for the same period of time with 50×10^{-5} M chelate followed by 40-fold dilution resulted in 75 ± 2% of control activity. In the same experiment, incubation with 50×10^{-5} chelate for 24 h yielded 45% of control activity.

These results are in marked contrast to observations made with various metal ions,[24,25] copper and nickel chelates,[15,26] and lanthanide ions,[16,27] all of which reversibly inhibit the enzyme. The irreversible inhibition exhibited by Co(MIDE)$_2$ and Co-(AIDE)$_2$ suggests chemical modification of the enzyme. This, in turn, may be due to hydrolysis of the chelates to species that are highly reactive. $(H_2O)_6Co^{III}$, for example, is an extremely powerful oxidant, capable even of oxidizing water,[22,28] and if $(H_2O)_6Co^{III}$ or similar species are formed from hydrolysis of the (2,2'-(alkylimino)diethanolato)cobalt(III) chelates, it seems likely that sulfhydryl or other sensitive functional groups on the enzyme could be susceptible to oxidation with concomitant loss of enzyme activity.

Acetylcholinesterase Reactivation. We concluded our investigation by determining the degree to which Co(MIDE)$_2$ and Co(AIDE)$_2$ restore activity to AChE inhibited by DFP. In these experiments AChE was incubated with excess DFP, separated from unreacted inhibitor, and diluted immediately into solutions containing 20×10^{-5} or 100×10^{-5} M Co-(MIDE)$_2$, Co(AIDE)$_2$, or 2-PAM. Aliquots were then withdrawn at 2-, 4-, and 24-h intervals and assayed for activity. At 20×10^{-5} and 100×10^{-5} M, 2-PAM restored AChE to greater than 96% of control activity for all incubation intervals; Co(MIDE)$_2$ and Co(AIDE)$_2$, however, were completely inactive as reactivators of AChE. In 12 experiments with the two chelates, AChE activity remained at 0.21 ± 0.2% of control activity for all concentrations and incubation periods investigated. Thus the chelates do not significantly restore activity to phosphorylated AChE under conditions where 2-PAM effectively reactivates inhibited enzyme.

Conclusions

Co(MIDE)$_2$ and Co(AIDE)$_2$ are unstable in near-neutral aqueous solution, hydrolytic cleavage of one of the two ligands proceeding at 25 °C with a half-life of 10–20 min depending on the reaction medium. The chelates or their solvolysis products irreversibly inhibit acetylcholinesterase, perhaps via oxidation of sulfhydryl or other sensitive functional groups on the enzyme.

Neither Co(MIDE)$_2$ nor Co(AIDE)$_2$ exhibit significant activity as reactivators of diisopropyl phosphorylacetylcholinesterase. These observations cast doubt on published claims[5–8] that Co(MIDE)$_2$ and Co(AIDE)$_2$ function as reactivators of dimethyl phosphorylacetylcholinesterase. We cannot attest to the claimed[5–8] antidotal efficacy of the chelates in dimethyl dichlorovinyl phosphate poisoning. However, our in vitro results with Co(MIDE)$_2$ and Co(AIDE)$_2$ largely exclude the possibility that any therapeutic properties derive from reactivation of inhibited acetylcholinesterase.

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Crystal and Molecular Structure of PPN[HRu$_4$(CO)$_{13}$]

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The water-gas shift reaction (CO + $H_2O \rightleftharpoons CO_2$ + H_2) has been found to be catalyzed by many different metal carbonyl complexes, both mono- and polynuclear.[1] The ruthenium carbonyls are clearly some of the most studied systems,[1a,b,g] and several mechanisms have been proposed to account for the observations. These proposals emphasize the intermediacy of trinuclear or tetranuclear clusters.[1a,g] In one scheme[1a] the species [HRu$_4$(CO)$_{13}$]$^-$ is formed by CO substitution for H_2 in [H$_3$Ru$_4$(CO)$_{12}$]$^-$. The monohydrido cluster is believed to react with H_2O, giving [H$_2$Ru$_4$(CO)$_{12}$(COOH)]$^-$, which loses CO_2, regenerating [H$_3$Ru$_4$(CO)$_{12}$]$^-$.

