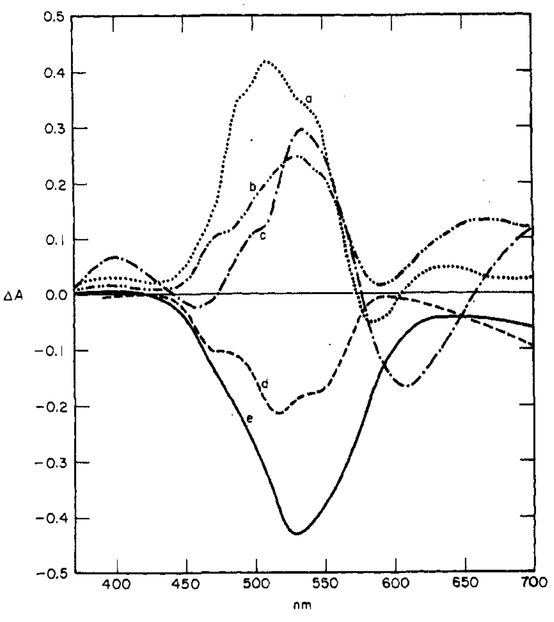

Figure 6. CD spectra of Co(II)-deprotonated hydroxy acid anion complexes with similar configurations on α and β carbons (multipliers to nominal Δ*A* scale in parentheses): (a) α-D-saccharine (×0.010); (b) α-D-glucoheptonate (×0.010); (c) D-arabonate (×0.010); (d) D-mannonate (×0.004); (e) L-erythronate (×0.020).

certain. Neither the absorption spectra nor the CD spectra for these complexes are like those for the cobalt(II)–dipeptide systems recorded for pH 9 and above.[16,17]

Registry No. L-Alanine, 56-41-7; L-valine, 72-18-4; L-

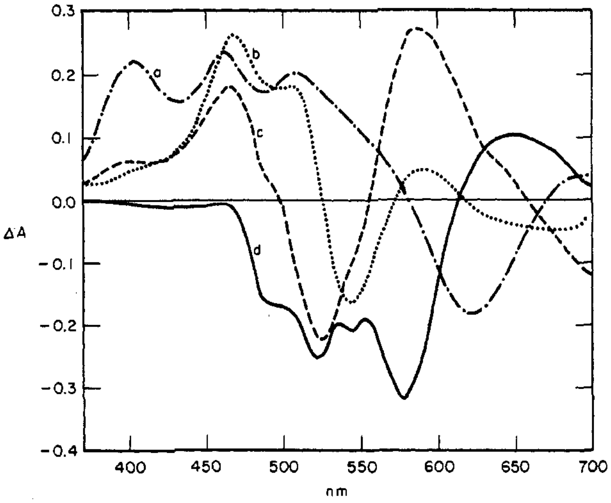

Figure 7. CD spectra of Co(II)-deprotonated hydroxy acid anion complexes with dissimilar configurations on α and β carbons (multipliers to nominal Δ*A* scale in parentheses): (a) D-gluconate, after 24-hr equilibration (×0.010); (b) D-galactonate (×0.004); (c) D-gluconate, on preparation (×0.010); (d) D-gulonate (×0.004).

serine, 56-45-1; L-methionine, 63-68-3; L-proline, 147-85-3; L-hydroxyproline, 51-35-4; L-lysine, 56-87-1; L-arginine, 74-79-3; L-ornithine, 70-26-8; L-aspartic acid, 56-84-8; L-glutamic acid, 56-86-0; L-asparagine, 70-47-3; L-lactic acid, 79-33-4; L-malic acid, 97-67-6; D-tartaric acid, 147-71-7; L-erythronic acid, 20703-66-6; D-ribonic acid, 642-98-8; D-arabonic acid, 488-30-2; D-gluconic acid, 526-95-4; D-gulonic acid, 20246-33-7; D-galactonic acid, 576-36-3; D-idonic acid, 488-33-5; D-mannonic acid, 642-99-9; D-pantoic acid, 1112-33-0; α-D-glucoheptonic acid, 87-74-1; α-D-saccharinic acid, 13962-35-1; cobalt, 7440-48-4.

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Contribution from the Department of Inorganic and Structural Chemistry,
The University, Leeds LS2 9JT, England, and the Anorganisch-Chemisches
Institut der Universitat, D-6900 Heidelberg, West Germany

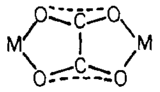
μ-Oxalato-cobalt(III) Complexes

K. L. SCOTT,[1a] K. WIEGHARDT,[1b] and A. G. SYKES*[1a]

Received July 11, 1972

Binuclear, trinuclear, and tetranuclear cobalt(III) complexes containing a single bridging oxalate ligand have been prepared and characterized. Elemental analyses and ultraviolet–visible and infrared spectra are reported. Behavior on reduction with Cr^{2+} and V^{2+} is consistent with the structures proposed.

Binuclear complexes in which both metal centers are linked to a planar tetradentate oxalate ligand to give two five-membered rings



have been known for some time. Well-established examples are the tri-*n*-butylphosphinepalladium(II) complex $[(n\text{-}Bu_3P)(Cl)PdC_2O_4Pd(Cl)(P\text{-}n\text{-}Bu_3)]^2$ and the pyridineruthenium(II) complex $[(C_5H_5N)_4RuC_2O_4Ru(C_5H_5N)_4](BF_4)_2$.[3] The mineral humboltine contains iron atoms linked by oxalate ligands to give planar polymeric chains, two water molecules completing the coordination about each iron.[4] The oxalate is similarly tetradentate in β-[Cu-

(1) (a) University of Leeds. (b) Heidelberg University.

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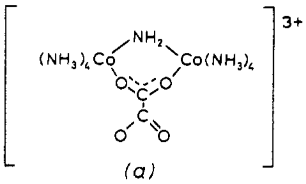
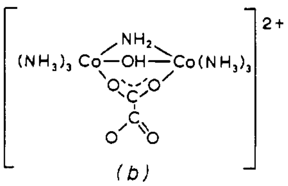


(a)



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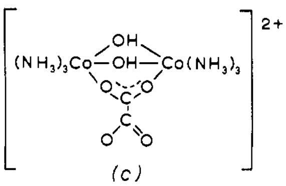
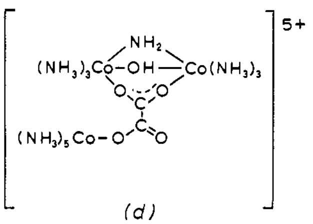


(c)



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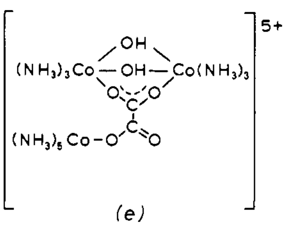

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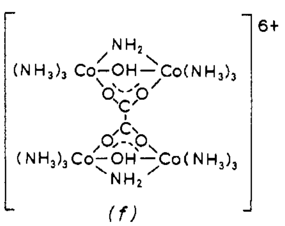

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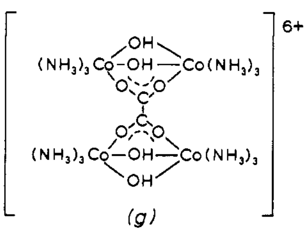
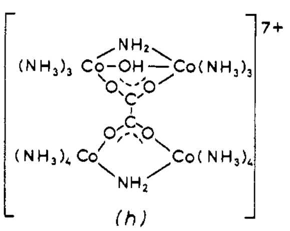
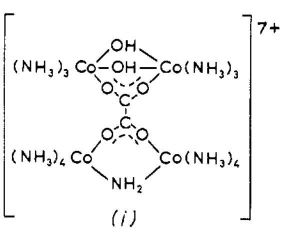


(g)



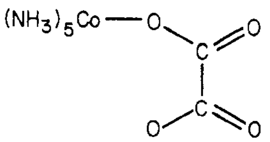
(h)

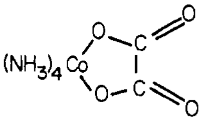


(i)

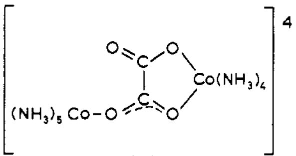
$(NH_3)_2C_2O_4]$[5] and $[Ti_2(C_2O_4)_3(H_2O)_6]\cdot 4H_2O$[6] and is tetradentate and tridentate in the complex $(NH_4)_2[(UO_2)_2(C_2O_4)_3]$.[7] Other claims for oxalate bonded to nickel(II), copper(II), and zinc(II) in a tetradentate manner have been made.[8,9] A crystal structure of the complex $[Cu(NH_3)(C_2O_4)]$ has indicated a distorted octahedral arrangement with one oxygen of the oxalate functioning as a bridge between two copper atoms.[10]

