

Communications

Synthesis and Structure of $(\text{Bu}^n_4\text{N})[\text{MoO}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]$. The First Mononuclear Molybdenum(V) Complex Containing both Coordinated Thiolate and Carboxylate Groups

Early solution EPR results for Mo(V) showed that one of the most promising mimics of the EPR spectrum of xanthine oxidase ($\langle g \rangle = 1.977$; $\langle A \rangle = 34$ G) is the species formed with thioglycolic acid¹ ($\langle g \rangle = 1.978$; $\langle A \rangle = 38$ G). In hydroxylic solvents, however, the EPR signal intensity accounted for only about 10% of the available Mo, indicating the presence of a labile equilibrium between a dimer or higher polymer and the paramagnetic monomeric species. Such an equilibrium could also explain why subsequent attempts to isolate the monomeric species have not been successful and only dimeric complexes containing a bridging oxygen² or sulfur³ atom were obtained. Thus, although the work of Meriwether et al.¹ was very influential, this monomeric complex has remained uncharacterized.

On the assumption that bulky ligands can prevent the formation of dimers,⁴ the $[\text{MoO}_2(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^{2-}$ complex, **1**, containing the sterically hindered 2,2-diphenyl-2-mercaptoacetic acid ligand (TBA) was previously synthesized and characterized.⁵ Here we show that reaction of **1** with thiols at acid pH yields the unique monomeric Mo(V) complex $[\text{MoO}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^-$ (**2**) whose structure has been determined by X-ray crystallography. The preparation of **2** in this way proves that inclusion of diphenyl groups on the ligand prevents the dimerization upon reduction. Complex **2** is the first example of a mononuclear five-coordinated Mo(V) species possessing a $\text{MoO}(\text{S}_2\text{O}_2)$ donor set. Such an environment is consistent with the minimal coordination unit $\text{MoOS}_{2,3}(\text{N}/\text{O})$ of several molybdoenzymes in their reduced forms as deduced from Mo EXAFS analysis.⁶ The spectroscopic (UV-vis, EPR) properties are also presented.

Figure 1 collects the spectra recorded during the reaction of the ammonium salt of complex **1** with a large excess of TBA. The time course of the reaction clearly shows decay of the reactant band at 26 700 cm^{-1} and buildup of the characteristic spectrum of a new chromophore with bands at 32 000, 25 000, and 19 800 cm^{-1} . The appearance of two tight isosbestic points strongly supports the formation of only one molybdenum complex product. Likewise, this reaction can be followed by EPR spectroscopy. The reduced complex exhibits an EPR spectrum ($\langle g \rangle = 1.978$; $\langle A \rangle$

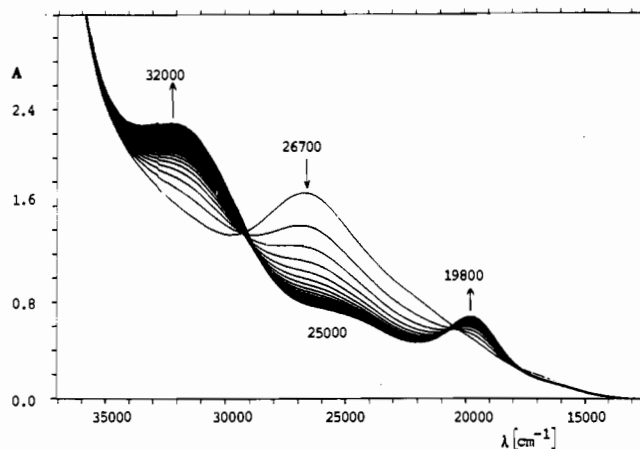


Figure 1. Spectral changes in the reaction of 0.48 mmol of $(\text{H}_4\text{N})_2(\mathbf{1})$ and 5.4 mmol of TBA in MeOH solution at 25 °C. Spectra were recorded every 30 min at a scan rate of 120 nm min^{-1} .

$= 38$ G) typical of Mo^{VO} complexes⁷ with no evidence of ^1H coupling to Mo(V).

The oxidation product of TBA is the dithiodibenzilic acid, DTDBA, detected in a stoichiometric amount by ^1H and ^{13}C NMR spectroscopy (Scheme I).

