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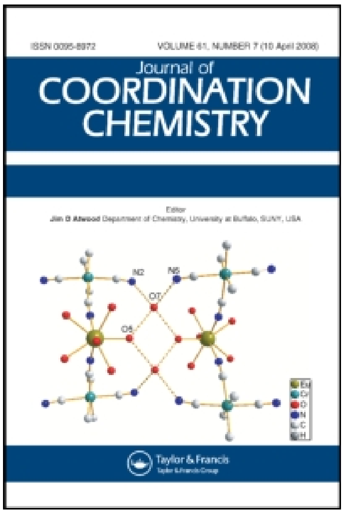

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Bis(triphenylphosphine)ethyltrithiocarbonatocopper(I)

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SHORT COMMUNICATION

Bis(triphenylphosphine)ethyltrithiocarbonatocopper(I)

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Transition metal complexes of alkyl trithiocarbonates (thioxanthates) have not received as much attention as have complexes with other monoanionic 1,1-dithiolates. Structural information about copper thioxanthates has not been reported. Edwald and Sinn[1] reported the preparation of Cu(II) thioxanthate but did not characterize nor isolate the dark-colored compound. Duncan, Ott, and Reid[2] studied the reaction of polymeric cuprous mercaptides with carbon disulfide in 1931 and reported the reddish-brown products as cuprous thioxanthates [Cu^I(RSCS$_2$)].

The instability (CS$_2$ elimination) of complexes with thioxanthate ligands,[3-7] the ease with which cuprous-sulfur systems polymerize to insoluble compounds,[2,8] and other complications[9,10] have made the study of cuprous thioxanthates difficult.

In light of the stabilizing and solubilizing effects of tertiary phosphines coordinated to copper,[11-13] it seemed reasonable that monomeric complexes of the sort L$_2$Cu^I X, where L = Ph$_3$P and X = RS^{-1}, RSCS$_2^{-1}$ could be formed.

For R = C$_2$H$_5$ the mercaptide and the thioxanthate compounds of the above type were prepared. The crystal structure of the latter compound, bis(triphenylphosphine)ethylthioxanthatocopper(I), I, is reported here.

The preparation of the title compound, I, was indirect since the formation of L$_2$CuSEt was desired. To a THF solution (200 ml) of NaH (0.23 g, 5.4 mmol, 57% oil disp.), cooled to 0°C and under N$_2$, EtSH (0.40 cc, 5.4 mmol) was slowly added. After 5 min of stirring, finely-ground powder of L$_2$CuBr · ½C$_6$H$_6$ (ref. 14) d(3.85 g, 5.4 mmol) was quickly added. A yellow solution formed immediately. After about 12 hrs of stirring at room temperature under N$_2$, the solution was quickly filtered in air into a flask. After the solvent was blown off by a brisk N$_2$ flow, the residue was dissolved in 300 ml C$_6$H$_6$ and filtered into another flask. The solution was concentrated under a slow nitrogen flow over a two-day period. The yellow solid, isolated by filtration, was dissolved in CS$_2$. To the yellow solution, some hexane was added and the mixture was allowed to stand in air until well-shaped yellow platelets of the title compound crystallized out.

The IR spectra of I is similar to that of L$_2$CuBr, except that two intense peaks, 990 and 895 cm^{-1}, are also present. Pmr spectra (Varian HA-100, FT) of I in CS$_2$ shows a singlet at 2.85τ (phenyl protons), a quartet centered at 7.03τ (J = 7 Hz, methylene protons), and a triplet at 8.78τ (methyl protons) with phenyl:ethyl intensity as 6:1. Osmometric molecular weight (37°C, CHCl$_3$) indicated a monomer.

