Pergamon

Polyhedron Vol. 14, No. 13 14, pp. 1799 1807, 1995
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0277-5387/95 $9.50+0.00

0277-5387(94)00478-1

SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COPPER(I) COMPLEXES CONTAINING HALIDES, TRIPHENYLARSINE AND *N,N*-DIMETHYL-*N′*-PHENYLTHIOUREA (dmptH), *N,N*-DIBUTYL-*N′*-PHENYLTHIOUREA (dbptH) OR 1,3-THIAZOLIDINE-2-THIONE (tzdtH). THE X-RAY CRYSTAL STRUCTURE OF $[Cu(PPh_3)_2(dmptH)Cl]$

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(*Received* 27 *September* 1994; *accepted* 18 *November* 1994)

Abstract—The arsine complexes $[Cu(AsPh_3)_2(LH)X]$ (LH = *N,N*-dimethyl-*N′*-phenylthiourea (dmptH), *N,N*-dibutyl-*N′*-phenylthiourea (dbptH) or 1,3-thiazolidine-2-thione (tzdtH); X = Cl, Br, I) have been prepared and characterized on the basis of analytical, IR, electronic (UV–vis), ^{1}H NMR, conductivity and magnetic measurements. In all cases there is a distorted tetrahedral environment around copper(I) and the ligands (LH) bind through thione sulphur atom to copper(I). We also report the crystal structure of complex $[Cu(PPh_3)_2(dmptH)Cl]$ which shows that metal ion has a distorted tetrahedral geometry with bond lengths Cu—S = 2.459(2), Cu—Cl = 2.308(1), Cu—P(1) = 2.305(1) and Cu—P(2) = 2.313(1) Å. The NH is intramolecularly hydrogen bonded to Cl with a bond distance NH···Cl = 2.31 Å.

The involvement of copper(I) in several biologically important reactions/copper–sulphur interactivations,[1–4] and the suitability of copper(I) complexes in providing models for the representation of several enzyme sites,[5,6] and the stereoelectronic factors responsible for stereoelectrochemical preferences of copper(I) compounds are some of the factors which have stimulated enhanced research activity. This is exemplified by reports on the ligating behaviour of heterocyclic thiones,[7] thioureas[8] and the N-substituted derivatives of thiourea.[9–11] Copper complexes with 1,3-thiazolidine-2-thione and its N-methyl and N-ethyl derivatives have been reported.[11,12] A number of copper(I) complexes with heterocyclic thiones, possessing an α-nitrogen heteroatom, and triaryl phosphines[13–20] and triarylarsines[21,22] have been recently characterized by single X-ray crystallography. The properties of triphenylphosphine heterocyclic thiones mixed ligand complexes are fairly well known, but their -arsine, -stibine and -bismuthine analogues are not well studied.

Following our interest in coordination properties of ligands containing the H—N—C═S group,[11,23–27] we have recently reported the -phosphine counterpart[11] of the complexes. For the sake of comparison and in view of the unique properties of copper coordinated triphenylarsine,[28,29] we describe the syntheses and characterization of novel copper(I) distorted tetrahedral complexes $[Cu(AsPh_3)_2(LH)X]$ with the title ligands. The IR spectral studies of the ligands and complexes show the involvement of thione sulphur in coordination. In this paper we also report the single crystal X-ray structure of the phosphine complex $[Cu(PPh_3)_2(dmptH)Cl]$. The structure of this complex matches the previously reported conclusion for the compound[11] on the basis of spectral studies. We are growing crystals of arsine complexes suitable for X-ray studies.

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EXPERIMENTAL

Materials and instruments

All the chemicals used were either of Analar or chemically pure grade. The ligands *N*,*N*-dimethyl-*N′*-phenylthiourea (dmptH) and *N*,*N*-dibutyl-*N′*-phenylthiourea (dbptH) were prepared by the direct addition of phenylisothiocyanate to the appropriate secondary amine in methanol in 1 : 1 ratio, and the products recrystallized from acetone. The ligand 1,3-thiazolidine-2-thione was purchased from Eastern Organic Chemicals and recrystallized from hot water before use. The cuprous halides[30] were freshly prepared according to the literature method just prior to use.

