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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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Synthesis and Characterization of Mixed- Ligand Complexes of Cu(I) Containing Halides, Triphenylstibine and Triphenylbismuthine, N,N-Dimethyl-N'-Phenylthiourea (Dmpth), N,N-Dibutyl-N'-Phenylthiourea (dbptH) and 1,3-thiazolidine-2-thione (tzdtH)

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SYNTHESIS AND CHARACTERIZATION OF MIXED- LIGAND COMPLEXES OF Cu(I) CONTAINING HALIDES, TRIPHENYLSTIBINE AND TRIPHENYLBISMUTHINE, N,N-DIMETHYL-N'-PHENYLTHIOUREA (dmptH), N,N-DIBUTYL-N'-PHENYLTHIOUREA (dbptH) AND 1,3-THIAZOLIDINE-2-THIONE (tzdtH).

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ABSTRACT

The triphenylstibine and bismuthine complexes $[Cu(EPh_3)(LH)_2X]$ (LH = N,N-dimethyl-N'-phenylthiourea) (dmptH), N,N-dibutyl-N'-phenylthiourea (dbptH) or 1,3-thiazolidine-2-thione (tzdtH); E = Sb or Bi; X = Cl, Br or I have been prepared and characterized on the basis of analytical, IR, electronic (UV-Vis), ¹H and ¹³C NMR, FAB mass and conductivity measurements. In all cases there is a distorted tetrahedral environment around Cu(I) and the ligand (LH) binds through the thione sulphur atom to copper(I). This is confirmed by FTIR spectra of the complexes. The complexes show v(Cu-Sb) in the range 180-195 cm⁻¹.

INTRODUCTION

The involvement of copper(I) in several biologically important reactions and coppersulphur interactions,¹⁴ the suitability of copper(I) complexes in providing models for the representation of several enzyme sites,^{5,6} and the stereochemical factors responsible for geometrical preferences of copper(I) compounds are some of the factors which have stimulated enhanced research activity in this area. This is exemplified by reports on the ligating behaviour of tetracyclic thiones,⁷ thioureas⁸ and N-substituted derivatives of thiourea.⁹⁻¹¹ Copper(I) complexes with 1,3-thiazolidine-2-thione and its N-methyl and N-ethyl derivatives have been reported.^{11,12} Karagiannidis and many other workers have characterized a number of copper(I) complexes with heterocyclic thiones, possessing an α -nitrogen hetero atom, and triphenylphosphines¹³ and triphenylarsines¹⁴ by single X-ray crystallography. The properties of transition metal complexes of triphenylphosphine, triphenylarsine and heterocyclic thiones are fairly well known, but their stibine and bismuthine analogues are rare.

Following our interest in the coordination properties of ligands containing the H-N-C=S group, $^{11.15}$ we have recently reported the phosphine and arsine counterparts¹¹ of the complexes. For the sake of comparison, we describe herein the synthesis and characterization of novel copper(I) distorted-tetrahedral complexes, [Cu(EPh₃)(LH)₂X], with the title ligands. The IR spectral studies of the ligands and complexes show the involvement of the thione sulphur in coordination. The ligands can be represented by the structures as shown in Fig. 1.

EXPERIMENTAL

Materials and Instruments

All chemicals used were either of AnalaR or chemically pure grade. The ligands, N,Ndimethyl-N'-phenylthiourea¹¹ (dmptH), N,N-dibutyl-N'-phenylthiourea¹¹ (dbptH) were prepared by the direct addition of phenylisothiocyanate to the appropriate secondary amine in methanol in 1:1 ratio, and the products were recrystallized from acetone. The ligand 1,3thiazolidine-2-thione was purchased from Eastern Organic Chemicals and recrystallised from hot water before use. The complexes [Cu(SbPh₃)₃X]¹⁶ were freshly prepared according to the literature method just prior to use.

