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SUBSTITUTION REACTIONS OF $[Cu^I(PPh_3)_3X]$ (X = Cl, Br OR I) WITH N,N-DIMETHYL-N′-PHENYLTHIOUREA (dmptH), N,N-DIBUTYL-N′-PHENYLTHIOUREA (dbptH) AND 1,3-THIAZOLIDINE-2-THIONE (tzdtH)

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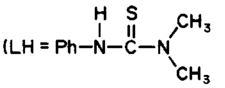
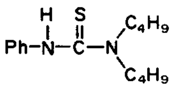
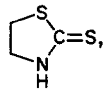
Abstract—Reactions of $[Cu(PPh_3)_3X]$ with the titled ligands yield

$[Cu(PPh_3)_2(LH)X]$, (LH =  $Ph{-}N(H){-}C(=S){-}N(CH_3)_2$ (dmptH);  $Ph{-}N(H){-}C(=S){-}N(C_4H_9)_2$

(dbptH) or  C=S, (tzdtH)).

The complexes have been characterized on the basis of analytical, IR, electronic (UV–vis), ^1H, ^{31}P and ^{13}C NMR, conductivity and magnetic measurements. In all cases there is a distorted tetrahedral environment around copper(I), and the ligands (LH) bind through the thione sulphur atom to copper(I).

The applications of heterocyclic thioamides in corrosion protection[1] and the biological importance of copper–sulphur interactions[2,3] have stimulated much of the research effort exemplified by reports on the ligating behaviour of heterocyclic thiones,[4] thioureas[5] and the N-substituted derivatives of thiourea.[6,7] Copper complexes with 1,3-thiazolidine-2-thione and its N-methyl and N-ethyl derivatives have been reported,[8] but copper salts invariably produce complexes with heterocyclic thiones which are unpredictable with respect to stoichiometry, stereochemistry and metal oxidation state.[3] This prompted us to study the reaction of $[Cu^I(PPh_3)_3X]$ with 1,3-thiazolidine-2-thione. In addition, we report the reaction of these copper(I) tetrahedral complexes with dmptH and dbptH as an extension of our work on soft-acid–soft-base interactions.[9,10]

EXPERIMENTAL

All the chemicals used were either of an Analar or chemically pure grade. The complexes of the type $[Cu(PPh_3)_3X]$ (X = Cl, Br or I)[11,12] were prepared by the literature method. The ligands N,N-dimethyl-N′-phenylthiourea (dmptH) and N,N-dibutyl-N′-phenylthiourea (dbptH) were prepared by the direct addition of phenyl isothiocyanate on the appropriate secondary amine in methanol in a 1 : 1 ratio, and recrystallization of the product using acetone as a solvent. The ligand 1,3-thiazolidine-2-thione was purchased from Eastern Organic Chemicals and recrystallized from hot water before use. Sulphur, halides and copper were estimated gravimetrically. The carbon, hydrogen and nitrogen analyses were done at the Microanalytical Laboratory, I.I.T., Kanpur. The IR spectra were recorded in KBr pellets in the range 4000–400 cm^{-1} on a Shimadzu IR-420 double beam spectrophotometer. The electronic spectra were recorded on a Shimadzu Double beam UV-160 spectrophotometer. All the NMR spectra were recorded in $CDCl_3$ solution. ^1H NMR spectra were recorded on a Jeol PMX-60 MHz spectrometer in the range 0–20 ppm (δ) using TMS as an internal calibrant. ^{31}P NMR (decoupled) were recorded on a Varian Associates XL-300 FT-NMR spectrometer using

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85% H_3PO_4 as an external calibrant. ^{13}C NMR (decoupled) were recorded on a Varian Associates XL-200 FT-NMR spectrometer and peaks are relative to TMS (0 ppm). Conductivity measurements were done on the Elico conductivity bridge type of CM 82T in nitrobenzene solution. Magnetic measurements were obtained using a parallel field vibrating sample magnetometer (VSM) model 150A (Princeton Applied Research Corporation, Princeton, NJ). M.p.s of the complexes were recorded on a Fisher John melting point apparatus and are uncorrected.

