Synthesis, spectroscopic and structural characterization of chlorobis(methyl pyruvate thiosemicarbazone)copper(I) and chlorobis(triphenylphosphine)(methyl pyruvate thiosemicarbazone)copper(I) toluene solvate (2/1)

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Abstract

Two new compounds, chlorobis(methyl pyruvate thiosemicarbazone)copper(I), [Cu(Hmpt)$_2$Cl] (**A**), and chlorobis(triphenylphosphine)(methyl pyruvate thiosemicarbazone)copper(I) toluene solvate (2/1), [Cu(PPh$_3$)$_2$(Hmpt)Cl]·0.5C$_7$H$_8$ (**B**) have been synthesized and characterized using spectroscopic studies and single-crystal X-ray diffraction methods at 293 K. Compound **A** crystallizes in space group *C2/c*, with $a=14.695(1)$, $b=13.775(1)$, $c=10.251(1)$ Å, $\beta=113.38(1)°$, $V=1904.7$ Å^3; compound **B** crystallizes in space group $P\bar{1}$, with $a=17.871(7)$, $b=10.681(2)$, $c=11.695(7)$ Å, $\alpha=74.90(1)$, $\beta=86.65(4)$, $\gamma=83.66(2)°$, $V=2141$ Å^3. The crystal structures were solved by the heavy-atom method for **A** and by direct methods for **B** and refined to *R* values of 0.053 for both compounds. In **A** the copper and chlorine atoms lie on a crystallographic two-fold axis and the trigonal coordination around copper involves, besides chlorine, two sulfur atoms from two Hmpt molecules. In **B** the copper is tetrahedrally four-coordinated involving a chlorine atom, a sulfur atom from the Hmpt molecule and the phosphorus atoms of the two PPh$_3$ molecules. In both compounds the ligand is neutral, monodentate through the sulfur atom and shows the configuration *Z E Z* about the C(2)–N(3), C(1)–N(2) and C(2)–C(3) bonds (with respect to possible donating centres O(1), N(3) and S). The main vibrational bands are also reported and discussed.

Introduction

In a recent research program concerning chemical and structural investigations on copper(I) complexes obtained by reaction of pseudo-cubane tetrameric [Cu(PPh$_3$)Cl]$_4$ with sulfur containing ligands, we examined complexes such as [Cu(PPh$_3$)(pptu)Cl], [Cu(pptu)$_2$Cl] (pptu = 1-phenyl-3-(2-pyridyl)-2-thiourea) [1] and [Cu(PPh$_3$)$_2$(dto)Cl] (dto = dithiooxamide) [2]. Now following this and also our interest in the chelating behaviour and subsequent biological activity of thiosemicarbazones [3, 4] we report studies on the synthesis, spectroscopic and structural characterization of two complexes obtained by the reaction of the tetrameric [Cu(PPh$_3$)Cl]$_4$ with the methyl pyruvate thiosemicarbazone (Hmpt)·0.5H$_2$O: [Cu(Hmpt)$_2$Cl] (**A**) and [Cu(PPh$_3$)$_2$(Hmpt)Cl]·0.5C$_7$H$_8$ (**B**). In previous works [5–7] we have considered the chemical and structural properties of this ligand and of some complexes obtained by reaction with Cu(II), Zn and Fe(II) salts. The aim of this research is to gain extensive information about: (i) the transformation of the pseudo-cubane stereochemistry when [Cu(PPh$_3$)Cl]$_4$ reacts with this ligand, similar as regards hindrance to dithiooxamide, under various experimental conditions employed in the synthesis reactions; (ii) the different stereochemistry of Cu(I) and Cu(II) complexes, possible models for the coordination geometries of a Cu^{I}–Cu^{II} redox couple in copper enzymes; (iii) the change of thiosemicarbazone ligand configuration and chelating behaviour related to its biological activities.

Experimental

Preparation of compounds

The methyl pyruvate thiosemicarbazone hemihydrate Hmpt·0.5H$_2$O was prepared as described previously [5].

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Solid $[Cu(PPh_3)Cl]_4$ (50 mg) was added to a boiling toluene solution (40 ml) of $Hmpt \cdot 0.5H_2O$ (25.5 mg) (ratio metal:Hmpt = 1:1) and the reaction mixture, which immediately became yellow, was refluxed for 10 min. The resulting solution was allowed to stand at room temperature and after slow evaporation gave yellow prismatic crystals of $[Cu(Hmpt)_2Cl]$ (**A**) which were collected by filtration (yield related to copper atom *c.* 19%). The filtrate was slowly evaporated to dryness at room temperature until a lemon yellow microcrystalline product (yield *c.* 44%) of formula $[Cu(PPh_3)_2(Hmpt)Cl] \cdot 0.5C_7H_8$ (**B**) was obtained. This complex **B** was isolated by a similar procedure when $[Cu(PPh_3)Cl]_4$ was reacted with $Hmpt \cdot 0.5H_2O$ (1:2 metal:ligand molar ratio) in the same solvent. In fact the reaction carried out by using 51 mg of $Hmpt \cdot 0.5H_2O$ provided only the complex $[Cu(PPh_3)_2(Hmpt)Cl] \cdot 0.5C_7H_8$ (**B**) which was isolated as single crystals suitable for an X-ray analysis, again together with the unreacted amounts of $Hmpt \cdot 0.5H_2O$. Since both the reactions of $[Cu(PPh_3)Cl]_4$ with Hmpt yield the complex **B** and solid CuCl (not reported in the next reaction scheme), we assume that, when equivalent amounts of metal ion and ligand are employed, CuCl partially disappears to produce $Cu(Hmpt)_2Cl$ in addition to complex **B**. In the other case, when we use a 1:2 metal:ligand molar ratio, Hmpt is also involved in the formation of different complexes of CuCl not isolable in the solid state.