The cluster [HRu$_4$(CO)$_{13}$]$^-$ has been found to be quite reactive,[2] and the determination of its molecular structure has not been reported. We have prepared [HRu$_4$(CO)$_{13}$]$^-$, by a serendipitous route starting with the isocyanato cluster [Ru$_4$(NCO)(CO)$_{13}$]$^-$, and report here its crystal and molecular structure.

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen, and the solvents were distilled under nitrogen from appropriate drying agents. The common reagents were obtained from the usual sources, and Ru$_3$(CO)$_{12}$ was synthesized by a literature procedure[3] with modifications suggested by Bradley.[4] PPN[Ru$_4$(NC-O)(CO)$_{13}$] was prepared from the reaction of Ru$_3$(CO)$_{12}$ and PPN(N$_3$) as reported elsewhere.[5]

Synthesis of PPN[HRu$_4$(CO)$_{13}$]. A stock solution of KOH in methanol (0.099 M) was prepared, and 2.5 mL of this solution was deoxygenated and added to a 25-mL methanol solution of PPN-[Ru$_4$(NCO)(CO)$_{13}$] (80 mg, 0.059 mmol). After 20 min of stirring at room temperature, the methanol was removed under vacuum. The brown residue was extracted with ether (20 mL), giving a deep red solution. The volume of ether was reduced to 10 mL, and slow diffusion of hexane into the ether resulted in the formation of dark red crystals of PPN[HRu$_4$(CO)$_{13}$] (9.1 mg, 12% yield).

The ether-insoluble material was extracted with tetrahydrofuran (20 mL); the resulting solution was concentrated to 15 mL and layered with 30 mL of hexane. Reddish brown crystals of (PPN)$_2$[Ru$_4$(CO)$_{13}$] formed slowly (39 mg, 35% yield).

Collection and Reduction of the X-ray Data. A red crystal of PPN[HRu$_4$(CO)$_{13}$] was mounted on a glass fiber and found to be triclinic by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs and by a Delauney reduction calculation.[6] The centrosymmetric space group $P\bar{1}$ was chosen and data collection begun. Successful refinement of the structure verified the choice of this space group. A summary of the crystal data is presented in Table I. The intensity data were measured with ω–2θ scans. Background counts of duration equal to one-fourth of the scan time for each peak were measured at the two ends of the scan range. In this manner, the total

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(2) Nagel, C.; Shore, S. G. *J. Chem. Soc., Chem. Commun.* **1980**, 530–1.
(3) Mantovani, A.; Cenini, S. *Inorg. Synth.* **1974**, *16*, 47–8.
(4) Bradley, J., personal communication.
(5) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.*, in press.
(6) All calculations were carried out on PDP 8A and 11/34 computers using the Enraf-Nonius CAD 4-SDP programs. This crystallographic computing package is described in: Frenz, B. A. In "Computing in Crystallography"; Schenk, H., Olthof-Hazekamp, R., van Konigsvel, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71. See also: "CAD 4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, 1978.

Table I

Crystal Parameters

cryst system triclinic	$V = 2506$ (3) Å³
space group $P\bar{1}$	$Z = 2$
$a = 15.296$ (3) Å	calcd density 1.73 g/cm³
$b = 19.195$ (7) Å	temp 22 °C
$c = 9.258$ (2) Å	abs coeff 12.83 cm⁻¹
$\alpha = 101.91$ (2)°	formula $C_{49}H_{31}NO_{13}P_2Ru_4$
$\beta = 93.27$ (1)°	
$\gamma = 108.15$ (2)°	

Measurement of Intensity Data

diffractometer: Enraf-Nonius CAD4

radiation: Mo Kα (λ = 0.710 69 Å)

monochromator: graphite crystal

scan speed: variable from 0.93 to 6.67°/min

scan range: $0 \leqslant 2\theta \leqslant 48°$

reflctns measd: $\pm h, \pm k, +l$

check reflctns: $\{6\bar{2}2\}$, $\{413\}$, $\{7\bar{5}1\}$; measd approximately every 50 reflctns

