1·986 (8)–2·110 (9) Å observed in the complex tri-μ-(2-chlorobenzoato)-μ-hydroxo-dizinc(II) dihydrate (Nakacho, Misawa, Fujiwara, Wakahara & Tomita, 1976). The long axial Zn—O(4′) bond probably results from steric crowding by bulky ligand molecules which occupy both the axial and equatorial positions of the trigonal bipyramid. The bond angles in the equatorial plane show large deviations from ideality (108·6–133·2°); these may be due to the difference in size of the bonding pairs of electrons which depend upon the electronegativity of O and Cl; the Zn—O(1) bond would hence exert less repulsion than Zn—Cl bonds giving a larger Cl—Zn—Cl bond angle.

The Zn—Cl distances are similar to those observed in other five-coordinate complexes, *e.g.* $ZnCl_2$.terpyridyl: 2·25 (1), 2·27 (1) Å (Penfold & Einstein, 1966).

No unusual non-bonding distances are observed and interchain distances indicate that they are held together by van der Waals forces.

References

Barnes, J. C., Sesay, L. J. & Nichols, B. H. (1977). *Inorg. Nucl. Chem. Lett.* **13**, 153–156.
Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Frey, M. & Monier, J. C. (1971). *Acta Cryst.* B**27**, 2487–2490.
Groth, P. & Hassel, O. (1964). *Acta Chem. Scand.* **18**, 1327–1332.
Juhasz, R. & Yntema, L. F. (1940). *J. Am. Chem. Soc.* **62**, 3522.
Main, P., Lessinger, L., Woolfson, M. M., Germain, G. & Declercq, J. P. (1977). *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Nakacho, Y., Misawa, T., Fujiwara, T., Wakahara, A. & Tomita, K. (1976). *Bull. Chem. Soc. Jpn*, **49**, 595–599.
Penfold, B. R. & Einstein, F. W. B. (1966). *Acta Cryst.* B**20**, 924–926.
Rheinboldt, H., Luyken, A. & Schmittmann, H. (1937). *J. Prakt. Chem.* **149**, 30–54.
Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1983). C**39**, 1007–1009

Structure of Tris(tetraphenylphosphonium) Tris[chlorocopper(I)]oxotrithiomolybdate(VI) Dichlorocuprate(I),* $[Ph_4P]_3[MoOS_3(CuCl)_3][CuCl_2]$

By William Clegg

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, *D*-3400 *Göttingen, Federal Republic of Germany*

C. David Garner and John R. Nicholson

*Department of Chemistry, University of Manchester, Manchester M*13 9*PL, England*

and Paul R. Raithby

*University Chemical Laboratories, Lensfield Road, Cambridge CB*2 1*EW, England*

(*Received* 22 *March* 1983; *accepted* 22 *April* 1983)

Abstract. $M_r = 1657\cdot8$, orthorhombic, $Pbca$, $a = 13\cdot714$ (2), $b = 17\cdot992$ (2), $c = 56\cdot964$ (9) Å, $U = 14055$ Å^3, $Z = 8$, $D_x = 1\cdot567$ Mg m^{-3}; Cu $K\alpha$ radiation, $\lambda = 1\cdot5418$ Å, $\mu = 6\cdot39$ mm^{-1}, $F(000) = 6686\cdot7$, $T = 291$ K; $R = 0\cdot047$ for 7347 reflections. The $[MoOS_3(CuCl)_3]^{2-}$ anion, co-crystallizing with a linear $[CuCl_2]^-$ anion as the tris-$[Ph_4P]^+$ salt, has a core of Mo, three S and three Cu atoms arranged on seven vertices of a trigonally distorted cube; the eighth vertex, diagonally opposite Mo, is unoccupied. Each S is bonded to Mo and two Cu; the oxo ligand is terminally bonded to Mo only.

Introduction. The title compound has been obtained as one product during studies of the preparation of $[MoS_4(CuX)_n]^{2-}$ complexes (X = halide); Cu—Mo—S systems are believed to be relevant to the biological antagonism between copper and molybdenum, which leads to copper deficiency in ruminant animals (Mills, Bremner, El-Gallad, Dalgarno & Young, 1978; Mills, 1979; Acott, Garner, Nicholson & Clegg, 1983).

