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Crystal and Molecular Structure of $((C_6H_5)_3P)_2$-$CuS_2MoS_2CuP(C_6H_5)_3 \cdot 0.8CH_2Cl_2$, a Compound with a Doubly Bridging MoS_4^{2-}-Ligand between Cu-Centers

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The MoS_4^{2-} ion, which was first used by us as a ligand [1] in transition metal complexes plays a key role in some biological processes [2–5]. Zumft has shown that acid treatment of the FeMo protein of C. pasteurianum leads to MoS_4^{2-} [5]. On the other hand Cu^{n+}/MoS_4^{2-} interactions have been claimed to be responsible for the Mo–Cu antagonism in biological processes [2–4]. The MoS_4^{2-} anion is the most effective antagonist of the copper metabolism [4]. In this paper we report the crystal and molecular structure of the title compound which is interesting as a model or Cu^{n+}/MoS_4^{2-} interactions. It is now evident that the MoS_4^{2-} ligand can act as a doubly and triply bridging one between Cu centers.

Experimental

Intensity data were collected from a crystal (0.15 × 0.3 × 0.5 mm) of $(PPh_3)_3Cu_2MoS_4 \cdot 0.8CH_2Cl_2$ with a Syntex $P2_1$ four circle diffractometer. Single crystals were obtained with the method described in [6].

$C_{54}H_{45}Cu_2MoP_3S_4 \cdot 0.8CH_2Cl_2$; monoclinic, space group $P2_1/c$: a = 18.394(4), b = 16.653(3), c = 17.714(3) Å, β = 95.53(1)°, V = 5400.9 Å^3; Z = 4, D_c = 1.48 g cm^{-3}; μ(Mo-K$_\alpha$) = 13.9 cm^{-1} The structure was solved by heavy atom methods. Least squares refinements (the phenyl rings being treated as regular hexagons, C–C = 1.395 Å) converged to R = 0.089 for 3699 independent reflexes ($4° \leqslant 2\theta \leqslant 45°$; $I \geqslant 1.96\sigma(I)$). Disordered solvent molecules at occupancy 0.8 were included in the calculations (see Table I; in contrast to the pseudo-isostructural compound $(PPh_3)_3Ag_2WS_4$ [7] where solvent molecules of CH_2Cl_2 at lower occupancy were distributed over several positions which did not allow the location). Empirical absorption, Lorentz, polarization and anomalous dispersion corrections were applied.

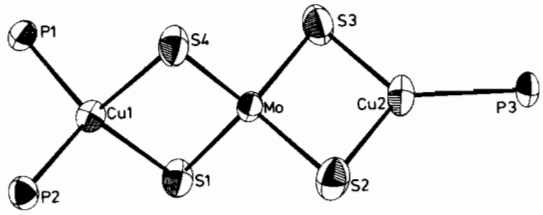

Fig. 1. Molecular structure of $(PPh_3)_3Cu_2MoS_4 \cdot 0.8CH_2Cl_2$; phenyl rings have been omitted for clarity. Mo···Cu1 = 2.775(2), Mo···Cu2 = 2.642(3), Mo–S1 = 2.204(5), Mo–S2 = 2.217(5), Mo–S3 = 2.219(5), Mo–S4 = 2.192(5), Cu1–S1 = 2.311(5), Cu1–S4 = 2.315(6), Cu2–S2 = 2.228(5), Cu2–S3 = 2.212(5), Cu1–P1 = 2.310(5), Cu1–P2 = 2.295(5), Cu2–P3 = 2.210(5) A.

The positional and thermal parameters are summarized in Table I. Selected bond distances are given in Fig. 1, containing the ORTEP-plot.

