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New Penta- and Tetraammine Complexes of Chromium(III) with Sulphato or μ-Dithionato Ligands

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The complex compounds $[CrSO_4(NH_3)_5]HSO_4\cdot 2H_2O$, $[CrSO_4(NH_3)_5]_2S_2O_6\cdot 3H_2O$, $[CrSO_4(H_2O)(NH_3)_4][Cr(SO_4)_2(NH_3)_4]\cdot 5H_2O$ *and* $[CrSO_4(H_2O)(NH_3)_4]_2S_2O_6\cdot 3H_2O$, *all containing* SO_4^{2-} *as a monodentate ligand, and also* $[Cr(NH_3)_5\text{–}S_2O_6\text{–}Cr(NH_3)_5](SO_4)_2\cdot 3H_2O$ *with* $S_2O_6^{2-}$ *bridging ligand have been prepared and characterized by chemical analysis, electronic and IR spectra, and conductivity measurements.*

The compound $[CrH_2O(NH_3)_4\text{–}S_2O_6\text{–}CrH_2O(NH_3)_4](SO_4)_2\cdot 2H_2O$ *(previously described) is converted, on standing both in the solid state and in solution, to* $[CrSO_4(H_2O)(NH_3)_4]_2S_2O_6$ *aq.*

Introduction

Three ammine complexes of chromium(III) containing sulphato as ligand have been reported [1, 2], but only one of them has been completely characterized. Recently, Ramasani *et al.* [1] have prepared the salt $[CrSO_4(NH_3)_5]ClO_4$ with cation exchange techniques. The authors, however, do not report the visible spectrum of the new complex cation $[CrSO_4(NH_3)_5]^+$ and indicate that "the unidentate nature of the ligand in this complex could not be inferred directly from the IR spectrum since the splittings of the ν(S=O) band have been overlapped by ClO_4^- ion vibration".

Hertzenberg and Bailar [2] prepared $[CrSO_4(H_2O)(NH_3)_4]_2SO_4$ and $[Cr(NH_3)_4(SO_4)_3Cr(NH_3)_4]$ from $[Cr(H_2O)_2(NH_3)_4]_2(SO_4)_3\cdot$aq in the solid state; according to the authors, these compounds are not pure as "some overlap of deaquation and deammination has occurred".

Four new ammine complexes of Cr(III) with monodentate sulphato: $[CrSO_4(NH_3)_5]HSO_4\cdot 2H_2O$ (I); $[CrSO_4(NH_3)_5]_2S_2O_6\cdot 3H_2O$ (II); $[CrSO_4(H_2O)(NH_3)_4][Cr(SO_4)_2(NH_3)_4]\cdot 5H_2O$ (III) and $[CrSO_4(H_2O)(NH_3)_4]_2S_2O_6\cdot 3H_2O$ (IV) are described and characterized in this paper.

With μ-S_2O_6 ligand, $[Cr(NH_3)_5\text{–}S_2O_6\text{–}Cr(NH_3)_5](SO_4)_2\cdot 3H_2O$ (V) is reported for the first time, along with the characterization of $[CrH_2O(NH_3)_4\text{–}S_2O_6\text{–}CrH_2O(NH_3)_4](SO_4)_2\cdot 2H_2O$ (VI), a compound previously reported by the authors [3].

Since II and V and, on the other hand, IV and VI have the same empirical formula, the possibility of their isomerization has been examined and reported in this paper.

Experimental

Preparative Methods

Preparation of Compound I, $[CrSO_4(NH_3)_5]HSO_4\cdot 2H_2O$

5 g of $[CrH_2O(NH_3)_5[(ClO_4)_3$ (obtained by adding concentrated $HClO_4$ to the nitrate salt) [4] were dissolved in 30 ml of water and to this solution maintained in an ice-water bath, concentrated H_2SO_4 (50–70 ml) was added dropwise and with constant stirring. A precipitate of $[CrH_2O(NH_3)_5]_2(SO_4)_3\cdot$aq is first formed, but this dissolves with the excess of H_2SO_4 and the colour of the mixture changes from orange to red. The solution was kept in the dark at room temperature for 3–4 days and then filtered. To the filtered solution a large excess of ethanol (500 ml) was added whereupon a rose readily soluble solid was precipitated. Analysis corresponds to I somewhat impure by $[CrH_2O(NH_3)_5]_2(SO_4)_3$. The mother liquor was left in the refrigerator at –20 °C for 24 hours, and compound (I) was precipitated in a pure state. *Anal.* Found: Cr, 14.09; NH_3, 23.13; SO_4^{2-}, 51.61; Calcd: Cr, 14.20; NH_3, 23.22; SO_4^{2-}, 52.45%.