Experimental. Reaction of $[Ph_4P]_2[MoS_4]$ with CuCl (1:4·3 molar ratio) in CH_3CN at room temperature gave three solid products. The first precipitate, with a Mo:Cu ratio of *ca* 1:4, has not yet been fully characterized; the second is $[Ph_4P]_2[MoS_4(CuCl)_3]$, obtained as its CH_3CN solvate and characterized by X-ray diffraction (Clegg, Garner & Nicholson, 1983). After separation of these and concentration and cooling of the filtrate, the third product was obtained as

---

* IUPAC name: tris(tetraphenylphosphonium) dichlorocuprate(I) oxo[1,2,3-trichloro-1,2;2,3;3,1-tri-μ-thio-tricuprato(I)-S^1,S^2,S^3]molybdate.

0108-2701/83/081007-03$01.50

bright-red single crystals. Chemical-analysis figures were in agreement with the structure reported here.

Data collection: crystal 0·66 × 0·45 × 0·23 mm, Nicolet $P2_1$ diffractometer, unit-cell parameters derived from 15 reflections with $44 < 2\theta < 52°$, intensities measured in $\omega/2\theta$ scan mode for 12647 reflections with $3 < 2\theta < 125°$ (*hkl* range: *h* 0–15, *k* 0–20, *l* 0–64); no significant intensity variation for three standard reflections.

Data reduction: empirical absorption correction based on 498 azimuthal scan data (R_{int} reduced from 0·147 to 0·030); relative transmission 0·423–1·000. 11017 unique reflections ($R_{\text{int}} = 0{\cdot}007$), 7347 with $F > 4\sigma(F)$.

Structure solution and refinement: automatic direct methods, difference syntheses. Blocked-cascade refinement on *F*, $w^{-1} = \sigma^2(F) + 0{\cdot}00092F^2$. Phenyl groups as rigid hexagons with 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; $U(\text{H}) = 1{\cdot}2U_{\text{eq}}(\text{C})$. Isotropic extinction correction $F_c' = F_c/(1 + xF_c^2/\sin 2\theta)^{1/4}$ with $x = 2{\cdot}2\,(2) \times 10^{-7}$. Scattering factors from *International Tables for X-ray Crystallography* (1974). 659 parameters, $R = 0{\cdot}047$, $wR = 0{\cdot}059$, slope of normal probability plot = 1·02. Maximum (shift/e.s.d.) = 0·07, mean = 0·02. Largest peak in final difference map = 0·44 e Å^{-3}, largest trough = –0·80 e Å^{-3}.

Programs: *SHELXTL* system (Sheldrick, 1978).

Discussion. Atomic coordinates, and bond lengths and angles for the anions, are given in Tables 1 and 2.* The $[MoOS_3(CuCl)_3]^{2-}$ anion is shown in Fig. 1.

The conversion of the original MoS_4^{2-} anion to a $MoOS_3^{2-}$ unit in the title compound is presumably due to reaction with atmospheric oxygen; no special precautions were taken to exclude this, and the compound is the third product of the reaction.

The $[MoOS_3(CuCl)_3]^{2-}$ anion contains a central core of Mo, three S and three Cu atoms, arranged on seven of the vertices of a distorted cube of edge 2·26 (2) Å. The eighth vertex, opposite Mo, is vacant. The distortion of the cube is a trigonal compression along the Mo-vacancy diagonal. Thus, the $MoCuS_2$ faces are rhombs with angles at S of 71·6 (1)° and at Mo and Cu of 109·4 (1)°. The shorter diagonal of each face is a 2·641 (1) Å Mo···Cu distance, typical of these Cu—Mo—S systems (Gheller, Gazzana, Masters, Brownlee, O'Connor, Wedd, Rodgers & Snow, 1981; Müller, Dartmann, Römer, Clegg & Sheldrick, 1981; Müller, Bögge, Tölle, Jostes, Schimanski & Dartmann, 1980; Müller, Bögge & Schimanski, 1980; Acott, Garner, Nicholson & Clegg, 1983; Clegg, Garner & Nicholson,