The infrared spectra were recordered on a Perkin-Elmer model 283 B spectrophotometer using KBr discs in the range 4000–200 cm^{-1}.

X-ray structure determination

Crystal data and information pertinent to data collection and structural determination are given in Table 1.

The structure was solved by the heavy-atom technique starting from the three-dimensional Patterson analysis for compound **A** and by direct methods using the SHELX-76 system of computer programs [8] for compound **B**. For both compounds successive Fourier syntheses gave the coordinates of all non-hydrogen

TABLE 1. Experimental data for the crystallographic analyses[a]

Compound	$[Cu(Hmpt)_2Cl]$ (**A**)	$[Cu(PPh_3)_2(Hmpt)Cl] \cdot 0.5C_7H_8$ (**B**)
Formula	$C_{10}H_{18}ClCuN_6O_4S_2$	$C_{45.5}H_{43}ClCuN_3O_2P_2S$
Molecular weight	449.4	856.9
Crystal symmetry	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	14.695(1)	17.871(7)
b (Å)	13.775(1)	10.681(2)
c (Å)	10.251(1)	11.695(7)
α (°)	90.0	74.90(1)
β (°)	113.38(1)	86.65(4)
γ (°)	90.0	83.66(2)
V (Å^3)	1904.7(3)	2141(2)
Z	4	2
D_{obs} (g/cm^3)	1.57	1.31
D_{calc} (g/cm^3)	1.57	1.33
$F(000)$	920	890
Crystal size (mm)	0.09×0.14×0.33	0.03×0.05×0.20
μ (cm^{-1})	52.0	27.7
θ-range (°)	3 to 70	3 to 60
h range	−17 to 16	−19 to 20
k range	0 to 16	−11 to 11
l range	0 to 11	0 to 12
Standard reflection	6 2 2	−1 3 0
Intensity variation	none	none
No. measured reflections	1960	6216
Conditions for observed reflections	$I>2\sigma(I)$	$I>3\sigma(I)$
Max./min. height in final difference synthesis	0.34, $0.\bar{2}\bar{6}$	0.24, $0.\bar{2}\bar{2}$
No. refined parameters	142	476
No. unique reflections	1066	2822
R	0.053	0.053
R'	0.059	0.059

[a] Data common to both compounds: Cu Kα radiation ($\lambda = 1.54178$ Å); Siemens-AED diffractometer; $T = 293 \pm 1$ K; unit weights are used.

TABLE 2. Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms for **A** and **B** and ($\times 10^3$) for hydrogen atoms in **A** and U_{eq} or U_{iso} ($\times 10^4$ Å^2)