Preparation of the compounds

In a benzene solution (50 cm^3) of $[Cu(PPh_3)_3X]$ (1 mmol), a solution of an equivalent amount of the ligand (1 mmol) in benzene (25 cm^3) was added slowly and the clear mixture was heated under reflux for *ca* 2 h. The resulting clear solution was concentrated to *ca* 20 cm^3 under reduced pressure. The addition of petroleum ether (60–80°C) (50 cm^3) and allowing to stand for 2–3 h with occasional stirring resulted in the isolation of the microcrystalline products. These complexes were centrifuged and washed several times with petroleum ether and dried *in vacuo*. M.p.s, colours and yields of the complexes are given in Table 1, along with the analytical data.

RESULTS AND DISCUSSION

The analytical data of the complexes are given in Table 1, which are consistent with the stoichiometries proposed. The conductivity of the complexes was found to be in the range 0.25–0.50 Ω^{-1} cm^2 mol^{-1} in nitrobenzene solution, indicating the non-electrolytic nature of the complexes.[13] All the complexes are diamagnetic at room temperature.

The IR spectra of the ligands dmptH, dbptH and their complexes are summarized in Table 2. Both the 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 2500 cm^{-1} region, and by the presence of ν(NH), in the range 2890–3310 cm^{-1}. Both the ligands contain the thioamide group (H—N—C=S) and should give rise to four characteristic thioamide bands, namely I, II, III and IV in the regions 1500, 1300, 1000 and 800 cm^{-1}, and have contributions from $\nu(C—N)+\delta(N—H)$, $\nu(C=S)+\nu(C=N)+\nu(C—H)$, $\nu(C—N)+\nu(C—S)$ and ν(C—S) modes of vibrations, respectively. All of these bands are found for the ligand dmptH, but band III of the ligand dbptH was too weak to be observed. The other bands useful for the identification of donor atoms are ν(NH) and ν(C=S). All complexes exhibited the characteristic bands of triphenylphosphine.[14] The mode of ligand bonding was decided on the basis of shifts on complexation of ν(N—H), ν(C=S) and four thioamide bands (Table 2). The thioamide bands II and III have

Table 1. Analytical data of the complexes with m.p.s and yields

	Compounds			Found (calculated) %				M.p.s (°C)	Yield (%)
		C	H	N	Cu	S	Halide		
(1)	$[Cu(PPh_3)_2(dmptH)Cl]$	67.3	5.2	3.5	7.6	3.9	4.4	169	89
	(white)	(67.3)	(5.3)	(3.5)	(7.9)	(4.0)	(4.4)		
(2)	$[Cu(PPh_3)_2(dmptH)Br]$	63.7	5.0	3.3	7.5	3.8	9.4	168	86
	(white)	(63.8)	(5.0)	(3.3)	(7.5)	(3.8)	(9.4)		
(3)	$[Cu(PPh_3)_2(dmptH)I]$	60.4	4.7	3.1	7.1	3.6	14.2	161	98
	(white)	(60.4)	(4.7)	(3.1)	(7.1)	(3.6)	(14.2)		
(4)	$[Cu(PPh_3)_2(dbptH)Cl]$	69.1	6.1	3.0	7.2	3.6	3.4	142	91
	(white)	(69.0)	(6.1)	(3.2)	(7.2)	(3.6)	(4.0)		
(5)	$[Cu(PPh_3)_2(dbptH)Br]$	65.7	5.8	3.0	6.8	3.4	8.6	150	86
	(white)	(65.8)	(5.8)	(3.0)	(6.8)	(3.4)	(8.6)		
(6)	$[Cu(PPh_3)_2(dbptH)I]$	62.6	5.5	2.9	6.5	3.3	13.0	141	93
	(white)	(62.6)	(5.6)	(2.9)	(6.5)	(3.3)	(13.0)		
(7)	$[Cu(PPh_3)_2(tzdtH)Cl]$	63.1	4.7	2.0	8.4	8.6	4.9	204	87
	(yellowish white)	(63.1)	(4.7)	(1.9)	(8.5)	(8.6)	(4.8)		
(8)	$[Cu(PPh_3)_2(tzdtH)Br]$	59.5	4.4	1.8	8.1	8.0	10.2	179d	77
	(yellowish white)	(59.5)	(4.5)	(1.8)	(8.1)	(8.1)	(10.1)		
(9)	$[Cu(PPh_3)_2(tzdtH)I]$	65.1	4.2	1.7	7.6	7.7	15.1	171d	72
	(yellowish white)	(65.1)	(4.2)	(1.7)	(7.6)	(7.7)	(15.2)		

d = decomposed.

