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Article

A Novel Ligand Modification and Diamond-core Molybdenum(IV) 2,6-Bis(2,2-diphenyl-2-thioethyl)pyridinate(2-) Complex

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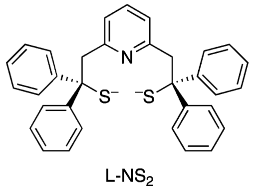
The reaction of $Mo^{VI}O_2(L\text{-}NS_2)$ [$L\text{-}NS_2$ = 2,6-bis(2,2-diphenyl-2-thioethyl)pyridinate(2-)] or $Mo^{V}{}_2O_3(L\text{-}NS_2)_2$ with excess PPh_3 in *N,N*-dimethylformamide at 70 °C results in the formation of gray-green $(L\text{-}NOS)Mo^{IV}(\mu\text{-}O)(\mu\text{-}S)Mo^{IV}(L\text{-}NS_2)$ [L-NOS = 2-(2,2-diphenyl-2-thioethyl)-6-(2,2-diphenyl-2-oxoethyl)pyridinate(2-)] (**1**). The crystal structure of **1** revealed a dinuclear complex comprised of two trigonal bipyramidal Mo centers bridged along an axial−equatorial edge (the μ-O-μ-S vector) such that the Mo−N bonds are trans to the bridging atoms and are anti with respect to the Mo−Mo bond (d(Mo−Mo) = 2.5535(5) Å); the remaining coordination sites are occupied by the S- and O-donor atoms of the L-NOS and $L\text{-}NS_2$ ligands. The diamond core is asymmetric, with Mo(1/2)−O(1) distances of 1.845(2) and 2.009(2) Å and Mo(1/2)−S(1) distances of 2.374(1) and 2.230(1) Å. Compound **1** is unique in possessing a planar, diamond-core unit devoid of terminal oxo ligation and a new tridentate L-NOS ligand formed via a novel intramolecular modification of the original $L\text{-}NS_2$ ligand.

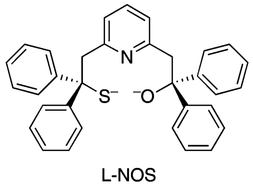
Introduction

High-valent molybdenum complexes containing the tridentate 2,6-bis(2,2-diphenyl-2-thioethyl)pyridinate(2-) ligand, $L\text{-}NS_2$, have been extensively studied by Holm and co-workers.[1−7] Initial reports described the synthesis and characterization of the five-coordinate, dioxo-Mo(VI) complex, $MoO_2(L\text{-}NS_2)$, and its reaction with PPh_3 in *N,N*-dimethylformamide (dmf) to produce an oxo-Mo(IV) complex, $MoO(L\text{-}NS_2)(dmf)$.[1,2] Subsequent papers probed the scope, kinetics, and mechanisms of bidirectional oxygen atom transfer (OAT) in this system. It was claimed that the system was the first to effect enzyme-like OAT between mononuclear complexes without comproportionation and the formation of biologically irrelevant, dinuclear μ-oxo-Mo(V) species.[8]

However, in 1998, we showed that "$MoO(L\text{-}NS_2)(dmf)$" was in fact the dinuclear μ-oxo-Mo(V) compound, $Mo_2O_3(L\text{-}NS_2)_2 \cdot 2dmf$.[9] We also reported that the reaction between $MoO_2(L\text{-}NS_2)$ and PPh_3 takes place in two stages, the first producing $Mo_2O_3(L\text{-}NS_2)_2$ and half an equivalent of $OPPh_3$ (based on Mo) while the second yields oxo-Mo(V) and/or -Mo(IV) complexes (depending on solvent) and additional $OPPh_3$. Moreover, we isolated a previously unreported gray-green compound after stage two of the reaction. This compound was initially formulated as the dmf solvate of $Mo^{IV}{}_2(\mu\text{-}O)_2(L\text{-}NS_2)_2$ on the basis of mass spectrometric (MS), infrared (IR), and preliminary crystallographic data.[9]



L-NS$_2$



L-NOS

Here, we report that the gray-green compound is in fact the dinuclear, μ-oxo-μ-sulfido-Mo(IV) complex, (L-NOS)-

