is expected to be more stable than the corresponding dibromide which agrees with the experimental observation.

Finally it should be mentioned that the reaction of $(C_5H_5)_2ZrBr_2$ ($9.7 \times 10^{-4}$ $M$) in tetrahydrofuran with LiCl ($3.7 \times 10^{-3}$ $M$) at 15° is complete within two minutes. Since Zr(IV) is larger than Ti(IV) the bond strength of Zr–Br probably is less than that of Ti–Br. Likewise the larger size of Zr(IV) will make it more susceptible to nucleophilic attack than is the smaller Ti(IV). Both of these factors may be responsible for the reactions of $(C_5H_5)_2ZrBr_2$ being faster than those of $(C_5H_5)_2TiBr_2$.

**Acknowledgment.**—We wish to thank Professor R. G. Pearson for his helpful suggestions and to acknowledge with pleasure the donation of samples of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2ZrCl_2$ by the Union Carbide Corporation. We also wish to acknowledge the support of this investigation by a Grant-in-Aid from the National Institutes of Health, Grant No. RG-4335.

EVANSTON, ILLINOIS

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

# Infrared Absorption Studies of Inorganic Coördination Complexes. XX. Cobalt(III) Ammine Complexes Containing Some Coördinated Anions[1]

BY E. P. BERTIN,[2] R. B. PENLAND, S. MIZUSHIMA, COLUMBA CURRAN AND J. V. QUAGLIANO

RECEIVED DECEMBER 30, 1958

Infrared spectra of cobalt(III) ammine complexes containing $NO_3^-$, $CO_3^=$, $SO_3^=$, $SO_4^=$ and $S_2O_3^=$ ligands have been measured in the 2–15 μ region. The portions of the spectra arising from these coördinated anions are greatly different from those of the corresponding free anions. Assignment of the absorption bands of $[Co(NH_3)_5NO_3]Cl_2$ and $[Co(NH_3)_4CO_3]Cl$ has been accomplished by comparison of their spectra with those of (a) the deuterated analogs and (b) the organic nitrates and carbonates.

## Introduction

The infrared spectra of the anions $NO_3^-$, $CO_3^=$, $SO_3^=$, $SO_4^=$ and $S_2O_3^=$ present as ligands in coördination complexes differ greatly from those of the free anions. These differences in spectra suggest the use of infrared spectroscopy as a method to determine if such groups are present inside or outside the coordination sphere in complex compounds. Differences in the infrared spectra of the free and coordinated anions in complex salts often result from the marked change in symmetry associated with a change in structure.[3,4] When an anion coördinates to a central metal atom of a complex, the character and configuration of the free anion are lost.

Infrared spectroscopy has been employed to determine which of several likely atoms present in a group is attached to the central metal atom in the formation of coördination complexes.[5] The infrared method should also serve to distinguish between coördination compounds in which a given group acts as a monodentate or as a bi- or polydentate ligand. Two types of complexes containing the $CO_3^=$ group are known. In one type the $CO_3^=$ group occupies one coördination position, and in the other it is said to act as a bidentate group, even though a four-membered ring results.

The present investigation was undertaken to study the change in structure of the above anions upon coördination, to determine the donor atoms in these groups and to report on the nature of the metal-to-ligand bond present in the metal coördination compounds.

## Experimental

**Preparation of Compounds.**—Nitratopentamminecobalt(III) chloride, $[Co(NH_3)_5NO_3]Cl_2$, was prepared by the method of Jorgensen.[6]

*Anal.* Calcd. for $[Co(NH_3)_5NO_3]Cl_2$: $NH_3$, 35.25. Found: $NH_3$, 35.15.

Carbonatotetramminecobalt(III) chloride, $[Co(NH_3)_4CO_3]Cl$, prepared by the method of Lamb and Damon[7] was recrystallized from hot water.

*Anal.* Calcd. for $[Co(NH_3)_4CO_3]Cl$: Co, 26.70; N, 25.19. Found: Co, 26.89; N, 24.93.

Carbonatopentamminecobalt(III) iodide, $[Co(NH_3)_5CO_3]I$, was prepared by the method of Basolo and Murmann.[8]

*Anal.* Calcd. for $[Co(NH_3)_5CO_3]I$: Co, 17.81. Found: Co, 17.85.

