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Trinuclear Oxothiomolybdates from the Reductive Cleavage of $[Mo_8O_{26}]^{4-}$ with Hexamethyldisilthiane

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Reaction of an isomeric mixture of $[Mo_8O_{26}]^{4-}$ (α:$\beta \sim 7$:1) with 1–8 equiv of $(Me_3Si)_2S$ in acetonitrile resulted in cleavage of the cage structure(s) and partial reduction of Mo(VI). From the 8-equiv reaction system conducted on a preparative scale, a dark red, diamagnetic crystalline material, $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$, was isolated. The crystals are monoclinic with a = 15.987 (3) Å, b = 15.344 (3) Å, c = 20.443 (3) Å, β = 103.75 (1)°, Z = 4, and space group $P2_1/c$. With 4391 unique data ($F_o^2 > 3\sigma(F_o)^2$) the structure was refined to R (R_w) = 4.4 (4.8)%. The crystal contains essentially equal amounts of two anions, $[Mo_3S_8O_2]^{2-}$ = $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoO(\mu\text{-}S)_2MoS_2]^{2-}$ and $[Mo_3S_7O_3]^{2-}$ = $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoO(\mu\text{-}S)_2MoOS]^{2-}$, differing only in the identity of one terminal ligand. These anions contain known structural fragments, which have not been previously assembled in a single species. Structural results suggest the Mo oxidation state description VI–IV–VI, with the central atom being Mo(IV). NMR spectra reveal four or five and three resolvably different ^{17}O and ^{95}Mo environments, respectively. Spectral assignments are proposed. The currently characterized set of oxothiomolybdates includes the foregoing complexes, $[MoOS_8]^{2-}$, $[Mo_2S_6O_2]^{2-}$, $[Mo_2S_7O_4]^{2-}$, and $[Mo_3OS_8]^{2-}$. The present results and those for systems containing $[Mo_2O_7]^{2-}$ show that O/S ligand substitution is accompanied by partial reduction of Mo(VI) and skeletal Mo–O bond cleavage. It appears unlikely that sulfide-substituted versions of intact polyoxomolybdate structures are attainable, at least with $(Me_3Si)_2S$ as the sulfide source.

Introduction

In previous investigations we have provided demonstrations of the replacement of terminal (M═O) and doubly bridging (M—O—M) oxo ligands with sulfide by use of the reagent hexamethyldisilthiane[1-3] ($(Me_3Si)_2S$). This reagent can also replace other types of oxygen ligands, such as those in $M(OEt)_5$, to give the open-cage complexes $[M_6S_{17}]^{4-}$ (M = Nb(V), Ta(V)).[4] These species are members of a rapidly enlarging set of new compounds, viz., soluble salts of oxothiometalates $[M_nO_xS_y]^{z-}$ and thiometalates $[M_nS_y]^{z-}$ in which the ligands are oxide (oxo), peroxide, sulfide, persulfide, and polysulfide or combinations of these. The rapid growth of this area is evident by, e.g., the synthesis and structural characterization of some eight polynuclear thiocuprates in 1983–1984[5] and, more pertinent to the present work, eleven oxothio-[6-9] and thiomolybdates[6,10-14] since 1979. Most of the latter compounds ultimately derive from reactions of the simplest members of the set, $[MoO_{4-n}S_n]^{2-}$[15,16] (n = 0–4).

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$

formula	$C_{32}H_{72}N_2Mo_3S_{7.45}O_{2.55}$
mol wt	1052.44
a, Å	15.987 (3)
b, Å	15.344 (3)
c, Å	20.443 (3)
β, deg	103.75 (1)
cryst syst	monoclinic
V, Å^3	4871 (1)
Z	4
d_{calcd}, g/cm^3	1.44
d_{obsd}, g/cm^3	1.43^a
space group	$P2_1/c$
cryst dimens, mm	0.30 × 0.42 × 0.50
radiation	Mo Kα (λ = 0.71069 Å)
abs coeff μ, cm^{-1}	10.8
scan speed, deg/min	2.0–29.3 (ω scan)
2θ limits	3° ≤ 2θ ≤ 52°
scan range, deg	0.8
bkgd/scan time ratio	0.25
no. of data collcd	8575 ($+h,+k,\pm l$)
no. of unique data ($F_o^2 > 3\sigma(F_o^2)$)	4391
no. of variables	434
goodness of fit (GOF)^b	1.16
R,^{c} %	4.4
R_w,^{d} %	4.8

^{a} Determined by the neutral buoyancy technique in CCl_4/n-hexane. ^{b} GOF = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$; $w = [\sigma^2(F) + gF_2]^{-1}$, with g = 0.00105. ^{c} $R = [\sum||F_o| - |F_c||/\sum|F_o|]$. ^{d} $R_w = [\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$.

We have been examining the possibility of synthesizing new polynuclear oxothio- and/or thiomolybdates by O/S substitution reactions of preformed polyoxomolybdates.[17] With the simplest such species, $[Mo_2O_7]^{2-}$, reaction 1 ensues, resulting in cleavage

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$$[Mo_2O_7]^{2-} + (Me_3Si)_2S \rightarrow [MoO_3(OSiMe_3)]^- + [MoO_2S(OSiMe_3)]^- \quad (1)$$

of the single Mo–O–Mo bridge.[3] Thereafter, terminal oxo substitution proceeds as in reaction 2. Mechanisms for these reactions

$$[MoO_{3-x}S_x(OSiMe_3)]^- + (Me_3Si)_2S \rightarrow [MoO_{3-x-1}S_{x+1}(OSiMe_3)]^- + (Me_3Si)_2O \quad (2)$$

have been proposed.[3] Product distributions in both reactions indicate that ligand substitution is accompanied by an extent of reduction of Mo(VI) by the sulfide reagent. With larger ions such as $[Mo_6O_{19}]^{2-}$ and $[Mo_8O_{26}]^{4-}$, the cage structure and different ratios of bridging and terminal ligands suggest a reaction pattern dissimilar to that of $[Mo_2O_7]^{2-}$,[3] possibly affording polynuclear products. This matter has been investigated in the system $[Mo_8O_{26}]^{4-}/(Me_3Si)_2S$, and the initial results are reported here.