reflctns collected: 8413 unique reflctns; 5811 with $I > 2.0\sigma(I)$

$p = 0.03$

$R = 0.054$

$R_w = 0.058$
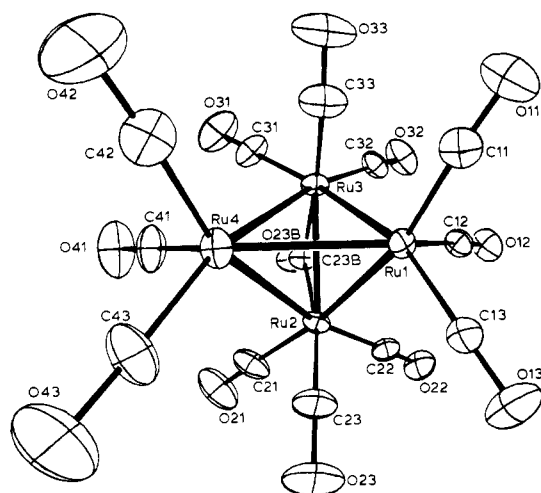
Figure 1. View showing the atom labels of $[HRu_4(CO)_{13}]^-$. The hydrogen atom is proposed to bridge the Ru(1)–Ru(4) bond. The thermal ellipsoids are shown at 30% probability level.

duration of measuring background is equal to half of the time required for the peak scan. The three check reflections showed no change intensity during data collection. A total of 8413 unique reflections were measured, of which 5811 had $I > 2.0\sigma(I)$, and were used in the structural determination.[7] The data were corrected for Lorentz, polarization, and background effects but not for absorption.

Solution and Refinement of the Structure. The structure was solved by conventional heavy-atom techniques. The positions of the four ruthenium atoms were determined by a Patterson synthesis. Subsequent structure factor and difference Fourier calculations revealed the positions of the non-hydrogen atoms.[8] All atoms in the cluster and the P and N atoms in the cation were refined with the use of anisotropic temperature factors. The hydrogen atom positions were

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(7) The intensity data were processed as described: "CAD 4 and SDP User's Manual"; Enraf-Nonius: Delft, Holland, 1978. The net intensity $I = (K/(\text{NPI}))(C - 2B)$, where $K = 20.1166x$ (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurements, C = total count, and B = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/(\text{NPI})^2[C + 4B + (pI)^2]$, where p is a factor used to downweight intense reflections. The observed structure factor amplitude F_o is given by $F_o = (I/Lp)^{1/2}$, where Lp = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o)$: $^1/_2(\sigma(I)/I)F_o$.

(8) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum w|F_o|)^2]^{1/2}$. The error in an observation of unit weight is $[w(|F_o| - |F_c|)^2/(\text{NO} - \text{NV})]^{1/2}$, where NO and NV are the number of observtions and variables, respectively.


Table II. Bond Distances (Å)

|			
Ru(1)–Ru(2)	2.791 (1)	C(11)–O(11)	1.143 (8)
Ru(1)–Ru(3)	2.756 (1)	C(12)–O(12)	1.132 (7)
Ru(1)–Ru(4)	2.930 (1)	C(13)–O(13)	1.153 (7)
Ru(2)–Ru(3)	2.835 (1)	C(21)–O(21)	1.136 (9)
Ru(2)–Ru(4)	2.770 (1)	C(22)–O(22)	1.126 (7)
Ru(3)–Ru(4)	2.765 (1)	C(23)–O(23)	1.171 (7)
Ru(1)–C(11)	1.885 (8)	C(23B)–O(23B)	1.165 (7)
Ru(1)–C(12)	1.893 (7)	C(31)–O(31)	1.137 (7)
Ru(1)–C(13)	1.869 (7)	C(32)–O(32)	1.130 (8)
Ru(2)–C(21)	1.902 (9)	C(33)–O(33)	1.155 (8)
Ru(2)–C(22)	1.918 (7)	C(41)–O(41)	1.120 (7)
Ru(2)–C(23)	1.872 (7)	C(42)–O(42)	1.145 (8)
Ru(2)–C(23B)	2.113 (7)	C(43)–O(43)	1.131 (8)
Ru(3)–C(31)	1.875 (7)	C–C$_{av}$	1.38 (4)
Ru(3)–C(32)	1.924 (8)	P(1)–C$_{av}$	1.79 (1)
Ru(3)–C(33)	1.876 (8)	P(2)–C$_{av}$	1.799 (7)
Ru(3)–C(23B)	2.161 (6)	P(1)–N	1.581 (4)
Ru(4)–C(41)	1.910 (8)	P(2)–N	1.567 (4)
Ru(4)–C(42)	1.864 (8)		
Ru(4)–C(43)	1.902 (8)		

calculated and used in the subsequent least-squares cycles, but their positions and temperature factors were not refined. The values of the atomic scattering factors used in the calculations were taken from the usual tabulation, and the effects of anomalous dispersion were included for the non-hydrogen atoms.[9] The hydrogen atom scattering factors were taken from Cromer and Ibers' list.[10]

