275. *Co-ordination Compounds of Semicarbazide, Phenylsemicarbazide,* m-*Tolylsemicarbazide, and Aminoguanidine.*

By G. Stanley Smith.

The objects of the investigation now described were the preparation and analysis of new complex metallic salts containing co-ordinated semicarbazide, or related compounds, with a view to determining their structure.

The results indicate that the organic molecule is bound to the metal atom or atoms at two points, semicarbazide giving 4- and 6-covalent nickel and cobalt, 4-covalent zinc and ferrous iron, and 2-covalent cadmium compounds; 4-phenyl- and 4-*m*-tolyl-semicarbazides giving 6-covalent nickel; and aminoguanidine giving 4-covalent nickel. 1-Phenyl- and 1-naphthyl-semicarbazides appeared not to link up with metal at all.

In the course of experiments conducted in 1928 for a different purpose, Professor J. Kenner observed the formation of a well-defined co-ordination compound of semicarbazide with ferrous sulphate. Reference to the literature having shown that, apart from compounds with copper nitrate and copper chloride (Thiele and Stange, *Annalen*, 1894, **283**, 24), with Roussin's salt (Bellucci and Cecchetti, *Gazzetta*, 1907, **37**, i, 169), and with sodium carbonylferrocyanide (Muller, *Bull. Soc. chim.*, 1905, **33**, 947), co-ordination compounds of semicarbazide had not previously been studied, the author, at Professor Kenner's suggestion, undertook a study of their formation.

The following compounds have been isolated (sem = semicarbazide) :

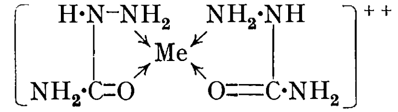
$[Fe(sem)_2]SO_4$
$[Co(sem)_2]SO_4$
$[Ni(sem)_3]Cl_2,3H_2O$
$*[Ni(sem)_2]SO_4$
$[Ni(sem)_3](NO_3)_2$

$[Cd(sem)]Cl_2$
$[Co(sem)_2]Cl_2$
$[Ni(sem)_3]SO_4,2H_2O$
$*[Co(sem)_3](NO_3)_2$

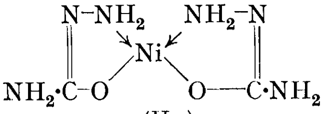
$[Zn(sem)_2]SO_4$
$*[Ni(sem)_2]Cl_2$
$*[Ni(sem)_3]Cl_2$
$[Ni(sem)_3]ClNO_3$

All these are new except those marked with an asterisk, which have been described by Jensen and Rancke-Madsen (*Z. anorg. Chem.*, 1936, **227**, 25), who were, however, unable to isolate a compound of nickel sulphate with 3 mols. of semicarbazide. As they pointed out, the results confirm the expectation that the co-ordinative value of the semicarbazide molecule would be twice that of the ammonia or water molecule. By analogy with the thiosemicarbazide complexes previously investigated by them (*ibid.*, 1934, **219**, 243; Jensen, *ibid.*, 1934, **221**, 11), the compounds would be of the type (I), in which the metal is bound both to the hydrazine group and to the oxygen atom.

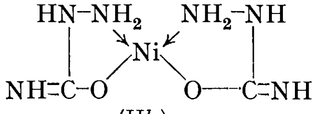
(I.)



Although the compounds of nickel salts with two and three molecules of semicarbazide are respectively green and blue, a pink precipitate was also observed both by Jensen and Rancke-Madsen and by the author when caustic alkali was carefully added to a concentrated solution of a nickel salt containing semicarbazide hydrochloride. The anions present in the solution do not enter into the composition of the product, which is represented by the Danish authors as an inner-complex, (II*a*) or (II*b*), the latter receiving preference since similar compounds were obtained with 2-methyl- and 1 : 2-dimethyl-semicarbazides.



(II*a*.)



(II*b*.)