Results and Discussion

The unit cell contains four $(PPh_3)_3Cu_2MoS_4$ molecules which are orientated nearly parallel to the b-axis. The P1, P2, Cu1, Mo, S2, S3, Cu2 and P3 atoms lie approximately in one plane and the Cu1···Mo···Cu2–P3 moiety is nearly linear (Cu1···Mo···Cu2 = 179.0(1), Mo···Cu2–P3 = 176.1(2)°). The Mo atom is tetrahedrally coordinated (107.0(2)–110.9(2)°). The compound contains two non-equivalent Cu atoms. The coordination polyhedron of Cu1 is a distorted tetrahedron (100.4(2)–118.0(2)°), while the coordination of Cu2 is nearly trigonally planar (106.9(2)–129.9(2)°).

Species containing Mo and Cu are interesting because of the interrelation of both metals in numerous biological processes (the so-called Mo–Cu antagonism). Polynuclear compounds containing Cu^+ and MoS_4^{2-} have a high formation tendency, the relative concentration of the reactants being the most important factor for the formation [6]. A corresponding compound with a cubane core and triply bridging MoS_4^{2-} ligands has also been characterized [8].

Acknowledgements

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TABLE I. Positional and Thermal (A^2) Parameters[a] for $(PPh_3)_3Cu_2MoS_4 \cdot 0.8CH_2Cl_2$[b] with Standard Deviations.

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
MO	0.2322(1)	0.4085(1)	0.1869(1)	2.45(9)	1.62(7)	2.68(9)	0.17(7)	0.47(8)	0.01(8)
CU1	0.1239(1)	0.2430(1)	0.1836(1)	2.63(13)	2.20(12)	2.82(13)	0.21(10)	0.21(10)	0.09(10)
CU2	0.2515(1)	0.5657(1)	0.1917(1)	4.45(16)	1.83(12)	3.62(14)	−0.02(11)	0.64(13)	−0.02(11)
S1	0.1671(3)	0.3376(3)	0.2612(3)	3.96(30)	2.35(24)	2.68(25)	0.07(21)	1.16(22)	0.10(21)
S2	0.1623(3)	0.4995(3)	0.1240(3)	4.60(34)	2.83(27)	3.69(27)	0.46(24)	−0.35(25)	0.50(23)
S3	0.3199(3)	0.4746(3)	0.2557(3)	3.93(32)	2.47(25)	4.33(30)	−0.60(23)	−0.62(26)	0.02(22)
S4	0.2783(3)	0.3253(3)	0.1083(3)	4.64(32)	2.24(23)	3.76(28)	0.04(24)	2.05(24)	−0.02(23)
P1	0.2941(3)	0.1664(3)	0.2620(3)	2.37(28)	2.04(24)	2.83(27)	0.39(21)	0.32(22)	0.21(21)
P2	0.1296(3)	0.1774(3)	0.1017(3)	2.83(28)	2.29(24)	2.79(26)	−0.17(23)	−0.10(22)	0.43(23)
P3	0.2640(3)	0.6976(3)	0.1877(3)	3.23(30)	1.37(24)	4.09(30)	−0.10(21)	0.70(25)	−0.49(21)