Although the generality of this reaction is demonstrated by oxidation at low pH of other thiols such as ethanethiol, it cannot be compared with other slower oxidations of aliphatic thiols and arenethiols reported for $\text{MoO}_2(\text{S}_2\text{CNEt}_2)_2$ ⁸ or $\text{MoO}_2(\text{LNS}_2)$ ⁹ because a more reduced Mo(IV) complex product is obtained. It is not at all evident why complex **1** reacts in such a way while others complexes do not, but there is no doubt that protons stabilize the Mo(VI)/Mo(V) conversion. In fact, Scheme I can be correlated with the electrochemical reduction of MoO_2 -tetradentate aromatic aminothiols complexes,¹⁰ which are among the few species that can be reduced to stable monomeric $\text{Mo}^{\text{VOL-}}$ species. It is significant that this unusual behavior appears to be a result of the deprotonation of the amino groups with elimination of H_2O upon reduction, which was in turn interpreted as indicating that coupled proton/electron transfer occurs in the redox reactions. In this regard the latter complexes and **1** mimic the redox behavior of the enzymes xanthine oxidase and sulfite oxidase.¹¹

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Scheme I

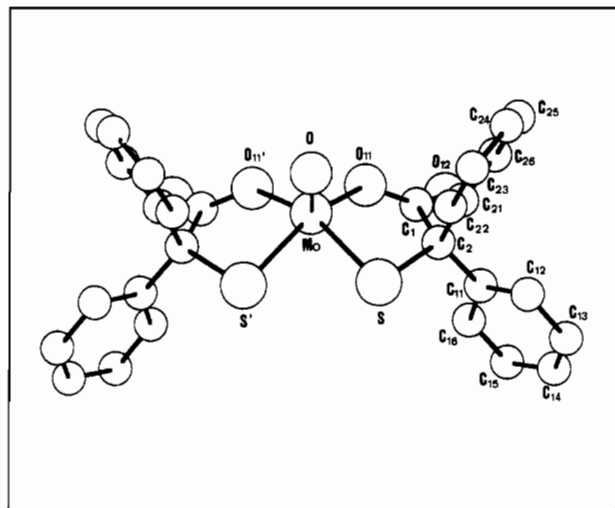
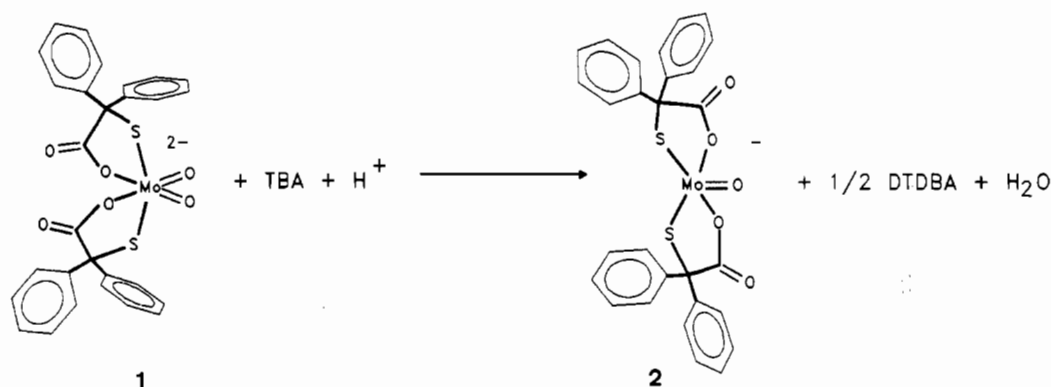


Figure 2. PLUTO drawing of $(\text{Bu}_4\text{N})(2)$. Selected bond lengths (Å) and angles (deg): Mo—S = 2.342 (3), Mo—O = 1.633 (8), Mo—O11 = 1.999 (6); O—Mo—S = 108.4 (2), O11—Mo—S = 81.0 (2), O11—Mo—O = 111.1 (3), S—Mo—S' = 86.3 (2), O11—Mo—O11' = 85.5 (4), C1—O11—Mo = 126.1 (6), C2—S—Mo = 98.4 (3). The Mo atom is 0.73 Å above the plane O11'—O11—S—S'.