The carbon, hydrogen and nitrogen analyses were performed at the Microanalytical Laboratory, Indian Institute Technology Kanpur. The IR spectra were recorded on a Shimadzu IR-420 spectrophotometer in KBr pellets in the range 4000-400 cm⁻¹ and FTIR spectra in Nujol mulls in polyethylene plates in the range 700-100 cm⁻¹ on a Perkin-Elmer Far-IR 1700X spectrophotometer. The electronic (UV-Vis) spectra were recorded on a Shimadzu Double beam UV-160 spectrophotometer in acetonitrile. ¹H and ¹³C NMR were recorded on a Bruker-WP-80 spectrometer. Conductivity measurements were performed on a Toshniwal Conductivity Bridge in acetonitrile. Sulphur, halides and copper were determined gravimetrically.^{17(a)} The melting points of the complexes were recorded on a Fisher-Johns melting point apparatus and are uncorrected.



N.N-Dimethyl-N'-phenylthiourea (dmptH)



N,N-Dibutyl-N'-phenylthiourea (dbptH)



Fig. 1. Structures of the Ligands

Syntheses

Preparation of [Cu(SbPh₃)(dmptH)₂X] (X = Cl, Br, l) [(1) - (3)]. In a benzene solution (50 mL) of [Cu(SbPh₃)₃X] {1 mmol, 1.16 g (X = Cl), 1.20 g (X = Br) 1.24 g (X = I)}, a solution of an equivalent amount of dmptH (2 mmol, 0.360 g) in benzene (25 mL) was added slowly with constant stirring at room temperature for 5 h (the iodide complex precipitated during the course of the reaction). The volume of the reaction mixture was then reduced to about 5 mL and stepwise addition of petroleum ether (60-80⁰C) with constant shaking initiated the precipitation of the desired complex. The complex was separated by centrifugation and washed several times with petroleum ether and dried in vacuo over P₄O₁₀ for several hours. Yields, 0.573 g (X = Cl), 0.493 g (X = Br), 0.570 g (X = I).

Preparation of $[Cu(SbPh_3)(dbptH)_2X]$ (X = Cl, Br, I) [(4) - (6)]. For the preparation of these complexes the above method was followed but in the case of X = Br, the desired complex were precipitated as a result of stirring for 5 h at room temperature. The complexes were recrystallised from CH₃CN-CHCl₃ (1:1). Yields, 0.332 g (X = Cl), 0.319 g (X = Br), 0.251 g (X = I).

Preparation of $[Cu(SbPh_3)(tzdtH)_2X]$ (X = CI, Br, I) [(7) - (9)]. In a benzene solution (50 mL) of $[Cu(SbPh_3)_3X]$ {1 mmol, 1.16 g (X = Cl), 1.20 g (X = Br) 1.24 g (X = I)}, a solution of an equivalent amount of tzdtH (2 mmol, 0.338 g) in benzene (25 mL) was added with constant stirring. The solution immediately became pale yellow, and was stirred for about 8 h at room temperature. During the course of the reaction the complexes precipitated. The

volume of the reaction mixture was then reduced to about 5 mL and an excess of petroleum ether (60-80⁰C) (150 mL) was added with constant shaking to ensure the complete precipitation of the complexes. The solution was left for a few hours to allow the complexes 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. Yields, 0.533 g (X = Cl), 0.703 g (X = Br), 0.537 g (X = 1).

Preparation of [Cu(BiPh₃)(dmptH)₂X] (X = Cl, Br, I) [(10) - (12)]. A quantity of 2.0 mmol (0.880 g) of BiPh₃ solution in benzene (30 mL) was flushed with argon for an hour and appropriate amounts of CuX (1.0 mmol) and the ligand dmptH (2.0 mmol, 0.360 g) were added to this solution. The reaction mixture was stirred for 7 h in an ice bath (temperature < 5^{0} C). During the course of the reaction, a clear solution was obtained followed by precipitation of the complexes. The reaction mixture was brought to room temperature and the solvent of the resulting solution was evaporated on a rotary evaporator to dryness. The complexes were washed with chloroform-petroleum ether (1:4). The complexes thus obtained were separated by centrifugation and dried in vacuo_over P₄O₁₀ for several hours. Yields, 0.451 g (X = Cl), 0.530 g (X = Br), 0.492 g (X = I).