Preparation of Compound II, $[CrSO_4(NH_3)_5]_2S_2O_6\cdot 3H_2O$

The compound II was obtained by dissolving 3 g of I (the impure fraction first obtained in the precipitate of I may also be used as starting material) in 50 ml of 10% $H_2S_2O_6$ solution and adding 100 ml of ethanol. The crude product was dissolved in the minimum amount of water and reprecipitated by addition of ethanol. The compound was filtered, washed with

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96% ethanol and ether, and air-dried. *Anal.* Found: Cr, 15.20; NH_3, 24.74; SO_4^{2-}, 28.02; $S_2O_6^{2-}$, 23.59. Calcd: Cr, 15.29; NH_3, 24.74; SO_4^{2-}, 28.23; $S_2O_6^{2-}$, 23.52%.

Preparation of Compound III, $[CrSO_4(H_2O)(NH_3)_4]$ $[Cr(SO_4)_2(NH_3)_4]5H_2O$

2 g of $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ [5] dissolved in 1*M* H_2SO_4 (30 ml) was heated on a sand bath at 70–80 °C for 10 min. The colour of the solution changes from light to dark red. The mixture was placed in an ice bath and 200 ml of ethanol at −20 °C was added slowly and with stirring. An oily product was separated. This was washed with ethanol and solidified by prolonged stirring in 1:1 ethanol:acetone. The product was collected, washed and dried as above. *Anal.* Found: Cr, 17.87; NH_3, 23.13; SO_4^{2-}, 50.10. Calcd: Cr, 17.87; NH_3, 23.32; SO_4^{2-}, 49.61%.

Preparation of Compound IV, $[CrSO_4(H_2O)(NH_3)_4]_2S_2O_6 \cdot 3H_2O$

Compound III (2 g) was dissolved in 40 ml of a 10% aqueous solution of $H_2S_2O_6$. The resulting solution was placed in an ice bath and ethanol (200 ml) was added with constant stirring. The precipitated product was filtered off, washed and dried as above. *Anal.* Found: Cr, 15.19; NH_3, 19.96; SO_4^{2-}, 28.26; $S_2O_6^{2-}$, 23.26. Calcd: Cr, 15.24; NH_3, 19.97; SO_4^{2-}, 28.26; $S_2O_6^{2-}$, 23.46%.

Preparation of Compounds V and VI

$[CrH_2O(NH_3)_5](ClO_4)_3$ (2g) or $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ (2 g) was dissolved in 20 ml of 10% $H_2S_2O_6$ and 1*M* H_2SO_4 (30 ml) was added. The solution was placed in an ice bath, and ethanol cooled to −20 °C was added with constant stirring. The products were filtered, washed and dried as above. *Anal.* (V): Found: Cr, 15.15; NH_3, 24.86; SO_4^{2-}, 28.38; $S_2O_6^{2-}$, 23.57. Calcd: Cr, 15.29; NH_3, 25.00; SO_4^{2-}, 28.23; $S_2O_6^{2-}$, 23.52. Compound VI: Found: Cr, 15.62; NH_3, 20.62; SO_4^{2-}, 24.20; $S_2O_6^{2-}$, 28.86. Calcd: Cr, 15.61; NH_3, 20.63; SO_4^{2-}, 24.13; $S_2O_6^{2-}$, 28.92%.

Analytical Methods [6]

Chromium was determined volumetrically with standard Fe(II) after oxidation to Cr(VI); ammonia was determined by distillation; sulphate was determined gravimetrically as $BaSO_4$ and dithionate was determined gravimetrically as $BaSO_4$, after oxidation with HNO_3.

Other Methods

Infrared spectra were recorded on a Beckman IR 20 A spectrophotometer purged with dry air. Samples were prepared using the KBr technique. Electronic absorption spectra were recorded on a Beckman DB-GT spectrophotometer. Conductivity measurements were obtained with a Radiometer model CDM-3 conductivity bridge.

