rangement of $[HRu_4(CO)_{13}]^-$ can be described as a hexacapped rectangular antiprism belonging to the point group D_{2d} and lying on the pathway of rearrangement of a bha to an omnicapped cube (Figure 3).

It is important to point out that in the $[HRu_4(CO)_{13}]^-$ structure each metal exists in a favorable octahedral environment of ligands and other metals. This raises the question of which factor is most important in determining the ligand arrangement: (a) the favorable octahedral metal environment or (b) interligand repulsions. Since both of these are energetically favorable in these structures, it seems unlikely that it will be possible to separate the effects.

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Registry No. 1-PPN, 84848-99-7; PPN$[HRu_4(CO)_{13}]$, 84848-97-5.

Supplementary Material Available: Listings of the observed and calculated structure factors and the positional and thermal parameters for all atoms (28 pages). Ordering information is given on any current masthead page.

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Preparation and Properties of a Novel $Co^{III}_2Cr^{III}$ Complex

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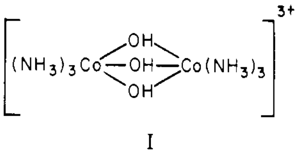
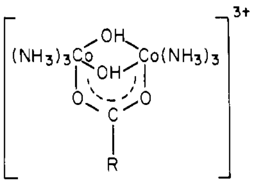
Reactions of the tris(μ-hydroxo)bis(triamminecobalt(III)) complex I have been extensively studied, and the formation of the μ-carboxylato derivatives II has been noted.[1-3] Properties of the aquo(ethylenediamine-*N,N,N',N'*-tetraacetato)chromium(III) complex, $[Cr(edta)(H_2O)]^-$ (III), or [Cr(Hedta)(H_2O)] when the uncoordinated carboxylate arm is protonated, have also been investigated, and the anomalous lability of the H_2O ligand (rates for anation are in the stopped-flow range) has been established.[4-6] Anation rate constants for replacement of the H_2O are less (1 order of magnitude) when the uncoordinated $CH_2CO_2^-$ arm of III is protonated and much less (2–4 orders of magnitude) when it is replaced by CH_3 (or H) as in the *N*-methylethylenediamine-*N,N',N'*-triacetate complex [Cr(medtra)(H_2O)] (IV).[4,5] These effects can be accounted for by transient coordination of the uncoordinated carboxylate arm to Cr(III).[5,6] Here we report the preparation of the complex V, in which the unattached carboxylate of III is incorporated into the binuclear Co(III) structure of I to give a product of the kind II. The properties and reactivity of this new trinuclear complex are also described.



I



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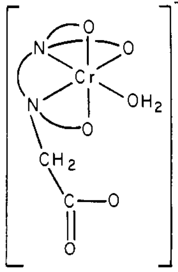
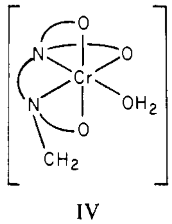
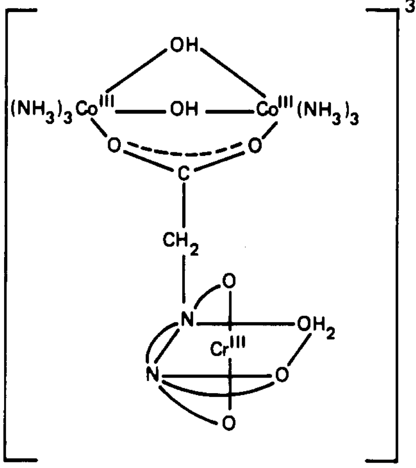


