Inorganic Chemistry

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The Solid-Phase Deaquation of *cis*-Diaquotetraamminecobalt(III) Sulfate and Some Related Complexes[1]

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The solid-phase deaquation reaction of *cis*-[Co(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O has been studied by thermogravimetric analysis, differential thermal analysis, X-ray powder diffraction, and infrared and visible spectra. The product was determined to be the dinuclear, sulfato-bridged complex *cis,cis*-[(SO₄)(NH₃)₄Co(SO₄)Co(NH₃)₄(SO₄)]. This product is unstable in air and aquates rapidly in solution to the *cis*-[Co(NH₃)₄(H₂O)(SO₄)]⁺ ion. The deaquation reactions of *cis*-[Co(NH₃)₄(H₂O)₂]₂-(SeO₄)₃·3H₂O, *cis*-[Cr(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O, and *cis*-[Co(NH₃)₄(H₂O)(SO₄)]₂MO₄·3H₂O (M = S, Se) were found to yield structurally analogous dinuclear complexes. The deaquation mechanism for each of the reactants is discussed.

Introduction

Numerous amine complexes of cobalt(III) and chromium(III) undergo thermally induced anation reactions in the solid phase.[2] However, a relatively unique situation is existent during the solid-phase deaquation of cis diaquo compounds containing oxyanion counterions, in that the entering anion may assume either monodentate, bidentate, or bridging coordination. In previously studied reactions of this type, it has been found that the deaquation of *cis*-[Co(NH₃)₄(H₂O)₂]-(IO₃)₃·2H₂O yields a monodentate iodato complex *cis*-[Co(NH₃)₄(H₂O)(IO₃)](IO₃)₂,[3] while *cis*-[Co(en)₂-(H₂O)₂](NO₃)₃ deaquates to form a monodentate nitrato complex [Co(en)₂(NO₃)₂]NO₃ of unknown configuration.[4] It has also been found that *cis*-[Co(NH₃)₄-(H₂O)₂]₂(ClO₄)₃ cannot be thermally deaquated without extensive decomposition.[5,6]

There have been conflicting reports as to the product formed in the solid-phase deaquation of *cis*-[Co(NH₃)₄-(H₂O)₂]₂(SO₄)₃·3H₂O. On the basis of precipitation tests and conductometric titration data, Ter Horst[7] proposed the formation of *cis,cis*-[(SO₄)(NH₃)₄Co(SO₄)-Co(NH₃)₄(SO₄)], a dinuclear complex containing a sulfato bridge and two monodentate sulfato groups. This product has also been represented as *cis*-[Co-(NH₃)₄(SO₄)]₂SO₄ in which the presence of one ionic sulfate and two chelated bidentate sulfato ligands is implied though not substantiated by experimental evidence.[6]

In this paper we report on a reinvestigation of this reaction and on the solid-phase deaquation of two additional diaquo complexes, *cis*-[Co(NH₃)₄(H₂O)₂]₂-(SeO₄)₃·3H₂O and *cis*-[Cr(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O. In addition, the deaquation reactions of two *cis*-sulfatoaquotetraammine complexes, *cis*-[Co(NH₃)₄-(H₂O)(SO₄)]₂SO₄·3H₂O and *cis*-[Co(NH₃)₄(H₂O)-(SO₄)]₂SeO₄·3H₂O, are described.

It should be noted at this time that bridged sulfato and chelated sulfato linkages have been found in other cobalt(III) complexes. Dinuclear complexes containing the sulfato group as one of two bridging ligands were prepared originally by Werner,[8] whereas the chelated sulfato complexes [Co(en)₂(SO₄)]Br and [Co-(en)₂(SO₄)]ClO₄ were prepared more recently by the solid-phase deaquation of *cis*-[Co(en)₂(H₂O)(SO₄)]Br·H₂O and *cis*-[Co(en)₂(H₂O)(SO₄)]ClO₄, respectively.[9] The relative scarcity of the chelated sulfato complexes has been rationalized by Finholt, *et al.*,[10] in terms of steric factors. From a consideration of bond distances and bond angles, the authors deduced that the distance between oxygen atoms in the sulfate ion (2.34 Å) is not large enough to allow occupation of the cis octahedral sites (which are separated by approximately 2.78 Å in complexes of both Cr(III) and Co(III)) without appreciable strain in the configuration.

Experimental Section

Thermogravimetric Analysis.—The thermogravimetric (tg) curves were obtained with a modified thermobalance employing the furnace and chain balance arrangement described by Groot and Toutner.[11] The change in weight was charted on a Heath recorder, while a second recorder continuously monitored the

(1) Abstracted from the Ph.D. thesis of E. P. H., University of Illinois, 1969.

(2) See W. W. Wendlandt and J. P. Smith, "The Thermal Properties of Transition-Metal Ammine Complexes," Elsevier, Amsterdam, 1967, Chapters 4, 5, and 7.

(3) N. I. Lobanov, *Russ. J. Inorg. Chem.*, **4**, 151 (1959).

(4) F. C. Chang and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **32**, 3775 (1970).

(5) J. P. Smith and W. W. Wendlandt, *Nature (London)*, **201**, 291 (1964).

(6) M. Mori, R. T. Tsuchiya, S. Takemura, and E. Matsuda, *Bull. Chem. Soc. Jap.*, **4**, 1757 (1961).

(7) M. G. Ter Horst, *Recl. Trav. Chim. Pays-Bas.*, **54**, 257 (1935).

(8) A. Werner, *Justus Liebigs Ann. Chem.*, **375**, 1 (1910).

(9) C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).

(10) (a) J. E. Finholt, R. W. Anderson, J. A. Fyfe, and K. G. Caulton, *Inorg. Chem.*, **4**, 43 (1965); (b) J. E. Finholt and S. N. Deming, *ibid.*, **6**, 1533 (1967).

(11) C. Groot and V. Troutner, *Anal. Chem.*, **29**, 835 (1957).

