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.

Acknowledgment.—The authors wish to acknowledge the support of the National Science Foundation (Grant GP-5318).

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The Solid-Phase Deaquation of Some *cis*-Sulfatoaquotetraaminecobalt(III) Complexes[1]

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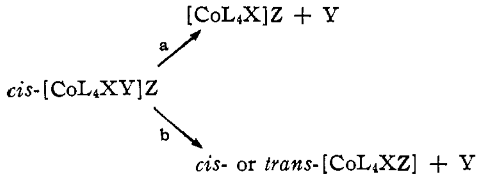
Received February 25, 1971

The solid-phase deaquation reactions of *cis*-$[Co(en)_2(H_2O)(SO_4)]Br\cdot H_2O$ and six *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Z$ complexes ($Z = Cl, Br, NO_3, ClO_4, BF_4, {}^1/_2PtCl_6$) have been studied by thermogravimetric analysis, differential thermal analysis, X-ray powder diffraction, and infrared and visible spectroscopy. Bidentate sulfato complexes of the type $[Co(NH_3)_4(SO_4)]Z$ are formed when $Z = ClO_4, BF_4$, and ${}^1/_2PtCl_6$. In addition, the bidentate sulfato complex $[Co(en)_2(SO_4)]Br$ is formed. Complexes of the type *cis*-$[Co(NH_3)_4(SO_4)Z]$ are formed when $Z = Cl$, Br, and NO_3. 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



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*-$[Co(en)_2(H_2O)(SO_4)]Br\cdot H_2O$ and *cis*-$[Co(en)_2(H_2O)(SO_4)]ClO_4$ deaquate at 120° to form the bidentate sulfato complexes $[Co(en)_2(SO_4)]Br$ and $[Co(en)_2(SO_4)]ClO_4$, 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*-$[Co(NH_3)_4(H_2O)(SO_4)]_2SO_4\cdot 3H_2O$ forms the dinuclear sulfato-bridged complex *cis,cis*-$[Co(NH_3)_4(SO_4)_3Co(NH_3)_4]$ rather than the bidentate sulfato complex *cis*-$[Co(NH_3)_4(SO_4)]_2SO_4$. An analogous selenato-bridged complex forms upon deaquation of *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2SeO_4\cdot 3H_2O$.[3]

In this paper we describe the solid-phase deaquation reactions of six additional *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Z$ complexes and discuss the factors which influence the paths by which the reactions proceed.

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*-$[Co(en)_2(H_2O)(SO_4)]Br\cdot H_2O$ and $[Co(en)_2(SO_4)]Br$ were prepared by the method of Barraclough and Tobe.[2]

The complexes *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Z$ ($Z = Cl$, Br, and NO_3) were prepared by the method of Ephraim and Flugel.[4]

The complex *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]ClO_4$ was prepared by a modification of a previously described procedure.[4] A solution of 0.7 g of *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Cl$ 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-$\mathbf{[Co(NH_3)_4(H_2O)(SO_4)]BF_4}$.—A solution of 1.6 g of the sulfatoaquo chloride in 20 ml of water was treated with a solution of 5 g of $NaBF_4$ 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-$\mathbf{[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6\cdot 2H_2O}$.—A mixture of 1.0 g of *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Br$ and 1.0 g of $H_2PtCl_6\cdot 6H_2O$ 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 $CaCl_2$. The yield was 1.0 g.

cis-$\mathbf{[Co(NH_3)_4(SO_4)Cl]}$.—This compound was prepared by heating *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Cl$ 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-$\mathbf{[Co(NH_3)_4(SO_4)Br]}$.—The blue-violet product was obtained by heating *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Br$ 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.

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[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).

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

TABLE I

ELEMENTAL ANALYSES

Compound	% N Calcd	% N Found	% H Calcd	% H Found	% Co Calcd	% Co Found
cis-$[Co(en)_2(H_2O)(SO_4)]Br \cdot H_2O$	12.28[a]	12.59[a]	5.12	5.22	15.08	15.22
cis-$[Co(NH_3)_4(H_2O)(SO_4)]Cl$	20.25	20.43	5.10	5.21	21.31	21.15
cis-$[Co(NH_3)_4(H_2O)(SO_4)]Br$	17.46	17.46	4.40	4.35	18.35	18.48
cis-$[Co(NH_3)_4(H_2O)(SO_4)]NO_3$	...	...	4.66	4.51	19.48	19.05
cis-$[Co(NH_3)_4(H_2O)(SO_4)]ClO_4$	16.46	16.53	...	...	17.35	17.05
cis-$[Co(NH_3)_4(H_2O)(SO_4)]BF_4$	17.08	17.79	4.30	4.35	17.98	17.56
cis-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6 \cdot 2H_2O$	...	...	3.48	3.44	12.73	12.62
$[Co(en)_2(SO_4)]Br$	...	...	9.46[b]	9.21[b]	...	...
cis-$[Co(NH_3)_4(SO_4)Cl]$	21.67	21.44	4.67	4.42	22.79	23.00
cis-$[Co(NH_3)_4(SO_4)Br]$	18.51	18.16	3.96	3.81	19.48	19.48
cis-$[Co(NH_3)_4(SO_4)(NO_3)]$	...	...	4.24	4.45	20.70	20.51
$[Co(NH_3)_4(SO_4)]ClO_4$	...	...	5.29[b]	5.45[b]	...	...
$[Co(NH_3)_4(SO_4)]BF_4$	18.10	17.80	3.90	3.87	19.05	18.60
$[Co(NH_3)_4(SO_4)]_2PtCl_6$	13.12	13.12	2.83	3.05	13.81	13.48

