The Magnetic Properties of [Co(NH₃)₅(NO)]Cl₂ (black)

and [Co(NH₃)₅(NO)](NO₃)₂ · ½H₂O (red)

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Magnetic susceptibility measurements of 6 independent preparates of the black [Co(NH₃)₅(NO)]Cl₂ show that the compound does not contain unpaired electrons. Our best samples give $\chi_g = +0.17 \times 10^{-6}$ at room temperature. It has been verified that the red [Co(NH₃)₅(NO)] (NO₃)₂ · ½H₂O is diamagnetic having $\chi_g = -0.20 \times 10^{-6}$. The absorption spectrum of this compound in aqueous solution has been measured. The similarity between this spectrum and the known absorption spectra of the ordinary Co(III)-pentammineacido complexes is evident. The possible structures of the compounds are discussed. The black pentahydrate [Co(NH₃)₅(NO)]Cl₂ · 5H₂O does not seem to exist.

In 1903 Sand and Genssler [1,2] showed that the action of NO(g) on [Co(NH₃)₆]⁺² solutions can result in two series of salts, "red salts" and "black salts". The empirical formula of both types of compounds is [Co(NH₃)₅(NO)]X₂. Later the preparation and the chemical properties of these compounds were critically studied and discussed by Werner and Karrer [3] and the magnetic properties were investigated by several authors [5-9].

These puzzling complexes have received great interest and many discussions concerning the possible structures, in particular their electronic structures on basis of the above mentioned chemical and magnetic investigations, have been published [3,7,10-12,19].

On account of the attention these compounds have received and the many contradictions concerning the experimental results and their interpretations, which are stated in the literature, we found it worth while to study thoroughly a typical example from each of the two series of salts, *viz.* "the black chloride" [Co(NH₃)₅(NO)]Cl₂ and the "red nitrate" [Co(NH₃)₅(NO)](NO₃)₂ · ½H₂O.

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1. *The black chloride*

Previously the magnetic susceptibility of this compound has been measured several times and effective magnetic moments μ_{eff} can be calculated. Thus Ray, and Bahr [6] obtained the value $\mu_{eff} = 2.78\ \mu_B$, Bose [5] found $\mu_{eff} = 2.81\ \mu_B$, Milward *et al.* [8] $\mu_{eff} = 1.63\ \mu_B$, Ghosh and Ray [7] $\mu_{eff} = 1.44\ \mu_B$, and Mellor and Craig [9] $\mu_{eff} = 1.60\ \mu_B$ (mean value) .

Our examinations of the preparation-methods described in the literature [1-3,7,13] revealed that a contamination of the black chloride with the strongly paramagnetic [14] cobalt(II)hexamminechloride is very difficult to avoid. We have modified the preparation-method (compare the results in the experimental part) and have then obtained samples of $[Co(NH_3)_5(NO)]Cl_2$ which under the microscope did not reveal even traces of reddish crystals of $[Co(NH_3)_6]Cl_2$. Some data from our measurements of the magnetic gram susceptibility at 295°K, 195°K and 85°K of 6 independent preparations are given in Table 1.

Table 1. The magnetic gram susceptibility χ_g of independent samples of $[Co(NH_3)_5(NO)]Cl_2$ (black). Analyses.

Sample No.	Analysis		$\chi_g \cdot 10^6$		
	Calc. %	Found %	295°K	195°K	85°K
17	28.94 Cl 34.75 NH₃		0.171	0.316	0.526
19	28.94 Cl 34.75 NH₃	29.06 Cl 34.79 NH₃	0.262	0.417	0.730
20	28.94 Cl 34.75 NH₃	28.89 Cl 34.90 NH₃	0.198	0.373	0.485
22	28.94 Cl 34.75 NH₃	28.75 Cl 34.63 NH₃	0.367	0.634	
23	28.94 Cl 34.75 NH₃	28.83 Cl 34.91 NH₃	0.173	0.366	0.807
25	28.94 Cl 34.75 NH₃ 24.06 Co	28.77 Cl 34.50 NH₃ 23.95 Co	0.277	0.508	1.26

It will be seen from Table 1 that we have succeeded in obtaining the compound in a higher and better reproducible magnetic purity than hitherto reported. The reproducibility of the magnetic measurements from sample to sample is far from the usual requirements. Our experiences prove, however, that it is very difficult to eliminate the last traces of paramagnetic impurities. The temperature dependence of the susceptibility can be explained as being due to such impurities still present even in our best samples.

We conclude from Table 1 that the expressions

$$\chi_g \;=\; +0.17 \times 10^{-6} \qquad (295°K) \tag{1}$$

$$\chi_M \;=\; 245 \times 0.17 \times 10^{-6} \;=\; +41 \times 10^{-6} \qquad (295°K) \tag{2}$$

give the best statement of the present measurements of the gram and the molar susceptibility, respectively. Since a compound with one unpaired electron ($\mu = 1.73 \; \mu_B$) has the molar susceptibility

$$\chi_M \;=\; 1\,260 \times 10^{-6} \tag{3}$$

at room temperature, it follows from (2) and (3) that no unpaired electrons are present. We consider this result more reasonable for a compound with an even number of electrons than the old values for the magnetic moment, which roughly correspond to — and also have been interpreted as originating from — one unpaired electron.