TABLE I

ELEMENTAL ANALYSES

Compound	% N		% H		% Co or Cr	
	Calcd	Found	Calcd	Found	Calcd	Found
cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O	16.76	16.69	5.73	5.49	17.61	17.40
cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SeO$_4$)$_3$·3H$_2$O	...	...	4.73	4.51	14.57	14.85
cis-[Cr(NH$_3$)$_4$(H$_2$O)]$_2$(SO$_4$)$_3$·3H$_2$O	17.13	16.76	5.85	5.82	15.89	15.88
cis-[Cr(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·2H$_2$O	...	...	5.31	5.23	17.31	17.59
cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·3H$_2$O	17.74	17.93	5.42	5.10	18.68	18.81
cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SeO$_4$·3H$_2$O	16.50	16.40	5.04	5.16	17.36	16.96
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$][a]	20.68	20.59	4.47	4.71	21.72	21.97
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$][b]	20.68	19.95	4.47	4.63	21.72	21.35
cis,cis-[Co(NH$_3$)$_4$(SeO$_4$)$_3$Co(NH$_3$)$_4$]	16.40	16.25	3.54	3.59	17.25	17.24
cis,cis-[Cr(NH$_3$)$_4$(SO$_4$)$_3$Cr(NH$_3$)$_4$]	...	...	19.41[c]	19.1[c]	...	...
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_2$(SeO$_4$)Co(NH$_3$)$_4$]	19.02	18.66	4.10	4.33	20.03	19.50

[a] Product derived from cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O.   [b] Product derived from cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·3H$_2$O.   [c] H$_2$O content determined from tg curve.

temperature with a calibrated iron–constantan thermocouple placed in a glass sheath directly above the sample cup. A thermocouple-controlled stepping motor was used to maintain a linear heating rate of 2°/min. All samples were passed through a 200-mesh screen, weighed 100 mg, and were loosely packed in the sample cup. A flowing nitrogen atmosphere (120 cm³/min) was used in all runs.

Differential Thermal Analysis.—The differential thermal analysis (dta) unit utilized the furnace, programmer, and recorders described above for the thermobalance. The system was wired according to the schematic diagram given by Wendlandt.[12] The differential thermocouple signal was magnified by an Analog Devices low-dc drift operational amplifier. The differential temperature axis was calibrated with an expanded-scale mercury thermometer. The sample and reference containers were made of truncated 5-mm nmr tubes which fit snugly into tap holes of 0.5-in. depth in a 1 in. × 1 in. cylindrical stainless steel block. The sample and reference thermocouples were made from 28-gauge iron–constantan wire and were protected from corrosion by sheating with 1.8-mm sealed glass capillaries. Chromatographic grade alumina (calcined at 800° for 3 hr) was used as a reference. The sample and reference materials each weighed 60 mg and had a particle size of less than 200 mesh. A heating rate of 2°/min and a nitrogen flow of 120 cm³/min were used. Except for the size and geometry of the sample, experimental conditions were the same for the tg and dta runs. Hence, good temperature correlations between the two methods were found.

Infrared Spectra.—The spectra were recorded either on a Beckman IR-5 spectrophotometer or a Perkin-Elmer 521 spectrophotometer. Spectra in the far-infrared region were recorded on a Beckman IR-5A spectrophotometer. Nujol mulls and KBr disks were employed.

Visible Spectra.—The visible spectra were recorded on a Cary 14 spectrophotometer. Solution spectra were obtained with 0.01 M HNO$_3$ as a solvent and reference. Solid-state spectra were recorded as Kel-F mulls sandwiched between quartz plates. A similar mull containing CaCO$_3$ was placed in the reference beam in an attempt to equalize scattering.

X-Ray Powder Diffraction.—Diffraction patterns were obtained with a 114.83-mm camera and a Philips X-ray unit. Nickel-filtered Cu Kα radiation was used (35 kV, 18 mA). An automatic scanning densitometer was used to determine the intensities of the diffraction lines.

Preparation of Compounds.—The analytical data for the compounds prepared in this study are presented in Table I. The formulas given for the previously uncharacterized thermal reaction products are those indicated by the evidence presented in this paper. The analyses were performed by Mr. J. Nemeth and his staff at the University of Illinois.

The complexes cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O,[13] cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·3H$_2$O,[14] and cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SeO$_4$·3H$_2$O[15] were prepared by methods described in the literature.

cis-[Cr(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·**3H$_2$O.**—A solution of 2 g of re-

crystallized cis-[Cr(NH$_3$)$_4$(H$_2$O)(OH)]SO$_4$·0.5H$_2$O[16] in 15 ml of H$_2$O was treated with 3 ml of 9 M sulfuric acid. An orange gum formed upon addition of ethanol to the orange solution. After decanting the liquor, the gum was dissolved in cold water, formed again by the addition of ethanol, and recrystallized by trituration with successive portions of fresh ethanol. The orange solid was then washed with ether. The air-dried product rapidly loses water and all experiments with it were initiated within 1 hr after the ether wash.

Within 6 hr after standing at room temperature (in the dark) the material had undergone a color change from orange to red; after 2 days the color had become violet-red. The color and elemental analyses at this time suggested the presence of a sulfatoaquo species. Attempts to recrystallize the material from aqueous solution gave only red-violet gums.

cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SeO$_4$)$_3$·**3H$_2$O.**—A solution of 2.7 g of cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]Cl$_3$ in 60 ml of water was ground in a mortar for a few minutes with 3.6 g of Ag$_2$SeO$_4$. After filtration to remove the precipitated silver chloride, 150 ml of cold ethanol was added slowly to the solution. After 30 min the red solid was filtered, washed successively with ethanol and ether, and then dried in air; yield, 2.5 g.

cis,cis-Co[(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$].—(a) This compound was prepared by heating cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O at 118° for 12 hr or by heating the diaquo sulfate in the thermobalance at 2°/min (to 160°) until a plateau corresponding to the total loss of water (calcd 18.60%) was reached (see curve A, Figure 1).
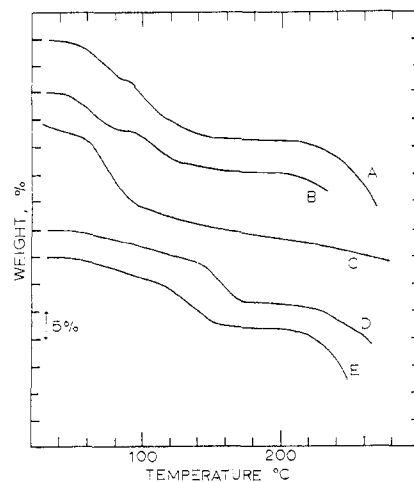

Figure 1.—Thermogravimetric analysis curves for cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O (A), cis-[Co(NH$_3$)$_4$(H$_2$O)]$_2$(SeO$_4$)$_3$·3H$_2$O (B), cis-[Cr(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O (C), cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·3H$_2$O (D), and cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SeO$_4$·3H$_2$O (E).

