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The Crystal and Molecular Structure of $\{[Mo(SCH_2CH_2SCH_2CH_2S)_2]_2Ag\}PF_6 \cdot \frac{1}{2}DMF$, a Thiolate-Bridged Mixed-Metal Cluster

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In recent years considerable interest has grown in the rational synthesis and chemical properties of heterometallic systems linked by sulfur donors because of the possible relationship of these species to metalloproteins [1] and in view of their unusual structural and physico-chemical properties [2]. Although tetrathiometallate ligands, such as MoS_4^{2-} and WS_4^{2-}, have been shown to display considerable chemistry in ligating other metals [3–5] the potential of metal–thiolate complexes to function in ligating groups has only recently been realized and exploited [6].

In the course of our investigations of the chemistry of Mo with sulfur-containing ligands [7], we have synthesized and characterized the Mo(IV) complex, $[Mo(mes)_2]$ [8]. Although the complex is well-behaved electrochemically, oxidizing to give the bright pink Mo(V) species, $[Mo(mes)_2]BPh_4$, chemical reaction with $AgPF_6$ in dimethylformamide provides a maroon, diamagnetic species analyzing as the 2:1 adduct $\{[Mo(mes)_2]_2Ag\}PF_6 \cdot \frac{1}{2}DMF$. Maroon diamagnetic crystals of $\{[Mo(mes)_2]_2Ag\}PF_6 \cdot \frac{1}{2}DMF$ were grown from dimethylformamide/methanol solution at 4 °C.

The infrared spectrum exhibited bands of medium intensity characteristic of ν(Mo–S) at 360 cm^{-1} and 418 cm^{-1}. The strong band at 840 cm^{-1} is attributed to ν(P–F). The electronic spectrum in dimethylformamide solution showed absorbances at 524 and 448 nm with extinction coefficients of

