ACTA CHEMICA SCANDINAVICA 17 (1963) 1029–1033

On the Properties of the Black $[Co(NH_3)_5(NO)]Cl_2$

Studies on NO Compounds 2 *

OLE BOSTRUP

Fredriksborg Statsskole, Hillerød, Denmark

An examination of the properties of the black $[Co(NH_3)_5(NO)]Cl_2$ has been carried out. From a chemical standpoint the compound could best be classified as a cobalt(II) complex with neutral nitrogen(II) oxide as ligand.

The black complex formed by treating an ammonia solution of cobalt(II) chloride with nitrogen(II) oxide has been studied extensively in the last 70 years. About 30 papers have been published dealing with this peculiar compound having the analytical composition $Co(NH_3)_5(NO)Cl_2$. On account of the several contradictory announcements it was considered interesting to make a thorough investigation. The results of some magnetic measurements have been published previously [1] together with a short description of the preparation of samples, and a detailed description of the mode of preparation will appear in *Inorganic Syntheses* [2] as number 3 in this series.

CHEMICAL PROPERTIES

The black chloride is formed from cobalt(II) chloride hexahydrate according to the scheme:

$$Co(OH_2)_6^{2+} + 6NH_3 \rightarrow Co(NH_3)_6^{2+} + 6H_2O \quad (1)$$

$$Co(NH_3)_6^{2+} + NO + 2Cl^- \rightarrow Co(NH_3)_5(NO)Cl_2 + NH_3 \quad (2)$$

The cobalt(II) ammine formation is well known from the investigations performed by Jannik Bjerrum [3]. During the preparation the average complexity $\bar{n} \cong 6$. Process (2) is demonstrated by numerous analyses on the samples formed, no pentahydrate is formed [1] contrary to an announcement by Frazer and Long [9].

Generally the black chloride behaves chemically as a Co(II) complex. This could be demonstrated by the following series of experiments:

* Part 1 in this series was published in *Acta Chem. Scand.* **12** (1958) 24.

Table 1. Treatment of the black chloride with 2 M H_2SO_4 in an N_2 atmosphere and measurement of volume evolved gas.

$[Co(NH_3)_5(NO)]Cl_2$	Evolved gas	Temp., pressure.	Gas volume corr. to 0°C, 1 atm.	Gas volume pr. mole $[Co(NH_3)_5(NO)]Cl_2$
0.1419 g = 0.00578 mole	13.1 ml	20°, 760 mm Hg	12.3 ml	21.2 l
0.1561 g = 0.00657 mole	14.3 ml	18°, 769 mm Hg	13.5 ml	20.5 l

Treatment of the black chloride with 2 M sulfuric acid yields almost quantitatively NO, as was shown gasometrically, Table 1. Thus the formation of N_2O found mass-spectrometrically by Griffith, Lewis and Wilkinson [4] is by no means the main reaction.

Treatment with diluted sulfuric or nitric acid gives cobalt(II) aquo solutions; the well known chemical properties of such solutions are easily identified. Fig. 1 gives absorption curves of some relevant solutions. The small deviation in absorption spectrum of solutions of $Co(NH_3)_5(NO)Cl_2$ and $Co(OH_2)_6Cl_2$, respectively, in 1 M HNO_3 can be explained as being due to a slight formation of $Co(OH_2)_5(NO)^{2+}$. This point was verified by measuring the absorption curves for $Co(OH_2)_6^{2+}$ treated with NO for 3 h, and the solution of the black chloride in 1 M HNO_3 flushed with H_2 for the same length of time.

Treatment of the black chloride with concentrated HCl gives quantitatively the well known blue $CoCl_4^{2-}$ solutions. This is confirmed by measurements of the absorption spectra, Fig. 2. Thus, neither the red isomer [5] nor purpureochloride [6] is formed as previously claimed.

