

Transition-Metal Complexes with Polyamino Alcohols. 1. Structures of a Dinuclear Chromium(III) Complex and a Trinuclear Cobalt Complex with *N*-(3-Aminopropyl)diethanolamine, a Bifurcated Quadridentate Tripod Ligand

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The reaction between *N*-(3-aminopropyl)diethanolamine (apdol-H₂) and CrCl₃·6H₂O (dehydrated in boiling DMF) results in the precipitation of violet [Cr₂Cl₂(μ-apdol-H-N,N',O,O')₂]Cl₂. Addition of NaClO₄·H₂O to an aqueous solution of this complex precipitates a perchlorate salt and X-ray quality crystals of [Cr₂Cl₂(μ-apdol-H_{0.5}-N,N',O,O')₂]ClO₄·DMF were obtained by diffusion of ethanol into a DMF solution of the perchlorate. The complex, C₁₇H₄₀N₅O₉Cl₃Cr₂, crystallizes in the monoclinic space group *P*₂₁/*c* with *a* = 10.458 (3) Å, *b* = 15.584 (4) Å, *c* = 17.711 (7) Å, β = 105.46 (3)°, and *Z* = 4 and was refined to a conventional *R* factor of 0.042. The crystal lattice consists of the Cr₂Cl₂(μ-apdol-H_{0.5}-N,N',O,O')₂²⁺ cation, a ClO₄⁻ anion, and one DMF of crystallization. Each Cr(III) is six-coordinated, four sites being occupied by two N atoms and two O atoms of the amino alcohol with the O, N, and O atoms of the diethanolamine component in a facial configuration. The fifth coordination site is occupied by a chloro ligand trans to a deprotonated O atom, which in turn acts as a bridge completing the octahedron. An intramolecular hydrogen bond between the other two O atoms accounts for the single positive charge on the dinuclear cation, and these two O atoms can be formally regarded as half-protonated. Spectrophotometrically determined kinetic parameters for the rate of loss of the chloro ligand from CrCl(apdol-H₂-N,N',O,O')(OH₂)²⁺ in 0.1 M HNO₃ are *k*(298) = 1.31 × 10⁻⁴ s⁻¹, *E*_a = 81.7 ± 0.6 kJ mol⁻¹, and Δ*S*₂₉₈[‡] = -53.6 ± 1.2 J K⁻¹ mol⁻¹. Reaction of apdol-H₂ and Na₃Co(NO₂)₆ in aqueous solution gives a brown, water-insoluble precipitate. This material readily dissolves in warm 3 M acetic acid, and the trinuclear Co complex [Co₃(μ-NO₂-N,O)₂(μ-CH₃CO₂-O,O')₂(μ-apdol-H-N,N',O,O')₂](ClO₄)₂·2H₂O can be isolated as dark brown, X-ray quality crystals by the addition of NaClO₄·H₂O. The complex, C₁₈H₄₄O₂₂N₆Cl₂Co₃, crystallizes in the monoclinic space group *P*₂₁/*n* with *a* = 13.794 (1) Å, *b* = 8.568 (1) Å, *c* = 14.958 (2) Å, β = 104.87 (1)°, and *Z* = 2 and was refined to *R* = 0.027. The centrosymmetric complex cation consists of a linear array of six-coordinate Co atoms with formal oxidation states Co(III)-Co(II)-Co(III). In the two terminal Co(III) atoms, the apdol-H adopts the same topology as in the Cr(III) complex with monodentate acetato-*O* and nitro-*N* ligands occupying the remaining two sites, trans to a protonated O donor and the N bridgehead, respectively. The central Co^{II}O₆ moiety is held in the trinuclear unit by pairs of bridging nitro-*O*, acetato-*O*, and deprotonated apdol-*O* atoms, in a trans-trans-trans configuration. Each cation is associated with two perchlorate anions and two molecules of water of crystallization, linked by hydrogen bonds.

Introduction

Linear and branched-chain polyamino polyalcohols are widely used in industry as bases or solvents.¹ They are also versatile ligands in transition-metal chemistry, and complexes using some of the simpler systems, e.g. ethanolamine, have been extensively investigated. The introduction of an -OH donor group into the ligand system can cause considerable modification to the chelating properties when compared with the analogous polyamine. For example, the -OH group may coordinate, remain uncoordinated,^{2,3} or, when coordinated, bridge between two metal centers,^{4,5} and for each of these modes there is the possibility of protonated⁶ or deprotonated⁷ oxygen atoms giving rise to intramolecular hydrogen bonds.⁸⁻¹¹ The number of potential geometric isomers may also increase, especially in multidentate polyamino polyalcohols when compared with the analogous multidentate polyamine.

N-(3-Aminopropyl)diethanolamine (apdol-H₂)¹⁰ is a diamino dialcohol of particular interest as it is a potentially quadridentate tripodal *N,N',O,O'*-donor ligand with unequal "arm" lengths. The coordination of all four donor groups will result in the formation of two five-membered and one six-membered chelate rings. In

this mode, there are two possible isomeric topological arrangements, with the O, N, and O atoms of the diethanolamine component either facial or meridional.

In this paper, we describe the structures of a dinuclear Cr(III) complex and a trinuclear Co complex formed by coordination of *N*-(3-aminopropyl)diethanolamine to these metal centers.

Experimental Section

N-(3-Aminopropyl)diethanolamine was purchased from Fluka and used as supplied. Although this compound is described as "practical" grade by the supplier, the ¹³C NMR spectrum (Varian CFT 20) showed the material to be free of other carbon-containing substances. ¹³C NMR (D₂O solution, ppm referenced to dioxane at 67.39): 59.53 (-CH₂OH), 56.19 (NCH₂CH₂OH), 52.88 (NCH₂CH₂CH₂NH₂), 39.94 (NH₂CH₂-), 29.50 (-CH₂CH₂CH₂-). All other chemicals were the best Reagent Grade available.

Caution! Although we have experienced no difficulties with the perchlorate salts described here, these should be regarded as potentially explosive and handled accordingly.

