[CpRu(coumarin-7)]$^+$, for instance, S_1 is only 440 cm^{-1} higher in energy ($\Delta\lambda_{max}$ = 9 nm) than in the coumarin-6 complex, but this change is sufficient to shut down the ligand-localized emission in the coumarin-7 complex. When ligand-centered emission *is* observed from a ruthenium complex, it is always much less intense than that of the corresponding uncomplexed arene. This decrease in fluorescence efficiency probably results from intersystem crossing within the dye manifold induced by the heavy ruthenium atom.

Acknowledgment. We thank Johnson Matthey Inc. for a generous loan of ruthenium trichloride. This material is based upon work supported in part by the National Science Foundation under Grant No. CHE-8722843.

Supplementary Material Available: Procedures for synthesizing [CpRu(coumarin-7)]PF_6, [CpRu(coumarin-30)]PF_6, [CpRu(9-phenylanthracene)]PF_6 (phenyl-bound and anthracene-bound isomers), and $[(CpRu)_2(rubrene)](PF_6)_2$ (4 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Three New Compounds Containing M_3S_4 (M = Mo, W) Cores Prepared from $M_3S_7X_4$ (M = Mo, W; X = Cl, Br) Starting Materials

F. Albert Cotton,* Piotr A. Kibala, and Charla S. Miertschin

Received August 10, 1990

$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot OPEt_3$ (**1**), $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (**2**), and $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (**3**) were prepared by reacting triethylphosphine with $Mo_3S_7Cl_4$, $Mo_3S_7Br_4$, and $W_3S_7Br_4$, respectively, in THF at room temperature. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 13.290 (2) Å, b = 18.282 (4) Å, c = 17.934 (4) Å, β = 93.95 (2)°, V = 4347 (3) Å^3, and Z = 4. Compounds **2** and **3** are isostructural and crystallize in the triclinic space group $P\bar{1}$. For **2**, a = 12.908 (4) Å, b = 18.299 (6) Å, c = 12.153 (4) Å, α = 98.26 (2)°, β = 116.69 (2)°, γ = 77.21 (2)°, V = 2498 (3) Å^3, and Z = 2. For **3**, a = 12.925 (4) Å, b = 18.318 (6) Å, c = 12.141 (4) Å, α = 98.41 (3)°, β = 116.51 (3)°, γ = 77.00 (3)°, V = 2503 (2) Å^3, and Z = 2. All three compounds belong to the B_1, M_3X_{13} structure family. An explanation for the formation of the Et_2HPO ligand in **2** and **3** is proposed.

Introduction

Much attention has recently been directed toward trinuclear transition-metal clusters. The discovery of new methods of synthesis has contributed to the rapid evolution of this field. Solution methods using mononuclear starting materials have been widely used to prepare molybdenum and tungsten trinuclear clusters with a variety of ligands.[1-6] Other methods involve ligand substitution on a preformed M_3 core with preservation of the triangular structure.[7-12] Recently, the synthesis and characterization of polymeric trimers having the formula $M_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3X_2X_{4/2}$ or, more simply, $M_3S_7X_4$ (M = Mo, W; X = Cl, Br) opened new routes for preparing substituted trimers.[13,14] Several new compounds have been prepared by utilizing $Mo_3S_7X_4$ as the starting material. For example, Federov et al. prepared $Mo_3S_7X_4\cdot 2PPh_3$ (X = Cl, Br) by reacting $Mo_3S_7X_4$ with PPh_3 in CH_3CN.[15] Saito et al. reported the synthesis of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_n(MeOH)_{5-n}$ (n = 3, 4) from $Mo_3S_7Cl_4$ reacted with PEt_3 in THF.[16] In this laboratory, $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)(H_2O)_2\cdot 3THF$ and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(PPh_3)(dmpe)_3]Cl\cdot 2MeOH$ were prepared by using this type of synthetic method.[17] So far only two compounds have been prepared by methods that make use of tungsten trinuclear polymeric starting materials, and only one of these contained substituted phosphines. They are $[W_6S_8(PEt_3)_6]$[18] and $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(H_2O)_3]^{2-}$.[19] We report here the syntheses and crystal structures of three new compounds that further exemplify the use of molybdenum and tungsten trinuclear chalcogenide halides as excellent synthons for trinuclear, triangular clusters of the M_3S_4 type having phosphine ligands in the outer coordination sites.

Experimental Section

Materials and Methods. All experiments 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 from the following sources: sulfur (precipitated grade), Fisher; triethylphosphine, S_2Cl_2, molybdenum (100-mesh powder), and tungsten (100-mesh powder), Strem. They were used without further purification. $Mo_3S_7Cl_4$, $Mo_3S_7Br_4$, and $W_3S_7Br_4$ were prepared

---

(1) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252.
(2) Dori, Z.; Cotton, F. A.; Llusar, R.; Schwotzer, W. *Polyhedron* **1986**, *5*, 907.
(3) Cotton, F. A.; Llusar, R. *Polyhedron* **1987**, *6*, 1741.
(4) Cotton, F. A.; Llusar, R. *Inorg. Chem.* **1988**, *27*, 1303.
(5) Cotton, F. A.; Llusar, R.; Eagle, C. T. *J. Am. Chem. Soc.* **1989**, *111*, 4332.
(6) Müller, A.; Reinsch, U. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 72.
(7) Shibahara, T.; Kohda, K.; Ohtsuji, A.; Yasuda, K.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 2757.
(8) Howlader, N. C.; Haight, G. P., Jr.; Hambley, T. W.; Lawrence, G. A.; Rahmoeller, K. M.; Snow, M. R. *Aust. J. Chem.* **1983**, *36*, 377.
(9) Halbert, T. R.; McGauley, K.; Pau, W.-H.; Czernuszewicz, R. S.; Steifel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849.
(10) Cotton, F. A.; Llusar, R.; Marler, D. O.; Schwotzer, W.; Dori, Z. *Inorg. Chim. Acta* **1985**, *102*, L25.
(11) Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 6734.
(12) Hegetschweiler, K.; Keller, T.; Zimmermann, H.; Schneider, W.; Schmalle, H.; Dubler, E. *Inorg. Chim. Acta* **1990**, *169*, 235.
(13) Federov, V. Ye.; Mironov, Yu. V.; Kuz'mina, O. A.; Fedin, V. P. *Zh. Neorg. Khim.* **1986**, *31*, 2476; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1986**, *31*, 1429.
(14) Marcoll, J.; Rabenau, A.; Mootz, D.; Wunderlich, H. *Rev. Chem. Miner.* **1974**, *11*, 607.
(15) Fedin, V. P.; Gubin, S. P.; Mishchenko, A. V.; Federov, V. Ye. *Koord. Khim.* **1984**, *10*, 901; *Sov. J. Coord. Chem.* (*Engl. Transl.*) **1985**, 501.
(16) Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *Chem. Lett.* **1987**, 2025.
(17) Cotton, F. A.; Kibala, P. A.; Matusz, M.; McCaleb, C. S.; Sandor, R. B. W. *Inorg. Chem.* **1989**, *28*, 2623.
(18) Saito, T.; Yoshikawa, A.; Yamagata, T.; Imoto, H.; Unoura, K. *Inorg. Chem.* **1989**, *28*, 3588.
(19) Fedin, V. P.; Sokolov, M. N.; Geras'ko, O. A.; Sheer, M.; Federov, V. Ye.; Mironov, Yu. V.; Slovokhotov, Y. L.; Strutchkov, Y. T. *Inorg. Chim. Acta* **1989**, *165*, 25.

