Table I. SCF–MS–Xα and Experimental Ionization Energies and He II:He I Intensity Ratios for *cis*-[$PtMe_2L_2$] Upper Valence Orbitals

	ionizn energy, eV			
orbital (C_{2v})	SCF–MS–Xα[a] L = C_2H_4	exptl L_2 = cod[c]	He II:He I L_2 = cod	compn[b]
$4a_1$	7.57	7.76, 7.93	1.00	spd (33%), σ_{Me} (16%), $\pi_{C=C}$ (24%)
$2b_2$	8.73	8.47	0.82	pd (9%), σ_{Me} (10%), $\pi_{C=C}$ (47%)
$3a_1$	8.93	8.76	1.05	sd (59%), σ_{Me} (7%), $\pi_{C=C}$ (8%)
$1b_1$	9.22	9.05	0.90	d (78%), $\pi_{C=C}$ (5%)
$1a_2$	9.41	9.39	1.05	d (66%), $\pi_{C=C}$ (11%)
$2a_1$	10.30	9.82	1.01	d (56%), $\pi_{C=C}$ (18%)

[a] The ionization energies were obtained by the removal of a half of an electron from the HOMO ($4a_1$). Geometric parameters assumed in the calculation: Pt–C_{Me} = 2.068 Å, Pt–ol [midpoint of C=C olefin (ol) bond] = 2.169 Å and $\angle C_{ol}$–Pt–C_{ol} = 91.25° (Day, C. S.; Day, V. W.; Shaver, A.; Clark, H. C. *Inorg. Chem.* **1981**, *20*, 2188); $\angle C_{Me}$–Pt–C_{Me} = 81.92° C=C = 1.375 Å, $C_{C=C}$–H = 1.087 Å, $\angle$H–$C_{C=C}$–H = 114.9°, and $\angle$H–$C_{1,C=C}$–$C_{2,C=C}$ = 121.08°: (Love, P. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653). Atomic and outer-sphere radii (bohr): outer, 6.8965; Pt, 2.6577; C, 1.6794; H, 1.2390. [b] Contributions in outer-sphere, intersphere, and hydrogen and contributions less than 5% are not included. [c] The ionization energy of the HOMO of free cod is 9.06 eV.

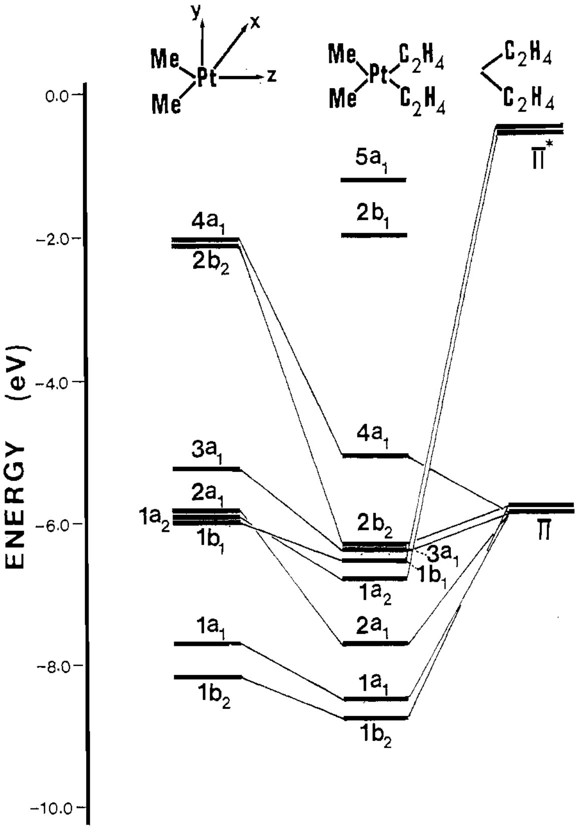

Figure 2. Orbital interaction diagram for *cis*-[$PtMe_2(C_2H_4)_2$]. For *cis*-[$PtMe_2$] the HOMO is $3a_1$. For *cis*-[$PtMe_2(C_2H_4)_2$] the HOMO is $4a_1$. For simplicity, only the major correlations are shown; for example, a correlation between $3a_1$ of the Me_2Pt fragment and $4a_1$ of *cis*-[$PtMe_2L_2$] is expected but is not shown in the diagram. This will be discussed in more depth in the full paper.

