Synthesis, Characterization and Crystal Structure of the Heterotrimetallic Complexes $[NEt_4][(Ph_3P)_2AgS_2MoS_2Cu(CN)]$ (Linear) and $[NEt_4][(Ph_3P)_2AgS_3MoOCu(CN)]$ (Butterfly)[†]

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Two novel heterometallic complexes with three different metals, the linear $[NEt_4][(Ph_3P)_2AgS_2MoS_2Cu(CN)]$ **1** and the butterfly-type $[NEt_4][(Ph_3P)_2AgS_3MoOCu(CN)]$ **2**, have been obtained by reaction of $[NEt_4]_2[MoS_4Cu(CN)]$ and $[NEt_4]_2[OMoS_3Cu(CN)]$ with $[Ag(PPh_3)_2]NO_3$, respectively. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ with a = 10.363(4), b = 35.74(1), c = 13.136(9) Å, β = 100.89(5)°, Z = 4; R = 0.069 for 2959 observed reflections with $I > 3\sigma(I)$ and 280 variables. Complex **2** crystallizes in the monoclinic space group $P2_1/n$ with a = 20.013(6), b = 10.529(3), c = 22.721(6) Å, β = 101.31(2)°, Z = 4; R = 0.064 for 3742 observed reflections with $I > 3\sigma(I)$ and 296 variables. In each synthetic procedure the fragment of the anion of the starting material, $S_2MoS_2Cu(CN)$ or $OMoS_3Cu(CN)$, remains almost unchanged in the product except for slight changes in bond lengths and angles. The chirality of the butterfly-type compound containing three different metals is discussed.

The tetrathiomolybdate anion, MoS_4^{2-}, which is a useful and versatile reagent, plays a key role in some biological processes.[1,2] One of its important functions is co-ordination.[3] Many types of compounds, which are interesting from the standpoint of structural chemistry, being formed on which it acts as a doubly, triply or quasi-quadruply bridging ligand. It has been proposed to be the most effective antagonist[2] of copper metabolism. Extensive research has been performed on MoS_4^{2-}–Cu^I complexes[4–9] which show rich structural varieties. Meanwhile a number of MoS_4^{2-}–Ag^I complexes[4b,9–12] have been obtained.

Recently, some heterometallic cubane-like and incomplete cubane-like clusters of the M–Cu–S or M–Ag–S (M = Mo or W) systems, such as those with $\{M_3CuS_4\}^{5+}$,[8a–f] $\{M_2M'S_4\}^{3+}$,[13,14] and $\{M_2Cu_2S_4\}^{4+}$ (ref. 15) (M = Mo or W, M′ = Cu or Ag) cores have been synthesised by the unit-construction method[16] from the trinuclear clusters $[M_3S_4\{S_2P(OEt)_2\}_4]\cdot H_2O$[17,18] and dinuclear complexes $[M_2S_4(SCH_2CH_2S)_2]^{2-}$ (ref. 19) in our laboratory. This method is convenient for obtaining multimetallic complexes or clusters by using reactive fragments which contain active sulfido atom(s) as building blocks. So far it has been used only to obtain bimetallic complexes. In this paper the use of this method to obtain a novel trimetallic complex is described.

Both the basal fragments of the anions $[MoS_4Cu(CN)]^{2-}$ (refs. 9 and 20) and $[OMoS_3Cu(CN)]^{2-}$ (ref. 9) may be expected to combine with another metal complex to form a trinuclear complex, *e.g.* the linear $[(NC)CuS_2MoS_2Cu(CN)]^{2-}$ (refs. 9 and 20) and the butterfly-type $[OMoS_3Cu_2(PPh_3)_3]$[21] clusters. However no trimetallic complex obtained in this way has been structurally determined. The greatest difficulty may be the statistical disorder between Cu and Ag atoms. Herein the first two examples are reported in which the Cu and Ag atoms have been located. As pointed out by Vahrenkamp,[22] higher-nuclearity clusters with three or more different types of metals should be chiral for most compositions and framework geometries. The chirality of the butterfly-type framework geometries will be discussed.

Experimental

All reagents and solvents purchased were of CP grade and were used with further purification. The complexes $[NEt_4]_2[MoS_4Cu(CN)]$[20] and $[NEt_4]_2[OMoS_3Cu(CN)]$[9] were synthesised according to the literature; $[Ag(PPh_3)_2]NO_3$ was obtained from a CH_2Cl_2–EtOH solution of PPh_3 and $AgNO_3$ (molar ratio 2:1). Elemental analyses were carried out by the Elemental Analysis Laboratories in our institute. The visible and UV electronic spectra were recorded on a Shimadzu UV-3000 spectrophotometer, infrared spectra on a Perkin-Elmer 577 spectrometer.