(b) It was also prepared by heating cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·3H$_2$O on the thermobalance (to 190°) until a nearly horizontal plateau corresponding to complete loss of the water

(12) W. W. Wendlandt, "Thermal Methods of Analysis," Interscience, New York, N. Y., 1964, p 187.

(13) S. M. Jorgensen, Z. Anorg. Allg. Chem., **2**, 279 (1892).

(14) F. Ephraim and W. Flugel, Helv. Chim. Acta, **7**, 724 (1924).

(15) J. Meyer and K. Grohler, Z. Anorg. Allg. Chem., **155**, 112 (1926).

(16) J. V. Dubsky, J. Prakt. Chem., **90**, 61 (1914).

(calcd 14.25%) was reached(see curve D, Figure 1). The slight nonzero slope of the plateau at this point suggests that deammination is occurring along with the final stages of the deaquation process. This is also evidenced in the low nitrogen content of the product.

The violet compound is extremely hygroscopic and it undergoes a pronounced color change toward red-violet if allowed to stand in humid air for 1 hr. The violet solid is soluble in water, but rapid aquation is apparent since the color of the solution changes within seconds toward red-violet. The material is insoluble in the common organic solvents.

cis,cis-[Co(NH₃)₄(SO₄)₂(SeO₄)Co(NH₃)₄].—The hygroscopic violet product was obtained by heating *cis*-[Co(NH₃)₄(H₂O)-(SO₄)]₂SeO₄·3H₂O on the thermobalance (to 170°) until a nearly horizontal plateau corresponding to the loss of three molecules of water (calcd 13.25%) was reached (see curve E, Figure 1). The material is soluble in water but aquates readily to give a red-violet solution.

cis,cis-[Cr(NH₃)₄(SO₄)₃Cr(NH₃)₄].—This compound was prepared by heating *cis*-[Cr(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O on the thermobalance (to 140°) until a plateau corresponding to the total loss of water (calcd 19.41%) was reached (see curve C, Figure 1). The plateau is not perfectly horizontal, indicating that some overlap of the deaquation and deammination steps has occurred. The violet solid dissolves in water and is insoluble in the common organic solvents.

cis,cis-[Co(NH₃)₄(SeO₄)₃Co(NH₃)₄].—The hygroscopic violet product was obtained by heating *cis*-[Co(NH₃)₄(H₂O)₂]₂(SeO₄)₃·3H₂O in the thermobalance (to 180°) until a plateau corresponding to the total loss of water (calcd 15.57%) was reached (see curve B, Figure 1). It is soluble in water and insoluble in ethanol.

Results and Discussion

Identification of Products.

The tg and dta curves for the diaquo and sulfatoaquo complexes are shown in Figures 1 and 2. Each tg curve has a distinct plateau
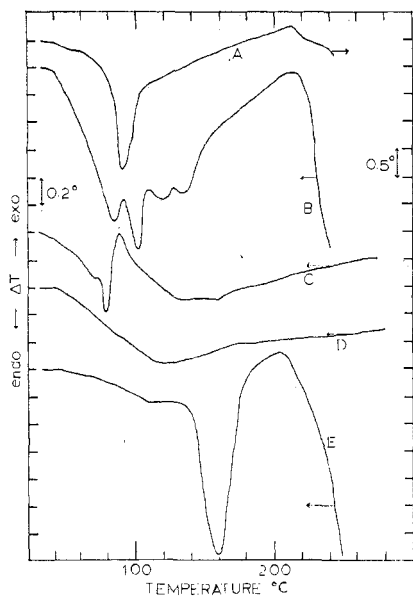

Figure 2.—Differential thermal analysis curves for *cis*-[Co-(NH₃)₄(H₂O)₂]₂(SeO₄)₃·3H₂O (A), *cis*-[Co(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O (B), *cis*-[Cr(NH₃)₄(H₂O)₂]₂(SO₄)₃·3H₂O (C), *cis*-[Cr(NH₃)₄-(H₂O)(SO₄)]₂SO₄·2H₂O (D), and *cis*-[Co(NH₃)₄(H₂O)(SO₄)]₂SO₄·3H₂O (E).

corresponding to the total loss of water, although those plateaus with a nonzero slope indicate that the latter stages of the deaquation reaction overlap with the beginning of the higher temperature deammination process. However, termination of the tg runs at the most nearly horizontal regions of the respective plateaus yielded products which gave satisfactory elemental analyses for the proposed formulas.
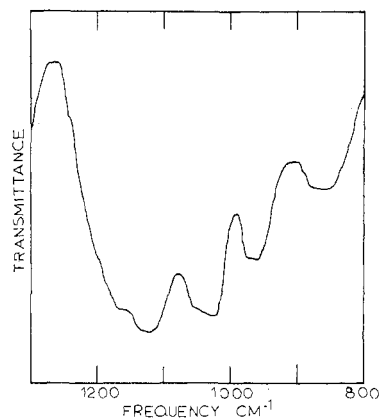

Figure 3.—Infrared spectrum of *cis,cis*-[Co(NH₃)₄(SO₄)₃Co(NH₃)₄].

When cold, freshly prepared solutions of the de-aquated complexes (or their immediate aquation products) were treated with barium ion, negative precipitation tests for the sulfate and selenate ions were obtained. This shows that all of the sulfate and selenate is coordinated and that [Co(NH₃)₄(SO)₄]₂SO₄ and other formulas containing ionic sulfate and selenate can be eliminated as possible deaquation products.