RESULTS AND DISCUSSION

The formation of the complexes may be depicted by the following general equations,

 $[Cu(SbPh_3)_3X] + 2LH \rightarrow [Cu(SbPh_3)(LH)_2X] + 2SbPh_3$ {Benzenc, room temperature, 5-8 h} (LH = dmptH, dbptH, tzdtH ; X = Cl, Br, I)

CuX + 2BiPh₃ + 2dmptH → [Cu(BiPh₃)(dmptH)₂X] + BiPh₃ (Benzene, temperature < 5^{0} C, 7 h) (X = Cl, Br, I)

The analytical data of the complexes are given in Table I and are consistent with the stoichiometries proposed. The conductivity of the complexes was found to be in the range 9-20 Ω^{-1} cm² mol⁻¹ in acetonitrile solution, indicating the non-electrolytic nature of the complexes.^{17(b)} In order to confirm the molecular weight of the synthesized copper complexes, FAB mass spectra were recorded. Theoretically calculated molecular weight for the representative compounds (1), (4), (8), (10) and (11) are 811.7, 899.0, 1023.2, 689.7 and 733.2 g respectively. The observed mass spectra of the compounds (1), (4), (8), (10) and (11) are 812, 900, 1025, 691 and 735 clearly indicating the formulated molecular weight.

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 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ **Conductivity**¹ 8.6 14.8 10.4 13.3 18.5 16.4 20.4 0.01 12.5 11.8 10.3 9.4 144.0 130.0 170.0 129.0 132.0 130.0 129.0 127.0 146.0 M.p.ª 71.0 94.0 84.0 ਉ (p) Ð (P **g** (g (p Ð (g Ð ઉ (g 63.0 72.4 33.9 54,4 68.8 Yield 70.6 57.7 37.0 25.4 50.2 65.4 63.1 (%) Halides (16.2) (12.8)(8.10) 16.0 (14.0)11.5 (5.1) (10.7)(8.4) 12.5 (3.6) 10.7 (4.3) (9.2) 14.1 4.0 (3.9) 8.4 3.5 1.7 5.0 4.3 9.3 5.7 (17.4) (16.3) (18.5) 16.0 (7.10) (0.7) (6.8) (6.4) (6.5) (6.0)18.5 17.5 (6.2) (7.9) (7.5) 6.6 6.6 6.2 6.0 8.3 7.0 6.2 7.5 7.0 S Found (Calc.) (%) (8.1) 8.0 7.8) (7.4) (0.7) 6.8 (0)2 (6.7) (6.4) (6.5) (6.2) (6.5) 9.2 (9.2) (8.7) 8.0 7.5 7.3 6.2 6.6 6.0 6.0 8.5 G 6.7 Analysis 5.9) (9.6) (5.7) 5.5 (5.5) (2.2) (4.0) (3.8) (3.6) (6.9) (5.5) 6.2) 6.4 (6.2) 5.9 5.6 5.5 4.0 3.8 3.7 6.9 6.5 6.4 5.7 z (3.6) (3.4)(3.2)(5.9) (6.4) (4.8) (4.5)(4.3) (4.3) (4.1) 4.0 (3.9) (0.1) 3.6 3.4 3.3 4.9 4.5 6.5 6.1 4.5 4.5 4.1 6.1 Ξ (56.3) 50.3) (58.8) (53.8) (4).7) (39.2)(36.8) (53.2)48.0 (47.8) (48.0)(45.7) 43.8 (43.5)59.0 56.3 53.5 41.7 39.2 37.0 53.5 50.5 45.7 48.1 Ċ Yellowish Yellowish Yellowish Colour white Yellow Yellow Yellow Yellow Yellow Yellow Yellow Yellow Yellow white white Light Dark {C₂₄H₂₅lCuN₂S₄Sb} (781.2) [C24H25CICuN2S4Sb] (689.7) {C₃₆H₃₉BrCuN₄S₂Bi} (942.5) C36H39CICuN4S2Sb} (811.7) {C₃₆H₃₉BrCuN₄S₂Sb} (855.2) (C₃₆H₃₉CICuN₄S₂Bi} (899.0) C48H63ClCuN4S2Sb} (979.5) C48H63BrCuN4S2Sb} (1023.2) {C48H63ICuN4S2Sb} (1071.2) {C₂₄H₂₅BrCuN₂S₄Sb} (733.2) {C₃₆H₃₉ICuN4S₂Bi} (990.5) {C₃₆H₃₉ICuN₄S₂Sb} (903.2) [Cu(SbPh₃)(tzdtH)₂CI] [Cu(SbPh₃)(tzdtH)₂Br] [Cu(SbPh₃)(tzdtH)₂I] (Formula weights in g) [Cu(SbPh₃)(dmptH)₂CI [Cu(SbPh₃)(dmptH)₂Br] {Empirical Formula} [Cu(BiPh₃)(dmptH)₂Cl] [Cu(BiPh₃)(dmptH)₂Br] (8) [Cu(SbPh₃)(dbptH)₂Br] (7) [Cu(SbPh₃)(dbptH)₂Cl] (3) [Cu(SbPh₃)(dmptH)₂I] (9) [Cu(SbPh₃)(dbptH)₂I] (6) [Cu(BiPh₃)(dmptH)₂I] Complex (0E) (12) (11) <u>a</u> Ξ 3 €

