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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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Synthesis, Characterization, Thermal Decomposition, and Antimicrobial Studies of Copper(I) Complexes of 1,3-Dihydro-4,5-Di(4-Methoxyphenyl)Imidazolin-2-Thione

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# Synthesis, Characterization, Thermal Decomposition, and Antimicrobial Studies of Copper(I) Complexes of 1,3-Dihydro-4,5-Di(4-Methoxyphenyl)Imidazolin-2-Thione

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The reaction between 1,3-dihydro-4,5-di-(4-methoxyphenyl) imidazolin-2-thione (MDPIT) with seven different copper(II) salts were carried out to synthesize and characterize the corresponding complexes. These complexes have the general formulae [CuLX(H<sub>2</sub>O)], where X = OAc, Cl, Br, NO<sub>3</sub>, ClO<sub>4</sub> or CNS, and [Cu<sub>2</sub>L<sub>2</sub>(SO<sub>4</sub>)(H<sub>2</sub>O)]. Characterization of the complexes was done by chemical analyses, molar conductance, magnetic susceptibility, electronic, infrared and <sup>1</sup>H NMR spectral studies. Thermogravimetric studies of complexes were carried out and kinetic parameters for the various decomposition stages were also calculated. Preliminary investigations on the antifungal and antibacterial activities of the ligand and some of its complexes were also made.

Keywords 1,3-Dihydro-4,5-di-(4-methoxyphenyl)imidazolin-2-thione, copper(I) complexes, synthesis, characterization, thermal decompression, antimicrobial studies

#### INTRODUCTION

Imidazolin-2-thiones are versatile ligands due to the presence of exocyclic sulfur and the ring nitrogen atoms. Their ability to reduce copper(II) to copper(I) producing complexes with unpredictable structures has created a lot of interest. Moreover, these compounds are biologically active and have applications in various other fields including corrosion prevention. The coordination behaviour of unsubstituted imidazolin-2-thione, their methyl- and ethyl derivatives and their saturated analogues have been reported (Creighton et al., 1985; Raper and Crackett, 1981; Shanmugam and Sathyanarayana, 1983; Raper et al., 1983). However, investigations on the omplexation behaviour of aryl substituted imidazolin-2-thiones are scanty (Mohanan and Aravindakshan, 1989). We describe the synthesis, characterization, thermal decomposition and antimicrobial studies of 1,3-dihydro-4,5-di(4-methoxyphenyl)imidazolin-2-thione (MDPIT) and its copper(I) complexes, which are formed by the reaction between copper(II) salts and the ligand (Figure 1).

#### **EXPERIMENTAL**

#### Synthesis of MDPIT

MDPIT was synthesized by a general method (Mohanan and Aravindakshan, 1989), which involved two steps.

#### Preparation of Anisoin (4,4'-dimethoxybenzoin)

Anisoin was prepared by refluxing a solution of anisaldehyde (100 mmol, 12 mL) in 50% ethanol (5 mL) with an aqueous solution of sodium cyanide (100 mmol in 10 mL) for 2.5 h. On refrigeration, anisoin separated out.

#### Preparation of the Ligand (MDPIT)

Anisoin (50 mmol, 11.2 g) and ammonium thiocyanate (120 mmol, 9.1 g) were refluxed in isoamyl alcohol (250 mL) for about 1 h. On cooling, an ivory coloured solid compound separated out, which was filtered and washed thoroughly with diethylether and dried over  $P_4O_{10}$ . It was then crystallized from ethanol.

#### Preparation of Copper(I) Complexes of MDPIT

A methanolic solution (20 mL) of the ligand (1 mmol, 0.313 g) was kept at refluxing temperature and to it was added slowly a methanolic solution (20 mL) of the copper(II) salt (1 mmol). Some complexes precipitated out instantly, while others formed only after refluxing for 1 h. The solid complexes were filtered, washed thoroughly with methanol and dried under reduced pressure over  $P_4O_{10}$ . The thiocyanate complex was prepared by adding a methanolic solution (20 mL) of copper(II) acetate (1 mmol, 0.200 g) to a methanolic

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FIG. 1. Structure of the ligand MDPIT.

solution (20 mL) of the ligand (1 mmol, 0.313 g) containing a stoichiometric quantity of ammonium thiocyanate (1 mmol, 0.076 g).

