Related literature. The structure of the triclinic form of $[Cu_2Cl_4(H_2O)_2$(pyridine *N*-oxide)$_2]$ has been reported by both Estes & Hodgson (1976) and Paulson, Krost, McPherson, Rogers & Atwood (1980). The main differences in the three structures are the Cu—OH_2 and Cu—O(pyridine *N*-oxide) distances. A copper complex of the starting material 2,6-pyridinedicarboxylic acid has been prepared by Nathan, Doyle, Mooring, Zapren, Larsen & Pierpont (1985) but no structural study was reported.

We thank the Center for Instructional Research Computing Activities, University of Florida, for a generous grant of computer time. Purchase of the Nicolet Instrumentation was funded in part by the NSF grant CHE 8316675.

References

ESTES, E. D. & HODGSON, D. J. (1976). *Inorg. Chem.* **15**, 348–351.
NATHAN, L. C., DOYLE, C. A., MOORING, A. M., ZAPREN, D. C., LARSEN, S. K. & PIERPONT, C. G. (1985). *Inorg. Chem.* **24**, 2763–2766.
PAULSON, J. A., KROST, D. A., MCPHERSON, G. L., ROGERS, R. D. & ATWOOD, J. L. (1980). *Inorg. Chem.* **19**, 2519–2525.
SHELDRICK, G. M. (1983). *SHELXTL User's Manual*, revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Acta Cryst. (1988). C**44**, 170–172

Structure of Bis(tetraphenylphosphonium) Tris[isothiocyanatocopper(I)]oxotrithiomolybdate(VI)*

BY WILLIAM CLEGG

Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, England

AND AZIZOLLA BEHESHTI AND C. DAVID GARNER

Chemistry Department, The University, Manchester M13 9PL, England

(*Received* 15 *July* 1987; *accepted* 3 *September* 1987)

Abstract. $[P(C_6H_5)_4]_2[MoOS_3\{Cu(NCS)\}_3]$, $Mr = 1251{\cdot}8$, triclinic, $P\bar{1}$, $a = 12{\cdot}480\ (2)$, $b = 12{\cdot}930\ (2)$, $c = 18{\cdot}646\ (2)$ Å, $\alpha = 83{\cdot}944\ (5)$, $\beta = 73{\cdot}177\ (6)$, $\gamma = 65{\cdot}188\ (6)°$, $V = 2613{\cdot}8$ Å^3, $Z = 2$, $D_x = 1{\cdot}590$ Mg m^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71073$ Å, $\mu = 1{\cdot}77$ mm^{-1}, $F(000) = 1260$, $T = 293$ K, $R = 0{\cdot}0392$ for 4965 unique reflections with $F > 4\sigma(F)$. The $[MoOS_3(CuNCS)_3]^{2-}$ anion has an MoS_3Cu_3 core with atoms at seven vertices of a trigonally distorted cube; the eighth vertex, opposite Mo, is vacant. Mo is tetrahedrally coordinated by one terminal O^{2-} ligand and by three bridging S^{2-} ligands, each of which also bonds to two Cu atoms. Two of the Cu atoms show trigonal-planar coordination by two S^{2-} and one NCS^- ligand bonded *via* N. The third Cu atom has distorted tetrahedral coordination, the fourth ligand atom being S of an NCS^- ligand of a neighbouring anion. Thus anions are linked by pairs of Cu—NCS—Cu bridges to form centrosymmetric dimers. The Mo—O bond length is 1·728 (5) Å; Mo—S range from 2·632 (1) to 2·668 (2) Å, Cu—S from 2·238 (2) to 2·279 (2) Å, Cu—N from 1·866 (5) to 1·893 (5) Å, Mo···Cu from 2·632 (1) to 2·668 (2) Å; Cu—SNC is 2·711 (2) Å. Bonds involving four-coordinate Cu are somewhat longer than those for three-coordinate Cu. The CuNCS linkages are essentially linear at C and only slightly bent at N, but Cu—S—CN for the bridging ligand is 122·0 (2)°.