Table I. Analytical and Physical Data of the Complexes

MIXED-LIGAND COMPLEXES OF Cu(l) HALIDES

^ad denotes decomposition temperature, ^bin acetonitrile solution.

IR Spectra

The IR spectral data of the ligands dmptH, dbptH and their complexes are summarized in Table II. Both ligands adopt the thione form in the free state and in their complexes. This is evident by the absence of the v(SH) band, in the 2500 cm⁻¹ region and by the presence of v(NH) in the range 3310-2900 cm⁻¹. Both 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 at 1500, 1300, 1000 and 800 cm⁻¹, having contributions from v(C-N) + δ (N-H), v(C=S) + v(C=N) + v(C-H), v(C-N) + v(C-S) and v(C-S) modes of vibrations, 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 v(NH) and v(C=S). All complexes exhibit the characteristic bands of triphenylstibine and triphenylbismuthine.¹⁸ The mode of ligand bonding is decided on the basis of the shifts of v(NH), v(C=S) and the four thioamide bands on complexation. The thioamide bands II and III have contributions from v(CN) and v(CS) vibrations, but v(CS) contributes more than v(CN)to the thioamide bands.¹⁹ therefore, band II can be utilized to decide the coordination site, but it is difficult to decide the coordination site on the basis of the shifts of band III.

The band at 3310 and 3240 cm⁻¹, assigned to v(NH) for both the free ligands dmptH and dbptH, respectively, are observed in the range 3200-3050 cm⁻¹ for the complexes (1)-(6), and in the range 3150-3050 cm^{-1} for the complexes (7)-(9). The red shift of the v(NH) bands is probably due to hydrogen bonding in the complexes. The thioamide band I, having contributions from $\delta(N-H) + v(C-N)$, shifts slightly towards the higher frequency region or remains almost unaffected, indicating the non-involvement of the NH group in coordination. The thioamide bands II, having more contribution from v(C=S), undergoes a red-shift or is split and intense bands are observed in the lower frequency region. In the case of compound (1) the broad thioamide bands II of the ligand dmptH at 1325 and 1295 cm⁻¹ is split into three bands at ca. 1320, 1275 and 1205 cm⁻¹, and in compound (4), the bands II are split into four bands at ca. 1320, 1300, 1265 and 1200 cm⁻¹, The broad thioamide bands II of the ligand dbptH observed at 1350, 1330 and 1325 cm⁻¹ are red-shifted on complexation, and the band at 1325 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 v(C=S) by <u>ca.</u> 30-40 cm⁻¹. A redshift or splitting of the thioamide band IV is also observed. The bands observed at 770 and 710 cm⁻¹ are assigned as the thioamide bands IV. The band at 770 cm⁻¹ is split into two bands at <u>ca.</u> 770 and 730 cm⁻¹ for compounds (1)-(6), but the band at 720 cm⁻¹ is not discernible in