Dichlorobis[*N*-(3-aminopropyl)diethanolamino-*N,N',O,O'*]dichromium(III) Dichloride, [Cr₂Cl₂(C₇H₁₇N₂O₂)₂]Cl₂. Hydrated chromium(III) chloride, CrCl₃·6H₂O (10 g) was boiled in DMF (40 mL) until a violet solution formed and the volume was reduced to about 30 mL. This solution was allowed to cool to about 100 °C, and a solution of apdol-H₂ (6 g) in DMF (20 mL) was slowly added. The color changed to green, and the solution was heated at just below boiling for about 30 min, during which time a violet microcrystalline product deposited. The solution was cooled to room temperature and filtered, and the product (1 g, 8%) as washed with 2-propanol and then ether and air-dried. This material was not recrystallized and attempts to crystallize further Cr(III) products from the green mother liquor were unsuccessful.

Anal. Calcd for [Cr₂Cl₂(C₇H₁₇N₂O₂)₂]Cl₂: C, 29.59; H, 6.03; N, 9.86. Found: C, 29.96; H, 6.20; N, 9.85. Visible absorption spectra (0.1 M HNO₃); λ, nm (ε, M⁻¹ cm⁻¹): 566 max (168), 474 min (44.0), 407 max (127); (H₂O) 555 max (159), 463 min (47.1), 400 max (115).

The perchlorate salt was obtained as a microcrystalline violet solid in an almost quantitative yield, by addition of NaClO₄·H₂O (5 g/1 g) to an aqueous solution of the chloride (1 g/20 mL). This salt is only sparingly soluble in water, but is readily soluble in DMF. Suitable crystals for the following single crystal X-ray structural analysis of [Cr₂Cl₂(apdol-H_{0.5}-N,N',O,O')₂]ClO₄·DMF were grown by ethanol diffusion into a DMF solution of the perchlorate salt in a closed vial. Visible

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Table I. Crystal Data

	Cr ₂	Co ₃
mol formula	C ₁₇ H ₄₀ N ₅ O ₉ Cl ₃ Cr ₂	C ₁₈ H ₄₄ O ₂₂ N ₆ Cl ₂ Co ₃
fw	668.9	944.4
space group	P2 ₁ /c	P2 ₁ /n
a, Å	10.458 (3)	13.794 (1)
b, Å	15.584 (4)	8.568 (1)
c, Å	17.711 (7)	14.958 (2)
β, deg	105.46 (3)	104.87 (1)
V, Å ³	2788 (1)	1708 (1)
Z	4	2
temp, °C	-150	-150
d _{calcd} , g cm ⁻³	1.59	1.84
F(000)	1389	970
abs coeff (μ), cm ⁻¹	11.0	16.9
abs cor	empirical	numerical
cryst size, mm	0.87 × 0.31 × 0.16	0.36 × 0.25 × 0.09
transmissn factors	0.59-0.73	0.62-0.83
λ(Mo Kα), Å	0.71069	0.71069
scan mode	θ/2θ	θ/2θ
octants	±h,+k,+l	±h,+k,+l
2θ _{max} , deg	50	55
no. of reflns measd	5401	4365
no. of reflns used (I > 3σ(I))	3734	3277
R(merge)	0.040	0.016
no. of params refined	328	241
weighting g	0.00084	0.00012
R	0.042	0.027
R ₂	0.056	0.034

absorption spectrum (DMF): 560 max (164), 464 min (49.3), 403 max (133).

Chloroqua[N-(3-aminopropyl)diethanolamine]chromium(III) Dichloride Sesquihydrate, [CrCl(apdol-H₂(OH)₂]₂Cl₂·³/₂H₂O. Violet [Cr₂Cl₂(apdol-H-N,N',O,O')₂Cl₂ (1 g) was dissolved in 0.1 M HCl (10 mL), MeOH (30 mL) was added, and ZnCl₂ (3 g) was stirred in. After about 1 h at room temperature, blue-violet crystals of the product (ca. 1 g) were collected by filtration, washed successively with 2-propanol and ether, and air-dried.

Anal. Calcd for [CrCl(C₇H₁₃N₂O₂)(OH₂)Cl₂·³/₂H₂O: C, 22.99; H, 6.34; N, 7.66. Found: C, 22.95; H, 5.58; N, 7.67. Visible absorption spectral parameters (0.1 M HNO₃) 567 max (83.8), 474 min (22.2), 406 max (63.4) were identical with those observed for the dimer in the same solvent (assuming 1 mol of dimer gives 2 mol of monomer).

Bis(μ-acetato-O,O')bis(μ-nitro-N,O)bis[N-(3-aminopropyl)diethanolamino-N,N',O,O']trichlorobis(Diperchlorate Dihydrate), [Co₃(NO₂)₂(CH₃CO₂)₂(apdol-H)₂](ClO₄)₂·2H₂O. A solution of apdol-H₂ (3 g) in water (10 mL) was added to an aqueous solution of Na₃Co(NO₂)₆ (7 g/40 mL) at room temperature. This mixture was heated to about 60 °C for 15 min. Effervescence occurred, and the orange-brown solid that deposited was collected from the ice-cooled solution, washed successively with water, 2-propanol, and ether, and air-dried (yield ca. 4 g). This solid (2 g) completely dissolved in warm 3 M acetic acid (50 mL, 30 °C) to give an orange solution.

After addition of NaClO₄·H₂O (5 g), dark brown crystals (1 g), suitable for single-crystal X-ray structural analysis, deposited over 3 days at room temperature.

Anal. Calcd for [Co₃(NO₂)₂(CH₃CO₂)₂(C₇H₁₇N₂O₂)₂](ClO₄)₂·2H₂O: C, 22.89; H, 4.69; N, 8.90. Found: C, 22.93; H, 4.59; N, 8.97. Visible absorption spectrum (DMF): ~530 sh (~150); ~445 sh (~250).

Kinetics. The rate of loss of the chloro ligand from CrCl(apdol-H₂)(OH₂)²⁺ (generated by dissolving [Cr₂Cl₂(apdol-H)₂]Cl₂ in 0.1 M HNO₃) was measured spectrophotometrically (Varian DMS 100). First-order rate constants were calculated from the variation of absorbance with time at 580, 532, and 420 nm in temperature-controlled, matched, 1.00-cm quartz cells. Activation parameters were computer calculated¹² from the variation of k_{obsd} with temperature over a 20 °C range.