#### Analytical Methods

Metal contents were determined by standard analytical or atomic absorption spectrophotometric methods. The anions present in the complexes were determined by standard methods (Vogel, 1978). Sulfate was determined gravimetrically as barium sulfate. Chorine and bromine were determined by Volhard's method after sodium carbonate fusion and dissolution in nitric acid (Vogel, 1978). Thiocyanate was determined gravimetrically as silver thiocyanate and for perchlorate, the Kurz method was used (Vogel, 1978). Carbon, hydrogen and nitrogen were determined by microanalysis using a Hitachi CHN-O rapid analyzer. Molar conductances of the complexes were determined using  $10^{-3}$  M solutions in DMF on a model 305 Systronic conductivity bridge and a dip-type cell, calibrated with a solution of AnalaR potassium chloride. Magnetic susceptibilities of the complexes were determined on a Gouy balance using  $Hg[Co(CNS)_4]$  as calibrant.

The electronic spectra of the compounds were recorded on a Shimadzu UV-Vis-1601 spectrophotometer using  $10^{-3}$  M solutions in DMF. The IR spectra were recorded using KBr discs on a 8101 Shimadzu FTIR spectrophotometer. The <sup>1</sup>H NMR spectra of the ligand and its copper(I) acetate complex were recorded in CDCl<sub>3</sub> on a Varian 300 NMR spectrometer. Thermal analyses were carried out on a Metler TA 4000 thermal analysis system with the following operational characteristics: heating rate,  $20^{\circ}$  min<sup>-1</sup>; atmosphere, static air; sample size, 2-10 mg; crucible, platinum. Kinetic parameters for the various stages of decomposition were calculated using different equations. The calculations were done using a computer programme written in Fortan 77. Antibacterial studies were conducted using the disc-diffusion method and antifungal studies using the cup-plate method (Murray et al., 1995).

#### **RESULTS AND DISCUSSION**

The reaction of anisoin with ammonium thiocyanate yielded 1,3-dihydro-4,5-di(4-methoxyphenyl)imidazolin-2-thione as ivory coloured, fine powder. There exist thione-thiol tautomerism of the ligand in solution, but in the solid, it exists as the thione (Shanmugam and Sathyanarayana, 1983) (Figure 2).



FIG. 2. Thione-thiol tautomeric forms of the ligand MDPIT.

The formation of the complexes may be represented by the following equation:

$$\begin{split} 3[C_{17}H_{16}O_2S] + CuX_2nH_2O \\ &\rightarrow [Cu(C_{17}H_{16}O_2S)XH_2O] + C_{17}H_{15}O_2 S - S - O_2H_{15}C_{17} \\ &+ HX + (n-1)H_2O + H^+ \end{split} \tag{1}$$

#### Formulae and General Properties of the Complexes

Reactions of CuX<sub>2</sub>, where X = OAc, Cl, Br, NO<sub>3</sub>,  $\frac{1}{2}$  SO<sub>4</sub>, ClO<sub>4</sub> or CNS, with MDPIT were carried out and in all cases light-coloured complexes were formed. The analytical data (Table 1) correspond to the formula [CuLX(H<sub>2</sub>O)], where X = OAc, Cl, Br, NO<sub>3</sub>, ClO<sub>4</sub> or CNS. The sulfato complex exists as a dimer of the formula [Cu<sub>2</sub>L<sub>2</sub>(SO<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>].

#### Molar Conductance

The molar conductance values of  $10^{-3}$  M solutions of all seven complexes in DMF were determined (Table 2). The values are lower than that expected for a 1:1 electrolyte in DMF, indicating that the complexes act as non-electrolytes, i.e., the anions are coordinated to the metal ions (Geary, 1971).

#### Magnetic Behaviour

The magnetic susceptibility values of the solid complexes were determined using a Gouy balance at room temperature and the values indicate that the complexes are diamagnetic in nature (Earnshaw, 1968). During complex formation, the copper(II) salts are reduced to copper(I) by the ligand and the excess of the ligand get oxidized to disulfide,  $C_{17}H_{15}O_{2-}S-S-O_{2}H_{15}C_{17}$  (Purushothaman, 1985) (Eq. (1)).