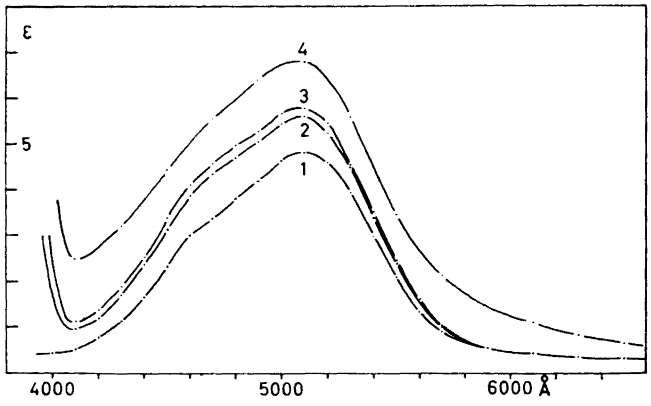

Fig. 1. Absorption spectra measured on a Beckman DU spectrophotometer. (1) $[Co(OH_2)_6]Cl_2$ in 1 M HNO_3. (2) $[Co(NH_3)_5(NO)]Cl_2$ in 1 M HNO_3 flushed with H_2. (3) $[Co(NH_3)_5(NO)]Cl_2$ in 1 M HNO_3. (4) $[Co(OH_2)_6]Cl_2$ in 1 M HNO_3 flushed with NO.

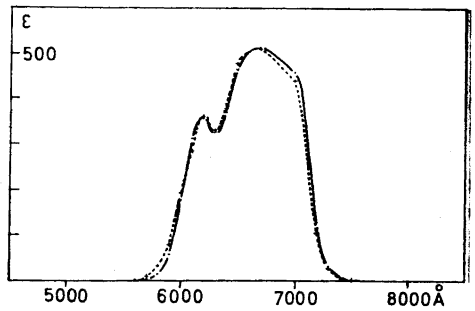

Fig. 2. Absorption spectra measured on a Beckman DU spectrophotometer. (1) $[Co(OH_2)_6](NO_3)_2$ in conc. HCl (12 M). (2) $[Co(NH_3)_5(NO)]Cl_2$ in the same solvent.

If $Co(NH_3)_5(NO)Cl_2$ or $Co(OH_2)_6Cl_2$ is treated first with 10 ml 50 % ammoniumthiocyanate and then with 50 ml acetone and finally diluted to 100 ml with water, blue solutions with identical absorptionspectra are formed. The procedure is a standard method in colorimetric cobalt(II) analyses[10].

Concentrated ammonia can convert the black chloride into bright red solutions of $Co(NH_3)_6^{2+}$ having the usual properties of this ion.

It must be emphasized that the exclusion of air in these experiments is most essential; the experiments here were carried out in an N_2 atmosphere. If air is admitted to ammonia-containing solutions of Co(II) compounds oxidation to Co(III) may happen; this must be the explanation of the findings of the carbonato- and aquocobalt(III) pentammines by Griffith *et al.*[4] and the purpureochloride by King and Moeller [6].

Treatment of the black chloride with KCN yields $K_3[Co(CN)_5(NO)]$ [7,4].