The carbon, hydrogen and nitrogen analyses were done at the Regional Sophisticated Instrumentation Center, Central Drugs Research Institute, Lucknow, India. The IR spectra were recorded in KBr pellets in the range 4,000–400 cm^{-1} on a Shimadzu IR-420 double beam spectrophotometer. The electronic (UV–vis) spectra were recorded on a Shimadzu Double beam UV-160 spectrophotometer in acetonitrile. ^1H NMR spectra were recorded on a Jeol PM-60 MHz spectrometer in the range 0–20 ppm(δ) using TMS as internal calibrant in $CDCl_3$ for the complexes of dmptH and dbptH, whereas dmso-d_6 was used as solvent for the complexes of tzdtH. Conductivity measurements were performed on an Elico conductivity bridge type CM 82T in nitrobenzene or acetonitrile solution. Magnetic measurements were carried out by using a parallel field vibrating sample magnetometer (VSM) model-150A (Princeton Applied Research Corporation, Princeton, NJ). The melting points (m.p.) of the complexes were recorded on a Fisher-John melting point apparatus and are uncorrected.

Preparation of compounds

Preparation of $[Cu(AsPh_3)_2(dmptH)X]$. A mixture of CuX (1 mmol) and $AsPh_3$ (4 mmol) was refluxed on a water bath with constant stirring in benzene (50 cm^3) until the reaction mixture became a clear solution (about 20 min for Cl, Br and >30 min for I). The solution thus obtained was cooled to room temperature and the appropriate ligand (1 mmol) was added with constant stirring. The solution immediately became pale yellow, and was stirred for about 3 h at room temperature. The volume of the reaction mixture was reduced to about 5 cm^3 and stepwise addition of petroleum ether (60–80°C) with constant shaking initiated the precipitation of the desired complex as a yellowish white turbidity. The addition of petroleum ether was stopped at a point where the turbidity just dissolved on shaking and the clear solution was left for slow evaporation at room temperature overnight, whereupon fine crystals of the complex appeared and were separated by centrifugation and washed several times with petroleum ether and dried *in vacuo* over P_4O_{10} for several hours. The complexes can also be separated by continuous excess addition of the petroleum ether (about 100 cm^3) to the reaction mixture after reducing its volume with constant shaking; however, the particle size of the compound obtained in this way was small or almost in powder form.

Preparation of $[Cu(AsPh_3)_2(dbptH)X]$. For the preparation of these complexes the above method of preparation for the dmpt-complexes was followed but in the case of Br, the desired complex was isolated during reaction and therefore for this case the following method for the preparation of tzdtH complexes was adopted.

Preparation of $[Cu(AsPh_3)_2(tzdtH)X]$. A mixture of CuX (1 mmol) and $AsPh_3$ (4 mmol) was refluxed on a water bath with constant stirring in benzene (50 cm^3) until the reaction mixture became a clear solution (about 20 min for Cl, Br and >30 min for I). The solution thus obtained was cooled to room temperature and the appropriate ligand (1 mmol) was added with constant stirring. The solution immediately became pale yellow, and was stirred for about 3 h at room temperature. During the course of the reaction, the desired complexes were precipitated. The volume of the reaction mixture was reduced to about 5 cm^3 and an excess petroleum ether (about 100 cm^3) was added with constant shaking to ensure the complete precipitation of the complex and left for a few hours to allow the complex to settle. The complexes thus obtained were separated by centrifugation and washed several times with petroleum ether and dried *in vacuo* over P_4O_{10} for several hours.

The m.p., colour and yield of the complexes are given in Table 1 together with the analytical data. Conductivity measurements in nitrobenzene or acetonitrile solution indicate the non-electrolytic nature of the complexes.[31] All complexes are diamagnetic at room temperature.

Collection and reduction of intensity data

Intensities were collected at room temperature, on an Enraf—Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator) in the $\theta-2\theta$ scan mode ($\theta < 25°C$). Lorentz and polarization corrections were applied. The structure was solved by the direct method using the Xtal-3.2 software

Table 1. Analytical data, colour, melting point (m.p.) and yield of the complexes

