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Short Communications

Tetrathio-oxalate as Side-on Bridging Ligand. Crystal and Molecular Structure of μ-Tetrathiooxalato-bis[bis(triphenylphosphine)-copper(I)]

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Tetrathio-oxalate is the last member of series of the thiooxalate anions, which are promising multipurpose bridging ligands. It is available by coupling of two CS_2 molecules via electroreductive dimerization[1] *i.e.* electrosynthesis from CS_2 in acetonitrile.

Due to its molecular design and multisulfur ligator capacity, it forms a variety of finite and infinite oligo- and multinuclear homo- or heterometallic complexes.[2,3]

In the present paper we describe the crystal and molecular structure of $(Ph_3P)_2Cu\ C_2S_4$-$Cu(PPh_3)_2$.

Structure determination. Deep blue crystals were obtained by direct combination of $(Et_4N)_2C_2S_4$ (as water/pyridine solution) with a pyridine solution of $(Ph_3P)_3CuCl$ after subsequent addition of water.[3] Suitable crystals were obtained after dissolving the crude complex in methylenechloride (containing some dissolved triphenylphosphine), covering the solution with a isopropanol layer and keeping the solution for some days at 20 °C.[4]

The X-ray measurements were carried out on a computer controlled Enraf-Nonius CAD 4 diffractometer using graphite monochromatized Mo$K\alpha$ radiation (λ=0.71069 Å). The unit cell dimensions were determined by a least squares calculation from the 2θ values of 25 high order reflections at 20 °C. A crystal of dimensions 0.05×0.05×0.40mm was used for all X-ray measurements.

Crystal data. $C_{74}H_{60}Cu_2P_4S_4$ F.W.=1331.5 triclinic, space group $P\bar{1}$ deep blue needles a=10.219(4)Å, b=13.059(3)Å, c=13.529(3) Å, α=63.44(2)°, β=89.26(3)°, γ=78.49(2)°, V=1576.5Å^3, D_c=1.40 gcm^{-3}, D_m=1.38 gcm^{-3} (flotation), Z=1, μ=7.65 cm^{-1} (Mo$K\alpha$)

Intensity data for 5654 reflections were collected at 20 °C within $2\theta \leqq 55°$ by the $\omega-2\theta$ scan technique. After data reduction, including *Lp*-correction but no absorption correction, 3430 reflections with net intensity $I \geqq 2\sigma(I)$, were regarded as observed. The structure was solved by direct methods (MULTAN).[5] Structure refinement was carried out by means of program CRYLSQ of the X-RAY 76 program system.[6] The hydrogen positions were found from difference maps and the atomic parameters were refined by full matrix least squares to an R factor of 0.040. In the final cycle a total of 500 parameters were refined simultaneously in 7 blocks. The average shift/error was then 0.25 with a maximum shift/error of 1.4.

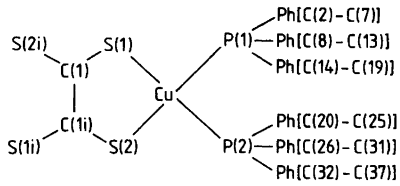

Fig. 1. Schematic drawing of the title compound showing the numbering of atoms. Atoms C(1i), S(1i) and S(2i) are over the inversion center.

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Table 1. Atomic coordinates and temperature parameters $\langle B \rangle$ (Å^2) for the non-hydrogen atoms. The coordinates for Cu, S and P are multiplied by 10^5 and for C by 10^4. $\langle B \rangle = 8\pi^2/3 \sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

ATOM	X	Y	Z	<B>
CU(1)	16870(7)	94612(6)	21114(6)	2.6
S(1)	21263(15)	97863(14)	3292(12)	3.1
S(2)	-4942(15)	95523(15)	16902(12)	3.2
P(1)	28936(15)	76668(13)	33104(12)	2.4
P(2)	18755(15)	111752(13)	21457(12)	2.5
C(1)	629(5)	10048(5)	-317(5)	2.6
C(1i)	-629(5)	9952(5)	317(5)	2.6
C(2)	3021(5)	7283(5)	4782(4)	2.5
C(3)	3153(6)	8150(5)	5093(5)	3.3
C(4)	3299(7)	7901(6)	6183(5)	4.3
C(5)	3299(7)	6787(7)	7002(5)	4.6
C(6)	3172(7)	5917(6)	6721(5)	4.8
C(7)	3039(6)	6167(5)	5618(5)	3.6
C(8)	2359(6)	6399(5)	3325(4)	2.6
C(9)	1037(6)	6314(5)	3515(5)	3.6
C(10)	618(7)	5335(6)	3599(6)	4.4
C(11)	1472(8)	4462(6)	3480(5)	4.6
C(12)	2791(7)	4543(5)	3271(5)	4.2
C(13)	3223(6)	5526(5)	3190(5)	3.4
C(14)	4645(5)	7459(5)	3009(5)	2.4
C(15)	5713(6)	7076(5)	3757(5)	3.1
C(16)	7017(6)	6992(6)	3464(6)	3.9
C(17)	7249(6)	7319(6)	2375(6)	4.0
C(18)	6216(7)	7681(6)	1600(5)	4.3
C(19)	4891(6)	7770(5)	1879(5)	3.7
C(20)	3442(5)	11593(5)	1605(5)	3.0
C(21)	3531(7)	12767(5)	1037(6)	4.6
C(22)	4770(8)	13009(7)	702(7)	6.0
C(23)	5868(8)	12159(8)	907(6)	5.4
C(24)	5797(7)	10994(8)	1489(6)	5.1
C(25)	4571(6)	10751(6)	1823(5)	3.9
C(26)	1890(6)	11267(4)	3448(4)	2.6
C(27)	3054(6)	11278(5)	3964(5)	3.2
C(28)	3073(7)	11216(6)	5009(5)	4.1
C(29)	1912(8)	11167(6)	5552(5)	4.6
C(30)	746(7)	11177(5)	5058(5)	4.0
C(31)	738(6)	11208(5)	4026(5)	3.5
C(32)	576(6)	12415(5)	1242(5)	2.8
C(33)	-118(7)	13262(6)	1505(5)	3.8
C(34)	-1150(7)	14138(6)	786(6)	4.4
C(35)	-1482(7)	14172(6)	-217(6)	4.6
C(36)	-801(8)	13338(6)	-485(6)	5.1
C(37)	230(7)	12476(5)	232(5)	4.2