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Complex	(HN)v	v(CS)		Thioamide	Bands		v(Cu-S)	v(Cu-X)	v(Cu-Sb)
			-	II	III	21			
Ligand	3310-3050 br,	1145 hr	1595 m,	1325 br,	1065 m	770 m, 710 br			
(dmptH)	m.		1535 W	1295 w					
()	3050 br	1100 s	1595 м	1320 br, 1275 w,	1065 м	770 s, 720 sh, 680 m	330 <i>s</i>	285 w	181 x
	2915 sh		1535 m	1205 m					
(2)	3140 br	1110 5	1600 w	1320 br, 1280 m,	1065 м	780 s. 740 w, 690 m	330 s	228 и	181 \$
	2985 sh		1550 m	1210 m					
(3)	3200 br	1115 s	1600 m	1320 br, 1275 m,	1065 w	780 s, 740 m, 690 s	332 s	157 м′	180 s
			1545 m	1205 m					
(1)	3150 br	1100 s	1595 w	1320 m, 1300 m,	1060 м ⁻	765 s, 720 w, 690 m	1	,	
	2900 sh		1540 w	1265 w, 1200 s					
(2)	3150 m	1100 5	1595 m	1320 m, 1300 m,	1060 w	770 s, 725 w, 685 m		,	•
			1540 m	1265 w, 1200 s					
(9)	3180 m	1105 5	1595 m	1320 m, 1305 w,	1065 w	770 s, 725 w, 690 w		l ı	
			1545 m	1265 w, 1200 m					
Ligand	3240 s	1145 br	1595 s, 1530 m	1350 w, 1330 w,		770 m, 710 br	,	ı	,
(dbptH)	2950 s, 2890		1500 m	1320 m					
	hs								
3	3050 sh	1105 s	1600 s. 1520 sh	1375 w, 1325 s,	,	735 s, 690 s	340 m	288 w	195 m
	2940 br		1500 hr	1240 m					
(8)	3150 w	1100 5	1590 s. 1520 w	1365 w, 1325 s,		730 s, 690 m	336 m	225 w	195 m
-	2940 br		1495 br	1230 m					
					-				
(6)	3150 W	1100 s	1595 х. 1525 w	1370 w, 1320 s.	ı	730 s, 690 m	336 m	157 w	195 m
	2950 br		1500 br	1230 w		-			

Table II. Major IR Bands of dmptH, dbptH and their Complexes $(cm^{-1})^{\sigma}$

^a w denotes weak, s sharp, sh shoulder, br broad and m medium peaks.

compound (1). The band at 710 cm⁻¹ in the compound is absent but may perhaps be coupled with the band due to the phenyl groups at 690 cm⁻¹. The band at 770 cm⁻¹ of the dbptH ligand shifts to 730 cm⁻¹ and the one at 710 cm⁻¹ shifts to 690 cm⁻¹. All these observations clearly indicate the involvement of the C=S group in coordination.

