

Table I. Mn 2p Binding Energies for Butterfly Complexes

complex	oxidn state	2p _{3/2} , eV	2p _{1/2} , eV
Mn ₄ O ₂ (O ₂ CCPh ₃) ₆ (OEt ₂) ₂ (1)	2.5	642.2	653.8
Mn ₄ O ₂ (O ₂ CCH ₃) ₆ (bpy) ₂ (2)	2.5	641.8	653.4
Mn ₄ O ₂ (O ₂ CCH ₃) ₇ (bpy) ₂ ⁺ (3)	3.0	642.2	653.8

photooxidize 1, and low-temperature EPR measurements have been used to detect ligand binding and redox reactions of 1. Figure 3a shows the EPR spectrum of 1 at 10 K in CH₂Cl₂. Addition of 2 equiv of triethylamine causes a pronounced change in the spectrum (Figure 3b), indicating that the amine coordinates to 1, probably by displacement of Et₂O. Photolysis (254 nm) at 77 K leads to the formation of a carbon-centered radical via ejection of an electron from a phenyl ring of one of the carboxylate ligands (Figure 3c, spectrum plotted with a 5-fold smaller amplitude). Essentially identical spectra were observed after photolysis of either 1 or 1 plus 2 equiv of triethylamine. However, after the sample of 1 plus 2 equiv of triethylamine was annealed at 200 K (below the melting point of CH₂Cl₂), the radical signal was replaced by a much broader signal, which we assign to a mixed-valence manganese compound, possibly a Mn^{III}₃Mn^{II} tetramer (Figure 3d).¹⁸ This new signal was not obtained in the absence of triethylamine; in this case, annealing did not cause any change in the EPR spectrum. Amine coordination does not alter the electrochemistry or optical spectrum of 1. If addition of triethylamine led to cluster decomposition, the Mn^{III} reduction at -1.9 V would certainly be affected, but coordination to Mn^{II} in the OEt₂ site would not be expected to change this potential, as we have observed.

The observation that 1 cannot be electrochemically oxidized to the (II, III, III, III) form can be understood in terms of the coordination environment for Mn^{II} in each cluster. In 1, each Mn^{II} center is five-coordinate with a very poor donor ligand, Et₂O, in the terminal position. The EPR experiment shown in Figure 3, however, demonstrates two important features of the complex. First, the weak diethyl ether ligands can be replaced by triethylamine (Figure 3b). This is a very useful feature for studying the binding of exogenous ligands to polynuclear Mn clusters; there is a large body of data for reactions of this type in the natural system.¹⁹ Second, the binding of triethylamine allows oxidation of a Mn^{II} center, showing that ligand binding can be used to tune the oxidation potential of the Mn₄O₂ core.

X-ray Spectroscopy. The Mn 2p binding energies for 1, 2, and Mn₄O₂(OAc)₇(bpy)₂⁺ (3) were determined by X-ray photoelectron spectroscopy (Table I). Upon oxidation of 2 from the Mn^{2.5+} level to the Mn^{3.0+} level (3), the binding energies increase by 0.4 eV. This observation is consistent with a decrease in electron density at Mn brought about by the oxidation. We have reported a 0.4-eV increase in binding energy for oxidation of Mn₂O₂(bpy)₄³⁺ (Mn^{3.5+}) to Mn₃O₄(bpy)₄(OH₂)₂⁴⁺.²⁰ The binding energies for 1 are 0.4 eV higher than those of the isoelectronic butterfly (2) and identical with those of 3. This supports the idea that the Mn^{II} centers of 1 are relatively electron-poor, giving binding energies identical with those of a complex containing Mn^{III} in the same sites.

Conclusions

The physical properties of a Mn tetramer having biologically relevant coordination have been presented. The data show that the molecule contains a unique type of Mn^{II} center that is relatively electron-poor. The effects of these unique centers are evident in the Mn 2p binding energies and the redox chemistry, as detected by electrochemistry and EPR. It is notable that binding of strongly donating ligands permits oxidation of the Mn^{II} centers to occur, since binding of NH₃ has been shown to modulate the redox and EPR properties of Mn in PS II.¹⁹ Finally, it has been suggested

that unusual Mn coordination environments could account for the X-ray absorption edge energies observed in PS II,⁷ and the characterization of the unique Mn^{II} centers in 1 provides some evidence that this may be an important consideration.

