Heterobimetallic Clusters of Copper(I) with MS_4^{2-} (M = Mo, W). Synthesis and Characterisation of $(PPh_4)_2(Cu_3MS_4Cl_3)\cdot CH_3CN$

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Thiometallates of Group VI can be directly coordinated to neutral species such as CuCN [1] or CuCl [2, 3] to form new bimetallic sulfur clusters. These clusters are easily obtained, owing to the high tendency of Cu(I) to form metal–sulfur bonds with MS_4^{2-}. By controlling the initial Cu/M ratio, different complexes were prepared and isolated as crystals. Their synthesis and some structural informations are reported herein.

The complexes were prepared by reacting a solution of $MS_4(PPh_4)_2$ in MeCN with CuCl previously dissolved in deaerated MeCN. The orange precipitate resulting from the mixture of the solutions was eliminated by filtration. Evaporation of the filtrates produced the heterometallic clusters $(Cu_3MS_4Cl_3)^{2-}$ with M = Mo (*1*) and W (*2*). Complex (*2*) crystallized under two distinct forms (*2a*) and (*2b*), related to the value of the initial Cu/W ratio. The evaporation of filtrates obtained from stoichiometric conditions (Cu/W = 3) led to the (*2a*) isomer. The other isomeric forms (*2b*) and (*1*) were prepared by slow evaporation at room temperature of filtrates obtained from solutions involving an initial ratio Cu/M = 2. The compounds have been characterized by full elemental analysis. The two isomers (*1*) and (*2*) have analogous IR spectra with main absorption bands (solid KBr pellet) at 460, 430 and 345 cm^{-1} for (*2*) and 475, 440 and 345 cm^{-1} for (*1*). The electronic spectra (in DMF solution) is characterized by absorption at 430(4350), 308(11900) and a shoulder at 330 nm for complex (*2*), at 508(3450), 372(6420), 292(15250) and a shoulder at 332 nm for complex (*1*) (molecular absorptivities in parentheses).

TABLE I. Results of the Crystal Structure Analysis.

Compound	(*1*)	(*2b*)
Space Group	$C_{2/c}$	$C_{2/c}$
a (Å)	34.015	34.053
b (Å)	27.045	27.069
c (Å)	26.850	26.898
β (°)	122.51	122.52
U ($Å^3$)	20830	20906
Z	16	16
Number of independent reflections $F_o^2 > 3\sigma(F_o^2)$	4093	4417
Number of variables	228 + 225[a]	228 + 225[a]
$\frac{\Sigma \lVert F_o \rvert - \lvert F_c \rVert}{\Sigma \lvert F_o \rvert}$	0.066	0.058

[a] The final model for the structures were refined in two blocks for computing economy.

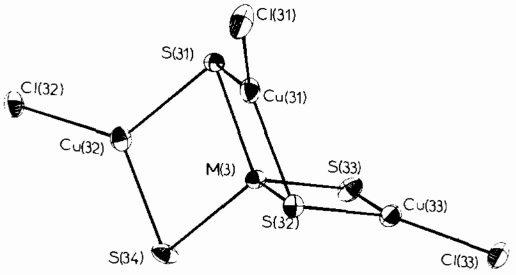

Fig. 1. $(Cu_3MS_4Cl_3)^{2-}$ in general position (M = Mo or W).

Crystals of $(Cu_3MS_4Cl_3)(PPh_4)_2\cdot CH_3CN$ could be isolated and examined by X-Ray structural analysis (Table I). Three-dimensional intensity data were collected with a PW 1100 four circle diffractomter (MoK_α radiation). Lorentz and polarisation corrections were applied to the data without absorption corrections. The structures were solved by direct methods using the MULTAN 77 program [4] and subsequent Fourier procedures. The structures were refined by least-squares using anisotropic thermal parameters for all atoms of the anion and the P atoms of the counter-anions (the phenyl rings of the PPh_4^+ cations being considered as rigid groups). Solvent molecules were included in the calculations and refined isotropically. Anomalous dispersion corrections were applied to the W (or Mo) and Cu atoms. The structures of the two isomorphous compounds consist of three indepen-

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TABLE II. Interatomic Distances (Å) and Bond Angles (°) of Interest with Standard Deviations for $(Cu_3MS_4Cl_3)^{2-}$ Anion.

