giving us very pure samples of several compounds. These afforded us a valuable check on the purity of our own preparations. We are also grateful to the personnel of the Argonne National Laboratory who permitted us to use their Beckman 1R-7 infrared spectrophotometer.

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An Infrared Study of Monosulfatopentaaquochromium(III) Chloride

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Solid monosulfatopentaaquochromium(III) chloride was prepared and the infrared spectrum of a Nujol mull obtained. From an analysis of the spectrum in the region from 900 to 1300 cm.$^{-1}$ the sulfate was found to be a monodentate ligand.

Introduction

The isolation of an aqueous solution of monosulfatochromium(III) ion was recently reported by Fogel and co-workers.[1] On the basis of entropy arguments and other considerations it was suggested that sulfate might be a bidentate ligand in this species. The question of whether or not the sulfate is a bidentate ligand is of considerable interest. Kinetic studies might be expected to show that aquation of the monosulfato ion proceeds in two steps if the sulfate is bidentate, since two Cr–O bonds would have to be broken. If the sulfate is monodentate, its aquation mechanism might be expected to resemble that of the monohalochromium(III) species. A knowledge of the way sulfate bonds to the chromium in this species will certainly be important in any attempt to interpret the visible and ultraviolet spectra of the species.

We were able to establish that sulfate is a monodentate ligand in the monosulfatochromium(III) ion by examining the infrared spectrum of its chloride salt. For this purpose we prepared and characterized solid monosulfatopentaaquochromium(III) chloride. It is believed that this is the first reported preparation of a solid containing the $Cr(OH_2)_5SO_4^+$ ion. The method used to analyze the infrared data was developed by Nakamoto and co-workers[2] in a study of sulfatoamminecobalt(III) compounds.

Experimental

Materials.—Dowex AG 50W X8 200–400 mesh resin in the hydrogen form was used in all experiments. The resin was obtained from the Bio Rad Laboratories, Richmond, Calif. All other materials were analytical reagent quality. Ordinary distilled water was used throughout.

Analytical Methods.—Chromium was determined spectrophotometrically after oxidation to chromate by alkaline peroxide. Chloride was determined by adding excess silver nitrate and carrying out a potentiometric back titration with potassium chloride solution using an Ag–AgCl electrode *vs.* a glass electrode. Sulfate was determined as barium sulfate after first oxidizing the chromium(III) to chromium(VI) to destroy the complex and then reducing the chromium(VI) to chromium(III) in the presence of acetic acid.[3]

Preparation of $[Cr(OH_2)_6]Cl_3$.—This compound was prepared by precipitation from a chromic nitrate solution at 0° upon treatment with hydrogen chloride gas.[4] The visible spectrum of a sample dissolved in 0.1 *M* perchloric acid agreed with that[5] reported for $Cr(OH_2)_6{}^{3+}$. When an aqueous solution of the solid was passed into an ion-exchange column in the hydrogen form only one band could be observed. This band was the violet color characteristic of $Cr(OH_2)_6{}^{3+}$.

Anal. Calcd. for $[Cr(OH_2)_6]Cl_3$: Cr, 19.5; Cl, 40.0. Found: Cr, 19.3; Cl, 39.9.

Preparation of $[Cr(OH_2)_5SO_4]Cl\cdot 0.5H_2O$.—A 2 *M* chromium(VI) and 0.02 *M* perchloric acid solution was prepared by mixing chromium trioxide, water, and perchloric acid. This solution was cooled to −10° and sulfur dioxide gas was bubbled into the solution. Care was taken to keep the temperature of the solution below 5°. The sulfur dioxide was oxidized to sulfate and the chromium(VI) was reduced to a mixture of chromium(III) species. When the reaction was complete, as evidenced by the cessation of heat evolution, more chromium(VI) solution was added to destroy any excess sulfite. The amount of chromium(VI) added was equal to about 10% of the original chromium(VI). This method was suggested by the work of Colson.[6]

The monosulfato species was isolated by an ion-exchange procedure. A glass column of 2.2 cm. i.d. and 40 cm. long with a sintered glass bottom was packed with hydrogen-form ion-exchange resin to a height of 27 cm. A 55-ml. portion of the solution obtained by the reduction of chromium(VI) was passed into the column. The column was then rinsed with 50 ml. of 0.0005 *M* perchloric acid. At this point the top 2 cm. of the column was violet and the rest of the column was green. The green monosulfato ion was eluted with 2 *M* hydrochloric acid. About 45 ml. of monosulfato solution was obtained.

