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Synthesis and Structural Characterization of Chlorobis(triphenylphosphine)(dithiooxamide)copper(I)

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Syntheses and X-ray structural studies of copper(I) complexes, obtained by reaction of pseudo-cubane tetrameric $[Cu(PPh_3)Cl]_4$ with sulphur containing ligands, are in progress in our laboratory to investigate the behaviour of the ligands and the factors which influence the nature of the products. Monomeric species such as $Cu(PPh_3)LCl$ and CuL_2Cl [L = 1-phenyl-3-(2-pyridyl)-2-thiourea = pptu], involving copper(I) with trigonal coordination, have been recently characterized [1]. In the present paper we report the synthesis and structural study of $Cu(PPh_3)_2LCl$ where L is dithiooxamide (dto). This compound was prepared to explore the effect on coordination observed with ligands such as dithiooxamide, less bulky than triphenylphosphine and phenylpyridylthiourea. The results show that the complex is monomeric with a tetrahedral co-ordination involving, besides chlorine and dithiooxamide, two PPh_3 molecules.

Experimental

To a boiling toluene solution of $[Cu(PPh_3)Cl]_4$ a hot red-orange solution of dithiooxamide (1:1 metal:ligand molar ratio) in the same solvent was added. The mixture was then refluxed until red-brown prismatic crystals of formula $Cu(PPh_3)_2(dto)Cl$ were isolated. When 1:2 or 2:1 metal:ligand molar ratios were used the complex was obtained again together with the unreacted amounts of dithiooxamide or tetramer respectively. Chloroform can also be employed as solvent following the same experimental conditions.

$Cu(PPh_3)_2(dto)Cl$ was also obtained from the reaction of dto in boiling toluene (1:1 metal:ligand molar ratio) with $Cu(PPh_3)(pptu)Cl$, whose synthesis has recently been reported [1]. In this case the complex $Cu(pptu)_2Cl$ [1] was also isolated by slow evaporation of the solvent at room temperature.

The infrared spectra were registered on a Perkin Elmer Mod. 283 B spectrophotometer in the 4000–200 cm^{-1} region by using KBr disks. A comparison of the main vibrational bands of the title compound with those of the reagents $[Cu(PPh_3)Cl]_4$ and dto is reported in Table I.

TABLE I. Selected Infrared Spectroscopic Data (cm^{-1}).

$[Cu(PPh_3)Cl]_4$	dto	$Cu(PPh_3)_2(dto)Cl$	
	3370(sh)	3325m	ν(NH)
	3295s	3260m	
	3210s	3210w,br	
	3140s	3190w	
		3120m	
3050m		3050m,br	ν(CH)
		1605(sh)	ν(CC), δ(NH)
	1585vs	1585vs	
1580w			ν(CC)
1480s		1475s	
1435vs		1435vs	ν(CC), ν(CN)
	1430vs	1410s,br	
		1215(sh)	$\delta(CH)_{in}$, ν(CS), ν(NCN)
	1195s	1190(sh)	
1185w		1180s,br	
1095s		1090s	$\delta(CH)_{in}$, ν(PC)

(continued overleaf)

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TABLE I. *(continued)*

$[Cu(PPh_3)Cl]_4$	dto	$Cu(PPh_3)_2(dto)Cl$	
1030m		1025m	$\delta(CH)_{in}$
1000m		995m	
	835vs	940vs	$\nu(CS)$
750(sh)		750(sh)	$\delta(CH)_{out}$
745vs		740vs	
700vs	700s	695vs	$\delta(CH)_{out}$, $\nu(NH)$, $\nu(NCN)$, $\nu(PC)$
	640vs	650s	$\nu(NCN)$
		605s	
530s		525s	ring skeletal, $\nu(PC)$
520vs		520vs	
500s		505vs	
495(sh)		495s	
440w,br		440w	
420(sh)			

TABLE II. Fractional Atomic Coordinates $\times 10^4$.

