

Introduction. The structure was investigated as part of a continuing research into Cu–Mo–S systems, which may be relevant to the biological antagonism between copper and molybdenum (Mills, Bremner, El-Gallad, Dalgarno & Young, 1978; Mills, 1979; Acott, Garner, Nicholson & Clegg, 1983). Thus, several $[(XCu)_nMoS_4]^{2-}$ complexes have been prepared by us and are under investigation.

Experimental. The complex was prepared from $[Ph_4P]_2[MoS_4]$ and CuCl (*ca* 1:3 molar ratio) in CH_3CN and recrystallized as dark-red blocks from CH_3CN . Chemical-analysis figures were in agreement with the formula given.

Data collection: crystal $0.27 \times 0.40 \times 0.42$ mm, Stoe–Siemens AED diffractometer. Unit-cell parameters derived from 2θ angles of 48 reflections centred at $\pm\omega$ ($20 < 2\theta < 25^\circ$). Intensities measured by profile analysis (Clegg, 1981) for 9934 reflections with $2\theta < 50^\circ$, $h \leq 0$, $k \geq 0$; no significant intensity variation for three standard reflections.

Data reduction: empirical absorption correction based on 276 azimuthal scan data; transmission 0.383–0.412. $R_{int} = 0.042$ ($0kl$ reflections only); 9191 unique reflections, 6091 with $F > 4\sigma(F)$.

Structure solution and refinement: some heavier atoms from automatic direct methods; difference syntheses; blocked-cascade refinement to minimize $\sum w\Delta^2$ with $\Delta = |F_o| - |F_c|$; $w^{-1} = \sigma_F^2 + 0.00096F^2$. Phenyl groups as rigid ideal hexagons, C–C = 1.395 Å, C–H = 0.96 Å on external C–C–C angle bisectors. Anisotropic thermal parameters for all non-H atoms; $U(H) = 1.2U_{eq}(C)$. No extinction correction. Two phenyl groups refined with twofold disorder of orientation [occupation factors 0.501 (5) and 0.523 (4) for major components]. CH_3CN as rigid group with C–C = 1.47 Å, C–N = 1.15 Å, C–C–N = 180° , no H atoms included. 567 parameters, $R = 0.068$, $wR = 0.081$, slope of normal probability plot = 1.49. Max.(shift/e.s.d.) = 0.02, mean = 0.004. Largest peak in final difference map = $0.78 e \text{ \AA}^{-3}$, largest hole = $-1.10 e \text{ \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Programs: *SHELXTL* by Professor G. M. Sheldrick (Göttingen), diffractometer control program by W. Clegg; Data General Eclipse and Nova computers.

Discussion. Atomic coordinates, and bond lengths and angles for the anions, are given in Tables 1 and 2.* One of the two crystallographically independent anions is shown in Fig. 1. Each lies on a twofold axis, which passes through Mo and a CuCl group. The MoS_4 unit is