The 45 ml. of monosulfato solution was concentrated by placing it on a vacuum line and removing about 20 ml. of water. Five-ml. portions of the concentrated solution were placed in 9-ml. test tubes, cooled to −10°, and treated with hydrogen chloride gas. Care must be taken to keep the temperature below 0° during the treatment with hydrogen chloride gas. A dark green precipitate formed and was separated by filtration. The product was immediately placed in a vacuum desiccator and dried for 6 hr. A weight change of only 0.1% took place during the last 3 hr. About 5 g. of product can be obtained from 45 ml. of

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[1] N. Fogel, J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84**, 1145 (1962).

[2] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *ibid.*, **79**, 4904 (1957).

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[5] R. Plane and J. Hunt, *J. Am. Chem. Soc.*, **79**, 3342 (1957).

[6] A. Colson, *Compt. rend.*, **142**, 402 (1906).

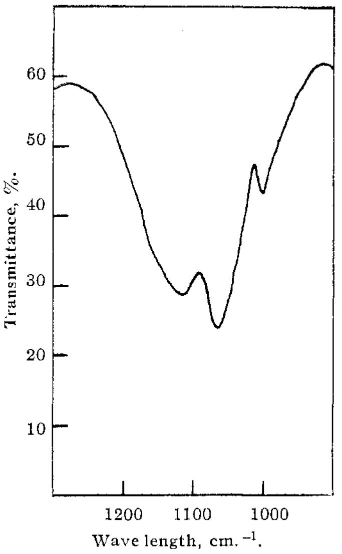

Figure 1.—Infrared spectrum of monosulfatopentaaquochromium(III) chloride in a Nujol mull.

solution from the ion-exchange column. The dry product is gray-green in color.

Monosulfatopentaaquochromium(III) ion was also isolated from solutions prepared by dissolving $Cr_2(SO_4)_3 \cdot xH_2O$ in water. The isolation was done using the same ion-exchange procedure used with the solutions prepared by the reduction of chromium(VI). The visible and ultraviolet spectra were the same for both preparations.

Characterization of $[Cr(OH_2)_5SO_4]Cl \cdot 0.5H_2O$.—In some experiments the monosulfato species was displaced from the ion-exchange column by a solution of 0.1 *M* cerous perchlorate and 0.1 *M* perchloric acid. From measurements of the total charge concentration (normality) of the displacing solution, together with the pH and chromium concentration of the collected monosulfato solution, the charge per chromium atom was found to be 1.00 ± 0.02. The procedure is described elsewhere.[7] The sulfate to chromium ratio of this solution was 0.99 ± 0.01.

The visible and ultraviolet spectrum of redissolved solid monosulfatopentaaquochromium(III) chloride was the same as that of material taken directly from an ion-exchange column within experimental error. A portion of redissolved solid was absorbed on a hydrogen-form ion-exchange column. The column was rinsed with two column volumes of water and eluted with seven column volumes of 0.2 *M* perchloric acid. The bulk of the material was eluted as a blue-green band during the perchloric acid elution, but a small green band remained near the top of the column. It was found that 2.1% of the chromium added to the column was removed during the water rinse, 96.5% during the elution with 0.2 *M* perchloric acid, and 1.4% was retained on the column. This indicates that between 96.5 and 97.9% of the chromium was present as the +1 monosulfatopentaaquochromium(III) ion. The 96.5% figure is more likely correct for the following reasons: four column volumes of perchloric acid were required to remove all visible traces of the blue-green band but the elution was continued until seven column volumes of acid had been used, some green material could be observed on the column after the acid elution, and the analytical results are consistent with this assumption. The chromium removed during the water rinse was probably neutral monochloromonosulfatotetraaquochromium(III) and the material retained on the column was probably +2 monochloropentaaquochromium(III) ion. The analytical results support this interpretation since the chloride is about 3% high and the sulfate 1% low.

Anal. Calcd. for $[Cr(OH_2)_5SO_4]Cl \cdot 0.5H_2O$: Cr, 18.41; Cl, 12.57; SO_4, 33.98. Found: Cr, 18.39; Cl, 12.97; SO_4, 33.61.