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Cu	1857(5)	1342(2)	2485(2)	C16	2792(36)	−1442(18)	1237(17)
Cl	526(7)	2373(4)	2412(4)	C17	1404(32)	−1311(18)	1160(15)
S1	4292(7)	1577(4)	2413(4)	C18	899(29)	−632(15)	1214(14)
S2	6594(9)	3490(5)	2499(6)	C19	1920(26)	1404(14)	4269(13)
P1	1437(8)	874(4)	3529(4)	C20	3231(33)	1715(16)	4291(17)
P2	1266(8)	788(4)	1474(4)	C21	3725(38)	2120(18)	4883(20)
N1	3695(26)	2893(14)	2327(14)	C22	2855(38)	2153(17)	5378(18)
N2	7132(21)	2220(12)	2252(12)	C23	1508(39)	1867(19)	5423(19)
C1	1983(28)	1203(15)	738(15)	C24	1046(36)	1469(18)	4823(19)
C2	2242(34)	1904(17)	767(17)	C25	2386(27)	77(14)	3704(15)
C3	2818(39)	2270(20)	207(22)	C26	2662(40)	−136(21)	4362(21)
C4	3035(39)	1881(20)	−382(20)	C27	3486(36)	−757(20)	4481(19)
C5	2801(36)	1179(19)	−436(17)	C28	3997(36)	−1145(19)	3936(19)
C6	2273(30)	866(16)	166(17)	C29	3658(31)	−895(16)	3301(17)
C7	−579(27)	768(14)	1315(14)	C30	2847(31)	−296(16)	3179(17)
C8	−1241(26)	1010(13)	683(13)	C31	−365(24)	715(13)	3617(12)
C9	−2717(31)	989(15)	578(15)	C32	−1399(31)	1194(15)	3596(15)
C10	−3585(33)	731(17)	1062(17)	C33	−2840(32)	1090(16)	3621(15)
C11	−2956(32)	468(16)	1632(16)	C34	−3420(37)	473(20)	3676(18)
C12	−1498(32)	508(16)	1752(16)	C35	−2448(36)	−75(18)	3715(17)
C13	1820(28)	−117(14)	1369(14)	C36	−949(31)	38(16)	3696(15)
C14	3248(33)	−241(17)	1481(16)	C37	4663(26)	2421(13)	2364(12)
C15	3729(36)	−941(19)	1426(18)	C38	6167(30)	2655(15)	2364(14)

X-ray Crystallography. Collection of Data

The crystal data of the red-brown crystals are: $C_{38}H_{34}ClCuN_2P_2S_2$, $M = 743.8$, $a = 9.394(2)$, $b = 19.333(6)$, $c = 19.662(6)$ Å, $\beta = 92.20(3)°$, $V = 3568(2)$ Å^3, space group $P2_1/n$, $Z = 5$, $D_c = 1.38$, $D_m = 1.37$ g cm^{-3}, $\mu(CuK\alpha) = 35.5$ cm^{-1}, $F(000) = 1536$.

Intensity data were collected at room temperature on a Siemens AED single-crystal computer-controlled diffractometer by the $\omega/2\theta$ scan technique [$7 < 2\theta < 100°$] with $CuK\alpha$ radiation. In the data collection the intensity of a standard reflection was measured every 20 reflections to check the stability of the crystal and the electronics. A total of 4108 independent reflections were measured, of which only 1157 having $I > 2\sigma(I)$ were considered observed and used in the subsequent analysis. No correction for absorption was made as the sample was sufficiently small (crystal size: 0.02 X 0.02 X 0.25 mm).

Solution and Refinement of the Structure

The structure was solved by a combination of Patterson and Fourier techniques. All non-hydrogen atoms were located and refined by full-matrix least-squares using isotropic and anisotropic temperature factors. Hydrogen atoms were included in calculated positions with each having an isotropic thermal parameter equivalent to that of the parent carbon or nitrogen atom. The best results were obtained using unit weights giving a final conventional $R(F) = 0.076$ (observed reflections only). Scattering factors for non-hydrogen atoms were taken from the International Tables for X-ray Crystallography, and both the real and imaginary components of anomalous dispersions were included [2]. Final positional parameters age given in Table II. Lists of observed and calculated structure factors and of thermal parameters are available from the authors on request.