Four thioamide bands of the ligand tzdtH, I at 1500 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 Tosi²⁰ who have reported various complexes with deprotonated ligands. Vibrational analysis of the ligands has also been carried out by Devillanova et al.¹⁹ The band at 650 cm⁻¹, which is assigned to v(CS)asym by Preti and Tosi²⁰ is mainly due to $v(C_1S_1)$, $(C_1 = \text{carbon atom bonded with the ring})$ sulphur, $S_1 = ring sulphur$), by Devillanova et al.¹⁹ Keeping this difference of opinion in mind we have taken various other bands to decide the coordination site and not only the thioamide bands.²⁰ The IR spectral data of the free ligand tzdtH and its complexes are summarized in Table III. This ligand tzdtH is also bonded to the metal through the thione sulphur as shown by the shifts of the v(CS) and v(CN) + δ (NH) bands. The IR bands, namely v(NH) at 3100 cm^{-1} , v(CN) + δ (NH) at 1500 cm⁻¹ v(CS) at 1090 and 545 cm⁻¹, v(CS₁) + δ (CS) + ring def (C = carbon atom bonded to thione sulphur and ring sulphur) at 585 cm⁻¹, $v(C_1S_1)$ + ring def. at 650 cm⁻¹ and $\Delta(CS)$ at 435 cm⁻¹ of the free ligand,¹⁹ are used to decide the donor site. Comparison of the IR spectra of the free ligand with its complexes shows that the v(CS) band shifts to the lower frequency region. The $\Delta(CS)$ band at 435 cm⁻¹ of the ligand is absent in the IR spectra of the complexes. The major shifts of the bands arising due to the C=S group indicate the involvement of the thione sulphur in the coordination. Other bands at 585, 650 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.

Fig. 2 shows representative far-FTIR spectra of the complexes (3), (8) and (10). The v(NH) absorption is moderately shifted towards lower frequencies with respect to the frequency in the free ligand solid phase spectrum. This is due to H-bonding in the complexes. The involement of nitrogen of the NH group is ruled out as no v(Cu-N) bands in the region 290-330 cm⁻¹ appear for any complex. In the IR spectra new bands present in the lower frequency region at 330-341 cm⁻¹ (Tables II and III) are tentatively assigned to v(Cu-S) according to literature data.²⁰⁻²² This assignment is supported by the noticeable shift of the v(C=S) band. The bands present at 285, 228 and 157 cm⁻¹ are typical for v(Cu-Cl), v(Cu-Br)



Fig. 2. The Far-FTIR Spectra of the Complexes (3), (8) and (10) in the Region 700-100 cm⁻¹.

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Complex	(HN)	v(CN)+8(NH)	v(CS ₁)	v(CS)	Δ(CS)	v(Cu-S)	v(Cu-X)	v(Cu-Sb)
Ligand	3100-2700	1500 br	650 m	1090 br	435 w	,	•	•
(tzdtH)	br		585 s	545 s				
(01)	3100 br	1530 br	654 m	1030 m	-	341 br	294 w	198 br
			595 s	540 s				
(11)	3125 br	1530 br	654 m	1030 m	•	341 br	225 m	198 br
			590 s	545 s				
(12)	3125 br	1520 br	654 m	1025 m	,	340 br	,	199 br
			590 s	545 s				
a undrate	and a share							

Table III. Major IR Bands of tzdtH and its Complexes $(cm^{-1})^a$

w denotes weak, s sharp, sh shoulder br broad and m medium peaks.

and v(Cu-I), respectively.²⁰⁻²² Goodfellow et al. and Park and Hendra measured the infrared spectra of alkylarsine and alkylstibine complexes of Pt and Pd and assigned v(M-As) and v(M-Sb).^{23(a)} According to Whiffen's normal coordinate analysis,^{23(b)} the normal mode of the t-vibration corresponds essentially to the Sb-C(Ph) stretching vibration on a qualitative basis. The t-vibration appears at 257 and 270 cm⁻¹ which shows an increase of 5-10 cm⁻¹ on complexation (Fig. 2). This indicates the involvement of the Sb atom of triphenylantimony in bond formation with copper(I). A similar kind of shift associated with P-C(Ph) and As-C(Ph) has been observed in [Cu(PPh₃)₂CN] and [Cu(AsPh₃)₂CN] by Cooper et al.^{23(c)} On the basis of this spectral analysis we assign the band in the region 195-180 cm⁻¹ as v(Cu-Sb).

