Inorganica Chimica Acta, 76 (1983) L245–L246

Synthesis of Heterometallic Clusters from Thiometalates by 'Unit Construction'*

ACHIM MÜLLER, UWE SCHIMANSKI and JÜRGEN SCHIMANSKI

Faculty of Chemistry, University, D-4800 Bielefeld, F.R.G.

Received November 15, 1982

Thioanions of the transition metals show interesting reactivities and can be used to produce multimetal complexes, which are either interesting from the structural point of view, or which have unusual electronic properties [1] (especially the MoS_4^{2-} and WS_4^{2-} ions and their complexes, which play a part in certain problems of bioinorganic chemistry [1]). In this note we report some novel heterometallic clusters (see Table I for crystallographic data; bond distances are shown in Figs. 1 and 2 and in the text). We intend to show that these clusters can be obtained deliberately by 'unit construction'.

According to the high formation tendency of M–S bonds (M = soft cations like Cu or Ag), coordinatively unsaturated species like CuCN, CuCl or $Cu(PPh_3)_n$ (n = 1, 2) *can be 'added' to thioanions* and stabilized. Following this principle polynuclear heterometallic compounds can be obtained with the intact thiometalate unit.

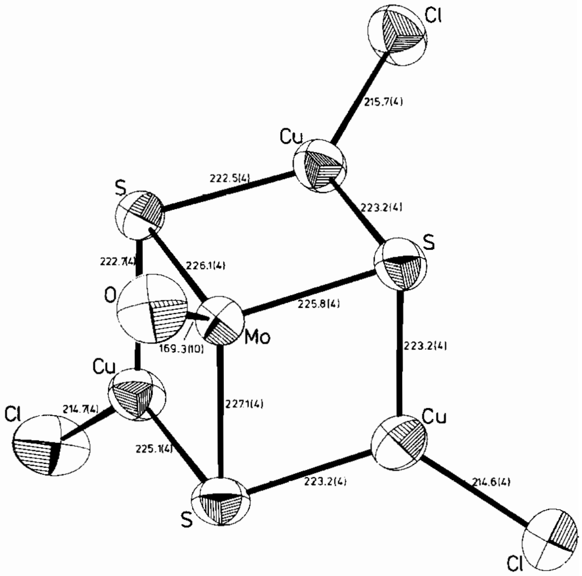

Fig. 1. ORTEP plot of $[(CuCl)_3(MoOS_3)]^{2-}$ in the PPh_4 salt *2* (bond lengths in [pm], bond angles in [°]: Cu–Mo 263.2(2)–264.2(2); Cu–Mo–Cu 84.6(1)–87.1(1), Mo–S–Cu 71.2(1)–72.1(1), Cu–S–Cu 105.8(2)–108.2(2), S–Mo–S 106.8(1)–107.5(1), O–Mo–S 111.5(4)–112.1(4), S–Cu–S 108.9(2)–109.4(2), S–Cu–Cl 121.8(2)–128.8(2)).

By heating a solution of $MoOS_3^{2-}$ *1* (PPh_4 salt) with CuCl (in the presence of sulfur) in organic solvents 3 CuCl are 'added' to *1* and the novel heterometallic species $[(CuCl)_3(MoOS_3)]^{2-}$ (having roughly C_{3v} symmetry) is formed, isolated as PPh_4 salt *2*.

TABLE I. Results of the Crystal Structure Analysis.[a]

Compound	*2*	*4*	*4a*	*6*	*6a*	*7*
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a [pm]	988.5(3)	1211.7(5)	1212.8(2)	2003.4(3)	2002.4(8)	1817.3(8)
b [pm]	1163.7(3)	1775.2(7)	1774.5(3)	1445.1(3)	1445.3(5)	1743.4(7)
c [pm]	2346.5(14)	2530.3(17)	2534.5(7)	1577.2(4)	1578.6(5)	1790.7(6)
α [°]	78.83(4)					
β [°]	78.42(4)	96.60(4)	96.41(2)	92.30(2)	92.35(3)	95.72(3)
γ [°]	70.94(2)					
$V\cdot10^{-6}$ [pm^3]	2475.3	5406.8	5420.4	4562.5	4564.7	5645.3
Z	2	4	4	4	4	4
Number of independent reflections $F_o > 3.92\sigma(F_o)$	4902	6372		7095	7825	3699
Number of variables	205	222		188	283	319
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.082	0.091		0.086	0.069	0.076

[a] *2*: $[Ph_4P]_2[(CuCl)_3(MoOS_3)]$
4: $[(CuPPh_3)(Cu(PPh_3)_2)(MoOS_3)]\cdot0.8CH_2Cl_2$
4a: $[(CuPPh_3)(Cu(PPh_3)_2)(WOS_3)]\cdot0.8CH_2Cl_2$
6: $[Ph_4P]_2[(AgCN)(MoS_4)]$
6a: $[Ph_4P]_2[(AgCN)(WS_4)]$
7: $[(PPh_3)_2AgSe_2WSe_2Ag(PPh_3)]\cdot0.8CH_2Cl_2$

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*This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Minister für Wissenschaft und Forschung (NRW).

