

Nickel Compounds of Aminoguanidine, Diaminoguanidine and Triaminoguanidine

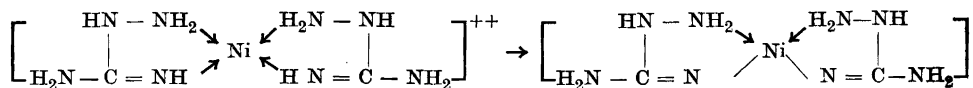
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In the course of investigations conducted in 1934—36 on coordination compounds of thiosemicarbazide and semicarbazide¹ it was noted that aminoguanidine also is able to combine with nickel sulphate to give a red complex salt, $[\text{Ni}(\text{CH}_5\text{N}_4)_2]\text{SO}_4$, (this was later described by Stanley Smith²). By addition of sodium hydroxide to this compound, sulphuric acid was split off, and another red compound, presumably an inner complex salt, was formed. Whereas the corresponding derivatives of thiosemicarbazide and semicarbazide are quite stable, the red aminoguanidine compound rapidly turned black during attempts to filter and decomposed with the evolution of nitrogen and ammonia. It was obvious that this transformation was due to oxidation, and the blackening of the red compound could also be effected by the addition of hydrogen peroxide to a suspension of the compound in water. This phenomenon has now been subjected to a closer examination.

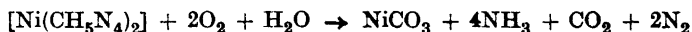
When oxygen is very carefully excluded, it is possible to isolate the above-mentioned red compound. The preparation, filtration and drying must be performed in an atmosphere absolutely free of oxygen. When dry, the compound is somewhat less susceptible to oxidation, but in the course of some hours it generally turns black.

The analyses of the red compound indicate the composition $\text{Ni}(\text{CH}_5\text{N}_4)_2$, and accordingly it is an inner complex compound derived from the cation of the red sulphate by the splitting off of two hydrogen ions:



According to the theory of Pauling ³, compounds of this type must have a planar configuration and must be diamagnetic. Measurements of the magnetism showed the sulphate to be diamagnetic; for the inner complex compound small paramagnetic values were found, but as the compound is very unstable and the black oxidation product is strongly paramagnetic, there is a little doubt that the pure compound really is diamagnetic.

The oxidation of the inner complex compound (suspended in water) in an atmosphere of oxygen was examined in the Van Slyke apparatus for gasometric determination of amino nitrogen. There was only a small change in the volume, because nitrogen was split off during the oxidation. The resulting gas was then analysed for nitrogen by passing it through a tube with hot copper filings and measuring the gas in an azotometer. Judging from these results, the oxidation mainly proceeds in accordance with the following equation:



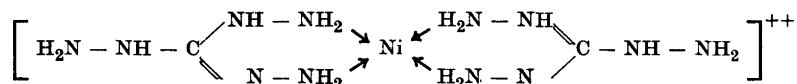
Almost all of the ammonia and carbon dioxide remains in the water. Part of the ammonia is bound to the nickel carbonate. A small trace of the nickel, however, forms nickel peroxide, which liberates iodine from potassium iodide in acidic solution. The reaction product further contains a trace of cyanide. It was shown that oxidation of aminoguanidine with potassium permanganate mainly proceeds in the same way. In that case, also, a small amount of cyanide is formed, especially in alkaline solution. The main process, however, is:



We think that the nickel atom functions as a catalyst during the oxidation in the following way: The nickel complex derived from divalent nickel is oxidized to a nickel compound with tervalent or quadrivalent nickel (in the last case a 6-coordinated complex, $[\text{Ni}(\text{CH}_5\text{N}_4)_2(\text{OH})_2]$, might be formed), but it is unstable and in its turn oxidizes aminoguanidine to ammonia and carbon dioxide. This hypothesis receives some support from the fact that the black compound liberates iodine from iodide and accordingly contains some nickel with a higher valency than two. It is remarkable that the compound should be black, as it only contains a trace of ter- or quadrivalent nickel. It has, however, been shown by le Blanc and Sachse ⁴ that NiO containing a few per cent Ni_2O_3 is quite black. This has been explained by de Boer and Verwey ⁵ by suggesting the possibility of electron transmission across the whole crystal lattice as soon as there is some deviation from the stoichiometric composition NiO.