Experimental Section

Preparation of $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$. All operations were performed under a pure dinitrogen atmosphere. To a vigorously stirred, colorless solution of 2.0 g (0.93 mmol) of α-$(n\text{-}Bu_4N)_4[Mo_8O_{26}]$[18] in 40 mL of DMF was added dropwise 1.56 mL (7.43 mmol) of $(Me_3Si)_2S$ (Petrarch Systems). A sequential color change to yellow, red, bright red, and then brown-red was observed upon stirring (24 h, room temperature). No precipitate formed during this time. The solution was treated with anhydrous ether until cloudiness became evident. After standing for 1–2 h at −20 °C, the mixture was filtered to remove a light orange solid material. The procedure was repeated until the formation of this material ceased. The red-brown filtrate was treated with sufficient ether to cause separation of a dark-red oily phase. The oil solidified upon vigorous scratching and storage at −20 °C. The crude product was collected by filtration, washed with ether, and dried in vacuo. Three recrystallizations from acetonitrile afforded 0.30 g (12%) of pure product as dark red crystals. Anal. Calcd for $C_{32}H_{72}Mo_3N_2O_{2.55}S_{7.45}$: C, 36.52; H, 6.90; Mo, 27.35; N, 2.66; S, 22.70. Found: C, 36.77; H, 6.94; Mo, 27.54; N, 2.68; S, 21.47. Absorption spectrum (acetonitrile): λ_{max} 272 nm (ϵ_M 19 600), 320 (sh, 11 600), 376 (10 200), 442 (8830), 480 (sh, 5640). IR spectrum (KBr): 962, 943, 910 (sh), 905 (all vs, $\nu_{Mo=O}$), 527 (m, $\nu_{Mo=S}$), 508 (s, ν_{S-S}), 480 (m, ν_{Mo-S}) cm^{-1}.

Collection and Reduction of X-ray Data. Dark red rectangular crystals were grown by slow vapor diffusion of ether into a solution of $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$ in DMF at room temperature. A suitable crystal was sealed in a glass capillary under dinitrogen. Diffraction experiments were performed with a Nicolet P3f four-circle automated diffractometer with graphite-monochromatized Mo Kα radiation. The orientation matrix and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections having 20° ≤ 2θ ≤ 25°. Data were collected at ~23 °C. No decay of the intensities of three standard reflections monitored every 123 reflections was observed. Details of the data collection and crystal parameters are summarized in Table I. Data reduction and an empirical absorption correction were performed with the programs XTAPE and XEMP, respectively, of the SHELXTL structure determination program package (Nicolet XRD Corp., Madison, WI). Maximum and minimum transmission factors were 0.672 and 0.630, respectively. After equivalent reflections were merged, R_{merg} was 1.9%. The systematic absences $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$) uniquely indicated the space group to be $P2_1/c$. This was confirmed by successful solution and refinement of the structure.

Structure Solution and Refinement. The direct-methods program SOLV revealed the positions of the three Mo atoms. The remaining nonhydrogen atoms of the anion and cations were found by successive difference Fourier maps and blocked cascade least-squares refinement. Atom scattering factors were taken from a standard source.[19] Further refinement of the structure with isotropic temperature factors of the cations and the anion formulated as $[Mo_3S_7O_3]^{2-}$ converged at R = 9.7%. However, this trial refinement yielded the curious Mo(3)–O(3) terminal distance of 1.97 Å. Anisotropic refinement of all but carbon atoms revealed two peaks, 1 and 2, disposed at 1.67 and 2.28 Å, respectively, from Mo(3) in the direction of the putative Mo(3)–O(3) bond. The positional parameters of peaks 1 and 2 were adopted as (new) positions of atoms O(3) and S(3) with site occupancy factors of 0.5. A series of refinements of all nonhydrogen atoms with anisotropic temperature factors gave a conventional R value of 5.2%. In the final stages of refinement the occupancy factors were optimized to 0.55 and 0.45 for O(3) and S(8), respectively, and hydrogen atoms were included in the cations at 0.96 Å from, and with isotropic thermal parameters 1.2 times those of, the bonded carbon atoms. A final difference Fourier map revealed several random features (≤0.57 e/Å^3) in the vicinity of the cations. Final R factors and other data are included in Table I; atom coordinates are listed in Table II.[20]

Table II. Atom Coordinates ($\times 10^4$) for $(n\text{-}Bu_4N)_2[Mo_3O_{2.55}S_{7.45}]$

atom[b]	x	y	z
Mo(1)	2591 (1)[a]	7692 (1)	4602 (1)
Mo(2)	2273 (1)	9495 (1)	4201 (1)
Mo(3)	2455 (1)	5721 (1)	4429 (1)
S(1)	3277 (1)	8585 (1)	3932 (1)
S(2)	1319 (1)	8536 (2)	4481 (1)
S(3)	1487 (1)	6617 (2)	4704 (1)
S(4)	3331 (1)	6639 (1)	4041 (1)
S(5)	1095 (2)	10275 (2)	3502 (1)
S(6)	2242 (2)	10361 (2)	3221 (1)
S(7)	1816 (2)	4842 (2)	3655 (1)
S(8)	3048 (4)	5103 (3)	5336 (3)
O(1)	3180 (4)	7801 (4)	5381 (2)
O(2)	2731 (4)	10095 (3)	4876 (3)
O(3)	3057 (8)	5115 (7)	5023 (10)
Na	3856 (4)	2430 (4)	−196 (3)
Nb	1151 (4)	7784 (4)	1912 (3)
C(11a)	3898 (6)	3211 (5)	−658 (5)
C(12a)	4732 (5)	3528 (6)	−691 (4)
C(13a)	4759 (7)	4334 (6)	−1055 (6)
C(14a)	5509 (7)	4664 (7)	−1217 (6)
C(21a)	4304 (6)	1658 (5)	−404 (4)
C(22a)	4085 (7)	1352 (6)	−1095 (5)
C(23a)	4531 (6)	503 (6)	−1195 (5)
C(24a)	4201 (8)	211 (8)	−1908 (6)
C(31a)	4221 (6)	2661 (7)	519 (4)
C(32a)	4119 (7)	2056 (8)	1039 (5)
C(33a)	4259 (13)	2384 (11)	1732 (6)
C(34a)	4047 (13)	1911 (14)	2213 (8)
C(41a)	2888 (5)	2210 (6)	−314 (4)
C(42a)	2326 (5)	2729 (7)	−52 (5)
C(43a)	1419 (5)	2518 (6)	−237 (5)
C(44a)	855 (7)	3055 (8)	90 (5)
C(11b)	701 (5)	7814 (5)	2484 (4)
C(12b)	−270 (5)	7681 (6)	2295 (4)
C(13b)	−664 (6)	7809 (7)	2892 (5)
C(14b)	−1623 (6)	7694 (7)	2713 (6)
C(21b)	1037 (6)	6892 (6)	1572 (4)
C(22b)	1340 (8)	6135 (7)	2011 (6)
C(23b)	1344 (8)	5278 (8)	1610 (7)
C(24b)	2042 (10)	5118 (10)	1414 (8)
C(31b)	2101 (5)	7977 (6)	2223 (4)
C(32b)	2662 (6)	7909 (9)	1713 (5)
C(33b)	3565 (8)	8166 (11)	2042 (7)
C(34b)	3644 (9)	9119 (13)	2144 (8)
C(41b)	772 (5)	8446 (5)	1374 (4)
C(42b)	790 (7)	9383 (6)	1621 (5)
C(43b)	492 (9)	10004 (8)	1033 (7)
C(44b)	878 (12)	10693 (11)	1018 (10)

