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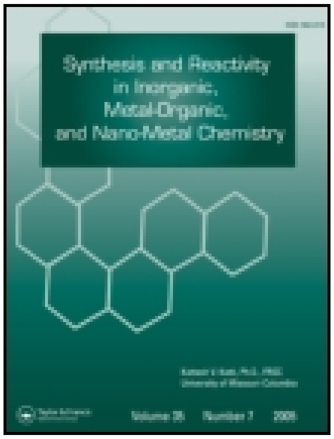

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SYNTHESIS AND CHARACTERIZATION OF COPPER(I) COMPLEXES OF N-CARBOETHOXY-4-CHLOROBENZENE AND N-CARBOETHOXY-4-BROMOBENZENE THIOAMIDES (Hcct AND Hcbt)

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SYNTHESIS AND CHARACTERIZATION OF COPPER(I) COMPLEXES OF N-CARBOETHOXY-4-CHLOROBENZENE AND N-CARBOETHOXY-4-BROMOBENZENE THIOAMIDES (Hcct AND Hcbt)

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ABSTRACT

Reactions of $[Cu(EPh_3)_3X]$ with the title ligands yield $[Cu(EPh_3)_2(LH)X]$ (LH = Hcct and Hcbt). Twelve complexes have been prepared and characterized on the basis of analytical, IR, electronic and NMR spectral and magnetic measurements. These complexes have a tetrahedral structure with the aromatic ligand bonded to copper(I) through sulfur.

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INTRODUCTION

The important feature of the chemistry of [Cu(EPh$_3$)$_3$X] (E = P or As; X = Cl, Br or I) is the facile replacement of one or two phosphine/arsine groups by neutral ligands,[1] and that of halides by mono-anionic ligands.[2,3] A number of copper(I) triarylphosphine and triarylarsine complexes having sulfur donor ligands have been reported.[4–7] These were either synthesized by the reaction of [Cu(EPh$_3$)$_3$X] and the sulfur ligands or by the reaction of copper(I) halide with sulfur donor ligands and triphenylphosphine or triphenylarsine. The synthesis, reactivity and ligating behaviour of N-carboethoxy-4-chlorobenzene thioamide (Hcct) and N-carboethoxy-4-bromobenzene thioamide (Hcbt) (Fig. 1) have been reported earlier.[8] In continuation of these studies, we report here the reactivity of these ligands with [Cu(EPh$_3$)$_3$X] to produce new complexes.

RESULTS AND DISCUSSION

The analytical data (Table I) are in good agreement with the stoichiometry in which one molecule of ligand displaces one EPh$_3$ in [Cu(EPh$_3$)$_3$X] (E = P or As); (X = Cl, Br or I) when allowed to react in benzene.

$$\left[\mathrm{Cu(EPh_3)_3X}\right] + \mathrm{HL} \rightarrow \left[\mathrm{Cu(EPh_3)_2(HL)X}\right] + \mathrm{EPh_3}$$
$$(\mathrm{E = P\ or\ As;\ X = Cl,\ Br\ or\ I;\ HL = Hcct\ or\ Hcbt})$$

All of the prepared complexes are diamagnetic at room temperature and are, in general air-stable and soluble in most of the organic solvents.

In all of the cases tetrahedral coordination with the thioamide ligands to copper(I) *via* the thiocarbonyl sulfur may be assigned. The diamagnetic nature and the stoichiometry confirm the oxidation state of copper as +1. Thus, these complexes may be represented as shown in Fig. 2.

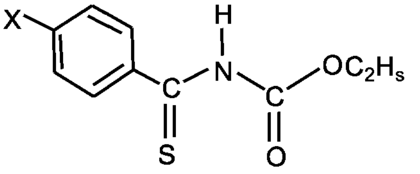

Figure 1. The ligands Hcct (X = Cl) and Hcbt (X = Br).

