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Supplementary Material Available: Tables S1–S7, listing complete crystallographic data, bond distances and angles including torsion angles, the derived hydrogen positions, thermal parameters, and least-squares planes (12 pages); Table S8, listing calculated and observed structure factors (16 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of Three New Trinuclear Group VI Clusters

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$Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot 3THF$ (**1**) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot 2MeOH$ (**2**) were prepared by reacting $Mo_3S_7Cl_4$ with the corresponding phosphine ligands at room temperature in THF. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.651$ (2) Å, $b = 20.227$ (4) Å, $c = 27.720$ (6) Å, $\beta = 96.25$ (2)°, $V = 7051$ (5) Å^3, and $Z = 4$. Compound **2** crystallizes in the monoclinic space group Pc with $a = 20.341$ (4) Å, $b = 13.307$ (3) Å, $c = 24.567$ (5) Å, $\beta = 141.08$ (2)°, $V = 4179$ (4) Å^3, and $Z = 4$. Both **1** and **2** belong to the B_1, M_3X_{13} structure family. In addition, we report the sealed-tube synthesis of $W_3S_7Br_4$ (**3**) from stoichiometric quantities of the elements. Crystallographic parameters for **3** are as follows: monoclinic space group $P2_1/c$; $a = 9.488$ (2), $b = 12.303$ (3), $c = 14.143$ (3) Å; $\beta = 121.62$ (2)°; $V = 1406$ (1) Å^3; $Z = 4$. Compound **3** is a B_2 type of trinuclear cluster and is isomorphous with $Mo_3S_7Cl_4$.

Introduction

Over the past three decades several routes to trinuclear transition-metal clusters have been discovered. The molecular clusters are typically prepared in solution by (1) reaction of a mononuclear starting material in the presence of a donating ligand and an appropriate amount (if any) of oxidizing/reducing agent[1-5] or (2) a ligand-exchange reaction that preserves the structural integrity of the M_3 core.[6-10] Several other less general methods have also been described.[11,12]

Fedorov et al. recently reported a promising new route to substituted molecular trimolybdenum chloro sulfido clusters from polymeric starting materials.[13] They prepared $Mo_3S_7X_4\cdot 2PPh_3$ (X = Cl, Br) by boiling $Mo_3S_7X_4$ ($Mo_3S_7X_4$ = $(Mo_3S(S_2)_3X_2X_{4/2})_\infty$) with PPh_3 in MeCN. In 1987, Saito prepared $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PEt_3)_n(MeOH)^{5-n}$ (n = 3, 4) by reacting $Mo_3S_7Cl_4$ with triethylphosphine in THF at room temperature.[14] We have extended this approach by preparing $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot 3THF$ (**1**) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot 2MeOH$ (**2**) by similar routes. We report here the syntheses and crystal structures of **1** and **2**.

Preparation of trinuclear solid-state, polymeric structures is typically carried out by reacting stoichiometric amounts of the starting materials at high temperatures.[15] Trimeric clusters have been prepared by reacting simple metal compounds that are in the required oxidation states[16,17] by comproportionation reactions[18] and by redox reactions.[19] A variety of trinuclear oxide/chalcogenide/halide clusters have been produced. However, until the present the only trinuclear chalcogenide halides had molybdenum as the transition element and these were the only compounds that yielded molecular clusters.[13] We anticipate that the tungsten congeners should provide an entry into the chemistry of analogous molecular tungsten clusters. We report here the synthesis and crystal structure of $W_3S_7Br_4$ (**3**), a complex that should be a useful synthon for the preparation of substituted molecular tritungsten bromo sulfido clusters.

Experimental Section

Materials and Methods. All manipulations were carried out under an argon atmosphere by using standard vacuum-line and Schlenk techniques. The solvents were freshly distilled under nitrogen from the appropriate drying agents. Chemicals were obtained from the following sources: phosphines, S_2Cl_2, and tungsten (100-mesh powder), Strem; sulfur, precipitated grade, Fischer; molybdenum (200-mesh powder), Alfa. All chemicals were used without further purification. The preparations of $Mo_3S_7Cl_4$ and $W_3S_7Br_4$ were carried out in Pyrex tubes with the following dimensions: 15 cm (length) × $2^1/_2$ cm (o.d.), wall thickness 4 mm.

Preparation of $Mo_3S_7Cl_4$. Molybdenum powder (1.00 g, 10.4 mmol), sulfur (0.34 g, 10.4 mmol), and S_2Cl_2 (0.94 g, 6.9 mmol) were placed in a tube. The contents was degassed by three freeze–pump–thaw cycles and then sealed under a vacuum of 2×10^{-4} Torr. The tube was placed in an oven that was slowly warmed to 425 °C (over ca. 8 h) and kept there for 48 h. The oven was then turned off, and the tube was cooled to room temperature over a period of 12 h. A homogeneous mass of red crystals was formed. The product was washed with dichloromethane and dried under vacuum. The isolated yield was 1.92 g, 85% based on Mo.

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Table I. Crystal Data for $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot 3THF$ (**1**), $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot 2MeOH$ (**2**), and $W_3S_7Br_4$ (**3**)

	1	2	3
formula	$C_{66}H_{73}Cl_4Mo_3O_5P_3S_4$	$C_{20}H_{56}Cl_4Mo_3O_2P_6S_4$	$Br_4S_7W_3$
fw	1705.3	1072.4	1095.6
space group	$P2_1/c$	Pc	$P2_1/c$
syst absences	$h0l$: $l = 2n + 1$	$h0l$: $l = 2n + 1$	$h0l$: $l = 2n + 1$
	$0k0$: $k = 2n + 1$		$0k0$: $k = 2n + 1$
a, Å	12.651 (3)	20.341 (4)	9.488 (2)
b, Å	20.227 (4)	13.307 (3)	12.303 (3)
c, Å	27.720 (5)	24.576 (5)	14.143 (3)
α, deg	90.0	90.0	90.0
β, deg	96.25 (2)	141.08 (2)	121.62 (2)
γ, deg	90.0	90.0	90.0
V, Å^3	7051 (5)	4179 (4)	1406 (1)
Z	4	4	4
d_{calc}, g/cm^3	1.606	1.704	5.176
cryst size, mm	0.50 × 0.30 × 0.25	0.55 × 0.45 × 0.40	0.30 × 0.20 × 0.05
μ(Mo Kα), cm^{-1}	8.970	15.640	372.583
data colln instrument	Syntex P3	Syntex P3	Rigaku AFC5R
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)		
orientation reflctns: no.; range (2θ), deg	25; $20 < 2\theta < 30$	25; $20 < 2\theta < 30$	25; $20 < 2\theta < 30$
temp, °C	21	21	21
scan method	ω–2θ	ω–2θ	ω–2θ
data collecn range (2θ), deg	$4 \leq 2\theta \leq 45$	$4 \leq 2\theta \leq 45$	$4 \leq 2\theta \leq 45$
no. of unique data, tot. with $F_o^2 > 3\sigma(F_o^2)$	8971, 3614	4976, 3962	1411, 920
no. of params refined	686	481	123
trans factors: max, min	1.000, 0.971	0.998, 0.956	1.000, 0.411
R^a	0.06010	0.05199	0.05167
$R_w{}^b$	0.06845	0.06121	0.06101
quality-of-fit indicator^c	1.168	1.173	1.142
largest shift/esd in final cycle	0.02	0.02	0.02
largest peak, e/Å^3	0.650	0.821	3.072

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^{c}Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

The identity of the product was confirmed by single-crystal X-ray diffraction.

Preparation of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot 3THF$ (1). $Mo_3S_7Cl_4$ (0.30 g, 0.46 mmol) and PPh_3 (0.80 g, 3.03 mmol) were vigorously stirred in 20 mL of THF for 48 h. The resulting dark orange mixture was filtered, leaving an orange solid (presumably unreacted $Mo_3S_7Cl_4$) and a dark green filtrate. The filtrate was layered with an equal volume of hexane. Dark green needles formed in 5 days. The yield based on $Mo_3S_7Cl_4$ was 0.26 g, 35%.

Preparation of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot 2MeOH$ (2). $Mo_3S_7Cl_4$ (0.5 g, 0.77 mmol), dmpe (2.00 g, 13.3 mmol), and 20 mL of THF were stirred at room temperature for 48 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The remaining solid was dissolved in acetone, and the solution was deposited on a silica gel column. The column was washed with acetone. A green band appeared, which was eluted with MeOH. The green eluate was allowed to evaporate in air, affording green needles of **2**. The isolated yield was 0.37 g, 48% based on $Mo_3S_7Cl_4$.

Preparation of $W_3S_7Br_4$ (3). Tungsten powder (1.62 g, 8.81 mmol), sulfur (0.66 g, 20.5 mmol), and bromine (1.03 g, 6.44 mmol) were placed in a tube. The contents was degassed by three freeze–pump–thaw cycles and then sealed under a vacuum of 2×10^{-4} Torr. The tube was placed in an oven that was slowly warmed to 425 °C (over ca. 8 h) and kept there for 48 h. The oven was then turned off, and the tube was cooled to room temperature over a period of 12 h. The product, a brown mass, was washed with dichloromethane and dried under vacuum. The isolated yield was 1.12 g, 35% based on W.