Compound (Colour)	Found (calc.) (%)						M.p. (θ/°C)	Yield (%)
	C	H	N	Cu	S	Halide		
1 $[Cu(AsPh_3)_2(dmptH)Cl]$	60.4	4.9	3.0	7.1	3.5	7.0	102	31
(pale yellow)	(60.6)	(4.8)	(3.1)	(7.1)	(3.6)	(7.0)		
2 $[Cu(AsPh_3)_2(dmptH)Br]$	57.6	4.4	3.1	6.6	3.5	8.4	98	38
(cream white)	(57.7)	(4.5)	(3.0)	(6.8)	(3.4)	(8.5)		
3 $[Cu(AsPh_3)_2(dmptH)I]$	55.2	4.4	2.8	6.6	3.3	12.8	154d	40
(pale yellow)	(55.0)	(4.3)	(2.9)	(6.5)	(3.3)	(12.9)		
4 $[Cu(AsPh_3)_2(dbptH)Cl]$	62.7	5.7	2.8	6.5	3.2	3.6	112	94
(cream white)	(62.8)	(5.6)	(2.9)	(6.6)	(3.3)	(3.6)		
5 $[Cu(AsPh_3)_2(dbptH)Br]$	60.2	5.2	2.9	6.2	3.0	7.9	127	96
(cream white)	(60.0)	(5.3)	(2.8)	(6.2)	(3.1)	(7.8)		
6 $[Cu(AsPh_3)_2(dbptH)I]$	57.3	5.0	2.5	6.1	3.2	11.8	132d	35
(pale yellow)	(57.4)	(5.1)	(2.6)	(6.0)	(3.0)	(11.9)		
7 $[Cu(AsPh_3)_2(tzdtH)Cl]$	56.5	4.2	1.8	7.6	7.8	4.3	178d	63
(cream white)	(56.4)	(4.3)	(1.7)	(7.7)	(7.7)	(4.3)		
8 $[Cu(AsPh_3)_2(tzdtH)Br]$	53.4	4.1	1.7	7.2	7.4	9.0	185d	66
(yellowish white)	(53.5)	(4.0)	(1.6)	(7.3)	(7.3)	(9.1)		
9 $[Cu(AsPh_3)_2(tzdtH)I]$	50.8	3.9	1.6	6.9	7.1	13.7	186d	60
(pale yellow)	(50.8)	(3.8)	(1.5)	(6.9)	(7.0)	(13.8)		

Table 2. Summary of crystal, intensity collection and refinement data

Formula	$CuC_{45}H_{42}N_2P_2SCl$
Formula weight	803.85
a (Å)	10.182(4)
b (Å)	13.480(3)
c (Å)	14.864(8)
α (°)	79.73(3)
β (°)	78.49(3)
γ (°)	84.82(3)
V (Å^3)	1964(1)
Z	2
Measured temperature (K)	293
D_{calc} (Mg m^{-3})	1.359
Space group	$P\bar{1}$
Radiation	Mo-K_α (λ = 0.71073 Å)
μ(cm^{-1})	13.4
Scan speed	Variable scan rate
Scan type	θ-2θ
Scan range (°)	0.60+0.35 tan θ
2θ range (°)	4–50
Data collected/unique	7022/6612
Data used	4696
Data form h, k, l	$0\rightarrow11$, $-14\rightarrow14$, $-16\rightarrow16$
Weighting scheme.	$w = 1/\sigma$
Goodness of fit (obs./all data)	2.40/2.07
F(000)	836
$(\Delta p)_{max}//(\Delta\rho)_{min}$(e Å^{-3})	0.580//−0.739
Number of refined parameters	469
R (obs./all data)	0.040/0.066
R_w (obs./all data)	0.032/0.034

package. Refinement was carried out by blocked full matrix least squares, in which $\Sigma w\Delta^2$ was minimized. The hydrogen atoms of the phenyl groups were calculated as 'riding' on carbon atoms at a distance of 0.95 Å. Refined parameters were calculated by using anisotropic thermal parameters for non-hydrogen atoms and isotropic factors for all hydrogen atoms.

A summary of the crystal, intensity collection and refinement data is presented in Table 2.

RESULTS AND DISCUSSION

Spectral characterization

The title ligands contain the NHCS group which may adopt either the thione form H—N—C═S or the thiol form N═C—S—H. The IR spectra of the ligands dmptH, dbptH and their complexes are summarized in Table 3. Both ligands adopt the thione form in the free state and in their complexes. This is evident by the absence of the ν(SH) band in the region of 2500 cm^{-1} and by the presence of ν(NH) in the range 2890–3310 cm^{-1}. Both ligands contain the thioamide group (HNCS) and should give rise to four characteristic thioamide bands namely I, II, III and IV in the region of 1500, 1300, 1000 and 800 cm^{-1} and have contributions from ν(C—N) + δ(N—H), ν(C═S) + ν(C═N) + ν(C—H); ν(C—N) + ν(C—S) and ν(C—S) modes of vibration, respectively. All these bands are found for the ligand dmptH but band III of ligand dbptH is too weak to be observed. The other bands useful for identification of donor atoms are ν(NH) and ν(C═S). All complexes exhibit the characteristic bands of triphenylarsine.[32] The mode of ligand bonding is decided on the basis of shifts of ν(NH), ν(C═S) and four thioamide bands on complexation (Table 3). The thioamide bands II and III have contributions from ν(CN) and ν(CS) vibrations but ν(CS) contributes more than ν(CN) to the thioamide band II;[33] therefore band II can be utilized to decide the coordination site but it is difficult to decide the coordination site on the basis of shifts of band III.