It has been found by Nakamoto, *et al.*,[17] that characteristic differences occur in the infrared spectra of complexes containing differing modes of sulfate coordination. For tetrahedral species (such as the sulfate ion) only the triply degenerate ν_3 (asymmetric stretch) and ν_4 (asymmetric bend) bands are infrared active, although a weak ν_1 (symmetric stretch) band is sometimes observed in solid-state spectra as a result of weak interactions between neighboring atoms or molecules. For a monodentate MO₄ ligand of C_{3v} symmetry, the ν_3 and ν_4 bands split into doublets, and the nondegenerate ν_4 and doubly degenerate ν_2 (symmetric bend) bands become allowed. A bidentate or bridged MO₄ ligand of C_{2v} symmetry has all degeneracies removed; the ν_3 and ν_4 bands split into triplets and the ν_2 band splits into a doublet. It has been shown by Eskanazi,[18] *et al.*, that the position of the highest frequency ν_3 band in a C_{2v} sulfato spectrum can be used to distinguish between chelated and bridging sulfato ligands; a ν_{3a} band[19] above 1200 cm⁻¹ is indicative of the chelate structure, while the bridged arrangement exhibits the ν_{3a} band below 1200 cm⁻¹.

The parent complexes containing the sulfate ion all give spectra with the typical T_d sulfate bands. The ν_3 band at about 1100 cm⁻¹ is broad and intense and in some cases is very slightly split due to lattice effects. A weak ν_1 band appears at about 970 cm⁻¹ and the strong ν_4 band occurs at about 610 cm⁻¹. In addition to the ionic sulfate bands, the complex *cis*-[Co(NH₃)₄-(H₂O)(SO₄)]₂SO₄·3H₂O shows absorptions attributed to the monodentate sulfato ligand. The ν_{3b} absorption is found at 1032 (s) cm⁻¹ and the slightly split ν_{3a} band, which overlaps partially with the ν_3 absorption of the sulfate ion, is found with peaks at 1119 (s) and 1160

(17) (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York N. Y., 1963, p 161; (b) N. Tanaka, H. Sugi, and J. Fujita, *Bull. Chem. Soc. Jap.*, **37**, 640 (1964).

(18) R. Eskanazi, J. Raskovan, and R. Levitus, *J. Inorg. Nucl. Chem.*, **28**, 521 (1966).

(19) The a, b, and c, subscripts are used to designate the bands resulting from the splitting of a degenerate vibrational mode. The highest frequency band is designated as the a band, *e.g.*, as in ν_{3a}.

Table II[a]

SULFATO VIBRATIONAL FREQUENCIES OF DEAQUATED COMPLEXES

Compound	ν_1	ν_3	ν_4	Symmetry
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] (a)	963 s, b	1190 s, sh, 1160 s, sh, 1125 s, 1050 s, sh, 1023 s	642 s, 614 s, 599 s	$C_{3v} + C_{2v}$
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] (b)	969 s, b	1185 s, sh, 1165 s, sh, 1110 s, b, 1022 s, b	642 m, 614 s, 599 s	$C_{3v} + C_{2v}$
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_2$(SeO$_4$)Co(NH$_3$)$_4$]	962 m	1160 s, sh, 1119 s, 1030 s	637 m, 612 m, 599 m	C_{3v}
cis,cis-[Cr(NH$_3$)$_4$(SO$_4$)$_3$Cr(NH$_3$)$_4$]	970 s	1175 s, sh, 1134 s, 1036 s	644 m, 609 s, b	$C_{3v} + C_{2v}$
cis-[Cr(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·2H$_2$O	970 s	1170 s, sh, 1125 s, 1105 s, sh	642 m, 605 s	$C_{3v} + T_d$

[a] Key: s, strong; m, medium; b, broad; sh, shoulder.

(s) cm^{-1}. This splitting has been attributed to a perturbation upon the C_{3v} symmetry by hydrogen bonding between the sulfato and the neighboring aquo group.[20] The ν_1 and the ν_4 bands apparently coincide at 969 and 613 cm^{-1} with the respective ν_1 and ν_4 bands of the ionic sulfate. The ν_{4a} band is seen at 645 cm^{-1}. Similar C_{3v} sulfato bands are seen in the spectrum of *cis*-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SeO$_4$·3H$_2$O.

The sulfato bands in the infrared spectra of the thermally deaquated complexes are listed in Table II. The spectrum of *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] prepared from the diaquo sulfate is shown in Figure 3. Although the prominent features of this spectrum are those of C_{3v} sulfato symmetry, there are also strong indications of the presence of a C_{2v} bridging sulfato group. The band appearing as a slight shoulder at about 1190 cm^{-1} is not found in the spectra of C_{3v} sulfato complexes and is probably the ν_{3a} vibration of the sulfato bridge. The shoulder at 1160 cm^{-1} and the peak at 1125 cm^{-1} are assigned to the ν_{3a} absorption of the monodentate sulfato group and they apparently mask the ν_{3b} band of the bridging group. The ν_{3b} band of the C_{3v} sulfato ligands appears at 1025 cm^{-1} and all but overlaps the ν_{3c} band of the bridge, which appears as a shoulder at 1050 cm^{-1}. The respective ν_1 bands also coincide, giving rise to the broad absorption at 963 cm^{-1}. The three ν_4 bands observed in the 600-cm^{-1} region are not inconsistent with the presence of a $C_{2v} + C_{3v}$ complex, although the possibility of completely overlapping bands precludes a definitive assignment.

The above evidence suggests that the molecular structure
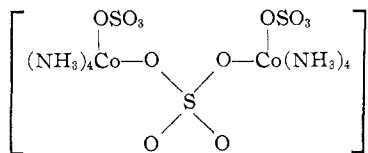
assigned by Ter Horst[7] is correct. The lack of a sulfato band above 1200 cm^{-1} indicates the absence of a chelated sulfato group and excludes [Co(NH$_3$)$_4$(SO$_4$)]-[Co(NH$_3$)$_4$(SO$_4$)$_2$] as a possible structure.

The sulfatoaquo-derived sample of *cis,cis*-[Co(NH$_3$)$_4$-(SO$_4$)$_3$Co(NH$_3$)$_4$] and the complex *cis,cis*-[Cr(NH$_3$)$_4$-(SO$_4$)$_3$Cr(NH$_3$)$_4$] both give sulfato bands virtually identical with those described directly above and the presence of combination $C_{2v} + C_{3v}$ structures is again indicated.

The complex *cis*-[Cr(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·2H$_2$O shows typical C_{3v} sulfato bands which apparently mask those resulting from the ionic sulfate. However, precipitation tests show that ionic sulfate is present.

(20) M. Drouin, J. P. Mathieu, and H. Poulet, *J. Chim. Phys.*, **58**, 322 (1961).