Concerning the chemical properties of the black chloride we shall mention the following facts: The chloride cannot be dissolved in water (even at 0°C) without decomposition to basic Co(II)-chlorides; treatment with conc. HCl or conc. NH_3 (in a N_2-atmosphere) yields $[CoCl_4]^{-2}$ and $[Co(NH_3)_6]^{+2}$-solutions, respectively, but on the other hand Nast and Rohmer [19] have shown recently that treatment of $[Co(NH_3)_5(NO)]Cl_2$ with aqueous KCN yields the yellow, diamagnetic $K_3[Co(CN)_5(NO)] \cdot 2H_2O$ which, as pointed out by Nast, very probable contains the unstable, diamagnetic [4,18] nitroxylate ion NO^- as a ligand. *I.e.*, in some reactions the black chloride behaves like a Co(II)- in other as a Co(III)-complex. The conversion from one oxidation state to another seems only to require a rather small energy.

It is, however, not only the chemical properties but also the magnetic properties and the intense black colour which may be interpreted on the basis of a structure formula represented as

$$(H_3N)_5 \overset{+3}{Co} NO^-$$
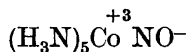
together with the further assumption of near lying Co(II)-states. We must, however, point out that further experimental investigations on other physical properties of the compound are necessary before further advance in the discussions of the structure of the black chloride can be expected.

2. The red nitrate (semihydrate)

The magnetic susceptibility of this compound has been measured several times previously. The first published values of χ_g were given by Ray and Bahr[6], who found $\chi_g = -0.109 \times 10^{-6}$. Later Milward *et al.*[8] published the

Table 2. The magnetic gram susceptibilities χ_g of independent samples of
$[Co(NH_3)_5(NO)](NO_3)_2 \cdot \frac{1}{2}H_2O$ (red). Analyses.

Sample No.	Analyses		$\chi_g \cdot 10^6$		
	Calc. %	Found %	295°K	195°K	85°K
1	19.19 Co 27.72 NH$_3$	19.11 Co 27.84 NH$_3$	−0.180		
2	19.19 Co 27.72 NH$_3$	19.21 Co 27.72 NH$_3$	−0.197	−0.156	−0.10
3		27.72 NH$_3$	27.75 NH$_3$	−0.159	−0.161	−0.03

value $\chi_g = -0.19 \times 10^{-6}$, and Ghosh and Ray [7] found $\chi_g = -0.201 \times 10^{-6}$.
In the papers by Bose [5] and Mellor and Craig [9] it is mentioned that they have
measured χ_g and found diamagnetism, but no values are given.

The results of our measurements on different preparations are given in
Table 2. The agreement with the data quoted above is obvious and the slight
temperature dependence of χ_g can be explained as being due to small amounts
of paramagnetic impurities.

The chemical properties of the red nitrate $[Co(NH_3)_5(NO)](NO_3)_2 \cdot \frac{1}{2}H_2O$
are very different from those of the black $[Co(NH_3)_5(NO)]Cl_2$. The former salt
is remarkably more stable and can, *e.g.*, be recrystallized from water with only
slight decomposition. Therefore it is possible to measure a reliable absorption-
spectrum and this is given in Fig. 1. The great similarity between this ab-
sorption-curve and the corresponding curves for ordinary Co(III)-pentammine
complexes is evident. (Compare, *e.g.*, the spectra measured by Linhard *et al.*[15]).

It is not only these physical properties (magnetism and absorption spect-
rum) which indicate that the compound is a Co(III)-complex, also the chemical
properties are in accordance with this assumption: The action of conc. HCl,
conc. HBr or 80 % HNO$_3$ on the red nitrate yields chloro-, bromo-, and nitrato-
pentammine salts, respectively, whereas treatment with a KCN-solution
yields [16],[19] $K_3[Co(CN)_6]$. We are therefore of the opinion that the red nitrate
is either a pentammine Co(III) complex or a binuclear decammine Co(III)-
complex.

3. The black chloride (penta-hydrate)]

Frazer and Long [4] have published data (preparation and magnetic measure-
ments) for a pentahydrate of the black chloride. We are, however, not con-
vinced of the existence of this hydrate. We have never been able to isolate a
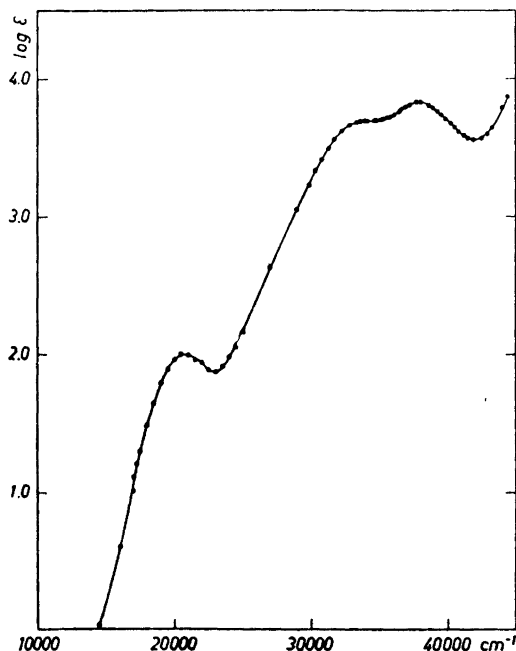hydrate of the black chloride. The procedure of Frazer and Long gives impure