Calculations were made on the CDC-CYBER 76 computer of the 'Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell' Italia Nord-Orientale' (CINECA, Casalecchio, Bologna) and on the GOULD-SEL 77/22 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma), using the SHELX-76 program [3] for solution and refinement of the structure, PARST [4] for the geometrical description of the structure, and PLUTO [5] for the structure drawings.

Results and Discussion

The structure of $Cu(PPh_3)_2(dto)Cl$ is shown in Fig. 1. The coordination polyhedron of the Cu atom is a distorted tetrahedron and involves the chlorine atom, a sulphur atom from dto and the phosphorus atoms of the two PPh_3 molecules. Comparing this molecule with that of $CuCl(PPh_3)(pptu)$, where coordination is trigonal planar [1], it appears that using the fairly small and rigid dithiooxamide ligand instead of the bulky phenylpyridylthiourea, a different stoichiometry and coordination geometry is observed for the resulting compound.

The Cl–Cu–S, S–Cu–P and Cl–Cu–P angles show small deviations (max 5.6°) from the tetrahedral value, while the P–Cu–P angle is much larger (by 13.6°) owing to the interactions between the two bulky phosphine ligands (H30...H14 = 2.57 Å). Some relevant bond distances and angles are given in Tables III and IV. The Cu–P distance (2.291(7); 2.307(9) Å) is within the range (2.24–2.31 Å) of

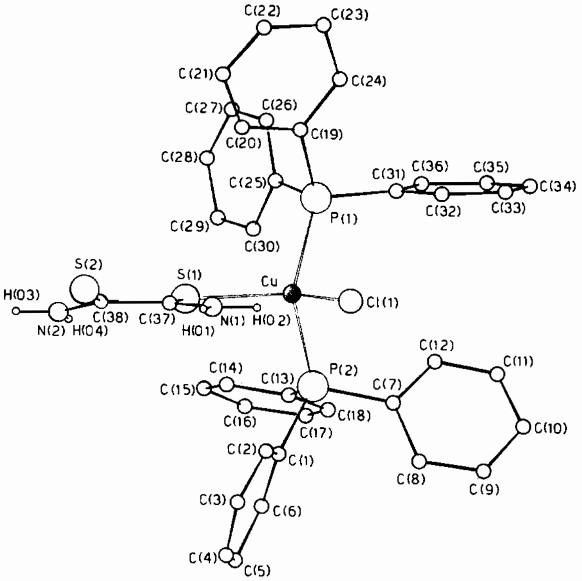


Fig. 1. Projection of the molecular structure on the (100) plane.

TABLE III. Selected Distances (Å).

Cu–Cl	2.354(8)	P(2)–C(7)	1.75(3)
Cu–S(1)	2.342(8)	P(2)–C(13)	1.84(3)
Cu–P(1)	2.291(9)	S(1)–C(37)	1.67(3)
Cu–P(2)	2.307(9)	S(2)–C(38)	1.68(3)
P(1)–C(19)	1.82(3)	N(1)–C(37)	1.29(4)
P(1)–C(25)	1.81(3)	N(2)–C(38)	1.26(4)
P(1)–C(31)	1.74(2)	C(37)–C(38)	1.48(4)
P(2)–C(1)	1.81(3)		

TABLE IV. Selected Bond Angles (Deg).

