1125. *The Preparation and Magnetic Susceptibility of Nitrosylpentamminecobalt Chloride (Black)*

By A. L. ODELL, R. W. OLLIFF, and A. A. TAGGART

The magnetic susceptibility of the black nitrosylpentamminecobalt chloride can be controlled by varying the conditions of its preparation. There would appear to be insufficient cobalt(II) impurity to account for the high susceptibilities sometimes found.

MAGNETIC-SUSCEPTIBILITY values for black nitrosylpentamminecobalt chloride $[Co(NH_3)_5NOCl_2]$ ranging from $\chi_M = 442 \times 10^{-6}$ to $\chi_M = +3258 \times 10^{-6}$ c.g.s.u. have been reported.[1] Recent *X*-ray structural studies [2] have not given any indication why this variation should occur. We have made a systematic study of the effect of conditions of preparation of this substance, and find that the susceptibility can be controlled by controlling these conditions.

Experimental.—The apparatus and method used were similar to that described by Moeller and King,[3] with an additional sintered-glass filter funnel attached above the reaction vessel so that solutions could be filtered before use. All parts of the apparatus could be flushed with hydrogen. Reactions were carried out in an ice-bath.

The nitric oxide was prepared by the method of Blanchard.[4] All other reagents were of AnalaR grade.

Analyses. Black nitrosylpentamminecobalt chloride [Found for sample 35 (high susceptibility): Cl, 29·0; Co, 24·0; $N(NH_3)$, 28·5; N(total), 34·2. Found for sample 17 (low susceptibility): Cl, 28·9; Co, 24·0; $N(NH_3)$, 28·5; N(total), 34·2. Calc. for $Co(NH_3)_5NOCl_2$: Cl,

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[1] R. W. Asmusson, O. Bostrup, and J. P. Jensen, *Acta Chem. Scand.*, 1958, **12**, 24, and references therein.

[2] (*a*) D. Hall and A. A. Taggart, *J.*, 1965, 1359; (*b*) D. Dale and D. Hodgkin, *J.*, 1965, 1364.

[3] T. Moeller and G. L. King, *Inorg. Synth.*, 1953, **4**, 168.

[4] A. A. Blanchard, *Inorg. Synth.*, 1946, **2**, 126.

28·9; Co, 24·05; N(NH_3), 28·6; N(total), 34·3%]. *Black nitrosylpentamminecobalt bromide* [Found: Co, 17·7. $Co(NH_3)_5NOBr_2$ requires Co, 17·7%]. *Black nitrosylpentamminecobalt nitrate* [Found: Co, 19·7. $Co(NH_3)_5NO(NO_3)_2$ requires Co, 19·8%]. Red nitrosylpentamminecobalt chloride (Found: Co, 24·0%).

Magnetic susceptibilities were measured on the Gouy balance described previously.[5] *X*-Ray powder photographs were recorded with a Unicam single-crystal camera and a Guinier focussing camera.

DISCUSSION AND RESULTS

Two factors in the preparation of the black chloride have been found to affect the susceptibility of the product.

(i) The rate of passage of nitric oxide, fast passage leading to rapid precipitation in high yield of high-susceptibility product. Slow passage gives a poor yield of low-susceptibility product.

(ii) Exposure of the ammoniacal solution of cobalt(II) chloride to air before the passage of nitric oxide. The longer this exposure the lower is the susceptibility of the black product. If the exposure is about 2 hr. both the red and black chlorides are formed together, and if the exposure is greater than 5 hr. only the red complex is formed. When both products are formed, fast passage of nitric oxide favours formation of the black complex. Such black complexes separated from red–black mixtures usually have low susceptibility.

It is now known that the black chloride is a monomer [2] and the red chloride a dimer.[6] It is probable that rapid passage of nitric oxide precipitates the monomer before dimerisation can occur, and that slower passage of nitric oxide allows the dimerisation to proceed before precipitation.

Even from the one preparation samples formed in different parts of the reaction vessel did not have the same susceptibility (*e.g.*, samples from preparation 38 gave $\chi_M = +448, +604, +375, +479 \times 10^{-6}$ c.g.s.u.). On the walls and around the nitric oxide inlet tube glistening black irregular prisms with many well-developed faces were formed. These were of low susceptibility. On the sintered-glass bed of the vessel the complex was formed as dull black plates with few well-developed faces but of high susceptibility.