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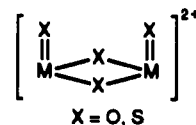
Synthesis and Characterization of a Dimeric Molybdenum(V) Anion [Br₂OMo(μ-S)₂MoOBr₂]²⁻: Conversion of Tetrahydrofuran to [PⁿBu₃P(CH₂)₄PⁿBu₃]²⁺

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Introduction

During our attempts to synthesize trinuclear sulfur-capped molybdenum clusters, we have inadvertently prepared and structurally characterized a molybdenum(V) dimer anion, [Br₂OMo(μ-S)₂MoOBr₂]²⁻. Many dinuclear molybdenum(V) and tungsten(V) compounds are known that have the general core formula M₂O_nS_{4-n}²⁺ (M = Mo, W; n = 0-4).¹⁻⁹



Typically, the dimers exhibit a bent MX₂M bridge with terminal syn M=X groups. A single metal-metal bond exists with an average length of 2.810 Å for molybdenum and 2.822 Å for tungsten.³ Other ligands, such as dithiolates^{2,5} and dithiocarbamates^{4,5} as well as phosphines,¹ coordinate to the metal atoms, completing a square-pyramidal geometry (minus the M-M bond) about each metal atom. We report here a molybdenum(V) dimer that exhibits these characteristics, but contains four bromide ions completing the coordination sphere of each metal atom. A similar tungsten compound with terminal chlorides is known,⁹ but this

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Table I. Crystal Data for $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4][(\text{nBu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{nBu})_3]$

formula	$\text{C}_{22}\text{H}_{62}\text{Br}_4\text{Mo}_2\text{O}_2\text{P}_2\text{S}_2$
fw	1068.40
space group	<i>Pnn2</i>
<i>a</i> , Å	14.534 (3)
<i>b</i> , Å	16.073 (4)
<i>c</i> , Å	8.904 (2)
<i>V</i> , Å ³	2080 (1)
<i>z</i>	2
<i>d</i> _{calc} , g/cm ³	1.706
μ (Mo K α), cm ⁻¹	45.907
radiation (monochromated in incident beam)	Mo K α ($\lambda = 0.71073$ Å)
temp, °C	-40.0
transm coeff: max, min	0.9979, 0.9224
<i>R</i> ^a	0.056
<i>R</i> _w ^b	0.072

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/\sigma^2|F_o|.$$

is the first example of this type for molybdenum. Also, we report and explain the fascinating formation of the cation $[(\text{nBu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{nBu})_3]^{2+}$, apparently from the reaction of tri-*n*-butylphosphine and THF under our experimental conditions.

Experimental Section

Materials and Methods. All operations were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. Solvents were distilled under nitrogen over the appropriate drying agents. Chemicals were obtained commercially and used without further purification. $\text{Mo}_2\text{S}_7\text{Br}_4$ was prepared according to the published procedure.¹⁰ The IR spectrum was obtained as a Nujol mull between CsI plates and was recorded on a Perkin-Elmer Model 783 infrared spectrophotometer. The electrochemical measurement was performed with a Bioanalytical Systems, Inc., Model BAS 100 electrochemical analyzer in conjunction with a Bausch and Lomb, Houston Instruments Model DMP 40 digital plotter. The experiment was carried out in a 0.2 M solution of tetra-*n*-butylammonium tetrafluoroborate in DMSO. A three-electrode cell configuration was used, with a glassy-carbon electrode (Model BAS MF 2012) and a platinum wire as working and auxiliary electrodes, respectively. A BAS MF 2020 Ag/AgCl cell was used as a reference electrode (against which ferrocene is oxidized at $E_{1/2} = +0.66$ V). The potential was referenced to the Ag/AgCl electrode at 22 ± 2 °C.