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$Mo^{IV}(\mu\text{-}O)(\mu\text{-}S)Mo^{IV}(L\text{-}NS_2)$ (**1**), containing the unexpected 2-(2,2-diphenyl-2-thioethyl)-6-(2,2-diphenyl-2-oxoethyl)pyridinate(2-) ligand, L-NOS. The formulation is consistent with previously reported data (IR, MS),[9] as well as with new data reported here (microanalysis, NMR, and an ordered crystal structure). The conversion of L-NS_2 to L-NOS represents a previously unrecognized ligand modification, and the asymmetric diamond-core structure of **1** is unprecedented in Mo chemistry. Compound **1** appears to be the only stable and isolable Mo(IV) compound formed in the reactions of MoO_2(L-NS_2) or Mo_2O_3(L-NS_2)$_2$ with PPh_3 in dmf; the mononuclear oxo-Mo(IV) complex, MoO(L-NS_2)(dmf),[1−7] is yet to be observed or isolated.

Experimental Section

Materials and Methods. Complexes MoO_2(L-NS_2),[2] Mo_2O_3(L-NS_2)$_2$,[9] and ^{18}O-labeled *N,N*-dimethylformamide (^{18}O-dmf)[10] were prepared by literature methods. All reactions were performed under dinitrogen using dried, deoxygenated solvents and standard Schlenk techniques, but workup procedures were performed in air. Solid-state IR (KBr disk) spectra were recorded on a Biorad FTS 165 FTIR spectrophotometer. Proton NMR spectra were obtained using a Varian FT UnityPlus 400 MHz spectrometer; spectra were referenced to residual protio-solvent peaks (for CHD_2CN $\delta = 1.93$). Mass spectra were recorded on a Bruker BioApex 47e FTMS fitted with an Analytica electrospray source operating with capillary voltages between 30 and 120 V. Microanalyses were performed by Atlantic Microlab Inc., Norcross, Georgia, U.S.A.

Synthesis of 1. A mixture of MoO_2(L-NS_2) (0.200 g, 0.32 mmol) and PPh_3 (0.625 g, 2.4 mmol) in dmf (50 mL) was heated at 70 °C for 24 h. The dark blue-brown mixture was reduced to dryness and then reconstituted with dichloromethane (5 mL). The solution was chromatographed on a silica gel column using chloroform as eluent. The main blue fraction was collected, reduced to low volume, and treated with methanol to precipitate the gray-green product. The compound was isolated by filtration, washed with methanol, and dried in vacuo. Yield: 0.085 g (43%). Anal. calcd for $C_{66}H_{54}N_2Mo_2O_2S_4$: C, 64.60; H, 4.43; N, 2.28; S, 10.45. Found: C, 64.85; H, 4.42; N, 2.26; S, 10.26. IR (cm^{-1}) KBr: 3054 w, 3027 w, 2927 w, 2857 w, 1604 m, 1575 m, 1491 m, 1458 m, 1444 s, 1385 w, 1233 w, 1183 w, 1123 w, 1090 w, 1041 m, 1023 m, 948 w, 915 w, 744 s, 698 vs, 655 m, 601 m, 416 w. ^1H NMR (CD_3CN): δ 4.21 and 3.54, 4.08 and 3.44, 3.96 and 3.80, 3.64 and 3.10 (each δ pair an AB quartet, 2H, $J_{AB} = 15$ Hz, CH_AH_B), 5.9−6.6 (4 × d, each 1H, 4 × 3- and 5-C*H* of pyridine unit), 6.4−7.4 (40H, m, Ph), 7.70 and 7.72 (each t, 1H, 2 × 4-C*H* of pyridine unit). ESI-MS (CH_2Cl_2/dmf/MeOH): *m/z* 1229.1 $[M + H]^+$, 1251.1 $[M + Na]^+$, 488.2 $[\text{L-NSO} + 3H]^+$, 510.2, $[\text{L-NSO} + H_2Na]^+$, 504.2 $[\text{L-NS}_2 + 3H]^+$, 526.2 $[\text{L-NS}_2 + H_2Na]^+$. UV−vis ($CH_2Cl_2$, nm ($\varepsilon$ M^{-1} cm^{-1})): 403 (2450), 566 nm (4170), 670 (sh, ca. 1500).

