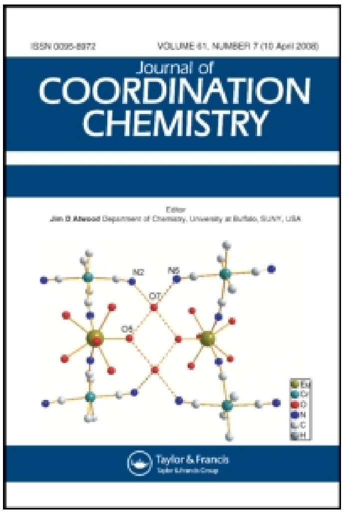

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A NOVEL PRISMANE CLUSTER. SYNTHESIS AND CRYSTAL STRUCTURE OF A DIMER OF [(TRIPHENYLPHOSPHINE) COPPER(2-PICOLINE)COPPER] OXOTRITHIOMOLYBDENUM, $[Cu_4Mo_2S_6][(C_6H_5)_3P]_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$

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The prismane cluster $[Cu_4Mo_2S_6][(C_6H_5)_3P]_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$ has been prepared by the reaction of $[NH_4]_2MoO_2S_2$ with CuBr and PPh_3 in 2-picoline. Its molecular structure was determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.149(2)$, $b = 17.152(2)$, $c = 15.793(2)$ Å, $\beta = 105.40(2)°$, and $Z = 2$. The X-ray structure (R; $R_w = 0.046$; 0.048) revealed a 12-atom $Cu_4Mo_2S_6$ prismane which can be envisaged as consisting of two $MoOS_3$ units connected on adjacent edges by two different groups, $[C_6H_7NCu]$ and $[(C_6H_5)_3PCu]$.

Keywords: Mo–Cu–S cluster; prismane cluster; synthesis; X-ray structure

INTRODUCTION

In the last two decades, molybdenum-sulfur clusters have been extensively studied because of their relevance to biological fixation of nitrogen[1] and catalytic processes.[2] Recently, Mo(W)–S–Cu(Ag) clusters have shown promise as non-linear optical (NLO) materials,[3] and prismane clusters are of great interest in regard to their excellent NLO properties.[4] Up to now,

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only six prismane clusters have been structurally reported, $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$,[5a] $[Cu_4W_2S_6](PPh_3)_4O_2$,[5e] $(PPh_3)_4Ag_4W_2S_8$,[5b] $(PPh_3)_4Ag_4Mo_2S_8$,[5c] $[(C_6H_5)_2PCH_3]_4Ag_4W_2S_8$,[5d] and $(Ph_3As)_4Ag_4W_2S_8$.[4b] Among these reported prismane clusters, no Mo-Cu-S analogue has been structurally characterized. This paper describes the synthesis and structure of a novel bimetallic sulfur cluster $(PPh_3)_2(C_6H_7N)_2Cu_4Mo_2S_6O_2 \cdot 2C_6H_7N$ (I), in which two different moieties, $\{Ph_3PCu\}$ and $\{C_6H_7NCu\}$, bridge $MoOS_3$ units. It is the first mixed-ligand prismane cluster as well as the first involving the coordination of an N atom.

EXPERIMENTAL

$[NH_4]_2Mo_2O_2$ was prepared according to the method[6] reported. All the other reagents were of AR grade, and used without further purification.

Preparation of $[Cu_4Mo_2S_6](PPh_3)_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$ (I)

A mixture of 0.22 g $[NH_4]_2MoO_2S_2$ (1 mmol), 0.43 g CuBr (3 mmol) and 0.79 g PPh_3 (3 mmol) was stirred in 2-picoline (9 cm^3) for about 8 h. The reaction mixture was filtered and allowed to stand in air at room temperature. After 5–6 days, black crystals of the title compound (0.22 g, yield 28%) and red crystals of $MoOS_3Cu_3(PPh_3)_3Br$ (yield *ca* 10%) were obtained, and which were separated mechanically. *Anal.* Calcd. for $Mo_2Cu_4S_6O_2N_4C_{60}P_2H_{58}$ (%): C, 45.97; H, 3.73; N, 3.57. Found: C, 46.06; H, 3.70; N, 3.42.