[a] Estimated standard deviations are given in parentheses in this and following tables. [b] Labeling scheme for cation: ⩾Ni–C*j*1i–C*j*2i–C*j*3i–C*j*4i; i = a, b, *j* = 1–4.

^{17}O Enrichments. A solution of 2.0 g of $(n\text{-}Bu_4N)_4[Mo_8O_{26}]$ in 50 mL of acetonitrile was treated with 100 μL of 50% $^{17}OH_2$ (Monsanto Research Corp.). After the solution was stirred for 1 h, sufficient ether was added to cause separation of 1.6 g of enriched product. This material, which was used in ^{17}O NMR monitoring of the reaction with $(Me_3Si)_2S$, was calculated to contain 9.4 atom % ^{17}O on the assumption of complete incorporation of the added isotope. Three times recrystallized $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$ (100 mg) was dissolved in 3.5 mL of CD_3CN to give a ~27 mM solution. After the ^{95}Mo NMR spectrum was recorded, 5 μL of 50% $^{17}OH_2$ was added. The solution was shaken for 20 min, and the ^{17}O NMR spectrum was recorded.

Other Physical Measurements. Electronic and infrared spectra were recorded on a Cary Model 219 and Perkin-Elmer 599B spectrophotometer, respectively. NMR spectra were determined at ~297 K with a

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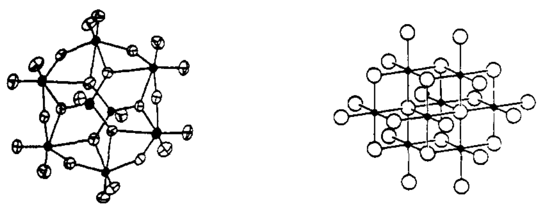
Bruker WM-300 spectrometer operating at 40.69 (^{17}O) or 19.56 (^{95}Mo) MHz. Chemical shifts are reported against 3:1 v/v H_2O (enriched)/CD_3CN (^{17}O) and 2 M Na_2MoO_4 in pH 11 aqueous solution (^{95}Mo). Diamagnetism of reaction products was established by the Faraday method.

Results and Discussion

Of the several previously characterized salts of polyoxomolybdates soluble in nonpolar solvents, reaction media required with the hydrolytically sensitive reagent $(Me_3Si)_2S$, $(n\text{-}Bu_4N)_4[Mo_8O_{26}]$[18] was selected for investigation. This compound has been obtained in anhydrous form and is sufficiently soluble in acetonitrile to facilitate ^{17}O NMR spectral observations. In the crystalline state of this salt the anion exists in the α form **1**,[21] but in acetonitrile solution the isomerization equilibrium (3) is established and favors **1**.[21a,22] The β isomer **2**, which was discovered first,[23] has since been structurally confirmed in several salts.[24]



$$\alpha\text{-}[Mo_8O_{26}]^{4-} \rightleftharpoons \beta\text{-}[Mo_8O_{26}]^{4-} \quad (3)$$

1 **2**

Reaction of $[Mo_8O_{26}]^{4-}$ and $(Me_3Si)_2S$. The ^{17}O NMR spectrum of a ~30 mM solution of ^{17}O-enriched $(n\text{-}Bu_4N)_4[Mo_8O_{26}]$ in CD_3CN exhibited the previously assigned resonances of the α and β isomers.[18,21a] Signal intensities corresponded to the mole ratio α:β ~ 7:1. As has been pointed out,[21] the α isomer can be formulated as $(MoO_4{}^{2-})_2(Mo_6O_{18})$, emphasizing the presence of two incipient molybdate ions (present as $[MoO(\mu_3\text{-}O)_3]^{2-}$) loosely bound above and below a Mo_6O_{18} ring composed of distorted $MoO_2(\mu\text{-}O)_2$ tetrahedra. This fragment formulation, together with dominance of the α isomer and the presence of terminal oxo ligands in the ring, raised the prospect of incorporation of bridging and terminal sulfide ligands in the cage structure.

The foregoing solution of $[Mo_8O_{26}]^{4-}$ was treated with n = 1, 2, 4, 6, and 8 equiv of $(Me_3Si)_2S$ in separate experiments, and the reactions were monitored by ^{17}O NMR (not shown). In the n = 1 case, prominent signals of $[MoO_3(OSiMe_3)]^-$ (131, 714 ppm) and $[MoO_2S(OSiMe_3)]^-$ (156, 779 ppm),[3] formed in a ~1:1 ratio, appeared. These increased in intensity up to n = 6, at which point the ratio $[MoO_2S(OSiMe_3)]^-$:$[MoO_3(OSiMe_3)]^-$ = 2.9:1, and then were strongly diminished at n = 8 (ratio 2.1:1). Coincident with these changes at n = 1–8 were a steady decline in the intensities of the $[Mo_8O_{26}]^{4-}$ resonances (most obviously in the α + β terminal oxo feature near 865 ppm), the appearance of a set of signals at ~800–850 ppm, and the growth of signals at 561, 881, and 933 ppm. Resonances of $[MoOS_2(OSiMe_3)]^-$ and $[MoS_3(OSiMe_3)]^-$, previously observed as products of reaction 2,[3] were not detected. These results demonstrate a significant extent of cleavage of the initial cage to produce mononuclear complexes, even at 1 equiv of the sulfide reagent, and the formation of other species, most evident in the n = 4–8 systems, that were not detected as products of reactions 1 and 2. All reaction systems clearly contained mixtures. Because of the virtual absence of $[Mo_8O_{26}]^{4-}$ at n = 8, this system was selected for product identification by synthesis and isolation.