Preparation of $[NEt_4][(Ph_3P)_2AgS_2MoS_2Cu(CN)]$ **1**.—A solution of $[Ag(PPh_3)_2]NO_3$ (0.40 g, 0.58 mmol) in CH_2Cl_2 (15 cm^3) was slowly added to a solution of $[NEt_4]_2[MoS_4Cu(CN)]$ (0.32 g, 0.56 mmol) in MeCN (15 cm^3). The colour changed from red to dark red. After stirring for a while, diethyl ether (10 cm^3) was added and then filtered. The filtrate was allowed to stand at 3–5 °C for 1 d, and 0.40 g analytically pure red crystals were obtained. After several days, 0.13 g red crystals was produced. Total yield 0.53 g (88%) (Found: C, 49.9; H, 4.6; Ag, 9.5; Cu, 5.7; Mo, 8.5; N, 3.4; P, 6.7; S, 11.9. $C_{45}H_{50}AgCuMoN_2P_2S_4$ requires C, 50.2; H, 4.7; Ag, 10.0; Cu, 5.9; Mo, 8.9; N, 2.6; P, 5.8; S, 11.9%). IR(KBr pellet): δ(C–H) in PPh_3, 754vs and 700s; Ag–P, 518s and 500s; Mo–μ-S, 468vs, 450 (sh) and 420w; C–N of CN ligand, 2130 cm^{-1}.

Preparation of $[NEt_4][(Ph_3P)_2AgS_3MoOCu(CN)]$ **2**.—A solution of $[Ag(PPh_3)_2]NO_3$ (0.44 g, 0.63 mmol) in CH_2Cl_2 (10 cm^3) was slowly added to a solution of $[NEt_4]_2[OMoS_3Cu(CN)]$ (0.35 g, 0.63 mmol) in MeCN (20 cm^3), the colour remaining red. After stirring for a while, diethyl ether (20 cm^3) was added and then filtered. The filtrate was allowed to stand at 3–5 °C for 1 d, and 0.35 g (53%) analytically pure red crystals were obtained (Found: C, 49.5; H, 4.7; Ag, 10.9; Cu, 6.4; Mo, 9.2; N, 2.8; P, 6.3; S, 9.1. $C_{45}H_{50}AgCuMoN_2OP_2S_3$ requires C, 51.0; H, 4.7; Ag, 10.2; Cu, 6.0; Mo, 9.1; N, 2.6; P, 5.9;, S, 9.1%). IR(KBr pellet): δ(C–H) in PPh_3, 754vs and 700vs; Ag–P, 520s and 510s; Mo–μ-S and Mo–μ$_3$-S, 495m, 475s, 465s, 430w and 410w; C–N of CN ligand, 2130m; Mo–O, 910vs cm^{-1}.

Crystal Structure Determinations.—The crystal data for

[†] *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx xxv.

Table 1 Crystal data and some experimental details for compounds **1** and **2**

Formula	**1** $C_{45}H_{50}AgCuMoN_2P_2S_4$	**2** $C_{45}H_{50}AgCuMoN_2OP_2S_3$
M	1076.44	1060.38
Crystal colour	Dark red	Orange red
Space group	$P2_1/c$	$P2_1/n$
a/Å	10.363(4)	20.013(6)
b/Å	35.74(1)	10.529(3)
c/Å	13.136(9)	22.721(6)
β/°	100.89(5)	101.31(2)
U/Å^3	4777(4)	4695(2)
μ/cm^{-1}	13.63	13.45
$F(000)$	2184	2152
$2\theta_{max}$/°	50.0	48.2
Maximum, minimum transmission factors	0.782, 1.099	0.658, 1.253
R, R'	0.069, 0.080	0.064, 0.082
Goodness of fit, S	1.48	1.83
No. of unique data	8588	7885
No. of observations with $I > 3\sigma(I)$	2959	3742
Maximum shift $(\Delta/\sigma)_{max}$ in final cycle	0.08	0.21
Largest, smallest feature in final difference map /eÅ^{-3}	1.05, −0.79	0.70, −0.59

Details in common: monoclinic; $Z = 4$; $D_c = 1.50$ g cm^{-3}; $T = 296$ K.

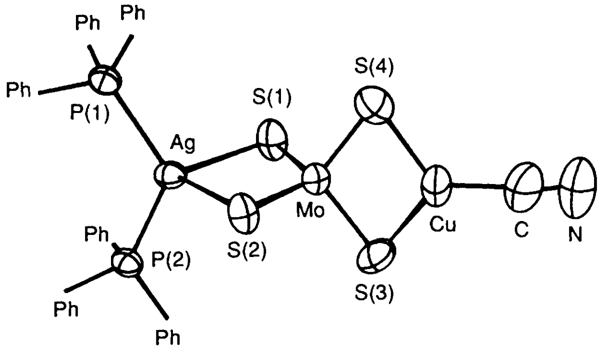


Fig. 1 The configuration of the anion of complex **1**, $[(Ph_3P)_2AgS_2MoS_2Cu(CN)]^-$

compounds **1** and **2** are summarized in Table 1, together with some experimental details. Data were collected on Rikagu AFC5R diffractometer using Mo-Kα radiation (λ = 0.710 69 Å) at 296 K. The ω scan speed was varied on the basis of the SEARCH intensity (maximum 16° min^{-1}). Three standard reflections were measured periodically in each case, and the absence of random deviations indicated crystal and electronic stability. The intensity error was defined as $\sigma(F^2) = [C + \frac{1}{4}(t_c/t_b)^2(b_1 + b_2) + (pI)^2]^{\frac{1}{2}}$, where I is the intensity and p a factor which downweights strong reflections, taken to be 0.05. The data were corrected for Lorentz and polarization effects and for absorption using empirical ψ-scan data and DIFABS.[23]

