5	0.92	-0.83
-5	2	-4	0.82	-0.48
-5	2	-1	3.61	3.68
-5	2	0	0.75	0.63
-4	-11	-2	1.36	1.19
-4	-11	-1	1.23	1.28
-4	-10	-5	1.35	-1.21
-4	-10	-4	0.92	0.71
-4	-10	-3	2.42	-2.39
-4	-10	-2	1.44	-1.56
-4	-10	-1	1.95	-1.90
-4	-9	-5	0.59	0.21
-4	-9	-4	0.59	-0.25
-4	-9	-3	2.37	-2.63
-4	-9	-2	3.02	-3.29
-4	-9	-1	0.58	[illegible]
-4	-9	0	0.61	0.53
-4	-8	-6	1.06	0.83
-4	-8	-5	0.60	0.88
-4	-8	-4	1.78	1.72
-4	-8	-3	2.72	2.62
-4	-8	-2	0.60	-0.59
-4	-8	-1	1.52	1.67
-4	-8	0	2.42	-2.52
-4	-7	-6	1.09	1.14
-4	-7	-5	0.00	0.23
-4	-7	-4	1.81	-1.88
-4	-7	-3	2.61	2.54
-4	-7	-1	3.82	3.66
-4	-7	0	2.03	-2.07
-4	-6	-6	0.58	0.51
-4	-6	-5	1.33	1.17
-4	-6	-4	0.62	0.34
-4	-6	-3	1.31	1.11
-4	-6	-2	1.90	1.88
-4	-6	-1	2.39	2.22
-4	-6	0	0.57	0.52
-4	-5	-6	2.90	2.86
-4	-5	-3	6.39	6.60
-4	-5	-2	0.00	0.05
-4	-5	-1	3.26	-3.09
-4	-5	0	0.89	0.75
-4	-4	-3	4.57	4.59
-4	-4	-2	3.17	3.09
-4	-4	-1	1.39	-1.56
-4	-4	0	1.46	1.21
-4	-3	-6	0.00	-0.00
-4	-3	-5	0.92	-0.90
-4	-3	-4	0.00	0.06
-4	-3	-3	1.07	1.03
-4	-3	-2	2.08	1.81
-4	-3	-1	1.78	1.73
-4	-3	0	1.84	1.64
-4	-2	-7	2.25	2.26
-4	-2	-6	1.20	-1.10
-4	-2	-5	2.22	2.31
-4	-2	-4	2.36	-2.39
-4	-2	-3	1.57	1.31
-4	-2	-2	3.80	-3.69
-4	-2	-1	2.17	-2.04
-4	-2	0	5.71	5.88
-4	-1	-7	1.91	-1.91
-4	-1	-6	3.22	-3.16
-4	-1	-5	2.34	2.41
-4	-1	-4	0.69	-0.72
-4	-1	-3	2.05	-2.16
-4	-1	-2	2.12	-2.28
-4	-1	-1	0.54	-0.43
-4	-1	0	0.50	-0.59
-4	0	-7	0.55	-0.30
-4	0	-6	3.81	-3.93
-4	0	-5	2.65	-2.60
-4	0	-4	2.26	-2.42
-4	0	-3	0.50	-0.21
-4	0	-2	2.38	2.40
-4	0	-1	0.92	0.73
-4	0	0	3.97	4.17
-4	1	-7	0.56	-0.39
-4	1	-6	0.56	0.71
-4	1	-4	1.45	1.57
-4	1	-3	4.55	-4.43
-4	1	-2	2.72	2.84
-4	1	-1	3.21	3.17
-4	1	0	0.75	-0.77
-4	2	-6	0.58	0.48
-4	2	-5	1.67	1.76
-4	2	-4	2.38	-2.53
-4	2	-3	5.20	-5.22
-4	2	-2	0.51	-0.61
-4	2	-1	1.96	-1.90
-4	2	0	0.48	0.42
-4	3	-4	4.38	4.41
-4	3	-3	3.25	-3.17
-4	3	-2	0.00	0.16
-4	3	-1	2.88	-3.07
-4	3	0	4.57	-4.71
-4	4	-6	0.00	0.07
-4	4	-4	2.67	-2.61
-4	4	-2	0.55	0.11
-4	4	-1	4.21	-4.58
-4	4	0	1.88	-1.75
-4	5	-5	2.91	-3.02
-4	5	-4	0.57	0.16
-4	5	-2	1.82	-1.98
-4	5	0	1.93	-1.99
-4	5	1	0.75	0.53
-4	6	-4	2.43	2.47
-4	6	-3	1.30	1.50
-4	6	-2	2.70	-2.82
-4	6	-1	2.05	2.11
-4	6	0	3.13	-3.08
-4	6	1	3.31	[illegible]
-4	7	-4	0.55	[illegible]
-4	7	-3	[illegible]	[illegible]
-4	[illegible]	[illegible]	[illegible]	[illegible]
-4	[illegible]	[illegible]	[illegible]	[illegible]
-4	[illegible]	[illegible]	[illegible]	[illegible]
-4	7	1	2.61	-2.67
-4	8	-3	1.75	1.64
-4	8	-2	0.94	1.06
-4	8	-1	2.81	3.00
-4	8	0	0.55	0.38
-4	8	1	0.00	-0.08
-4	9	-2	0.88	0.81
-4	9	-1	1.09	1.00
-4	9	0	2.13	2.32
-4	9	1	0.00	-0.22
-4	10	0	1.90	-1.98
-4	10	1	1.05	-0.69
-3	-13	-2	0.58	0.47
-3	-13	-1	0.57	0.39
-3	-12	-3	0.58	-0.11
-3	-12	-2	1.23	-1.18
-3	-12	-1	0.58	-0.44
-3	-11	-5	2.11	2.21
-3	-11	-4	1.16	-1.12
-3	-11	-3	2.28	2.32
-3	-11	-2	0.00	0.17
-3	-11	-1	2.47	-2.41
-3	-10	-5	1.50	1.42
-3	-10	-4	0.57	-0.67
-3	-10	-3	0.00	0.02
-3	-10	-2	0.96	0.81
-3	-10	-1	3.21	2.95
-3	-9	-6	0.00	0.09
-3	-9	-5	2.31	2.30
-3	-9	-4	0.57	0.51
-3	-9	-3	0.56	0.29
-3	-9	-2	3.34	3.40
-3	-9	-1	0.83	0.85
-3	-8	-6	0.58	-0.34
-3	-8	-4	3.28	-3.22
-3	-8	-3	0.60	0.94
-3	-8	-2	1.25	0.93
-3	-8	-1	0.94	-0.86
-3	-7	-7	0.59	-0.73
-3	-7	-5	1.65	1.58
-3	-7	-4	0.00	-0.40
-3	-6	-7	0.58	-0.38
-3	-6	-6	1.04	1.16
-3	-6	-5	6.46	-6.88
-3	-5	-7	0.55	0.07
-3	-5	-6	1.72	-1.73
-3	-5	-5	1.32	1.23
-3	-5	-4	1.29	-1.27
-3	-5	-3	3.81	-3.73
-3	-5	-2	1.03	0.96
-3	-5	-1	7.58	-8.57
-3	-5	0	0.47	0.29
-3	-4	-7	1.65	-1.49
-3	-4	-6	0.58	0.66
-3	-4	-5	5.43	-5.94
-3	-4	-4	0.50	-0.05
-3	-4	-3	2.12	2.01
-3	-4	-2	2.52	-2.30
-3	-4	-1	2.28	2.23
-3	-4	0	1.61	-1.61
-3	-4	2	1.79	1.65
-3	-3	-8	0.57	-0.22
-3	-3	-7	0.00	-0.58
-3	-3	-6	4.07	-4.12
-3	-3	-5	4.45	-4.36
-3	-3	-4	0.54	-0.71
-3	-3	-3	3.94	3.76
-3	-3	-2	1.62	-1.68
-3	-3	-1	1.05	0.85
-3	-2	-8	0.57	0.57
-3	-2	-7	0.57	0.59
-3	-2	-6	2.91	2.92
-3	-1	-8	0.00	0.17
-3	-1	-7	0.00	-0.15
-3	-1	-5	0.52	0.47
-3	0	-7	3.66	-3.59
-3	0	-6	4.14	4.14
-3	0	-5	1.23	1.21
-3	1	-7	2.16	2.05
-3	1	-6	0.61	0.66
-2	-11	0	1.93	-1.96
-2	-11	1	0.57	0.75
-2	-10	-6	0.37	-0.96
-2	-10	-5	2.35	-2.26
-2	-10	-4	1.05	1.00
-2	-10	-3	1.72	1.75
-2	-10	-2	0.58	-0.32
-2	-10	-1	1.35	1.21
-2	-10	0	1.14	-0.78
-2	-10	1	3.78	-3.90
-2	-9	-6	2.73	2.99
-2	-9	-5	1.13	-1.18
-2	-9	-4	1.00	-0.90
-2	-9	-3	0.56	-0.48
-2	-8	-7	0.58	0.52
-2	-8	-6	1.27	-1.18
-2	-8	-5	0.57	-0.86
-2	-8	-4	3.02	-3.22
-2	-7	-7	3.12	-3.46
-2	-7	-6	1.24	-1.32
-2	-7	-5	0.56	-0.16
-2	-6	-8	0.54	0.63
-2	-6	-7	0.00	-0.17
-2	-6	-6	0.55	0.42
-2	-6	-5	1.55	1.62
-2	-6	-2	1.34	1.19
-2	-6	-1	4.27	4.56
-2	-5	-8	1.27	[illegible]