The mononuclear amminecobalt(III) complexes containing monodentate[11] and bidentate[12] oxalate are well known, *i.e.*

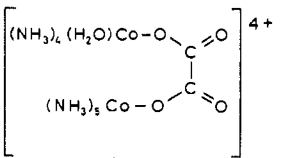




Whereas the complex containing monodentate oxalate will protonate readily (protonation constant $K \approx 114$ l. mol^{-1} at 25°, $\mu = 1.0M$),[11] there is no observable tendency for the complex containing bidentate oxalate to protonate.[12] We now consider the series of bi-, tri-, and tetranuclear cobalt(III) complexes, (a)-(i), in which a single oxalate ligand is either bi-, tri-, or tetradentate. The preparation and some details of the characterization of complexes (a),[13] (c) and (e),[14] and (g)[15] have been reported previously. The preparations of other related complexes are now described, and a comparison is made of their properties including ultraviolet-visible spectra, infrared spectra, and the mechanisms of reduction by Cr^{2+} and V^{2+}. Elemental analyses and the properties displayed by each complex are consistent with structures (a)-(i). The preparation of the complex (j) and

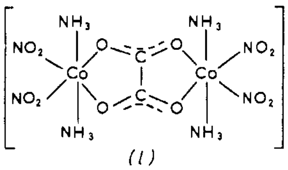


(j)



(k)

its conversion to (k) is also described. Finally, independently of this work, the preparation of (l) has been confirmed.[16]



(l)

Experimental Section

The following complexes were prepared by procedures already described in the literature: oxalatopentaamminecobalt(III), $[Co(NH_3)_5C_2O_4H](ClO_4)_2$,[11,17] carbonatotetraamminecobalt(III), $[Co(NH_3)_4CO_3](ClO_4)$,[18] μ-amido-μ-chloro-bis[tetraamminecobalt(III)], $[(NH_3)_4Co\text{-}\mu(NH_2,Cl)\text{-}Co(NH_3)_4]Cl_4\cdot 4.5H_2O$,[19] tri-$\mu$-hydroxo-bis[triamminecobalt(III)], $[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3\cdot 2H_2O$,[20] and μ-amido-μ-hydroxo-bis[aquotriamminecobalt(III)], $[(NH_3)_3(H_2O)Co\text{-}\mu(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3](NO_3)_4\cdot$

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Table I. Elemental Analysis (%) for μ-Oxalato Complexes, (a)–(k)

		C	H	N	NH_3	Cl or Br	Co	H_2O
(a) $[Co_2(NH_3)_8(NH_2)(C_2O_4)]Br_3 \cdot H_2O$	Calcd	3.9	4.6	20.5		38.9		
	Found	4.2	4.8	20.2		38.7		
(b) $[Co_2(NH_3)_6(NH_2)(OH)(C_2O_4H)](ClO_4)_3 \cdot H_2O$	Calcd	3.6	3.6	14.9				2.7
	Found	3.8	3.6	14.4				2.9
(c) $[Co_2(NH_3)_6(OH)_2(C_2O_4)](ClO_4)_2 \cdot 3H_2O$	Calcd	4.0	4.4		17.1	11.9	19.8	
	Found	3.9	4.9		17.2	12.2	19.9	
(d) $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)](ClO_4)_5 \cdot H_2O$	Calcd	2.4	3.8	16.8				1.8
	Found	2.2	3.85	16.1				1.4
(d) $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)]Br_5 \cdot 3H_2O$	Calcd	2.6	4.5			42.6		
	Found	2.9	4.5			41.5		
(e) $[Co_3(NH_3)_{11}(OH)_2(C_2O_4)]Br_5 \cdot 3H_2O$	Calcd	2.6	4.4		19.9	42.5		
	Found	2.7	4.5		19.9	42.3		
(f) $[Co_4(NH_3)_{12}(NH_2)_2(OH)_2(C_2O_4)](ClO_4)_6 \cdot 4H_2O$	Calcd	1.9	4.0	15.5				5.7
	Found	2.1	4.0	15.3				5.6
(g) $[Co_4(NH_3)_{12}(OH)_4(C_2O_4)](ClO_4)_6 \cdot 4H_2O$	Calcd	1.9	3.8	13.3		16.8		
	Found	2.3	4.0	13.4		16.8		
(h) $[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)](ClO_4)_7 \cdot 4H_2O$	Calcd	1.7	4.0	16.2				5.2
	Found	1.7	4.0	15.9				5.4
(h) $[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)]Br_7 \cdot 5H_2O$	Calcd	1.9	4.5	17.8		44.4		7.1
	Found	2.3	4.6	17.5		44.5		6.5
(i) $[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)](ClO_4)_7 \cdot 3H_2O$	Calcd	1.8	3.9	15.4		18.2	17.3	
	Found	2.0	3.8	15.2		18.3	17.2	
(i) $[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)]Br_7 \cdot 4H_2O$	Calcd	1.9	4.4		20.5	45.0	18.9	
	Found	2.1	4.2		20.5	45.4	18.8	
(j) $[Co_2(NH_3)_9(C_2O_4)](ClO_4)_4 \cdot 2H_2O$	Calcd	3.0	3.9		19.3	17.9	14.8	
	Found	3.2	4.0		19.2	17.5	14.7	
(j) $[Co_2(NH_3)_9(C_2O_4)](S_2O_6)_2 \cdot 5H_2O$	Calcd	3.1	4.9		19.9		15.3	
	Found	3.3	5.0		19.8		15.3	
(k) $[Co_2(NH_3)_9(H_2O)(C_2O_4)](ClO_4)_4 \cdot H_2O$	Calcd	3.0	3.9		19.3	17.9	14.9	
	Found	3.2	3.9		19.2	17.9	15.0	
(k) $[Co_2(NH_3)_9(H_2O)(C_2O_4)]Br_4 \cdot 2H_2O$	Calcd	3.3	4.5		20.9	43.6	16.1	
	Found	3.4	4.4		20.9	43.2	16.0	

$2H_2O$.[21] The latter was converted to the bromide salt by dissolving 0.4 g in water (10 ml) at *ca.* 40° and adding half the volume of concentrated HBr. It was also converted into the perchlorate salt of the related μ-amido-di-μ-hydroxo complex, $[(NH_3)_3Co\text{-}\mu(NH_2,OH,OH)\text{-}Co(NH_3)_3]^{3+}$, by dissolving 3 g in water (60 ml) at 40°, adding $NaClO_4 \cdot H_2O$ (25 g), and leaving the solution at 0° for 2 hr. Both solids were washed with ethanol and ether; yields 0.25 and 1.6 g, respectively. The hydration numbers were not determined. Oxalic acid dihydrate and other reagents were of Analar grade purity. The preparations of binuclear, trinuclear, and tetranuclear cobalt(III)–μ-oxalato complexes are described below, and their analyses are given in Table I. Hydration numbers were obtained by determining the loss in weight after leaving to stand over P_2O_5 for about 2 weeks.

Preparation of the μ-Amido-μ-oxalato-bis[tetraamminecobalt(III)] Complex, Formula (a). The chloride salt of the protonated form of (a), $[(NH_3)_4Co\text{-}\mu(NH_2,C_2O_4H)\text{-}Co(NH_3)_4]Cl_4 \cdot H_2O$, was prepared from $[(NH_3)_4Co\text{-}\mu(NH_2,Cl)\text{-}Co(NH_3)_4]Cl_4 \cdot 4.5H_2O$ and then converted into the perchlorate salt, which is half-protonated, by the procedure already described.[13] The unprotonated form of (a) was obtained as the bromide salt by neutralizing a solution of the perchlorate salt with 0.1 *M* NaOH and then adding a saturated solution of NaBr.

Preparation of the μ-Amido-μ-hydroxo-μ-oxalato-bis[triamminecobalt(III)] Complex, Formula (b). The perchlorate salt was prepared by first adding 10 ml of 1 *M* oxalic acid at 50° to 0.5 g of the complex $[(NH_3)_3(H_2O)Co\text{-}\mu(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3](NO_3)_4 \cdot 2H_2O$ and maintaining the temperature at 50° for 1 hr. The reaction mixture was left overnight at 5°. An extremely insoluble purple powder (8.4% carbon) settled out as an impurity and was filtered off and discarded. An equal volume of concentrated $HClO_4$ was added to the filtrate which was then kept at 0° for 3 hr. The orange-red product was filtered off and washed with ethanol and ether. Two recrystallizations were effected: first, dissolving in a minimum of hot water, filtering, and adding an equal volume of 12 *M* $HClO_4$ with cooling; second, repeating the method with more generous volumes, so that recrystallization only took place when the solution 6 *M* in $HClO_4$ was left exposed to the atmosphere for 48 hr. The orange needles which were obtained were filtered off and washed with ethanol and ether.