The structures were solved by direct methods using MITHRIL;[24] the Mo, Ag and Cu atoms were located in the E map. Most non-hydrogen atoms were located using the DIRDIF program;[25] some non-hydrogen atoms were located in the succeeding Fourier difference syntheses. The structures were refined by the full-matrix least-squares technique with anisotropic thermal parameters for Mo, Ag, Cu, S, P, C and N atoms (CN ligand) and isotropic thermal parameters for all C atoms in the PPh_3 ligands. Final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| =$ 0.069(0.064), $R' = [\Sigma(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}} = 0.080(0.082)$ and $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}} = 1.48(1.83)$ (N_o = number of observations, N_v = number of variables) for compound **1** (compound **2**). The weighting scheme was $w = 1/\sigma^2(F_o)$. All calculations were performed on a VAX 785 computer using the TEXSAN program package.[26] Non-hydrogen scattering factors were taken from Cromer and Waber.[27]

Atomic coordinates, bond lengths and bond angles for the two compounds are given in Tables 2–7, respectively. Table 8 compares the main bond lengths with those of the two starting materials and related compounds.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—Since cyano ligands are easily displaced the complexes of thiomolybdates with copper(I) and silver(I) cyanides are useful starting materials for the synthesis of related species. Displacement by thiolato ligands produced thiolatocopper(I)–tetrathiomolybdate(VI) complex anions [equations (1) and (2)]. Displacement by triphenylphosphine ligands

$$[(NC)CuS_2MoS_2]^{2-} + PhS^- \longrightarrow [(PhS)CuS_2MoS_2]^{2-} \quad (1)$$

$$[(NC)CuS_2MoS_2Cu(CN)]^{2-} + 2PhS^- \longrightarrow [(PhS)CuS_2MoS_2Cu(SPh)]^{2-} \quad (2)$$

leads to triphenylphosphinecopper(I)–tetrathiomolybdate(VI) complexes[9] [equations (3) and (4)]. However, in our

$$[NPr^n{}_4]_2[(NC)CuS_2MoS_2] + [Cu(PPh_3)_2]NO_3 \longrightarrow [(Ph_3P)_2CuS_2MoS_2Cu(PPh_3)] \quad (3)$$

$$[NPr^n{}_4]_2[(NC)AgS_2WS_2] + [Cu(PPh_3)_2]NO_3 \longrightarrow [(Ph_3P)_3CuAgWS_4] \quad (4)$$

procedures the cyano ligands are not displaced by triphenylphosphine ligands [equations (5) and (6)]. The only difference

$$[NEt_4]_2[(NC)CuS_2MoS_2] + [Ag(PPh_3)_2]NO_3 \longrightarrow [(NC)CuS_2MoS_2Ag(PPh_3)_2] \quad (5)$$

$$[NEt_4]_2[(NC)CuS_3MoO] + [Ag(PPh_3)_2]NO_3 \longrightarrow [(NC)CuS_3OMoAg(PPh_3)_2] \quad (6)$$

between our procedure and that in equations (3) and (4) is the reaction temperature. At 3–5 °C the cyano ligands are relatively difficult to displace, unlike the case at room temperature. The high yield of the products means that the $MoS_2Cu(CN)$ moiety of the products is relatively stable in solution at 3–5 °C. When the products are recrystallized at room temperature only the complexes with PPh_3 ligands are obtained, $[(Ph_3P)_3CuAgMoS_4]$ and $[(Ph_3P)_3CuAgMoOS_3]$.

Structure of Compound **1**.—The structure of the anion of $[NEt_4][(Ph_3P)_2AgS_2MoS_2Cu(CN)]$ **1** is shown in Fig. 1. The arrangement of the three metal atoms (Ag, Mo, Cu) and the CN ligand is almost linear. The idealized symmetry of the anion is C_{2v}. In the anion, the Mo atom retains its tetrahedral co-ordination by four sulfur atoms as in $MoS_4{}^{2-}$. The two metal atoms attached to the MoS_4 moiety have different geometries; Cu has approximately trigonal-planar co-ordination, while Ag is tetrahedrally co-ordinated by two μ-S and two PPh_3 ligands. This causes the four Mo–S bonds to be separated into two groups: those which involve the tetrahedrally co-ordinated

