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Solid state syntheses and crystal structures of $[Cu(HOC_6H_4CHNNHCSNH_2)(PPh_3)_2X]$ (X = I, Br)

He-Gen Zheng,[a] Dong-Xiang Zeng,[a] Xin-Quan Xin[a]* and Wing-Tak Wong[b]

[a] State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093, P.R. China

[b] Department of Chemistry, Nanjing University, Pokfulam Road, Hong Kong

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Abstract—The complexes $[Cu(L)(PPh_3)_2X]$ [L_1 = 2-[(4-hydroxyphenyl methylene)]hydrazinecarbothioamine, X = I(**I**) and L_2 = 2-[(2-hydroxyphenyl methylene)]hydrazinecarbothioamine, X = Br(**II**) were obtained by the solid state reaction of L, CuX, PPh_3 and characterized by elemental analysis, IR and UV–Vis spectroscopy. The crystal structures have been determined by single crystal X-ray diffraction. The copper atom is coordinated tetrahedrally by two phosphine atoms from PPh_3, one halogen atom and one sulfur atom from L acting as a monodentate ligand. In the compound (**I**), two molecules and two solvents MeCN molecules are in the asymmetric unit. The Cu—S bond lengths are 2.402(3) Å for molecule A and 2.376(3) Å for molecule **B**; respectively. In the compound (**II**), one solvate MeCN molecule is in the asymmetric unit; the Cu—S bond length is 2.379(3) Å. © 1997 Elsevier Science Ltd

Keywords: copper(I) complexes; thiosemicarbazone complexes; solid state syntheses; spectroscopic characterization; crystal structures.

The coordination compounds of copper(I) with heterocyclic thione donors as ligands have been of considerable interest because of their stereochemistry [1,2]. Many Cu^I complexes coordinated by sulfur atom donors have been synthesized and characterized by X-ray analysis [3–5]. Skoulika and Aubry [5] have investigated ligand behaviour in connection with different factors such as the complexing properties of the ligands containing N, S and P as donors and the experimental conditions employed in the synthesis reactions. In order to further explore coordination modes of Cu^I complexes containing S atom as donor, we used thiosemicarbazone L to replace heterocyclic thione to react with CuX, PPh_3 by solid state reaction at low heating temperature; the title complexes $[Cu(L)(PPh_3)_2X]$ were thus obtained. The X-ray crystal structures, IR, far-IR, UV–vis spectra have been investigated.

EXPERIMENTAL

Preparation

The ligands were prepared by a literature method [6]. Other chemicals were reagent grade and used without further purification.

$[Cu(L)(PPh_3)_2I]$ (**I**). A well-ground mixture CuI (0.38 g, 2.0 mmol), PPh_3 (1.05 g, 4.0 mmol), and L_1 (0.38 g, 2.0 mmol) was placed in a reaction tube. A white solid was obtained by heating the mixture at 95°C for 5 h. After extracting the product with CH_3CN (30 cm^3), filtering the yellow–white extract and layering the filtrate with $(CH_3)_2CHOH$ (10 cm^3), white-needle crystals were obtained several days later. The crystals for elemental analyses were dried *in vacuo*. Yield 87.0%. Found: C, 58.0; H, 4.4; N, 5.9; Calc. for $C_{46}H_{42}N_4OCuISP_2$; C, 58.1; H, 4.4; N, 5.9%.

$[Cu(L_2)(PPh_3)_2Br]$ (**II**). Compound (**II**) was prepared in the same way as (**I**) using CuBr, L_2 instead of CuI, L_1, white-needle crystals were obtained, yield 86.6%. Found: C, 61.3; H, 4.6; N, 6.3; Calc. for $C_{46}H_{42}N_4OCuISP_2$: C, 61.1; H, 4.7; N, 6.2%.

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* Author to whom correspondence should be addressed.

Physical measurements

Elemental analyses were performed on a Perkin–Elmer 240 elemental analyzer, IR, far-IR spectra were recorded on a Nicolet 170SX FTIR spectrometer, electronic spectra were recorded on a Shimadzu. UV-240 spectrophotometer ($CHCl_3$ solution, 10^{-3}M).

