rearrangements in the cobaltacarborane cage (340°) and the carborane cage (400°) were observed only at much higher temperatures; therefore, we proposed that the 2′,4′-$C_2B_5H_6$ cage migration must occur by means of a direct shift mechanism possibly involving intermediates in which the carborane cage boron B3′ adopts a bridging position across cobaltacarborane cage atoms B2 and B3. We have, in fact, recently reported[13] the first structural characterization of this type of single three-center boron cage linkage in another coupled-cage cobaltacarborane complex, 6:4′,5′-[1-(η-C_5H_5)Co-2,3-$(CH_3)_2C_2B_4H_3$][2′,3′-$(CH_3)_2C_2B_4H_5$], providing additional support for the involvement of such species in these rearrangements. The observation of a lengthened B2–B3 distance is also consistent with a direct shift mechanism of rearrangement since it would indicate a lower bonding interaction between these two atoms, which should facilitate the transfer of the 2′,4′-$C_2B_5H_6$ cage by means of a three-center, B2, B3′, B3, intermediate. It should be noted, however, that the B3′–B3 distance, 3.305 Å, and the HB3–B2′ distance, 2.814 Å, indicate little interaction between these atoms in the solid state at room temperature.

The structure of the 2′,4′-$C_2B_5H_6$ cage is based on a pentagonal bipyramid, with atoms B1 and B7 occupying the apex positions. The cage bond distances and angles are again normal and are consistent with those determined in a microwave study[14] of the parent carborane, 2,4-$C_2B_5H_7$, apparently indicating that there has been little perturbation of the cage bonding caused by the attachment of the cobaltacarborane fragment at the B3′ position.

Further studies are now in progress concerning the synthesis and structural characterizations of related linked cage clusters, and these will be reported in future publications.

Acknowledgment. We thank the Army Research Office, the National Science Foundation, and the University of Pennsylvania Materials Research Laboratory for support of this research.

Registry No. 3′:2-[2′,4′-$C_2B_5H_6$][1,8,5,6-$(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_6$], 70480-08-9.

Supplementary Material Available: Tables of selected molecular planes, hydrogen atom positional parameters, anisotropic thermal parameters, and observed and calculated structure factors and an ORTEP molecular packing diagram (19 pages). Ordering information is given on any current masthead page.

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(13) Borelli, A. J., Jr.; Plotkin, J. S.; Sneddon, L. G. *Inorg. Chem.* **1982**, *21*, 1328.

(14) Beaudet, R. A.; Poynter, R. L. *J. Chem. Phys.* **1965**, *43*, 2166.

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Structure Proofs of Ligated and Polymeric Dioxomolybdenum(VI)–Tridentate Complexes: $MoO_2(C_5H_3N\text{-}2,6\text{-}(CH_2S)_2)(C_4H_8SO)$ and $[MoO_2(C_5H_3N\text{-}2,6\text{-}(CH_2O)_2)]_n$

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The dioxomolybdenum(VI) complexes $MoO_2(L\text{-}NS_2)\cdot$TMSO and $[MoO_2(L\text{-}NO_2)]_n$ (where L-NS_2 = pyridine-2,6-dimethanethiolate, L-NO_2 = pyridine-2,6-dimethanolate, and TMSO = tetramethylene sulfoxide) have been prepared and structurally characterized by single-crystal X-ray diffraction methods. Crystals of the former compound consist of isolated mononuclear units, each having a distorted octahedral environment around Mo with cis-oxo groups and trans-thiolate donors. The remaining coordination sites are occupied by the N atom of the pyridine and an O-bound sulfoxide. Crystals of the latter consist of polymeric chains of Mo complexes, each of which has a distorted octahedral environment similar to that in the former complex with alkoxide replacing thiolate and an oxo group, unsymmetrically bridging from an adjacent complex, replacing the sulfoxide oxygen. Both compounds crystallize in the space group $P2_1/c$ with $a = 8.508$ (4) Å, $b = 10.784$ (7) Å, $c = 16.961$ (4) Å, and $\beta = 110.08$ (4)° for $MoO_2(L\text{-}NS_2)\cdot$TMSO and $a = 7.490$ (2) Å, $b = 14.335$ (4) Å, $c = 8.310$ (2) Å, and $\beta = 113.72$ (2)° for $[MoO_2(L\text{-}NO_2)]_n$. The final agreement factors are $R = 2.85\%$, $R_w = 2.91\%$ and $R = 2.50\%$, $R_w = 2.55\%$, respectively. These compounds provide the first structurally characterized examples of MoO_2(tridentate) systems, which may be important as models of the catalytic sites of certain molybdenum-containing enzymes.