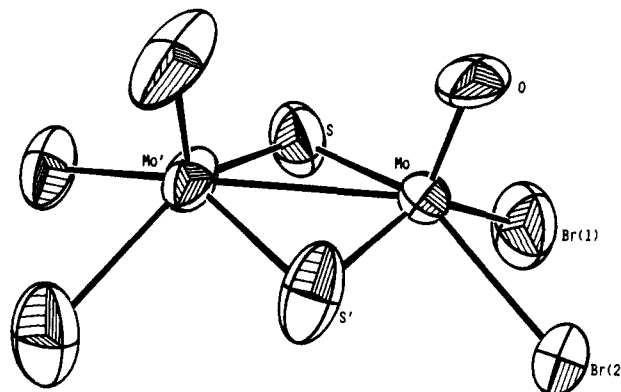
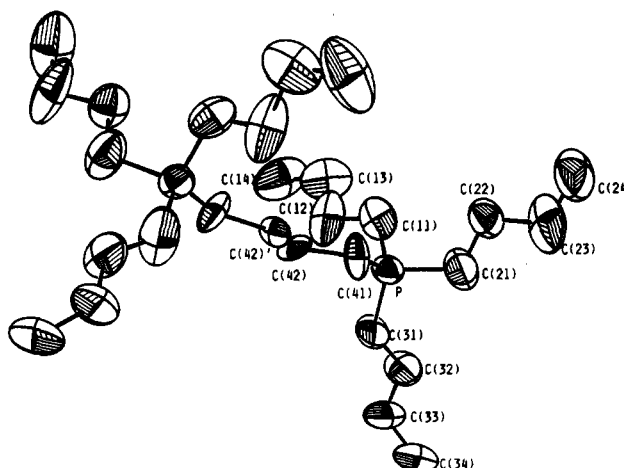
Preparation. $\text{Mo}_2\text{S}_7\text{Br}_4$ (0.2058 g, 0.2474 mmol) and $(\text{nBu})_3\text{P}$ (0.80 mL, 3.2 mmol) were refluxed in 20 mL of THF for 48 h. The resulting dark brown mixture was filtered to give a dark gold-colored filtrate. When the filtrate was allowed to stand, large, orange, needle-like crystals formed in the bottom of the Schlenk tube. The yield based on $\text{Mo}_2\text{S}_7\text{Br}_4$ was 0.11 g, 27%.

X-ray Crystallography. A suitable crystal was mounted on the end of a thin quartz fiber with epoxy resin. Some crystallographic and refinement data are provided in Table I. The general procedures used for the data collection were as described previously.¹¹ The unit cell constants determined from 25 reflections with 2θ values in the range of 20–30° indicated that the crystal system was orthorhombic. The axial lengths and Laue class were then confirmed with rotation photographs. The data set was corrected for Lorentz and polarization effects. Absorption corrections were also applied by using an empirical method based on ψ scans for χ angles near 90°. Systematic absences determined the space group to be either *Pnnm* or *Pnn2*. Attempts to solve the structure in the space group *Pnnm* failed as the solutions obtained from the Patterson map or direct methods were not meaningful. However, with the space group *Pnn2*, a likely position for the molybdenum atom was apparent from a three-dimensional Patterson function. The remaining non-hydrogen at-

Table II. Positional and Isotropic Equivalent Displacement Parameters and Their Estimated Standard Deviations for $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4][(\text{nBu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{nBu})_3]^a$

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} , Å ²
Mo	0.0741 (1)	0.94165 (8)	0.740	4.40 (3)
Br(1)	0.0847 (1)	0.7929 (1)	0.6239 (3)	6.25 (5)
Br(2)	0.2307 (1)	0.9524 (1)	0.5963 (4)	8.31 (7)
S	0.0772 (3)	1.0817 (3)	0.7004 (8)	6.7 (2)
O	0.095 (1)	0.9282 (9)	0.923 (1)	10.6 (6)
P	0.1179 (3)	0.1887 (3)	0.2245 (6)	4.9 (1)
C(11)	0.064 (2)	0.293 (1)	0.186 (3)	9.0 (8)
C(12)	0.020 (2)	0.304 (1)	0.042 (3)	7.4 (6)
C(13)	-0.026 (2)	0.390 (1)	0.028 (5)	13 (1)
C(14)	-0.064 (2)	0.405 (2)	-0.109 (5)	14 (1)
C(21)	0.180 (3)	0.199 (1)	0.391 (3)	14 (1)
C(22)	0.192 (2)	0.264 (1)	0.473 (3)	8.7 (7)
C(23)	0.252 (2)	0.265 (2)	0.609 (3)	9.0 (7)
C(24)	0.232 (3)	0.328 (2)	0.714 (3)	15 (1)
C(31)	0.186 (1)	0.167 (1)	0.065 (3)	7.3 (6)
C(32)	0.253 (1)	0.097 (1)	0.082 (4)	9.4 (8)
C(33)	0.314 (2)	0.091 (2)	-0.055 (4)	10.2 (9)
C(34)	0.379 (2)	0.023 (2)	-0.043 (5)	14 (1)
C(41)	0.022 (1)	0.1169 (9)	0.242 (3)	6.1 (5)
C(42)	0.044 (1)	0.0235 (9)	0.259 (2)	4.6 (4)

^a Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter, *B*_{eq}, defined as $1/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + 2ab(\cos \gamma)a^*b^*B_{12} + 2ac(\cos \beta)a^*c^*B_{13} + 2bc(\cos \alpha)b^*c^*B_{23}]$.