The band at 3310–3340 and 3230 cm^{-1} assigned to ν(NH) for both the free ligands dmptH and dbptH, respectively, are observed in the region of 3150–3200 cm^{-1} for the dmptH complexes and in the region of 3200 cm^{-1} for the dbptH complexes, respectively. The red shift of the ν(N-) bands are probably due to the hydrogen bonding in the complexes. The thioamide band I, having a contribution from ν(C—N) + δ(N—H) shifts slightly towards the higher region or remains almost unaffected indicating the non-involvement of the NH group in

Table 3. Major IR bands of dmptH, dbptH and their complexes (cm^{-1})

			Thioamide bands			
Compound	ν(NH)	ν(CS)	I	II	III	IV
Ligand (dmptH)	3310–3340	1145	1595	1325	1065	770
			1535	1300		710
1 [Cu(AsPh$_3$)$_2$(dmptH)Cl]	3150	1115	1600	1330	1070	770
			1535	1280		735
2 [Cu(AsPh$_3$)$_2$(dmptH)Br]	3160	1115	1600	1315	1060	770
			1520	1275		750
3 [Cu(AsPh$_3$)$_2$(dmptH)I]	3200	1115	1595	1325	1060	770
			1550	1315		735
				1270		
Ligand (dbptH)	3230	1150	1595	1355	—	765
			1530	1330		715
			1505	1320		—
4 [Cu(AsPh$_3$)$_2$(dbptH)Cl]	3150	1160	1600	1380	—	810
		1130	1525	1330		685
			1505	1245		—
5 [Cu(AsPh$_3$)$_2$(dbptH)Br]	3150	1165	1600	1375	—	800
		1130	1525	1330		685
			1505	1245		
6 [Cu(AsPh$_3$)$_2$(dbptH)I]	3225	1110	1600	1325	—	765
			1515			
			1500			

coordination. The thioamide bands II, having more contribution from $\nu(C{=}S)$ undergo a red shift or split in which intense bands are observed in the lower frequency region. In the case of compound **1** the broad thioamide band II of the ligand dmptH at 1325 and 1300 cm^{-1} splits into two bands at *ca* 1330 and 1280 cm^{-1}, and in compounds **2** and **3** these bands are observed at 1325 and 1275 cm^{-1}. The broad thioamide band II of the ligand dbptH, observed at 1355, 1330 and 1320 cm^{-1} split into the three bands at 1380, 1330 and 1245 cm^{-1} on complex formation, from which the band at 1330 cm^{-1} becomes sharp. These shifts indicate the involvement of the C═S group in coordination. This is also supported by the red shift of the $\nu(C{=}S)$ band at $\Delta\bar{\nu}$ = *ca* 25–30 cm^{-1} in the case of the complexes of the dmptH ligand, and the red shift or splitting of the $\nu(C{=}S)$ band of the complexes of the dbptH ligand in which the red shifted bands are found to be strong. The bands observed at 770 and 710 cm^{-1} for the ligand dmptH and at 765 and 715 cm^{-1} for the ligand dpbtH are assigned as thioamide band IV. The band at 770 cm^{-1} splits into two ($\Delta\bar{\nu}$ = *ca* 35 and 30 cm^{-1}) for compounds **1** and **2**, but for compound **3**, the band is not discernible. The band at 710 cm^{-1} in the compounds is absent which may perhaps be coupled with the band due to phenyl groups at 695 cm^{-1}. The band at 765 cm^{-1} of the dbptH ligand, splits into two bands (*ca* 810 cm^{-1} and 685 cm^{-1}) or shifts to 685 cm^{-1} in all three compounds **4**, **5** and **6**, and the band at 715 cm^{-1} is not observed in the complexes. All these observations clearly indicate the involvement of the C═S group in coordination. Bonding through the sulphur atom is also favoured because copper(I), being a soft acid, should prefer to interact with a soft base such as sulphur and indeed the presence of the sulphur—copper(I) bond is confirmed by the X-ray single crystal structure of many complexes of ligands containing the thioamide group[34] and of substituted thiourea ligands.[35] In particular Cu^{I}—S bond with heterocyclic thione donors having thioamide groups[36,37] has been extensively studied.

