THE ACTION OF CERTAIN INORGANIC SALTS
ON
SEMICARBAZIDES AND SEMICARBAZONES

by

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LIST OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Annalen.	Justus Liebig's Annalen der Chemie.
Ann. Reports Ch.Soc.	Annual Reports of the Chemical Society.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Bull.Soc.Chim.	Bulletin de la Société chimique de France.
Chem. Reviews.	Chemical Reviews.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. rend.	Comptes rendu hebdomadaires des Séances de l'Académie des Sciences.
Gazzetta.	Gazzetta chimica italiana.
Hand. der anorg. Chem.	Handbuch der Anorganischen Chemie - Abegg.
J.Amer.Chem.Soc.	Journal of the American Chemical Society.
J.Chem.Physics.	The Journal of Chemical Physics.
J.C.S.	Journal of the Chemical Society.
J.pr.Chem.	Journal für praktische Chemie.
J.R.T.C.	Journal of the Royal Technical College - Glasgow.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Qual. Anal.	Qualitative Analysis by Spot Tests - Feigl (Matthews).
Rec.Trav.chim.	Recueil de Travaux chimiques des Pays-Bas et de la Belgique.
Sci.Pro.	Science Progress.
Trans.Faraday Soc.	Transactions of the Faraday Society.

Z.anorg.Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z.Krist.	Zeitschrift für Kristallographie.
Z.physik.Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.

INTRODUCTION.

INTRODUCTION

When carrying out experimental work for a different purpose in 1924, A.B.Crawford observed the formation of a deep red colouration when an aqueous solution of semicarbazide hydrochloride came in contact with an aqueous solution of potassium ferrocyanide. The intensity of the colour suggested that the organic molecule had probably entered into some type of complex union with the inorganic ions. However, a survey of the literature published before 1936 indicated that apart from compounds of semicarbazide with copper nitrate and copper chloride (Thiele & Stange, Annalen, 1894,283,24), with sodium carbonyl ferrocyanide (Müller, Bull.soc.chim.,1905,33, 947) and with Roussins' Salt, (Bellucci & Cechetti, Gazetta,1907, 37,(i), 169), of acetone-semicarbazone with zinc chloride (Thiele & Heuser; Annalen, 1895, 288, 312), and of 4-substituted semicarbazides with copper chloride (Hopper; J.R.T.C. 1927, 4, 57), co-ordination compounds of semicarbazide had not previously been systematically investigated, while on the other hand a systematic study of inorganic complex compounds with thio-semicarbazides had been undertaken by K.A.Jensen and E. Ranke-Madsen (Z.anorg. Chem., 1934, 219, 243). The author, therefore, at the suggestion of Doctors M.M.J.Sutherland and A.B.Crawford, undertook to investigate the possibility of the formation of complex co-ordination compounds between semicarbazide and inorganic salts.

With this aim in view, experiments were carried out, on the test-tube scale, using the salts of several metals, whereupon immediate indications, such as pronounced changes in the colours of the products isolated, from the colours of the original inorganic salts, were obtained which pointed to the probability that new compounds had been formed. The formation of highly coloured products was very marked, particularly in the cases of the chlorides of iron, cobalt and nickel, and so a more intensive study of the reactions which take place between semicarbazide and the salts of the members of this triad, was initiated.

While work was progressing in this direction, a paper was published by K.A.Jensen (Z.anorg.Chem.1936,227,25), dealing with complex compounds of semicarbazide, in which complex compounds of semicarbazide with nickel chloride, nickel sulphate and cobalt nitrate were described. This was followed by a paper by G.S.Smith published in the Journal of the Chemical Society (J.C.S. 1937, 1354), which extended the field to include complex compounds of semicarbazide with ferrous sulphate, cobalt sulphate, cobalt chloride, nickel sulphate, cadmium chloride and zinc sulphate. It is evident that the results recorded in these two papers anticipated those of the work already undertaken by the author and it was, therefore, deemed advisable that this work should be brought to a conclusion. The results of the author's work pertaining to the chlorides of iron, cobalt and nickel constitute the first portion of this thesis.

On abandoning the work carried out on the salts of iron, cobalt and nickel, the author turned his attention to the effect of substituent groups in the semicarbazide molecule on the ability of the organic molecule to form complex compounds with copper salts, thus furthering a section of the research work which is at present being carried out by M.M.J.Sutherland and A.B. Crawford. Although the results of this latter research work have not, as yet, been published, the results of the work performed by the author on the formation of complex compounds of "4"-substituted semicarbazides with cupric chloride, are recorded in the second portion of this thesis.

The final section is in the form of Appendices, the first of which summarises the methods of analysis which have been employed throughout this work, while the second Appendix gives an account of the methods used to prepare the substituted semicarbazides.

THE THEORY OF CO-ORDINATION.

GENERAL DISCUSSION OF THE THEORY OF CO-ORDINATION.

In 1891 Alfred Werner introduced his theory of co-ordination, in an attempt to explain the formation of what have been called "molecular compounds", and the generalisations which resulted from his work on the cobaltammines have had a very far reaching influence on modern chemical philosophy and chemical practice.

The term"molecular compounds" referred to compounds which were apparently formed by the association of several molecules, the components of which were already completely satisfied with respect to their normal valencies. For example, 4 $KCNFe(CN)_2$, $(NH_4)_2SO_4Al_2(SO_4)_3 \cdot 24H_2O$, $6NH_3 \cdot CoCl_3$, highly hydrated molecules and other double salts were all classified under the heading of "molecular compounds". To explain the formation of such substances Werner, without invoking the aid of theories of valency, postulated that it was possible for a central atom to become co-ordinated with several ions of opposite charge, and with neutral molecules. The number of entities with which the central atom united he termed the co-ordination number of that specific atom, its value being defined only by spatial and symmetrical considerations. On this basis, Werner was of the opinion that in general the co-ordination number assumed the values 2,3,4, 6 and 8, the values 4 and 6 being the most common.

This conception proved to be very useful for explaining the mode of formation of very many of these "molecular compounds", but to prevent the application of the theory becoming too artificial it has become necessary to define the term more critically. X-ray analysis has shown that in certain cases the crystal lattice is made up of separate units which are not combined in any chemical sense , but which crystallise together to form a more stable lattice structure. For example ,Hassel and Mark (Z. physic. Chem., 1924, 27,89) showed that in the case of the fluozirconates of the type $(NH_4)_3 ZrF_7$, these are not compounds in which the zirconium atom shows a co-ordination number of 7, but are to be considered as being built up in the following manner; $(NH_4)_2ZrF_6 + NH_4F$. Similarly, in 1935 Powell and Wells (J.C.S. 1935, 359), as a result from the study of $CsCoCl_5$ by X-ray analysis found that the crystal lattice contained the anions $\left[CoCl_4\right]''$ and Cl' only, and that there was no evidence to support the existence of an anion of the type $\left[CoCl_5\right]'''$. Similar results have been forthcoming when the methods of X-ray analysis have been employed in the examination of the alums and other double salts. When compounds such as those mentioned above go into solution,the complex lattice is broken down and the units become separated, thus ending the existence of the "molecular compounds" . Such compounds may be termed "lattice compounds".

The criterion for a true "molecular compound" may be taken as being the persistence of the co-ordinated complex in solution (Emeléus and Anderson; Modern Aspects of Inorganic Chemistry 1938 p.80). In 1927, Biltz (Z. anorg. Chem.1927 164,345) further subdivided the true "molecular compounds" into "normal complexes" and "penetration complexes". The "normal complexes" included compounds of the types $[Co\ (NH_3)_6]Cl_2$ and $K_2\ [Cd(CN)_4]$ which, either in the solid phase or in solution, are reversibly dissociated into their components. In such combinations he regarded the linkings as being very loose. The term "penetration complexes" on the other hand, Biltz applied to compounds in which there is no evidence of reversible dissociation, such as $K_4\ [Fe(CN)_6]$ and $[Co(NH_3)_6]\ Cl_3$.

As will be seen later, this classification is one of limiting types as there is no sharp line of demarkation between the subdivisions.

It has already been stated that the conceptions put forward by Werner inspired a great number of investigations along the same lines, with the result that, since the beginning of this century a tremendous number of new complex compounds has been amassed in the literature, without any attempts to bring the mechanism of their modes of formation into line with the newer developments in the theories of the structure of matter. The first attempt to interpret the co-ordination linking of Werner in terms of the electronic theory of valency was carried out in 1923 by Sidgwick ("Electronic Theory of Valency" p.109 et.seq.).

Before dealing with the application of the electronic theory of valency to the co-ordinate linkage, it may be advisable to survey the salient points of the modern conception of the structure of matter.

THE STRUCTURE OF THE ATOM. - As is well known, the modern theory of the structure of the atom originated from the spectroscopic observations made by Moseley and Bohr, which led to the postulation that the atom consists of a nucleus, built up of positively charged protons and negatively charged electrons, the protons being in excess of the electrons, surrounded by planetary electrons which neutralise this excess positive charge. According to Bohr's theory, the atomic nucleus is surrounded by a finite number of orbits or stationary states, of different potential energy, which the extranuclear electrons may occupy. Each orbit or "shell" has a different total energy content from its neighbour and is distinguished from it by its principal quantum number n; n may have the values 1, 2, 3, ... corresponding to the different shells.

When n = 1, the electrons are referred to as the K electrons and are said to be in the K shell; when n = 2, 3, 4 .... the electrons and shells are designated by the letters L, M, N ....respectively. The principal quantum number n however, is not sufficient to account for all the spectral lines of the elements, so that other quantum numbers require to be introduced. For each value of the principal quantum number n, there are n sub-levels, distinguished from one another by the subsidiary or azimuthal quantum number ℓ. The electrons in each of the new sub-levels are designated by the letters s, p, d, f ..... Other two quantum numbers are required to account satisfactorily for all the observed lines in the spectrum of an element, and these are called the magnetic quantum number m, and the spin quantum number s. The introduction of the magnetic quantum number is necessary to account for the well known Zeeman effect, while the spin quantum number refers to the quantisation of the energy of spin of an electron about its own axis.

Before applying the classification of electrons in terms of quantum numbers as a basis for the discussion of atomic structure, two important principles must be borne in mind. The first of these is the Pauli Exclusion Principle, which states that no two electrons in the same atom may have the same values for the four quantum numbers n, ℓ, m and s. This means that there can be as many electrons in each of the shells as there are possible different arrangements of the four quantum numbers. It follows from this, that the maximum numbers of electrons in the K, L, M, N and O shells are 2, 8, 18, 32 and 50 respectively. The second principle is known as the Hund Rule of Maximum Multiplicity which states that as many orbits as possible are occupied singly before any pairing of the electrons takes place.

ELECTRONIC THEORIES OF VALENCY. - As the electronic structures of the elements were systematically established it became evident that some relationship exists between the periodicity in chemical properties and the periodicity in atomic structures, and this realisation led to attempts to formulate a theory of valency on an electronic basis. The electronic theories of valency conceive of three types of combining link, the electrovalent link, the co-valent link and the co-ordinate link, but it must be recognised that satisfactory as they are for ordinary chemical purposes, the theories give only an approximation to what really happens when atoms combine.

The electrovalent link, or ionised link, occurs when one electron is transferred from one atom to another, the resultant ions being held together by electrostatic forces which have, in general, no directive properties.

The covalent link on the other hand results from the sharing of two electrons between two atoms, each atom contributing one electron. This link is non-ionised. Heitler and London consider that the union is achieved by the mutual neutralisation of electronic spins, while Pauling and Slater, from a consideration of the wave functions of the electrons in the isolated atoms, have shown how the quantum theory leads to the conception of directed valency (Emeleus and Anderson ibid. p.16).

The co-ordinate link is also non-ionised and is identical with the co-valent link except in that both the electrons which effect the union are denoted by only one of the two atoms involved. However, before discussing the actual mechanism of the co-ordinate linkage it may be profitable to examine in fuller detail the nature of the bonding.

NATURE OF THE CO-ORDINATE BONDING. - An examination of the distribution amongst the metallic ions of the ability to form hydrates, ammoniates and stable complex salts indicates that this tendency is greater among the metals of small ionic radius and high ionic potential. Fajan's theory of ionic distortion states that the maximum distorting effect is exerted by small cations of high ionic charge, acting on large polarisable anions, and this conception may be applied to complex formations in which, in place of anions, polarisable dipolar molecules, such as water or ammonia, are subjected to the influence of a central positive ion. It may also be noted in this connection that the firmness with which univalent negative ions are bound within the co-ordinated complex follows, in general, the order of their polarisabilities (Emeléus and Anderson ibid. p.167).

On the basis of Fajan's theory it may, therefore, be permissible to conceive of a co-ordinated complex as being bound, in the limiting case, by electrostatic forces, and as the polarising effect of the cation increases a state may be attained in which the distorting effect is such that the electrostatic linking passes over to a true co-valent bonding. However, that the co-ordinating properties of ions are not determined solely by their ionic potentials is evidenced by the facts that, on this assumption, the ferric ion (ionic potential $I = 4.5$) should equal the cobaltic ion ($I = 4.5$) in ability to form complex ions, while the aluminium ion ($I = 5.3$) should be the trivalent ion most prone to the formation of complex compounds. Similarly, the cuprous ion ($I = 1.0$) should have as little ability as the sodium ion ($I = 1.0$) for forming complex compounds. These facts are contrary to chemical experience, so that some additional factor or factors must be involved which confer upon the ions of the metals of the transition series the property of co-ordinating with neutral atoms and with anions, to an extent out of all proportion to their ionic potentials.

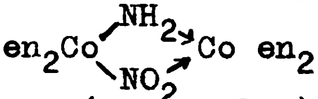
Mention has already been made to the classification of complex compounds, by Biltz, into "normal complexes" and "penetration complexes", and it may be permissible to identify the two classes with the operation of electrostatic bondings and with the operation of true directed chemical valencies. From dimensional, optical, magnetic and stereochemical considerations, observations are forthcoming which indicate that in the case of the "penetration complexes" true chemical linkages are involved.

DIMENSIONAL EVIDENCE. - In the case of $\left[Co(NH_3)_6\right]Cl_2$ and $\left[Co(NH_3)_6\right]Cl_3$, which exemplify the two classes, the total molecular volumes are almost identical, and this can be shown to be due to the contraction of the ammonia in the luteo-cobaltic chloride. There is a considerable shortening of the Co-N distance, which must be due to the formation of a true chemical bond. In fact, the Co-N distance in the luteo-cobaltic ion is approximately equal to the sum of the co-valent bond radii of cobalt and nitrogen.

OPTICAL EVIDENCE. - The profound changes of colour which are evidenced in the formation of co-ordination complexes indicates that some modification of the electronic orbits of the central atom has taken place. The coloured ions of the transition elements owe their selective absorption to interaction with the incompletely filled d levels, and according to current theories it is these d electrons which are concerned in co-ordination, so that their rearrangement must modify the absorption spectrum of the central ion. This may be illustrated by comparing the pink colour of the $[Co(NH_3)_6]^{++}$ ion with the yellow colour of the $[Co(NH_3)_6]^{+++}$ ion.

MAGNETIC EVIDENCE. - From energy considerations it has been shown that the presence of an unpaired electron in an atom or molecule introduces a magnetic moment which thus renders the atom or molecule paramagnetic. In the case of the first transition period the Hund principle of maximum multiplicity is valid, so that the magnetic moments of the ions may be calculated from the resultant electron spin. On the other hand, any change in the magnetic moment of an ion must be associated with a change in the number of unpaired electrons and indicates that a rearrangement of orbits has taken place. Comparison of the magnetic susceptibilities of the simple and complex salts of 16 metals of the transition series, establishes the fact that just those compounds of 6 - co-ordinate trivalent cobalt and ferrous iron, and of 4 - co-ordinate nickel, are diamagnetic, which would on general grounds be regarded as being "penetration complexes". It is evident that in these compounds, the electrons which are originally, on Hund's principle, singly distributed among the 3d orbits have been fully paired, and the inference drawn from this is, that the orbits which have thus been made available, have been utilised for the direct co-valent linking of the co-ordinated groups. On the other hand, the chemically less stable "normal complexes" exhibit the full paramagnetism of the central ion.

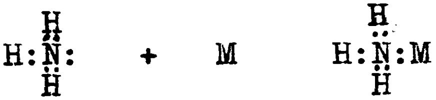
STEREOCHEMICAL EVIDENCE. - The stereochemistry of co-ordination compounds implies at once the existence of directed valency forces. Were the bonding forces due purely to electrostatic attraction, the configuration of an assemblage of entities around a central atom would be dictated entirely by considerations of symmetry, due to the mutual repulsion of the attached ions or dipoles. In the cases where the central atom is associated with 4 and with 6 groups, the configurations adopted would be tetrahedral and octohedral respectively. However, as will be seen later, in the most stable of the compounds of co-ordination number four, the configuration is not tetrahedral, but planar, and in this fact the operation of directed valency forces is implicit. Further evidence which points to the functioning of directed valency forces is to be found in the existence of stable cis- and trans- isomerides of both 4- co-ordinate and 6- co-ordinate compounds, and also in the existence of optically active complex salts, which show very little tendency towards auto-racemisation.

From the very beginning, Werner maintained that no distinction could be drawn between the functioning of principal valency forces and co-ordinate valency forces, and all the evidence forthcoming up-to-date serves to substantiate that view, which is further endorsed by the existence of non-resolvable meso-forms of poly-nuclear complex salts of the type  $en_2Co\begin{matrix}\diagup NH_2 \searrow\\ \diagdown NO_2 \nearrow\end{matrix}Co\ en_2$.

Emeléus and Anderson (ibid.p.170), in summing up, are of the opinion that the purely electrostatic binding represents only a limiting type, and that it is likely that the co-ordinate link is, in many cases, a bond of "fractional order", intermediate between a purely physical linkage and a true chemical linkage.

<u>THE MECHANISM OF THE CO-ORDINATE LINK.</u> - It has been stated above, that the first attempt to interpret the mechanism of the co-ordinate link was made by Sidgwick, who put forward the hypothesis that this linkage is a special case of the semipolar type of bond, the co-ordinated group acting as the donor, and the central atom acting as the acceptor. He based the hypothesis on the evidence that the common characteristic of all co-ordinating groups seems to be the possession of at least one "lone pair" of electrons,

and an examination of the complex compounds, including polynuclear complexes, indicates that in no case does the number of co-ordinate links, which may be formed by a co-ordinating group, exceed the number of available "lone pairs" of electrons. This conception may be illustrated graphically as follows :-



$$\mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{N}}}}}: \quad + \quad \mathrm{M} \qquad \mathrm{H}:\overset{\mathrm{H}}{\underset{\mathrm{H}}{\ddot{\underset{\cdot\cdot}{\mathrm{N}}}}}:\mathrm{M}$$

The application of this principle proved to become very successful, and it early became evident that the formation of stable complex compounds is apparently connected with the attainment of some type of closed electronic structure around the central atom. In certain cases the "effective atomic number" of the central atom in the complex reaches the atomic number of the next inert gas in the periodic system, and it is concluded that the attainment of this inert gas structure contributes to the stability of the complex ions or atoms. Thus, in hexammine-cobaltic chloride the atomic number 24 of the cobaltic ion is increased to the effective atomic number 36, of krypton, by the donation of twelve electrons, or rather six "lone pairs", from the ammonia molecules. It is noteworthy, that in all cases in which the "effective atomic number" reaches that of an inert gas, the compounds are diamagnetic (Emeléus and Anderson ibid. p.172).

That the attainment of an inert gas configuration is not the governing factor, is demonstrated by the existence of stable complex ions in which the effective atomic number may be two electrons short of, or two electrons in excess of that of the next inert gas. For example, the effective atomic number of the $[\mathrm{Ni(CN)_4}]''$ ion is 34, while that of the $[\mathrm{Ni(dipyridyl)_3}]^{++}$ ion is 38. Sidgwick and Bose attempted to correlate this difference between the effective atomic number of the central atom and the atomic number of the next inert gas, with the paramagnetism of the complex salts, assuming that this difference indicated the number of unpaired electrons. They met with some considerable success in the cases of the complex salts of copper, chromium, and 6- co-ordinate nickel, but in some cases stable complex salts of the type $\mathrm{K_2[Ni(CN)_4]}$ and $\mathrm{Pt(NH_3)_2Cl_2}$, in which the central atom, according to the Sidgwick-Bose rule, contains two unpaired electrons, are found to be diamagnetic, and special hypotheses require to be advanced to deal with these.

Two objections have been brought forward against this conception of a valency link effected by this simple "lone-pair" bonding. The first objection is on the grounds that this type of anion results in the improbable accumulation of negative charges on the central atom. To meet this objection Sugden (The Parachor and Valency", 1930 p.138 et.seq.) introduced his "singlet link" theory in which he postulates that the co-ordinate bond is achieved by the co-ordinating groups donating one electron each to the central atom, each group therefore bearing a charge of plus half a unit or minus half a unit. In the case of the water molecule and of the ammonia molecule, the "lone-pair" of electrons which carry out the union, correspond to the $2s^2$ electrons; the "singlet link" theory implies the breaking up of this partnership, a procedure which is precluded by energy considerations. However, if, as has been suggested above, the co-ordinate link is mesomeric between a true electron pair bonding and a state of electrostatic attraction, it may be that each bond will amount statistically to the sharing of a single electron, between the central atom and the attached groupings.

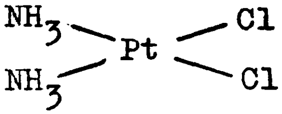
The second objection to the simple "lone-pair" bonding, was put forward by Hunter and Samuel (J.C.S.,1934, 1180; Chem. & Ind., 1935,635) on the grounds that a completed sub-level, such as the $2s^2$ levels in the water and ammonia molecules, has no bonding properties and that therefore these electrons cannot be considered as taking part in the co-ordinate link. Current theories dispense with this objection, by considering that the linking is effected by a reorganisation of the orbits with the formation of new hybrid orbits, rather than by the direct donation of two electrons from an s level.

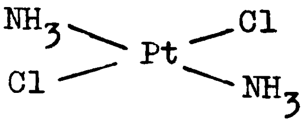
Emeléus and Anderson (ibid.p.174) point out that the functions of the central atom and of the attached group are to be considered as being reciprocal. In other words, it is as true to consider the cobalt atom in hexammine cobaltic chloride as completing the fourfold co-ordination shell of the nitrogen atoms, as it is to take the cobalt as being the central atom in the complex ion.

THE STEREOCHEMISTRY OF CO-ORDINATION COMPOUNDS - SIX - CO-ORDINATE COMPOUNDS. - The application of Werner's theory to the realm of stereochemistry proved to be very fruitful in its results. It became apparent at once that if a central atom is surrounded symmetrically by say, six groups, under certain conditions stereo-isomers should exist. There are three possible spatial configurations which have six points equidistant from the centre of the system, namely, the planar hexagon, the triangular prism and the octahedron. In the case of a complex ion of the type $[Ma_4b_2]$ three distinct isomers are possible if the configuration is either that of the hexagon or that of the triangular prism. In the numerous cases examined only two isomers have ever been isolated and this number of isomers agrees with the configuration of the

octohedron. In 1911 Werner further established this configuration by resolving into their optically active enantiomerides complex compounds of cobalt containing two or three chelate groupings. For example,
$[CoClNO_2(en)_2]X$ and $[Co(en)_3]X_3$ (en = ethylenediamine) were found to be resolvable, as were also compounds of the type $K_3[Cr(C_2O_4)_3]$. Modern physical methods of analysis by means of X-rays and electron diffraction measurements have shown that the octohedral configuration is apparently general when a central atom has a co-ordination number of six.