-2	-5	-7	3.35	3.73
-2	-5	-6	0.84	-0.88
-2	-5	-5	1.65	1.66
-2	-5	-4	1.94	-1.73
-2	-5	-3	2.11	-2.07
-2	-5	-2	1.40	1.17
-2	-5	-1	3.81	3.72
-2	-4	-8	0.97	-0.93
-2	-4	-7	1.47	1.49
-2	-4	-6	1.21	1.37
-2	-4	-5	4.32	4.37
-2	-4	-4	2.61	-2.43
-2	-4	-3	4.22	4.31
-2	-4	-2	1.26	-1.06
-2	-4	-1	3.20	-3.13
-2	-4	0	0.50	-0.52
-2	-3	-8	2.50	2.58
-2	-3	-7	2.34	2.45
-2	-3	-6	1.17	-0.89
-2	-3	-5	0.98	0.82
-2	-3	-4	2.72	2.66
-2	-3	-3	3.27	3.13
-2	-3	-2	1.79	1.82
-2	-3	-1	3.11	-2.99
-2	-3	0	0.81	0.65
-2	-2	-8	1.59	1.65
-2	-2	-7	2.55	2.53
-2	-2	-6	0.56	0.05
-2	-2	-5	3.71	-3.39
-2	-2	-4	3.25	3.29
-2	-2	-3	3.26	-3.41
-2	-2	-2	1.30	1.09
-2	-2	-1	1.26	1.40
-2	-2	0	[illegible]	[illegible]
-2	-1	[illegible]	[illegible]	[illegible]
-2	-1	[illegible]	[illegible]	[illegible]
-2	-1	[illegible]	[illegible]	[illegible]
-2	-1	-5	1.59	1.37
-2	-1	-4	0.51	-0.15
-2	-1	-3	0.98	-1.00
-2	-1	-2	2.35	-2.31
-2	-1	-1	2.20	-2.11
-2	-1	0	5.99	6.46
-2	0	-8	0.00	0.15
-2	0	-7	1.02	-1.17
-2	0	-6	1.94	-2.02
-2	0	-5	5.12	5.04
-2	0	-4	6.09	5.90
-2	0	-3	0.99	-0.97
-2	0	-2	2.70	-2.64
-2	0	-1	1.97	1.87
-2	0	0	3.33	-3.25
-2	1	-8	2.62	-2.72
-2	1	-7	0.57	-0.08
-2	1	-6	3.16	-3.48
-2	1	-5	1.63	-1.96
-2	1	-4	0.46	-0.10
-2	1	-3	1.87	1.88
-2	1	-2	1.77	1.74
-2	1	-1	0.57	0.38
-2	1	0	3.97	3.85
-2	2	-8	1.33	-1.24
-2	2	-7	0.56	-0.30
-2	2	-6	1.49	1.68
-2	2	-5	2.37	-2.34
-2	2	-4	3.94	3.85
-2	2	-3	0.39	0.30
-2	2	-2	3.34	3.44
-2	2	-1	4.43	4.36
-2	2	0	2.28	-2.13
-2	3	-7	0.83	-1.00
-2	3	-6	1.99	2.17
-2	3	-5	3.68	3.91
-2	3	-4	1.90	-2.06
-2	3	-3	3.34	-3.39
-2	3	-2	2.02	-1.97
-2	3	-1	3.24	-3.18
-2	3	0	1.40	-1.11
-2	4	-7	2.40	-2.75
-2	4	-6	0.88	1.23
-2	4	-5	5.91	-7.13
-2	4	-4	2.80	[illegible]
-2	4	-3	1.14	-1.16
-2	4	-2	0.46	-0.47
-2	4	-1	2.66	-2.62
-2	4	0	2.88	-2.64
-2	5	-7	2.27	-2.43
-2	5	-6	0.98	-1.10
-2	5	-5	0.00	-0.07
-2	5	-4	2.88	-3.02
-2	5	-3	0.48	0.10
-2	5	-2	3.43	3.32
-2	5	-1	5.28	-5.44
-2	5	0	3.90	3.67
-2	6	-6	0.98	1.11
-2	6	-5	4.22	-4.62
-2	6	-4	2.96	-3.12
-2	6	-3	2.18	-2.05
-2	6	-2	1.84	-1.73
-2	6	-1	1.29	1.31
-2	6	0	3.41	3.34
-2	7	-6	0.58	-0.73
-2	7	-5	0.55	0.18
-2	7	-4	0.58	0.57
-2	7	-3	2.06	2.01
-2	7	-2	3.23	-3.20
-2	7	-1	2.69	2.75
-2	7	0	1.47	-1.35
-2	8	-5	1.22	1.20
-2	8	-4	2.46	-2.50
-2	8	-3	0.57	0.40
-2	8	-2	0.54	-0.32
-2	8	-1	1.85	-1.81
-2	8	0	0.50	-0.66
-2	9	-4	1.57	-1.41
-2	9	-3	0.55	0.38
-2	9	-2	0.57	-0.42
-2	9	-1	2.38	2.40
-2	9	0	2.67	-2.66
-2	10	-4	0.00	-0.10
-2	10	-3	0.57	-0.47
-2	10	-2	0.58	-0.54
-2	10	-1	0.57	0.85
-2	10	0	1.59	1.66
-2	10	1	2.13	2.21
-2	11	-2	0.55	0.56
-2	11	-1	1.43	-1.48
-2	11	0	3.33	-3.24
-2	11	1	0.00	-0.61
-2	12	0	1.44	-1.50
-2	12	1	0.56	0.45
-1	-13	-3	2.93	3.16
-1	-13	-2	1.32	1.94
-1	-12	-4	0.57	-0.42
-1	-12	-3	0.93	-0.89
-1	-12	-2	1.96	1.86
-1	-12	-1	1.68	1.83
-1	-11	-5	0.68	-0.75
-1	-11	-4	0.65	0.69
-1	-11	-3	1.47	-1.66
-1	-11	-2	1.42	-1.13
-1	-11	-1	1.10	1.14
-1	-10	-6	0.56	-0.63
-1	-10	-5	0.55	0.34
-1	-10	-4	0.89	0.68
-1	-10	-3	2.49	2.56
-1	-10	-2	2.16	2.37
-1	-10	-1	1.99	-1.95
-1	-9	-7	1.61	1.69
-1	-9	-6	3.29	-3.60
-1	-9	-5	0.57	-0.83
-1	-9	-4	1.57	1.62
-1	-9	-3	0.69	1.02
-1	-9	-2	0.78	0.87
-1	-9	-1	5.61	5.62
-1	-8	-7	1.70	2.00
-1	-8	-6	1.51	1.61
-1	-8	-5	1.09	1.55
-1	-8	-4	0.55	0.49
-1	-8	-3	1.36	-1.47
-1	-8	-2	0.88	0.88
-1	-8	-1	1.68	1.48
-1	-7	-8	0.55	0.29
-1	-7	-7	1.16	1.01
-1	-7	-6	2.37	2.63
-1	-7	-5	0.84	0.59
-1	-7	-4	2.12	2.17
-1	-7	-3	1.16	1.27
-1	-7	-2	3.26	-3.19
-1	-7	-1	0.46	0.14
-1	-6	-8	0.00	0.20
-1	-6	-7	0.55	0.44
-1	-6	-6	0.55	0.30
-1	-6	-5	2.69	2.81
-1	-6	-4	0.86	-0.86
-1	-6	-3	1.60	-1.67
-1	-6	-2	1.65	-1.59
-1	-6	-1	5.16	[illegible]
-1	[illegible]	[illegible]	[illegible]	[illegible]
-1	[illegible]	[illegible]	[illegible]	[illegible]
-1	[illegible]	[illegible]	[illegible]	[illegible]
-1	[illegible]	[illegible]	[illegible]	[illegible]
-1	-5	-4	1.33	-1.11
-1	-5	-3	[illegible]	-3.05
-1	-5	-2	0.44	0.26
-1	-5	-1	4.61	4.78
-1	-4	-8	0.87	-0.81
-1	-4	-7	0.57	-0.69
-1	-4	-6	0.55	-0.49
-1	-4	-5	1.63	1.57
-1	-4	-4	0.80	-0.72
-1	-4	-3	3.86	-4.10
-1	-4	-2	5.00	5.23
-1	-4	-1	8.08	-9.61
-1	-3	-8	0.57	-0.46
-1	-3	-7	2.69	-2.98
-1	-3	-6	4.44	4.70
-1	-3	-5	1.67	-1.73
-1	-3	-4	0.71	0.80
-1	-3	-3	1.15	1.23
-1	-3	-2	2.79	-2.84
-1	-3	-1	0.66	-0.68
-1	-2	-6	4.73	-5.13
-1	-2	-5	3.26	-3.31
-1	-2	-4	0.44	-0.59
-1	-2	-3	5.53	6.09
-1	-2	-2	0.39	0.08
-1	-2	-1	0.32	0.24
-1	-2	0	4.53	-4.90
-1	-1	-6	1.50	1.42
-1	-1	-5	1.00	0.96
-1	-1	-4	1.12	-1.10
-1	-1	-3	0.41	-0.50
-1	-1	-2	0.36	-0.25
-1	-1	-1	3.16	-3.26
-1	-1	0	3.51	-3.67
-1	0	-8	0.63	-0.62
-1	0	-7	1.69	1.61
-1	0	-6	3.32	-3.41
-1	0	-5	2.25	2.30