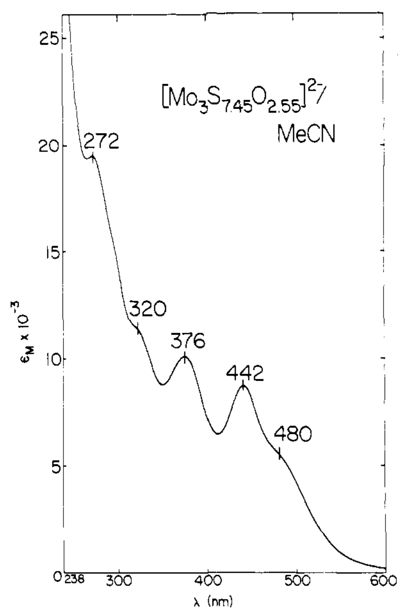


Figure 1. Absorption spectrum of $[Mo_3S_{7.45}O_{2.55}]^{2-}$ in acetonitrile solution.

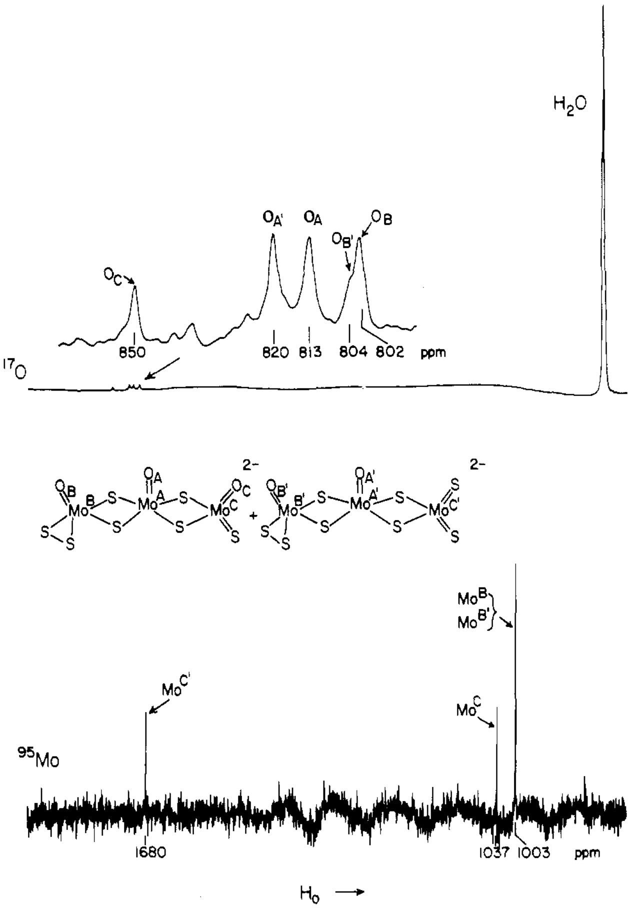


Figure 2. ^{17}O (upper, enriched sample) and ^{95}Mo (lower) NMR spectra of $[Mo_3S_{7.45}O_{2.55}]^{2-}$ in CD_3CN solution. Chemical shifts and tentative assignments are indicated.

On a preparative scale, $(n\text{-}Bu_4N)_4[Mo_8O_{26}]$ in acetonitrile solution was treated with 8.0 equiv of $(Me_3Si)_2S$. After fractionation of a light orange amorphous material (not further examined) by differential solubility, further workup and purification by recrystallization afforded a dark red, highly crystalline, diamagnetic product in modest yield. Its UV–visible absorption spectrum, shown in Figure 1, contains five discernible features, which, on the basis of intensities, are LMCT bands. The spectrum

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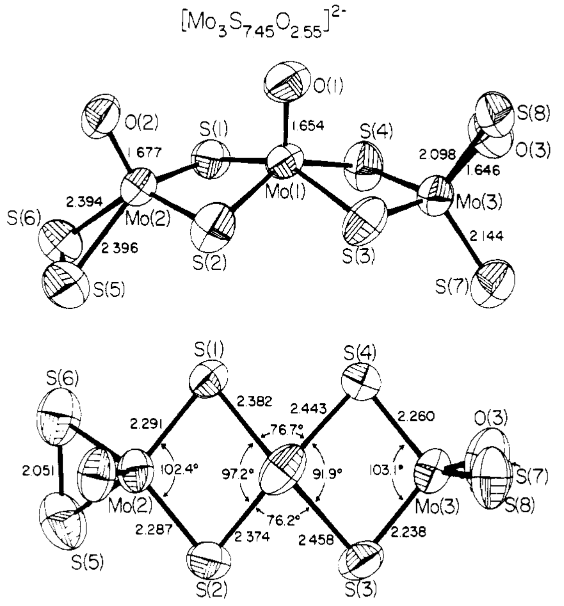
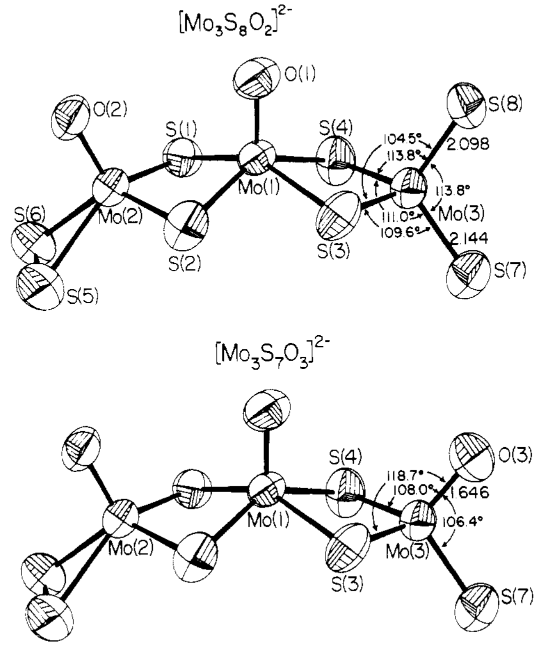

$[Mo_3S_{7.45}O_{2.55}]^{2-}$

Figure 3. Two views of the superimposed structure of $[Mo_3S_8O_2]^{2-}$ and $[Mo_3S_7O_3]^{2-}$ in a crystal of $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$. In this and the following figure, the atom-labeling scheme, 50% probability ellipsoids, and selected bond angles and distances are given.