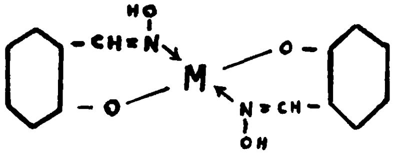
FOUR - CO-ORDINATE COMPOUNDS. - In the case of central atoms with the co-ordination number of four no such universality of structure is apparent. By analogy with the carbon atom it was assumed that the four co-ordinating groups would be tetrahedrally disposed around the central atom. However, Werner was of the opinion that it was possible that the complex ion with four attached groupings might be a special case of the six - co-ordinate complex ion, in which two of the octahedrally disposed valencies are not satisfied, in which case the remaining four groups would be distributed in a planar fashion around the central atom. In support of this view Werner obtained the cis and trans isomerides of platinous and palladous chlorides.





Between 1899 and 1926 classical methods of organic chemistry indicated that tin, sulphur, selenium, nitrogen(?) beryllium, copper and zinc, all formed compounds in which the configuration was tetrahedral and the only support for Werner's claim arrived in 1920 by the isolation of "cis" and "trans" forms of the compound $Te(CH_3)_2I_2$ by Vernon (J.C.S. 1920, 117, 86, 889; ibid. 1921, 119,105, 687). However, in 1929 Drew, (J.C.S. 1929, 560) dispensed with this support on showing, by X-ray analysis, that while the one form of the compound was $Te(CH_3)_2I_2$, the other form corresponded to $[Te(CH_3)_3][Te(CH_3)I_4]$. On the other hand, in 1922 physical evidence in support of the planar structure of Werner was put forward by Dickinson (J.Amer.Chem.Soc. 1922,44,2404), who showed by X-ray methods that in the ions $[PtCl_4]''$ and $[PdCl_4]''$, the four chlorine atoms are in the same plane as the metal atom. The fact that, outside of platinum and palladium, there existed no evidence in support of the existence of a planar structure, made these two elements somewhat unique, and stimulated a great deal of work in this sphere.

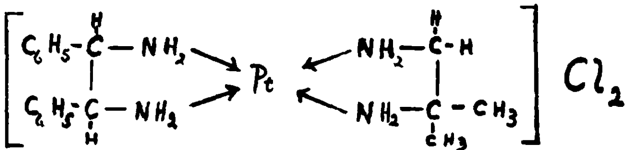
In 1931, Pauling (J.Amer. Chem. Soc.1931,53,1367) predicted, on wave mechanical grounds, that the planar structure should be possible in the case of four - covalent nickel, as well as in the cases of four co-valent palladium and four co-valent platinum. This was an entirely new suggestion and widened the scope of the investigations, with the result that in 1932 Pauling's prediction was fulfilled by the isolation by Sugden (J.C.S. 1932, 246) of two isomeric forms of a nickelous derivative of unsymetrical benzyl-methyl-glyoxime. This compound proved to be diamagnetic, which is in keeping with Pauling's views. Sugden also prepared nickel derivatives of dimethyl-glyoxime and of diphenyl-glyoxime, and in 1935 Cox and his co-workers (J.C.S. 1935, 459) prepared the salicylaldoxime derivatives of platinum, palladium and nickel.



The properties of all the compounds where M= nickel, platinum or palladium, show that they are definitely co-valent structures, while analysis by means of X-rays, indicates that in each case there is a centre of symmetry, which demonstrates that each has a trans-planar structure. The nickel derivative is again diamagnetic.

In 1936, Sugden (Nature, 1936, 137, 543) summarised the evidence for the existence of a planar structure for compounds of four-covalent nickel, platinum and palladium, along the following lines. Firstly, there is the evidence from the existence of isomeric derivatives of nickel and benzyl-methyl-glyoxime, and the glycine derivatives of platinum (Grunberg and

Ptizyn, J.pr.Chem., 1933, ii, 136, 143) and of palladium (Pinkard, Sharratt, Wardlaw and Cox, J.C.S.,1934, 1012). Secondly, there is the evidence from the resolution into its optically active antimers, of the compound



by Mills and Quibell (J.C.S., 1935, 839), and finally there is the evidence from X-ray analytical work carried out by Cox and Wardlaw (J.C.S., 1935, 459, 1475) demonstrating the existence of the planar configuration in the dithio-oxalate derivatives of nickel, platinum and palladium.

Prior to 1934, copper was considered to belong to the class of elements which gives rise to a tetrahedral configuration in complex formations. This assumption was based on the work of Mills and Gotts (J.C.S.,1926, 3121) who claimed to have i isolated an optically active derivative of cupri-benzoyl - pyruvic acid. However in 1934 Beevers and Lipson (Proc. Roy. Soc.,1934, A,146,570) determined the crystal structure of $CuSO_4.5H_2O$, and found that the four water molecules in the ion $[Cu(H_2O)_4]^{++}$ are in the same plane as the copper atom. Further support for the planar configuration in copper compounds was forthcoming when Cox and Webster (J.C.S.,1935,731), on examining a number of copper derivatives of β -diketones, found that the copper valencies are directed towards the corners of a square. At the same time Robertson (J.C.S.,1935,613) found that the phthalocyanine derivatives of copper and nickel possessed planar structures, while the following year Cox, Sharratt, Wardlaw and Webster (J.C.S. 1936,129) found that dipyridinocupric chloride, $CuCl_2(C_5H_5N)_2$, has a trans-planar configuration.

Co-ordination compounds of cobalt, in which the co-ordination number is four, until recently have received very little attention. These compounds introduce another problem. Two forms of dipyridinocobaltous chloride, $CoCl_2(C_5H_5N)_2$, are known and one form has been shown to be definitely trans-planar (Cox and Wardlaw, J.C.S. 1937,1556); the nature of the other form has not yet been explained. On the other hand Powell and Wells (J.C.S. 1935,359) have demonstrated that, in the compound Cs_3CoCl_5, the complex ion $[CoCl_4]''$ exists, in which the four chlorine atoms are arranged tetrahedrally around the central cobalt atom. Cobalt, therefore, appears to offer an example of an element in one valency state giving rise to more than one configuration, when associated with unchelated groups. The only other element which shows this tendency is beryllium, which gives rise to a planar configuration in its phthalocyanine derivative (Linstead and Robertson, Chem. Reviews, 1936, 19, 55). However, as in many other quadri-covalent derivatives of beryllium the structure is apparently tetrahedral, Cox and Wardlaw (Sci. Pro. XXXII, 127, 463-478) suggest that the planar structure may be forced on the central beryllium atom due to the very rigid planar configuration of the phthalocyanine molecule. It is interesting to note that the opposite tendency in the case of nickel and platinum has also been recorded. In 1926 Mann (J.C.S. 1926,482) prepared complex compounds of nickel iodide and of platinous iodide with β,β',β'' - triaminotriethylamine, $N(CH_2CN_2NH_2)_3$, in which the organic radical acts as a quadridentate group satisfying all four positions in the co-ordination shell. It has been shown above that the configuration around the nickel and platinum atoms is always planar, but the triaminotriethylamine is unable to span all four positions of a planar square structure without great strain, so that presumably, the configuration around the central atom adopted in this case, is tetrahedral in which the strain is at a minimum.

<u>THE INFLUENCE OF CHANGES IN PRINCIPAL VALENCY ON THE STEREOCHEMISTRY OF 4-CO-ORDINATE COMPOUNDS</u>. - Recent investigations have shown that a change in the principal valency of an element, very often results in an alteration in the spatial arrangement of the associated groups about the central atom. For example, in the compound $Pt(CH_3)_3Cl$, in which the platinum is quadricovalent and also quadrivalent the platinum valencies are not co-planar, but are tetrahedrally disposed (Cox and Webster, Z.Krist, 1935,A,90,561).

Again, in 1932, Cox, Wardlaw and Webster (J.C.S.1936,775) found tetrahedral configurations in the following complex con compounds; $[Ag(CH_3CSNH_2)_4]Cl$, $[Cu(CH_3CSNH_2)_4]Cl$, and $K_3[Cu(CN)_4]$. On the other hand these same authors have shown (J.C.S. ibid.) that the picolinate of bivalent silver is isomorphous with that of cupric copper, and this latter has a trans-planar structure. Similarly nickel carbonyl, $Ni(CO)_4$, in which the nickel has zero valency, has been shown to have a tetrahedral structure. Further examples are to be found in the cases of tin and lead. The four valencies of stannic tin are tetrahedrally placed (Dickinson, J.Amer. Chem. Soc., 1923, 45, 958) while in the case of bivalent tin, in the compound $K_2[SnCl_4]2H_2O$ the four co-valencies are directed towards the corners of a square (Cox, Shorter and Wardlaw, Nature, 1937, 139, 72). Again, in lead tetraphenyl (George, Proc. Roy. Soc. A. 1927, 113, 585) the configuration is tetrahedral, while in $PbCl_2 2CS(NH_2)_2$, in which the lead is bivalent, a planar structure has been found (Cox, Shorter and Wardlaw, ibid.)

The position of the stereochemistry of the four - covalent elements has been well dealt with in a paper by E.G.Cox and W.Wardlaw (Science Progress XXXII, 127, 463-478) and the following table, taken from that paper, summarises the position at the beginning of 1938.

Principal Valency	Ni	Pd	Pt	Cu	Ag	Au	Pb	Sn	Co	Mn*	Be
0	△										
1				△	△	?					
2	□	□	□	□	□		□	□	□ △	□	□ △ ?
3						□				□	
4		?	△				△	△			

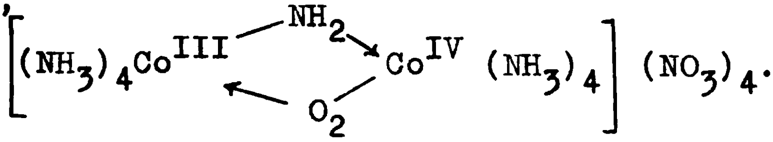
□ ≡ planar structure △ ≡ tetrahedral structure

* △ for principal valency 6 and 7.

EIGHT CO-ORDINATE COMPOUNDS. - Complex compounds in which the central atom exhibits a co-ordination number of eight also exist, although the number of elements which show this property is limited. Penney and Anderson (Trans.Faraday Soc. 1937, 33, 1363) have shown that eight elements, namely zirconium, molybdenum, ruthenium, cerium, hafnium, tungsten, arsenic and thallium, show this tendency. The reasons underlying the co-ordination number eight are still obscure and the configuration of the eight associated groups round the central atom has not as yet been ascertained, although it is presumed to be cubic.

COMPOUNDS WITH ODD CO-ORDINATION NUMBERS. - Mention has been made earlier in this paper of the existence of complex compounds in which the central atom in the complex is apparently associated with odd numbers of co-ordinating groups. However, X-ray examinations of such compounds by Hassel and Mark (Z.physic.Chem., 1924,27,89) and by Powell and Wells (J.C.S. 1935,359) have shown that, in many cases, they are lattice compounds, and not true co-ordination complexes.

STABILISATION OF VALENCY STATES BY MEANS OF CO-ORDINATION. - One other aspect of co-ordination compounds should be mentioned, and that is the stabilising effect which the co-ordinated groups, in some cases, have on otherwise unstable valency states. A familiar example of this is found in the case of the cobaltammines. Cobalt in the trivalent state has very strong oxidising properties, due to the readiness with which it reverts to the bivalent condition. In the presence of ammonia on the other hand the opposite tendency is evident, as is shown by the fact that the $\left[Co(NH_3)_6\right]^{++}$ ion is readily oxidised to the $\left[Co(NH_3)_6\right]^{+++}$ ion by atmospheric oxygen at room temperature. Under similar conditions compounds have actually been isolated in which the cobalt exhibits a valency of four. The following compound is an example of a complex compound containing both trivalent and quadrivalent cobalt, isolated by Werner in 1910 (Annalen, 1910,375,15);



$$\left[(NH_3)_4Co^{III}\overset{NH_2}{\underset{O_2}{\rightleftarrows}}Co^{IV}(NH_3)_4\right](NO_3)_4.$$

In the case of copper both the higher and the lower valency states may be stabilised by appropriate co-ordinating groups. The unstable cupric iodide may be stabilised by ethylene-diamine in such a complex formation as $\left[Cu(en)_2\right]I_2$ 1 or $2H_2O$ (Morgan and Burstall, J.C.S. 1926,2018,2027; 1927, 1259), while the cuprous state may be stabilised by co-ordination with acetonitrile (Morgan J.C.S. 1923,2901) with thio-carbamide (Rosenheim and Loewenstamm, Z.anorg.Chem., 1903, 34, 62; Kollschütter, Ber., 1903, 36, 1151; Annalen, 1906, 349, 232), or with ethylene thio-carbamide (Morgan and Burstall J.C.S. 1928, 143).

Univalent silver is stabilised by co-ordination with ethylene thio-carbamide (etu) in so far that $\left[Ag(etu)_3\right]Cl$ is not sensitive to light (Spacu and Murgulescu, Chem.Zentr.1931 (1) 1426), while biv alent silver is stabilised by o-phenanthroline (Hieber and Mühlbauer, Ber. 1928, 61,2149) and by dipyridyl (Sugden, J.C.S. 1932, 161).

Univalent manganese is stabilised in the complex $R_5\left[Mn(CN)_6\right]$ while tervalent manganese is stabilised in $R_3\left[Mn(CN)_6\right]$. Acetyl-acetone forms an inner complex with tervalent manganese only (Urbain and Debierne, Compt.rend., 1899,129,302) which is parallel with the fact that β-diketones combine only with tervalent iron. Ferrous iron on the other hand is strongly stabilised by co-ordination with such groups as dipyridyl and o-phenanthroline (Cf. Emeléus and Anderson, Modern Aspects of Inorganic Chem. 1938,p.153).

CORRELATION OF CONFIGURATION OF ASSOCIATED GROUPS WITH THE ELECTRONIC THEORY OF VALENCY. - It remained now to find some theoretical explanation for the variations in configuration which occur, particularly in the case where the central atom is associated with four co-ordinating groups.

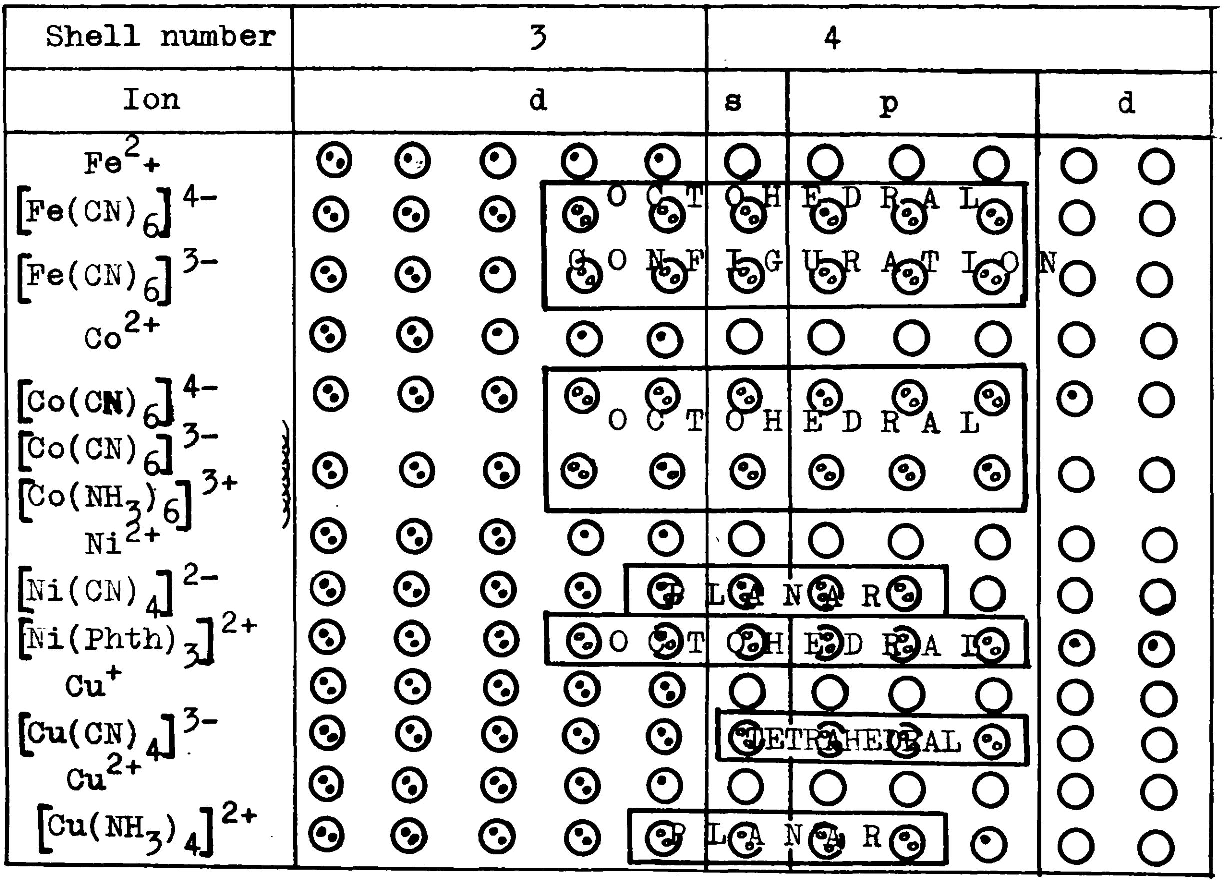
In 1931, Pauling (J.Amer. Chem. Soc. 1931,53,1367, 3225) endeavoured to give this explanation by developing along quantum mechanical lines Sidgwick's "lone-pair" theory, with particular reference to the complex compounds of the transition elements. It is generally accepted that, in the case of the heavier metals, a certain overlapping of the energy levels takes place between the different quantum groups, as is evidenced by the fact that in the first transition series the $4s^2$ levels become filled before the 3d levels, and also by the variable valencies of these elements. This indicates that the 3d levels and the 4s levels can vary very little in energy, and when this is the case Pauling is of the opinion that the normal quantisation may be broken down and new hybrid orbits formed. In this manner four or six equivalent new orbits may be obtained according to the number of orbits available for hybridisation.

It has been pointed out already that the Hund rule of maximum multiplicity is followed throughout the first transition series, but the diamagnetic properties of the complex compounds, indicate that the electrons, originally present singly, have become paired up, and in this way some orbits have been vacated and made available for hybridisation.

Pauling found that, with six bond functions available - two d, one s and two p bond functions - six equivalent orbits, may be formed, directed towards the apices of a regular octohedron. On the other hand, with four bond functions, two distinct configurations may result. When the four bonds are formed by means of d and s electrons alone or by s and p electrons alone, their distribution is tetrahedral. If, however, as well as the s and p electrons one d electron is available and the bond is of the type dsp^2, four new co-planar bonds result, directed towards the corners of a square. Each new orbit formed may accommodate two electrons, which may be obtained by sharing either with a negative ion or with the "lone pair" of a neutral molecule.

It is to be noted also, that each set of hybrid orbits represents a closed configuration, so that if the levels below them are completely filled, the resulting complex must be diamagnetic. In this manner Pauling predicted the diamagnetism and planar structure of four co-ordinate bivalent nickel. On the other hand if there is an unpaired electron below the hybridised orbits the resultant complex is paramagnetic. The ferricyanide ion is found to be paramagnetic and reference to the accompanying diagram shows that it has an unpaired electron.

The following diagram, after Emeléus and Anderson (ibid.1938 p.176) shows in a graphical manner, how well the application of Pauling's theory explains the experimental facts.



● = occupied electronic orbit.

o = unoccupied electronic orbit.

It is seen from the diagram that if, in the ferrous ion the electrons become paired up in the three lowest d orbits, two d orbits are made available for combination with one s orbit and three p orbits, to form six new octohedtrally disposed bonds. Also in the ferrocyanide ion, all the lower levels are completely filled and the ion is consequently diamagnetic, while in the ferricyanide ion one electron is still unpaired, and this ion is therefore paramagnetic.

In the cobaltous ion after pairing, one electron requires to be promoted to the 4d level, to make available the six bond functions required for the octohedral configuration. It is reasonable to consider that this electron will be readily lost, thus accounting for the stability of the trivalent state, in the cobaltammines.

In the case of the nickelous ion after pairing, it is seen that one 3d orbit is available for combination with one 4s and two 4p orbits, resulting in a planar structure. In the case of the six co-ordinate nickel ion two electrons require to be promoted, and by analogy with the cobalt complexes, it would be expected that in such cases the nickel should be readily oxidised to the quadrivalent state, a fact which is contrary to experience. However, the six-co-ordinate complex compounds of nickel are found to be paramagnetic, and the paramagnetism is in accordance with the existence of two unpaired electrons.

Again, in the case of cupric copper, one electron requires to be promoted to allow for a planar configuration, but trivalent copper is unknown. However, the paramagnetism of the complex ion is in accordance with the presence of one unpaired electron.

Cuprous copper on the other hand, has all the 3d levels filled, and hybridisation can be effected only by 4s and 4p orbits, thus giving rise to tetrahedral diamagnetic complex compounds of co-ordination number four.

At the present time the formulation of co-ordination compounds has been brought fairly well into line with the modern quantum mechanical conceptions of valency, although there are still points at which a complete reconciliation between theory and experiment has not, as yet, been achieved. Pauling's theory has had a very stimulating effect on experimental work since 1931, but as Cox and Wardlaw point out (Sci.Pro.1938,XXXII, 127, 463-478) it is limited by the fact that, although, for any given combination of orbits, it can predict the resultant configuration, where more than one combination of orbitals seems valid, it offers no criterion whereby it is possible to predict which configuration will be adopted.

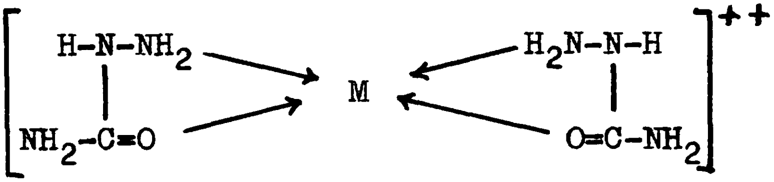
Again, there is some doubt as to whether, on theoretical grounds, any distinction may be drawn between the covalent linkage and the co-ordinate linkage. However, there may be some significance in the fact that while, in the planar complex compounds of bivalent cobalt co-ordinate links are involved, in the tetrahedral ion $[CoCl_4]''$ only co-valent bonds are present (Cox and Wardlaw, ibid. loc. cit.)

PART ONE

COMPLEX COMPOUNDS BETWEEN SEMICARBAZIDE AND THE SALTS OF IRON, COBALT AND NICKEL.

SEMICARBAZIDE AS A CO-ORDINATING GROUP, with special reference to its complex compounds with the salts of Iron, Cobalt and Nickel.

