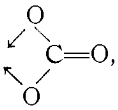
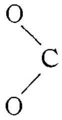
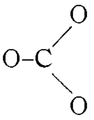
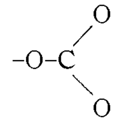
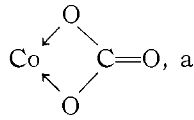
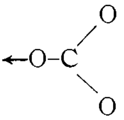
deformation vibrations of coördinated NH_3 gives added strength to the assignments. A similar approach is suitable for the coördinated NO_3^- and $SO_4^=$ groups.

The band observed at 1604 cm.$^{-1}$ in the spectrum of $[Co(NH_3)_4CO_3]Cl$ decreases to some extent in intensity on deuteration, indicating that this band is an overlapping of two bands. One band is assigned to the NH_3 degenerate deformation and the other to a stretching vibration of the  in which the terminal CO group has considerable double bond character. The band at 1287 cm.$^{-1}$, which is shifted considerably upon deuteration, is assigned to the NH_3 symmetric deformation; its observed value is compatible with the calculated value.[14] The band at 1268 cm.$^{-1}$ does not shift, and may be attributed to one of the  stretching vibrations. This frequency would correspond to the observed 1284 cm.$^{-1}$ band of dimethyl carbonate, $(CH_3O)_2CO$, assigned to the O-C-O stretching vibration.[20] The very broad absorption observed at *ca.* 845 cm.$^{-1}$ in the spectrum of $[Co(NH_3)_4CO_3]Cl$ is associated with the NH_3 rocking vibration, as is evident from the degree of isotopic shift and from the comparison with calculated values.[15] A sharp band at 832 cm.$^{-1}$ which does not shift on deuteration can be assigned to one of the carbonate skeletal vibrations.

In the spectrum of $[Co(NH_3)_5CO_3]I$, the bands at 1448 and 1364 cm.$^{-1}$ are assigned to the  stretching vibrations. That at 908 cm.$^{-1}$ corresponds to the  deformation. The absorption frequencies at 1612, 1310 and 849 cm.$^{-1}$ are assigned to the NH_3 degenerate deformation, symmetric deformation and rocking vibrations, respectively.

Thus the infrared spectra of $[Co(NH_3)_4CO_3]Cl$ and $[Co(NH_3)_5CO_3]I$ confirm the bidentate structure of the first,  and the monodentate structure of the second, Co← 

In the spectrum of $[Co(NH_3)_5SO_4]Cl$ four well-defined bands, observed at 1278, 1137, 1045 and 975 cm.$^{-1}$ appear in addition to the characteristic NH_3 deformation bands. These four replace the single, rather broad, and very intense infrared absorption frequency characteristic of the free $SO_4^=$ ion,[21,22] which appears at about 1120 cm.$^{-1}$. It is evident that upon coördination the tetrahedral symmetry of the free $SO_4^=$ is lost, and that this ligand involves an essentially covalent bond.

In the spectra of $[Co(NH_3)_5S_2O_3]Cl$ and $[Co(NH_3)_5Cl]S_2O_3$, the absorption frequencies in the 8–10 μ region are almost the same in regard to shape and relative intensity. It is noticed, however, that the frequencies in the spectrum of the compound containing coördinated $S_2O_3^=$ are appreciably higher than those of the isomer containing free $S_2O_3^=$. This implies that the symmetry of the free $S_2O_3^=$ ion remains essentially unchanged upon coördination, even though an essentially covalent bond is formed.

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[21] T. Wu, "Vibrational Spectra and Structure of Polyatomic Molecules," National University of Peking, Kun-Ming, China, 1939, p. 217, 233.

[22] F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Infrared Absorption Studies of Inorganic Coördination Complexes. XXI. Nitrosopentamminecobalt Halides and Nitrate[1]

BY E. P. BERTIN,[2] SAN-ICHIRO MIZUSHIMA, T. J. LANE AND J. V. QUAGLIANO

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The infrared absorption spectra of the black nitrosopentamminecobalt halides and the red nitrosopentamminecobalt nitrate were studied. From a consideration of the deformation vibration frequencies of the coördinated ammonia group, it is concluded that both series contain cobalt in the +3 oxidation state and that the difference between the series lies in the nature of the NO linkage.

Introduction

The black shiny crystalline substance formed by bubbling nitric oxide gas through an ammoniacal solution of cobalt(II) chloride satisfies the empirical formula $Co(NH_3)_5NOCl_2$.[3] It liberates nitric oxide when treated with water or dilute acid but is thoroughly stable when dry.[4] Many workers have investigated the nature of this compound in the

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[1] Paper XX in this series, THIS JOURNAL, **81**, 3818 (1959).