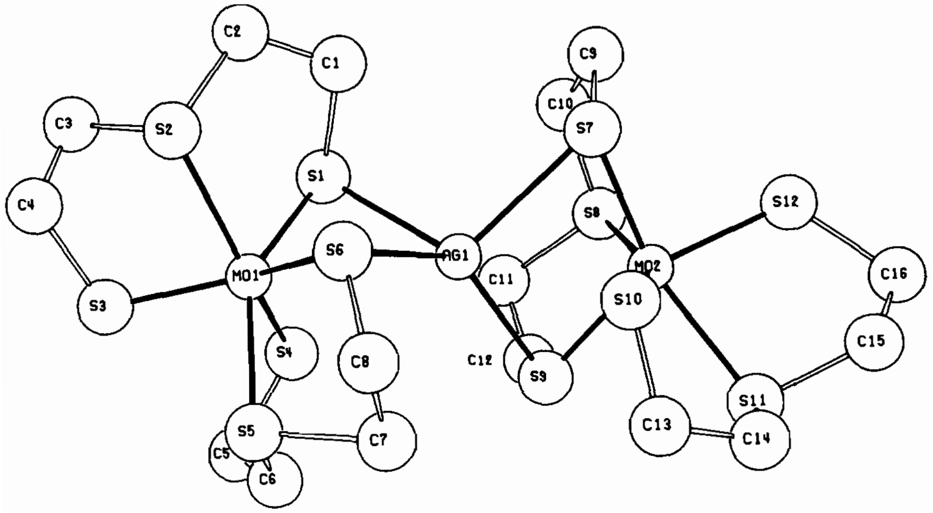

Fig. 1. A perspective view of the conformation of one cation of the asymmetric unit; the stereochemistry of the second cation is essentially identical. The relevant bond lengths and angles for the $\{[Mo(mes)_2]_2Ag\}^{1+}$ complex cation are: Mo1–Ag, 3.137(8) Å; Mo2–Ag, 2.968(8); Mo1–S1, 2.35(1); Mo1–S2, 2.50(1); Mo1–S3, 2.26(1); Mo1–S4, 2.36(1); Mo1–S5, 2.43(1); Mo1–S6, 2.38(1); Mo2–S7, 2.32(2); Mo2–S8, 2.50(2); Mo2–S9; 2.45(2); Mo2–S10, 2.33(2); Mo2–S11, 2.50(2), Mo2–S12, 2.31(2); Ag–S1, 2.62(1); Ag–S6, 2.61(1); Ag–S7, 2.70(2); Ag–S9, 2.59(2); <Mo1–Ag–Mo2, 170.1(3); <S1–Ag–S6, 80.1(5); <S1–Ag–S7, 104.1(7); <S1–Ag–S9, 123.2(6); <S6–Ag–S7, 111.9(7); <S6–Ag–S9, 136.4(6); <S7–Ag–S9, 98.3(7); <S1–Mo1–S2, 80.1(6); <S1–Mo1–S3, 121.5(7); <S1–Mo1–S4, 77.8(6); <S1–Mo1–S5, 144.8(6); <S1–Mo1–S6, 90.5(6); <S2–Mo1–S3, 77.9(6); <S2–Mo1–S4, 145.0(7); <S2–Mo1–S5, 130.4(6); <S2–Mo1–S6, 81.2(6); <S3–Mo1–S4, 91.0(7); <S3–Mo1–S5, 86.2(6); <S3–Mo1–S6, 137.3(7); <S4–Mo1–S5, 80.7(6); <S4–Mo1–S6, 125.5(6); <S5–Mo1–S6, 79.7(6); <S7–Mo2–S8, 81.3(9) <S7–Mo2–S11, 156.2(9); <S7–Mo2–S12, 92.9(7); <S8–Mo2–S9, 79.7(8); <S8–Mo2–S10, 154.0(9); <S8–Mo2–S11, 119.8(8); <S8–Mo2–S12, 83.1(7); <S9–Mo2–S10, 90.7(9); <S9–Mo2–S11, 82.4(7); <S9–Mo2–S12, 145.1(8); <S10–Mo2–S11, 82.2(6); <S10–Mo2–S12, 116.4(9); <S11–Mo2–<S12, 80.2(6).

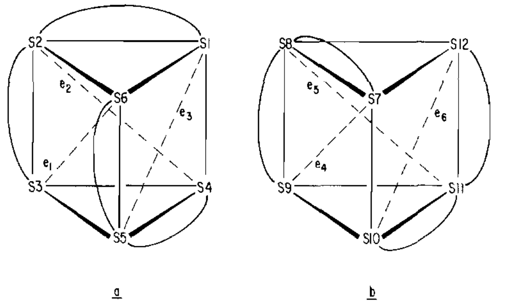

Fig. 2. Schematic representations, *a* and *b*, of the coordination polyhedra about Mo1 and Mo2, respectively, showing the crossover pattern of tridentate ligand coordination about Mo1, *a*, and about Mo2, *b*. The labelled edges define the shape-determining dihedral angles: <S2S3S4–S1S2S4, 22.8°; <S1S4S5–S1S5S6, 9.8°; <S2S3S6–S3S5S6, 20.2°; <S7S8-S9–S7S9S10, 34.5°; <S7S10S12–S10S11S12, 34.2°; <S8S9S11–S8S11S12, 26.0°. The dihedral angle between the triangular faces S1S2S6 and S3S4S5 is 4.7°, while that between S7S8S12 and S9S10S11 is 7.0°. The non-binding distances generating the polyhedral edge lengths about Mo1 are: S1···S2 3.12 A; S1···S4, 2.96 A; S2···S6, 3.18 A; S2···S3, 2.99 A; S1···S6, 3.36 A; S6···S5, 3.08 A; S3–S4, 3.29 A; S3···S5, 3.20 A; S4···S5, 3.10 A. The corresponding distances for the coordination polyhedron of Mo2 are: S7–S8, 3.14 A; S7···S10, 3.01 A; S8···S12, 3.20 A; S8···S9, 3.17 A; S7···S12 3.36 A; S12···S11, 3.10 A; S9···S10, 3 40 A; S9···S11, 3.26 A; S10···S11, 3.17 A. The intraligand thiolate S-thiolate S bite distances are: S1···S3, 4.02 A; S4···S6, 3.81 A; S7···S9, 4.00 A; S10···S12, 3.94 A.