	M = W	M = Mo		M = W	M = Mo
M_1-S_{12}	2.195(4)	2.191(5)	M_3-S_{34}	2.197(4)	2.195(5)
M_1-S_{11}	2.253(4)	2.251(5)	M_3-S_{33}	2.204(4)	2.196(5)
M_1-Cu_{11}	2.638(3)	2.620(4)	M_3-S_{32}	2.250(4)	2.250(5)
M_1-Cu_{12}	2.629(2)	2.613(2)	M_3-S_{31}	2.260(4)	2.259(5)
M_2-S_{22}	2.203(5)	2.200(5)	M_3---Cu_{31}	2.627(2)	2.613(2)
M_2-S_{21}	2.259(4)	2.254(5)	M_3---Cu_{32}	2.630(2)	2.620(3)
M_2-Cu_{21}	2.633(3)	2.616(4)	M_3---Cu_{33}	2.630(2)	2.611(3)
M_2-Cu_{22}	2.638(2)	2.618(2)			
$S_{12}-M_1-S_{12}'$	113.1(3)	113.5(3)	$S_{34}-M_3-S_{33}$	112.9(2)	112.8(2)
$S_{12}-M_1-S_{11}$	108.9(2)	109.2(2)	$S_{34}-M_3-S_{32}$	108.6(2)	108.9(2)
$S_{12}-M_1-S_{11}'$	108.6(2)	108.1(2)	$S_{34}-M_3-S_{31}$	108.7(2)	108.2(2)
$S_{11}-M_1-S_{11}'$	108.5(2)	108.5(3)	$S_{33}-M_3-S_{32}$	108.7(2)	108.4(2)
			$S_{33}-M_3-S_{31}$	109.3(2)	109.9(2)
$S_{22}-M_2-S_{22}'$	113.1(3)	112.9(3)	$S_{32}-M_3-S_{31}$	108.6(2)	108.4(2)
$S_{22}-M_2-S_{21}$	109.5(2)	109.6(2)			
$S_{22}-M_2-S_{21}'$	108.5(2)	108.3(2)			
$S_{21}-M_2-S_{21}'$	107.5(2)	107.9(3)			

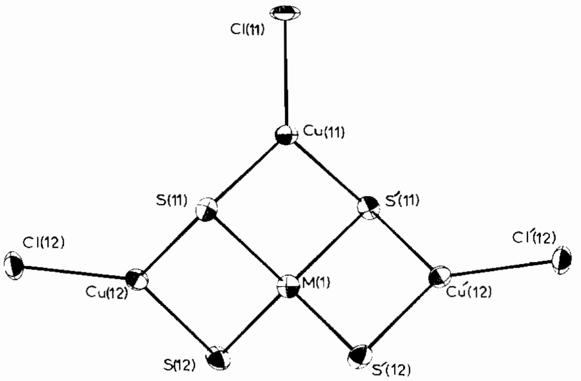

Fig. 2. One of the special positions of the $(Cu_3MS_4Cl_3)^{2-}$ anion. M(1), Cu(11), Cl(11) lie on a twofold axis. Atoms related by the diad axis are primed.

dent species. Figure 1 shows the $(Cu_3MS_4Cl_3)^{2-}$ anion in general position. One of the two special positions (binary symmetry) of the same anion is represented on Fig. 2. Selected structural parameters are given in Table II.

The $(Cu_3MS_4Cl_3)^{2-}$ unit is a slightly distorted MS_4^{2-} tetrahedron coordinated by three CuCl molecules leaving an open S–M–S angle. In both compounds the copper(I) atoms have a trigonal planar coordination geometry and lie in the plane of two S and one Cl atoms (maximum deviation 0.36 Å for (*1*), and (*2b*).

The W–S bonds involving triply bonded S (average value 2.255(5) Å) are longer than those for doubly bonded S (average value 2.200(5) Å). Similarly a significant angular distortion from tetrahedral geometry at the central M atom is observed for only the open S–W–S angle (maximum angle 113.1(3)° for (*2b*). These variations were not so significant in the orthorhombic (*2a*) isomer [2].

The Cu–S distances are not clearly influenced by the different S coordination and are comparable with the corresponding values found in other complexes in which Cu(I) is coordinated by two S and one Cl atoms in a trigonal array [3, 5] for (*1*), [2] for (*2b*). Complexes (*1*) and (*2b*) involve short Cu··· M distances (average values: 2.633(4) Å for (*2b*) and 2.616(3) Å for (*1*)) as observed for equivalent three coordinated Cu(I) in other complexes [2, 3, 5]. These values, together with the very acute angles about the S atoms bridging Cu and M, are indicative of a possible Cu···M bonding interaction.

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