Spectra.—The visible and ultraviolet spectra of $Cr(OH_2)_5SO_4^+$ were determined six times, by three different workers, using both a Beckman DU spectrophotometer and a Cary Model 15 spectrophotometer. All spectra were taken at 25° in 0.1 *M* perchloric acid. The average deviation in the molar absorptivity at all wave lengths greater than 290 mμ was ±0.1 molar absorptivity unit. The position and molar absorptivity of spectral peaks are as follows: possible shoulder at 260 mμ, 12.4 cm.$^{-1}$ mole^{-1} l.; 417 mμ, 18.8 cm.$^{-1}$ mole^{-1} l.; 587 mμ, 19.0 cm.$^{-1}$ mole^{-1} l.; shoulder at 671 mμ, 5.28 cm.$^{-1}$ mole^{-1} l.[8]

Infrared measurements of the monosulfato species were made using a Nujol mull on a Perkin-Elmer Model 531 spectrophotometer. In the 900 to 1300 cm.$^{-1}$ region the following peaks were recorded: 1002 (m), 1068 (s), and 1118 (s) cm.$^{-1}$. The spectrum is shown in Figure 1. Infrared measurements of the $[Cr(OH_2)_6]Cl_3$ were made on a Nujol mull using a Perkin-Elmer Model 237 spectrophotometer. No bands were observed in the 900–1500 cm.$^{-1}$ region.

Discussion

The molar absorptivity values reported here for the visible and ultraviolet spectra of $Cr(OH_2)_5SO_4^+$ are about 20% higher than those reported by Fogel.[1] We are unable to explain this discrepancy.

The vibrational properties of a sulfate ion are not drastically changed when the sulfate ion is bound to a metal ion. The bonding to the metal ion acts as a perturbation which decreases the symmetry of the sulfate. The results of such a decrease in symmetry on the infrared spectrum are summarized in Table I, a correlation table prepared by Nakamoto.[2] Nakamoto's work[2] shows that for sulfatoamminecobalt(III) complexes ν_1 is about 1000 cm.$^{-1}$, ν_2 is about 450 cm.$^{-1}$, ν_3 is about 1100 cm.$^{-1}$, and ν_4 is about 600 cm.$^{-1}$. The splitting as the symmetry decreases is less than 100 cm.$^{-1}$. In the region from 900 to 1300 cm.$^{-1}$ three infrared lines should be observed for a monodentate ligand and four for a bidentate ligand.

Table I

Correlation Table for Infrared-Active Vibrations

Species	Symmetry	ν_1	ν_2	ν_3	ν_4
Free sulfate	T_d			F_2	F_2
Monodentate	C_{3v}	A_1	E	$A_1 + E$	$A_1 + E$
Bidentate	C_{2v}	A_1	A_1	$A_1 + B_1 + B_2$	$A_1 + B_1 + B_2$

Hexaaquochromium(III) chloride was prepared and its infrared spectrum determined in the range 900–1500 cm.$^{-1}$ since its spectrum in this range has not previously been reported. The absence of any peaks in the hexaaquochromium(III) spectrum indicates that coordinate water groups do not absorb in this region. Thus, any observed peaks in this region in the spectrum of the monosulfato species can be attributed to sulfate group vibrations. We assign the lines at 1068 and 1118 cm.$^{-1}$ to be ν_3 and the line at 1002 cm.$^{-1}$ to be ν_1. On this basis it is concluded that sulfate is a mono-

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[7] J. E. Finholt, Lawrence Radiation Lab. Rept. UCRL 8879, University of California, Berkeley, 1960, pp. 23–24; H. W. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958).

[8] A tabulation of the molar absorptivity values has been deposited as Document No. 8118 with the ADI Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and by remitting $1.25 for photoprints, or $1.25 for microfilm. Advance payment is required. Make checks or money order payable to: Chief, Photoduplication Service, Library of Congress.

dentate ligand in the monosulfatopentaaquochromium(III) ion. Because of the many lines due to water vibrations in the 400–700 cm.$^{-1}$ region,[9] no attempt was made to determine the degree of splitting of ν_4.

Barraclaugh and Tobe[10] have reported the preparation of salts containing the $CoSO_4H_2O(C_2H_8N_2)_2^+$ ion. From infrared studies of these salts the sulfate was found to be a monodentate ligand. Upon heating, a conversion to salts containing $CoSO_4(C_2H_8N_2)_2^+$ took place, and the sulfate was found to be bidentate. When dissolved in water, $CoSO_4(C_2H_8N_2)_2^+$ was found to revert to $CoSO_4H_2O(C_2H_8N_2)_2^+$, indicating that the monodentate form is the more stable of the two. It would be interesting to determine if a chromium species containing sulfate as a bidentate ligand could be prepared in a similar fashion.