Fig. 1. Absorption spectrum of [Co(NH₃)₅(NO)](NO₃)₂ in aqueous solution.

samples of the anhydrous complex; furthermore we consider the analytical methods used to be unnecessarily complicated. The susceptibility was measured in rather weak fields (300 Ørsted). The value given by Frazer and Long corresponds to between 2 and 4 unpaired electrons.

EXPERIMENTAL

Preparation of the compounds

[Co(NH₃)₅(NO)]Cl₂. 1 000 ml of 12 % ammonia placed in the apparatus shown in Fig. 2 is cooled to 0°C by immersion of the apparatus in an ice-water bath. After the apparatus has been freed from oxygen by passing a stream of purified nitrogen through A, 50 ml of 2.50 M CoCl₂ is introduced at H maintaining a vigorous stream of nitrogen in order to prevent oxydation of the cobaltoammine solution formed. This solution is now treated with nitric oxide at 0°C for 5 h. Nitric oxide is then replaced by nitrogen and suction is applied at C in order to get rid of the original liquor. The crystals are purified by careful flotation with alcohol in a nitrogen atmosphere and are finally washed with alcohol and ethyl ether and dried by evacuating the apparatus. The hard, black, octahedral crystals are stored in a nitrogen atmosphere. The yield is approximately 20 % of the cobalt used.

[Co(NH₃)₅(NO)](NO₃)₂ · ½H₂O was prepared according to Werner and Karrer [3] and recrystallized from water containing ammonia [8].

NO was prepared in an ordinary Kipp-apparatus from NaNO₂ (p.a. *in rotulis*) and 20 % H₂SO₄ and purified by passing through a 30 % NaOH solution and four U-tubes with solid NaOH (p.a. *in bacillis*).
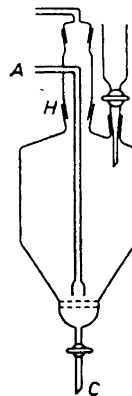
Fig. 2. Apparatus for the preparation of [Co(NH₃)₅(NO)]Cl₂, black.

Quantitative analysis. Co was determined as CoSO₄ after destruction of the complex by means of H₂SO₄. Cl was estimated as AgCl by weighing. NH₃ was determined acidimetrically (distillation of the complex with 30 % NaOH solution). The results of the analyses are given in Tables 1 and 2. In this connection it may be of interest to point out that the theoretical Co-, Cl-, and N-contents of the black chloride and those of Co(NH₃)₆Cl₂ do not differ very much, which will be seen from Table 3.

Table 3. Comparison of the analytical composition of [Co(NH₃)₆]Cl₂, [Co(NH₃)₅(NO)]Cl₂ and a mixture of these containing 10 % [Co(NH₃)₆]Cl₂.

Substance	% Co	% Cl	% NH₃	% N
Co(NH₃)₅(NO)Cl₂	24.06	28.94	34.75	34.31
Co(NH₃)₆Cl₂	25.40	30.56	44.04	36.22
Mixture of the composition: 10 % Co(NH₃)₆Cl₂ 90 % Co(NH₃)₅(NO)Cl₂	24.19	29.10	35.70	34.50

In Table 3 is furthermore given the calculated Co-, Cl-, NH₃-, and N per cents for a mixture of the composition: 10 % [Co(NH₃)₆]Cl₂ and 90 % [Co(NH₃)₅(NO)]Cl₂. The presence of as much as 10 % [Co(NH₃)₆]Cl₂ in a black chloride sample has, as will be seen, practically no influence upon the composition compared to that of chemical pure [Co(NH₃)₅(NO)]Cl₂. The magnetic gram susceptibility of this 10 % mixture is 4.6×10^{-6} and the magnetic moment is $\mu_{eff} = 1.73 \; \mu_B$. The gram susceptibilities for [Co(NH₃)₆]Cl₂ and [Co(NH₃)₅(NO)]Cl₂ are 47.0×10^{-6} and 0.17×10^{-6} respectively, at 22°C. The following diamagnetic corrections were applied for Cl⁻, NO⁻ and NH₃ [18,20], respectively: -21×10^{-6}, -18×10^{-6} and -15×10^{-6} (gram ion susceptibilities).

Magnetic measurements

The measurements were carried out as described previously [17].

Absorption spectrum

In the region below 800 mμ the measurements were carried out by means of a Cary MS recording spectrophotometer kindly placed at our disposal by professor Jannik Bjerrum. In the region 800—1 250 mμ the measurements were carried out by means of a Beckman DU spectrophotometer.

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