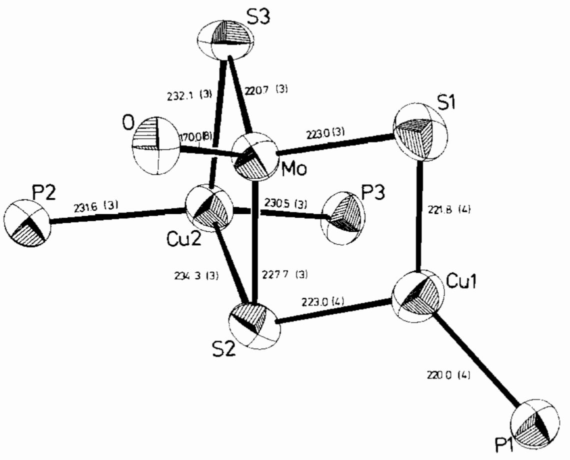
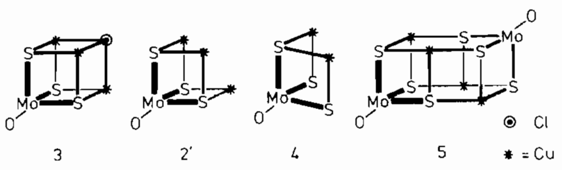


Fig. 2. ORTEP plot of the central unit of [(CuPPh$_3$)(Cu(PPh$_3$)$_2$)(MoOS$_3$)] *4* (bond lengths in [pm], bond angles in [°]: Cu1–Mo 264.1(2), Cu2–Mo 279.7(2); Cu–Mo–Cu 90.0(1), Mo–μ_3S–Cu 71.7(1)–74.5(1), Mo–μ_2S–Cu 72.9(1)–76.3(1), S–Mo–S 106.7(1)–111.0(1), O–Mo–S 109.7(3)–111.6(3), P1–Cu1–S 124.0(1)–124.6(1), P2–Cu2–P3 120.3(1), P–Cu2–S 107.3(1)–109.1(1), μ_2S–Cu–μ_3S 101.5(1)–108.7(1), Cu–μ_3S–Cu 114.4(1)).

The central unit of *2* (see Fig. 1) corresponds to a distorted cube with one missing corner (the Cu atoms are trigonally planar coordinated). Remarkably, the {Cu$_3$MoS$_3$} unit can be completed by 'addition' of another atom, for example chlorine (see below the schematic structure of [(CuPPh$_3$)$_3$(MoOS$_3$)Cl] *3* [2] with the {Cu$_3$MoS$_3$Cl} cube).

We can also obtain the novel compound with two missing corners having the central {Cu$_2$MoS$_3$} moiety. By extraction of an aqueous solution of *1* (Cs salt) with CH$_2$Cl$_2$ containing CuCN and PPh$_3$*, crystals of [(CuPPh$_3$)(Cu(PPh$_3$)$_2$)(MoOS$_3$)]·0.8CH$_2$Cl$_2$ *4* (see Fig. 2) could be isolated. The corresponding W compound *4a* was obtained in the same way (Table I).

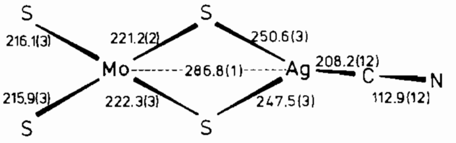


If we compare the structure of *4* with that of [(CuPPh$_3$)$_4$(MOS$_3$)$_2$] (M = Mo *5* [3a], W *5a* [3b]; see above), we realize that *4* represents almost one half of *5* (*4* has only one more PPh$_3$ ligand at one of the two non-equivalent Cu atoms). Due to the preferred formation of Cu–S bonds in solution (CH$_2$Cl$_2$/acetone), the following reaction takes place

$$2[(\mathrm{CuPPh_3})(\mathrm{Cu(PPh_3)_2})(\mathrm{MoOS_3})]\ 4 \xrightarrow{-2\mathrm{PPh_3}} [(\mathrm{CuPPh_3})_4(\mathrm{MoOS_3})_2]\ 5$$

which is an impressive example for the construction of a cage from two halves.

This type of chemistry can be extended for instance to Ag complexes and to selenometalates. By 'adding' AgCN to MS$_4^{2-}$ [(AgCN)(MS$_4$)]$^{2-}$ (PPh$_4$ salt: M = Mo *6* [1, 5], W *6a* [5]) was obtained in the same way as the corresponding, structurally similar complex [(CuCN)(MoS$_4$)]$^{2-}$ [4] (but having a linear C–Cu–Mo moeity; in *6*: C–Ag–Mo: 169.1(3)°).



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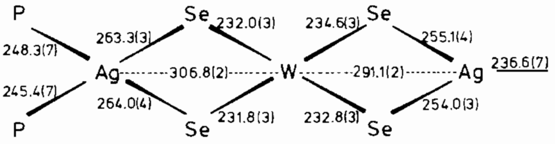

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(Bond lengths in [pm]; see also Table I).

We can now also isolate a selenometalato complex [(PPh$_3$)$_2$AgSe$_2$WSe$_2$(PPh$_3$)]·0.8CH$_2$Cl$_2$ *7*, using a method analogous to the preparation of the corresponding sulfur compound [6].

There seems to be a promising future in this type of chemistry concerned with cluster synthesis by using intact thio- and selenometalates or their derivates.

References

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*CuCN is soluble in CH$_2$Cl$_2$ in the presence of PPh$_3$.