Precession film methods revealed triclinic symmetry for I, which was confirmed by a Delaunay reduction.[15] The lattice parameters, deduced from a least-squares fit to the angular settings of 33 carefully centered reflections on a Picker automatic four-circle (card-controlled) diffractometer equipped with a graphite monochromator ($2\theta_{av} = 30°$, MoK$_\alpha$, $\lambda = 0.70926$Å), are $a = 10.437(1)$, $b = 12.912(1)$, $c = 15.124(1)$Å, $\alpha = 82.24(1)°$, $\beta = 113.99(1)°$, $\gamma = 103.52(1)°$, and $V = 1808.6$Å^3. The observed density (flotation), 1.34(2) g/cm^3, agrees with the calculated value, 1.332 g/cm^3, assuming $z = 2$. Data (5759 reflections, $2\theta_{max} = 50°$) were collected using molybdenum radiation ($\lambda = 0.7107$Å). Using two strong reflections as standards to monitor the stability of the crystal, no decomposition was observed. The data were corrected for Lorentz and polarization[16] effects. No absorption correction was made ($\mu = 9.1$ cm^{-1}, crystal: 0.2 x 0.33 x 0.80 mm, mounted along the long direction, $3\bar{1}2$).

The intensities and associated errors used were defined previously[17] (p = 0.02). The intensities chosen for the structure solution numbered 3981 ($I/\sigma(I) \geqslant 3$).

The centrosymmetric space group P1 was chosen

TABLE I

Positional parameters and estimated standard deviations for $(Ph_3P)_2\underline{C}u(Et\text{-}txan)$

	x	y	z		x	y	z
Cu	.6650(1)	.3354(1)	.2540(1)	CC3	.7802(11)	.6405(8)	.0352(7)
S1	.8691(2)	.3180(2)	.2283(2)	CC4	.8179(12)	.7457(9)	.0541(8)
S2	.5726(2)	.2401(2)	.1007(2)	CC5	.7878(12)	.7810(8)	.1244(8)
S3	.8186(3)	.1772(3)	.0802(2)	CC6	.7256(10)	.7082(8)	.1806(7)
P1	.6206(2)	.2040(1)	.3592(1)	CX1	.6683(8)	.0768(6)	.3566(5)
P2	.6224(2)	.5010(1)	.2369(1)	CX2	.8086(10)	.0785(7)	.3723(6)
C	.7480(8)	.2446(6)	.1365(5)	CX3	.8563(11)	-.0179(8)	.3779(7)
CE1	.6653(16)	.1057(13)	-.0149(11)	CX4	.7571(11)	-.1124(7)	.3639(7)
CE2	.7200(24)	.0597(16)	-.0755(13)	CX5	.6140(11)	-.1152(8)	.3463(7)
CA1	.6988(8)	.5656(6)	.3553(5)	CX6	.5691(9)	-.0194(6)	.3436(6)
CA2	.8484(9)	.5824(7)	.4035(6)	CY1	.4288(8)	.1659(5)	.3335(5)
CA3	.9126(10)	.6244(7)	.4961(7)	CY2	.3749(9)	.1515(6)	.4049(6)
CA4	.8286(10)	.6459(7)	.5400(7)	CY3	.2272(9)	.1257(7)	.3786(6)
CA5	.6811(10)	.6287(7)	.4914(7)	CY4	.1353(10)	.1154(7)	.2846(6)
CA6	.6140(9)	.5883(6)	.3979(6)	CY5	.1878(10)	.1268(8)	.2121(7)
CB1	.4359(8)	.5082(6)	.1947(5)	CY6	.3360(10)	.1547(7)	.2367(6)
CB2	.3496(9)	.4301(7)	.2308(6)	CZ1	.7008(8)	.2290(6)	.4889(5)
CB3	.2039(10)	.4301(6)	.2006(7)	CZ2	.7524(10)	.1539(7)	.5593(6)
CB4	.1424(11)	.5070(8)	.1373(7)	CZ3	.8120(12)	.1765(9)	.6576(8)
CB5	.2273(12)	.5856(9)	.0994(8)	CZ4	.8209(11)	.2776(8)	.6851(7)
CB6	.3732(10)	.5856(7)	.1271(6)	CZ5	.7684(10)	.3543(7)	.6127(7)
CC1	.6955(8)	.5999(6)	.1648(5)	CZ6	.7091(9)	.3301(6)	.5169(6)
CC2	.7199(9)	.5642(7)	.0919(6)				
H1	.6708	.1287	-.0758	HC5	.8140	.8545	.1376
H2	.6645	.0314	-.0043	HC6	.7081	.7317	.2308
H3	.7809	.0126	-.0363	HX2	.8761	.1439	.3838
H4	.6516	.0216	-.1262	HX3	.9531	-.0157	.3887
H5	.7721	.1157	-.1025	HX4	.7857	-.1779	.3671
HA2	.9040	.5606	.3756	HX5	.5479	-.1813	.3368
HA3	.0136	.6361	.5295	HX6	.4738	-.0200	.3357
HA4	.8722	.6743	.6026	HY2	.4380	.1612	.4706
HA5	.6234	.6433	.5214	HY3	.1886	.1155	.4268
HA6	.5127	.5703	.3668	HY4	.0350	.0978	.2685
HB2	.3899	.3765	.2764	HY5	.1234	.1195	.1462
HB3	.1460	.3766	.2255	HY6	.3729	.1666	.1874
HB4	.0432	.5055	.1178	HZ2	.7475	.0845	.5419
HB5	.1863	.6399	.0551	HZ3	.8473	.1231	.7055
HB6	.4297	.6392	.1014	HZ4	.8613	.2929	.7517
HC2	.6986	.4900	.0817	HZ5	.7732	.4237	.6296
HC3	.7979	.6178	-.0152	HZ6	.6735	.3835	.4691
HC4	.8580	.7957	.0155				