The knowledge that sulfate behaves as a monodentate ligand should be of use in investigating the kinetics of chromium(III) reactions. Most ligands of -2 or -3 charge are multidentate and attempts to distinguish effects due to ligand charge are obscured by the multidentate character of the ligands. Straightforward investigation of ligand charge effects should be possible by comparing monodentate sulfate to ligands of -1 and 0 charge.

The monodentate nature of the sulfate in the monosulfatopentaaquochromium(III) ion can be rationalized by consideration of bond distances and angles. The Cr–O bond distances in *trans*-dioxalatodiaquochromate(III)[11] and trisoxalatochromate(III)[12] range from 1.92 to 2.02 Å. If one assumes the Cr–O distance to be about 1.97 Å. in a bidentate sulfatochromium(III) species, and, further, that the O–Cr–O angle would be 90°, the distance between the two oxygen atoms is 1.39 Å. The S–O bond distance in sulfate is 1.44 Å.[13] Assuming that the oxygen atoms are arranged tetrahedrally around the sulfur, the distance between two oxygen atoms is 1.17 Å. Thus, if the sulfate is to be a bidentate ligand one or more of the following must occur: the S–O bond must be stretched, the O–S–O bond angle increased, the Cr–O bond shrunk, or the O–Cr–O bond angle decreased. The idea that geometrical factors prevent sulfate from acting as a bidentate ligand with chromium(III) would be supported if a bidentate selenatochromium(III) species could be prepared. The Se–O distance is 1.61 Å. in selenate,[14] so much less distortion would be required for the selenate to act as a bidentate ligand than for the sulfate.

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(11) J. N. van Nieckerk and F. R. Schoening, *Acta Cryst.*, **5**, 196, 499 (1952).

(12) J. N. van Nieckerk and F. R. Schoening, *ibid.*, **4**, 35 (1951).

(13) F. Mazzi, *ibid.*, **8**, 137 (1955).

(14) M. Bailey and A. F. Wells, *J. Chem. Soc.*, 968 (1951).

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The Absolute Configurations of Disubstituted Cobalt(III) Triethylenetetramine Complexes

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The rotatory dispersion and circular dichroism curves for the following complex ions are recorded[1]: (+)-α-$[Co(trien)Cl_2]^+$, (+)-α-$[Co(trien)ClOH_2]^{+2}$, (+)-α-$[Co(trien)CO_3]^+$, $(+)_{546}$-α-$[Co(trien)(OH_2)_2]^{+3}$, $(+)_{546}$-α-$[Co(trien)(NO_2)_2]^+$, (+)-β-$[Co(trien)Cl_2]^+$, (+)-β-$[Co(trien)ClOH_2]^{+2}$, (+)-β-$[Co(trien)CO_3]^+$, $(+)_{546}$-β-$[Co(trien)(OH_2)_2]^{+3}$, and $(+)_{546}$-$[Co(trien)(NO_2)_2]^+$. The relative and absolute configurations of the complex ions are discussed in the light of recent advances in the interpretation of circular dichroism curves and in conjunction with reactions which interrelate the compounds and are known to occur with retention of configuration.

Introduction

The absolute and relative configurations of a series of optically active disubstituted bis(ethylenediamine)-cobalt(III) complexes have been assessed by an analysis of their rotatory dispersion (RD) curves, correlated with kinetic and mechanistic evidence which interrelates the configurations of the compounds independently of rotatory dispersion.[2] The present paper is concerned with a similar series of complexes containing the quadridentate ligand triethylenetetramine (trien) which may be regarded as two ethylenediamine (en) molecules linked by an ethylene bridge. The distinction between the $[Co(en)_2X_2]^{+n}$ and $[Co(trien)X_2]^{+n}$ complexes arises from the manner in which the quadridentate can attach to the cobalt. Whereas $[Co(en)_2X_2]^{+n}$

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(1) The optical isomers are denoted by the sign of rotation in the Na D or if another wave length is used then the wave length appears as a subscript, *e.g.*, $(+)_{546}$.

(2) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).