**Figure 1.** ORTEP drawing of the $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4]^{2-}$ anion. Atoms are represented by their ellipsoids at the 50% probability level.**Figure 2.** ORTEP drawing of the $[(\text{nBu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{nBu})_3]^{2+}$ cation. Atoms are represented by their ellipsoids at the 50% probability level.

oms were located by alternating least-squares full-matrix cycles of refinement and difference Fourier maps. Anisotropic convergence was accomplished with the SHELX-76 package.¹² The hydrogen atoms were

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Table III. Listing of Selected Bond Distances (Å) and Angles (deg) for $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4][(\text{}^n\text{Bu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{}^n\text{Bu})_3]^{2+}$

Mo-Mo'	2.857 (2)	C(12)-C(13)	1.54 (3)
Mo-Br(1)	2.610 (2)	C(13)-C(14)	1.36 (6)
Mo-Br(2)	2.616 (3)	C(21)-C(22)	1.29 (3)
Mo-S	2.279 (5)	C(22)-C(23)	1.50 (4)
Mo-S'	2.259 (5)	C(23)-C(24)	1.40 (4)
Mo-O	1.67 (1)	C(31)-C(32)	1.50 (3)
P-C(11)	1.88 (2)	C(32)-C(33)	1.52 (4)
P-C(21)	1.75 (3)	C(33)-C(34)	1.44 (4)
P-C(31)	1.77 (2)	C(41)-C(42)	1.54 (2)
P-C(41)	1.82 (2)	C(42)-C(42)'	1.49 (2)
C(11)-C(12)	1.44 (4)		
Mo'-Mo-Br(1)	130.23 (7)	C(11)-P-C(31)	105 (1)
Mo'-Mo-Br(2)	127.78 (7)	C(11)-P-C(41)	105 (1)
Mo'-Mo-S	50.7 (1)	C(21)-P-C(31)	114 (2)
Mo'-Mo-S'	51.3 (1)	C(21)-P-C(41)	112 (1)
Mo'-Mo-O	102.7 (6)	C(31)-P-C(41)	112 (1)
Br(1)-Mo-Br(2)	79.41 (8)	P-C(11)-C(12)	117 (2)
Br(1)-Mo-S	147.5 (2)	C(11)-C(12)-C(13)	112 (2)
Br(1)-Mo-S'	81.0 (1)	C(12)-C(13)-C(14)	114 (3)
Br(1)-Mo-O	104.9 (5)	P-C(21)-C(22)	128 (2)
Br(2)-Mo-S	80.9 (1)	C(21)-C(22)-C(23)	122 (2)
Br(2)-Mo-S'	141.4 (2)	C(22)-C(23)-C(24)	115 (2)
Br(2)-Mo-O	109.3 (7)	P-C(31)-C(32)	115 (2)
S-Mo-S'	99.2 (2)	C(31)-C(32)-C(33)	110 (3)
S-Mo-O	105.9 (5)	C(32)-C(33)-C(34)	112 (3)
S'-Mo-O	107.7 (7)	P-C(41)-C(42)	118 (1)
Mo-S-Mo'	78.0 (2)	C(41)-C(42)-C(42)'	108 (1)
C(11)-P-C(21)	107 (1)		

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

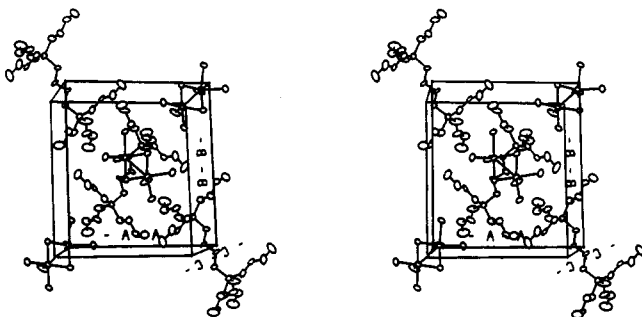


Figure 3. Unit cell drawing of $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4][(\text{}^n\text{Bu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{}^n\text{Bu})_3]^{2+}$. Axes orientation: b, down; a, across; c, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

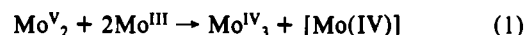
inserted at calculated positions and their thermal parameters constrained to one value, which was refined. The atomic positional parameters are listed in Table II, and selected bond distances and angles are listed in Table III.

