

COMPLEXES OF Cu(I) AND Zn(II) WITH SOME N-ARYL, N'-2-(5-HALO-PYRIDYL) THIOUREAS

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METAL complexes of the substituted thioureas having a heterocyclic group as one of the substituents have been studied by many workers¹⁻⁴. In these complexes pyridyl nitrogen and thiocarbonyl sulfur act as donor atoms, giving rise to a stable six membered chelate ring. The present paper reports the studies made on the complexes of Cu (I) and Zn (II) with some N-aryl, N'-2-(5-halo-pyridyl) thioureas.

The following are the substituted thioureas that were chosen :

- (i) N-phenyl, N'-2-(5-chloro-pyridyl) thiourea (PCT),
- (ii) N-phenyl, N'-2-(5-bromo-pyridyl) thiourea (PBT),
- (iii) N-phenyl, N'-2-(5-iodo-pyridyl) thiourea (PIT),
- (iv) N-*o*-tolyl, N'-2-(5-chloro-pyridyl) thiourea (TCT),
- (v) N-*o*-tolyl, N'-2-(5-bromo-pyridyl) thiourea (TBT), and
- (vi) N-*o*-tolyl, N'-2-(5-iodo-pyridyl) thiourea (TIT).

EXPERIMENTAL

Preparation of the Cu (I) Complexes.—0.01 mole of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (BDH, AnalaR) in ethanol was added slowly and with stirring to a hot solution (0.025 mole) of the substituted thiourea in *n*-butanol. The complex was precipitated just after the addition. It was filtered, washed with butanol and dried in air oven at 60–70° C.

A hot solution (0.01 mole) of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in *n*-butanol was added with stirring to a boiling solution (0.025 mole) of the ligand in the same solvent. The mixture was concentrated and cooled. The precipitate was filtered, washed with *n*-butanol and dried at 60–70° C.

The composition of the complexes was determined by the estimation of the elements, N, S, Cl [ClO_4 in case of Zn (II) complexes] and the metal. Copper and zinc were estimated by the pyridine method⁵, as $[\text{M}(\text{C}_5\text{H}_5\text{N})_4](\text{CNS})_2$. The other elements were estimated by standard methods.

The conductance measurements were made on a conductivity meter, type LBR, WTW, Germany, using a dip type cell. Ultra-violet spectra were obtained on a UV-VIS Perkin Elmer Hitachi

Spectrophotometer (Model-139) using 0.5 cm matched quartz cuvettes. Infrared spectra, in nujol-mull were recorded on a Perkin Elmer Grating Infrared Spectrophotometer (Model 237-B).

RESULTS AND DISCUSSION

The Cu (I) complexes, white in colour, were soluble in chloroform, dimethylformamide, nitrobenzene, pyridine and dioxane. These complexes, on the basis of elemental analysis can be represented by the general formula CuClL_2 , where L is the ligand. The Zn (II) complexes were also white in colour and were soluble in acetone, pyridine, tetrahydrofuran and dimethylformamide. The elemental analysis of these compounds revealed their composition to be $\text{Zn}(\text{ClO}_4)_2\text{L}_2$. The results of elemental analysis along with their melting points, molar conductances and magnetic moments have been recorded in Table I.

The Cu (I) Complexes.—The composition of these complexes shows that Cu is present in + 1 oxidation state. The reduction of Cu (II) to Cu (I) is a peculiar property of thioureas and has been observed by earlier workers also¹⁻³.

The low molar conductance range (0.04–0.22 mhos, cf. Table I) shows that these complexes are non-electrolytes, having chlorine coordinated to the metal ion.

Two bands are exhibited in the uv spectra of these complexes which have been assigned to thiocarbonyl $\pi-\pi^*$ transition (~ 275 nm) and pyridyl $\pi-\pi^*$ transition (~ 310 nm)⁶. On comparison of these spectra with those of the ligands it has been found that the λ_{max} of thiocarbonyl $\pi-\pi^*$ transitions is shifted upto 10 nm to shorter wavelengths. In the case of ligands E_{max} for thiocarbonyl $\pi-\pi^*$ transition is found to be greater than that for pyridyl $\pi-\pi^*$ transition but in the case of Cu (I) complexes the order is reversed (cf. Table II). These observations are indicative of strong interactions between the ligand and the metal ion. Cu (I) is a soft acid according to the Pearson's classification⁷ and belongs to the (b) class of metals according to Ahland *et al.*⁸. Therefore its coordination with a soft donor, like thiocarbonyl sulfur with strong π -interactions is quite obvious. This however, has not been reported in the case of complexes of substituted thioureas by earlier workers¹⁻³.

TABLE I

Copper (I) chloride and Zinc (II) perchlorate complexes of some *N*-aryl, *N'*-2-(5-halo-pyridyl) thiourcas