Experimental. The compound was obtained by reaction of CuSCN with $[P(C_6H_5)_4]_2[MoOS_3]$ (3:1 molar ratio) in acetone solution and recrystallized from dichloromethane. Crystal size 0·19 × 0·27 × 0·50 mm, Siemens AED2 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, cell parameters from 2θ values (20–22°) of 32 reflections measured on both sides of the direct beam. Intensity-data collection in ω/θ scan mode, scan width = 0·51° below α_1 to 0·51° above α_2, scan time = 14–56 s, $2\theta_{max} = 45°$, h −13→0, k −13→13, l −20→20, no significant variation of three standard reflections, semi-empirical absorption correction, transmission 0·614–0·845, no extinction correction. 6837 reflections measured, all unique, 4965 with $F > 4\sigma(F)$ for structure solution by automatic direct methods and difference syntheses, blocked-cascade refinement on F with $w^{-1} = \sigma^2(F) + 0{\cdot}00003F^2$, anisotropic thermal parameters and constrained phenyl groups [C—C = 1·395, C—H = 0·96 Å, C—C—C =

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

0108-2701/88/010170-03$03.00

C–C–H = 120°, $U(H) = 1{\cdot}2U_{eq}(C)$]. 508 parameters, $R = 0{\cdot}0392$, $wR = 0{\cdot}0369$, mean $\Delta/\sigma = 0{\cdot}008$, max. = 0·028, max. $\Delta\rho = 0{\cdot}45$, min. = −0·42 e Å^{-3}, slope of normal probability plot = 1·68. Scattering factors from *International Tables for X-ray Crystallography* (1974); *SHELXTL* programs (Sheldrick, 1985).

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

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

	x	y	z	U_{eq}
Mo	3825·0 (4)	4334·5 (4)	2768·6 (2)	487 (2)
O	2769 (3)	4191 (3)	2403 (2)	685 (20)
Cu(1)	6192·9 (6)	3036·2 (6)	2423·4 (4)	594 (3)
N(1)	7779 (4)	1908 (4)	2066 (2)	675 (24)
C(1)	8627 (5)	1273 (4)	1653 (3)	560 (28)
S(1)	9825 (2)	415 (1)	1054 (1)	877 (9)
Cu(2)	3999·4 (7)	4269·1 (6)	4152·8 (4)	704 (4)
N(2)	3920 (5)	4348 (4)	5161 (3)	776 (29)
C(2)	3823 (5)	4517 (4)	5777 (3)	555 (27)
S(2)	3642 (1)	4775 (1)	6651 (1)	765 (8)
Cu(3)	4459·8 (7)	6076·5 (6)	2719·3 (4)	795 (4)
N(3)	4242 (4)	7599 (4)	2479 (3)	676 (26)
C(3)	3864 (5)	8566 (5)	2411 (3)	656 (32)
S(3)	3361 (2)	9918 (1)	2314 (1)	1342 (16)
S(4)	4786 (1)	2751 (1)	3384 (1)	580 (7)
S(5)	2914 (1)	5810 (1)	3589 (1)	621 (7)
S(6)	5294 (1)	4649 (1)	1844 (1)	567 (7)
P(1)	2690 (1)	3238 (1)	269 (1)	424 (6)
C(112)	1524 (3)	2319 (3)	−355 (2)	570 (29)
C(113)	1309	1941	−952	722 (35)
C(114)	1927	2066	−1687	767 (37)
C(115)	2760	2569	−1825	726 (34)
C(116)	2975	2947	−1228	600 (29)
C(111)	2357	2822	−493	450 (24)
C(122)	1873 (3)	5394 (3)	−293 (2)	586 (29)
C(123)	1781	6510	−385	712 (32)
C(124)	2489	6854	−89	722 (34)
C(125)	3289	6081	299	676 (33)
C(126)	3382	4964	390	527 (27)
C(121)	2674	4621	94	448 (24)
C(132)	4395 (3)	2150 (3)	1065 (2)	627 (31)
C(133)	5556	1428	1141	762 (37)
C(134)	6469	798	523	832 (39)
C(135)	6221	890	−169	820 (36)
C(136)	5060	1612	−244	680 (32)
C(131)	4147	2242	373	451 (25)
C(142)	517 (3)	4332 (2)	1350 (2)	512 (27)
C(143)	−458	4356	1958	615 (29)
C(144)	−437	3347	2317	642 (32)
C(145)	560	2316	2068	625 (31)
C(146)	1535	2292	1460	508 (26)
C(141)	1514	3301	1101	395 (23)
P(2)	8376 (1)	8810 (1)	4305 (1)	406 (6)
C(212)	8358 (3)	10446 (3)	5168 (2)	565 (29)
C(213)	8132	11559	5333	728 (35)
C(214)	7759	12427	4830	744 (35)
C(215)	7612	12182	4163	729 (36)
C(216)	7837	11070	3998	632 (32)
C(211)	8210	10202	4501	417 (23)
C(222)	9645 (4)	7272 (3)	3146 (2)	747 (33)
C(223)	10546	6809	2480	1180 (47)
C(224)	11321	7342	2122	1380 (61)
C(225)	11196	8338	2430	1177 (51)
C(226)	10296	8800	3096	765 (34)
C(221)	9520	8267	3453	541 (27)
C(232)	6271 (3)	8381 (3)	4665 (2)	577 (28)
C(233)	5210	8427	4529	668 (32)
C(234)	4859	8976	3897	615 (30)
C(235)	5569	9479	3401	668 (32)
C(236)	6630	9433	3537	612 (31)
C(231)	6981	8884	4169	405 (23)
C(242)	7996 (2)	8126 (2)	5782 (2)	542 (27)
C(243)	8293	7375	6358	677 (34)
C(244)	9357	6369	6207	744 (37)
C(245)	10124	6114	5479	690 (32)
C(246)	9827	6865	4902	544 (28)
C(241)	8763	7871	5053	399 (24)