#### **Electronic Spectra**

The electronic spectra of the complexes were recorded in DMSO, but they do not register any bands characteristic of Cu(II) ions in the visible region. This confirms the observation that the complexes contain copper in the +1 oxidation state (Figgis, 1967). The pale colours of the complexes further support this observation.

#### **Infrared Spectra**

The important IR spectral bands and their tentative assignments are given in Table 3. The ligand spectrum contains a broad band of strong intensity at  $3045 \text{ cm}^{-1}$ . This may be

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	Found (Calculated) %	C H N Anion	65.23 5.20 8.69 —	(65.17) $(5.30)$ $(8.74)$	7 50.36 4.70 6.02 —	(1)  (50.33)  (4.63)  (6.18)	3 47.54 4.09 6.51 8.26	(1) (47.55) (4.19) (6.52) (8.29)	t 43.04 3.70 6.02 16.57	(1) (43.08) (3.79) (5.90) (16.68)	× 44.52 3.90 9.18 —	() (44.73) (3.94) (9.21)	0 46.08 4.08 6.42 10.88	(1) (46.10) (4.06) (6.32) (10.84)	3 41.32 3.62 5.88 20.02	(1) (41.38) (3.65) (5.87) (20.17)	3 47.62 3.96 9.32 12.86	(12.83) (47.78) (3.98) (9.29) (12.83)
	-	-		,	1	(17	1	(17	1	(1)	1	(1)	1	(12	12	(1)	17	(1
mpounds	Viol	1 Iel( (%)	60	l	70		60		55		60		52		50		09	
I data of the co	Docement	temp. (°C)	245		302		260		250		206		230				300	
ytical and physica		Colour	Ivory	:	Yellow		Bluish-violet		Light blue		Yellow		Yellow		Yellow		Yellow	
Anal	Emain of framing	Empirical formula (Formula weight)	$C_{17}H_{16}N_2O_2S$		$C_{19}H_{21}CuN_2O_5S$ (453)		$C_{17}H_{18}CICuN_2O_3S$ (429)		$C_{17}H_{18}BrCuN_2O_3S$ (474)		$C_{17}H_{18}CuN_3O_6S$ (456)		$C_{34}H_{36}Cu_2N_4O_{10}S_3$	(885)	$C_{17}H_{18}CICuN_2O_6S$ (493)		$C_{18}H_{18}CuN_3O_3S_2$ (452)	
		Compound	L		$[CuL(OAc)(H_2O)]$		$[CuLCI(H_2O)]$		$[CuLBr(H_2O)]$		$[CuL(NO_3)(H_2O)]$		$[Cu_2L_2(SO_4)(H_2O)_2]$		$[CuL(ClO_4)(H_2O)]$		$[CuL(CNS)(H_2O)]$	
		Sl. no.	(1)	į	(2)		(3)		(4)		(5)		(9)		(-)		(8)	

√t th∽ TABLE 1 nhvsical data of -, locitulo

TABLE 2 Molar conductances of copper(I) complexes of 1,3-dihydro-4,5di(4-methoxyphenyl)imidazolin-2-thione (MDPIT) (L)

S1. no.	Complex	Molar conductance in DMF ( $ohm^{-1} cm^2 mol^{-1}$ )
(1)	[CuL(OAc)(H <sub>2</sub> O)]	6.3
(2)	$[CuLCl(H_2O)]$	12.27
(3)	$[CuLBr(H_2O)]$	15.43
(4)	$[CuL(NO_3)(H_2O)]$	15.72
(5)	$[Cu_2L_2(SO_4) (H_2O)_2]$	9.5
(6)	$[CuL(ClO_4) (H_2O)]$	9.7
(7)	[CuL(CNS)(H <sub>2</sub> O)]	12.5

assigned to the vibrational frequency of the NH group. The position of this band and its broad nature indicate the presence of NH....S hydrogen bonding. The absence of  $\nu$  (SH) near 2500 cm<sup>-1</sup> in the ligand spectrum indicates the dominance of the thione form of the ligand in the solid state (Bellamy, 1978).

