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### STUDIES OF COPPER(I) COMPLEXES WITH N,N'-SUBSTITUTED THIOUREAS

THIOUREA is potentially capable of forming coordinate bonds through both 'S' and 'N', even though the extremely low basicity<sup>1</sup> of ligand militates against the formation of M-N bonds. Cu(I) complexes derived from substituted thioureas are of increasing interest to coordinate chemists. Several Cu(I) complexes of N-ethyl thiourea<sup>2</sup> showed M-S bonding, but Lane *et al.*<sup>3</sup> observed M-N bonding in Cu(I) complex derived from N-methyl thiourea. The present study describes the synthesis of Cu(I)Cl complexes with benzoylthiourea (bztu), N-benzoyl-N'-methylthiourea(bzmetu), N-benzoyl-N'-ethylthiourea(bzetu), N-benzoyl-N'-o-chlorophenylthiourea(bz-o-clptu), N-benzoyl N'-phenyl thiourea(bzptu), N-benzoyl-N'-o-

tolythiourea(bz-o-totu) and N-benzoyl-N'-o-methoxyphenylthiourea(bz-o-meoptu). These complexes are characterized with the aid of conductance, spectral and thermal studies.

The standard methods were used for the preparation of substituted thioureas<sup>4</sup>. All the chemicals used were of B.D.H. reagent grade. The purity of ligands was confirmed by nitrogen and sulphur estimations.

The complexes were prepared by treating  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and ligand in the appropriate ratio in ethanol. The complex separated on concentration of the solution. In the case of bz-o-meoptu complex, cooling in a freezing mixture was necessary. The products were washed with hot ethanol and dried over  $\text{P}_2\text{O}_5$  in vacuum. The complexes were analysed for copper, nitrogen, sulphur and chlorine by standard procedures. The analytical data are presented in Table I.

The molar conductivity was measured in DMF ( $1 \times 10^{-3} \text{ M}$ ) with the aid of ELICO conductivity bridge. The infrared spectra have been recorded on PE-257 ( $4000\text{--}600 \text{ cm}^{-1}$ ) and far i.r. from Beckman IR-12 spectrophotometer ( $600\text{--}200 \text{ cm}^{-1}$ ).

TABLE I

Complex	*Elemental analysis				Infrared frequencies		
	Cu%	N%	S%	Cl%	C=S	M-Cl	M-S
bztu	..	..	..	..	710s	..	..
CuCl · bztu	22.45 (22.74)	10.32 (10.00)	11.61 (11.43)	13.02 (12.68)	705ms	252ms(b)	235ms
bzmtu	..	..	..	..	700mbr	..	..
CuCl · bzmtu	21.57 (21.45)	9.75 (9.55)	11.18 (10.91)	11.79 (12.12)	685ms	..	247br**
bzetu	..	..	..	..	710s	..	..
CuCl · 2bzetu	12.33 (12.28)	11.23 (10.92)	12.10 (11.43)	7.03 (6.89)	695ms	..	246mw**
bzptu	..	..	..	..	720ms	..	..
CuCl · 2bzptu	11.55 (11.18)	9.09 (9.17)	10.72 (10.47)	6.14 (5.81)	710w	249w (b)	245w
bz-o-meoptu	..	..	..	..	695s	..	..
CuCl · 2bz-o-meoptu	9.72 (9.39)	8.40 (8.44)	9.74 (9.54)	4.89 (5.30)	692ms	251s (b)	250s
bz-o-clptu	..	..	..	..	706s	..	..
CuCl · 2bz-o-clptu	9.38 (9.35)	8.32 (8.25)	9.18 (9.44)	16.19 (15.70)	740s	251w (b)	..
bz-o-totu	..	..	..	..	741s	..	..
CuCl · 3bz-o tuto	6.80 (7.00)	9.12 (9.24)	10.43 (10.56)	3.70 (3.90)	727w	298w (t)	230w

\* The figures in the parenthesis show expected values.

\*\* Overlapped with M-Cl band.

s = sharp; ms = medium sharp; w = weak; br = broad; b = bridge; t = terminal.