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Table I. Analytical Data of the Complexes [CuX(HL)(EPh$_3$)$_2$] [E = P or As; X = Cl, Br or I; HL = (Hcct) or (Hcbt)]

				% Found (Calculated)					
Compound	Empirical Formula (Formula Weight)	Colour	M.p.[a] (°C) (Yield, %)	C	H	N	M	S	Halide
[CuCl(Hcct)(PPh$_3$)$_2$]	$C_{46}H_{40}Cl_2CuNO_2P_2S$ (866.48)	Greenish yellow	178 (82)	63.62 (63.71)	4.58 (4.62)	1.60 (1.62)	7.28 (7.33)	3.65 (3.69)	8.02 (8.19)
[CuBr(Hcct)(PPh$_3$)$_2$]	$C_{46}H_{40}BrClCuNO_2P_2S$ (910.88)	Bright yellow	163 (65)	61.48 (61.55)	4.45 (4.46)	1.52 (1.56)	7.02 (7.08)	3.55 (3.57)	12.82 (12.87)
[CuI(Hcct)(PPh$_3$)$_2$]	$C_{46}H_{40}ClCuINO_2P_2S$ (957.88)	Red	113 (57)	57.54 (57.63)	4.09 (4.18)	1.50 (1.46)	6.70 (6.63)	3.35 (3.34)	16.90 (16.95)
[CuCl(Hcct)(AsPh$_3$)$_2$]	$C_{46}H_{40}As_2Cl_2CuNO_2S$ (954.38)	Dark orange	145 (55)	57.80 (57.84)	4.15 (4.19)	1.50 (1.47)	6.65 (6.66)	3.32 (3.35)	7.40 (7.44)
[CuBr(Hcct)(AsPh$_3$)$_2$]	$C_{46}H_{40}As_2BrClCuNO_2S$ (998.78)	Orange	111 (49)	55.30 (55.27)	4.05 (4.00)	1.45 (1.40)	6.40 (6.36)	3.25 (3.20)	11.60 (11.55)
[CuI(Hcct)(AsPh$_3$)$_2$]	$C_{46}H_{40}As_2ClCuINO_2S$ (1045.78)	Orange	195 d (45)	52.80 (52.78)	3.87 (3.82)	1.40 (1.34)	6.13 (6.08)	3.12 (3.06)	15.60 (15.53)
[CuCl(Hcbt)(PPh$_3$)$_2$]	$C_{46}H_{40}BrClCuNO_2P_2S$ (910.88)	Greenish yellow	175 (80)	60.65 (60.60)	4.40 (4.39)	1.55 (1.54)	6.93 (6.98)	3.35 (3.51)	12.70 (12.67)

(continued)

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Table I. Continued

Compound	Empirical Formula (Formula Weight)	Colour	M.p.[a] (°C) (Yield, %)	% Found (Calculated)					
				C	H	N	M	S	Halide
[CuBr(Hcbt)$(PPh_3)_2$]	$C_{46}H_{40}Br_2CuNO_2P_2S$ (955.28)	Dark yellow	161 (67)	57.80 (57.78)	4.25 (4.19)	1.56 (1.47)	6.70 (6.65)	3.40 (3.35)	16.81 (16.73)
[CuI(Hcbt)$(PPh_3)_2$]	$C_{46}H_{40}BrCuINO_2P_2S$ (1002.28)	Shining Red	111 (52)	55.12 (55.07)	4.02 (3.99)	1.45 (1.40)	6.40 (6.34)	3.25 (3.19)	20.70 (20.63)
[CuCl(Hcbt)$(AsPh_3)_2$]	$C_{46}H_{40}As_2BrClCuNO_2S$ (998.78)	Dark orange	144 (56)	55.30 (55.27)	4.05 (4.00)	1.45 (1.40)	6.40 (6.36)	3.25 (3.20)	11.62 (11.55)
[CuBr(Hcbt)$(AsPh_3)_2$]	$C_{46}H_{40}As_2Br_2CuNO_2S$ (1043.18)	Orange	110 (54)	53.00 (52.92)	3.90 (3.83)	1.35 (1.34)	6.10 (6.09)	3.10 (3.07)	15.42 (15.32)
[CuI(Hcbt)$(AsPh_3)_2$]	$C_{46}H_{40}As_2BrCuINO_2S$ (1090.18)	Orange	166 (52)	50.12 (50.63)	3.59 (3.67)	1.25 (1.28)	5.80 (5.83)	3.00 (2.94)	19.00 (18.97)

[a] Melting points are uncorrected; d = decomposes.