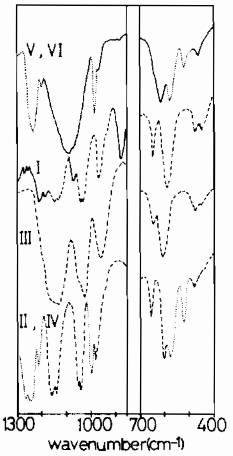

Figure 1. Infrared spectra (1300–400 cm^{-1}). ········ free or bridging $S_2O_6^{2-}$; ------monodentate SO_4^{2-}; —— free SO_4^{2-} or HSO_4.

Results and Discussion

Infrared Spectra (Fig. 1)

The six new compounds show the bands due to H_2O and NH_3, according to the literature [7]. On the other hand, an ill-defined band at about 3150 cm^{-1}, a very broad one in the region 3000–2000 cm^{-1}, and particularly, a weak but defined band at about 2500 cm^{-1} are evidence for the existence of hydrogen bond interactions [8–10] in the complexes I, V and VI.

Compounds II, IV, V and VI show the five bands typical of the dithionate ion [11] (Fig. 1).

For compounds V and VI, the IR spectra show the presence of the bands due to free sulphate [7] (Fig. 1). The modes forbidden in the free ion appear weakly due to lattice effects.

The four complexes I, II, III and IV, containing the ligand sulphato show the bands due to this group functioning as monodentate (C_{3v} symmetry) [7] (Fig. 1; ν_3 shows additional splitting due to lattice effects).

Compound I exhibits, along with the bands due to monodentate sulphato, those typical of HSO_4^- [12], overlapped between themselves and with those of monodentate sulphato.

Conductivity Measurements

Conductivity measurements for the new compounds in water indicate remarkable stability for compound I, II and IV (with ligand sulphato), high lability for compounds V and VI (with ligand μ-$S_2O_6^{2-}$) and an intermediate stability for the anion of the salt III, $[Cr(SO_4)_2(NH_3)_4]^-$.

TABLE I. Conductivity Measurements (Λ_{1000}, ohm^{-1} mol^{-1} cm^2)

Compound	Solvent			
	Water		Methanol Water (35%)	Dioxane Water (30%)
	0 °C	20 °C	20 °C	20 °C
I	250	390	–	–
II	155	260	–	–
III	105	185	–	–
IV	165	275	–	–
V	215	440	145	165
VI	220	450	130	160
VII[a]	230	365	240	255
VIII[b]	245	385	235	260

[a]VII = $[CrH_2O(NH_3)_5](ClO_4)_3$ [b]VIII = $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$

Values of molar conductivity of the new compounds along with those of the starting materials $[CrH_2O(NH_3)_5](ClO_4)_3$ (VII) and $[Cr(H_2O)_2(NH_3)_4]ClO_4)_3$ (VII) are given in Table I. From this data and the values given in the literature [13] it may be concluded that compounds II and IV behave as AB_2 electrolytes in aqueous solution, in accord with the proposed formulations. Values of conductivity remain unchanged for 3–4 hours and the aqueous solutions do not give precipitate with Ba^{2+} salt. At 20 °C, compounds V and VI show values of conductivity corresponding to five-ion electrolytes, indicating a rapid aquation of the complex species containing the ligand dithionato. The aquation process is not complete at 0 °C.

The extremely high value of Λ for compound I is explained in terms of the high mobility of the H^+set free.

Finally, the initial values of Λ for compound III agree with the assigned character of AB electrolyte. The aqueous solution does not give precipitate with Ba^{2+} until after 10–15 minutes. However, an appreciable variation of Λ with time is observed at 20 °C. After 20 minutes a value of Λ = 255 ohm^{-1} mol^{-1} cm^2 is obtained, which indicates a greater lability of the anion $[Cr(SO_4)_2(NH_3)_4]^-$ in the first step of aquation. The study of the visible spectrum of the aqueous solution confirms this interpretation.

It is not possible to draw conclusions on the existence of binuclear ions from conductivity measurements in aqueous solution, in view of the rapid aquation which must occur. However, molar conductivity in hydroalcoholic mixtures (media involved in their preparation) and particularly in 1 2 methanol water and 1 2 dioxane water at 20 °C indicates constant values of Λ which correspond to electrolytes of the type AB_2 [14].