-1	0	-4	0.68	-0.64
-1	0	-3	2.16	-2.45
-1	0	-2	2.06	-2.01
-1	0	-1	3.27	3.38
-1	0	0	4.32	-4.79
-1	1	-8	2.04	1.88
-1	1	-7	6.44	-6.13
-1	1	-6	0.48	-0.25
-1	1	-5	1.33	1.39
-1	1	-4	2.65	3.06
-1	1	-3	1.95	2.18
-1	1	-2	0.36	0.19
-1	1	-1	1.71	-1.81
-1	1	0	3.52	-3.55
-1	2	-8	2.15	1.97
-1	2	-7	1.35	1.25
-1	2	-6	1.27	-1.00
-1	2	-5	1.37	-1.64
-1	2	-4	2.56	-2.97
-1	2	-3	2.13	-2.32
-1	2	-2	1.26	1.35
-1	2	-1	2.64	2.65
-1	2	0	0.99	-1.01
-1	3	-8	0.61	-0.39
-1	3	-7	1.44	1.31
-1	3	-6	3.35	-3.06
-1	3	-5	0.49	0.19
-1	3	-4	3.16	-3.21
-1	3	-3	[illegible]	-3.70
-1	3	-2	0.43	-0.09
-1	3	-1	2.67	2.45
-1	3	0	1.05	1.02
-1	4	-8	1.46	-1.28
-1	4	-7	0.60	0.22
-1	4	-6	1.90	1.62
-1	4	-5	2.99	2.80
-1	4	-4	1.33	1.13
-1	4	-3	4.54	4.46
-1	4	-2	0.72	0.62
-1	4	-1	3.27	3.05
-1	4	0	3.37	3.19
-1	5	-7	2.31	2.16
-1	5	-6	2.75	[illegible]
-1	5	-5	1.41	[illegible]
-1	5	-4	1.12	1.13
-1	6	-7	2.96	2.68
-1	6	-6	1.28	1.11
-1	6	-5	0.60	0.31
-1	6	-4	1.10	-1.17
-1	6	-3	1.45	1.51
-1	6	-2	[illegible]	[illegible]
-1	6	-1	[illegible]	[illegible]
-1	6	0	2.71	2.64
-1	7	-6	1.36	[illegible]
-1	7	-5	1.49	1.39
-1	7	-4	0.00	-0.18
-1	7	-3	[illegible]	2.51
-1	7	-2	4.44	-4.30
-1	7	-1	0.00	[illegible]
-1	7	0	[illegible]	[illegible]
-1	8	-6	1.71	1.40
-1	8	-5	0.57	-0.44
-1	8	-4	4.72	4.43
-1	8	-3	5.05	-5.01
-1	8	-2	0.48	0.63
-1	8	-1	3.92	-3.96
-1	8	0	2.48	-2.36
-1	9	-5	1.64	-1.52
-1	9	-4	0.60	0.16
-1	9	-3	1.66	1.49
-1	9	-2	1.90	1.83
-1	9	-1	0.60	-0.53
-1	9	0	7.42	7.50
-1	10	-4	0.60	0.70
-1	10	-3	0.62	-0.88
-1	10	-2	1.46	1.26
-1	10	-1	0.93	0.84
-1	10	0	0.60	-0.74
-1	11	-3	0.60	-0.34
-1	11	-2	0.62	-0.66
-1	11	-1	0.60	-0.53
-1	11	0	0.60	0.67
-1	12	-2	1.53	1.26
-1	12	-1	0.60	-0.72
-1	12	0	2.21	-2.22
-1	12	1	1.51	-1.52
0	-13	-2	6.82	7.50
0	-13	-1	2.10	-2.31
0	-12	-4	2.36	-2.43
0	-12	-3	1.19	1.27
0	-12	-2	1.15	-1.16
0	-12	-1	0.51	0.11
0	-11	-5	0.54	-0.13
0	-11	-4	2.79	-2.83
0	-11	-3	1.29	-1.37
0	-11	-2	3.37	3.34
0	-11	-1	1.17	0.74
0	-10	-6	1.49	1.28
0	-10	-5	1.32	1.30
0	-10	-4	0.85	0.72
0	-10	-3	0.52	-0.23
0	-10	-2	3.54	-3.48
0	-10	-1	5.59	-5.68
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
0	-9	-2	5.07	-4.75
0	-9	-1	1.71	-1.63
0	-9	0	3.06	-3.11
0	-9	1	1.12	-0.80
0	-8	-7	3.88	-4.09
0	-8	-6	0.00	0.01
0	-8	-5	0.69	-0.71
0	-8	-4	1.79	-1.85
0	-8	-3	1.36	-1.37
0	-8	-2	0.53	-0.23
0	-8	-1	1.84	1.72
0	-8	0	4.56	-4.56
0	-8	1	2.48	2.60
0	-8	2	4.68	-4.67
0	-7	-8	1.28	-1.35
0	-7	-7	1.56	1.50
0	-7	-6	0.89	-1.09
0	-7	-5	0.50	0.65
0	-7	-4	0.70	-0.46
0	-7	-3	6.99	-7.16
0	-7	-2	6.57	-6.65
0	-7	-1	1.86	-1.80
0	-7	0	2.20	2.30
0	-7	1	0.52	0.42
0	-6	-8	1.25	-1.39
0	-6	-7	2.34	-2.41
0	-6	-6	1.72	-1.62
0	-6	-5	1.00	0.90
0	-6	-4	2.23	[illegible]
0	-6	-3	0.55	0.47
0	-6	-2	0.54	-0.67
0	-6	-1	1.02	0.75
0	-6	0	1.35	1.39
0	-6	1	4.20	-4.06
0	-5	-8	1.93	-1.76
0	-5	-7	1.18	-0.91
0	-5	-6	0.53	0.12
0	-5	-5	2.64	2.65
0	-5	-4	1.40	1.25
0	-5	-3	5.53	5.04
0	-5	-2	0.98	0.96
0	-5	-1	3.76	3.66
0	-5	0	5.75	-5.85
0	-4	-8	0.54	-0.28
0	-4	-7	5.56	5.77
0	-4	-6	0.00	-0.19
0	-4	-5	0.52	0.20
0	-4	-4	1.45	1.23
0	-4	-3	1.74	-1.57
0	-4	-2	0.44	-0.08
0	-4	-1	5.34	5.41
0	-4	0	4.27	-4.11
0	-4	1	5.88	-6.33
0	-3	-9	0.87	0.76
0	-3	-8	3.51	-3.42
0	-3	-7	1.58	1.42
0	-3	-6	0.54	0.68
0	-3	-5	3.38	3.39
0	-3	-4	4.56	-4.75
0	-3	-3	2.97	2.62
0	-3	-2	2.62	-2.36
0	-3	-1	1.07	1.05
0	-3	0	0.78	-0.64
0	-2	-9	1.60	1.44
0	-2	-8	0.57	0.24
0	-2	-7	1.43	1.39
0	-2	-6	1.57	-1.40
0	-2	-5	1.50	1.42
0	-2	-4	1.02	0.99
0	-2	-3	5.37	4.95
0	-2	-2	1.53	1.40
0	-2	-1	0.54	0.21
0	-2	0	5.46	5.79
0	-1	-9	1.65	1.75
0	-1	-8	1.48	1.45
0	-1	-7	0.51	0.53
0	-1	-6	0.24	[illegible]
0	-1	-5	4.91	-5.18
0	-1	-4	4.17	4.53
0	-1	-3	0.43	-0.29
0	-1	-2	2.71	2.53
0	-1	-1	3.77	3.05
0	-1	0	[illegible]	0.01
0	0	-9	1.23	1.10
0	0	-8	1.39	-1.21
0	0	-7	1.87	1.76
0	0	-6	1.37	[illegible]
0	0	-5	[illegible]	-2.14
0	0	-4	3.31	-3.50
0	0	-3	0.46	[illegible]
0	0	-2	4.10	3.98
0	0	-1	3.44	[illegible]
0	1	-9	0.51	[illegible]
0	1	-8	2.18	2.23
0	1	-7	[illegible]	[illegible]
0	1	-6	[illegible]	0.29
0	1	-5	3.88	3.63
0	1	-4	5.00	4.60
0	1	-3	1.17	1.14
0	1	-2	[illegible]	3.41
0	1	-1	3.21	3.37
0	2	-8	0.98	-0.79
0	2	-7	0.54	[illegible]
0	2	-6	0.52	-0.46
0	2	-5	0.49	-0.17
0	2	-4	3.09	-2.93
0	2	-3	0.42	[illegible]
0	2	-2	3.11	2.82
0	3	-8	0.65	0.48
0	3	-7	0.52	0.04
0	3	-6	[illegible]	[illegible]
0	3	-3	0.44	-0.32
0	3	-2	[illegible]	2.60
0	3	-1	1.04	0.96
0	4	-8	1.15	1.23
0	4	-7	[illegible]	0.31
0	4	-6	1.18	1.15
0	4	-5	6.53	6.76
0	4	-4	1.61	-1.46
0	4	-3	2.49	-2.43
0	4	-2	3.02	-2.73
0	5	-8	0.00	0.39
0	5	-7	1.66	-1.64
0	5	-6	2.34	2.15
0	5	-5	6.84	-6.72
0	5	-3	1.38	-1.31