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$)

$U_{\text{eq}} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix)

	x	*y*	*z*	U_{eq}
Mo	3922 (1)	–165 (1)	1984 (1)	524 (2)
O	3880 (3)	–442 (3)	2268 (1)	885 (21)
S(1)	5485 (1)	29 (1)	1870 (1)	550 (5)
S(2)	3273 (1)	–1024 (1)	1737 (1)	616 (5)
S(3)	3089 (1)	914 (1)	1927 (1)	587 (5)
Cu(1)	4635 (1)	1075 (1)	1806 (1)	559 (3)
Cl(1)	5180 (1)	2084 (1)	1652 (1)	677 (6)
Cu(2)	4831 (1)	–837 (1)	1635 (1)	570 (3)
Cl(2)	5647 (1)	–1429 (1)	1372 (1)	826 (7)
Cu(3)	2402 (1)	24 (1)	1705 (1)	553 (3)
Cl(3)	1099 (1)	151 (1)	1497 (1)	718 (6)
Cu(4)	2616 (1)	1658 (1)	89 (1)	646 (3)
Cl(4)	1390 (1)	1892 (1)	–118 (1)	786 (7)
Cl(5)	3826 (1)	1388 (1)	295 (1)	805 (7)
P(1)	8045 (1)	2837 (1)	2287 (1)	394 (4)
C(112)	8918 (3)	3924 (2)	2553 (1)	553 (21)
C(113)	9290	4227	2760	638 (23)
C(114)	9183	3845	2971	607 (23)
C(115)	8704	3161	2976	545 (21)
C(116)	8332	2859	2769	468 (19)
C(111)	8439	3240	2557	401 (17)
C(122)	7033 (3)	4137 (2)	2206 (1)	494 (19)
C(123)	6640	4689	2062	636 (24)
C(124)	6772	4657	1820	685 (25)
C(125)	7297	4071	1720	750 (27)
C(126)	7690	3519	1864	562 (22)
C(121)	7558	3552	2107	379 (16)
C(132)	6185 (2)	2248 (2)	2275 (1)	474 (19)
C(133)	5488	1702	2320	530 (21)
C(134)	5761	1042	2431	565 (22)
C(135)	6730	928	2496	589 (21)
C(136)	7427	1474	2451	485 (19)
C(131)	7155	2134	2340	403 (17)
C(142)	8915 (2)	1783 (2)	2002 (1)	556 (21)
C(143)	9700	1474	1881	665 (25)
C(144)	10625	1792	1901	671 (25)
C(145)	10764	2418	2041	672 (25)
C(146)	9978	2727	2162	533 (21)
C(141)	9053	2410	2143	402 (17)
P(2)	1517 (1)	3749 (1)	757 (1)	425 (4)
C(212)	3077 (3)	3312 (2)	488 (1)	597 (22)
C(213)	3773	3397	312	667 (25)
C(214)	3820	4059	184	735 (28)
C(215)	3171	4635	234	726 (27)
C(216)	2475	4550	410	582 (22)
C(211)	2428	3889	538	440 (18)
C(222)	548 (3)	5085 (2)	753 (1)	541 (20)
C(223)	276	5773	846	655 (24)
C(224)	595	5983	1068	609 (23)
C(225)	1186	5506	1199	611 (23)
C(226)	1458	4818	1106	520 (20)
C(221)	1139	4608	884	408 (17)
C(232)	2938 (3)	3352 (2)	1071 (1)	631 (23)
C(233)	3318	2946	1259	780 (29)
C(234)	2780	2364	1356	807 (30)
C(235)	1863	2188	1266	740 (27)
C(236)	1484	2594	1079	591 (22)
C(231)	2021	3176	981	477 (19)
C(242)	–379 (3)	3263 (2)	753 (1)	586 (22)
C(243)	–1209	2958	649	661 (25)
C(244)	1186	2736	415	689 (26)
C(245)	–333	2821	284	633 (24)
C(246)	496	3126	388	528 (20)
C(241)	473	3348	622	450 (18)
P(3)	8520 (1)	116 (1)	811 (1)	441 (4)
C(312)	8660 (2)	1171 (2)	1163 (1)	637 (23)
C(313)	8308	1563	1356	751 (27)
C(314)	7387	1402	1447	708 (26)
C(315)	6818	848	1344	648 (24)
C(316)	7170	455	1151	572 (22)
C(311)	8091	617	1060	455 (18)
C(322)	8286 (4)	–1149 (2)	1084 (1)	1005 (35)
C(323)	8403	–1905	1131	1201 (41)
C(324)	8876	–2361	969	806 (29)
C(325)	9233	–2062	760	805 (29)
C(326)	9116	–1306	713	692 (25)
C(321)	8643	–850	875	472 (19)
C(332)	10450 (3)	341 (2)	893 (1)	607 (23)
C(333)	11361	661	853	694 (26)
C(334)	11513	1094	653	820 (30)
C(335)	10754	1208	494	702 (26)
C(336)	9843	888	534	581 (22)
C(331)	9691	455	734	471 (19)
C(342)	7333 (3)	994 (2)	544 (1)	599 (23)
C(343)	6642	1139	370	730 (27)
C(344)	6271	557	235	708 (27)