cod compound. This band shows resolved vibrational structure, and the observed splitting of 0.17 ± 0.02 eV (~1400 cm^{-1}) correlates well with the expected C=C stretching frequency for [$PtMe_2$(cod)][6] of 1428 cm^{-1}. This is strong evidence that the HOMO has substantial Pt–L character, and this is supported by the calculation. Although such a ligand vibrational splitting is not common, CO vibrational splittings have been seen on M–C MO's in $W(CO)_6$.[13] This vibrational structure has also been observed on the lowest IE band of [$PtMe_2$NBD] (NBD = norbornadiene) and [$Pt(CF_3)_2$(cod)], again strongly suggesting that the splitting is due to C=C bond vibrations.

The agreement between the calculations and experiment for the remaining five peaks is again good. However, with the orbitals so closely spaced, the exact ordering cannot be considered highly reliable, even when the calculations allow for relaxation and relativistic effects.[11]

An orbital correlation diagram is shown in Figure 2, with values calculated by the SCF–MS–Xα method for the ground state only for both of the fragments *cis*-$PtMe_2$ and (C_2H_4) and for *cis*-[$PtMe_2(C_2H_4)_2$]. This illustrates the mixing of the "d" and "σ" orbitals in the complex. As for *trans*-[$PtCl_2L_2$] complexes,[10] the HOMO shows large mixing of Pt 5d and ligand orbitals (Table I). The next orbital has high $\pi_{C=C}$ character, while the mainly 5d orbitals have higher ionization energies. Because of the small differences in energy in this and other *cis*-[$PtMe_2L_2$] complexes, interpretation of the reactivity of these molecules based on selective attack of electrophiles at the HOMO is problematic.[14] However, when electronic effects are dominant electrophilic attack on the σ orbitals rather than on the d orbitals might be predicted.

Acknowledgment. We are grateful to the NSERC for financial support.

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Rational Synthesis of Monooxo Thioanions from [$OMo(SPh)_4$]$^-$. Structural Characterization of the [Ph_4P]$^+$ Salts of the [(η^2-S_2)MoO(μ-S)$_2$MoS(η^2-S_2)]$^{2-}$, [(η^2-S_2)MoO(MoS_4)]$^{2-}$, [(S_4)MoX(μ-S)$_2$MoSX(η^2-S_2)]$^{2-}$ (X = S, O), and [(S_4)MoO(MoS_4)]$^{2-}$ Anions

Sir:

In a previous communication we reported[1] on the systematic synthesis and chemical interconversions of the [$Mo_2(S)_n(S_2)_{6-n}$]$^{2-}$ anions and various isomeric forms of these compounds. More recently we have been able to obtain many of the corresponding [$Mo_2(O)_2(S)_n(S_2)_{4-n}$]$^{2-}$ complexes by a rational synthesis that employs the recently characterized[2] [$Mo_2O_2S_4(DMF)_3$] and [$Mo_2O_2S_2(DMF)_6$]$^{2+}$ complexes.

The availability of series of related Mo/S and Mo/O/S complexes is highly desirable for systematic studies that probe the

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0020-1669/89/1328-0002$01.50/0

Table I. Interatomic Distances (Å) and Angles (deg) in the $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$ (III), $[(\eta^2\text{-}S_2)MoO(MoS_4)]^{2-}$ (IV), $[(\eta^2\text{-}S_2)MoX(\mu\text{-}S)_2MoX(S_4)]^{2-}$ (X = S, O) (V),[a] and $[(S_4)MoO(MoS_4)]^{2-}$ (VI) Anions