A small amount of complex (0.07 g) was converted to the bromide salt for infrared studies as follows. The complex was dissolved in a minimum of water, an equal volume of concentrated HBr was added, and the solution was cooled to 0°, for 4 hr. The crystals collected were washed with ethanol and ether; yield 0.04 g.

Preparation of the Di-μ-hydroxo-μ-oxalato-bis[triamminecobalt(III)] Complex, Formula (c). To prepare the perchlorate salt of the protonated complex an aqueous solution of $[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3 \cdot 2H_2O$ was treated with oxalic acid (ratio 1:1) and perchloric acid, at 55°, as described previously.[14] The bromide salt of the protonated complex was prepared by dissolving the perchlorate salt in water and adding concentrated HBr. Samples of the perchlorate and bromide salts of the unprotonated complex were prepared by dissolving the protonated complex in water at 0° and neutralizing rapidly with 0.1 *M* NaOH. The unprotonated complex was precipitated by addition of $NaClO_4$ (or NaBr) and ethanol.

Preparation of the μ_3-Oxalato-[μ-amido-μ-hydroxo-bis{triamminecobalt(III)}][pentaamminecobalt(III)] Complex, Formula (d). The perchlorate salt was prepared by the following procedure. Solutions of the perchlorate salt of $[(NH_3)_3Co\text{-}\mu(NH_2,OH,OH)\text{-}Co(NH_3)_3]^{3+}$ (0.49 g) in 0.1 *M* $HClO_4$ (10 ml) and $[(Co(NH_3)_5\text{-}(C_2O_4H)](ClO_4)_2$ (0.42 g) in water (15 ml), both at 50°, were mixed together and the temperature was maintained for 100 min. Sodium perchlorate (20 g) was added to the cooled solution, which was kept at 0° for 2 hr. An orange powder was collected, dissolved in water, filtered, and recrystallized by addition of sodium perchlorate. The recrystallized product was filtered off, dried by suction, and washed with ethanol and ether; yield 0.24 g. The remaining impurity is less soluble than the trinuclear complex and was removed in the following way. An aqueous solution was allowed to evaporate slowly in the atmosphere. When it was judged that approximately half the complex had crystallized out, the solid was filtered off and discarded. The filtrate was allowed to evaporate to dryness overnight and orange crystals were collected.

A sample of the bromide salt was prepared by dissolving the perchlorate salt in a minimum of water and adding an equal volume of concentrated HBr. The solution was left for 3 hr at 0°, when crystals were obtained. These were filtered off and washed with ethanol and ether.

Preparation of the μ_3-Oxalato-[di-μ-hydroxo-bis{triamminecobalt(III)}][pentaamminecobalt(III)] Complex, Formula (e). A solution of the tri-μ-hydroxo-bis[triamminecobalt(III)] complex, $[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3 \cdot 2H_2O$, in *ca.* 0.3 *M* $HClO_4$, was treated with an equivalent amount of the oxalatopentaamminecobalt(III) complex $[Co(NH_3)_5C_2O_4H](ClO_4)_2$ at 55°.[14]

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The perchlorate salt was obtained on addition of $NaClO_4$ at 0°. Conversion to the bromide salt was effected by addition of NaBr to a solution of the perchlorate in 0.03 *M* $HClO_4$. Analyses for the bromide salt, Table I, indicated a purer sample than for the original perchlorate salt (high C analysis). It was possible to convert the bromide to the perchlorate by first adding a slight excess of silver perchlorate crystals to a solution in a minimum of 0.1 *M* $HClO_4$ at 40°. After filtering off the silver bromide, crystallization occurred at 0°.

Preparation of the μ_4-Oxalato-bis[μ-amido-μ-hydroxo-bis{triamminecobalt(III)}] Complex, Formula (f). The perchlorate salt of the complex $[(NH_3)_3Co\text{-}\mu(NH_2,OH,OH)\text{-}Co(NH_3)_3]^{3+}$ (0.53 g) was dissolved in 0.1 *M* $HClO_4$ (10 ml) at 40°. Analar oxalic acid dihydrate (0.053 g) in the required 1:2 ratio was added, and the solution was maintained at 50° for 2 hr. After a further 3 hr at room temperature crystals of the crude perchlorate salt were filtered off, dried by suction, and washed with ethanol and ether; yield 0.31 g. No second crop of crystals should be taken. To recrystallize, the solid was dissolved in 0.1 *M* $HClO_4$ (300ml) at 40° and filtered, and 30 ml of 10 *M* $HClO_4$ was added. On leaving overnight at room temperature orange crystals were obtained and separated as before; yield 0.2 g.

The bromide salt of the complex cannot readily be prepared from the perchlorate because of the differences in solubilities. Instead a solution of the bromide salt of the diaquo complex $[(NH_3)_3(H_2O)Co\text{-}\mu(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3]^{4+}$ (0.25 g) in 15 ml of water was used as starting material. To this 1 drop of concentrated HBr and oxalic acid dihydrate (0.026 g) were added, and the solution was warmed to 50° at which temperature it was maintained for 2 hr. Concentrated HBr (15 ml) was added to the cooled solution which was then kept for 48 hr at 5°. The crystals obtained were dried by suction and washed with ethanol and ether. These were recrystallized twice, first of all by dissolving in a minimum (*ca.* 4 ml) of water at 40° and adding an equal volume of concentrated HBr. Better crystals were obtained from a second recrystallization in which a concentrated solution in water at 40° was allowed to cool and then to stand at room temperature. Dark red crystals were collected, washed with ethanol and ether, and dried by suction; yield 0.06 g. A second fraction obtained on evaporating to dryness was contaminated with impurity. A 3.6% loss in weight was observed on dehydration over P_2O_5 (3.2% calculated for dihydrate). Absorption coefficients are identical with those for the perchlorate salt assuming the formula to be as in (f) with six bromide counteranions and two water molecules of crystallization.

Preparation of the μ_4-Oxalato-bis[di-μ-hydroxo-bis{triamminecobalt(III)}] Complex, Formula (g). The perchlorate salt of the complex was prepared by treating an aqueous 0.5 *M* $HClO_4$ solution of $[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3 \cdot 2H_2O$ (12 g) with oxalic acid (1.3 g, ratio 2:1), at 50°; details are as previously described.[15] Recrystallization was from 400 ml of H_2O by addition of 15 ml of saturated $NaClO_4$.

Preparation of the μ_4-Oxalato-[μ-amido-μ-hydroxo-bis{triamminecobalt(III)}][μ-amido-bis{tetraamminecobalt(III)}] Complex, Formula (h). The perchlorate salt was prepared by addition of $[(NH_3)_3(H_2O)Co\text{-}\mu(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3](NO_3)_4 \cdot 2H_2O$ (0.5 g) and the perchlorate salt of half-protonated (a) (0.55 g) to 0.05 *M* $HClO_4$ (15 ml) at 50°. The mixture was stirred until all the crystals had dissolved and the temperature was maintained at 50° for 3.5 hr. The solution was left overnight at 5°, after which a sample of crude product (0.6 g) was filtered off, washed with ethanol and ether, and then dried by suction. To recrystallize, the solid was dissolved in 0.1 *M* $HClO_4$ (50 ml) with slight warming and filtered, and an equal volume of concentrated $HClO_4$ was added. The precipitate obtained was filtered off, redissolved in a minimum of 0.1 *M* $HClO_4$ at 50°, and allowed to crystallize overnight at 5°; yield 0.46 g. A third recrystallization which gives fine red crystals was effected by dissolving the product in 0.1 *M* $HClO_4$ and allowing the solution to evaporate at room temperature. Evaporation was stopped when about 2–4 ml of liquid remained; yield 0.26 g.

The bromide salt was obtained from the crude material (0.6 g) by dissolving in a minimum of water, adding an equal volume of concentrated HBr, and allowing the solution to stand at 0° for 1 hr. The solid was filtered off and washed with ethanol and ether. It was redissolved in a minimum of water (40°), 1 drop of concentrated HBr was added, and the solution was left to stand at 0°. The bromide salt was filtered off, washed with ethanol and ether, and dried by suction; yield 0.16 g. A second crop of crystals obtained by adding a further amount of concentrated HBr to the mother liquor improved the yield.

