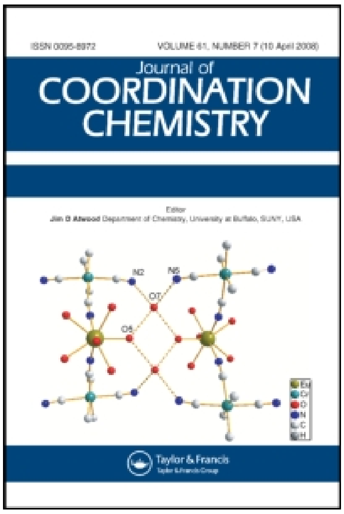

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REACTIONS OF CLUSTER COMPOUND $[(C_2H_5)_4N]_4[Mo_2O_2S_6Cu_6I_4Br_2]$:

Synthesis, Crystal Structures of $[MoOS_3Cu_3(AsPh_3)_3I]\cdot 2DMF$ and $MoOS_3Cu_3(PPh_3)_3I$

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The title compounds $[MoOS_3Cu_3(AsPh_3)_3I]\cdot 2DMF$ (**II**) and $MoOS_3Cu_3(PPh_3)_3I$ (**III**) were obtained by reaction of twin-nest shaped cluster $[(C_2H_5)_4N]_4[Mo_2O_2S_6Cu_6I_4Br_2]$ (**I**) with $AsPh_3$ and PPh_3 in solution, respectively. The compounds have been studied by single crystal X-ray methods. The structure of (**II**) has been refined to show a cubane-like structure containing a $\{MoS_3Cu_3\}$ core and $AsPh_3$ ligands attached to three Cu atoms. Reaction properties of (**I**) are also described and discussed.

Keywords: thiomolybdate; synthesis; substitution; X-ray structure

INTRODUCTION

Mo(W)-Cu(Ag)-S cluster compounds have been extensively studied because of their relevance to biological systems, [1] catalysis [2] and non-linear optical properties. [3-5] Many methods have been employed to prepare such clusters. It is known that in the presence of PPh_3, reactions of $MO_nS_{(4-n)}^{2-}$ (n = 1, 2) with Cu^+ result in the formation of several different types of clusters. [6,7] On the contrary, only a few $AsPh_3$-containing cluster compounds, $Ag_4(AsPh_3)_4W_2S_8$, [5] $MoS_4Cu_3(AsPh_3)_3I$ [8] have been structurally reported, in contrast with the

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relatively great number of PPh_3-containing cluster compounds. Both the $AsPh_3$ compounds were obtained by solid state syntheses at low temperature, [5,9] the method first introduced in our group to prepare cluster compounds. Herein we present the syntheses of $AsPh_3$-containing clusters through reactions in solution using $[(C_2H_5)_4N]_4[Mo_2O_2S_6Cu_6I_4Br_2]$ [10] as reactive precursor.

EXPERIMENTAL

$[(C_2H_5)_4N]_4[Mo_2O_2S_6Cu_6I_4Br_2]$ (**I**) was prepared according to the literature. [10] Other chemicals were of A.R. grade. Infrared spectra (KBr pellets) were recorded on a Nicolet FT-170 SX spectrophotometer. Carbon, nitrogen and hydrogen analyses were performed on a JA-1100 ICP instrument.

$MoOS_3Cu_3(AsPh_3)_3I{\cdot}2DMF$ (II)

A DMF solution (5 cm^3) of $[(C_2H_5)_4N]_4[Mo_2O_2S_6Cu_6I_4Br_2]$ (0.15 g, 0.075 mmol) was added to a DMF solution (5 cm^3) of $AsPh_3$ (0.15 g, 0.45 mmol), then stirred for about 10 mins. The resulting solution was filtered and the filtrate allowed to evaporate in atmosphere at room temperature. Several days later, deep red cubic crystals (0.09 g) were obtained. *Anal.* Calcd. for $MoO_3S_3Cu_3IC_{60}H_{59}N_2As_3$(%): C, 45.1; H, 3.8; N, 1.9. Found: C, 45.1; H, 3.7; N, 1.8. IR spectra: $\nu(Mo\text{-}O_t)$, 920cm^{-1}; $\nu(Mo\text{-}S_{br})$, 446cm^{-1}.