Atomic parameters are given in Table 1,* selected bond distances and angles in Table 2. Atomic numbering for the anion is shown in Fig. 1.

Related literature. The MoS_3Cu_3 core with a terminal Mo=O bond is found also in $[MoOS_3(CuCl)_3]^{2-}$ (Müller, Schimanski & Schimanski, 1983; Clegg, Garner, Nicholson & Raithby, 1983). CuNCS is attached to a WS_4^{2-} central unit in $[WS_4(CuNCS)_4]^{2-}$ (Manoli, Potvin, Secheresse & Marzak, 1986): here all the NCS^- ligands are involved in bridging between Cu

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44331 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Mo–Cu(1)	2·632 (1)	Mo–Cu(2)	2·642 (1)
Mo–Cu(3)	2·668 (2)	Mo–O	1·728 (5)
Mo–S(4)	2·277 (2)	Mo–S(5)	2·250 (2)
Mo–S(6)	2·269 (2)	Cu(1)–N(1)	1·873 (4)
Cu(1)–S(4)	2·238 (2)	Cu(1)–S(6)	2·244 (2)
N(1)–C(1)	1·149 (6)	C(1)–S(1)	1·618 (5)
Cu(2)–N(2)	1·866 (5)	Cu(2)–S(4)	2·244 (2)
Cu(2)–S(5)	2·243 (2)	N(2)–C(2)	1·153 (8)
C(2)–S(2)	1·631 (7)	Cu(3)–N(3)	1·893 (5)
Cu(3)–S(5)	2·258 (2)	Cu(3)–S(6)	2·279 (2)
Cu(3)–S(2^i)	2·711 (2)	N(3)–C(3)	1·144 (8)
C(3)–S(3)	1·601 (7)		

O–Mo–S(4)	112·3 (1)	O–Mo–S(5)	111·0 (1)
S(4)–Mo–S(5)	107·3 (1)	O–Mo–S(6)	110·7 (1)
S(4)–Mo–S(6)	107·4 (1)	S(5)–Mo–S(6)	108·0 (1)
N(1)–Cu(1)–S(4)	122·5 (2)	N(1)–Cu(1)–S(6)	126·6 (1)
S(4)–Cu(1)–S(6)	109·7 (1)	Cu(1)–N(1)–C(1)	158·9 (5)
N(1)–C(1)–S(1)	178·0 (5)	N(2)–Cu(2)–S(4)	130·2 (2)
N(2)–Cu(2)–S(5)	120·2 (1)	S(4)–Cu(2)–S(5)	108·7 (1)
Cu(2)–N(2)–C(2)	172·9 (5)	N(2)–C(2)–S(2)	178·3 (5)
C(2)–S(2)–Cu(3^i)	122·0 (2)	N(3)–Cu(3)–S(5)	117·3 (1)
N(3)–Cu(3)–S(6)	123·4 (1)	S(5)–Cu(3)–S(6)	107·3 (1)
N(3)–Cu(3)–S(2^i)	105·3 (2)	S(5)–Cu(3)–S(2^i)	104·3 (1)
S(6)–Cu(3)–S(2^i)	95·0 (1)	Cu(3)–N(3)–C(3)	165·9 (5)
N(3)–C(3)–S(3)	178·9 (7)	Mo–S(4)–Cu(1)	71·3 (1)
Mo–S(4)–Cu(2)	71·5 (1)	Cu(1)–S(4)–Cu(2)	105·6 (1)
Mo–S(5)–Cu(2)	72·0 (1)	Mo–S(5)–Cu(3)	72·6 (1)
Cu(2)–S(5)–Cu(3)	99·8 (1)	Mo–S(6)–Cu(1)	71·4 (1)
Mo–S(6)–Cu(3)	71·9 (1)	Cu(1)–S(6)–Cu(3)	106·1 (1)