	III	IV	V	VI
		Distances		
Mo(1)–Mo(2)	2.820 (1)	2.864 (1)	2.850 (1)	2.888 (3)
Mo(1)–S(7)	2.055 (2)		1.862 (7)	
Mo(1)–S(1)	2.377 (2)	2.175 (3)	2.396 (4)	2.182 (7)
Mo(1)–S(2)	2.397 (3)	2.132 (3)	2.405 (5)	2.135 (7)
Mo(1)–S(5)	2.318 (2)	2.285 (3)	2.285 (3)	2.262 (7)
Mo(1)–S(6)	2.320 (2)	2.281 (3)	2.320 (3)	2.275 (7)
Mo(2)–O	1.677 (4)	1.680 (7)	2.014 (5)	1.669 (13)
Mo(2)–S(3)	2.402 (2)	2.413 (2)	2.401 (3)	2.371 (8)
Mo(2)–S(4)	2.396 (2)	2.400 (3)	2.423 (3)	2.405 (8)
Mo(2)–S(5)	2.330 (2)	2.332 (3)	2.370 (3)	2.382 (8)
Mo(2)–S(6)	2.322 (2)	2.352 (3)	2.331 (3)	2.365 (6)
S(1)–S(2)	2.059 (3)			
S(3)–S(4)	2.068 (3)	2.154 (7)		
		Angles[b]		
S(5,6)–Mo(1)–S(7)	109.6 ± 4		107.2 ± 1.6	
S(5,6)–Mo(2)–O	108.3 ± 0.5 106.6 ± 1.1	106.9 ± 1.2	107.6 ± 0.4	
S(1,2)–Mo(1)–S(7)	109.0 ± 0.5		110.7 ± 1.6	
S(3,4)–Mo(2)–O	110.4 ± 1.3 108.6 ± 2.1	110.0 ± 1.5	108.1 ± 2.6	
Mo(1)–S(5,6)–Mo(2)	74.8 ± 0.1	76.5 ± 0.2	75.6 ± 0.1	76.9 ± 0.1

[a] Subject to orientational disorder. [b] In all cases the average value of two chemically equivalent, crystallographically independent angles is given.

influence of specific Mo coordination environments on the reactivity of the Mo-coordinated S^{2-}, S_2^{2-}, and S_4^{2-} ligands. Certain aspects of the unique reactivity characteristics of these ligands already have been discussed.[3] A reliable general synthesis of molybdothioanion dimers containing both Mo=S and Mo=O units is not available, and the small number of such complexes that have been reported, such as $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoO(\mu\text{-}S)_2MoOS]^{2-}$[4] and $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$,[5] have been obtained by serendipitous means.

In this communication we report on the rational synthesis of complexes that contain both Mo=S and Mo=O units. This synthesis is based on the $[(PhS)_2Mo(O)(MoS_4)]^{2-}$ anion (I) and the ligand substitution or oxidation reactions that this molecule undergoes. The synthesis of I is accomplished in dimethylformamide (DMF) solution by the substitution of two of the thiophenolate ligands in the $[(PhS)_4Mo(O)]^-$ complex[6] (II) by the MoS_4^{2-} chelating ligand (Figure 1). Both the $[Ph_4P]^+$ and $[Et_4N]^+$ microcrystalline salts of I give satisfactory elemental analyses,[7] and the integration of the resonances in the ^1H NMR spectrum of the $[Et_4N]^+$ salt of I is consistent with the proposed formulation.

The reduction of the Mo ion from the +5 oxidation state in II to the +4 oxidation state in I apparently is facilitated by the reducing nature of the displaced PhS^- ligands and the concomitant formation of PhSSPh (eq 1). Oxidation of I by dibenzyl trisulfide

$$[(PhS)_4Mo(O)]^- + MoS_4^{2-} \rightarrow [(PhS)_2Mo(O)(MoS_4)]^{2-} + PhS^- + {}^1/_2PhSSPh \quad (1)$$

(BzSSSBz) in DMF, in a 1:4 molar ratio, proceeds readily at ambient temperature and affords the $[Mo_2OS_7]^{2-}$ anion.[8] The latter, with $[Ph_4P]^+$ as a counterion, is obtained in ~65% yield as red-black crystals (III).[9] The utility of the BzSSSBz reagent as an oxidizing agent for thiophenolate ligands with the concomitant generation of S_x^{2-} ligands has been reported previously[1] in the synthesis of various binary metal sulfide complexes. The reaction of III with 1 equiv of Ph_3P in DMF solution affords in high yield the $[Ph_4P]^+$ salt of the $[Mo_2OS_6]^{2-}$ anion (IV).[10] The latter reaction is similar to the one employed previously for the synthesis of $[Mo_2S_7]^{2-}$ from $[Mo_2S_8]^{2-}$. The oxidation of I with BzSSSBz in a 1:9 molar ratio, under conditions similar to those employed for the synthesis of III, affords $[Mo_2OS_9]^{2-}$ as a mixture of the $[(S_x)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$ and $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoS(S_x)]^{2-}$ anions (x = 3, 4 in equal amounts). The latter cocrystallize (vide infra) with $[Ph_4P]^+$ as a counterion and can be isolated as a black crystalline material (V)[11] in ~85% yield.