h	k	l	Fo	Fc
0	5	-2	3.28	-3.02
0	5	-1	2.95	-3.01
0	6	-7	2.76	-2.54
0	6	-6	3.24	-3.23
0	6	-5	0.52	0.45
0	6	-2	4.47	4.69
0	7	-7	0.53	0.08
0	7	-6	1.59	1.62
0	7	-5	1.71	-1.85
0	7	-4	0.49	-0.31
0	8	-6	1.20	-1.09
0	8	-5	0.48	-0.17
0	8	-4	3.38	3.29
0	8	-3	1.26	1.19
0	9	-6	0.52	-0.56
0	9	-5	1.91	1.93
0	9	-4	0.27	0.14
0	9	-3	0.51	0.48
0	9	-2	0.90	-1.00
0	10	-5	0.50	0.41
0	10	-4	1.76	-1.69
0	10	-3	0.82	0.82
0	10	-2	1.45	-1.45
0	10	-1	4.46	4.50
0	10	0	4.57	-4.42
0	11	-4	1.55	-1.59
0	11	-3	0.00	0.08
0	11	-2	1.95	-2.05
0	11	-1	2.80	2.77
0	11	0	1.83	1.85
0	12	-3	0.49	-0.38
0	12	-2	0.52	0.53
0	12	-1	1.04	0.90
0	12	0	0.51	0.30
0	13	-1	0.50	-0.65
0	13	0	0.50	0.23
1	-12	-4	4.35	-4.26
1	-12	-3	2.18	2.17
1	-12	-2	0.86	-0.87
1	-11	-5	0.00	-0.13
1	-11	-4	2.24	-2.31
1	-11	-3	1.22	0.94
1	-11	-2	1.16	0.69
1	-11	-1	0.61	0.35
1	-10	-6	1.67	1.71
1	-10	-5	1.53	-1.20
1	-10	-4	[illegible]	0.48
1	-10	-3	0.00	0.18
1	-10	-2	3.40	-3.35
1	-10	-1	1.77	-1.73
1	-9	-7	0.61	-0.54
1	-9	-6	1.65	1.45
1	-9	-5	1.36	1.27
1	-9	-4	2.41	2.35
1	-9	-3	4.35	4.14
1	-9	-2	2.89	2.61
1	-9	-1	7.72	-7.71
1	-8	-7	1.41	1.19
1	-8	-6	1.54	-1.44
1	-8	-5	0.61	-0.31
1	-8	-4	4.73	4.57
1	-8	-3	4.74	4.97
1	-8	-2	3.30	3.40
1	-8	-1	2.79	2.60
1	-7	-8	0.63	-0.57
1	-7	-7	0.63	0.50
1	-7	-6	2.22	2.06
1	-7	-5	3.29	3.16
1	-7	-4	2.33	2.44
1	-7	-3	1.48	-1.39
1	-7	-2	3.44	3.27
1	-7	-1	2.48	-2.35
1	-6	-8	0.63	0.52
1	-6	-7	0.00	-0.51
1	-6	-6	2.66	2.38
1	-6	-5	1.70	1.74
1	-6	-4	1.45	1.51
1	-5	-8	0.65	0.67
1	-5	-6	3.58	-3.31
1	-5	-5	5.86	5.68
1	-5	-4	2.20	2.10
1	-5	-3	0.44	-0.18
1	-5	-2	1.21	1.06
1	-5	-1	2.38	-2.43
1	-4	-9	0.61	0.09
1	-4	-8	1.52	1.30
1	-4	-7	3.14	-2.81
1	-4	-6	2.58	2.75
1	-4	-5	6.35	-6.92
1	-4	-4	1.34	-1.45
1	-4	-3	1.59	-1.46
1	-4	-2	0.96	1.09
1	-4	-1	8.95	9.72
1	-3	-9	3.25	-2.80
1	-3	-6	3.33	-4.27
1	-3	-5	0.48	-0.83
1	-3	-4	0.82	-1.03
1	-3	-3	5.35	-5.79
1	-3	-2	9.48	11.22
1	-3	-1	0.74	-0.47
1	-2	-9	2.06	-1.95
1	-2	-8	0.61	0.41
1	-2	-7	2.68	-2.43
1	-2	-6	5.96	5.72
1	-2	-5	1.34	1.19
1	-2	-4	2.36	2.15
1	-2	-3	2.67	-2.85
1	-2	-2	1.85	-2.00
1	-1	-9	0.93	-0.58
1	-1	-8	1.22	1.00
1	-1	-7	0.57	-0.24
1	-1	-5	3.92	-4.02
1	-1	-4	1.39	-1.45
1	-1	-3	0.39	0.44
1	-1	-2	2.83	-3.01
1	-1	-1	2.63	2.55
1	0	-9	0.62	-0.69
1	0	-8	0.62	0.65
1	0	-7	0.61	-0.63
1	0	-6	0.49	-0.09
1	0	-5	0.78	-0.74
1	0	-4	1.39	-1.34
1	0	-3	1.21	-1.00
1	0	-2	2.30	-2.14
1	0	-1	2.65	-2.53
1	1	-9	0.63	-0.80
1	1	-8	2.14	-2.08
1	1	-7	5.39	5.19
1	1	-6	1.50	-1.71
1	1	-5	1.20	1.11
1	1	-4	3.47	-3.56
1	1	-3	3.50	-3.61
1	1	-2	6.47	-7.13
1	1	-1	2.80	2.88
1	2	-9	0.59	-0.19
1	2	-8	0.61	0.65
1	2	-7	4.13	-4.05
1	2	-6	0.49	-0.79
1	2	-5	0.47	-0.39
1	2	-4	1.20	-1.39
1	2	-3	2.14	2.29
1	2	-2	3.35	-3.24
1	2	-1	2.29	-2.27
1	3	-8	0.93	-0.62
1	3	-7	0.60	0.65
1	3	-6	1.36	1.33
1	3	-5	1.04	-1.17
1	3	-4	1.95	-2.01
1	3	-3	1.11	1.09
1	3	-2	1.09	-1.06
1	3	-1	1.03	1.14
1	3	0	0.91	-0.94
1	4	-8	1.19	-0.93
1	4	-7	1.87	1.63
1	4	-6	1.33	-1.37
1	4	-5	0.43	-0.61
1	4	-4	1.90	-2.07
1	4	-3	1.39	-1.33
1	4	-2	1.79	-1.84
1	4	-1	1.62	-1.54
1	4	0	0.72	0.75
1	5	-8	1.70	-1.41
1	5	-7	1.00	-1.01
1	5	-6	2.29	2.16
1	5	-5	1.95	2.13
1	5	-4	1.95	1.91
1	5	-3	5.90	6.43
1	5	-2	0.44	0.44
1	5	-1	2.86	-2.82
1	5	0	2.96	2.97
1	6	-7	1.53	1.35
1	6	-6	1.63	-1.35
1	6	-5	1.00	0.87
1	6	-4	2.39	2.77
1	6	-3	3.24	3.53
1	6	-2	4.58	5.12
1	6	-1	3.23	-3.12
1	6	0	1.77	-1.59
1	7	-7	1.47	1.48
1	7	-6	0.60	0.63
1	7	-5	0.60	0.30
1	7	-4	1.33	-1.20
1	7	-3	0.75	0.80
1	7	-2	0.98	-1.07
1	7	-1	1.01	-0.86
1	8	-6	0.61	-0.21
1	8	-5	1.91	1.72
1	8	-4	2.14	-2.10
1	8	-2	1.92	-1.87
1	8	-1	1.29	1.32
1	8	0	9.19	9.86
1	9	-6	0.58	0.26
1	9	-5	0.61	0.57
1	9	-4	5.10	5.00
1	9	-3	3.53	-3.44
1	9	-2	2.99	2.77
1	9	-1	0.49	0.29
1	9	0	2.30	-2.37
1	10	-5	0.61	-0.72
1	10	-4	0.00	0.15
1	10	-3	0.00	-0.04
1	10	-2	4.30	4.19
1	10	-1	0.57	-0.49
1	10	0	7.04	7.02
1	11	-4	1.12	1.05
1	11	-3	1.91	-1.80
1	11	-2	3.78	3.49
1	11	-1	3.07	2.83
1	11	0	0.00	0.09
1	12	-3	1.83	-1.90
1	12	-2	0.00	-0.23
1	12	-1	0.00	0.07
1	12	0	0.00	-0.36
1	13	-1	0.00	-0.12
1	13	0	1.89	-1.93
2	-12	-3	2.46	-2.28