Four characteristic thioamide bands I, II, III, and IV (Rao, 1963) are seen in the spectrum of MDPIT. The thioamide I bands are at 1570 and 1458 cm<sup>-1</sup>, with shoulders at 1514 and 1373 cm<sup>-1</sup>. These are the coupled bands arising from  $\nu$ (CN) and  $\delta$ (NH). A medium-intensity band at 1249 cm<sup>-1</sup> is assigned to the thioamide band II, which has major contributions from  $\nu$ (C=S),  $\nu$ (CN) and  $\delta$ (NH). The thioamide

TABLE 3

Significant	infrared s	spectral	bands (	$(cm^{-1})$	of	MDPIT,	its	copper(I)	complexes,	and their	assignments
0		1	(					II \/	1 /		0

Compound	$\nu$ (OH) of coord. water	$\nu$ (N–H)	TA I	TA II	TA III	TA IV	$\nu(C=S)$	Anion
MDPIT (L)	_	3045 b	1570 s 1514 sh 1458 s 1373 sh	1249 s 1211 m	1090 s	792 m	536 s	_
[CuL(OAc)(H <sub>2</sub> O)]	3242 b	3060 b	1575 sh 1528 s 1506 sh 1458 s 1373 sh	1247 s	1029 s	773 m	532 s	1640 s 1400 s
[CuLCl(H <sub>2</sub> O)]	3136 b	3053 b	1550 s 1514 sh 1458 s 1370 sh	1253 s	1028 s	780 m	532 s	_
[CuLBr(H <sub>2</sub> O)]	3251 b	3143 b	1558 s 1508 sh 1458 s 1378 sh	1253 s	1026 s	773 m	522 s	_
[CuL(NO <sub>3</sub> )(H <sub>2</sub> O)]	3420 b	3109 b	1571 s 1515 sh 1458 s 1384 sh	1251 s	1076 s	770 m	534 s	1408 s 1299 m 1000 s
$[Cu_2L_2(SO_4)(H_2O)_2]$	3327 b	3049 b	1571 s 1519 sh 1460 s	1251 s	1070 s	770 m	536 s	1140 s 1030 m 990 s 577 m 680 m 461 m
[CuL(ClO <sub>4</sub> )(H <sub>2</sub> O)]	3421 b	3145 b	1575 s 1512 sh 1460 s 1388 sh	1253 s	1063 s	770 m	530 s	1130 s 1081 s 921 m 623 m
CuL(CNS)(H <sub>2</sub> O)]	3246 b	3060 b	1570 s 1506 sh 1458 s 1373 sh	1247 s	1028 s	771 m	536 s	2123 m 727 s

b = broad; sh = shoulder; TA = thioamide band.

-	
δ (ppm)	Proton
2.50 (s, 1H)	-SH
3.55 (s, 3H)	
3.35 (s, 3H)	OCH <sub>3</sub>
7.27-7.24 (m, 10H)	Aromatic protons
6.92-6.88 (m)	and imidazole NH
3.50 (m, 6H)	OCH <sub>3</sub>
3.76 (s, 2H)	Coord. water
7.41-6.85 (m, 10H)	Aromatic protons
	and imidazole NH
	$\frac{\delta \text{ (ppm)}}{2.50 \text{ (s, 1H)}}$ 3.55 (s, 3H) 3.35 (s, 3H) 7.27-7.24 (m, 10H) 6.92-6.88 (m) 3.50 (m, 6H) 3.76 (s, 2H) 7.41-6.85 (m, 10H)

 TABLE 4

 Significant <sup>1</sup>H NMR spectral assignment of MDPIT and its copper(I) nitrate complex

s = singlet, m = multiplet.

band III at  $1090 \text{ cm}^{-1}$  has contributions from  $\nu(\text{CN})$  and  $\nu(\text{C=S})$ . The thioamide band IV is present at  $792 \text{ cm}^{-1}$ . The  $\nu(\text{C=S})$  is assigned at  $536 \text{ cm}^{-1}$ . Thus the presence of four characteristic thioamide bands and the absence of  $\nu(\text{SH})$ , confirm the ligand to be in the thione form in the solid state.