X-ray Data Collection and Analysis (Table I). Intensity data were collected with a Nicolet R3m four-circle diffractometer by using graphite-monochromatized Mo Kα radiation. Cell parameters were determined by least-squares refinement of 25 accurately centered reflections (2θ > 25°). Throughout data collections the intensities of three standard reflections were monitored at regular intervals, and no significant vari-

Table II. Final Atomic Parameters for [Cr₂Cl₂(apdol-H_{0.5}-N,N',O,O')₂](ClO₄)₂DMF

atom	10 ⁴ x	10 ⁴ y	10 ⁴ z
Cation			
Cr(1)	3317 (1)	5037 (1)	7439 (1)
Cl(1)	4781 (1)	3973 (1)	7325 (1)
N(11)	4421 (3)	6116 (2)	7303 (2)
C(11)	5786 (4)	6191 (3)	7861 (2)
C(12)	5863 (4)	6101 (3)	8721 (2)
C(13)	5486 (4)	5222 (3)	8969 (2)
N(12)	4057 (3)	5041 (2)	8637 (2)
C(14)	3610 (4)	6891 (2)	7390 (2)
C(15)	2149 (4)	6685 (2)	7225 (2)
O(11)	2019 (2)	5889 (2)	7586 (1)
C(16)	4572 (4)	6029 (3)	6498 (2)
C(17)	3270 (4)	5784 (3)	5926 (2)
O(12)	2640 (2)	5137 (2)	6279 (2)
Cr(2)	424 (1)	5162 (1)	7343 (1)
Cl(2)	-1152 (1)	6229 (1)	7248 (1)
N(21)	-843 (3)	4132 (2)	6995 (2)
C(21)	-1884 (3)	4018 (2)	7433 (2)
C(22)	-1377 (4)	3944 (3)	8316 (2)
C(23)	-727 (4)	4750 (3)	8728 (2)
N(22)	511 (3)	4966 (2)	8512 (2)
C(24)	-9 (4)	3337 (2)	7066 (2)
C(25)	1400 (4)	3534 (2)	7029 (2)
O(21)	1823 (2)	4294 (2)	7474 (2)
C(26)	-1568 (4)	4332 (3)	6169 (2)
C(27)	-608 (4)	4648 (3)	5720 (2)
O(22)	306 (2)	5237 (2)	6203 (1)
H(12e) ^a	1623 (39)	5199 (25)	6222 (23)
Anion			
Cl(3)	2635 (1)	8061 (1)	4839 (1)
O(31)	3512 (4)	7977 (2)	5606 (2)
O(32)	1429 (4)	7631 (3)	4829 (2)
O(33)	2430 (4)	8945 (2)	4672 (2)
O(34)	3209 (4)	7664 (3)	4274 (2)
DMF			
C(1)	1332 (5)	2700 (4)	4767 (3)
C(2)	3483 (5)	3455 (3)	5036 (3)
N(1)	2698 (4)	2695 (2)	4754 (2)
C(3)	3221 (4)	2033 (3)	4471 (3)
O(1)	2648 (3)	1352 (2)	4232 (2)

^aBridging H atom.

ation was observed. The space groups were uniquely determined from systematic absences and the intensities were corrected for Lorentz-polarization and absorption effects. Reflections with intensities I > 3σ(I) were used for structure solution and refinement.

Both structures were solved by conventional Patterson and Fourier methods and refined by blocked-cascade least-squares procedures. All non-hydrogen atoms were refined with anisotropic thermal parameters. No disorder of the perchlorate ions was observed. Hydrogen atoms were included in calculated positions except for the hydroxyl and water hydrogens, which were refined from the positions found from difference maps. All hydrogen atoms were assigned isotropic thermal parameters 1.2 times the isotropic equivalent of their carrier atoms. The function minimized was Σw(|F_o - |F_c||)², with w = [σ²(F_o) + gF_c²]⁻¹. The magnitude of residual electron density in final Fourier syntheses was <0.6 e Å⁻³. No correction was applied for secondary extinction. Tables II and III list atomic coordinates for [Cr₂Cl₂(apdol-H_{0.5}-N,N',O,O')₂](ClO₄)₂DMF and [Co₃(NO₂)₂(CH₃CO₂)₂(apdol-H-N,N',O,O')₂](ClO₄)₂·2H₂O respectively, with standard deviations in parentheses.

All calculations (including diagrams) were performed on a Nova 4X computer using SHELXTL.¹³ Atomic scattering factors of SHELXTL¹³ were used. Tabulations of structure factors, hydrogen atom coordinates, and anisotropic thermal parameters are available as supplementary material.

Results

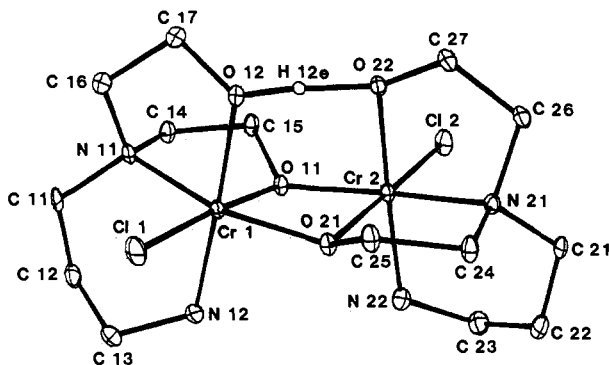
Cr(III) Complexes. Reaction of CrCl₃·6H₂O (dehydrated in boiling DMF) with apdol-H₂ gives a low yield of a violet crystalline product with elemental analysis corresponding to CrCl₂(apdol-H); however, subsequent evidence shows this is best formulated as

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Table III. Final Atomic Parameters for $[\text{Co}_3(\text{NO}_2)_2(\text{CH}_3\text{CO}_2)_2(\text{apdol-H-N,N',O,O'})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$