Atom	x/a	y/b	z/c	$U_{eq/iso}$
A				
Cu	0	2139(1)	2500	610(7)
Cl	0	489(2)	2500	830(18)
S	585(2)	2956(2)	1122(2)	680(10)
O(1)	1436(7)	4028(4)	−2343(8)	1225(48)
O(2)	1917(5)	3628(4)	−4073(6)	773(31)
N(1)	826(6)	1224(5)	122(8)	793(40)
N(2)	1131(5)	2573(5)	−947(7)	661(33)
N(3)	1370(5)	1966(5)	−1832(7)	644(32)
C(1)	861(6)	2161(6)	54(8)	611(39)
C(2)	1601(6)	2352(6)	−2821(8)	596(39)
C(3)	1637(7)	3411(6)	−3032(9)	741(44)
C(4)	1902(11)	4642(7)	−4429(14)	1353(97)
C(5)	1856(7)	1678(6)	−3752(9)	704(42)
H(11)	63(5)	91(6)	60(7)	807(210)
H(21)	80(5)	83(5)	−52(7)	1066(230)
H(1)	115(5)	318(5)	−101(7)	843(217)
H(14)	176(8)	464(7)	−524(11)	1488(367)
H(24)	162(8)	501(7)	−410(10)	1435(354)
H(34)	240(8)	487(7)	−427(11)	1508(372)
H(15)	177(5)	117(5)	−364(7)	662(217)
H(25)	132(5)	188(5)	−497(7)	837(213)
H(35)	244(5)	177(5)	−360(7)	884(215)
B				
Cu	1935(1)	4427(1)	6945(1)	431(5)
Cl	1304(1)	3766(2)	5502(2)	586(10)
S	1476(1)	6575(2)	6972(2)	552(9)
O(1)	108(4)	10346(7)	7067(7)	854(33)
O(2)	−897(4)	11671(7)	6400(6)	736(32)
P(1)	1691(1)	3012(2)	8751(2)	445(9)
P(2)	3123(1)	4640(2)	6117(2)	445(9)
N(1)	232(4)	6188(7)	6006(7)	622(35)
N(2)	235(4)	8106(7)	6537(7)	590(37)
N(3)	−461(4)	8484(8)	6067(7)	610(37)
C(1)	592(5)	6918(9)	6452(8)	514(34)
C(2)	−810(5)	9622(9)	6084(8)	573(42)
C(3)	−468(6)	10522(10)	6567(9)	604(45)
C(4)	−589(6)	12657(10)	6865(10)	808(52)
C(5)	−1576(5)	9923(10)	5555(9)	665(43)
C(6)	3546(5)	3237(9)	5585(7)	479(35)
C(7)	4083(5)	3311(10)	4717(9)	644(42)
C(8)	4370(6)	2226(12)	4344(10)	819(53)
C(9)	4089(7)	1064(12)	4825(12)	906(60)
C(10)	3523(8)	971(12)	5680(12)	1129(69)
C(11)	3258(6)	2061(11)	6073(10)	881(49)
C(12)	3838(5)	4962(10)	7032(7)	516(40)
C(13)	4508(6)	4164(10)	7314(9)	655(45)
C(14)	5013(7)	4485(14)	8023(11)	960(68)
C(15)	4866(8)	5554(15)	8451(10)	908(63)
C(16)	4206(7)	6348(13)	8187(11)	879(63)
C(17)	3698(5)	6014(11)	7501(9)	710(51)
C(18)	3202(5)	6001(9)	4811(8)	498(38)
C(19)	3776(6)	6789(11)	4599(10)	762(51)
C(20)	3803(8)	7822(12)	3590(12)	965(65)
C(21)	3235(9)	8054(13)	2782(11)	995(67)
C(22)	2686(7)	7273(14)	2952(10)	951(62)
C(23)	2641(6)	6213(11)	3980(9)	734(54)
C(24)	702(5)	2894(9)	9205(7)	488(36)
C(25)	407(6)	1792(9)	9870(8)	612(42)
C(26)	−340(7)	1806(12)	10234(9)	796(55)
C(27)	−813(6)	2921(12)	9917(10)	763(53)
C(28)	−529(6)	4071(11)	9255(10)	746(53)
C(29)	218(6)	4045(10)	8881(8)	616(43)
C(30)	2017(5)	1325(8)	8801(8)	470(36)
C(31)	2549(7)	561(11)	9584(10)	848(57)
C(32)	2796(8)	−710(12)	9512(11)	1038(60)
C(33)	2504(7)	−1225(10)	8717(10)	747(52)
C(34)	1984(6)	−490(10)	7947(9)	669(46)
C(35)	1736(5)	774(9)	7988(8)	544(38)
C(36)	2092(5)	3341(8)	10048(7)	474(36)
C(37)	1848(7)	2765(11)	11216(10)	865(53)
C(38)	2152(9)	3103(13)	12145(10)	1037(67)
C(39)	2696(8)	3908(14)	11951(11)	963(64)
C(40)	2915(7)	4526(14)	10799(13)	1055(73)
C(41)	2614(6)	4197(12)	9866(9)	772(48)
C(42)	4700(14)	687(22)	−696(14)	1250(138)
C(43)	4394(14)	1422(22)	77(14)	1411(107)
C(44)	4620(14)	1096(22)	1249(14)	1995(321)
C(45)	5153(14)	34(22)	1648(14)	1296(101)
C(46)	5459(14)	−701(22)	876(14)	1603(198)
C(47)	5233(14)	−375(22)	−296(14)	1292(96)
C(48)	5483(36)	−1123(49)	−1203(40)	1602(426)

atoms, which were refined by means of isotropic and anisotropic least-squares calculations. The hydrogen atoms, located on a ΔF synthesis, were refined isotropically for **A** and not refined for **B** (the isotropic thermal parameters are equivalent to that of the parent carbon or nitrogen atom). In **B** no attempt was made to locate the hydrogen atoms of the unexpected toluene molecule which was refined as a rigid body. This moiety is statistically distributed in two positions around a symmetry centre with s.o.f. 0.5. The final atomic fractional coordinates and U_{eq} or U_{iso} are given in Table 2 for **A** and **B**. Atomic scattering factors were taken from ref. 9. All calculations were performed partly on a Cray X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) and partly on a GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma) using the PARST [10] program for the geometrical description of the structure, ORTEP [11] and PLUTO [12] for the structure drawings.

Results and discussion

The structure of **A** is shown in Fig. 1. The copper and chlorine atoms lie on a crystallographic two-

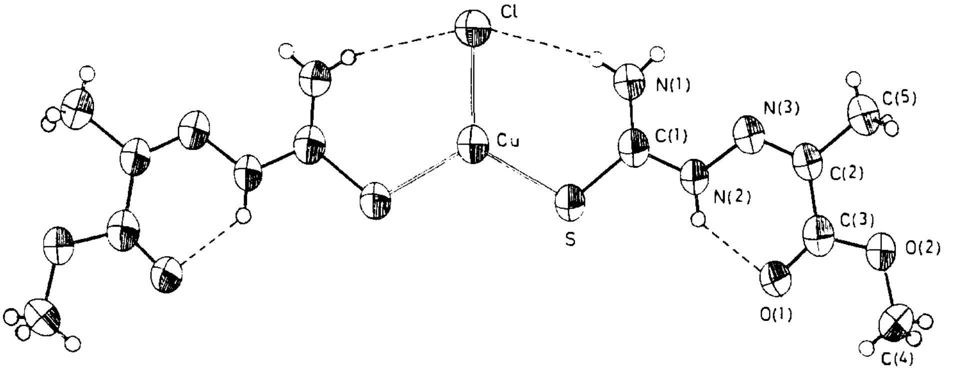

Fig. 1. Perspective view of complex **A** with thermal ellipsoids at 50% probability level.