In the spectra of all complexes of MDPIT,  $\nu$ (NH) is shifted to higher frequency indicating the non-participation of cyclic nitrogen atoms in coordination. Broad bands observed near  $3200 \text{ cm}^{-1}$  in the spectra of all complexes may be assigned to  $\nu(\text{OH})$  of coordinated water. The thioamide bands I and II do not show much change upon coordination. In the spectra of the complexes, the thioamide band III shows a shift to lower frequency of  $60-70 \text{ cm}^{-1}$ . Similarly, the thioamide band IV shows a shift to lower frequency of  $20 \text{ cm}^{-1}$  in the spectra of the complexes. These changes indicate the coordination of the ligand through the thione sulfur atom.

Thermal decomposition data of copper(1) complexes of MDPIT										
		Decomp		Mass-loss fr	om					
Complex	Decomp. stage	temp. range (°C)	TG	Independent pyrolysis	Calculated	Stages of decomposition				
[CuL(OAc)(H <sub>2</sub> O)]	1 2 3	100-150 250-400 450-600	4.00 17.56 83.00	 83.20	3.97 16.97 82.44	$[CuL(OAc)H_2O] \rightarrow CuL(OAc)$ $[CuL(OAc)H_2O] \rightarrow CuL$ $[CuL(OAc)H_2O] \rightarrow CuO$				
[CuLCl(H <sub>2</sub> O)]	1 2 3 4	100-180 250-300 300-400 500-700	3.00 12.00 25.50 84.00	  81.76	4.10 12.45 26.84 81.46	$[CuLCl(H_2O)] \rightarrow CuLCl$ $[CuLCl(H_2O)] \rightarrow CuL$ $[CuLCl(H_2O)] \rightarrow CuL-2 \text{ OCH}_3$ $[CuLCl(H_2O)] \rightarrow CuO$				
[CuLBr(H <sub>2</sub> O)]	1 2 3 4	100-150 220-300 300-450 500-700	4.30 16.50 35.00 85.00		3.74 16.85 33.72 83.24	$[CuLBr(H_2O)] \rightarrow CuLBr$ $[CuLBr(H_2O)] \rightarrow Cu(L-2 \text{ OCH}_3)Br]$ $[CuLBr(H_2O)] \rightarrow Cu(L-2 \text{ OCH}_3)$ $[CuLBr(H_2O)] \rightarrow CuO$				
[CuL(NO <sub>3</sub> )(H <sub>2</sub> O)]	1 2 3 4	100-150 150-300 200-450 450-600	4.00 10.50 30.50 84.00	  83.46	3.97 10.73 31.10 82.60	$\begin{split} & [\operatorname{CuL}(\operatorname{NO}_3)\operatorname{H}_2\operatorname{O}] \to \operatorname{CuL}(\operatorname{NO}_3) \\ & [\operatorname{CuL}(\operatorname{NO}_3)\operatorname{H}_2\operatorname{O}] \to \operatorname{Cu}(\operatorname{L}\text{-2 OCH}_3)\operatorname{NO}_3 \\ & [\operatorname{CuL}(\operatorname{NO}_3)\operatorname{H}_2\operatorname{O}] \to \operatorname{Cu}(\operatorname{L}\text{-2 OCH}_3) \\ & [\operatorname{CuL}(\operatorname{NO}_3)\operatorname{H}_2\operatorname{O}] \to \operatorname{CuO} \end{split}$				
$[Cu_2L_2(SO_4)(H_2O)_2]$	1 2 3 4 5	$100-150 \\ 150-200 \\ 200-400 \\ 400-500 \\ 650-750$	4.40 11.04 46.16 76.60 81.11	  82.00	4.05 11.11 46.33 74.63 82.07	$\begin{split} [\mathrm{Cu}_2\mathrm{L}_2(\mathrm{SO}_4)(\mathrm{H}_2\mathrm{O})_2] &\to \mathrm{Cu}_2\mathrm{L}_2\mathrm{SO}_4 \\ &\to \mathrm{Cu}_2(\mathrm{L},\mathrm{L}\text{-}2\;\mathrm{OCH}_3)\mathrm{SO}_4 \\ &\to \mathrm{Cu}_2(\mathrm{L}\text{-}2\;\mathrm{OCH}_3)\mathrm{SO}_4 \\ &\to \mathrm{Cu}_2\mathrm{SO}_4 \\ &\to 2\mathrm{Cu}\mathrm{O} \end{split}$				