NMR Spectra. The $^{31}P\{^1H\}$ NMR spectra of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot 2MeOH$ (**2**) in MeOH were run on a Varian XL-400 spectrometer in a tube with an insert containing a 1.0% solution of $P(OC_6H_5)_3$ in C_6D_6. The peaks were referenced to $P(OC_6H_5)_3$ at 128.23 ppm. The ^{31}P shifts are reported relative to 85% H_3PO_4 by using the chemical shift difference, $\delta - 128.23$. After the spectrum of **2** was recorded, an attempt was made to prepare $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3H_3(dmpe)_3]^+$ in situ. An excess of $LiBH_4$ dissolved in MeOH was added to the solution of **2**. The color immediately changed to red, and $^{31}P\{^1H\}$ NMR spectra were taken.

X-ray Crystallography

All crystals in this study were mounted in thin-walled capillaries filled with degassed mineral oil to prevent decomposition in the air. Axial lengths and Laue class were confirmed with oscillation photographs. The general procedures were routine to this laboratory and have already been described.[20] Lorentz, polarization, and empirical absorption corrections were applied to the data. The crystal parameters and basic information relating to data collection and structure refinements are summarized in Table I.

Crystal Structure of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot 3THF$ (1). A green acicular crystal was selected from the product and was 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 refinement of the structure proceeded straightforwardly in the monoclinic space group $P2_1/c$. The positions of the molybdenum atoms were found by using the direct-methods part of the SHELXS-86 package. Additional least-squares cycles and difference Fourier maps revealed the positions of the remaining atoms. Hydrogen atoms were not included in the refinement. No disorder or other nonroutine problems arose. The atomic positional and isotropic equivalent displacement parameters are listed in Table II.

Crystal Structure of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot 2MeOH$ (2). A thin green needle was selected from the product and mounted on the goniometer head of a Syntex P3 diffractometer. Periodically monitored check reflections displayed an average decrease of 7.9% during the data collection. This decay was corrected by the use of an anisotropic decay correction. The systematic absences appeared to indicate that the space group was $P2_1/c$. However, attempts to solve the structure in this space group proved unsuccessful. The structure was finally solved in the monoclinic space group Pc by using the direct-methods part of the SHELXS-86 package, which revealed a large portion of the molecule. An alternating series of least-squares refinements and difference electron-density maps revealed the positions of the remaining atoms. Hydrogen atoms were not included in the refinement. Of the two possible enantiomorphs, the one with the better agreement factors is reported here. No disorder or other nonroutine problems arose. The atomic positional and isotropic equivalent displacement parameters are listed in Table III.

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Table II. Positional and Isotropic Equivalent Displacement Parameters and Their Estimated Standard Deviations for $Mo_3S_4Cl_4(PPh_3)_3(H_2O)\cdot 3THF$[a]

atom	*x*	*y*	*z*	B_{eq}, Å^2	atom	*x*	*y*	*z*	B_{eq}, Å^2
Mo(1)	0.3061 (1)	0.22063 (8)	0.11744 (6)	2.31 (3)	C(131)	0.334 (2)	0.391 (1)	0.003 (1)	8.8 (7)
Mo(2)	0.3104 (1)	0.09217 (8)	0.14904 (5)	2.11 (3)	C(132)	0.366 (3)	0.459 (2)	0.006 (1)	12 (1)
Mo(3)	0.2288 (1)	0.19014 (9)	0.20418 (6)	2.31 (3)	C(133)	0.326 (3)	0.501 (2)	0.044 (1)	13 (1)*
Cl(11)	0.4718 (4)	0.2335 (3)	0.0812 (2)	3.5 (1)	C(134)	0.257 (2)	0.478 (1)	0.073 (1)	9.7 (9)
Cl(22)	0.4784 (4)	0.0502 (3)	0.1277 (2)	3.2 (1)	C(135)	0.233 (2)	0.410 (1)	0.0755 (9)	9.1 (8)
Cl(31)	0.2914 (4)	0.1408 (3)	0.2851 (2)	3.7 (1)	C(136)	0.271 (2)	0.370 (1)	0.0399 (8)	6.0 (6)
Cl(32)	0.2927 (4)	0.2939 (3)	0.2469 (2)	3.7 (1)	C(211)	0.046 (2)	0.010 (1)	0.0776 (8)	4.8 (6)
S(1)	0.2443 (4)	0.1301 (3)	0.0741 (2)	2.7 (1)	C(212)	−0.066 (2)	−0.006 (1)	0.0625 (9)	5.6 (6)
S(2)	0.1516 (4)	0.0906 (3)	0.1813 (2)	2.8 (1)	C(213)	−0.103 (2)	−0.070 (1)	0.0637 (8)	5.4 (6)
S(3)	0.1471 (4)	0.2519 (3)	0.1422 (2)	3.0 (1)	C(214)	−0.038 (2)	−0.121 (1)	0.0805 (8)	5.5 (6)
S(4)	0.4063 (4)	0.1798 (2)	0.1873 (2)	2.6 (1)	C(215)	0.070 (2)	−0.109 (1)	0.0988 (7)	4.1 (5)
P(11)	0.2305 (4)	0.2814 (3)	0.0381 (2)	3.3 (1)	C(216)	0.110 (1)	−0.041 (1)	0.0967 (6)	3.3 (5)
P(21)	0.2522 (4)	−0.0243 (3)	0.1129 (2)	2.6 (1)	C(221)	0.309 (2)	−0.1197 (9)	0.0474 (7)	4.0 (5)
P(31)	0.0447 (4)	0.2192 (3)	0.2383 (2)	2.8 (1)	C(222)	0.352 (2)	−0.142 (1)	0.0042 (8)	5.5 (6)
O(1)	0.3605 (9)	0.3219 (6)	0.1457 (4)	3.3 (3)	C(223)	0.388 (1)	−0.098 (1)	−0.0283 (7)	4.7 (6)
O(2)	0.3660 (9)	0.0358 (6)	0.2180 (4)	3.4 (3)	C(224)	0.378 (2)	−0.030 (1)	−0.0190 (7)	5.0 (6)
O(3)	0.566 (1)	0.0178 (9)	0.2544 (6)	7.9 (5)*	C(225)	0.342 (2)	−0.008 (1)	0.0231 (7)	4.3 (5)
O(4)	0.558 (2)	0.382 (1)	0.1393 (7)	9.6 (6)*	C(226)	0.308 (1)	−0.0533 (9)	0.0573 (6)	2.8 (4)
O(5)	0.350 (2)	0.693 (2)	0.076 (1)	18 (1)*	C(231)	0.236 (2)	−0.098 (1)	0.1959 (8)	5.4 (6)
C(31)	0.632 (3)	0.073 (2)	0.250 (1)	14 (1)*	C(232)	0.282 (2)	−0.141 (1)	0.2329 (9)	5.5 (6)
C(32)	0.754 (3)	0.049 (2)	0.263 (1)	15 (1)*	C(233)	0.382 (2)	−0.167 (1)	0.2344 (8)	6.3 (7)
C(33)	0.731 (3)	−0.024 (2)	0.287 (2)	16 (1)*	C(234)	0.441 (2)	−0.153 (1)	0.1971 (9)	5.9 (7)
C(34)	0.633 (3)	−0.038 (2)	0.251 (1)	13 (1)*	C(235)	0.404 (2)	−0.1102 (9)	0.1569 (7)	3.7 (5)
C(41)	0.641 (3)	0.367 (2)	0.106 (1)	12 (1)*	C(236)	0.299 (1)	−0.0855 (9)	0.1577 (6)	3.0 (4)
C(42)	0.715 (3)	0.417 (2)	0.112 (1)	10.2 (9)*	C(311)	−0.026 (1)	0.346 (1)	0.2073 (8)	3.7 (5)
C(43)	0.676 (3)	0.472 (2)	0.141 (1)	12 (1)*	C(312)	−0.032 (2)	0.414 (1)	0.2120 (8)	5.1 (6)
C(44)	0.564 (3)	0.450 (2)	0.150 (1)	12 (1)*	C(313)	0.009 (2)	0.448 (1)	0.254 (1)	7.4 (8)
C(51)	0.347 (4)	0.696 (3)	0.127 (2)	20 (2)*	C(314)	0.060 (2)	0.411 (1)	0.2913 (7)	5.3 (6)
C(52)	0.449 (3)	0.680 (2)	0.143 (2)	16 (1)*	C(315)	0.073 (2)	0.339 (1)	0.2869 (7)	4.7 (5)
C(53)	0.494 (3)	0.640 (2)	0.105 (1)	12 (1)*	C(316)	0.027 (1)	0.3086 (9)	0.2445 (6)	2.1 (4)
C(54)	0.446 (4)	0.667 (2)	0.060 (2)	17 (2)*	C(321)	−0.077 (2)	0.168 (1)	0.1527 (7)	4.8 (6)
C(111)	0.215 (2)	0.282 (1)	−0.0634 (8)	5.2 (6)	C(322)	−0.176 (2)	0.157 (1)	0.1248 (7)	4.8 (6)
C(112)	0.236 (2)	0.259 (1)	−0.1102 (8)	6.9 (7)	C(323)	−0.271 (2)	0.171 (1)	0.144 (1)	7.6 (8)
C(113)	0.305 (2)	0.208 (1)	−0.1117 (7)	6.5 (6)	C(324)	−0.271 (1)	0.199 (1)	0.1887 (8)	5.0 (6)
C(114)	0.357 (2)	0.172 (1)	−0.0698 (7)	6.0 (6)	C(325)	−0.174 (1)	0.211 (1)	0.2182 (8)	4.7 (6)
C(115)	0.333 (1)	0.196 (1)	−0.0241 (7)	3.8 (5)	C(326)	−0.079 (1)	0.199 (1)	0.1985 (6)	3.5 (5)
C(116)	0.268 (2)	0.247 (1)	−0.0215 (7)	4.1 (5)	C(331)	0.043 (1)	0.1180 (9)	0.3035 (7)	3.6 (5)
C(121)	0.033 (2)	0.226 (1)	0.0216 (7)	5.7 (6)	C(332)	0.023 (2)	0.087 (1)	0.3467 (7)	4.8 (6)
C(122)	−0.079 (2)	0.221 (2)	0.013 (1)	8.0 (8)	C(333)	−0.027 (2)	0.122 (1)	0.3812 (9)	6.0 (6)
C(123)	−0.133 (2)	0.277 (1)	0.0101 (9)	8.0 (8)	C(334)	−0.056 (2)	0.188 (1)	0.3727 (7)	5.8 (6)
C(124)	−0.086 (2)	0.341 (2)	0.014 (1)	10 (1)	C(335)	−0.035 (2)	0.221 (1)	0.3294 (7)	4.6 (5)
C(125)	0.028 (2)	0.344 (1)	0.0243 (9)	6.4 (7)	C(336)	0.019 (1)	0.183 (1)	0.2956 (6)	3.7 (5)
C(126)	0.084 (1)	0.285 (1)	0.0279 (6)	3.3 (5)					