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TABLE II

Thermal parameters[a] and estimated standard deviations for $(Ph_3P)_2Cu(Et\text{-}txan)$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	.0113(1)	.0052(1)	.0052(1)	.0016(1)	.0046(1)	-.0001(1)
S1	.0086(3)	.0094(2)	.0063(1)	.0014(2)	.0035(1)	-.0008(1)
S2	.0102(3)	.0098(2)	.0058(1)	.0020(2)	.0029(1)	-.0016(1)
S3	.0190(4)	.0148(3)	.0081(2)	.0087(3)	.0049(2)	-.0021(2)
P1	.0107(3)	.0047(1)	.0053(1)	.0016(1)	.0042(1)	.0001(1)
P2	.0108(3)	.0046(1)	.0050(1)	.0014(1)	.0040(1)	-.0002(1)
C	.0124(11)	.0071(6)	.0052(4)	.0044(6)	.0035(5)	.0005(4)
CE1	.0270(25)	.0207(17)	.0136(12)	.0055(16)	.0046(13)	-.0099(12)
CE2	.0566(52	.0240(22)	.0166(16)	-.0001(26)	.0138(23)	-.0120(16)

	B(Å^2)		B(Å^2)		B(Å^2)
CA1	3.56(13)	CC1	3.82(14)	CY1	3.49(13)
CA2	4.60(16)	CC2	4.91(17)	CY2	4.22(15)
CA3	5.33(18)	CC3	6.14(21)	CY3	4.73(16)
CA4	5.19(18)	CC4	6.70(23)	CY4	5.28(18)
CA5	5.21(18)	CC5	6.58(22)	CY5	5.72(19)
CA6	4.12(15)	CC6	5.60(19)	CY6	4.94(17)
CB1	3.64(13)	CX1	3.70(13)	CZ1	3.69(13)
CB2	4.81(16)	CX2	5.32(18)	CZ2	5.24(18)
CB3	5.36(18)	CX3	5.81(20)	CZ3	6.67(23)
CB4	6.05(20)	CX4	5.61(19)	CZ4	6.31(21)
CB5	7.06(24)	CX5	5.86(20)	CZ5	5.67(19)
CB6	5.13(17)	CX6	4.55(16)	CZ6	4.53(16)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$

and later proved to be the correct one. Using Dewar's and Stone's[18] FAME-MAGIC-LINK-SYMPL direct methods package, the E-map from the solution with the least contradictions (other than the all + solution) showed clearly the positions of Cu, sulfurs, phosphines, and one complete phenyl ring at $R = 0.43$ [$R = \Sigma \| F_0 \| F_c | / \Sigma | F_0 |$]