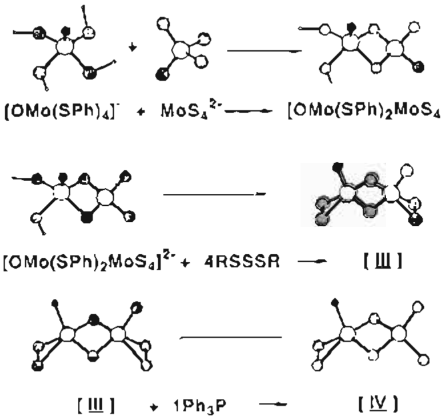

Figure 1. Synthesis of $[Mo_2OS_7]^{2-}$ (anion of III) and $[Mo_2OS_6]^{2-}$ (anion of IV) from the $[OMo(SPh)_4]^-$ anion.[6]

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(7) Anal. Calcd for I·DMF, $Mo_2S_6P_2O_2NC_{63}H_{57}$: Mo, 14.70; S, 14.74; P, 4.74; N, 1.07; C, 57.92; H, 4.37. Found: Mo, 14.07; S, 14.72; P, 4.58; N, 0.37; C, 58.12; H, 4.31. Uncoordinated DMF was detected in the IR spectrum of this compound. Electronic spectrum (λ, nm): 438. Infrared spectrum (cm^{-1}): Mo—S, 504 (m), 469 (w); Mo—SPh, 485 (m); Mo=O, 940 (s).

(8) Throughout the text the designations $[Mo_2OS_7]^{2-}$ (III), $[Mo_2OS_6]^{2-}$ (IV), $[Mo_2OS_9]^{2-}$ (V), and $[Mo_2OS_8]^{2-}$ (VI) refer to $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$, $[(\eta^2\text{-}S_2)MoO(MoS_4)]^{2-}$, $[(S_4)MoX(\mu\text{-}S)_2MoX(\eta^2\text{-}S_2)]^{2-}$ (X = S, O), and $[(S_4)MoO(MoS_4)]^{2-}$, respectively.

(9) Anal. Calcd for III, $Mo_2S_7P_2NO_2C_{51}H_{47}$: Mo, 16.22; S, 18.97; P, 5.23; N, 1.18; C, 51.72; H, 3.97. Found: Mo, 16.26; S, 19.23; P, 5.28; N, 0.9; C, 50.95; H, 3.64. One molecule of DMF of solvation was found in the ^1H NMR spectrum and in the crystal structure determination of III. Electronic spectrum (λ, nm): 550 (sh), 470, 390. Infrared spectrum (cm^{-1}): Mo—S, 456 (w), 354 (w); Mo=O, 938 (m).

(10) Anal. Calcd for IV, $Mo_2S_6P_2NO_2C_{51}H_{47}$: Mo, 16.67; S, 16.71; P, 5.38; N, 1.21; C, 53.16; H, 4.08. Found: Mo, 16.69; S, 17.35; P, 5.96; N, 0.7; C, 52.07; H, 3.87. One molecule of DMF of solvation was found in the ^1H NMR spectrum and in the crystal structure determination of IV. Electronic spectrum (λ, nm): 476 (sh), 412. Infrared spectrum (cm^{-1}): Mo—S, 503 (m), 483 (w), 461 (w); Mo=O, 945 (m).

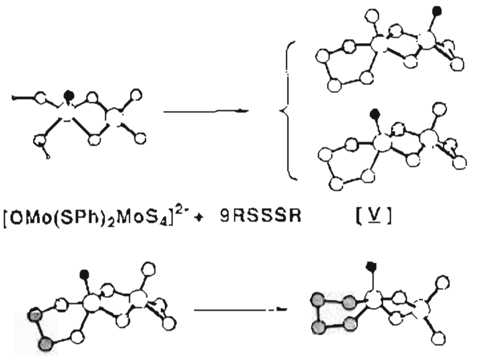

Figure 2. Synthesis of $[Mo_2OS_9]^{2-}$ (anion of V, two isomers) and $[Mo_2OS_8]^{2-}$ (anion of VI).