With diaminoguanidine nickel sulphate forms complexes quite analogous to the derivatives of aminoguanidine, viz. a red, slightly soluble sulphate, $[\text{Ni}(\text{CH}_7\text{N}_5)_2]\text{SO}_4$, and a red inner complex salt, $[\text{Ni}(\text{CH}_6\text{N}_5)_2]$, which is still more easily oxidable than the aminoguanidine compound. In this case, too, the sulphate was found to be diamagnetic, while for the inner complex salt a slight paramagnetism was found, which however, without a doubt is due to beginning decomposition.

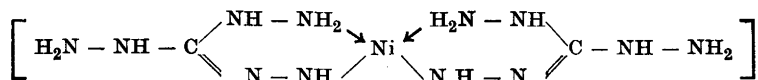
Finally we have investigated the reaction of nickel salts with triaminoguanidine. To judge from the change of colour to red-violet, a complex is formed by the addition of triaminoguanidine to a solution of a nickel salt, but the sulphate is easily soluble. The explanation of this difference is perhaps that in this case a six-membered ring may be formed:



or that triaminoguanidine behaves as a tridentate group, so that a 6-coordinated complex is formed.

By the addition of an excess of sodium hydroxide or potassium hydroxide to the above-mentioned solution, a red inner complex compound, $[\text{Ni}(\text{CH}_7\text{N}_6)_2]$, is formed, as in the case of mono- and diaminoguanidine. The triaminoguanidine compound is somewhat soluble in water. It is still more easily oxidable than the two lower homologues. In a glass tube with a well-fitting stopper it may be kept for some time without decomposition, but as soon as the stopper is removed the oxidation starts with perceptible evolution of heat; when the stopper is replaced, the evolution of heat stops, and the content soon regains room temperature. This experiment may be repeated several times. When the red compound is filtered on a Büchner-funnel in air, the heat evolution is so great that the compound deflagrates. (The corresponding mono- and diaminoguanidine compounds also deflagrate on gentle heating).

By making magnetic measurements just after the preparation, the triaminoguanidine compound was found to be practically diamagnetic. This circumstance, in addition to the colour of the compound, indicates that the nickel atom is 4-covalent, not 6-covalent and that the complex has the square configuration. Presumably a six-membered, not a five-membered, ring is formed, so that the formula of the complex is the following:



Several resonance forms of this formula are of course possible.

EXPERIMENTAL

Aminoguanidine compounds

$[\text{Ni}(\text{CH}_6\text{N}_4)_2]\text{SO}_4$. Aminoguanidine sulphate⁶ (3.5 g = 0.02 mole) and nickel sulphate (2.9 g = 0.01 mole) were dissolved in 50 ml of water. Upon the addition of sodium hydroxide the green solution at first turned blue, but when the amount equivalent to the aminoguanidine sulphate (10 ml of 2 N NaOH) had been added, a red precipitate separated. This was filtered off on a Büchner-funnel, washed with water and ethanol, and dried at 50–60°. The compound is a heavy, brick-red, crystalline powder, which is almost insoluble in water. Yield 3 g ~ 100 %.

Calc.	Ni 19.37	N 37.00
Found	» 19.15 (as dimethylglyoxime-nickel)	» 36.60 (Micro-Dumas)
Magnetism:	$\chi_g = -0.35 \times 10^{-6}$ (3750 Ørsted and 21.5°)	
	$\chi_g = -0.33 \times 10^{-6}$ (6970 Ørsted and 21.5°)	

$[\text{Ni}(\text{CH}_5\text{N}_4)_2]$. As this compound is extremely sensitive to oxygen, the preparation and filtering were carried out in an atmosphere of nitrogen. The synthesis was performed in an apparatus similar to that employed by Steinkopff⁷. Oxygen must be removed from the nitrogen employed by passing the nitrogen over copper filings. It is important that all solvents be thoroughly boiled to expel all air.

To a solution of 1 g of aminoguanidine sulphate and 0.9 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 25 ml of water and 25 ml of 10 N NaOH were added. A red solution was formed, and then almost instantaneously a red precipitate separated, which was filtered as quickly as possible and thoroughly washed with water, alcohol, and ether (dried over sodium).