Symmetry operator: (i) 1−x, 1−y, 1−z.

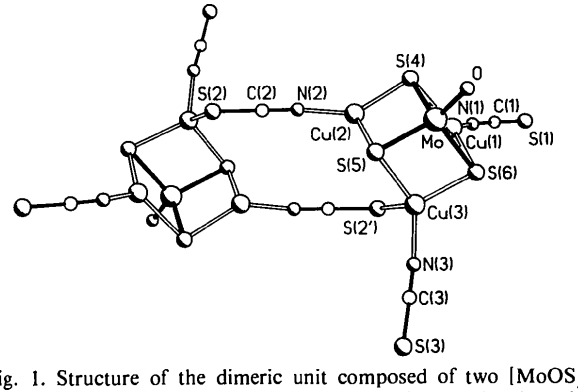

Fig. 1. Structure of the dimeric unit composed of two $[MoOS_3(CuNCS)_3]^{2-}$ anions linked by NCS bridges, showing the atom-labelling scheme.

atoms, to give a polymeric anion structure. More restricted bridging between Cu atoms by chloride ligands is observed in $[MoS_4(CuCl)_4]^{2-}$, to give a chain polymer (Nicholson, Flood, Garner & Clegg, 1983), and in $[WS_4(CuCl)_4]^{2-}$, to give dimeric units (Clegg, Scattergood & Garner, 1987).

We thank the SERC for financial support.

References

CLEGG, W., GARNER, C. D., NICHOLSON, J. R. & RAITHBY, P. R. (1983). *Acta Cryst.* C**39**, 1007–1009.

CLEGG, W., SCATTERGOOD, C. D. & GARNER, C. D. (1987). *Acta Cryst.* C**43**, 786–787.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 99, 149. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

MANOLI, J. M., POTVIN, C., SECHERESSE, F. & MARZAK, S. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1557–1558.

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

NICHOLSON, J. R., FLOOD, A. C., GARNER, C. D. & CLEGG, W. (1983). *J. Chem. Soc. Chem. Commun.* pp. 1179–1180.

SHELDRICK, G. M. (1985). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Revision 5. Univ. of Göttingen, Federal Republic of Germany.

Acta Cryst. (1988). C**44**, 172–174

Structures of Tetraphenylphosphonium Bis(ethane-1,2-dithiolato)oxorhenium(V) and Tetraphenylphosphonium Bis(benzene-1,2-dithiolato)oxorhenium(V)

BY WILLIAM CLEGG

Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, England

AND STEPHEN BOYDE AND C. DAVID GARNER

Chemistry Department, The University, Manchester M13 9PL, England

(*Received* 15 *July* 1987; *accepted* 3 *September* 1987)

