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Binuclear Chromium(III) Complexes with μ-Oxalato Ligand

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Three novel binuclear complexes of Chromium(III) with ligand μ-oxalato are described: $[(NH_3)_5Cr(C_2O_4)Cr(NH_3)_5](S_2O_6)_2\cdot 4H_2O$; $[(NH_3)_4(H_2O)Cr(C_2O_4)Cr(H_2O)(NH_3)_4](S_2O_6)_2\cdot H_2O$ *and* $[(NH_3)_4Cr(C_2O_4)_2Cr(NH_3)_4]S_2O_6\cdot 9H_2O$; *and a new salt of oxalatotetraamminechromium(III) cation:* $[Cr(C_2O_4)(NH_3)_4]_2S_2O_6\cdot 4H_2O$. *The infrared spectra of these substances are studied and interpreted, and a criterion based on infrared spectroscopy to differenciate between the oxalato group acting as a chelate or bridging ligand is proposed: the presence of only two bands in the 1600–1700 cm*$^{-1}$ *zone when oxalato acts as a bridging ligand, and the presence of three bands when it acts a bidentate ligand.*

Introduction

Several Chromium(III) ammines with mono or bidentate oxalato have been prepared and described[1,2] but no references exist for polynuclear ammines of this cation with oxalate acting as a bridging ligand. The following substances have been prepared in the course of the research on Chromium(III) tetra- and pentaammine complexes carried out in this Department of Inorganic Chemistry:

$$[(NH_3)_5Cr(C_2O_4)Cr(NH_3)_5](S_2O_6)_2\cdot 4H_2O \quad \text{(I)}$$

$$[(NH_3)_4(H_2O)Cr(C_2O_4)Cr(H_2O)(NH_3)_4](S_2O_6)_2\cdot H_2O \quad \text{(II)}$$

and

$$[(NH_3)_4Cr(C_2O_4)_2Cr(NH_3)_4]S_2O_6\cdot 9H_2O \quad \text{(III)}$$

which are the first Chromium(III) complexes reported with the ligand μ-oxalato. Furthermore, a new salt of the oxalatotetraamminechromium(III) class has been prepared:

$$[Cr(C_2O_4)(NH_3)_4]_2S_2O_6\cdot 4H_2O \quad \text{(IV)}$$

using a different procedure from that used for other salts of the same cation.

Neat differences have been appreciated in the 1600–1700 cm^{-1} zone (zone of C=O stretching vibrational modes) depending on whether oxalato group acts as a chelate or as a bridging ligand (Figure 1). This could well be a criterion to determine precisely the character of such a ligand.

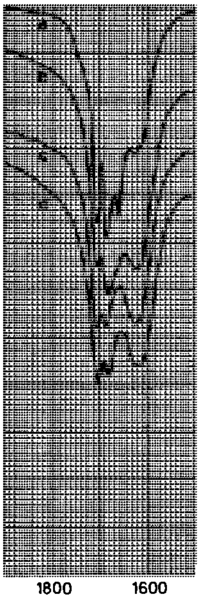

Figure 1. Infrared Spectra of: a) Compound IV; b) Compound I; c) Compound II; d) Compound III.

Preparation and Characterization of the New Compounds

Compound (IV)

By reaction of yellow $[Cr(S_2O_6)(NH_3)_5]_2S_2O_6\cdot 5H_2O$ with ammonium oxalate at room temperature, yellow $[Cr(S_2O_6)(NH_3)_5]_2C_2O_4\cdot 7H_2O$ is obtained[3]; but it has been observed that a red product separates out from the mother liquor of this preparation. The same red product (which turns out to be $[Cr(C_2O_4)(NH_3)_4]_2S_2O_6\cdot 4H_2O$) is obtained by treating directly $[Cr(S_2O_6)(NH_3)_5]_2S_2O_6\cdot 5H_2O$ with ammonium oxalate and warming the mixture. The visible and ultraviolet spectra of this compound show absorption maxima at 505, 375 and 209 mμ in agreement with the values reported in the literature for the visible spectra of other salts