Table 2 Atomic coordinates for $[NEt_4][(Ph_3P)_2AgS_2MoS_2Cu(CN)]$ **1**

Atom	*x*	*y*	*z*
Ag	0.688 6(1)	0.101 18(4)	0.184 7(1)
Mo	0.521 1(2)	0.160 99(5)	0.266 9(1)
Cu	0.361 2(2)	0.208 45(8)	0.331 4(2)
S(1)	0.730 4(5)	0.168 4(1)	0.265 8(4)
S(2)	0.449 4(5)	0.106 9(1)	0.201 5(4)
S(3)	0.481 9(6)	0.165 5(2)	0.426 1(4)
S(4)	0.407 8(6)	0.205 2(2)	0.174 4(4)
C	0.236(2)	0.241 0(7)	0.369(2)
N	0.151(2)	0.260 4(6)	0.377(2)
P(1)	0.724 6(4)	0.101 9(1)	0.003 1(4)
P(2)	0.802 9(5)	0.056 5(1)	0.316 4(4)
C(111)	0.715(2)	0.055 7(5)	−0.060(1)
C(112)	0.829(2)	0.038 2(5)	−0.081(1)
C(113)	0.821(2)	0.000 6(6)	−0.120(2)
C(114)	0.702(2)	−0.017 3(6)	−0.139(2)
C(115)	0.590(2)	0.000 4(7)	−0.122(2)
C(116)	0.595(2)	0.037 0(5)	−0.079(1)
C(121)	0.889(2)	0.117 7(5)	−0.001(1)
C(122)	0.985(2)	0.108 6(6)	0.087(2)
C(123)	1.116(2)	0.119 5(6)	0.087(2)
C(124)	1.153(2)	0.137 9(6)	0.001(2)
C(125)	1.055(2)	0.147 4(6)	−0.085(2)
C(126)	0.918(2)	0.136 3(6)	−0.086(2)
C(131)	0.612(2)	0.129 7(5)	−0.089(1)
C(132)	0.599(2)	0.123 6(7)	−0.197(2)
C(133)	0.509(3)	0.147 8(8)	−0.266(2)
C(134)	0.437(3)	0.175 3(8)	−0.222(2)
C(135)	0.455(2)	0.181 8(7)	−0.116(2)
C(136)	0.545(2)	0.158 2(7)	−0.051(2)
C(211)	0.978(2)	0.067 3(5)	0.350(1)
C(212)	1.073(2)	0.039 8(5)	0.355(1)
C(213)	1.211(2)	0.050 0(6)	0.377(1)
C(214)	1.243(2)	0.087 2(6)	0.395(1)
C(215)	1.145(2)	0.115 3(6)	0.388(2)
C(216)	1.013(2)	0.105 0(6)	0.366(1)
C(221)	0.750(2)	0.055 9(5)	0.440(1)
C(222)	0.615(2)	0.052 6(6)	0.439(2)
C(223)	0.571(2)	0.049 4(7)	0.536(2)
C(224)	0.661(2)	0.049 6(6)	0.630(2)
C(225)	0.794(2)	0.054 5(6)	0.630(2)
C(226)	0.841(2)	0.057 0(5)	0.537(1)
C(231)	0.795(2)	0.006 6(5)	0.281(1)
C(232)	0.798(2)	−0.003 3(6)	0.178(2)
C(233)	0.797(2)	−0.040 7(6)	0.144(2)
C(234)	0.784(2)	−0.068 0(7)	0.215(2)
C(235)	0.778(2)	−0.058 7(7)	0.322(2)
C(236)	0.788(2)	−0.021 5(7)	0.356(2)
N(1)	0.882(2)	0.226 2(6)	0.589(2)
C(1)	0.946(4)	0.255(1)	0.662(3)
C(2)	0.997(3)	0.290(1)	0.628(2)
C(3)	0.985(4)	0.213(1)	0.525(3)
C(4)	1.129(4)	0.200(1)	0.595(3)
C(5)	0.857(5)	0.193(2)	0.661(4)
C(6)	0.838(4)	0.157(1)	0.591(3)
C(7)	0.778(4)	0.246(1)	0.496(3)
C(8)	0.667(6)	0.243(2)	0.573(4)

Table 3 Bond lengths (Å) for complex **1**

Ag ··· Mo	3.075(2)	Cu–S(3)	2.208(7)
Mo ··· Cu	2.622(3)	Cu–S(4)	2.209(7)
Ag–S(1)	2.629(5)	Cu–C	1.87(2)
Ag–S(2)	2.538(5)	P(1)–C(111)	1.84(2)
Ag–P(1)	2.483(5)	P(1)–C(121)	1.81(2)
Ag–P(2)	2.485(5)	P(1)–C(131)	1.81(2)
Mo–S(1)	2.188(5)	P(2)–C(211)	1.82(2)
Mo–S(2)	2.189(5)	P(2)–C(221)	1.81(2)
Mo–S(3)	2.211(6)	P(2)–C(231)	1.84(2)
Mo–S(4)	2.193(6)	N–C	1.15(3)