Table 2. Major IR bands of dmptH, dbptH and their complexes (cm^{-1})

	Compounds	ν(NH)	ν(C=S)	Thioamide bands I	II	III	IV
	Ligand [dmptH]	3310	1145	1595	1325	1065	770
		2950		1535	1300		710
(1)	$[Cu(PPh_3)_2(dmptH)Cl]$	2950	1115	1605	1330	1070	785
				1540	1315		735
					1280		
(2)	$[Cu(PPh_3)_2(dmptH)Br]$	3100	1115	1600	1315	1060	770
		2950		1540	1305		750
		2900			1270		
(3)	$[Cu(PPh_3)_2(dmptH)I]$	3150	1120	1595	1315	1065	775
				1540	1305sh		
					1270		
	Ligand [dbptH]	3230	1150	1595	1355	—	765
		2940		1530	1330		715
		2890		1505	1320		
(4)	$[Cu(PPh_3)_2(dbptH)Cl]$	2940	1125	1605	1325	—	730
		2890sh		1520			
				1505			
(5)	$[Cu(PPh_3)_2(dbptH)Br]$	—	1125	1600	1325	—	730
		2950		1520			
		2895		1500			
(6)	$[Cu(PPh_3)_2(dbptH)I]$	3150	1125	1605	1325	—	730
		2950		1515sh			
		2895		1500			

contributions from ν(CN) and ν(CS) vibrations, but ν(CS) contributes more than ν(CN) to the thioamide band II.[15] 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 bands at 3310 and 3230 cm^{-1}, assigned to ν(NH) for both the ligands dmptH and dbptH, respectively, become too weak to be observable in the IR spectra of the complexes. The thioamide band I, having contributions from $\delta(N—H)+\nu(C—N)$, shifts slightly towards the higher region, indicating the non-involvement of the NH group on coordination. The thioamide bands II, having more contribution from $\nu(C{=}S)$, undergo a red shift or split giving intense bands in the lower frequency region. In the case of compound **1** the broad thioamide band II of ligand dmptH, at 1325 and 1300 cm^{-1}, is split into three bands at *ca* 1330, 1315 and 1280 cm^{-1}; in compounds **2** and **3** these bands are observed at 1315, 1305 and 1270 cm^{-1}. The broad thioamide band II of the ligand dbptH is observed at 1355, 1330 and 1320 cm^{-1} and becomes a sharp single band at 1325 cm^{-1} on complexation. 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, *ca* $\Delta\nu = 25–30$ cm^{-1}, and the red shift or splitting of the thioamide band IV (see Figs 1 and 2). The bands observed at 770 and 710 cm^{-1} for the ligand dmptH (Fig. 1), and at 765 and 715 cm^{-1} for the ligand dbptH (Fig. 2), are assigned as thioamide band IV. The band at 770 cm^{-1} splits into two *ca* $\Delta\nu = 50$ cm^{-1} for compound **1** (Fig. 1), and *ca* $\Delta\nu = 20$ cm^{-1} for compound **2**; 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 the phenyl groups at 695 cm^{-1} [14] (Fig. 1). The band at 765 cm^{-1} (Fig. 2) splits into two bands, *ca* 780 and 730 cm^{-1}, or shifts to 730 cm^{-1} (Fig. 2) in all the three compounds **4**, **5** and **6**, and the band at 715 cm^{-1} is not observed. All these observations clearly indicate the involvement of the C=S group in the coordination. Bonding through the sulphur atom is also favoured because copper(I), being soft, should prefer to interact with a soft donor such as sulphur and indeed the presence of the sulphur–copper(I) bond was confirmed by the X-ray single structure of many complexes of the ligands having the thioamide group[16] and of substituted thiourea ligands.[17] The $Cu^I—S$ bond with heterocyclic thione donors having thioamide groups[18–29] have been extensively studied.