Atom	x	y	z	B	Atom	x	y	z	B
C1	0.2464(6)	0.0968(7)	0.3197(6)	2.3(4)	C30	0.1736(6)	0.0253(6)	0.0516(6)	3.4(4)
C2	0.2038(6)	0.1278(7)	0.3738(6)	2.6(4)	C31	0.0602(5)	0.1157(6)	0.1425(7)	1.9(4)
C3	0.1691(6)	0.0759(7)	0.4207(6)	2.9(4)	C32	0.0646(5)	0.1067(6)	0.2211(7)	3.2(4)
C4	0.1771(6)	−0.0070(7)	0.4135(6)	4.2(5)	C33	0.0135(5)	0.0594(6)	0.2539(7)	4.0(5)
C5	0.2198(6)	−0.0380(7)	0.3594(6)	5.6(6)	C34	−0.0419(5)	0.0210(6)	0.2081(7)	3.5(4)
C6	0.2545(6)	0.0139(7)	0.3125(6)	3.9(4)	C35	−0.0462(5)	0.0300(6)	0.1295(7)	5.0(5)
½7	0.3614(6)	0.1061(6)	0.2155(7)	3.3(4)	C36	0.0048(5)	0.0773(6)	0.0967(7)	3.8(5)
C8	0.4201(6)	0.0686(6)	0.2571(7)	2.9(4)	C37	0.2731(7)	0.7355(7)	0.0923(5)	3.1(4)
C9	0.4704(6)	0.0246(6)	0.2199(7)	3.9(5)	C38	0.2179(7)	0.7152(7)	0.0359(5)	4.6(5)
C10	0.4621(6)	0.0182(6)	0.1410(7)	4.8(5)	C39	0.2236(7)	0.7380(7)	−0.0391(5)	5.5(6)
C11	0.4034(6)	0.0557(6)	0.0994(7)	4.1(5)	C40	0.2844(7)	0.7811(7)	−0.0577(5)	4.2(5)
C12	0.3531(6)	0.0996(6)	0.1366(7)	3.9(5)	C41	0.3395(7)	0.8014(7)	−0.0014(5)	5.0(5)
C13	0.3551(6)	0.2247(6)	0.3315(7)	2.1(4)	C42	0.3339(7)	0.7786(7)	0.0736(5)	4.7(5)
C14	0.3570(6)	0.2170(6)	0.4101(7)	3.6(5)	C43	0.3413(5)	0.7410(7)	0.2485(6)	2.6(4)
C15	0.4072(6)	0.2613(6)	0.4572(7)	4.7(5)	C44	0.3985(5)	0.6901(7)	0.2749(6)	3.1(4)
C16	0.4555(6)	0.3133(6)	0.4259(7)	4.1(5)	C45	0.4570(5)	0.7200(7)	0.3227(6)	4.0(5)
C17	0.4536(6)	0.3211(6)	0.3473(7)	3.9(4)	C46	0.4584(5)	0.8006(7)	0.3440(6)	5.7(6)
C18	0.4035(6)	0.2768(6)	0.3001(7)	3.4(4)	C47	0.4013(5)	0.8515(7)	0.3176(6)	3.5(5)
C19	0.0723(6)	0.2450(7)	0.0373(7)	3.6(4)	C48	0.3427(5)	0.8216(7)	0.2698(6)	3.0(4)
C20	0.0485(6)	0.3155(7)	0.0697(7)	3.5(4)	C49	0.1844(5)	0.7519(7)	0.2158(6)	2.8(4)
C21	0.0029(6)	0.3683(7)	0.0262(7)	4.2(5)	C50	0.1421(5)	0.7161(7)	0.2678(6)	3.3(4)
C22	−0.0189(6)	0.3506(7)	−0.0496(7)	4.0(5)	C51	0.0815(5)	0.7564(7)	0.2908(6)	4.1(5)
C23	0.0050(6)	0.2801(7)	−0.0819(7)	5.3(5)	C52	0.0632(5)	0.8324(7)	0.2617(6)	3.9(4)
C24	0.0506(6)	0.2273(7)	−0.0385(7)	5.2(5)	C53	0.1055(5)	0.8681(7)	0.2097(6)	4.3(5)
C25	0.1739(6)	0.1079(6)	0.0386(6)	2.1(4)	C54	0.1661(5)	0.8278(7)	0.1867(6)	2.9(4)
C26	0.2126(6)	0.1392(6)	−0.0187(6)	4.0(5)	C	0.3630(8)	0.5546(16)	0.0351(22)	4.6(12)
C27	0.2508(6)	0.0879(6)	−0.0630(6)	4.7(5)	C′	0.4394(24)	0.4981(9)	0.0722(17)	6.9(15)
C28	0.2505(6)	0.0053(6)	−0.0499(6)	3.8(4)	CL1	0.4354(7)	0.5992(8)	0.0852(7)	17.4(5)
C29	0.2118(6)	−0.0260(6)	0.0074(6)	3.9(5)	CL2	0.3874(9)	0.4689(8)	−0.0077(9)	23.3(7)

[a]The anisotropic temperature factor used is defined as exp $[-¼(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$. [b]The carbon atom in the CH_2Cl_2 solvent molecule occupies two positions (C and C′), which were both defined with an occupancy factor of 0.4.

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