 TABLE 5

 "hermal decomposition data of copper(I) complexes of MDPIT

#### IR Features of Coordinated Anions in the Complexes

In all the complexes, the anions except sulfate act as monadentate ligands. The wide separation between two  $\nu$ (C=O) bands of acetate ion shows its monodentate nature. The denticity of nitrate ion is clear from the separation between  $\nu_1$  and  $\nu_4$ , which is of the order of  $100 \text{ cm}^{-1}$  in the present case. Therefore, the nitrate ion is acting as a monodentate one (Babu and Indrasenan, 1988). The sulfate ion in [Cu<sub>2</sub>L<sub>2</sub>(SO<sub>4</sub>)(H<sub>2</sub>O)] is acting as a bidentate-bridging ligand, which is evident from the positions and the natures of  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  bands. The split nature of the  $\nu_3$  band of the perchlorate ion indicates its monodentate nature (Nakamoto, 1986). In the thiocyanate complex,  $\nu_1$  is present near 2100 cm<sup>-1</sup> indicating that the thiocyanate ligand is S-bonded to the metal ion (Rao, 1963).

## <sup>1</sup>H NMR SPECTRA

The spectra of the ligand and its copper(I) nitrate complex, recorded in CDCl<sub>3</sub> (Table 4) show multiplets near 7 ppm. They

may be assigned to the aromatic protons and the imidazole NH (Purushothaman, 1985). The singlet at 2.50 ppm in the ligand spectrum is due to -SH, which is absent in the spectrum of the complex. This shows that the ligand exists in the thiol form in solution (Shanmugam and Sathyanarayana, 1983). Hence, the peaks of protons of two OCH<sub>3</sub> groups are slightly different in the ligand spectrum while they form a set of multiplets in the spectrum of the complex. This confirms the fact that the ligand coordinates to the metal ion in the thione form. A singlet at 3.76 ppm in the spectrum of the coordinated water.

#### THERMAL DECOMPOSITION STUDIES

The thermal analyses data of the complexes are summarized in Table 5 and the thermograms are shown in Figure 3. The kinetic parameters, such as energy of activation (E),



 $[Cu_2L_2(SO_4)(H_2O)_2]$ 

FIG. 3. TG and DTG curves of metal complexes.

pre-exponential factor (A) and change in entropy ( $\Delta$ s) were calculated for the important stages of decomposition using three different equations, the Coats and Redfern (1963), Horowitz and Metzger (1963) and MacCallum and Tanner (Ninan et al., 1986) equations and the results are summarized in Table 6.

The copper(I) acetate complex decomposed in three stages. In the first stage, loss of coordinated water and in the second stage, loss of coordinated acetate ion resulted. In the third stage, the complex completely decomposed to CuO. The kinetic parameters for the 2<sup>nd</sup> and 3<sup>rd</sup> stages were calculated. The values of energy of activation for the two stages are comparable as they involve rupture of metal-ligand bonds.

The copper(I) chloride complex followed a four-staged decomposition, in which the coordinated water, chloride ion, methoxy groups and the rest of the ligand decomposed successively giving CuO as the final product. The kinetic parameters for the  $2^{nd}$ ,  $3^{rd}$  and  $4^{th}$  stages were calculated. Comparatively high values of activation energies for the  $2^{nd}$  and  $4^{th}$  steps may be due to the rupture of metal-ligand