Abstract. (1): $[P(C_6H_5)_4][ReO(C_2H_4S_2)_2]$, $M_r = 726{\cdot}0$, orthorhombic, *Pbca*, $a = 19{\cdot}650\ (1)$, $b = 18{\cdot}679\ (1)$, $c = 15{\cdot}104\ (1)$ Å, $V = 5543{\cdot}8$ Å^3, $Z = 8$, $D_x = 1{\cdot}739$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 4{\cdot}81$ mm^{-1}, $F(000) = 2864$, $T = 293$ K, $R = 0{\cdot}0279$ for 2935 unique reflections with $F > 4\sigma(F)$. (2): $[P(C_6H_5)_4][ReO(C_6H_4S_2)_2]$, $M_r = 822{\cdot}0$, monoclinic, *Cc*, $a = 12{\cdot}511\ (1)$, $b = 15{\cdot}749\ (2)$, $c = 16{\cdot}581\ (2)$ Å, $\beta = 93{\cdot}55\ (1)°$, $V = 3260{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}674$ Mg m^{-3}, $\mu(\text{Mo } K\alpha) = 4{\cdot}10$ mm^{-1}, $F(000) = 1624$, $T = 293$ K, $R = 0{\cdot}0253$ for 5431 unique reflections with $F > 4\sigma(F)$. In both anions, Re has square-based pyramidal coordination with axial O^{2-} and the bidentate edt^{2-} ($=C_2H_4S_2^{2-}$) and bdt^{2-} ($=C_6H_4S_2^{2-}$) ligands in basal positions. Mean bond lengths for (1) are: Re—O = 1·673 (4), Re—S = 2·308 (10) Å; for (2): Re—O = 1·663 (4), Re—S = 2·315 (3) Å, the Re—S distances showing significant variations within the anion of (1).

Experimental. The compounds were obtained by reaction of $[ReOCl_3(PPh_3)_2]$ with H_2edt or H_2bdt in MeOH/Et_3N solution, followed by addition of $[PPh_4]$-Br, and were recrystallized from CH_2Cl_2/Et_2O. Crystals were mounted in air on glass fibres and examined on a Siemens AED2 diffractometer with graphite-monochromated Mo $K\alpha$ radiation.

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

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

	x	y	z	U_{eq}
Re	5347·9 (1)	7948·5 (1)	4302·9 (2)	399 (1)
O	5509 (3)	7183 (2)	4837 (3)	745 (19)
S(1)	5971 (1)	8020 (1)	3010 (1)	634 (6)
S(2)	4435 (1)	7714 (1)	3375 (1)	548 (6)
S(3)	4571 (1)	8615 (1)	5077 (1)	637 (6)
S(4)	6124 (1)	8793 (1)	4785 (1)	780 (8)
C(1)	5426 (4)	7694 (5)	2127 (5)	933 (36)
C(2)	4828 (4)	7327 (5)	2406 (5)	876 (34)
C(3)	5021 (4)	9214 (4)	5815 (4)	692 (28)
C(4)	5757 (4)	9205 (5)	5748 (5)	956 (37)
P	3499 (1)	5361 (1)	3895 (1)	374 (5)
C(11)	3363 (3)	5820 (3)	4924 (3)	383 (19)
C(12)	2959 (3)	5518 (3)	5579 (4)	517 (22)
C(13)	2813 (3)	5902 (3)	6328 (4)	627 (25)
C(14)	3067 (4)	6582 (4)	6439 (5)	735 (30)
C(15)	3458 (4)	6887 (3)	5792 (4)	648 (27)
C(16)	3610 (3)	6518 (3)	5025 (4)	550 (24)
C(21)	3102 (3)	5882 (3)	3033 (3)	406 (20)
C(22)	3305 (3)	5809 (3)	2158 (4)	544 (23)
C(23)	2953 (3)	6174 (4)	1506 (4)	652 (27)
C(24)	2409 (4)	6599 (4)	1714 (5)	637 (28)
C(25)	2207 (3)	6669 (4)	2579 (4)	642 (26)
C(26)	2554 (3)	6316 (3)	3241 (4)	572 (23)
C(31)	3075 (3)	4509 (3)	3939 (3)	382 (19)
C(32)	3404 (3)	3896 (3)	4228 (4)	445 (20)
C(33)	3041 (3)	3261 (3)	4299 (4)	537 (22)
C(34)	2365 (3)	3242 (3)	4088 (4)	542 (24)
C(35)	2039 (3)	3851 (3)	3797 (4)	534 (22)
C(36)	2392 (3)	4484 (3)	3725 (4)	485 (22)
C(41)	4379 (3)	5235 (3)	3628 (4)	400 (19)
C(42)	4888 (3)	5662 (3)	3978 (4)	488 (21)
C(43)	5545 (3)	5593 (4)	3689 (4)	615 (26)
C(44)	5707 (3)	5100 (4)	3061 (4)	586 (25)
C(45)	5216 (3)	4661 (3)	2711 (4)	593 (25)
C(46)	4547 (3)	4727 (3)	2993 (4)	478 (21)

0108-2701/88/010172-03$03.00