0020-1669/91/1330-0548$02.50/0 © 1991 American Chemical Society

Table I. Crystal Data for $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot OPEt_3$ (**1**), $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(H_2O)(OPEt_2H)\cdot 2THF$ (**2**), and $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(H_2O)(OPEt_2H)\cdot 2THF$ (**3**)

	1	**2**	**3**
formula	$C_{24}H_{64}Cl_4Mo_3O_3P_4S_4$	$C_{30}H_{74}Br_4Mo_3O_4P_4S_4$	$C_{30}H_{74}Br_4O_4P_4S_4W_3$
fw	1082.56	1358.53	1622.21
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a, Å	13.290 (2)	12.908 (4)	12.925 (4)
b, Å	18.282 (4)	18.299 (6)	18.318 (6)
c, Å	17.934 (4)	12.153 (4)	12.141 (4)
α, deg	90.0	98.26 (2)	98.41 (3)
β, deg	93.95 (2)	116.69 (2)	116.51 (3)
γ, deg	90.0	77.21 (2)	77.00 (3)
V, Å^3	4347 (3)	2498 (3)	2503 (2)
Z	4	2	2
d_{calc}, g/cm^3	1.654	1.806	2.152
μ(Mo Kα), cm^{-1}	14.363	42.123	105.093
radiation (monochromated in incident beam)		Mo Kα (λ = 0.71073 Å)	
temp, °C	21	21	21
trans coeff: max, min	0.9992, 0.9792	0.9987, 0.9651	0.9974, 0.5914
R^a	0.042	0.065	0.042
$R_w{}^b$	0.054	0.079	0.053

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

according to published procedures.[13,17]

Preparation of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot OPEt_3$ (1). $Mo_3S_7Cl_4$ (0.244 g, 0.374 mmol), PEt_3 (0.320 g, 2.71 mmol), and 25 mL of THF were stirred at room temperature for 24 h. The brown mixture was filtered, giving a dark green filtrate and an orange residue (presumably unreacted starting material). The filtrate was layered with an equal volume of hexane. Dark green crystals formed within 2 weeks. Based on $Mo_3S_7Cl_4$, the yield was 0.18 g, 45%.

Preparation of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (2). $Mo_3S_7Br_4$ (0.205 g, 0.247 mmol) and PEt_3 (0.200 g, 1.69 mmol) were stirred in 25 mL of THF for 24 h. The brown reaction mixture was filtered, leaving a brown residue (unreacted $Mo_3S_7Br_4$) and a dark green filtrate. The filtrate was layered with hexane, which upon mixing produced dark green crystals. The yield was 0.11 g, 32% based on $Mo_3S_7Br_4$.

Preparation of $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (3). $W_3S_7Br_4$ (0.200 g, 0.183 mmol) and PEt_3 (0.160 g, 1.35 mmol) were added to 15 mL of THF and stirred for 4 h. Within 1 h the original dark orange mixture turned green. A brown solid containing unreacted $W_3S_7Br_4$ and a very dark green filtrate were obtained upon filtering. An equal volume of hexane was used as a layering solvent for the filtrate. Dark green crystals formed in 2 months. The yield based on $W_3S_7Br_4$ was 0.06 g, 20%.

X-ray Crystallography. In each case a crystal was mounted on the end of a thin glass fiber and fixed with epoxy glue. Axial lengths and Laue classes were confirmed with rotation photographs. General procedures and practices common to this laboratory have already been described.[20] Lorentz, polarization, and empirical absorption corrections based on ψ scans for χ angles near 90° were applied to the data. Crystal parameters and basic information relating to data collection and structure refinement are summarized in Table I.

Crystal Structure of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot OPEt_3$ (1). A suitable crystal was selected and mounted on the goniometer head of an Enraf-Nonius CAD4 diffractometer. The choice of the monoclinic space group $P2_1/n$ proved correct, and refinement proceeded straightforwardly. The direct-methods program in SHELXS-86 aided in locating the positions of the molybdenum atoms. Additional least-squares cycles and difference Fourier maps revealed the positions of the remaining atoms. Hydrogen atoms were not included in the refinement. Disorder was found for C(6), and this atom was subsequently refined at two positions each with half-multiplicity. No other problems arose. The atomic positional and isotropic equivalent displacement parameters are listed in Table II.

Crystal Structure of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (2). A crystal was selected from the product and shown to be of good quality by polarized light microscopy. The crystal was mounted on the goniometer head of a Syntex P3 diffractometer. The solution and

Table II. Positional and Isotropic Equivalent Displacement Parameters and Their Estimated Standard Deviations for $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot(OPEt_3)$ (**1**)

atom	x	y	z	B_{eq},^{a} Å^2
Mo(1)	0.22441 (6)	0.15499 (4)	0.37027 (5)	2.83 (2)
Mo(2)	0.20429 (6)	0.30463 (5)	0.38688 (5)	2.88 (2)
Mo(3)	0.06543 (6)	0.22856 (5)	0.29552 (5)	3.10 (2)
Cl(1)	0.4035 (2)	0.1290 (1)	0.3581 (1)	3.88 (5)
Cl(2)	0.2052 (2)	0.3970 (1)	0.4897 (1)	4.32 (6)
Cl(3)	0.0383 (2)	0.3311 (2)	0.2026 (2)	4.67 (6)
Cl(4)	0.0616 (2)	0.1514 (2)	0.1804 (2)	4.90 (7)
S	0.2366 (2)	0.2438 (1)	0.2767 (1)	3.11 (5)
S(1)	0.2372 (2)	0.2215 (1)	0.4786 (1)	3.50 (6)
S(2)	0.0313 (2)	0.3082 (1)	0.3888 (1)	3.67 (5)
S(3)	0.0569 (2)	0.1270 (1)	0.3713 (1)	3.43 (5)
P(1)	0.2526 (2)	0.0461 (2)	0.4611 (2)	4.13 (6)
P(2)	0.3942 (2)	0.3483 (2)	0.3976 (2)	3.90 (6)
P(3)	−0.1278 (2)	0.2103 (2)	0.2774 (2)	4.41 (7)
P(4)	0.4004 (2)	0.0826 (2)	0.1163 (2)	3.90 (6)
O(1)	0.2187 (5)	0.0699 (3)	0.2782 (4)	3.8 (1)
O(2)	0.1966 (5)	0.4026 (3)	0.3129 (3)	3.6 (1)
O(3)	0.3320 (5)	0.0433 (4)	0.1670 (4)	4.2 (2)
C(1)	0.1463 (8)	0.0186 (6)	0.5158 (6)	4.5 (2)
C(2)	0.1132 (9)	0.0787 (7)	0.5687 (7)	6.0 (3)
C(3)	0.3623 (9)	0.0641 (7)	0.5307 (7)	6.1 (3)
C(4)	0.383 (1)	0.0072 (9)	0.5938 (8)	8.2 (4)
C(5)	0.287 (1)	−0.0380 (6)	0.4126 (8)	7.6 (4)
C(6a)	0.213 (2)	−0.082 (1)	0.388 (1)	6.3 (7)
C(6b)	0.268 (2)	−0.112 (1)	0.437 (2)	9.9 (8)
C(7)	0.4068 (8)	0.4482 (5)	0.3948 (6)	4.4 (3)
C(8)	0.5167 (8)	0.4766 (6)	0.4023 (7)	5.1 (3)
C(9)	0.4591 (9)	0.3257 (7)	0.4959 (8)	6.7 (3)
C(10)	0.503 (1)	0.2523 (7)	0.5019 (9)	7.4 (4)
C(11)	0.4802 (9)	0.3191 (6)	0.3278 (7)	7.3 (3)
C(12)	0.453 (1)	0.3533 (8)	0.2521 (7)	8.3 (4)
C(13)	−0.203 (1)	0.2777 (9)	0.2197 (9)	9.5 (5)
C(14)	−0.208 (1)	0.3520 (8)	0.272 (1)	10.6 (6)
C(15)	−0.187 (1)	0.1985 (9)	0.3647 (8)	8.0 (4)
C(16)	−0.306 (1)	0.1843 (9)	0.3562 (9)	9.2 (5)
C(17)	−0.173 (1)	0.1266 (9)	0.2194 (8)	7.9 (4)
C(18)	−0.146 (1)	0.0531 (7)	0.2577 (8)	7.3 (4)
C(19)	0.5132 (8)	0.0298 (7)	0.1080 (8)	6.6 (3)
C(20)	0.572 (1)	0.0195 (9)	0.180 (1)	9.7 (5)
C(21)	0.3428 (9)	0.0927 (7)	0.0220 (6)	5.7 (3)
C(22)	0.247 (1)	0.142 (1)	0.0228 (9)	10.2 (5)
C(23)	0.433 (1)	0.1716 (6)	0.1516 (7)	6.3 (3)
C(24)	0.503 (1)	0.2145 (7)	0.1002 (7)	9.1 (4)

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter, B_{eq}, defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

---

(20) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. J. *J. Organomet. Chem.* **1973**, *50*, 227. (c) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Gen. Theor. Crystallogr.* **1968**, *24*, 351. (d) Calculations were performed with the Enraf-Nonius Structure Determination Package on the Microvax II computer at the Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, TX 77843. (e) Sheldrick, G. M. SHELX-86, Program for Crystal Structure Determination. University of Göttingen, Federal Republic of Germany, 1986.