Preparation of the μ_4-Oxalato-[di-μ-hydroxo-bis{triamminecobalt(III)}][μ-amido-bis{tetraamminecobalt(III)}] Complex, Formula (i). The perchlorate salt of the half-protonated form of (a) (0.44 g) was dissolved in 10 ml of water and a solution of 0.37 g of $[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3 \cdot 2H_2O$ in 10 ml of water with 0.5 ml of 2.5 *M* $HClO_4$ was added with stirring. The temperature was raised to 55° for 1 hr. While the solution cooled, solid $NaClO_4$ (15 g) was added in small amounts. The solution was left for 12 hr at 0°. Red crystals of the perchlorate salt were filtered off and washed with ethanol and ether. To recrystallize the solid, it was dissolved in a minimum of 0.01 *M* $HClO_4$ at 30°, and $NaClO_4$ was added; yield 0.4 g.

To convert to the bromide the perchlorate salt (0.16 g) was dissolved in 10 ml of water at 40°. The solution was saturated with solid NaBr, and 5 ml of ethanol was added. The solution was left at *ca.* 0° for a few hours. Red crystals were filtered off and washed with ethanol and ether.

Preparation of the μ-Oxalato-[tetraamminecobalt(III)][pentaamminecobalt(III)] Complex, Formula (j). The perchlorate salt was prepared as follows. To 50 ml of water at 40° were added $[Co(NH_3)_5C_2O_4H](ClO_4)_2$ (4.32 g), $[Co(NH_3)_4CO_3]ClO_4$ (3.1 g), and 4 ml of 2.5 *M* $HClO_4$ with stirring. The temperature was maintained at 60° for 15 min, after which the solution was cooled to 20°, and a solution of 50 g of $NaClO_4$ in 50 ml of water was added. This solution was cooled rapidly to 0°, and the perchlorate salt was precipitated by adding 70 ml of ethanol (0°). The poorly crystallized product was filtered off and washed with ethanol and ether. The resulting perchlorate salt is extremely soluble in water, and the number of water molecules of crystallization is variable. Double salts with 1.5 mol of $NaClO_4$ are formed. The $Co:NH_3:C_2O_4$ ratio is however always 1:4.5:0.5, and infrared spectra of all products were in good agreement. To recrystallize, 5.0 g of the crude product were dissolved as quickly as possible in 50 ml of water at 0°. The filtered solution was rapidly saturated with solid $NaClO_4$ and cooled for 10 min in an ice bath. The crystals were filtered off, washed with ethanol and ether, and dried *in vacuo* over P_2O_5 at 20° for 10 hr; yield 3.1 g.

It was not possible to obtain the bromide salt owing to the high solubility in water. Instead, an insoluble dithionate salt was prepared. A 2.1-g amount of $[Co(NH_3)_5C_2O_4H](ClO_4)$ and 1.6 g of $[Co(NH_3)_4CO_3](ClO_4)$ were dissolved in 25 ml of water at 40°, and 2 ml of 2.5 *M* $HClO_4$ was added with stirring. The temperature was maintained at 60° for 15 min. The solution was cooled to 20°, and 50 ml of water with 0.5 ml of 2.5 *M* $HClO_4$ was added. The solution was quickly cooled to 0° and 25 ml of concentrated $Na_2S_2O_6$ solution was added. After leaving the solution for 5 min at 0°, crystals of the dithionate formed. These were filtered off and washed with ethanol and ether.

Preparation of the μ-Oxalato-[aquotetraamminecobalt(III)][pentaamminecobalt(III)] Complex, Formula (k). To prepare the perchlorate salt 4.0 g of the crude perchlorate of (i) was dissolved in 80 ml of water with 30 ml of 2.5 *M* $HClO_4$. The solution was allowed to stand at 20° for 6 hr, after which 40 g of $NaClO_4$ was added and the solution was left for 6 hr at 20°. A further 40 g of $NaClO_4$ was added and the solution was left for 12 hr at *ca.* 0°. Pink crystals (thin needles) were filtered off and washed with ethanol and ether. To recrystallize the solid, it was dissolved in a minimum of 0.1 *M* $HClO_4$, at 10°, and $NaClO_4$ was added; yield 2.0 g. A different perchlorate salt of the above complex with 3.5 water molecules of crystallization was obtained, when a solution of the perchlorate (2.0 g) in water (50 ml) with 1 ml of 2.5 *M* $HClO_4$ was allowed to stand for 2 hr. After addition of 40 g of $NaClO_4$, the solution was left *ca.* 4 hr at *ca.* 0°. Red crystals were filtered off and washed with ethanol and ether; yield 1.8 g.

It was possible to prepare a bromide salt by dissolving 2.0 g of the crude μ-oxalato-[aquotetraamminecobalt(III)][pentaamminecobalt(III)] perchlorate in 50 ml of water at 20°. After addition of saturated NaBr solution (15 ml in small amounts), the solution was left to stand for a few hours at 0°. Long, thin crystals were filtered off and washed with ethanol and ether. To recrystallize the solid, it was dissolved in water and precipitated with NaBr; yield 1.7 g.

Other Complexes. Two attempts were made to prepare the 8+ tetranuclear complex with just two amido bridges in addition to the oxalate. The first involved treating the μ-amido-μ-chloro complex with oxalic acid (ratio 2:1), and the second, mixing solutions of the μ-amido-μ-chloro and μ-amido-μ-oxalato complexes. Both were unsuccessful. Two procedures for the preparation of the μ-oxalato-bis[pentaamminecobalt(III)] complex, the analog of (k), were also unsuccessful. These involved first treatment of (k) with liquid ammonia (in one experiment liquid NH_3 was used, in another liquid

NH_3-NH_4Cl) and second treating oxalatopentaamminecobalt(III) with aquopentaamminecobalt(III) at 90°.

Results

General Properties. Analysis figures are given in Table I, where, from these and values given previously,[13-15] it can be seen that carbon analyses in particular are diagnostic of the type of complex. Thus in the series of perchlorate salts, tetranuclear complexes are distinguished by having 1.8, trinuclear 2.3, and binuclear >3% calculated carbon content. Whereas protonation of the binuclear complexes (a)-(c) is observed (the protonation constant for (a) is 18 l. mol^{-1} at 25°, $\mu = 2.0$ *M*),[13] it was not possible to isolate protonated forms of either the trinuclear or tetranuclear complexes (d)-(i) or of the binuclear complexes (j) and (k). Derivatives of the μ-amido-di-μ-hydroxo-bis[triamminecobalt(III)] complex are orange rather than pink-red, and those of the tri-μ-hydroxo-bis[triamminecobalt(III)] complex are maroon. Of the perchlorate salts of the oxalato complexes described here only (j) could be described as very soluble. The 6+ tetranuclear complexes in particular have low solubilities, and kinetic studies had to be carried out in perchlorate media, $\mu = 0.2$ *M*. Significant reaction of (j) to (k) is observed in aqueous solution where $[HClO_4] = 1.0$ *M*, at room temperature over times >15 min.

Chemical Evidence for the Proposed Structures. It is evident from details of the preparations that (b) is obtained by treating the parent μ-amido-di-μ-hydroxo-bis[triamminecobalt(III)] complex with ratio of oxalic acid (ratio 1:1), whereas (f) is obtained with 2 mol of complex to 1 mol of oxalic acid. Similarly (c) and (g) are obtained from the tri-μ-hydroxo-bis[triamminecobalt(III)] complex depending on whether 1 or 2 equiv of oxalic acid is used. It has also been shown that in aqueous solution (1.0 *M* $HClO_4$) (c) reacts with an equivalent amount of the tri-μ-hydroxo complex to give (g).

The existence of the chelate ring in (j) is substantiated by the identification of the products obtained on reacting with ammonia. With concentrated ammonia the products are $Co(NH_3)_4C_2O_4^+$ and $Co(NH_3)_5H_2O^{3+}$, and with liquid ammonia $Co(NH_3)_4C_2O_4^+$ and $Co(NH_3)_6^{3+}$.

Ultraviolet-Visible Spectra. Details of peak positions, λ_{max}, and absorption coefficients (here and elsewhere in units of l. mol^{-1} cm^{-1}, and *not* per cobalt atom) of parent complexes are listed in Table II. Spectra for binuclear complexes with a bridging oxalate ligand, (a)-(c), in 1.0 *M* $HClO_4$ are shown in Figure 1. Spectra of μ-amido-μ-formato-bis[tetraamminecobalt(III)] (λ_{max} 515 nm, ϵ 360 l. mol^{-1} cm^{-1}) and μ-amido-μ-acetato-bis[tetraamminecobalt(III)] (λ_{max} 517, ϵ 368 l. mol^{-1} cm^{-1}) are virtually identical with that of (a) (λ_{max} 517 nm, ϵ 370 l. mol^{-1} cm^{-1}). Evidence that complexes of this type have six-membered ring structures has been considered previously.[13,22] Similarly the spectra of di-μ-hydroxo-μ-formato, di-μ-hydroxo-μ-acetato, and di-μ-hydroxo-μ-chloroacetato complexes are similar to (c), Table III. For the hydrogen ion concentration chosen, the protonated complexes are dominant. Protonation does not affect the spectrum of (a) at wavelengths >380 nm, and there is a <10% effect at the 360-nm peak. More significant shifts are observed below 350 nm. The presence of one or two hydroxo bridges gives rise to intense charge-transfer bands which mask the 360-nm peak. At the same time the peak at *ca.* 500 nm moves to higher wavelengths with increasing number of hydroxo groups.