A compound of this composition would contain Ni, 28·37; N, 40·64%, whereas analysis gave Ni, 26·80; N, 40·41%. The discrepancy in the nickel figures was explained on the assumption that a compound containing more than 2 mols. of semicarbazide was co-precipitated. The precipitate appears as a powder when obtained in the manner described, but by slow precipitation from an alkaline tartrate solution it is obtained in crystalline form. Analysis appears to indicate that it is a complex oxide, $Ni(sem)_2O$. The compound is basic, for not only can it be titrated with acid (*Z. anorg. Chem.*, 1936, **227**, 27), but it liberates ammonia from ammonium salts. No evidence of the formation of a carbonate has been obtained. The compound is insoluble in all the common organic solvents, a fact that is not so easily explained if the complex is formulated as an "inner-complex" compound of nickel. It is precipitated also by free guanidine but not by sodium carbonate, and it can be obtained from hydrazine sulphate and potassium cyanate, without the intermediate isolation of semicarbazide. (Phillips and Williams, *J. Amer. Chem. Soc.*, 1928, **50**, 2465, obtained a complex nickel oxide with nitroaminoguanidine, $NiO[NH{:}C(NH{\cdot}NO_2){\cdot}NH{\cdot}NH_2]_2$, as a fawn-coloured precipitate, though this compound is soluble in sodium hydroxide.)

In view of the interest attaching to the configuration of 4-covalent compounds (cf. *Ann. Reports*, 1935, **32**, 160; 1936, **33**, 158), attempts were made to prepare tartrates of the various 4-covalent types now described, but only viscous masses could be obtained.

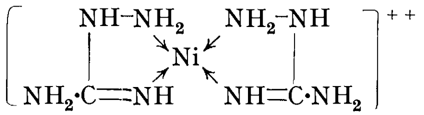
The opportunity has also been taken to study the co-ordinative behaviour of certain compounds related to semicarbazide. Thus, 4-phenylsemicarbazide (phsem) has yielded the compounds:

$[Fe(phsem)_2]SO_4$	$[Ni(phsem)_3]SO_4$	$[Ni(phsem)_3]Cl_2$
$[Ni(phsem)_3](NO_3)_2$	$[Cd(phsem)_2]Cl_2$	$[Co(phsem)_3]Cl_2$

of which only that from nickel nitrate was described by Jensen and Rancke-Madsen.

4-*m*-Tolylsemicarbazide yielded *compounds* analogous to these with cadmium chloride and nickel nitrate. On the other hand, 1-phenyl-, 1-α- and 1-β-naphthyl-semicarbazides did not participate in complex formation, and semioxamazide and oxalic dihydrazide both gave blue, amorphous compounds with nickel salts. [With alkali, the latter compounds give red or orange precipitates containing the alkali metal as well as nickel (Hofmann and Ehrhardt, *Ber.*, 1913, **46**, 1461).]

Aminoguanidine combines with nickel salts to give red salts of the type $[Ni(CH_6N_4)_2]X_2$. By analogy with the red nickel salts of 4-phenylselenosemicarbazide (Jensen and Frederiksen, *Z. anorg. Chem.*, 1936, **230**, 31), they may be formulated as:



The *chloride* and the *nitrate* of this complex are slightly soluble in water, giving red solutions, but the sulphate is practically insoluble. They are decomposed on boiling with water, nickel hydroxide being precipitated.

EXPERIMENTAL.

Free Semicarbazide.—In order to obtain several of the semicarbazide complexes it was necessary to employ the free base. This was prepared in small quantities as required by evaporating to dryness on a water-bath a concentrated solution of the hydrochloride, neutralised with potassium hydroxide, followed by extraction with hot absolute alcohol. Crystals of semicarbazide separated as the solution cooled.

Analysis.—All nitrogen data were determined by the Dumas method. Semicarbazide and aminoguanidine were determined by addition of excess potassium iodate and titration of the excess with thiosulphate (see this vol., p. 1325).

Disemicarbazidoferrous Sulphate.—2·8 G. of crystalline ferrous sulphate and 2·5 g. of semicarbazide hydrochloride were dissolved in the minimum of warm water, and a concentrated solution of 3·5 g. of crystalline sodium acetate added. Crystals formed almost at once on scratching the sides of the vessel with a glass rod, but larger crystals were obtained when the solution was left for several hours. The *compound* could be recrystallised from hot water containing an excess of free semicarbazide. It forms white, compact crystals, moderately soluble in water, giving a solution which rapidly oxidises with the separation of ferric hydroxide. The crystals showed no signs of oxidation or decomposition in the air during several years [Found: N, 28·0; Fe, 18·5; SO_4, 31·9. $(CH_5ON_3)_2,FeSO_4$ requires N, 27·8; Fe, 18·5; SO_4, 31·8%].