Table III. Positional and Isotropic Equivalent Displacement Parameters and Their Estimated Standard Deviations for $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(H_2O)(OPEt_2H)\cdot 2THF$ (**2**)

atom	x	y	z	B_{eq},[a] Å^2
Mo(1)	0.1821 (1)	0.17923 (8)	0.0150 (1)	2.49 (3)
Mo(2)	0.1671 (1)	0.27666 (8)	−0.1509 (1)	2.21 (3)
Mo(3)	0.2908 (1)	0.30361 (8)	0.1017 (1)	2.46 (3)
Br(1)	0.0956 (2)	0.1713 (1)	0.1696 (2)	4.49 (5)
Br(2)	−0.0557 (1)	0.2588 (1)	−0.3196 (2)	3.83 (5)
Br(3)	0.2419 (2)	0.4518 (1)	0.1001 (2)	3.86 (5)
Br(4)	0.2594 (2)	0.3299 (1)	0.3065 (1)	4.11 (5)
S	0.0871 (3)	0.3059 (2)	−0.0048 (3)	2.7 (1)
S(1)	0.2185 (3)	0.1487 (2)	−0.1554 (3)	3.0 (1)
S(2)	0.3558 (3)	0.2974 (2)	−0.0472 (3)	2.8 (1)
S(3)	0.3713 (3)	0.1809 (2)	0.1539 (4)	3.1 (1)
P(1)	0.2424 (4)	0.0357 (3)	0.0433 (4)	4.1 (1)
P(2)	0.2131 (4)	0.2660 (3)	−0.3410 (3)	2.8 (1)
P(3)	0.5049 (4)	0.3270 (3)	0.2463 (4)	4.2 (1)
P(4)	0.0001 (4)	0.4528 (3)	−0.2049 (4)	3.8 (1)
O(1)	0.0014 (8)	0.1500 (6)	−0.1126 (9)	3.4 (3)
O(2)	0.0955 (8)	0.3888 (5)	−0.2118 (9)	2.8 (3)
O(3)	0.255 (3)	0.949 (2)	0.463 (2)	40 (1)
O(4)	0.208 (1)	0.7912 (8)	0.089 (1)	7.0 (4)
C(1)	0.276 (2)	0.001 (1)	0.196 (2)	6.5 (6)
C(2)	0.377 (2)	0.026 (1)	0.297 (2)	8.6 (8)
C(3)	0.126 (1)	−0.018 (1)	−0.058 (2)	5.2 (6)
C(4)	0.104 (2)	−0.026 (1)	−0.192 (2)	6.0 (6)
C(5)	0.372 (1)	−0.008 (1)	0.013 (2)	4.3 (5)
C(6)	0.414 (2)	−0.092 (1)	0.032 (2)	6.1 (6)
C(7)	0.349 (1)	0.200 (1)	−0.319 (1)	3.5 (4)
C(8)	0.389 (1)	0.193 (1)	−0.427 (1)	5.3 (5)
C(9)	0.102 (1)	0.237 (1)	−0.494 (1)	4.3 (5)
C(10)	0.092 (2)	0.154 (1)	−0.503 (2)	5.4 (6)
C(11)	0.226 (1)	0.356 (1)	−0.384 (1)	4.2 (4)
C(12)	0.324 (2)	0.393 (1)	−0.289 (2)	5.8 (6)
C(13)	0.545 (2)	0.417 (1)	0.237 (2)	6.1 (7)
C(14)	0.534 (2)	0.428 (1)	0.110 (2)	6.7 (6)
C(15)	0.555 (2)	0.320 (2)	0.417 (2)	7.4 (8)
C(16)	0.514 (3)	0.403 (2)	0.476 (3)	13 (1)
C(17)	0.615 (1)	0.256 (1)	0.213 (2)	5.3 (6)
C(18)	0.748 (2)	0.267 (2)	0.295 (2)	7.1 (7)
C(19)	0.043 (2)	0.5444 (9)	−0.178 (2)	4.7 (6)
C(20)	0.075 (2)	0.566 (1)	−0.270 (2)	8.4 (7)
C(21)	−0.141 (2)	0.455 (1)	−0.334 (2)	5.6 (6)
C(22)	−0.128 (2)	0.449 (1)	−0.456 (2)	7.3 (8)
C(23)	0.334 (3)	0.889 (3)	0.515 (5)	26 (2)
C(24)	0.317 (3)	0.959 (2)	0.639 (3)	13 (1)*
C(25)	0.244 (4)	0.920 (3)	0.619 (4)	16 (1)*
C(26)	0.164 (3)	0.940 (2)	0.498 (4)	15 (2)
C(27)	0.293 (2)	0.771 (2)	0.203 (2)	11 (1)
C(28)	0.316 (3)	0.691 (2)	0.204 (3)	12 (1)
C(29)	0.261 (4)	0.664 (2)	0.079 (4)	17 (2)
C(30)	0.211 (3)	0.730 (2)	0.001 (2)	12 (1)
H	−0.052	0.446	−0.103	4.0[b]

[a] Starred values indicate atoms that were refined isotropically. *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter, B_{eq}, defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. [b] Hydrogen atom was not refined but was used in structure factor calculations.

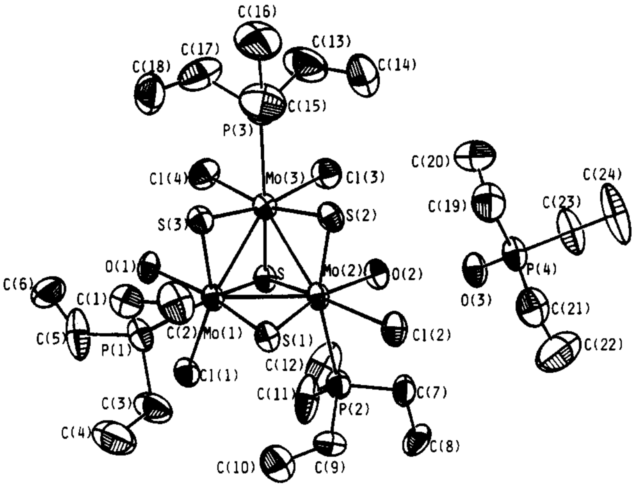


Figure 1. ORTEP drawing of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot OPEt_3$ (**1**). Atoms are represented by their ellipsoids at the 50% probability level.