As early as 1894, Thiele and Stange (Annalen, 1894, 283, 24) prepared two molecular compounds between semicarbazide, $\overset{1}{N}H_2\overset{2}{N}H\overset{3}{C}O\overset{4}{N}H_2$, and copper nitrate and copper chloride. On the one hand, a dark blue crystalline product in which two molecules of semicarbazide united with one molecule of copper nitrate, was obtained, while on the other hand a sky blue crystalline product resulted, in which the organic molecule and the copper chloride were present in equal molecular proportions, both products being soluble in water, but very sparingly so in alcohol. Later, in 1905, Müller (Bull. de. Soc. chim. de France (3) 33, 947) by the interaction between semicarbazide and sodium carbonylferrocyanide, obtained a white hygroscopic crystalline powder which was very sparingly soluble in water, while in 1907 Bellucci and Oechetti (Gazetta, 1907, 37, I, 169,176), prepared a molecular compound of Roussin's Salt, $Na\left[Fe_4(NO)_7S_3\right]$, which contained one molecule of semicarbazide. Apart from a compound between acetone semicarbazone and zinc chloride reported by Thiele and Heuser (Annalen, 1895,288,312) and one or two complex compounds of copper salts and substituted semicarbazides, (see later), nothing further was recorded in this field until 1936, when a systematic study of the co-ordination properties of semicarbazide was undertaken by Jensen (Z.anorg. chem. 1936, 227, 25) who assigned the following structure to the complex compounds which he prepared.

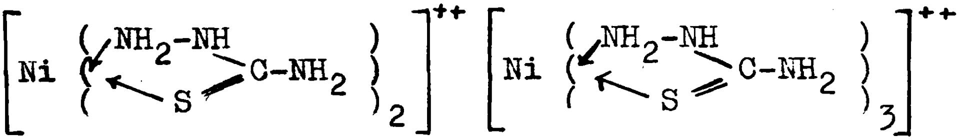


This structure of course applies to compounds in which the central metallic atom has a co-ordination number of four, and it will be seen that this metallic atom is represented as being linked to the organic molecule through the oxygen atom and through the number one nitrogen atom. Going back to Sidgwick's original conception that co-ordination is effected through a "lone pair" of electrons, it is noted that each of the nitrogen atoms, and the oxygen atom in the semicarbazide molecule, possesses such a pair of electrons, and this, coupled with the general structure of the organic molecule, suggests that co-ordination at two points might possibly be anticipated. Stearic considerations however, indicate that the points at which co-ordination might be expected to take place are either at the No.I

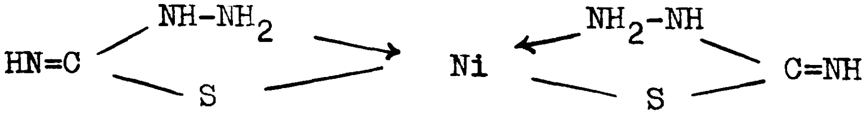
Nitrogen atom and at the oxygen atom, or at the No.I Nitrogen atom and at the No.4 Nitrogen atom.

As many of the arguments on which Jensen (Z.anorg. Chem. 1934, 219, 243) based his configuration of the complexes, were derived from evidence which he obtained from previous work carried out on the co-ordinating properties of thiosemicarbazide, it is deemed advisable to consider this evidence before proceeding further.

In 1934, Jensen and Ranke-Madsen (ibid.) investigated the formation of complex compounds between thio-semicarbazide and substituted thio-semicarbazides and the salts of the common metals iron, copper, cobalt and nickel. The compounds to which most attention was given, were those with the nickel salts. In the case of thio-semicarbazide itself red compounds containing two molecules of the organic radical were obtained, while those containing three molecules of thio-semicarbazide were deep blue in colour. It is noteworthy also that a blue dithiosemicarbazido-nickel nitrate was isolated. In the case of the substituted thiosemicarbazides it was found that substitution in the 2-position or the 4-position in no way hinders the ability of the organic molecule to enter into complex formation, although the nature of the substituted group in the 4-position apparently has some bearing on the number of molecules which become associated with the central nickel atom. On the other hand, substitution in the 1-position prevents the formation of complex compounds completely, as is also the case with the sulphur substituted thio-semicarbazides. From these facts it was therefore deduced that co-ordination to the central atom, in the case of the thiosemicarbazides, is effected through the number 1 nitrogen atom and the sulphur atom, and the following structures are thereby ascribed to the complex ions.



It is interesting to record that at the same time these authors isolated complex compounds of nickel and thiosemicarbazide from alkaline solution, which are insoluble in water, but soluble in organic solvents, to give solutions which do not conduct electricity. These are considered to be covalent complexes of the type,

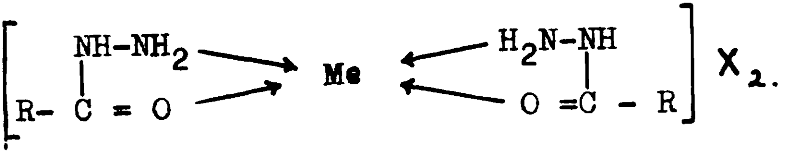


in which one hydrogen of the thiosemicarbazide molecule is replaced by its nickel equivalent. That the metal is joined to the sulphur atom was confirmed by the fact, that, on investigating the formation of nickel derivatives with several other sulphur/nitrogen compounds, only in cases where there is the possibility of a thiol-formation, is there any evidence of complex formation.

In 1936 Jensen (Z.anorg. chem. 1936, 227,25) extended his investigations to a study of the formation of complex compounds between semicarbazide and the salts of copper, cobalt and nickel. With simple semicarbazide green salts of nickel sulphate and of nickel chloride containing two organic molecules were isolated along with a blue compound of nickel chloride containing three molecules of semicarbazide. As is the case with thiosemicarbazide, substitution in the 2-position and in the 4-position does not hinder the co-ordinating ability of semicarbazide, but when the substituent group is in the 1-position, it is found that in some cases the formation of complex compounds is completely prohibited, in others it is unaffected. Thus, whereas 1-benzyl, and 1-phenyl semicarbazide form no metallic complexes, 1:2 dimethyl semicarbazide behaves normally as does also 1:2 dimethyl-4-phenyl semicarbazide.

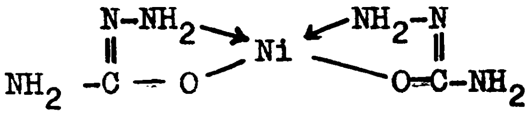
To confirm the structure of these complexes Jensen also isolated metallic complexes of hydrazine-carbonic acid ethyl ester and of acethydrazide, in which they possess two co-ordinating places (see under).

On consideration of the above evidence, and by analogy with the thio-semicarbazide complexes, for combination of semi-carbazide with metals of co-ordination number four, Jensen suggests the following structural formula.

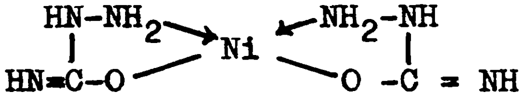


$R = -NH_2$; $-OC_2H_5$; $-CH_3$.

From alkaline solution Jensen obtained a bright red compound which he considers to be derived from semicarbazide by the substitution of hydrogen atoms by their nickel equivalent, and to which he ascribes one or other of the following structures, A or B, preference



A



B

being given to B on the grounds that similar compounds were obtained from 2-methyl, and from 1:2 dimethyl-semicarbazides, while acethydrazide and hydrazine carbonic acid ethyl ester yield no such compounds. This compound appears as a red powder and is definitely basic, as it may be titrated with acid (Jensen; ibid. 227,27). G.S.Smith (J.C.S.1937 1355) on the other hand isolated this complex in a crystalline form from alkaline tartrate solution, and from the analysis and from the fact that it is insoluble in organic solvents he considers it to be a complex oxide of the type $Ni(sem)_2O$ rather than an inner complex.

In 1937 Smith (ibid.1354-1358), as well as repeating some of Jensen's work, extended the field to include complex compounds of semicarbazide with Iron, Cadmium and Zinc salts. Whereas Jensen was unable to isolate a nickel sulphate complex containing three molecules of semicarbazide, Smith prepared such a compound, consisting of deep blue feathery crystals, containing two molecules of crystallisation.

It is of interest to note that both Jensen and Smith endeavoured to utilise the complex compounds which they prepared, to elucidate the structure of the 4-covalent nickel complex ion, but they met with little success. Jensen and Ranke-Madsen (Z.anorg.Chem.1934,219,243) succeeded in forming the well crystallised (+)-bromcamphorsulphonate of the $[\mathrm{Ni(Thio\text{-}sem)_2}]^{++}$ ions, but were unable to effect a resolution of the product into its optically active components, while at the same time they found no evidence of the existence of cis- and trans-isomerides. On the other hand Smith (J.C.S. 1937, p.1355) attempted to prepare the tartrates of the various 4-covalent types which he had isolated, but in all cases he obtained viscous masses.

Introduction to Experimental Work.

On reviewing the literature with reference to the formation of complex metallic compounds of semicarbazide, it is apparent that, prior to 1936, no such complex compounds with the metals of this triad have been recorded, with the exception of the molecular compounds with sodium carbonylferrocyanide reported by Muller (ibid., loc. cit.), and with Roussin's Salt reported by Bellucci and Cechetti (ibid.,loc.cit.).

In 1936, Jensen (ibid.,loc.cit.), reported several compounds with the salts of cobalt and nickel, and a list of these complex compounds is given in Table I. In 1937, Smith (ibid.,loc.cit.) recorded a further list of complex compounds with the salts of iron, cobalt and nickel, which is given in Table II.

Table I.

Complex	Colour	Complex	Colour
$[Ni(sem)_2]SO_4$	Green	$[Ni(I{:}2DiMe.4Ph.sem)_2]Cl_2$	cinnamon brown.
$[Ni(sem)_2]Cl_2$	Green	$[Ni(4Ph.sem)_3](NO_3)_2$	blue
$[Ni(sem)_3]Cl_2$	Blue	$[Co(sem)_3](NO_3)_2$	red.
Complex Compounds formed in Alkaline Solution.			
$[Ni(CON_3H_4)_2]$	red	$\left[Ni\begin{matrix}(NH{=}C(O{-})N.CH_3NHCH_3)_2\\ NH_2CON.CH_3NHCH_3\end{matrix}\right]$	garnet red.
$[Ni(NH{=}C(O{-})N.CH_3NH_2)_2]$	brick red		

Table II

Complex	Colour	Complex	Colour
$[Ni(sem)_2]Cl_2$	Green	$[Co(sem)_2]SO_4$	Pink
$[Ni(sem)_3]Cl_2$	-	$[Co(sem)_2]Cl_2$	Red
$[Ni(sem)_3]Cl_2 3H_2O$	Blue	$[Co(sem)_3](NO_3)_2$	Deep Red
$[Ni(sem)_2|SO_4$	Dark Green	$[Fe(sem)_2]SO_4$	White
$[Ni(sem)_3]SO_4 2H_2O$	Deep Blue	$[Cd(sem)\ ]Cl_2$	White
$[Ni(sem)_3](NO_3)_2$	Deep Blue	$[Zn(sem)_2]SO_4$	White
$[Ni(sem)_3]ClNO_3$	Deep Blue	$Ni(sem)_2O$ (?)	Deep Pink or Red

Between 1936 and 1938 the author investigated the interaction between semicarbazide and semicarbazones and the chlorides of iron cobalt and nickel, with the object of preparing new compounds and of studying their structures. The list of compounds which resulted from this investigation is given in Table III.

Table III

Complex	Colour	Complex	Colour
$[Fe(sem)_2]Cl_2$	White	$[Co_2(sem)_5]Cl_4 2EtOH$	Rose Pink
$[Fe(sem)_3]Cl_2$	White	$[Co(sem)_2(en)]Cl_2H_2O$) or) $[Co_2(sem)_4(en)_2]Cl_4 2H_2O$)	Dark Reddish Brown
$[Fe(Ac/sem)_2]Cl_2$	White		
$[Co(sem)_2]Cl_2$	Pale Pink or Lilac	$[Co(sem)(en)_2]Cl_2H_2O$	Dark Reddish Brown
$[Co(sem)_2]Cl_2H_2O$	Rose Pink	$[Co(Ac/sem)_2]Cl_2$	Lilac
$[Co(sem)_2]Cl_2 2H_2O$	Reddish Brown	$[Ni(sem)_2]Cl_2$	Pale Green
$[Co(sem)_3]Cl_2$	Deep Pink	$[Ni(Ac/sem)_2]Cl_2$	Pale Green

DISCUSSION OF EXPERIMENTAL WORK.

I.

Complex Compounds of Iron.

When an alcoholic solution of semicarbazide is added to an alcoholic solution of ferric chloride, a blood red colour is produced, which disappears on standing and after much gassing, to give a colourless solution from which small buff-coloured crystals separate. On the other hand, on the addition of the semicarbazide solution to a ferrous chloride solution, a white crystalline product is immediately formed, without the formation of the intermediate red colouration. (Note; Jensen(Z.anorg.Chem. 1934,219,243), observed the production of a transient red colouration on adding a solution of thiosemicarbazide to a ferric salt solution.) In both cases the resultant products contain iron in the ferrous state only.

From ferrous chloride and semicarbazide base, small white crystals, which were readily soluble in water but insoluble in organic solvents, were obtained, containing two molecules of semicarbazide associated with the ferrous atom. The analysis of this compound indicates that it corresponds with the structure $[Fe(NH_2NH.CO.NH_2)_2]Cl_2$. However, when semicarbazide hydrochloride was used in place of the base, small white rectangular prisms were obtained which contain three molecules of semicarbazide, $[Fe(NH_2NH.CO.NH_2)_3]Cl_2$. This product was obtained both when the ratio of ferrous chloride to semicarbazide hydrochloride was I:2 and when it was I:3, which seems to indicate that the acidity of the solution influences the number of groups which co-ordinate with the ferrous atom.

The action of acetone semicarbazone on ferric chloride and on ferrous chloride was also studied, As before, with the ferric solution, a deep red colour is at first formed but this disappears and from the colourless solution small white rectangular plates are deposited. This compound contains two molecules of acetone semicarbazone and its analysis shows that it conforms with the structure $[Fe((CH_3)_2C=N.NH.CO.NH_2)_2]Cl_2$. The same product is obtained from ferrous solutions. In some cases, the product, when formed from ferric chloride, appeared to be pale yellow in colour, but in spite of this the iron was present totally in the ferrous condition, and the analysis remained unaltered.

Attention should be drawn to the fact that although, in some cases, as many as six molecules of acetone semicarbazone for each molecule of metallic salt, were employed, in no case did the resultant complex compound contain more than two molecules of acetone semicarbazone.

The actions of methyl-ethyl-ketone semicarbazone, acetophenone semicarbazone and benzaldehyde semicarbazone on ferric chloride were also examined qualitatively, but there was no evidence forthcoming of the formation of complex compounds with these semicarbazones.

It is of interest to note that the complex compounds which have been described above, have shown no signs of decomposition while they have been stored in dry tubes for a period of three years, but in the presence of air and moisture oxidation to the ferric state gradually takes place.

SUMMARY AND REMARKS. - Three new compounds of ferrous

$[Fe(NH_2NH.CO.NH_2)_2]Cl_2$, trisemicarbazido-ferrous chloride loride
$[Fe(NH_2NH.CO.NH_2)_3]Cl_2$, and bis-acetonesemicarbazono-ferrous
chloride $[Fe((CH_3)_2C{=}N.NH.CO.NH_2)_2]Cl_2$. us

chloride $[Fe((CH_3)_2C{=}N.NH.CO.NH_2)_2]Cl_2$.

Reference to the literature shows that complex compounds of ferrous iron in which the metallic atom displays co-ordination numbers of four and of six have been recorded, although the value of six is apparently the more common. The diammine of ferrous chloride prepared by Biltz and Huttig (Z.anorg.Chem., 1919, 109, 89) and formulated in the manner $[Fe2NH_3Cl_2]$ by Morgan and Burstall (Inorganic Chemistry-Modern developments 1936,p204 exemplifies the first class of compounds, while hexammine ferrous chloride $[Fe6NH_3]Cl_2$ (Biltz and Huttig, ibid., loc.cit) represents the second class.

On examining the compounds prepared by the author, in this light it follows that the semicarbazide molecule effects co-ordination at two points which is in keeping with views expressed by Jensen. Moreover, the fact that only complex compounds of ferrous chloride have been obtained, indicates that the reducing nature of the semicarbazide molecule comes into play.

II.

Complex Compounds of Cobalt

COBALTOUS CHLORIDE HEXAHYDRATE WITH SEMICARBAZIDE HYDROCHLORIDE:-

From the preliminary qualitative study of the reaction between semicarbazide hydrochloride and cobaltous chloride hexahydrate, it was found that the tendency to form complex compounds is apparently greater when an aqueous alcoholic medium, rather than a totally aqueous medium is employed.

In consequence of this, several quantitative experiments were carried out using fifty per cent aqueous alcohol as the solvent, in which the molecular ratio of semicarbazide hydrochloride to hydrated cobaltous chloride employed was two to one. In all cases good yields of mauve-coloured crystals were obtained. However, on examining these products under the microscope, it was evident that in no case was the product of a homogeneous nature, but consisted of a mixture of clusters of very small compact crystals and medium sized hexagonal plates. A great deal of time was spent in endeavouring to separate these two crystalline forms by methods of fractional crystallisation, and by utilising various proportions of water and alcohol. It became evident that as the proportion of water in the aqueous-alcohol medium increased, a larger proportion of the hexagonal crystals in the product was obtained, whereas when a large proportion of alcohol was used, the small mauve crystals predominated.

On comparing the mixed product obtained by the author with the disemicarbazido-cobaltous chloride isolated by Smith (J.C.S. 1937,1356), it was seen that the descriptions varied, and as the latter was prepared from a totally aqueous medium it was decided to repeat the preparation according to Smith's method, for further comparison. The product obtained in this manner tallied with the description given by Smith, and consisted of small flat hexagonal crystals of a dark red colour, and they appeared to be very similar to the hexagonal crystals which formed part of the mixed product obtained by the author. The evidence now pointed to the probability that the mixed product consisted of crystals of the complex with varying proportions of water of crystallisation, and subsequent investigation proved this to be the case.

On recrystallising the mixed product from a small quantity of water, small red flat hexagonal crystals were isolated which correspond very closely in appearance with those which were obtained by the method of Smith. The analysis of this recrystallised product indicates that it corresponds to disemicarbazido-cobaltous chloride dihydrate with the constitution $[Co(NH_2NH.CO.NH_2)_2]Cl_2 2H_2O$, or to diaquodisemicarbazido-cobaltous chloride with the constitution $[Co(NH_2NH.CO.NH_2)_2 2H_2O]Cl_2$. The two molecules of water are driven off on heating the substance for ten hours at 110°C, the resultant residue consisting of a pale lilac amorphous powder, the analysis of which agrees with the formula $[Co(NH_2NH.CO.NH_2)_2]Cl_2$.

Attempts were next made to prepare the anhydrous disemicarbazido-cobaltous chloride from solution by dissolving the semicarbazide hydrochloride in the minimum quantity of warm water and mixing it with the cobaltous chloride hexahydrate dissolved in a large quantity of absolute alcohol. Finally, a homogeneous product was obtained which consists of very small rose-pink crystals and which, by analysis, corresponds to disemicarbazido-cobaltous chloride monohydrate, $[Co(NH_2NH.CO.NH_2)_2] Cl_2H_2O$. This compound is very soluble in water and from the aqueous solution the dihydrate separates out. Also, on heating for several hours at 110°C. the single molecule of water is lost yielding a pale lilac powder which corresponds to disemicarbazido-cobaltous chloride.

It should also be noted that the pale lilac products obtained by the action of heat on the monohydrate and on the dihydrate are soluble in water on slight heating, and from the aqueous solutions thus formed flat red hexagonal plates of the dihydrate crystallise.

It is evident, therefore, that the presence of even a very small quantity of water tends to promote the formation of a hydrated compound.

ANHYDROUS COBALTOUS CHLORIDE WITH SEMICARBAZIDE FREE BASE:- Experiments were then undertaken to study the reaction under entirely anhydrous conditions. Absolute alcohol was used as the medium along with semicarbazide free base and anhydrous cobaltous chloride. When one molecule of cobalt chloride was added slowly, and with stirring, to three molecules of semicarbazide base, a product was isolated which consists of very small pale pink crystals. The analysis of this product shows that it is anhydrous disemicarbazido-cobaltous chloride, $[Co(NH_2NH.CO.NH_2)_2]Cl_2$. It is soluble in water on the application of a small amount of heat, and from the aqueous solution flat red hexagonal plates of the dihydrate are deposited.

Each of these products which have just been described, is fairly stable if stored under dry conditions. Their solutions in water are neutral to litmus, but on standing for three or four days the solutions become alkaline and deposit hydrazodicarbonamide. This change is effected at once when the aqueous solutions are heated. They give no true melting points, decomposition setting in at about 200°C, but they finally fuse to deep blue masses at temperatures varying from 238°C for the anhydrous product, 243° C for the monohydrate and 248°C for the dihydrate. In each case the decomposition is accompanied with the evolution of a large amount of gas. It should be noted in this connection, that the melting point of hydrazodicarbonamide is 244° - 246°C, while anhydrous cobaltous chloride gives no melting, but sublimes. With Fehling's Solution in the cold much gas is evolved and a green solution is obtained; complete reduction however is effected on the application of heat.

The affinity of the anhydrous compound for water seems to indicate that the central cobalt atom is attempting to satisfy the two vacant co-ordinate valencies. Were this the case it would be expected, that in the preparation in which three molecules of semicarbazide were employed, trisemicarbazido -cobaltous chloride would at once have been formed. This did not happen, the disemicarbazido-complex being the one which was isolated. On the other hand, the comparative ease with which the associated water molecules are driven off, indicates that these molecules are not very firmly bound, so that with the evidence available and in the absence of physical measurements, it is unsafe to come to a decision as to whether the water molecules are held within the co-ordination sphere, or whether they are present as water of crystallisation.

On comparing the compound disemicarbazido-cobaltous chloride recorded by Smith (J.C.S. 1937,loc.,cit.), with the three compounds which have just been described, and on considering the manner in which the complex was prepared, the author is of the opinion that it corresponds to the dihydrate rather than to the anhydrous complex, as stated.

TRISEMICARBAZIDO-COBALTOUS CHLORIDE:- Both Jensen and Smith have isolated trisemicarbazido-cobaltous nitrate, and the author has succeeded in preparing the corresponding complex compound with cobaltous chloride. In the preparation of this compound, an excess of five molecules of semicarbazide base was required, a large yield of very small deep pink crystals being obtained. The analysis of this product indicates that it is in agreement with the structure $\left[Co(NH_2NH.CO.NH_2)_3\right]Cl_2$. it is soluble in cold water to give a deep red solution and it decomposes with the evolution of gas at 224°C, fusing to a deep blue mass.

COBALTOUS CHLORIDE MONOHYDRATE WITH SEMICARBAZIDE FREE BASE:- Several preparations were also carried out using cobaltous chloride monohydrate in place of the hexahydrate or of the anhydrous salt. On three occasions the ratio, one molecule of the salt to three molecules of semicarbazide free base, was employed, and the preparations were effected in absolute alcoholic media. In each case homogeneous products were obtained which consist of very small rose-pink crystals, the analyses of which all point to the empirical formula $\left[Co_2(NH_2NH.CO.NH_2)_5\right] Cl_4 . 2C_2H_5OH$.