atom	10^4x	10^4y	10^4z
Cation			
Co(1)	3032 (1)	6550 (1)	5476 (1)
Co(2)	5000	5000	5000
N(11)	3083 (1)	8863 (2)	5599 (1)
C(11)	2253 (2)	9718 (3)	4946 (2)
C(12)	1222 (2)	9269 (3)	5045 (2)
C(13)	915 (2)	7624 (3)	4713 (2)
N(12)	1568 (1)	6405 (2)	5272 (1)
C(14)	4053 (2)	9298 (2)	5389 (2)
C(15)	4835 (2)	8135 (2)	5879 (2)
O(11)	4428 (1)	6629 (2)	5642 (1)
C(16)	3146 (2)	9302 (3)	6590 (1)
C(17)	2871 (2)	7949 (3)	7124 (2)
O(12)	3202 (1)	6505 (2)	6789 (1)
N(21)	3136 (1)	4292 (2)	5528 (1)
O(21)	3868 (1)	3591 (2)	5348 (1)
O(22)	2521 (1)	3527 (2)	5805 (1)
O(31)	2740 (1)	6695 (2)	4173 (1)
O(32)	3960 (1)	5400 (2)	3743 (1)
C(31)	3147 (2)	6108 (2)	3575 (1)
C(32)	2547 (2)	6306 (3)	2586 (2)
Anion			
Cl(4)	4660 (1)	8589 (1)	1732 (1)
O(41)	5193 (2)	9907 (2)	1500 (1)
O(42)	4582 (1)	8687 (2)	2661 (1)
O(43)	5220 (2)	7219 (2)	1628 (2)
O(44)	3688 (2)	8508 (3)	1114 (1)
H_2O			
O(51)	5012 (1)	4391 (2)	2429 (1)
H Atoms			
H(12e)	3823 (18)	6261 (26)	7115 (16)
H(51a)	4726 (19)	4488 (30)	2778 (17)
H(51b)	5074 (19)	5192 (29)	2215 (17)

**Figure 1.** Perspective view of the Cr(III) dimer.

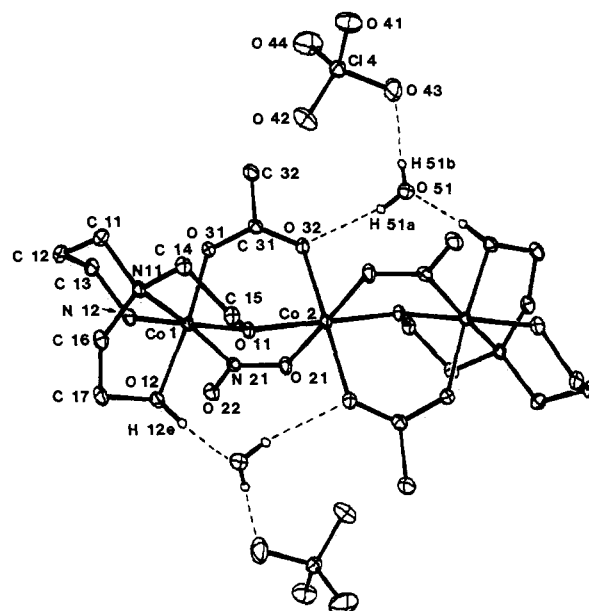
$[\text{Cr}_2\text{Cl}_2(\text{apdol-H-N,N',O,O'})_2]\text{Cl}_2$. The violet complex is soluble in water and 0.1 M HNO_3 (the visible absorption spectral parameters are different in these two media) and addition of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ to an aqueous solution results in the precipitation of a perchlorate salt. This perchlorate is soluble in DMF, and X-ray quality crystals of $[\text{Cr}_2\text{Cl}_2(\text{apdol-H}_{0.5}\text{-N,N',O,O'})_2]\text{ClO}_4 \cdot \text{DMF}$ were obtained by ethanol diffusion into a concentrated DMF solution, the stoichiometry and structure being determined by single-crystal X-ray analysis (Figure 1).

The crystal lattice consists of the $\text{Cr}_2\text{Cl}_2(\text{apdol-H}_{0.5}\text{-N,N',O,O'})_2^+$ cation, a perchlorate anion, and one DMF of crystallization. Each Cr(III) is six-coordinate, four sites being occupied by two N atoms and two O atoms of the tripodal ligand, with the O, N, and O atoms of the diethanolamine component in a facial configuration. The fifth site is occupied by a chloro ligand trans to a deprotonated O atom, which in turn acts as a bridge, completing the octahedron. An unsymmetrical hydrogen bond between the other two O atoms accounts for the single positive charge on the dinuclear cation, and these two O atoms can be formally regarded as half-protonated.

Table IV. Observed and Calculated Pseudo-First-Order Rate Constants for the Aquation of $[\text{CrCl}(\text{apdol-H}_2)(\text{OH}_2)]^{2+}$ in 0.1 M HNO_3

$T, ^\circ\text{C}$ [K]	$10^4k_{\text{obsd}}^a$	$10^4k_{\text{calcd}}^b$
49.8 [323.0]	16.3 ± 0.3	16.4
45.0 [318.2]	10.4 ± 0.2	10.4
40.0 [313.2]	6.48 ± 0.1	6.35
30.0 [303.2]	2.23 ± 0.04	2.26
25.0 [298.2]		1.31

^a Mean \pm standard deviation of at least two determinations at each particular temperature. All rate constants were included in the calculation of the activation parameters. ^b Calculated from the following activation parameters: $E_a = 81.7 \pm 0.6 \text{ kJ mol}^{-1}$; $\log(PZ) = 10.428$; $\Delta S_{298.2}^\ddagger = -53.6 \pm 1.2 \text{ J K}^{-1} \text{ mol}^{-1}$.

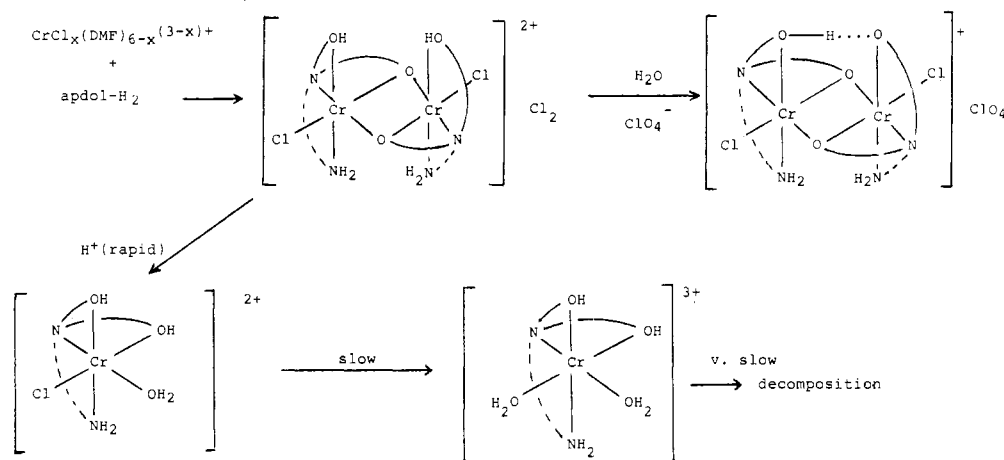
**Figure 2.** Perspective view of the Co trimer.

