JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (© Copyright, 1960, by the American Chemical Society)

VOLUME 82 APRIL 12, 1960 NUMBER 7

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Infrared Spectra Studies on the *cis* and *trans* Isomers of Diacidobis-(ethylenediamine)-cobalt(III) Complexes

BY MELVIN L. MORRIS AND DARYLE H. BUSCH

RECEIVED AUGUST 31, 1959

The infrared spectra of the *cis*- and *trans*-diacidobis-(ethylenediamine)-cobalt(III) complexes were studied with a view toward differentiating between the *cis* and *trans* configurations. The compounds were deuterated in order to unambiguously assign the bands associated with the NH_2 group. The *cis* isomers of dinitrobis-(ethylenediamine)-cobalt(III) and dichlorobis-(ethylenediamine)-cobalt(III) complexes showed a splitting of the NH_2 asymmetrical deformation frequency, whereas in the *trans* complexes this absorption band showed, in general, no splitting. The carbon-hydrogen deformation frequencies of the ethylene linkages of these compounds also were assigned. In general, these assignments gave a definite indication that the ligand ethylenediamine, when complexed, exists in a *gauche* form and not in a *cis* form.

Introduction

Several methods[1] have been applied with varying degrees of success to the problem of differentiating between the *cis* and *trans* isomers of hexacovalent cobalt(III) complexes. Chemical approaches to the solution of this problem have been attempted, but in general proof of structure on this basis alone is open to question. However, the *cis* isomers of compounds of the type $[M(AA)_2a_2]$, $[M(AA)_2ab]$ and $[M(AA)a_2b_2]$ (where AA represents a bidentate ligand), which can be resolved into their optically active antipodes, give a definite proof of the structure. X-Ray diffraction and ultraviolet and visible absorption spectra also have been used. Another method which might be applicable to the distinction between *cis* and *trans* configurations is infrared absorption spectra.

Faust and Quagliano[2] first applied infrared spectral measurements to *cis* and *trans*-diacidotetramminecobalt(III) complexes. These investigators studied the spectra of *cis* and *trans*-dinitrotetramminecobalt(III) ion, $[Co(NH_3)_4(NO_2)_2]^+$. The vibrations associated with the coördinated NH_3 and NO_2^- groups were assigned on the basis of the spectra of hexamminecobalt(III), $[Co(NH_3)_6]^{+3}$ and hexanitrocobaltate(III), $[Co(NO_2)_6]^{-3}$. The two absorption bands in the 3200 cm.$^{-1}$ region correspond to the NH_2 stretching vibration; the absorption band at 1600 cm.$^{-1}$, to the asymmetric deformation frequency; the band at 1350 cm.$^{-1}$, to the symmetric deformation frequency; and the absorption band at 850 cm.$^{-1}$, to the NH_3 rocking frequency. These assignments have been discussed in later publications by a number of other investigators.[3-6]

The infrared spectra of the *cis* and *trans* isomers studied by Faust and Quagliano were found to differ only as a consequence of the splitting of some of the low frequency bands in the case of the *cis* isomer. This splitting may be rationalized on the basis of the lower symmetry of the *cis* isomer.

Infrared spectral measurements[7] also have been reported on the *cis* and *trans* isomers of diacidobis-(ethylenediamine)-cobalt(III) compounds. In the case of the dinitro- and dichloro-compounds, complexities were encountered. The band at approximately 1600 cm.$^{-1}$, which is assigned to the asymmetric deformation mode of the NH_2 group is split in the case of the *cis* isomer, while the *trans* isomer exhibits only a single band in this region.

The presence of the ethylene links in the ethylenediamine introduces a number of additional absorption bands which complicate the assignment of the low frequency absorptions of the NH_2

---

[1] F. Basolo, *Chem. Revs.*, **52**, 459 (1953).

[2] J. P. Faust and J. V. Quagliano, THIS JOURNAL, **76**, 5346 (1954).

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

[4] D. G. Hill and A. F. Rosenberg, *ibid.*, **22**, 148 (1954).

[5] S. Mizushima, I. Nakagawa and J. V. Quagliano, *ibid.*, **23**, 1367 (1955).

[6] M. Kobayashi and J. Fujitu, *ibid.*, **23**, 1354 (1955).

[7] D. H. Busch, Thesis, University of Illinois (1954).