Table 4 Bond angles (°) for complex **1**

Cu–Mo–Ag	175.2(1)	Mo–S(1)–Ag	78.7(2)
S(2)–Ag–S(1)	88.9(2)	Mo–S(2)–Ag	80.8(2)
P(1)–Ag–S(1)	109.7(2)	Cu–S(3)–Mo	72.8(2)
P(1)–Ag–S(2)	114.2(2)	Mo–S(4)–Cu	73.1(2)
P(1)–Ag–P(2)	122.5(2)	C(121)–P(1)–C(111)	103.8(8)
P(2)–Ag–S(1)	106.5(2)	C(131)–P(1)–C(111)	102.5(8)
P(2)–Ag–S(2)	109.6(2)	C(121)–P(1)–C(131)	107.6(8)
S(1)–Mo–S(2)	111.6(2)	C(121)–P(1)–Ag	110.2(6)
S(1)–Mo–S(3)	110.9(2)	C(131)–P(1)–Ag	116.9(7)
S(1)–Mo–S(4)	109.7(2)	C(111)–P(1)–Ag	114.7(6)
S(2)–Mo–S(3)	109.1(2)	C(221)–P(2)–C(211)	104.2(8)
S(2)–Mo–S(4)	108.2(2)	C(211)–P(2)–C(231)	105.1(8)
S(4)–Mo–S(3)	107.2(2)	C(221)–P(2)–C(231)	102.3(8)
C–Cu–S(3)	129.1(8)	C(221)–P(2)–Ag	116.4(6)
C–Cu–S(4)	124.1(8)	C(211)–P(2)–Ag	110.6(6)
C–Cu–Mo	175.3(7)	C(231)–P(2)–Ag	116.9(6)
S(3)–Cu–S(4)	106.8(2)	N–C–Cu	170(2)

Ag are a little shorter than those to the trigonally co-ordinated Cu.

The MoS_2Cu and MoS_2Ag cores are planar to within 0.02 and 0.005 Å, respectively. Their dihedral angle is 89.92° which means they are very closely perpendicular to each other. The six atoms P(1), P(2), Ag, S(3), S(4), Mo are also in a plane within 0.06 Å, but the atoms of the CN ligand have unexpectedly large deviations from this least-squares plane of 0.35 (C) and 0.58 Å (N), on account of the bend at Cu. The bond lengths in the $(NC)CuS_2MoS_2$ unit arc almost the same as those in $[PPh_4]_2[(NC)CuS_2MoS_2]$,[20] except that the two bond lengths between the terminal sulfido atoms and the Mo atom are elongated slightly from 2.150(3) to 2.189(5) Å.

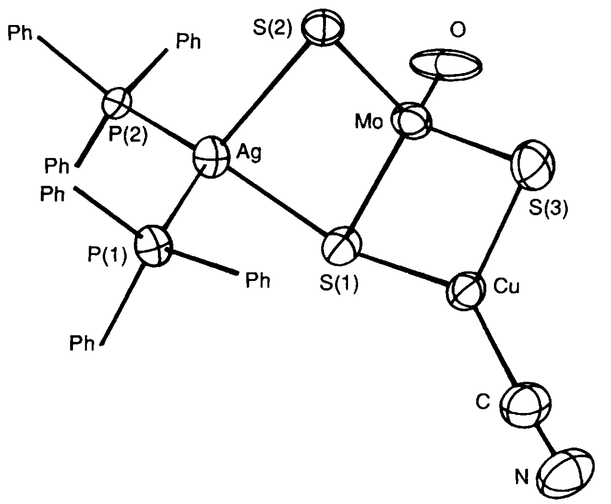


Fig. 2 The configuration of the anion of complex **2**, $[(Ph_3P)_2AgS_3MoOCu(CN)]^-$

The structure of the anion is quite similar to that of $[(Ph_3P)_2AgS_2MoS_2Ag(PPh_3)]\cdot CH_2Cl_2$ (Table 8) in which one Ag atom is tetrahedrally co-ordinated while the other is trigonally co-ordinated. Although the replacement of a $Ag(PPh_3)$ group by Cu(CN) does not reduce the symmetry of the linear fragment of the complex, it does produce a novel trimetallic complex.

Structure of Compound **2**.—The structure of the anion of $[NEt_4][(Ph_3P)_2[AgS_3MoOCu(CN)]$ **2** is shown in Fig. 2. The three different metal atoms (Ag, Mo, Cu) and the three bridging