The visible absorption spectrum of 0.1 M HNO_3 solutions of $[\text{Cr}_2\text{Cl}_2(\text{apdol-H-N,N',O,O'})_2]\text{Cl}_2$ slowly changes with time (isosbestic points at 394, 460 and 555 nm), and chloride ion is released. Table IV lists the spectrophotometrically determined pseudo-first-order rate constants for the reaction $\text{CrCl}(\text{apdol-H}_2)(\text{OH}_2)^{2+} \rightarrow \text{Cr}(\text{apdol-H}_2)(\text{OH}_2)_2^{3+} + \text{Cl}^-$ (see Discussion). Chloride ion release is greatly accelerated by addition of Hg^{2+} , and heated (60 $^\circ\text{C}$) solutions of the product slowly lose absorption intensity without the generation of isosbestic points.

Co Complexes. Reaction of apdol-H_2 with $\text{Na}_3\text{Co}(\text{NO}_2)_6$ in aqueous solution results in the precipitation of an orange-brown powder of unknown composition. This water-insoluble solid readily dissolves in 3 M acetic acid to give an orange solution, and on addition of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$, X-ray quality, lustrous, dark brown crystals of $\text{meso-}[\text{Co}_3(\mu\text{-NO}_2\text{-N,O})_2(\mu\text{-CH}_3\text{CO}_2\text{-O,O'})_2(\mu\text{-apdol-H-N,N',O,O'})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ deposit over three days at room temperature. The stoichiometry and structure of this product were determined by single-crystal X-ray analysis (Figure 2).

In the cation, each Co is six-coordinate, four sites on each of the tripodal amino alcohol, with the O, N, and O atoms of the diethanolamine component in the facial configuration. A coordinated nitro-N group is trans to the N bridgehead of the amino alcohol and an acetato-O ligand completes the coordination sphere.

The central Co atom is held by bridging pairs of nitro-O, acetato-O, and deprotonated apdol-O atoms in a trans, trans, trans configuration. The water molecules of crystallization and the perchlorate anions are linked to the cation by hydrogen bonds. Hydrogen atoms on the protonated arms of the apdol ligands are bonded to the O atoms of the water molecules, and in turn, two H atoms on a water molecule are linked to an acetato-O (bridging) atom and one of the perchlorate oxygen atoms, respectively.

Scheme I. Synthetic and Kinetic Pathways for the Cr(III) Complexes^a

^aFive-membered chelate rings are indicated by a solid curve, six-membered rings are indicated by a dashed curve, and hydrogen bonds are depicted as O-H...O.

Table V. Comparable Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg)

Cr ₂		Cr ₂		Co ₃	
Bond Lengths					
N(11)-C(11)	1.509 (4)	N(21)-C(21)	1.507 (5)	N(11)-C(11)	1.492 (3)
N(11)-C(14)	1.506 (5)	N(21)-C(24)	1.501 (5)	N(11)-C(14)	1.497 (3)
N(11)-C(16)	1.482 (5)	N(21)-C(26)	1.491 (5)	N(11)-C(16)	1.510 (3)
C(11)-C(12)	1.509 (6)	C(21)-C(22)	1.517 (5)	C(11)-C(12)	1.517 (3)
C(12)-C(13)	1.523 (6)	C(22)-C(23)	1.518 (6)	C(12)-C(13)	1.518 (3)
C(13)-N(12)	1.479 (5)	C(23)-N(22)	1.484 (6)	C(13)-N(12)	1.488 (3)
C(14)-C(15)	1.512 (5)	C(24)-C(25)	1.524 (6)	C(14)-C(15)	1.512 (3)
C(15)-O(11)	1.419 (5)	C(25)-O(21)	1.425 (4)	C(15)-O(11)	1.416 (2)
C(16)-C(17)	1.515 (5)	C(26)-C(27)	1.519 (6)	C(16)-C(17)	1.516 (3)
C(17)-O(12)	1.436 (5)	C(27)-O(22)	1.432 (4)	C(17)-O(12)	1.445 (3)
Bond Angles					
N(11)-Cr(1)-O(12)	82.7 (1)	N(21)-Cr(2)-O(22)	83.2 (1)	N(11)-Co(1)-O(12)	86.2 (1)
C(11)-N(11)-C(16)	108.2 (3)	C(21)-N(21)-C(26)	106.3 (3)	C(11)-N(11)-C(16)	111.2 (2)
C(14)-N(11)-C(16)	112.3 (3)	C(24)-N(21)-C(26)	112.8 (3)	C(14)-N(11)-C(16)	108.3 (2)
C(11)-N(11)-C(14)	109.3 (3)	C(21)-N(21)-C(24)	110.1 (3)	C(11)-N(11)-C(14)	108.5 (2)
O(11)-Cr(1)-O(12)	90.9 (1)	O(21)-Cr(2)-O(22)	90.2 (1)	O(11)-Co(1)-O(12)	90.8 (1)
N(11)-Cr(1)-N(12)	92.8 (1)	N(21)-Cr(2)-N(22)	92.2 (1)	N(11)-Co(1)-N(12)	95.0 (1)
O(11)-Cr(1)-N(11)	83.9 (1)	O(21)-Cr(2)-N(21)	84.2 (1)	O(11)-Co(1)-N(11)	86.6 (1)
Torsion Angles					
N(11)-C(14)-C(15)-O(11)	42.6 (4)	N(21)-C(24)-C(25)-O(21)	41.0 (4)	N(11)-C(14)-C(15)-O(11)	50.5 (2)
N(11)-C(16)-C(17)-O(12)	-42.8 (4)	N(21)-C(26)-C(27)-O(22)	-43.0 (4)	N(11)-C(16)-C(17)-O(12)	34.0 (2)
N(11)-C(11)-C(12)-C(13)	65.1 (4)	N(21)-C(21)-C(22)-C(23)	66.3 (5)	N(11)-C(11)-C(12)-C(13)	-69.7 (2)
C(11)-C(12)-C(13)-N(12)	-67.9 (5)	C(21)-C(22)-C(23)-N(22)	-65.3 (4)	C(11)-C(12)-C(13)-N(12)	64.3 (3)