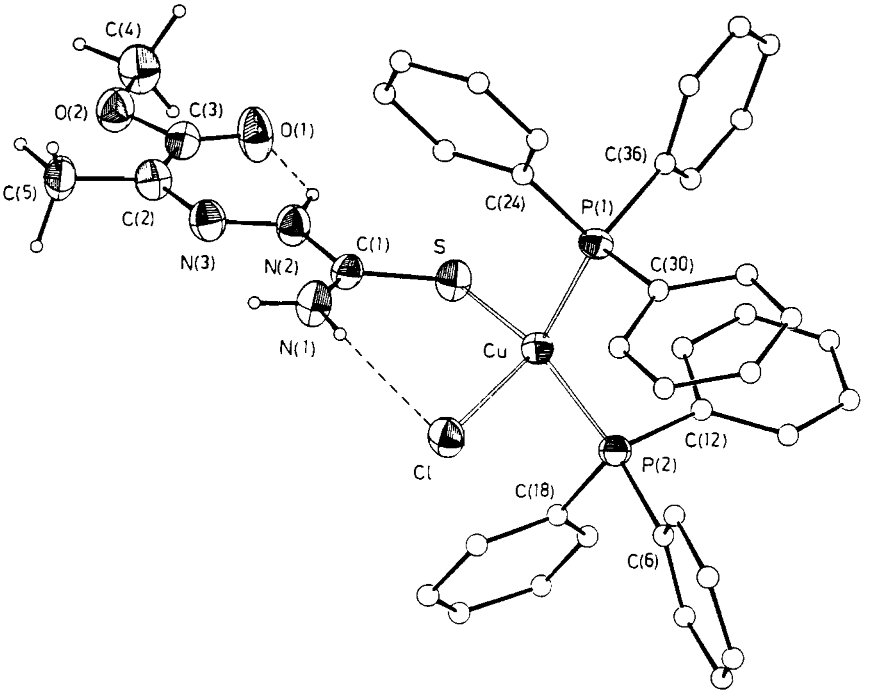

Fig. 2. Perspective view of the copper complex of **B** with thermal ellipsoids at 50% probability level.

fold axis. The coordination around copper is trigonal planar and involves a chlorine and the two sulfur atoms from two symmetrically related Hmpt molecules. The Cu–Cl bond length (2.273 Å) is comparable to those found in trigonal [Cu(PPh$_3$)(pptu)Cl] and [Cu(pptu)$_2$Cl] [1] and in other trigonal copper complexes [13–15] and is shorter than that found in the tetrameric [Cu(PPh$_3$)Cl]$_4$ starting material (2.444 Å) [16] which shows a tetrahedral coordination with triply bridging chlorine atoms. The Cu–S distance (2.228(3) Å) falls in the lower range of values (2.213–2.280 Å) reported for other trigonally coordinated copper(I) complexes [17]. This trigonal copper(I) complex is coordinately unsaturated as are the previously studied [Cu(PPh$_3$)(pptu)Cl] and [Cu(pptu)$_2$Cl] compounds. The coordination geometry in the two compounds obtained by reaction of Hmpt with Cu(II) salts [5] is a square pyramid (4+1) or elongated square bipyramid (4+2). This fact might be related to the biological activity of thiosemicarbazones and might also explain the possible geometries of a Cu^{I}–Cu^{II} redox couple in copper enzymes.

The structure of **B** (Fig. 2) consists of discrete molecular units of [Cu(PPh$_3$)$_2$(Hmpt)Cl] and toluene as a solvate. The geometry about Cu(I) is a distorted tetrahedron and involves a chlorine atom, the phosphorus atoms of the two PPh$_3$ molecules and a sulfur atom from the thiosemicarbazone moiety.

TABLE 3. Bond distances (Å) and angles (°) for **A**

Cu–Cl	2.273(3)	N(1)–C(1)	1.29(1)
Cu–S	2.228(3)	N(2)–N(3)	1.38(1)
S–C(1)	1.71(1)	N(2)–C(1)	1.36(1)
O(1)–C(3)	1.21(1)	N(3)–C(2)	1.30(1)
O(2)–C(3)	1.32(1)	C(2)–C(3)	1.48(1)
O(2)–C(4)	1.44(1)	C(2)–C(5)	1.48(1)
N(1)–H(11)	0.79(9)	C(4)–H(34)	0.75(11)
N(1)–H(21)	0.84(7)	C(5)–H(15)	0.72(7)
N(2)–H(1)	0.85(7)	C(5)–H(25)	1.21(6)
C(4)–H(14)	0.77(11)	C(5)–H(35)	0.82(8)
C(4)–H(24)	0.81(12)		
Cl–Cu–S	120.34(9)	S–C(1)–N(1)	125.5(7)
Cu–S–C(1)	109.4(3)	N(3)–C(2)–C(5)	117.1(7)
C(3)–O(2)–C(4)	116.4(7)	N(3)–C(2)–C(3)	123.5(7)
N(3)–N(2)–C(1)	118.0(7)	C(3)–C(2)–C(5)	119.4(7)
N(2)–N(3)–C(2)	118.5(7)	O(2)–C(3)–C(2)	112.5(7)
N(1)–C(1)–N(2)	119.0(8)	O(1)–C(3)–C(2)	125.1(8)
S–C(1)–N(2)	115.5(6)	O(1)–C(3)–O(2)	122.5(8)
H(11)–N(1)–H(21)	103(8)	H(14)–C(4)–H(34)	94(12)
C(1)–N(1)–H(21)	126(5)	H(14)–C(4)–H(24)	119(11)
C(1)–N(1)–H(11)	127(6)	C(2)–C(5)–H(35)	107(5)
C(1)–N(2)–H(1)	120(5)	C(2)–C(5)–H(25)	107(3)
N(3)–N(2)–H(1)	122(5)	C(2)–C(5)–H(15)	113(6)
O(2)–C(4)–H(34)	116(8)	H(25)–C(5)–H(35)	111(6)
O(2)–C(4)–H(24)	118(8)	H(15)–C(5)–H(35)	111(8)
O(2)–C(4)–H(14)	104(7)	H(15)–C(5)–H(25)	107(6)
H(24)–C(4)–H(34)	105(11)		