For further comparison two samples were chosen. One of high susceptibility (sample 35, $\chi_M = +828 \times 10^{-6}$ c.g.s.u.) was prepared by rapid passage of nitric oxide into an ammoniacal solution of cobalt(II) chloride which had not been exposed to air. The other was of low susceptibility (sample 17, $\chi_M = +120 \times 10^{-6}$ c.g.s.u.) in which the ammoniacal solution had been exposed to air for 1 hr. This low-susceptibility sample was that used for the single-crystal structure determination.[2a]

X-Ray powder photographs showed no differences between the high- and low-susceptibility samples, unequivocal indexing was possible, and all the observed lines were in excellent agreement with the single-crystal data.[2a]

The infrared spectra of the black salts have been discussed by Quagliano and co-workers [7] who considered these salts to be cobalt(III) complexes. Their spectra, compared to cobalt(II) hexammine complexes, contained a band at 1300 cm.$^{-1}$ (NH_3 symmetric deformation) of normal intensity together with one at 1600 cm.$^{-1}$ (NH_3 degenerate deformation), the intensity of which was considerably enhanced. An intense band at 1170 cm.$^{-1}$ [absent in cobalt(III) hexammine complexes] was also present and had been assigned by these workers to the presence of cobalt(II) hexammine which shows strong absorption in this region. The presence of such impurities would provide a ready explanation for the paramagnetism of some of the specimens of the black salts (*e.g.*, sample 35). Griffith *et al* [8] have shown, however, using isotopic-substitution evidence, that the 1170 cm.$^{-1}$ band is associated with the

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[5] H. C. Clark and A. L. Odell, *J.*, 1955, 3431.

[6] R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 1038.

[7] E. P. Bertin, S. Mizushima, T. J. Lane, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1959, **81**, 3821.

[8] W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38; *J.*, 1961, 775.

hyponitrito-group rather than the ammonia group and have assigned it to NO^- stretching, so that the presence of this band is not of itself evidence of the presence of cobalt(II) hexammine impurities. Such impurities would, however, lead to an enhancement of the 1170 cm.$^{-1}$ band but none was observed. 10·7% of cobalt(II) hexammine would be needed to account for the observed paramagnetism of sample 35, and about 1·5% for sample 17. The ratio of peak heights 1170 : 1260 cm.$^{-1}$ is 0·64 for sample 17. If cobalt(II) hexammine is the cause of the paramagnetism in sample 35 this ratio should be 0·71. The observed ratio for sample 35 is 0·63 (cf. 0·64 for sample 17). It is unlikely therefore that sufficient cobalt(II) hexammine is present to account for the paramagnetism of sample 35.

No obvious explanation for the enhancement of the 1600 cm.$^{-1}$ band can be suggested. It may be that this is related to the presence of a long Co–(NH_3) bond (2·28 Å)[2a] *trans* to the NO group.

If 10% of cobalt(II) hexammine were present in sample 35 (as required by the susceptibility) this should be detectable in the analysis, especially of ammonia nitrogen which should rise from 28·6 to 29·1%. The observed analytical figure is 28·50 ± 0·05%. Again it would appear that insufficient cobalt(II) hexammine is present to account for the paramagnetism of sample 35.

Electron spin resonance measurements did not detect resonance of either sample, even at low temperatures. This is in contrast with other paramagnetic nitrosyl complexes which do show absorption.[9] This negative result does not rule out the possibility that the paramagnetism is due to cobalt(II) impurities as cobalt(II) compounds often do not show e.s.r. absorption.[10]

The black bromide and nitrate can be prepared in a manner similar to the black chloride. They show similar variations in magnetic susceptibility.

We have found that the susceptibility of the black chloride can be controlled by varying the conditions of preparation. We also find that, at least in our samples, there is probably insufficient cobalt(II) impurity present to account for the paramagnetism.

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CHEMISTRY DEPARTMENT, UNIVERSITY OF AUCKLAND,
AUCKLAND, NEW ZEALAND.

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[9] H. B. Gray, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3404.

[10] D. M. S. Bagguley, B. Bleaney, J. H. E. Griffiths, R. P. Penrose, and B. I. Plumpton, *Proc. Phys. Soc.*, 1948, **61**, 551.