TABLE I

INFRARED SPECTRA OF *cis* AND *trans*-DIACIDOBIS-(ETHYLENEDIAMINE)-COBALT(III) COMPLEXES (CM.$^{-1}$)

Compound	NH_2(str.)	NH_2(def.(a))	NH_2(def.(S))	NH_2(rock.)	NO_2	NO_2	NO_3
$[Co(en)_3]Cl_3$	3172 3086	1575(S) 1529(sh)	1366	810(sh) 735(W)	..	..	..
cis-$[Co(en)_2(NO_2)_2]Cl$	3227 3138 3051	1615(M) 1598(M) 1566(S)	1364	797 778 742 718	1412	1341	831 818
trans-$[Co(en)_2(NO_2)_2]NO_2$	3245 3227 3100	1633(vW) 1617 1606	1358	800 778 740	1407(S)	1328	827 818
cis-$[Co(en)_2(NO_2)_2]NO_2$	3204 3171 3030	1581(S) 1571(sh) 1553(M)	1358	809 796 774	1410 1394(sh) 1381(sh)	1340	828 817
trans-$[Co(en)_2(NO_2)_2]NO_3$	3272 3103	1610(S)	1360	802	1428	1346	827 818
cis-$[Co(en)_2(NO_2)_2]NO_3$	3272 3239 3138	1617(W) 1575(S)	Obscured	800 774 714 708	1428	1345	827 819
trans-$[Co(en)_2Cl_2]Cl$	3237 3182 3061	1596(S)	1386 1363	805 733	..	..	..
cis-$[Co(en)_2Cl_2]Cl$	3195 3109	1630(M) 1561(S)	1366 1356	785 768 708	..	..	..

group. The assignment of absorption bands associated with the ethylene group may be accomplished by making use of the work of Mizushima and Sweeney.[8,9] These investigators have pointed out the fact that the ethylene group may exist in *trans*, *gauche* or *cis* forms. They also have shown that the *trans* form cannot exist in coördination compounds and that the *gauche* form is encountered. The bands expected of a *cis* form were not observed in the spectra of complex compounds containing bidentate ligands of the type X-CH_2-CH_2-X.

In the work reported here, the infrared spectra were obtained on the salts of *cis* and *trans*-dinitro-bis-(ethylenediamine)-cobalt(III) and dichloro-bis-(ethylenediamine)-cobalt-(III). The assignments of bands due to the NH_2 groups were made unambiguous by deuteration.

Experimental

Preparation of Tris-(ethylenediamine)-cobalt(III) Chloride.[10]—This compound was prepared by the method of Work. *Anal.* Calcd. for $[Co(C_2H_8N_2)_3]Cl_3$: C, 20.85; H, 7.00; N, 24.32. Found: C, 20.57; H, 7.06; N, 24.35.

Preparation of *cis* and *trans*-Dichloro-bis-(ethylenediamine)-cobalt(III) Chloride.—These compounds were prepared by the method of Bailar.[11] *Anal.* Calcd. for (*cis* and *trans*)-$[Co(C_2H_8N_2)_2Cl_2]Cl$: C, 16.83; H, 5.65; N, 19.62. Found for *trans*-$[Co(C_2H_8N_2)_2Cl_2]Cl$: C, 16.72; H, 5.59; N, 19.47. Found for *cis*-$[Co(C_2H_8N_2)_2Cl_2]Cl$: C, 16.89; H, 5.57; N, 19.63.

Preparation of *cis* and *trans*-Dinitro-bis-(ethylenediamine)-cobalt(III) Nitrate.—These compounds were prepared by the method of Holtzclaw, Sheetz and McCarthy.[12] *Anal.* Calcd. for (*trans* and *cis*)-$[Co(C_2H_8N_2)_2(NO_2)_2]NO_3$: C, 14.42; H, 4.84; N, 29.43. Found for *trans*-$[Co(C_2H_8N_2)_2(NO_2)_2]NO_3$: C, 14.47; H, 4.64; N, 29.58. Found for *cis*-$[Co(C_2H_8N_2)_2(NO_2)_2]NO_3$: C, 14.39; H, 4.63; N, 29.52.