$[Mo_3S_8O_2]^{2-}$

$[Mo_3S_7O_3]^{2-}$

Figure 4. Separate structures of $[Mo_3S_8O_2]^{2-}$ and $[Mo_3S_7O_3]^{2-}$, emphasizing differences at the Mo(3) site.

is somewhat similar to those of certain perturbed $[MoS_4]^{2-}$ chromophores in binuclear complexes of this ion.[25,26] The ^{17}O NMR spectrum shown in Figure 2 reveals at least four, and probably five, oxygen atom environments. The chemical shift range of 802–850 ppm falls within the interval for terminal $Mo^{VI}{=}O$ groups.[3,27] The ^{95}Mo NMR spectrum (Figure 2) is characterized by narrow lines ($\Delta_{1/2}$ = 12–24 Hz) generally observed for (distorted) tetrahedral Mo(VI). On the basis of the value for $[MoO_2S_2]^{2-}$ (997 ppm), chemical shifts of the three Mo environments are consistent with the presence of at least two sulfide ligands at tetrahedral Mo(VI) sites.[3,28] The ^{17}O NMR signals are those observed in the $n = 8$ reaction system. Resonances at 561, 881, and 933 ppm were not found in the synthetic product and remain unidentified. The collective spectral observations of this product are not sufficiently restrictive to reveal its complete structure, which was obtained by single-crystal X-ray analysis.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$

Mo(1)–S(1)	2.382 (2)	Mo(2)–S(1)	2.291 (2)
Mo(1)–S(2)	2.374 (2)	Mo(2)–S(2)	2.287 (3)
Mo(1)–S(3)	2.458 (2)	Mo(2)–S(5)	2.396 (3)
Mo(1)–S(4)	2.443 (2)	Mo(2)–S(6)	2.394 (3)
Mo(1)–O(1)	1.654 (5)	Mo(2)–O(2)	1.677 (5)
Mo(3)–S(3)	2.238 (3)	S(5)–S(6)	2.051 (4)
Mo(3)–S(4)	2.260 (2)		
Mo(3)–S(7)	2.144 (3)	Mo(1)···Mo(2)	2.896 (1)
Mo(3)–S(8)	2.098 (6)	Mo(1)···Mo(3)	3.047 (1)
Mo(3)–O(3)	1.646 (14)		
S(1)–Mo(1)–S(2)	97.2 (1)	O(1)–Mo(1)–S(1)	105.1 (2)
S(2)–Mo(1)–S(3)	76.2 (1)	O(1)–Mo(1)–S(2)	108.9 (2)
S(3)–Mo(1)–S(4)	91.9 (1)	O(1)–Mo(1)–S(3)	104.0 (2)
S(4)–Mo(1)–S(1)	76.7 (1)	O(1)–Mo(1)–S(4)	106.9 (2)
S(1)–Mo(2)–S(2)	102.4 (1)	O(2)–Mo(2)–S(1)	109.8 (2)
S(2)–Mo(2)–S(5)	89.7 (1)	O(2)–Mo(2)–S(2)	109.5 (2)
S(5)–Mo(2)–S(6)	50.7 (1)	O(2)–Mo(2)–S(5)	110.2 (2)
S(6)–Mo(2)–S(1)	90.8 (1)	O(2)–Mo(2)–S(6)	107.6 (2)
S(3)–Mo(3)–S(4)	103.1 (1)	S(3)–Mo(3)–O(3)	118.7 (6)
S(3)–Mo(3)–S(7)	109.6 (1)	S(4)–Mo(3)–O(3)	108.0 (5)
S(3)–Mo(3)–S(8)	104.5 (2)	S(7)–Mo(3)–O(3)	106.4 (5)
S(4)–Mo(3)–S(7)	111.0 (1)		
S(4)–Mo(3)–S(8)	113.8 (2)		
S(7)–Mo(3)–S(8)	113.8 (2)	Mo(2)–Mo(1)–Mo(3)	155.9 (1)
Mo(1)–S(1)–Mo(2)	76.6 (1)	Mo(1)–S(3)–Mo(3)	80.7 (1)
Mo(1)–S(2)–Mo(2)	76.8 (1)	Mo(1)–S(4)–Mo(3)	80.7 (1)
Mo(2)–S(5)–S(6)	64.6 (1)	Mo(2)–S(6)–S(5)	64.7 (1)

Table IV. Dihedral Angles (deg) between and Atom Position Deviations (Å) from Selected Unweighted Least-Squares Planes of $[Mo_3S_{7.45}O_{2.55}]^{2-}$

plane			angle	
no.	atoms	dev (±)	planes	value
1	S(1–4)	0.064	1/2	11.2
2	Mo(1,2)S(1,2)	0.201	1/3	14.3
3	Mo(1,3)S(3,4)	0.144	1/4	89.2
4	Mo(1,2)O(1,2)	0.016	1/11	48.0
5	Mo(1,3)O(1,3)	0.050	1/12	6.0
6	Mo(1,3)O(1)S(8)	0.025	2/4	91.1
7	S(1,2,5,6)	0.032	4/5	4.7
8	Mo(3)S(3,4)	0	3/2	3.2
9	Mo(3)S(7,8)	0	8/9	87.1
10	Mo(3)S(7)O(3)	0	8/10	97.2
11	Mo(2)S(5,6)	0		
12	Mo(2)S(1,2)	0		