TABLE I. Observed Infrared Bands.

a	b	c	d	e	f	g	Attributable to
1664 (B_{1g})	1704	1705(s)	1705(s)	1705(s)	1705(s)	1705(s)	$C_2O_4^{2-}$
1627 (B_{2u})		1680–1690(s)	1680–1690(s)	1680(s)	1680(s)	1680(s)	$C_2O_4^{2-}$
	1668	1660(s)	1660(s)	–	–	–	$C_2O_4^{2-}$
		1625(m)	1625(m)	1620(m)	1620(m)	1620(m)	NH_3; H_2O
1400–1485 (A_g)	1393	1380(s)	1390(s)	1395(s)	1390(s)	1390(s)	$C_2O_4^{2-}$; NO_3^-
1338 (B_{3u})	1258	1250(m)	1245(s)	1240(s)	1240(s)	1235(s)	$S_2O_6^{2-}$; NO_3^-, $C_2O_4^{2-}$
898 (A_g)	914, 890	(920)890(w)	890(920)(w)	920(895)(w)	900(w)	(920)895(w)	$C_2O_4^{2-}$
768 (B_{3u})	804	805(m)	805(m)	805(m)	805(m)	805(m)	$C_2O_4^{2-}$
545 (B_{1g})	545	540(w)	(580)560(m)	575(s)	570(m)	575(s)	$C_2O_4^{2-}$; $S_2O_6^{2-}$
443 (A_g)	486	475(w)	475(w)	475(w)	475(w)	475(w)	$C_2O_4^{2-}$; NH_3 (M–NH_3)
–	469						$C_2O_4^{2-}$
–	366						$C_2O_4^{2-}$
–	347						$C_2O_4^{2-}$
–	328						$C_2O_4^{2-}$

Reported in the literature: a) for free ion $C_2O_4^{2-}$ (1R and Raman spectra)[12]; b) for $[CrC_2O_4(NH_3)_4]Cl$.[6]
Observed bands: c) for $[CrC_2O_4(NH_3)_4]NO_3$; d) for Compound IV; e) for Compound I; f) for Compound II; g) for Compound III.
The values in parentheses correspond to bands only insinuated because of the overlapping with other more intense bands.

of the same complex cation.[4,5] The bands which may be attributed to the $C_2O_4^{2-}$ group in the infrared spectrum agree very well with those specified in the literature for this ion[6] (Table I). The same complex salt can be obtained by other methods as indicated in the Experimental Section. *Anal.* Found: Cr, 21.2; NH_3, 16.0; $C_2O_4^{2-}$, 27.1; $S_2O_6^{2-}$, 24.6; Calcd.: Cr, 21.01; NH_3, 16.04; $C_2O_4^{2-}$, 27.14; $S_2O_6^{2-}$, 24.69.

Compound (I)

DTA curve of $[CrS_2O_6(NH_3)_5]_2C_2O_4 \cdot 7H_2O$ shows a first endothermic peak at 110° C.[3] The very insoluble compound (I) is obtained by a thermal treatment of $[CrS_2O_6(NH_3)_5]_2C_2O_4 \cdot 7H_2O$ at this temperature involving dehydratation and internal reorganization of the complex in the solid phase. Visible spectrum in $HClO_4$ solution (1:3) shows absorption maxima at 510 and 375 mμ; diffuse reflectance spectrum in the solid state shows reflectance minima at 515 and 384 mμ. The infrared spectrum exhibits the bands given in Table I. *Anal.* Found: Cr, 13.8; NH_3, 22.2; $C_2O_4^{2-}$, 11.2; $S_2O_6^{2-}$, 42.6; Calcd: Cr, 13.78; NH_3, 22.67; $C_2O_4^{2-}$, 11.27; $S_2O_6^{2-}$, 42.42.