The same reaction, performed on a 70 mg scale using ^{18}O-dmf (0.75 mL), yielded **1** with the same spectroscopic and mass spectrometric properties as the product produced using unlabeled dmf.

Crystal Structure Determination. Gray-green crystals of the acetonitrile disolvate of **1** were grown from an undisturbed, saturated acetonitrile solution of the complex. Crystallographic data were collected at 130(2) K on a Bruker CCD area detector using graphite monochromated Mo Kα radiation (0.710 73 Å) using 30 s frames over the range $2° < 2\theta < 50°$. Cell parameters were acquired by the SMART software package, and data reduction was performed with SAINT. Structures were solved by direct methods (SHELXS-97)[11] and refined using full-matrix least-squares on F^2 (SHELXL-97).[12] Unless stated, all non-hydrogen atoms were found in difference electron density maps and were refined using anisotropic thermal parameters. Hydrogen atoms were included with fixed isotropic temperature factors in idealized positions and were refined as riding atoms. Molecular diagrams were generated using ORTEP 3[13] and CAChe software.[14] Crystallographic data are summarized in Table 1, and selected bond distances and angles are presented in Table 2.

Table 1. Crystallographic data for $\mathbf{1}\cdot 2MeCN$

formula	$C_{70}H_{60}Mo_2N_4O_2S_4$
fw	1309.34
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	15.1892(12)
b, Å	15.4013(12)
c, Å	16.1475(13)
α, deg	62.1480(10)
β, deg	67.628(2)
γ, deg	78.459(2)
V, Å^3	3087.3(4)
Z	2
ρ_{calc}, g·cm^{-3}	1.408
μ, cm^{-1}	5.90
GOF (on F^2)	1.119
R^a	0.0487
$R_w{}^b$	0.0800

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

Table 2. Selected Distances and Angles for $\mathbf{1}\cdot 2MeCN$

Distances (Å)			
Mo(1)−Mo(2)	2.5535(5)	Mo(2)−O(1)	2.009(2)
Mo(1)−O(1)	1.845(2)	Mo(2)−S(1)	2.2298(10)
Mo(1)−S(1)	2.3744(10)	Mo(2)−S(4)	2.3121(10)
Mo(1)−S(2)	2.3190(11)	Mo(2)−O(2)	1.904(3)
Mo(1)−S(3)	2.3260(10)	Mo(2)−N(2)	2.254(3)
Mo(1)−N(1)	2.303(3)		
Angles (deg)			
Mo(1)−O(1)−Mo(2)	82.87(9)	N(1)−Mo(1)−S(3)	93.18(8)
Mo(1)−S(1)−Mo(2)	67.28(3)	N(1)−Mo(1)−S(1)	170.67(7)
S(1)−Mo(1)−O(1)	104.98(7)	S(1)−Mo(2)−S(4)	117.70(4)
S(1)−Mo(2)−O(1)	104.87(7)	S(1)−Mo(2)−O(2)	122.47(8)
S(2)−Mo(1)−O(1)	119.20(8)	S(4)−Mo(2)−O(2)	119.53(8)
S(2)−Mo(1)−S(3)	117.58(4)	N(2)−Mo(2)−S(1)	86.02(7)
O(1)−Mo(1)−S(3)	123.16(8)	N(2)−Mo(2)−O(2)	87.22(11)
S(1)−Mo(1)−S(2)	86.19(4)	N(2)−Mo(2)−S(4)	91.47(8)
S(1)−Mo(1)−S(3)	80.93(3)	O(1)−Mo(2)−O(2)	85.00(10)
N(1)−Mo(1)−O(1)	84.29(10)	O(1)−Mo(2)−S(4)	85.48(7)
N(1)−Mo(1)−S(2)	90.19(8)	O(1)−Mo(2)−N(2)	168.89(10)