Structure of $[Mo_3S_{7.45}O_{2.55}]^{2-}$. Electron density maps obtained after final anisotropic refinement corresponded to the superimposition of the two trinuclear structures, shown in two perspectives in Figure 3. Structures of the individual anions, which differ significantly only in certain distances and angles involving Mo(3), are set out in Figure 4. Metric parameters are collected in Table III. Significant differences between the two ions do not extend to the bond distances Mo(3)–S(3,4) or the bond angles S(3)–Mo(3)–S(4). Optimization of site occupancies of atoms O(3) and S(8) in the final refinement cycles afforded the species ratio $[Mo_3S_7O_3]^{2-}$:$[Mo_3S_8O_2]^{2-}$ = 1.22:1, corresponding to $[Mo_3S_{7.45}O_{2.55}]^{2-}$. The elemental analysis is sensibly consistent with this formulation, which is taken to correspond closely to the actual composition of bulk samples used in spectroscopic measurements.[29] Among related compounds, mixed-anion site oc-

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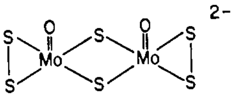
cupancies have been observed in crystals of the Ph_4P^+ salts of $[(Mo_2S_{10})_{0.72}(Mo_2S_{12})_{0.28}]^{2-}$[6b] and $[(CuS_{13})_{0.5}(CuS_{14})_{0.5}]^{2-}$.[5b] In these cases the anions differ in the sizes of the MS_n chelate rings. Here, mixed occupancy is observed for two anions that have the same overall structure and vary in only one atom, oxygen or sulfur, bonded distances to which differ by 0.45 Å.

The conformation of the anions in Figure 4 is concave in the sense that the angle Mo(2)–Mo(1)–Mo(3) = 155.9 (1)°. A more detailed description of anion shape can be drawn from the dihedral angles in Table IV. Among these, angle 1/11 = 48.0° further emphasizes the bent conformation, which may be adopted in part to increase the separation of electron-rich terminal oxo ligands. The structures may be visualized as built from a central unit, $Mo(1)OS_4$, to which are bound the fragments $Mo(2)O(S_2)$ and $Mo(3)S_2$ or Mo(3)SO. The central unit is rectangular pyramidal with deviations of ±0.064 Å from the S(1–4) least-squares plane, and Mo(1) is situated at 0.674 Å above this plane toward O(1). Similarly, Mo(2), which coordinates a persulfide group, is located 0.771 Å above the plane S(1,2,5,6). On the basis of bond angles and the dihedral angles 8/9 and 8/10, the coordination about Mo(3) is distorted tetrahedral.

The anions $[Mo_3S_8O_2]^{2-}$ and $[Mo_3S_7O_3]^{2-}$ contain certain structural fragments a–f, some of which have been encountered

a = $MoO(\eta^2\text{-}S_2)$
b = $MoO(\mu\text{-}S)_4$
c = $MoO(\eta^2\text{-}S_2)(\mu\text{-}S)_2$
d = $Mo_2O_2(\eta^2\text{-}S_2)(\mu\text{-}S)_2$
e = $Mo_2O_2S(\mu\text{-}S)_2$
f = $Mo_2OS_2(\mu\text{-}S)_2$

previously but never all in the same molecule. Fragment a is present in the Mo(VI) complexes $MoO(S_2)(S_2CNPr_2)_2$,[30] $[MoO(S_2)_2(C_2O_3S)]^{2-}$,[31] and $[Cl_2FeS_2MoO(S_2)]^{2-}$[32] and in a number of Mo(V) species,[7-11,33] including $[Mo_2O_2S_2(S_2)_2]^{2-}$[7] (**3**)



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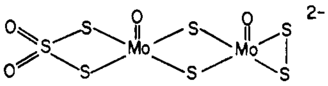

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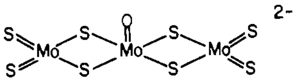

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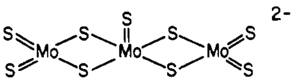

6

and $[Mo_2O_2S_2(S_2)(S_3O_2)]^{2-}$[8] (**4**). Fragment b is approached in **4** and achieved in $[Mo_3OS_8]^{2-}$[9] (**5**). Complexes **3**, **4**, and $[Cl_2FeS_2MoO(S_2)]^{2-}$ include fragment c, and **4** contains the larger unit d. Fragments e and f differ in one terminal atom. Fragment e has not been found previously, but f is anticipated by the $Mo_2S_3(\mu\text{-}S)_2$ portion of $[Mo_3S_9]^{2-}$[13] (**6**) and is realized in **5**. The fragment approach, in conjunction with the substantial body of structural data for Mo complexes, leads to an assignment of oxidation states to be three inequivalent Mo atoms. The possibilities are limited to V–V–VI and VI–IV–VI.[34] These are the same for **5** and **6**, in which the latter clearly applies inasmuch as the end groups $MoS_2(\mu\text{-}S)_2$ are simply perturbed forms of $[MoS_4]^{2-}$. For the same or analogous reasons Mo(3) in fragments e and f of the present anions is Mo(VI). Fragment b adopts the (distorted) square-pyramidal stereochemistry observed for oxo–Mo(IV) complexes,[35] some of which have a less strongly bound ligand trans to the oxo group.[36] In metric terms, the mean Mo(1)–S distance of 2.41 Å is much closer to the corresponding values for $[MoOS_8]^{2-}$ (2.38 Å), $[MoS_9]^{2-}$ (2.36 Å), **5** (2.41 Å), and **6** (2.39 Å) than to mean Mo–μ-S distances in fragments b, c, or d of **3**,[7b,c] **4**,[8] and other Mo(V) complexes.[6b,10-12] The range of mean values is 2.30–2.33 Å, with no individual value exceeding 2.35 Å. Assignment of the IV state of Mo(1) leaves Mo(2) as VI. As noted already, the Mo(VI) fragment a is precedented.[30-32] However, available data[6b,7b,c,10,11,32] do not reveal sufficient dimensional differences in fragment a alone or incorporated in c and d to distinguish Mo(V) and Mo(VI). Assignment of Mo(2) to oxidation state VI implies that $\eta^2\text{-}S_2^{2-}$, as O^{2-} and S^{2-}, functions as a 4-electron donor in order that, e.g., fragment d be isoelectronic with e, f, and the Mo_2S_5 portion of **5**. This simple idea is consistent with information on related Mo(VI) complexes. Peroxide is a functional electronic replacement for oxo ligands,[37] as in, e.g., $[Mo(O_2)_4]^{2-}$, where the midpoints of the bonds of $\eta^2\text{-}O_2^{2-}$ are tetrahedrally disposed around the Mo atom.[38] Substituted deprotonated hydroxylamines act as analogous side-on ligands in the compounds $MoO_2(RR'NO)_2$, $MoOS(RR'NO)_2$, and $MoS_2(RR'NO)_2$.[39] While we cannot insist on the VI–IV–VI description, it does appear to be the more consistent with structural features of related complexes whose Mo oxidation states are uniquely defined.