Four thioamide bands of the ligand tzdtH, I at 1490 cm^{-1}, II at 1245 cm^{-1}, III at 990 cm^{-1} and IV at 690 cm^{-1}, 650 cm^{-1} were assigned by Preti and Tosi[38] and they have reported various complexes including copper(I) with the deprotonated ligand. Vibrational analysis of the ligand has been carried out by Devillanova *et al.*,[33] who have also reported the various copper(I) complexes[9] with the neutral ligand. The bands at 690 and 650 cm^{-1} which are assigned to ν(CS) *sym* and *asym* by Preti and Tosi,[38] are mainly due to ΔNH and $\nu(C_1S_1)$ (C_1 = carbon atom bonded with ring sulphur, S_1 = ring sulphur), respectively, according to Devillanova *et al.*[33] Keeping this difference of opinion in mind, we have taken various other bands to decide the coordination site and not only the thiomamide bands.[38] Principal IR bands of the free ligand tzdtH and its complexes are given in Table 4. This ligand, tzdtH, is also bonded to the metal through the thione sulphur as shown by the shifts of the ν(CS) and $\nu(CN)+\delta(NH)$ bands. The IR bands namely, ν(NH) at 3130 cm^{-1}, $\nu(CN)+\delta(NH)$ at 1500 cm^{-1}, ν(CS) at 1085 and 545 cm^{-1}, $\nu(CS_1)+\delta(CS)+$ring def. (C = carbon atom bonded with thione sulphur and ring sulphur) at 585 cm^{-1}, $\nu(C_1S_1)+$ring def. at 653 cm^{-1} and Δ(CS) at 435 cm^{-1} of the free ligand[33] are used to decide the donor site. Comparison of IR spectra of the free ligand with its complexes shows that the ν(CS) band at 1085 cm^{-1} either couples with the characteristic band of triphenylarsine[32] at 1088 cm^{-1} or shifts to the lower region and the band at 585 cm^{-1} remains almost unaffected. The Δ(CS) band at 434 cm^{-1} of the ligand is absent in the IR spectra of the complexes. This shows the major shift of the bands arising due to the C═S group which indicates the involvement of thione sulphur in the coordination. Other bands at 585, 653 and 1500 cm^{-1} of the free ligand are observed either as such or shift towards the higher frequency region due to complex formation, which indicates the non-involvement of the ring sulphur and NH group. The ν(NH) band which shifts to the lower region may be due to hydrogen bonding. In fact very recently many copper(I) complexes of the triphenylarsine and the heterocyclic thione donors have been reported[21,22] having the same stoichiometry with different heterocyclic thione donors and some of them have been characterized by single X-ray crystallography.

Electronic (UV–vis) and the ^{1}H NMR spectral data for the complexes and free ligands are given in Table 5 with assignment. As expected, only UV absorption bands are observed which are assigned as intra-ligand (IL) transitions. The very weak band of the ligand tzdtH at 336 nm is not observed in its complexes. This band probably shifts to the higher region on complex formation. The ^{1}H NMR spectra of the complexes clearly show the peaks due to the ligands and triphenylarsines. The ^{1}H NMR peak of the >NH proton of the complexes appears as a broad signal. The broadening of the signal may be due to hydrogen bonding.[14,15,18,21,22] The fine resolution ^{1}H NMR spectra at different concentrations in the >NH region show almost no shift of the >NH proton signal which indicates the >NH hydrogens are intramolecularly bonded to the halides. The ^{1}H NMR spectra are recorded for the complexes after shaking the NMR solution with a few drops of D_2O. The peak due to the >NH group

Table 4. Major IR bands of tzdtH and its complexes (cm^{-1})

Compound	ν(NH)	ν(CN) + δ(NH)	$\nu(\mathrm{CS}_1)$	ν(CS)	Δ(CS)	Vibrations between 600 cm^{-1} and 400 cm^{-1}
Ligand (tzdtH)	3130–2700	1500	653, 585	1085, 545	434	585, 545, 434
7 $[\mathrm{Cu(AsPh_3)_2(tzdtH)Cl}]$	3125–3060	1535	660, 585	1025, 535	—	585, 535, 470
8 $[\mathrm{Cu(AsPh_3)_2(tzdtH)Br}]$	3130	1530	660, 585	1025, 530	—	585, 535, 465
9 $[\mathrm{Cu(AsPh_3)_2(tzdtH)I}]$	3160	1525	650, 585	1025, 530	—	585, 530, 465