If one starts with the Bu_4N^+ salt of complex 1, the Bu_4N^+ salt of complex 2 may be obtained¹² through the reaction shown in Scheme I as a green crystalline solid, which upon redissolution displays the same UV-vis and EPR spectra as observed for the final solution of the reaction shown in Scheme I (see Figure 1). The $[\text{MoO}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]^-$ structure¹³ (Figure 2) reveals a nearly square-pyramidal arrangement of ligand atoms (C_3 symmetry), thus resembling those found for other tetrathiolate $\text{Mo}^{\text{V}}\text{O}_2^-$ complexes ($L = \text{benzene-1,2-dithiolate}^{15}$ or $1,2\text{-ethanedithiolate}^{16}$)

having a MoOS_4 environment and longer Mo=O and Mo—S bond lengths. This conformation places the stronger π -donor thiolate ligands cis to the oxo atom and trans to the carboxylate groups where they can more effectively compete for available empty d orbitals. The M=O (1.636 (9) Å) and Mo—S (2.349 (3) Å) distances are in good agreement with those (1.67, 2.38 Å) derived from EXAFS analysis of reduced nitrate reductase,¹⁷ which also suggests one N/O atom at 2.07 Å. The Mo—O distance (2.013 Å) is consistent with that possibility. Lastly, as proposed for the Mo-cofactor (Mo-co),¹⁸ complex 2 presents the postulated cis coordination by two thiolate groups which are also cis to a terminal oxo group.

The powder EPR spectrum of $(\text{Bu}_4\text{N})(2)$ is characterized by broad spectral features, but in methanol the EPR spectra are well resolved. The point symmetry at the Mo atom is C_3 , and therefore, complete anisotropy in the principal components of the g tensor is permitted. The values of g_i were obtained by direct measurement from the X-band frozen-solution EPR spectra. At 100 K, these values are $g_1 = 2.002$, $g_2 = 1.961$, and $g_3 = 1.934$, with $^{95,97}\text{Mo}$ hyperfine parameters $A_1 = 62 \times 10^4 \text{ cm}^{-1}$, $A_2 = 42 \times 10^4 \text{ cm}^{-1}$, and $A_3 = 48 \times 10^4 \text{ cm}^{-1}$, respectively. In all cases, $\sum g_i/3$ is in good agreement with $\langle g \rangle = 1.978$ obtained directly from fluid-solution measurements at room temperature.

In noncoordinating solvents (THF or Cl_3CH), a very similar spectrum is observed ($\langle g \rangle = 1.985$; $\langle A \rangle = 36 \times 10^4 \text{ cm}^{-1}$); the poor ligating ability of these solvents ensures that these g_i values are the molecular parameters of the complex. These values lead us to suggest that the EPR-active species generated by Meriwether et al.¹ with thioglycolic acid was $[\text{MoO}(\text{O}_2\text{CC}(\text{S})\text{H}_2)]^-$, an interpretation consistent with the 2:1 thiol:Mo ratio predicted by these authors.

A comparison of the g_i parameters for complex 2 with those reported for a tetrathiolate complex such as $[\text{MoO}(\text{S}(\text{CH}_2)_2\text{S})_2]^-$ ($g = 2.012, 1.997, \text{ and } 1.975$)¹⁶ shows that both complexes have similar g_1 values, but the latter has larger values for g_2 and g_3 and hence for $\langle g \rangle$. This follows the general rule that substitution of sulfur for oxygen in the ligands gives lower g values and slightly larger A values.¹⁹ We conclude, therefore, that complex 2 with only two thiolate groups has g values closer to those found for sulfite oxidase²⁰ (1.9872, 1.9641, and 1.9531) or nitrate reductase²¹ (1.995, 1.967, and 1.954) than any tetrathiolate complex. This finding is consistent with EXAFS results for both enzymes.¹⁶

The foregoing results indicate that thiocarboxylate coordination of molybdenum results in properties consistent with the molybdenum enzymatic activity and with the structural and electronic features observed for certain oxomolybdo enzymes.