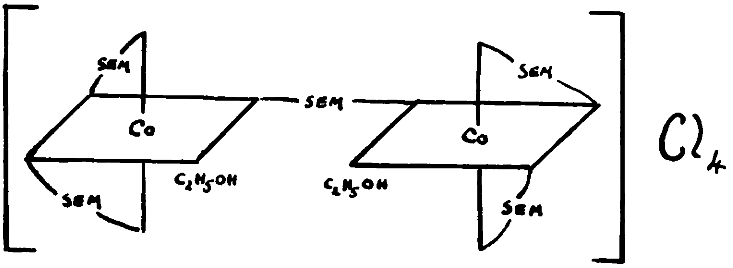
In each case the ratio of semicarbazide to cobalt is almost exactly two and a half to one. The product is decomposed by cold water, gas being evolved, and the solution is alkaline litmus. On allowing the solution to evaporate slowly flat red crystals of disemicarbazido-cobaltous chloride dihydrate separate out. On heating the solid, decomposition sets in at 217°C, the colour changing to pale lilac, and at 237° - 239°C it fuses to a deep blue mass, accompanied with the evolution of a great deal of gas. On heating this product for six hours at 110°C the colour changes from rose-pink to light brown and the loss in weight is equivalent to two molecules of ethyl alcohol. However, on prolonged heating during seventy-five hours at 140°C, weight is progressively lost and a constant weight is not achieved. After such treatment the residue is pale lilac in colour and contains semicarbazide and cobalt in the ratio 2:1.

The presence of the alcohol of crystallisation was demonstrated in the following manner. About 1.5 grams of the rose-pink product were dried under vacuum at room temperature for two days, after which they were subjected to controlled heat treatment, and the distillate collected. This distillate gave negative tests for water, but gave a positive reaction with hydroxylamine hydrochloride and ferric chloride, thus indicating the presence of alcohol (Feigl, Qual.Anal. p.250).

The empirical formula $\left[Co_2\ (NH_2NH.CO.NH_2)_5\right]Cl_4.2C_2H_5OH$, may be interpreted in one or other of the following ways.

Firstly, this formula would result from an equimolecular mixture of dialcoholated disemicarbazido-cobaltous chloride, and trisemicarbazido-cobaltous chloride. However, the fact that the product is homogeneous, coupled with the unlikelihood that an equimolecular mixture would be formed in each of the three preparations, suggests that some other explanation may be more fitting.

Secondly, this empirical formula is in accordance with the formation of a polynuclear complex compound, in which two molecules of disemicarbazido-cobaltous chloride are linked together through one molecule of semicarbazide. Such a compound may be represented by the following structure.



A complex ion of this type would probably be unstable, and it has already been pointed out that the product under discussion is readily decomposed by cold water, the aqueous solution depositing dihydrated disemicarbazido-cobaltous chloride.

Two other observations with respect to this product should also be noted. In each of these preparations, on filtering off the rose-pink compound, the filtrate appeared to be pale pink in colour, but on standing, a very small quantity of a brownish-red solid separated out and the solution turned deep blue in colour. The solid melts with decomposition at 115° - 120°C and reduces Fehling's Solution, while the blue alcoholic filtrate is neutral to litmus and has no effect on Fehling's Solution. The second point to note is that, if the rose-pink product, after filtration and washing with alcohol, is not completely dried with respect to alcohol, it becomes discoloured with greenish-blue patches. If, however, the discoloured product is left in contact with the air, or is placed under vacuum, until the odour of alcohol disappears, the original rose-pink colour is regained.

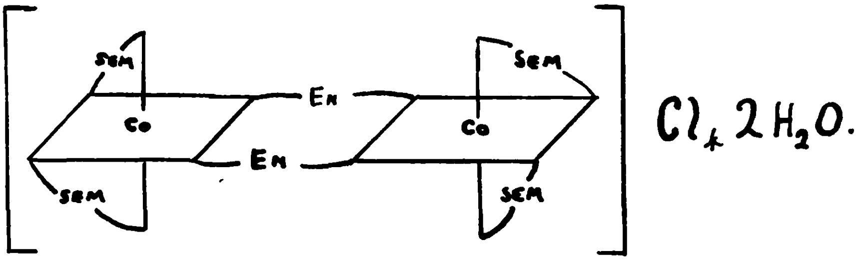
ACTION OF ETHYLENEDIAMINE ON THE PRODUCT CONTAINING TWO AND A HALF MOLECULES OF SEMICARBAZIDE:- On considering the polynuclear structure which has been suggested above for this compound, it is seen that two of the co-ordination valencies are represented as being satisfied by the two molecules of alcohol. It seemed possible therefore, that some support for this structure would be forthcoming if a compound were prepared in which these two co-ordination positions are linked together by some molecule other than semicarbazide.

Reference to the literature indicated that a suitable molecule for this purpose is ethylenediamine as a great number of complex compounds formed between ethylenediamine and cobalt salts has been recorded (Cf.Abegg, Hand.der anorg.Chem.,1935,4,2, 652-657, et seq.) For example, in 1899 Jorgensen (J.pr.Chem., 1899, 39,8) isolated a yellow-brown compound of cobaltic chloride containing three molecules of ethylenediamine $\left[Co(en)_3\right]Cl_3 3H_2O$, and in 1898 Werner (Z.anorg. Chem. 1898,21,229) prepared triethylenediamino-cobaltous sulphate $\left[Co(en)_3\right]SO_4$ which is also yellow in colour. It is noteworthy that in the case of the complex compounds of ethylenediamine, as it is in the case of the simple cobaltammines, unless special precautions are taken to exclude the air, compounds of trivalent cobalt are formed. Complex compounds which contain both cobaltous and cobaltic cobalt are also known. A recent example of such a compound isolated by Drew and Pratt (J.C.S. 1937,506) is hydroxoaquobisethylenediaminocobaltic cobaltochloride $\left[(en)_2Co(OH)H_2O\right]CoCl_4$, which consists of very minute pink crystals.

Experiments were then undertaken with the aim of adding one molecule of ethylenediamine to one molecule of the supposedly polynuclear compound.

When equimolecular quantities were employed in an aqueous medium, a dark-brown solution resulted. This solution after standing for two days deposited a quantity of hydrazodicarbonamide, and on taking the filtrate down almost to dryness, a dark reddish-brown product was obtained. The analysis of this product indicates that it corresponds empirically with $\left[Co(NH_2NH.CO.NH_2)_2(NH_2CH_2CH_2NH_2)\right]Cl_2H_2O$.

The deposition of hydrazodicarbonamide shows that throughout the reaction semicarbazide was being displaced, so that even yet a polynuclear structure may be possible, built up in the following manner.



On the other hand, this product may be monomolecular disemicarbazido-ethylenediamino-cobaltous chloride monohydrate formed from a stoichiometric mixture of disemicarbazido-cobaltous chloride and trisemicarbazido-cobaltous chloride, by the addition of one molecule of ethylenediamine to the disemicarbazido-compound and by the simultaneous displacement of semicarbazide by one molecule of ethylenediamine from the trisemicarbazido-compound. Subsequent experiment showed that such displacement of semicarbazide by ethylenediamine from trisemicarbazido-cobaltous chloride does take place, so that in the absence of further evidence it is inadvisable to come to any definite conclusion with regard to the configuration of this compound.

ACTION OF ETHYLENEDIAMINE ON DISEMICARBAZIDO-COBALTOUS CHLORIDE:- Following along similar lines, attempts were made to form this same compound by the direct addition of one molecule of ethylenediamine to one molecule of disemicarbazido-cobaltous chloride, but here again the displacement of semicarbazide took place and the resultant dark reddish-brown product contained two molecules of ethylenediamine, but only one molecule of semicarbazide. The analysis of this compound shows that it is semicarbazido-diethylenediamino-cobaltous chloride monohydrate $\left[Co(NH_2NH.CO.NH_2)(NH_2CH_2CH_2NH_2)_2\right] Cl_2H_2O$.

On attempting this preparation again, a dark reddish-brown substance was obtained which contains 16.41% of cobalt and 32.32% of nitrogen. These figures agree very closely with the cobalt and nitrogen values in the structure $\left[Co(NH_2NH.CO.NH_2)_2(NH_2CH_2CH_2NH_2)\right] Cl_2H_2O$, which contains 16.46% of cobalt and 31.30% of nitrogen. The semicarbazide figure is low being 35.53% against 41.91%, and this is probably indicative of a disproportioning between the semicarbazide and the ethylenediamine.

ACTION OF SEMICARBAZONES ON COBALTOUS CHLORIDE MONOHYDRATE:- The action of semicarbazones on cobaltous chloride monohydrate in alcoholic solution was also studied.

Benzaldehyde semicarbazone and acetophenone semicarbazone did not form complex compounds, but with acetone semicarbazone a pale lilac product was obtained which melts with decomposition at 255° - 258°C. The analysis of this compound indicates that it contains two molecules of acetone semicarbazone and that it conforms with the structure $\left[Co((CH_3)_2C{=}N.NH.CO.NH_2)_2\right] Cl_2$.

<u>SUMMARY AND REMARKS</u>:- Three forms of disemicarbazido-cobaltous chloride, $\left[Co(NH_2NH.CO.NH_2)_2\right] Cl_2$, have been prepared; the anhydrous complex, the monohydrate and the dihydrate. The last two may be "aquo" salts. The author is of the opinion that the anhydrous disemicarbazido-cobaltous chloride reported by Smith (J.C.S.1937,1356) corresponds rather with the complex compound which contains two molecules of water.

Trisemicarbazido-cobaltous chloride and bisacetone-semicarbazono-cobaltous chloride have also been isolated.

A compound in which the ratio of semicarbazide to cobalt is two and a half to one and which contains two molecules of ethyl alcohol has been prepared. This may be a polynuclear compound of the type $\left[Co_2(sem)_5 2EtOH\right] Cl_4$ or it may be a mixture of disemicarbazido-cobaltous chloride and trisemicarbazido-cobaltous chloride.

Two compounds containing both semicarbazide and ethylenediamine have been prepared; disemicarbazido-ethylenediamino-cobaltous chloride monohydrate,

$[Co(sem)_2(en)]Cl_2H_2O$, and semicarbazido-diethylenediamino-cobaltous chloride monohydrate $[Co(sem)(en)_2]Cl_2H_2O$.

That the semicarbazide molecule effects co-ordination at two points has again been demonstrated. The fact that only cobaltous compounds have been obtained in contradistinction to the more usual chemical experience that co-ordination stabilizes the cobaltic state, which is particularly evident in complex compounds containing ethylenediamine, indicates that once again the reducing nature of the semicarbazide molecule comes into play.

Evidence has also been obtained that the ethylenediamine molecule tends to displace the semicarbazide molecule from complex formations.

III.

Complex Compounds of Nickel

It has already been stated in the Introduction to this paper, that the publishing of communications by Jensen and by Smith anticipated the results of the work which has been undertaken by the author and this is particularly applicable in the case of the compounds of nickel. However, the author has independently isolated two compounds of nickel chloride, the one containing two molecules of semicarbazide and the other containing two molecules of acetone semicarbazone.

Disemicarbazido-nickelous chloride, $[Ni(NH_2NH.CO.NH_2)_2]Cl_2$, was prepared from alcoholic solution, one molecule of nickelous chloride hexahydrate being added to two molecules of semicarbazide hydrochloride. The product obtained is pale green in colour which conforms with the descriptions of the same compound isolated both by Jensen and by Smith.

Bisacetonesemicarbazono-nickelous chloride, $[Ni((CH_3)_2C{=}N.NH.CO.NH_2)_2]\ Cl_2$, on the other hand, has not been described in the literature. This product is also pale green in colour and was prepared from alcoholic solution by the addition of one molecule of nickelous chloride hexahydrate to two molecules of acetone semicarbazone.

In both of these preparations, on the first addition of the alcoholic nickel solution to the alcoholic solution of the organic molecule, a deep blue colour developed, but on the total addition of the nickel salt the blue colouration gradually paled off, the final mixed solution being green in colour. This blue colour is probably due to the formation of the trisemicarbazido-complex, as the nickel complexes containing three molecules of semicarbazide isolated by Jensen and by Smith (Cf. p.43 above) are deep blue in colour.

EXPERIMENTAL SECTION

Purification of Semicarbazide Hydrochloride.

The semicarbazide hydrochloride used throughout the experimental work was purified by precipitation from saturated aqueous solution by means of an excess of ethyl alcohol. The melting point of the purified product is 173°C.

Preparation of Semicarbazide Base.

Semicarbazide free base was prepared in the following manner. The required quantity of finely powdered semicarbazide hydrochloride was suspended in a fairly large volume of absolute alcohol and the suspension titrated with an approximately 2N alcoholic solution of potassium hydroxide. After the addition of almost the calculated amount of alkali, the suspension was vigorously shaken and allowed to stand for half an hour. The titration was then resumed until a permanent end point with phenolphthalein was obtained, after which the solution was made faintly acid again by the addition of a small quantity of semicarbazide hydrochloride. The precipitated potassium chloride was filtered off, and the semicarbazide base obtained by crystallisation from the filtrate. The melting point of the free base is 96°C.

In many of the following experiments the solid base was not isolated, the alcoholic solution containing a known quantity of the base, being employed.

1.

COMPLEX COMPOUNDS OF IRON.

The following reactions were investigated.

FERROUS CHLORIDE WITH SEMICARBAZIDE HYDROCHLORIDE.

Molecular Ratio 1:2:- 1.1 grams (1mol) of iron wire were dissolved in ten cubic centimetres of concentrated hydrochloric acid and the solution filtered into eighty cubic centimetres of an aqueous-alcoholic (1:3) solution of 4.4 grams (2 mols) of semicarbazide hydrochloride. After a few minutes, white crystals began to separate out and these proved to be semicarbazide hydrochloride (m.pt.174°C), a yield of 2.1 grams being obtained. After the semicarbazide hydrochloride had been removed, the filtrate was allowed to stand for sixteen hours during which time 1.3 grams of small white crystals were deposited.

This product is TRISEMICARBAZIDO-FERROUS CHLORIDE, $\left[Fe(NH_2NH.CONH_2)_3\right]Cl_2$, and the yield obtained on this basis was 27%.

Found: N = 35.04%; Fe = 15.95%; Cl = 19.41%:

Theory: N = 35.84%; Fe = 15.87%; Cl = 20.16%:

Properties:- This product consists of very small white rectangular plates which dissolve slowly in cold water to give a solution which is neutral to litmus. The iron is present totally in the ferrous state, and the aqueous solution gives an immediate precipitation of silver chloride with silver nitrate solution. With Fehling's Solution it gives a dark green solution in the cold, and a dirty green precipitate on heating, but on boiling the normal reduction takes place. The complex does not fuse below 300°C, and it has shown no tendency to become oxidised to the ferric state on being stored in a dry tube for three years.

NOTE:- The reaction between ferrous chloride and semicarbazide hydrochloride was also examined in the absence of the excess of hydrochloric acid which was left from the preparation of the ferrous chloride solution in the above experiment.

2.5 grams (1mol) of solid ferrous chloride were dissolved in twenty cubic centimetres of absolute alcohol and the solution was added to one hundred and fifty cubic centimetres of an aqueous alcoholic solution (1:6) of 4.4 grams (2mols) of semicarbazide hydrochloride. The resultant solution was pale yellow in colour and on standing over night this colour became intensified, and a small quantity (0.7 grams) of semicarbazide hydrochloride had been deposited. No further reaction took place.

Molecular Ratio 1:3 :- 1.1 grams (1mol) of iron wire were dissolved in ten cubic centimetres of concentrated hydrochloric acid and the solution was filtered, in the cold, into eighty cubic centimetres of an aqueous-alcoholic (1:3) solution of 6.7 grams (3mols) of semicarbazide hydrochloride. The resultant solution was pale green in colour, and after two days' time a deposit of 0.7 grams of very small rectangular plates separated out: the supernatant liquor, at the end of this time, was pale yellow in colour. The small crystals do not fuse below 300°C, they reduce Fehling's Solution on boiling, and they give an immediate precipitation with silver nitrate solution.

This compound corresponds to TRISEMICARBAZIDO-FERROUS CHLORIDE, $\left[Fe(NH_2NH.CO.NH_2)_3\right]Cl_2$.

Found: Fe = 15.82%

Theory: Fe = 15.87%

NOTE:- On working up the mother liquor 4.3 grams of semicarbazide hydrochloride were recovered.

FERROUS CHLORIDE WITH SEMICARBAZIDE BASE.

Molecular Ratio 1:2 :- 1.1 grams (1mol) of iron wire were dissolved in five cubic centimetres of concentrated hydrochloric acid, and the solution diluted with absolute alcohol. This solution, which was slightly acid to litmus, was added to an alcoholic solution of 3.0 grams (2mols) of semicarbazide base. An oily pale green mass was immediately precipitated. This mass was allowed to stand in contact with the mother liquor for sixteen hours, after which time it was removed from the solution and broken up in a mortar. During this procedure the solid became definitely crystalline. The product was then washed thoroughly with alcohol and dried in a desiccator; when dry, a yield of 2.7 grams of very small white crystals was obtained.

This compound is DISEMICARBAZIDO-FERROUS CHLORIDE, $\left[Fe(NH_2NH.CO.NH_2)_2\right]Cl_2$, and on this basis, the yield obtained, was 48%.

Found: N = 31.85%; sem = 55.33%; Fe = 20.03%; Cl = 23.79%;
Theory: N = 30.37%; sem = 54.19%; Fe = 20.17%; Cl = 25.62%;

Properties:- This compound consists of very small white flat rectangular crystals which are readily soluble in water to give a solution which is neutral to litmus. It is quite insoluble in organic solvents such as ether, alcohol and benzene

The iron is present only in the ferrous state, and the aqueous solution gives an immediate precipitate with silver nitrate solution. With Fehling's Solution, in the cold, a green precipitate is formed, and on boiling the normal reduction takes place. The complex does not fuse below 300°C.

With concentrated hydrochloric acid, the complex turns yellow, without going into solution, but with concentrated sulphuric acid solution is effected accompanied by the evolution of gas; after a few seconds a small white residue is deposited which deliquesces on exposure to the atmosphere. With concentrated nitric acid decomposition is again evident, but in this case a yellow deliquescent deposit is obtained.

ANHYDROUS FERRIC CHLORIDE WITH SEMICARBAZIDE HYDROCHLORIDE.

This reaction was studied in a qualitative manner. The molecular proportions employed were approximately 1:3. When the alcoholic solution of ferric chloride was added to the alcoholic solution of semicarbazide hydrochloride a blood red coloured solution was obtained. This red colour disappeared, after about half an hour, accompanied by the evolution of nitrogen, and from the colourless solution a small quantity of a buff-coloured product separated out. These crystals consist of small elongated rectangular plates which contain semicarbazide and ferrous iron.

This compound corresponds to TRISEMICARBAZIDO-FERROUS CHLORIDE, $\left[Fe(NH_2NH.CO.NH_2)_3\right] Cl_2$.

Found:	Fe	=	15.10%
Theory:	Fe	=	15.87%

FERROUS CHLORIDE WITH ACETONE SEMICARBAZONE.

Molecular Ratio 1:3 :- 1.1 grams (1mol) of iron wire were dissolved in five cubic centimetres of concentrated alcoholic hydrochloric acid with the aid of heat, and the slightly warm solution filtered into an alcoholic solution of 4.6 grams (3mols) of acetone semicarbazone. On mixing, the solution turned pale yellow in colour and almost immediately a white crystalline precipitate was formed. After about fifteen minutes had elapsed, this product was filtered off and washed with alcohol, a yield of 5.3 grams being obtained.

This compound is BISACETONESEMICARBAZONO-FERROUS CHLORIDE, $\left[Fe((CH_3)_2C{=}N.NH.CO.NH_2)_2\right]Cl_2$, and on this basis the yield obtained was 74%.

Found: N = 23.74%; Fe = 15.47%; Cl = 19.11%;
Theory: N = 23.56%; Fe = 15.65%; Cl = 19.87%;

Properties:- This compound consists of small white rectangular plates which dissolve slowly in cold water to give a solution which is neutral to litmus, The iron is present in the ferrous state and the aqueous solution gives an immediate precipitation with silver nitrate solution. A green precipitate is formed with Fehling's Solution, which turns dirty yellow on boiling. On heating the complex with dilute hydrochloric acid a distinct odour of acetone is detectable, and after such treatment the solution reduces Fehling's Solution in the normal manner, on gentle heating. The complex does not fuse below 300°C.

FERRIC CHLORIDE HEXAHYDRATE WITH ACETONE SEMICARBAZONE.

Molecular Ratio 1:2 :- 6.9 grams (2mols) of acetone semicarbazone were dissolved with the aid of heat, in one hundred cubic centimetres of alcohol and the solution, while still slightly warm, was filtered into fifty cubic centimetres of an alcoholic solution of 8.1 grams (1mol) of ferric chloride hexahydrate. The mixed solution was deep red in colour, but there were no signs of the immediate formation of a precipitate. On standing, the evolution of nitrogen commenced and after about an hour and a half's time the solution turned yellow in colour, and a finely divided pale yellow solid separated. The yield of solid was 5.6 grams.

This compound is BISACETONESEMICARBAZONO-FERROUS CHLORIDE, $\left[Fe((CH_3)_2C{=}N.NH.CO.NH_2)_2\right]Cl_2$, and the yield obtained, on this basis is 52.3%.

Found;	N = 23.70%;	Fe = 15.53% ;	Cl = 19.70%:
Theory:	N = 23.56%;	Fe = 15.65% ;	Cl = 19.87%:

Properties:- Except for the colour, which in this case is pale yellow, the properties of this compound are identical with those of the foregoing compound. It is noteworthy that before it goes into solution in water, the compound turns white.

Molecular Ratio 1:6 :- On adding an alcoholic solution of 2.7 grams (1mol) of ferric chloride hexahydrate to an alcoholic solution of 6.9 grams (6mols) of acetone semicarbazone a deep red mixed solution was again obtained. After a period of about half an hour had elapsed, the red colour disappeared along with the evolution nitrogen, and at the end of a further half hour a yield of 3.5 grams of small white crystals had been deposited on the bottom of the beaker.

The properties and the analysis show that this compound is BISACETONESEMICARBAZONO-FERROUS CHLORIDE, $\left[Fe((CH_3)_2C=N.NH.CO.NH_2)_2\right]Cl_2$, and on this basis the yield obtained is 97%.

Found:	N = 23.36%;	Fe = 15.89%;	Cl = 19.17%;
Theory:	N = 23.56%;	Fe = 15.65%;	Cl = 19.87%;

ANHYDROUS FERRIC CHLORIDE WITH ACETONE SEMICARBAZONE

Molecular Ratio 1:3:- 3.2 grams (1 mol) of anhydrous ferric chloride were dissolved in alcohol and the solution was added to an alcoholic solution of 6.9 grams (3 mols) of acetone semicarbazone, both solutions being slightly warm when mixed. The red colouration again appeared, but after an interval of about fifteen minutes had elapsed, a pale yellow crystalline deposit formed, accompanied with the evolution of nitrogen and with the disappearance of the red colour. The yield of solid obtained was 6.1 grams.