Complex	Decomp. stage	Eqn. used	E, kcals $mol^{-1}$	A, $s^{-1}$	$\Delta$ S, kcals deg <sup>-1</sup> mol <sup>-1</sup>
[CuL(OAc)(H <sub>2</sub> O)]	2nd	Coats-Redfern (CR)	17.01	$2.01 \times 10^{3}$	-44.96
		Horowitz-Metzger (HM)	15.29	$2.98 \times 10^{3}$	-48.76
		MacCallum-Tanner (MT)	17.54	$2.89 \times 10^{3}$	-39.67
	3rd	CR	16.79	68.38	-52.16
		HM	20.75	92.95	-41.40
		MT	18.07	93.91	-37.80
[CuLCl(H <sub>2</sub> O)]	2nd	CR	11.89	$5.9 \times 10^{5}$	-49.80
		HM	11.93	$9.5 \times 10^{5}$	-50.70
		MT	13.46	$3.6 \times 10^{5}$	-41.14
	3rd	CR	9.16	$2.5 \times 10^{2}$	-58.19
		HM	11.72	$2.3 \times 10^{2}$	-53.77
		MT	9.75	$3.0 \times 10^{2}$	-51.91
	4th	CR	12.48	1.4	-60.02
		HM	14.13	1.6	-54.92
		MT	11.67	1.2	-58.32
[CuLBr(H <sub>2</sub> O)]	2nd	CR	6.75	0.75	-60.31
		HM	6.50	0.38	-61.66
		MT	6.87	0.76	-46.54
	4th	CR	15.67	9.66	-56.33
		HM	19.98	12.09	-51.31
		MT	17.45	18.60	-41.30
$[CuL(NO_3)(H_2O)]$	2nd	CR	7.60	7.62	-55.31
		HM	9.85	11.9	-49.83
		MT	7.31	15.81	-42.58
	3rd	CR	9.01	2.80	-57.96
		HM	7.69	5.08	-61.35
		MT	8.39	4.08	-60.49
	4th	CR	12.53	4.28	-57.66
		HM	16.27	5.42	-52.62
		MT	13.80	6.72	-51.66
$[Cu_2L_2(SO_4)(H_2O)_2]$	3rd	CR	14.84	$3.89 \times 10^{3}$	-40.01
		HM	16.38	$4.95 \times 10^{3}$	-43.01
		MT	13.76	$2.5 \times 10^{3}$	-35.18
	4th	CR	11.08	$5.4 \times 10^{3}$	-56.99
		HM	14.51	$7.1 \times 10^{3}$	-51.89
		MT	12.03	$7.4 \times 10^{3}$	-53.95

 TABLE 6

 Kinetic parameters for thermal decomposition of copper(I) complexes of MDPIT

	Diameter of inhibition zone (mm)										
		Fungal st	rains	Bacterial strains							
Compound	Aspergillus niger	Aspergillus parasiticus	Rhizopus oryzae	Candida albicans	Staphylococcus aureus	Escherichia coli	Pseudomonas aeruginosa				
DMSO	8	8	8	8							
Nystatin	10	12	10	0							
Ampicillin	_	_			15	10	10				
L	10	10		10	_		_				
[CuL(OAc)H <sub>2</sub> O]	10	10		10	_	_	_				
[CuLClH <sub>2</sub> O]	10	10	—	10	11	—	10				

TABLE 7 Antimicrobial activities of copper(I) complexes of MDPIT

bonds. The copper(I) bromide complex also decomposed in four stages. Here the OCH<sub>3</sub> groups decomposed before the elimination of bromide ion. This may be due to the low energy of activation for the decomposition of OCH<sub>3</sub> groups.

The thermal decomposition of the copper(I) nitrate complex took place in four stages. The coordinated water, two OCH<sub>3</sub> groups, nitrate ion and the rest of the ligand decomposed successively. The values of kinetic parameters are also comparable. The copper(I) sulfate complex decomposed in five stages. Coordinated water molecules, two OCH<sub>3</sub> of one of the ligand, one of the ligand and rest of the ligand decomposed successively giving  $Cu_2SO_4$ , which finally decomposed to CuO. The activation energies of the steps involving M-L bond breaking are found to be appreciably higher than those of the other stages.

#### ANTIMICROBIAL STUDIES

Preliminary screening for antifungal and antibacterial activities of the ligand and some of its complexes (2000 ppm solutions in DMSO) were performed against four different fungal and three different bacterial strains. The cup-plate method was used for testing antifungal activity using



FIG. 4. Suggested structure of the complexes.

Nystatin as standard (Murray et al., 1995). The disk-diffusion (Murray et al., 1995) method was used for testing antibacterial activity using Ampicillin as standard (Table 7).

The above investigations revealed that these compounds have higher fungicidal activity than bactericidal activity. None of these compounds were found to be active against *Rhizopus oryzae* and *Escherichia coli*. Of the compounds tested, none other than [CuLCl(H<sub>2</sub>O)] showed activity against bacterial strains. The lower activities of some of the complexes may be due to their inert nature, which prevent their substitution reaction with metal ion centres (Murray et al., 1995).