Discussion

Previous work on the transition-metal chemistry of amino alcohols suggests that, although the expected analogues of polyamine complexes can be prepared,^{14,15} the introduction of the -OH group in the ligand more often than not introduces unusual structural modifications.⁴ Thus, while the synthetic routes used here give polyamine complexes of the type CrCl₃L and Co(NO₂)₃L (L = dien, 2,3-tri)^{16,17} the amino alcohol analogues, aeol-H and apol-H yield green dinuclear alkoxo-bridged complexes Cr₂L₂Cl₄ (L = aeol, apol) for Cr(III)¹⁶ and a variety of products¹⁸⁻²⁰ for Co(III), including [Co(NO₂)₂(aeol-H-N,N')₂]ClO₄¹⁶ and [Co(NO₂)₂(aeol-N,N',O)(aeol-H-N,N')₂]ClO₄.¹⁶

Although the violet complex formed with Cr(III) and apdol-H₂ has the nonelectrolyte empirical formula [CrCl₂(apdol-H)], it

behaves in water as a typical 1:1 electrolyte giving a monoperochlorate salt and in dilute HNO₃ as a typical monochloro cation. The structure of [Cr₂Cl₂(apdol-H_{0.5}N,N',O,O')₂]ClO₄·DMF (Figure 1) suggests that the original complex is best formulated as [Cr₂Cl₂(apdol-H)₂]Cl₂ (Scheme I).

In acid solution, these dimers are rapidly protonated to give two monomeric units of CrCl(apdol-H₂)(OH₂)²⁺ and the chloride salt can be isolated (Scheme I). However, we cannot at this stage entirely exclude the less likely formulation CrCl(apdol-H₂-N,N')(OH₂)₃²⁺ for this complex. Nevertheless, the above behavior entirely parallels that of Cr₂(enol-H_{0.5})₆³⁺,⁹ and we have no evidence for a two-phase chloride-release reaction that would be expected if the dimeric unit were maintained.

The resulting *cis*-chloroaqua complex slowly aquates with kinetic parameters (Table IV) similar to those observed for the chloride release from *cis*-CrCl(en)(tn)(OH₂)²⁺ (*k*(298.2), 0.1 M HClO₄ = 1.03 × 10⁻⁴ s⁻¹, E_a = 78.7 kJ mol⁻¹, ΔS₂₉₈[‡] = -66 J K⁻¹ mol⁻¹).²¹ The diaqua product (Scheme I) is generated more rapidly in Hg²⁺/HNO₃ (μ = 1.0 M) solutions, and the resulting

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Table VI. Interatomic Distances (Å) in $[\text{Cr}_2\text{Cl}_2(\text{apdol}-\text{H}_{0.5}-\text{N},\text{N}',\text{O},\text{O}')_2]\text{ClO}_4\cdot\text{DMF}$ and $[\text{Co}_3(\text{NO}_2)_2(\text{CH}_3\text{CO}_2)_2(\text{apdol}-\text{H}-\text{N},\text{N}',\text{O},\text{O}')_2](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$

		Cr_2	
Cr(1)–Cl(1)	2.301 (1)	Cr(2)–Cl(2)	2.315 (1)
Cr(1)–N(12)	2.056 (3)	Cr(2)–N(22)	2.069 (4)
Cr(1)–N(11)	2.090 (3)	Cr(2)–N(21)	2.068 (3)
Cr(1)–O(12)	1.993 (3)	Cr(2)–O(22)	1.994 (3)
Cr(1)–O(11)	1.965 (3)	Cr(2)–O(21)	1.960 (3)
Cr(1)–O(21)	1.959 (3)	Cr(2)–O(11)	1.967 (3)
O(12)–O(22)	2.414 (3)	O(12)–H(12e)	1.046 (41)
O(22)–H(12e)	1.370 (42)	Cr(1)–Cr(2)	2.992 (1)
Cl(3)–O(31)	1.428 (3)	Cl(3)–O(32)	1.424 (4)
Cl(3)–O(33)	1.414 (4)	Cl(3)–O(34)	1.436 (5)
C(1)–N(1)	1.435 (7)	C(2)–N(1)	1.452 (6)
N(1)–C(3)	1.327 (6)	C(3)–O(1)	1.236 (5)
		Co_3	
Co(1)–N(11)	1.990 (2)	Co(1)–N(12)	1.968 (2)
Co(1)–O(11)	1.878 (1)	Co(1)–O(12)	1.917 (1)
Co(1)–N(21)	1.940 (2)	Co(1)–O(31)	1.891 (1)
Co(2)–O(32)	2.080 (1)	Co(2)–O(11)	1.970 (1)
Co(2)–O(21)	2.140 (2)	Co(2)–O(32)	2.080 (1)
N(21)–O(21)	1.262 (3)	N(21)–O(22)	1.226 (3)
O(31)–C(31)	1.275 (3)	O(32)–C(31)	1.243 (3)
C(31)–C(32)	1.508 (3)	Cl(4)–O(41)	1.438 (2)
Cl(4)–O(42)	1.424 (2)	Cl(4)–O(43)	1.436 (2)
Cl(4)–O(44)	1.421 (2)	O(32)–O(51)	2.860 (3)
O(12)–O(51)	2.559 (3)	O(51)–O(43)	2.751 (3)
O(32)–H(51a)	2.143 (28)	H(51a)–O(51)	0.735 (29)
O(51)–H(51b)	0.772 (26)	H(51b)–O(43)	1.979 (31)
O(12)–H(12e)	0.895 (22)	H(12e)–O(51a)	1.672 (23)

spectral changes indicate slow decomposition, again similar to but less rapid than that observed in the $\text{Cr}(\text{enol}-\text{H})_3^{3+}$ system.⁹

The topology of the tripodal ligand in both the Cr_2 and Co_3 complexes is similar, as are the majority of the comparable bond lengths (Table V), and in both cases, the six-membered rings adopt a chair conformation. In the $\text{Cr}(\text{III})$ dimer, both halves of the cation have the same chirality with the five-membered rings in the δ, λ conformation, and the structure consists of equal amounts of the $\Delta\Delta$ and $\Lambda\Lambda$ forms. Consequently, the chloro ligands have a trans orientation with respect to the Cr_2O_2 core.