2	-12	-2	7.46	7.87
2	-11	-4	1.45	1.48
2	-11	-3	3.14	3.17
2	-11	-2	0.00	0.30
2	-10	-6	0.63	0.89
2	-10	-5	1.42	-1.40
2	-10	-4	0.62	-0.79
2	-10	-3	1.35	-1.30
2	-10	-2	2.09	2.06
2	-9	-6	0.60	-0.13
2	-9	-5	0.60	-0.52
2	-9	-4	2.42	2.45
2	-9	-3	2.62	2.47
2	-9	-2	1.33	-1.34
2	-9	-1	1.25	-1.27
2	-8	-7	3.2	2.85
2	-8	-6	3.21	-3.10
2	-8	-5	3.02	-2.93
2	-8	-4	0.57	0.50
2	-8	-3	3.08	2.99
2	-8	-2	6.42	-6.46
2	-7	-7	3.67	-3.59
2	-7	-6	3.66	-3.63
2	-7	-5	3.77	-3.49
2	-7	-4	3.60	-3.44
2	-7	-3	2.09	1.93
2	-7	-2	0.48	-0.48
2	-7	-1	6.50	6.65
2	-6	-8	3.03	-2.82
2	-6	-7	0.00	0.10
2	-6	-6	1.91	-1.98
2	-6	-5	0.62	-0.96
2	-6	-4	1.70	-1.65
2	-6	-3	2.53	-2.53
2	-6	-2	5.66	-5.73
2	-6	-1	1.20	1.19
2	-5	-8	0.63	-0.83
2	-5	-7	2.00	-1.90
2	-5	-6	1.03	-0.39
2	-5	-5	0.48	0.57
2	-5	-4	0.48	-0.41
2	-5	-3	1.37	-1.33
2	-5	-2	2.88	-2.80
2	-5	-1	1.67	-1.67
2	-4	-8	1.00	-0.61
2	-4	-7	3.73	-3.33
2	-4	-6	0.89	-0.62
2	-4	-5	1.65	1.91
2	-4	-4	1.63	-1.48
2	-4	-3	2.40	2.23
2	-4	-2	0.64	0.52
2	-4	-1	1.06	-1.08
2	-3	-9	1.22	0.87
2	-3	-8	1.18	1.13
2	-3	-7	4.53	4.43
2	-3	-6	0.94	0.30
2	-3	-5	1.17	-1.11
2	-3	-4	0.45	-0.53
2	-3	-3	4.32	-4.12
2	-3	-2	0.77	-0.65
2	-3	-1	0.82	-0.72
2	-2	-9	1.63	1.77
2	-2	-8	1.19	-1.24
2	-2	-7	1.14	0.85
2	-2	-6	1.02	0.93
2	-2	-5	3.60	3.35
2	-2	-4	7.92	-7.91
2	-2	-3	2.79	-2.73
2	-2	-2	3.33	-3.45
2	-2	-1	4.63	-4.69
2	-1	-9	0.60	0.54
2	-1	-8	0.53	-0.75
2	-1	-7	0.60	0.63
2	-1	-6	1.57	-1.37
2	-1	-5	4.10	4.11
2	-1	-4	2.65	-2.56
2	-1	-3	2.18	1.93
2	-1	-2	1.47	1.31
2	-1	-1	4.05	-4.14
2	0	-9	0.62	1.13
2	0	-8	1.65	1.53
2	0	-7	0.60	0.32
2	0	-6	0.73	0.86
2	0	-5	0.74	-0.60
2	0	-4	5.53	6.04
2	0	-3	1.33	1.50
2	0	-2	3.53	3.45
2	1	-9	0.60	0.56
2	1	-8	0.98	-1.10
2	1	-7	1.70	1.52
2	1	-6	2.26	2.36
2	1	-5	0.00	0.20
2	1	-4	1.61	-1.53
2	1	-3	3.02	-2.92
2	1	-2	4.09	4.22
2	1	-1	4.70	-4.75
2	2	-9	1.45	-1.49
2	2	-8	2.91	2.56
2	2	-7	0.61	-0.68
2	2	-6	1.13	1.12
2	2	-5	2.71	2.73
2	2	-4	6.58	6.82
2	2	-3	0.79	0.73
2	2	-2	3.70	3.86
2	2	-1	3.59	3.82
2	3	-8	0.60	-0.34
2	3	-7	0.00	-0.04
2	3	-6	1.04	1.06
2	3	-5	2.08	1.85
2	3	-4	2.27	2.30
2	3	-3	0.84	0.85
2	3	-2	4.38	4.22
2	3	-1	3.11	-3.09
2	4	-8	0.59	0.50
2	4	-7	0.59	0.45
2	4	-6	2.62	2.32
2	4	-5	5.10	-5.32
2	4	-4	0.48	0.53
2	4	-3	0.44	-0.59
2	4	-2	3.15	3.26
2	4	-1	4.48	4.83
2	5	-8	0.59	0.16
2	5	-7	0.92	0.72
2	5	-6	1.85	-1.76
2	5	-5	3.68	4.22
2	5	-4	0.93	1.15
2	5	-3	0.44	-0.16
2	5	-2	0.00	-0.11
2	5	-1	2.09	2.06
2	5	0	1.39	-1.26
2	6	-7	0.61	-0.83
2	6	-6	2.38	2.45
2	6	-5	5.76	-5.58
2	6	-4	0.71	0.53
2	6	-3	1.27	1.12
2	6	-2	4.60	-4.98
2	6	-1	2.66	2.71
2	6	0	3.11	-2.94
2	7	-7	1.57	-1.53
2	7	-6	4.68	-4.33
2	7	-5	1.85	-1.67
2	7	-4	1.14	-1.08
2	7	-1	0.77	0.80
2	7	0	0.90	1.03
2	8	-7	0.59	-0.47
2	8	-6	1.21	1.2
2	8	-5	1.30	-1.23
2	8	-4	0.61	-0.77
2	8	-3	1.10	-0.95
2	8	-2	1.63	-2.02
2	8	-1	0.82	0.61
2	8	0	3.93	3.77
2	9	-6	0.00	0.54
2	9	-5	0.91	-1.14
2	9	-4	0.93	0.72
2	9	-3	0.00	0.25
2	9	-2	5.74	-5.41
2	9	-1	0.92	1.01
2	9	0	2.15	-2.19
2	10	-5	1.26	1.03
2	10	-4	0.95	-1.03
2	10	-3	1.17	-0.98
2	10	-2	2.21	-2.12
2	11	-4	2.69	-2.88
2	11	-3	0.61	0.24
2	11	-2	2.22	-0.15
2	12	-3	0.58	0.29
2	12	-2	1.95	-2.07
2	12	-1	1.23	-1.09
2	13	-1	1.00	-0.73
2	13	0	0.00	-0.01
3	-11	-3	0.93	0.69
3	-11	-2	1.11	1.09
3	-10	-5	0.61	-0.53
3	-10	-4	3.10	-3.28
3	-10	-3	0.95	0.63
3	-10	-2	3.77	3.72
3	-9	-6	0.58	-0.19
3	-9	-5	1.36	-1.40
3	-9	-4	0.89	-0.32
3	-9	-3	0.58	-0.29
3	-9	-2	1.23	-1.09
3	-8	-6	0.58	-0.28
3	-8	-3	1.15	-1.00
3	-8	-2	1.28	1.66
3	-7	-7	2.42	2.26
3	-7	-6	1.73	-1.67
3	-7	-5	2.47	-2.28
3	-7	-4	3.79	3.63
3	-7	-3	0.00	0.38
3	-7	-2	1.13	1.20
3	-7	-1	3.61	3.69
3	-6	-7	1.39	2.03
3	-6	-6	1.56	1.46
3	-6	-5	1.07	0.96
3	-6	-4	4.03	3.90
3	-6	-3	4.27	-4.43
3	-6	-2	1.35	1.98
3	-6	-1	3.40	-3.60
3	-5	-8	1.02	1.32
3	-5	-7	0.63	0.67
3	-5	-6	3.83	3.72
3	-5	-5	0.61	-0.30
3	-5	-4	1.13	1.14
3	-5	-3	4.02	-4.13
3	-5	-2	3.17	-3.17
3	-5	-1	1.50	1.23
3	-4	-8	0.00	0.25
3	-4	-7	0.63	0.64
3	-4	-6	3.05	-2.57
3	-4	-5	3.38	3.35
3	-4	-4	3.53	3.43
3	-4	-3	0.53	0.45
3	-4	-2	1.13	1.31
3	-4	-1	0.46	0.27
3	-3	-8	1.34	1.13
3	-3	-7	1.36	-1.85