X-ray structure determination

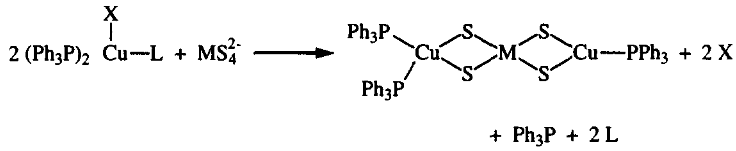
A selected single crystal with the dimensions $0.30 \times 0.32 \times 0.33$ mm for compound (**I**) or $0.26 \times 0.31 \times 0.35$ mm for compound (**II**) was mounted on a glass fiber. Intensity data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) using ω–2θ scans at room temperature. The data were corrected for Lorentz, polarization effects and absorption corrections using ψ-scan method. The crystallographic parameters are summarized in Table 1.

All calculations were performed on a Silicon-Graphics computer using the TEXSAN program package [7]. The structure was solved by direct methods (SIR92) [8]. The structure was refined by the full-matrix least squares methods. All hydrogen atoms were generated geometrically and included isotropically in the structure-factor calculation but not refined. The final R, R_w values are 0.056, 0.069 for compound (**I**) and 0.053, 0.049 for compound (**II**).

RESULTS AND DISCUSSION

Synthesis

The new tetrahedral mononuclear copper(I) complexes $[Cu(L)(PPh_3)_2X]$ were prepared by the solid state reaction method at 95°C, which was developed in recent years and has been applied in synthesizing more than 200 clusters and coordination compounds [9]. This method is different from solution reactions because it needs no solvent and sometimes generates unusual products [10]. Since CuX is usually insoluble in organic solvents and hard to react with other materials, the solid state reaction method was applied to synthesize title compounds with high yields. Thiosemicarbazone (L) is usually a bidentate ligand as reported in the literature, but the ligand L coordinated with Cu^I as monodentate in the presence of PPh_3. When the title compounds reacted with MoS_4^{2-} or WS_4^{2-}, a known compound was obtained [11,12]. The reactions is as follows:



M = Mo, W; L = L$_1$, L$_2$; X = Br, I.

Table 1. Crystal data for compounds (I) and (II)

Formula	$C_{46}H_{42}N_4OCuIP_2S$ (I)	$C_{46}H_{42}N_4OCuBrP_2S$ (II)
Formula weight	951.32	904.32
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)
a(Å)	11.756(1)	19.604(4)
b(Å)	32.030(3)	9.616(3)
c(Å)	23.994(3)	23.457(3)
β(°)	98.23	98.27(1)
V(Å)^3	8941(1)	4375(1)
Z	8	4
T(K)	295	301
D_{calc}(g/cm^3)	1.413	1.373
F(000)	3856.00	1856.00
μ(Mo–K$_\alpha$)(cm^{-1})	13.36	15.75
No. of observations ($I > 3\sigma(I)$)	6445	2909
No. of variables	499	250
R	0.056	0.053
Rw	0.069	0.049
Goodness of fit indicator	2.53	2.12
Maximum shift in final cycle	0.06	0.03
Maximum peak in final diff. map (e/Å^3)	1.50	0.51
Minimum peak in final diff. map (e/Å^3)	−0.56	−0.39

Description of the structure of complexes (**I**) *and* (**II**)