The Co_3 complex is meso, with Δ and Λ chelate ring arrangements on each of the terminal Co atoms. This results in the $\lambda\lambda$ conformation for the five-membered rings, and the ring involved in the bridging is considerably flattened (Table V). One other difference between the structures is that in the Cr_2 case, the arm trans to the monodentate ligand (chloro) is bridging, whereas in the Co_3 structure it is the arm trans to the terminal NH_2 of the six-membered ring.

Within the $\text{Cr}(\text{III})$ dimer, the Cr–Cr distance is 2.992 (1) Å, comparable to similar distances observed for μ -dihydroxo $\text{Cr}(\text{III})$ dimers (3.05 Å),^{22–25} and despite the fact that the coordinated chloro ligand is trans to a deprotonated alkoxo group, the Cr–Cl distance of 2.31 (1) Å is similar to that observed when the Cl ligand is trans to a nitrogen donor (2.33 Å).²⁶

The five-membered amino alcohol chelate rings are more regular in the $\text{Cr}(\text{III})$ complex than in the Co trimer. In the former, the rings are remarkably similar to those observed for 1,2-diaminoethane coordinated to $\text{Cr}(\text{III})$ with mean N–Cr–O bond angles of 83.5° (cf. 83.1° for N–Cr–N in $\text{Cr}(\text{en})(\text{ox})_2^{-}$)²⁷ and mean torsion angles of $\pm 42.4^\circ$. The mean of the N–Cr–N angles subtended in the six-membered rings (92.5°) is again similar to those observed when 1,3-diaminopropane is bound to $\text{Cr}(\text{III})$.²⁸

Table VII. Selected Bond Angles (deg)

		Cr_2	
Cr(1)–O(11)–Cr(2)	99.0 (1)	Cr(1)–O(21)–Cr(2)	99.5 (1)
O(11)–Cr(1)–O(21)	79.1 (1)	O(11)–Cr(2)–O(21)	79.0 (1)
N(11)–Cr(1)–Cl(1)	99.7 (1)	N(21)–Cr(2)–Cl(2)	98.6 (1)
Cl(1)–Cr(1)–O(21)	79.6 (1)	Cl(2)–Cr(2)–O(11)	98.5 (1)
O(12)–Cr(1)–Cl(1)	91.6 (1)	O(22)–Cr(2)–Cl(2)	91.9 (1)
O(12)–H(12e)–O(22)	175.5 (3.7)		
		Co_3	
N(12)–Co(1)–O(12)	90.5 (1)	N(12)–Co(1)–N(21)	90.3 (1)
O(11)–Co(1)–N(21)	88.1 (1)	O(12)–Co(1)–N(21)	87.2 (1)
N(11)–Co(1)–O(31)	91.3 (1)	N(12)–Co(1)–O(31)	84.6 (1)
O(11)–Co(1)–O(31)	94.2 (1)	N(21)–Co(1)–O(31)	95.8 (1)
O(11)–Co(2)–O(21)	82.7 (1)	O(11)–Co(2)–O(32)	93.1 (1)
O(21)–Co(2)–O(32)	86.4 (1)		
O(32)–H(51a)–O(51)	165.1 (1.5)	O(12)–H(12e)–O(51)	170.3 (1.5)
H(51a)–O(51)–H(51b)	109.3 (2.9)	O(51)–H(51b)–O(43)	178.2 (1.5)

The five-membered rings in the Co complex are rather distorted with torsion angles of 50.5 and 43.1°, but the N–Co–O angles ($\sim 86.4^\circ$) subtended in these amino alcohol rings are similar. The observed N–Co–N bond angle of 95.0° for the six-membered ring is similar to the values observed for other $\text{tn}-\text{Co}(\text{III})$ complexes.

The apdol ligand also allows a comparison of tertiary amine bonding vs primary amine bonding to the metal centers. The tertiary nitrogen to Co bond length is 0.02 Å longer than the Co– NH_2 distance, but there appears to be no systematic difference between the two distances in the $\text{Cr}(\text{III})$ dimer.

Both structures contain hydrogen bonds (Tables VI and VII). The unsymmetrical intramolecular hydrogen bond in the $\text{Cr}(\text{III})$ dimer is apparently formed in aqueous solution (Scheme I), and although similar hydrogen-bonded systems have been observed previously for amino alcohol complexes, these seem to be restricted to intermolecular situations, eg. $\text{Co}_2(\text{enol}-\text{H}_{0.5})_6^{3+}$.⁸ For the single hydrogen bond observed (Figure 1) the O–O distance is 2.414 (3) Å with O–H distances of 1.37 (4) and 1.05 (4) Å. These are quite similar to previously observed unsymmetrical intermolecular hydrogen bonds formed by coordinated amino alcohols (O–O = 2.33 Å; O–H = 1.38, 1.09 Å).¹¹

The protonated arms of the apdol ligand in the Co trimer are also involved in hydrogen bonding, in this case to the O atoms of the lattice water (O–O distances = 2.559 (3) Å (Figure 2). The H atoms of these water molecules are in turn linked to the bridging acetate oxygens (at the central Co), and to an oxygen atom of the perchlorate anions, respectively. Here the bonds are somewhat longer, with O–O distances of 2.860 (3) and 2.751 (3) Å, respectively.

Finally there is the question of the oxidation state of the central atom in the Co trimer. From the following evidence, we suggest a $\text{Co}(\text{III})-\text{Co}(\text{II})-\text{Co}(\text{III})$ arrangement: (a) no product is obtained in the initial reaction between apdol- H_2 and $\text{Na}_3\text{Co}(\text{NO}_2)_6$ until effervescence has occurred, indicating the formation of $\text{Co}(\text{II})$; (b) the trimer is paramagnetic, and no meaningful 13-C NMR spectrum could be obtained; (c) dissolution of the trimer in 12 M HCl immediately produces a deep blue-green color, indicating the facile formation of CoCl_4^{2-} ; (d) it is not expected that $\text{Co}(\text{III})$ would be stable in an O_6 donor environment; (e) the stoichiometry, charge balance, and symmetry nicely fit a $\text{Co}(\text{III})-\text{Co}(\text{II})-\text{Co}(\text{III})$ array.³¹ In this respect, a similar structural arrangement has been proposed for $[\text{Co}_3(\text{enol})_6]\text{Cl}_2$,⁵ although here the central $\text{Co}(\text{II})$ is trigonal prismatic.