* Tables of structure factors, anisotropic thermal parameters, hydrogen-atom parameters and cation geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38339 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Mo(1)	7500	888 (1)	7500	544 (3)
Cu(11)	7500	−1042 (1)	7500	610 (4)
Cl(11)	7500	−2616 (2)	7500	1124 (15)
Cu(12)	6781 (1)	839 (1)	6423 (1)	651 (3)
Cl(12)	6140 (1)	895 (1)	5562 (1)	757 (7)
S(11)	6469 (1)	−87 (1)	7177 (1)	596 (6)
S(12)	7807 (1)	1785 (1)	6758 (1)	810 (8)
Mo(2)	7500	6088 (1)	2500	578 (3)
Cu(21)	7500	4148 (1)	2500	691 (5)
Cl(21)	7500	2564 (2)	2500	947 (13)
Cu(22)	6662 (1)	6018 (1)	1466 (1)	632 (3)
Cl(22)	5983 (1)	5904 (1)	621 (1)	722 (7)
S(21)	6446 (1)	5104 (2)	2254 (1)	666 (7)
S(22)	7700 (1)	6979 (2)	1725 (1)	794 (8)
P(1)	1736 (1)	−1 (1)	5675 (1)	624 (7)
C(112)	2886 (3)	−638 (4)	6519 (5)	1457 (56)
C(113)	3658	−725	6791	1801 (69)
C(114)	4271	−225	6561	1088 (44)
C(115)	4111	360	6059	1284 (53)
C(116)	3339	447	5787	1187 (48)
C(111)	2727	−52	6017	662 (27)
C(122)	1816 (4)	350 (3)	4495 (2)	1396 (56)
C(123)	1780	948	3996	1501 (62)
C(124)	1600	1949	4037	932 (39)
C(125)	1456	2351	4577	1995 (77)
C(126)	1491	1752	5077	1950 (74)
C(121)	1671	751	5036	626 (26)
C(132)	1332 (4)	1146 (6)	6595 (4)	718 (57)
C(133)	828	1588	6959	1059 (81)
C(134)	51	1258	6949	771 (63)
C(135)	−221	486	6576	814 (66)
C(136)	282	44	6213	630 (53)
C(131)	1059	373	6222	423 (39)
C(13b)	1405 (6)	614 (8)	6738 (4)	998 (80)
C(13c)	913	1017	7124	1254 (103)
C(13d)	195	1443	6905	1211 (100)
C(13e)	−32	1466	6298	1124 (92)
C(13f)	459	1063	5912	961 (77)
C(13a)	1178	637	6131	508 (45)
C(142)	1037 (6)	−1563 (7)	4946 (4)	706 (62)
C(143)	766	−2516	4808	928 (91)
C(144)	820	−3244	5243	760 (78)
C(145)	1144	−3018	5816	728 (64)
C(146)	1414	−2064	5954	734 (64)
C(141)	1361	−1337	5519	489 (61)
C(14b)	729 (5)	−1450 (7)	5562 (4)	775 (60)
C(14c)	472	−2391	5382	1035 (86)
C(14d)	940	−2983	5062	1203 (117)
C(14e)	1666	−2634	4921	772 (61)
C(14f)	1923	−1693	5100	615 (50)
C(14a)	1455	−1100	5421	504 (53)
P(2)	1670 (1)	4996 (1)	709 (1)	428 (5)
C(212)	2736 (3)	4980 (6)	1723 (2)	1588 (65)
C(213)	3494	4988	2027	2277 (95)
C(214)	4153	5021	1716	1044 (42)
C(215)	4054	5046	1101	1225 (50)
C(216)	3297	5038	797	1145 (47)
C(211)	2638	5005	1108	504 (22)
C(222)	2046 (2)	5256 (3)	−426 (2)	611 (25)
C(223)	2059	5775	−953	703 (29)
C(224)	1695	6697	−1022	715 (29)
C(225)	1320	7100	−565	1257 (48)
C(226)	1308	6581	−39	1012 (39)
C(221)	1671	5659	31	429 (20)
C(232)	1189 (2)	6489 (3)	1408 (2)	837 (32)
C(233)	652	6965	1730	978 (38)
C(234)	−69	6520	1802	705 (29)
C(235)	−254	5599	1550	733 (30)
C(236)	283	5122	1228	581 (24)
C(231)	1004	5567	1156	419 (19)
C(242)	918 (3)	3513 (3)	27 (2)	735 (28)
C(243)	626	2558	−68	902 (35)

Table 1 (cont.)

	x	y	z	U _{eq}
C(244)	775	1842	369	742 (30)
C(245)	1217	2081	902	714 (30)
C(246)	1509	3037	998	615 (25)
C(241)	1360	3753	560	437 (20)
N(3)	127 (8)	3042 (11)	2110 (6)	2757 (106)
C(31)	-22	2640	2528	1817 (100)
C(32)	-212	2125	3061	2724 (128)

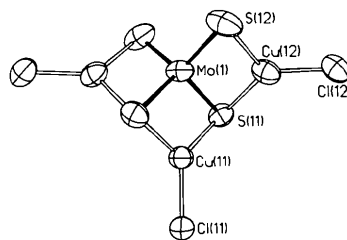
Fig. 1. One of the [MoS₄(CuCl)₃]²⁻ anions. Thermal motion is represented as 50% probability ellipsoids.

Table 2. Bond lengths (Å) and angles (°) for the anions

The prime denotes a symmetry-related atom.