Preparation of *cis*-Dinitro-bis-(ethylenediamine)-cobalt(III) Nitrite.—This compound was prepared by the method of Holtzclaw, Sheetz and McCarthy.[12] *Anal.* Calcd. for *cis*-$[Co(C_2H_8N_2)_2(NO_2)_2]NO_2$: C, 15.15; H, 5.08; N, 30.92. Found: C, 15.35; H, 5.27; N, 30.92.

Preparation of *trans*-Dinitro-bis-(ethylenediamine)-cobalt(III) Nitrite.—This compound was prepared by a modification of the method used by Holtzclaw, Sheetz and McCarthy[12] to prepare the *cis* isomer. Forty eight g. of a 10% ethylenediamine solution is added to 20 g. of potassium hexanitrocobaltate(III). The mixture is stirred constantly while it is heated slowly on a steam-bath to about 70°, whereupon the reaction occurs, as evidenced by the dissolving of the yellow hexanitrocobaltate to form a dark brown solution. While it is still hot, the reaction mixture is filtered to remove any traces of unreacted hexanitrocobaltate, and the filtrate is cooled in an ice-salt bath to precipitate the brown *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) nitrite. The crystals are isolated by filtration.

The *cis* compound is converted to the *trans* by dissolving the *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) nitrite in a minimum amount of boiling water and heating the solution for thirty minutes. This procedure is carried out three more times. After the final heating, the solution is filtered and the product obtained. *Anal.* Calcd. for $[Co(C_2H_8N_2)_2(NO_2)_2]NO_2$: C, 15.15; H, 5.08; N, 30.92. Found: C, 15.82; H, 4.99; N, 31.11.

Preparation of *cis*-Dinitro-bis-(ethylenediamine)-cobalt (III) Chloride.—This product was prepared by a modification of the method of Holtzclaw, Sheetz and McCarthy.[12]

A mixture of 6.85 g. of 10% ethylenediamine and 10 ml. of water is partially neutralized by the addition of 4 ml. of concentrated hydrochloric acid. The resulting solution is added to a solution of 9.52 g. of cobalt(II) chloride 6-hydrate and 6.0 g. of sodium nitrite in 10 ml. of water. A vigorous stream of air is drawn through the solution. The yellow *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) chloride begins to

---

(8) D. M. Sweeney, S. Mizushima and J. V. Quagliano, THIS JOURNAL, **77**, 6521 (1955).

(9) S. Mizushima, I. Ichishima, I. Nakagawa and J. V. Quagliano, *J. Phys. Chem.*, **59**, 293 (1955).

(10) J. B. Work, "Inorganic Syntheses," **II**, 221 (1946).

(11) J. C. Bailar, Jr., *ibid.*, p. 223.

(12) H. Holtzclaw, D. Sheetz and W. McCarthy, *ibid.*, **IV**, 176 (1953).

TABLE II

INFRARED SPECTRA OF *cis* AND *trans*-DIACIDOBIS-(ETHYLENEDIAMINE)-COBALT(III) COMPLEXES (CM.$^{-1}$)

Compound	C–N	CH_2(str.)	CH_2(bend.)	CH_2(wag.)	CH_2(twist.)	CH_2(rock.)
cis-$[Co(en)_2(NO_2)_2]Cl$	1058	2967 2908	1460	1307 1276 1211	1182 1171 1131 1058	899 890 883 873
$[Co(en)_3]Cl_3$	1064	2982 2895	1465	1331 1268 1253	1169 1157 1110 1024	906 895 890
cis-$[Co(en)_2(NO_2)_2]NO_2$	1047	2942 2878	1451	1337 1266 1236	1159 1129 1098 1007	890 870
trans-$[Co(en)_2(NO_2)_2]NO_2$	1058	2953 2932 2900	1453	1270 1215	1124 1107 1000(M)	883
trans-$[Co(en)_2(NO_2)_2]NO_3$	1053	2992 2935	1472	1220 1199 1334 1330 1294 1281	1121 1109 1002	891
cis-$[Co(en)_2(NO_2)_2]NO_3$	1060	2970 2915	1469	1314 1294	1159 1143 1125 1107 1047	894 888 875 869
trans-$[Co(en)_2Cl_2]Cl$	1049	2943	1446	1308 1292 1273 1208	1120 1091 1002	886
cis-$[Co(en)_2Cl_2]Cl$	1055	2936	1446 1448	1318 1277 1269 1206 1193	1158 1126 1113 1000	896 873

precipitate in a few minutes and the reaction is allowed to proceed for one hour. The mixture is cooled in an ice-salt bath and filtered. The product is recrystallized from hot water and dried in the air. *Anal.* Calcd. for $[Co(C_2H_8N_2)_2(NO_2)_2]Cl$: C, 15.67; H, 5.26; N, 27.41. Found: C, 15.80; H, 5.15; N, 27.28.