[a] Starred values are for atoms refined isotropically. The equivalent isotropic displacement parameter, B_{eq}, is calculated as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

Crystal Structure of $W_3S_7Br_4$ (3). A small red crystal was selected from the product and was shown to be of good quality by polarized light microscopy. The crystal was mounted on the goniometer head of a Rigaku diffractometer. Because the cell dimensions of **3** implied that it was isomorphous with $Mo_3S_7Cl_4$, the atomic positions from that structure determination were used as a starting point in the present investigation. The refinement proceeded straightforwardly. All atoms were given anisotropic thermal parameters except for one sulfur atom. An observed systematic dependence of $w(|F_o| - |F_c|)^2$ on $(\sin\theta)/\lambda$ implied the need for a secondary extinction correction, *g*, of the form $F_c = |F_c|/(1 + gI_c)$. The refined extinction coefficient was 2.21×10^{-8}. The final difference Fourier map showed three peaks near tungsten atoms of height 3.07, 2.86, and 2.50 e/Å^3. The remaining peaks were randomly located and had heights of <2.23 e/Å^3. No disorder or other nonroutine problems arose. The atomic positional and isotropic equivalent displacement parameters are listed in Table IV.

Results

Compound 1. The structure consists of a normal packing of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2$ and THF molecules, each residing on a general position. An ORTEP drawing of the molecule is shown in Figure 1, where the atom-numbering scheme is also defined. A unit cell diagram is shown in Figure 2. Although the molecule has no crystallographically imposed symmetry, it has idealized C_s symmetry with the mirror plane perpendicular to the plane of metal atoms, passing through Mo(3) and bisecting the Mo(1)–Mo(2) edge. The Mo(1)–Mo(2) distance is 0.025 Å

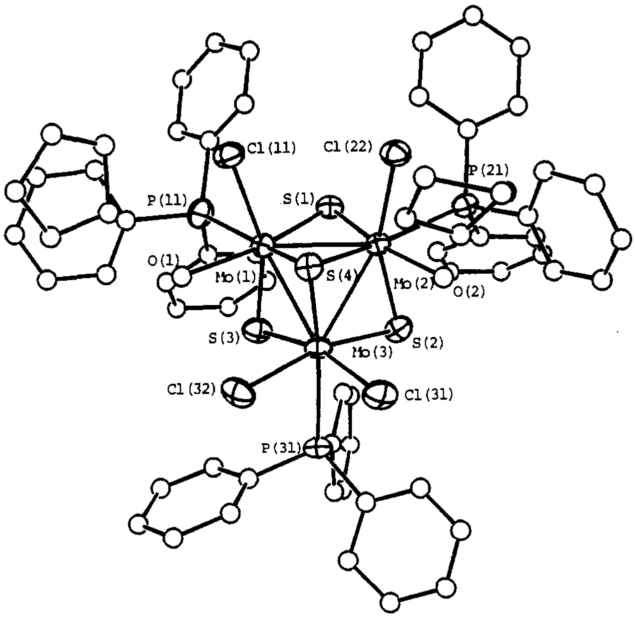

Figure 1. ORTEP drawing of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2$ molecule in **1**. Atoms are represented by their ellipsoids at the 50% probability level.

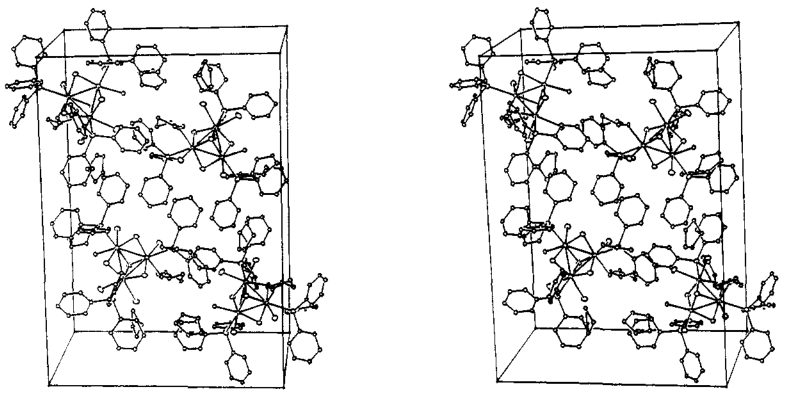

Figure 2. Unit cell of $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot3THF$ (**1**). Axes orientation: *c*, down; *b*, across; *a*, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

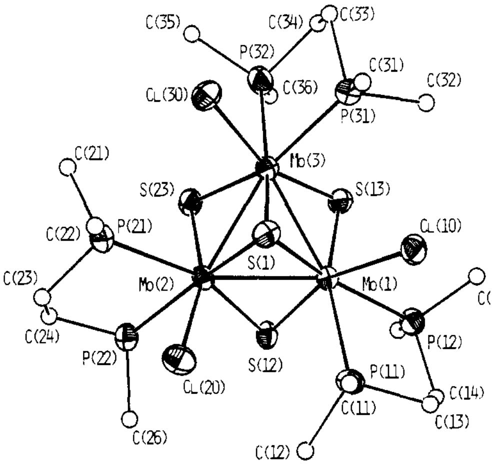

Figure 3. ORTEP drawing of the $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]^+$ cation in compound **2**. Atoms are represented by their ellipsoids at the 50% probability level.

shorter than the average of the other two edges, 2.766 [4] Å. The Mo_3 triangle is surrounded by a capping sulfur atom (S_c) and three edge-bridging sulfur atoms. Mo(1) and Mo(2) are coordinated to a PPh_3 ligand, a water molecule, and a chlorine atom, while Mo(3) is coordinated to two chlorine atoms and one PPh_3 ligand. All phosphine ligands are trans to the capping sulfur atom, while the chlorine atoms and water molecules are cis. The two chlorine ligands bound to Mo(3) have an average Mo–Cl distance of 2.503 [2] Å, which is 0.07 Å longer than the average of the other two. The Mo–S_c and Mo–P distances show variations inconsistent with the idealized C_s symmetry; we presume these variations are due to crystal packing effects. The bond distances and angles are similar to those reported for other Mo_3S_4 clusters. Also, two THF molecules are hydrogen bonded to the coordinated water molecules and there is one interstitial THF molecule. Selected important bond distances and angles for **1** are given in Table V.