[2] Rev. Ernest P. Bertin, S.J., Seattle University; supported in part under A.E.C. contract AT (11-1)-38, Radiation Project of the University of Notre Dame; presented at the 133rd meeting of the American Chemical Society, San Francisco, April, 1958.

[3] J. Sand and O. Genssler, *Ber.*, **36**, 2083 (1903).

[4] A. Werner and P. Karrer, *Helv. Chim. Acta*, **1**, 54 (1918).

past.[5-8] However, it has been established recently by Asmussen,[9] *et al.*, that all previous workers who reported that the compound was paramagnetic were using an impure material and that unless a very pure specimen was prepared and used for investigation, any conclusion drawn concerning the structure must be regarded as invalidated.

The oxidation state of the cobalt atom has been designated by some authors[3,4,8,10] as +2 and by others,[11,12] as +3. One group[6] postulates a resonance between Co(I) and Co(III). Another group[8] suggests an equilibrium mixture between two forms: one in which the promoted electron of the cobalt(II) atom (presupposing $3d^2 4s 4p^3$ electron configuration) has its spin parallel to the odd electron of the three-electron bond in the NO group; the other in which the spin of this promoted electron is antiparallel to that of the NO group. Dimeric[3,13] and monomeric[4,6,11] structures have both been assigned to this black compound.

Since Asmussen has shown that the paramagnetism is due to the impurity $[Co(NH_3)_6]Cl_2$, suggested structures[6-8] which attempt to reconcile the paramagnetism with other properties need not be seriously considered.

Red nitrosopentamminecobalt nitrate is apparently stable in water and acids,[3,6] is diamagnetic[6,8] and is explained on the basis of cobalt(III) and a NO^- group coördinating like CN^- or Cl^-.

Short[13] has reported the NO infrared absorption frequencies at 1172 and 1614 cm.$^{-1}$ for $[Co(NH_3)_5NO]Cl_2$ and 1047 cm.$^{-1}$ for $[Co(NH_3)_5NO](NO_3)_2$.

The purpose of the present study is to determine the oxidation state of the cobalt atom in the black nitrosopentamminecobalt halides and the red nitrosopentamminecobalt nitrate.

It has been shown[14] that the deformation frequencies of the coördinated NH_3 group characteristic of spin-free (*i.e.*, "outer orbital") hexamminecobalt(II) halides differ greatly from those for the corresponding vibrations in spin-paired (*i.e.*, "inner orbital") hexamminecobalt(III) complexes. Consequently, in order to determine the oxidation state of the cobalt atom in the black and red nitrosopentamminecobalt coördination complexes, it will suffice to compare the spectra of our complexes with those previously reported.

Experimental

Preparation of Compounds.—Nitric oxide was prepared by the reaction of sodium nitrite with acidic iron(II) sulfate, the higher oxides of nitrogen being removed with sodium hydroxide.[15]

Black nitrosopentamminecobalt chloride was prepared by bubbling nitric oxide gas for 4 hr. through an ammonia solution of cobalt(II) chloride at 0° and in the absence of air.[16] A closed system was employed and kept under partial vacuum to facilitate the flow of NO.

Black nitrosopentamminecobalt bromide and iodide were prepared in the same way as for the corresponding chloride, but the aqueous solutions of the cobalt(II) halides used were more dilute. $CoBr_2 \cdot 6H_2O$ and $CoI_2 \cdot 6H_2O$ were prepared, and HI was regenerated, as previously reported.[14]

Red nitrosopentamminecobalt nitrate was prepared in the same way as $[Co(NH_3)_5NO]Cl_2$ but at room temperature and in the presence of air.

Cobalt analysis was carried out by cathodic electrodeposition.[17]

Anal. Calcd. for $[Co(NH_3)_5NO]Cl_2$: Co, 24.05. Found: Co, 24.00. Calcd. for $[Co(NH_3)_5NO]Br_2$: Co, 17.69. Found: Co, 17.85. Calcd. for $[Co(NH_3)_5NO]I_2$: Co, 13.78. Found: Co, 13.40. Calcd. for $[Co(NH_3)_5NO](NO_3)_2$: Co, 19.20. Found: Co, 19.25.

Absorption Measurements.—The infrared spectra were obtained by means of a model 21 Perkin–Elmer recording infrared spectrophotometer with a sodium chloride prism. The potassium bromide disk technique was employed[18] and the results were checked in Nujol mulls.

Results

Table I lists the infrared absorption frequencies of the black nitrosopentamminecobalt halides and of red nitrosopentamminecobalt nitrate. Figure 1 shows the infrared absorption spectra of hexamminecobalt(III) chloride, hexamminecobalt(II) chloride and black nitrosopentamminecobalt chloride.