X-ray Structure Determination

A suitable crystal of the title compound for X-ray analysis was mounted on a glass fibre using epoxy resin. Crystal and refinement data are summarized in Table I. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) using the ω-2θ scan method. The stability of the crystal was monitored at regular intervals using three standard reflections and no significant variation was observed. Intensity data was corrected for Lorentz and polarization effects and semi-empirical absorption corrections (ψ-scan method) were also applied.[7] The structure was solved by a combination of direct methods (SIR88)[8] and difference Fourier techniques and refined on F by full-matrix least-squares analysis. The hydrogen atoms of the organic

TABLE I Crystallographic data for the complex

Empirical formula	$Mo_2Cu_4S_6O_2N_4C_{60}P_2H_{58}$
Formular weight	1567.52
Crystal dimensions (mm)	0.30 × 0.32 × 0.35
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell parameters	
a (Å)	12.149(2)
b (Å)	17.152(2)
c (Å)	15.793(2)
β (°)	105.40(2)
V (Å^3)	3172.8(8)
Z	2
μ (cm^{-1})	19.91
$F(000)$	1576.00
2θmax (°)	44.9
d_c (g cm^{-1})	1.641
Temperature (K)	296.0
Diffractometer	Enraf-Nonius CAD4
Radiation	MoKα ($\lambda = 0.71069$Å)
Scan type	ω-2θ
Scan width (°)	$0.70 + 0.35\tan\theta$
Solution method	Direct Methods (SIR88)
Correction	Lorentz-polarization, Adsorption
No. of observations with $I > 3\ (\sigma(I))$	2753
Residuals: R, R_w	0.046; 0.048; $w = \sigma^2(F_o)^{-1}$
Goodness of fit: S	1.98
Max. shift in final cycle	0.19
No. of variables	201
Max./Min. peaks in final diff. map (e-/Å^3)	0.60/−0.54

moieties were placed in their idealized positions (C–H, 0.95 Å). All calculations were performed on a Silicon Graphics computer using the program package teXsan[9] from the Molecular Structure Corporation. Final atomic positions are listed in Table II, and bond lengths and angles in Tables III and IV.

RESULTS AND DISCUSSION

There are two $(PPh_3)_2(C_6H_7N)_2Cu_4Mo_2S_6O_2 \cdot 2C_6H_7N$ molecules per unit cell. The crystal structure reveals a discrete 12-atom $Mo_2S_6Cu_4$ prismane (Figure 1). Each Mo atom is bonded to a terminal oxygen atom, while the four Cu atoms are equally divided into two types. One is additionally bonded to PPh_3 and the other to a 2-picoline ligand. Four 2-picoline solvent molecules are distributed in every unit cell.

A centre of symmetry lies within the molecule. Therefore, each molecule can be regarded as a dimer fused by two identical $(Ph_3P)CuMoOS_3Cu(NC_6H_7)$ moieties. The asterisked atoms are related to the

TABLE II Atomic Coordinates and B_{eq} values for $[Cu_4Mo_2S_6][(C_6H_5)_3P]_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$

atom	x/a	y/b	z/c	B_{eq}* ($\AA^2$)
Mo(1)	0.094391(7)	0.08845(4)	0.09542(5)	3.09(2)
Cu(1)	0.86143(10)	−0.05779(7)	0.06171(8)	3.76(3)
Cu(2)	1.15891(9)	0.03047(7)	0.11767(7)	3.52(3)
S(1)	1.0168(2)	−0.0206(1)	0.1699(1)	3.56(6)
S(2)	1.0806(2)	0.1416(1)	0.0436(2)	3.50(6)
S(3)	0.7908(2)	0.0553(1)	−0.0125(2)	3.44(6)
O(1)	0.9051(6)	0.1520(4)	0.1635(4)	4.9(2)
P(1)	1.3199(2)	0.0557(1)	0.2234(2)	3.15(6)
N(1)	0.7415(6)	−0.1169(4)	0.1036(5)	3.9(2)
C(1)	1.2951(7)	0.1261(5)	0.3034(5)	3.2(2)
C(2)	1.2074(9)	0.1132(6)	0.3389(7)	5.4(2)
C(3)	1.182(1)	0.1671(7)	0.3993(8)	6.7(3)
C(4)	1.2494(9)	0.2324(6)	0.4211(7)	4.9(2)
C(5)	1.3350(10)	0.2450(6)	0.3862(7)	5.5(2)
C(6)	1.3601(8)	0.1934(6)	0.3265(6)	4.4(2)
C(19)	0.6372(9)	−0.0843(6)	0.0879(7)	5.0(2)
C(20)	0.551(1)	−0.1168(8)	0.1189(8)	7.0(3)
C(21)	0.573(1)	−0.1819(8)	0.1670(9)	7.7(3)
C(22)	0.675(1)	−0.2160(8)	0.1838(9)	7.8(3)
C(23)	0.7605(10)	−0.1815(7)	0.1505(7)	5.7(3)
C(24)	0.874(1)	−0.2189(9)	0.1650(9)	8.9(4)