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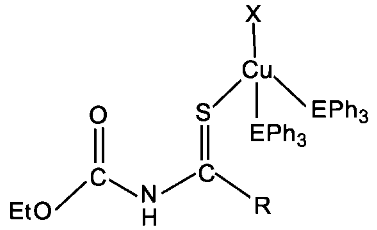

E=P or As; R=4-ClC$_4$H$_4$ or 4-BrC$_6$H$_4$; X=Cl, Br, or I

Figure 2. Copper(I) complexes of Hcct or Hcbt.

The major IR bands of interest in the spectra of the ligands and complexes are given in Table II. All complexes exhibit the characteristic bands of PPh$_3$ or AsPh$_3$. The vibrations are mainly due to the phenyl groups of the PPh$_3$ or AsPh$_3$ ligands for which the characteristic bands are at 1088 and 1075 cm^{-1}, respectively.[9,10]

The band at ~3225 cm^{-1} in the ligands and assigned to υ(N–H), could not be used reliably for ascertaining the bonding through nitrogen because of unsystematic shifts after complexation. The presence of NH in the complexes was confirmed by the ^{1}H NMR spectrum in CDCl$_3$ which displayed a signal at $\delta = 11.3$ ppm (singlet, intensity 1H) [for the uncomplexed ligand, $\delta = 11.8$ ppm (s, 1H, NH)].[11] The position of the band at around 1765 cm^{-1} assigned to υ(C=O) either remains stationary or shifts towards higher wave number (*ca.* 5 cm^{-1}) in the complexes, ruling out coordination through the carbonyl group. The band around 1585 cm^{-1} assigned to υ(C$\overset{\cdots}{—}$N), shifts to higher wave number (Δυ *ca.* 25–35 cm^{-1}). This indicates non-involvement of nitrogen in bonding. The thioamide band I [υ(C$\overset{\cdots}{—}$N) + δ(NH)] shifts to lower wave numbers (*ca.* 10–30 cm^{-1}). The thioamide band II around 1360 cm^{-1} either remains stationary or shifts to higher energy by 5–10 cm^{-1}. The position of thioamide band IV (850–830) cm^{-1} is invariant but the band at 830 cm^{-1} appears with appreciable reduced intensity in the complexes. The band around 1130 cm^{-1} assigned to υ(C=S) systematically shifts to lower energy to an extent of 5–20 cm^{-1}. This observation supports involvement of sulfur as the donor site.

The electronic spectra of the complexes formed with the ligand Hcct were taken in dichloromethane and assigned on the basis of earlier reports.[9,12–14] The values of λ_{max} and their assignments are given in Table III.

The spectra of the ligand, Hcct, exhibit bands at 445 nm, 305 nm and 265 nm. The higher energy band at 265 nm has been assigned to intraligand

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Table II. Major IR Bands[a] (cm^{-1}) of the Ligands and Complexes $[CuX(HL)(EPh_3)_2]$ (E = P or As; X = Cl, Br or I; HL = Hcct or Hcbt)

				Thioamide Bands			
Compound	υ(NH)	υ(C=O)	υ(C=S)	I	II	III	IV
[Ligand(Hcct)]	3225 m	1765 s	1130 m	1540 s	1360 s	1075 s	850 s
$[CuCl(Hcct)(PPh_3)_2]$	–	1765 s	1120 w	1530 s	1360 s	1060 s	830 s
$[CuBr(Hcct)(PPh_3)_2$	–	1765 s	1125 w	1520 s	1360 s	1050 s	850 s
$[CuI(Hcct)(PPh_3)_2$	–	1765 s	1120 w	1520 m	1360 s	1055 s	850 s
$[CuCl(Hcct)(AsPh_3)_2$	–	1770 s	1120 w	1525 s	1360 s	1050 s	850 s
$[CuBr(Hcct)(AsPh_3)_2$	–	1770 s	1120 w	1500 s	1360 s	1050 s	850 s
$[CuI(Hcct)(AsPh_3)_2$	–	1770 s	1110 w	1500 s	1360 s	1060 s	830 s
[Ligand(Hcbt)]	3220 m	1765 s	1130 m	1540 s	1360 s	1080 s	850 s
$[CuCl(Hcbt)(PPh_3)_2$	–	1765 s	1120 w	1525 s	1360 s	1075 s	830 s
$[CuBr(Hcbt)(PPh_3)_2$	–	1770 s	1115 w	1530 s	1360 s	1070 s	840 s
$[CuI(Hcbt)(PPh_3)_2$	–	1765 s	1120 w	1520 s	1360 s	1060 s	850 s
$[CuCl(Hcbt)(AsPh_3)_2$	–	1770 s	1125 w	1500 s	1360 s	1050 s	850 s
$[CuBr(Hcbt)(AsPh_3)_2$	–	1765 s	1120 w	1500 s	1360 s	1060 s	840 s
$[CuI(Hcbt)(AsPh_3)_2$	–	1765 s	1115 w	1510 s	1360 s	1050 s	830 s