Electronic Spectra

Absorption maxima in aqueous solution for the new compounds are indicated in Table II. Visible spectra of I, II and IV do not change with time. Maxima in aqueous solution are identical with whose obtained in Nujol dispersions and with minima of diffuse reflectance spectra.

The electronic spectra of compounds V and VI in aqueous solution are identical with those of the cations $[CrH_2O(NH_3)_5]^{3+}$ and $[Cr(H_2O)_2(NH_3)_4]^{3+}$ (compounds VII and VIII) respectively, since the aquation is very rapid. Compounds V and VI exhibit maxima in the solid state (Nujol dispersion or diffuse reflectance) at 480, 360 nm and 494, 367 nm respectively. Therefore, $S_2O_6^{2-}$ and H_2O are situated almost identically in the spectrochemical series [15].

A shift in the visible absorption maxima towards higher wavelengths is observed when aquo ligands are replaced by sulphato. Aqueous solutions of compounds III show a shift of absorption maxima with time towards lower wavelength. Thus, after 10 minutes maxima are observed at 520 and 385 nm, after 70 minutes at 510 and 375 nm (already practically constant), thus confirming a gradual aquation of the initial species $[Cr(SO_4)_2(NH_3)_4]^-$ to $[CrSO_4(H_2O)(NH_3)_4]^+$.

The absorption spectrum of III is practically identical with that reported by Hertzenberg and Bailar [2] for the product obtained by heating $[Cr(H_2O)_2(NH_3)_4]_2(SO_4)_3$ in the thermogravimetric balance and formulated as $[Cr(NH_3)_4(SO_4)_3Cr(NH_3)_4]$, even though the mentioned authors indicate partial loss of ammonia during the dehydration process. This compound, with bridging sulphato ligand, should exhibit additional splitting of the E mode of both $\nu_3(T_d)$ and

TABLE II. Electronic Spectra (nm)

Compound	I	II	III	IV	V	VI	VII[a]	VIII[b]
Absorption Maxima (in water)	494–496 365 205	494–496 365 212	523 385 210	508–510 372 215	478 358 218	494 367 208	478 358 210	494 367 210

[a]VII = $[CrH_2O(NH_3)_5](ClO_4)_3$ [b]VIII = $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$

$\nu_4(T_d)$ as observed in Co(III) complexes containing bridging SO_4^{2-} ligand [7]. Anyway, it seems more likely that the IR spectrum reported by Hertzenberg corresponds to a product with monodentate sulphato rather than to one containing bridging or chelate SO_4^{2-}, since this IR spectrum (showing the ν_3 band clearly split into two components) is practically identical with that of $[CrSO_4(H_2O)(NH_3)_4]_2SO_4$, also prepared by the same authors.

Transformations in the Solid State and in Solution

Compound VI is gradually converted to compound IV both in the solid state and in solution (even at room temperature and in the dark). The maximum of absortion shifts from 494 to 510 nm and the IR spectrum shows the presence of SO_4^{2-} functioning as a ligand. After about 30 days the aqueous solution gives practically negative test with Ba^{2+}. The transformation is more rapidly achieved on heating the solid salt at 80–90 °C.

This isomerization process is most conveniently carried out by heating an acidified aqueous solution of VI at 60 °C for 30 minutes. The colour of the solution gradually changes to wine-red (due to $[CrSO_4(H_2O)(NH_3)_4]^+$ cation). The compound IV is isolated in a 20% yield by precipitation with ethanol.

On the other hand, the transformation V to II is not attained. At room temperature complex V is quite stable. It shows only very slight features attributable to monodentate sulphate in the IR spectrum after standing in the dessicator for about one month, and its aqueous solution still gives immediate precipitate with Ba^{2+}. The aqueous solution of V is also quite stable; the solid obtained by precipitation with ethanol from this aqueous solution maintained at 0 °C or 20 °C for one month is identical with the product kept in the solid state. The same result is obtained if solid V is heated below 100 °C; above this temperature the dithionate anion is gradually decomposed. On heating the aqueous solution, partial aquation of the pentaammine species occurs with formation of aquotetraammine cations which are more stable in solution.

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