Semicarbazidocadmium Chloride.—4 G. of $CdCl_2,2\frac{1}{2}H_2O$, 2·5 g. of semicarbazide hydrochloride, and 3·5 g. of sodium acetate were dissolved in nearly boiling water, and the solution allowed to cool slowly. Long, white prisms separated, which were moderately soluble in water. From fairly concentrated solutions stout crystals, over 1″ long, were often obtained when the volume of the solution was as small as 5 ml. (Found: N, 16·3; Cl, 27·3; Cd, 43·4; CH_5ON_3, 28·9. $CH_5ON_3,CdCl_2$ requires N, 16·3; Cl, 27·45; Cd, 43·5; CH_5ON_3, 29·05%). The same *compound* was obtained when the proportions of cadmium chloride and semicarbazide were varied considerably.

Disemicarbazidozinc Sulphate.—The theoretical quantities of zinc sulphate, semicarbazide hydrochloride, and sodium acetate were dissolved in hot water and the solution allowed to cool slowly. Small white crystals separated, sparingly soluble in water and in dilute sulphuric acid [Found: N, 27·0; Zn, 21·0; SO_4, 30·5; CH_5ON_3, 48·2. $(CH_5ON_3)_2,ZnSO_4$ requires N, 27·0; Zn, 21·0; SO_4, 30·8; CH_5ON_3, 48·2%].

Disemicarbazidocobalt Sulphate.—Prepared like the zinc sulphate compound, this formed small pink crystals, sparingly soluble in water [Found: N, 27·6; Co, 19·3; CH_5ON_3, 48·0. $(CH_5ON_3)_2,CoSO_4$ requires N, 27·55; Co, 19·3; CH_5ON_3, 49·2%].

Disemicarbazidocobalt Chloride.—The theoretical quantities of cobalt chloride, semicarbazide hydrochloride, and sodium acetate, dissolved in the minimum amount of hot water, gave a red solution, from which small red crystals, moderately soluble in water, separated on cooling [Found: N, 30·1; Co, 20·9; CH_5ON_3, 52·6. $(CH_5ON_3)_2,CoCl_2$ requires N, 30·0; Co, 21·1; CH_5ON_3, 53·6%].

Disemicarbazidonickel Chloride.—2·4 G. of hydrated nickel chloride and 1·4 g. of free semicarbazide were dissolved in a few ml. of water, and the bluish-green solution left on a water-bath for about ½ hour, and then cooled; 2—3 vols. of alcohol were added, and the small green crystals were filtered off, washed with alcohol, and dried in the air. The compound is moderately soluble in water [Found: N, 29·9; Cl, 25·9; Ni, 21·1; CH_5ON_3, 53·4. Calc. for $(CH_5ON_3)_2,NiCl_2$: N, 30·05; Cl, 25·35; Ni, 21·0; CH_5ON_3, 53·7%].

Trisemicarbazidonickel Chloride Trihydrate.—To 1·5 g. of free semicarbazide, dissolved in a few drops of water, a very concentrated solution of 1·5 g. of nickel chloride was added. The solutions were mixed by gentle agitation and not by stirring, since touching the sides of the vessel with a glass rod causes the compound to separate in a solid mass. After the solution had stood for a short time, blue, feathery crystals filled the liquid. The compound may be recrystallised from hot water if the solution is removed from the source of heat as soon as the complex is in solution. (If heating is continued the less soluble green complex is produced.) The *trihydrate* was collected, washed with dilute alcohol, and dried in the air [Found: N, 30·8; Cl, 17·2; Ni, 14·4; H_2O, 13·1; CH_5ON_3, 55·0. $(CH_5ON_3)_3,NiCl_2,3H_2O$ requires N, 30·8; Cl, 17·3; Ni, 14·35; H_2O, 13·2; CH_5ON_3, 55·1%]. When heated at 105°, this afforded the anhydrous compound [Found: N, 35·2; Cl, 19·5; Ni, 16·2; CH_5ON_3, 62·9. Calc. for $(CH_5ON_3)_3,NiCl_2$: N, 35·5; Cl, 20·0; Ni, 16·5; CH_5ON_3, 63·5%].