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 (12) Synthesis of $(\text{Bu}_4\text{N})(2)$ is as follows. Under argon, 0.25 g (0.29 mmol) of $(\text{Bu}_4\text{N})(1)$ was added to 0.18 g of TBA (0.74 mmol) previously dissolved in 10 mL of MeOH. After argon was bubbled through the reaction, the vessel was sealed. Cooling the solution gave 0.1 g of green air-sensitive crystals (yield: 40%). IR (KBr pellet, cm^{-1}): 970 (Mo=O). Cyclic voltammetry (Pt, Pt, SCE): $E' = -485$ (MeOH), -595 mV (DMF); reversible reduction.
 (13) Crystal data for $(\text{Bu}_4\text{N})[\text{MoO}(\text{O}_2\text{CC}(\text{S})\text{Ph}_2)_2]$: $M = 838.99$, monoclinic, space group $P2_1/m$, $a = 9.567$ (9) Å, $b = 24.077$ (9) Å, $c = 10.419$ (12) Å, $\beta = 114.95$ (3)°, $V = 2176$ (3) Å³, $Z = 4$, $D_{\text{calc}} = 1.28 \text{ g cm}^{-3}$, $\lambda_{\text{Mo}}(\text{K}\alpha_1) = 0.7093$ Å, $\mu(\text{Mo K}\alpha) = 3.98 \text{ cm}^{-1}$. The intensities of 3921 reflections were measured at room temperature on a CAD-4 diffractometer using monochromated Mo K α radiation. The structure was solved by direct methods using MULTAN 84 and developed with SHELX-76.¹⁴ Atomic scattering factors and corrections for anomalous scattering taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–149. For 1549 unique reflections with $I > 3\sigma(I)$ and 257 parameters the reliability factors were $R = 0.062$, $R_w = 0.065$ [$w = 1/(\sigma^2(F) + 0.0046F^2)$].
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Acknowledgment. We thank the CICYT for financial support (Grant PB86-0290).

Supplementary Material Available: For complex $(\text{Bu}^n\text{N})(2)$, tables of crystallographic data, complete atomic coordinates and anisotropic and isotropic thermal parameters, bond lengths, and bond angles (4 pages); a table of structure factors (9 pages). Ordering information is given on any current masthead page.

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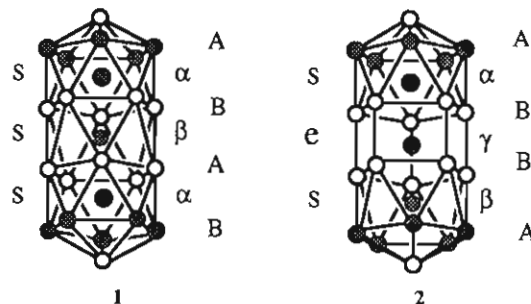
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Received January 8, 1991

Cluster of Clusters. Structure of a New 25-Metal-Atom Cluster $[(p\text{-Tol}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Cl}_7](\text{SbF}_6)_2$ Containing a Nearly Staggered-Eclipsed-Stacked Metal Configuration and Five Doubly Bridging Ligands

Clusters of increasing nuclearity can often be obtained by fusing together smaller cluster units.^{1–11} Recently we reported the synthesis and structural characterization of a 25-metal-atom cluster $[(p\text{-Tol}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Br}_8]^+$ (**1**),^{6a} which can be described as two centered icosahedra sharing a common vertex. The metal

framework is characterized by the staggered–staggered–staggered (sss) configuration of the four metal pentagons, giving rise to an idealized symmetry of D_{3d} for the metal core. We now wish to report the structure of a novel 25-metal-atom cluster $[(p\text{-Tol}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Cl}_7]^{2+}$ (**2**), which has a nearly staggered–eclipsed–stacked (ses) metal configuration with an idealized symmetry of D_5 for the metal core.