$MoOS_3Cu_3(PPh_3)_3I$ (III)

A CH_3CN solution (15 cm^3) of $[(C_2H_5)_4N]_4[Mo_2O_2S_6Cu_6I_4Br_2]$ (0.15 g, 0.075 mmol) was added to a CH_3CN solution (10 cm^3) of PPh_3 (0.13 g, 0.45 mmol), then stirred for about 40 mins. The resulting solution was filtered and the filtrate allowed to evaporate in atmosphere at room temperature. Deep red crystals (0.10 g) precipitated after several days. *Anal.* Calcd. for $MoOS_3Cu_3IP_3C_{54}H_{45}$(%): C, 49.4; H, 3.4. Found: C, 49.2; H, 3.4.

Crystal Structure Analysis

Single crystals were mounted in random orientation on glass fibres. The crystal data for the two title compounds are summarized in Table I, together with other experimental details. Intensity data were corrected for Lorentz and polarization effects. The structure of compound (**II**) was solved by direct methods and successive Fourier syntheses and refined by full-matrix least-squares procedures.

TABLE I Crystallographic data.

Formula	$C_{60}H_{59}As_3O_3N_2MoCu_3S_3I$	$C_{54}H_{45}P_3OMoCu_3S_3I$
Formula Weight	1589.7	1311.8
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	12.027(2)	11.902(5)
b (Å)	13.263(2)	28.296(4)
c (Å)	20.517(3)	19.360(6)
α (°)	74.10(0)	
β (°)	84.79(1)	101.45(5)
γ (°)	63.55(1)	
Z	2	4
V (Å^3)	2816.3	6390.3
T (K)	294	293
D_c (g cm^{-1})	1.72	1.36
μ (Mo-K_α) (cm^{-1})	39.2	18.5
λ (Å)	0.71073	0.70930
Crystal size (mm)	0.28×0.32×0.40	0.10×0.15×0.35
Maximum 2θ (°)	48	46
Collection instrument	R3M/E	Enraf-Nonius CAD4
Number of unique reflection	9397	
Number of observed reflection	6280 ($I > 3\sigma$) (I)	
R	0.0338	
R_w	0.0315	
Number of variables	611	
Residual extrema in final difference map (e Å^{-3})	0.831 to −0.420	

Details of data collection together and structure refinement are summarized in Table I. Atomic coordinates and isotropic thermal parameters of compound (II) are given in Table II. Anisotropic thermal parameter, H atom coordinates full lists of bond lengths and angles, and observed and calculated structure factors are available from the authors on request.

RESULTS AND DISCUSSION

Structure of [$MoOS_3Cu_3(AsPh_3)_3I$]·2DMF (II)

The structure of [$MoOS_3Cu_3(AsPh_3)_3I$]·2DMF consists of two neutral molecules in the unit cell of space group $P\bar{1}$. A diagram of one molecule is shown in Figure 1. Selected bond lengths and angles are listed in Table III.

The structure is similar to that of $MoOS_3Cu_3(PPh_3)_3Cl$. [6] {MoS_3Cu_3I} is a cubane-like core, completed by three Cu atoms, one I atom and one terdentate [$MoOS_3$]$^{2-}$ ligand. Three $AsPh_3$ ligands coordinate to the three copper atoms.

TABLE II Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for (**1**).