5.3×10^4 and 7.3×10^4, respectively, and tentatively assigned as S → Mo change transfer bands. The complex is sparingly soluble in dmf and acetonitrile.

Crystal data: $\{[Mo(SCH_2CH_2SCH_2CH_2S)_2Ag\}$-$PF_6 \cdot \frac{1}{2}DMF$, triclinic, space group $P\bar{1}$, with a = 12.644(3) Å, b = 17.052(4) Å, c = 18.269(4) Å, α = 98.32(2)°, β = $105.60(^1)^\circ$, (two molecules per asymmetric unit): F(000) = 2156.0. Axial photographs and Delauney reduction revealed no hidden symmetry. The structure analysis is based on 1804 independent reflections with $F_{obs} \geqslant 6.0\sigma\ F_{obs}$ (Mo–Kα, μ = 19.15 cm^{-1}) and R is currently 0.072.

The asymmetric unit contains two units $\{[Mo(mes)_2]_2Ag\}PF_6 \cdot \frac{1}{2}DMF$ of essentially identical stereochemistries. Figure 1 demonstrates the geometry of the heterometallic cation, with pertinent bond lengths and angles displayed in the caption.

The metal aggregate is nearly linear (<Mo1–Ag–Mo2, 170.1(3)°) with the Ag atom bridging the two $[Mo(mes)_2]$ units through coordination to two thiolatesulfur donors of each Mo^{IV} center, utilizing thiolate sulfurs from each mes ligand above Mo1 and the thiolato-donors from the same *mes* group about Mo2. The average Ag–S distance of 2.63(1) Å is consistent with four coordinate Ag(I) in a thiolate coordination environment [6].

The geometry about the Ag atom is severely distorted from regular tetrahedral as a consequence of the constrained ligand geometries required to generate the Mo coordination polyhedra.

The geometry about Mo1, in common with that observed for the parent species $[Mo(mes)_2]$, is pseudo-trigonal prismatic. The average torsion angle between the triangular faces S(1)S(2)S(6) and S(4)-S(5)S(6) of *ca.* 12.0° is significantly closer to the trigonal prismatic limit of 0° than to the ideal octahedral value of 60°. The shape-determining dihedral angles, associated with the edges labelled in Fig. 2 are also consistent with the rectangular faces of the trigonal prism. In common with the parent compound $[Mo(mes)_2]$, the tridentate ligands span the triangular faces of the trigonal prism to compress the polyhedron along its pseudo-C_3 axis. The thiolate-sulfur groups participating in the bridging interaction with the central Ag atom occupy the same triangular face and consequently derive from different *mes* groups.

The polyhedron for Mo2, on the other hand, is significantly distorted toward the octahedral limit, wih an average torsion angle of *ca.* 23.4° between the triangular faces S(7)S(8)S(12) and S(9)S(10)S(11), and with shape-determining dihedral angles consistent with a geometry intermediate between the octahedral and trigonal prismatic limits (Fig. 2). The distortion from the geometry associated with the parent $[Mo(mes)_2]$ appears to be a consequence of the use of the two thiolate-sulfur donors of a single *mes* ligand in bridging to the Ag atom.

Although not as versatile as MoS_4^{2-} in forming heterometallic clusters, $[Mo(mes)_2]$ possesses a rich and varied chemistry as a metal complex ligand forming clusters of the types $\{[Mo(mes)_2]M\}PF_6$ (M = Ag^{1+} and Cu^{1+}) and $\{[Mo(mes)_2M\}(PF_6)_2$ (M = Fe^{2+} and Cu^{2+}). We are currently investigating the structural and spectroscopic properties of this new class of compounds.

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