Complex	m pt. (C)	Molar conduc- tance (mhos)	Magnetic moment (BM)	% Metal		% Nitrogen		% Sulfur		% chlorine perchlorate	
				Calcu- lated	Found	Calcu- lated	Found	Calcu- lated	Found	Calcu- lated	Found
CuCl(PCT) ₂	246d	0.10	Diamag- netic	12.77	12.65	13.42	13.32	12.87	12.75	17.01	16.50
Zn(PCT) ₂ (ClO ₄) ₂	208d	70.2	do.	8.26	8.15	10.61	10.41	8.09	8.01	25.15	25.02
CuCl(PBT) ₂	248d	0.04	do.	8.88	8.75	11.75	11.62	8.95	8.82	4.97	4.85
Zn(PBT) ₂ (ClO ₄) ₂	210d	72.9	do.	7.43	7.31	9.54	9.38	7.27	7.12	22.60	22.42
CuCl(PIT) ₂	239d	0.18	do.	7.85	7.70	10.39	10.18	7.91	7.80	4.39	4.12
Zn(PIT) ₂ (ClO ₄) ₂	221d	74.0	do.	6.71	6.51	8.62	8.51	6.57	6.47	20.42	20.30
CuCl(TCT) ₂	230d	0.10	do.	9.71	9.61	12.84	12.64	9.79	9.60	16.29	16.09
Zn(TCT) ₂ (ClO ₄) ₂	215d	73.1	do.	7.98	7.85	10.75	10.05	7.81	7.65	24.29	24.02
CuCl(TBT) ₂	224d	0.08	do.	8.55	8.43	11.31	11.11	8.61	8.41	4.78	4.65
Zn(TBT) ₂ (ClO ₄) ₂	210d	76.2	do.	7.20	7.02	9.25	9.15	7.05	6.91	21.91	21.75
CuCl(TIT) ₂	222d	0.22	do.	7.59	7.45	10.03	9.95	7.65	7.48	4.24	4.15
Zn(TIT) ₂ (ClO ₄) ₂	210d	79.0	do.	6.33	6.21	8.38	8.29	6.39	6.32	19.86	19.73

d = decomposes.

In the spectra of the complexes (Table III), the ν (N—C—N+C=S) and ν (C=S) bands occurring at ~ 1060 cm⁻¹ and ~ 720 cm⁻¹ respectively⁴ are either shifted to lower frequencies or are reduced in their intensities. The band assigned to ν (C=C+C=N) mode is shifted in an irregular fashion which precludes any unambiguous assertion of metal ligand bonding through the pyridyl nitrogen, which however is suggested by the uv spectra.

On the basis of these observations the complex can be considered five coordinated (2 pyridyl nitrogens, 2 thiocarbonyl sulphurs and 1 chlorine).

The Zn (II) Complexes.—The molar conductances of these complexes fall in the range 70–80 mhos predicting these to be 1:1 electrolytes. But the ir spectra of these complexes do not show the characteristic bands of coordinated perchlorate⁵.

Thus, the complexes should be 1:2 electrolytes. It has been observed by Dutta Ahmed and Mandal¹ that in non-aqueous solvents the conductances of 1:2 electrolytes are less than the normal values.

The uv spectra of these complexes (Table II) show little variation from the corresponding ligand spectrum.

The band at ~ 1600 nm assigned for (C=C+C=N) mode is found to be shifted to lower frequencies showing thereby bonding through pyridyl nitrogen. The ν (N—C—N+C=S) and is either missing, as in the case of TBT and TIT, or is found to become less intense and shifted to lower frequencies. Similarly ν (C=S) band (~ 720 nm) is also reduced in intensity. Thus, the ir spectra of these complexes indicate that the pyridyl nitrogen and thiocarbonyl sulfur act as donors, and the complex is 4-coordinated.

TABLE II

Ultraviolet spectral data on the Cu (I) and Zn (II) complexes

Compound	Solvent	λ_{\max} (nm)	E_{\max} ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)
CuCl (PCT) ₂	Chloroform	273	36160
		313	39120
CuCl (PBT) ₂	do.	271	40790
		317	47400
CuCl (PIT) ₂	do.	276	34020
		317	42240
CuCl (TCT) ₂	do.	261	30660
		313	37480
CuCl (TBT) ₂	do.	262	31960
		314	40190
CuCl (TIT) ₂	do.	276	31700
		319	42030
Zn (PCT) ₂ (ClO ₄) ₂	DMF	276	24730
		311	22650
Zn (PBT) ₂ (ClO ₄) ₂	do.	276	22810
		309	20120
Zn (PIT) ₂ (ClO ₄) ₂	do.	282	20250
		314	18950
Zn (TCT) ₂ (ClO ₄) ₂	do.	274	21310
		311	19270
Zn (TBT) ₂ (ClO ₄) ₂	do.	278	28110
		309	24890
Zn (TIT) ₂ (ClO ₄) ₂	do.	281	30900
		315	26720

DMF = Dimethylformamide.

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TABLE III

Infrared spectral peaks on the Cu (I) and Zn (II) Complexes (in mijoI-mull)

Compound	ν (C=C + C=N) (cm^{-1})	ν (N-C-N + C=S) (cm^{-1})	ν (C=S) (cm^{-1})
PCT	1598 s	1070 m	720 m
CuCl (PCT) ₂	1600 s	1065 w	715 m
Zn (PCT) ₂ (ClO ₄) ₂	1600 s	1025 w	715 sh
PBT	1595 s	1070 m	720 m
CuCl (PBT) ₂	1598 s	1065 vw	710 w,b
Zn (PBT) ₂ (ClO ₄) ₂	1590 s	1017 vw	715 vw
PIT	1592 s	1077 m	716 m
CuCl (PIT) ₂	1585 s	1070 m	705 vw
Zn (PIT) ₂ (ClO ₄) ₂	1590 s	1015 vw	710 vw
TCT	1600 s	1042 m	705 m
CuCl (TCT) ₂	1598 s	1045 w	710 m
Zn (TCT) ₂ (ClO ₄) ₂	1600 s	1045 vw	700 w
TBT	1595 s	1042 m	705 m
CuCl (TBT) ₂	1598 vs	1040 w	705 w
Zn (TBT) ₂ (ClO ₄) ₂	1592 s	..	700 w
TIT	1590 s,b	1077 m	703 m
CuCl (TIT) ₂	1595 s	1077 m	715 w
Zn (TIT) ₂ (ClO ₄) ₂	1590 s,b	..	700 w

Note : w = weak, v = very, sh = shoulder, m = medium, s = strong and b = broad.

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