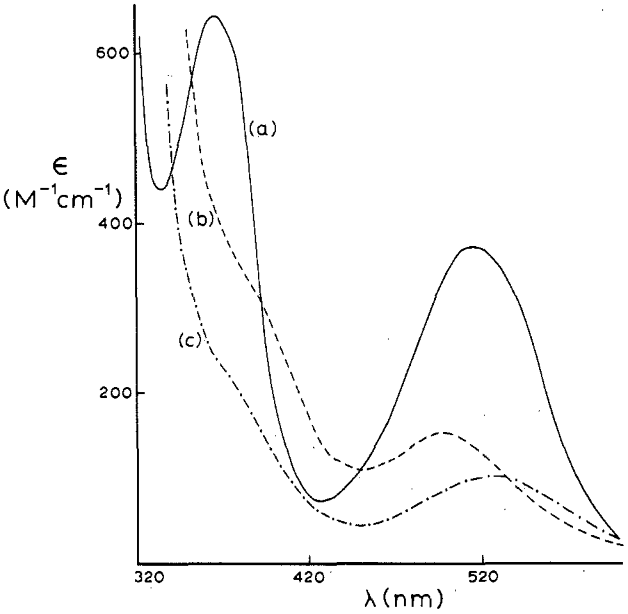

Figure 1. Ultraviolet-visible spectra of μ-oxalato binuclear cobalt(III) complexes (a)-(c).

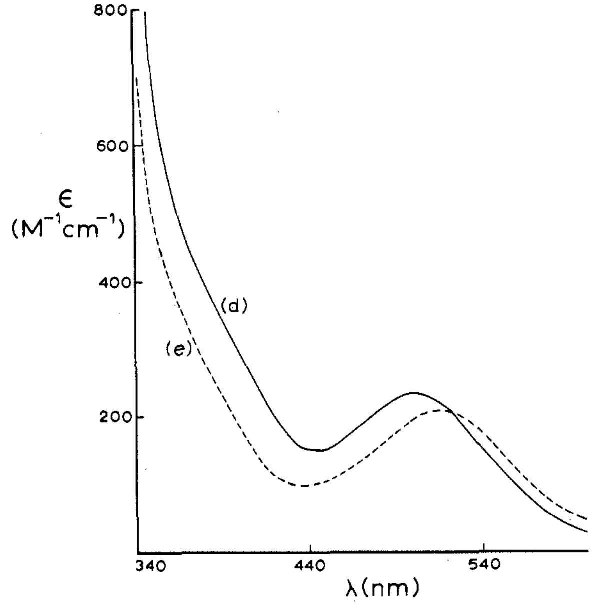

Figure 2. Ultraviolet-visible spectra of μ-oxalato trinuclear cobalt(III) complexes (d)-(e).

These features are repeated in the spectra of the trinuclear complexes (d) and (e), Figure 2, and the tetranuclear complexes (f)-(i), Figure 3. The spectra of (j) and (k) are illustrated in Figure 4. Here an interesting observation is the presence of an intense charge-transfer band for (j). Peak positions and absorption coefficients are listed in Table IV.

Infrared Spectra. As far as infrared spectra are concerned the number of oxalate oxygens which are coordinated is more important than the number of cobalt atoms bonded to the oxalate. Thus the infrared spectrum of the tridentate oxalate in the trinuclear complex (e) is similar to that of tridentate oxalate in the binuclear complex (j). Details of infrared bands in the 1800-1200-cm^{-1} region are therefore classified in terms of the bidentate, tridentate and tetradentate nature of the oxalate, Table V. We are reluctant to give more detailed assignments because X-ray structures are lacking (symmetries are uncertain) and the complete vibrational spectra of the complexes are not known.

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[22] K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, in press.

Table II. Ultraviolet-Visible Range Spectra, Peak Positions λ (nm) and Absorption Coefficients ε (l. mol^{-1} cm^{-1}), for Parent Mononuclear and Binuclear Complexes

Complex	λ	ε	λ	ε	Ref
$[(NH_3)_5CoC_2O_4H]^{2+}$	502	74			This work
$[(NH_3)_4CoC_2O_4]^{+}$	500	93	357	144	*b*
$[(NH_3)_4Co\text{-}\mu(NH_2,OH)\text{-}Co(NH_3)_4]^{4+}$	520	149	360[a]	405[a]	*c*
$[(NH_3)_3Co\text{-}\mu(NH_2, OH,OH)\text{-}Co(NH_3)_3]^{3+}$	510	170	*Ca.* 360[a]	*Ca.* 360[a]	*d*
$[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3]^{3+}$	526	135	364[e]	263[e]	20

[a] Inflection. [b] A. Kiss and D. Czegledy, *Z. Anorg. Allg. Chem.*, **235**, 411 (1938). [c] R. S. Taylor, Ph.D. Thesis, University of Leeds, 1970. [d] R. S. Taylor and A. G. Sykes, *J. Chem. Soc. A*, 1427 (1971). [e] Shoulder.

Table III. Ultraviolet-Visible Range Spectra (Similarity of Peak Positions λ (nm) and Absorption Coefficients ε (l. mol^{-1} cm^{-1}) for Analogs of (c))

Complex	λ	ε	Ref
$[(NH_3)_3Co\text{-}\mu(OH,OH,O_2CH)\text{-}Co(NH_3)_3]^{3+}$	529	95.5	*a*
$[(NH_3)_3Co\text{-}\mu(OH,OH,O_2CCH_3)\text{-}Co(NH_3)_3]^{3+}$	529	102	*a*
$[(NH_3)_3Co\text{-}\mu(OH,OH,O_2CCH_2Cl)\text{-}Co(NH_3)_3]^{3+}$	524	105	*a*
$[(NH_3)_3Co\text{-}\mu(OH,OH,C_2O_4)\text{-}Co(NH_3)_3]^{2+}$	525	103	This work

[a] G. Tremmel, Ph.D Dissertation, University of Heidelberg, 1970, p 46.

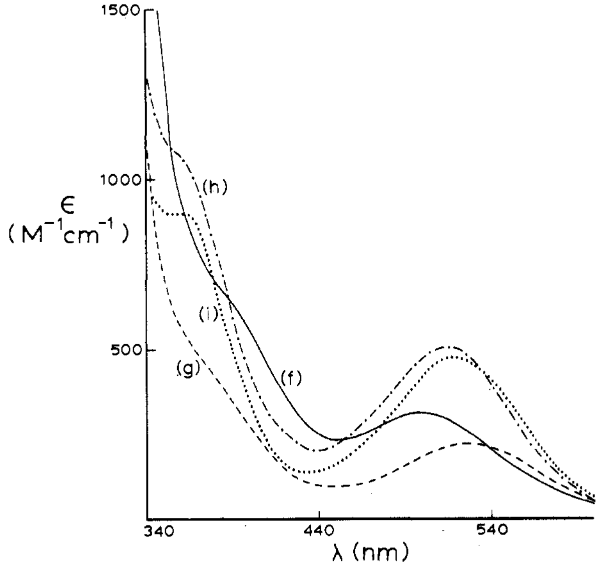


Figure 3. Ultraviolet-visible spectra of μ-oxalato tetranuclear cobalt(III) complexes (f)-(i).

Tetradentate oxalato complexes in which the four oxygen atoms interact equally with four cobalt atoms yield the simplest spectra. The positions of the two bands (1629 and 1344 cm^{-1}) are very similar to those observed for ionic oxalate in sodium oxalate (1625 and 1317 cm^{-1})[23] and for other tetradentate oxalato complexes.[9,10] This indicates that in spite of interactions of four cobalt ions the character of the C-O bonds does not change drastically when compared to that of the ionic oxalate. Although the oxalate ion in sodium oxalate is planar and symmetrical,[24] it should be noted that a tetradentate oxalate coordinated to four cobalt atoms need not necessarily be planar. A staggered configuration of the carboxylate groups (D_{2d}) is consistent with the infrared data. The same two bands are observed for tetradentate oxalate in the binuclear complex (l), where the oxalate may be assumed planar (D_{2h}) as in ref 3.