Scattering factors given by Cromer and Mann[7] were used for copper, phosphorus, sulfur and carbon. For hydrogen the scattering factor curve given by Stewart *et al.*[8] was used. The numbering of atoms is shown in Fig. 1. Final coordinates and temperature parameters for the non-hydrogen atoms are listed in Table 1; for the hydrogen atoms in Table 2. Lists of structure factors and anisotropic thermal parameters are available on request from one of the authors (L.K. H.).

Discussion. The molecular structure of the title compound is shown in Fig. 2. Selected bond distances and angles for the non-hydrogen atoms are given in Table 3.

The most interesting fact of the structure is the presence of a single bond between the two carbon atoms C(1)–C(1i) of the tetrathiooxalate (1.531(8)Å). Obviously, this is a consequence of the synthesis of the complex starting with the true isolated tetrathiooxalate dianion (as Et_4N-salt). Other compounds containing a bridging C_2S_4 moiety obtained by a metalactivated head-to-head dimerization of carbon disulfide on transition-metal centers have a quite shorter C–C bond.[10,11] Thus, the nickel complex $(\eta^5\text{-}C_5Me_5Ni)_2C_2S_4$ should be described better as an ethylene-tetrathiolato bridge containing compound (C–C 1.360(11)Å, C–S 1.718(3)Å). Despite the difference between such tetrathiolene-like complexes and the tetrathiooxalato arrangement in our compound, both cases have

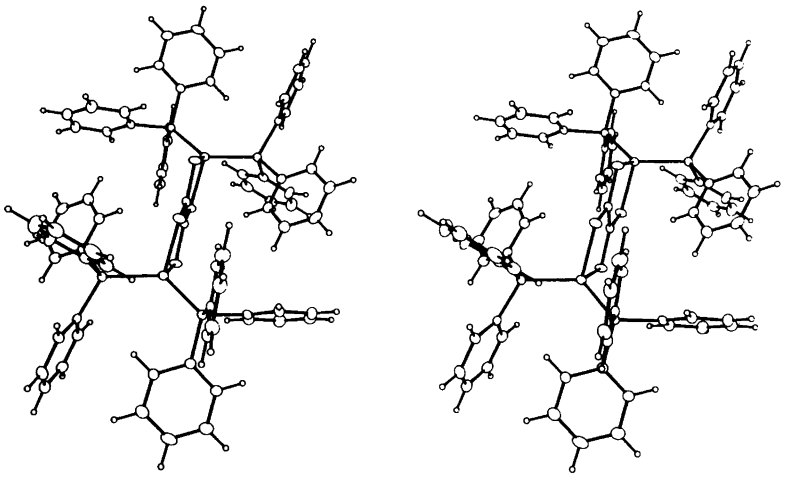

Fig. 2. Stereoscopic view of the molecular structure of the title compound.[9]

$MS_2C_2S_2M$ cores which are strictly planar. Both differ in this respect from the $(Ph_4P)_2C_2S_4$, where a torsion angle of 79° was found.[1b] The C(1)–C(1i) bond length in the bridging tetrathiooxalate is near that of dithiooxalato ligands linking two equal or different metal ions,[12,13] however somewhat longer than in the non-coordinated tetrathiooxalate (1.461(19)Å).[1b] The C–S bond lengths show a similar behavior. As expected, also the Cu–C and Cu–P bond lengths in the compound under investigation and in KSn $(S_2C_2O_2)_2O_2C_2S_2Cu$ $(PPh_3)_2$,[14] both having $S_2Cu(PPh_3)_2$ units, do not differ significantly.