The known molybdenum-containing enzymes,[2] with the exception of nitrogenase, catalyze transformations that may be described as oxygen atom transfer reactions (e.g., $NO_3^- \rightarrow NO_2^-$, $SO_3^{2-} \rightarrow SO_4^{2-}$). Evidence from EPR[2-4] and EXAFS[5,6] studies indicates that the oxidized enzymes contain Mo(VI), which is coordinated by one or more terminal (t) oxo and at least two sulfur ligands. Those Mo–S distances of ~2.4 Å deduced from EXAFS analysis involve thiolate ligands. We are engaged in research directed toward the attainment of credible synthetic representations of the catalytic sites of certain molybdoenzymes in oxidized and reduced forms. A potentially useful feature of such species is the presence of a labile coordination site for substrate binding and activation. This feature is presumably present in complexes of the type MoO_2(tridentate)·D, examples of which have been described[7-10] (D = neutral monodentate ligand). Additionally,

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(1) National Science Foundation Predoctoral Fellow, 1980–1983.

(2) Bray, R. C. *Enzymes, 3rd ed.* **1975**, *12*, Chapter 6.

(3) Gutteridge, S.; Bray, R. C. In "Molybdenum and Molybdenum-Containing Enzymes"; Coughlan, M., Ed.; Pergamon Press: New York, 1980; pp 221–239.

(4) Lamy, M. T.; Gutteridge, S.; Bray, R. C. *Biochem. J.* **1980**, *185*, 397.

(5) Cramer, S. P.; Wahl, R.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1981**, *103*, 7721.

(6) Bordas, J.; Bray, R. C.; Garner, C. D.; Gutteridge, S.; Hasnain, S. S. *Biochem. J.* **1980**, *199*, 499.

(7) Liebeskind, L. S.; Sharpless, K. B.; Wilson, R. D.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 7061.

(8) Rajan, O. A.; Chakravorty, A. *Inorg. Chim. Acta* **1979**, *37*, L503; *Inorg. Chem.* **1981**, *20*, 660.

(9) Topich, J. *Inorg. Chim. Acta* **1980**, *46*, L37; *Inorg. Chem.* **1981**, *20*, 3704.

(10) Dey, K.; Maiti, R. K.; Bhar, J. K. *Transition Met. Chem. (N.Y.)* **1981**, *6*, 345.

0020-1669/83/1322-1768$01.50/0

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters

quantity	$MoO_2(L\text{-}NS_2)\cdot$ TMSO	$[MoO_2(L\text{-}NO_2)]_n$
formula (mol wt)	$C_{11}H_{15}MoNO_3S_3$ (401.37)	$C_7H_7MoNO_4$ (265.08)
a, Å	8.508 (4)	7.490 (2)
b, Å	10.784 (7)	14.335 (4)
c, Å	16.961 (4)	8.310 (2)
β, deg	110.08 (4)	113.72 (2)
V, Å^3	1462 (1)	816.8 (4)
Z	4	4
space group	$P2_1/c$	$P2_1/c$
d_{calcd}, g/cm^3	1.82	2.16
data collected	$3° < 2\theta < 60°$; $+h, +k, \pm l$	$3° < 2\theta < 60°$; $+h, +k, \pm l$
unique data ($F_o^2 > 3\sigma(F_o^2)$)	1984	1381
no. of variables	172	118
R, %	2.85	2.50
R_w, %	2.91	2.55
goodness of fit	1.17	1.07