Results and Discussion

Synthesis and Characterization. Reaction of orange MoO_2(L-NS_2) or purple Mo_2O_3(L-NS_2)$_2$ with ca. 10 equivalents of PPh_3 in dmf at 70−80 °C for 24 h (or over weeks at room temperature) resulted in the formation of a blue-brown solution containing **1**. Gray-green **1** was isolated by column chromatography on silica gel using chloroform as

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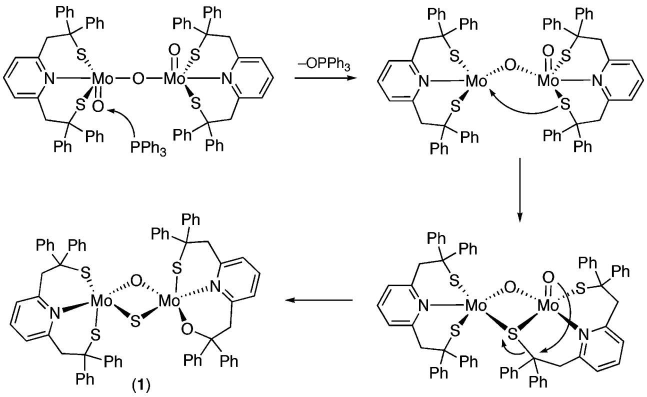
eluent. It is air-stable in the solid state and is soluble in dmf, chlorinated solvents, and (to a lesser extent) acetonitrile but is insoluble in hexane, alcohols, and diethyl ether. Reaction of MoO_2(L-NS_2) with excess PPh_3 in acetonitrile produced only Mo_2O_3(L-NS_2)$_2$, whereas brown, unidentified Mo(V) species were produced when the reactions were performed in chlorinated solvents. The use of ^{18}O-labeled dmf in the reaction did not lead to the incorporation of ^{18}O into the isolated product. The overall equation for the formation of **1** from $Mo^{V}{}_2O_3$(L-NS_2)$_2$ (the initial product of the reaction of MoO_2(L-NS_2) with PPh_3[9]) can be written as shown in eq 1.

$$Mo_2^{V}O_3(\text{L-NS}_2)_2 + PPh_3 \rightarrow (\text{L-NOS})Mo^{IV}(\mu\text{-O})(\mu\text{-S})Mo^{IV}(\text{L-NS}_2) + OPPh_3 \quad (1)$$

Microanalytical, mass spectrometric, and IR data were consistent with the proposed formulation. Mass spectra showed peak clusters attributable to the parent ions as well as the two different ligands. The IR spectrum of **1** showed bands characteristic of the chelate ligands but was devoid of bands typical of terminal oxo or sulfido ligands. Bands assignable to the Mo(μ-O)(μ-S)Mo core unit could not be identified because strong ligand bands occur in the regions of interest.

The ^{1}H NMR spectra of **1** (in various solvents) were indicative of a dinuclear complex possessing C_1 molecular symmetry. In d_3-acetonitrile, four AB quartets assigned to the eight diastereotopic CH_2 protons were observed in the region δ 3.0−4.3 (see Experimental Section for assignments). Many factors influence the chemical shifts of CH_AH_B groups and an unambiguous assignment of the resonances to particular H-atoms is not practicable. However, for a given CH_AH_B proton pair, it is reasonable to conclude that the endo protons (pointed toward the bridging unit) are shielded relative to the exo protons (by the ring current associated with the Mo−Mo bond). Moreover, it is likely that the most-shielded of the resonances belongs to the proton on C(8) (see crystal structure below), which is closest to the center of the core unit (3.2 Å vs >3.6 Å for the others). Three of the four pyridine 3- and 5-CH proton doublet resonances were also clearly visible in the region δ 5.9−6.6; the fourth is obscured by intense, multiplet, phenyl resonances in the region δ 6.4−7.5. Finally, two closely spaced triplets assigned to the pyridine 4-CH protons are observed around δ 7.7. The duplication of most resonances is consistent with the presence of a second stereoisomer (<15% of total sample). Four diastereomeric isomers are possible for **1**; each of these is chiral, leading to four enantiomeric pairs of isomers. A pair of anti enantiomers was present in the crystal characterized by X-ray diffraction (vide infra). A second anti enantiomeric pair, with the N atom of L-NOS trans to μ-S, and two syn enantiomeric pairs are also possible. It is likely that the minor diastereomer observed by NMR is the second anti isomer, as the syn isomers would be subject to severe ligand steric interactions across the bridging unit. Broadly similar NMR spectra are observed in d-chloroform, d_6-dimethyl sulfoxide, d_6-benzene, and d_7-dmf, although some bands are obscured by solvent or water peaks in these solvents.