In the syntheses of III and V from I (Figures 1 and 2), the organic trisulfide serves as both an oxidizing and a sulfur-transfer agent. The amounts of the reagent used have been optimized to ensure completeness of the reactions under the conditions employed in the syntheses. As reported previously[1] for the conversion of $[Mo_2S_{10}]^{2-}$ to $[Mo_2S_8]^{2-}$, V reacts with 2 equiv of Ph_3P to give III in excellent yield.

The reaction of V with only 1 equiv of Ph_3P affords $[Ph_4P]_2[Mo_2OS_8]$ (VI)[12] in modest (50%) yield (Figure 2). This reaction appears to take place preferentially with the $[(S_4)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$ component of V and is not unexpected in view of the greater steric crowding of the $MoS(\eta^2\text{-}S_2)$ unit in comparison to that of the $MoO(\eta^2\text{-}S_2)$ unit. A similar preferential sulfur abstraction from a $MoS(\eta^2\text{-}S_2)$ functional group also is apparent in the conversion of III to IV.

The structures of III–VI have been determined[13] (Figure 3), and the analogous structural features of the anions (Table I) are very similar to those of the $[(\eta^2\text{-}S_2)MoS(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$,[14] $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoO(\eta^2\text{-}S_2)]^{2-}$,[15] $[(S_4)MoS(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$,[16] and $[(S_4)MoS(MoS_4)]^{2-}$ complexes.[1] Of the four anions, only the one in V shows disorder with the two isomers (Figure 2) occupying the same site in an approximate 1:1 ratio.

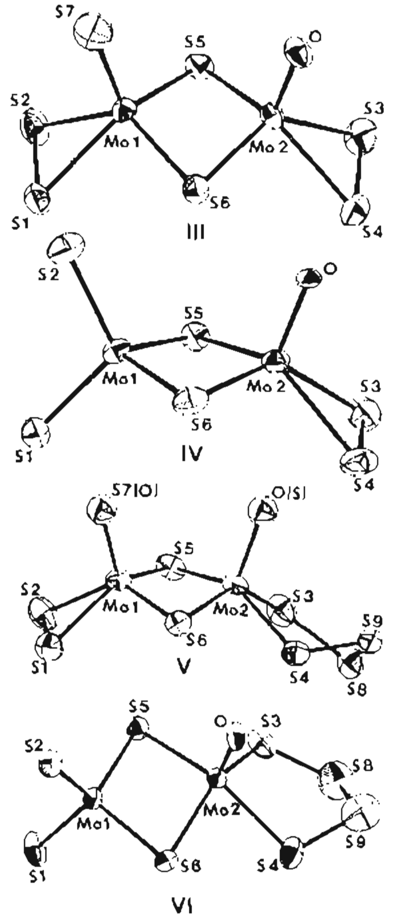

Figure 3. Structure and labeling of $[Mo_2OS_7]^{2-}$ (III), $[Mo_2OS_6]^{2-}$ (IV), $[Mo_2OS_9]^{2-}$ (V), and $[Mo_2OS_8]^{2-}$ (VI) anions. Thermal ellipsoids as drawn by ORTEP[17] represent the 40% probability surfaces.

The structure of the $[Bu_4N]^+$ salt of III has been reported previously;[5] in that structure the anion was subject to orientational disorder and as a result only mean values for the Mo=S and Mo=O bonds could be obtained. In this study[5] the formulation of the anion as $[Mo_2OS_7]^{2-}$ (rather than a solid solution of $[Mo_2S_8]^{2-}$ and $[Mo_2O_2S_6]^{2-}$) was based on analytical and spectroscopic data. The correctness of this earlier formulation is verified by our work, which shows the structurally characterized, nondisordered anion in III with essentially the same spectroscopic characteristics as those reported earlier.