The properties and the analysis of this compound show that it is BISACETONESEMICARBAZONO-FERROUS CHLORIDE, $\left[Fe((CH_3)_2C{=}N.NH.CO.NH_2)_2\right]Cl_2$, and on this basis the yield obtained is 86%.

Found: Fe = 15.87%; Cl = 19.84%:

Theory: Fe = 15.65%; Cl = 19.87%:

FERRIC CHLORIDE HEXAHYDRATE WITH OTHER SEMICARBAZONES.

The following experiments were entirely of a qualitative nature.

Methyl-ethyl-ketone Semicarbazone.

When an alcoholic solution of methyl-ethyl-ketone semicarbazone was added to an alcoholic solution of hydrated ferric chloride, there was a slight deepening of the yellow colour, but there was no sign of a red colouration. On standing for twenty-four hours the solution deposited crystals of the original semicarbazone.

Acetophenone Semicarbazone.

An alcoholic solution containing both acetophenone semicarbazone and hydrated ferric chloride on standing for a few days deposited crystals of the original semicarbazone. There were no indications of the appearance of the intermediate red colouration.

Benzaldehyde Semicarbazone.

An alcoholic solution containing both benzaldehyde semicarbazone and hydrated ferric chloride on standing overnight deposited crystals of the original semicarbazone. There were no indications of the appearance of the intermediate red colouration.

11.

COMPLEX COMPOUNDS OF COBALT.

The following reactions were investigated.

COBALTOUS CHLORIDE HEXAHYDRATE WITH SEMICARBAZIDE HYDROCHLORIDE.

Several experiments were carried out in aqueous-alcoholic media containing various proportions of water and alcohol, in which one molecule of cobaltous chloride hexahydrate was added to two molecules of semicarbazide hydrochloride. In the majority of these experiments, bright mauve-coloured products were obtained, which consisted of mixtures of very small compact pink crystals and larger flat red hexagonal plates. As the proportion of alcohol increased, the number of small pink crystals increased, but as the proportion of water in the medium increased the flat red hexagonal plates predominated. Bearing this fact in mind, the following experiments were performed.

Molecular Ratio 1:2 :- 13.2 grams (2 mols) of semicarbazide hydrochloride were dissolved in the minimum quantity of warm water necessary for solution, and about twice this volume of absolute alcohol added. This solution was filtered into an alcoholic solution of 14.4 grams (1 mol) of cobaltous chloride hexahydrate, the resultant mixed solution being pale violet in colour. After an interval of about ten minutes, crystallisation commenced, and this was allowed to proceed for a further period of twenty minutes, in the ice-chest. A yield of 14.4 grams of rose-pink crystals was obtained.

This compound is DISEMICARBAZIDO-COBALTOUS CHLORIDE MONOHYDRATE, $\left[Co(NH_2NH.CO.NH_2)_2\right]Cl_2H_2O$, and on this basis the yield obtained was 80%.

Found: sem = 49.94%; Co = 19.70%; Cl = 24.00%; loss at 110°C = 5.30%:

Theory: sem = 50.35%; Co = 19.79%; Cl = 24.35%; water = 6.04%:

<u>Properties</u>:- This compound consists of very small compact rose-pink plates which are very soluble in water to give a deep red solution. With Fehling's Solution, much gas is evolved in the cold, and a green solution is produced, but on heating, the normal reduction takes place. The aqueous solution gives an immediate precipitation with silver nitrate solution. On heating the complex, it turns pale lilac at 110°C and decomposition commences at 235°C, fusion to a deep blue mass along with the evolution of gas, finally taking place at 243°C.

The pale lilac powder which is left after heating disemicarbazido-cobaltous chloride monohydrate at 110°C until a constant weight is achieved, corresponds to anhydrous DISEMICARBAZIDO-COBALTOUS CHLORIDE, $\left[Co(NH_2NH.CO.NH_2)_2\right] Cl_2$.

Found: sem = 52.26%:

Theory: sem = 53.59%:

ACTION OF WATER ON DISEMICARBAZIDO-COBALTOUS CHLORIDE MONOHYDRATE

On dissolving disemicarbazido-cobaltous chloride monohydrate in cold water, a deep red solution was obtained which deposited flat red hexagonal plates on being allowed to evaporate slowly to the atmosphere.

This compound is DISEMICARBAZIDO-COBALTOUS CHLORIDE DIHYDRATE, $\left[Co(NH_2NH.CO.NH_2)_2\right]Cl_2.2H_2O$.

Found:	sem = 47.07%;	Co = 18.65%;	Cl = 21.42%;	loss at 110°C = 11.64%:
Theory:	sem = 47.49%;	Co = 18.66%;	Cl = 22.45%;	water = 11.40%:

Properties:- This compound consists of flat red hexagonal plates which are very soluble in water to give a deep red solution. It reduces Fehling's Solution on boiling, and gives an immediate precipitation with silver nitrate solution. On heating, the complex turns pale lilac at 100°C, begins to decompose at 200°C, and finally fuses, with the evolution of gas, to a deep blue mass at 248°C.

The pale lilac powder which is left after heating disemicarbazido-cobaltous chloride dihydrate at 110°C, until a constant weight is achieved, corresponds to anhydrous DISEMICARBAZIDO-COBALTOUS CHLORIDE, $\left[Co(NH_2NH.CO.NH_2)_2\right]Cl_2$.

Found: sem = 52.50%:

Theory: sem = 53.59%:

NOTE:- The pale lilac powders which were obtained by the action of heat at 110°C, on the monohydrate and on the dihydrate, were soluble in cold water to give red solutions from which small red hexagonal plates of disemicarbazido-cobaltous chloride dihydrate separated, when the solutions were allowed to evaporate slowly to the atmosphere.

COBALTOUS CHLORIDE HEXAHYDRATE WITH SEMICARBAZIDE BASE.

Molecular Ratio 1:2 :- On adding an alcoholic solution containing 3.0 grams (2 mols) of semicarbazide base to an alcoholic solution of 4.8 grams (1 mol) of cobaltous chloride hexahydrate, a yield of 3.7 grams of small rose-pink crystals immediately separated. These crystals were dissolved in cold water, and on allowing this solution to evaporate slowly, flat red hexagonal plates of DISEMICARBAZIDO-COBALTOUS CHLORIDE DIHYDRATE, $\left[Co(NH_2NH.CO.NH_2)_2\right] Cl_2 2H_2O$, were formed.

Found: sem = 47.61%:

Theory: sem = 47.49%:

ANHYDROUS COBALTOUS CHLORIDE WITH SEMICARBAZIDE BASE.

Molecular Ratio 1:3 :- 6.5 grams (1 mol) of anhydrous cobaltous chloride were dissolved in one hundred and fifty cubic centimetres of absolute alcohol and the solution added slowly and with stirring to an alcoholic solution of 11.3 grams (3 mols) of semicarbazide base. Immediately very small pale pink crystals were formed which were filtered off and washed with alcohol. The yield obtained was 12.0 grams.

This compound is anhydrous DISEMICARBAZIDO-COBALTOUS CHLORIDE, $\left[Co(NH_2NH.CO.NH_2)_2\right]Cl_2$, and on this basis the yield obtained was 86% .

Found: sem = 51.66%; Co = 20.95%;
Theory: sem = 53.59%; Co = 21.07%;

Properties:- This compound consists of very small compact pale pink crystals, which are partially soluble in cold water to give a red solution. On standing, gassing takes place, and hydrazodicarbonamide is deposited. At first the solution is neutral to litmus, but gradually an alkaline reaction develops. On boiling with water, solution is effected at once and the red solution gives an alkaline reaction to litmus, but on standing for a short time, hydrazodicarbonamide is again deposited. On removing the hydrazodicarbonamide, the red solution yields small red hexagonal plates of disemicarbazido-cobaltous chloride dihydrate. With Fehling's Solution in the cold, a green solution is formed, but on boiling the normal reduction takes place. The chloride portion of the complex is immediately precipitated by silver nitrate solution. On heating the complex, the following changes are noted; at 120°C the colour pales off to white, and as heating progresses decomposition sets in at 213°C, fusion, accompanied with the evolution of gas, finally taking place at 238°C.

On storing the crystals in a dry tube for three years the colour has changed from pale pink to pale lilac.

Molecular Ratio 1:5 :- 6.5 grams (1 mol) of anhydrous cobaltous chloride were dissolved in one hundred cubic centimetres of absolute alcohol and the solution poured slowly and with stirring into two hundred cubic centimetres of an alcoholic solution of 18.8 grams (5 mols) of freshly prepared semicarbazide base. A very bulky, light purple precipitate was immediately formed, which was filtered off with suction and washed thoroughly with alcohol. On drying the product in a vacuum desiccator, a yield of 16.8 grams of deep pink crystals was obtained.

This compound is TRISEMICARBAZIDO-COBALTOUS CHLORIDE, $\left[Co(NH_2NH.CO.NH_2)_3\right]Cl_2$, and on this basis the yield obtained was 95%.

Found: sem = 62.87%; Co = 16.05%;

Theory: sem = 63.40%; Co = 16.62%;

Properties :- This compound consists of very small deep pink crystals which are soluble in water to give a red solution. On allowing the aqueous solution to evaporate almost to dryness, trisemicarbazido-cobaltous chloride is again obtained. Fehling's Solution is reduced on the application of heat, and an immediate precipitation of silver chloride is obtained with silver nitrate solution. The complex melts, with the evolution of gas, to a deep blue mass at 224°C.

On storing for three years the colour of this compound has changed very little.

COBALTOUS CHLORIDE MONOHYDRATE WITH SEMICARBAZIDE BASE.

Molecular Ratio 1:3 :- An alcoholic solution containing 3.7 grams (1 mol) of cobaltous chloride monohydrate was added slowly and with stirring to an alcoholic solution of 5.6 grams (3 mols) of semicarbazide base. A bulky bluish-pink product was immediately precipitated. This product was filtered off with suction, and washed thoroughly with alcohol and on drying it in a vacuum desiccator a yield of 7.9 grams of pale rose-pink crystals was obtained.

Empirically, this compound contains semicarbazide and cobalt in the molecular ratio 2.5 : 1, and corresponds either to $\left[Co_2(NH_2NH.CO.NH_2)_5\right]Cl_4.\ 2C_2H_5OH$, or to a mixture of DIALCOHOLATED DISEMICARBAZIDO-COBALTOUS CHLORIDE, $\left[Co(NH_2NH.CO.NH_2)_2\right]Cl_2.2C_2H_5OH$, and TRISEMICARBAZIDO-COBALTOUS CHLORIDE, $\left[Co(NH_2NH.CO.NH_2)_3\right]Cl_2$, and on this basis the yield obtained was 87%.

Found: N= 30.62%; sem=53.20%; Co=16.10%; Cl=18.84%; loss at 110°C=11.85%

Theory; N= 28.89%; sem=51.59%; Co=16.22%; Cl=19.51%; EtOH=12.66%:

Properties:- This compound consists of very small pale rose-pink crystals which dissolve slowly in cold water. On standing for a short time, nitrogen is evolved and hydrazodicarbonamide is deposited. The red solution is alkaline to litmus, and on allowing it to evaporate slowly, small flat red hexagonal crystals of disemicarbazido-cobaltous chloride dihydrate separate. With hot water, the initial decomposition is more vigorous, but the red solution again deposits the flat red hexagonal crystals.

With Fehling's Solution, there is very little reaction in the cold, but on slight heating a light green precipitate is formed, and on boiling, the normal reduction takes place. With insufficient Fehling's Solution, a deep red solution is produced on boiling.

An immediate precipitation of silver chloride is obtained with silver nitrate solution.

If the complex is not completely dried with respect to alcohol, it becomes discoloured blue in patches, however, on completely drying it, either in a vacuum desiccator or by leaving it exposed to the atmosphere, the blue patches disappear and the product becomes homogeneously pale rose-pink.

With concentrated hydrochloric acid the compound turns deep blue; with concentrated sulphuric acid it turns green, and with concentrated nitric acid a deep violet colour is produced. When it is treated with ammonium hydroxide solution, the complex becomes reddish brown in colour.

In the melting point tube, the complex turns white at 217°C; the decomposition begins at 229°C, and finally, fusion, accompanied with the evolution of gas, takes place at 239°C.

The action of heat on this compound was examined on a larger scale. 1.5 grams of the complex were placed in a tube which was closed at one end, the other end consisting of a capillary tube leading into a receiver which was surrounded by ice. On gentle heat being applied the sides of the tube became moist, but on driving this distillate over into the receiver prolonged heating caused further decomposition to occur. The colour changed from pink to violet and vigorous evolution of ammonia gas followed. A white sublimate, which was probably ammonium chloride, condensed on the cooler parts of the tube. On strong heating the evolution of ammonia continued, and the residue in the tube turned deep blue. This residue on cooling, solidified to a deep blue glass.

A few drops of a pink coloured distillate were collected and examined by means of "spot" tests, for water and for alcohol.

The test for water, using anhydrous copper sulphate, was negative, while the test for alcohol by means of hydroxylamine hydrochloride and ferric chloride (Feigl, Qual. Anal.p.250) was definitely positive.

On heating the complex in an open dish for six hours at 110°C, a light brown powder was formed, and the loss in weight was equivalent to two molecules of alcohol. On prolonged heating for seventy-five hours at 140°C, weight was progressively lost and a constant weight was not achieved. After such heat treatment, a pale lilac powder was left which contains both semicarbazide and cobalt in the molecular ratio 2:1, thus indicating that semicarbazide as well as alcohol was lost.

This lilac residue corresponds to anhydrous DISEMICARBAZIDO-COBALTOUS CHLORIDE $\left[Co(NH_2NH.CO.NH_2)_2\right]Cl_2$.

Found: sem = 51.06%; Co = 20.25%:

Theory: sem = 53.59%; Co = 21.07%:

NOTE:- On storing the pale rose-pink crystals for three years, in the case of one sample the colour has changed to light brown, while in another sample the colour has changed to pale lilac.

ETHYLENEDIAMINE ON COMPLEX CONTAINING 2.5 MOLECULES OF SEMICARBAZIDE.

Molecular Ratio 1:1:- 3.2 grams (1 mol) of the complex $[Co_2(NH_2NH.CO.NH_2)_5]Cl_4 2C_2H_5OH$ were dissolved in a small quantity of water and 0.3 grams (1 mol) of ethylenediamine were immediately added. A deep brown solution resulted, and after some time hydrazodicarbonamide was deposited. On removing the hydrazodicarbonamide, and on allowing the filtrate to evaporate slowly, a dark brown glass was obtained, which broke up readily to give a dark reddish brown powder.

This compound is DISEMICARBAZIDO-ETHYLENEDIAMINO-COBALTOUS CHLORIDE MONOHYDRATE, $[Co(sem)_2(en)]Cl_2.H_2O$.

Found:	sem = 39.75%;	Co = 16.26%;	Cl = 20.60%:
Theory:	sem = 41.91%;	Co = 16.46%;	Cl = 19.81%:

Properties:- The compound consists of a dark reddish brown powder, which on heating in the melting point tube increases in volume at 115°C and melts to a reddish brown mass at 140°C. It should be noted that the fused melt is not deep blue in colour.

ETHYLENEDIAMINE ON DISEMICARBAZIDO-COBALTOUS CHLORIDE

Molecular Ratio 1:1 :- 1.4 grams (1 mol) of disemicarbazido-cobaltous chloride were dissolved in fifteen cubic centimetres of cold water and 0.3 grams (1 mol) of ethylenediamine were added. Heat was evolved and a dark brown solution resulted. On allowing this solution to evaporate slowly, hydrazodicarbonamide was deposited in stages. Finally, a dark red glass was obtained which broke up easily to produce a dark reddish-brown powder; the yield obtained was 1.3 grams.

This compound is SEMICARBAZIDO-DIETHYLENEDIAMINO-COBALTOUS CHLORIDE MONOHYDRATE, $[Co(sem)(en)_2]Cl_2.H_2O$.

Found: sem = 21.48%; N = 29.56%; Co = 17.40%:
Theory: sem = 21.88%; N = 28.59%; Co = 17.20%:

Properties:- This compound consists of a dark reddish-brown powder which is insoluble in alcohol. On heating, the complex decomposed with gassing at 113°C, a green melt being obtained.

NOTE:- On attempting to repeat this experiment, a dark reddish-brown powder was isolated which corresponds to DISEMICARBAZIDO-ETHYLENEDIAMINO-COBALTOUS CHLORIDE MONOHYDRATE, $[Co(sem)_2(en)] Cl_2H_2O$.

Found : sem = 35.53%; Co = 16.41%; Cl = 20.86%; N = 32.32%:
Theory: sem = 41.91%; Co = 16.46%; Cl = 19.81%; N = 31.30%:

COBALTOUS CHLORIDE HEXAHYDRATE WITH ACETONE SEMICARBAZONE.

Molecular Ratio 1:2 :- 3.5 grams (1 mol) of Cobaltous Chloride Hexahydrate were dissolved in fifty cubic centimetres of alcohol, and the solution added to one hundred cubic centimetres of alcohol containing 3.4 grams (2 mols) of acetone semicarbazone. Immediately, a bulky precipitate of mauve-coloured crystals separated, a yield of 4.6 grams being obtained.

This compound is BISACETONE-SEMICARBAZONO-COBALTOUS CHLORIDE $[Co((CH_3)_2C{=}N.NH.CO.NH_2)_2]Cl_2$, and the yield obtained on this basis was 87%.

Found: N = 24.07%:
Theory: N = 23.40%:

Properties:- This compound consists of very small mauve-coloured crystals which reduce Fehling's Solution on strong boiling. When heated with dilute hydrochloric acid the odour of acetone may be detected. It fuses to a deep blue mass at 258°C.

COBALTOUS CHLORIDE MONOHYDRATE WITH OTHER SEMICARBAZONES.

The following experiments were entirely of a qualitative nature.

Acetophenone Semicarbazone.

When an alcoholic solution of acetophenone semicarbazone was added to an alcoholic solution of cobaltous chloride monohydrate, the mixed solution retained the deep blue colour of the $[\mathrm{CoCl}_4]''$ ion in alcohol, and no solid was deposited. On standing, crystals of the original semicarbazone separated.

Benzaldehyde Semicarbazone.

When an alcoholic solution of benzaldehyde semicarbazone was added to an alcoholic solution of cobaltous chloride monohydrate no colour change took place and on standing crystals of the original semicarbazone were deposited from the solution.

111.

Complex Compounds of Nickel.

The following reactions were investigated.

NICKELOUS CHLORIDE HEXAHYDRATE WITH SEMICARBAZIDE HYDROCHLORIDE.

Molecular Ratio 1:2 :- 3.9 grams (1 mol) of nickelous chloride hexahydrate were dissolved in alcohol and the solution added to an aqueous-alcoholic solution of 6.7 grams (2 mols) of semicarbazide hydrochloride. The mixed solution was greenish blue in colour, and deposited a yield of 5.0 grams of small green crystals after standing for ten minutes.

This compound is DISEMICARBAZIDO-NICKELOUS CHLORIDE, $\left[Ni(NH_2NH.CO.NH_2)_2\right]Cl_2$.

Found:	N = 27.80%:
Theory:	N = 29.99%:

NICKELOUS CHLORIDE HEXAHYDRATE WITH ACETONE SEMICARBAZONE.

Molecular Ratio 1:2 :- An alcoholic solution of 7.9 grams (2 mols) of acetone semicarbazone were filtered into an alcoholic solution of 3.8 grams (1 mol) of nickelous chloride hexahydrate. As filtration proceeded two distinct layers were formed; a lower layer which was brighter green and an upper layer which was light blue in colour. On mixing, the two layers a green solution was formed, from which a yield of 5.7 grams of a light green product separated, after standing for half an hour.

This compound is BISACETONE-SEMICARBAZONO-NICKELOUS CHLORIDE, $\left[Ni((CH_3)_2\ C{=}N.NH.CO.NH_2)_2\right] Cl_2$.

Found: N = 23.56%:

Theory: N = 23.36%:

PART TWO.

THE INFLUENCE OF SUBSTITUTION IN THE 4-POSITION ON THE CO-ORDINATING PROPERTIES OF SEMICARBAZIDE.

SUMMARY OF THE LITERATURE

COMPLEX COMPOUNDS OF COPPER:- Up to date very little has appeared in the literature with reference to the formation of complex compounds between semicarbazide and its derivatives, and copper salts.

In 1894, Thiele and Stange (Annalen, 283,23) isolated a deep blue compound of copper nitrate with semicarbazide, which they represented as being $2CH_5ON_3 + Cu(NO_3)_2$, and also a sky-blue product with cupric chloride of the type $CH_5ON_3 + CuCl_2$. Both products were very soluble in water, but only very sparingly so in alcohol.

Nothing more was recorded until 1927, when I.V.Hopper (J.R.T.C., 1927, 4,56) prepared compounds of copper chloride with 4-benzyl-semicarbazide hydrochloride and with 4-phenyl-semicarbazide hydrochloride. In the case of 4-benzyl-semicarbazide hydrochloride, two products were obtained, the one being royal blue in colour, and the other olive green. These compounds were represented as being of the type $PhCH_2NH.CO.N(CuCl).NH_2HCl.4\frac{1}{2}H_2O$, differing only in the degree of hydration. In the case of 4-phenyl-semicarbazide hydrochloride, only one product was obtained, which was light green in colour, and this was represented by the formula $PhNH.CO.N(CuCl).NH_2HCl.10H_2O$. At the same time, an olive-green compound was isolated from the interaction of copper chloride and 1-ethyl-4-phenyl-semicarbazide hydrochloride.

In 1936, K.A.Jensen (Z.anorg.Chem.,227,25)prepared a bright blue compound which has the structure $[Cu(PhNH.CO.NHNH_2)_2](NO_3)_2$. This compound was soluble in water, but very difficultly so in alcohol. At the same time he isolated an ultramarine blue powder from the interaction of 1-2-dimethyl-semicarbazide and hydrated copper sulphate, to which he assigned the structure $[Cu(NH_2.CO.N(CH_3).NH(CH_3))_2] SO_4$.

4-SUBSTITUTED-SEMICARBAZIDO-COMPLEXES:- Apart from the complex compounds of copper chloride and of copper nitrate, prepared by Hopper and by Jensen, the only other reference to metallic salt complex formations with 4-substituted-semicarbazides is recorded by Smith (J.C.S.1937,1354), who isolated complex compounds of 4-phenyl-semicarbazide with the salts of iron cobalt, nickel and cadmium.

INTRODUCTION TO EXPERIMENTAL WORK.

At present, a systematic study of the formation of complex compounds between semicarbazide and its derivatives and copper salts, is being carried out by M.M.J.Sutherland and A.B. Crawford, but the results of their work have not, as yet, been published. This paper deals with a section of this work, which was undertaken by the author, with a view to investigating the influence of various substituent groupings in the "4"-position on the co-ordinating ability of the semicarbazide molecule, with particular reference to the complex compounds of copper chloride.