Atom	*x/a*	*y/b*	*z/c*	U^*
I	4454(1)	−1806(1)	3084(1)	48(1)
Mo	1309(1)	237(1)	1659(1)	41(1)
As(1)	3375(1)	1648(1)	2903(1)	41(1)
As(2)	1615(1)	−2750(1)	3770(1)	41(1)
As(3)	5494(1)	−2534(1)	1182(1)	49(1)
Cu(1)	2718(1)	574(1)	2453(1)	51(1)
Cu(2)	1895(1)	−1455(1)	2833(1)	57(1)
Cu(3)	3725(1)	−1368(1)	1664(1)	58(1)
S(1)	874(1)	504(1)	2714(1)	44(1)
S(2)	1992(2)	−1696(1)	1773(1)	43(1)
S(3)	2944(1)	640(1)	1327(1)	47(1)
O	52(4)	1073(4)	1127(3)	81(3)
C(1)	5117(5)	1303(5)	2773(3)	44(2)
C(2)	5727(5)	755(5)	2276(4)	59(3)
C(3)	6948(6)	552(7)	2152(4)	74(4)
C(4)	7544(6)	878(6)	2524(4)	75(3)
C(5)	6945(6)	1412(7)	3032(4)	78(4)
C(6)	5729(6)	1603(6)	3155(4)	61(3)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

The molybdenum atom retains the tetrahedral geometry of the free $[\text{MoOS}_3]^{2-}$ ligand with S-Mo-S(O) angles ranging from 106.4(1) to 113.0(2)°. Although the coordination geometry of each Cu atom is tetrahedrally distorted, the three Cu atoms are approximately equivalent. The three Cu-I bond distances are in the range 2.894(1)-2.973(1)Å. However, in the $\text{MoOS}_3\text{Cu}_3(\text{PPh}_3)_3\text{Cl}$ cluster, [6] which crystallizes space group, in $P2_12_12_1$ there exists one short Cu-Cl bond [2.4714 Å] and two long bonds [av. 2.744(4) Å].

In addition, the main difference between the structure of compound (**II**) and that of $[\text{MoS}_4\text{Cu}_3(\text{AsPh}_3)_3\text{I}]$ (**IV**) [8] is that the terminal sulfur ligand in (**IV**) has been replaced by an oxo ligand (**II**). Compound (**IV**) crystallizes in space group $P\bar{1}$ and has three Cu-I bonds in the range 2.900(2)-2.949(2)Å. It seems that replacement of the terminal sulfur by the oxo ligand only makes a slight difference.

Structure of $[\text{MoOS}_3\text{Cu}_3(\text{PPh}_3)_3\text{I}]$ (III)

The structure of (**III**) was not refined, because compounds (**III**) and $[\text{WOS}_3\text{Cu}_3(\text{PPh}_3)_3\text{I}]\cdot 2\text{Py}$ [11] are isomorphous according to the crystallographic data $[\text{WOS}_3\text{Cu}_3(\text{PPh}_3)_3\text{I}]\cdot 2\text{Py}$: $P2_1/c$; a = 11.920(2), b = 28.5456(3), c = 19.444(2)Å), elemental analyses and chemical reactivity. The structure is also cubane-like, almost the same as that of compound (**II**) except for the difference of $AsPh_3$ and PPh_3 ligands.

Synthesis and Reactivity

To our knowledge, no compound (**II**) could be obtained by the direct reaction of $[NH_4]_2MoO_2S_2$ with CuI and $AsPh_3$ in solution. As a pervasive theme in thiomolybdate and thiotunstate chemistry is tetrahedral coordination about the group 6B metal, so it seems reasonable to use Cu(Ag)-Mo-S clusters in which the metals have not achieved tetrahedral coordination as starting materials to further