Ultraviolet Spectra.—In order to establish the geometrical configuration of the compounds containing the $[Co(en)_2(NO_2)_2]^+$ cation, their ultraviolet spectra were obtained by use of a Cary Model 10 Recording Spectrophotometer. Distilled water was used as the solvent. The wave lengths of maximum absorption of the *cis* and *trans*-$[Co(en)_2(NO_2)_2]^+$ compounds agreed with those reported by Basolo.[13]

Deuteration and Infrared Spectral Measurements.—The samples were deuterated by addition of 2 ml. of 99.5% deuterium oxide to about 10 mg. of sample contained in a small plastic stoppered bottle. The bottle was shaken vigorously to dissolve the samples and the solution was allowed to stand overnight. The deuterated sample was isolated by distillation of the deuterium oxide. The infrared spectra of the original and deuterated samples were obtained by use of solid potassium bromide disks.[14] The measurements were made on a Perkin–Elmer Model 21 Recording Spectrophotometer.

Results and Discussion

The NH_2 stretching frequencies, the asymmetric and symmetric deformation frequencies and the rocking frequencies of the dichloro-bis-(ethylenediamine)-cobalt(III) and dinitro-bis-(ethylenediamine)-cobalt(III) complexes are listed in Table I. The NH_2 stretching frequencies are in the 3200 cm.$^{-1}$ range. This region includes both the symmetric and asymmetric modes. The asymmetric deformation vibration occurs at about 1600 cm.$^{-1}$, the symmetric deformation in the vicinity of 1350 cm.$^{-1}$ and the NH_2 rocking vibration is near 800 cm.$^{-1}$. The infrared spectral measurements were carried out in order to determine the feasibility of a differentiation between the *cis* and *trans* isomers. A major difference in the spectra of the *cis* and *trans* isomers was observed in the NH_2 asymmetric deformation frequencies. In the case of the *cis* isomers, a splitting of this band was observed. An examination of the spectrum of *trans*-dichloro-bis-(ethylenediamine)-cobalt(III) (Table I) reveals a strong symmetric band occurring at 1596 cm.$^{-1}$. In contrast, the *cis*-dichloro-bis-(ethylenediamine)-cobalt(III) complex (Table I) exhibits a strong band at 1561 cm.$^{-1}$ and a moderate band at 1630 cm.$^{-1}$. Deuteration confirms the assignment of both bands to the asymmetric deformation mode.

Upon deuteration, these bands are shifted to lower frequencies, thus establishing their relationship to the NH_2 group. The vibrational modes of

---

[13] F. Basolo, THIS JOURNAL, **72**, 4393 (1950).

[14] M. M. Stimson and M. L. O'Donnell, *ibid.*, **74**, 1805 (1952).

the NH_2 groups in this region previously have been assigned to the asymmetric deformation modes.

The *cis* and *trans*-dinitrobis-(ethylenediamine)-cobalt(III) complexes also were investigated. The bands corresponding to the nitro groups[2,15] were assigned. These were observed at approximately 1400, 1340 and 830 cm.$^{-1}$ in the five salts of this type which were studied. A splitting of the band in the 800 cm.$^{-1}$ region occurred in both the *cis* and *trans*-dinitro compounds. The absorption peaks occurred at 828 and 817 cm.$^{-1}$. In the case of the complexes which contained nitrate as the anion a strong peak was observed at 1376 cm.$^{-1}$, which was assigned to the nitrate ion.

Investigation of the NH_2 asymmetric deformation frequencies of the *cis* and *trans*-dinitro complexes again revealed a splitting of this band in the case of the *cis* isomer. The *trans*-dinitro complex, containing nitrate as the anion (Table I) showed a strong fairly symmetrical band at 1610 cm.$^{-1}$. However, as had been observed previously in the case of the *cis*-dichloro compound, the *cis*-dinitro complex (Table I) gave two peaks in this region, a strong band which occurred at 1575 cm.$^{-1}$ and a weaker one at 1617 cm.$^{-1}$. The chloride salt of the *cis*-dinitro complex gave three absorption bands in this region. These involved a strong band at 1566 cm.$^{-1}$ and bands at 1615 and 1598 cm.$^{-1}$, both of moderate intensity.