The bidentate oxalate in oxalatotetraamminecobalt(III) exhibits four C-O stretching frequencies which is consistent with C_{2v} symmetry of the oxalate group.[25,26] The infrared spectrum of (k) is similar and four CO stretching frequencies are observed. If it is assumed that the oxalate ligand is planar, there are two possible configurations

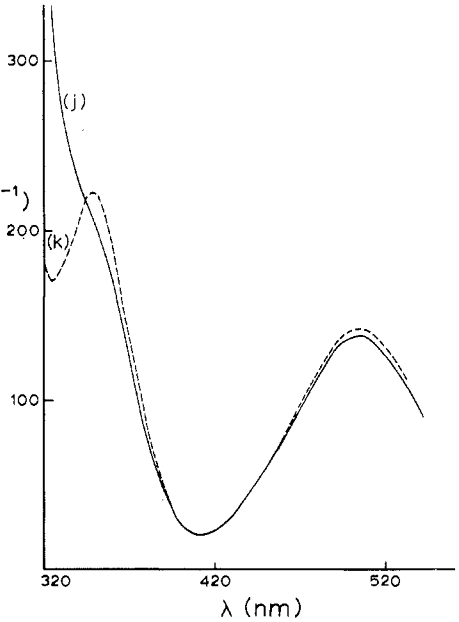
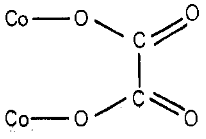
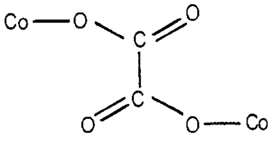


Figure 4. Ultraviolet-visible spectra of μ-oxalato binuclear cobalt(III) complexes (j)-(k).



cis (C_{2v})



trans (C_{2h})

The data for the crystalline solids cannot be interpreted on the basis of a planar trans configuration (C_{2h}) because for such a case only two C-O frequencies would be infrared active. A planar cis configuration (C_{2v} symmetry) and a structure in which the carboxylate groups deviate from a planar configuration by rotation about the C-C bond (C_2 symmetry) are both possible. It is of interest that dimethyl oxalate, $(CH_3)_2C_2O_4$, exhibits C_{2h} symmetry and has the trans structure.[27]

Finally the fact that (d) and (e) have three strong CO stretching frequencies (1652, 1607, and 1320 cm^{-1}) excludes a bidentate structure in which one of the cobalt atoms of the di-μ-hydroxo unit is bonded to an H_2O ligand rather than to the oxalate. Cis and trans structures would be possible for

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(23) K. M. Begum and W. H. Fletcher, *Spectrochim. Acta*, **19**, 1343 (1963).

(24) G. A. Jeffrey and G. S. Parry, *J. Amer. Chem. Soc.*, **76**, 5283 (1954).

(25) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, **79**, 4904 (1957).

(26) H. Siebert, *Z. Anorg. Allg. Chem.*, **298**, 51 (1959).

(27) J. K. Wilmshurst and J. F. Horwood, *J. Mol. Spectrosc.*, **21**, 48 (1966); M. W. Dougill and G. A. Jeffrey, *Acta Crystallogr.*, **6**, 831 (1953).

Table IV. Ultraviolet-Visible Spectra, Peak Positions λ (nm) and Absorption Coefficients ε (l. mol⁻¹ cm⁻¹), for Perchlorate Salts of Binuclear, Trinuclear, and Tetranuclear Cobalt(III) μ-Oxalato Complexes

	λ	ε	λ	ε
	Binuclear Complexes[a]			
(a) $[Co_2(NH_3)_8(NH_2)(C_2O_4H)]^{4+}$	517	370	366	642
(b) $[Co_2(NH_3)_6(NH_2)(OH)(C_2O_4H)]^{3+}$	498	154	*Ca.* 390[b]	*Ca.* 300
(c) $[Co_2(NH_3)_6(OH)_2(C_2O_4H)]^{3+}$	525	103	*Ca.* 375[b]	*Ca.* 215
	Trinuclear Complexes			
(d) $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)]^{5+}$	500	235	*Ca.* 380[b]	
(e) $[Co_3(NH_3)_{11}(OH)_2(C_2O_4)]^{5+}$	514	207	*Ca.* 380[b]	
	Tetranuclear Complexes			
(f) $[Co_4(NH_3)_{12}(NH_2)_2(OH)_2(C_2O_4)]^{6+}$	500	315	*Ca.* 390[b]	*Ca.* 650
(g) $[Co_4(NH_3)_{12}(OH)_4(C_2O_4)]^{6+}$	525	227	*Ca.* 380	*Ca.* 400
(h) $[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)]^{7+}$	513	505	360 sh	1060
(i) $[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)]^{7+}$	518	480	360 sh	910
	Binuclear Complexes[c]			
(j) $[Co_2(NH_3)_9(C_2O_4)]^{4+}$	504	138	*Ca.* 345[b]	*Ca.* 217
(k) $[Co_2(NH_3)_9(H_2O)(C_2O_4)]^{4+}$	504	143	350	222

[a] Recorded at pH ~0; oxalate ligand is protonated. Protonation does not have significant effect on the ~500-nm peak. [b] Inflection. [c] $[HClO_4] = 1\ M$.

Table V. Infrared C-O Stretching Frequencies (KBr Disks) for Oxalato Complexes (Bromide Salts) (Classification in Terms of Extent of Bonding of Oxalate to Cobalt)[a]

	Symmetry C_2O_4	Bands						
				Bidentate Oxalate (Type 1)				
(a) $[Co_2(NH_3)_8(NH_2)(C_2O_4)]^{3+}$	C_{2v}			1640 sh, s	1616 s		1325 s	
(c) $[Co_2(NH_3)_6(OH)_2(C_2O_4)]^{2+}$	C_{2v}			1634 vs	1600 ms		1318 s	
(a) $[Co_2(NH_3)_8(NH_2)(C_2O_4H)]^{4+}$		1755 vs		1626 s			1320 s	1270 s
(b) $[Co_2(NH_3)_8(NH_2)(OH)(C_2O_4H)]^{3+}$		1762 vs		1626 vs			1318 s	1284 s
(c) $[Co_2(NH_3)_6(OH)_2(C_2O_4H)]^{3+}$		1765 s		1625 s			1310 m	1273 ms
				Bidentate Oxalate (Type 2)				
$[Co(NH_3)_4(C_2O_4)]^{+}$	C_{2v}		1696 vs	1667 vs, b		1410 vs		1268 ms
(k) $[Co_2(NH_3)_9(H_2O)(C_2O_4)]^{4+}$	C_{2v} or C_2		1721 ms } 1701 s }	1629 vs } 1670 ms }		1439 vs } 1430 sh, s }		1276 ms } 1250 m }
				Tridentate Oxalate				
(d) $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)]^{5+}$				1650 sh	1610 s		1322 vs	
(e) $[Co_3(NH_3)_{11}(OH)_2(C_2O_4)]^{5+}$				1652 s	1607 s		1320 vs	
(j) $[Co_2(NH_3)_9(C_2O_4)]^{4+}$				1690 m, sh	1630 vs, b		1315 s	
				Tetradentate Oxalate				
(f) $[Co_4(NH_3)_{12}(NH_2)_2(OH)_2(C_2O_4)]^{6+}$	D_{2h} or D_{2d}				1628 vs		1345 ms	
(g) $[Co_4(NH_3)_{12}(OH)_4(C_2O_4)]^{6+}$	D_{2h} or D_{2d}				1628 vs		1344 ms	
(h) $[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)]^{7+}$	D_{2h} or D_{2d}				1631 vs		1346 ms	
(i) $[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)]^{7+}$	D_{2h} or D_{2d}				1629 vs		1342 ms	
(l) $[Co_2(NH_3)_4(NO_2)_4(C_2O_4)]$	D_{2h}				1650 vs		1348 ms } 1307 }	

[a] Key: sh, shoulder; vs, very strong; s, strong; m, moderate; b, broad.

such a structure as previously considered for (k). Alternative structures for (d) and (e) in which the oxalate forms a large ring with the cobalt atoms of the di-μ-hydroxo unit cannot be ruled out on the basis of infrared spectra.