Thiosulfatopentamminecobalt(III) chloride, $[Co(NH_3)_5S_2O_3]Cl$, was prepared by Ray's method.[9]

*Anal.* Calcd. for $[Co(NH_3)_5S_2O_3]Cl$: Co, 20.21. Found: Co, 20.40

Chloropentamminecobalt(III) thiosulfate, $[Co(NH_3)_5Cl]S_2O_3$, was prepared according to the method of Jorgensen.[10]

*Anal.* Calcd. for $[Co(NH_3)_5Cl]S_2O_3$: $NH_3$, 29.19. Found: $NH_3$, 29.19.

Sulfitopentamminecobalt(III) chloride, $[Co(NH_3)_5SO_3]Cl$ prepared by the method of Vortman and Magdeburg,[11] was recrystallized from aqueous solution.

*Anal.* Calcd. for $[Co(NH_3)_5SO_3]Cl$: Co, 22.70. Found: Co, 22.72.

Sulfatopentamminecobalt(III) chloride, $[Co(NH_3)_5SO_4]Cl$, was prepared by the method of Ephraim and Flugel.[12]

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(1) Paper XIX in series, *Spectrochim. Acta*, 77 (1959).

(2) Rev. Ernest P. Bertin, S.J., Seattle University, Seattle, Washington. Supported in part under A.E.C. Contract AT(11-1)-38. Radiation Project of the University of Notre Dame; presented at the 131st meeting of the American Chemical Society, Miami, Florida, April, 1957.

(3) S. Mizushima and J. V. Quagliano, THIS JOURNAL, **75**, 4870 (1953).

(4) B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

(5) (a) R. B. Penland, T. J. Lane and J. V. Quagliano, THIS JOURNAL, **78**, 887 (1956); (b) R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, *ibid.*, **79**, 1575 (1957).

(6) S. M. Jorgensen, *J. prakt. Chem.*, **23**, 237 (1881).

(7) A. B. Lamb and E. B. Damon, THIS JOURNAL, **59**, 385 (1937).

(8) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 173 (1953).

(9) R. R. Ray, *J. Indian Chem. Soc.*, **4**, 71 (1927).

(10) S. M. Jorgensen, *J. prakt. Chem.*, **18**, 233 (1878).

(11) G. Vortman and G. Magdeburg, *Ber.*, **22**, 2636 (1889).

(12) F. Ephraim and W. Flugel, *Helv. Chim. Acta*, **7**, 737 (1924).

*Anal.* Calcd. for [Co(NH$_3$)$_5$SO$_4$]Cl: NH$_3$, 30.98. Found: NH$_3$, 30.98.

Deuterated compounds were prepared by precipitation of the complexes from D$_2$O solution with dry acetone.

**Absorption Measurements.**—Infrared spectra were obtained by means of a Perkin-Elmer infrared spectrophotometer model 21 using a sodium chloride prism. The potassium bromide disk technique was applied as described in previous communications,[13] and the results were checked by measurements in Nujol mull.

## Results

The infrared frequencies of the metal ammine complexes containing nitrato, carbonato, sulfito, sulfato and thiosulfato groups are listed in Table I.

TABLE I[a]

ABSORPTION MAXIMA IN CM.$^{-1}$ OF METAL AMMINE COMPLEXES CONTAINING NITRATO, CARBONATO, SULFITO, SULFATO AND THIOSULFATO GROUPS

| [Co(NH$_3$)$_5$NO$_3$]Cl$_2$ | Deuterated [Co(NH$_3$)$_5$NO$_3$]Cl$_2$ | [Co(NH$_3$)$_4$CO$_3$]Cl | [Co(NH$_3$)$_5$CO$_3$]I |
|---|---|---|---|
| 3230s | 3190m | 3290s | 3210s |
| 3100s | 2425s | 3180s | 3050s |
| 1600m | 2280s | 1604s | 1612m |
| 1475s | 1485s | 1287s | 1448m |
| 1315s | 1385w | 1268s | 1364s |
| 1280s | 1297s | *ca.* 845m | 1310m |
| 1017m | 1152w | 832m | 1290sh |
| 860m | 1085w | 768m | 1276sh |
| 800w | 1014s | 674w | 908w |
|  | 797w |  | 849m |
|  | 670w |  |  |

| [Co(NH$_3$)$_5$SO$_3$]Cl | [Co(NH$_3$)$_5$SO$_4$]Cl | [Co(NH$_3$)$_5$S$_2$O$_3$]Cl | [Co(NH$_3$)$_5$Cl]S$_2$O$_3$ |
|---|---|---|---|
| 3270s | 3200s | 3220s | 3220s |
| 3150s | 1613m | 3120s | 3120s |
| 1620m | 1315s | 1615m | 1600m |
| 1297s | 1278m | 1335s | 1320s |
| 1105s | 1137s | 1318m | 1305m |
| 994s | 1045s | 1168s | 1130s |
| 982s | 975s | 1139s | 1097s |
| 847m | 830m | 997s | 983s |
| 750w | 645m | 850m | 834m |
| 621m |  | *ca.* 640s | 647s |

[a] Abbreviations: w, weak; m, medium; s, strong; v, very; sh, shoulder.