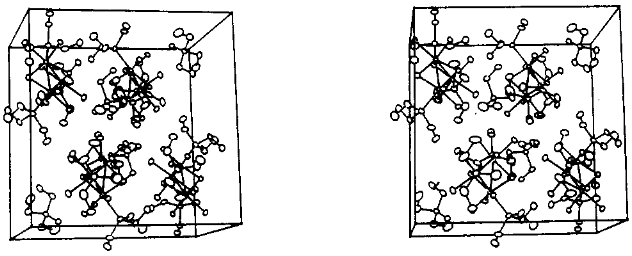


Figure 2. Unit cell of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot OPEt_3$ (**1**). Axes orientation: *b*, down; *c*, across; *a*, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

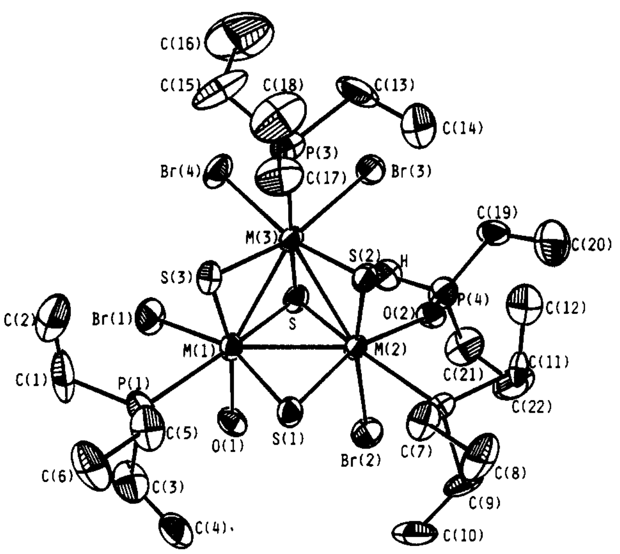


Figure 3. ORTEP drawing of the $M_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ molecule in, for M = Mo, **2** and, for M = W, **3**. The hydrogen shown was found for compound **2** only. Atoms are represented by their ellipsoids at the 50% probability level.

refinement of the structure proceeded straightforwardly in the triclinic space group $P\bar{1}$. The molybdenum atoms were located from a three-dimensional Patterson function. The remaining non-hydrogen atoms were found by alternating least-squares full-matrix cycles of refinement and difference Fourier maps. During anisotropic refinement two carbon atoms gave nonpositive definite values and were subsequently refined isotropically. The position of the hydrogen atom on P(4) was located in the final Fourier map. The atom was not refined but was included in structure factor calculations. No disorder or other problems arose. The atomic positional and isotropic equivalent displacement parameters are listed in Table III.

Crystal Structure of $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)_2(H_2O)\cdot 2THF$ (3). A green needle was selected and mounted on the goniometer head of a Syntex P3 diffractometer. The unit cell constants determined from 25 reflections with 2θ values in the range of 20 to 30° indicated that **3** was isostructural with **2**. Three check reflections monitored throughout data collection displayed a decay of 8.4%. An appropriate anisotropic decay correction was made. The atomic positions from **2** were used as a starting point in the refinement. A semiempirical absorption correction was also applied to the data.[21] Hydrogen atoms were not included in the refinement. Disorder was found for C(16), and this atom was subsequently refined at two positions each with half-multiplicity. A problem arose in the refinement of one solvent molecule. The oxygen atom in the THF molecule was indistinguishable from the carbon atoms, presumably because of a 5-fold disorder. Attempts to refine the disorder were un-

---

(21) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *39*, 158.

Table IV. Positional and Isotropic Equivalent Displacement Parameters and Their Estimated Standard Deviations for $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(H_2O)(OPEt_2H)\cdot 2THF$ (**3**)

atom	x	y	z	B_{eq},[a] Å^2
W(1)	0.18422 (5)	0.17897 (4)	0.01454 (5)	2.84 (2)
W(2)	0.16905 (5)	0.27587 (4)	−0.15095 (5)	2.59 (1)
W(3)	0.29195 (5)	0.30318 (4)	0.10073 (5)	2.86 (2)
Br(1)	0.0973 (2)	0.1723 (1)	0.1691 (2)	5.01 (5)
Br(2)	−0.0526 (1)	0.2582 (1)	−0.3184 (2)	4.44 (5)
Br(3)	0.2405 (2)	0.4515 (1)	0.0986 (2)	4.67 (5)
Br(4)	0.2585 (2)	0.3309 (1)	0.3037 (1)	4.79 (5)
S	0.0887 (3)	0.3050 (2)	−0.0061 (3)	3.1 (1)
S(1)	0.2204 (3)	0.1472 (2)	−0.1572 (3)	3.1 (1)
S(2)	0.3578 (3)	0.2976 (2)	−0.0485 (3)	2.96 (9)
S(3)	0.3740 (3)	0.1805 (2)	0.1540 (4)	3.4 (1)
P(1)	0.2418 (4)	0.0362 (3)	0.0415 (4)	4.2 (1)
P(2)	0.2141 (3)	0.2655 (3)	−0.3413 (4)	3.5 (1)
P(3)	0.5041 (4)	0.3272 (3)	0.2457 (4)	4.5 (1)
P(4)	0.0007 (4)	0.4519 (3)	−0.2053 (5)	4.7 (1)
O(1)	0.0029 (8)	0.1505 (7)	−0.1086 (9)	3.9 (3)
O(2)	0.0967 (8)	0.3867 (6)	−0.2116 (8)	3.2 (3)
O(4)	0.202 (1)	0.788 (1)	0.088 (1)	8.3 (5)
C(1)	0.275 (2)	−0.000 (1)	0.190 (2)	6.9 (6)
C(2)	0.378 (2)	0.028 (2)	0.302 (2)	10 (1)
C(3)	0.123 (1)	−0.016 (1)	−0.060 (2)	6.2 (5)
C(4)	0.103 (2)	−0.027 (1)	−0.189 (2)	8.4 (7)
C(5)	0.371 (1)	−0.007 (1)	0.014 (2)	4.8 (5)
C(6)	0.417 (2)	−0.091 (1)	0.032 (2)	6.5 (7)
C(7)	0.355 (1)	0.201 (1)	−0.318 (1)	4.7 (5)
C(8)	0.387 (1)	0.193 (1)	−0.427 (2)	6.2 (6)
C(9)	0.108 (1)	0.234 (1)	−0.494 (2)	5.5 (5)
C(10)	0.097 (2)	0.154 (1)	−0.502 (2)	6.7 (6)
C(11)	0.227 (1)	0.353 (1)	−0.385 (1)	4.5 (5)
C(12)	0.326 (2)	0.393 (1)	−0.289 (2)	6.7 (6)
C(13)	0.542 (2)	0.418 (1)	0.241 (2)	7.0 (6)
C(14)	0.534 (2)	0.431 (1)	0.114 (2)	7.9 (7)
C(15)	0.552 (2)	0.325 (2)	0.414 (2)	8.7 (7)
C(16a)	0.578 (5)	0.253 (5)	0.450 (5)	16 (3)
C(16)	0.520 (4)	0.403 (3)	0.478 (3)	7 (1)
C(17)	0.616 (1)	0.258 (1)	0.210 (2)	5.7 (6)
C(18)	0.749 (2)	0.266 (1)	0.290 (2)	7.4 (7)
C(19)	0.042 (2)	0.542 (1)	−0.176 (2)	6.0 (6)
C(20)	0.073 (2)	0.564 (2)	−0.275 (3)	10.1 (9)
C(21)	−0.139 (2)	0.456 (1)	−0.336 (2)	6.4 (7)
C(22)	−0.127 (2)	0.444 (1)	−0.454 (2)	8.5 (8)
C(23)	0.698 (4)	0.111 (3)	0.519 (5)	25 (3)
C(24)	0.799 (4)	0.055 (3)	0.569 (4)	17 (2)
C(25)	0.839 (3)	0.058 (2)	0.480 (4)	17 (2)
C(26)	0.729 (4)	0.068 (3)	0.367 (3)	19 (2)
C(27)	0.665 (3)	0.050 (2)	0.429 (5)	24 (2)
C(28)	0.288 (2)	0.768 (2)	0.198 (3)	12 (1)
C(29)	0.321 (3)	0.689 (2)	0.203 (3)	12 (1)
C(30)	0.271 (4)	0.667 (2)	0.083 (4)	18 (2)
C(31)	0.210 (2)	0.728 (2)	0.004 (2)	11 (1)