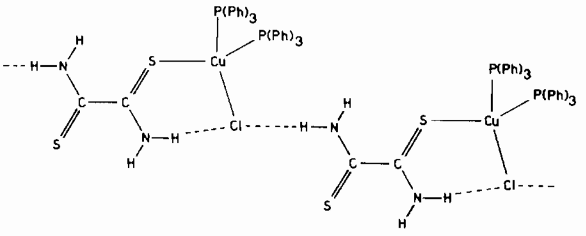
P(1)–Cu–P(2	123.0(3)
S(1)–Cu–P(2)	104.0(3)
S(1)–Cu–P(1)	109.5(3)
Cl–Cu–P(2)	103.3(3)
Cl–Cu–P(1)	106.2(3)
Cl–Cu–S(1)	110.5(3)
Cu–S(1)–C(37)	113.5(9)
Cu–P(1)–C(31)	111.2(9)
Cu–P(1)–C(25)	114.0(9)
Cu–P(1)–C(19)	116.6(9)
Cu–P(2)–C(13)	118.6(9)
Cu–P(2)–C(7)	111.6(1.0)
Cu–P(2)–C(1)	113.5(1.0)
C(25)–P(1)–C(31)	107.8(1.2)
C(19)–P(1)–C(31)	103.5(1.2)
C(19)–P(1)–C(25)	102.8(1.3)
C(7)–P(2)–C(13)	104.0(1.3)
C(1)–P(2)–C(13)	102.5(1.3)
C(1)–P(2)–C(7)	105.3(1.3)
S(1)–C(37)–N(1)	123.1(2.1)
N(1)–C(37)–C(38)	117.0(2.4)
S(1)–C(37)–C(38)	119.9(1.9)
N(2)–C(38)–C(37)	119.2(2.5)
S(2)–C(38)–C(37)	120.9(2.1)
S(2)–C(38)–N(2)	119.9(2.2)

those found in a number of copper(I) compounds with two phosphine ligands [6]. The Cu–Cl and Cu–S distances (2.354(8); 2.342(8) Å) are comparable with the corresponding bonds in other similar four-coordinate copper(I) compounds [6–9].

In the triphenylphosphine molecules the P–C distances range from 1.74(2) to 1.84(3) Å. The Cu–P–C angles are, as usual, larger than the tetrahedral angle (mean 114.4(12)°) and the C–P–C angles correspondingly smaller (mean 104.1(9)°) (Table IV). All these parameters are consistent with those commonly found in other phosphine–metal complexes [1].

The distances and angles in the dithiooxamide molecule agree with those found for the uncoordinated dithiooxamide [10]. The molecule is not planar $\Sigma(\Delta/\sigma)^2 = 341.6$, and exhibits a *trans* configuration, similar to other ligands [11]. There are two N...S intramolecular contacts (2.97(2), 2.97(3) Å) that could be considered hydrogen bonds with S...H distances of 2.58(8) and 2.55(7) Å.

The dto ligand is monodentate through one S atom, contrary to the behaviour found in $SbCl_3$-(NN'-diethyldithiooxamide)$_{1.5}$ [11] where the ligand is acting as a bidentate bridging group. Unlike the spectroscopic data previously reported for dto-complexes [11] in $Cu(PPh_3)_2(dto)Cl$, all the IR bands remain practically unchanged with respect to free dto with the exception of some ν(NH) bands which undergo small shifts (Table I). In particular the ν(C=S) bands at 1195 and 835 cm^{-1} are scarcely influenced by coordination of sulphur to metal.



The dihedral angle between the CuPP and CuSCl plane is 90.7(3)°. It is worth noting that the orientation of the dithiooxamide molecule relative to the CuPP plane appears to be determined by hydrogen-bond interactions between N(1), N(2) and the chlorine atom (N(1)...Cl = 3.15(2); Cl...N(2^i)* = 3.20(2) Å). So CuSCNH...Cl rings almost planar are formed, linked by N(2)...Cl hydrogen bonds in polymer chains running along the *a* axis,

where the dithiooxamide molecule acts as a bridging group. The connection between the chains is ensured by Van der Waals contacts. The shortest are between nitrogens and the carbon atoms of the phenyl rings.

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*$i = x - 1, y, z$.