NMR Assignments. The established structures of $[Mo_3S_7O_3]^{2-}$ and $[Mo_3S_8O_2]^{2-}$ lead to the proposed signal assignments shown in Figure 2. The feature at 1003 ppm in the ^{95}Mo spectrum is assigned to the degenerate resonances of $Mo^{B,B'}$ in fragment a, which is common to both anions and farthest removed from the sites of structural difference, $Mo^{C,C'}$. The resonances at 1037 and 1680 ppm are associated with Mo^C and $Mo^{C'}$, respectively, on the basis that the deshielding of tetrahedral Mo(VI) decreases with increasing number of sulfide ligands.[3,28] These atoms are in fragments e and f, which contain $[MoOS_3]^{2-}$ (1586 ppm) and $[MoS_4]^{2-}$ (2209 ppm) ions, respectively, perturbed by coordination to $Mo^{A,A'}$. Displacement of $Mo^{C,C'}$ shifts to higher fields vs. the indicated values of the free ions[3] is consistent with upfield shifts induced by coordination of Cu(I) or Ag(I) to these ions.[26,28,40] The

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(29) Deviation of the sulfur analysis by −5.4% from this composition suggests that the bulk sample may be slightly richer in $[Mo_3S_7O_3]^{2-}$ than the crystal used in the single-crystal X-ray experiments. We do not regard this possible difference as significant. The bulk sample (also used in NMR experiments) was examined by X-ray powder diffraction using Ni-filtered Cu Kα radiation. The first 15 lines, corresponding to 11 ≳ *d* ≳ 3.3 Å, could be indexed in a monoclinic cell of the dimensions in Table I. Visually estimated intensities and F_c values of the *hkl* reflections appropriate to the observed *d* spacings were qualitatively consistent. This evidence supports the essential identity of the single crystal and bulk samples.

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(34) On the basis of present information, several pertinent structural exclusions are recognized. No Mo═O or Mo═S group occurs in any complex for which the Mo oxidation state is less than IV. No discrete Mo(IV,V) species containing at least one such group is tetrahedral.

(35) (a) $[MoO(C_2O_2S_2)_2]^{2-}$: Mennemann, K.; Mattes, R. *J. Chem. Res., Synop.* **1979**, 102. (b) $MoO(S_2CN\text{-}n\text{-}Pr_2)_2$: Ricard, L.; Estienne, J.; Karagiannidis, P.; Toledano, P.; Fischer, J.; Mitschler, A.; Weiss, R. *J. Coord. Chem.* **1974**, *3*, 277. (c) MoO(TTP): Diebold, T.; Chevrier, B.; Weiss, R. *Inorg. Chem.* **1979**, *18*, 1193. (d) $MoO(S_2CS\text{-}i\text{-}Pr)_2$: Hyde, J.; Venkatasubramanian, K.; Zubieta, J. *Ibid.* **1978**, *17*, 414. (e) $MoO(SCH_2CH_2PPh_2)_2$: Chatt, J.; Dilworth, J. R.; Schmutz, J. A.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1979**, 1595. This molecule has a structure intermediate between square pyramidal and trigonal bipyramidal.

(36) (a) $[MoO(CN)_4(H_2O)]^{2-}$: Wieghardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44. (b) $[Mo_2O_2(16\text{-}ane[S_4])_2(OEt)]^{3+}$: DeSimone, R. E.; Cragel, J., Jr.; Ilsley, W. H.; Glick, M. D. *J. Coord. Chem.* **1979**, *9*, 167. (c) $[MoO(16\text{-}ane[S_4])(SH)]^+$: DeSimone, R. E.; Glick, M. D. *Inorg. Chem.* **1978**, *17*, 3574. (d) $[MoO(diphos)_2(OH)]^+$: Churchill, M. R.; Rotella, F. J. *Ibid.* **1978**, *17*, 668. (e) $[MoO(diphos)_2Cl]^+$: Adam, V. C.; Gregory, V. A.; Kilbourn, B. T. *J. Chem. Soc. D* **1970**, 1400.

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failure to detect a signal of a Mo atom with oxidation state less than VI, here $Mo^{A,A'}$, under conditions where those of tetrahedral Mo(VI) are readily observed, has been recorded previously.[3,41] This effect presumably results from quadrupolar line broadening owing to a strongly noncubic environment. The relative intensities of the $Mo^{C,C'}$ signals support the presence of essentially equimolar quantities of the two anions in the preparative sample. In the ^{17}O NMR spectrum, the chemical shifts of $O^{B,B'}$ in common fragment a would be expected to be nearly identical, leading to the assignment of the 802 and 804 ppm features to these sites.[42] Because ^{17}O NMR resonances at tetrahedral Mo(VI) become progressively deshielded as the number of sulfide ligands increases, the 850 ppm signal is ascribed to O^C of fragment e. The remaining resonances at 813 and 820 ppm are assigned to $O^{A,A'}$, whose environments are resolvably differentiated by the terminal ligands in fragments e and f. Other than the result for **3**,[42] we are unaware of previous data for ^{17}O NMR chemical shifts of $Mo^{IV,V}{=}O$ units. At least for **3**, $[Mo_3S_8O_2]^{2-}$, and $[Mo_3S_7O_3]^{2-}$, these shifts fall into the same interval associated with $Mo^{VI}{=}O$ groups of polyoxoanions.[3,27]