An inspection of the data in Table I shows that IV and VI contain two sets of Mo–S_b bonds. The shorter of these bonds (associated with the "MoS_4" structural units) indicate considerable localization of charge within the dimers and suggest significant $Mo^{VI}S_4$–$Mo^{IV}O(S_x)$ character. Similar, but less pronounced, differences in the Mo–S_b bond lengths were found previously[1] in the thio analogues of IV and VI. The Mo–S_b bond lengths in the structures of III and V do not show significant differences and suggest Mo(V)–Mo(V) as an appropriate description for the formal metal oxidation states in these dimers. The η^2-S_2 ligand

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(11) Anal. Calcd for V, $Mo_2S_{8.5}P_2N_{0.5}O_{1.5}C_{49.5}H_{43.5}$: Mo, 16.05; S, 22.81; P, 5.18; N, 0.58; C, 49.71; H, 3.64. Found: Mo, 17.77; S, 20.03; P, 5.10; N, 0.66; C, 49.95; H, 3.57. A half-molecule of DMF of solvation per anion was detected in the ^{1}H NMR spectrum and in the crystal structure determination of V. Electronic spectrum (λ, nm): 430, 370 (sh). Infrared spectrum (cm^{-1}): Mo—S, 458 (w), 354 (w); Mo=O, 949 (m), 932 (m).

(12) Anal. Calcd for VI $Mo_2S_8P_2N_{0.5}O_{1.5}C_{49.5}H_{43.5}$: Mo, 16.28; S, 21.75; P, 5.25; N, 0.59; C, 50.39; H, 3.69. Found: Mo, 17.29; S, 19.56; P, 5.04; N, 0.12; C, 50.16; H, 3.50. A half-molecule of DMF of solvation per anion was detected in the ^{1}H NMR spectrum and in the crystal structure determination of VI. Electronic spectrum (λ, nm): 408. Infrared spectrum (cm^{-1}): Mo—S, 506 (m), 489 (m), 482 (w); Mo—S_b, 461 (w); Mo=O, 944 (m).

(13) Crystal and refinement data: red-black crystals of $[Ph_4P]_2[Mo_2OS_7]\cdot$DMF (III) are triclinic, space group $P\bar{1}$, with a = 11.549 (2) Å, b = 13.039 (3) Å, c = 18.667 (4) Å, α = 78.04 (2)°, β = 74.39(1)°, γ = 79.72 (2)°, and Z = 2; orange-red crystals of $[Ph_4P]_2[Mo_2OS_6]\cdot$DMF (IV) are triclinic, space group $P\bar{1}$, with a = 10.213 (2) Å, b = 12.914 (4) Å, c = 20.707 (4) Å, α = 89.9 (2)°, β = 100.1 (1)°, γ = 101.4 (2)°, and Z = 2; black crystals of $[Ph_4P]_2[Mo_2OS_{8/9}]\cdot 0.5$DMF (V) are triclinic, space group $P\bar{1}$, with a = 10.424 (5) Å, b = 11.701 (4) Å, c = 22.073 (8) Å, α = 76.46 (3)°, β = 85.59 (3)°, γ = 77.85 (3)°, and Z = 2; orange crystals of $[Ph_4P]_2[Mo_2OS_8]\cdot 0.5$DMF (VI) are triclinic, space group $P\bar{1}$, with a = 10.649 (6) Å, b = 12.611 (12) Å, c = 19.846 (21) Å, α = 87.61 (8)°, β = 80.17 (7)°, γ = 83.09 (7)°, and Z = 2. Single-crystal X-ray diffraction data were collected for all compounds on a Nicolet P3F four-circle diffractometer using Mo Kα radiation, and the solutions of the structures were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. The refinement of the structures by full-matrix least-squares methods was based on 3880 unique reflections ($2\theta_{max}$ = 40°, $I > 3\sigma$) for III, on 4627 unique reflections ($2\theta_{max}$ = 45°, $I > 3\sigma$) for IV, on 3734 unique reflections ($2\theta_{max}$ = 40°, $I > 3\sigma$) for V, and on 2194 unique reflections ($2\theta_{max}$ = 35°, $I > 3\sigma$) for VI. (For VI, the marginal quality of the crystals precluded collection of data at $2\theta >$ 35°.) Anisotropic temperature factors were used for the non-hydrogen, nondisordered atoms, and isotropic factors were used for the positionally disordered sulfur atoms. The numbers of refined parameters were 587 for III, 534 for IV, 578 for V, and 327 for VI. At the current stage of refinement with all atoms present in the asymmetric units R = 0.035 for III, 0.062 for IV, 0.059 for V, and 0.072 for VI.