Four thioamide bands of the ligand tzdtH, I at

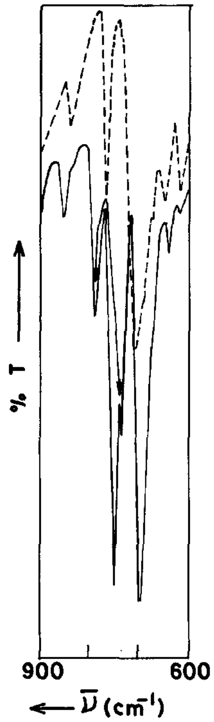


Fig. 1. Thioamide band IV of the ligand dmptH (---) and its splitting into two bands in complex [Cu(PPh$_3$)$_2$ (dmptH)Cl] (——).

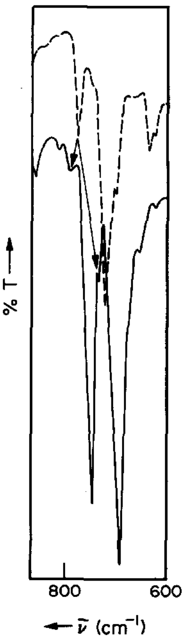


Fig. 2. Thioamide band IV of the ligand dbptH (---) and its splitting into two bands in complex [Cu(PPh$_3$)$_2$ (dbptH)Cl] (——).

1490 cm^{-1}, II at 1245 cm^{-1}, III at 990 cm^{-1} and IV at 690 and 650 cm^{-1}, were assigned by Preti and Tosi[30] who reported various complexes including copper(I) with the deprotonated ligand. Vibrational analysis of the ligand has been done by Devillanova *et al.*[15] who also reported the various copper(I) complexes[8] with the protonated ligand. The bands at 690 and 650 cm^{-1}, which were assigned to ν(CS) sym and asym by Preti and Tosi,[30] were assigned mainly due to Δ(NH) and $\nu(C_1S_1)$ (C_1 = carbon atom bonded with ring sulphur, S_1 = ring sulphur), respectively, by Dewillanova *et al.*[15] Keeping this difference of opinion in mind, we have taken various other bands[15] to decide the coordination site.[30] The principal IR bands of the free ligand tzdtH and its complexes are given in Table 3. This ligand, tzdtH, is also bonded to the metal through the thione sulphur as shown by the shifts of the ν(CS) and ν(CN)+δ(NH) bands. The IR bands, namely ν(NH) at 3130 cm^{-1}, ν(CN)+δ(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[15] (Fig. 3) were used to decide the donor sites. Comparison of the 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 phosphine[14] at 1088 cm^{-1}, or is absent and the band at 545 cm^{-1} (Fig. 3) probably shifts to the lower frequency region and couples with the band around 505 cm^{-1} of the complex [Cu(PPh$_3$)$_3$X].[11] The Δ(CS) band at 435 cm^{-1} of the ligand is absent in the IR spectra of the complexes (Fig. 3). This

Table 3. Major IR bands of tzdtH and its complexes (cm^{-1})

	Compound	ν(NH)	ν(CN)+δ(NH)	$\nu(CS_1)$	ν(CS)	Δ(CS)	Vibrations between 600 and 400 cm^{-1}
	Ligand [tzdtH]	3130–2700	1500	653, 585	1085 545	434	585, 545, 434
(7)	[Cu(PPh$_3$)$_2$(tzdtH)Cl]	3050–2800	1520	655, 585	—	—	585, 505, 485
(8)	[Cu(PPh$_3$)$_2$(tzdtH)Br]	3050–2800	1525	655, 585	—	—	585, 505, 485
(9)	[Cu(PPh$_3$)$_2$(tzdtH)I]	3140–2900	1515	655, 585	—	—	585, 520–490