---

* Tables of structure factors, anisotropic thermal parameters, H-atom parameters and cation geometry have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38544 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1 (*cont.*)

	x	y	z	U_{eq}
C(345)	6590	−169	273	706 (26)
C(346)	7280	−313	447	607 (22)
C(341)	7651	268	582	461 (18)

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

Mo–Cu(1)	2·640 (1)	Mo–Cu(2)	2·640 (1)
Mo–Cu(3)	2·643 (1)	Mo–O	1·693 (4)
Mo–S(1)	2·267 (2)	Mo–S(2)	2·273 (2)
Mo–S(3)	2·276 (2)	Cu(1)–S(1)	2·245 (2)
Cu(2)–S(1)	2·242 (2)	Cu(2)–S(2)	2·239 (2)
Cu(3)–S(2)	2·240 (2)	Cu(1)–S(3)	2·249 (2)
Cu(3)–S(3)	2·247 (2)	Cu(1)–Cl(1)	2·151 (2)
Cu(2)–Cl(2)	2·151 (2)	Cu(3)–Cl(3)	2·156 (2)
Cu(4)–Cl(4)	2·095 (2)	Cu(4)–Cl(5)	2·091 (2)
O–Mo–S(1)	110·5 (2)	O–Mo–S(2)	112·3 (2)
S(1)–Mo–S(2)	107·3 (1)	O–Mo–S(3)	111·7 (2)
S(1)–Mo–S(3)	107·6 (1)	S(2)–Mo–S(3)	107·2 (1)
S(1)–Cu(1)–S(3)	109·3 (1)	S(1)–Cu(1)–Cl(1)	126·4 (1)
S(3)–Cu(1)–Cl(1)	124·2 (1)	S(1)–Cu(2)–S(2)	109·4 (1)
S(1)–Cu(2)–Cl(2)	123·5 (1)	S(2)–Cu(2)–Cl(2)	127·0 (1)
S(2)–Cu(3)–S(3)	109·3 (1)	S(2)–Cu(3)–Cl(3)	125·1 (1)
S(3)–Cu(3)–Cl(3)	125·5 (1)	Mo–S(1)–Cu(1)	71·6 (1)
Mo–S(1)–Cu(2)	71·7 (1)	Cu(1)–S(1)–Cu(2)	106·1 (1)
Mo–S(2)–Cu(2)	71·6 (1)	Mo–S(2)–Cu(3)	71·7 (1)
Cu(2)–S(2)–Cu(3)	111·2 (1)	Mo–S(3)–Cu(1)	71·4 (1)
Mo–S(3)–Cu(3)	71·5 (1)	Cu(1)–S(3)–Cu(3)	108·3 (1)
Cl(4)–Cu(4)–Cl(5)	178·1 (1)		

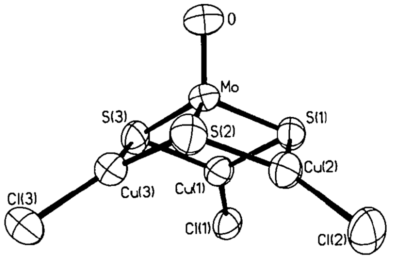

Fig. 1. Structure of the $[MoOS_3(CuCl)_3]^{2-}$ anion. Thermal motion is represented as 50% probability ellipsoids.