$^*B_{eq} = (8\pi^2/3)[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$.

TABLE III Selected bond distances for $[Cu_4Mo_2S_6](PPh_3)_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$ (Å)

Mo(1)-S(1)	2.261(3)	Mo(1)-S(2)	2.232(3)
Mo(1)-S(3)	2.237(2)	Mo(1)-O(1)	1.684(6)
Mo(1)-Cu(1)	2.701(1)	Mo(1)-Cu(2)	2.729(1)
Cu(1)-S(1)	2.275(3)	Cu(1)-S(2*)	2.440(3)
Cu(1)-S(3)	2.310(3)	Cu(1)-N(1)	2.024(8)
Cu(2)-S(1)	2.277(3)	Cu(2)-S(2)	2.306(3)
Cu(2)-S(3*)	2.415(3)	Cu(2)-P(1)	2.251(3)

TABLE IV Selected bond angles for $[Cu_4Mo_2S_6](PPh_3)_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$ (°)

S(1)-Mo(1)-S(2)	107.56(9)	S(2)-Mo(1)-S(3)	111.93(9)
S(1)-Mo(1)-S(3)	108.52(9)	S(2)-Mo(1)-O(2)	109.4(2)
S(1)-Mo(1)-O(1)	109.9(2)	S(3)-Mo(1)-O(1)	109.5(2)
S(1)-Cu-S(2*)	110.19(10)	S(1)-Cu(1)-S(3)	105.53(10)
S(2*)-Cu(1)-S(3)	106.51(9)	S(1)-Cu(1)-N(1)	114.9(2)
S(2*)-Cu(1)-N(1)	106.9(2)	S(3)-Cu(1)-N(1)	112.6(2)
S(1)-Cu(2)-S(2)	104.56(9)	S(1)-Cu(2)-S(3*)	111.68(9)
S(2)-Cu(2)-S(3*)	107.47(9)	S(1)-Cu(2)-P(1)	113.47(10)
S(2)-Cu(2)-P(1)	112.19(10)	S(3*)-Cu(2)-P(1)	107.37(9)