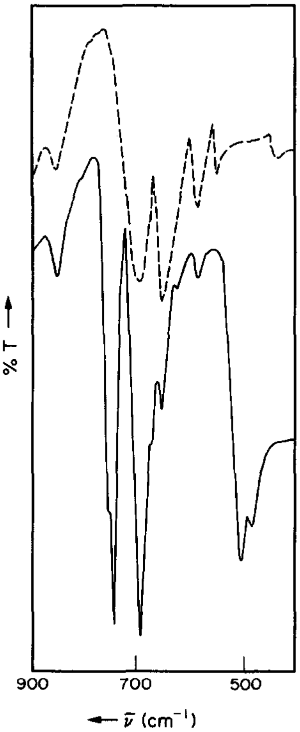


Fig. 3. The bands ν(CS) and Δ(CS) of the free ligand tzdtH (– – –) at 545 and 435 cm^{-1}, shifted to the lower frequency or absent in the complex $[Cu(PPh_3)_2(tzdtH)_2Br]$ (——).

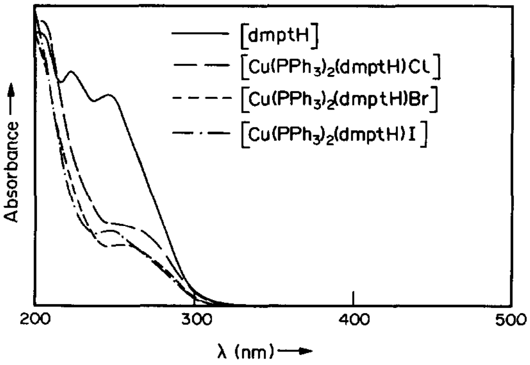


Fig. 4. Electronic spectra of the ligand dmptH and its complexes.

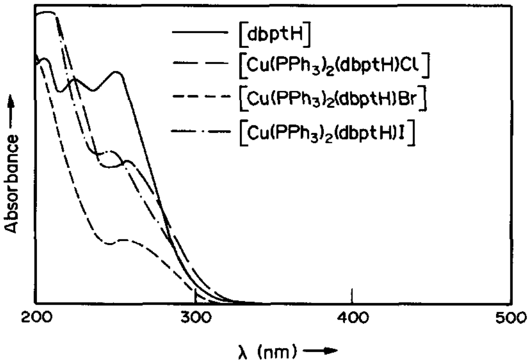


Fig. 5. Electronic spectra of the ligand dbptH and its complexes.

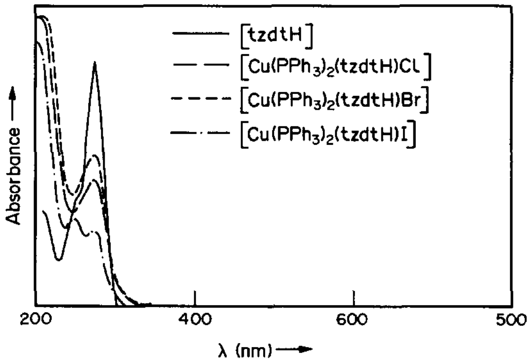


Fig. 6. Electronic spectra of the ligand tzdtH and its complexes.

shows the major shift of the ν(CS) band at 545 cm^{-1} and the Δ(CS) band at 435 cm^{-1} to the lower region, which indicates the involvement of the thione sulphur in the coordination. Other bands at 585, 653 (Fig. 3) 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 triphenylphosphine and the heterocyclic thione donors have been reported[20,28,31] of the same stoichiometry but with different heterocyclic thione donors and many of them have been characterized by single X-ray crystallography.[20,28]

The electronic (UV–vis) spectral data and the ^{1}H NMR spectra of the complexes and free ligands are given in Table 4, with assignments. As expected, only UV absorption bands are observed which are assigned as intraligand (IL) bands (Figs 4, 5 and 6). The ^{1}H NMR spectra of the complexes clearly show the peaks due to the ligands and triphenylphosphines (Figs 7, 8 and 9). On complexation, the peaks shift slightly towards the higher magnetic field [less ppm(δ)] (Figs 7, 8 and 9). The proportions of the protons, observed by integration, are exactly matching with the proposed stoichiometry of the complexes.