The *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)(SeO$_4$)Co(NH$_3$)$_4$(SO$_4$)] complex exhibits a typical C_{3v} sulfato spectrum which is very similar to that of its parent compound, *cis*-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SeO$_4$·3H$_2$O. This shows that the sulfato groups remain monodentate and implies that the selenate ion forms the bridge during the deaquation reaction. Unfortunately, direct evidence for the selenato bridge could not be obtained since the selenate ν_1 and ν_3 absorptions occur in the 830–880-cm^{-1} region[21] and are masked by the degenerate NH$_3$ rocking vibration of the cobalt(III)–tetraammine portion of the molecule. The ν_4 band observed in the 410–420-cm^{-1} region is split into a doublet,[4] indicating that the selenate is coordinated but is of no help in the bonding assignment. In the absence of evidence to the contrary, the structure
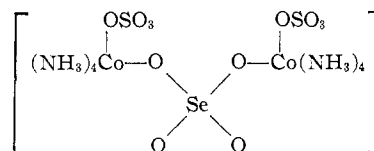
is proposed for this compound.

The infrared spectrum of the deaquated diaquo selenate complex shows an intense band with three poorly resolved minima in the 850-cm^{-1} region. Assignments could not be made due to overlap of the selenato bands with the NH$_3$ rocking absorption.

The visible absorption maxima for the diaquo-, sulfatoaquo-, and sulfato-bridged complexes are listed in Table III. Because the bridged complexes are

Table III[a]

VISIBLE SPECTRA OF THE COMPLEXES[b,c]

Complex	λ_{max}, nm (ϵ)	
cis-[Co(L)$_4$(H$_2$O)$_2$]$^{3+}$	503 (54)	355 (45)
cis-[Cr(L)$_4$(H$_2$O)$_2$]$^{3+}$	497 (36)	368 (29)
cis-[Co(L)$_4$(H$_2$O)(SO$_4$)]$^+$	517 (71)	362 (49)
cis,cis-[CoL$_4$(SO$_4$)$_3$CoL$_4$] (a)	590 sh, 533	362
cis-cis-[CoL$_4$(SO$_4$)$_3$CoL$_4$] (b)	590 sh, 533	365 sh[d]
cis,cis-[CoL$_4$(SO$_4$)$_2$(SeO$_4$)CoL$_4$]	590 sh, 535	355 sh[d]
cis,cis-[CoL$_4$(SeO$_4$)$_3$CoL$_4$]	509 sh, 532	361
cis,cis-[CrL$_4$(SO$_4$)$_3$CrL$_4$]	528	385
cis-[CrL$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·2H$_2$O	512	378

[a] sh = shoulder. [b] L = NH$_3$. [c] Values for thermal products are taken from mull spectra. [d] Band appears as shoulder on charge-transfer band.

unstable in aqueous solution, the maxima have been taken from the mull spectra. The shorter wavelength maximum in each of the mull spectra is markedly dependent upon the mull thickness and the degree of overlap with nearby charge-transfer bands.

(21) A. Muller and B. Krebs, *J. Mol. Spectrosc.*, **24**, 180 (1967).

Compound	*d*, Å
cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O	10.32 (3), 6.00 (10), 5.60 (7), 4.64 (5), 4.26 (7), 4.10 (10), 3.82 (6), 3.56 (7)
cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SeO$_4$)$_2$·3H$_2$O	10.45 (3), 6.19 (7), 5.71 (7), 4.65 (7), 4.50 (7), 4.35 (10), 3.93 (7), 3.50 (8)
cis-[Cr(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O	10.33 (3), 6.19 (10), 5.68 (7), 4.68 (5), 4.27 (10), 3.81 (5), 3.59 (8)
cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$	6.48 (5), 5.53 (9), 4.18 (10), 3.73 (6), 3.09 (3), 2.78 (2)
cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SeO$_4$)$_3$	6.63 (3), 5.69 (9), 4.27 (10), 3.82 (7), 3.18 (3), 2.84 (5)
cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·3H$_2$O	8.98 (5), 8.58 (2), 6.80 (5), 5.96 (10), 5.14 (3), 4.69 (10), 4.43 (8), 4.22 (7)
cis-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SeO$_4$·3H$_2$O	9.11 (7), 8.62 (7), 6.80 (4), 5.98 (7), 5.09 (5), 4.73 (10), 4.45 (8), 4.15 (9)
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] (a)	6.19 (10), 5.24 (7), 3.96 (8), 3.59 (7), 1.99 (2)
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] (b)	No diffraction lines
cis,cis-[Co(NH$_3$)$_4$(SeO$_4$)$_3$Co(NH$_3$)$_4$]	10.16 (2), 6.32 (4), 5.37 (4), 5.09 (3), 3.97 (10), 3.65 (8)
cis,cis-[Cr(NH$_3$)$_4$(SO$_4$)$_3$Cr(NH$_3$)$_4$]	6.23 s, b, 5.14 s, b, 4.07 m, b, 3.60 w, 1.99 s
cis,cis-[Co(NH$_3$)$_4$(SO$_4$)$_2$(SeO$_4$)Co(NH$_3$)$_4$]	No diffraction lines
cis-[Cr(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$_2$SO$_4$·2H$_2$O	6.32 w, 5.37 w, 5.34 w, 4.15 w, 3.75 w

[a] Key: s, strong; m, medium; w, weak; b, broad.

If it is assumed that the spectrum of each dinuclear cobalt(III) complex consists of contributions from two independently absorbing cobalt(III) centers of the type CoN$_4$O$_2$, then it should be possible to assign a geometrical configuration based upon analogy with the spectra of similar CoN$_4$O$_2$ species. As a model, the *cis*- and *trans*-[Co(en)$_2$(H$_2$O)$_2$]$^{3+}$ complexes were chosen. The cis isomer exhibits a spectrum in which the $^1A_1 \rightarrow$ $^1T_1$ (octahedral) transition is seen as a single band with a maximum at 492 nm.[22] The tetragonal distortion of the ligand field of the trans isomer is twice that of the cis, and the $^1T_1$ band splits into two clearly resolved bands ($^1A_2$ and $^1E_1$) with maxima at 550 and 444 nm.[22] The $^1T_1$ band in the spectrum of *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co-(NH$_3$)$_4$] consists of a single maximum at about 530 nm and a shoulder at about 590 nm. The absence of a second maximum leads us to assign tentatively the cis,cis configuration, although the presence of the shoulder could be indicative of minor amounts of the trans,trans or cis,trans isomers. Since this complex rapidly aquates in solution, purification or separation of isomers could not be effected.