TABLE 4. Selected bond distances (Å) and angles (°) for **B**

Cu–Cl	2.374(3)	S–C(1)	1.694(9)
Cu–S	2.357(2)	O(1)–C(3)	1.19(1)
Cu–P(1)	2.304(2)	O(2)–C(3)	1.35(1)
Cu–P(2)	2.291(3)	O(2)–C(4)	1.47(1)
P(1)–C(24)	1.824(9)	N(1)–C(1)	1.29(1)
P(1)–C(3)0	1.818(9)	N(2)–N(3)	1.37(1)
P(1)–C(36)	1.84(1)	N(2)–C(1)	1.38(1)
P(2)–C(6)	1.84(1)	N(3)–C(2)	1.31(1)
P(2)–C(12)	1.83(1)	C(2)–C(3)	1.44(2)
P(2)–C(18)	1.825(8)	C(2)–C(5)	1.50(1)
P(1)–Cu–P(2)	123.2(1)	C(12)–P(2)–C(18)	100.0(4)
S–Cu–P(2)	103.5(1)	C(6)–P(2)–C(18)	102.6(4)
S–Cu–P(1)	110.1(1)	C(6)–P(2)–C(12)	105.0(4)
Cl–Cu–P(2)	102.6(1)	C(3)–O(2)–C(4)	115.0(8)
Cl–Cu–P(1)	107.0(1)	N(3)–N(2)–C(1)	118.2(8)
Cl–Cu–S	109.9(1)	N(2)–N(3)–C(2)	120.5(8)
Cu–S–C(1)	109.8(4)	N(1)–C(1)–N(2)	118.3(8)
Cu–P(1)–C(36)	116.1(3)	S–C(1)–N(2)	115.0(7)
Cu–P(1)–C(30)	113.0(3)	S–C(1)–N(1)	126.7(8)
Cu–P(1)–C(24)	116.5(3)	N(3)–C(2)–C(5)	115.7(9)
Cu–P(2)–C(18)	115.5(3)	N(3)–C(2)–C(3)	121.3(9)
Cu–P(2)–C(12)	117.0(3)	C(3)–C(2)–C(5)	122.9(9)
Cu–P(2)–C(6)	114.6(3)	O(2)–C(3)–C(2)	111.2(9)
C(30)–P(1)–C(36)	105.6(4)	O(1)–C(3)–C(2)	128(1)
C(24)–P(1)–C(36)	102.4(4)	O(1)–C(3)–O(2)	121(1)
C(24)–P(1)–C(30)	101.6(4)		

TABLE 5. Comparison of bond lengths in the thiosemicarbazone moiety

	Hmpt·0.5H$_2$O	[Cu(Hmpt)$_2$Cl]	[Cu(PPh$_3$)$_2$(Hmpt)Cl]	{[Cu(Hpt)Cl]·2H$_2$O}$_n$	[{Cu(ept)Cl}$_2$]	[Fe(Hept)Cl$_2$]	[Zn(Hpt)$_2$]
S–C(1)	1.684(4)	1.707(9)	1.694(9)	1.710(3)	1.745(8)	1.68(1)	1.684(5)
C(1)–N(1)	1.325(5)	1.30(1)	1.29(1)	1.301(4)	1.321(11)	1.34(2)	1.337(7)
C(1)–N(2)	1.363(4)	1.36(1)	1.38(1)	1.355(5)	1.327(10)	1.36(2)	1.336(9)
N(2)–N(3)	1.367(4)	1.38(1)	1.37(1)	1.358(4)	1.346(8)	1.36(1)	1.385(6)
C(2)–N(3)	1.285(4)	1.30(1)	1.31(1)	1.291(5)	1.297(9)	1.29(1)	1.261(9)
C(2)–C(3)	1.506(6)	1.48(1)	1.44(2)	1.523(6)	1.455(11)	1.50(2)	1.537(7)
C(3)–O(1)	1.208(4)	1.21(1)	1.19(1)	1.224(7)	1.258(10)	1.22(2)	1.259(8)^a
C(3)–O(2)	1.337(4)	1.32(1)	1.35(1)	1.273(6)^a	1.318(9)	1.32(2)	1.22(1)
C(4)–O(2)	1.457(5)	1.44(1)	1.47(2)		1.465(11)	1.48(2)	
Reference	5	this work	this work	5	5	6	7

^{a}Coordinated atom.