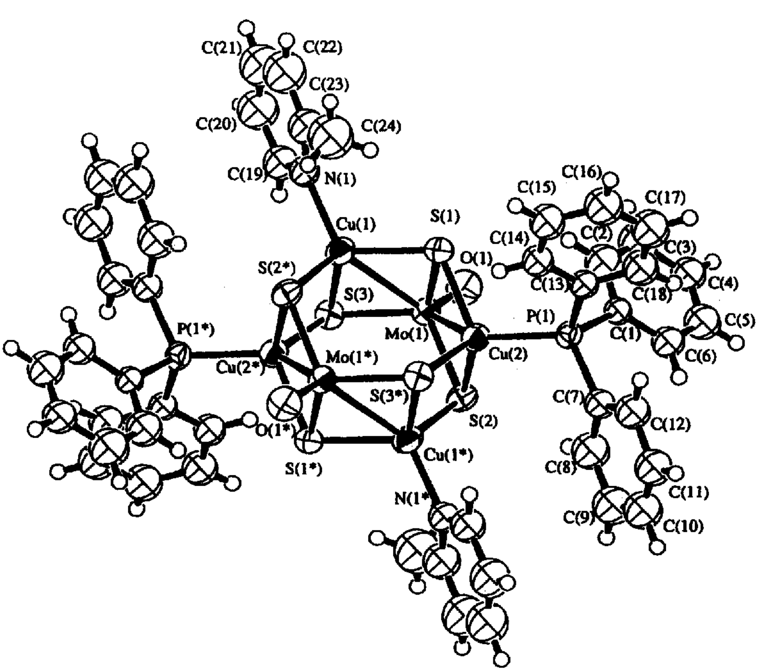

FIGURE 1 ORTEP diagram of $[Cu_4Mo_2S_6](PPh_3)_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$.

unasterisked atoms by the symmetry centre. As shown in Table IV, the $MoOS_3$ group has tetrahedral geometry, with S–Mo–S(O) angles ranging from 107.56(9) to 111.93(9)°. The terminal bond length of 1.684(6) Å (Table III) is characteristic of an Mo = O double bond.

Although the two crystallographically independent copper atoms both adopt tetrahedral geometry, they have very different ligand arrangements as mentioned above. For the $\{S_3Cu(NC_6H_7)\}$ moiety, S–Cu–S and S–Cu–N angles range from 105.53(10) to 114.9(2)°, with a mean of 109.4°; for $\{S_3CuPPh_3\}$, S–Cu–S and S–Cu–P range from 104.56(9) to 113.47(10)°, with a mean of 109.5°. Thus bond angles about copper atoms are closer to the ideal than in $[Cu_4W_2S_6][(C_7H_7)_3P]_4O_2$[5a] [102.7(3)–121.2(3)°] and $[Cu_4W_2S_6](PPh_3)_4O_2$[5e] [108.49(13)–121.08(13)°].

There are three crystallographically independent four-atom faces in the molecule (Table V). These faces are not strictly planar. The two $CuMoS_2$ faces have average displacements from the plane of 0.0023 and 0.0045 Å, while for the Cu_2S_2 plane the average displacement is 0.0241 Å.

Cu(1)-S(2*) [2.440(3) Å] and Cu(2)-S(3*) [2.415(3) Å], linking the two symmetrically related parts of the molecule, are longer than the other four

TABLE V Least-Squares Planes for $[Cu_4Mo_2S_6](PPh_3)_2(C_6H_7N)_2O_2 \cdot 2C_6H_7N$

Plane 1		Plane 2		Plane 3	
Atom	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)
Mo(1)	−0.0004	Mo(1)	−0.0009	Cu(1*)	0.0086
Cu(1)	−0.0009	Cu(2)	−0.0018	Cu(2)	0.0086
S(1)	0.0037	S(1)	0.0077	S(2)	−0.0399
S(3)	0.0039	S(2)	0.0078	S(3*)	−0.0393
	Planes		Dihedral Angle (°)		
	1 and 2		58.88		
	2 and 3		59.94		
	1 and 3		61.18		

Cu-S distances [2.275(3)–2.310(3) Å]. From a chemical point of view, it is more reasonable to consider the prismane as being formed by the dimerization of two $(Ph_3P)CuMoOS_3Cu(NC_6H_7)$ units, rather than two 6-membered MoS_3Cu_2 rings.

As reported by Müller,[5e] two clusters, $(PPh_3)_4Cu_4W_2S_6O_2$ and $[Cu_3WS_3Cl](PPh_3)_3O$, form in the course of the same reaction. As mentioned in the experimental section, starting from $[NH_4]_2MoO_2S_2$, CuBr, PPh_3 and 2-picoline, $[Cu_3MoS_3Br](PPh_3)_3O$ also forms, accompanied by production of (I). This shows that there might exist a competition between the cubane-like cluster and the prismane cluster. Apparently, in the reaction process, $[MoO_2S_2]^{2-}$ is transformed into $[MoOS_3]^{2-}$. We have no idea how the transformation occurs.

Supplementary Material

Lists of bond lengths and angles, H atom positions, thermal parameters and observed and calculated structure factors are available from the authors.

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