Synthesis and Crystal and Molecular Structure of $MoS_4(AuPEt_3)_2$:
A Linear Trinuclear Heterobimetallic Species

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Metal sulfur aggregates have received considerable attention of late [1–6]. This interest has arisen for several reasons. Many of the new metal sulfide species prepared and characterized in recent years, have revealed novel structures and bonding modes. Recent reviews have summarized the current thinking in these areas [7, 8]. The relevance of such compounds to bioinorganic chemistry is another reason for intense interest. Biological systems involved with electron transfer and fixation of nitrogen are thought to contain metal sulfur aggregates. A variety of metal sulfur compounds containing biologically relevant metals have been characterized in attempts to model specific enzymatic sites. This work has also been recently reviewed [9, 10]. Our interest [11–13] in the synthesis, structure and chemistry of mixed metal systems has prompted us to investigate sulfur-bridged heterobimetallic species. Such compounds containing two different metals in close proximity are expected to yield unusual structure and bonding relationships as well as unique reactivity patterns. In this paper we report the preparation and structural characterization of a Au derivative of the tetrathiometallate MoS_4^{2-}. The structure of this linear trinuclear heterobimetallic species is described and the implications of the chemistry are discussed below.

Experimental

The preparations were done under an atmosphere of dry O_2-free, N_2. Solvents used were reagent grade, distilled from the appropriate drying agents under N_2 and degassed by the freeze-thaw method at least three times prior to use. ^{31}P NMR spectra were recorded on a Bruker CXP 100 spectrometer operating at 36.5 MHz with broad-band proton decoupling. The ^{31}P chemical shifts are reported relative to 85% H_3PO_4. UV-vis data were recorded employing a Shimadzu 240 spectrometer. Combustion analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario. PEt_3 was purchased from the Strem Chemical Co. Et_3PAuCl was prepared by literature methods [14], employing $HAuCl_4$ received on loan from Johnson-Matthey Ltd.

Preparation of $(NEt_4)_2MoS_4$, (1)

$(NH_4)_2MoS_4$ was prepared by a literature method [15]. This compound was dissolved in a 10% aqueous solution of Et_4OH. This solution was placed under vacuum for 2 h to remove NH_3. The lost H_2O was replaced and the solution filtered into 400 ml of isopropanol. The resulting precipitate was isolated by filtration, washed with isopropanol and diethylether and recrystallized from CH_3CN/diethylether. After drying *in vacuo* the yield was 68% (based on starting amount of $Na_2MoO_4 \cdot 2H_2O$).

Preparation of $MoS_4(AuPEt_3)_2$, (2)

69 mg (0.143 mmol) of (1) was dissolved in 10 ml of ethanol. This solution was added to an ethanol solution of 100 mg (0.286 mmol) of Et_3PAuCl. A red crystalline precipitate forms immediately. This product was isolated by filtration and recrystallized from CH_3CN/diethylether to yield 60 mg (48%) of (2). M.p. 133 °C(d). *Anal.* Calcd: C, 16.88; H, 3.54. Found: C, 17.22; H, 3.67. $^{31}P\{^1H\}$ NMR (CH_3CN): δ, 41.9 ppm (s). UV-vis (CH_3CN): λ: 490 nm ($\epsilon = 3590$ M^{-1} cm^{-1}), 430 nm ($\epsilon = 1540$ M^{-1} cm^{-1}), 375 nm ($\epsilon = 2050$ M^{-1} cm^{-1}), 345 nm ($\epsilon = 5120$ M^{-1} cm^{-1}).

X-ray Data Collection and Reduction

Wine-red crystals of (2) were obtained by vapor diffusion of diethylether into a CH_3CN solution of (2). Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with a graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with a monoclinic crystal system. Ultimately, 31 high-angle reflections ($15 < 2\theta < 35°$) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group $P2_1/c$. $\pm h$, $\pm k$, $+l$ data were collected in one shell ($4.5 < 2\theta < 45.0°$). Three standard reflections were recorded every 197 reflections; their intensities show no statistically significant change over the duration of data collection. The data were processed by using the SHELX-76 program package on

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TABLE I. Summary of Crystal Data, Intensity Collection and Structure Solution.

formula	$MoS_4(AuPEt_3)_2$
crystal color, form	wine red, blocks
a, Å	18.370(3)
b, Å	7.928(1)
c, Å	18.733(4)
β, deg	120.87(1)
crystal system	monoclinic
space group	$P2_1/c$
V, Å^3	2341.7(6)
d calc., g cm^{-3}	2.42
Z	4
crystal dimensions, mm	0.31 × 0.12 × 0.25
abs. coeff. (μ), cm^{-1}	129.72
radiation (λ, Å)	Mo Kα (0.71069)
	(graphite monochromator)
temp, °C	24
scan speed, deg/min	2.0–5.0° ($\theta/2\theta$ scan)
scan range, deg	2.0° below Kα_1, 1.0° above Kα_2
bkgd/scan time ratio	0.5
data collected	2θ of 4.5–50.0° ($\pm h$, $\pm k + l$)
total no. of data collected	6230
no. of unique data, $F_o^2 > 3\sigma(F_o^2)$	2760
no. of variables	189
R, %	4.88
R_w, %	5.25

the computing facilities at the University of Windsor. A total of 2760 reflections with $Fo^2 < 3\sigma(Fo^2)$ were used in the refinement.