Selected bond distances and bond angles of the complexes are given in Table 2 and 3, respectively. ORTEP diagrams are given in Figures 1 (molecule 1 of compound (**I**)) and 2 (compound (**II**)). The Cu^I metal ion is four-coordinated forming a distorted tetrahedron. The ligand L acts as a monodentate ligand coordinating through the S atom. The other positions of the tetrahedron are occupied by one halogen atom and two triphenylphosphine ligands. In the compound(I), the Cu—S bond lengths are 2.402(3) Å for molecule A, 2.376(3) Å for molecule B, as usually found for tetrahedrally coordinated copper(I) and S atom donors [3,5]. The Cu—P distances [2.310(3), 2.282(3) Å for molecule A, 2.290(3), 2.306(3) Å for molecule B] are comparable to those found in (PPh_3)$_2$Cu($C_2H_4N_2S_2$)Br [13] and [Cu(SC(Ph)NHPh (PPh_3)$_2$Cl] [14]. The P-Cu-P angles [123.1(1)° for molecule A, 120.2(1)° for molecule B] are in good agreement with values reported for other bis(triphenylphosphine)copper(I) compounds such as 125.0(2)° for Cu(Py2SH)(PPh_3)$_2$Br [15], 121.71(3) for [Cu(PPh_3)$_2$(bzimtH_2)Cl] [5], 123.8(2) for [Cu (PPh_3)$_2$($C_2H_4N_2S_2$)Br [13]. In compound(**II**), the Cu—Br distance of 2.536(3) Å is significantly longer than those observed in Cu(PPh)$_3$Br (2.35Å) [16]. Moreover, it is slightly longer than corresponding Cu—Br distance of 2.462(2) Å in Cu(Py2SH) (PPh_3)$_2$Br [15]. The Cu—S bond length (2.379(3) Å) is comparable to those observed in (**I**). Cu—P bond lengths [2.267(3), 2.279(3) Å] are shorter than 2.304(2) Å in [Cu(PymtH)(PPh_3)$_2$Br] [17]. The P—Cu—P angles [135.4(1)] is wider than those found in compound (**I**) and other compounds mentioned above. In the compound (**I**) and (**II**), the P—Cu—P angles deviate considerably from the tetrahedral value of 109.47°. A possible explanation for the large value is the steric interaction between the PPh_3 group and the CuSX entity. Besides, some other differences exist

Table 2. Selected bond lengths and angles for compound (**I**)

molecule (A)		molecule (B)	
I(1)—Cu(1)	2.661(2)	I(2)—Cu(2)	2.640(2)
Cu(1)—S(1)	2.402(3)	Cu(2)—S(2)	2.376(3)
Cu(1)—P(1)	2.310(3)	Cu(2)—P(3)	2.290(3)
C(1)—N(2)	1.36(1)	C(45)—N(5)	1.33(1)
C(2)—N(3)	1.27(1)	C(46)—N(6)	1.29(1)
Cu(1)—P(2)	2.282(3)	Cu(2)—P(4)	2.306(3)
S(1)—C(1)	1.70(1)	S(2)—C(45)	1.72(1)
C(1)—N(1)	1.33(1)	C(45)—N(4)	1.32(1)
N(2)—N(3)	1.38(1)	N(5)—N(6)	1.41(1)
C(6)—O(1)	1.39(1)	C(50)—O(2)	1.40(1)
I(1)—Cu(1)—S(1)	110.18(9)	I(2)—Cu(2)—S(2)	110.33(9)
I(1)—Cu(1)—P(1)	104.40(9)	I(2)—Cu(2)—P(3)	108.72(10)
I(1)—Cu(1)—P(2)	108.96(9)	I(2)—Cu(2)—P(4)	103.72(9)
S(1)—Cu(1)—P(1)	107.6(1)	S(2)—Cu(2)—P(3)	104.3(1)
S(1)—Cu(1)—P(2)	102.4(1)	S(2)—Cu(2)—P(4)	109.5(1)
P(1)—Cu(1)—P(2)	123.1(1)	P(3)—Cu(2)—P(4)	120.2(1)
Cu(1)—S(1)—C(1)	112.2(4)	Cu(2)—S(2)—C(45)	112.1(4)
S(1)—C(1)—N(1)	121.4(9)	S(2)—C(45)—N(4)	120.6(9)
S(1)—C(1)—N(2)	118.1(8)	s(2)—C(45)—N(5)	117.8(8)
N(1)—C(1)—N(2)	120.6(10)	N(4)—C(45)—N(5)	121(1)

Table 3. Selected bond lengths and angles for compound (**II**)