[a] Per cent carbon. [b] Per cent H_2O.

cis-$[Co(NH_3)_4(SO_4)(NO_3)]$.—This compound was prepared by heating the sulfatoaquo nitrate at 110° for 18 hr. An identical material was obtained by heating the nitrate on the thermobalance (to 200°) until a plateau corresponding to the loss of one molecule of water (calcd 5.71%) was reached. The hygroscopic, violet solid is insoluble in water.

$[Co(NH_3)_4(SO_4)]ClO_4$.—This compound was prepared by heating the sulfatoaquo perchlorate at 115° for 16 hr. The violet solid is insoluble in water.

$[Co(NH_3)_4(SO_4)]BF_4$.—The light violet product was obtained by heating the sulfatoaquo tetrafluoroborate on the thermobalance (to 170°) until a plateau corresponding to the loss of one molecule of water (calcd 5.44%) was reached. The product is insoluble in water.

$[Co(NH_3)_4(SO_4)]_2PtCl_6$.—This compound was prepared by heating *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6 \cdot 2H_2O$ (to 160°) on the thermobalance until a plateau corresponding to the loss of four molecules of water (calcd 7.76%) was reached. The hygroscopic brown-violet solid is insoluble in water.

Results and Discussion

Identification of the Products.—The elemental analysis data given in Table I and the tg curves for the sulfatoaquo complexes (all except the perchlorate) shown in Figure 1 indicate that stable, well-defined products were formed upon the total loss of water from each of the reactants. The dta curves for these reactants are shown in Figure 2. Only *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Br$ gave a tg deaquation plateau (see Figure 1, curve B) which was not very nearly horizontal and for which the corresponding data endotherm (see Figure 2, curve F) did not return to the base line ($\Delta T = 0$)[5] before the start of the higher temperature deamination endotherm. Overlapping deaquation and deamination steps have been observed during the thermal decomposition of other cobalt(III)–tetraamine complexes.[3,6]

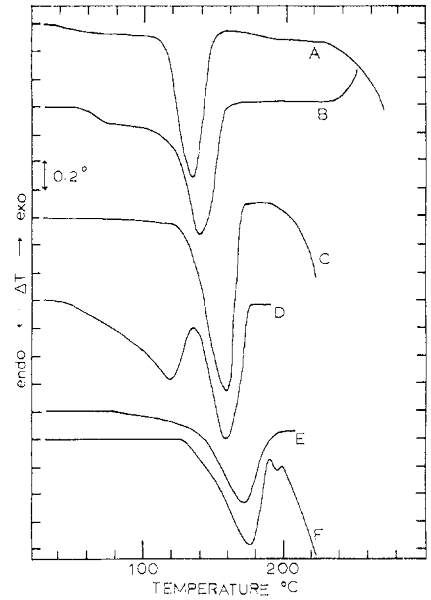

Figure 2.—Differential thermal analysis curves for *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]BF_4$ (A), *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6 \cdot 2H_2O$ (B) *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Cl$ (C), *cis*-$[Co(en)_2(H_2O)(SO_4)]Br \cdot H_2O$ (D), *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]NO_3$ (E), and *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Br$ (F).

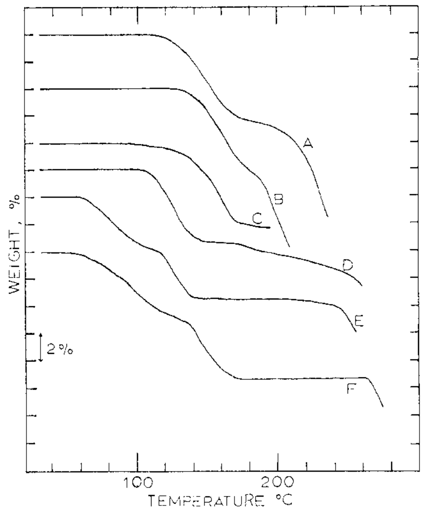

Figure 1.—Thermogravimetric analysis curves for *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Cl$ (A), *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Br$ (B), *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]NO_3$ (C), *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]BF_4$ (D), *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6 \cdot 2H_2O$ (E), and *cis*-$[Co(en)_2(H_2O)(SO_4)]Br \cdot H_2O$ (F).