[a] s = strong; m = medium; w = weak.

Table III. Electronic Spectra of the Ligand Hcct and the Complexes [CuX(Hcct)-(Eph$_3$)$_2$] in Dichloromethane (conc. = 10^{-4} M) (E = P or As; X = Cl, Br or I)

Compounds	Band Position λ_{max} (nm)	$(\varepsilon)^a$	Assignments
Ligand [Hcct]	445	(1498)	$n \rightarrow \pi^*$
	305	(2667)	$\pi \rightarrow \pi^*$
	265	(2954)	CT
[CuCl(Hcct)(PPh$_3$)$_2$]	280	(952)	CT
	265	(721)	CT
[CuBr(Hcct)(PPh$_3$)$_2$]	390		M → L CT
	278	(615)	CT
	265	(527)	CT
[CuI(Hcct)(PPh$_3$)$_2$]	280	(767)	CT
	265	(652)	CT
[CuCl(Hcct)(AsPh$_3$)$_2$]	270	(733)	CT
	260	(891)	CT
[CuCl(Hcct)(AsPh$_3$)$_2$]	275	(761)	CT
	265	(531)	CT
[CuI(Hcct)(AsPh$_3$)$_2$]	300	(373)	$\pi \rightarrow \pi^*$
	275	(306)	CT

$^a\varepsilon$, L mol^{-1} cm^{-1}.

charge transfer (IL-CT) while the bands at 445 nm and 305 nm are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ intraligand (IL) bands, respectively. The $n \rightarrow \pi^*$ transition usually occurs at the low-energy side and is less intense in comparison with $\pi \rightarrow \pi^*$ in the system involving nitrogen and sulfur atoms.[15] The spectra of the copper(I) complexes exhibit only intraligand transitions. The d-d transitions for Cu(I) (d^{10}) are not observed.

EXPERIMENTAL

The ligands, Hcct and Hcbt, were synthesized as reported.[8] The complexes [Cu(EPh$_3$)$_3$X] (E = P or As; X = Cl, Br or I) were prepared by literature methods.[1,9,16,17] Cuprous halides were freshly prepared just prior to use for the preparation of the phosphine and arsine complexes.

A benzene solution (25 mL) containing an equivalent amount of ligand (1 mmol) was mixed slowly with a benzene solution (25 mL) of [Cu(EPh$_3$)$_3$X] (1 mmol) at room temperature. The colour of the solution intensified and it was then heated under reflux for 0.5 to 1 h and concentrated to *ca.* half of its volume under reduced pressure. Addition of petroleum ether (60–80 °C)

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(10 mL) and allowing the mixture to stand for 2–3 h produced coloured crystals. These were filtered, washed several times with petroleum ether and dried *in vacuo*.

Copper, halide, phosphorus and sulfur were determined gravimetrically. Analyses of C, H and N were done at the Microanalytical Laboratory, Indian Institute of Technology, Kanpur. The IR spectra of the ligands and complexes were recorded in KBr pellets in the range 4000–250 cm^{-1}. The electronic spectra were recorded on a Cary model 17D UV-Visible spectrophotometer using dichloromethane as solvent. Magnetic susceptibilities of the complexes at room temperature (298 K) were determined by using a model 150A parallel field vibrating sample magnetometer (VSM).

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