Br(1)—Cu(1)	2.536(2)	Br(1)—Cu(1)—S(1)	114.81(9)
Cu(1)—S(1)	2379(3)	Br(1)—Cu(1)—P(1)	99.95(9)
Cu(1)—P(1)	2.267(3)	Br(1)—Cu(1)—P(2)	99.21(9)
C(1)—N(2)	1.31(1)	S(1)—Cu(1)—P(1)	103.9(1)
C(2)—N(3)	1.25(1)	S(1)—Cu(1)—P(2)	103.9(1)
Cu(1)—P(2)	2.279(3)	P(1)—Cu(1)—P(2)	135.4(1)
S(1)—C(1)	1.66(1)	Cu(1)—S(1)—C(1)	107.0(4)
C(1)—N(1)	1.38(1)	S(1)—C(1)—N(1)	121.0(9)
N(2)—N(3)	1.37(1)	S(1)—C(1)—N(2)	124.0(9)
C(8)—O(1)	1.31(1)	N(1)—C(1)—N(2)	114.9(10)

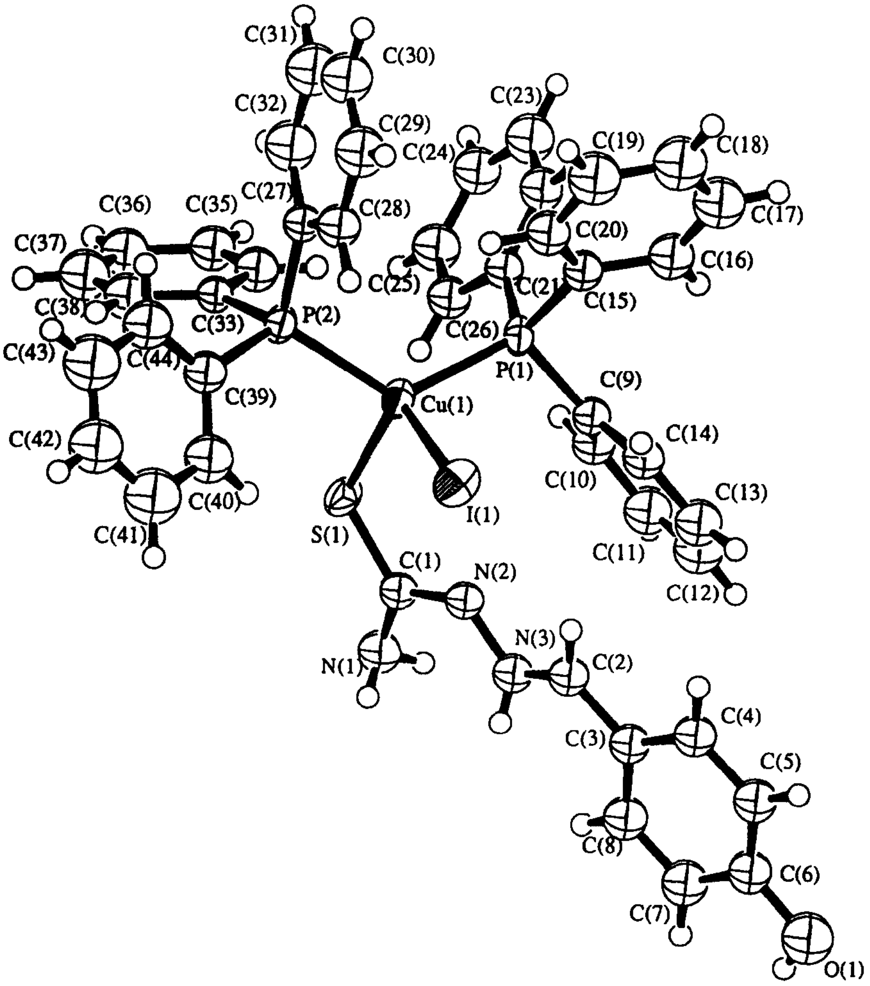


Fig. 1. ORTEP diagram of molecule 1 of compound **I**.

in these two title compounds. Firstly, in the compound (**I**), two molecules and two solvate MeCN exist in an asymmetric unit, but only one molecule and one solvate MeCN are in present the unit of (**II**). Secondly, the coordination polyhedra of both compounds are different due to the P—Cu—P coordination angles: the Cu coordination polyhedron in (**I**) is close to a regular tetrahedron [102.4(1)° < L—Cu—L′ < 123.1(1)° for molecule A, 103.72(9)° < L—Cu—L < 120.2(1)° for molecule B], whereas the L—Cu—L′ bond angles in (**II**) are in the range of 99.21(9)° and 135.4(1)°.