Conclusion

Of pedagogical interest is the fact that in both $\text{Cr}(\text{III})$ dimers and for the terminal $\text{Co}(\text{III})$ atoms in the Co trimer there are formally six different types of donor groups bound to the central metal. Four common but different groups arise from the N-, N,O,O-donor atoms of the bifurcated tripodal ligand, viz. a primary amine, a tertiary nitrogen bridgehead, a bridging alkoxo oxygen, and a protonated or internally hydrogen bonded oxygen donor.

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For the two Cr(III) dimers, the remaining two sites are occupied by a chloro ligand and a bridging alkoxo oxygen from the second apdol ligand, while in the Co trimer, the remaining two sites are occupied by nitro-*O* and acetato-*O* oxygen donors. Perhaps these are not quite as spectacular as Geldman's example²⁹ [Pt(py)-

(NH₃)(NO₂)(Cl)(Br)(I)], but they are certainly members of this rather rare situation.

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Supplementary Material Available: Listings of atomic parameters for non-hydrogen atoms, bond lengths, bond angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom parameters for the Cr(III) dimer and Co trimer (10 pages); listings of structure factors for both compounds (42 pages). Ordering information is given on any current masthead page.

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(30) The nomenclature adopted here is that the free ligand will be given an abbreviation, followed by the number of H atoms attached to oxygen in the alcohol form. On successive deprotonation, these will be reduced from the ligand abbreviation to give the number of H atoms remaining. The number and type of coordinated donor atoms will be indicated in the formula of the complex, after the ligand abbreviation. We use the following: NH₂(CH₂)₂OH, enol-H; NH₂(CH₂)₃OH, tnol-H; NH₂(C-H₂)₂NH(CH₂)₂OH, 2-((2-aminoethyl)amino)ethanol, aeol-H; NH₂(C-H₂)₃NH(CH₂)₂OH, 2-((3-aminopropyl)amino)ethanol, apol-H; NH₂(CH₂)₃N(CH₂CH₂OH)₂, *N*-(3-aminopropyl)diethanolamine; apdol-H₂; NH₂(CH₂)₂NH₂, en; NH₂(CH₂)₃NH₂, tn; NH₂(CH₂)₂NH(CH₂)₂NH₂, diethylenetriamine, dien (2,2-tri); NH₂(CH₂)₂NH(CH₂)₃NH₂, *N*-(2-aminoethyl)-1,3-diaminopropane (2,3-tri). Thus, the completely chelated *N*-(3-aminopropyl)diethanolamine with all H atoms present will be represented as (apol-H₂-*N,N',O,O*).

(31) Further support for this arrangement is provided by the X-ray bonding geometry in which the Co-O bond lengths to the central cobalt are significantly longer than those to the terminal cobalt atoms, consistent with the greater ionic radius of Co(II) relative to Co(III). We thank a reviewer for this observation.

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Synthesis and Cluster Interconversion Chemistry of a Linear Trinuclear Hexakis(μ -benzenethiolato)triiron(II) Hexacarbonyl Compound

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The neutral compound Fe₃(SPh)₆(CO)₆ (**1**) assembles in a solution containing NaSPh and FeCl₂ in a 2:1 ratio in ethanol under an atmosphere of carbon monoxide at room temperature. It also forms in the reaction of the Fe₄(SPh)₁₀²⁻ ion with CO and FeBr₂ and by the oxidative addition of PhSSPh to an Fe(0) carbonyl species with UV irradiation in an inert atmosphere under ambient conditions. Product **1** was characterized by X-ray diffraction and found to be a linear trinuclear complex in which the benzenethiolate ligands occupy bridging positions and the carbonyl ligands are exclusively terminally bonded. Crystal data are space group *P*2₁/*n* with *a* = 11.077 (1) Å, *b* = 10.488 (1) Å, *c* = 19.052 (2) Å, β = 95.41 (6)°, *V* = 2203.52 Å³, and *Z* = 2. On the basis of the observed octahedral coordination of each of the iron atoms in **1**, it is suggested that octahedral coordination may occur in the limit of unrestricted CO binding in the CO-inhibited states of iron-sulfur enzymes. Compound **1** converts to Fe(SPh)₄²⁻ (**2**) in neat Me₂SO solution where the counterion is probably Fe(Me₂SO)₆²⁺. The compound [Fe(Me₂SO)₆][Fe₄(SPh)₁₀] (**3**) is formed in a mixed solution of Me₂SO/THF (1:25, v/v) and can be isolated as brown crystals. The self-assembly of these clusters in lieu of others that could form with the same Fe:thiolate ratio suggests that those which are obtained represent clusters with particularly stable structures. The formation of clusters in such "stoichiometrically free" environments suggests new approaches to the study of cluster formation.

The role of carbon monoxide as a potent dead end inhibitor of the iron-sulfur enzyme hydrogenase^{1,2} and the molybdenum-iron-sulfur enzyme nitrogenase³ has stimulated our interest in synthetic iron-sulfur carbonyl complexes. In tandem with our study of CO binding to preformed iron-sulfur clusters in proteins and model compounds, we have attempted syntheses of iron-sulfur carbonyl compounds from simple precursors. This report delineates syntheses of a series of iron-sulfur (Fe-S) compounds, beginning with the neutral carbonyl cluster Fe₃(SPh)₆(CO)₆ (**1**) (Ph = C₆H₅), which forms under carbon monoxide in a solution containing sodium benzenethiolate and ferrous chloride in a 2:1 ratio. This complex provides insight into the preferred stereochemistry of Fe(II)-sulfur carbonyl complexes and is relevant to the interaction of CO and Fe-S enzyme active sites. In the coordinating solvent Me₂SO, CO is displaced as a terminal ligand in complex **1** followed by cluster rearrangement, leading to the formation of Fe(SPh)₄²⁻ (**2**) with solvated Fe(II) as a counterion in solution, and [Fe(Me₂SO)₆][Fe₄(SPh)₁₀] (**3**), which is isolated as a crystalline solid.

In the area of iron-sulfur carbonyl chemistry there has traditionally been an emphasis on compounds derived from the oxidative addition reactions of iron carbonyl compounds with alkyl or phenyl disulfides, resulting in Fe(I) compounds with bridging mercaptides or disulfides.⁴⁻¹¹ Recently, studies have appeared which focus on iron(II)-sulfur carbonyl compounds whose ster-

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