Scheme 1. Possible Mechanism for the Formation of **1**



The mechanism of the ligand modification remains unclear. *N,N*-Dimethylformamide is required for the reaction but it does not appear to be the source of the oxygen atom in L-NOS, as there is no incorporation of ^{18}O into the isolated product when the reaction is performed in ^{18}O-dmf. The formation of a small amount of $SPPh_3$ in the reaction has been reported,[9] but it is unlikely to be associated with the formation of **1**. Thus, the mechanism of formation of **1** is most likely to involve oxygen atom transfer from Mo_2O_3(L-NS_2)$_2$ to PPh_3, followed by intramolecular rearrangement (ligand modification) of the resulting dinuclear species. One of a number of possible mechanisms based on this general mechanistic concept is shown in Scheme 1. The initial step involves attack of PPh_3 on a terminal oxo group of Mo_2O_3(L-NS_2)$_2$, leading to the formation of $OPPh_3$ and the net two-electron reduction of the metal center (this process may be assisted by the binding of dmf trans to the oxo group, accounting for the solvent dependence of the reaction). The reduction of mononuclear oxo-Mo(V) complexes to Mo(III) species by phosphines has been reported by Maverick and co-workers.[15] A change in the coordination mode of a thiolate donor, such that it functions as a bridging ligand (as observed in the zinc complex Zn_2(L-NS_2)$_2$[16]) could be induced by the formation of the unsaturated Mo(III) center formed by OAT. This would position and prime the thiolate sulfur atom for conversion into the μ-sulfido ligand (the L-NS_2 ligand is the sole source of sulfur in this system) and facilitate electron transfer to generate two Mo(IV) centers. Severe steric interactions in this intermediate may provide the driving force for C−S bond cleavage early in the thiolate-to-sulfido conversion. In the next step, an exchange of sulfur for oxygen on the ligand side-chain takes place, converting L-NS_2 to L-NOS. Other mechanisms, differing in the order and nature (concerted, stepwise, etc) of the aforementioned processes, are also possible.

Description of Structure. Crystallographic difficulties, including very small crystals, high mosaicity, disorder, and possible twinning, persistently hampered attempts to obtain

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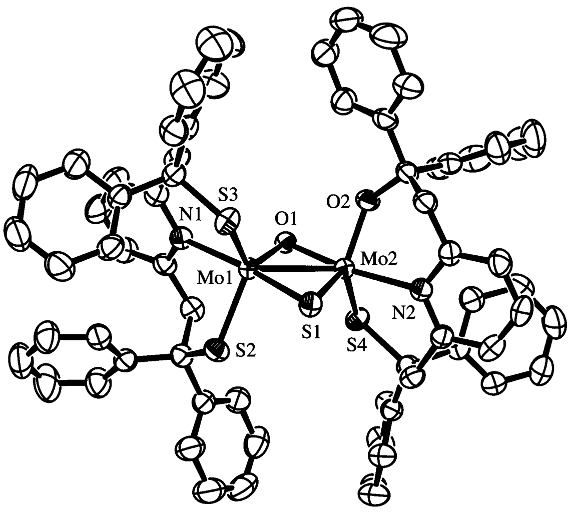

Figure 1. ORTEP projection of **1** drawn at the 30% probability level and with H atoms omitted for clarity.