3	-3	-6	5.14	4.33
3	-3	-5	2.02	-1.93
3	-3	-4	1.03	0.87
3	-3	-3	3.41	3.52
3	-3	-2	3.02	-2.99
3	-3	-1	7.06	7.32
3	-2	-8	0.93	-0.87
3	-2	-7	1.77	1.50
3	-2	-6	2.28	-2.07
3	-2	-5	0.00	-0.34
3	-2	-4	0.47	0.05
3	-2	-3	1.31	-1.26
3	-2	-2	6.21	6.35
3	-2	-1	1.12	1.00
3	-1	-8	0.60	-0.36
3	-1	-7	2.92	-2.67
3	-1	-6	6.18	6.03
3	-1	-5	3.46	3.49
3	-1	-4	4.53	4.54
3	-1	-3	3.72	3.77
3	-1	-2	1.73	-1.69
3	-1	-1	3.76	-3.38
3	0	-8	0.59	0.43
3	0	-6	0.61	0.36
3	0	-5	2.02	-2.15
3	0	-4	0.75	-0.85
3	0	-3	3.34	3.27
3	0	-2	3.20	-3.16
3	0	-1	0.42	-0.40
3	1	-8	0.61	0.58
3	1	-7	3.55	-3.25
3	1	-6	1.28	-1.34
3	1	-5	2.34	-2.37
3	1	-4	2.71	-2.57
3	1	-3	1.25	1.18
3	1	-2	1.40	1.34
3	1	-1	0.42	-0.23
3	2	-8	3.14	-3.32
3	2	-7	2.82	2.72
3	2	-6	1.44	-1.43
3	2	-5	1.94	1.65
3	2	-3	1.57	-1.50
3	2	-2	4.90	-5.14
3	2	-1	3.12	3.20
3	3	-8	0.62	0.34
3	3	-7	2.92	-3.02
3	3	-6	3.19	-2.99
3	3	-5	0.00	0.23
3	3	-4	3.32	-3.42
3	3	-3	0.87	1.02
3	3	-2	1.75	-1.62
3	3	-1	1.92	-1.94
3	4	-8	1.36	-1.21
3	4	-7	1.15	-1.04
3	4	-6	0.93	-1.00
3	4	-5	0.50	-0.69
3	4	-4	0.69	-2.78
3	4	-3	0.00	1.99
3	4	-1	2.24	2.13
3	5	-8	0.63	-0.64
3	5	-7	2.21	2.12
3	5	-6	1.96	-1.99
3	5	-5	0.97	-0.74
3	5	-4	3.12	-3.13
3	5	-3	3.77	-3.63
3	5	-2	0.77	0.70
3	5	-1	1.30	1.32
3	6	-7	0.00	-0.43
3	6	-6	0.62	0.86
3	6	-5	1.19	1.37
3	6	-4	0.81	-0.96
3	6	-3	0.48	-0.65
3	6	-2	0.48	-0.76
3	6	-1	3.09	-3.03
3	7	-7	1.42	1.19
3	7	-6	1.57	-1.31
3	7	-5	0.59	-0.10
3	7	-4	2.90	2.60
3	7	-3	1.44	-1.71
3	7	-2	3.21	3.15
3	7	-1	3.69	-3.64
3	8	-6	0.59	0.43
3	8	-5	0.00	-0.58
3	8	-4	0.99	0.62
3	8	-3	2.18	-2.08
3	8	-2	0.00	-0.34
3	8	-1	2.40	-2.48
3	8	0	4.44	-4.35
3	9	-6	0.00	[illegible]
3	9	-5	0.59	0.57
3	9	-4	2.05	-2.09
3	9	-3	0.61	0.63
3	9	-2	1.81	-1.53
3	9	-1	0.58	0.13
3	9	0	5.80	5.27
3	10	-5	0.62	0.30
3	10	-4	4.38	4.92
3	10	-3	1.22	-1.35
3	10	-2	1.00	1.08
3	10	-1	[illegible]	3.11
3	10	0	3.42	-3.52
3	11	-4	1.77	1.39
3	11	-3	[illegible]	[illegible]
3	11	-2	1.98	1.97
3	11	-1	1.31	-1.33
3	11	0	2.79	2.74
3	12	-3	0.59	0.70
3	12	-2	1.73	1.57
3	12	-1	1.90	1.95
3	13	-1	0.00	0.18
3	13	0	0.00	0.13
4	-10	-3	3.45	3.55
4	-10	-2	0.90	-0.57
4	-9	-5	0.99	-1.19
4	-9	-4	2.21	-2.31
4	-9	-3	1.58	-1.69
4	-9	-2	0.52	-0.96
4	-8	-6	0.63	0.30
4	-8	-5	0.59	-0.29
4	-8	-4	0.62	-0.50
4	-8	-3	0.62	0.56
4	-8	-2	0.59	0.50
4	-7	-5	0.62	0.73
4	-7	-4	0.59	0.55
4	-7	-3	2.86	[illegible]
4	-7	-2	3.30	-3.64
4	-6	-7	1.26	-1.15
4	-6	-6	2.56	-2.57
4	-6	-5	1.11	-0.92
4	-6	-4	2.73	-2.55
4	-6	-3	0.64	0.78
4	-6	-2	0.00	0.55
4	-5	-7	0.00	-0.20
4	-5	-6	2.36	-2.31
4	-5	-5	2.50	2.21
4	-5	-4	1.35	-1.23
4	-5	-3	0.73	0.73
4	-5	-2	1.53	[illegible]
4	-4	-8	1.37	-1.15
4	-4	-7	0.90	-0.13
4	-4	-6	0.66	-0.75
4	-4	-5	3.05	2.90
4	-4	-4	0.58	0.69
4	-4	-3	0.50	-0.35
4	-4	-2	0.50	0.08
4	-4	-1	2.86	-2.73
4	-3	-8	0.61	-0.50
4	-3	-7	2.97	-3.03
4	-3	-6	2.50	-2.32
4	-3	-5	1.46	1.46
4	-3	-4	1.92	-1.87
4	-3	-3	0.50	0.34
4	-3	-2	2.63	2.63
4	-3	-1	2.05	-2.00
4	-2	-8	0.61	-0.66
4	-2	-7	2.18	1.91
4	-2	-6	0.55	-0.73
4	-2	-5	3.56	-3.45
4	-2	-4	1.31	1.16
4	-2	-3	3.35	-3.32
4	-2	-2	2.04	1.30
4	-2	-1	0.50	-0.45
4	-1	-8	0.61	-0.95
4	-1	-7	0.59	-0.34
4	-1	-6	0.94	-0.92
4	-1	-5	0.50	-0.05
4	-1	-4	2.79	-2.66
4	-1	-3	2.88	-2.64
4	-1	-2	1.71	-1.57
4	-1	-1	2.82	-2.72
4	0	-8	2.27	-2.26
4	0	-7	0.60	-0.59
4	0	-6	3.23	-3.16
4	0	-5	0.50	-0.24
4	0	-4	1.33	-1.34
4	0	-3	1.24	1.20
4	0	-2	0.58	0.49
4	0	-1	3.62	-3.32
4	1	-8	0.63	0.76
4	1	-7	0.60	0.33
4	1	-6	0.60	-0.58
4	1	-5	2.80	-2.91
4	1	-4	4.97	5.01
4	1	-3	3.65	3.56
4	1	-2	1.36	1.61
4	1	-1	6.66	6.35
4	2	-8	0.97	-0.78
4	2	-6	2.47	2.50
4	2	-5	0.67	-0.49
4	2	-4	1.13	-1.02
4	2	-3	3.67	-3.76
4	2	-2	0.60	-0.60
4	2	-1	2.06	-1.98
4	3	-8	2.05	2.19
4	3	-7	0.00	0.29
4	3	-4	3.14	3.28
4	3	-3	2.03	-2.22
4	3	-2	3.42	-3.42
4	3	-1	3.38	3.43
4	4	-6	1.42	1.33
4	4	-5	1.94	1.85
4	4	-4	2.73	2.80
4	4	-3	1.07	0.97
4	4	-2	0.82	0.72
4	4	-1	3.13	-3.19
4	5	-6	4.25	4.03
4	5	-5	3.98	-3.36
4	5	-4	0.98	-0.95
4	5	-3	0.52	-0.79
4	5	-2	1.03	0.99
4	5	-1	2.05	1.86
4	6	-7	0.93	0.91
4	6	-6	1.06	-1.03
4	6	-5	2.74	2.83
4	6	-4	0.58	-0.33
4	6	-3	0.47	-0.27