Summary. Reaction of an $\alpha:\beta \sim 7:1$ isomeric mixture of $[Mo_8O_{26}]^{4-}$ in acetonitrile with 1–8 equiv of $(Me_3Si)_2S$ resulted in cleavage of the cage structures **1** and **2**. A significant extent of cage fracture was observable even at 1–2 equiv, in which the systems $[MoO_3(OSiMe_3)]^-$ and $[MoO_2S(OSiMe_3)]^-$ were formed in appreciable amounts. Both isomers were essentially absent in the 8-equiv system, which exhibited a series of new ^{17}O NMR signals. On a preparative scale this system afforded a diamagnetic crystalline n-Bu_4N^+ salt containing virtually equimolar amounts of $[Mo_3S_8O_2]^{2-}$ and $[Mo_3S_7O_3]^{2-}$. The formation of trinuclear products discouraged a study of reaction systems with >8 equiv of the sulfide reagent. The two anions contain a set of structural fragments not previously assembled in a single molecule. The oxidation state description $[(S_2)Mo^{VI}O(\mu\text{-}S)_2Mo^{IV}O(\mu\text{-}S)_2Mo^{VI}S(S/O)]^{2-}$ is offered, and assignments of the ^{17}O and ^{95}Mo NMR spectra are proposed. The species $[MoOS_8]^{2-}$, $[Mo_2S_6O_2]^{2-}$ (**3**), $[Mo_2S_7O_4]^{2-}$ (**4**), $[Mo_3OS_8]^{2-}$ (**5**), $[Mo_3S_8O_2]^{2-}$, and $[Mo_3S_7O_3]^{2-}$ constitute the current set of characterized oxothiomolybdates.[43] From the present results and those for $[Mo_2O_7]^{2-}$,[3] the reagent $(Me_3Si)_2S$ is capable of effecting O/S ligand substitution, but with partial reduction to Mo(IV,V) and Mo–O skeletal bond cleavage. It is apparent that the latter events preclude sustenance of a sulfide-substituted version of the initial polyoxoanion structure, at least with $(Me_3Si)_2S$ as the sulfide source. If reduction precedes cage disruption, polyoxotungstates may be more amenable to extensive substitution, provided reduction potentials follow the usual order W < Mo.

Acknowledgment. This research was supported by NSF Grant CHE 81-06017. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247 and NMR equipment by NSF Grant CHE 80-08891.

Registry No. **1**, 97295-50-6; **2**, 59054-50-1; $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$, 97295-49-3; $(Me_3Si)_2S$, 3385-94-2.

Supplementary Material Available: X-ray crystallographic data for $(n\text{-}Bu_4N)_2[Mo_3S_{7.45}O_{2.55}]$ including tables of anisotropic temperature factors for non-hydrogen atoms, positional and isotropic temperature factors for hydrogen atoms, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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(42) In earlier work we observed that treatment of $[Mo_2S_6O_2]^{2-}$ (**3**) with $^{17}OH_2$ produced a signal at 804 ppm, which was also found in the spectra of the $[Mo_2O_7]^{2-}/(Me_3Si)_2S$ reaction systems.[3] Because **3**, $[Mo_3S_8O_2]^{2-}$, and $[Mo_3S_7O_3]^{2-}$ contain the common fragment a, we cannot exclude the possibility that one or both of the latter anions are (very minor) products of those systems. The occurrence of significant quantities of **3** in the present preparative samples is unlikely on the basis of elemental analysis and the lack of a suitably intense single signal for sites O^B and $O^{B'}$.

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Contribution from the Department of Chemistry,
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Electron Transfer. 74. Reduction of Carboxylato-Bound Chromium(V) with Iron(II). Intervention of Chromium(IV)[1a]

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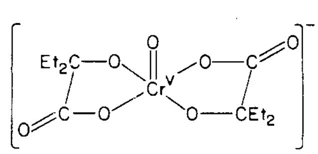
The chelated (carboxylato)chromium(V) anion bis(2-ethyl-2-hydroxybutyrato)oxochromate(V) (I) reacts rapidly with iron(II) at pH 2–4 in aqueous perchlorate, yielding a chromium(III) product, the electronic spectrum and ion-exchange behavior of which correspond to that of a bis-chelated hydroxycarboxylato complex of $(H_2O)_2Cr^{III}$. Reactions in the presence of an excess of the ligand anion, 2-ethyl-2-hydroxybutyrate (Lig^-), are found to pass through a strongly absorbing (λ_{max} 515 nm, $\epsilon = 1.5 \times 10^3$ M^{-1} cm^{-1}) intermediate, the properties of which indicate it to be a complex of the unusual oxidation state Cr(IV). The formation of this intermediate entails a combination of two routes, the first an inverse-[acid] path and the second with a rate proportional to $[Fe(Lig)^+]$. The reduction of the intermediate by excess Fe(II) proceeds at a specific rate $(2.7 \pm 0.4) \times 10^4$ M^{-1} s^{-1} (21 °C, $\mu = 0.50$ M), independent of both $[H^+]$ and $[Lig^-]$. Unlike reductions by N_2H_4 and NH_2OH, the initial reaction with Fe(II) does not require loss of ligand from the Cr(V) complex prior to the redox process. As with reduction by Ti(III), it appears that both steps of the electron-transfer sequence, $Cr^V \rightarrow Cr^{IV} \rightarrow Cr^{III}$, proceed with preservation of the ligand connectivity about chromium, suggesting that the Cr^{IV} intermediate, like the Cr^V reactant, is a bis chelate. Whereas the specific rate for reduction of Cr(IV) by Ti(III) is thought to be at least 15-fold greater than that for reduction of Cr(V) to Cr(IV), rate contants for the corresponding 1e reductions by Fe(II) are more nearly comparable. If the reductions by Ti(III) are taken to be outer sphere, this change in relative rates is in the direction consistent with a significant inner-sphere contribution to the initial step in the reduction by Fe(II).

The preparation of water-soluble chelates of chromium(V) was described in 1979.[2] For several years we have been interested in redox reactions involving this unusual oxidation state. Earlier studies indicated that reductions of the bis chelate I with hydrazine[3] and with hydroxylamine,[4] as well as the disproportionation of Cr(V) as catalyzed by Ce(III),[5] entail preliminary loss of a



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(2) Krumpolc, M.; Roček, J. *J. Am. Chem. Soc.* **1979**, *101*, 3206.

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