Table 5 Atomic coordinates for complex **2**

Atom	*x*	*y*	*z*
Mo	0.935 24(6)	0.028 7(1)	0.751 40(6)
Ag	1.028 55(5)	0.244 8(1)	0.736 01(4)
Cu	0.888 0(1)	0.129 4(2)	0.841 78(8)
S(1)	0.906 2(2)	0.234 4(3)	0.761 5(2)
S(2)	1.039 6(2)	0.003 6(3)	0.737 2(2)
S(3)	0.923 8(3)	−0.066 6(4)	0.834 3(3)
O	0.881 0(6)	−0.034(1)	0.692 5(7)
P(1)	1.107 7(2)	0.319 2(3)	0.825 7(2)
P(2)	1.019 0(2)	0.328 9(3)	0.633 7(2)
N	0.818(1)	0.198(2)	0.943 0(7)
C	0.845(1)	0.175(2)	0.904 0(8)
C(111)	1.102 1(6)	0.231(1)	0.893 2(5)
C(112)	1.042 4(7)	0.247(1)	0.914 8(7)
C(113)	1.031 0(8)	0.175(2)	0.966 4(7)
C(114)	1.082 4(9)	0.089(2)	0.990 5(7)
C(115)	1.140 5(9)	0.071(2)	0.969 5(7)
C(116)	1.152 5(7)	0.147(1)	0.920 8(6)
C(121)	1.197 3(6)	0.308(1)	0.818 5(6)
C(122)	1.218 2(7)	0.193(1)	0.799 3(6)
C(123)	1.284 6(9)	0.180(2)	0.788 3(7)
C(124)	1.329 5(8)	0.285(2)	0.799 4(7)
C(125)	1.308 6(8)	0.398(2)	0.816 8(7)
C(126)	1.239 9(7)	0.411(1)	0.827 7(6)
C(131)	1.097 2(6)	0.483(1)	0.845 6(6)
C(132)	1.121 2(7)	0.531(1)	0.903 0(6)
C(133)	1.113 4(8)	0.660(2)	0.915 6(7)
C(134)	1.079 8(9)	0.738(2)	0.869 4(8)
C(135)	1.054 0(9)	0.694(2)	0.811 9(8)
C(136)	1.064 1(8)	0.562(1)	0.799 8(7)
C(211)	0.992 9(7)	0.494(1)	0.629 1(6)
C(212)	1.030 0(7)	0.590(1)	0.608 6(6)
C(213)	1.007 5(8)	0.717(1)	0.608 4(7)
C(214)	0.949 5(8)	0.746(2)	0.627 3(7)
C(215)	0.909 9(9)	0.652(2)	0.647 7(8)
C(216)	0.931 7(8)	0.521(2)	0.650 3(7)
C(221)	1.098 0(6)	0.328(1)	0.605 9(6)
C(222)	1.158 8(8)	0.323(1)	0.648 6(7)
C(223)	1.222(1)	0.322(2)	0.628 5(8)
C(224)	1.221 4(9)	0.323(2)	0.566 2(8)
C(225)	1.159 8(9)	0.330(2)	0.525 2(7)
C(226)	1.097 5(7)	0.333(1)	0.543 6(6)
C(231)	0.959 3(6)	0.248(1)	0.574 5(6)
C(232)	0.912 8(8)	0.318(2)	0.532 7(7)
C(233)	0.867(1)	0.244(2)	0.485 7(8)
C(234)	0.875(1)	0.117(2)	0.482 3(9)
C(235)	0.923(1)	0.051(2)	0.524(1)
C(236)	0.966 2(8)	0.118(2)	0.571 7(7)
N(1)	0.694 8(7)	0.102(1)	0.629 3(6)
C(1)	0.761(3)	0.195(6)	0.632(3)
C(2)	0.746(1)	0.306(3)	0.609(1)
C(3)	0.642(3)	0.155(5)	0.579(3)
C(4)	0.577(1)	0.044(3)	0.586(1)
C(5)	0.665(3)	0.101(6)	0.692(3)
C(6)	0.705(2)	0.049(3)	0.736(2)
C(7)	0.731(2)	−0.016(4)	0.619(2)
C(8)	0.764(2)	−0.025(3)	0.563(1)
C(1′)	0.737(4)	0.222(7)	0.655(3)
C(3′)	0.620(2)	0.138(4)	0.609(2)
C(5′)	0.710(3)	−0.011(5)	0.668(3)
C(7′)	0.710(2)	0.028(4)	0.558(2)

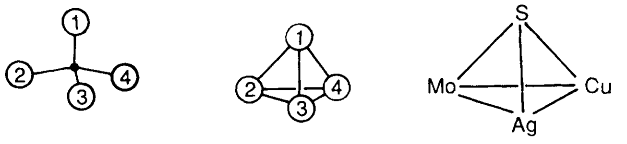
Table 6 Selected bond lengths (Å) for complex **2**

Mo···Ag	3.007(2)	Cu–C	1.86(2)
Mo···Cu	2.645(2)	Cu–S(1)	2.223(4)
Mo–O	1.68(1)	Cu–S(3)	2.201(5)
Mo–S(1)	2.266(4)	P(1)–C(111)	1.81(1)
Mo–S(2)	2.191(4)	P(1)–C(121)	1.84(1)
Mo–S(3)	2.186(5)	P(1)–C(131)	1.80(1)
Ag–S(1)	2.627(4)	P(2)–C(211)	1.82(1)
Ag–S(2)	2.549(4)	P(2)–C(221)	1.81(1)
Ag–P(1)	2.452(4)	P(2)–C(231)	1.82(1)
Ag–P(2)	2.459(4)	N–C	1.15(2)

Table 7 Selected bond angles (°) for complex **2**

Cu–Mo–Ag	96.41(6)	C–Cu–Mo	169.8(6)
O–Mo–S(1)	108.5(5)	S(3)–Cu–S(1)	107.2(2)
O–Mo–S(2)	108.7(4)	Cu–S(1)–Mo	72.2(1)
O–Mo–S(3)	110.2(7)	Cu–S(1)–Ag	120.7(2)
S(3)–Mo–S(1)	106.2(2)	Mo–S(1)–Ag	75.4(1)
S(3)–Mo–S(2)	109.6(2)	Mo–S(2)–Ag	78.3(1)
S(2)–Mo–S(1)	113.7(1)	Mo–S(3)–Cu	74.2(1)
P(1)–Ag–S(1)	108.0(1)	C(131)–P(1)–C(111)	104.3(6)
P(1)–Ag–S(2)	105.6(1)	C(131)–P(1)–C(121)	104.5(6)
P(1)–Ag–P(2)	126.0(1)	C(111)–P(1)–C(121)	105.3(6)
P(2)–Ag–S(1)	108.7(1)	C(221)–P(2)–C(211)	104.1(6)
P(2)–Ag–S(2)	111.1(1)	C(221)–P(2)–C(231)	103.3(6)
S(2)–Ag–S(1)	92.2(1)	C(211)–P(2)–C(231)	105.4(6)
C–Cu–S(3)	120.4(5)	N–C–Cu	177(2)
C–Cu–S(1)	132.2(5)		