4	6	-2	1.62	1.81
4	6	-1	2.22	2.23
4	7	-6	3.79	3.69
4	7	-5	0.00	-0.11
4	7	-4	0.58	0.30
4	7	-3	2.12	2.09
4	7	-2	3.23	-3.33
4	7	-1	0.95	1.01
4	8	-5	1.01	0.99
4	8	-4	0.60	-0.75
4	9	-2	1.24	1.16
4	9	-1	0.90	-0.83
4	10	-4	0.00	-0.16
4	10	-3	0.60	0.64
4	10	-2	2.18	-2.08
4	10	-1	1.09	0.80
4	10	0	2.46	-2.35
4	11	-4	0.60	-0.52
4	11	-3	1.53	-1.57
4	11	-2	0.55	0.35
4	11	-1	2.61	-2.34
4	11	0	1.47	-1.50
4	12	-2	0.00	-0.14
4	12	-1	1.35	1.43
4	12	0	0.00	0.09
5	-8	-4	0.60	0.70
5	-8	-3	[illegible]	0.36
5	-8	-2	1.52	-1.63
5	-7	-5	0.59	0.51
5	-7	-4	1.52	1.39
5	-7	-3	0.50	-0.71
5	-7	-2	0.53	-0.39
5	-6	-6	0.57	-0.57
5	-6	-5	2.33	-2.45
5	-6	-4	1.03	1.34
5	-6	-3	0.99	0.36
5	-6	-2	1.21	-1.07
5	-5	-6	0.61	0.69
5	-5	-5	0.61	-0.58
5	-5	-4	2.15	2.35
5	-5	-3	0.95	-0.89
5	-5	-2	3.96	3.93
5	-4	-7	1.62	-1.55
5	-4	-6	3.27	3.59
5	-4	-5	1.25	-1.22
5	-4	-4	0.50	-0.37
5	-4	-3	1.51	-1.33
5	-4	-2	0.61	-0.36
5	-3	-6	2.14	-2.30
5	-3	-5	0.00	0.13
5	-3	-4	0.00	0.17
5	-3	-3	1.06	1.05
5	-3	-2	4.55	4.56
5	-2	-7	1.59	-1.98
5	-2	-6	3.33	3.03
5	-2	-5	0.90	-0.55
5	-2	-4	0.59	-0.31
5	-2	-3	5.50	5.62
5	-2	-2	0.51	-0.10
5	-2	-1	4.03	3.73
5	-1	-7	2.56	2.36
5	-1	-6	0.60	-0.98
5	-1	-5	0.59	0.39
5	-1	-4	2.06	-2.21
5	-1	-3	1.30	-1.15
5	-1	-2	2.33	2.51
5	0	-7	1.13	-1.24
5	0	-6	2.03	2.39
5	0	-5	2.83	2.32
5	0	-4	1.73	1.30
5	0	-3	2.42	2.54
5	0	-2	1.29	-1.09
5	1	-7	1.32	1.46
5	1	-6	0.57	0.29
5	1	-5	0.58	0.15
5	1	-4	0.57	-0.07
5	1	-3	1.59	1.47
5	1	-2	3.90	-3.91
5	1	-1	1.93	-1.75
5	2	-7	1.10	-1.00
5	2	-6	1.58	-1.83
5	2	-5	1.96	-2.10
5	2	-4	1.80	-1.75
5	2	-3	1.79	-1.82
5	2	-2	1.06	0.89
5	3	-7	1.62	1.90
5	3	-6	0.59	-0.82
5	3	-5	1.97	2.10
5	3	-4	0.55	0.21
5	3	-3	1.71	-1.61
5	3	-2	3.23	-3.27
5	4	-7	0.56	-0.46
5	4	-6	1.45	-1.80
5	4	-5	2.08	2.24
5	4	-4	0.57	0.66
5	4	-3	1.44	-1.33
5	5	-7	0.34	-0.95
5	5	-6	1.00	-1.23
5	5	-5	0.54	0.28
5	5	-4	0.00	-0.08
5	5	-3	1.56	1.64
5	6	-6	1.15	-1.25
5	6	-5	1.19	-0.34
5	6	-4	0.56	-0.61
5	6	-3	1.54	-1.70
5	6	-2	0.56	0.35
5	7	-6	0.56	0.82
5	7	-5	0.56	0.52
5	7	-4	1.19	-1.24
5	7	-3	0.58	-0.73
5	7	-2	1.34	-1.31
5	7	-1	1.73	-1.67
5	8	-5	1.31	-1.82
5	8	-4	1.20	1.23
5	8	-3	1.12	-1.25
5	8	-2	1.53	1.46
5	8	-1	2.20	-2.20
5	9	-5	1.74	-1.30
5	9	-4	0.97	0.82
5	9	-3	0.56	-0.54
5	9	-2	1.27	1.30
5	9	-1	0.56	-0.71
5	10	-4	1.83	-2.19
5	11	-1	2.42	2.57
6	-7	-2	2.15	2.12
6	-6	-2	0.60	0.35
6	-5	-5	0.57	0.52
6	-5	-4	0.59	-0.34
6	-5	-3	0.59	-0.42
6	-5	-2	0.59	0.33
6	-4	-6	1.22	-1.43
6	-4	-5	0.58	0.26
6	-4	-4	2.26	-2.37
6	-4	-3	0.58	-0.18
6	-4	-2	1.35	-1.45
6	-3	-6	0.00	0.26
6	-3	-5	0.56	0.62
6	-3	-4	0.57	-0.15
6	-3	-3	0.59	-0.65
6	-3	-2	2.20	-2.04
6	-2	-6	1.11	-1.00
6	-2	-4	2.63	-2.69
6	-2	-3	0.59	-0.38
6	-2	-2	1.33	-1.14
6	-1	-6	0.58	0.44
6	-1	-5	4.23	-4.36
6	-1	-4	0.57	-0.27
6	-1	-3	2.29	-2.38
6	-1	-2	0.00	-0.23
6	0	-7	0.00	-0.44
6	0	-6	0.57	0.64
6	0	-5	0.57	-0.72
6	2	-1	1.77	1.63
6	3	-6	1.23	1.38
6	3	-5	0.99	1.09
6	3	-4	0.55	0.17
6	4	-5	0.00	0.07
6	4	-4	0.57	0.64
6	4	-3	2.02	-2.01
6	4	-2	2.52	-2.40
6	4	-1	1.77	1.75
6	5	-6	1.00	-1.03
6	5	-5	1.34	1.64
6	5	-3	0.35	0.34
6	5	-2	2.39	2.38
6	5	-1	0.55	-0.11
6	6	-6	2.04	2.14
6	6	-5	1.40	-1.35
6	6	-4	0.00	-0.16
6	6	-3	0.00	[illegible]
6	6	-2	1.80	1.34
6	6	-1	1.73	[illegible]
6	7	-5	0.97	1.03
6	7	-4	0.90	-0.32
6	7	-3	0.56	-0.21
6	7	-2	2.50	2.61
6	7	-1	1.73	2.75
6	8	[illegible]	0.00	0.52
6	8	-1	1.52	1.54
6	9	-4	[illegible]	-0.21
6	9	-3	1.17	1.25
6	9	-2	0.57	0.33
6	10	-2	0.00	[illegible]
6	10	-1	0.57	0.29
7	-4	-3	1.51	-1.50
7	-3	-5	1.35	2.37
7	-3	-4	[illegible]	0.45
7	-3	-3	1.10	-1.73
7	-3	-2	0.99	-0.26
7	-2	-5	0.55	[illegible]
7	-2	-4	1.22	1.24
7	-2	-3	1.15	-1.15
7	-2	-2	1.60	1.53
7	-1	-5	[illegible]	[illegible]
7	-1	-4	1.28	1.32
7	-1	-3	4.30	4.33
7	-1	-2	0.96	0.51
7	0	-5	0.91	0.94
7	0	-4	[illegible]	0.15
7	0	-3	0.61	[illegible]
7	0	-2	0.00	[illegible]
7	1	-5	1.16	1.11
7	1	-4	0.93	-0.73
7	1	-3	1.66	1.69
7	1	-2	[illegible]	[illegible]
7	2	-5	0.57	0.54
7	2	-4	0.59	[illegible]
7	2	-3	2.73	2.77
7	2	-2	2.17	-1.72
7	3	-5	1.26	[illegible]
7	3	-4	0.59	-0.52
7	3	-2	1.21	1.14