1983). The oxo ligand is bonded terminally to Mo only, with no Cu–O bonding. The apparent clear preference for Cu^I to bond to S rather than O produces the pyramidal $MoCu_3$ arrangement described here, in contrast to the planar T-shaped $MoCu_3$ arrangement in the $[MoS_4(CuCl)_3]^{2-}$ anion (Clegg, Garner & Nicholson, 1983). Although the MoS_4^{2-} unit has six S···S edges available for bridging by Cu^I (complexes with up to three bridges have so far been crystallographically characterized), the $MoOS_3^{2-}$ unit provides only three such edges, and the anion described here seems to represent the maximum attainable Mo:Cu ratio in this case; additional Cu^I does not bridge a S···O edge, but co-precipitates as the $[CuCl_2]^-$ anion from a solution containing a high Cu:Mo ratio (particularly in this reaction after separation of the major products). The $[MoOS_3(CuCl)_3]^{2-}$ anion can be obtained in high yield from the reaction of $[MoOS_3]^{2-}$ with CuCl (1:3 molar ratio).

The structure of the $[MoOS_3(CuCl)_3]^{2-}$ anion resembles that of $MoOS_3(CuPPh_3)_3Cl$ (Müller, Bögge & Schimanski, 1980, 1983), except that the latter has the eighth vertex of the cubane-like core occupied by Cl, which bonds to all three Cu atoms. $[MoOS_3(CuCl)_3]^{2-}$ is converted to $MoOS_3(CuPPh_3)_3Cl$ by addition of PPh_3 (1:3 molar ratio).

The three chemically equivalent Mo–S bonds in the $[MoOS_3(CuCl)_3]^{2-}$ anion are all essentially equal, in contrast to those in $[MoS_4(CuCl)_3]^{2-}$ (Clegg, Garner & Nicholson, 1983), which contains two doubly-bridging and two-triply bridging S atoms. Cu–S and Cu–Cl bonds are comparable in the two anions; the Cu–Cl bonds in the $[CuCl_2]^-$ anion are shorter, as expected for two-coordinate as against three-coordinate Cu. The $[CuCl_2]^-$ ion is essentially linear and symmetrical, and is well separated from the $[MoOS_3(CuCl)_3]^{2-}$ anion (shortest distance > 8 Å).

We thank the SERC and the Verband der Chemischen Industrie for financial support.

Note added in proof: The direct preparation and crystal structure of $[Ph_4P]_2[MoOS_3(CuCl)_3]$ have been reported (Müller, Schimanski & Schimanski, 1983). The geometry of the anion is essentially the same as that described here.

References

Acott, S. R., Garner, C. D., Nicholson, J. R. & Clegg, W. (1983). *J. Chem. Soc. Dalton Trans.* pp. 713–719.

Clegg, W., Garner, C. D. & Nicholson, J. R. (1983). *Acta Cryst.* C**39**, 552–554.

Gheller, S. F., Gazzana, P. A., Masters, A. F., Brownlee, R. T. C., O'Connor, M. J., Wedd, A. G., Rodgers, J. R. & Snow, M. R. (1981). *Inorg. Chim. Acta*, **54**, L131–L132.

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. & Schimanski, U. (1983). *Inorg. Chim. Acta*, **69**, 5–16.

Müller, A., Bögge, H., Tölle, H. G., Jostes, R., Schimanski, U. & Dartmann, M. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 654–655.

Müller, A., Dartmann, M., Römer, C., Clegg, W. & Sheldrick, G. M. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 1060–1061.

Müller, A., Schimanski, U. & Schimanski, J. (1983). *Inorg. Chim. Acta*, **76**, L245–L246.

Sheldrick, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.