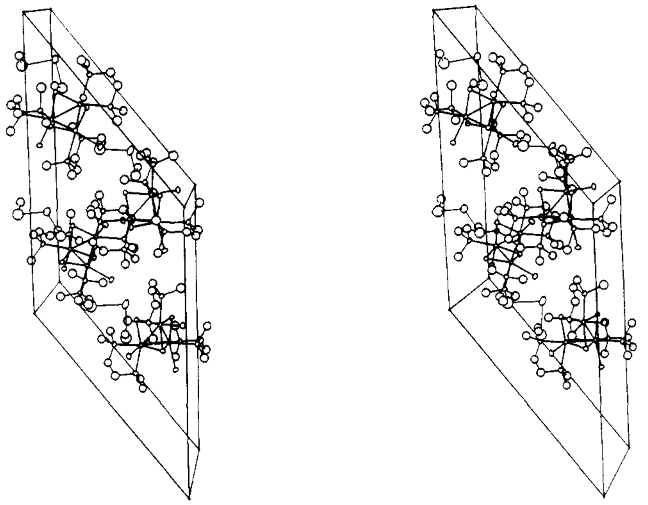

Figure 4. Unit cell of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot2MeOH$ (**2**). Axes orientation: *c*, down; *a*, across; b, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

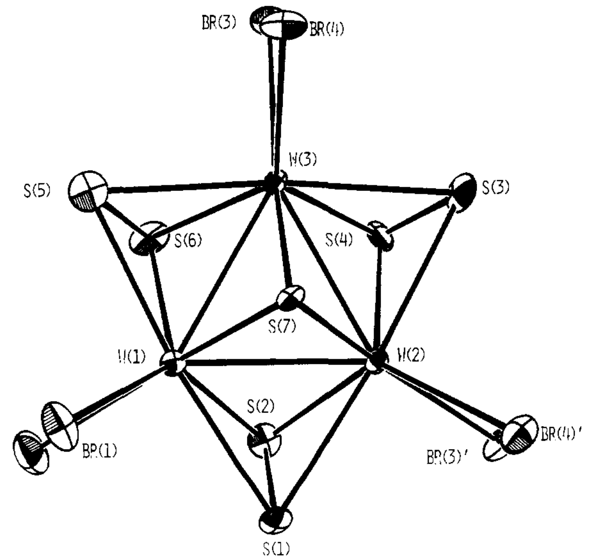

Figure 5. ORTEP drawing of the $W_3S_7Br_2Br_{4/2}$ (**3**) molecule. Atoms are represented by their ellipsoids at the 50% probability level.

Compound 2. There are two independent trinuclear cations in the asymmetric unit. The structures of the two cations are nearly identical, and an ORTEP drawing of one of these is shown in Figure 3. A unit cell diagram is shown in Figure 4. Although the trinuclear cations sit on general positions, they do have virtual C_3 symmetry. The Mo_3 core of each cation is a nearly equilateral triangle with an average Mo–Mo distance of 2.772 [2] Å. Each metal atom is coordinated to one capping and two bridging sulfur atoms, one chelating dmpe ligand, and one chlorine atom, which is cis to the capping sulfur atom. The presence of a chelating phosphine ligand results in significant deviations in the C_{3v} symmetry of the Mo_3S_4 core. The Mo–μ-S distances that are trans to the Mo–P bonds are significantly longer, by an average value of 0.04 Å, than the Mo–μ-S distances trans to the Mo–Cl bonds. In addition, the Mo–P distances that are trans to the capping sulfur atom are an average of 0.06 Å shorter than those that are cis. The metal–ligand bond distances and angles are similar to those reported for other structures of this type, and important values are given in Table VI. Each cation is associated with a crystallographically independent chloride counterion. These chloride ions are each hydrogen bonded to two methanol molecules. Although hydrogen atoms were not identified, the average Cl–O distance, 3.07 [1] Å, and Cl–O–C angle, 106 [1]°, clearly imply the presence of hydrogen bonding.

Compound 3. $W_3S_7Br_4$ is isostructural with $Mo_3S_7Cl_4$. An ORTEP drawing of the asymmetric unit appears in Figure 5, where

Table III Positional and Isotropic Equivalent Displacement Parameters and Their Estimated Standard Deviations for $[Mo_3S_4Cl_3(dmpe)_3]Cl\cdot 2MeOH$[a]

atom	x	y	z	B_{eq}, Å^2
Mo(1)	0.382	0.2714 (1)	0.311	2.03 (4)
Mo(2)	0.18867 (9)	0.1771 (1)	0.18780 (7)	2.03 (4)
Mo(3)	0.23862 (9)	0.3094 (2)	0.13635 (8)	2.25 (4)
S(1)	0.2197 (3)	0.3515 (4)	0.2164 (2)	2.5 (1)
S(12)	0.3527 (3)	0.1043 (4)	0.3036 (2)	2.4 (1)
S(13)	0.4099 (3)	0.2673 (5)	0.2352 (2)	2.7 (1)
S(23)	0.1690 (3)	0.1483 (4)	0.0836 (2)	2.5 (1)
Cl(10)	0.4495 (3)	0.4442 (4)	0.3710 (3)	3.0 (1)
Cl(20)	0.1465 (3)	0.1890 (5)	0.2592 (2)	3.5 (1)
Cl(30)	0.0715 (3)	0.4060 (4)	0.0189 (2)	3.3 (1)
P(11)	0.4244 (3)	0.2744 (5)	0.4413 (2)	2.9 (1)
P(12)	0.5764 (3)	0.2335 (5)	0.4367 (2)	2.7 (1)
P(21)	−0.0124 (3)	0.1982 (5)	0.0598 (3)	3.0 (1)
P(22)	0.1279 (3)	−0.0016 (5)	0.1654 (2)	2.5 (1)
P(31)	0.2995 (3)	0.4876 (5)	0.1471 (3)	3.0 (2)
P(32)	0.2236 (3)	0.3038 (5)	0.0234 (2)	3.2 (1)
C(11)	0.365 (1)	0.373 (2)	0.4451 (9)	7.1 (5)*
C(12)	0.405 (1)	0.157 (2)	0.467 (1)	7.7 (6)*
C(13)	0.569 (1)	0.295 (2)	0.540 (1)	8.6 (7)*
C(14)	0.628 (1)	0.222 (2)	0.539 (1)	7.4 (6)*
C(15)	0.618 (1)	0.119 (2)	0.429 (1)	7.9 (6)*
C(16)	0.654 (1)	0.328 (2)	0.454 (1)	7.8 (6)*
C(21)	−0.085 (1)	0.192 (2)	−0.054 (1)	7.8 (6)*
C(22)	−0.067 (1)	0.305 (2)	0.061 (1)	8.9 (7)*
C(23)	−0.069 (1)	0.088 (2)	0.0590 (9)	7.4 (6)*
C(24)	−0.017 (1)	−0.011 (2)	0.0700 (9)	6.8 (5)*
C(25)	0.168 (1)	−0.100 (2)	0.145 (1)	9.1 (7)*
C(26)	0.167 (1)	−0.053 (2)	0.257 (1)	7.8 (6)*
C(31)	0.261 (1)	0.598 (2)	0.166 (1)	9.4 (7)*
C(32)	0.442 (1)	0.508 (2)	0.229 (1)	9.1 (7)*
C(33)	0.247 (1)	0.515 (2)	0.045 (1)	8.2 (6)*
C(34)	0.278 (1)	0.419 (2)	0.026 (1)	7.8 (6)*
C(35)	0.088 (1)	0.296 (2)	−0.095 (1)	10.2 (8)*
C(36)	0.294 (1)	0.207 (2)	0.032 (1)	8.1 (6)*
Mo(4)	0.68672 (9)	0.2312 (1)	0.10980 (8)	2.18 (4)
Mo(5)	0.74039 (9)	0.3270 (1)	0.24086 (7)	2.06 (4)
Mo(6)	0.87907 (9)	0.1950 (1)	0.28110 (8)	2.12 (4)
S(2)	0.7144 (3)	0.1530 (4)	0.2115 (2)	2.4 (1)
S(45)	0.6698 (3)	0.3992 (4)	0.1171 (2)	2.5 (1)
S(46)	0.8504 (3)	0.2369 (4)	0.1729 (2)	2.6 (1)
S(56)	0.9135 (3)	0.3572 (4)	0.3341 (2)	2.4 (1)
Cl(40)	0.6391 (3)	0.0578 (4)	0.0507 (3)	3.6 (2)
Cl(50)	0.5729 (3)	0.3139 (5)	0.1857 (3)	3.7 (1)
Cl(60)	0.9444 (3)	0.0998 (5)	0.4040 (2)	3.2 (1)
P(41)	0.4851 (3)	0.2246 (5)	−0.0093 (3)	2.9 (1)
P(42)	0.6243 (3)	0.2673 (5)	−0.0267 (3)	2.9 (1)
P(51)	0.8008 (3)	0.3092 (5)	0.3794 (2)	2.9 (1)
P(52)	0.7304 (3)	0.5064 (5)	0.2678 (3)	2.9 (1)
P(61)	1.0728 (3)	0.2030 (5)	0.3847 (5)	2.8 (1)
P(62)	0.9163 (3)	0.0161 (5)	0.2672 (3)	2.9 (1)
C(41)	0.432 (1)	0.123 (2)	−0.001 (1)	10.1 (8)*
C(42)	0.417 (1)	0.339 (2)	−0.0336 (9)	7.2 (5)*
C(43)	0.432 (1)	0.199 (2)	−0.114 (1)	8.2 (6)*
C(44)	0.484 (1)	0.275 (2)	−0.122 (1)	8.4 (6)*
C(45)	0.663 (1)	0.178 (2)	−0.052 (1)	9.1 (7)*
C(46)	0.666 (1)	0.385 (2)	−0.033 (1)	8.4 (6)*
C(51)	0.942 (1)	0.310 (2)	0.483 (1)	8.9 (7)*
C(52)	0.754 (1)	0.197 (2)	0.388 (1)	8.9 (7)*
C(53)	0.752 (1)	0.420 (2)	0.3854 (9)	7.4 (6)*
C(54)	0.781 (1)	0.518 (2)	0.370 (1)	9.1 (7)*
C(55)	0.598 (1)	0.559 (2)	0.185 (1)	8.0 (6)*
C(56)	0.804 (1)	0.600 (2)	0.280 (1)	9.2 (7)*
C(61)	1.119 (1)	0.307 (2)	0.370 (1)	8.0 (6)*
C(62)	1.157 (1)	0.219 (2)	0.498 (1)	8.9 (7)*
C(63)	1.118 (1)	0.090 (2)	0.380 (1)	8.5 (7)*
C(64)	1.058 (1)	−0.006 (2)	0.364 (1)	9.1 (7)*
C(65)	0.900 (1)	−0.005 (2)	0.181 (1)	9.4 (7)*
C(66)	0.860 (1)	−0.095 (2)	0.265 (1)	8.1 (6)*
Cl(1)	0.9346 (4)	0.7613 (6)	0.1320 (4)	6.0 (2)
Cl(2)	0.4236 (4)	0.7424 (7)	0.1299 (4)	7.1 (3)
C(1)	1.150 (2)	0.579 (3)	0.250 (2)	8 (1)*
O(1)	1.149 (2)	0.661 (3)	0.286 (2)	15 (1)*
C(2)	0.905 (2)	0.531 (3)	0.198 (1)	7.4 (9)*
O(2)	0.870 (2)	0.629 (3)	0.187 (1)	13 (1)*
C(3)	0.403 (2)	0.981 (3)	0.191 (1)	7.0 (8)*
O(3)	0.409 (2)	0.886 (3)	0.220 (1)	14 (1)*
C(4)	0.650 (2)	0.921 (4)	0.254 (2)	10 (1)*
O(4)	0.648 (2)	0.817 (3)	0.271 (2)	16 (1)*