TABLE 6. Hydrogen bonds (Å) in compounds **A** and **B**

Bond D–H...A[a]	Position of A	D–H	H...A	D...A	Angles (°) D–H...A
Compound **A**					
N(1)–H(11)...Cl	*x*, *y*, *z*	0.79(9)	2.53(8)	3.28(1)	160(8)
N(1)–H(21)...Cl	−*x*, −*y*, −*z*	0.84(8)	2.63(7)	3.42(1)	156(7)
N(1)–H(21)...N(3)	*x*, *y*, *z*	0.84(8)	2.42(8)	2.64(1)	96(5)
N(2)–H(1)...O(1)	*x*, *y*, *z*	0.85(7)	1.96(8)	2.60(1)	132(6)
Compound **B**					
N(1)–H(3)...Cl	*x*, *y*, *z*	1.07(-)[b]	2.31(-)[b]	3.21(1)	140(-)[b]
N(1)–H(2)...Cl	−*x*, −*y*+1, −*z*+1	0.96(-)	2.42(-)	3.34(1)	158(-)
N(1)–H(2)...N(3)	*x*, *y*, *z*	0.96(-)	2.38(-)	2.64(1)	94(-)
N(2)–H(1)...O(1)	*x*, *y*, *z*	1.00(-)	1.81(-)	2.61(1)	133(-)

[a]Donor–hydrogen...acceptor, D–H is at *x*, *y*, *z* and A is in the position given. [b]In **B** the hydrogen atoms have not been refined.

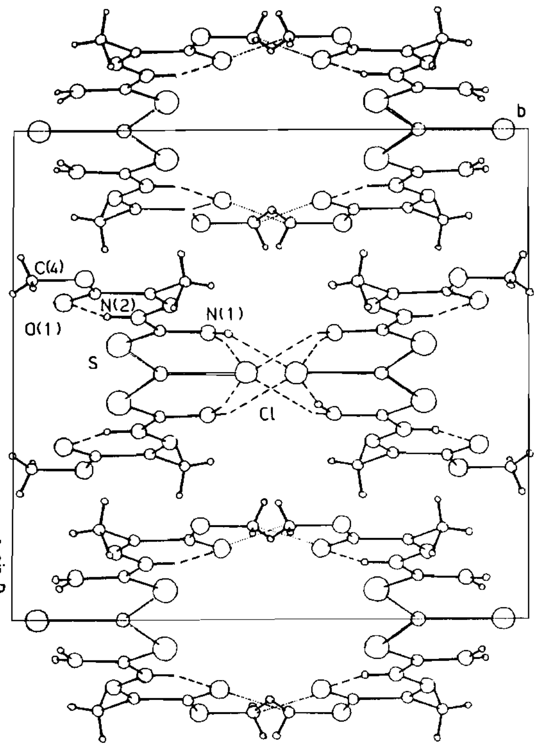

Fig. 3. The packing arrangement of **A** projected on the (001) plane.

We have observed that from the reaction of pseudocubane $[Cu(PPh_3)Cl]_4$ with sulfur containing ligands, pptu, dto, Hmpt (1:1 or 1:2 metal–ligand molar ratio), in toluene, a series of different copper(I) complexes is formed

$$[Cu(PPh_3)Cl]_4 + pptu \longrightarrow [Cu(PPh_3)(pptu)Cl]$$

$$[Cu(PPh_3)Cl]_4 + dto \longrightarrow [Cu(PPh_3)_2(dto)Cl]$$

$$[Cu(PPh_3)Cl]_4 + Hmpt\cdot 0.5H_2O \longrightarrow [Cu(PPh_3)_2(Hmpt)Cl]\cdot 0.5C_7H_8$$

The nature and geometry of the ligands together with the basicity of triphenylphosphine are the main factors which affect the stoichiometry and the stereochemistry of the complexes. On the basis of our recent works, at the present time, we can observe that the formation of monomeric complexes, containing two triphenylphosphine molecules and a tetrahedral coordination, seems to be favoured when nearly planar ligands, such as dto and Hmpt, are employed. Steric effects, which are prevalent in the pptu ligand, seem to favour the formation of complexes with a trigonal planar coordination where only one PPh_3 molecule is present.

The Cu–P (2.304(2), 2.291(3) Å) distances are near the upper limit of the range (2.24–2.31 Å) of those found in a number of copper(I) compounds with two phosphine ligands [2, 13]. The Cu–Cl and Cu–S bond lengths (2.374(3) and 2.357(2) Å respectively) agree with the corresponding bonds in other similar tetrahedral copper(I) compounds and are longer than those in **A** and in other three-coordinated copper(I) complexes [13–15, 16]. This variation is consistent with expectations on the effect of an increase of the coordination number on molecular geometry. The coordination angles Cl–Cu–S, S–Cu–P and Cl–Cu–P deviate slightly from the tetrahedral value (max. 6.9°). The P–Cu–P angle is much larger (123.2°) owing to the interactions between the two bulky phosphine ligands (C(17)...H(41) = 2.52(1) Å, C(35)...H(11) = 2.61(1) Å). The same behaviour is presented in ref. 2. The lower value of the P–Cu–P (123.2°) angle in comparison with that found in $Cu_2Cl_2(PPh_3)_3$ (131.8°) [18] is in agreement with the lengthening of the