examples of MoO_2(tridentate) have been prepared by Rajan and Chakravorty,[8] who proposed a Mo═O···Mo chainlike structure in which an oxo atom in one molecule acts as a ligand to another. In the course of our investigations we have prepared the complexes $MoO_2(L\text{-}NS_2)$ and $MoO_2(L\text{-}NO_2)$ containing the ligands pyridine-2,6-dimethanethiolate and pyridine-2,6-dimethanolate, respectively. Crystallization of the former from tetramethylene sulfoxide (TMSO) yielded a 1:1 adduct, $MoO_2(L\text{-}NS_2)\cdot$TMSO, whereas similar treatment of the latter afforded the unsolvated complex. These compounds have provided an opportunity for accurate structural characterization of the foregoing two types of complexes, structurally defined examples of which are lacking.

Experimental Section

Preparation of Compounds. Pyridine-2,6-dimethanol and TMSO were commercial samples (Aldrich) and were used as received. Pyridine-2,6-dimethanethiol was prepared by the method of Partyka,[11] and $MoO_2(acac)_2$, by the procedure of Chen et al.[12] The compounds $MoO_2(L\text{-}NS_2)$ and $MoO_2(L\text{-}NO_2)$ were prepared by the reaction of equimolar quantities of $MoO_2(acac)_2$ and the ligand in methanol. Precipitates appeared within 1 min; after a ~30-min reaction time the complexes were isolated by filtration in ≳90% yield. Crystallization of $MoO_2(L\text{-}NS_2)$ from TMSO gave $MoO_2(L\text{-}NS_2)\cdot$TMSO as a highly crystalline orange solid in a form suitable for X-ray study. When exposed to the atmosphere, the compound rapidly lost TMSO, precluding analysis; the unsolvated form was analyzed. Anal. Calcd for $C_7H_7MoNO_2S_2$: C, 28.29; H, 2.37; Mo, 32.28; N, 4.71; S, 21.57. Found: C, 28.46; H, 2.36; Mo, 32.23; N, 4.71; S, 21.61. Infrared spectrum (mull): ν_{MoO} 916, 800 (br) cm^{-1}. $MoO_2(L\text{-}NO_2)$ was recovered unchanged from TMSO solution as colorless crystals, which were used in the X-ray diffraction study. Anal. Calcd for $C_7H_7MoNO_4$: C, 31.72; H, 2.66; Mo, 36.19; N, 5.28. Found: C, 31.60; H, 2.61; Mo, 35.97; N, 5.19. Infrared spectrum (mull): ν_{MoO} 909, 850 (br) cm^{-1}.

X-ray Structural Analysis. A crystal of $MoO_2(L\text{-}NS_2)\cdot$TMSO was mounted in a sealed glass capillary in the presence of mother liquor. A crystal of $MoO_2(L\text{-}NO_2)$ was mounted on a glass fiber. Diffraction studies were performed on a Nicolet R3M four-circle diffractometer with use of Mo K$\bar{\alpha}$ radiation. Twenty-five machine-centered reflections were used in the least-squares refinement of the orientation matrix and lattice parameters for each crystal. Crystal data are summarized in Table I. For each crystal ω scans had full widths at half-height of <0.25°. The lack of any significant fluctuations in the intensities of three standard reflections throughout each data set collection indicated suitable crystal and machine stability. Empirical absorption corrections were applied to both data sets. The systematic absences *h*0*l* ($l \neq 2n$) and 0*k*0 ($k \neq 2n$) revealed that both crystals belong to space group $P2_1/c$. Both structures were solved by the heavy-atom method and were refined by using weighted blocked-cascade least squares as described previously,[13] with weights calculated from $w = [(\sigma(F_o))^2 + 0.0005F_o^2]^{-1}$. All non-hydrogen atoms were refined anisotropically. Calculated hydrogen atom contributions were included with C–H distances of 0.98 Å and thermal parameters set to 1.2 times the effective isotropic thermal parameter of the bonded carbon atom. Final agreement factors are given in Table I. Positional parameters are compiled in Table II, and selected interatomic distances and angles are presented in Table III.[14]