It has been established that differences in the infrared spectra can be used to distinguish between complexes containing the monodentate C_{3v} and the bidentate or bridged C_{2v} sulfato group.[7] For a monodentate MO_4 ligand, the ν_3 (asymmetric stretch) and ν_4 (asymmetric bend) peaks are split into doublets, whereas in the MO_4 ligand with C_{2v} symmetry all degeneracies are re-

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(5) In some of the curves the base line after an endotherm appears to be shifted, due possibly to changes in the packing and thermal conductivity of the remaining solid.

(6) H. F. LeMay, Jr., and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **89**, 5577 (1967).

(7) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 161.

TABLE II[a]

SULFATO VIBRATIONAL FREQUENCIES OF DEAQUATED COMPLEXES

Compound	ν_1	ν_{3a}	ν_{3b}	ν_{3c}	ν_{4a}	ν_{4b}	ν_{4c}	Symmetry
$[Co(en)_2(SO_4)]Br$	998 s	1215 s	1180 s	1077 s	650 s	632 s	?	C_{2v}
cis-$[Co(NH_3)_4(SO_4)Cl]$	991 s	1183 s 1117 s	1020 s	. . .	641 m	598 m	. . .	C_{3v}
cis-$[Co(NH_3)_4(SO_4)Br]$	989 s	1185 s 1118 s	1024 s	. . .	640 m	600 m	. . .	C_{3v}
cis-$[Co(NH_3)_4(SO_4)(NO_3)]$	973 s	1138 s	1040 s	. . .	646 s	616 s 596 s	. . .	C_{3v}
$[Co(NH_3)_4(SO_4)]ClO_4$	966 s	1221 s 1198 s	1120 s	1030 s	665 s		600 m	C_{3v}
$[Co(NH_3)_4(SO_4)]BF_4$	970 m	1216 s	1116 s	1040 s	665 m	611 m	594 m	C_{2v}
$[Co(NH_3)_4(SO_3)]_2PtCl_6$	977 s	1212 s	1120 s	1050 s	670 m	620 m	590 m	C_{2v}

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

moved and the ν_3 and ν_4 bands are split into triplets. For C_{2v} bidentate sulfato complexes, it has been shown that the ν_{3a} band appears above 1200 cm^{-1}, while for the bridged configuration the ν_{3a} band appears below 1200 cm^{-1}.[8]

The mull spectra of the sulfatoaquotetraamine complexes show sulfato ν_1 bands in the 964–976-cm^{-1} region, very weak ν_2 bands at about 500 cm^{-1}, and ν_{4a} and ν_{4b} bands centered at 599–613 and 635–645 cm^{-1}, respectively. The ν_{3b} bands are found at 1030–1039 cm^{-1}, while the ν_{3a} bands appear at about 1140 cm^{-1} but, with the exception of those in the perchlorate and tetrafluoroborate spectra, are slightly split into doublets with peaks at 1118–1124 and 1158–1165 cm^{-1}. This splitting has been attributed to a perturbation upon the C_{3v} symmetry as a result of hydrogen bonding between the sulfato group and the neighboring aquo group.[9] This splitting is seen in the spectrum of *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6 \cdot 2H_2O$ shown in Figure 3.

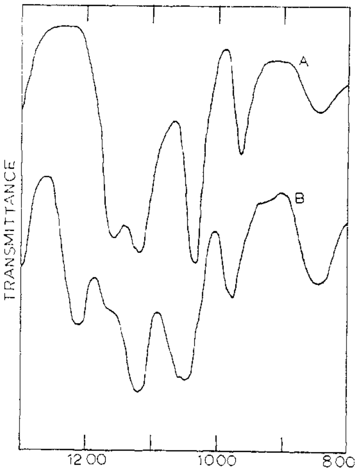

Figure 3.—Infrared spectra of *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6 \cdot 2H_2O$ (A) and $[Co(NH_3)_4(SO_4)]_2PtCl_6$ (B).

The sulfato vibrations in *cis*-$[Co(en)_2(H_2O)(SO_4)]Br \cdot H_2O$ are found at 620 (s), 642 (m), 986 (s), 1071 (s), and 1131 (s) cm^{-1}, and are in excellent agreement with the spectrum previously reported.[2]

The peaks attributed to sulfato vibrations in the thermally deaquated products are shown in Table II. A chelated sulfato configuration is indicated for the perchlorate, tetrafluoroborate, and hexachloroplatinate products by the presence of three ν_3 bands and by the ν_{3a} band appearing above 1200 cm^{-1}. In addition, the ν_{4a} bands for the three complexes occur at a higher frequency (665–670 cm^{-1}) than do the ν_{4a} bands of the C_{3v} sulfato spectra (635–656 cm^{-1}). Figure 3 shows the ν_3 sulfato bands in the spectrum of $[Co(NH_3)_4(SO_4)]_2PtCl_6$, for which there is no interference from absorptions of the hexachloroplatinate ion.