Electronic (UV-Vis) and NMR Spectra

The electronic (UV-Vis) and ¹H NMR spectral data of the complexes and free ligands with assignments are collected in Table IV. As expected, intraligand (IL) bands are observed in the UV region for the complexes (1)-(12).

The ¹H NMR spectra of the complexes clearly show the peaks due to the ligands and triphenylstibine and triphenylbismuthine. On complexation, the peaks shift slightly towards higher magnetic field. These shifts towards lower δ values indicate the non-involvement of the nitrogen atom in dmptH and dbptH, as well as the nitrogen and ring sulphur atoms in tzdtH as donor sites in the respective complexes. The ¹H NMR signals due to the >NH group of the ligands dmptH and dbptH are not discernible, whereas for the ligand tzdtH it is observed as a very broad weak signal. The ¹H NMR spectra in the >NH region show a downfield shift on going from iodide to bromide to chloride, indicating the non-involvement of the >NH group in the complexation. This unusual phenomenon may be due to a gradual decrease in intramolecular hydrogen bonding strength.^{14(b)} The proportion of protons observed by integration exactly matches with the proposed stoichiometry of the complexes.

¹³C NMR spectra of representative complexes with assignments are given in Fig. 3 and the data are collected in Table V. In the substituted thiourea and its metal complexes, the ¹³C NMR signals for the C=S carbon²⁴⁻²⁶ are found in the range 170-194 ppm, which is in very good agreement with our observations. ¹³C NMR data of 1,3-thiazolidine-2-thione are given as 51.3, 33.8 and 202.0 ppm for C-N, C-S and C=S carbon atoms respectively.²⁷ In the complexes there is a shift towards higher field [lower values ppm (δ)]. Other peaks due to phenyl rings and alkyl groups are observed in the expected characteristic range (Fig. 3).

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Table IV. Electronic (UV-Vis) Spectral Data of the Ligands and the Complexes in CH₃CN and ¹H NMR Spectral Data of the Ligand and Complexes in CDCl₃.

Compound	Band position Assignment λ_{max} (nm) { $\epsilon = 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	<pre>1 [H NMR signals with Assignment [ppm (δ)]</pre>
Ligand	223	3.27 (s, 6H, -N-CH3 groups), 7.20 (s, 5H, -C ₆ H ₅ group)
	1 (0 5/0 8/0	210 (c 12H N CH. croning) 7 00 7 54 (m 35H - C.H. droning)
(1)	1 (0.c) 0.042	10.47 (s. 12tt, -N-Cri groups), /.00-7.54 (iii, 25tt, - Coris groups)
(2)	248.0 (7.3)	L 3.17 (s, 12H, -N-CH ₃ groups), 7.00-7.48 (m, 25H, -C ₆ H ₅ groups)
	-	9.64 (s, 2H, > N-H groups)
(3)	245.5 (11.9)	L 3.20 (s, 12H, -N-CH ₃ groups), 7.00-7.55 (m, 25H, -C ₆ H ₅ groups)
		9.45 (s, 2H, > N-H groups)
(4)	249.5 (5.2)	 3.07 (s, 12H, -N-CH₃ groups), 6.96-7.53 (m, 25H, -C₆H₅ groups)
		9.26 (s, 2H, > N-H groups)
(2)	249.5 (4.9)	L 3.00 (s, 12H, -N-CH ₃ groups), 6.93-7.50 (m, 25H, -C ₆ H ₅ groups)
		9.03 (s, 2H, > N-H groups)
(9)	245.5 (8.5)	. 3.03 (s, 12H, -N-CH3 groups), 6.93-7.50 (m, 25H, -C ₆ H5 groups)
		8.97 (s, 2H, > N-H groups)
Ligand	251.5, 225.5	0.67-2.00 (m, 6H,-N-CH ₃ groups), 3.63 (t, 12H, J = 10.6 Hz, > CH ₂ groups)
(dbptH)	212.0	6.95-7.35 (m, 5H,-C ₆ H ₅ groups), 7.01 (s[broad], 1H, > N-H group)
6	248.5 (7.9)	IL 0.60-1.87 (m, 12H,-N-CH ₃ groups), 3.48 (t. 24H, J = 10.6 Hz, > CH ₂ groups)
	212.0 (11.7)	IL 7.09-7.40 (m, 25H,-C ₆ H ₅ groups), 9.57 (s, 2H, > N-H group)
(8)	251.0 (7.0)	IL 0.65-1.90 (m, 12H,-N-CH ₃ groups), 3.51 (t, 24H, J = 10.5 Hz, > CH ₂ groups)
	213.0 (13.4)	IL 7.05-7.35 (m, 25H,-C ₆ Hs groups), 9.50 (s, 2H, > N-H group)
(6)	248.0 (8.0)	IL 0.67-1.85 (m, 12H,-N-CH ₃ groups), 3.50 (t, 24H, J = 10.3 Hz, > CH ₂ groups)
	214.0 (14.4)	II. 7.05-7.40 (m, 25H,-C ₆ H ₅ groups), 9.17 (s, 2H, > N-H group)