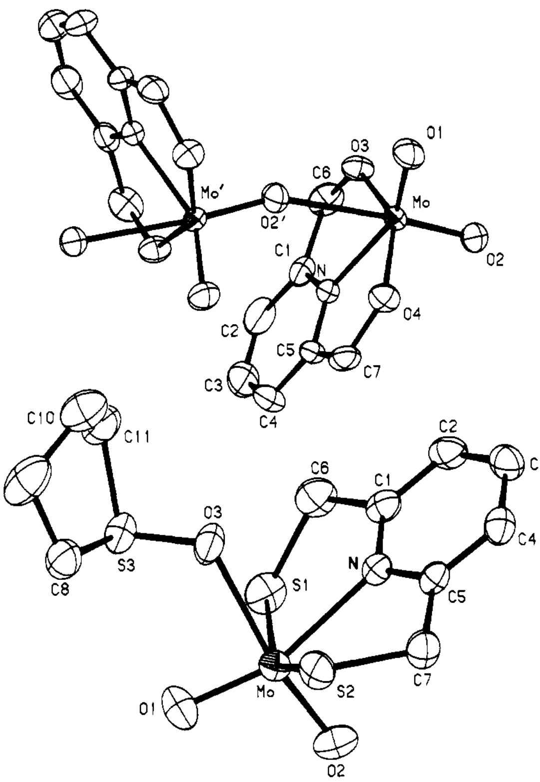

Figure 1. Structures of $MoO_2(L\text{-}NS_2)\cdot$TMSO (lower) and $[MoO_2(L\text{-}NO_2)]_n$ (upper), showing the atom-labeling scheme and 50% probability ellipsoids (hydrogen atoms omitted).

Results and Discussion

The structures of $MoO_2(L\text{-}NS_2)\cdot$TMSO and $MoO_2(L\text{-}NO_2)$ are presented in Figure 1. No symmetry is imposed on either molecule.

$MoO_2(L\text{-}NS_2)\cdot$TMSO. The crystal structure consists of well-separated mononuclear molecules. These have a distorted octahedral structure common to most dioxomolybdenum(VI) complexes,[15] with cis terminal oxo ligands, Mo–O_t distances of 1.723 (3) and 1.694 (3) Å and a O_t–Mo–O_t angle of 106.0 (2)°. Ligand constraints require trans sulfur atoms. The Mo–S distances of 2.438 (1) and 2.402 (1) Å are similar to those in other $Mo^{VI}O_2$ complexes with thiolate ligands,[16-18] including those with nonoctahedral geometries.[17] With the cis-O_t, trans-sulfur atom arrangement the TMSO molecule is necessarily coordinated trans to an O_t atom. The structure of $MoO_2(L\text{-}NS_2)\cdot$TMSO shows significant deviations from

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(11) Partyka, R. A. U.S. Patent 3290319, 1966; *Chem. Abstr.* **1967**, *66*, P115609*k*.

(12) Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612.

(13) Christou, G.; Mascharak, P. K.; Armstrong, W. H.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2820.

(14) See the paragraph at the end of this article concerning supplementary structural data.

(15) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

(16) Berg, J. M.; Hodgson, K. O.; Cramer, S. P.; Corbin, J. L.; Elsberry, A.; Pariyadath, N.; Stiefel, E. I. *J. Am. Chem. Soc.* **1979**, *101*, 2774.

(17) Stiefel, E. I.; Miller, K. F.; Bruce, A. E.; Corbin, J. L.; Berg, J. M.; Hodgson, K. O. *J. Am. Chem. Soc.* **1980**, *102*, 3624.