The spectra given in Fig. 1 illustrate the effect of deuteration of nitratopentamminecobalt(III) chloride, which helps to assign the observed bands.

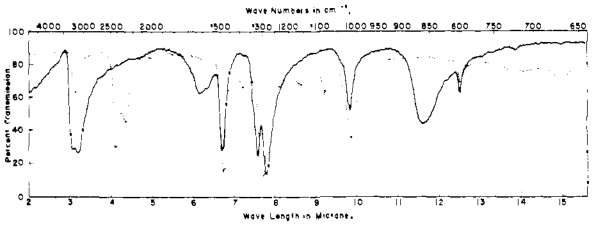

Fig. 1.—Nitratopentamminecobalt(III) chloride, [Co(NH$_3$)$_5$NO$_3$]Cl$_2$ ———; – – – –, deuterated nitratopentamminecobalt(III) chloride.

Figure 2 gives a comparison of the infrared spectra of carbonatotetramminecobalt(III) chloride and its deuterated derivative. Figure 3 illustrates differences of that part of the spectrum relating to the free, and coördinated, thiosulfate group.

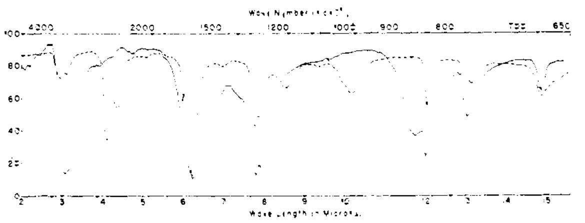

Fig. 2.—Carbonatotetramminecobalt(III) chloride, [Co(NH$_3$)$_4$CO$_3$]Cl ———; – – –, deuterated carbonatotetramminecobalt(III) chloride.

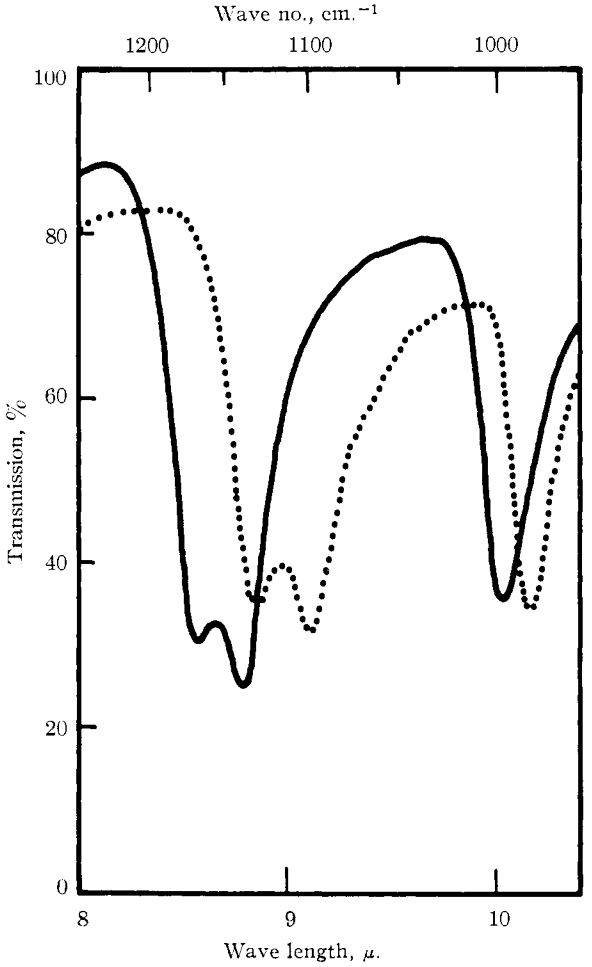

Fig. 3.—Thiosulfatopentamminecobalt(III) chloride, [Co(NH$_3$)$_5$S$_2$O$_3$]Cl ———; – – –, chloropentamminecobalt(III) thiosulfate, [Co(NH$_3$)$_5$Cl]S$_2$O$_3$.