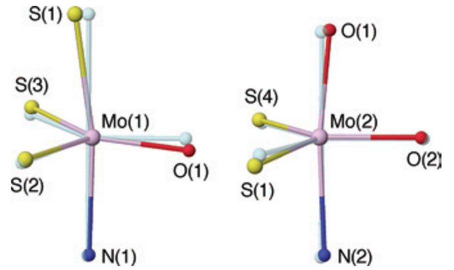

Figure 2. Superposition of Mo(1) and Mo(2) coordination spheres on idealized trigonal bipyramidal units (drawn using experimental bond distances). The idealized trigonal bipyramidal units are shown in light blue. Atom colors: Mo (mauve), S (yellow), N (blue), O (red).

a quality X-ray structure for **1** and led to its incorrect initial formulation.[9] The true identity of the compound was revealed only after an ordered crystal of **1**·2MeCN was examined by X-ray diffraction. The complex is composed of two five-coordinate, trigonal bipyramidal Mo centers bridged by μ-oxo and μ-sulfido ligands, each Mo being further coordinated by either an L-NS$_2$ or an L-NOS ligand (Figure 1).

At Mo(1), the (trigonal) equatorial plane is defined by atoms O(1), S(2), and S(3), with Mo(1) lying only 0.031(1) Å out of the plane toward S(1). The N(1) and S(1) atoms occupy axial positions, with the N(1)−Mo(1)−S(1) angle being 170.67(7)°. The S(1), O(1), and S(3) atoms show the greatest displacements, 0.26, 0.23, and 0.16 Å, respectively, from idealized trigonal bipyramidal positions; the mean atom displacement from an idealized trigonal bipyramidal structure (for the 6 atoms) is 0.14 Å (see Figure 2). Atoms S(1), S(4), and O(2) define the equatorial plane of Mo(2), with the metal being 0.067(1) Å out of the plane toward O(1). The axial donors, N(2) and O(1), subtend an angle of 168.9(1)° at Mo(2). The greatest atomic displacements from an idealized trigonal bipyramidal structure are for O(1), S(1), and S(4) (0.25, 0.20, and 0.11 Å, respectively), and the mean atom displacement for this trigonal bipyramidal center is 0.13 Å (see Figure 2). The equatorial angles average 120°, with an average variation of 2.1° for Mo(1) and 1.7° for Mo(2).

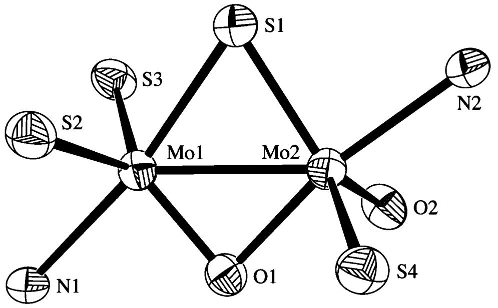

Figure 3. Diamond core of **1** showing the metal centers and donor atoms.

Addison, Reedijk, and co-workers[17] introduced the τ index, defined as $(\alpha - \beta)/60$, where α and β are the two largest metal-centered angles, to describe the structural continuum between trigonal bipyramidal ($\tau = 1$) and rectangular (or square) pyramidal ($\tau = 0$) geometries. The τ indices for Mo(1) and Mo(2) are 0.78 and 0.77, respectively, indicative of coordination geometries approaching trigonal bipyramidal; the values deviate from the τ value of 1 because the S(1)−Mo(1)−N(1) and O(1)−Mo–N(2) angles are less obtuse (mean 170.2°) than the idealized value of 180°.

The two trigonal bipyramidal units are linked along a shared equatorial−axial edge defined by atoms S(1) and O(1); the two polyhedra are geometrically opposed, the N-donor atoms are anti with respect to the Mo−Mo vector, and the molecules belong to the C_1 point group (Figure 3). The NMo(μ-O)(μ-S)MoN unit is essentially planar, with a mean atom displacement of 0.027 Å. The displacement of the bridging atoms from idealized positions (vide supra) is a result of the acute bond angles at O(1) (82.87(9)°) and S(1) (67.28(3)°) and the close approach of the Mo atoms. The Mo−Mo distance of 2.5535(5) Å and the diamagnetism of the complex are consistent with the presence of a metal−metal double bond. The diamond core is asymmetric, as atom S(1) lies closer to Mo(2) (2.230(1) Å) than to Mo(1) (2.374(1) Å), and O(1) lies closer to Mo(1) (1.845(2) Å) than to Mo(2) (2.009(2) Å). In each case, the longer of the two bonds is found trans to an axial Mo−N bond, and the shorter lies in one of the two equatorial planes. The Mo(1)−N(1) and Mo(2)−N(2) bond distances are significantly different at 2.303(3) and 2.254(3) Å, respectively.