Results and Discussion

The reaction of azide with $Ru_3(CO)_{12}$ has been shown to give $[Ru_4(NCO)(CO)_{13}]^-$ (**1**) in good yield.[5] It was the re-

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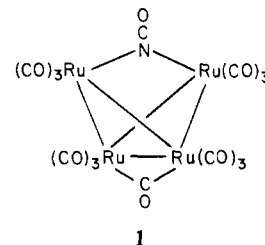
lation between this structure and the unknown nitrido cluster $[Ru_4N(CO)_{12}]^-$, formally involving loss of two CO groups, that led us to study the reaction of **1** with hydroxide. Possible cleavage of the N–C bond of the coordinated isocyanate could be facilitated by nucleophilic attack at the carbon, ultimately leading to CO_2 formation and a coordinated nitrogen atom. The reaction of hydroxide does occur, but the entire isocyanate group is displaced to give low yields of $[HRu_4(CO)_{13}]^-$ and $[Ru_4(CO)_{13}]^{2-}$ (eq 1). The analysis of these products is based

$$[Ru_4(NCO)(CO)_{13}]^- + OH^- \xrightarrow{CH_3OH}$$
$$[HRu_4(CO)_{13}]^- + [Ru_4(CO)_{13}]^{2-} \quad (1)$$
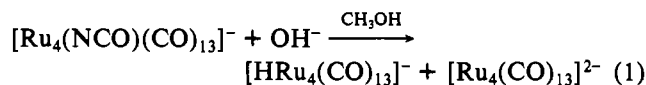
on a spectral comparison with the reported data, and not surprisingly, the relative amounts of these can vary.

The structure of $[HRu_4(CO)_{13}]^-$ consists of four $Ru(CO)_3$ groups bound to each other in the form of a distorted tetrahedron. Figures 1 and 2 show the atomic labeling scheme and a stereoview of the structure. The $Ru(CO)_3$ groups themselves are structurally very similar with an average C–Ru–C bond angle of 96 (2)°. The metal–metal bond lengths vary according to whether or not they are bridged, the unbridged bonds being the shortest, averaging 2.77 (1) Å. Ru(2) and Ru(3) are bridged by C(23B)–O(23B) and are separated by

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(9) Cromer, D. T.; Waber, J. R. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. Cromer, D. T. *Ibid.*, Table 2.3.1.

(10) Cromer, D. R.; Ibers, J. A. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2C.
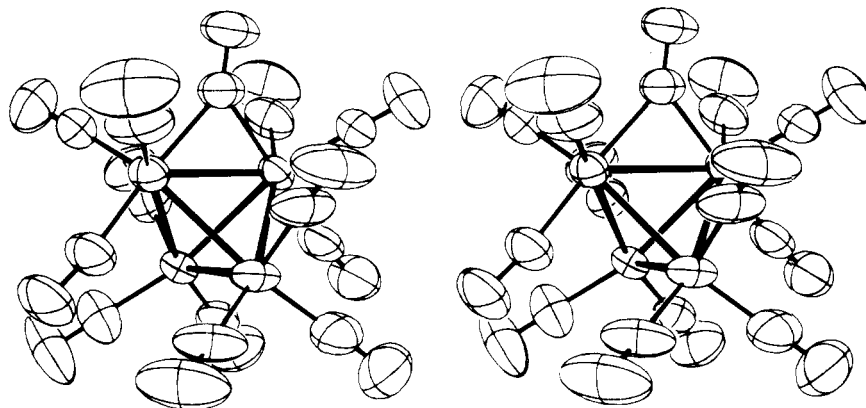
Figure 2. Stereoview of $[HRu_4(CO)_{13}]^-$ with the thermal ellipsoids at the 40% probability level.