Compound (II)

This substance has been obtained from the not previously described salt $[Cr(S_2O_6)(NH_3)_4]_2C_2O_4 \cdot 4H_2O$, which in turn has been prepared from two other new compounds by the methods outlined in the Experimental Section. The study of the new tetraammine salts of Chromium(III) with dithionato ligand will be reported elsewhere.

The visible and ultraviolet spectra of the substance show absorption maxima at 506, 376 and 215–218 mμ, and the infrared spectrum exhibits the bands given in Table I. *Anal.* Found: Cr, 14.8; NH_3, 19.4; $C_2O_4^{2-}$, 12.4; $S_2O_6^{2-}$, 45.2; Calcd: Cr, 14.80; NH_3, 19.30; $C_2O_4^{2-}$, 12.53; $S_2O_6^{2-}$, 45.00. The diffuse reflectance spectrum shows transmittance minima at 506–508 and 375–377 mμ.

Compound (III)

The substance has been obtained by the two methods outlined in the Experimental Section; the aqueous solution does not yield precipitate with Ag^+ and neither does the cold solution acidified with acetic acid, with Ca^{2+} ion. The visible and ultraviolet spectra of this substance show absorption maxima at 503, 373 and 213 mμ, and the infrared spectrum exhibits the bands listed in Table I. *Anal.* Found: Cr, 14.0; NH_3, 18.5; $C_2O_4^{2-}$, 23.6; $S_2O_6^{2-}$, 21.4; Calcd: Cr, 14.09; NH_3, 18.42; $C_2O_4^{2-}$, 23.84; $S_2O_6^{2-}$, 21.68.

Infrared Spectra of the Compound with μ-Oxalato Ligand

The assignment of bands for the oxalate ion has been carried out by a number of authors, using the infrared and Raman spectra in the solid state and in aqueous solution.[7–9] On the basis of these authors' conclusions, a $D_{2h}(V_h)$ symmetry for the free oxalate ion as well as the assignment of bands, consistent with this point group, given in Table I, may be accepted.

The coordination of the oxalate group to metallic ion as a mono or bidentate ligand lowers the symmetry to C_s and C_{2v}, respectively. Bridging coordination on the other hand can occur through two *cis*-oxygens or through two *trans*-oxygens (*cis* or *trans* with respect to oxalate) which leads to different symmetries for the μ-oxalato group: C_{2v} or C_{2h}, respectively. Several authors[10] point out that μ-oxalato in some polynuclear complexes of Co(III) would coordinate through the two oxygens attached to the same atom of carbon, whereby the symmetry of the oxalato group would be also C_{2v}, in this case.

The interpretation of the infrared spectra of the compounds with mono- or bidentate oxalato has been undertaken by several authors using the treatment of correlations among point groups.[11–13]

Fujita, Martell and Nakamoto in 1961 concluded that the interactions existing among the vibrational modes of bidentate oxalato make impossible this simplified treatment; and on the basis of a 1 : 1 model of C_{2v} symmetry, they carried out a normal-coordinate analysis and proposed an assignment of bands for the $[CrC_2O_4(NH_3)_4]^+$ ion, in very good agreement with the experimental data. It does not seem reasonable not to use the correlation treatment with μ-oxalato polynuclear complexes, since in such cases the coupling of vibrations must not be important. The situation would be analogous in the case of complexes with di-μ-oxalato ligand, since the infrared spectra (at least those studied in this work) are very similar.

It is inferred from Table I and Figure 1 that the main differences observed in the infrared spectra of Cr(III) compounds with bidentate or bridging oxalato occur within the 1600–1700 cm^{-1} zone; and specially in the existence of a well-defined band at 1660 cm^{-1} appearing in the complexes with bidentate oxalato group and not in those with bridging oxalato. This band has not yet been assigned or accounted for.