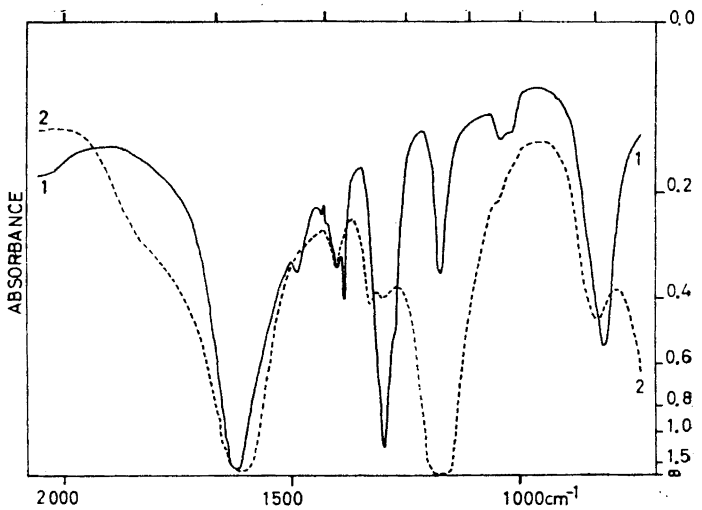

Fig. 3. Absorption curves for: (1) black $[Co(NH_3)_5(NO)]Cl_2$, and (2) $[Co(NH_3)_6]Cl_3$ in KBr-disks. The measurements were most kindly carried out for me in the Cyanamid Research Institute (Geneve) by courtesy of Dr. Chr. Klixbüll Jørgensen and Dr. Klaus Noack. The instrument was a Perkin Elmer — 221.

PHYSICAL PROPERTIES

The magnetic measurements revealed a compound with no unpaired electrons [1] contrary to earlier experiments on impure samples. This statement has later been verified [4].

IR spectra have previously been measured and discussed [4]; our curves are found in Fig. 3, the data are collected in Table 2. The bands in the 1170 cm^{-1} region are particularly interesting. Griffith, Lewis and Wilkinson [4] observed a band here in the black chloride and identified it as the stretching frequency of NO and from this point drew further conclusions as to the nature of the compound. We found the same band in the black chloride, but we also found a very strong band at the same place in pure cobalt(II) hexamminechloride. However, since this compound does not contain NO, and since it is a frequently

Table 2. IR absorption frequencies (in cm^{-1}). *Cf.* Fig. 3.

$[Co(NH_3)_5(NO)]Cl_2$	$[Co(NH_3)_5(NO)]Cl_2$ Ref.[4]	$[Co(NH_3)_6]Cl_2$
1620	1610	1600
1486		
1400		1400
1384		1325
1296	1290	1295
1172	1170	1170
1040		
808	809	735

appearing impurity in the black chloride,[1] the identification of the band as an NO stretching frequency may be subject to doubt. On standing in air the band in the black chloride disappears,[4] but it would also disappear from cobalt(II) hexammine since oxidation products like, *e.g.*, cobalt(III) hexammine does not have a band here. For these reasons the disappearance of the 1170 cm^{-1} band in moist air is therefore not an argument in favor of the identification.

The density was found (pycnometer) to 1.65 g/ml (22°C) in fair agreement with the value of Ghosh and Ray,[8] 1.73 g/ml (30°C).

RESULT

According to chemical experience the black chloride $[Co(NH_3)_5(NO)]Cl_2$ should be classified as cobalt(II) pentamminenitrosochloride. The investigation is being continued.

Acknowledgements. The author is indebted to professor R. W. Asmussen for inspiration and help during the work and to *Statens Almindelige Videnskabsfond* and *Tipsfonden* for financial support.

REFERENCES

1. Asmussen, R. W., Bostrup, O. and Jensen, J. P. *Acta Chem. Scand.* **12** (1958) 24.
2. Bostrup, O. *Inorg. Syn. To be published.*
3. Bjerrum, J. *Metal Ammine Formation.* Copenhagen 1941.
4. Griffith, W. P., Lewis, J. and Wilkinson, G. *J. Inorg. Nucl. Chem.* **7** (1958) 38.
5. Moeller, T. and King, G. *Inorg. Syn.* **4** (1953) 168.
6. Moeller, T. and King, G. *Inorg. Syn.* **5** (1957) 185.
7. Nast, R. and Rohmer, M. *Z. anorg. Chem.* **285** (1956) 271.
8. Ghosh, S. P. and Ray, P. *J. Indian Chem. Soc.* **20** (1943) 409.
9. Frazer, J. H. and Long, N. O. *J. Chem. Phys.* **6** (1938) 462.
10. Charlot, G. *Les Methodes de la Chimie Analytique* Paris (1961) 711.

Received December 20, 1962.