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter, B_{eq}, defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

Table V. Listing of Selected Bond Distances (Å) and Angles (deg) for $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2\cdot(OPEt_3)$ (**1**)[a]

Distances			
Mo(1)–Mo(2)	2.767 (1)	Mo(2)–S(1)	2.260 (3)
Mo(1)–Mo(3)	2.771 (1)	Mo(2)–S(2)	2.302 (3)
Mo(1)–Cl(1)	2.452 (3)	Mo(2)–P(2)	2.642 (3)
Mo(1)–S	2.349 (3)	Mo(2)–O(2)	2.227 (6)
Mo(1)–S(1)	2.288 (3)	Mo(3)–Cl(3)	2.518 (3)
Mo(1)–S(3)	2.285 (3)	Mo(3)–Cl(4)	2.499 (3)
Mo(1)–P(1)	2.584 (3)	Mo(3)–S	2.339 (3)
Mo(1)–O(1)	2.266 (6)	Mo(3)–S(2)	2.286 (3)
Mo(2)–Mo(3)	2.758 (1)	Mo(3)–S(3)	2.308 (3)
Mo(2)–Cl(2)	2.500 (3)	Mo(3)–P(3)	2.588 (3)
Mo(2)–S	2.333 (3)	P(4)–O(3)	1.511 (7)
Angles			
Mo(2)–Mo(1)–Mo(3)	59.74 (3)	Cl(2)–Mo(2)–O(2)	83.9 (2)
Mo(2)–Mo(1)–Cl(1)	107.62 (7)	S–Mo(2)–S(1)	104.96 (9)
Mo(2)–Mo(1)–S	53.51 (6)	S–Mo(2)–S(2)	105.55 (9)
Mo(2)–Mo(1)–S(1)	52.07 (7)	S–Mo(2)–P(2)	88.59 (9)
Mo(2)–Mo(1)–S(3)	96.82 (7)	S–Mo(2)–O(2)	83.2 (2)
Mo(2)–Mo(1)–P(1)	134.82 (7)	S(1)–Mo(2)–S(2)	98.7 (1)
Mo(2)–Mo(1)–O(1)	139.3 (2)	S(1)–Mo(2)–P(2)	90.83 (9)
Mo(3)–Mo(1)–Cl(1)	139.77 (7)	S(1)–Mo(2)–O(2)	166.7 (2)
Mo(3)–Mo(1)–S	53.59 (6)	S(2)–Mo(2)–P(2)	160.1 (1)
Mo(3)–Mo(1)–S(1)	99.35 (7)	S(2)–Mo(2)–O(2)	88.9 (2)
Mo(3)–Mo(1)–S(3)	53.27 (7)	P(2)–Mo(2)–O(2)	78.7 (2)
Mo(3)–Mo(1)–P(1)	138.73 (7)	Mo(1)–Mo(3)–Mo(2)	60.05 (3)
Mo(3)–Mo(1)–O(1)	89.7 (2)	Mo(1)–Mo(3)–Cl(3)	138.71 (8)
Cl(1)–Mo(1)–S	87.44 (9)	Mo(1)–Mo(3)–Cl(4)	95.57 (7)
Cl(1)–Mo(1)–S(1)	99.37 (9)	Mo(1)–Mo(3)–S	53.93 (6)
Cl(1)–Mo(1)–S(3)	155.47 (9)	Mo(1)–Mo(3)–S(2)	97.93 (7)
Cl(1)–Mo(1)–P(1)	78.90 (9)	Mo(1)–Mo(3)–S(3)	52.52 (6)
Cl(1)–Mo(1)–O(1)	77.7 (2)	Mo(1)–Mo(3)–P(3)	135.65 (8)
S–Mo(1)–S(1)	103.57 (9)	Mo(2)–Mo(3)–Cl(3)	94.44 (7)
S–Mo(1)–S(3)	105.99 (9)	Mo(2)–Mo(3)–Cl(4)	138.61 (8)
S–Mo(1)–P(1)	165.76 (9)	Mo(2)–Mo(3)–S	53.72 (6)
S–Mo(1)–O(1)	87.4 (2)	Mo(2)–Mo(3)–S(2)	53.32 (7)
S(1)–Mo(1)–S(3)	97.3 (1)	Mo(2)–Mo(3)–S(3)	96.51 (7)
S(1)–Mo(1)–P(1)	82.81 (9)	Mo(2)–Mo(3)–P(3)	139.21 (8)
S(1)–Mo(1)–O(1)	168.6 (2)	Cl(3)–Mo(3)–Cl(4)	83.07 (9)
S(3)–Mo(1)–P(1)	85.49 (9)	Cl(3)–Mo(3)–S	84.96 (9)
S(3)–Mo(1)–O(1)	82.5 (2)	Cl(3)–Mo(3)–S(2)	89.1 (1)
P(1)–Mo(1)–O(1)	85.8 (2)	Cl(3)–Mo(3)–S(3)	167.96 (9)
Mo(1)–Mo(2)–Mo(3)	60.21 (3)	Cl(3)–Mo(3)–P(3)	85.2 (1)
Mo(1)–Mo(2)–Cl(2)	138.76 (7)	Cl(4)–Mo(3)–S	84.98 (9)
Mo(1)–Mo(2)–S	54.04 (6)	Cl(4)–Mo(3)–S(2)	166.0 (1)
Mo(1)–Mo(2)–S(1)	52.98 (7)	Cl(4)–Mo(3)–S(3)	91.9 (1)
Mo(1)–Mo(2)–S(2)	97.66 (7)	Cl(4)–Mo(3)–P(3)	82.0 (1)
Mo(1)–Mo(2)–P(2)	102.00 (7)	S–Mo(3)–S(2)	105.88 (9)
Mo(1)–Mo(2)–O(2)	137.0 (2)	S–Mo(3)–S(3)	105.58 (9)
Mo(3)–Mo(2)–Cl(2)	138.39 (7)	S–Mo(3)–P(3)	164.5 (1)
Mo(3)–Mo(2)–S	53.91 (6)	S(2)–Mo(3)–S(3)	93.5 (1)
Mo(3)–Mo(2)–S(1)	100.43 (7)	S(2)–Mo(3)–P(3)	85.9 (1)
Mo(3)–Mo(2)–S(2)	52.79 (7)	S(3)–Mo(3)–P(3)	83.21 (9)
Mo(3)–Mo(2)–P(2)	142.42 (7)	Mo(1)–S–Mo(2)	72.54 (8)
Mo(3)–Mo(2)–O(2)	92.9 (2)	Mo(1)–S–Mo(3)	72.48 (8)
Cl(2)–Mo(2)–S	162.74 (9)	Mo(2)–S–Mo(3)	72.37 (8)
Cl(2)–Mo(2)–S(1)	85.82 (9)	Mo(1)–S(1)–Mo(2)	74.94 (8)
Cl(2)–Mo(2)–S(2)	85.63 (9)	Mo(2)–S(2)–Mo(3)	73.90 (8)
Cl(2)–Mo(2)–P(2)	77.65 (9)	Mo(1)–S(3)–Mo(3)	74.21 (8)

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

successful. This molecule was refined anisotropically with all five atoms as carbon atoms. The final difference Fourier map showed seven peaks with heights ranging from 1.165 to 1.584 e/Å^3 in the vicinity of the heavy atoms. No other problems arose. The atomic positional and isotropic equivalent displacement parameters are listed in Table IV.