Table III. Selected Bond Angles (deg)

Ru(2)-Ru(1)-Ru(3)	61.47 (2)	Ru(4)-Ru(2)-C(21)	100.0 (2)
Ru(2)-Ru(1)-Ru(4)	57.86 (2)	Ru(4)-Ru(2)-C(22)	159.4 (2)
Ru(3)-Ru(1)-Ru(4)	58.10 (2)	Ru(4)-Ru(2)-C(23)	78.9 (2)
Ru(2)-Ru(1)-C(11)	166.6 (2)	Ru(4)-Ru(2)-C(23B)	94.8 (2)
Ru(2)-Ru(1)-C(12)	87.8 (2)	C(21)-Ru(2)-C(22)	100.0 (3)
Ru(2)-Ru(1)-C(13)	98.8 (2)	C(21)-Ru(2)-C(23)	92.6 (3)
Ru(3)-Ru(1)-C(11)	106.3 (2)	C(21)-Ru(2)-C(23B)	81.8 (3)
Ru(3)-Ru(1)-C(12)	85.4 (2)	C(22)-Ru(2)-C(23)	95.5 (3)
Ru(3)-Ru(1)-C(13)	160.3 (2)	C(22)-Ru(2)-C(23B)	92.7 (3)
Ru(4)-Ru(1)-C(11)	112.1 (2)	C(23)-Ru(2)-C(23B)	170.8 (3)
Ru(4)-Ru(1)-C(12)	137.9 (2)	Ru(1)-C(11)-O(11)	176.3 (7)
Ru(4)-Ru(1)-C(13)	112.6 (2)	Ru(1)-C(12)-O(12)	176.3 (6)
C(11)-Ru(1)-C(12)	96.8 (3)	Ru(1)-C(13)-O(13)	178.7 (7)
C(11)-Ru(1)-C(13)	93.4 (3)	Ru(2)-C(21)-O(21)	177.1 (9)
C(12)-Ru(1)-C(13)	94.8 (3)	Ru(2)-C(22)-O(22)	176.9 (6)
Ru(1)-Ru(2)-Ru(3)	58.64 (2)	Ru(2)-C(23)-O(23)	172.0 (6)
Ru(1)-Ru(2)-Ru(4)	63.58 (2)	Ru(2)-C(23B)-O(23B)	141.2 (6)
Ru(3)-Ru(2)-Ru(4)	59.10 (2)	Ru(3)-C(23B)-O(23B)	135.8 (6)
Ru(1)-Ru(2)-C(21)	162.7 (2)	P(1)-N-P(2)	146.3 (3)
Ru(1)-Ru(2)-C(22)	96.0 (2)	C-P(1)-C_{av}	107 (2)
Ru(1)-Ru(2)-C(23)	79.5 (2)	C-P(2)-C_{av}	107 (1)
Ru(1)-Ru(2)-C(23B)	103.9 (2)	C-P(1)-N_{av}	112 (2)
Ru(3)-Ru(2)-C(21)	119.0 (3)	C-P(2)-N_{av}	111 (4)
Ru(3)-Ru(2)-C(22)	114.0 (2)	P-C-C_{av}	120 (2)
Ru(3)-Ru(2)-C(23)	129.8 (2)	C-C-C_{av}	120 (2)
Ru(3)-Ru(2)-C(23B)	49.2 (2)		

a distance of 2.835 (1) Å. The bridging carbonyl is close to being fully symmetric with respect to its distances to Ru(2) and Ru(3). However, there is some asymmetry with respect to the plane defined by Ru(2), Ru(3), and the center of the Ru(1)-Ru(4) bond. This can be best shown by comparing the dihedral angle between the planes comprising C(23B)-Ru(2)-Ru(3) and Ru(2)-Ru(3)-Ru(4) (162.1°) with that of C(23B)-Ru(2)-Ru(3) and Ru(2)-Ru(3)-Ru(1) (122°).

The location of the hydrogen, which was not observed in the final difference Fourier map, is almost certainly bridging the Ru(1)-Ru(4) bond. This distance is 2.930 (1) Å, which is consistent with the usual M-M bond lengthening that occurs upon addition of one bridging hydrogen.[11] This also is the only site in the cluster that is unencumbered by carbonyl ligands. Tables II and III list selected distances and angles.