Reductions by Cr^{2+} and V^{2+}. This represents the most sophisticated method of distinguishing between binuclear, trinuclear, and tetranuclear complexes (a)-(i). The distinction is based on the observation that a carboxylate oxygen bonded directly to a cobalt(III) center is not an available site for inner-sphere attack by Cr^{2+}.[28] Thus with tetranuclear complexes an inner-sphere mechanism is not possible because of the nonavailability of the oxygen atoms of the oxalate ligand for bridging. Reduction proceeds instead by a slow outer-sphere mechanism with second-order rate constants *ca.* 10^{-3} l. mol^{-1} sec^{-1} at 25°. The assignment of outer-sphere mechanisms has been placed on a sound quantitative footing by determination of the ratio of rate constants k_{Cr} and k_V for the reduction by Cr^{2+} and V^{2+}. Toppen and Linck[29] have drawn attention to the fact that for reactions with a common oxidant the ratio k_{Cr}/k_V is *ca.* 0.02 at 25° when both reductions occur by an outer-sphere mechanism. [This ratio now seems well established for amminecobalt(III) complexes. It is less well established with other metal ions as oxidants.] This approach has been used to assign outer-sphere mechanisms to the reductions of the complexes $[(NH_3)_5Co\text{-}\mu(NH_2)\text{-}Co(NH_3)_5]^{5+}$ (0.021), $[(NH_3)_5Co\text{-}\mu(O_2)\text{-}Co(NH_3)_5]^{5+}$ (0.023), $[(trenen)Co\text{-}\mu(O_2)\text{-}Co(trenen)]^{5+}$ (0.020), $[(NH_3)_4Co\text{-}\mu(OH,OH)\text{-}Co(NH_3)_4]^{4+}$ (0.017), $[(NH_3)_4Co\text{-}\mu(NH_2,O_2CH)\text{-}Co(NH_3)_4]^{4+}$ (0.028), and $[(NH_3)_4Co\text{-}\mu(NH_2,O_2CCH_3)\text{-}Co(NH_3)_4]^{4+}$ (0.021) which have k_{Cr}/k_V values of the required magnitude.[28] The method is of particular value in cases where ion-exchange separation of the primary chromium(III) products is not easy because of the slowness of the reaction.

The kinetic data and k_{Cr}/k_V ratios summarized in Table VI are consistent with outer-sphere mechanisms for complexes (f)-(i). This therefore supports the assignment of tetranuclear structures to these complexes. Similarly the

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(29) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971).

Table VI. Second-Order Rate Constants for the Cr^{2+} (k_{Cr}) and V^{2+} (k_V) Reductions of Binuclear, Trinuclear, and Tetranuclear μ-Oxalato Complexes at 25° (Ionic Strength μ Adjusted with $LiClO_4$)

	μ, *M*	k_{Cr}, l. mol^{-1} sec^{-1}	k_V, l. mol^{-1} sec^{-1}	k_{Cr}/k_V	Proposed mechanism k_{Cr}	Proposed mechanism k_V
		Binuclear Complexes				
(a) $[Co_2(NH_3)_8(NH_2)(C_2O_4H)]^{4+}$	2.0	1.45[a]	3.51[a]	0.41	Inner	Inner
(a) $[Co_2(NH_3)_8(NH_2)(C_2O_4)]^{3+}$	2.0	35.2[a]	22.7[a]	1.55	Inner	Inner
(b) $[Co_2(NH_3)_6(NH_2)(OH)(C_2O_4)]^{3+}$	1.0	Fast[b]			Inner	
		Trinuclear Complexes				
(d) $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)]^{5+}$	0.2	3.4×10^{-3} [c]	0.103[d]	0.033	Some inner	
(e) $[Co_3(NH_3)_{11}(OH)_2(C_2O_4)]^{5+}$	1.0	$>3 \times 10^{-2}$ [e]	0.42[f]	>0.07	Some inner	
		Tetranuclear Complexes				
(f) $[Co_4(NH_3)_{12}(NH_2)_2(OH)_2(C_2O_4)]^{6+}$	0.2	$<10^{-3}$	*Ca.* 8×10^{-3}		Outer	Outer
(g) $[Co_4(NH_3)_{12}(OH)_4(C_2O_4)]^{6+}$	0.2	3.6×10^{-3}	0.21	0.017	Outer	Outer
(h) $[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)]^{7+}$	1.0	4.4×10^{-3}	0.217	0.020	Outer	Outer
(i) $[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)]^{7+}$	1.0	8.1×10^{-3}	0.363	0.022	Outer	Outer

[a] Reference 13. [b] Requires stopped-flow method to study; reaction complete in *ca.* 12.5 sec with $[Cr^{2+}] = 2.42 \times 10^{-2}$ *M* and $[H^+] = 0.025$ *M*, at 25° and $\mu = 1.0$ *M* ($LiClO_4$). [c] Two runs; $[(Co^{III})_3] = 4.2 \times 10^{-4}$ *M*, $[Cr^{2+}] = 2.7 \times 10^{-2}$ *M*, $[H^+] = 0.10$ *M*. Linearity of first-order plots 90% completion. [d] Two runs; $[(Co^{III})_3] = 4.2 \times 10^{-4}$ *M*, $[V^{2+}] = 1.53 \times 10^{-2}$ and 2.95×10^{-2} *M*, $[H^+] = 0.11$ and 0.16 *M*, $k_V = 0.109$ and 0.096 l. mol^{-1} sec^{-1}, respectively. Linearity of first-order plots *ca.* 95% completion. [e] Runs with $[(Co^{III})_3] = 3 \times 10^{-4}$ *M*, $[Cr^{2+}] = 2.14 \times 10^{-2}$ *M*, and $[H^+] = 0.97$ *M* give k_{Cr} for first stage as $>3 \times 10^{-2}$ l. mol^{-1} sec^{-1}. [f] Two runs; $[(Co^{III})_3] = 3 \times 10^{-4}$ *M*, $[V^{2+}] = 0.93 \times 10^{-2}$ and 1.83×10^{-2} *M*, $[H^+] = 0.72$ and 0.95 *M*, $k_V = 0.425$ and 0.42 l. mol^{-1} sec^{-1}, respectively. Linearity of first-order plots *ca.* 95% completion.

fast rates of reduction of the binuclear complexes, Table VI, are consistent with the structures proposed. The formation and spectrophotometric identification of a cobalt(III)-chromium(III) binuclear intermediate is also evidence for an inner-sphere mechanism in the case of the Cr^{2+} reduction of (a).[13] It is noteworthy that although rate constants for the reduction of the tetranuclear complexes are slow, the reactions are appreciably faster than the Cr^{2+} reduction of $Co(NH_3)_6^{3+}$ ($k_{Cr} = 9 \times 10^{-5}$ l. mol^{-1} sec^{-1} at 25°), a point which will be discussed elsewhere.[30] Inner-sphere attack at the free carboxyl group in the trinuclear complexes would be expected to be sterically hindered, as in the case of the Cr^{2+} reduction of pivalatopentaamminecobalt(III) (rate constant 7×10^{-3} l. mol^{-1} sec^{-1} at 25°, $\mu = 1.0$ *M*).[31] Parallel inner- and outer-sphere paths might therefore compete in the Cr^{2+} reduction of the trinuclear complexes. Results obtained, Table VI, are we believe consistent with this. The ratios k_{Cr}/k_V are outside the acceptable range for purely outer-sphere reactions, indicating that there is some contribution from an inner-sphere process. Moreover, while the reduction of (d) is straightforward, the reaction of (e) is more complicated and at least two stages are apparant in the reduction with Cr^{2+}. Further details of the Cr^{2+} and V^{2+} reductions of (g)-(i) will be reported elsewhere.[30]

Discussion

The remarkable versatility of oxalate as a bridging and chelating ligand is illustrated in the series of cobalt(III) complexes considered in this paper. It has furthermore been reported[10] that in the solid state $[Cu(NH_3)(C_2O_4)]$ exists as a distorted octahedral structure, with one of the oxygens of the oxalate ligand bonded to two metals. This type of structure has not so far been identified in the cobalt(III) series of complexes, and the inability of Cr^{2+} to utilize an oxygen of the oxalate ligand which is already bonded to cobalt(III) in an inner-sphere electron-transfer process[28] suggests that such a structure may not be possible.

The preparation of trinuclear and tetranuclear cobalt(III) complexes and the high charges of these complexes are also of considerable interest. Werner has described the preparation of linear trinuclear complexes with two bridges, $[(en)_2Co\text{-}\mu(OH,OH)\text{-}Co(H_2O)_2\text{-}\mu(OH,OH)\text{-}Co(en)_2]^{5+}$,[32] and three bridges, $[(NH_3)_3Co\text{-}\mu(OH,OH,OH)\text{-}Co\text{-}\mu(OH,OH,OH)\text{-}Co(NH_3)_3]^{3+}$,[33] between each cobalt(III). Examples of tetranuclear complexes are the tris[di-μ-hydroxo-tetraamminecobalt(III)] cobalt(III) complex, $[\{(NH_3)_4Co(OH)_2\}_3Co]^{6+}$,[34,35] and the ethylenediamine analog $[\{(en)_2Co(OH)_2\}_3Co]^{6+}$.[36] Higher polynuclear cobalt(III) complexes do not appear to have been characterized.