(18) Bruce, A.; Corbin, J. L.; Dahlstrom, P. L.; Hyde, J. R.; Minelli, M.; Stiefel, E. I.; Spence, J. T.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 917.

Table II. Positional Parameters (Fractional Coordinates × 10^4)

$MoO_2(L\text{-}NS_2)\cdot TMSO$				$[MoO_2(L\text{-}NO_2)]_n$			
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Mo	2133 (1)	2290 (1)	3667 (1)	Mo	2566 (1)	2492 (1)	997 (1)
S(1)	205 (1)	728 (1)	3849 (1)	O(1)	4043 (4)	3449 (2)	1692 (4)
S(2)	3298 (1)	4351 (1)	3899 (1)	O(2)	2497 (4)	2217 (2)	−1040 (4)
S(3)	3957 (1)	1149 (1)	5606 (1)	O(3)	16 (4)	3035 (2)	279 (4)
O(1)	3948 (4)	1449 (3)	3841 (2)	O(4)	4263 (4)	1514 (2)	2340 (4)
O(2)	1225 (4)	2406 (3)	2610 (2)	N	701 (4)	1414 (2)	1381 (4)
O(3)	2970 (4)	2286 (2)	5145 (2)	C(1)	−1228 (5)	1578 (3)	751 (5)
N	103 (3)	3450 (3)	3953 (2)	C(2)	−2446 (7)	912 (3)	973 (6)
C(1)	−1050 (4)	2929 (4)	4243 (2)	C(3)	−1654 (8)	110 (4)	1866 (8)
C(2)	−2311 (5)	3632 (4)	4357 (2)	C(4)	367 (7)	−33 (3)	2548 (6)
C(3)	−2394 (5)	4891 (4)	4185 (2)	C(5)	1534 (6)	647 (3)	2281 (5)
C(4)	−1222 (5)	5419 (4)	3895 (2)	C(6)	−1710 (5)	2517 (3)	−110 (5)
C(5)	12 (4)	4678 (3)	3786 (2)	C(7)	3703 (6)	677 (3)	2902 (5)
C(6)	−831 (5)	1577 (4)	4452 (3)				
C(7)	1315 (5)	5175 (4)	3460 (3)				
C(8)	6130 (5)	1659 (4)	6007 (3)				
C(9)	6652 (6)	1789 (5)	6954 (3)				
C(10)	5083 (7)	2102 (5)	7151 (3)				
C(11)	3775 (5)	1198 (4)	6634 (3)				

Table III. Selected Bond Distances (Å) and Angles (deg)

quantity	$MoO_2(L\text{-}NS_2)\cdot TMSO^{a,c}$	$[MoO_2(L\text{-}NO_2)]_n{}^{b,d}$
Mo-O(1)	1.723 (3)	1.710 (3)
Mo-O(2)	1.694 (3)	1.719 (3)
Mo-X(1)	2.438 (1)	1.922 (3)
Mo-X(2)	2.402 (1)	1.919 (3)
Mo-N	2.311 (3)	2.190 (3)
Mo-Y	2.357 (3)	2.518 (3)
Mo-Mo′		4.155 (1)
S(3)-O(3)	1.536 (3)	
O(1)-Mo-O(2)	106.0 (2)	106.0 (2)
O(1)-Mo-X(1)	102.5 (1)	101.9 (1)
O(1)-Mo-X(2)	99.5 (1)	101.7 (1)
O(1)-Mo-N	159.3 (1)	151.7 (1)
O(1)-Mo-Y	83.8 (1)	78.6 (1)
O(2)-Mo-X(1)	95.9 (1)	98.9 (1)
O(2)-Mo-X(2)	96.7 (1)	99.0 (1)
O(2)-Mo-N	94.6 (1)	102.3 (1)
O(2)-Mo-Y	170.1 (1)	175.4 (1)
X(1)-Mo-X(2)	150.4 (1)	145.0 (1)
X(1)-Mo-N	76.3 (1)	73.6 (1)
X(1)-Mo-Y	80.5 (1)	80.1 (1)
X(2)-Mo-N	76.1 (1)	73.3 (1)
X(2)-Mo-Y	82.5 (1)	79.7 (1)
N-Mo-Y	75.7 (1)	73.1 (1)
Mo-O(3)-S(3)	117.0 (2)	
Mo-O(2)-Mo′		157.1 (2)