Interpretation of the Infrared Spectra of the Binuclear Compounds with μ-Oxalato Ligand

Assuming C_{2v} symmetry for the μ-oxalato group and the band assignment for the oxalate ion proposed by Fujita, Nakamoto and Kobayashi[1] and Murata and Kawai[8] (Table I), the infrared spectra of polynuclear Chromium(III) complexes with μ-oxalato ligand may be interpreted as follows:

B_{2u} modes (infrared active) are transformed into infrared active A_1 modes of point group C_{2v}, the band appearing at 1680 cm^{-1} in the complexes studied and which appears at 1627 cm^{-1} for the free oxalate ion must be assigned to this symmetry species. The frequency calculated at 295 cm^{-1} would appear in the KBr absorption zone and cannot be observed for this reason.

B_{3u} modes (also infrared active) are transformed into B_1 of point group C_{2v} (infrared active). The band at 1250–1260 cm^{-1} observed in the complexes with bidentate oxalato ligand (also of C_{2v} symmetry) and containing no dithionate, is assigned to the same vibrational mode observed in the free ion at 1338 cm^{-1}. In the binuclear compounds with μ-oxalato ligand containing also dithionate, the assignment is ambiguous due to the presence of the $\nu_7(E_u)$ and $\nu_{10}(E_g)$ bands of the $S_2O_6^{2-}$ ion (point group D_{3d})[14] in the same zone. The other band calculated at 757 cm^{-1} for the free oxalate ion and observed at 768 cm^{-1}, corresponds to that appearing at 805 cm^{-1} in all of these complexes.

B_{1u} mode (infrared active) is transformed into B_2 of point group C_{2v} (also infrared active). The band corresponding to this out-of-plane vibrational mode has not yet been unambiguously assigned. Several authors set it at 665 cm^{-1} [7] even though some doubt exists as to this assignment.

B_{1g} modes (infrared inactive) are transformed into B_2 of point group C_{2v} (infrared active), which may usually appear with weak intensity. The band observed at 1705 cm^{-1} in all of these substances is assigned to these vibrational modes; this band corresponds to the line appearing in the Raman spectrum of the free oxalate ion at 1664 cm^{-1}. The other band calculated at 550 cm^{-1} and appearing in the Raman spectrum of the free ion at 545 cm^{-1}, cannot be observed in these compounds due to the overlapping with the $[\nu_6(A_{2u})]$ band of the dithionate group.[14] In fact this band appears at 540–560 cm^{-1} in the compounds with bidentate oxalato ligand containing no dithionate.

B_{2g} mode (infrared inactive) is transformed into A_2 of point group C_{2v} (also infrared inactive). The band corresponding to this out-of-plane vibrational mode has not been assigned.

A_g modes (infrared inactive) are transformed into A_1 of point group C_{2v} (infrared active) and may usually appear with weak intensity. There are three bands belonging to these modes, to which the lines observed in the Raman spectrum at 443, 898 and 1400–1485 cm^{-1} are assigned. In the complexes studied, the broad and weak band at 475 cm^{-1} overlapped with the metal–nitrogen bands of ammonia, the weak band at 890–920 cm^{-1} and the strong band at 1385–1390 cm^{-1} correspond to the above modes respectively.

From all this it may be concluded that bridging oxalato group is likely to coordinate to the two Chromium(III) ions in such a way that its symmetry becomes C_{2v} (probably involving the two carbonyl groups with a *cis* geometry with respect to the oxalate ion).

Interpretation of the Infrared Spectrum of the $[Cr(C_2O_4)(NH_3)_4]^+$ Ion

According to what has been previously pointed out, Fujita, Martell and Nakamoto give the following band assignment, calculated with a normal-coordinate analysis: A_1 modes [ν_1, 1665; ν_2, 1400; ν_3, 910; ν_4, 543; ν_5, 345; ν_6, 214 cm^{-1}]; B_2 modes [ν_7, 1697; ν_8, 1251; ν_9, 825; ν_{10}, 479; ν_{11}, 386 cm^{-1}], but they do not calculate or assign the out-of-plane vibrational modes, which are probably found below 300 cm^{-1}. On the other hand a band at 1660 cm^{-1}, not reported or assigned by these authors, is observed in the spectrum of $[Cr(C_2O_4)(NH_3)_4]_2S_2O_6\cdot4H_2O$ and in those of other salts of the same cation.