One of the more interesting aspects of the structures is the way the oxalate is bonded. In the case of tris-oxalato complexes, *e.g.*, $Co(C_2O_4)_3^{3-}$, and related complexes containing chelated oxalate, five-membered rings are formed by utilizing oxygen atoms from the adjacent carboxyl groups. Complexes (a)-(i) described here use instead the two oxygens of a single carboxylate group to bridge two cobalt(III) ions in forming a ring structure. This gives rise to six-membered rings, whereas more orthodox bonding of the oxalate would give rise to seven-membered ring structures.

Registry No. $[Co_2(NH_3)_8(NH_2)(C_2O_4)]Br_3 \cdot H_2O$, 37540-60-6; $[Co_2(NH_3)_6(NH_2)(OH)(C_2O_4H)](ClO_4)_3 \cdot H_2O$, 37540-61-7; $[Co_2(NH_3)_6(OH)_2(C_2O_4)](ClO_4)_2 \cdot 3H_2O$, 37540-62-8; $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)](ClO_4)_5 \cdot H_2O$, 37540-63-9; $[Co_3(NH_3)_{11}(NH_2)(OH)(C_2O_4)]Br_5 \cdot 2H_2O$, 37540-64-0; $[Co_3(NH_3)_{11}(OH)_2(C_2O_4)]Br_5 \cdot 3H_2O$, 37540-65-1; $[Co_4(NH_3)_{12}(NH_2)_2(OH)_2(C_2O_4)](ClO_4)_6 \cdot 4H_2O$, 37540-66-2; $[Co_4(NH_3)_{12}(OH)_4(C_2O_4)](ClO_4)_6 \cdot 4H_2O$, 37540-67-3; $[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)](ClO_4)_7 \cdot 4H_2O$, 37540-68-4; $[Co_4(NH_3)_{14}(NH_2)_2(OH)(C_2O_4)]Br_7 \cdot 5H_2O$, 37540-69-5; $[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)](ClO_4)_7 \cdot 3H_2O$, 37523-50-5; $[Co_4(NH_3)_{14}(NH_2)(OH)_2(C_2O_4)]Br_7 \cdot 4H_2O$, 37540-70-8; $[Co_2(NH_3)_9(C_2O_4)](ClO_4)_4 \cdot 2H_2O$, 37540-71-9; $[Co_2(NH_3)_9(C_2O_4)](S_2O_6)_2 \cdot 5H_2O$, 37540-72-0; $[Co_2(NH_3)_9(H_2O)(C_2O_4)]$-

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$(ClO_4)_4\cdot H_2O$, 37540-73-1; $[Co_2(NH_3)_9(H_2O)(C_2O_4)]Br_4\cdot 2H_2O$, 37523-51-6; $[(NH_3)_5Co(C_2O_4H)](ClO_4)_2$, 15293-41-1; $[Co_2(NH_3)_4(NO_2)_4(C_2O_4)]$, 37548-99-5; $[(NH_3)_3(H_2O)Co\text{-}\mu\,(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3](NO_3)_4\cdot 2H_2O$, 36593-60-9; $[(NH_3)_3Co\text{-}\mu\,(NH_2,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3$, 37549-00-1; $[(NH_3)_3(H_2O)Co\text{-}\mu\,(NH_2,OH)\text{-}Co(H_2O)(NH_3)_3]Br_4$, 37523-52-7; $[(NH_3)_3Co\text{-}\mu\,(OH,OH,OH)\text{-}Co(NH_3)_3](ClO_4)_3\cdot 2H_2O$, 37540-75-3; $[Co(NH_3)_4CO_3]ClO_4$, 37549-01-2.

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Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

Synthesis of Peroxo- and Superoxodicobalt(III) Complexes of 2,2′,2″-Triaminotriethylamine

CHEN-HWA YANG and MERLAND W. GRIEB*

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Complex compounds $[NH_3(tren)CoOOCo(tren)NH_3]X_4\cdot nH_2O$, where X = Cl with $n = 2$ and X = Br, I, NO_3, or ClO_4 with $n = 0$, were prepared by aeration of stoichiometric amounts of 2,2′,2″-triaminotriethylamine (tren), ammonia, and the corresponding cobalt(II) salt in aqueous solution. The pyridine (py) analog $[py(tren)CoOOCo(tren)(py)]I_4\cdot H_2O$ was made similarly. The cations of these salts were somewhat unstable in aqueous solution and gradually transformed to stable $[(tren)Co(O_2,OH)Co(tren)]^{3+}$ ion, the perchlorate salt of which also was prepared directly by aeration of solutions of tren and Co^{2+}. The rate of transformation was retarded by excess ammonia in the solution. The compounds $[(tren)Co(O_2,NH_2)Co(tren)]X_3\cdot nH_2O$, where X = I with $n = 0$ and X = ClO_4 with $n = 1$, were obtained by ligand replacement. The corresponding superoxo complexes $[NH_3(tren)CoOOCo(tren)NH_3](ClO_4)_5\cdot 2H_2O$, $[(tren)Co(O_2,NH_2)Co(tren)](ClO_4)_4\cdot 2H_2O$, and (probably) $[H_2O(tren)CoOOCo(tren)H_2O](ClO_4)_5$ were prepared by oxidation of peroxo compounds. The electronic absorption spectra of these complexes were obtained and compared with the spectra of related binuclear species.

Introduction

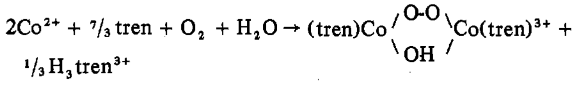
Binuclear, peroxo-bridged complexes of cobalt, which form upon reaction of cobalt(II)-amine complexes with molecular oxygen have evoked much recent interest.[1] Stoichiometric studies of solutions containing the linear ligand triethylenetetramine (trien) showed that the oxygen uptake reaction involved 2 mol of triethylenetetramine and cobalt(II) and 1 mol of oxygen.[2,3] Further investigations revealed that the ultimate product was doubly bridged $[(trien)Co(O_2,OH)Co(trien)]^{3+}$ [4] but that a singly bridged intermediate with nonbridging hydroxide ion ligand was consistent with kinetic observations.[5] A singly bridged peroxo compound, $[NH_3(trien)CoOOCo(trien)NH_3](ClO_4)_4\cdot 2H_2O$ has been isolated,[6] as well as doubly bridged $[(trien)Co(O_2,NH_2)Co(trien)]^{4+}$, although details of the latter superoxo complex are not available.[7]

Doubly bridged peroxo complexes of cobalt in which the second bridge is the hydroxide ion have been recognized recently,[4,5,8] and two, with ethylenediamine[9] and *l*-propylenediamine[10] ligands, have been isolated.

We report herein the synthesis of singly and doubly bridged peroxo- and superoxocobalt(III) complexes containing 2,2′,2″-triaminotriethylamine corresponding to each type described above. Interest in this ligand derives from the fact that it affords fewer possibilities for isomerism in coordination complexes than does its linear isomer. While the methods employed in this study did not show isomerism in the binuclear ions, we have reported the two possible isomers of a mononuclear decomposition product of one of them.[11]

Results and Discussion

Addition of 2,2′,2″-triaminotriethylamine [tren, $N(CH_2CH_2NH_2)_3$] to an aerated solution of cobalt(II) ion results in a change of color from pink to brown. It was found spectrophotometrically that only one product, which had an absorption maximum at 350 nm, was formed at room temperature independent of the ratio of amine to cobalt. The reaction was very fast and quantitative, going to completion well within 10 min in a 10^{-4} *M* unbuffered solution. Oxygen uptake measurements taken at 30° (Figure 1) also showed a single reaction up to the ratio of 1.16 mol of 2,2′,2″-triaminotriethylamine to 1 mol of cobalt(II), at which point 0.5 molar equiv of O_2 was absorbed. Consistent with the known triprotic basicity of 2,2′,2″-triaminotriethylamine,[12] the reaction stoichiometry is best expressed by eq 1. When the experiment was repeated at ice tem-



$$2Co^{2+} + {}^{7}/_{3}\,tren + O_2 + H_2O \rightarrow (tren)Co\overset{/\,O\text{-}O\,\backslash}{\underset{\backslash\,OH\,/}{\quad}}Co(tren)^{3+} + {}^{1}/_{3}H_3tren^{3+} \qquad (1)$$

perature, the break in the oxygen uptake curve corresponded to formation of $[H_2O(tren)CoOOCo(tren)H_2O]^{4+}$ without

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