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Ligand	277.0	3.27-4.17 (m, 4H. > CH ₂ groups), 8.00 (s [broad], > N-H group)
(tzdtH)	212	
$(10)^{d}$	273.0 (4.7) IL	2.50-4.10 (m, 8H, > CH ₂ groups), 7.33 (s. 15H,- C ₆ H ₅ groups)
	254.0 (4.2) IL	10.47 (s, 2H, > N-H groups)
	212.0 (9.6) IL	
(11) ^a	[273.0 (4.1) IL	2.50-4.10 (m, 811, > CH ₂ groups), 7.37 (s, 15H, - C ₆ H ₅ groups)
	254.5 (3.6) IL	10.33 (s, 211, > N-H groups)
	213.5 (9.4) IL	
(12) ^a	273.0 (6.7) II.	2.50-4.10 (m, 8H, > CH ₂ groups), 7.40 (s, 15H,- C ₆ H ₅ groups)
	245.0 (4.7) IL	10.30 (s, 2H, > N-H groups)
	212.5 (14.2) IL	
" Recorded in	DMSO-d ⁶	



Fig. 3. ¹³C NMR Spectra of the Complexes (2), (8) and (10).

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Table V.¹³C NMR Chemical Shifts (5/ppm) of Representative Complexes in CDCl₃ (peak multiplicity in parentheses)



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Compound	1	2	m	4	а	q	c	q	Other peaks
(2)	۰	136.6 (d)	126.5 (d)	129.4 (s)	140.0 (s)	122.6 (s)	128.7 (s)	123.9 (s)	178.6 (s) C=S
									44.3 (s) N-C
(8)	•	136.6 (d)	126.8 (d)	129.4 (s)	139.3 (s)	122.6 (s)	129.1 (s)	123.8 (s)	171.2 (s) C=S
					_				54.6 (s) A
									28.7 (s) B
									18.8 (s) C
									12.6 (s) D
(10) ^a	•	135.7 (d)	118.1 (d)	129.0 (s)	-	•		-	192.6 (s) C=S
						1			50.1 (s) N-C
									31.3 (s) S-C
^a Recorded ir	DMSO-de								

MIXED-LIGAND COMPLEXES OF Cu(l) HALIDES



Fig. 4. Suggested Structure of the Complex, [Cu(SbPh₃)(dmptH)₂X].

Conclusion

On the basis of the spectral analysis we infer that these complexes adopt distorted tetrahedral geometry. In these cases the ligands LH were found to be coordinating through the thione sulphur. In all cases there is an intramolecular N-H....X hydrogen bond (Fig. 4).

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