[a] X(1) = S(1), X(2) = S(2), Y = O(3). [b] X(1) = O(3), X(2) = O(4), Y = O(2)′. [c] Ligand bond distances: N–C(1), 1.358 (5); N–C(5), 1.348 (4); C(1)–C(2), 1.378 (6); C(2)–C(3), 1.382 (6); C(3)–C(4), 1.375 (6); C(4)–C(5), 1.378 (6); C(1)–C(6), 1.493 (5); C(5)–C(7), 1.494 (6); C(6)–S(1), 1.808 (5); C(7)–S(2), 1.815 (4); C(8)–S(3), 1.819 (4); C(11)–S(3), 1.801 (5); C(8)–C(9), 1.517 (6); C(9)–C(10), 1.518 (8); C(10)–C(11), 1.510 (6). [d] Ligand bond distances: N–C(1), 1.344 (5); N–C(5), 1.336 (5); C(1)–C(2), 1.383 (7); C(2)–C(3), 1.367 (7); C(3)–C(4), 1.401 (8); C(4)–C(5), 1.385 (7); C(1)–C(6), 1.500 (6); C(5)–C(7), 1.494 (6); C(6)–O(3), 1.411 (5); C(7)–O(4), 1.411 (5).

the highest idealized symmetry of C_s, as is indicated by inspection of the distances and angles in Table III. This situation is most clearly reflected by the twisting of the mean pyridine ring plane with respect to the $Mo(O_t)_2$ plane, which is accompanied by puckering of the two chelate rings. The dihedral angle of these planes is 71.3° instead of the idealized value of 90°, a situation presumably due to the size of the chelate rings. In the structure of $[MoO_2(L\text{–}NO_2)]_n$ this angle is 85.5°.

The TMSO molecule is coordinated through its oxygen atom, as would be anticipated from hard and soft acid–base considerations.[19] The S–O distance and geometry of the TMSO molecule are unexceptional compared to those of other O-bonded sulfoxide complexes.[19,20] However, the Mo–O distance of 2.357 (3) Å is definitely longer than the distances to neutral donors in $MoO_2X_2(OPPh_3)_2$[21] (X = Cl, Br; 2.17–2.20 Å) and $MoO_2Cl_2(DMF)_2$[22] (2.20 (1) Å). In these molecules, which are the only other structurally characterized neutral monodentate ligand adducts of $Mo^{VI}O_2$, the neutral ligands are trans to O_t atoms.

$[MoO_2(L\text{–}NO_2)]_n$. The asymmetric unit in the crystal structure consists of one formula weight. The two O_t atoms and the tridentate ligand provide five donor atoms of the Mo center. The sixth site in the distorted octahedral coordination sphere is occupied by an oxo atom of an adjacent molecule related by a *c*-glide operation. This atom functions as a bridge (b) and $Mo{=}O_b{\cdots}Mo'$ interactions lead to a "linear" polymeric structure, with dimensions of the repeating bridge unit being 1.719 (3) Å ($Mo\text{–}O_b$), 2.518 (3) Å ($Mo{\cdots}O_b$), 151.7 (2)° ($Mo'\text{–}O_b\text{–}Mo$), and 4.155 (1) Å (Mo···Mo′). Similar structures have been estalished for $MoO_2Cl_2(H_2O)$[23,24] and $MoO_2Cl_2(OPCl_3)$,[25] in which comparably unsymmetrical bridge units are found. The N–Mo–Mo′–N′ torsional angle of 100.7° demonstrates the twist of adjacent molecules along the polymeric chain. Other structural features include typical dimensions of the MoO_2 group (which is more symmetrical than that in the preceding structure), trans Mo–O(RO^-) distances that are comparable to those (1.91–1.98 Å) in other $Mo^{VI}O_2$ complexes,[21,26-28] and a $Mo(O_t)_2NO_2O'$ unit that more closely approximates C_s symmetry than does the analogous unit in the preceding structure. Deviations from this symmetry persist nonetheless. The Mo–O(3)–C(6)–C(1)–N chelate ring is substantially puckered with maximum displacements from the least-squares plane of +0.124 Å for C(1) and −0.103 Å for C(6). In the other chelate ring no displacement exceeds 0.004 Å. The chelate rings in $MoO_2(L\text{–}NS_2)\cdot TMSO$ are puckered;