[a] Starred values are for atoms refined isotropically. The equivalent isotropic displacement parameter, B_{eq}, is calculated 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 IV. Positional and Isotropic Equivalent Displacement Parameters and Their Estimated Standard Deviations for $W_3S_7Br_4$[a]

atom	x	y	z	B_{eq}, Å^2
W(1)	0.1187 (2)	0.2455 (1)	0.2061 (2)	1.02 (4)
W(2)	0.3986 (2)	0.1659 (1)	0.2229 (2)	0.86 (4)
W(3)	0.3516 (2)	0.3828 (2)	0.2167 (2)	0.85 (4)
S(1)	0.182 (1)	0.0482 (9)	0.220 (1)	1.3 (3)
S(2)	0.125 (1)	0.121 (1)	0.080 (1)	1.7 (3)
S(3)	0.610 (1)	0.298 (1)	0.2473 (9)	1.6 (3)
S(4)	0.406 (1)	0.286 (1)	0.093 (1)	1.6 (3)
S(5)	0.096 (1)	0.446 (1)	0.207 (1)	2.2 (3)*
S(6)	0.068 (1)	0.381 (1)	0.070 (1)	1.6 (3)
S(7)	0.392 (1)	0.2671 (8)	0.3632 (9)	1.0 (2)
Br(1)	0.0507 (5)	0.2347 (4)	0.3618 (4)	2.0 (1)
Br(2)	−0.1971 (6)	0.2086 (5)	0.0858 (5)	2.5 (1)
Br(3)	0.4795 (5)	0.0193 (4)	0.1218 (4)	1.5 (1)
Br(4)	0.6283 (6)	0.0550 (4)	0.3911 (4)	1.7 (1)

[a] Starred value is for atom refined isotropically. The equivalent isotropic displacement parameter, B_{eq}, is calculated as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

the atom-numbering scheme is also defined. A unit cell diagram is shown in Figure 6. The three crystallographically independent tungsten atoms form an isosceles triangle with the W(2)–W(3) distance 0.022 Å shorter than the other two edges. Each W–W edge is bridged by a disulfide ligand, and there is also a capping sulfur atom. Two bromine atoms at each metal center complete the coordination sphere. The bromine atoms at W(1) are terminal and are opposite the short W(2)–W(3) edge. The other four bromine atoms link with other trimeric units to form an extended zig chain with the expanded formula $[(W_3S(S_2)_3Br_2Br_{4/2})_\infty]$. The trimeric moieties are related crystallographically by a 2-fold screw axis along the b-axis direction. The shortest W–W distance between adjacent trimers is 4.044 (2) Å.

If we ignore metal–metal interactions, each tungsten atom can be considered heptacoordinate. The $W(S_2)_2$ and WS_cBr_2 units are both nearly planar and are perpendicular to one another. However, we can simplify the geometrical picture by imagining bonding to the midpoint of the S–S bond, in which case the resulting geometry around tungsten atoms is distorted trigonal bipyramidal, as shown in Figure 7. Selected important bond distances and angles for **3** are given in Table VII.

NMR Spectra. The 162-MHz $^{31}P\{^1H\}$ NMR spectrum of **2** is shown in Figure 8. Each phosphorus atom on a chelating dmpe ligand is in a different magnetic environment resulting in two signals (δ = 30.52 and 20.74 ppm, each of which is split into a doublet of doublets. The four peaks of the signal centered at 30.52 ppm are at 4950.8, 4945.7, 4935.6, and 4930.1 Hz. The four peaks of the signal centered at 20.74 ppm are at 3367.8, 3361.9, 3352.5, and 3346.5 Hz. The pattern of coupling constants is the same for both signals within experimental error.

It has previously been demonstrated[21,22] that *gem* phosphorus coupling can be so small as to be undetectable. Hence, the observed splitting pattern is consistent with the interpretation that, each phosphorus atom is coupled to its *gem* neighbor, ^2J(P–Mo–P) = 5.6 Hz, as well as to one other magnetically equivalent phos-

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(21) Grim, S. O.; Barth, R. C.; Mitchell, J. D.; DelGaudio, J. *Inorg. Chem.* **1977**, *16*, 1776.

(22) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Table V. Selected Bond Distances (Å) and Angles for $Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2 \cdot 3THF$[a]

Mo(1)–Mo(2)	2.741 (2)	Mo(2)–Mo(3)	2.770 (2)	Mo(3)–Cl(32)	2.501 (5)	P(21)–C(216)	1.84 (2)
Mo(1)–Mo(3)	2.762 (2)	Mo(2)–Cl(22)	2.420 (5)	Mo(3)–S(2)	2.296 (5)	P(21)–C(226)	1.86 (2)
Mo(1)–Cl(11)	2.434 (5)	Mo(2)–S(1)	2.286 (5)	Mo(3)–S(3)	2.279 (5)	P(21)–C(236)	1.81 (2)
Mo(1)–S(1)	2.281 (5)	Mo(2)–S(2)	2.287 (5)	Mo(3)–S(4)	2.352 (5)	P(31)–C(316)	1.83 (2)
Mo(1)–S(3)	2.285 (5)	Mo(2)–S(4)	2.336 (5)	Mo(3)–P(31)	2.674 (5)	P(31)–C(326)	1.86 (2)
Mo(1)–S(4)	2.347 (5)	Mo(2)–P(21)	2.634 (5)	P(11)–C(116)	1.90 (2)	P(31)–C(336)	1.81 (2)
Mo(1)–P(11)	2.608 (5)	Mo(2)–O(2)	2.272 (12)	P(11)–C(126)	1.84 (2)	O(1)–O(4)	2.80 (2)
Mo(1)–O(1)	2.273 (12)	Mo(3)–Cl(31)	2.505 (5)	P(11)–C(136)	1.87 (2)	O(2)–O(3)	2.65 (2)