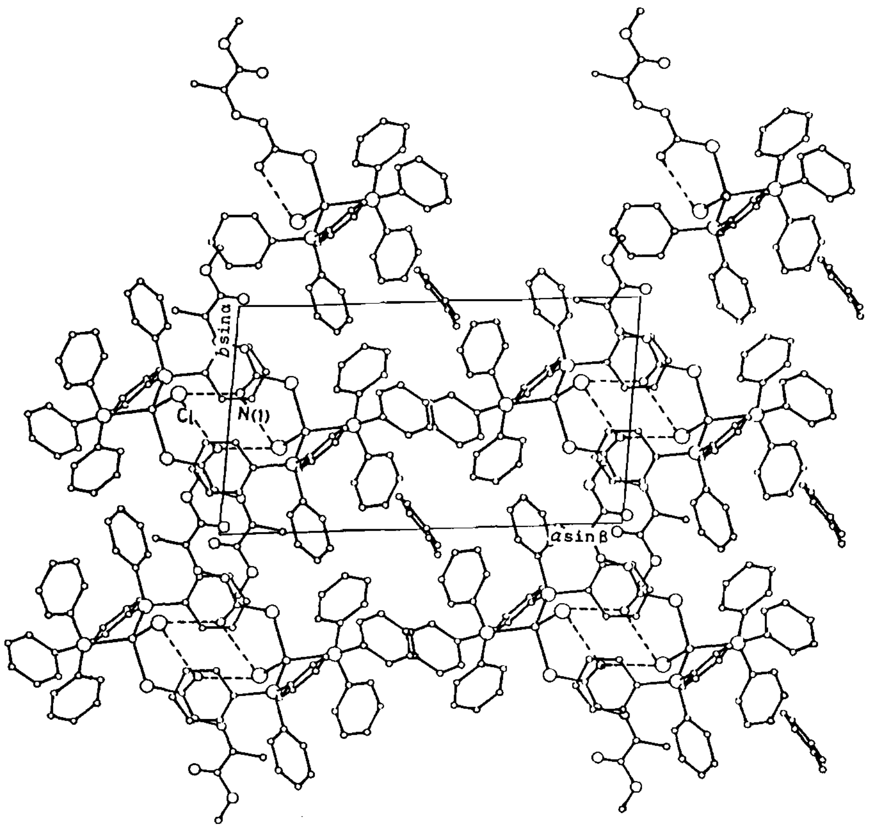

Fig. 4. Projection of **B** on the (001) plane. The hydrogen atoms have been omitted for clarity and only one of the two disordered toluene molecules is shown.

Cu–P distances (2.304(2), 2.291(3) Å versus 2.236(5) and 2.245(5) Å in $Cu_2Cl_2(PPh_3)_3$ [18]). Some relevant bond distances and angles with their estimated standard deviations are shown in Table 3 for **A** and in Table 4 for **B**. In the triphenylphosphine molecules the six independent P–C bond lengths range from 1.818(9) to 1.843(10) Å. As has been noted for other phosphine–metal complexes [2], the angles around the phosphorus atoms deviate significantly and systematically from the ideal tetrahedral value of 109° 28′. In fact Cu–P–C angles are all greater than the tetrahedral angle and range from 113.0(3) to 117.0(3)°, while C–P–C angles are all correspondingly smaller with values ranging from 100.0(4) to 105.6(4)° (Table 4). The six phenyl rings are planar within the limits of experimental error, and the C–C distances are in the usual range.

In both compounds the ligand is neutral, monodentate through the sulfur atom, contrary to the behaviour found in Cu(II), Zn and Fe(II) complexes [5–7] where the ligand (transesterificated or hydrolized) acts as an anionic tridentate group. The configuration of the ligand in both **A** and **B** compounds is *Z E Z* about the C(2)–N(3), C(1)–N(2) and C(2)–C(3) bonds (with respect to possible donating centres O(1), N(3) and S), while the uncoordinated thiosemicarbazone shows an *E E Z* configuration. The *Z E Z* configuration is stabilized by an intramolecular hydrogen bond between the hydrazinic NH group and the carbonylic oxygen of the pyruvic group. In **A** the Hmpt molecule is nearly planar, the largest deviation from the best plane being 0.09(2) Å for the terminal methyl carbon C(4). The thiourea moiety and the pyruvic group are planar and the dihedral angle between them is 1.7(4)°. In **B** the whole ligand deviates significantly from planarity; the thiourea moiety and the pyruvic group are planar but the dihedral angle between them is 8.3(3)°. The comparison of bond lengths in the thiosemicarbazone moiety is reported in Table 5 for the free ligand and some complexes. It can be observed that the charge delocalization is particularly influenced by the deprotonation on the hydrazinic nitrogen atom (see the compound $[\{Cu(ept)Cl\}_2]$ [5]). In both complexes of the present work the bond distances are similar to each other and to those found in the free ligand (in spite of the change of configuration) and show an extended π delocalization. The greatest differences are found in the C(2)–C(3) bonds.