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(19) Davies, J. A. *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 115.

(20) Reynolds, W. L. *Prog. Inorg. Chem.* **1970**, *12*, 1.

(21) Butcher, R. J.; Penfold, B. R.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1979**, 668.

(22) Florian, L. R.; Corey, E. R. *Inorg. Chem.* **1968**, *7*, 722.

(23) Atovmyan, L. O.; Aliev, Z. G. *J. Struct. Chem. (Engl. Transl.)* **1971**, *12*, 668.

(24) Schulz, H.; Schröder, F. A. *Acta Crystallogr., Sect. A* **1973**, *A29*, 322.

(25) Beyendorff-Gulba, G.; Strähle, J.; Liebelt, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1981**, *483*, 26.

(26) Atovmyan, L. O.; Sokolova, Yu. A. *J. Chem. Soc., Chem. Commun.* **1969**, 649.

(27) Atovmyan, L. O.; Krasochka, O. N. *J. Chem. Soc., Chem. Commun.* **1970**, 1670.

(28) Schröder, F. A.; Scherle, J.; Hazell, R. G. *Acta Crystallogr., Sect. B* **1975**, *B31*, 531.

maximum deviations from the appropriate least-squares planes are +0.249 Å for C(6), −0.217 Å for S(1), +0.344 Å for S(2), and −0.359 Å for C(7).

Summary. The structures presented here represent prototypes for MoO_2(tridentate) complexes in ligated and unligated (polymeric) forms. The polymeric structure of $[MoO_2(L-NO_2)]_n$ provides clear support for the claim of a similar chainlike arrangement in unligated MoO_2(salicylaldimato) complexes.[8] The infrared spectrum of unligated $MoO_2(L-NS_2)$, $MoO_2(L-NO_2)$, and the latter complexes[8] exhibits a broad IR band at ~800–850 cm^{-1}, which appears to be diagnostic of Mo=O···Mo bridges and is presumably the perturbed $\nu_{Mo=O}$ stretching frequency. The structure of $MoO_2(L-NS_2)\cdot$TMSO tends to substantiate earlier ligated formulations of MoO_2(tridentate)·D complexes.[7-10] The long Mo···O(TMSO) distance is a consequence of a neutral ligand and the trans effect of a Mo=O$_t$ unit and leads to a higher degree of lability of ligands in this position. Research is continuing on complexes of the general type $MoO_{1,2}$(tridentate–NS_2), including those with labile binding sites and steric features that obviate formation of Mo(V)–O–Mo(V) complexes in the course of enzyme-related

$$Mo^{IV}O \underset{}{\overset{[O]}{\rightleftharpoons}} Mo^{VI}O_2$$

oxo-transfer reactions.

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Registry No. $MoO_2(L-NS_2)\cdot$TMSO, 85534-01-6; $[MoO_2(L-NO_2)]_n$, 85534-02-7; $MoO_2(acac)_2$, 17524-05-9.