The $[HRu_4(CO)_{13}]^-$ anion fits into a large series of isoelectronic clusters that have been structurally characterized and includes $[HOs_4(CO)_{13}]^-$,[12] $[HFeRu_3(CO)_{13}]^-$,[13] $[HFe_2Ru_2(CO)_{13}]^-$,[13] and $[HFe_4(CO)_{13}]^-$,[14] along with some related

(11) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843–53.
(12) Dawson, P. A.; Johnson, B. F. G.; Lewis, J.; Kaner, D. A.; Raithby, P. R. *J. Chem. Soc. Chem. Commun.* **1980**, 961–2.
(13) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Steinmetz, G. R.; Rosen, R. P.,; Gladfelter, W. L.; Geoffroy, G. L.; Bruck, M. A.; Bau, R. *Inorg. Chem.* **1981**, *20*, 3823–8.
(14) Manassero, M.; Sansoni, M.; Longoni, G. *J. Chem. Soc., Chem. Commun.* **1976**, 919–20.
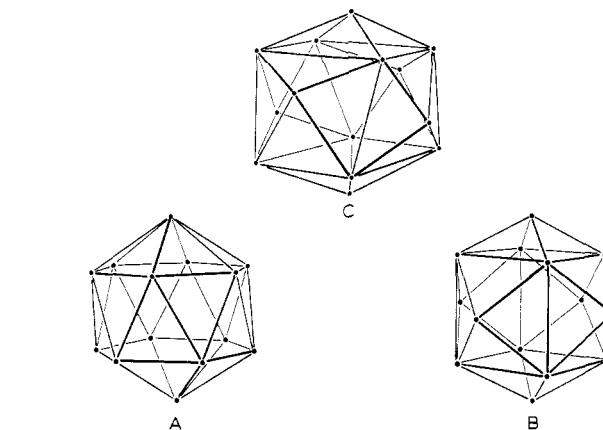

Figure 3. Relationship of three 14-vertex polyhedra: A, bicapped hexagonal antiprism; B, omnicapped cube; C, hexacapped rectangular antiprism.

compounds such as $[Ru_4Cl(CO)_{13}]^-$ [15] and $[Ru_4(NCO)(CO)_{13}]^-$.[5] Despite the isoelectronic nature of the first four of these, three distinctly different structures have been observed. The tetrairon cluster $[HFe_4(CO)_{13}]^-$ contains a unique η^2-CO within a butterfly arrangement of metals.[14] $[HRu_4(CO)_{13}]^-$ is similar to $[HOs_4(CO)_{13}]^-$ [11] and $[HFe_2Ru_2(CO)_{13}]^-$,[13] and these have the highest symmetry (C_{2v}) of the series. $[HFeRu_3(CO)_{13}]^-$ [13] has two asymmetric bridging carbonyls and is closely related to the structure of $H_2FeRu_3(CO)_{13}$.[16] Since $H_2Ru_4(CO)_{13}$ is also isostructural with $H_2FeRu_3(CO)_{13}$, it is not obvious which form $[HRu_4(CO)_{13}]^-$ would adopt. The compounds $[Ru_4Cl(CO)_{13}]^-$ [15] and $[Ru_4(NCO)(CO)_{13}]^-$ have C_{2v} symmetries and are related to $[HRu_4(CO)_{13}]^-$ structurally by the replacement of H with Cl or NCO. The additional two electrons donated by these ligands open the Ru-Ru bond that they bridge. If the hydride is included, each of these clusters has 14 ligands, which must result in substantial nonbonded repulsions among these groups. This is clearly evident in $HRu_4(CO)_{13}^-$, as exemplified by the following contacts (Å): C(33)-C(11), 2.86 (1); C(33)-C(42), 2.99 (1); C(23)-C(43), 2.92 (1); C(23)-C(13), 2.88 (1).