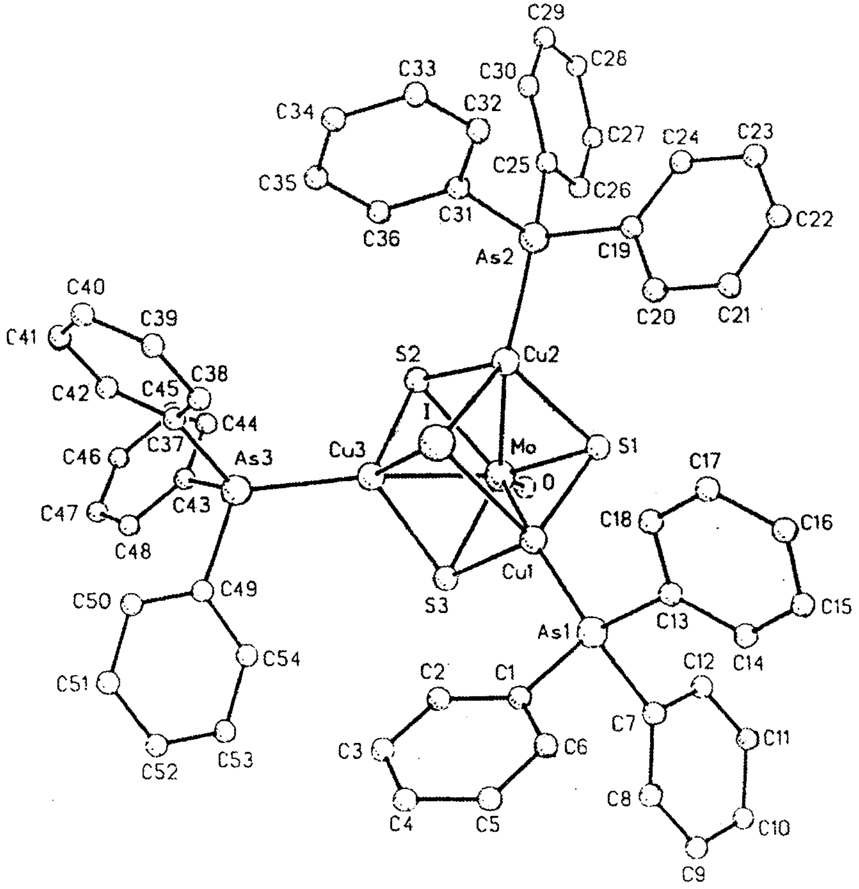


FIGURE 1 Structure $[MoOS_3Cu_3(AsPh_3)_3I]\cdot 2DMF$.

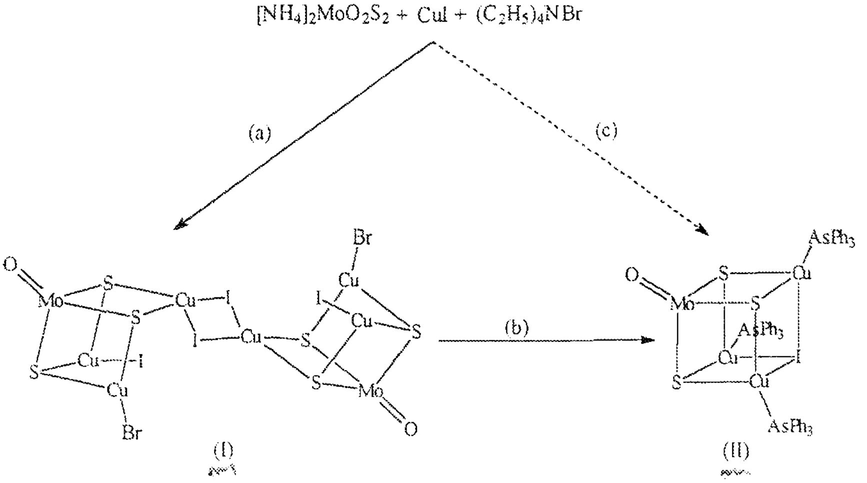
TABLE III Selected bond lengths (Å) and angles (°) for $[MoOS_3Cu_3(AsPh_3)_3I]\cdot 2DMF$.