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in IV shows an unusually long S–S bond at 2.154 (7) Å. A similarly long bond (2.136 (6) Å) was found previously for the same ligand in the $[(\eta^2\text{-}S_2)MoS(MoS_4)]^{2-}$ anion.[1] In the structures of IV, VI, $[(\eta^2\text{-}S_2)MoS(MoS_4)]^{2-}$, and $[(S_4)MoS(MoS_4)]^{2-}$, the two terminal Mo–S bond lengths within the "MoS_4" ligands are significantly different. In all cases, the bonds syn to the "$Mo^{IV}{=}X_t$" unit are shorter than those in the anti orientation.

The chemical reactivity of the various coordinated ligands in III–VI and of the same ligands in the analogous thio complexes currently are under investigation in systematic reactivity studies.

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Supplementary Material Available: Listings of positional and thermal parameters for the $[Ph_4P]^+$ salts of $[(\eta^2\text{-}S_2)MoO(\mu\text{-}S)_2MoS(\eta^2\text{-}S_2)]^{2-}$ (III), $[(\eta^2\text{-}S_2)MoO(MoS_4)]^{2-}$ (IV), $[(S_4)MoX(\mu\text{-}S)_2MoX(\eta^2\text{-}S_2)]^{2-}$ (X = S, O) (V), and $[(S_4)MoO(MoS_4)]^{2-}$ (VI) (Tables S1–S4) (20 pages); listings of structure factors (Tables S5–S8) (56 pages). Ordering information is given on any current masthead page.

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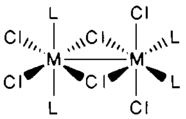
An Equilibrium Involving Edge- and Face-Shared Bioctahedral d^3–d^3 Ditungsten Complexes: $W_2Cl_6(PEt_3)_4$ and $W_2Cl_6(PEt_3)_3$

Sir:

There is now a diverse chemistry surrounding W_2^{6+}-containing compounds for which the green crystalline salt $NaW_2Cl_7(THF)_5$[1] provides an excellent starting material. (1) Metathetic reactions employing LiO-*t*-Bu or $LiNMe_2$ give access to $X_3W{\equiv}WX_3$ compounds.[2] (2) Addition of neutral donor ligands such as pyridine[3] and PMe_3[4,5] give edge-shared bioctahedral complexes of type I.



I

The latter finding prompted us to question why the $W_2Cl_7(THF)_2^-$ anion[6] did not exist in THF (tetrahydrofuran) solution as $W_2Cl_6(THF)_4$.[7] Could there be an equilibrium involving edge-shared bioctahedra and face-shared bioctahedra and, if so, what factors influence the equilibrium? We describe here our discovery of an equilibrium of the above type, eq 1, and our structural characterization of both W_2^{6+}-containing compounds.

$$W_2Cl_6(PEt_3)_4 \rightleftarrows W_2Cl_6(PEt_3)_3 + PEt_3 \qquad (1)$$

Addition of PEt_3 (>4 equiv) to a solution of $NaW_2Cl_7(THF)_5$ in THF leads to $W_2Cl_6(PEt_3)_4$, which can be crystallized from toluene. The molecular structure determined from a single-crystal X-ray diffraction study[8] showed this to be a member of a now fairly extensive family of edge-shared bioctahedra[9] of structural type I with W–W = 2.7397 (7) Å.[10] The terminal W–L axial bond distances are slightly shorter than the terminal W–L equatorial distances; cf. W–Cl = 2.41 (1) (axial) vs 2.45 (1) Å, and W–P = 2.56 (1) (axial) vs 2.61 (1) Å.

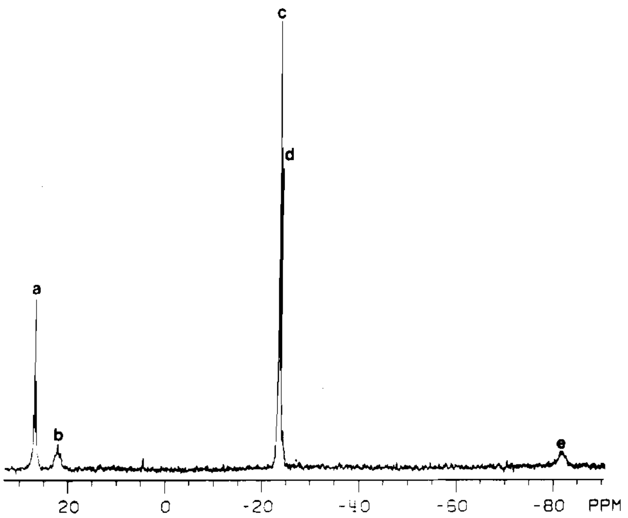
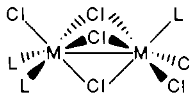