In one case we succeeded in preparing a sample which gave correct values for nickel and nitrogen:

Calc.	N 54.7	Ni 28.6
Found	» 55.6	» 28.3

In most cases, however, the compound turned more or less black during drying and then gave smaller values for the nitrogen content.

We did not succeed in preparing a diamagnetic sample of this compound. For all preparations a weak paramagnetic susceptibility, varying from 1×10^{-6} to 2×10^{-6} ($\chi_M = 200-400 \times 10^{-6}$) was found. When the preparations turn black, the paramagnetism is increased and approaches the theoretical values for Ni^{++} , calculated from nickel analyses. As the red compound is very unstable, we conclude that the pure compound must be diamagnetic.

Diaminoguanidine compounds

$[\text{Ni}(\text{CH}_7\text{N}_5)_2]\text{SO}_4$. A dilute (about 0.1 N) solution of sodium hydroxide was added dropwise to a solution of 1 g of diaminoguanidine-hydrobromide⁸, 0.25 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 1 g of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ in 10 ml of water (tepid) until the green colour turned violet. By rubbing with a spatula and heating, a dark-red, crystalline substance was precipitated. This was filtered, washed with water, ethanol, and ether, and dried in vacuo over H_2SO_4 .

Calc.	Ni 17.63	N 42.09
Found	» 17.56	» 42.17
Magnetism: $\chi_g = -0.02 \times 10^{-6}$ (6970 Ørsted and 24.1°)		

[Ni(CH₆N₅)₂]. The compound was prepared with the same precautions as employed in the preparation of the monoaminoguanidine compound: 1.70 g of diaminoguanidine-hydrobromide and 0.30 g of nickel nitrate were dissolved in 30 ml of water and a concentrated solution of 8 g of sodium hydroxide was added. At first the solution turned dark-red, then a red, crystalline precipitate separated. The compound is very unstable, and although it was analysed just after preparation, we were not able to obtain values in exact agreement with the theoretical ones:

Calc.	Ni 25.00	N 59.7
Found	» 23.2–23.7	» 58.0–59.1

In air the compound — especially when moist — soon darkens and smells of ammonia.

By measuring magnetically, small paramagnetic values were found ($\chi_g = 2-3 \times 10^{-6}$). When the substance turns black, the paramagnetism increases. At the same time the nitrogen content falls to about 30 %. The nickel content of the black preparations was between 21 and 28 %. From corresponding values of the paramagnetic susceptibility and the nickel content, it was calculated that the values of μ_{eff} increases until about 2.5.

Triaminoguanidine compound

[Ni(CH₇N₆)₂]. Upon the addition of triaminoguanidine hydrochloride to a solution of nickel sulphate or nickel nitrate and neutralization, the colour turns red-violet; the complex formed could not be isolated. Upon the addition of sodium hydroxide in excess, a red solution is obtained and from this a pink crystalline precipitate separated: To a solution of 1.40 g of triaminoguanidine hydrochloride and 0.50 g of nickel nitrate in 50 ml of water a solution of 8 g NaOH in 50 ml of water was added. Pink needles separated. The compound is somewhat soluble in water, and the washing water was pink. In 50 % water-alcohol it is almost insoluble. When potassium hydroxide was employed instead of sodium hydroxide, the crystals had a darker red colour; the compound did not contain alkali. During the preparation and isolation of the compound, oxygen was carefully excluded. In air the compound soon gets warm and sometimes deflagrates.

Calc.	Ni 22.15	N 63.5
Found	» 21.60	» 51.7–52.9

As in the case of the other two inner complex salts, the samples of this compound were found to be weakly paramagnetic.

SUMMARY

Nickel compounds containing mono-, di- and triaminoguanidine have been prepared, viz. [Ni(CH₆N₄)₂]SO₄, [Ni(CH₇N₅)₂]SO₄, [Ni(CH₅N₄)₂], [Ni(CH₆N₅)₂] and [Ni(CH₇N₆)₂]. The three last-mentioned compounds were formulated as

inner complex salts. Magnetic measurements indicate that these compounds have a square configuration. They are highly oxidable and are quickly decomposed in air under the formation of nitrogen, ammonia, and carbon dioxide. It is supposed that the oxidation is initiated by the formation of a complex with tervalent or quadrivalent nickel.

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