Characteristic infrared absorptions for the tetrahedral perchlorate and tetrafluoroborate ions are seen in the spectra of $[Co(NH_3)_4(SO_4)]ClO_4$ and $[Co(NH_3)_4(SO_4)]BF_4$, respectively, indicating that the counterions remain uncoordinated and thus providing additional evidence in support of the chelated sulfato assignments. The perchlorate ion in the spectrum of the sulfatoaquo perchlorate precursor exhibits ν_1, ν_3, and ν_4 bands at 933 (w), 1103 (s, b), and 628 (s) cm^{-1}, respectively, which appear virtually unchanged after deaquation. (There is some overlap of these bands with the sulfato absorptions, however.) The tetrafluoroborate ion gives a characteristic ν_1 absorption which appears at about 1080 (s) cm^{-1} and is unsplit in both the *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]BF_4$ and $[Co(NH_3)_4(SO_4)]BF_4$ complexes. A weak ν_1 band found at 758 (w) cm^{-1} in the sulfatoaquo spectrum does not appear at all after deaquation. If the tetrafluoroborate ion were to coordinate (and assume C_{3v} symmetry), the ν_1 band would than be allowed and would be expected to appear with an increase in intensity.

The spectra of the deaquated sulfatoaquo chloride, bromide, and nitrate complexes exhibit two ν_3 sulfato and two ν_4 sulfato absorptions, indicating that the sulfato group has C_{3v} symmetry. The doubly degenerate ν_{3a} band is not split, whereas the ν_{3a} absorptions centered at about 1150 cm^{-1} in the chlorosulfato and bromosulfato spectra show splittings of approximately 65–70 cm^{-1}. However, this splitting, which is possibly due to a perturbation upon the C_{3v} sulfato symmetry either by the neighboring halo group or by a restrictive lattice arrangement, is considerably less than that observed (>90 cm^{-1}) in the C_{2v} sulfato complexes. In addition, the higher frequency peaks arising from the split ν_{3a} band in each of the halosulfato complexes is located considerably below 1200 cm^{-1}.

The spectrum of *cis*-$[Co(NH_3)_4(SO_4)Cl]$ exhibits a weak absorption at 296 cm^{-1} which lies within the region expected for the Co(III)–Cl stretching vibration.[10] This provides direct evidence for coordination of the chloride species.

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

(9) M. Drouin, J. P. Mathieu, and H. Paulet, *J. Chim. Phys. Physicochim. Biol.*, **58**, 322 (1961).

(10) G. W. Watt and D. S. Klett, *Inorg. Chem.*, **3**, 782 (1964).

The assignment of the sulfatonitrate configuration in *cis*-$[Co(NH_3)_4(SO_4)(NO_3)]$ is supported by the infrared absorptions of the nitrate group. The ν_2, ν_3, and ν_4 bands of the nitrate ion (D_{3h} symmetry) in *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]NO_3$ are found at 840 (m), 1380 (s), and 710 (w) cm^{-1}, respectively, while the ν_1 band expected[11] at about 1050 cm^{-1} is apparently hidden under the ν_{3a} sulfato band centered at 1030 cm^{-1}. Upon coordination through one of the oxygen atoms, the nitrate group assumes C_{2v} symmetry and the doubly degenerate ν_3 and ν_4 modes each split into doublets. In *cis*-$[Co(NH_3)_4(SO_4)(NO_3)]$ the ν_3 doublet bands are found at 1470 (s) and 1280 (s) cm^{-1}, the ν_4 bands are found at 714 (vw) and 745 (vw) cm^{-1}, and the ν_1 and ν_2 bands are found at 1012 (m, sh) and 802 (w) cm^{-1}, respectively. The positions of these bands are very close to those reported for a similar C_{2v} monodentate nitrato complex, $[Co(NH_3)_5(NO_3)]PtCl_4$.[12]

The visible absorption maxima obtained from the transmittance mull spectra of the reactants and products are listed in Table III. The use of solid-state spectra was necessitated by the very low solubility of the products. The sulfatoaquotetraamine complexes in aqueous solution have absorption maxima at 517 nm (ϵ 71) and 362 nm (ϵ 49) due, respectively, to the $^1A_1 \rightarrow {}^1T_1$ (octahedral) and $^1A_1 \rightarrow {}^1T_2$ (octahedral) ligand field transitions. It is seen that in the mull spectra of these compounds the anions (all but the hexachloroplatinate are colorless) have a strong influence upon the positions of the bands. However, it is not known whether a similar anion effect occurs in the spectra of the products. In addition, it was found that the $^1T_2$ band maxima all depend somewhat upon the thickness of the mull.