Results

Compound 1. The structure consists of normal packing of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_3(H_2O)_2$ and Et_3PO molecules, each residing on a general position. An ORTEP drawing of the molecule is shown in Figure 1, where the atom-numbering scheme is defined. A unit cell diagram is shown in Figure 2. The three Mo–Mo bond lengths are nearly equal with an average distance of 2.765 [4] Å. The Mo_3 core is capped by one sulfur atom and edge-bridged by three additional sulfurs. The Mo–S bond distances and the Mo–S–Mo angles are comparable to those in other Mo_3S_4 complexes. No symmetry is shown by the molecule, as the coordination sphere of each molybdenum is different. Both Mo(1) and Mo(2) are coordinated to a PEt_3 ligand, a chlorine atom, and a water molecule. However, the phosphine ligand lies trans to the capping sulfur atom on Mo(1) and the chlorine atom is trans to the capping sulfur atom on Mo(2). The change in coordination site for Mo(2) is accompanied by a hydrogen-bond interaction between the bound water molecule and the phosphine oxide molecule. This configuration permits a satisfactory packing interaction between the bound phosphine and the phosphine oxide. Selected important bond distances and angles for **1** are given in Table V.

Compounds 2 and 3. The trinuclear complexes crystallize in general positions, and the unit cell is completed by two interstitial THF molecules. A representative ORTEP drawing for molecules **2** and **3** and the atom-numbering scheme are shown in Figure 3, where M = Mo for **2** and M = W for **3**. A unit cell diagram is shown in Figure 4. In each case the metal–metal bonds are nearly equal, the average values being 2.780 [8] Å and 2.774 [6] Å for

Table VI. Listing of Selected Bond Distances (Å) and Angles (deg) for $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(H_2O)(OPEt_2H)\cdot 2THF$ (**2**)[a]

Distances

Mo(1)–Mo(2)	2.795 (2)	Mo(2)–S(1)	2.288 (4)
Mo(1)–Mo(3)	2.767 (2)	Mo(2)–S(2)	2.275 (4)
Mo(1)–Br(1)	2.614 (3)	Mo(2)–P(2)	2.604 (5)
Mo(1)–S	2.360 (4)	Mo(2)–O(2)	2.144 (10)
Mo(1)–S(1)	2.291 (5)	Mo(3)–Br(3)	2.646 (2)
Mo(1)–S(3)	2.265 (4)	Mo(3)–Br(4)	2.658 (2)
Mo(1)–P(1)	2.595 (5)	Mo(3)–S	2.345 (4)
Mo(1)–O(1)	2.279 (9)	Mo(3)–S(2)	2.291 (5)
Mo(2)–Mo(3)	2.779 (2)	Mo(3)–S(3)	2.305 (4)
Mo(2)–Br(2)	2.740 (2)	Mo(3)–P(3)	2.618 (5)
Mo(2)–S	2.373 (5)	P(4)–O(2)	1.523 (11)

Angles

Mo(2)–Mo(1)–Mo(3)	59.95 (5)	S–Mo(2)–S(1)	104.6 (2)
Mo(2)–Mo(1)–Br(1)	140.48 (7)	S–Mo(2)–S(2)	105.3 (2)
Mo(2)–Mo(1)–S	54.0 (1)	S–Mo(2)–P(2)	167.0 (1)
Mo(2)–Mo(1)–S(1)	52.3 (1)	S–Mo(2)–O(2)	89.0 (3)
Mo(2)–Mo(1)–S(3)	98.4 (1)	S(1)–Mo(2)–S(2)	94.8 (2)
Mo(2)–Mo(1)–P(1)	136.0 (1)	S(1)–Mo(2)–P(2)	84.6 (2)
Mo(2)–Mo(1)–O(1)	92.5 (3)	S(1)–Mo(2)–O(2)	160.8 (3)
Mo(3)–Mo(1)–Br(1)	104.18 (7)	S(2)–Mo(2)–P(2)	82.7 (2)
Mo(3)–Mo(1)–S	53.7 (1)	S(2)–Mo(2)–O(2)	94.4 (3)
Mo(3)–Mo(1)–S(1)	98.0 (1)	P(2)–Mo(2)–O(2)	80.0 (3)
Mo(3)–Mo(1)–S(3)	53.4 (1)	Mo(1)–Mo(3)–Mo(2)	60.51 (5)
Mo(3)–Mo(1)–P(1)	136.9 (1)	Mo(1)–Mo(3)–Br(3)	141.09 (7)
Mo(3)–Mo(1)–O(1)	139.5 (3)	Mo(1)–Mo(3)–Br(4)	96.47 (8)
Br(1)–Mo(1)–S	86.9 (1)	Mo(1)–Mo(3)–S	54.2 (1)
Br(1)–Mo(1)–S(1)	157.7 (1)	Mo(1)–Mo(3)–S(2)	96.8 (1)
Br(1)–Mo(1)–S(3)	98.1 (1)	Mo(1)–Mo(3)–S(3)	52.1 (1)
Br(1)–Mo(1)–P(1)	81.4 (2)	Mo(1)–Mo(3)–P(3)	135.6 (1)
Br(1)–Mo(1)–O(1)	77.6 (3)	Mo(2)–Mo(3)–Br(3)	96.64 (6)
S–Mo(1)–S(1)	105.0 (2)	Mo(2)–Mo(3)–Br(4)	140.99 (8)
S–Mo(1)–S(3)	105.8 (2)	Mo(2)–Mo(3)–S	54.4 (1)
S–Mo(1)–P(1)	166.0 (2)	Mo(2)–Mo(3)–S(2)	52.2 (1)
S–Mo(1)–O(1)	86.5 (3)	Mo(2)–Mo(3)–S(3)	97.9 (1)
S(1)–Mo(1)–S(3)	96.7 (2)	Mo(2)–Mo(3)–P(3)	134.4 (2)
S(1)–Mo(1)–P(1)	83.7 (2)	Br(3)–Mo(3)–Br(4)	82.36 (7)
S(1)–Mo(1)–O(1)	84.3 (3)	Br(3)–Mo(3)–S	87.0 (1)
S(3)–Mo(1)–P(1)	83.6 (2)	Br(3)–Mo(3)–S(2)	90.8 (1)
S(3)–Mo(1)–O(1)	166.9 (3)	Br(3)–Mo(3)–S(3)	164.9 (1)
P(1)–Mo(1)–O(1)	83.6 (3)	Br(3)–Mo(3)–P(3)	83.2 (1)
Mo(1)–Mo(2)–Mo(3)	59.53 (5)	Br(4)–Mo(3)–S	86.7 (1)
Mo(1)–Mo(2)–Br(2)	94.73 (7)	Br(4)–Mo(3)–S(2)	165.6 (1)
Mo(1)–Mo(2)–S	53.6 (1)	Br(4)–Mo(3)–S(3)	89.0 (1)
Mo(1)–Mo(2)–S(1)	52.4 (1)	Br(4)–Mo(3)–P(3)	84.5 (1)
Mo(1)–Mo(2)–S(2)	96.4 (1)	S–Mo(3)–S(2)	105.7 (1)
Mo(1)–Mo(2)–P(2)	136.9 (1)	S–Mo(3)–S(3)	105.0 (2)
Mo(1)–Mo(2)–O(2)	142.6 (3)	S–Mo(3)–P(3)	167.6 (2)
Mo(3)–Mo(2)–Br(2)	139.02 (9)	S(2)–Mo(3)–S(3)	94.7 (2)
Mo(3)–Mo(2)–S	53.44 (9)	S(2)–Mo(3)–P(3)	82.1 (2)
Mo(3)–Mo(2)–S(1)	97.8 (1)	S(3)–Mo(3)–P(3)	83.6 (2)
Mo(3)–Mo(2)–S(2)	52.8 (1)	Mo(1)–S–Mo(2)	72.4 (1)
Mo(3)–Mo(2)–P(2)	135.4 (1)	Mo(1)–S–Mo(3)	72.1 (1)
Mo(3)–Mo(2)–O(2)	101.2 (2)	Mo(2)–S–Mo(3)	72.2 (1)
Br(2)–Mo(2)–S	85.8 (1)	Mo(1)–S(1)–Mo(2)	75.2 (1)
Br(2)–Mo(2)–S(1)	87.6 (1)	Mo(2)–S(2)–Mo(3)	75.0 (2)
Br(2)–Mo(2)–S(2)	167.6 (1)	Mo(1)–S(3)–Mo(3)	74.5 (1)
Br(2)–Mo(2)–P(2)	85.4 (1)	Mo(2)–O(2)–P(4)	137.4 (8)
Br(2)–Mo(2)–O(2)	79.9 (3)		