Table 5. Electronic (UV–vis) spectral data of the ligands and the complexes in $\mathrm{Ch_3CN}$ and ^{1}H NMR spectral data of the ligands and complexes in $\mathrm{CDCl_3}$

Compound	Band position, λ (nm), with assignments	^{1}H NMR signal with assignments [ppm(δ)]
Ligand (dmptH)	223.0 246.5	3.27 (s, 6H, $-\mathrm{CH_3}$ groups) 7.20 (s, 5H, $-\mathrm{C_6H_5}$ group)
1 $[\mathrm{Cu(AsPh_3)_2(dmptH)Cl}]$	228.0 IL	3.07 (s, 6H, $-\mathrm{CH_3}$ groups) 6.83–7.33 (m, 35H, $-\mathrm{C_6H_5}$ groups) 10.27(s, 1H > NH group)
2 $[\mathrm{Cu(AsPh_3)_2(dmptH)Br}]$	227.0 IL	3.07 (s, 6H, $-\mathrm{CH_3}$ groups) 6.83–7.33 (m, 35H, $-\mathrm{C_6H_5}$ groups) 9.93 (s, 1H, > NH group)
3 $[\mathrm{Cu(AsPh_3)_2(dmptH)I}]$	228.0 IL 245.0 IL	3.10 (s, 6H, $-\mathrm{CH_3}$ groups) 7.00–7.50 (m, 35 H, $-\mathrm{C_6H_5}$ groups) 9.58 (s, 1H, > NH group)
Ligand (dbptH)	207.0 225.0 251.0	0.67–2.00 (m, 6H, $-\mathrm{CH_3}$ groups) 3.63 (t, 12H, > $\mathrm{CH_2}$ groups) 6.67–7.33 (m, 35H, $-\mathrm{C_6H_5}$ groups) 6.95(s[broad], 1H, > NH group)
4 $[\mathrm{Cu(AsPh_3)_2(dbptH)Cl}]$	226.0 IL 247.0 IL	0.67–1.83 (m, 6H, $-\mathrm{CH_3}$ groups) 343 (t, 12H, > $\mathrm{CH_2}$ groups) 6.83–7.50 (m, 35H, $-\mathrm{C_6H_5}$ groups) 9.97(s, 1H, > NH group)
5 $[\mathrm{Cu(AsPh_3)_2(dpbtH)Br}]$	256.5 IL	0.67–1.83 (m, 6H, $-\mathrm{CH_3}$ groups) 3.50 (t, 12H, > $\mathrm{CH_2}$ groups) 7.00–7.67 (m, 35H, $-\mathrm{C_6H_5}$ groups) 9.53 (s, 1H, > NH group)
6 $[\mathrm{Cu(AsPh_3)_2(dbptH)I}]$	211.5 IL 247.0 IL	0.67–1.83 (m, 6H, $-\mathrm{CH_3}$ groups) 353 (t, 12H, > $\mathrm{CH_2}$ groups) 6.83–7.40 (m, 35H, $-\mathrm{C_6H_5}$ groups) 9.07 (s, 1H, > NH group)
Ligand (tzdtH)	221.0 336.0 276.0	3.27–4.17 (m, 4H, > $\mathrm{CH_2}$ groups) 7.97 (s[broad], 1H, > NH group)
7 $[\mathrm{Cu(AsPh_3)_2(tzdtH)Cl}]^a$	229.0 IL 247.0 IL	2.50–4.00 (m, 4H, > $\mathrm{CH_2}$ groups) 7.37 (s, 30H, $-\mathrm{C_6H_5}$ groups) 8.11 (s, 1H, > NH group)
8 $[\mathrm{Cu(AsPh_3)_2(tzdtH)Br}]^a$	215.0 IL 274.0 IL	2.50–4.00 (m, 4H, > $\mathrm{CH_2}$ groups) 7.37 (s, 30H, $-\mathrm{C_6H_5}$ groups) 7.84 (s, 1H, > NH group)
9 $[\mathrm{Cu(AsPh_3)_2(tzdtH)I}]^a$	248.0 IL 275.0 IL	2.50–4.00 (m, 4H, > $\mathrm{CH_2}$ groups) 7.37 (s, 30H, $-\mathrm{C_6H_5}$ groups) 7.50 (s, 1H, > NH group)

[a] ^{1}H NMR spectra recorded in dmso-d_6.