TABLE III[a]

VISIBLE MULL SPECTRA OF COBALT(III) COMPLEXES[b]

Compound	λ_{max}, nm	λ_{max},[c] nm
cis-$[Co(en)_2(H_2O)(SO_4)]Br \cdot H_2O$	499	358
cis-$[Co(L)_4(H_2O)(SO_4)]Cl$	513	356
cis-$[Co(L)_4(H_2O)(SO_4)]Br$	510	360 sh[d]
cis-$[Co(L)_4(H_2O)(SO_4)]NO_3$	501	348
cis-$[Co(L)_4(H_2O)(SO_4)]ClO_4$	502	356
cis-$[Co(L)_4(H_2O)(SO_3)]BF_4$	508	349
cis-$[Co(L)_4(H_2O)(SO_4)]_2PtCl_6 \cdot 2H_2O$	494	350 sh[d]
$[Co(en)_2(SO_4)]Br$	590 sh, 506	365 sh[d]
cis-$[Co(L)_4(SO_4)Cl]$	544	360 sh[d]
cis-$[Co(L)_4(SO_4)Br]$	550	375 sh[d]
cis-$[Co(L)_4(SO_4)(NO_3)]$	580 sh, 508	355
$[Co(L)_4(SO_4)]ClO_4$	585 sh, 510	360
$[Co(L)_4(SO_4)]BF_4$	585 sh, 505	362
$[Co(L)_4(SO_4)]_2PtCl_6$	585 sh, 503	365 sh[d]

[a] sh = shoulder. [b] L = NH_3. [c] Position of band is dependent upon mull thickness. [d] Band appears as shoulder on charge-transfer band.

The absorption maxima for *cis*-$[Co(en)_2(H_2O)(SO_4)]Br \cdot H_2O$ in aqueous solution were observed at 503 nm (ϵ 102) and 365 nm (ϵ 74), while those for $[Co(en)_2(SO_4)]Br$ were found at 505 nm (ϵ 104) and 369 nm (ϵ 74). All values are in good agreement with those given in the literature.[2] The relatively small shift in the corresponding bands upon deaquation implies that the cis sulfatoaquo and bidentate sulfato configurations have in-plane ligand field strengths of comparable magnitude. The shifts of less than 10 nm in the $^1T_1$ band observed upon formation of the perchlorate, tetrafluoroborate, and hexachloroplatinate products are consistent with the assignment of the chelated sulfato configuration.

The deaquation of *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]NO_3$ to form *cis*-$[Co(NH_3)_4(SO_4)(NO_3)]$ results in a shift of maxima from 501 nm to 508 nm. This shift, while similar in magnitude to that observed in forming the bidentate sulfato complexes, is not inconsistent with that expected for the replacement of an aquo group by a monodentate nitrato group, *e.g.*, in comparing the spectra of $[Co(NH_3)_5(NO_3)]^{2+}$ (λ_{max} 500 nm) and $[Co(NH_3)_5(H_2O)]^{3+}$ (λ_{max} 490 nm).[13]

The $[Co(NH_3)_4(SO_4)(NO_3)]$ complex belongs to the structural type CoN_4O_2, and its geometrical configuration can be assigned tentatively by comparison of its spectrum with those of other CoN_4O_2 complexes. The $^1T_1$ (octahedral) band in the spectrum of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ has a single maximum at 492 nm,[14] whereas in the trans isomer this band is split into two clearly resolved peaks with maxima at 550 and 444 nm.[14] The $^1T_1$ band in the sulfatonitrato spectrum has a single maximum at 508 nm but with a marked asymmetry on the longer wavelength side. This more closely fits the cis description, although the presence of minor amounts of the trans isomer cannot be discounted.

The formation of *cis*-$[Co(NH_3)_4(SO_4)Cl]$ and *cis*-$[Co(NH_3)_4(SO_4)Br]$ upon deaquation of the respective sulfatoaquo halide parent is shown conclusively by the visible spectra. The chlorosulfato and bromosulfato products show shifts of 31 nm (from 513 to 544 nm) and 40 nm (from 510 to 550 nm) which are of the same magnitude observed when comparing the spectra of $[Co(NH_3)_5Cl]^{2+}$ and $[Co(NH_3)_5Br]^{2+}$ with that of $[Co(NH_3)_5(H_2O)]^{3+}$; the aquo ion has a maximum at 490 nm, while the chloro and bromo ions have maxima at 533 and 550 nm, respectively.[13] The deaquation path leading to the formation of bidentate sulfato complexes would be expected to produce spectral shifts of 10 nm or less. The broad, unsplit $^1T_1$ (octahedral) bands of the halosulfato complexes again suggest the presence of the cis isomers in major amounts.