Figure 1. ^{31}P NMR spectrum of a single crystal of $W_2Cl_6(PEt_3)_4$ dissolved in toluene-d_8 at −80 °C and 146.2 MHz showing the presence of free PEt_3, δ −22.1 s (c), and signals due to the equilibrium involving I, δ 23.2 t (b), and −81.4 t (e), J_{P-P} = 87 Hz, and II, δ 27.8 t (a), and −22.3 d (d), J_{P-P} = 44 Hz. Tungsten satellites are resolved for II but not for I. Chemical shifts are in ppm relative to H_3PO_4 (85% aqueous) external reference.

The ^{31}P NMR spectrum of a crystalline sample of $W_2Cl_6(PEt_3)_4$ dissolved in toluene-d_8 is temperature dependent, and only at low temperatures are signals present that can be correlated with a compound of structural type I, namely two triplets of equal intensity. The major species present in solution gives rise to a doublet and a triplet in the intensity ratio 2:1, respectively. This is consistent with the presence of a confacial bioctahedral isomer having a mirror plane of symmetry as shown in II. In addition there is a singlet assignable to free PEt_3 (see Figure 1). The equilibrium



II

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(1) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C.; Ontiveros, C. D.; Streib, W. E.; Van Der Sluys, W. G. *Inorg. Chem.* **1987**, *26*, 3182.

(2) Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 21.

(3) Jackson, R. B.; Streib, W. E. *Inorg. Chem.* **1971**, *10*, 1760.

(4) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430.

(5) The structure of $W_2Cl_6(PMe_3)_4$ has been determined and shown to be of type I: Chisholm, M. H.; Huffman, J. C.; Van Der Sluys, W. G. Results to be submitted for publication.

(6) Bergs, D. J.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Stahl, K. A. *Inorg. Chem.* **1988**, *27*, 2950.

(7) I.e., as originally suggested in ref 4.

(8) Crystal data for $W_2Cl_6(PEt_3)_4$ at −144 °C: a = 11.220 (2) Å, b = 18.462 (3) Å, c = 18.519 (3) Å, β = 98.32 (1)°, Z = 4, d_{calcd} = 1.843 g cm^{-3}, and space group $P2_1/n$. Of 6359 reflections collected (6° ≤ 2θ ≤ 45°), 4975 were unique and the 4288 reflections having $F > 3\sigma(F)$ were used in the refinement. Hydrogen atoms were placed in idealized positions during the final refinement. All non-hydrogen atoms were refined anisotropically. Final residuals are $R(F)$ = 0.0397 and $R_w(F)$ = 0.0397. Crystal data for $W_2Cl_6(PEt_3)_3{\cdot}CH_2Cl_2$ at −144 °C: a = 14.097 (2) Å, b = 12.992 (2) Å, c = 18.798 (3) Å, β = 97.96 (1)°, Z = 4, d_{calcd} = 1.987 g cm^{-3}, and space group $P2_1/n$. Of 6111 reflections collected, 4324 were unique and the 4125 reflections that had $F > 3\sigma(F)$ were used in the full least-squares refinement. Hydrogen atoms were introduced in fixed, calculated positions; all other atoms were refined anisotropically, leading to $R(F)$ = 0.0437 and $R_w(F)$ = 0.0445. General operating procedures and listings of programs have been given: Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(9) For a review of edge-shared bioctahedra for d^n–d^n complexes where n = 0–5, see: Cotton, F. A. *Polyhedron* **1987**, *6*, 677. Evidence for an equilibrium involving mononuclear octahedral Mo(III) and a confacial bioctahedral dimer

$$2MoCl_3(THF)_3 \rightleftarrows Mo_2Cl_6(THF)_3 + 3THF$$

has been reported previously: Boyd, I. W.; Wedd, A. G. *Aust. J. Chem.* **1976**, *29*, 1829. We thank Professor R. A. Walton for bringing this to our attention.

(10) The distance in the closely related d^2–d^2 complex $Ta_2Cl_6(PMe_3)_4$ is 2.721 (1) Å: Sattelberger, A. P.; Wilson, B. R. Jr.; Huffman, J. C. *Inorg. Chem.* **1982**, *21*, 2392.