## Discussion

All the coördination complexes listed in Table I contain NH$_3$ ligands whose stretching and deformation frequencies appear in the sodium chloride region. These frequencies can be identified easily by comparing them with the spectra of the corresponding deuterated compounds. Thus the bands present at about 3000 cm.$^{-1}$ are assigned to NH stretching vibrations. The shifts in the NH stretching vibrations to lower frequencies upon coördination of ammonia to a metal atom are in

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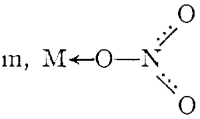
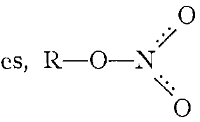
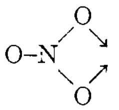
[13] J. P. Faust and J. V. Quagliano, THIS JOURNAL, **76**, 5346 (1954); T. J. Lane, D. N. Sen and J. V. Quagliano, *J. Chem. Phys.*, **22**, 1855 (1954).

accord with the observations of previous investigators.[14] The bands present at about 1600, 1300 and 850 cm.$^{-1}$ are assigned to $NH_3$ degenerate deformation, symmetric deformation and rocking vibrations, respectively, by means of the normal vibration calculation as well as by observation of the isotopic shifts.[15] Most of the infrared frequencies observed in the rock salt region, other than those described above, can be assigned to the vibrations characteristic of the anion ligands and from these frequencies the structure of the ligands can be determined.

If the coördinated nitrato ligand present in $[Co(NH_3)_5NO_3]Cl_2$ coördinates through an oxygen atom,  $\mathrm{M{\leftarrow}O{-}N}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$, its structure will be similar to that of organic nitrates,  $\mathrm{R{-}O{-}N}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$ Pauling and Brockway[16] concluded from electron diffraction measurements that in organo-nitrate compounds two of the three N–O bonds in the nitrate group have double bond character while the remaining N–O bond has essentially single bond character. Since the frequencies involving the nitrogen-to-oxygen double bonds are much higher than the nitrogen-to-oxygen single bonds, the vibrations of the $NO_2$ part may be treated separately from those of the other parts of the molecule.

From the observed Raman[17] and infrared spectra of organo-nitrate compounds, the antisymmetric and symmetric $NO_2$ stretching vibrations may be considered to have frequencies of about 1640 and 1260 cm.$^{-1}$, respectively. Thus similar infrared bands observed at 1475 and 1280 cm.$^{-1}$ for $[Co(NH_3)_5NO_3]Cl_2$ may be assigned to the antisymmetric and symmetric stretching vibrations of the $NO_2$ part in the coördinated nitrate group $-ONO_2$. The band observed at 1017 cm.$^{-1}$ in the spectrum of the $[Co(NH_3)_5NO_3]Cl_2$ complex can be assigned to the O–N stretching frequency from a comparison with the Raman effect of ethyl nitrate, $C_2H_5ONO_2$, in this region. A moderately intense Raman band, observed at 1013 cm.$^{-1}$, for ethyl nitrate, can be considered to result from the overlapping of the CON stretching and $CH_3$ rocking vibrations. This rocking vibration alone would show only a very weak Raman line similar, for example, to that observed in the spectrum of $CH_3Cl$ at 1015 cm.$^{-1}$.

A moderately intense infrared absorption band in the spectrum of ethyl nitrate observed at 863 cm.$^{-1}$ corresponds to a Raman line of moderate intensity at 864 cm.$^{-1}$. This Raman line has been assigned to a $NO_3$ deformation vibration.[17] (The $CH_2$ rocking vibration would give rise to only a weak Raman line in this region.) On this basis a similar band observed in the infrared spectrum of $[Co(NH_3)_5NO_3]Cl_2$ at 800 cm.$^{-1}$ may be assigned to the  $\mathrm{O{-}N}\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}$ deformation vibration. The three bands assigned to the $NO_2$ part of the $ONO_2$ group, 1475, 1280 and 800 cm.$^{-1}$, thus correspond to the antisymmetric stretching, symmetric stretching and deformation vibrations of the coördinated nitro group in the complex $[Co(NH_3)_5NO_2]Cl_2$, which appear at 1430, 1315 and 825 cm.$^{-1}$, respectively.[5a]

The fact that the four absorption values 1475, 1280, 1017 and 800 cm.$^{-1}$, in the nitrato complex remain essentially unchanged in frequency and intensity, upon deuteration, confirms their assignment to vibrations involving the coördinated nitrate group.