The nitrite salt of the *trans*-dinitro complex, however, exhibited three absorption bands in the 1600 cm.$^{-1}$ region. The two strongest bands were at 1617 and 1606 cm.$^{-1}$. The other band, which was extremely weak, occurred at 1633 cm.$^{-1}$. The band containing these peaks was symmetrical. It should be noticed that in this case the strongest absorption peak is observed at 1606 cm.$^{-1}$.

The strongest band of the *cis* complex was found at 1581 cm.$^{-1}$ and the others at 1571 and 1553 cm.$^{-1}$. In general, examination of the spectra reveals a more distinct and a greater splitting of the asymmetric deformation modes of the NH_2 groups in *cis* isomers than is observed in the corresponding *trans* isomers.

Mizushima and co-workers[5] have proposed that a bidentate ligand of the type $X\text{-}CH_2\text{-}CH_2\text{-}X$ exists in the *gauche* form when it is complexed. The calculated hydrogen deformation frequencies of the *gauche* form of $NCS\text{-}CH_2\text{-}CH_2\text{-}SCN$ have been reported.[5] These values have been used in making assignments of the absorption peaks observed for the ethylene groups. Due to the multiplicity of the peaks observed in the spectra of the diacido-bis-(ethylenediamine)-cobalt(III) complexes, which could be assigned to carbon–hydrogen vibrations, the observed peaks have been categorized and assigned by region. These assignments are listed in Table II. The absorption bands assigned fall into the general regions which are expected for the *gauche* form of the ethylene group. Furthermore, the low frequency rocking vibration expected of a *cis*-ethylene group at 740 cm.$^{-1}$ is not observed. No correlation was observed between the splittings of these absorption bands and the isomeric nature of the complex ion.

COLUMBUS 10, OHIO

---

[15] M. L. Morris and D. H. Busch, THIS JOURNAL, **78**, 5178 (1956).

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, AND THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XXV. A *trans* Complex of Triethylenetetramine[1]

BY J. SELBIN[2] AND JOHN C. BAILAR, JR.

RECEIVED JULY 20, 1959

The isolation of both green and violet forms of the cation [Co trien Br_2]$^+$ is reported. That these are *trans* and *cis* isomers, as their respective colors would indicate, is confirmed by a comparison of the infrared spectrum for the known *cis*-[Co trien Cl_2]$^+$ with the spectra for the two dibromo cations. The large size of the bromide ion doubtless helps in forcing the formation of the planar configuration of the *trien* molecule, since adjacent (*cis*) bromide ions will introduce instability, particularly in the close-packed solid state.

Introduction

In 1948, Basolo[3] reported the preparation of [Co trien Cl_2]$^+$ and [Co trien $(NO_2)_2$]$^+$, where *trien* is an abbreviation for the quadridentate ligand, triethylenetetramine. Theoretically, these ions may exist in three different stereoisomeric forms, two *cis* and one *trans*, as shown in Fig. 1. Both *cis* forms, being asymmetric, should be capable of resolution into optical antipodes. Although he used several different preparative methods, Basolo obtained only one dichloro compound and on the basis of its blue-violet color he assigned to it a *cis* configuration. The colors of dihalo cobalt complexes are characteristic of the configurations and have long been used in structure determination, for all known *cis*-dichloro-tetrammine cobalt (and chromium) cations are violet, while their *trans* isomers are green. Likewise he obtained only one dinitro compound, although several different methods were used for its preparation. He could not resolve either of the complex cations.

Das Sarma and Bailar[4] observed that a purple solution of [Co trien Cl_2]Cl in methanol slowly changes to light gray-violet in color on standing,

---

[1] Based in part upon a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Illinois, 1957.

[2] Socony-Mobil Laboratories Fellow in Chemistry, University of Illinois, 1956–1957.

[3] F. Basolo, THIS JOURNAL, **70**, 2634 (1948).

[4] B. Das Sarma and John C. Bailar, Jr., *ibid.*, **77**, 5480 (1955).