It has been pointed out in Part One of this thesis (p.40), when discussing the work which was carried out by Jensen with regard to the formation of complex nickel compounds with substituted semicarbazides, that substitution in the "4"-position does not, in general, prohibit co-ordination. The work under consideration here, confines itself to a discussion of the influence of various substituent groupings on the nature of the complex compound which is formed.

On reviewing the literature, it is evident that with the exception of the contributions by Hopper, by Jensen and by Smith, this field has not been investigated. A list of the compounds which were prepared by these authors is given in Table IV.

TABLE IV.

Complex	Colour	Authority
$PhCH_2NH.CO.N(CuCl).NH_2HCl.4\frac{1}{2}H_2O$	Royal blue or Olive green	Hopper
$Ph.NH.CO.N(CuCl).NH_2.HCl.10H_2O$	Light green	
$[Cu(4.Ph.sem)2](NO_3)_2$	Blue	Jensen
$[Ni(4.Ph.sem)_3]SO_4$	Blue	Smith
$[Ni(4.Ph.sem)_3]Cl_2$	Blue	
$[Ni(4.Ph.sem)_3](NO_3)_2$	Blue	
$[Co(4.Ph.sem)_3]Cl_2$	Red	
$[Fe(4.Ph.sem)_2]SO_4$	White	
$[Cd(4.Ph.sem)_2]Cl_2$	White	

The author has examined the reactions between cupric chloride and 4-benzyl, 4-phenyl, and 4-methyl semicarbazides, and a list of the compounds which have been isolated by him is given in Table V.

TABLE V.

Complex	Description
$[Cu(4.Ph.sem)_2]Cl_2.H_2O$	Dark green: hexagonal plates
$(4.Ph.sem)_2.CuCl_2.CuCl$	Light green: small needles
$[Cu(4.PhCH_2.sem)_2]Cl_2$	Royal blue:hexagonal plates
$[Cu(4.PhCH_2.sem)_2]Cl_2.H_2O$	Royal blue:hexagonal plates
$(4.PhCH_2.sem)_2.CuCl_2.CuCl$	Green: flat parallelograms
$(4.PhCH_2.sem).CuCl_2.CuCl.(6H_2O?)$	Green: flat parallelograms

DISCUSSION OF EXPERIMENTAL WORK.

I.

Reaction between Cupric Chloride and 4-phenyl-semicarbazide.

In the preliminary examination of this reaction, absolute alcohol was used as the solvent medium.

On adding an alcoholic solution of anhydrous cupric chloride to an alcoholic solution of 4-phenyl-semicarbazide, a light green product was immediately precipitated. This product on standing for a short time, turned brown in colour, but after a further period of twenty-four hours this brown colour vanished, leaving a dark green, apparently homogeneous, substance. The filtrate from this experiment turned deep red in colour on standing for a few days. Similar results were obtained when solid cupric chloride was added to an alcoholic solution of the base, but in this case, evidence of the formation of turquoise blue crystals on the sides of the reaction vessel, was obtained.

When the addition of the reagents was carried out in the opposite order, that is, on adding the alcoholic solution of the base to the alcoholic solution of cupric chloride, there was a slight darkening of the green colour of the solution, but no permanent precipitate was obtained, until a considerable quantity of the base had been added. The product obtained in this case behaved in the same manner as that which has just been described. The filtrate from this experiment did not turn deep red in colour, but as the solution evaporated, long needle-shaped crystals became deposited on the sides of the beaker, those at the top being yellow in colour, while those lower down were turquoise blue.

EXAMINATION OF THE REACTION IN ALCOHOLIC SOLUTION :-

Experiments were carried out on a quantitative basis using one molecule of anhydrous cupric chloride to two molecules of 4-phenyl-semicarbazide,and in this manner, grass-green products were immediately formed which were filtered off, only with difficulty. Filtration was facilitated by heating the precipitates with alcohol, but even after such treatment homogeneous products were not obtained. It should be noted that the washings from these filtrations turned deep red on standing.

Reaction between Cupric Chloride and 4-phenyl-semicarbazide Hydrochloride.

EXAMINATION OF THE REACTION IN ALCOHOLIC SOLUTION :-

Experiments were also carried out in which 4-phenyl-semicarbazide hydrochloride was employed in place of the free base. When the molecular ratio used was one molecule of anhydrous cupric chloride to two molecules of the base-hydrochloride, a dark green solution was obtained, but there was no separation of a solid product until a period of half an hour had elapsed. At the end of this period, a dark green precipitate was formed, and on scratching the sides of the beaker a further yield of a light green product was obtained. The filtrates from these experiments were slightly acid to litmus and reduced Fehling's Solution on the application of heat, thus indicating that they contained an excess of 4-phenyl-semicarbazide hydrochloride, but even on standing, no development of a red colouration was observed, nor were there any indications of the formation of turquoise blue crystals.

The rapidity with which these compounds were precipitated, rendered their purification a matter of some difficulty, and as an examination under the microscope indicated that they were not homogeneous, no attempt was made to carry out their analyses.

The green products remained stable for about a week; they then gradually darkened and after about ten days' time, they appeared to be very dark green, almost black, in colour. The resultant dark green residues were intermingled with white particles. During this decomposition very acrid odours were given off, indicating the presence of phenylisocyanate.

It should also be noted that, whereas, in the case of 4-phenyl-semicarbazide base, the formation of the green compound was spontaneous with the mixing of the solutions, in in the case of the hydrochloride, the presence of the acid apparently retarded the initiation of the reaction. Also, in the case of the hydrochloride, if the mixed solution were shaken, the evolution of gas took place, but if the mixed solution were not agitated no gas was evolved.

EXAMINATION OF THE REACTION IN AQUEOUS SOLUTION :- Several experiments were carried out in aqueous media using various proportions of the reactants.

When the molecular ratio of 4-phenyl-semicarbazide hydrochloride to anhydrous cupric chloride employed, was two to one, a dark green solution was obtained from which dark green crystals were deposited after an interval of from ten to fifteen minutes. On examining this product under the microscope, it was seen to consist of a mixture of hexagonal plates and of small needles, the former definitely predominating. The analysis, which was unsatisfactory since the product was a mixture, indicated that the ratio of copper to 4-phenyl-semicarbazide was approximately one to two. The filtrate from this preparation on further standing deposited a yield of light green crystals which were for the most part small needles mingled with a few of the hexagonal plates.

Similar results were obtained when equimolecular proportions of the reactants were employed.

Ultimately, a separation of the two crystalline forms was achieved by removing the crystals in stages as they were formed, and in this manner two distinct homogeneous products were isolated.

The dark green compound which consists of small hexagonal plates corresponds to bis-4-phenyl-semicarbazido-cupric chloride monohydrate with the structure $\left[Cu(C_6H_5NH.CO.NH.NH_2)_2\right]Cl_2.H_2O$. Cold water wets it with difficulty, but on boiling, solution is effected and acrid odours of phenylisocyanate are evolved; the aqueous solution, even after prolonged boiling is acid to litmus. When the compound is heated with alkali, aniline is liberated, and the copper is reduced to cuprous oxide. It is sparingly soluble in alcohol and completely insoluble in carbon tetrachloride. On heating, the compound turns colourless at 180°C and fuses to a colourless melt at 224°C - 226°C; aniline and phenylisocyanate are products of this decomposition by heat treatment.

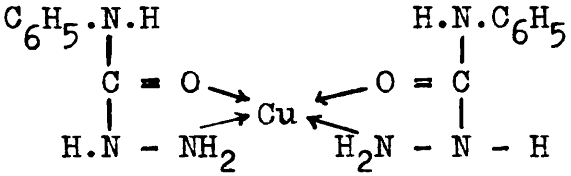
The light green compound, which consists of very small needles, has not as yet been completely characterised. It contains copper in both of its valency states, and empirically, it conforms to the structure, $(C_6H_5NH.CO.NH.NH_2)_2.CuCl_2.CuCl$.

This compound is similar in its behavious to the one which has just been described, and it is decomposed on heating, melting to a colourless mass at 218°C - 220°C.

SUMMARY AND REMARKS:- Two complex compounds of copper chloride with 4-phenyl-semicarbazide have been isolated; bis-4-phenyl-semicarbazido-cupric chloride monohydrate, $\left[Cu(4.Ph.sem)_2\right] Cl_2 H_2O$, and a compound of the type $(4.Ph.sem)_2.CuCl_2CuCl$.

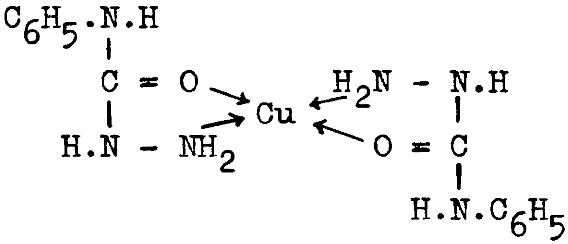
On comparing the dark green compound which has been prepared by the author with the light green compound which was recorded by Hopper (Cf.p.95) it is evident that each of the products has been isolated under similar conditions, but that the latter has been represented as being a compound in which the copper has replaced a hydrogen atom in the semicarbazide molecule. The present author is of the opinion that, as this compound has been isolated from acid solution, replacement of the hydrogen in the semicarbazide molecule is unlikely to take place. In addition, compounds of this type in which the metal atom enters into direct covalent union with the organic molecule, tend, as a rule, to be soluble in organic solvents (Cf. the nickel compounds which were prepared by Jensen - p.39), so that the compound which is under discussion may be more truly represented as being a co-ordination complex.

It is of interest to compare the dark green bis-4-phenyl-semicarbazido-cupric chloride monohydrate with the bright blue bis-4-phenyl-semicarbazido-cupric nitrate which was isolated by Jensen (Cf.p.95), and with the royal blue compound bis-4-benzyl-semicarbazido-cupric chloride which has also been prepared by the author (see under). The discrepancy in colour requires to be explained. It has already been pointed out in the theoretical introduction to this thesis that, in the cupric ion, the four co-ordinate valencies are co-planar, and also that when the central atom is associated with two unsymmetrical chelate groupings, such as 4-substituted-semicarbazides, cis- and trans-isomerism is possible. The variation in the colour of the products which have just been mentioned may probably be accounted for by some such case of isomerism.



$$\begin{array}{lcccr}
C_6H_5.N.H & & & & H.N.C_6H_5 \\
| & & & & | \\
C = O & \searrow & & \swarrow & O = C \\
| & & Cu & & | \\
H.N - NH_2 & \nearrow & & \nwarrow & H_2N - N - H
\end{array}$$

Cis-



$$\begin{array}{lcccr}
C_6H_5.N.H & & & & \\
| & & & & \\
C = O & \searrow & & \swarrow & H_2N - N.H \\
| & & Cu & & | \\
H.N - NH_2 & \nearrow & & \nwarrow & O = C \\
 & & & & | \\
 & & & & H.N.C_6H_5
\end{array}$$

Trans-

Evidence of the formation of a turquoise blue product in the reaction between cupric chloride and 4-phenyl-semicarbazide was recorded in the preliminary investigations which were carried out in alcoholic media, but so far this compound has not been isolated.

The reducing effect of the semicarbazide molecule has again been demonstrated.

II.

Reaction between Cupric Chloride and 4-benzyl-semicarbazide Hydrochloride.

EXAMINATION OF THE REACTION IN ALCOHOLIC SOLUTION :- As an alcoholic solution of one molecule of anhydrous cupric chloride was added to an alcoholic solution of two molecules of 4-benzyl-semicarbazide hydrochloride, the colour of the resultant solution was, to begin with, pale blue, but on the addition of the total amount of the copper solution the final solution was dark green in colour. From this solution a dark green powder separated after an interval of half-an-hour, but this product was unstable, as it rapidly turned yellow, and after fourteen days it had turned very dark green, almost black, in colour. The decomposition was accompanied by the evolution of exceedingly acrid, lachrymatory fumes of the isocyanate type, which were probably due to the presence of benzylisocyanate.

When the addition was carried out in the opposite manner, namely, on adding the solution of the base-hydrochloride to the cupric chloride solution, no blue colour was formed, only a dark green solution resulted, from which, after several hours, a dark green product separated. This product behaved exactly in the same manner as the one which has just been described.

The reaction with the free base was also investigated. In this case the molecular ratio which was employed, was again one to two, and the product which was obtained was bright green in colour. This compound was again very unstable.

In each of these reactions the green product which was obtained decomposed too rapidly for its analysis to be carried out.

EXAMINATION OF THE REACTION IN AQUEOUS SOLUTION :- The course of the reaction in totally aqueous media was also studied.

On the addition of one molecule of cupric chloride to two molecules of 4-benzyl-semicarbazide hydrochloride, a deep blue solution resulted, from which after an interval of a few seconds, royal blue crystals separated. This compound consists of royal blue hexagonal plates and corresponds to bis-4-benzyl-semicarbazido-cupric chloride monohydrate which has the structure $\left[Cu(C_6H_5CH_2.NH.CO.NH.NH_2)_2\right]Cl_2.H_2O$.

When equimolecular proportions were employed, royal blue hexagonal plates of anhydrous bis-4-benzyl-semicarbazido-cupric chloride, $\left[Cu(C_6H_5CH_2.NH.CO.NH.NH_2)_2\right]Cl_2$, were obtained.

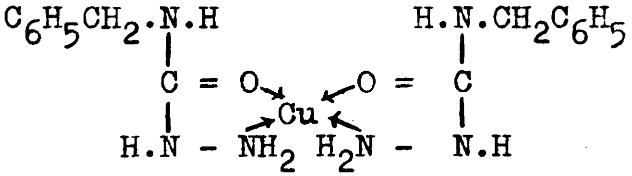
The blue compounds are slowly decomposed by cold water, a white deposit being formed, accompanied by the evolution of gas. The aqueous solution is acid to litmus, and the odour of benzyl-isocyanate may be detected. On boiling with water, the presence of the isocyanate is more marked and the solution becomes more acidic, and as the heating is continued, complete reduction to cuprous oxide ultimately takes place. The white product which is deposited during the decomposition is probably cuprous chloride, as the addition of 4-benzyl-semicarbazide hydrochloride to the partially reduced complex, causes the formation of a green compound to take place. Total reduction of the blue compound may be effected in the cold, by treating it with sodium carbonate solution; again, the acrid odour of the isocyanate is present, but on boiling, the characteristic smell which is associated with amines, is detectable.

Heat also causes the decomposition of the compounds to take place. The anhydrous compound turns green at 87°C, changes to white at 167°C and finally fuses to a colourless melt at 222°C. In the case of the monohydrate, these changes take place at slightly higher temperatures, namely, 95°C, 171°C and 223°C - 226°C.

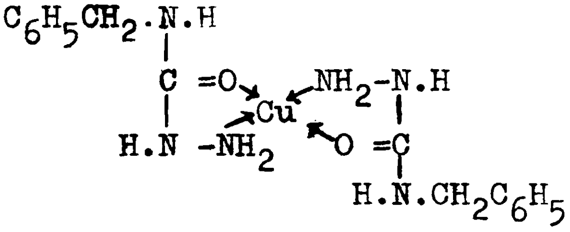
When these compounds are heated under controlled conditions, several stages in the decomposition are observed: first of all, the acrid odour of benzyl isocyanate appears and this is followed by the amine odour along with the evolution of ammonia gas, and on further heating the residue turns black, and a heavy distillate which smells of benzaldehyde is obtained.

When they are treated with cold alcohol, the colours of these compounds change from blue to green and on prolonged heating, gas is evolved and white residues of cuprous chloride are left, while the alcoholic solutions give acid reactions to litmus.

The blue compounds are insoluble in carbon tetrachloride, but on prolonged boiling in this medium, the colour changes from blue to green. However, on cooling the suspensions in carbon tetrachloride, the blue colour reappears. This temporary change in colour from blue to green and back to blue, particularly in the case of the anhydrous product, may be interpreted as being evidence in support of the existence of cis- and trans-isomerides of the following type, although, as yet, the green compound has not been isolated.



Cis-



Trans-

The filtrates from the preparations of the blue compounds were still blue in colour, and on standing they deposited light green products. In each case, this light green product consists of small plates in the form of parallelograms, which very soon decompose with the development of a yellow colour. This compound begins to melt at 110°C and fuses to a dark brown mass at 116°C. The analysis indicates that it contains both cupric and cuprous copper and that it conforms empirically with the formula $(C_6H_5CH_2NH.CO.NH.NH_2).CuCl_2.CuCl(6H_2O?)$.

EXAMINATION OF THE REACTION UNDER VARIOUS CONDITIONS:-

In the Presence of Sodium Acetate :- The mixed solution in water was buffered by the addition of sodium acetate but the royal blue crystals of bis-4-benzyl-semicarbazido-cupric chloride separated out as before.

In the Presence of a High Concentration of Acid :- The effect of the presence of a high concentration of hydrochloric acid was also studied with the aim of promoting oxidising conditions, but this resulted in the co-precipitation of cupric chloride and 4-benzyl-semicarbazide hydrochloride.

In the Presence of Excess Cupric Chloride and Free Copper :- The aim in this case was to promote the formation of the reduced form of the complex compound. A homogeneous green product, consisting of small parallelogrammatic plates, was obtained. This compound remains stable, if it is stored under dry conditions, for about ten days, after which decomposition sets in. The analytical figures indicate that it contains copper in both of its valency states, and that it agrees with the empirical formula $(C_6H_5CH_2NH.CO.NH.NH_2)_2.CuCl_2.CuCl$.

This formula requires a total copper content of 22.55%, and the value which was found is 22.33%. Cuprous copper estimations were carried out on freshly prepared samples of the compound, by means of potentiometric titrations using N/40 potassium dichromate, but although good graphs were obtained, only 4.14% of cuprous copper was found, against the theoretical value of 11.25%. This anomaly has not been explained.

SUMMARY AND REMARKS:- Four complex compounds of copper chloride with 4-benzyl-semicarbazide have been prepared; the anhydrous and monohydrated forms of bis-4-benzyl-semicarbazido-cupric chloride, $[Cu(C_6H_5CH_2NH.CO.NH.NH_2)_2]Cl_2$, which are blue in colour, and two green products which have not as yet been completely characterised, but which both contain cuprous and cupric copper, and which conform to the empirical structures, $(4.PhCH_2.sem).CuCl_2.CuCl.(6H_2O?)$ and $(4.PhCH_2.sem)_2.CuCl_2.CuCl$.

The remarks which have already been made in the previous section (p.102) with reference to the comparison of the compounds which have been recorded by Hopper (Cf.p.95) with the compounds which have been isolated by the author, are also applicable in the case of 4-benzyl-semicarbazido-complexes.

Qualitative evidence of the probable existence of cis- and trans- isomerides of 4-benzyl-semicarbazido-cupric chloride has been obtained, and the reducing nature of the semicarbazide molecule has again been demonstrated.

III.

Reaction between Cupric Chloride and 4-methyl-semicarbazide.

Difficulty has been experienced in procuring a satisfactory method for preparing 4-methyl-semicarbazide. The synthesis which was employed was efficient in procuring a solution of the sulphate, but the attempts to convert this salt to the hydrochloride or to the free base met with little success, very poor yields of these substances being obtained.

A sufficient quantity of 4-methyl-semicarbazide hydro-chloride was obtained to enable qualitative experiments to be carried out, and these indicated that a blue complex, which very quickly changes into a green compound, does exist.

One quantitative experiment was performed in which the molecular ratio of anhydrous cupric chloride to 4-methyl-semicarbazide hydrochloride employed was one to two, and a yield of a pale green powder was obtained from the alcoholic solution. This product is exceedingly unstable, decomposition setting in overnight, even when the sample is stored in a stoppered tube. The decomposition is accompanied with the evolution of fumes of methylisocyanate which are followed by the fumes of methyl carbylamine.

The filtrate from this preparation yielded on standing, a grass-green crystalline product which is apparently more stable.

Neither product has, as yet, been characterised, and further work requires to be performed in this connection.

EXPERIMENTAL SECTION.

I.

Cupric Chloride with 4-phenyl-semicarbazide.

PRELIMINARY EXAMINATION OF THE REACTION IN ALCOHOLIC SOLUTION.

(a) On the addition of one drop of an alcoholic solution of anhydrous cupric chloride to a small quantity of an alcoholic solution of 4-phenyl-semicarbazide, a bulky light green precipitate was immediately formed. This product on standing overnight turned dark brown in colour, but after a further twenty-four hours the brown colour disappeared leaving a dark green, apparently homogeneous substance.

The filtrate, on standing, deposited a brown precipitate, and after an interval of a few days the solution turned deep red in colour. The deposit which had formed on the sides of the beaker was also red in colour.

(b) A second similar experiment was performed, but in this case the alcoholic solution of 4-phenyl-semicarbazide was added to the cupric chloride solution. On the addition of the first few drops, a light green precipitate was formed, which was immediately soluble on shaking to produce a dark green solution. A considerable quantity of the solution of the base required to be added before a permanent bluish green precipitate was obtained. This product turned brown on standing overnight but after a period of twenty-four hours a dark green residue was left.

The filtrate remained green in colour, and after a few days it deposited a very small quantity of a pale yellow solid. The residue which had formed on the sides of the beaker due to evaporation, consisted of long fine needles, those at the top being yellow in colour, while those lower down were turquoise blue.

(c) A third experiment was carried out in which a single crystal of anhydrous cupric chloride was added to a small quantity of an alcoholic solution of 4-phenyl-semicarbazide. On standing, a turquoise blue precipitate was formed. The supernatant liquid turned dark brown in colour and the residue, which was left on the upper sides of the tube due to evaporation, was deep red.

QUANTITATIVE EXAMINATION OF THE REACTION IN ALCOHOLIC SOLUTION.

Molecular Ratio 1:2 :- An alcoholic solution of 0.67 grams (1 mol) of anhydrous cupric chloride was added slowly and with stirring to an alcoholic solution of 1.50 grams (2 mols) of 4-phenyl-semicarbazide. A grass green product was immediately formed, but the solution could not be filtered properly because of the pasty nature of the precipitate. Even on standing for one and a half days in a vacuum desiccator this precipitate was not completely dried. The yield at this stage was 1.8 grams.

The filtrate was colourless, and after a few days it deposited crystals of 4-phenyl-semicarbazide.

An attempt was made to purify the product by boiling it with twenty cubic centimetres of alcohol, but although this treatment facilitated the filtration, the pale green solid which resulted was not homogeneous. The yield at this stage was 1.1 grams.

The filtrate from the attempted purification was yellow in colour, and on standing overnight deposited a further small quantity of the pale green product, but after twenty-four hours the solution had turned deep red in colour and the small green deposit had disappeared.

Cupric Chloride with 4-phenyl-semicarbazide Hydrochloride.

EXAMINATION OF THE REACTION IN ALCOHOLIC SOLUTION.

Molecular Ratio 1:2 :- On adding 0.67 grams (1 mol) of anhydrous cupric chloride dissolved in alcohol, to an alcoholic solution of 1.88 grams (2 mols) of 4-phenyl-semicarbazide hydrochloride, a dark green solution resulted. There was no indication of the evolution of gas unless the flask were shaken. After half an hour a dark green precipitate began to settle on the bottom of the vessel, and after twenty-four hours a yield of 0.2 grams was obtained. On scratching the sides of the containing vessel the filtrate yielded 0.8 grams of a light green product.