APPENDIX II

THE SETTING-UP OF CRYSTALS ON A FOUR-CIRCLE NEUTRON DIFFRACTOMETER

by Murdoch Currie

Department of Chemistry,
The University,
Glasgow, W.2.

1.1. INTRODUCTION

Basically there are three ways of setting up a crystal on the Ferranti four-circle diffractometer:

(1) with a real axis vertical at $\chi \neq 0°$

(2) with a reciprocal axis vertical at $\chi \doteq 0°$

(3) in a general orientation.

If the crystal possesses orthorhombic or higher symmetry the real and reciprocal axes are coincident and (1) and (2) become identical. If, however, the crystal is monoclinic, with the b-axis unique, only b and b* are coincident. In the triclinic case the real and reciprocal axes do not coincide.

To calculate the setting angles for a crystal on the diffractometer it is necessary to use a program originally written by M.J.D. Powell for the STRETCH computer, and subsequently modified for use on ATLAS and the IBM 360/65. This program is fully described elsewhere (Powell, 1965) but some notes are included here as an Appendix. The diffractometer itself is described by Bunce and Wheeler (1965).

2.1. REAL AXIS VERTICAL

A crystal may be set up with a real axis vertical (at $\chi = 0°$) in one of several ways, viz. by X-ray oscillation or back-reflexion Laue photographs, after which it is transferred to the diffractometer on which its position is defined by setting of Φ, Ω and θ for a strong zero-layer reflexion and by turning the goniometer by hand until the peak is indicated on the rate-meter. This peak is centred as well as possible, the goniometer is clamped in position, and, if the crystal has been set up properly, general reflexions, for which $\chi \neq 0°$, will appear where predicted.

This method has several disadvantages, the greatest of which is that the adjustments to the arcs are made on the basis of X-ray photographs from which no better accuracy that 0·10 – 0·20° may be obtainable, whilst the accuracy of the instrument is specified as 0·01°. It is also difficult to make adjustments to the arcs once the crystal is mounted on the instrument as χ scans of a zero-layer reflexion tend to show little variation of peak intensity over ranges of 3·00 to 4·00°.

2.2. RECIPROCAL AXIS VERTICAL

The second, and most satisfactory, approach to the problem is to orient the crystal so that a reciprocal axis is vertical at $\chi = 0^\circ$. The main advantage of this method is that the crystal is set up on the diffractometer itself, though, of course, its approximate orientation has to be known first. This is easily obtained optically or from an X-ray oscillation photograph.

The crystal is mounted on the diffractometer and a strong reflexion, for which $\chi = \pm 90{\cdot}00^\circ$ (i.e. an $0k0$ or $0\bar{k}0$ reflexion if b^* is vertical) is chosen, Ω and θ being positioned appropriately. For such a reflexion, viz. at $\chi = \pm 90{\cdot}00^\circ$, Φ is insensitive, as rotating Φ, when the crystal is properly set, merely rotates the reciprocal vector without altering its position. Φ is positioned so that one arc of the goniometer is horizontal and the other vertical. The horizontal arc is then adjusted, preferably by means of an extended arc key, until the intensity of the peak, indicated on the rate-meter, is maximised; Φ is then turned through ± 90° and the other arc similarly adjusted. The crystal is now set with the reciprocal axis vertical at $\chi = 0^\circ$. Finally, the goniometer is clamped in position for a reflexion at $\chi = 0^\circ$ as described in the previous section.

2.3. GENERAL ORIENTATION

This method requires that the orientation of the crystal be known approximately, and setting angles should be calculated for this approximate orientation. The goniometer is clamped in position as described previously. General reflexions for which $\chi = 0^\circ$ are then sought, Ω and θ being sent to the positions calculated for the reflexion: θ is dependent on the cell dimensions of the crystal, and in general $\Omega = \theta$, thus the orientation of the crystal, with respect to the diffractometer, is defined by Φ and χ. As the crystal is not set properly i.e. not with an axis vertical, a general reflexion will not be found exactly where predicted but, by movements of Φ and χ, it should be located without undue difficulty, and, once located, refinement of Φ and χ are successively carried out until peak maximisation is obtained.

This procedure is carried out for several reflexions which should be, if possible, in different regions of reciprocal space and at high values of θ. The positions of these reflexions are then put into the Powell program and a new set of angles calculated from which every reflexion should be located where predicted.

The results obtained by this approach tend to be unsatisfactory and consequently it is very seldom used. One likely reason for this is the insensitivity of γ when carrying out the refinement of the peak position. In many cases little variation in intensity may be indicated over a range of 3·00 to 4·00°.

References

L.J. Bunce and D.A. Wheeler (1965), U.K.A.E.A. document A.E.R.E.-R4841.

M.J.D.Powell (1965), A.E.R.E. report.

Dept. of Chemistry,
The University,
Glasgow, W.2.

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APPENDIX

(1) The setting angles obtained from the ATLAS and 360/65 versions of the Powell program are entirely equivalent but differ in their definition of the direction of the reciprocal lattice vector for a given reflexion, e.g.

	ATLAS		360/65	
REFLEXION	Φ	χ	Φ	χ
221	141·45	-37·31	-38·55	37·31
$\bar{2}\bar{2}\bar{1}$	- 38·55	37·31	141·45	-37·31

Ω and θ are of course identical for the 221 and 221 reflexions in each case.

(2) A version of the Powell program modified by P.J. Brown is available to calculate angles for the Ferranti two-circle diffractometer (with cryostat). This is not available on ATLAS.

(3) The "fitting" procedure for crystals in a general orientation, as described in Section 2.3 is available only on the 360/65.

(4) Prior to using the Powell program the following data must be known:

(a) Accurate cell dimensions of the crystal

(b) Current neutron wqvelength

(c) Current limit switch positions; these comprise the first four cards of the "Powell Data".