In both compounds dimer-like molecules are formed by N(1)–H...Cl hydrogen bonds across the

TABLE 7. Selected infrared spectroscopic data (cm^{-1})

$[Cu(PPh_3)Cl]_4$	$Hmpt \cdot 0.5H_2O$	$[Cu(Hmpt)_2Cl]$	$[Cu(PPh_3)_2(Hmpt)Cl] \cdot 0.5C_7H_8$	Assignment
	3510			ν(OH)
		3340m,br	3340m	ν(NH)
	3290m,br	3290(sh)		
			3280m	
	3230ms		3230ms	
		3220ms		
		3160m	3160m	
	3150ms			
			3080m,br	ν(CH)
3050m			3050m	
	2990vw	2990vw		
	2950w	2950w		
			2940w	
	1720vs			ν(C=O)
		1690ms,br	1690m	
	1625s			ν(C=N)
	1610s			
		1600vs	1600s,br	
1580w			1580(sh)	ν(CC), ν(NCS)
1480s			1480s	
1435vs	1435s	1435s,br	1435vs	
		1415s		
		1295vs,br		$\delta(CH)_{in}$, ν(NCS) ν[C–C(=O)–O] system
	1290vs,br		1290s	
	1280(sh)			
	1260vs			
		1255s,br	1255ms	
		1220s	1220(sh)	
	1210m			
		1205s		
			1200ms,br	
1185w				
		1170s		
	1165m,br		1165s	
		1110vs	1110vs	
	1105vs,br			
1095s				
			1090ms	
		1060m	1060m	
	1040(sh)			
1030m	1030(sh)	1030mw		
			1025m	
		1010m		
1000m	1000w			
			995mw	
		975ms		ν(C=S)
			970mw,br	
	965m			
		860ms		
		855ms		
			850m	

(*continued*)

TABLE 7. (*continued*)

$[Cu(PPh_3)Cl]_4$	$Hmpt \cdot 0.5H_2O$	$[Cu(Hmpt)_2Cl]$	$[Cu(PPh_3)_2(Hmpt)Cl] \cdot 0.5C_7H_8$	Assignment
		770ms	770mw	$\delta(CH)_{out}$, $\nu(NCS)$
750(sh)			750(sh)	
745vs	745ms			
			740ms,br	
			730(sh)	
		725mw,br		
700vs				$\delta(CH)_{out}$, $\nu(PC)$
	695ms		690s	$\delta(CH)_{out}$, $\nu(NH)$, $\nu(NCS)$
		625ms	625m	
530s				ring skeletal
520vs			520(sh)	
			515ms,br	
			505ms,br	
500s				

symmetry centres at 0 0 0 in **A** and at 0 $\frac{1}{2}$ $\frac{1}{2}$ in **B** (Table 6). In **A** the dimers exchange a weak interaction C(4)–H...O(1) (x, $1-y$, $z-\frac{1}{2}$) = 3.34(2) Å around the symmetry centre at 0 $\frac{1}{2}$ 0, so forming chains running along b and an elliptical section channel along the z axis (Fig. 3). Considering the van der Waals radii of the atoms which face the channel surface, the free space for a hypothetic filling-in molecule has a radius of only about 1 Å, too small to host a molecule of the solvent (toluene). In **B** a weak interaction C(35)–H...O(1) (x, $y-1$, z) 3.28(1) Å links the dimers in chains running along the crystallographic b axis. The toluene molecules, surrounded by phenyl rings from PPh_3, occupy interstitial sites centered at $\frac{1}{2}$ 0 0 between the dimer chains (Fig. 4).

The main vibrational bands of $[Cu(PPh_3)Cl]_4$ and $Hmpt \cdot 0.5H_2O$ and their reaction products are given in Table 7. The $\nu(NH)$ bands of the thiosemicarbazone ligand are observed as medium bands in the 3290–3150 cm^{-1} region. The slight shift of these bands and the appearance of a new medium band at 3340 cm^{-1} in the spectra of Cu(I) complexes suggest the participation of both secondary and primary nitrogen atoms in hydrogen bonding. Upon complex formation, the $\nu(C{=}O)$ and $\nu(C{=}N)$ stretching vibrations are shifted to lower frequencies by 30 and *c*. 20 cm^{-1}, respectively. These shifts are often proposed to show coordination of a carbonylic oxygen and an imine nitrogen. In our case, the X-ray structural analysis clearly excluded any possibility of oxygen or nitrogen atoms of the ligand being bound to the Cu(I) ion. The differences in the position of the $\nu(C{=}O)$ and $\nu(C{=}N)$ bands are due to an intramolecular hydrogen bonding between C=O...HN which incorporates the C=N group into a six-membered cyclic ring. The $\nu(C{=}S)$ vibrations in free Hmpt located at 965 and 860 cm^{-1} exhibit opposite shifts in both complexes. The band at 965 cm^{-1} is positively shifted by 5–10 cm^{-1} while the band at 860 cm^{-1} is shifted to lower frequency. These observations and the appearance of medium bands having $\nu(CS)$ character at 770–725 cm^{-1} and at 625 cm^{-1} in the spectra of both complexes suggest coordination of the thiocarbonyl sulfur to the metal ion. In the region below 500 cm^{-1} the spectra are very similar and new bands are not present, so the assignment of the $\nu(M{-}S)$ stretching vibrations cannot be made. Finally both bands observed in the spectra of $[Cu(PPh_3)Cl]_4$ and $[Cu(PPh_3)_2(Hmpt)Cl] \cdot 0.5C_7H_8$ at 1095 and 1090 cm^{-1}, respectively, have a significant contribution (assignments omitted in Table 7) from the P–C bonds of the triphenylphosphine molecule.

Supplementary material

Tables listing structure factors, hydrogen positional and isotropic thermal parameters, and anisotropic thermal parameters for the heavy atoms are available from the authors on request.

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