Table 6. Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses

Cu—S	2.459(2)	C(37)—N(1)	1.358(5)
Cu—Cl	2.308(1)	C(37)—N(2)	1.337(5)
Cu—P(1)	2.305(1)	N(2)—C(44)	1.458(6)
Cu—P(2)	2.313(1)	N(2)—C(45)	1.461(5)
S—C(37)	1.708(4)	N(1)—C(38)	1.426(5)

Cl—Cu—S	108.61(4)	C(37)—N(1)—C(38)	131.2(3)
Cl—Cu—P(1)	107.36(5)	C(37)—N(2)—C(44)	120.7(3)
Cl—Cu—P(2)	111.51(5)	C(37)—N(2)—C(45)	124.4(4)
S—Cu—P(1)	109.18(5)	C(37)—N(1)—H1	114.2(3)
S—Cu—P(2)	94.98(4)	C(38)—N(1)—H1	114.6(4)
P(1)—Cu—P(2)	123.89(4)	N(1)—C(37)—N(2)	120.5(3)
Cu—S—C(37)	114.5(2)	C(44)—N(2)—C(45)	113.1(3)
S—C(37)—N(1)	119.0(2)	N(1)—C(38)—C(39)	116.9(4)
S—C(37)—N(2)	120.5(3)	N(1)—C(38)—C(43)	122.7(4)

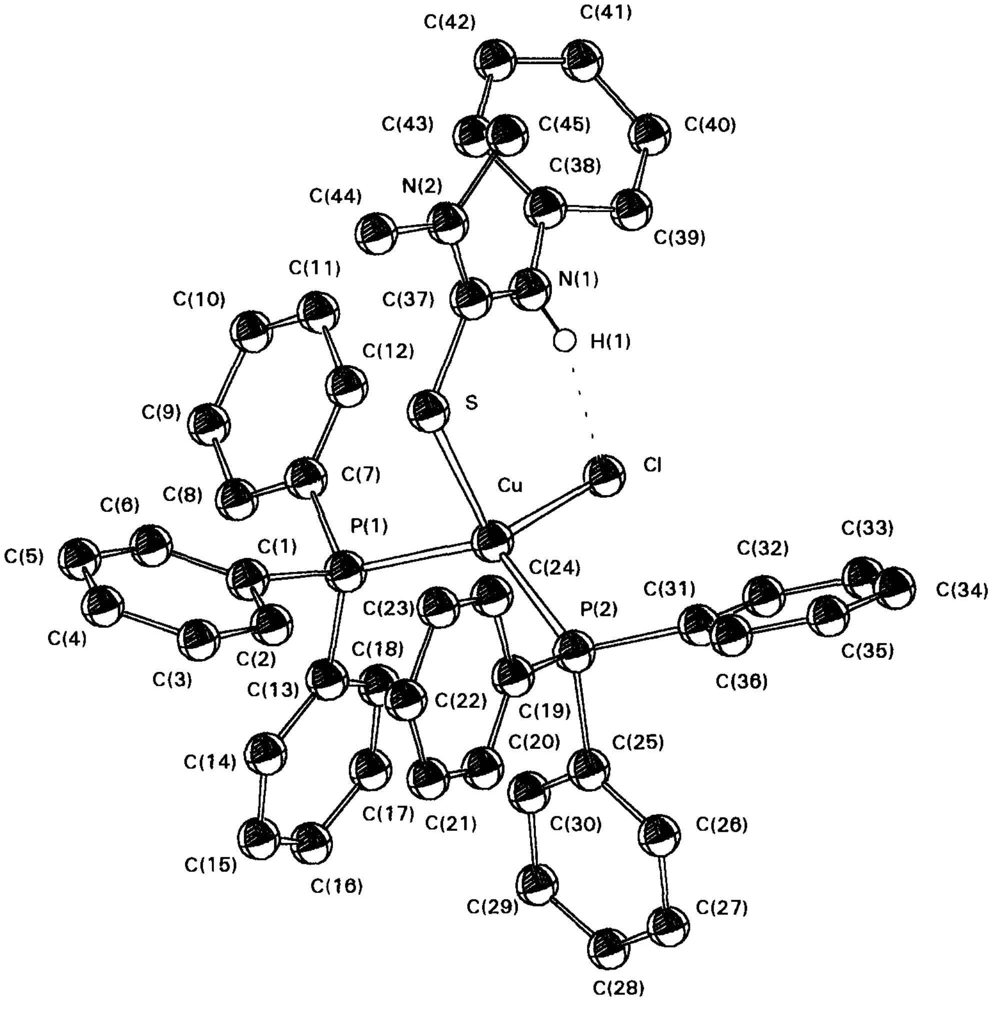

Fig. 1. Ortep diagram of the molecule [Cu(PPh$_3$)$_2$ (dmptH)Cl] with 50% probability ellipsoid. Hydrogen atoms are omitted for clarity except H(1). Hydrogen bonding is shown as a dashed line.