The most intense lines in the X-ray powder patterns of the sulfatoaquo and the deaquated complex are shown in Table IV. The products all have ordered crystal lattices which, with the exception of the perchlorate, appear to be somewhat similar to those of the respective parents. The sulfatoaquotetraamine chloride and bromide lattices are similar though apparently not isomorphous, as are those of the chlorosulfato and bromosulfato products. The deaquation of the hexachloroplatinate complex appears to have done little to the lattice except to cause a slight shrinkage of the original unit cell. The stability of this lattice is probably due in great part to the dominant presence of the bulky anions.

Mechanism of Deaquation.—The tg and dta curves in Figures 1 and 2 show that the loss of coordinated water from each of the nonhydrated sulfatoaquo complexes is characterized by a single tg step and a single dta endotherm. Minima were found at 135, 160, 170,

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[11] See ref 7, p 92.

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

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TABLE IV[a]

PROMINENT LINES IN X-RAY POWDER PATTERNS OF COBALT(III) COMPLEXES

Compound	*d*, Å
cis-$[Co(en)_2(H_2O)(SO_4)]Br\cdot H_2O$	11.62 (3), 6.75 (4), 6.34 (10), 5.27 (2), 4.18 (2), 3.90 (3), 3.69 (2), 3.37 (3)
cis-$[Co(NH_3)_4(H_2O)(SO_4)]Cl$	6.46 (10), 5.05 (4), 4.03 (10), 3.91 (4), 3.50 (5), 3.09 (1), 2.99 (2), 2.54 (2)
cis-$[Co(NH_3)_4(H_2O)(SO_4)]Br$	6.48 (3), 5.18 (2), 4.02 (10), 3.95 (6), 3.46 (5), 3.03 (2), 2.76 (2), 2.53 (2)
cis-$[Co(NH_3)_4(H_2O)(SO_4)]NO_3$	6.70 (4), 5.10 (10), 4.86 (4), 4.44 (4), 4.21 (6), 4.04 (10), 3.78 (10), 3.13 (5)
cis-$[Co(NH_3)_4(H_2O)(SO_4)]ClO_4$	6.34 (3), 4.46 (10), 4.25 (3), 4.00 (3), 3.64 (3), 3.47 (2), 2.90 (2), 2.69 (2)
cis-$[Co(NH_3)_4(H_2O)(SO_4)]BF_4$	6.41 (4), 5.30 (10), 4.87 (4), 4.49 (4), 4.26 (3), 4.09 (8), 3.94 (4), 3.71 (9)
cis-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6\cdot 2H_2O$	9.11 (6), 6.43 (8), 5.64 (10), 5.20 (10), 4.88 (2), 4.57 (2), 4.13 (4), 4.04 (4)
$[Co(en)_2(SO_4)]Br$	10.91 (1), 6.80 (4), 6.30 (10), 4.92 (2), 4.56 (2), 4.25 (4), 3.70 (4), 3.14 (3)
cis-$[Co(NH_3)_4(SO_4)Cl]$	7.37 (2), 6.48 (10), 5.21 (3), 4.82 (2), 4.26 (7), 3.87 (2), 3.75 (7), 3.12 (3)
cis-$[Co(NH_3)_4(SO_4)Br]$	6.63 (4), 5.37 (2), 4.30 (10), 3.91 (10), 3.77 (10), 3.10 (3), 2.97 (3), 2.75 (5)
cis-$[Co(NH_3)_4(SO_4)(NO_3)]$	6.88 (5), 6.28 (10), 5.30 (6), 5.09 (10), 4.84 (5), 4.13 (5), 4.02 (10), 3.79 (9)
$[Co(NH_3)_4(SO_4)]ClO_4$	7.82 (9), 5.62 (8), 5.37 (7), 4.84 (3), 4.40 (9), 4.11 (9), 3.77 (10), 3.14 (3)
$[Co(NH_3)_4(SO_4)BF_4$	7.69 (10), 6.52 (4), 5.60 (8), 4.49 (6), 4.30 (2), 3.87 (3), 3.61 (4), 3.46 (2)
$[Co(NH_3)_4(SO_4)]_2PtCl_6$	8.84 (3), 6.23 (10), 5.45 (8), 5.02 (7), 4.29 (1), 3.89 (3), 3.70 (3), 3.15 (1)

[a] Numbers in parentheses are the relative intensities, based on 10.