The title compound **2** was isolated as the SbF_6^- salt from the reduction of a mixture of $p\text{-Tol}_3\text{P}$, HAuCl_4 , and AgSbF_6 with NaBH_4 in ethanol.¹² Other structurally characterized clusters of this series include the 37-metal-atom cluster $[(p\text{-Tol}_3\text{P})_{12}\text{Au}_{18}\text{Ag}_{19}\text{Br}_{11}]^{2+}$ (**3**),⁷ the 38-metal-atom cluster $[(p\text{-Tol}_3\text{P})_{12}\text{Au}_{18}\text{Ag}_{20}\text{Cl}_{14}]$ (**4**),⁸ and the 46-metal-atom cluster $[(\text{Ph}_3\text{P})_{12}\text{Au}_{22}\text{Ag}_{24}\text{Cl}_{12}]$ (**5**).⁹

The title cluster **2** conforms to the crystallographic site symmetry C_{2v} . Figure 1a depicts the metal core which can be described as two 13-atom-Au-centered icosahedra sharing a vertex (Au13). As shown in Figure 1b, there are 10 phosphine ligands, coordinated to the 10 peripheral Au atoms. Five doubly bridging chloride ligands connect the two Ag_5 pentagons and two terminal chloride ligands ($\text{Cl}11$ and $\text{Cl}11'$) coordinate to the two apical Ag atoms ($\text{Ag}11$ and $\text{Ag}11'$).

Several novel features of the structure of **2** are noteworthy. First, the most significant structural characteristic of **2** is the observed (nearly) staggered–eclipsed–stacked (ses) configuration for the metal core¹³ (cf. Figure 1a,c), which is to be contrasted with the staggered–staggered–staggered (sss) metal configuration of **1**.^{6a} Second, there are five bridging chloride ligands in **2** instead of six as in **1**. As shown in Figure 1c, all five bridging chloride ligands are symmetrical with an average Ag–Cl distance of 2.44 Å. Third, cluster **2** is a dication instead of a monocation (as in **1**). The last two observations are related in that removal of one halide ligand in **1** causes the increase of the overall charge of the cluster from +1 to +2 (as in **2**). As a result, the number of electrons remains the same (25 (metals) – 7 (Cl) – 2 (charges) = 16).

The intricosahedral metal–metal distances (Au11-centered icosahedra) are significantly shorter than intericosahedral distances (Au13-centered bicapped pentagonal prism), suggesting that intricosahedral bondings are substantially stronger than intericosahedral bonding (cf. Figure 1 caption). This observation is consistent with the cluster of clusters concept^{10,11} wherein the individual icosahedra serve as the basic building blocks.

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- (12) The cluster $[(p\text{-Tol}_3\text{P})_{10}\text{Au}_{13}\text{Ag}_{12}\text{Cl}_7](\text{SbF}_6)_2 \cdot n\text{EtOH}$ forms dark red prismatic crystals. It crystallizes in the tetragonal space group $P4_32_12$, with $a = 20.510(6)$ Å, $c = 61.78(1)$ Å, $V = 25988.1$ Å³, and $Z = 4$. Single-crystal X-ray diffraction data were collected by using an Enraf-Nonius diffractometer (Mo $K\alpha$ radiation). The tolyl groups and the SbF_6^- anion were refined as rigid bodies with C(methyl)–C(ring), C(ring)–C(ring), and Sb–F distances of 1.47, 1.395, and 1.86 Å, respectively (see ref 8a for details). Anisotropic refinement gave $R_1 = 9.6\%$ for 5811 independent reflections ($2\theta \leq 46^\circ$) with $I > 3\sigma$. Crystallographic (Tables I–VI and VIII) and preparative (Table VII) details can be found in the supplementary material.
- (13) One can envision the successive buildup of a one-dimensional structure of nuclearities 1, 7, 13, 19, 25, 31, 37, ... by adding one atom and one pentagon at a time. The infinite chain analogue is observed in the solid-state compounds Ta_2S (Franzen, H. F.; Smeggil, J. G. *Acta Crystallogr.* **1969**, *B25*, 1736) and Ta_6S (Franzen, H. F.; Smeggil, J. G. *Acta Crystallogr.* **1970**, *B26*, 125). The structural relationship of the high nuclearity clusters and the solid-state compounds therefore provides a link between clusters and the bulk.^{11c}