Table I[a]

$[Co(NH_3)_5NO]Cl_2$	$[Co(NH_3)_5NO]Br_2$	$[Co(NH_3)_5NO]I_2$	$[Co(NH_3)_5NO](NO_3)_2$	Assignments
3240vs	3210vs	3230vs	3280vs	NH stretching
3150vs	3110vs	3150vs	3180vs	NH stretching
....	....	....	1770vw	Combination or overtone
1620vs	1628vs	1644vs	1628w	NH_3 degenerate deformation (+ NO vibration in halides)
....	....	....	1495m	
....	....	....	1370vs	NO_3^- degenerate frequency
1295s	1295s	1298m	1268m	NH_3 symmetric deformation
1170m	1174m	1192s	...	NH_3 symmetric deformation of $[Co(NH_3)_6]X_2$ impurities
....	....	....	1042vw	NO_3^- symmetric stretching
....	....	....	1010vw	
....	....	....	830m	NO_3^- out-of-plane bending
812m	798m	784m	*ca.* 830m	NH_3 rocking

[a] s = strong; m = medium; w = weak; v = very.

Discussion

Comparison of Table I with the infrared absorption values of hexamminecobalt(II) and (III) halides previously reported[14] and inspection of Fig. 1 makes it evident that the deformation frequencies

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[8] S. P. Ghosh and P. Ray, *J. Indian Chem. Soc.*, **20**, 409 (1943).

[9] R. W. Asmussen, O. Bostrup and J. P. Jensen, *Acta Chem. Scand.*, **12**, 24 (1958).

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[11] N. Sidgwick and R. Bailey, *Proc. Roy. Soc.* (*London*), **A144**, 521 (1934).

[12] D. P. Mellor and D. P. Craig, *J. Proc. Roy. Soc. N.S. Wales*, **78**, 25 (1944).

[13] L. N. Short, *Rev. Pure Appl. Chem.*, **4**, 41 (1954).

[14] E. P. Bertin, I. Nakagawa, S. Mizushima, T. J. Lane and J. V. Quagliano, This Journal, **80**, 525 (1958).

[15] A. A. Blanchard, *Inorg. Syn.*, **2**, 126 (1946).

[16] T. Moeller and G. L. King, *ibid.*, **4**, 168 (1953).

[17] W. F. Hillebrand and G. E. Lundell, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 419.

[18] J. P. Faust and J. V. Quagliano, This Journal, **76**, 5346 (1954).

of the coördinated NH_3 group in the black nitrosopentamminecobalt halides are essentially the same as those of the hexamminecobalt(III) halides. On the other hand, they differ greatly from the absorption values of the hexamminecobalt(II) halides. For example, the NH_3 rocking vibration appears at *ca.* 820 cm.$^{-1}$ in hexamminecobalt(III) halides, whereas this same vibration is at *ca.* 630 cm.$^{-1}$ in hexamminecobalt(II) halides.[14] The conclusion, therefore, is that the cobalt atom in the black nitrosopentamminecobalt halides has an oxidation state of +3.

The only appreciable differences in spectra between those of the black nitrosopentamminecobalt halides and the corresponding hexamminecobalt(III) halides are in the 6 and 8.5 μ regions. We have previously shown[14] that hexamminecobalt(II) and hexamminecobalt(III) complexes are distinguished from one another by the fact that the NH_3 rocking vibration in the Co(II) appears in the region 630 cm.$^{-1}$ whereas that of the Co(III) appears at about 820 cm.$^{-1}$. The 1620 cm.$^{-1}$ band in the black nitrosopentamminecobalt chloride is considerably more intense than the 1285 cm.$^{-1}$ band. In hexamminecobalt(III) chloride, however, the 1600 cm.$^{-1}$ band is far less intense than that at 1325 cm.$^{-1}$. This suggests that the high intensity of the absorption band at 1620 cm.$^{-1}$ in the spectrum of the black nitrosopentamminecobalt chloride arises from the superposition of two separate bands of nearly the same frequency. The other difference in spectra is in the 8.5 μ region. The peak at 1170 cm.$^{-1}$ in the spectrum of black nitrosopentamminecobalt chloride is absent in that of the hexamminecobalt(III) chloride. The absorption values at 1170 cm.$^{-1}$ (for the chloride), 1174 cm.$^{-1}$ (for the bromide) and 1192 cm.$^{-1}$ (for the iodide) are best explained as NH_3 symmetric deformation frequencies of hexamminecobalt(II) halide impurities (1160, 1165 and 1190 cm.$^{-1}$ for chloride, bromide and iodide, respectively).[14] Apparent magnetic susceptibilities of the samples whose spectra are given above were kindly determined by Fergusson[19] to be the following: $[Co(NH_3)_5NO]Cl_2$—$\mu_{eff} = 1.5$; $[Co(NH_3)_5NO]Br_2$—$\mu_{eff} = 1.6$. In the light of the work of Asmussen and co-workers,[9] this implies contamination by hexamminecobalt(II) halides.