Disemicarbazidonickel Sulphate.—2·8 G. of hydrated nickel sulphate and 1·4 g. of free semicarbazide were dissolved in about 5 ml. of hot water, and the solution allowed to cool slowly. Deep green crystals, adhering to the glass, separated. They were collected, washed with water, and dried in the air. The compound is difficultly soluble in hot water [Found: N, 27·8. Calc. for $(CH_5ON_3)_2,NiSO_4$: N, 27·6%].

Trisemicarbazidonickel Sulphate.—1·5 G. of free semicarbazide, dissolved in a little water, were mixed with a concentrated solution of 1·2 g. of nickel sulphate and 2 drops of glacial acetic acid. To the quite cold solution about the same volume of methyl alcohol was added all at once. Deep blue, feathery crystals separated immediately. They were collected, and washed with 50% methyl alcohol. The *dihydrate* was dried in the air [Found: N, 30·7, 30·6, 30·1; Ni, 14·0, 14·5, 14·4. $(CH_5ON_3)_3,NiSO_4,2H_2O$ requires N, 30·3; Ni, 14·1%]. It showed no appreciable loss in a vacuum desiccator over sulphuric acid, but although it lost in weight at 105°, no constant figure could be obtained. Obvious decomposition sets in at 130° and the compound slowly turns greenish-blue. The complex is easily soluble in water and may be reprecipitated by methyl alcohol. On warming the deep blue aqueous solution, a change of colour is apparent almost at once and a green precipitate of $Ni(sem)_2SO_4$ forms.

Trisemicarbazido-nickel and -cobalt Nitrates.—These compounds were prepared by adding alcohol to concentrated solutions of the metal nitrate (1 mol.) and free semicarbazide (3 mols.). The precipitates were dissolved in the minimum of hot water, and the solutions allowed to cool very slowly. Very large compact crystals, deep blue and deep red respectively, separated. The compounds are very soluble in water but practically insoluble in alcohol. The solutions appear to be unchanged on boiling [Found, for *nickel* compound : N, 38·0; Ni, 14·4; CH_5ON_3, 55·0. $(CH_5ON_3)_3,Ni(NO_3)_2$ requires N, 37·8; Ni, 14·4; CH_5ON_3, 55·2%. Found, for cobalt compound : N, 37·6. Calc. for $(CH_5ON_3)_3,Co(NO_3)_2$: N, 37·75%].

Trisemicarbazidonickel Chloronitrate.—This *compound* was obtained (1) by adding sodium acetate to a solution containing nickel nitrate and semicarbazide hydrochloride, (2) by adding sodium acetate to nickel chloride and semicarbazide nitrate, and (3) by adding free semicarbazide to a solution containing both nickel chloride and nickel nitrate. The deep blue solution is apparently unaltered on boiling. On slow crystallisation the compound forms deep blue, elongated prisms, easily soluble in water but less so than the corresponding nitrate or chloride. There is no tendency for this compound to lose one equivalent of semicarbazide [Found : N, 36·7; Ni, 15·1; Cl, 9·4; CH_5ON_3, 59·8. $(CH_5ON_3)_3,NiClNO_3$ requires N, 36·7; Ni, 15·4; Cl, 9·3; CH_5ON_3, 59·1%].

Disemicarbazidonickelous Oxide (?).—A very finely divided, but dense, pink precipitate was obtained by adding sodium hydroxide solution to an aqueous solution of a nickel salt containing excess of semicarbazide, but the composition varied (Found : N, 37·5—41·0; Ni, 24·5—27·5%). A crystalline compound was obtained by adding a hot solution (12 ml.) containing 0·6 g. of $NiCl_2,6H_2O$, 0·6 g. of tartaric acid, and 5 ml. of 5*N*-sodium hydroxide to 1 g. of semicarbazide in about 2 ml. of hot water. No immediate precipitation occurred, but overnight small, well-defined red crystals (0·4 g.) separated [Found : N, 38·0; Ni, 26·2. Calc. for $(CH_5ON_3)_2NiO$: N, 37·4; Ni, 26·1%. Calc. for $(CH_4ON_3)_2NiO$: N, 37·7; Ni, 26·3%].