As organic nitrates have an oxygen-to-carbon bond, it can be concluded that coördination of the $NO_3^-$ group to a central metal ion involves oxygen as the donor atom and that the metal-to-ligand bond must be essentially covalent. It is to be noted that the absorption bands characteristic of the free $NO_3^-$ ion are not observed in the spectrum of the complex $[Co(NH_3)_5NO_3]Cl_2$. Evidently, upon coordination the structure and consequently the vibrations of the $NO_3^-$ ligand become quite different from those of the $NO_3^-$ ion present both in simple salts, and outside the coördination sphere of complexes.[3] After the completion of this work, we noticed that Nakomoto and co-workers[18] investigated the carbonatoammine cobalt complexes in the sodium chloride region and, passing over the discussion of the $NH_3$ deformation vibrations in this region, considered the $CO_3^{=}$ vibrations in terms of those of the free ion. In explaining the change of spectrum, on coördination, in relation to the change of symmetry of the ion, they seem to imply that the bond nature is essentially ionic. However, since the $NH_2$ deformation vibrations are found to be quite similar to the $CH_3$ deformation vibrations, it is quite natural to conclude that the nitrogen-to-metal bond is of considerably covalent character. (This has been discussed in our previous papers.[5a,15,19]) Therefore it seems difficult to consider just one or two bonds of the total six to be ionic while the others are essentially covalent. In the infrared spectrum of $[Co(NH_3)_5NO_3]^{+2}$ the $NH_3$ bands are very similar to those in $[Co(NH_3)_6]^{+3}$ and consequently the $NO_3^-$ group is effectively like the $NH_3$ group. It seems more appropriate to consider all six of the octahedral complex bonds as essentially covalent, including those between the metal and the carbonate group. The superiority of this approach is evident from the great change of spectrum of the free carbonate ion in the 6–8 $\mu$ region when this ion undergoes coördination. Furthermore, the use of deuteration techniques to distinguish between vibrations of the coördinated $CO_3^{=}$ group and the

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(14) G. F. Svatos, D. M. Sweeny, S. Mizushima, C. Curran and J. V. Quagliano, THIS JOURNAL, **79**, 3313 (1957).

(15) S. Mizushima, I. Nakagawa and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

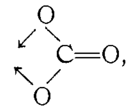
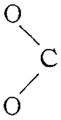
(16) L. Pauling and L. Brockway, THIS JOURNAL, **59**, 13 (1937).

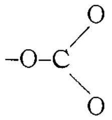
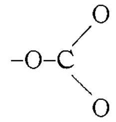
(17) J. H. Hibben, "The Raman Effect and Chemical Applications," Reinhold Publ. Co., New York, N. Y., 1939, p. 284.

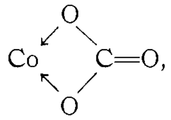
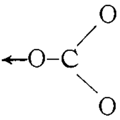
(18) K. Nakamoto, J. Fujita, S. Tanaka and M. Kobayashi, THIS JOURNAL, **79**, 4904 (1957). See also, B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, 3137 (1958).

(19) S. Mizushima, I. Nakagawa and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955); S. Mizushima, G. Svatos and J. V. Quagliano, *Anal. Chem.*, **27**, 325 (1955); I. Nakagawa and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 589 (1955).

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  $\begin{smallmatrix}\mathrm{O}\\ \swarrow\ \searrow\\ \mathrm{C{=}O}\\ \nwarrow\ \nearrow\\ \mathrm{O}\end{smallmatrix}$, 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  $\begin{smallmatrix}\mathrm{O}\\ \diagdown\\ \mathrm{C}\\ \diagup\\ \mathrm{O}\end{smallmatrix}$ 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  $\mathrm{-O-C}\begin{smallmatrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix}$ stretching vibrations. That at 908 cm.$^{-1}$ corresponds to the  $\mathrm{-O-C}\begin{smallmatrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix}$ 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,  $\mathrm{Co}\begin{smallmatrix}\mathrm{O}\\ \swarrow\ \searrow\\ \mathrm{C{=}O}\\ \nwarrow\ \nearrow\\ \mathrm{O}\end{smallmatrix}$, and the monodentate structure of the second, Co←O-  $\mathrm{Co{\leftarrow}O-C}\begin{smallmatrix}\diagup\mathrm{O}\\ \diagdown\mathrm{O}\end{smallmatrix}$

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 $\mu$ 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.

NOTRE DAME, INDIANA

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[20] H. Tschamler and R. Leutner, *Monatsh. Chem.*, **83**, 1502 (1952).

[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

RECEIVED DECEMBER 30, 1958

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).