The fact that the NH_3 rocking vibration, the most distinctive deformation frequency, has slightly different values in the spectra of black nitrosopentamminecobalt chloride (812 cm.$^{-1}$) and in hexamminecobalt(III) chloride (827 cm.$^{-1}$) is not unexpected. Among other factors, coördinated electronegative groups, such as Cl^-, $CO_3^=$, NO_3^-, may influence the deformation frequencies of coördinated NH_3.[20] On the other hand, the difference between the NH_3 rocking frequency of hexamminecobalt(II) chloride (634 cm.$^{-1}$) and that of black nitrosopentamminecobalt chloride (812 cm.$^{-1}$) is so great that one can exclude the existence of cobalt(II) in the latter compound. The same reasoning holds for the corresponding bromides and iodides.

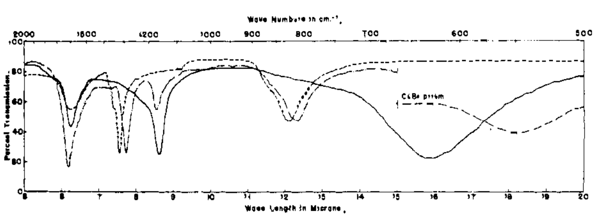

Fig. 1.—Infrared absorption spectra: the spectra were obtained by means of a model 21 Perkin–Elmer recording infrared spectrophotometer with sodium chloride and cesium bromide prisms. The concentrations were *ca.* 0.6 mg. of each sample per 298 mg. of potassium bromide. The temperature was 25°: ———, hexamminecobalt(II) chloride, $[Co(NH_3)_6]Cl_2$; - - - -, hexamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$; - · - · -, black nitrosopentamminecobalt chloride $[Co(NH_3)_5NO]Cl_2$.

In the spectrum of nitrosopentamminecobalt nitrate, the frequencies at 1770, 1370 and 830 cm.$^{-1}$ are assigned to the free nitrate ion, from a comparison with the spectra of $NaNO_3$, KNO_3 and $AgNO_3$.[21] The very weak absorption peak at 1042 cm.$^{-1}$ may be another example of the infrared inactive totally symmetrical NO_3^- stretching vibration becoming infrared active because of its arrangement in the crystal lattice.[22] The NH_3 deformation frequencies, though partly masked by NO_3^- vibrations, are clearly discernible as those of the NH_3 group coördinated to cobalt(III). The most distinctive of these NH_3 deformation frequencies, that of the rocking vibration, is at *ca.* 830 cm.$^{-1}$. This peak is clearly recognized in the original spectrum as a superposition of a sharp, intense NO_3^- deformation absorption frequency upon a broad, less intense NH_3 rocking frequency. The NH_3 degenerate deformation frequency is found at 1628 cm.$^{-1}$. That of the NH_3 symmetric deformation would be expected at about 1320 cm.$^{-1}$ but is obscured by the strong NO^- absorption in that region.

The NO frequencies characteristic of the black nitrosopentamminecobalt halides are not present in the same part of the spectrum of the red nitrosopentamminecobalt nitrate. Hence, it may be concluded that the isomerism of the black and red series is dependent upon the nature of the coördinated NO linkages and not upon a difference in oxidation state of the central cobalt atoms.[23]

Acknowledgment.—Gratitude is expressed to Professor Therald Moeller for first sending us a sample of black nitrosopentamminecobalt chloride and arousing our interest in this problem.

SEATTLE, WASHINGTON

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(19) J. E. Fergusson, University College, London, private communication, August, 1958.

(20) D. G. Hill and A. F. Rosenberg, *J. Chem. Phys.*, **24**, 1219 (1956).

(21) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

(22) T. J. Lane, D. N. Sen and J. V. Quagliano, *J. Chem. Phys.*, **22**, 1855 (1954).

(23) The reviewer brought to our attention the paper of W. P. Griffith, J. Lewis and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 38 (1958), which appeared after the completion of our work. Evidence for the hyponitrite structure for the black series suggested by Mellor and Craig[12] apparently has been confirmed by Wilkinson, *et al.*, on the basis of chemical evidence. The black complex salts, similar to the simple hyponitrites, react with carbon dioxide to form nitrous oxide and a carbonato complex. They also, upon reaction with water, turn pink and produce mainly the aquopentammine with a little carbonato complex. Analysis of the gas, obtained by heating the black salt with water or dilute acid and then treating with solid potassium hydroxide, showed strong absorptions characteristic of nitrous oxide. The black chloride has been obtained, in small yields, by the addition of solid sodium hyponitrite to a solution of anhydrous cobaltous chloride in liquid ammonia.