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

Table VII. Listing of Selected Bond Distances (Å) and Angles (deg) for $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(H_2O)(OPEt_2H)\cdot 2THF$ (**3**)[a]

Distances

W(1)–W(2)	2.786 (1)	W(2)–S(1)	2.300 (4)
W(1)–W(3)	2.764 (1)	W(2)–S(2)	2.289 (4)
W(1)–Br(1)	2.609 (2)	W(2)–P(2)	2.595 (5)
W(1)–S	2.350 (4)	W(2)–O(2)	2.123 (10)
W(1)–S(1)	2.302 (4)	W(3)–Br(3)	2.648 (2)
W(1)–S(3)	2.279 (3)	W(3)–Br(4)	2.647 (2)
W(1)–P(1)	2.580 (5)	W(3)–S	2.348 (4)
W(1)–O(1)	2.278 (9)	W(3)–S(2)	2.302 (5)
W(2)–W(3)	2.773 (1)	W(3)–S(3)	2.309 (4)
W(2)–Br(2)	2.733 (2)	W(3)–P(3)	2.611 (4)
W(2)–S	2.359 (5)	P(4)–O(2)	1.537 (11)

Angles

W(2)–W(1)–W(3)	59.95 (2)	S–W(2)–S(1)	104.9 (2)
W(2)–W(1)–Br(1)	140.11 (5)	S–W(2)–S(2)	105.8 (1)
W(2)–W(1)–S	53.9 (1)	S–W(2)–P(2)	166.6 (1)
W(2)–W(1)–S(1)	52.7 (1)	S–W(2)–O(2)	88.9 (3)
W(2)–W(1)–S(3)	98.5 (1)	S(1)–W(2)–S(2)	95.5 (1)
W(2)–W(1)–P(1)	136.2 (1)	S(1)–W(2)–P(2)	84.4 (2)
W(2)–W(1)–O(1)	93.4 (3)	S(1)–W(2)–O(2)	160.2 (3)
W(3)–W(1)–Br(1)	103.96 (5)	S(2)–W(2)–P(2)	82.5 (1)
W(3)–W(1)–S	53.9 (1)	S(2)–W(2)–O(2)	94.3 (3)
W(3)–W(1)–S(1)	98.5 (1)	P(2)–W(2)–O(2)	79.9 (3)
W(3)–W(1)–S(3)	53.5 (1)	W(1)–W(3)–W(2)	60.42 (2)
W(3)–W(1)–P(1)	137.64 (9)	W(1)–W(3)–Br(3)	140.62 (5)
W(3)–W(1)–O(1)	139.3 (3)	W(1)–W(3)–Br(4)	96.62 (6)
Br(1)–W(1)–S	86.7 (1)	W(1)–W(3)–S	54.0 (1)
Br(1)–W(1)–S(1)	157.4 (1)	W(1)–W(3)–S(2)	97.3 (1)
Br(1)–W(1)–S(3)	98.1 (1)	W(1)–W(3)–S(3)	52.47 (9)
Br(1)–W(1)–P(1)	81.4 (1)	W(1)–W(3)–P(3)	135.8 (1)
Br(1)–W(1)–O(1)	76.2 (3)	W(2)–W(3)–Br(3)	96.52 (4)
S–W(1)–S(1)	105.1 (2)	W(2)–W(3)–Br(4)	140.54 (5)
S–W(1)–S(3)	106.1 (1)	W(2)–W(3)–S	54.1 (1)
S–W(1)–P(1)	165.3 (2)	W(2)–W(3)–S(2)	52.63 (8)
S–W(1)–O(1)	85.8 (3)	W(2)–W(3)–S(3)	98.13 (9)
S(1)–W(1)–S(3)	97.0 (2)	W(2)–W(3)–P(3)	134.8 (1)
S(1)–W(1)–P(1)	83.5 (2)	Br(3)–W(3)–Br(4)	81.68 (7)
S(1)–W(1)–O(1)	85.4 (3)	Br(3)–W(3)–S	86.7 (1)
S(3)–W(1)–P(1)	84.2 (1)	Br(3)–W(3)–S(2)	90.7 (1)
S(3)–W(1)–O(1)	166.7 (3)	Br(3)–W(3)–S(3)	164.81 (9)
P(1)–W(1)–O(1)	83.0 (3)	Br(3)–W(3)–P(3)	83.4 (1)
W(1)–W(2)–W(3)	59.63 (2)	Br(4)–W(3)–S	86.5 (1)
W(1)–W(2)–Br(2)	94.72 (5)	Br(4)–W(3)–S(2)	165.2 (1)
W(1)–W(2)–S	53.6 (1)	Br(4)–W(3)–S(3)	89.5 (1)
W(1)–W(2)–S(1)	52.8 (1)	Br(4)–W(3)–P(3)	84.4 (1)
W(1)–W(2)–S(2)	97.0 (1)	S–W(3)–S(2)	105.7 (1)
W(1)–W(2)–P(2)	137.1 (1)	S–W(3)–S(3)	105.2 (2)
W(1)–W(2)–O(2)	142.4 (3)	S–W(3)–P(3)	167.4 (2)
W(3)–W(2)–Br(2)	139.01 (6)	S(2)–W(3)–S(3)	95.0 (2)
W(3)–W(2)–S	53.74 (8)	S(2)–W(3)–P(3)	82.2 (2)
W(3)–W(2)–S(1)	98.27 (9)	S(3)–W(3)–P(3)	83.4 (2)
W(3)–W(2)–S(2)	53.1 (1)	W(1)–S–W(2)	72.5 (1)
W(3)–W(2)–P(2)	135.53 (9)	W(1)–S–W(3)	72.1 (1)
W(3)–W(2)–O(2)	101.3 (2)	W(2)–S–W(3)	72.2 (1)
Br(2)–W(2)–S	85.49 (9)	W(1)–S(1)–W(2)	74.5 (1)
Br(2)–W(2)–S(1)	87.36 (9)	W(2)–S(2)–W(3)	74.3 (1)
Br(2)–W(2)–S(2)	167.1 (1)	W(1)–S(3)–W(3)	74.1 (1)
Br(2)–W(2)–P(2)	85.3 (1)	W(2)–O(2)–P(4)	138.4 (8)
Br(2)–W(2)–O(2)	79.5 (2)		

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

Mo–Mo and W–W, respectively. The M_3 triangle is enclosed by a capping sulfur and three edge-bridging sulfur atoms. Each metal atom is in a different coordination environment. M(1) is coordinated to a PEt_3 ligand, a bromine atom, and a water molecule. M(3) has a PEt_3 ligand and two bromine atoms bound to it. M(2) is coordinated to a PEt_3 ligand and a bromine atom, as well as a novel and unexpected molecule, Et_2HPO. All phosphine ligands are trans to the capping sulfur atom, and all other ligands are cis. In **2** the two bromine atoms bound to Mo(3) have an average Mo–Br distance of 2.652 [2] Å, which is 0.038 Å longer than the Mo(1)–Br(1) distance and 0.088 Å shorter than the Mo(2)–Br(2) distance. A similar situation prevails for **3** with the average W(3)–Br distance of 2.648 [2] Å being 0.039 Å longer than W(1)–Br(1) and 0.085 Å shorter than W(2)–Br(2). In general, all metal–ligand bond distances and angles correspond to those reported for similar compounds. Important bond lengths and angles for **2** and **3** are given in Tables VI and VII, respectively.