These products remained fairly stable when stored in a desiccator. The dark green product after a few days turned reddish brown and at the end of ten days a very dark green almost black powder, mingled with white particles, was left. The light green product behaved similarly, but after ten days the residue appeared to be homogeneous and had a sweetish odour.

The filtrate from the experiment was green in colour and it was slightly acid to litmus. On boiling, the solution turned yellow and became more definitely acidic. It also reduced Fehling's Solution on the application of heat.

NOTE:- A second experiment was carried out in which the solution of 4-phenyl-semicarbazide hydrochloride was added to the cupric chloride solution. The result was similar to that in the above experiment but in this case a single yield of a green product was obtained. This product was a mixture, and it decomposed in a manner similar to the products which have just been described.

EXAMINATION OF THE REACTION IN AQUEOUS SOLUTION.

Molecular Ratio 1:2 :- 0.67 grams (1 mol) of anhydrous cupric chloride were dissolved in twenty cubic centimetres of water and the solution added slowly and with stirring to twenty cubic centimetres of an aqueous solution of 1.88 grams (2 mols) of 4-phenyl-semicarbazide hydrochloride. A dark green solution resulted, from which, after fifteen seconds, a yield of 0.8 grams of dark green crystals was obtained.

This dark green product, when examined under the microscope proved to be a mixture of small hexagonal plates and very small needles, the former predominating. On heating, it turned white at 180°C, and at 215°C a purple colouration appeared on the sides of the melting point tube, well above the solid; the solid began to melt at 217°C, and it finally fused to a pale yellow mass at 219°C.

The analysis of this substance was unsatisfactory as it was a mixture, but in spite of this the analytical figures indicated that the ratio of 4-phenyl-semicarbazide to copper was of the order of 2:1.

Found: N $\doteqdot$ 18%; Cu $\doteqdot$ 12%:

THE FILTRATE on standing for a few days, yielded 0.4 grams of a light green substance which was again a mixture of hexagonal plates and small needles, but in this case the needles predominated.

Molecular Ratio 1:1 :- 1.88 grams (1 mol) of 4-phenylsemicarbazide hydrochloride dissolved in twenty cubic centimetres of water, was added slowly and with stirring to twenty cubic centimetres of an aqueous solution of 1.34 grams (1 mol) of anhydrous cupric chloride. Immediately, from the dark green solution, a yield of 1.45 grams of a bright green crystalline product separated.

This compound is BIS-4-PHENYL-SEMICARBAZIDO-CUPRIC CHLORIDE MONOHYDRATE, $\left[Cu(C_6H_5NH.CO.NH.NH_2)_2\right]Cl_2H_2O$.

Found: N = 18.75%; Cu = 13.90%; Cl = 13.84%:
Theory: N = 18.48%; Cu = 13.98%; Cl = 15.59%:

Properties:- This compound consists of small dark green hexagonal plates which do readily become wet in cold water. Cold water dissolves it slowly and the solution gives a slightly acid reaction with litmus. On boiling, much gas is evolved and phenylisocyanate is liberated, a greenish brown residue being formed. Complete reduction to cuprous oxide takes place when the compound is warmed with aqueous sodium carbonate, and on strong boiling a faint odour of aniline may be detected.

Fehling's Solution is readily reduced, and an immediate precipitation of silver chloride is obtained with silver nitrate solution.

The compound is apparently slightly soluble in alcohol since the solvent becomes pale green in colour and the undissolved residue appears to be almost black. It is insoluble in carbon tetrachloride.

In the melting point tube the green colour changes to white at 180°C and the solid begins to melt at 224°C, fusion to a colourless melt finally taking place at 226°C.

When stored in a stoppered tube, this compound remains stable for about ten days.

NOTE:- The action of heat on this compound was further investigated. A quantity of the blue compound was placed in a tube, closed at one end and provided with a capillary tube leading into a receiver at the other end. On gentle heating, the green colour gave way to black, and a white sublimate and a colourless condensate formed on the cooler portions of the tube. On driving over the sublimate and the condensate into the receiver by further heating, the presence of aniline was noticed, and a few drops of a colourless liquid were collected in the receiver. This colourless liquid evolved the extremely lachrymatory fumes of phenylisocyanate. The black residue in the tube possessed a slight aromatic odour.

THE FILTRATE from the foregoing experiment was green in colour and on standing deposited a small quantity of light green crystals.

This compound contains both cupric and cuprous copper and it conforms empirically to the following formula -

$$(C_6H_5NH.CO.NH.NH_2)_2.CuCl_2.CuCl.$$

Found: $N = 16.37\%$; $Cu = 21.88\%$; $Cl = 19.44\%$:

Theory: $N = 15.70\%$; $Cu = 23.73\%$; $Cl = 19.86\%$:

Properties:- This compound consists of very small light green needle-shaped crystals which turn white at 200°C and melt to a colourless mass over the range 218°C - 220°C.

It reduces Fehling's Solution and gives an immediate precipitation with silver nitrate solution.

On being stored in a stoppered tube it remains stable for about a week to ten days.

II.

Cupric Chloride with 4-benzyl-semicarbazide Hydrochloride.

EXAMINATION OF THE REACTION IN ALCOHOLIC SOLUTION.

Molecular Ratio 1:2 :- On the first addition of an alcoholic solution of 0.67 grams (1 mol) of anhydrous cupric chloride to an alcoholic solution of 2.02 grams (2 mols) of 4-benzyl-semicarbazide hydrochloride, the resultant solution was light blue in colour, but as the addition proceeded the blue colour deepened and then gave way to dark green on the total addition of the copper salt solution. No gas was evolved unless the flask were shaken. After half an hour, a dark green powder began to separate out and after twenty-four hours a total yield of 0.9 grams was obtained.

This product turned yellow on being exposed to the atmosphere for a short time, and on storing it in a stoppered tube for several weeks it developed a very dark green, almost black, colour. This decomposition was accompanied by the evolution of acrid fumes of the isocyanate type - probably benzylisocyanate.

THE FILTRATE from the experiment was green in colour and it gave a slightly acid reaction with litmus, but on boiling, the colour changed to yellow and fumes of benzylisocyanate were given off, while the acidity of the solution increased.

The filtrate also reduced Fehling's Solution on the application of heat.

NOTE:- A similar experiment was carried out in which the solution of 4-benzyl-semicarbazide hydrochloride was added to the cupric chloride solution. In this case, there was no evidence of the appearance of a blue colour, a dark green solution being obtained. After twenty-four hours this solution yielded 0.9 grams of a dark green compound, which turned yellow on exposure to the atmosphere for a short time. On storage, this product behaved exactly in the same manner as the one which has just been described.

EXAMINATION OF THE REACTION OF THE PRESENCE OF ALKALI.

Molecular Ratio 1:2:- An alcoholic solution of 0.67 grams (1 mol) of anhydrous cupric chloride was added to an alcoholic solution of 2.02 grams (2 mols) of 4-benzylsemicarbazide hydrochloride, but in this case the blue colour did not give way to green. To the blue solution, 0.56 grams (2 mols) of potassium hydroxide dissolved in ten cubic centimetres of alcohol, were added, which caused the immediate precipitation of a bright green product, a yield of 1.9 grams being obtained.

This product, which necessarily contained a quantity of precipitated potassium chloride, smelt strongly of benzylisocyanate and it was apparently insoluble in cold water, the supernatant liquid being neutral to litmus. On boiling with water, the isocyanate fumes became more prolific and the green colour disappeared, leaving a yellowish brown insoluble residue; the solution still gave a neutral reaction with litmus.

After two days, the colour of the product changed from green to yellow; the acrid odour was still in evidence but on further standing this gave way to a more pleasant odour, similar to that of unripe apples.

THE FILTRATE from this reaction was pale blue in colour, and on standing overnight it deposited a very small quantity of fine white crystals. The solution, which was acid to litmus, turned almost colourless on boiling, and it also reduced Fehling's Solution on fairly strong heating.

EXAMINATION OF THE REACTION IN AQUEOUS SOLUTION.

Molecular Ratio 1:2 :- 0.67 grams (1 mol) of anhydrous cupric chloride were dissolved in twenty cubic centimetres of water and the solution added slowly to twenty cubic centimetres of an aqueous solution of 2.02 grams (2 mols) of 4-benzyl-semicarbazide hydrochloride. The resultant solution was deep blue in colour and after a few seconds royal blue crystals separated out, a yield of 0.9 grams being obtained.

This compound is BIS-4-BENZYL-SEMICARBAZIDO-CUPRIC CHLORIDE MONOHYDRATE, $[Cu(C_6H_5CH_2NH.CO.NH.NH_2)_2]Cl_2.H_2O$.

Found: N = 17.48%; Cu = 13.39%; Cl = 14.62%:
Theory: N = 17.43%; Cu = 13.17% Cl = 14.70%:

Properties:- This compound consists of small royal blue hexagonal plates which are soluble in water. The aqueous solution soon decomposes, turning green, and gas is evolved. The compound readily reduces Fehling's Solution and gives an immediate precipitation with silver nitrate solution.

In the melting point tube the blue colour changes to green at 95°C, then to white at 171°C and the compound ultimately fuses to a colourless melt at 223°C - 226°C.

When it is stored in a stoppered tube the compound remains stable for several weeks.

THE FILTRATE from this reaction was pale blue in colour and deposited a small quantity of bright green crystals. These crystals were in the shape of small flat parallelograms, and they very soon decomposed, turning yellow. In the melting point tube, they turned darker at 100°C and fused to a dark brown mass at 116°C.

Molecular Ratio 1:1 :- Twenty cubic centimetres of an aqueous solution containing 2.02 grams (1 mol) of 4-benzylsemicarbazide hydrochloride were slowly added to twenty cubic centimetres of an aqueous solution of 1.34 grams (1 mol) of anhydrous cupric chloride. The resultant solution was deep blue in colour, and after thirty seconds a yield of 0.85 grams of royal blue crystals separated out.

This compound is BIS-4-BENZYL-SEMICARBAZIDO-CUPRIC CHLORIDE, $\left[Cu(C_6H_5CH_2NH.CO.NH.NH_2)_2\right] Cl_2$.

Found: N = 18.41%; Cu = 13.68%; Cl = 15.09%:
Theory: N = 18.10%; Cu = 13.69%; Cl = 15.26%:

Properties:- This compound consists of small royal blue hexagonal plates. In cold water slight gassing takes place and a small white deposit is formed; the solution is acid to litmus and a faint odour of benzylisocyanate may be detected. On heating the aqueous solution, this acrid odour becomes more marked and a white deposit is again formed, but on continued heating the reduction goes completely to cuprous oxide. The solution is again acid to litmus. When a small quantity of 4-benzyl-semicarbazide hydrochloride is added to the partially reduced complex, a green product is formed, which indicates that the small white deposit may probably be cuprous chloride.

With cold aqueous sodium carbonate, a small white deposit is again obtained and the presence of benzylisocyanate is detected; complete reduction of the complex is almost effected in the cold, red cuprous oxide being deposited on the application of very little heat. On boiling this suspension, a strong odour, similar to that which is associated with amines, is given off.

Fehling's Solution is readily reduced, and an immediate precipitate of silver chloride is obtained with silver nitrate solution.

In the melting point tube the blue colour gives way to green at 87°C, and at 167°C the compound turns white; fusion begins at 219°C and is completed at 222°C, a colourless melt being formed.

The compound is insoluble in cold alcohol, but slight gassing takes place and the colour changes from blue to green. The alcohol is neutral to litmus, but on boiling, the green colour of the solid is discharged and a white insoluble residue is formed. The supernatant liquid is now acid to litmus and on cooling, a pale green bulky precipitate settles out.

When the blue compound is boiled with carbon tetrachloride, solution is not effected, but the blue colour of the solid changes to green and on cooling, the original blue colour reappears.

THE FILTRATE from the foregoing experiment was pale blue in colour and on standing, it deposited a yield of 0.9 grams of light green crystals.

This compound has not been fully characterised, but it conforms empirically to the following structure, $(C_6H_5CH_2NH.CO.NH.NH_2).\ CuCl_2.\ CuCl.(6H_2O?)$.

Found: $N = 8.37\%$; $Cu = 25.27\%$; $Cl = 20.67\%$:

Theory: $N = 8.30\%$; $Cu = 25.09\%$; $Cl = 21.00\%$:

<u>Properties:-</u> This compound consists of light green parallelogrammatic plates. In the melting point tube it darkens in colour at 97°C and the first indication of fusion occurs at 117°C, a black melt being finally obtained at 123°C.

EXAMINATION OF THE REACTION UNDER VARIOUS CONDITIONS.

In the Presence of Sodium Acetate.

Molecular Ratio 1:2 :- Fifteen cubic centimetres of an aqueous solution containing 0.67 grams (1 mol) of anhydrous cupric chloride were added to twenty cubic centimetres of an aqueous solution of 2.02 grams (2 mols) of 4-benzyl-semicarbazide hydrochloride and to the deep blue resultant solution ten cubic centimetres of an aqueous solution of 2.0 grams of anhydrous sodium acetate were added. This resulted in a deepening of the blue colour and after a period of thirty seconds, 1.0 grams of the royal blue crystals of bis-4-benzyl-semicarbazido-cupric chloride separated out.

In the Presence of an Excess of Hydrochloric Acid.

On examining, in a qualitative manner, the effect of excess hydrochloric acid on the action of 4-benzyl-semicarbazide hydrochloride on cupric chloride, both before and after mixing the aqueous solutions, green products were formed instead of blue. These products appeared to be homogeneous, consisting of very small needles arranged in starlike clusters.

(Note:- A corresponding result was obtained when the acidification was carried out by means of glacial acetic acid).

The reaction was also examined quantitatively, in the following manner.

To thirty-five cubic centimetres of a deep blue aqueous solution containing 0.67 grams (1 mol) of cupric chloride and 2.02 grams (2 mols) of 4-benzyl-semicarbazide hydrochloride, ten cubic centimetres of concentrated hydrochloric acid were slowly added. The deep blue colour of the solution remained until eight cubic centimetres of the acid had been added, but on the addition of the remainder of the acid the solution turned bright green in colour. On scratching the sides of the vessel a yield of 1.75 grams of a bulky bright green product was obtained.

This product consisted of long colourless plates mixed with green coloured conglomerates and on standing exposed to the atmosphere the green particles were deliquescent; after a few days the whole mass turned yellow.

When the bright green product was treated with a small quantity of water, blue crystals very similar to bis-4-benxyl-semicarbazido-cupric chloride, were formed, which indicated that the green product was probably a mixture of cupric chloride and 4-benzyl-semicarbazide hydrochloride, co-precipitated in the ratio 1:2 by the concentrated hydrochloric acid, due to the common ion effect.

In the Presence of Free Copper.

Molecular Ratio 1:2 :- The reaction was carried out in the presence of free copper in an endeavour to promote the formation of a complex compound containing copper in its lower valency state.

Ten cubic centimetres of an aqueous solution of 0.67 grams (1 mol) of cupric chloride were added to fifteen cubic centimetres of an aqueous solution of 2.02 grams (2 mols) of 4-benzyl-semicarbazide hydrochloride and to the resultant deep blue solution a piece of freshly cleaned copper foil was immediately added. After thirty seconds, royal blue crystals were formed, but these were not removed, being left in suspension in contact with the copper foil. At the end of three days the crystals had turned green, a yield of 0.4 grams being obtained.

A further yield of green crystals was obtained by adding 0.5 grams of anhydrous cupric chloride to the peacock blue filtrate from the above reaction; this yield, at the end of two days, amounted to 0.9 grams.

The total yield of green crystals obtained after five days was 1.3 grams.

This compound consisted of light green plates in the form of parallelograms and it decomposed after ten days. On decomposing it turned yellow and gave off acrid fumes of benzylisocyanate.

Molecular Ratio 1:1 :- In the above experiment the formation of the reduced compound was carried out at the expense of the copper in the blue cupric compound and consequently the yield of the reduced compound was impaired. The experiment was therefore repeated using a larger proportion of cupric chloride.

The experiment was carried out in exactly the same manner as the above experiment using 1.34 grams (1 mol) of anhydrous cupric chloride and 2.02 grams (1 mol) of 4-benzylsemicarbazide hydrochloride. The blue crystals formed after thirty seconds, as before, but the conversion to the green compound was more rapid, taking place in two days. The yield of green crystals obtained was 1.5 grams.

This compound contains both cupric and cuprous copper and it conforms to the empirical formula,

$(C_6H_5CH_2NH.CO.NH.NH_2)_2.\ CuCl_2CuCl.$

Found: N = 15.31%; Cu(total) = 22.33%; Cu(ous)=4.14%; Cl=18.57%:
Theory: N = 14.92%; Cu(total) = 22.55%; Cu(ous)=11.25%;Cl=18.88%:

NOTE:- The cuprous copper was estimated by the potentiometric titration method using N/40 potassium dichromate and except for this result the figures are in good agreement.

Properties:- This compound consists of small green plates in the shape of parallelograms. It reduces Fehling's Solution and gives an immediate precipitate with silver nitrate solution.

This compound remains stable for about ten days after which it turns yellow; the decomposition is accompanied by the evolution of fumes of benzylisocyanate.

III.

Cupric Chloride with 4-methyl-semicarbazide Hydrochloride.

On the addition of a small amount of solid 4-methyl-semicarbazide hydrochloride to an alcoholic solution of anhydrous cupric chloride, a deep blue product was formed which rapidly turned light green in colour.

Molecular Ratio 1:2 :- 0.75 grams (2 mols) of 4-methyl-semicarbazide sulphate were suspended in ten cubic centimetres of alcohol and the suspension titrated with an alcoholic solution of potassium hydroxide until the solution was just permanently alkaline to litmus, used as an external indicator. The solution was then made faintly acid by the addition of a few drops of dilute hydrochloric acid and after standing for sixteen hours, the precipitated potassium sulphate was filtered off. To the filtrate, ten cubic centimetres of an alcoholic solution of 0.27 grams (1 mol) of anhydrous cupric chloride were added. This resulted in the formation of a peacock blue solution from which almost immediately, a yield of 0.12 grams of a pale green finely divided product was precipitated.

This product was placed in a stoppered sample bottle but it decomposed overnight turning dark green and smelling strongly of methylisocyanate. After one more day it had turned almost brown in colour and the odour of isocyanate had given way to that of methyl carbylamine.

Due to the rapidity with which this compound decomposed a complete analysis was unable to be carried out.

THE FILTRATE from the above experiment was peacock blue in colour and after standing for several hours it deposited a very small quantity of a grass green product.

This compound consists of very small diamond-shaped crystals and it remains stable for several days when it is stored in a desiccator over calcium chloride.

GENERAL SUMMARY

PART ONE

Complex compounds of the chlorides of iron, cobalt and nickel with semicarbazide have been prepared in which one atom of the metal becomes associated with either two molecules, or with three molecules of the base.

Compounds of the chlorides of iron, cobalt and nickel have been prepared containing two molecules of acetone semicarbazone, but so far compounds containing three molecules of acetone semicarbazone have not been isolated.

Methyl-ethyl-ketone semicarbazone, benzophenone semicarbazone and benzaldehyde semicarbazone apparently do not enter into complex formation with the chlorides of iron cobalt and nickel.

A compound has also been prepared in which one atom of cobalt is associated with two and a half molecules of semicarbazide, but sufficient evidence is not, as yet, forthcoming to determine whether this is a polynuclear compound, or whether it is a statistical mixture of disemicarbazido-cobaltous chloride and trisemicarbazido-chloride.

Two compounds of cobaltous chloride containing both semicarbazide and ethylenediamine have been isolated; the one contains two molecules of semicarbazide and one molecule of ethylenediamine, while the other contains one molecule of semicarbazide and two molecules of ethylenediamine.

The complex compounds of iron, cobalt and nickel which have been isolated all contain the metals in their divalent state even although, as in the case of iron, the salt of the triadic metal was employed in their formation.

The above compounds have been listed in Table III (p.44)

PART TWO

Complex compounds of cupric chloride with 4-benzyl-semicarbazide and with 4-phenyl-semicarbazide have been isolated and evidence has been obtained that similar compounds have been formed with 4-methyl-semicarbazide, but due to their great instability the latter have not been characterised. In the compounds of 4-benzyl, and of 4-phenyl-semicarbazide, the metal atom is associated with two molecules of the base.

Qualitative evidence is forthcoming that cis- and trans-isomerides of bis-4-benzylsemicarbazido-cupric chloride and of bis-4-phenyl-semicarbazido cupric chloride may exist.

Two green compounds have been formed, one with 4-benzyl-semicarbazide, and one with 4-phenyl-semicarbazide, which contain both cuprous and cupric copper and which conform empirically to the structures $(4.PhCH_2sem)_2CuCl_2.CuCl.$ and

$(4.Phsem)_2CuCl_2.CuCl$. They are both crystalline compounds and their crystalline forms differ from those of the cupric compounds already mentioned.

One other compound which has not been reconciled with theoretical conceptions has been isolated, and it is empirically represented by the formula $(4.PhCH_2sem).CuCl_2.CuCl.(6H_2O?)$.

The stabilities of all these copper compounds progressively decrease as the substituent group changes from benzyl to phenyl and then to methyl. Aryl or alkyl isocyanates appear among the decomposition products, and in the case of the compounds of 4-methyl-semicarbazide the methyl isocyanate is further reduced to methyl carbylamine.

The above compounds have been listed in Table V (p.96).

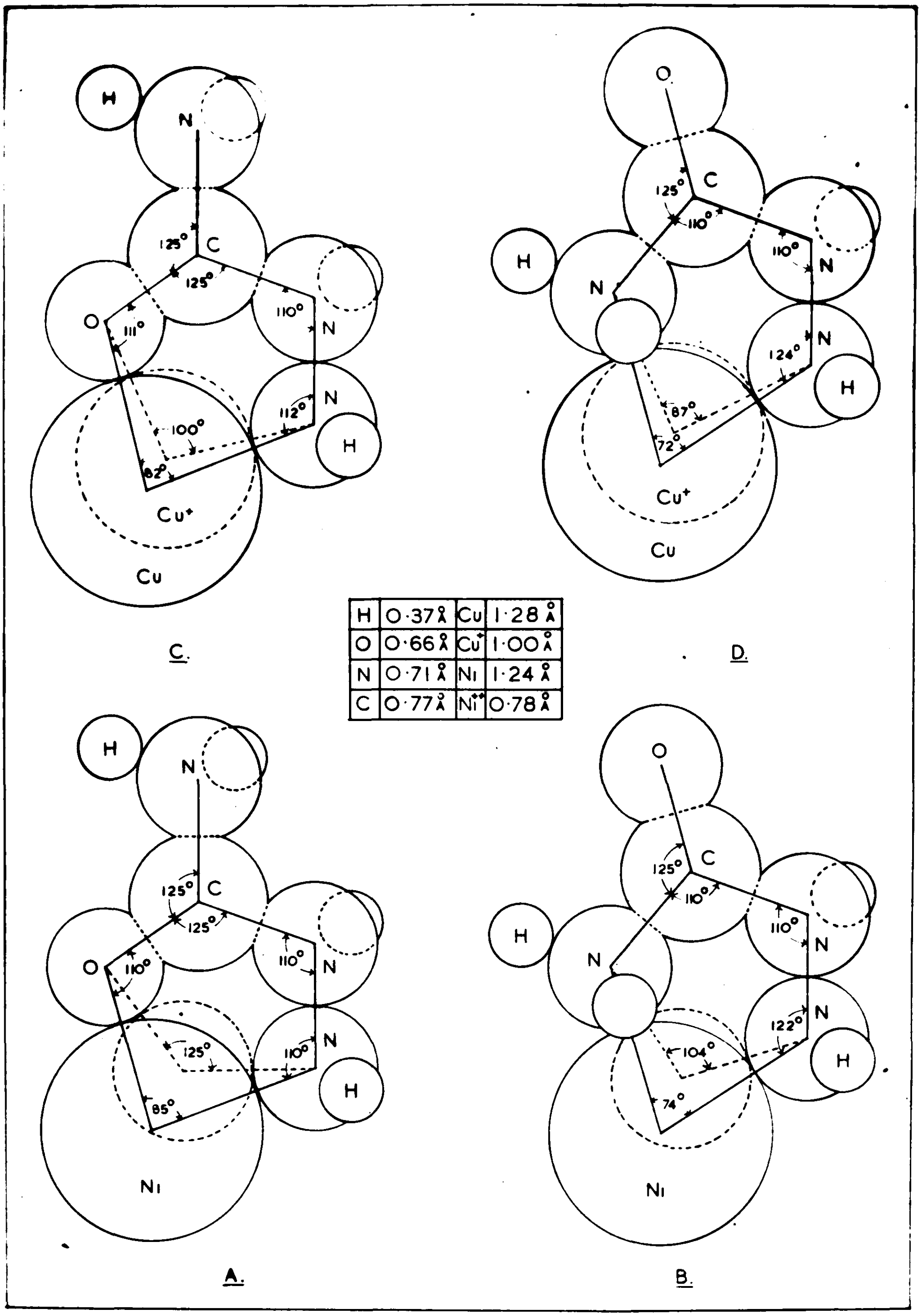
CONCLUSIONS

Semicarbazide as a Co-ordinating Molecule.