The complexes possess pale yellow colour and are amorphous in nature. These complexes are insoluble in common organic solvents but are difficultly soluble in DMF and DMSO. The molar conductivity values lie in the range  $4\text{--}17\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$  suggesting non-electrolytic nature of the complexes. The complexes did not show any magnetic moment. This might be due to the reduction of Cu(II) to Cu(I) by the above ligands. The reduction of copper(II) to copper(I) by organic sulphides has been extensively studied<sup>5,6</sup>.

The infrared spectral data are presented in Table I. The  $\nu\text{NH}$  band of the ligand ( $3100\text{--}3300\text{ cm}^{-1}$ ) in general shows a blue shift on complexation, except in the case of bz-*o*-Clptu where a red shift is observed ( $110\text{ cm}^{-1}$ ). A strong band ( $1650\text{--}1675\text{ cm}^{-1}$ ) of the ligand is assigned to stretching C=O frequency. The coordination of the carbonyl oxygen is ruled out from the positive shift of the above band<sup>7</sup>. A medium strong band in the range  $710\text{--}685\text{ cm}^{-1}$  is assigned to  $\nu\text{C}=\text{S}$  vibration<sup>8</sup>. This is in accordance with assignments made by other investigators. The above band experiences red shift ( $3\text{--}15\text{ cm}^{-1}$ ) with reduction in intensity in all complexes except in bz-*o*-Clptu, where a blue shift of the order of  $34\text{ cm}^{-1}$  is experienced. These observations clearly suggest that in the case of bz-*o*-Clptu, the ligand is coordinated through 'N' while in the remaining complexes through 'S'. The bands at  $201\text{--}250\text{ cm}^{-1}$  and  $250\text{--}300\text{ cm}^{-1}$  are assigned to  $\nu\text{Cu}\text{--Cl}$  bridging and terminal types respectively<sup>9,10</sup>. These complexes also exhibit a band in the region  $250\text{--}320\text{ cm}^{-1}$  except in  $\text{Cu}(\text{bz-}o\text{-Clptu})_2\text{Cl}$  complex which is assigned to  $\nu\text{Cu}\text{--S}$  vibration<sup>10</sup>. The latter complex exhibits  $\nu\text{Cu}\text{--N}$  band<sup>11</sup> at  $354\text{ cm}^{-1}$ . The values of energy of dissociation for  $\text{CuCl}\cdot 2\text{bz-}o\text{-Clptu}$  and  $\text{CuCl}\cdot 2\text{hz-metu}$  lie at  $36.8\text{ K cal}$ , and  $20.2\text{ K cal}$  respectively as deduced from TG curves utilizing Freeman and Corroll's procedure<sup>12</sup>. This shows that the former complex is more stable than the latter.

From the above discussion it is evident that  $\text{CuCl}\cdot\text{L}$  type complexes are polymers where both 'S' and 'Cl' atoms act as alternative bridging units. The complexes of the type  $\text{CuCl}\cdot 2\text{L}$  have a dimeric halogen bridged structure<sup>13</sup> and in the case of  $\text{CuCl}\cdot 3\text{L}$ , the structure proposed is obviously tetrahedral.

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#### COLORIMETRIC METHOD FOR THE ESTIMATION OF *p*-PHENYLENEDIAMINE

A SIMPLE colorimetric method of estimation of *p*-Phenylenediamine (PPDA) is reported. In an alkaline (sodium hydroxide) medium, PPDA forms an orange coloured complex with 1,2-Naphthaquinone, 4-sulphonic acid (NQSA) ( $\lambda_{\text{max}}\text{—}485\text{ nm}$ ) and a red complex with 1-amino, 2-naphthol, 4-sulphonic acid (ANSA) ( $\lambda_{\text{max}}\text{—}490\text{ nm}$ ). Beer's law is obeyed upto  $9\text{ }\mu\text{g/ml}$  of the PPDA. The results obtained compare well with those obtained from the official method.

*p*-Phenylenediamine is a white to slightly red crystalline solid, which darkens on oxidation, or on exposure to air. It is used for dyeing furs, also in photochemical measurements, accelerating vulcanization; manufacture of azodyes, etc. It is mainly used in hair dyes. The pure compound or the intermediate oxidation products may produce eczematoid contact dermatitis, bronchial asthma. When used as a hair dye, it has been reported to produce vertigo, anaemia, gastritis, exfoliative dermatitis and even death.

The official method<sup>1</sup> of quantitative estimation of PPDA consists of extracting it with chloroform using continuous extractor and then precipitating it with