^{13}C *NMR and* ^{31}P *NMR chemical shifts*

^{13}C NMR and ^{31}P NMR data of the representative complexes are given in Table 5, with

Table 4. Electronic spectra of the ligands and the complexes in CH_3CN and ^1H NMR spectra of the ligands and complexes in $CDCl_3$

Compound	Band position λ_{max}	Assignment	^1H NMR signal with assignments (δ)
[dmptH]	223.0 246.5		3.27 (s, 6H, $-N\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ group); 7.20 (s, 5H, $-C_6H_5$ group)
(**1**) $[Cu(PPh_3)_2(dmptH)Cl]$	253.0	IL	3.10 (s, 6H, $-N\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ group); 7.00–7.50 (m, 35H, $-C_6H_5$ groups)
(**2**) $[Cu(PPh_3)_2(dmptH)Br]$	250.0	IL	3.13 (s, 6H, $-N\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ group); 7.00–7.50 (m, 35H, $-C_6H_5$ groups)
(**3**) $[Cu(PPh_3)_3(dmptH)I]$	248.0	IL	3.10 (s, 6H, $-N\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$ group); 7.00–7.50 (m, 35H, $-C_6H_5$ groups)
[dbptH]	207.0 225.0 251.0		0.67–2.00 (m, 12H, $-CH_2$ groups); 3.63 (t, 6H, $-CH_3$ groups); 6.67–7.33 (m, 35H, $-C_6H_5$ groups)
(**4**) $[Cu(PPh_3)_2(dbptH)Cl]$	212.0 255.0	IL IL	0.67–1.80 (m, 12H, $-CH_2$ groups); 3.50 (t, 6H, $-CH_3$ groups); 6.83–7.50 (m, 35H, $-C_6H_5$ groups)
(**5**) $[Cu(PPh_3)_2(dbptH)Br]$	256.5	IL	0.67–1.83 (m, 12H, $-CH_2$ groups); 3.50 (t, 6H, $-CH_3$ groups); 7.00–7.67 (m, 35H, $-C_6H_5$ groups)
(**6**) $[Cu(PPh_3)_2(dbptH)I]$	211.5 247.0	IL IL	0.67–1.83 (m, 12H, $-CH_2$ groups); 3.53 (t, 6H, $-CH_3$ groups); 6.83–7.40 (m, 35H, $-C_6H_5$ groups)
[tzdtH]	276.0		3.27–4.17 (m, 4H, $-CH_2$ groups)
(**7**) $[Cu(PPh_3)_2(tzdtH)Cl]$	208.0 274.0	IL IL	3.07–3.73 (m, 4H, $-CH_2$ groups); 6.83–7.67 (m, 30H, $-C_6H_5$ groups)
(**8**) $[Cu(PPh_3)_2(tzdtH)Br]$	215.0 274.0	IL IL	3.07–3.70 (m, 4H, $-CH_2$ groups); 6.83–7.67 (m, 30H, $-C_6H_5$ groups)
(**9**) $[Cu(PPh_3)_2(tzdtH)I]$	248.0 275.0	IL IL	3.07–3.73 (m, 4H, $-CH_2$ groups); 6.83–7.67 (m, 30H, $-C_6H_5$ groups)