On examining the compounds of iron, cobalt, nickel and copper which have been prepared, it is evident that in the case of a central atom which may possess a co-ordination number of either four or six, the number of semicarbazide molecules which become associated with this central atom is either two or three. It follows therefore, that the organic radical possesses two positions at which co-ordination may be effected.

The fact that methyl-ethyl-ketone semicarbazone, benzophenone semicarbazone and benzaldehyde semicarbazone do not enter into complex formation with metallic salts, indicates that substitution at the No. 1 nitrogen atom prohibits co-ordination, and consequently, it is this nitrogen atom which enters into the mechanism of the linkage. However, that compounds containing acetone semicarbazone have been isolated, suggests that in the case of the semicarbazones stearic hindrance effects may govern the ability of the No.1 nitrogen atom to form a co-ordinate bond.

On the other hand, an examination of the copper compounds which have been prepared, shows that substitution in the "4" position does not prohibit the formation of a complex compound, and this indicates that the No.4 nitrogen atom does not enter into the mechanism of the linkage.



H	0·37 Å	Cu	1·28 Å
O	0·66 Å	Cu^+	1·00 Å
N	0·71 Å	Ni	1·24 Å
C	0·77 Å	Ni^{++}	0·78 Å

FIG I METALLIC ATOMS AND IONS IN POSITION IN THE ALTERNATIVE FORMS OF THE SEMICARBAZIDE MOLECULE.

The evidence which has just been discussed serves to support the structural formula which has been put forward by Jensen (p.37), in which the semicarbazide molecule is represented as effecting co-ordination through the No.1 nitrogen atom and through the oxygen atom.

The alternative spatial arrangements of the atoms in the semicarbazide molecule with relation to the nickelous atom and the nickelous ion, are represented diagrammatically in Figures 1A and 1B.

In the diagrams, the semicarbazide molecule is assumed to be built up from hydrazine and urea. The distance between the No.1 nitrogen atom and the No.2 nitrogen atom is assumed to be twice the atomic radius of nitrogen, and the value of the NNC angle (110°) is that of the nitrogen valency angle in hydrazine, found by Penney and Sutherland (Trans.Faraday Soc., 1934,30,898; J.Chem.Physics, 1934, 2, 492). The values employed for the C-N distance (1.37Å) and for the C=O distance (1.25Å) are those found for the corresponding linkages in urea by Wyckoff and Corey (Z.Krist.1934,89,462; Cf.Reinicke, ibid.,1935,87,417), while the value 125° for the angle N-C=O is that of the angle C-C=O in acetone and in acetophenone recorded by Groves and Sugden (J.C.S.,1937,1995). The values used for the atomic and ionic radii are those given by Sidgwick (Covalent Link in Chemistry, 1933,83-85).

In the diagrams the atoms are represented as being in one plane which is not strictly true, but suffices for illustrative purposes. The overlap of the carbon and oxygen atoms is due to the presence of the double bond, and the shortening of the C-N distance is probably accounted for by the resonance of this double bond round the carbon atom.

Co-ordination between the No.1 Nitrogen Atom and the Oxygen Atom - Fig. 1A :- In Fig.1A the nickel atom and the nickelous ion are shown in position in the case where co-ordination takes place between the oxygen atom and the No.1 nitrogen atom, and the resultant valency angles are recorded. It has been pointed out earlier in this paper that the nickel valencies are directed towards the corners of a square, so that the nickel valency angle should be 90°. In the diagram it is seen that the nickel valency angle in the case of the nickel atom is 85°, and the Ni-N-N angle is 110° thus indicating that there is room for a nickel atom in this position, without any great distortion of the valency angles resulting.

In the case of the nickel ion, on the other hand, considerable distortion of the valency angles takes place. In any case, the mechanism of the co-ordinate bond implies the donation of electrons to the metallic ion, by virtue of which, the effective radius of the ion becomes increased, so that the diagram showing the nickel atom in position is in all probability the truer picture.

Co-ordination between the No.1 Nitrogen Atom and the No.4 Nitrogen Atom - Fig.1B :- Fig.1B represents the semicarbazide molecule built up in the alternative manner, in which the No.1 nitrogen atom and the No.4 nitrogen atom are in adjacent positions. Again, the nickel atom and the nickelous ion are shown in position, but in this case the valency angle of the nickel atom is reduced to 74°C, while that of the No.1 nitrogen atom is increased from 110° to 122°, and that of the No.4 nitrogen atom is increased to 124°. It is evident therefore, that for co-ordination to take place through the nitrogen atoms, considerable strain requires to be exerted on the valency angles of the atoms concerned.

From this theoretical consideration of the configuration of the semicarbazide molecule, it is perhaps permissible to anticipate that co-ordination of semicarbazide with the metal is effected through the No.1 nitrogen atom and through the oxygen atom, rather than through the nitrogen atoms in the 1-4 positions.

Fig. 1C and Fig.1D show the corresponding diagrams with the copper atom and the cuprous ion in position, and again, Fig.1C illustrates the configuration in which the strain on the valency angles is at a minimum.

Nature of the Complex Compounds.

The complex compounds of the chlorides of iron, cobalt and nickel are definitely crystalline and tend to be unstable in the presence of water.

There has been no fundamental colour change in any of the compounds, such as might be expected to result from the formation of the "penetration" type of complex of Biltz, or such as might be associated with the formation of covalent bonds. For example, the $[CoCl_4]''$ ion is deep blue in colour, and in this ion the cobalt atom is surrounded by four covalent bonds, so that by analogy, the disemicarbazido-cobaltous ion might also be expected to be blue in colour, if the bonds are of the covalent type. In actual fact, the disemicarbazido-cobaltous compounds are coloured in various shades of pink which do vary fundamentally from the colour of the hydrated cobaltous ion.

Hill and Howell (Ann.Reports Ch.Soc., 1927,24,288) have advanced the general theory, which has been confirmed by Howell and Jackson (J.C.S.,1937,621), that the colour of cobaltous compounds is determined by the number of groups which are associated with the central cobalt atom; with six groups the colour of the ion is red, while with four groups the colour of the ion is blue. On this basis, it might be argued that the disemicarbazido-cobaltous chloride compound which is associated with two molecules of water is actually the diaquo-compound, but again the anhydrous compound should be blue in colour.

Similarly, in the case of the disemicarbazido-ferrous ion and of the disemicarbazido-nickelous ion, there is no fundamental colour change.

On the other hand, the intensification of the colour to chocolate brown, which occurs as the semicarbazide molecules in the cobaltous chloride compounds are replaced by ethylenediamine molecules, may be interpreted as indicating that in the case of the ethylenediamine molecule the co-ordinate bonds are tending to be of the covalent type.

The displacement of semicarbazide by ethylenediamine suggests that the latter has the greater co-ordinating ability. This may well be due to the fact that in the case of ethylenediamine the co-ordinating bonds are effected through the extreme nitrogen atoms of a linear molecule, whereas, in the case of semicarbazide the union is effected in one instance through an oxygen atom which is doubly linked to the main molecule.

Reducing Effect of the Semicarbazide Molecule.

It has been pointed out earlier in this paper that in the case of the cobalt atom it is, as a rule and particularly in the case of the compounds containing ethylenediamine, the trivalent state of the metal which is stabilised by co-ordination, and Pauling has shown theoretically that this is due to the loss of the electron which has been promoted to an outer orbit, to allow for hybridisation to take place. The fact that this oxidation does not occur in the semicarbazido-complexes of cobalt may mean one of two things; firstly, that hybridisation has taken place and the single electron has been promoted, but that the reducing nature of the semicarbazide molecule has prevented the migration of this electron, or secondly, that hybridisation has not taken place and the semicarbazide molecules are held loosely to the central cobalt atom by electrostatic attraction.

From the above discussion of the appearance of the products and on considering their comparative instability in water, the second explanation seems to be the more fitting.

The reducing effect of the semicarbazide molecule is further demonstrated by the formation of the ferrous complex compounds from ferric chloride and by the formation of the cupro-cupric compounds.

In the absence of physical measurements, facilities for which have not been available, it is inadvisable to attempt an ultimate classification of these complex compounds of semi-carbazide, but the general and theoretical considerations which have been discussed seem to indicate that they belong to the "normal" type of compound, in the classification of Biltz.

Influence of Substituents in the "4" Position.

Substitution in the "4" position does not prevent the formation of complex compounds between semicarbazide and cupric chloride, but the nature of the substituent group influences the stability of the resultant complex. The stability of the compound decreases as the substituent group passes from the benzyl radical to the phenyl radical, and then to the methyl radical.

APPENDICES.

APPENDIX A.

Methods of Analysis.

IRON:- In the case of the iron complex compounds, the iron was precipitated directly as ferric hydroxide after destroying the organic portion of the molecule by boiling the aqueous solution with concentrated nitric acid. The precipitated ferric hydroxide was dissolved in hydrochloric acid and the iron content of this solution estimated in the usual manner by means of decinormal potassium dichromate, using diphenylamine as the internal indicator.

COBALT:- In the preliminary estimations of cobalt the organic portion of the molecule was destroyed by igniting a weighed quantity of the compound with concentrated nitric acid. As the solution was taken to dryness, the residue became incandescent and a series of small explosions resulted, a second ignition with nitric acid being required before complete solution of the residue in sulphuric acid could be obtained. The solution of cobalt sulphate was then made strongly ammoniacal with ammonium hydroxide (sp.g. 0.88) and electrolysed using platinum electrodes. A current of 0.3 amperes - 0.5 amperes, from a twelve volt source, was passed through the solution for periods varying from two to three hours. The results obtained in this manner were low and inconsistent due to loss of cobalt oxide during the initial ignition.

Consistent and accurate results were obtained by depositing the cobalt directly from an ammoniacal solution of the complex compound. The period of electrolysis varied from one and a half to two hours, and its completion was indicated by treating one drop of the electrolyte with a small quantity of ammonium sulphide solution.

COPPER:- On applying the electro-deposition method to the compounds of copper with 4-substituted-semicarbazides, the copper could not be completely removed from the solution without first of all destroying the organic portion of the molecule. This was best achieved by digesting a weighed quantity of the substance with concentrated nitric acid on the water-bath for one hour, followed by a further hour's treatment with concentrated sulphuric acid. Throughout this procedure the solution was not allowed to go to dryness. The solution of copper sulphate was then diluted to two hundred cubic centimetres and ten cubic centimetres of concentrated nitric acid added, after which the electrolysis was carried out for a period of two hours, using platinum electrodes, and a current of 1.5 amperes, from a twelve volt source. The completion of the electrolysis was indicated by means of ammonium sulphide. At the end of the electrolysis solid urea was added to the electrolyte to destroy the free nitrous acid and the cathode was removed before cutting off the current.

NOTE:- In the electro-deposition of cobalt and of copper a rotating anode was employed. In the case of the cobalt estimation, the cathode used weighed fifteen grams which necessitated the use of five-hundred milligrams of the complex compound, but in the case of the copper estimation the cathode used weighed only two grams which allowed the amount of material to be cut down to one hundred milligrams.

CUPROUS COPPER:- The estimation of cuprous copper in the compound $(C_6H_5CH_2NH.CO.NH.NH_2)_2.CuCl_2.CuCl$, was carried out by means of potentiometric titrations. The amount of freshly prepared material used, was of the order of one hundred milligrams, and the titration was carried out by means of N/40 potassium dichromate, precautions being taken throughout the experiment to exclude the air by passing a continuous stream of carbon dioxide through the solution. Good graphs were obtained and the figure for the cuprous copper was calculated from the differential curves.

CHLORINE:- In each case the organic portion of the complex compound was destroyed by boiling a weighed quantity with dilute nitric acid. The chloride was then precipitated as silver chloride by the addition of an excess of standard silver nitrate solution and on the removal of the precipitate the excess of silver nitrate was titrated against standard decinormal ammonium thiocyanate solution, using ferric alum as the indicator.

In the case of the compounds of iron, the chloride was estimated in the filtrate from the precipitation of the ferric hydroxide.

SEMICARBAZIDE:- In the case of the complex compounds of iron and of cobalt the semicarbazide was estimated directly by the method described by G.S.Smith (J.C.S.,1937,1325) using potassium iodate and sodium thiosulphate. About one hundred milligrams of the compound were dissolved or suspended in 20 c.cs. of water contained in a bottle fitted with a ground glass stopper. To this solution, 20 c.cs. of 5N sulphuric acid were added followed by 50 c.cs. of M/60 potassium iodate. The bottle was then stoppered and the contents shaken at intervals during a period of five minutes, after which an excess of potassium iodide was added, and the total iodine liberated immediately titrated against N/10 sodium thiosulphate. From the difference between the amount of thiosulphate equivalent to the total volume of iodate added, and the amount of thiosulphate used in the titration, the semicarbazide content of the solution was calculated - one cubic centimetre of N/10 thiosulphate being equivalent to 0.001877 grams of semicarbazide.

NITROGEN:- In the earlier estimations of nitrogen the large scale method of Dumas was employed in which the amount of material used was of the order of two hundred milligrams, but latterly, and particularly in the case of the complex compounds of copper, the hemi-macro modification of this method in which the amount of material used is of the order of thirty milligrams, was employed.

APPENDIX B.

Preparation of 4-substituted-semicarbazides.

4-phenyl-semicarbazide Hydrochloride:- This preparation was carried out exactly in the manner which has been described by I.V.Hopper (J.R.T.C. 1927,4,53). Equimolecular quantities of aniline and finely powdered acetone semicarbazone were refluxed together at 140°C for a period of one hour, until the first evolution of ammonia had ceased. The product was then cooled and mixed with an equal volume of alcohol and the mixture poured into 600 c.cs. of cold water. The precipitated acetone 4-phenyl-semicarbazone was collected and hydrolysed by boiling with 22 ccs. of concentrated hydrochloric acid and 120 ccs. of water for thirty minutes. The impurities were filtered off and the 4-phenyl-semicarbazide hydrochloride was recovered from the filtrate by concentrating the solution under vacuum.

The hydrochloride melted at 215°C.

The free base was prepared by treating a concentrated aqueous solution of the hydrochloride with sodium carbonate until the solution was faintly alkaline, and the precipitated base was recrystallised from water, under vacuum.

The free base melted at 125°C.

4-benzyl-semicarbazide Hydrochloride:- This preparation was carried out on similar lines to the above. (Hopper,J.R.T.C., 1927,4,50). Equimolecular quantities of benzylamine and finely powdered acetone semicarbazone were refluxed together at 138°C for a period of half an hour. The precipitated acetone 4-benzyl-semicarbazone was collected and hydrolysed, and the 4-benzyl-semicarbazide hydrochloride isolated as before.

The melting point of the hydrochloride was 225°C.

4-methyl-semicarbazide Hydrochloride:- No satisfactory method has as yet, been obtained for the preparation of 4-methyl-semicarbazide hydrochloride. Attempts were made to prepare the semicarbazide by the electrolytic reduction of symmetrical nitro-methylurea along the lines of the method recorded by H.J.Backer (Rec.Trav.Chim.,1915, 34,187), but although yields of benzaldehyde 4-methyl-semicarbazone were obtained, the conversion of this product either to the base or the hydrochloride, met with very little success.

45 grams of methylurea nitrate were converted into symmetrical nitro-methylurea in the following manner.

15 grams of powdered methylurea nitrate were added in small quantities to 50 c.cs. of concentrated sulphuric acid, cooled to -15°C and rapidly agitated by means of a mechanical stirrer. When the addition was finished, after 20 minutes, the stirring was allowed to proceed for a further 10 minutes,

without allowing the temperature to rise; the liquid was then poured on to a mixture of 100 grams of ice and 150 grams of crystalline sodium carbonate. The mixture, which was still acid, was then filtered with suction and the filtrate extracted several times with ethyl acetate. The solid portion was also shaken up with this ethyl acetate extract to dissolve any nitrated product which it might have contained, after which the extract was dried over anhydrous sodium sulphate. The ethyl acetate was removed by vacuum distillation and the symmetrical nitro-methylurea separated by fractional crystallisation. In this manner a yield of 8 grams of symmetrical nitro-methylurea was obtained from the 45 grams of methylurea nitrate. This compound melted at 159°C.

It is of interest to note that the mother liquor from the crystallisation, yielded long thin needles of a substance which melted at 35°C - this was probably the unsymmetrical isomer, which however was not isolated by Backer.

Reduction of symmetrical nitro-methylurea:- The reduction was carried out electrolytically using a cathode of copper gauze (area = 120 sq. cms.) and a lead anode; the anode was kept cool throughout the reaction by passing cold water through it. The cathode liquor consisted of 40 ccs. of 5% sulphuric acid and the anode liquor, which was placed in the porous pot, consisted of 10% sulphuric acid, and the whole reaction vessel was immersed in ice. The current was maintained at 2 amperes for a period of 80 minutes and during this time 2 grams of finely powdered symmetrical nitro-methylurea was added in small quantities.

After the passage of the theoretical quantity of electricity (161 amp/mins), the sulphuric acid was almost neutralised with sodium carbonate and an alcoholic solution of benzaldehyde added, whereupon the condensation product separated.

From the 8 grams of symmetrical nitro-methylurea 5 grams of long white needles melting at 166°C, of benzaldehyde 4-methyl-semicarbazone were obtained.

The semicarbazone was hydrolysed with 20% sulphuric acid and the solution then neutralised with sodium carbonate, after which the solution was taken to dryness on the water-bath. On extracting the residue with benzene a yield of 0.5 grams of small colourless rods melting at 118°C was obtained. This product was 4-methyl-semicarbazide.

NOTE:- In a subsequent preparation on concentrating the sulphuric acid solutions obtained after the reductions, a total yield of 2.25 grams of 4-methyl-semicarbazide sulphate was obtained. This product melted at 195°C.

APPENDIX C.

Note on the Development of the Red Colouration in the Reaction between Semicarbazide Hydrochloride and Potassium Ferrocyanide.

In the introduction to this thesis it has been stated that the starting point of this work was the observation by A.B.Crawford of the development of a red colouration when semicarbazide was allowed to react with potassium ferrocyanide.

Before embarking on a systemmatic study of the action of inorganic salts on semicarbazide, the author spent some time in attempting to isolate the red intermediate product in the ferrocyanide reaction.

When an aqueous solution containing equimolecular quantities of potassium ferrocyanide and semicarbazide hydrochloride is gently warmed, a green product gradually separates out accompanied by the evolution of gas. On filtering off this precipitate the filtrate is pale yellow in colour, but on standing exposed to the atmosphere, after a period of half an hour it becomes deep red. Similar results are obtained when acetone semicarbazone is employed.

All attempts to isolate this red compound by methods of crystallisation and by extraction with organic solvents have so far proved to be fruitless, as have also attempts to promote the formation of the red colour in the pale yellow filtrate by oxidation, reduction, the action of carbon dioxide or by the action of ammonia.

The red solution is neutral to litmus but on boiling, the red colour gives way to yellow and the solution becomes alkaline. On cooling,the red colour redevelops after a period of three hours and the solution is again neutral to litmus. Hydrochloric acid changes the red colour to yellow, but on neutralising the solution with ammonia or with caustic soda the red colour reappears.

It is of interest to compare this red colouration with the "spot tests" for hydrazine and for semicarbazide by means of sodium penta-cyano-ammine-ferroate, $Na_3[Fe(CN)_5NH_3]$, reported by Feigl (Qual.Anal.,286) in which deeply coloured soluble compounds are formed probably by the replacement of the ammonia by the organic radical. In the case of semicarbazide a cherry red colour is produced in neutral solution, and a dark yellow colour is formed in alkaline solution. It is probable that in the case which is under consideration some similar compound is formed due to hydrolysis.

The development of red colourations have also been noted in the reactions between semicarbazide and acetone semicarbazone and ferric chloride (pp.45,46,69,71,73), and between 4-phenyl-semicarbazide and cupric chloride (pp.97,98, 112-114). Attempts to isolate the red products were made in each case, but so far no success has been achieved.

BIBLIOGRAPHY

M.M.J.Sutherland.	"The Metal Ammines." A Text-Book of Inorganic Chemistry - J.Newton Friend Vol X. - 1928 (Griffen).
N.V.Sidgwick.	"The Electronic Theory of Valency" - 1927 (Oxford Press). "The Covalent Link in Chemistry." - 1933 (Oxford Press).
S.Sugden.	"The Parachor and Valency." - 1930. Nature - 1936,137,543.
L.Pauling.	Journal of the American Chemical Society,1931,53,1367: 1932, 54,995.
R.Abegg.	"Handbuch der Anorganischen Chemie." Band.4.,3 Abt.,3 Teil, 2 - 1935 (Hirzel).
G.T.Morgan and F.H.Burstall.	"Inorganic Chemistry - A Survey of Modern Developments." - 1936 (Heffer).
K.A.Jensen	"Complex Compounds of Semicarbazide." Z.anorg.Chem., 1936,227,25.
G.S.Smith.	"Co-ordination Compounds of Semicarbazide." J.C.S.,1937,1354.
H.J.Emeléus and J.S.Anderson.	"Modern Aspects of Inorganic Chemistry." - 1938 (Routledge).
E.G.Cox and W.Wardlaw.	"Co-ordination Compounds." Science Progress. - 1938, 463-478.

Annual Reports of the Chemical Society - 1936 - 1938.

<u>NOTE</u>:- All references are given as they occur in the text.

INDEX OF COMPOUNDS.