Structure Solution and Refinement

Non-hydrogen atomic scattering factors were taken from the tabulation of Cromer and Waber [16, 17]. The two Au atom positions were determined by a direct methods technique using the program MULTAN. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Full-matrix least-squares refinement, in which all non-hydrogen atoms were assigned isotropic temperature factors gave $R = 21.83\%$. Hydrogen atom contributions for the ethyl hydrogens were included. C–H bond lengths of 0.95 Å were assumed, and hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the bonded carbon atom. An empirical absorption correction was applied. In the final cycles of full matrix refinement the Au, Mo, S, P and methylene carbon atoms were assigned anisotropic temperature factors, the methyl groups were refined as rigid rotors with isotropic thermal parameters, and all hydrogen atom contributions were included but not refined.

This gave $R = 4.88\%$ and $R_w = 5.25\%$. The maximum Δ/σ on any of the parameters excluding those associated with the methyl groups in the final cycles was 0.051. The shift on the parameters of the methyl groups were larger reflecting the disordered nature of these CH_3 moieties. Since no information regarding the partial occupancy positions of the methyl hydrogen atoms could be derived from difference map calculations no attempt was made to model their disorder. The final difference Fourier map calculation showed no peaks of chemical significance; the largest peak was 1.0 electrons and was associated with the Au1–S1 moiety. The following data are tabulated: positional parameters (Table II); interatomic distances and angles (Table III). Temperature factors (Table S-I), Hydrogen atom parameters (Table S-II) angles and distances associated with the PEt_3 groups. (Table S-III) and values of $10|Fo|$ and $10|Fc|$ (Table S-IV) have been deposited as supplementary material.

Results and Discussion

The reaction of Et_3PAuCl and $(NEt_4)_2MoS_4$ **(1)** was performed in ethanol. An microcrystalline

TABLE II. Positional Parameters.[a]

Atom	x	y	z
Au1	1673(1)	3080(1)	5804(1)
Au2	3200(1)	4509(1)	3918(1)
Mo	2477(1)	3681(2)	4887(1)
S1	1229(3)	2418(6)	4379(2)
S2	3050(3)	4273(6)	6233(3)
S3	3322(3)	1986(6)	4702(3)
S4	2278(3)	6110(6)	4226(3)
P1	948(3)	2784(5)	6481(2)
P2	3830(3)	5196(6)	3178(3)
C1	1389(12)	4081(23)	7419(9)
C2	1376(13)	5986(26)	7235(13)
C3	916(11)	645(22)	6836(10)
C4	395(11)	412(22)	7224(10)
C5	−163(9)	3446(22)	5823(9)
C6	−670(12)	2274(22)	5062(12)
C7	4575(13)	3497(32)	3228(14)
C8	5181(15)	2905(33)	4112(14)
C9	4448(14)	7150(33)	3533(14)
C10	4006(20)	8656(36)	3563(19)
C11	3086(11)	5517(24)	2078(11)
C12	3466(15)	5878(30)	1532(14)

[a]Parameters given $\times 10^4$.

orange-red precipitate formed immediately. This product could be recrystallized from acetonitrile/diethylether yielding wine red crystals. The $^{31}P\{^1H\}$ NMR spectrum of this material shows a singlet at 41.9 ppm. This is consistent with equivalent uncoupled phosphorus atoms. The visible spectrum of this compound showed absorptions at 490, 430, 375, and 345 nm. These spectral features are reminiscent of the spectrum of $(NCH_4)_2[NCCu(MoS_4)]$ [8] thus suggesting a bridging MoS_4^{2-} in the present compound. These observations as well as combustion analysis data resulted in the formulation of this species as $MoS_4(AuPEt_3)_2$ (2).