sulfido ligands are arranged in a butterfly structure, very similar to that of the bimetallic complex $[(Ph_3P)CuMoOS_3Cu(PPh_3)_2]$[21] (Table 8). The angle of Ag–Mo–Cu is approximately 96°. In the anion the Mo atom has a tetrahedral co-ordination involving two μ-S, one μ_3-S and one terminal oxygen atom as in $MoOS_3^{2-}$. The Cu atom has approximately trigonal-planar co-ordination with one μ_3-S, one μ-S and one CN ligand, but the Ag is tetrahedrally co-ordinated by one μ-S, one μ_3-S and two PPh_3 ligands. The bond length of Mo–(μ_3-S) is 0.08 Å longer than the two M–(μ-S) bonds.



Methane
ML_4 complex

Tetrahedrane
M_4 or EM_3 complex

MoCuAg(μ_3-S) complex

Fig. 3 The asymmetric tetrahedra and the MoCuAg(μ_3-S) tetrahedrane framework.

The MoS_2Cu and MoS_2Ag core are planar to within 0.04 and 0.05 Å, respectively. Their dihedral angle is 52.9(1)°. As the Mo and Ag atoms both have tetrahedral co-ordination geometries, the atoms P(1), P(2), Ag, Mo, O, S(3) and Mo, S(1), S(3), Cu, C, N are almost planar. The CN ligand is in the metallic plane of MoCuAg within 0.02 Å. The Mo–Cu bond is 2.645(2) Å, but the Mo–Ag and the Cu–Ag distances are too long to be described as bonding.

The MoCuAg(μ_3-S) moiety may also be regarded as having a tetrahedral framework (see Fig. 3). It has been demonstrated[22] that the EM_3 tetrahedral framework ensures chirality for a cluster with three different metal atoms in which there are metal–metal bonds between any two of the metals. With respect to their possible application, it is important to know the configurative stability of the optically active clusters. It is certain that the structure of the anion of **2** shares the framework chirality. In the unit cell there exist two groups of enantiomers, but is each enantiomer stable after separation? The tetrahedral geometry of the $OMoS_3$ moiety is very stable, preventing one enantiomer inverting into the other, so the two enantiomers could be separated. However in solution the simplest way to racemize each enantiomer is to break the Ag–(μ_3-S) bond to form a new Ag–(μ_3-S) bond; is this easy to perform? It will be interesting and significant to study the enantiomer separation.

In Table 8 the major bond lengths of related complexes are

Table 8 Comparison of main bond lengths of some related complexes[a]

Complex	Mo–S_t	Mo–μ-S	Mo–μ_3-S	M′–μ-S	M′–μ_3-S	M–M′	M′–L	Ref.
$[PPh_4]_2[MoS_4Cu(CN)]$	2.163(2)	2.245(2)		2.215(2)		2.630(1)	1.892(10)	20
$[MoS_4Cu_2(PPh_3)_3]\cdot0.8CH_2Cl_2$		2.218(5)		2.220(5)		2.642(3)	2.210(5)	28
		2.198(5)*		2.313(5)*		2.775(2)*	2.303(5)*	
$[MoS_4Ag_2(PPh_3)_3]\cdot0.8CH_2Cl_2$		2.215(5)		2.459(5)		2.860(2)	2.380(4)	4*b*
		2.195(5)*		2.572(5)*		3.030(2)*	2.471(4)*	
$[NEt_4][(Ph_3P)_2AgS_2MoS_2Cu(CN)]$		2.202(6)		2.209(7)		2.622(3)	1.87(2)	*b*
		2.189(5)*		2.584(5)*		3.075(2)*	2.484(5)*	
$[OMoS_3Cu_2(PPh_3)_3]$	[1.713(3)]	2.224(1)	2.272(2)	2.218(1)	2.235(1)	2.6489(6)	2.202(2)	21, 29
		2.213(1)*		2.317(1)*	2.328(1)*	2.7869(6)*	2.304(1)*	
$[NEt_4][(Ph_3P)_2AgS_3MoOCu(CN)]$	1.68(1)	2.186(5)	2.266(4)	2.201(5)	2.223(4)	2.645(2)	1.86(2)	*b*
		2.191(4)*		2.549(4)*	2.627(4)	3.007(2)*	2.456(4)*	

[a] The M′ atom is Cu or Ag; the starred bond lengths are those when the M′ has tetrahedral co-ordination or the S atom is bonded to this M′. [b] This work.