III



IV



V

Experimental Section

Preparation of Complexes. The complex $[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3](ClO_4)_3\cdot 2H_2O$ (I) was obtained by an adaptation of the procedure of Siebert and co-workers,[7-9] as already indicated.[2] The protonated form of III, $[Cr(Hedta)(H_2O)]$, was prepared by the method previously described.[10,11] To prepare the trinuclear complex V, essentially the same procedure as described for the conversion of I to II was used. Thus, to a solution of 1.5 g of $[Cr(Hedta)H_2O]$ in 40 mL of 0.5 M $HClO_4$ was added 2.8 g of I at 65 °C. The temperature was maintained for 15 min. Upon addition of 15 mL of concentrated $HClO_4$ to 0 °C violet crystals were obtained, which were filtered off and washed with ethanol and ether (yield 2.5 g). Anal. Calcd for $[Co_2CrC_{10}H_{34}N_8O_{11}](ClO_4)_3\cdot 6H_2O$: C, 11.8; H, 4.5; N, 11.0; Cr, 5.1; H_2O 10.6. Found: C, 11.7; H, 4.3; N, 11.0; Cr, 5.3; H_2O, 11.2. The Cr was determined by oxidation to CrO_4^{2-} (λ 372 nm, ϵ 4815 M^{-1} cm^{-1}) with H_2O_2 in 6 M NaOH and H_2O content was obtained by determining the loss in weight by leaving the complex to stand >4 days over P_2O_5 in a dessicator (it was assumed that the H_2O coordinated to the Cr was retained). A sample of the (μ-acetato)bis(μ-hydroxo)bis[triamminecobalt(III)] complex, $[(NH_3)_3Co(\mu\text{-}CH_3CO_2)(\mu\text{-}OH)_2Co(NH_3)_3](ClO_4)_3$ (II), was prepared as follows. The tris(μ-hydroxy) complex I (120 mg, 0.2 mmol) was dissolved in 12 mg (0.2 mmol) of concentrated acetic acid and 0.5 M $HClO_4$ (0.6 mL) and kept at 60 °C for 30 min. When 0.6 mL of saturated $NaClO_4$ was added and the mixture was left at 0 °C, crystallization took place overnight. Recrystallization was from dilute acetic acid (0.7 mL) with addition of saturated $NaClO_4$ (0.4 mL).

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Table I. Details of the UV–Visible Spectra (Peak Positions) for Relevant Complexes

complex	λ, nm (ε M^{-1} cm^{-1})
$[(NH_3)_3Co(\mu\text{-}OH)_3Co(NH_3)_3]^{3+}$ (I)	526 (135), 364 (263)
$[(NH_3)_3Co(\mu\text{-}CH_3CO_2)(\mu\text{-}OH)_2Co(NH_3)_3]^{3+}$ (II)	522 (111), 370 (234)
$[Cr(edta)(H_2O)]^-$ (III)[a]	540 (205), 390 (119)
$[Cr(Hedta)H_2O]$ (protonated III)[b]	540 (147), 390 (113)
$Co^{III}{}_2Cr^{III}$ complex (V)	534 (253), 367 (325)

[a] pH 4-5. [b] pH 1.9.

Table II. Acid Dissociation (K_a) Constants as pK_a Values for the H_2O Ligand of Cr(III) Complexes at 25 °C, $I = 0.10$ M ($NaClO_4$)[a]

complex	pK_a	complex	pK_a
$[Cr(edta)(H_2O)]^-$ (III)	7.39[b]	$[Cr(edtra)(H_2O)]$	6.25
$[Cr(medtra)(H_2O)]$ (IV)	6.25	complex V	5.76
$[Cr(hedtra)(H_2O)]$	6.02		

[a] Abbreviations: hedtra = *N*-(hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate; edtra = ethylenediamine-*N*,*N*′,*N*′-triacetate.
[b] See also: Schwarzenbach, G.; Heller, J. *Helv. Chim. Acta* 1951, *34*, 576. Furlani, C.; Morpurgo, G.; Sartori, G. *Z. Anorg. Allg. Chem.* 1960, *303*, 1.

The UV–visible spectrum gave a peak at 522 nm (ε 111 M^{-1} cm^{-1}) and a shoulder at 370 nm in agreement with a previous report.[2]

Spectra and pH Measurements. UV–visible spectra were recorded on Perkin-Elmer 550 and 554 spectrophotometers and IR spectra (KBr disks) on a Perkin-Elmer 598 instrument. All pH measurements were carried out with a Radiometer PHM 62 fitted with a Russell (CWR/322) glass electrode with a built-in Ag/AgCl reference.

Results and Discussion

Analyses were in accordance with the hexahydrate of the perchlorate salt of the $Co^{III}{}_2Cr^{III}$ complex as in V. The IR spectrum of $[Cr(Hedta)(H_2O)]$ gives bands at 1640 and 1743 cm^{-1} assigned to monodentate (O-coordinated) CO_2^- and free CO_2H groups.[12] The trinuclear complex V has bands at 1570 and 1630 cm^{-1} assigned to the μ-carboxylato and monodentate CO_2^- groups but no band at ~1740 cm^{-1} corresponding to free CO_2H, consistent with the formulation given in V.