Table 2. Atomic coordinates $\times 10^3$ and temperature factors B(Å^2) for the H-atoms.

ATOM	X	Y	Z	B
H(3)	324(5)	881(4)	457(4)	4.3
H(4)	346(5)	853(4)	643(4)	3.8
H(5)	341(5)	666(5)	772(4)	5.9
H(6)	320(5)	511(5)	729(4)	5.2
H(7)	296(5)	558(4)	542(4)	3.7
H(9)	40(5)	697(4)	354(4)	5.0
H(10)	-29(5)	538(5)	364(4)	5.9
H(11)	118(5)	371(5)	353(4)	5.8
H(12)	340(5)	395(4)	318(4)	5.0
H(13)	420(5)	555(4)	316(4)	5.0
H(15)	561(5)	688(4)	448(4)	5.3
H(16)	771(5)	674(4)	397(4)	3.9
H(17)	813(5)	724(5)	217(4)	5.6
H(18)	632(5)	790(5)	80(4)	5.5
H(19)	412(5)	803(4)	136(4)	4.0
H(21)	270(5)	1357(4)	89(4)	4.5
H(22)	472(5)	1377(5)	50(4)	5.7
H(23)	665(6)	1230(5)	75(5)	7.1
H(24)	663(5)	1036(4)	171(4)	4.5
H(25)	462(5)	981(4)	228(4)	3.7
H(27)	383(5)	1122(4)	363(4)	4.4
H(28)	391(5)	1116(4)	544(4)	4.5
H(29)	199(4)	1108(4)	627(4)	2.5
H(30)	-4(5)	1120(4)	540(4)	4.4
H(31)	-9(5)	1124(4)	368(4)	3.4
H(33)	23(5)	1316(4)	229(4)	4.3
H(34)	-160(5)	1463(5)	103(4)	5.1
H(35)	-215(5)	1484(5)	-73(4)	6.2
H(36)	-107(6)	1342(5)	-124(5)	6.7
H(37)	67(5)	1188(4)	8(4)	4.1

Table 3. Selected bond lengths (Å) and angles (°) for the non-hydrogen atoms.

BOND	(Å)
CU(1)-S(1)	2.308(2)
CU(1)-S(2)	2.275(2)
CU(1)-P(1)	2.268(1)
CU(1)-P(2)	2.303(2)
S(1)-C(1)	1.668(6)
S(2)-C(1i)	1.689(6)
P(1)-C(2)	1.822(6)
P(1)-C(8)	1.837(7)
P(1)-C(14)	1.826(6)
P(2)-C(20)	1.832(6)
P(2)-C(26)	1.820(7)
P(2)-C(32)	1.816(5)
C(1)-C(1i)	1.531(8)

ANGLE	(°)
S(1)-CU(1)-S(2)	89.18(7)
S(1)-CU(1)-P(1)	108.41(7)
S(1)-CU(1)-P(2)	103.79(7)
CU(1)-S(1)-C(1)	104.69(23)
S(2)-CU(1)-P(1)	115.89(7)
S(2)-CU(1)-P(2)	109.51(7)
CU(1)-S(2)-C(1i)	105.30(21)
P(1)-CU(1)-P(2)	123.58(8)
CU(1)-P(1)-C(2)	118.40(20)
CU(1)-P(1)-C(8)	116.45(18)
CU(1)-P(1)-C(14)	112.36(16)
CU(1)-P(2)-C(20)	111.01(25)
CU(1)-P(2)-C(26)	120.65(18)
CU(1)-P(2)-C(32)	112.55(26)
S(1)-C(1)-C(1i)	120.6(5)
S(2)-C(1i)-C(1)	119.7(5)
C(2)-P(1)-C(8)	101.8(3)
C(2)-P(1)-C(14)	102.9(3)
P(1)-C(2)-C(3)	118.8(4)
P(1)-C(2)-C(7)	123.6(6)
C(8)-P(1)-C(14)	102.9(3)
P(1)-C(8)-C(9)	117.9(6)
P(1)-C(8)-C(13)	122.6(5)
P(1)-C(14)-C(15)	125.0(5)
P(1)-C(14)-C(19)	116.8(5)
C(20)-P(2)-C(26)	102.7(4)
C(20)-P(2)-C(32)	104.2(3)
P(2)-C(20)-C(21)	121.6(5)
P(2)-C(20)-C(25)	119.0(5)
C(26)-P(2)-C(32)	104.4(3)
P(2)-C(26)-C(27)	122.3(5)
P(2)-C(26)-C(31)	120.1(6)
P(2)-C(32)-C(33)	125.2(6)
P(2)-C(32)-C(37)	116.8(6)

The planar tetrathiooxalato bridge contains the inversion center of the whole molecule, a situation similar to that found in molecules with a briding trans-dithiooxalate.[8,10] Besides oxalate[15] and dithiooxalate, tetrathiooxalate is the third bridging ligand of this topology capable of linking two equal or different central metal ions.

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