Table 9 Electronic spectra in MeCN

Complex	λ/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})
$[NEt_4]_2[MoS_4]$[a]	477 (14.25), 324 (20.60)
$[NEt_4]_2][(NC)CuS_2MoS_2]$	470 (6.1), 314 (18), 245 (15), 214 (22)
$[NEt_4][(Ph_3P)_2AgS_2MoS_2Cu(CN)]$	480 (5.4), 314 (17), 252 (33), 218 (22)
$[MoOS_3]^{2-}$[b]	465, 392
$[NEt_4]_2[(NC)CuMoOS_3]$	430 (4.36), 390 (5.27), 320 (sh), 295 (12.4), 235 (12.9)
$[NEt_4][(Ph_3P)_2AgS_3MoOCu(CN)]$	415 (1.71), 350 (2.69), 250 (14.8), 225 (17.5)

[a] See ref. 9. [b] See ref. 3.

given. It is noted that when Cu (or Ag) has trigonal-planar co-ordination the Cu–S (or Ag–S), Cu–L (or Ag–L) and Mo–Cu (or Mo–Ag) bond lengths are shorter, and at the same time the Mo–S bond lengths are longer than those in tetrahedral co-ordination. In other cases[4–12] almost no exception to this generalization has been found. This situation may be due to the low co-ordination number of trigonal co-ordination. It is well known that the Mo–Cu–S complexes have[5] special stabilities and properties, such as antoxidation, easy formation of polymerization, low solubility, deep colour and always the +1 oxidation state for Cu, *etc*. As regards the electronic structure, Müller *et al.*[3] have pointed out that the electron density on a MoSCu bridge is delocalized among the three atoms. Obviously, when Cu has trigonal co-ordination, its remaining vacant 4p orbital may be used to form a large π bond involving the three atoms of the MoSCu bridge, and we presume that this large bond comprises a kind of π conjugation like that of the allyl cation, *i.e.* the conjugation for the MoSCu bridge is d(Mo)–p(S)–p(Cu). The presence of the conjugation results in a special stability, for compounds containing it. When the Cu atom has distorted-tetrahedral co-ordination this type of conjugation may also exist, but to a relatively lower extent. This presumption may help us understand the essence of biochemical MoCu antagonism in the presence of sulfur ligands, and to explain why Mo^{VI}–Cu–S complexes are stable to oxidation and why Cu always has the +1 oxidation state.

The presence of co-ordinated cyanide is confirmed by the presence of medium, sharp absorptions at around 2130 cm^{-1}. The bands due to PPh_3 ligands are obviously distinguished. The two bands at around 520 and 510 cm^{-1} are attributed to the Ag–P bonds.

The electronic spectra of the anions $[MoS_4]^{2-}$, $[MoOS_3]^{2-}$, $[MoOS_3Cu(CN)]^{2-}$, $[MoS_4Cu(CN)]^{2-}$, $[(Ph_3P)_2AgS_2MoS_2Cu(CN)]^-$ and $[(Ph_3P)_2AgS_3MoOCu(CN)]^-$ are listed in Table 9. It has been demonstrated[3] that the spectra of complexes of MoS_4^{2-} with d^{10} metal atoms show essentially internal transitions corresponding to those of the free thiometalate ions. A simple molecular orbital (MO) scheme for the MS_4^{2-} ions (T_d symmetry) may be devized[3] by assuming *n*d, (*n* + 1)s and (*n* + 1)p valence orbitals on M and 3s and 3p valence orbitals on S. The longest-wavelength absorption at 477 nm can be unambiguously assigned[3] to the one-electron transition ν_1 $t_1(n,\pi) \longrightarrow 2e(d)$ on the basis of magnetic circular dichroism measurements. In addition, the absorption at 324 nm is plausibly assigned to ν_2 $3t_2(\pi,\sigma) \longrightarrow 2e(d)$, and those at 240–280 nm are assigned to ν_3 $t_1(n,\pi) \longrightarrow 4t_2(d)$ which also originate in $t_1(n,\pi)$ as ν_1. Our results are also consistent with these conclusions:[3,9] (*i*) the bi- and tri-nuclear complexes absorb in the same energy regions as does MoS_4^{2-}, (*ii*) the incorporation of the d^{10} Cu^I or Ag^I into MoS_4^{2-} only changes the first (ν_1) and third (ν_3) bands, while the second (ν_2) is practically unaltered in its position and intensity. It is interesting that the longest-wavelength band ν_1 is somewhat red-shifted after the incorporation of a $Ag(PPh_3)_2^+$ group, as has frequently been found[6a,7,30] in other d^{10} Cu^I–MoS_4^{2-} complexes. The anion $[MoOS_3Cu(CN)]^{2-}$ also exhibits some bands in the same region as does $[MoOS_3]^{2-}$, and the spectra appear to be little influenced by co-ordination of the Cu(CN) fragment. However, a relatively large influence has been observed in the spectra of $[(Ph_3P)_2AgMoOS_3Cu(CN)]^-$. It is interesting that the longest-wavelength band is slightly blue shifted in the order $[MoOS_3]^{2-}$, $[MoOS_3Cu(CN)]^{2-}$, $[(Ph_3P)_2AgMoOS_3Cu(CN)]^-$ upon incorporation of the d^{10} metal atoms.

Acknowledgements

This research was supported by grants from the Structural Chemistry Research Laboratory of the Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences and the National Science Foundation of China.

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Received 20*th May* 1991; *Paper* 1/02359D