Details of the UV–visible peak positions for relevant complexes are indicated in Table I. Spectra of the $Co^{III}{}_2$ and Cr^{III} chromophores are additive (±3%) over the range 350–650 nm (see Figure 1), and there is no evidence for interaction of the two chromophores.

Titration of a 5×10^{-4} M solution (25 mL) of the $Co^{III}{}_2Cr^{III}$ complex in 0.1 M $NaClO_4$ with 10^{-2} M NaOH at 25 °C using a glass electrode to monitor pH changes (range pH 4–11) gave only a single end point with acid dissociation pK_a = 5.76 (5.83 with $I = 1.0$ M ($NaClO_4$)). There is no uncoordinated CO_2H to titrate, and the pK_a observed is for the Cr(III)-coordinated H_2O. For comparison other relevant pK_a values are listed in Table II. The trends observed indicate a dependence on whether an uncoordinated CO_2^- arm is present or not. The presence of the positively charged $Co^{III}{}_2$ section of the complex may also be influential in bringing about a further lowering of the pK_a to 5.76.

The reactivity of the trinuclear complex V has been investigated by UV–visible spectrometer with (a) 0.10 M NCS^- in 0.10 M $HClO_4$ and (b) 1 M $CH_3CO_2^-/CH_3CO_2H$ at pH 5.0 and found to differ from that of the separate $Co^{III}{}_2$ and Cr^{III} complexes. Evidence obtained clearly indicates that the H_2O ligand attached to Cr(III) in V is no longer labile. With NCS^-, for example, the reaction of I (cleavage of a single μ-hydroxo bridge and coordination of NCS^-)[7] is complete within 25 min, and that of III (replacement of H_2O by NCS^-)[5] is rapid and complete in 1 min. In the case of the μ-acetato complex II, if there is a reaction, it is rapid and complete within 1 min of mixing. With the $Co^{III}{}_2Cr^{III}$ complex V, on the other hand, a slow process ($t_{1/2} \approx 3$ h) is observed with an ~25% increase in absorbance at ~540 nm. In the studies with 1 M acetate (pH 5.0) no reaction was observed with the $Co^{III}{}_2$ complexes I and II, and the reaction with the Cr^{III} complex III was observed to be rapid as reported elsewhere.[5] With V a slow reaction (monitored over 5 h) was observed, giving small (~4%) absorbance increases at ~540 nm and isosbestic points at 392, 455, and 530 nm. The only explanation of these observations is that slow anation at the H_2O coordination site of Cr(III) occurs in the case of V.

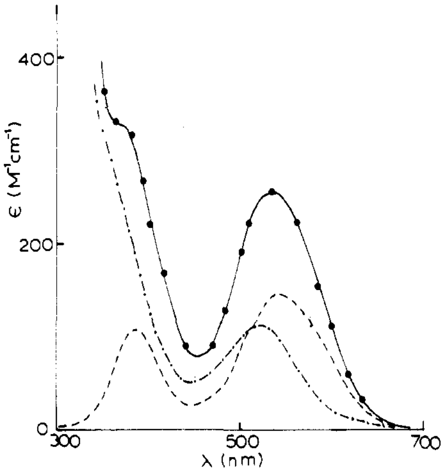

Figure 1. UV–visible spectra in 0.10 M $HClO_4$ for $(CH_3)_3Co(\mu\text{-}CH_3CO_2)(\mu\text{-}OH)_2Co(NH_3)_3^{3+}$ (–·–·) and $Cr(Hedta)(H_2O)$ (---) and the spectrum obtained on addition of these two (—), together with experimental points for the $Co^{III}{}_2Cr^{III}$ complex V.

All the properties observed and reactions studied are consistent with the formation of a trinuclear $Co^{III}{}_2Cr^{III}$ complex as in V, where the unattached carboxylate of the edta forms a carboxylato bridge to $Co^{III}{}_2$ and results in a loss of lability of the H_2O coordinated to Cr^{III}.

Further support is also provided for the lability of the H_2O ligand in III resulting from the presence of the free uncoordinated carboxylate arm of the edta and its ability to form a transient chelate to Cr^{III}.

Acknowledgment. We thank the Swiss National Science Foundation for a fellowship to P.L.

Registry No. I, 22445-08-5; III, 15955-81-4; V, 84895-75-0.

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Uniaxial Stress Measurements on $Rb_2BaCu(NO_2)_6$

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$Rb_2BaCu(NO_2)_6$ is one of a series of $M_2M'Cu(NO_2)_6$ compounds in which the crystallographic site symmetry of