Cu(1)-Mo	2.703(1)	Cu(2)-As(2)	2.312(1)
Cu(2)-Mo	2.697(1)	Cu(3)-As(3)	2.329(1)
Cu(3)-Mo	2.731(1)	Cu(1)-I	2.894(1)
Cu(1)-S(1)	2.269(2)	Cu(2)-I	2.973(1)
Cu(1)-S(3)	2.284(2)	Cu(3)-I	2.947(1)
Cu(2)-S(1)	2.277(2)	Mo-S(1)	2.266(2)
Cu(2)-S(2)	2.268(2)	Mo-S(2)	2.265(2)
Cu(3)-S(2)	2.291(2)	Mo-S(3)	2.261(2)
Cu(3)-S(3)	2.310(2)	Mo-O	1.687(5)
Cu(1)-As(1)	2.315(1)		
Cu(1)-Mo-Cu(2)	71.3(1)	S(3)-Cu(3)-I	99.9(1)
Cu(1)-Mo-Cu(3)	70.7(1)	O-Mo-S(1)	111.0(2)
Cu(2)-Mo-Cu(3)	70.1(1)	O-Mo-S(2)	112.9(2)
As(1)-Cu(1)-S(1)	122.1(1)	O-Mo-S(3)	113.0(2)
As(1)-Cu(1)-S(3)	119.6(1)	S(1)-Mo-S(2)	106.4(1)
As(1)-Cu(1)-I	102.6(1)	S(1)-Mo-S(3)	106.5(1)
S(1)-Cu(1)-S(3)	105.6(1)	S(2)-Mo-S(3)	106.6(1)
S(1)-Cu(1)-I	101.2(1)	Cu(1)-I-Cu(2)	64.9(1)
S(3)-Cu(1)-I	102.0(1)	Cu(1)-I-Cu(3)	65.1(1)
As(2)-Cu(2)-S(1)	120.8(1)	Cu(2)-I-Cu(3)	63.6(1)
As(2)-Cu(2)-S(2)	121.9(1)	Cu(1)-S(1)-Cu(2)	87.7(1)
As(2)-Cu(2)-I	102.6(1)	Mo-S(1)-Cu(2)	72.8(1)
S(1)-Cu(2)-S(2)	106.0(1)	Mo-S(1)-Cu(1)	73.2(1)
S(1)-Cu(2)-I	98.7(1)	Cu(2)-S(2)-Cu(3)	86.3(1)
S(2)-Cu(2)-I	102.4(1)	Mo-S(2)-Cu(2)	73.0(1)
As(3)-Cu(3)-S(3)	120.6(1)	Mo-S(2)-Cu(3)	73.7(1)
As(3)-Cu(3)-S(2)	120.5(1)	Cu(1)-S(3)-Cu(3)	86.3(1)
As(3)-Cu(3)-I	105.8(1)	Mo-S(3)-Cu(1)	73.0(1)
S(2)-Cu(3)-S(3)	104.1(1)	Mo-S(3)-Cu(3)	73.4(1)
S(2)-Cu(3)-I	102.6(1)		

react with other ligands (*e.g.*, $AsPh_3$) to prepare new clusters. The synthetic route is thus modified and the cluster (**I**) is a "building block". The reaction path is illustrated in Scheme 1.

As shown, the structure of (**I**) can be viewed as two nest-shaped $[MoOS_3Cu_3I_2Br]$ cores linked together by a double iodine bridge. The six Cu atoms exhibit two types of geometry, trigonal and tetrahedral. The trigonal Cu atoms are attacked by ligands (*e.g.*, $AsPh_3$), and finally the halogen ligands are substituted by $AsPh_3$ and μ_3-I is formed to complete a closed cubane-like structure.

Although the reaction processes are not very clear, it seems reasonable to think that it is one of the atoms in the double iodine bridge that becomes the μ_3-I atom, because there no Br atom has been found in (**II**) or (**III**). It could be concluded that the halogen ligand in a trigonal coordination environment has been substituted by $AsPh_3$ or PPh_3 and the iodine in the bridge remains in the final



SCHEME 1 Synthesis of compound (**II**); (a) solid state synthesis; (b) (**I**) + $AsPh_3$ in DMF solution; (c) reaction with $AsPh_3$ in solution directly cannot obtain (**II**).

structure. The successful synthesis of (**II**) and (**III**) imply that (**I**) may be a useful material to prepare new clusters.

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