Interligand steric repulsion has been hypothesized to play a major role in determining the structures of binary metal carbonyl clusters.[18] The two most favorable 14-vertex polyhedra for minimizing interligand repulsions are the bicapped hexagonal antiprism (bha) and the omnicapped (hexacapped) cube (A and B, respectively, in Figure 3). The ligand ar-

(15) Steinmetz, G.; Harley, A. D.; Geoffroy, G. L. *Inorg. Chem.* **1980**, *19*, 2985–9.
(16) Gilmore, C. J.; Woodward, P. *J. Chem. Soc. A* **1971**, 3453.
(17) Yawney, D. B. W.; Doedens, R. J. *Inorg. Chem.* **1972**, *11*, 838.
(18) Benfield, R. E.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1980**, 1743–67.

rangement of [HRu$_4$(CO)$_{13}$]$^-$ can be described as a hexa-capped 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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Preparation and Properties of a Novel Co^{III}$_2$Cr^{III} Complex

Peter Leupin, A. Geoffrey Sykes,* and Karl Wieghardt*

Reactions of the tris(μ-hydroxo)bis(triamminecobalt(III)) complex I have been extensively studied, and the formation
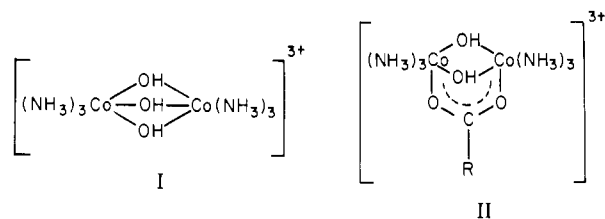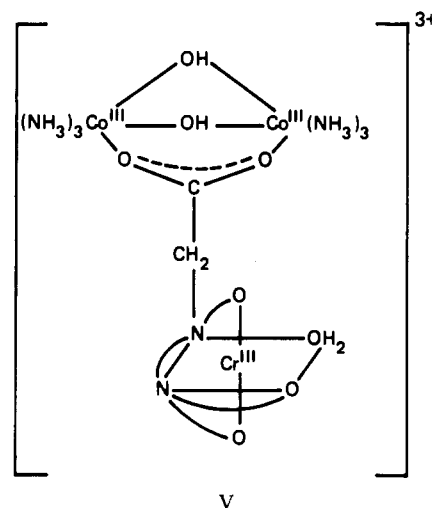

of the μ-carboxylato derivatives II has been noted.[1-3] Properties of the aquo(ethylenediamine-*N,N,N',N'*-tetraacetato)-chromium(III) complex, [Cr(edta)(H$_2$O)]$^-$ (III), or [Cr-
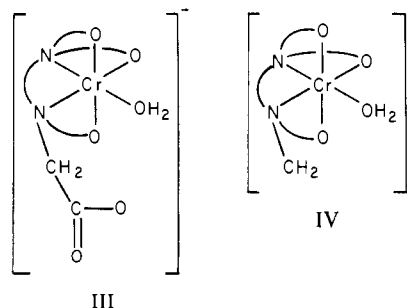
(Hedta)(H$_2$O)] when the uncoordinated carboxylate arm is protonated, have also been investigated, and the anomalous lability of the H$_2$O ligand (rates for anation are in the stop-

ped-flow range) has been established.[4-6] Anation rate constants for replacement of the H$_2$O are less (1 order of magnitude) when the uncoordinated CH$_2$CO$_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$_2$O)] (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

V

and reactivity of this new trinuclear complex are also described.

Experimental Section

Preparation of Complexes. The complex [(NH$_3$)$_3$Co(μ-OH)$_3$Co-(NH$_3$)$_3$](ClO$_4$)$_3$·2H$_2$O (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$_2$O)], 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$_2$O] 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$_2$CrC$_{10}$H$_{34}$N$_8$O$_{11}$](ClO$_4$)$_3$·6H$_2$O: C, 11.8; H, 4.5; N, 11.0; Cr, 5.1; H$_2$O 10.6. Found: C, 11.7; H, 4.3; N, 11.0; Cr, 5.3; H$_2$O, 11.2. The Cr was determined by oxidation to CrO$_4$$^{2-}$ (λ 372 nm, ϵ 4815 M^{-1} cm^{-1}) with H$_2$O$_2$ in 6 M NaOH and H$_2$O content was obtained by determining the loss in weight by leaving the complex to stand >4 days over P$_2$O$_5$ in a dessicator (it was assumed that the H$_2$O coordinated to the Cr was retained). A sample of the (μ-acetato)bis(μ-hydroxo)bis[triamminecobalt(III)] complex, [(NH$_3$)$_3$Co(μ-CH$_3$CO$_2$)(μ-OH)$_2$Co(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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