The construction of isomeric [Co(NH$_3$)$_4$(SO$_4$)$_3$Co-(NH$_3$)$_4$] molecules with Fisher–Hirschfelder molecular models indicates not only that the cis,cis configuration has less steric strain than the cis,trans or the trans,-trans but that ten or more different cis,cis conformers are possible. Two of the conformers are quite free of strain and appreciable rotational movement about the cobalt–oxygen bonds is possible.

The spectrum of a freshly prepared solution of di-aquo-derived *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] differs from the mull spectrum in that the 590-nm shoulder is gone and the $^1T_1$ band has shifted to 528 nm (ϵ 78). This is not inconsistent with the proposal that *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] immediately aquates in solution to form the *cis*-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$^+$ and *cis*-[Co(NH$_3$)$_4$(SO$_4$)$_2$]$^-$ ions.[7] After 3 hr the solution showed maxima at 517 nm (ϵ 68) and 362 nm (ϵ 49), indicating that aquation of *cis*-[Co(NH$_3$)$_4$(SO$_4$)$_2$]$^-$ to the *cis*-[Co-(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$^+$ ion had occurred. The latter ion has maxima at 517 nm (ϵ 71) and 362 nm (ϵ 49) and is quite resistant toward further aquation.

Similar aquation behavior was observed for the sulfatoaquo-derived *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$] complex, although the lower extinction coefficient calculated for the $^1T_1$ band (ϵ 58) after the 3-hr aquation period suggests that appreciable amounts of impurity

were present. Other evidence for the presence of impurities has been mentioned earlier in the discussion.

The visible mull spectrum of *cis,cis*-[Co(NH$_3$)$_4$-(SeO$_4$)$_3$Co(NH$_3$)$_4$] is similar to that of its sulfato analog, indicating a predominantly cis,cis configuration. The rate of aquation of the selenato complex is not as rapid, however, and a freshly prepared solution shows a spectrum virtually identical with that of the compound in the solid state. Maxima were observed at 369 nm (ϵ 48) and 531 nm (ϵ 59) with a shoulder on the latter at 590 nm. A spectrum recorded after 45 min showed maxima at 367 nm (ϵ 47) and 527 nm (ϵ 57) (the shoulder had disappeared), while after 6 hr maxima were found at 361 nm (ϵ 47) and 518 nm (ϵ 54). The latter spectrum is virtually identical with that recorded for the *cis*-[Co(NH$_3$)$_4$(H$_2$O)(SeO$_4$)]$^+$ ion.[23]

The mull spectrum of *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_2$(SeO$_4$)-Co(NH$_3$)$_4$] is similar to that of its sulfato-bridged analog and a cis,cis configuration is again indicated. The spectrum of a freshly prepared solution shows similar changes from the mull spectrum as in the case of *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_3$Co(NH$_3$)$_4$]. It is probable that *cis*-[Co(NH$_3$)$_4$(H$_2$O)(SO$_4$)]$^+$ and *cis*-[Co(NH$_3$)$_4$(SO$_4$)-(SeO$_4$)]$^-$ form immediately upon dissolution in water. Although the anionic complex aquates readily, it is not known whether the sulfatoaquo or selenatoaquo ion is formed.

The complex *cis,cis*-[Cr(NH$_3$)$_4$(SO$_4$)$_3$Cr(NH$_3$)$_4$] gives a solid-state visible spectrum with maxima at 385 and 528 nm. The absence of splitting in the latter band ($^4A_2 \rightarrow$ $^4T_2$ (octahedral)) indicates the presence of the cis,cis configuration.

The most intense lines in the X-ray diffraction patterns of the reactant and product complexes are listed in Table IV. The three diaquo parents are isomorphous, as are the respective deaquation products. This strongly infers that the latter have formally similar molecular structures, in agreement with the spectral results discussed above. The sulfatoaquo sulfate and selenate are also isomorphous, while their respective products do not give diffraction lines and are apparently amorphous.

The Nature of the Solid-Phase Reactions.—It is seen from examination of the dta curve (Figure 2, curve B) that *cis*-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$_2$(SO$_4$)$_3$·3H$_2$O loses water in four steps to form *cis,cis*-[Co(NH$_3$)$_4$(SO$_4$)$_3$-Co(NH$_3$)$_4$]. On the basis of the subsequent discussion

(22) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **9**, 1265 (1952).

(23) E. P. Hertzenberg, Ph.D. Thesis, University of Illinois, 1969.

the following reaction sequence is proposed

$$cis\text{-}[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$$

$$(1) \downarrow -3H_2O$$

$$cis\text{-}[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$$

$$(2) \downarrow -2H_2O$$

$$cis\text{-}[Co(NH_3)_4(H_2O)(SO_4)]_2SO_4$$

$$(3) \downarrow -H_2O$$

$$[cis\text{-}Co(NH_3)_4(H_2O)(SO_4)] [cis\text{-}Co(NH_3)_4(SO_4)_2]$$

$$(4) \downarrow -H_2O$$

$$cis,cis\text{-}[Co(NH_3)_4(SO_4)_3Co(NH_3)_4]$$
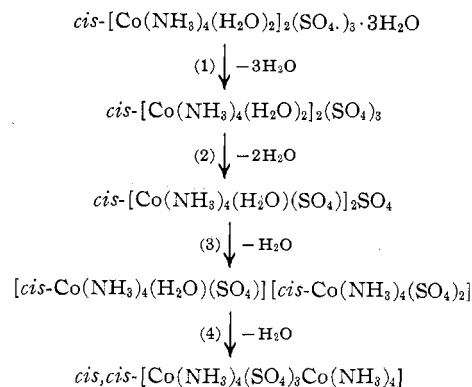
The first endotherm (at 84°) corresponds to the loss of lattice water, and a clearly distinguished plateau for this step is seen in the tg curve (Figure 1, curve A). The product isolated at this point, $cis\text{-}[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$, has a color identical with that of its parent, produces a distinctly different X-ray pattern (see Table IV), and gives a dta curve similar to that of the parent but without the 84° endotherm. The second endotherm (at 102°) corresponds to a loss of one aquo ligand from each diaquo cation and the formation of the sulfatoaquo sulfate intermediate. This step is indicated only by a slight change of slope in the tg curve; the lack of a well-defined plateau discouraged any attempt to isolate the intermediate for further characterization. Although the endotherm (at 120°) corresponding to step 3 is clearly observed, there is no evidence for this step in the tg curve and, again, no attempt was made to isolate the intermediate product. The fourth endotherm (at 134°) and the well-defined plateau correspond to the formation of the dinuclear product described above.