TABLE V

ACTIVATION ENERGIES FOR THE DEAQUATION OF SOME SULFATOAQUO COMPLEXES

Complex	E_a, kcal mol^{-1}	Complex	E_a, kcal mol^{-1}
cis-$[Co(NH_3)_4(H_2O)(SO_4)]Cl$	29 ± 4[a]	*cis*-$[Co(NH_3)_4(H_2O)(SO_4)]NO_3$	23 ± 3
cis-$[Co(NH_3)_4(H_2O)(SO_4)]Br$	34 ± 4	*cis*-$[Co(NH_3)_4(H_2O)(SO_4)]BF_4$	23 ± 3

[a] Error limits are estimated.

and 176° for the tetrafluoroborate, chloride, bromide, and nitrate reactions, respectively. The *cis*-$[Co(en)_2(H_2O)(SO_4)]Br\cdot H_2O$ and *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6\cdot 2H_2O$ complexes lose their lattice water and coordinated water in two distinct steps. The respective products isolated after the first deaquation steps have been identified by infrared and visible spectra as *cis*-$[Co(en)_2(H_2O)(SO_4)]Br$ and *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]_2PtCl_6$. Hence, in both cases the loss of lattice water precedes the loss of coordinated water. An X-ray powder pattern of the bromide is identical with that of its bromide monohydrate parent, indicating that very little disruption of the lattice occurs during the first deaquation step.

The activation energies for the deaquation of four of the sulfatoaquo complexes were determined from the tg curves by the method of Fuoss, Salyer, and Wilson.[15] Calculations were made only for those compounds which have no lattice water, so that the activation energies would not be influenced by preliminary disruption of the crystal lattice. The values are shown in Table V and are the average of at least two determinations. It is seen that the energy needed for the formation of the acidosulfato complexes is highly dependent upon the anion and is probably a reflection both of the different crystal structures of the reactants and of the different coordination tendencies of the anions. However, in view of the similarity between the chloride and bromide lattices, it may also be that the higher activation energy for deaquation of the latter is due in part to more hindered movement of the bulky bromide ion.

The reluctance of the sulfato ligand to assume a bidentate chelate configuration because of steric requirements has been discussed previously.[3,16] The distance between two *cis* ligand sites (2.78 Å) is larger than the oxygen–oxygen distance (2.34 Å) afforded by the tetrahedral O–S–O bond angle. The tendency to relieve the steric strain in the bidentate sulfato configuration is seen by the aquation of $[Co(en)_2(SO_4)]^+$ to *cis*-$[Co(en)_2(H_2O)(SO_4)]^+$ with a half-life of 3 hr (in weakly acidic solution).[2,17] Aside from the steric factor, it is apparent that when a cis sulfatoaquo complex is deaquated, relatively little atomic movement is needed to replace the departing aquo ligand with one of the three noncoordinated oxygen atoms of the monodentate sulfato group. Yet among the sulfatoaquotetraammine complexes, this reaction path occurs only in the presence of anions such as perchlorate, tetrafluoroborate, and hexachloroplatinate, which have very weak coordination tendencies. Moreover, the packing of the sulfatoaquo cations and the chloride, bromide, and nitrate anions in the respective crystal lattices appears to be such that these anions can compete effectively for the vacated coordination site on the cobalt atom. Even the dinuclear sulfato-bridged and selenato-bridged complexes, which result from substitution by the counter ions as in path b (see Introduction), form in preference to the chelated species.[3]

It is of interest that while *cis*-$[Co(NH_3)_4(H_2O)(SO_4)]Br$ deaquates to form the bromosulfato complex, the bidentate sulfato bromide is produced from *cis*-$[Co(en)_2(H_2O)(SO_4)]Br\cdot H_2O$. Assuming that the two reactants are chemically similar, the difference in reaction paths perhaps is caused by topochemical factors.[18] Possibly the bulky ethylene bridges connecting the cis amine ligands in *cis*-$[Co(en)_2(H_2O)(SO_4)]Br\cdot H_2O$ prevent the relatively large bromide ion from reaching the reactive site, or possibly the bromide ion is otherwise located in the lattice such that a restrictively large amount of energy is needed for migration to a position favorable for anation. Hence, the formation of the chelated sulfato group is forced upon the molecule. The bromide ion in the tetraammine complex, by contrast, should meet less hindrance from the relatively compact ammonia ligands and is probably in a lattice

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position within close distance to the departing aquo ligand. X-Ray structural determinations would be be most enlightening in this regard.

Acknowledgment.—The authors gratefully acknowledge the support of the National Science Foundation (Grant GP 5318).

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The Stereoisomers of the Bis(L-hydrogen aspartato)-*l*-propylenediamine- and L-Aspartatobis(*l*-propylenediamine)cobalt(III) Complexes

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Received February 23, 1971

The bis(L-hydrogen aspartato)-*l*-propylenediamine- and L-aspartatobis(*l*-propylenediamine)cobalt(III) complexes have been prepared from the reaction of the *trans*-$CoCl_2(l\text{-pn})_2^+$ complex with L-aspartic acid. The stereoisomers of these complexes have been separated by an ion-exchange chromatographic method. The isolated complexes are Λ- and Δ-trans(O), Λ- and Δ-cis(O),cis(N), and Λ-trans(N) isomers for the bis(L-hydrogen aspartato)-*l*-propylenediamine complexes. On the other hand, for the bis(*l*-propylenediamine) complexes eight possible stereoisomers have been separated and the four Λ isomers and one Δ isomer have been crystallized. All of the complexes isolated as crystals have been characterized by their electronic absorption, circular dichroism, and proton magnetic resonance spectra. The stereoselectivity in these complexes has also been discussed based on the results of the formation ratios of the isomers.