All non-hydrogen atoms were located by Fourier synthesis. At $R = 0.20$, full-matrix least-squares refinement was initiated. Subsequently, the temperature factors of the Cu, P, and the thioxanthate atoms were converted to anisotropic

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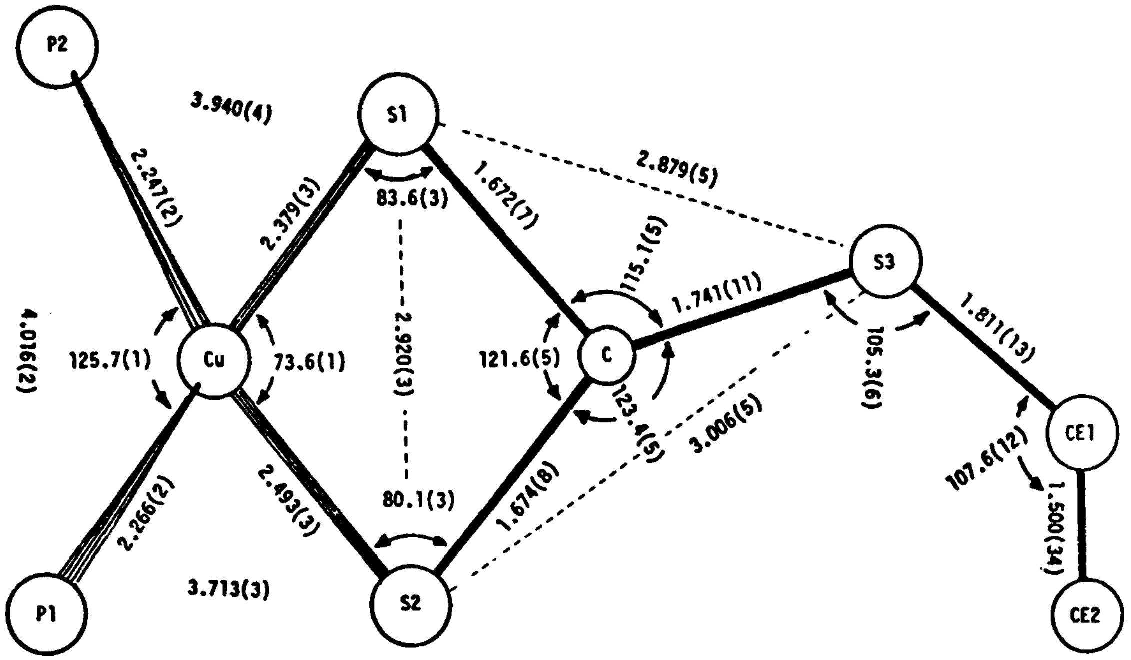

P-C_{av} = 1.827A phenyl: C-C_{av} = 1.392A, C-C-C_{av} = 1200,0° Cu-P-C_{av} = 115.2°

FIGURE 1 Structural dimensions for $(Ph_2P)_2Cu^I(S_2CSC_2H_5)$.

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forms. Refinement converged at $R = 0.073$ and $R_w = 0.098$ [$R_w = \Sigma w(|F_0| - |F_c|)^2 / \Sigma w \mid \Sigma w \, |F_0|^2 \, ½$ $w = \sigma(F_0)^{-1}$, Cruickshank type weighting scheme[17]]. When hydrogens were included at calculated positions, $R = 0.067$ and $R_w = 0.089$. The final difference Fourier had peaks as high as ±1.2 e/Å^3, mostly in the region of the isotropically refined phenyl rings. The dimensions of the molecule are shown in Figure 1.

The dimensions of the thioxanthate ligand are significantly different from those observed in other complexes.[4-7] The S. . .S "bite" distance is larger than usual. Consequently so is the S1-C-S2 angle. The S1. . .S3 distance is smaller than the "bite" distance. More importantly, the two sulfurs atoms (S1,S2) do not coordinate to the copper equivalently. The shorter Cu-S1 distance is typical of tetrahedral Cu-S complexes.[19] The immediate environment about the copper is that of a highly distorted tetrahedron.

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