was not found which confirms the presence of the $>$NH group, its assignment and, in turn, the hydrogen bonding in the complexes. The gradual decrease in intramolecular hydrogen bonding strength is reflected by the corresponding lowering of δ values for $>$NH proton on going from chloride to bromide to iodide complexes.[22] The intramolecular hydrogen bonding in such systems has been confirmed by X-ray crystallography.[18,21,22,36] On complexation the ^{1}H NMR signals of $>CH_2$ and $-CH_3$ groups shift slightly towards the higher magnetic field (lower δ value). The proportions of the protons, observed by integration, are exactly matching with the proposed stoichiometry of the complexes.

Description of structure

Selected bond distances and angles are presented in Table 6. The coordination around copper is a distorted tetrahedral, with one sulphur, two phosphorus and one chlorine atoms in the vicinity of copper (Figure 1). This result is a consequence of the approximately equal steric factors near the copper coordination sphere.

The Cu—S bond length is 2.459(2) Å, as usually found for tetrahedrally coordinated copper(I) with thione-S donors.[20,39,40] The Cu—P(1) and Cu—P(2) distances of 2.305(1) and 2.313(1) Å, respectively, are in agreement with the distances in [Cu $(PPh_3)_2$(bzimtH_2)Cl].[15] The Cu—Cl distance of 2.308(1) Å is similar to those found in two complexes of the type [Cu$(PPh_3)_2$(L)Cl] (L = bzimtH_2, nbzimtH_2).

For comparison purposes, selected interatomic distances and angles of the three related complexes [Cu$(PPh_3)_2$(dmptH)Cl], [Cu$(PPh_3)_2$(bzimtH_2)Cl] and [Cu$(PPh_3)_2$(nbzimtH_2)Cl] are included in Table 7. Three of the angles around copper in the two known complexes, as well as in the present, are nearly those of a regular tetrahedron. The P(1)—Cu—P(2) angle deviates 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 CuSCl entity; but as the angle has opened up considerably, these steric interactions are not likely to be the sole cause for the distortion.

Table 7. Interatomic distances (Å) and angles (°) in [Cu$(PPh_3)_2$(dmptH)Cl] (A), [Cu$(PPh_3)_2$(bzimtH_2)Cl] (B) and [Cu$(PPh_3)_2$(nbzimtH_2)Cl] (C)

	A	B	C
Cu—S	2.459(2)	2.377(1)	2.381(2)
Cu—Cl	2.308(1)	2.376(1)	2.384(2)
Cu—P	2.305(1)	2.278(1)	2.265(2)
	2.313(1)	2.295(1)	2.282(2)
P—Cu—P	123.89(4)	121.71(3)	124.75(7)
P—Cu—Cl	107.36(5)	103.67(4)	103.75(8)
	111.51(5)	111.74(4)	110.41(7)
S—Cu—Cl	108.61(4)	106.62(4)	108.09(7)
S—Cu—P	109.18(5)	109.62(4)	108.21(8)
	94.98(4)	103.03(4)	100.86(9)

In comparison with the other two complexes B and C, it is seen that the Cu—S distance is lengthened upon coordination, which suggests that the π-character in this bond is reduced.

Geometries within the phosphine and the thione ligands are standard. The average P—C (1.827 Å) and S—C (1.708 Å) bond lengths are close to those found in other similar complexes.[20]

The NH hydrogen is intramolecularly hydrogen bonded to Cl. The NH $\cdots$ Cl bond distance is 2.31 Å.

Acknowledgements—The authors are grateful to Dr P. K. Bhardwaj, Department of Chemistry, Indian Institute of Technology (Kanpur, India) for the use of the X-ray facility for data collection and refinement. One of the authors (R.S.) is grateful to the Indian Institute of Technology (Kanpur, India) for providing financial assistance for a Research Associateship.

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