All previously reported oxosulfido-bridged Mo complexes are Mo(V) species possessing terminal oxo ligands (at one or usually both metal centers) and a nonplanar core.[18−29]

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These features are also characteristic of most di-μ-oxo and di-μ-sulfido-Mo(V) species.[30−32] Uniquely for oxosulfido-bridged Mo complexes, the Mo centers of **1** are in the +4 oxidation state, the complex itself is devoid of terminal oxo ligation, and it contains an asymmetric diamond core. The Mo−Mo distance is shorter in **1** than in other oxosulfido-bridged compounds (2.5535(5) Å for **1** vs 2.65−2.81 Å), but the angles subtended at O(1) and S(1) are within or are close to established ranges (Mo−O−Mo = 82.9(1)° for **1** vs 76.4−90.7°; Mo−S−Mo = 67.28(3)° for **1** vs 69.3−73.5°).[18−29] The O−Mo−S angles of **1** (av. 104.9°) are more obtuse than those of most other relevant species (ca. 97−102°; exceptions include $Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(\mu$-pyridazine)$\{S_2P(O^iPr)_2\}_2$ (mean 105.7°)[21] and $Mo_2O_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SO_4)(p\text{-}NC_5H_4Me)_4$ (mean 104.2°)[26]). Oxosulfido-bridged Mo(V) complexes are generally symmetrical with respect to Mo-(μ-O) and Mo-(μ-S) distances, an exception being the asymmetric complex $(\eta^5\text{-}MeC_5H_4)MoO(\mu\text{-}O)(\mu\text{-}S)Mo(\eta^5\text{-}MeC_5H_4)\{\eta^4\text{-}C_4(p\text{-}C_6H_4Me)_4\}$.[28] Other dinuclear Mo(IV) compounds are known, but few exhibit an unsupported 2-atom bridge of the type observed in **1**;[30−32] examples include the di-μ-sulfido species $[Mo(\mu\text{-}S)(SCN^nPr_2)(S_2CN^nPr_2)]_2$[33] and $[Mo(\mu\text{-}S)(L\text{-}S_4)]_2$ (L-S_4 = 1,2-bis(3,5-di(*t*-butyl)-2-mercaptophenylthio)ethane(2-)).[34] The asymmetric, diamond core of **1** is consistent with an electronic contribution from distinguishable oxo-Mo(IV) and sulfido-Mo(IV) centers stabilized by complementary Mo−S/Mo−Mo and Mo−O/Mo−Mo bonding.

The Mo−S distances of the tridentate ligands average at 2.32 Å, close the value expected for Mo−S coordinate bonds (2.314 Å), whereas the Mo(2)−O(2) bond distance of 1.904(3) Å is typical of Mo−OR groups (mean 1.911 Å).[35] The distances and angles within the L-NS_2 and L-NOS ligands are unexceptional.

Conclusions

We have established that the product of extended reactions of MoO_2(L-NS_2) or Mo_2O_3(L-NS_2)$_2$ with PPh_3 is the unusual, diamond-core Mo(IV) complex (**1**). This result is significant in a number of contexts. First, a novel ligand modification that converts an L-NS_2 ligand into an L-NOS ligand accompanies the formation of **1**. Second, the planar, unsupported, diamond-core structure of **1** is unprecedented in Mo chemistry. Third, **1** represents the only well-characterized Mo(IV) complex yet detected or isolated in OAT reactions involving oxo-Mo L-NS_2 complexes and PPh_3.[1−7,9] To date, we have been unable to isolate any mononuclear oxo-Mo(IV) complexes, including putative MoO(L-NS_2)(dmf),[1−7] from this system.

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Supporting Information Available: Crystallographic data of **1**·2MeCN in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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