Mo(2)–Mo(1)–Mo(3)	60.44 (6)	Cl(22)–Mo(2)–S(1)	98.1 (2)	Cl(31)–Mo(3)–Cl(32)	81.7 (2)	Mo(2)–S(2)–Mo(3)	74.4 (2)
Cl(11)–Mo(1)–S(1)	97.4 (2)	Cl(22)–Mo(2)–S(2)	157.3 (2)	Cl(31)–Mo(3)–S(2)	88.9 (2)	Mo(1)–S(3)–Mo(3)	74.5 (2)
Cl(11)–Mo(1)–S(3)	157.0 (2)	Cl(22)–Mo(2)–S(4)	87.1 (2)	Cl(31)–Mo(3)–S(3)	165.2 (2)	Mo(1)–S(4)–Mo(2)	71.6 (1)
Cl(11)–Mo(1)–S(4)	88.0 (2)	Cl(22)–Mo(2)–P(21)	79.1 (2)	Cl(31)–Mo(3)–S(4)	85.8 (2)	Mo(1)–S(4)–Mo(3)	72.0 (1)
Cl(11)–Mo(1)–P(11)	81.7 (2)	Cl(22)–Mo(2)–O(2)	80.2 (3)	Cl(31)–Mo(3)–P(31)	88.5 (2)	Mo(2)–S(4)–Mo(3)	72.4 (1)
Cl(11)–Mo(1)–O(1)	78.7 (3)	S(1)–Mo(2)–S(2)	96.3 (2)	Cl(32)–Mo(3)–S(2)	166.5 (2)	Mo(1)–P(11)–C(116)	117.4 (7)
S(1)–Mo(1)–S(3)	96.8 (2)	S(1)–Mo(2)–S(4)	106.2 (2)	Cl(32)–Mo(3)–S(3)	89.6 (2)	Mo(1)–P(11)–C(126)	114.7 (6)
S(1)–Mo(1)–S(4)	106.0 (2)	S(1)–Mo(2)–P(21)	84.0 (2)	Cl(32)–Mo(3)–S(4)	84.4 (2)	Mo(1)–P(11)–C(136)	110.9 (7)
S(1)–Mo(1)–P(11)	82.0 (2)	S(1)–Mo(2)–O(2)	169.3 (3)	Cl(32)–Mo(3)–P(31)	84.0 (2)	Mo(2)–P(21)–C(216)	118.8 (7)
S(1)–Mo(1)–O(1)	168.2 (3)	S(2)–Mo(2)–S(4)	105.5 (2)	S(2)–Mo(3)–S(3)	97.4 (2)	Mo(2)–P(21)–C(226)	118.9 (6)
S(3)–Mo(1)–S(4)	105.3 (2)	S(2)–Mo(2)–P(21)	85.2 (2)	S(2)–Mo(3)–S(4)	104.7 (2)	Mo(2)–P(21)–C(236)	107.0 (6)
S(3)–Mo(1)–P(11)	82.5 (2)	S(2)–Mo(2)–O(2)	82.4 (3)	S(2)–Mo(3)–P(31)	86.0 (2)	Mo(3)–P(31)–C(316)	111.8 (6)
S(3)–Mo(1)–O(1)	83.7 (3)	S(4)–Mo(2)–P(21)	164.0 (2)	S(3)–Mo(3)–S(4)	105.3 (2)	Mo(3)–P(31)–C(326)	116.9 (6)
S(4)–Mo(1)–P(11)	167.8 (2)	S(4)–Mo(2)–O(2)	84.3 (3)	S(3)–Mo(3)–P(31)	78.7 (2)	Mo(3)–P(31)–C(336)	117.9 (6)
S(4)–Mo(1)–O(1)	85.2 (3)	P(21)–Mo(2)–O(2)	85.4 (3)	S(4)–Mo(3)–P(31)	167.8 (2)	Mo(1)–O(1)–O(4)	127.5 (7)
P(11)–Mo(1)–O(1)	86.3 (3)	Mo(1)–Mo(3)–Mo(2)	59.40 (6)	Mo(1)–S(1)–Mo(2)	73.8 (1)	Mo(2)–O(2)–O(3)	125.8 (7)
Mo(1)–Mo(2)–Mo(3)	60.16 (6)						

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

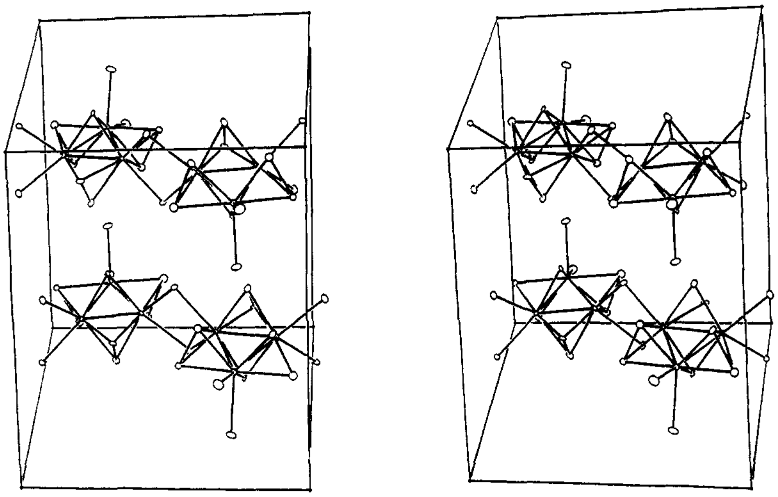

Figure 6. Unit cell diagram of $W_3S_7Br_4$ (**3**). Axes orientation: *c*, down; *b*, across; *a*, toward viewer. Atoms are represented by their ellipsoids at the 20% probability level.

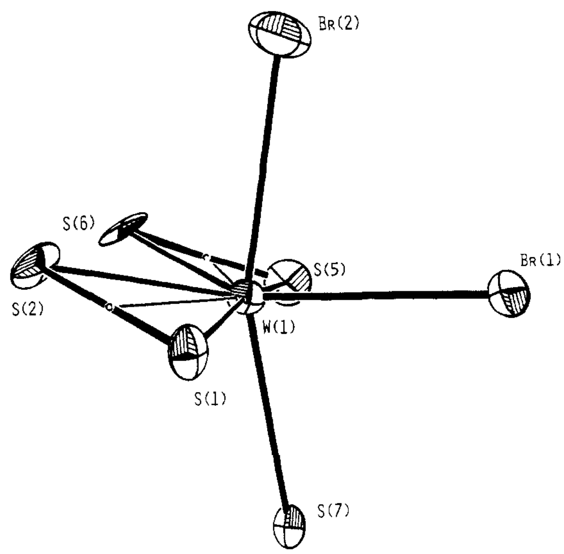

Figure 7. ORTEP drawing representing local geometry around the W(1) atom in $W_3S_7Br_4$ (**3**). Atoms are represented by their ellipsoids at the 50% probability level.

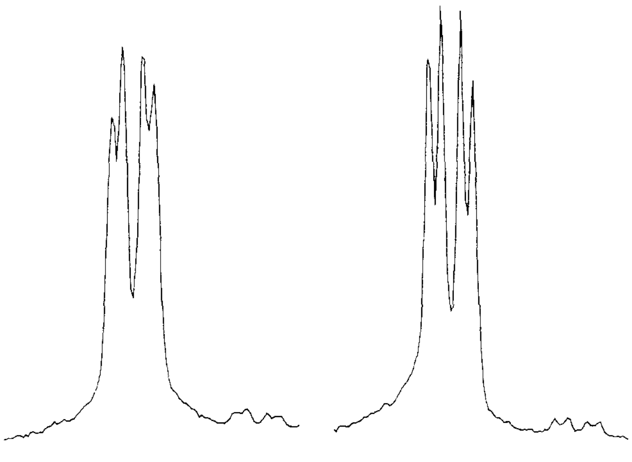

Figure 8. $^{31}P\{^1H\}$ NMR spectrum of $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl \cdot 2MeOH$ (**2**).

phorus atom, ^3J(P–Mo–Mo–P) = 15.4 Hz. Since each of the two nonequivalent phosphorus nuclei has only one phosphorus neighbor

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Mo_3S_4Cl_3(dmpe)_3]Cl \cdot 2MeOH$[a]

Mo(1)–Mo(2)	2.772 (2)	Mo(2)–P(21)	2.584 (4)	Mo(4)–Cl(40)	2.487 (6)	Mo(6)–S(56)	2.329 (6)
Mo(1)–Mo(3)	2.770 (1)	Mo(2)–P(22)	2.535 (6)	Mo(4)–P(41)	2.592 (4)	Mo(6)–Cl(60)	2.501 (6)
Mo(1)–S(1)	2.346 (5)	Mo(3)–S(1)	2.348 (8)	Mo(4)–P(42)	2.543 (7)	Mo(6)–P(61)	2.531 (5)
Mo(1)–S(12)	2.274 (6)	Mo(3)–S(13)	2.277 (4)	Mo(5)–Mo(6)	2.771 (3)	Mo(6)–P(62)	2.600 (7)
Mo(1)–S(13)	2.325 (7)	Mo(3)–S(23)	2.330 (6)	Mo(5)–S(2)	2.359 (6)	Cl(1)–O(1)	3.07 (3)
Mo(1)–Cl(10)	2.490 (5)	Mo(3)–Cl(30)	2.504 (4)	Mo(5)–S(45)	2.333 (6)	Cl(1)–O(2)	3.07 (4)
Mo(1)–P(11)	2.598 (7)	Mo(3)–P(31)	2.592 (7)	Mo(5)–S(56)	2.293 (4)	Cl(2)–O(3)	3.10 (5)
Mo(1)–P(12)	2.533 (4)	Mo(3)–P(32)	2.547 (8)	Mo(5)–Cl(50)	2.509 (6)	Cl(2)–O(4)	3.04 (3)
Mo(2)–Mo(3)	2.780 (3)	Mo(4)–Mo(5)	2.778 (3)	Mo(5)–P(51)	2.578 (7)	C(1)–O(1)	1.41 (7)
Mo(2)–S(1)	2.364 (6)	Mo(4)–Mo(6)	2.763 (1)	Mo(5)–P(52)	2.528 (7)	C(2)–O(2)	1.41 (5)
Mo(2)–S(12)	2.323 (4)	Mo(4)–S(2)	2.336 (7)	Mo(6)–S(2)	2.354 (6)	C(3)–O(3)	1.41 (6)
Mo(2)–S(23)	2.295 (7)	Mo(4)–S(45)	2.290 (6)	Mo(6)–S(46)	2.304 (7)	C(4)–O(4)	1.46 (7)
Mo(2)–Cl(20)	2.486 (7)	Mo(4)–S(46)	2.337 (6)				