Formation of compound (2) takes place regardless of the Au:Mo ratio. In experiments where the ratio of Au:Mo was varied between 1:1 and 2:1 no other species could be observed by spectroscopy or

TABLE III. Selected Bond Distances and Angles.[a]

Mo–S1	2.258(4)	Mo–S2	2.182(4)
Mo–S3	2.234(4)	Mo–S4	2.205(5)
Au1–S1	2.362(4)	Au1–S2	2.466(5)
Au2–S3	2.409(5)	Au2–S4	2.432(4)
Au1–P1	2.277(4)	Au2–P2	2.275(4)
Au1–Mo	2.815(1)	Au2–Mo	2.814(1)
S1–Mo–S2	111.5(2)	S1–Mo–S3	109.5(2)
S1–Mo–S4	108.3(2)	S2–Mo–S3	109.1(2)
S2–Mo–S4	106.4(2)	S3–Mo–S4	112.0(2)
S1–Au1–S2	99.0(1)	S3–Au2–S4	99.0(1)
S1–Au1–P1	127.8(2)	S2–Au1–P1	133.1(2)
S3–Au2–P2	129.6(2)	S4–Au2–P2	131.4(2)
Au1–S1–Mo	75.0(1)	Au1–S2–Mo	74.3(1)
Au2–S3–Mo	74.5(1)	Au2–S2–Mo	74.5(1)

[a]Bond lengths in A, angles in degrees.

isolated from the reaction mixtures. Of course the yield of (2) was dependent on the initial Au:Mo ratio. This result is consistent with the known affinity of Au for sulphur ligands [18] as well as the propensity of MoS_4^{2-} to act as a tetradentate bridging unit.

Single crystals of (2) were obtained by vapor diffusion of diethylether into a CH_3CN solution of (2). An X-ray crystallographic study of this species revealed that the crystals are made of unit cells each containing four discrete molecules. The closest non-bonded contact between molecules was 2.852 Å (H11B–Au1). Selected interatomic distances and angles are tabulated in Table II. An ORTEP drawing of the core of the molecule is shown in Fig. 1. The P–Au–Mo–Au–P fragment of the molecule is essentially linear. The geometry of the Mo atom is pseudo-tetrahedral while the geometries of the Au atoms are pseudo-trigonal. There are four sulphur atoms about the Mo atom with an average Mo–S bond length of 2.220(9) Å. Bonded to each of the two chemically equivalent Au atoms are two bridging sulphur atoms and a phosphorus atom of a PEt_3 moiety. Au–S and Au–P bond lengths are similar
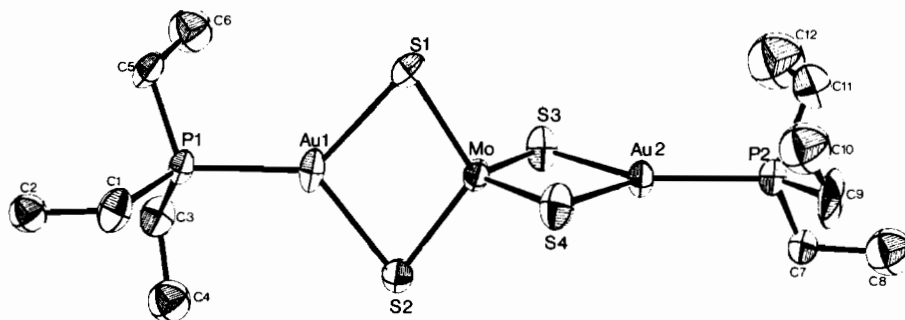

Fig. 1. ORTEP Drawing of the molecule, $MoS_4(AuPEt_3)_2$ 50% thermal ellipsoids are shown. Hydrogen atoms are omitted for clarity.

to those observed for other complexes [18]. The bond lengths and angles within the PEt$_3$ moieties are typical [19].

Molecular orbital calculations have been described for compounds containing the M$'$S$_2$MS$_2$M$'$ unit [8]. These theoretical studies show that a delocalized molecular orbital occurs over the M$'$–M moiety. The overlap integral function between the metals shows that at a separation of approximately 2.8 Å a direct metal–metal interaction should be considered. The average of the two Mo–Au distances in (2) is 2.815(1) Å. The angles at S (*i.e.*, Au–S–Mo) are constrained to an average of 74.6(2)°, while the S1–Mo–S2 and S3–Mo–S4 angles open up slightly averaging 3.5° greater than the other S–Mo–S angles. These structural parameters determined herein confirm the presence of a direct metal–metal (*i.e.* Au–Mo) interaction in (2).

Metal–metal bonding in other derivatives of tetrathiometalates is well documented [7–9]. Such interactions are expected to be the logical consequence of putting two metals of diverse oxidation states in close proximity. However, it is also clear that on formation of the metal–metal bond the formal oxidation states of the metal centers is altered. It is this aspect of heterobimetallic species that will undoubtedly give rise to unique reactivity properties. Further studies designed to examine the effect of metal–metal interactions on the chemistry of heterobimetallic species is currently underway and will be reported in due course.

Supplementary Material Available

Tables S-I–S-IV list temperature factors, hydrogen atom parameters, angles and distances associated with PEt$_3$ groups, and observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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