Results and Discussion

The structure consists of discrete $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4]^{2-}$ anions and $[(\text{}^n\text{Bu})_3\text{P}(\text{CH}_2)_4\text{P}(\text{}^n\text{Bu})_3]^{2+}$ cations lying on a 2-fold axis, which bisects the Mo-Mo' bond of the anion and the C(42)-C(42)' bond of the cation. ORTEP drawings of the anion and cation are shown in Figures 1 and 2, respectively, where the atom-numbering scheme is also defined. A stereoview of the unit cell diagram is shown in Figure 3. The Mo-Mo distance of 2.857 (2) Å is consistent with that reported for similar compounds, as are the Mo-S-Mo and S-Mo-S angles and the terminal Mo-O distance.⁴⁻⁶ The MoS₂Mo bridge is bent, but the average Mo-S distance of 2.269 [7] Å falls below the range reported for other compounds with Mo₂S₂ bridges.^{4,6}

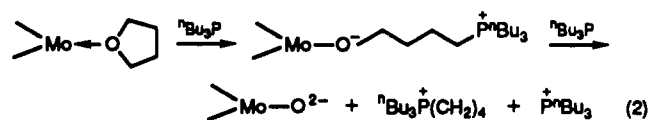
The infrared spectrum showed bands at 965 (m) and 954 (w) cm⁻¹, which are probably assignable to the terminal Mo-O stretching vibrations since this is consistent with reported data.⁸ A cyclic voltammogram in dimethyl sulfoxide (for comparison with previous results⁴ in that solvent) indicates that an irreversible reduction occurs at -1.672 V. The low solubility precluded the measurement of NMR spectra.

The syntheses of such M^V₂ compounds are usually carried out by the reduction of M(VI) compounds, such as MoO₄²⁻,⁸ MS₂²⁻,^{2,3,6} and Mo₇O₂₄⁶⁻.^{5,6} However, $[\text{Mo}_2\text{O}_2\text{S}_2\text{Br}_4]^{2-}$ resulted from the oxidation of Mo₃S₇Br₄. In 1987, Martinez et al. reported the formation of triangular molybdenum complexes from the reduction of molybdenum(V) dimers.¹³ They also proposed several reaction schemes by which this reaction might have occurred. The route to a μ₃-sulfido-capped trimer from the reduction of Mo₂O₂S₂²⁺ was shown to proceed via a cuboidal Mo₄S₄⁴⁺ intermediate. Equation 1 formally summarizes the overall reaction. The



$[\text{Mo}(\text{IV})]$ moiety is described as a "transient" that produces Mo^{IV}₃ or is reoxidized to Mo^V₂.¹³ We suggest that the oxidation of Mo₃S₇Br₄ can be regarded as the reverse of reaction 1. It is unclear, however, whether the trimer breaks down to give a dimer and monomer or if the oxidation step described below occurs first. It is doubtful that a cuboidal intermediate is formed.

The present reaction is effected by the transfer of an oxygen atom from THF and the participation of ⁿBu₃P, as indicated in reaction 2. While this scheme is speculative and intermediates were not



characterized, we do feel that this is a viable route and is the most probable for the products formed.

Acknowledgment. We thank the Robert A. Welch Foundation for support under Grant No. A494.

Supplementary Material Available: Full listings of crystallographic data, bond distances and angles, positional and isotropic parameters, and anisotropic displacement parameters (8 pages); a listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Contribution from the Coordination Chemistry and Catalysis Division, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

First Catalytic Sulfur Atom Transfer Reaction by a Novel (μ-Persulfido)ruthenium(IV) Complex, $[(\text{Edta-H})\text{Ru}^{\text{IV}}]_2\text{S}_2^{2-}$

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The interaction of $\text{K}[\text{Ru}^{\text{II}}(\text{Edta-H})\text{Cl}]\cdot 2\text{H}_2\text{O}$ (1) with elemental sulfur in 1:1 water-ethanol leads to the formation of the μ-persulfido complex $[\text{Ru}^{\text{IV}}(\text{Edta-H})]_2(\mu\text{-}\eta^1\text{-S}_2^{2-})$ (2) (Edta-H = protonated ethylenediaminetetraacetic acid). In the absence of a substrate the S₂²⁻ bond undergoes a heterolytic cleavage to give a μ-sulfido complex, $[\text{Ru}^{\text{IV}}(\text{Edta-H})]_2(\mu\text{-}\eta^1\text{-S}^{2-})$ (3), and elemental sulfur. Complexes 2 and 3 catalyze sulfur atom transfer to cyclohexene to form cyclohexene sulfide.

The activation of diatomic molecules such as H₂, O₂, N₂, and CO has attained significant relevance in chemistry and homogeneous catalysis.^{1,2} Despite several papers and monographs,^{3,4}

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