Discussion

The preparations reported here prove further the usefulness of the $M_3S_7X_4$ compounds as starting materials for the preparation of compounds containing the $M_3S_4^{4+}$ cores, with M = Mo and W. The conversion of μ-S_2^{2-} ligands appears to proceed efficiently by the action of excess PEt_3 in desulfurizing the S_2^{2-} ions (eq 1).

$$PEt_3 + S_2^{2-} \rightleftharpoons Et_3PS + S^{2-} \tag{1}$$

In addition to this, however, the triethylphosphine undergoes other reactions. One, which is not surprising, is reaction with adventitious oxygen to give Et_3PO. In **1** a molecule of Et_3PO is

Inorg. Chem. 1991, 30, 553-558

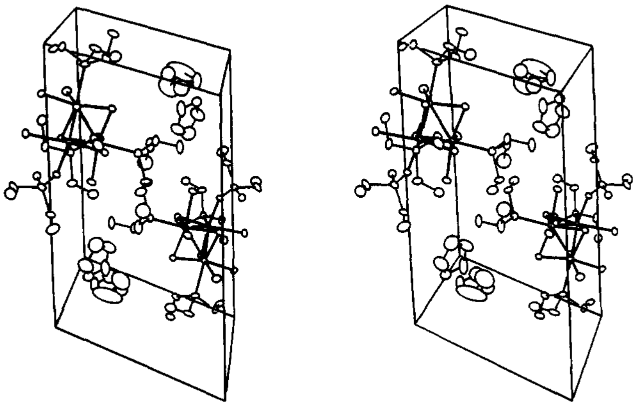
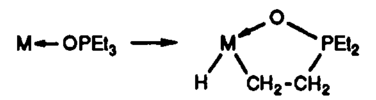


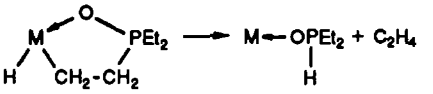
Figure 4. Unit cell of $M_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2THF$ (M = Mo, **2**; M = W, **3**). The hydrogen atom was found for compound **2** only. Axes orientation: *b*, down; *a*, across; *c*, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

attached by a hydrogen bond to a coordinated H_2O molecule. In compounds **2** and **3**, however, a far more interesting product is to be found, namely, a Et_2HPO ligand attached to one metal atom. We suggest the following explanation for the formation of this unusual molecule. First, Et_3P is oxidized to Et_3PO, which then coordinates to a metal atom through the oxygen atom. This is then followed by reactions 2 and 3, where (3) may take place in two stages with a hydrido intermediate.

The structures of the three products are not unusual, apart from the Et_2HPO ligand in **2** and **3**. All three structures are of the



(2)



(3)

B_1 type of M_3X_{13} structure.[22] Compound **1** is much like one reported by Saito[16] except that in that case there were two coordinated methanol molecules instead of two H_2O molecules. There is, however, also a difference in the position of the PEt_3 ligand on Mo(2), cis rather than trans to the capping sulfur atom. The isomorphous compounds **2** and **3** have all phosphine ligands trans to μ_3-S. They are the first such isomorphous pair of Mo_3S_4 and W_3S_4 compounds, and it is interesting that the mean W–W distance appears to be slightly shorter than the mean Mo–Mo distance, although statistically the difference is not real, 0.006 (10) Å.

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, and anisotropic displacement parameters for **1**–**3** (17 pages); listings of observed and calculated structure factors for **1**–**3** (62 pages). Ordering information is given on any current masthead page.

---

(22) Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

Contribution from the Departments of Chemistry, Louisiana State University,
Baton Rouge, Louisiana 70803-1804, and Washington University, St. Louis, Missouri 63130

Photophysics and Photochemistry of Hexachlororhenate(IV) and Hexabromorhenate(IV)

Andrew W. Maverick,*,† Marc D. Lord,‡ Qin Yao,‡ and Leslie J. Henderson, Jr.†

Received October 25, 1989

A study of the solution photophysical and photoredox properties of $ReCl_6^{2-}$ and $ReBr_6^{2-}$ is reported. The solutions are phosphorescent at room temperature, with emission maxima (lifetimes) of 1340 nm (80 ns) and 1380 nm (40 ns) for $(Bu_4N)_2[ReCl_6]$ and $(Bu_4N)_2[ReBr_6]$, respectively, in CH_3CN. The phosphorescences are assigned to the $\Gamma_8(^2T_{1g}) \rightarrow \Gamma_8(^4A_{2g})$ transition. Although the ions also phosphoresce from upper excited states when they are doped into host crystals, no such phosphorescence is observed for the pure solids or for solutions, either at room temperature or at 77 K. Both ions undergo one-electron oxidation on irradiation in the presence of 2,3,5,6-tetrachloro- (chloranil) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ); with $ReCl_6^{2-}$, this process is reversible, and back-electron-transfer reactions are essentially diffusion-controlled. Photochemical reactions with some acceptors, such as tetracyanoethylene, are complicated by the formation of charge-transfer complexes. Irradiation of $ReCl_6^{2-}$ with $C(NO_2)_4$ in CH_3CN or CH_2Cl_2 yields ReO_4^-, along with NOCl (produced by reaction of NO_2 with $ReCl_6^{2-}$ or Cl^-) and $C(NO_2)_3^-$.

Introduction

We have begun an exploration of the photophysical and photochemical properties of d^3 complexes of the early transition metals. These experiments have been designed to combine the attractive photophysical properties of the d^3 configuration with the multiple stable oxidation states of elements such as V, Mo, W, and Re. We have described the photoinitiated two-electron oxidation of $V(phen)_3^{2+}$ (phen = 1,10-phenanthroline) to VO^{2+}[1] and $Mo(NCS)_6^{3-}$ to $Mo_2O_4(NCS)_6^{4-}$.[2] More recently, we have reported that, like the extensively studied complexes of chromium(III), room-temperature solutions of species such as $MoCl_6^{3-}$ and $ReCl_6^{2-}$ phosphoresce in the near-infrared region (1100–1400 nm).[3] We have now studied the properties of $ReCl_6^{2-}$ and $ReBr_6^{2-}$ in more detail. $ReCl_6^{2-}$ is photooxidized to perrhenate by $C(NO_2)_4$; this is an unusual example of a photoinitiated three-electron oxidation.[4]

Experimental Section

Materials. Chloranil (MCB) and DDQ (Aldrich) were purified by recrystallization from 1,2-dichloroethane and chloroform, respectively. For experiments to be conducted in the absence of H_2O, CH_3CN and CH_2Cl_2 were distilled from CaH_2 under N_2 and stored in an inert-atmosphere drybox. $H_2{}^{18}O$ (10 atom %, Aldrich) was handled in a glovebag. Other materials and solvents were of the highest grade commercially available and were used as received. Samples for photochemical measurements were prepared by degassing on a Schlenk or high-vacuum line; Ar was added in some cases (especially for CH_2Cl_2 solutions) to inhibit boiling during flash-photolysis experiments.

The method of Rulfs and Meyer[5] was used to prepare K_2ReCl_6, substituting an equimolar mixture of $HReO_4$ (Aesar) and KCl for $KReO_4$.

---

† Louisiana State University.
‡ Washington University.

(1) Shah, S. S.; Maverick, A. W. *Inorg. Chem.* **1987**, *26*, 1559–1562.
(2) Yao, Q.; Maverick, A. W. *J. Am. Chem. Soc.* **1986**, *108*, 5364–5365.
(3) Yao, Q.; Maverick, A. W. *Inorg. Chem.* **1988**, *27*, 1669–1670.
(4) Several chromium(III) complexes can be photooxidized to Cr(VI): Marchaj, A.; Stasicka, Z.; Rehorek, D. *Polyhedron* **1983**, *2*, 1281–1286. Stopa, G.; Stasicka, Z. *Polyhedron* **1984**, *3*, 247–250.
(5) Rulfs, C. L.; Meyer, R. J. *J. Am. Chem. Soc.* **1955**, *77*, 4505–4507.

0020-1669/91/1330-0553$02.50/0