On the basis of C_{2v} symmetry for bidentate oxalato and the previous assignment, the $2\nu_9(B_2)$ overtone could be predicted to interact with the $\nu_1(A_1)$ fundamental mode forming a doublet made up of the bands observed at 1680–1690 and 1660 cm^{-1}. It should be pointed out that the ν_9 fundamental band is a vibrational mode involving the Cr–O bond[6] and that Fermi's interaction would be a consequence of coordination and formation of the chelate ring.

Therefore, it may be concluded that it is possible to distinguish between the two forms of coordination of the oxalate group, by inspection of the infrared spectra in the 1600–1700 cm^{-1} zone. Three strong bands (at 1705, 1680–1690, and 1660 cm^{-1}) will be observed in the compounds with bidentate oxalato, whereas only the two first will be observed in the compounds containing bridging oxalato group.

Experimental Section

Preparation of the Substances

$[Cr(S_2O_6)(NH_3)_5]_2S_2O_6\cdot5H_2O$ and $[Cr(S_2O_6)(NH_3)_5]_2C_2O_4\cdot7H_2O$ were prepared as indicated in reference[3]; and $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ as in reference.[15]

Preparation of compound IV

a) A solution formed with 1 g of $[CrS_2O_6(NH_3)_5]_2S_2O_6\cdot5H_2O$ and 2.5 g of $H_2C_2O_4$ in the minimum amount of water is heated on the water bath at 80° C for 45–60 min; the mixture is allowed to cool and the red precipitate formed is filtered, washed with alcohol and ether, and dried in a dessicator over concentrated sulphuric acid.

b) 2 g of $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ are dissolved in 25 ml of water and the mixture is treated with 4–5 g of oxalic acid dissolved in 20 ml of a solution containing 2 g of dithionic acid. The solution is heated on the water bath at 70° C for ten minutes and then it is filtered.

c) 10 g of $[CrClH_2O(NH_3)_4]Cl_2$ are treated with a solution of Ag_2O_{aq} in a solution containing 15 g of dithionic acid.

The Ag_2O_{aq} used is obtained from the reaction between 20.8 g of $AgNO_3$ and an excess of NaOH (*ca.* 10 g) and washed six times with boiling water.

The mixture is heated at 70–75° C on the water bath for 10–15 min, and the solid product is filtered and washed. This product shows a Cr:NH_3 ratio between 1:4 and 1:5 and might be a mixture of $(NH_4)[Cr(S_2O_6)_2(NH_3)_4]$ and $[(H_2O)(NH_3)_4Cr(S_2O_6)Cr(NH_3)_4(H_2O)](S_2O_6)_2$ (aq).

Upon heating the mixture formed with the solutions of 2 g of this solid product in 25 ml of water and 2 g of oxalic acid in 20 ml of water, on the water bath at 70° C for 10 min, red crystals of $[CrC_2O_4(NH_3)_4]_2S_2O_6\cdot4H_2O$ separate out.

d) A solution of 2 g of $NH_4[Cr(S_2O_6)_2(NH_3)_4]$ (aq)[16] in 30–40 ml of water is mixed with a solution of 4–5 g of oxalic acid in 20 ml of water. The mixture is heated on the water bath at 70° C for 10 min. Red crystals begin to separate out within a few minutes.

e) It is also obtained from $[Cr(S_2O_6)(NH_3)_4]_2S_2O_6\cdot3H_2O$ (obtained as indicated below) by a procedure identical to that indicated in d).

f) A suspension of 2 g of $[Cr(C_2O_4)(NH_3)_4]NO_3$ in 30 ml of water is treated with 1 g of $Na_2S_2O_6\cdot2H_2O$ in a nearly saturated solution, or with the equivalent quantity of $H_2S_2O_6$ solution, and is heated on the water bath to 50° C. After the solid has disolved the product separates out with an almost theoretical yield, if $Na_2S_2O_6$ has been used. If dilute dithionic acid is used, some alcohol (20 ml) should be used to precipitate the substance.