IR spectra

IR spectra are in agreement with the X-ray diffraction data with respect to the monodentate sulfur donating character. The presence of $\nu_{(OH)}$, $\nu_{(NH2)}$, $\nu_{(NH)}$, values [3416, 3290, 3128.1 cm^{-1} for (**1**); 3435, 3304 and 3164 cm^{-1} for (**II**) confirms that O, N atoms are not bonded to the Cu^{I} atom. The monodentate nature of the ligand is further confirmed by far IR spectra, wherein a new band is observed about 361 cm^{-1} which can be assigned to Cu—S vibrations [8]. This assignment is supported by the absence of absorptions in the region where ν_{Cu-N} generally lies [18].

UV–vis spectra

The UV–vis spectra of the compound in CHCl$_3$ solutions, as expected, show only two absorption bands at ~245 and ~325 nm which can be assigned as intraligand transitions.

Supplementary material

The atomic coordinates, thermal parameters, bond distances, bond angles and observed and calculated structure factors for the title compounds are available from the authors upon request.

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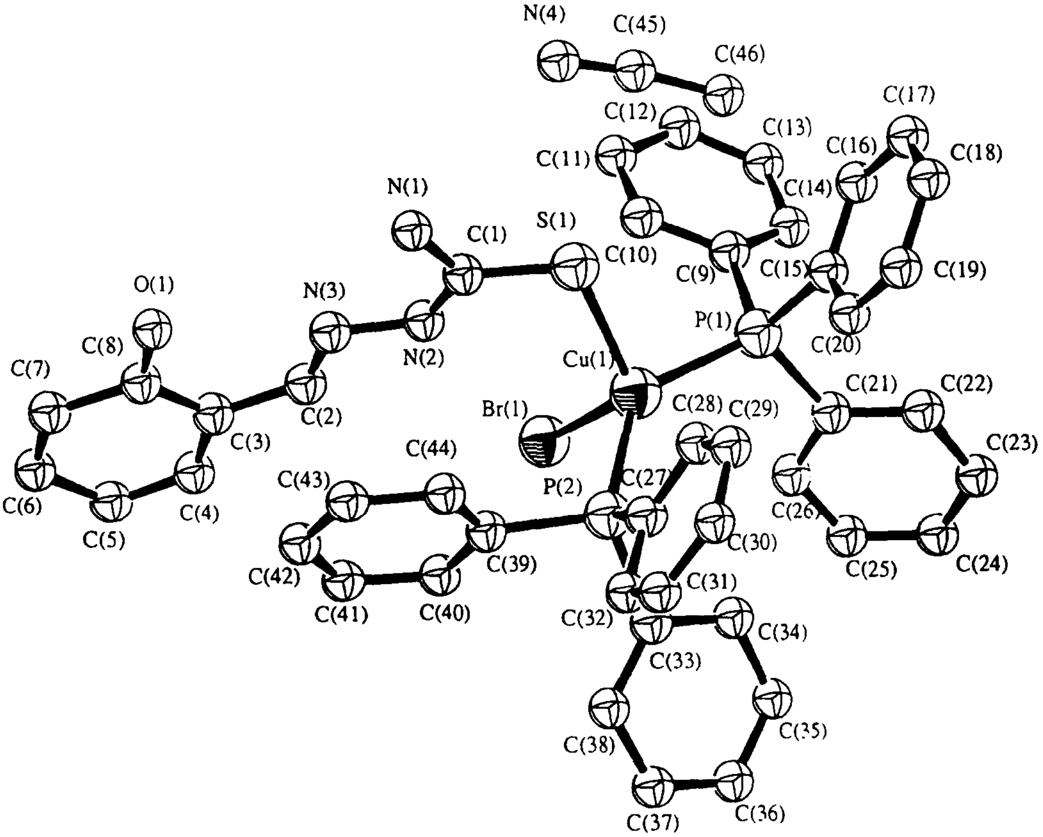

Fig. 2. ORTEP diagram of compound **II**.

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