M(2)–Mo(1)–Mo(3)	60.21 (6)	Cl(20)–Mo(2)–P(21)	76.3 (2)	S(2)–Mo(4)–P(41)	92.6 (2)	Mo(4)–Mo(6)–Mo(5)	60.27 (6)
S(1)–Mo(1)–S(12)	106.5 (2)	Cl(20)–Mo(2)–P(22)	80.5 (2)	S(2)–Mo(4)–P(42)	162.3 (2)	S(2)–Mo(6)–S(46)	106.2 (2)
S(1)–Mo(1)–S(13)	104.6 (2)	P(21)–Mo(2)–P(22)	78.2 (2)	S(45)–Mo(4)–S(46)	98.0 (2)	S(2)–Mo(6)–S(56)	105.4 (2)
S(1)–Mo(1)–Cl(10)	82.5 (2)	Mo(1)–Mo(3)–Mo(2)	59.93 (5)	S(45)–Mo(4)–Cl(40)	159.7 (1)	S(2)–Mo(6)–Cl(60)	82.9 (2)
S(1)–Mo(1)–P(11)	94.1 (2)	S(1)–Mo(3)–S(13)	106.1 (2)	S(45)–Mo(4)–P(41)	85.4 (2)	S(2)–Mo(6)–P(61)	164.2 (2)
S(1)–Mo(1)–P(12)	163.0 (2)	S(1)–Mo(3)–S(23)	105.1 (2)	S(45)–Mo(4)–P(42)	88.1 (2)	S(2)–Mo(6)–P(62)	94.7 (2)
S(12)–Mo(1)–S(13)	97.4 (2)	S(1)–Mo(3)–Cl(30)	83.3 (2)	S(46)–Mo(4)–Cl(40)	97.1 (2)	S(46)–Mo(6)–S(56)	96.7 (2)
S(12)–Mo(1)–Cl(10)	159.9 (2)	S(1)–Mo(3)–P(31)	94.2 (2)	S(46)–Mo(4)–P(41)	159.5 (2)	S(46)–Mo(6)–Cl(60)	159.5 (2)
S(12)–Mo(1)–P(11)	85.6 (2)	S(1)–Mo(3)–P(32)	164.1 (2)	S(46)–Mo(4)–P(42)	82.0 (2)	S(46)–Mo(6)–P(61)	87.1 (2)
S(12)–Mo(1)–P(12)	88.1 (2)	S(13)–Mo(3)–S(23)	97.5 (2)	Cl(40)–Mo(4)–P(41)	75.7 (2)	S(46)–Mo(6)–P(62)	84.7 (2)
S(13)–Mo(1)–Cl(10)	97.6 (2)	S(13)–Mo(3)–Cl(30)	159.1 (3)	Cl(40)–Mo(4)–P(42)	80.6 (2)	S(56)–Mo(6)–Cl(60)	98.5 (2)
S(13)–Mo(1)–P(11)	159.2 (1)	S(13)–Mo(3)–P(31)	84.4 (2)	P(41)–Mo(4)–P(42)	77.9 (2)	S(56)–Mo(6)–P(61)	81.0 (2)
S(13)–Mo(1)–P(12)	81.6 (2)	S(13)–Mo(3)–P(32)	86.6 (2)	Mo(4)–Mo(5)–Mo(6)	59.72 (6)	S(56)–Mo(6)–P(62)	158.5 (2)
Cl(10)–Mo(1)–P(11)	75.6 (2)	S(23)–Mo(3)–Cl(30)	98.0 (2)	S(2)–Mo(5)–S(45)	104.0 (2)	Cl(60)–Mo(6)–P(61)	81.8 (2)
Cl(10)–Mo(1)–P(12)	81.0 (2)	S(23)–Mo(3)–P(31)	159.1 (2)	S(2)–Mo(5)–S(56)	106.4 (2)	Cl(60)–Mo(6)–P(62)	76.1 (2)
P(11)–Mo(1)–P(12)	77.9 (2)	S(23)–Mo(3)–P(32)	82.0 (2)	S(2)–Mo(5)–Cl(50)	83.1 (2)	P(61)–Mo(6)–P(62)	77.6 (2)
Mo(1)–Mo(2)–Mo(3)	59.86 (5)	Cl(30)–Mo(3)–P(31)	76.1 (2)	S(2)–Mo(5)–P(51)	94.4 (2)	Mo(4)–S(2)–Mo(5)	72.5 (2)
S(1)–Mo(2)–S(12)	104.4 (2)	Cl(30)–Mo(3)–P(32)	81.7 (2)	S(2)–Mo(5)–P(52)	164.2 (3)	Mo(4)–S(2)–Mo(6)	72.2 (2)
S(1)–Mo(2)–S(23)	105.7 (2)	P(31)–Mo(3)–P(32)	77.3 (2)	S(45)–Mo(5)–S(56)	98.0 (2)	Mo(5)–S(2)–Mo(6)	72.0 (2)
S(1)–Mo(2)–Cl(20)	83.5 (2)	Mo(1)–S(1)–Mo(2)	72.1 (2)	S(45)–Mo(5)–Cl(50)	97.2 (2)	Mo(4)–S(45)–Mo(5)	73.9 (2)
S(1)–Mo(2)–P(21)	93.4 (2)	Mo(1)–S(1)–Mo(3)	72.3 (2)	S(45)–Mo(5)–P(51)	159.6 (2)	Mo(4)–S(46)–Mo(6)	73.1 (2)
S(1)–Mo(2)–P(22)	163.3 (3)	Mo(2)–S(1)–Mo(3)	72.3 (2)	S(45)–Mo(5)–P(52)	81.9 (2)	Mo(5)–S(56)–Mo(6)	73.7 (2)
S(12)–Mo(2)–S(23)	97.8 (2)	Mo(1)–S(12)–Mo(2)	74.2 (2)	S(56)–Mo(5)–Cl(50)	159.5 (2)	O(1)–Cl(1)–O(2)	84 (1)
S(12)–Mo(2)–Cl(20)	96.7 (2)	Mo(1)–S(13)–Mo(3)	74.0 (2)	S(56)–Mo(5)–P(51)	85.0 (2)	O(3)–Cl(2)–O(4)	83 (1)
S(12)–Mo(2)–P(21)	160.2 (2)	Mo(2)–S(23)–Mo(3)	73.9 (2)	S(56)–Mo(5)–P(52)	87.0 (2)	Cl(1)–O(1)–C(1)	105 (1)
S(12)–Mo(2)–P(22)	82.4 (2)	Mo(5)–Mo(4)–Mo(6)	60.01 (6)	Cl(50)–Mo(5)–P(51)	76.0 (2)	Cl(1)–O(2)–C(2)	106 (3)
S(23)–Mo(2)–Cl(20)	160.3 (1)	S(2)–Mo(4)–S(45)	106.1 (2)	Cl(50)–Mo(5)–P(52)	81.6 (2)	Cl(2)–O(3)–C(3)	103 (3)
S(23)–Mo(2)–P(21)	85.6 (2)	S(2)–Mo(4)–S(46)	105.7 (2)	P(51)–Mo(5)–P(52)	78.1 (2)	Cl(2)–O(4)–C(4)	109 (2)
S(23)–Mo(2)–P(22)	88.2 (2)	S(2)–Mo(4)–Cl(40)	82.6 (2)				

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

Table VII. Selected Bond Distances (Å) and Angles (deg) for $W_3S_7Br_4$[a]

W(1)–W(2)	2.722 (3)	W(1)–Br(1)	2.601 (7)	W(2)–S(7)	2.37 (1)	W(3)–S(7)	2.37 (1)
W(1)–W(3)	2.722 (3)	W(1)–Br(2)	2.595 (5)	W(2)–Br(3)	2.653 (6)	W(3)–Br(3)	2.601 (5)
W(1)–S(1)	2.48 (1)	W(2)–W(3)	2.700 (3)	W(2)–Br(4)	2.614 (4)	W(3)–Br(4)	2.674 (6)
W(1)–S(2)	2.37 (1)	W(2)–S(1)	2.50 (1)	W(3)–S(3)	2.49 (1)	S(1)–S(2)	1.97 (2)
W(1)–S(5)	2.48 (1)	W(2)–S(2)	2.37 (1)	W(3)–S(4)	2.39 (2)	S(3)–S(4)	2.03 (1)
W(1)–S(6)	2.39 (1)	W(2)–S(3)	2.47 (1)	W(3)–S(5)	2.48 (2)	S(5)–S(6)	1.98 (2)
W(1)–S(7)	2.384 (9)	W(2)–S(4)	2.39 (1)	W(3)–S(6)	2.39 (1)		