4-*Phenylsemicarbazide Complexes.*—These, with the exception of the ferrous sulphate compound, were obtained as difficultly soluble crystals by adding a solution of the semicarbazide (0·75 g.) in 10—15 ml. of boiling water to a hot solution of $\frac{1}{2}$ mol. of the simple metal salt. Splendid crystals formed almost at once. The compounds were collected, washed with water, and left to dry in the air. The ferrous sulphate compound was obtained as a white crystalline powder by adding a cold solution of phenylsemicarbazide in dilute acetic acid to a cold solution of ferrous sulphate.

Complex ferrous sulphate. White [Found : N, 18·4. $(C_7H_9ON_3)_2,FeSO_4$ requires N, 18·5%]. *Complex cadmium chloride.* White [Found : N, 17·6. $(C_7H_9ON_3)_2,CdCl_2$ requires N, 17·3%]. Complex nickel nitrate. Blue [Found : N, 24·2; Ni, 9·3. Calc. for $(C_7H_9ON_3)_3,Ni(NO_3)_2$: N, 24·2; Ni, 9·2%]. *Complex nickel chloride.* Blue [Found : N, 21·3; Ni, 10·1. $(C_7H_9ON_3)_3,NiCl_2$ requires N, 21·6; Ni, 10·1%]. *Complex nickel sulphate.* Blue [Found : Ni, 9·7. $(C_7H_9ON_3)_3,NiSO_4$ requires Ni, 9·6%]. *Complex cobalt chloride.* Red [Found : N, 21·2. $(C_7H_9ON_3)_3,CoCl_2$ requires N, 21·6%].

All these compounds are less soluble in water than the corresponding semicarbazide compounds.

No compound of nickel or cobalt containing only 2 mols. of phenylsemicarbazide could be obtained.

4-m-*Tolylsemicarbazide Complexes.*—4-*m*-Tolylsemicarbazide (m. p. 108° from amyl alcohol; acetone compound, m. p. 157° from aqueous alcohol and from benzene; methyl ethyl ketone compound, m. p. 112°; benzaldehyde compound, m. p. 172°) was prepared from *m*-tolylurea and hydrazine (cf. Sah, Wang, and Kao, *J. Chinese Chem. Soc.*, 1936, 187). It gave the following complexes: *cadmium chloride* [Found : N, 16·1. $(C_8H_{11}ON_3)_2,CdCl_2$ requires N, 16·4%]; *nickel nitrate* [Found : Ni, 8·5. $(C_8H_{11}ON_3)_3,Ni(NO_3)_2$ requires Ni, 8·7%].

Aminoguanidine Compounds.—A solution of aminoguanidine sulphate, neutralised with sodium acetate and mixed with solutions of nickel and cobalt salts, gave no indications, either by reason of a change in colour of the solution or of the formation of a precipitate, of the presence of a complex, but on careful addition of ammonia or of sodium hydroxide, the nickel solution yielded a heavy, crystalline, red precipitate, and the cobalt solution a jade-green, amorphous precipitate, both compounds containing the sulphate radical. The chloride and nitrate, and also the sulphate, of the nickel–aminoguanidine complex were prepared from aminoguanidine carbonate.

Aminoguanidine carbonate (2 mols.) was treated with a measured volume, in slight excess, of 5*N*-hydrochloric, nitric, or sulphuric acid. After effervescence had ceased, sodium hydroxide (5*N*), exactly equivalent to the acid previously used, was added, and the warmed solution poured through a disc filter into a concentrated solution of nickel chloride, nitrate, or sulphate (1 mol.). The red solutions so obtained were allowed to cool slowly. Crystals of the sulphate formed at once; the chloride and nitrate crystallised less rapidly. The sulphate is practically insoluble in water, but the other salts are slightly soluble to red solutions, which appear to be stable in the cold: *Complex chloride* [Found: Cl, 25·5; Ni, 21·2; CH_6N_4, 53·0. $(CH_6N_4)_2,NiCl_2$ requires Cl, 25·5; Ni, 21·1; CH_6N_4, 53·3%]; *complex nitrate* [Found: Ni, 17·3; CH_6N_4, 44·4. $(CH_6N_4)_2,Ni(NO_3)_2$ requires Ni, 17·7; CH_6N_4, 44·8%].

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