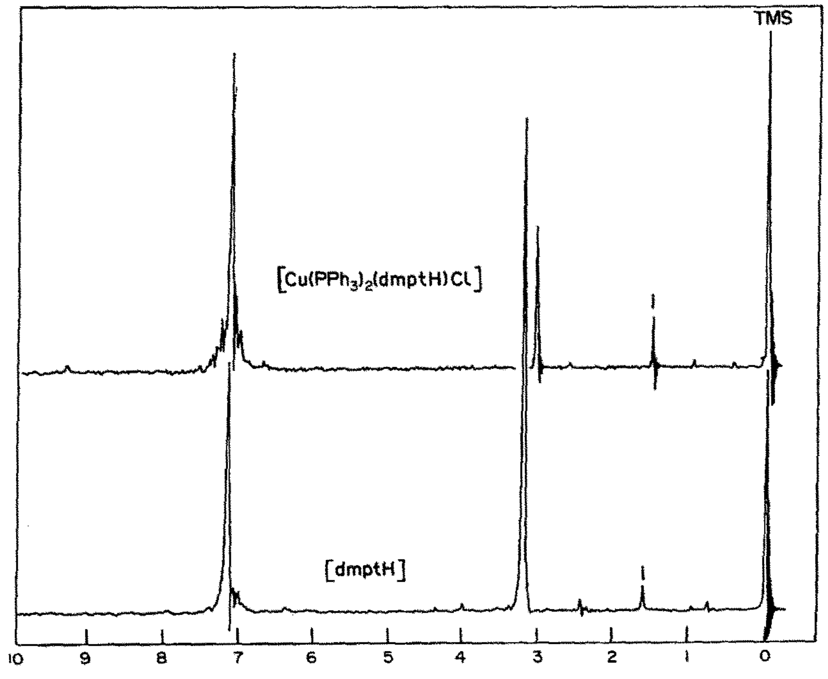


Fig. 7. ^1H NMR spectra of the ligand dmptH and the complex $[Cu(PPh_3)_2(dmptH)Cl]$ at room temperature. Peaks indicated by i are due to the acetone impurity.

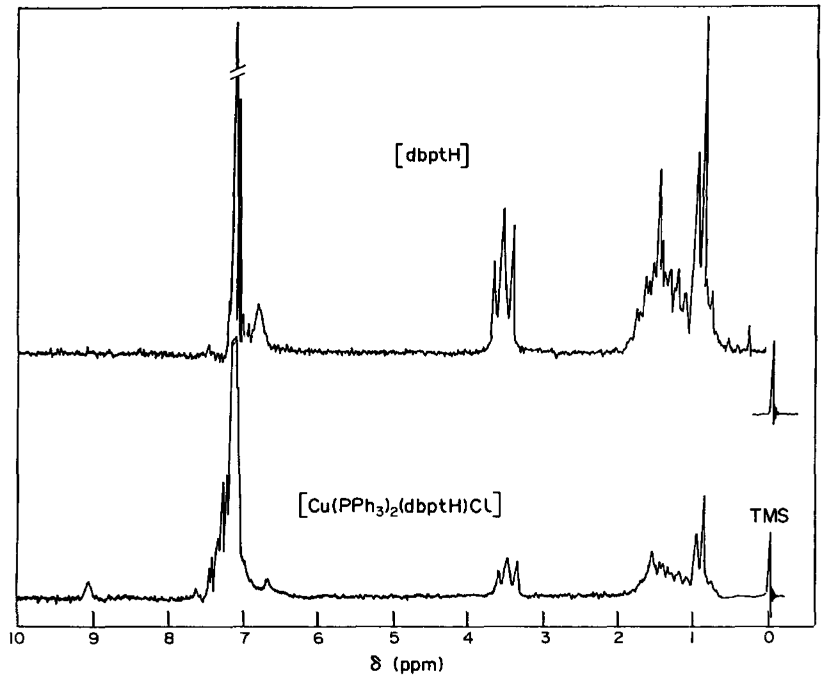


Fig. 8. ^{1}H NMR spectra of the ligand dbptH and the complex [Cu(PPh$_3$)$_2$(dbptH)Cl] at room temperature.

assignments. Data for phosphine, tetramethylthiourea and N,N-diethylaniline are also given from the literature for comparison and assignment. In the substituted thiourea and the metal complexes the ^{13}C NMR signals for C=S carbon[32–34] are found in the range 180–194 ppm, which is in very good agreement with our observations. The ^{13}C NMR data of 1,3-thiazolidine-2-thione are