W(2)–W(1)–W(3)	59.47 (7)	S(7)–W(1)–Br(2)	161.4 (4)	S(4)–W(2)–Br(3)	82.5 (4)	S(5)–W(3)–Br(3)	88.8 (3)
S(1)–W(1)–S(2)	47.9 (5)	Br(1)–W(1)–Br(2)	80.4 (2)	S(4)–W(2)–Br(4)	132.5 (3)	S(5)–W(3)–Br(4)	94.5 (4)
S(1)–W(1)–S(5)	172.4 (4)	W(1)–W(2)–W(3)	60.28 (7)	S(7)–W(2)–Br(3)	161.9 (2)	S(6)–W(3)–S(7)	110.1 (4)
S(1)–W(1)–S(6)	133.0 (5)	S(1)–W(2)–S(2)	47.7 (4)	S(7)–W(2)–Br(4)	83.6 (3)	S(6)–W(3)–Br(3)	131.7 (4)
S(1)–W(1)–S(7)	86.3 (3)	S(1)–W(2)–S(3)	171.3 (5)	Br(3)–W(2)–Br(4)	78.3 (2)	S(6)–W(3)–Br(4)	84.1 (4)
S(1)–W(1)–Br(1)	92.3 (4)	S(1)–W(2)–S(4)	134.6 (3)	W(1)–W(3)–W(2)	60.25 (7)	S(7)–W(3)–Br(3)	83.0 (3)
S(1)–W(1)–Br(2)	91.6 (3)	S(1)–W(2)–S(7)	86.2 (4)	S(3)–W(3)–S(4)	49.1 (3)	S(7)–W(3)–Br(4)	161.0 (3)
S(2)–W(1)–S(5)	133.0 (5)	S(1)–W(2)–Br(3)	93.8 (3)	S(3)–W(3)–S(5)	171.2 (5)	Br(3)–W(3)–Br(4)	78.1 (2)
S(2)–W(1)–S(6)	85.3 (5)	S(1)–W(2)–Br(4)	90.0 (3)	S(3)–W(3)–S(6)	135.1 (5)	W(1)–S(2)–W(2)	70.0 (3)
S(2)–W(1)–S(7)	109.2 (4)	S(2)–W(2)–S(3)	136.0 (4)	S(3)–W(3)–S(7)	84.6 (4)	W(2)–S(3)–W(3)	66.1 (3)
S(2)–W(1)–Br(1)	135.9 (4)	S(2)–W(2)–S(4)	87.0 (4)	S(3)–W(3)–Br(3)	91.1 (3)	W(2)–S(4)–W(3)	68.7 (4)
S(2)–W(1)–Br(2)	82.5 (3)	S(2)–W(2)–S(7)	109.7 (5)	S(3)–W(3)–Br(4)	94.1 (3)	W(1)–S(5)–W(3)	66.6 (4)
S(5)–W(1)–S(6)	47.9 (5)	S(2)–W(2)–Br(3)	83.1 (4)	S(4)–W(3)–S(5)	134.2 (4)	W(1)–S(6)–W(3)	69.4 (3)
S(5)–W(1)–S(7)	86.5 (3)	S(2)–W(2)–Br(4)	132.3 (3)	S(4)–W(3)–S(6)	86.4 (4)	W(1)–S(7)–W(2)	69.8 (3)
S(5)–W(1)–Br(1)	89.2 (5)	S(3)–W(2)–S(4)	49.4 (3)	S(4)–W(3)–S(7)	110.0 (4)	W(1)–S(7)–W(3)	69.8 (3)
S(5)–W(1)–Br(2)	96.0 (3)	S(3)–W(2)–S(7)	85.0 (4)	S(4)–W(3)–Br(3)	134.1 (3)	W(2)–S(7)–W(3)	69.3 (4)
S(6)–W(1)–S(7)	109.6 (4)	S(3)–W(2)–Br(3)	94.6 (4)	S(4)–W(3)–Br(4)	82.5 (3)	W(2)–Br(3)–W(3)	100.6 (2)
S(6)–W(1)–Br(1)	132.9 (4)	S(3)–W(2)–Br(4)	89.3 (3)	S(5)–W(3)–S(6)	48.0 (5)	W(2)–Br(4)–W(3)	99.7 (2)
S(6)–W(1)–Br(2)	85.2 (3)	S(4)–W(2)–S(7)	110.3 (4)	S(5)–W(3)–S(7)	86.7 (5)	W(1)–S(1)–W(2)	66.2 (3)
S(7)–W(1)–Br(1)	81.2 (4)						

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

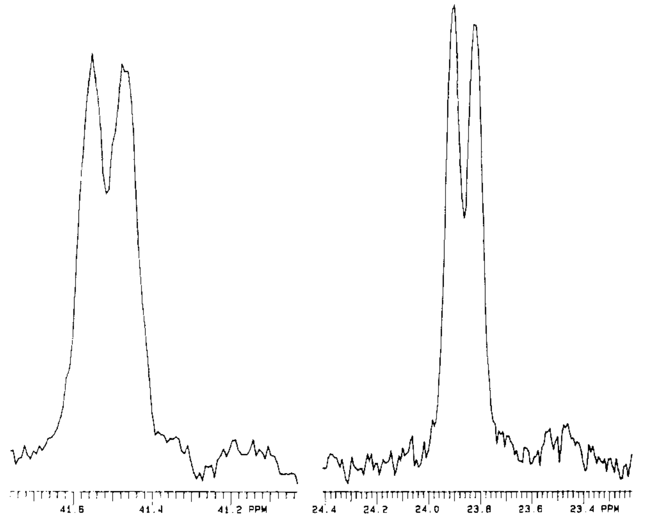

Figure 9. $^{31}P\{^1H\}$ NMR spectrum of the $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3H_3(dmpe)_3]^+$ cation.

that can be considered trans, we presume that this one causes the latter coupling.

The 162-MHz $^{31}P\{^1H\}$ NMR spectrum of the presumed $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3H_3(dmpe)_3]^+$ cation is shown in Figure 9. Both signals have been shifted downfield with respect to the signals found for **2** and appear as doublets centered at 41.52 and 23.87 ppm with ^3J(P–Mo–Mo–P) = 12.4 Hz. The broadening of the signals in this spectrum relative to the spectrum of **2** obscures the small *gem* phosphorus coupling.

Discussion

Synthesis of the discrete trinuclear complexes, **1** and **2**, from polymeric trinuclear starting materials provides further evidence of the robust nature of the Mo_3 core. During the preparation of **1** and **2**, $Mo_3S_7Cl_4$ is presumed to undergo sulfur abstraction by phosphine from the disulfide ligands, resulting in sulfide bridges in the products. Simultaneously, chlorine–molybdenum bonds are broken as the trinuclear monomeric units are extracted from the pristine polymer. The reactive species presumably has the $[Mo_3S_4]^{4+}$ core intact and carries some number of chlorine ligands as well. The nature of the $[Mo_3S_4]^{4+}$ core is such that the bridging and capping sulfur atoms occupy a set of facial positions around the octahedrally coordinated metal atoms, leaving the other three labile facial sites available to other ligands. If we assume that the $[Mo_3S_4]^{4+}$ core does not undergo any redox process during the reaction, then in order to maintain charge balance, the presence of four chloride ions is required in the vicinity of the core. The requirement of two coordination sites for the chelating dmpe ligand in the case of **2** leaves one open site for coordination of a chloride ion on each metal atom and results in the formation of a cationic species with the fourth chloride ion acting as a counterion.

Because of steric requirements, in the case of **1**, only one triphenylphosphine ligand can be accommodated by the remaining three mutually cis coordination sites on each metal atom, leaving two sites per metal atom capable of binding chloride ions or solvent. Four chloride ligands can now bind to the core, resulting in a neutral species, and the remaining sites are occupied by solvent molecules. The triphenylphosphine ligand chooses the position trans to the capping sulfur atom because this position is unique among three octahedra that share edges in that it is furthest away from terminal ligands on adjacent octahedra. Results obtained by Saito et al. support the above hypothesis.[14] They also employed $Mo_3S_7Cl_4$ as a starting material. When this was treated with excess PEt_3, a sterically less demanding ligand than PPh_3, $Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2$ or $Mo_3S_4Cl_4(PEt_3)_4(MeOH)$ was obtained depending on the workup procedure. In both compounds three PEt_3 ligands occupy sites that are trans to capping sulfur atoms, while the fourth PEt_3 ligand in the latter compound is cis.

Compounds **1** and **2** both belong to the B_1, M_3X_{13} structure family.[23] The basic structure of **1** is similar to that of Saito's complex, $Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2$, with H_2O replacing MeOH and PPh_3 replacing PEt_3.[14] The only significant differences in the intramolecular geometries of the two compounds are in the Mo–P distances. In $Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2$, the Mo–P distances are nearly equivalent with an average value of 2.599 [3] Å whereas in **1** the values vary from 2.608 (5) to 2.674 (5) Å. The cation of **2** is identical with that prepared by Cotton and Llusar, and there are no significant differences between the structures.[3]

As stated earlier, $W_3S_7Br_4$ (**3**) is isostructural with $Mo_3S_7Cl_4$, a compound that has been demonstrated to be a useful starting material in the synthesis of discrete trinuclear clusters. The interatomic bond distances and angles of **3** are similar to those of $Mo_3S_7Cl_4$ and show differences consistent with changes in ionic radii. It is interesting that compound **3** was prepared from the elements and that nature has serendipitously given a product that not only is interesting in its own right but should have great potential for further synthetic development.

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

Supplementary Material Available: Full listings of bond distances, bond angles, and anisotropic displacement parameters for $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4(PPh_3)_3(H_2O)_2\cdot 3THF$ (**1**), $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(dmpe)_3]Cl\cdot 2MeOH$ (**2**), and $W_3S_7Br_4$ (**3**) (29 pages); listings of observed and calculated structure factors for **1**–**3** (44 pages). Ordering information is given on any current masthead page.

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