Supplementary Material Available: Anisotropic temperature factors (Table S-I), calculated hydrogen atom coordinates (Table S-II), and calculated and observed structure factors (Table S-III) for $MoO_2(L-NS_2)\cdot$TMSO and $[MoO_2(L-NO_2)]_n$ (24 pages). Ordering information is given on any current masthead page.

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Molecular Structure of a Mixed-Ligand Chlorinated Sulfur-Containing Phosphorane[1]

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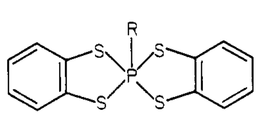
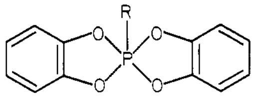
The synthesis and crystal structure of 5-phenyl-2,3-tetrachlorobenzo-7,8-(2′-methyl-5′,6′-benzo)-1,4-dioxa-6,9-dithia-5λ^5-phosphaspiro[4.4]nona-2,7-diene, $(Cl_4C_6O_2)(CH_3C_6H_3S_2)PPh$ (**7**), is reported. It crystallizes in the monoclinic space group $C2/c$ (Z = 8) with a = 22.534 (8) Å, b = 8.710 (3) Å, c = 21.419 (7) Å, and β = 94.11 (3)°. The structure was refined to R = 0.072 and R_w = 0.083. The geometry around the phosphorus atom is rectangular pyramidal, being 93.0% (97.4% using unit vectors) displaced from the trigonal bipyramid toward the rectangular pyramid. Achievement of this structure is aided by the electron-delocalizing effect of the chlorine ring substituents, resulting in reduced bond electron-pair repulsions at phosphorus. It represents the least distorted rectangular-pyramidal phosphorane so far reported.

Introduction

Although only a few spirocyclic phosphorane structures that contain sulfur atoms bonded to phorphorus have been investigated,[2-5] it appears that thio-containing derivatives undergo considerable structural change with relatively small variations in ligand character, especially variations in the composition of the acyclic ligand.[2] For example, the spirocycle **1** is not far displaced from a trigonal bipyramid[2] (TP) (31% from the TP toward the rectangular pyramid (RP) along the Berry coordinate based on unit bond distances[6]) while **2**,[4] containing an acyclic methyl group in place of the phenyl group, is close to a rectangular pyramid (79% displaced from a TP[2]). The corresponding oxaphospholes, **3**[7] and **4**,[8] are 72% and 82% displaced toward the RP,[6] respectively, on the basis of actual bond distances in these derivatives (based on unit bond distances in parentheses). It has been commented[2] that the presence of the less electronegative sulfur atoms bonded to phosphorus causes enhanced bond electron-pair repulsions[9] between apical and basal bonds of a RP that tend to favor the TP.



	R	% TP → RP
1	Ph	31
2	CH_3	79



	R	% TP → RP
3	Ph	72.0 (74.6)
4	CH_3	82.5 (85.0)

In a further comparison of substituent effects, phosphoranes **5** and **6**, containing chlorinated rings, are nearly ideal rec-

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(1) (a) Pentacoordinated Molecules. 47. (b) Previous paper in this series: Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 3916.

(2) Day, R. O.; Sau, A. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3790.

(3) Holmes, R. R. *ACS Monogr.* **1980**, *No. 175*, Chapter 2.

(4) (a) Eisenhut, M.; Schmutzler, R.; Sheldrick, W. S. *J. Chem. Soc., Chem. Commun.* **1973**, 144. (b) Sheldrick, W. S., personal communication.

(5) Duff, E.; Russell, D. R.; Trippett, S. *Phosphorus Relat. Group V Elem.* **1974**, *4*, 203.

(6) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(7) Brown, R. K.; Holmes, R. R. *J. Am. Chem. Soc.* **1977**, *99*, 3326.

(8) Wunderlich, H. *Acta Crystallogr., Sect. B* **1974**, *B30*, 939.

(9) Gillespie, R. J. "Molecular Geometry"; Van Nostrand-Reinhold, New York, 1972.

0020-1669/83/1322-1771$01.50/0