The complex $cis\text{-}[Co(NH_3)_4(H_2O)_2]_2(SeO_4)_3 \cdot 3H_2O$ also shows a distinct pleateau (see Figure 1, curve B) for the loss of the lattice water and the product isolated at this point, $cis\text{-}[Co(NH_3)_4(H_2O)_2]_2(SeO_4)_3$, is isomorphous with its sulfate analog. The dta curve (see Figure 2, curve A), however, shows a very weak thermal effect for the loss of lattice water and a strong, sharp endotherm (at 90°) corresponding to the formation of a short-lived $cis\text{-}[Co(NH_3)_4(H_2O)(SeO_4)]_2SeO_4$ intermediate. The formation of $cis,cis\text{-}[Co(NH_3)_4(SeO_4)_3Co(NH_3)_4]$ after this step is apparently characterized by a slight change in slope in the tg curve for loss of the last two molecules of coordinated water and by a shoulder (on the 90° endotherm) which slowly returns to the dta base line.

A remarkable difference occurs between the rate of deaquation of $cis\text{-}[Cr(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$ and its isomorphous cobalt(III) analog. The latter complex undergoes no change in composition over a period of 2 years, whereas the chromium(III) compound releases water within hours at room temperature and has reacted further in a few days to form $cis\text{-}[Cr(NH_3)_4(H_2O)(SO_4)_2]_2SO_4 \cdot 2H_2O$. It is apparent from the tg curve (Figure 1, curve C) that the losses of lattice water and coordinated water partially coincide. The dta curve (Figure 2, curve C) shows a broad endotherm for the first process which then merges into a sharp endotherm at 78° corresponding to formation of $cis\text{-}[Cr(NH_3)_4(H_2O)(SO_4)]_2SO_4$. The deaquation of this intermediate is characterized by a broad endotherm

centered at about 140° which is slightly resolved into two separate steps corresponding to those in the analogous cobalt(III) reaction and which merges with the deammination endotherm.

The dta curve (Figure 2, curve D) for $cis\text{-}[Cr(NH_3)_4(H_2O)(SO_4)]_2SO_4 \cdot 2H_2O$ shows a broad shallow endotherm for the deaquation process and is similar to the diaquo curve except for the absence of the sharp endotherm at 78°. This confirms the assignment of the latter peak to the formation of the sulfatoaquo intermediate in the diaquo sulfate reaction.

A comparison of the thermoanalytical curves (Figure 1, curves D and E; Figure 2, curve E) of the isomorphous sulfatoaquo sulfate and selenate complexes shows that the two deaquate in a similar manner, although closer inspection shows that the selenato-bridged complex is formed more readily. The tg curves show that the loss of coordinated water begins before the lattice water is completely removed. The dta curves show a weak endotherm for the loss of the lattice water and a single peak for the loss of the co-ordinated water. The lack of splitting in the latter peak indicates that on the dta time scale used in this study both ends of the bridge form simultaneously. The infrared data have shown that in $cis,cis\text{-}[Co(NH_3)_4(SO_4)_2(SeO_4)Co(NH_3)_4]$ the selenate ion has become the bridge during deaquation of the sulfatoaquo selenate complex. Since this reactant is isomorphous with $cis\text{-}[Co(NH_3)_4(H_2O)(SO_4)]_2SO_4 \cdot 3H_2O$, it is assumed that during deaquation of the latter the sulfate ion forms the bridge.

The apparent difference in activity of the $cis\text{-}[Co(NH_3)_4(H_2O)(SO_4)]_2SO_4$ intermediate common to both the $cis\text{-}[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3 \cdot 3H_2O$ and $cis\text{-}[Co(NH_3)_4(H_2O)(SO_4)]_2SO_4 \cdot 3H_2O$ deaquation reactions is perhaps due to a topochemical effect. (The topochemical principle recognizes that the location of potentially reactive centers relative to one another in an ordered lattice profoundly effects the rate and path of a solid-state reaction; reaction in the solid state occurs with a minimum amount of atomic or molecular movement.[24]) It is seen from Table IV that the crystalline diaquo and sulfatoaquo parents have different lattice arrangements and that the diaquo-derived $cis,cis\text{-}[Co(NH_3)_4(SO_4)_3Co(NH_3)_4]$ product retains considerable crystallinity while the sulfatoaquo-derived product is apparently amorphous. The greater degree of disruption in the lattice of the latter product implies that the sulfate ion has traversed a longer or more restricted path in order to reach positions favorable for bonding to the vacated coordination sites. This is reflected in the higher temperature needed to complete the deaquation reaction (compare curves A and D in Figure 1). The topochemical factor also rationalizes the observed differences in the dta curves (compare curves B and E in Figure 2). Whereas a step corresponding to the formation of $cis\text{-}[Co(NH_3)_4(H_2O)(SO_4)]$-$cis\text{-}[Co(NH_3)_4(SO_4)_2]$ is seen in the diaquo reaction, evidence for this intermediate is not observed in the sulfatoaquo reaction as both ends of the bridge apparently form at the same time.