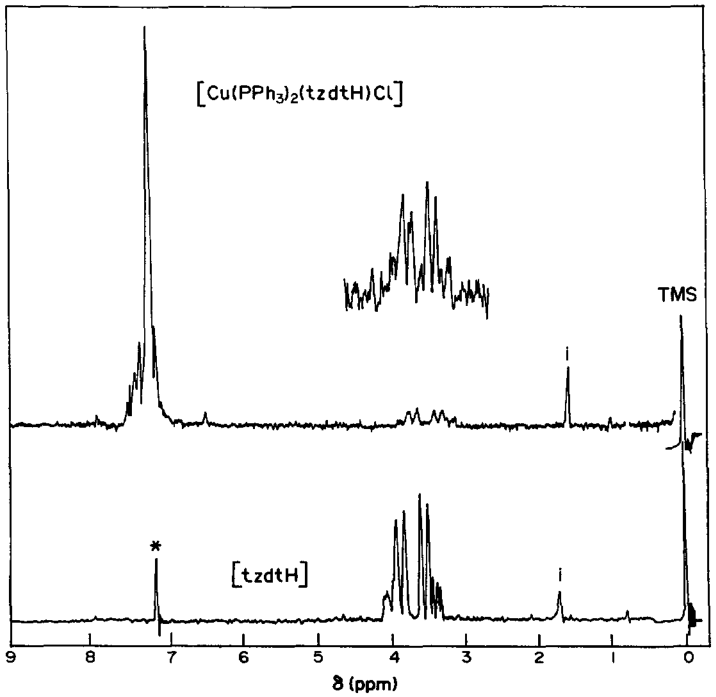
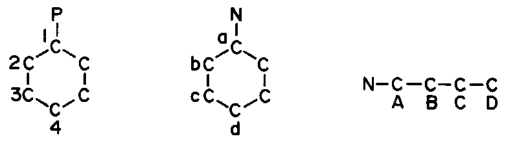


Fig. 9. ^{1}H NMR spectra of the ligand tzdtH and the complex [Cu(PPh$_3$)$_2$(tzdtH)Cl] at room temperature. The peak indicated by an asterisk (*) is due to the solvent and peaks indicated by i are due to the impurity.

Table 5. ^{13}C NMR chemical shifts (δ/ppm from Me_4Si) and ^{31}P NMR chemical shifts (δ/ppm from 85% H_3PO_4 ext. ref.) of representative complexes in $CDCl_3$, peak multiplicities in brackets



Compounds	^{13}C NMR 1	2	3	4	a	b	c	d	Other peaks	^{31}P NMR
(**1**) $[Cu(PPh_3)_2(dmptH)Cl]$	—	133.91(2)	128.41(2)	129.42(1)	139.50(1)	122.23(1)	128.91(1)	124.48(1)	181.04(1) C═S; 42.50(1) N—CH_3	−4.89(1)
(**4**) $[Cu(PPh_3)_2(dbptH)Cl]$	—	133.93(2)	128.43(2)	129.45(1)	140.08(1)	122.92(1)	129.08(1)	124.68(1)	180.84(1) C═S; 51.55(1)A; 29.13(1)B; 19.77(1)C; 13.72(1)D	−4.94(1)
(**8**) $[Cu(PPh_3)_2(tzdtH)Br]$	—	133.96(2)	128.33(2)	129.16(1)	—	—	—	—	198.92(1) C═S; 51.30(1) N—C; 32.65(1) S—C	−5.50(1)
PPh_3[a]	137.2(2)	133.6(2)	128.4(2)	128.5(1)	—	—	—	—	—	−6.00(1)
$SC[N(CH_3)_2]_2$[b]	—	—	—	—	—	—	—	—	193.9(1) C═S; 43.0(1) N—C	—
Ph—$N(C_2H_5)_2$[b]	—	—	—	—	147.8(1)	112.0(1)	129.1(1)	115.5(1)	44.2(1) N—CH_2—; 12.5(1) —CH_3	—

[a] ^{13}C NMR data from ref. 32. ^{31}P NMR data from ref. 36.

[b] ^{13}C NMR data from ref. 32.

given as 51.3, 33.8 and 202.0 ppm for C—N, C—S and C═S carbon atoms, respectively.[35] In the complexes there is a shift towards higher field [less ppm (δ)]. Other peaks due to phenyl rings and alkyl groups are observed in the expected characteristic range (Table 5). As expected, only one sharp ^{31}P NMR signal of triphenylphosphine is observed in all the complexes with a shift towards lower field [higher ppm (δ)].

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