Introduction

We reported, in the previous paper, the isolation of a series of stereoisomers of the glycinato-*l*-propylenediaminecobalt(III) complexes.[1] Recently, the preparation of tris-type mixed complexes of cobalt(III) with glycinato and L-aspartato ligands was also reported from our laboratory.[2] The present work has been undertaken in connection with those studies and in order to isolate the mixed complexes with L-aspartato and *l*-propylenediamine ligands and investigate their stereoselectivity.

Experimental Section

Preparations.—The complex *trans*-$[CoCl_2(l\text{-pn})_2]Cl \cdot H_2O$,[3] 9 g (0.027 mol), was dissolved in 20 ml of water, and L-aspartic acid, 7.4 g (0.055 mol), was dissolved in the solution, adding simultaneously an aqueous sodium hydroxide solution. After that, the resulting solution was adjusted to pH ~10 with the alkali solution. After adding active charcoal (1.2 g), the mixture was stirred at 55° for 15 min; then the color of the solution became red-brown. After the removal of the active charcoal by hot filtration, the filtrate was adjusted to pH ~8 with aqueous hydrochloric acid. A portion of the solution was added to an ion-exchange column (diameter, 6 cm; height of resin, 40 cm) containing 100–200 mesh Dowex 50W-X8 resin in the sodium form. At this stage, the absorbed complexes formed two bands at the top of the column (a red-brown band and a red band, up and down). After the column was swept with water, the bands were eluted with a 0.1 *M* aqueous solution of sodium perchlorate at a rate about 0.2 ml/min. Through elution over a period of about 2 months, the red band was completely separated into seven bands colored red or red-violet. These eluted bands were collected in seven fractions and numbered according to the order of the eluted bands (no. 1–7). The other red-brown band remaining in the column was then eluted with a 0.4 *M* sodium perchlorate solution over a period of about 3 months. At this stage, four bands colored red-brown were separated from the original band, and these eluted bands were collected in fractions (no. 8–11). When the rest of the red-brown band still remaining in the column was eluted with a 1 *M* sodium perchlorate solution, two bands came down and collected in fractions (no. 12–13). The last fraction (no. 13) was rechromatographed using a smaller column and 0.5 *M* $NaClO_4$ at a slower rate (0.1 ml/min). Three overlapped bands were obtained and these were collected in fractions (no. 13′, 13″, and 13‴). A yellow band still remained at the top of the original column and it was the tris(*l*-propylenediamine)cobalt(III) species. The chromatographic separation was repeated over and over again from the beginning in order to store up the same fractions.

Each fraction was evaporated to about dryness at 40° along with the simultaneous removal of a large amount of the perchlorate. After that, the residue was dissolved in a few milliliters of water, and to it a large amount of an acetone–ether mixture (1:4) was added. After the solution had stood for some time, the desired complex was separated as an oil from the organic solvent. After this treatment was repeated several times, a large amount of acetone was added to the resulting oil to precipitate the product. The precipitates were collected by means of the centrifuge and washed with acetone. The precipitates were again dissolved in a minimum amount of water and the solution was allowed to stand for several days at room temperature to crystallize the desired complex. Results of the elemental analyses for the isolated complexes will be given in the Results and Discussion.

Formation Ratios of Isomers.—The relative concentrations and the formation ratios of the eluted bands were spectrophotometrically determined using the ϵ values of the first absorption band of each of the isomers obtained from no. 1–13, but the ϵ values of the isomers from no. 6 and 7 were assumed to be the same as that of the isomer from no. 5.

Reagents.—Optically active *l*-propylenediamine (*l*-pn) used in the above experiment was obtained by resolving its commercial racemate according to the usual method.[4] The observed $[\alpha]^{25}D$ in dry benzene was $-34.6°$. L-Aspartic acid (L-$aspH_2$) used was reagent grade and the observed $[\alpha]^{25}D$ was $+25.3°$.

Measurements.—The electronic absorption, circular dichroism (CD), and proton magnetic resonance (pmr) spectra were measured with the same instruments as were used in the previous investigation.[1]

Results and Discussion

Results of the elemental analyses are summarized in Table I. For the sake of convenience, the isolated complexes are numbered as E-1, E-2, . . . , E-13 corresponding to the numbers of the fractions. No results

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