The results of this study indicate that none of the reaction products contains a chelated sulfato ligand. This can be ascribed to steric factors[10] which have

(24) See M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1996 (1964).

been mentioned in the Introduction. Since the selenate ion has a larger oxygen-to-oxygen distance (2.62 Å) than that in the sulfate ion (2.34 Å), the bidentate selenato linkage ought to be formed with less strain. It is of interest that the deaquation of the diaquo

selenate yields the bridged selenato complex in preference to a bidentate selenato product.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE MATERIALS RESEARCH LABORATORY,
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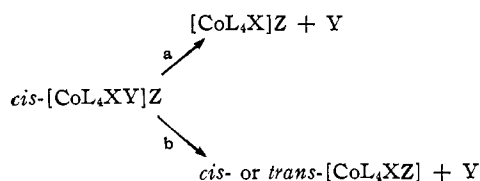# The Solid-Phase Deaquation of Some *cis*-Sulfatoaquotetraaminecobalt(III) Complexes[1]

BY E. P. HERTZENBERG AND JOHN C. BAILAR, JR.*

The solid-phase deaquation reactions of *cis*-[Co(en)₂(H₂O)(SO₄)]Br·H₂O and six *cis*-[Co(NH₃)₄(H₂O)(SO₄)]Z complexes (Z = Cl, Br, NO₃, ClO₄, BF₄, ½PtCl₆) have been studied by thermogravimetric analysis, differential thermal analysis, X-ray powder diffraction, and infrared and visible spectroscopy. Bidentate sulfato complexes of the type [Co(NH₃)₄(SO₄)]Z are formed when Z = ClO₄, BF₄, and ½PtCl₆. In addition, the bidentate sulfato complex [Co(en)₂(SO₄)]Br is formed. Complexes of the type *cis*-[Co(NH₃)₄(SO₄)Z] are formed when Z = Cl, Br, and NO₃. The factors which influence the reaction paths are discussed.

Introduction

Few solid-phase anation reactions of cobalt(III) complexes are known in which two or more potential ligands are able to compete for a single position in the coordination sphere. The situation arises when an easily replaceable ligand occupies a position cis to a potentially multidentate ligand

$$
\begin{array}{c}
\text{[CoL}_4\text{X]Z + Y} \\
\nearrow {}^{a} \\
cis\text{-[CoL}_4\text{XY]Z} \\
\searrow {}_{b} \\
cis\text{- or } trans\text{-[CoL}_4\text{XZ] + Y}
\end{array}
$$

Upon the loss of ligand Y, either the denticity of X is increased (path a) or the counterion Z becomes coordinated (path b). In an example of the first type, Barraclough and Tobe[2] found that *cis*-[Co(en)₂(H₂O)(SO₄)]Br·H₂O and *cis*-[Co(en)₂(H₂O)(SO₄)]ClO₄ deaquate at 120° to form the bidentate sulfato complexes [Co(en)₂(SO₄)]Br and [Co(en)₂(SO₄)]ClO₄, respectively, in preference to products in which the bromide and perchlorate anions replace the aquo group. A reaction of the second type has been illustrated in the preceding paper,[3] in that the deaquation of *cis*-[Co(NH₃)₄(H₂O)(SO₄)]₂SO₄·3H₂O forms the dinuclear sulfato-bridged complex *cis,cis*-[Co(NH₃)₄(SO₄)₃Co(NH₃)₄] rather than the bidentate sulfato complex *cis*-[Co(NH₃)₄(SO₄)]₂SO₄. An analogous selenato-bridged complex forms upon deaquation of *cis*-[Co(NH₃)₄(H₂O)(SO₄)]₂SeO₄·3H₂O.[3]

In this paper we describe the solid-phase deaquation reactions of six additional *cis*-[Co(NH₃)₄(H₂O)(SO₄)]Z complexes and discuss the factors which influence the paths by which the reactions proceed.

(1) Abstracted in part from the Ph.D. thesis of E. P. Hertzenberg, University of Illinois, 1969.

(2) C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).

(3) E. P. Hertzenberg and J. C. Bailar, Jr., *Inorg. Chem.*, **10**, 2371 (1971).

Experimental Section

The tg, dta, infrared, ultraviolet–visible, and X-ray powder diffraction instrumentation and techniques have been described.[3]

The analytical data for the compounds prepared in this study are presented in Table I. Formulas for the thermal reaction products are those indicated by the evidence presented in this paper.

The complexes *cis*-[Co(en)₂(H₂O)(SO₄)]Br·H₂O and [Co(en)₂(SO₄)]Br were prepared by the method of Barraclough and Tobe.[2]

The complexes *cis*-[Co(NH₃)₄(H₂O)(SO₄)]Z (Z = Cl, Br, and NO₃) were prepared by the method of Ephraim and Flugel.[4]

The complex *cis*-[Co(NH₃)₄(H₂O)(SO₄)]ClO₄ was prepared by a modification of a previously described procedure.[4] A solution of 0.7 g of *cis*-[Co(NH₃)₄(H₂O)(SO₄)]Cl in 20 ml of water was treated with 3 g of sodium perchlorate. The red crystalline product was filtered, washed generously with ethanol, and then dried in air; yield 0.4 g.

cis-[Co(NH₃)₄(H₂O)(SO₄)]BF₄.—A solution of 1.6 g of the sulfatoaquo chloride in 20 ml of water was treated with a solution of 5 g of NaBF₄ in 10 ml of water. Upon addition of 30 ml of ethanol, a light red precipitate formed. The solid was reprecipitated in a similar manner, filtered, washed successively with 1:1 ethanol–water and ethanol, and dried in air. The yield was 1.0 g.

cis-[Co(NH₃)₄(H₂O)(SO₄)]₂PtCl₆·2H₂O.—A mixture of 1.0 g of *cis*-[Co(NH₃)₄(H₂O)(SO₄)]Br and 1.0 g of H₂PtCl₆·6H₂O was dissolved in 50 ml of water. The resulting solution was treated with 30 ml of ethanol added in small portions. The gold-red flakes were recrystallized by dissolving in 75 ml of water and slowly adding 50 ml of ethanol. The solid was filtered, washed generously with ethanol, and then dried over CaCl₂. The yield was 1.0 g.

cis-[Co(NH₃)₄(SO₄)Cl].—This compound was prepared by heating *cis*-[Co(NH₃)₄(H₂O)(SO₄)]Cl on the thermobalance (to 175°) until a plateau corresponding to the loss of one molecule of water (calcd 6.51%) was reached. The complex may also be prepared by isothermal heating of the sulfatoaquo chloride at 110° for about 17 hr. The blue-violet solid is insoluble in water and the common organic solvents.

cis-[Co(NH₃)₄(SO₄)Br].—The blue-violet product was obtained by heating *cis*-[Co(NH₃)₄(H₂O)(SO₄)]Br on the thermobalance (to 178°) until a plateau corresponding to the loss of one molecule of water (calcd 5.61%) was reached. The material is insoluble in water and the common organic solvents.

(4) F. Ephraim and W. Flugel, *Helv. Chim. Acta*, **7**, 724 (1924).