Mo(1)—Cu(11)	2.615 (2)	Mo(2)—Cu(21)	2.628 (2)
Mo(1)—Cu(12)	2.621 (1)	Mo(2)—Cu(22)	2.619 (1)
Mo(1)—S(11)	2.255 (2)	Mo(2)—S(21)	2.257 (2)
Mo(1)—S(12)	2.196 (2)	Mo(2)—S(22)	2.198 (2)
Cu(11)—Cl(11)	2.131 (3)	Cu(21)—Cl(21)	2.146 (4)
Cu(11)—S(11)	2.240 (2)	Cu(21)—S(21)	2.235 (2)
Cu(12)—Cl(12)	2.141 (2)	Cu(22)—Cl(22)	2.140 (2)
Cu(12)—S(11)	2.240 (2)	Cu(22)—S(21)	2.247 (2)
Cu(12)—S(12)	2.233 (2)	Cu(22)—S(22)	2.222 (2)
Cu(11)—Mo(1)—Cu(12)	88.5 (1)	Cu(21)—Mo(2)—Cu(22)	87.9 (1)
Cu(11)—Mo(1)—S(11)	54.2 (1)	Cu(21)—Mo(2)—S(21)	53.8 (1)
Cu(12)—Mo(1)—S(11)	54.1 (1)	Cu(22)—Mo(2)—S(21)	54.3 (1)
Cu(11)—Mo(1)—S(12)	123.6 (1)	Cu(21)—Mo(2)—S(22)	123.3 (1)
Cu(12)—Mo(1)—S(12)	54.4 (1)	Cu(22)—Mo(2)—S(22)	54.1 (1)
S(11)—Mo(1)—S(12)	108.4 (1)	S(21)—Mo(2)—S(22)	108.4 (1)
Cu(12)—Mo(1)—Cu(12')	177.1 (1)	Cu(22)—Mo(2)—Cu(22')	175.8 (1)
Cu(12)—Mo(1)—S(11')	123.9 (1)	Cu(22)—Mo(2)—S(21')	122.7 (1)
S(11)—Mo(1)—S(11')	108.3 (1)	S(21)—Mo(2)—S(21')	107.6 (1)
Cu(12)—Mo(1)—S(12')	127.6 (1)	Cu(22)—Mo(2)—S(22')	128.8 (1)
S(11)—Mo(1)—S(12')	109.4 (1)	S(21)—Mo(2)—S(22')	109.5 (1)
S(12)—Mo(1)—S(12')	112.8 (1)	S(22)—Mo(2)—S(22')	113.4 (1)
Mo(1)—Cu(11)—Cl(11)	180.0	Mo(2)—Cu(21)—Cl(21)	180.0
Mo(1)—Cu(11)—S(11)	54.7 (1)	Mo(2)—Cu(21)—S(21)	54.6 (1)
Cl(11)—Cu(11)—S(11)	125.3 (1)	Cl(21)—Cu(21)—S(21)	125.4 (1)
S(11)—Cu(11)—S(11')	109.4 (1)	S(21)—Cu(21)—S(21')	109.2 (1)
Mo(1)—Cu(12)—Cl(12)	175.5 (1)	Mo(2)—Cu(22)—Cl(22)	178.0 (1)
Mo(1)—Cu(12)—S(11)	54.6 (1)	Mo(2)—Cu(22)—S(21)	54.6 (1)
Cl(12)—Cu(12)—S(11)	125.8 (1)	Cl(22)—Cu(22)—S(21)	124.1 (1)
Mo(1)—Cu(12)—S(12)	53.1 (1)	Mo(2)—Cu(22)—S(22)	53.2 (1)
Cl(12)—Cu(12)—S(12)	126.3 (1)	Cl(22)—Cu(22)—S(22)	128.0 (1)
S(11)—Cu(12)—S(12)	107.7 (1)	S(21)—Cu(22)—S(22)	107.9 (1)
Mo(1)—S(11)—Cu(11)	71.1 (1)	Mo(2)—S(21)—Cu(21)	71.6 (1)
Mo(1)—S(11)—Cu(12)	71.3 (1)	Mo(2)—S(21)—Cu(22)	71.1 (1)
Cu(11)—S(11)—Cu(12)	109.3 (1)	Cu(21)—S(21)—Cu(22)	108.7 (1)
Mo(1)—S(12)—Cu(12)	72.6 (1)	Mo(2)—S(22)—Cu(22)	72.7 (1)

essentially tetrahedral; two opposite S...S edges are bridged by CuCl groups, as is a third edge, in such a way that two S atoms are bonded to Mo and one Cu, the other two to Mo and two Cu atoms. This arrangement appears to be the first such example for a

M₃MoS₄ complex, and is in contrast to that found for (Ph₃PCu)₃MoS₃XCl (X = S or O), in which the Mo, 3Cu, 3S and Cl atoms form a cubane-like core and the O or fourth S atom is non-bridging (Müller, Bögge & Schimanski, 1980; Müller, Bögge, Tolle, Jostes, Schimanski & Dartmann, 1980). The S—Mo—S angles which are bridged by CuCl are all smaller than those which are open. Mo—S bonds involving triply bonded S are longer than those for doubly bonded S. This angular and radial distortion of the central MoS₄²⁻ unit from a regular tetrahedral geometry affects its spectroscopic properties (Clegg, Garner & Nicholson, 1983).

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References

- ACOTT, S. R., GARNER, C. D., NICHOLSON, J. R. & CLEGG, W. (1983). *J. Chem. Soc. Dalton Trans.* In the press.
- CLEGG, W. (1981). *Acta Cryst.* **A37**, 22–28.
- CLEGG, W., GARNER, C. D. & NICHOLSON, J. R. (1983). To be submitted.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press.
- MILLS, C. F. (1979). *Philos. Trans. R. Soc., London Ser. B*, **288**, 51–63.
- MILLS, C. F., BREMNER, I., EL-GALLAD, T. T., DALGARNO, A. C. & YOUNG, B. W. (1978). *Trace Element Metabolism in Man and Animals*, edited by M. KIRCHGESSNER, pp. 150–158. Freising-Weihenstephan: Institut für Ernährungsphysiologie.
- MÜLLER, A., BÖGGE, H. & SCHIMANSKI, U. (1980). *J. Chem. Soc. Chem. Commun.* pp. 91–92.
- MÜLLER, A., BÖGGE, H., TOLLE, H. G., JOSTES, R., SCHIMANSKI, U. & DARTMANN, M. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 654–655.