Preparation of compound (I)

This substance is obtained by heating $[Cr(S_2O_6)(NH_3)_5]_2C_2O_4\cdot7H_2O$ at 110° C for an hour.

Preparation of $[Cr(S_2O_6)(NH_3)_4]_2C_2O_4\cdot4H_2O$

The following sequence of preparations is required.

a) Preparation of $[(H_2O)(NH_3)_4Cr(S_2O_6)Cr(NH_3)_4(H_2O)](S_2O_6)_2\cdot3H_2O$. A solution of 1 g of $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ in the minimum amount of water is treated with excess of $H_2S_2O_6$ solution. The product is precipitated upon adding 10 ml of glacial acetic acid to this mixture.

b) Preparation of $[Cr(S_2O_6)(NH_3)_4]_2S_2O_6\cdot3H_2O$. This product is obtained by thermal treatment of $[(H_2O)(NH_3)_4Cr(S_2O_6)Cr(NH_3)_4(H_2O)](S_2O_6)_2\cdot3H_2O$ at 80° C for an hour.

c) Preparation of $[Cr(S_2O_6)(NH_3)_4]_2C_2O_4\cdot4H_2O$. An excess of $H_2C_2O_4$ (2–3 g) is added to a solution of $[Cr(S_2O_6)(NH_3)_4]_2S_2O_6\cdot3H_2O$ (1 g) in the minimum of water, and the product is precipitated upon adding and equal volume of alcohol.

Preparation of compound (II)

Solid $[Cr(S_2O_6)(NH_3)_4]_2C_2O_4\cdot4H_2O$ is converted into this product by standing for some time (1–5 days).

Preparation of compound (III)

It is obtained via one of the following methods.

a) One gram of $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ is dissolved in the minimum amount of a 1:1 water–alcohol mixture and the resulting solution is cooled to –30° C. A solution of $H_2S_2O_6$ (0.5 g) and 2 g of $H_2C_2O_4$ in 10 ml of a 1:1 water–alcohol mixture is also prepared and cooled to –30° C. On mixing the two solutions, the product is precipitated as an oil which becomes crystalline by constant stirring for some time.

b) For this second method, the previous preparation of $[(NH_3)_4H_2OCr(S_2O_6)CrH_2O(NH_3)_4](C_2O_4)_2 \cdot 3H_2O$ is required. A solution of $[Cr(H_2O)_2(NH_3)_4](ClO_4)_3$ (2 g) and $H_2C_2O_4$ (2 g) in 25 ml of water is treated with an excess of $H_2S_2O_6$ (obtained from 2 g of BaS_2O_6 and the stoichiometric quantity of H_2SO_4). Upon adding 100 ml of alcohol, $[(NH_3)_4(H_2O)Cr(S_2O_6)Cr(H_2O)(NH_3)_4](C_2O_4)_2 \cdot 3H_2O$ separates out. This latter product is transformed into $[(NH_3)_4Cr(C_2O_4)_2(NH_3)_4]S_2O_6 \cdot 9H_2O$ on standing in the solid state for some 15 days.

Visible and Ultraviolet Spectra

Spectra were recorded on a Beckman DB–GT spectrophotometer.

Diffuse Reflectance Spectra

The spectra were measured on a Beckman model DU2 spectrophotometer equipped with a reflectance attachment provided by the manufacturers.

Infrared Spectra

The spectra were obtained on a Beckman model IR 20A spectrophotometer, and samples were prepared using the pressed KBr disk technique.

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