FIG. 5. Suggested structure of the sulfato complex.

#### CONCLUSIONS

From the magnetic susceptibility and electronic spectral data it was confirmed that copper is in the +1 oxidation state in the complexes. The pale colours of the complexes support this observation. Analytical data indicated that the complexes are of the type [CuLX(H<sub>2</sub>O)], where X = OAc, Cl, Br, NO<sub>3</sub>, ClO<sub>4</sub> or CNS and  $[Cu_2L_2(SO_4)(H_2O)_2]$ . The IR and <sup>1</sup>H NMR spectral studies showed that in the complexes, MDPIT acts as a neutral monodentate ligand coordinating through the thione sulfur atom. As copper is in the +1oxidation state, magnetic and electronic spectral data are of little use in assigning the geometries of the complexes. In comparison with similar complexes (Creighton et al., 1985; Raper and Crackett, 1981; Shanmugam and Sathyanarayana, 1983; Raper et al., 1983), the following geometries may be proposed for the Cu(I) complexes of MDPIT (Figures 4 and 5).

#### REFERENCES

- Babu, K.; Indrasenan, P. Thorium(IV) nitrate complexes with some substituted pyrazol-5-ones. *Indian J. Chem.* 1988, 27A, 1005–1007.
- Bellamy, L. H. The Infrared Spectra of Complex Molecule; Chapman and Hall: London, 1978.
- Coats, A. W.; Redform, J. P. Thermogravimetric analysis. *Analyst* 1963, 88, 906–918.
- Creighton, J. R.; Gardiner, D. J.; Gorvin, A. C.; Gutteridge, C.; Jackson, A. R. W.; Raper, E. S.; Sherwood, P. M. A. Copper(I) halide complexes of imidazole thiones: Crystal structure of dimeric monochlorobis(1-methylimadazoline-2-thione) copper(I). *Inorg. Chim. Acta* **1985**, *103*, 195–205.
- Earnshaw, A. Introduction to Magnetochemistry; Academic Press: London, 1968.

- Figgis, B. N. Introduction to Ligand Fields; Wiley Interscience: New York, 1967.
- Geary, W. J. The use of conductivity measurements in organic solvents for the characterization of coordination compounds. *Coord. Chem. Rev.* 1971, 7, 81–122.
- Horowitz, H. H.; Metzger, G. A new analysis of thermogravimetric traces. Anal. Chem. 1963, 35, 1464–1468.
- Mohanan, A.; Aravindakshan, K. K. Synthesis and characterisation of Cu(I) and Ag(I) complexes of 4,5-diphenylimidazole-2-thione. *Proc. Indian Acad. of Sci. (Chem. Sci.)* **1989**, *101* (1), 13–17.
- Murray, P. R.; Baron, E. J.; Pfaller, M. A.; Tenover, F. C.; Yolken, R. H. *Manuel of Clinical Microbiology*, 4th ed.; American Society for Microbiology Press: Washington, DC, 1995; pp. 1407.
- Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds; John Wiley and Sons: New York, 1986.
- Ninan, K. N.; Krishnan, K.; Mathew, J. Addition polyimides, kinetics of cure reaction and thermal decomposition of bismaleimides. *J. Appl. Poly. Sci.* **1986**, *32*, 6033–6042.
- Purushothaman, E. Ph.D. Studies in the photochemistry of Imidazole-Derivatives; Calicut University, 1985.
- Rao, C. N. R. Chemical Applications of IR Spectroscopy, Academic Press: New York, 1963.
- Raper, E. S.; Crackett, P. H. Complexes of imidazoline (1,3H)-2thione with Co(II) and Zn(II) salts. *Inorg. Chim. Acta* 1981, 50, 159–165.
- Raper, E. S.; Jordan, B. M.; Creighton, J. R. Thermal analysis of heterocyclic thione donor complexes. Part V. Nickel(II) complexes of imidazoline-2-thiones. *Thermochim. Acta* **1983**, *65*, 135–141.
- Shanmugam, R.; Sathyanarayana, D. N. Complexes of imidazoline-2thione and its 1-methyl analogue with Cu(II), Zn(II), Cd(II) and Hg(II) salts. J. Coord. Chem. 1983, 12, 151–156.
- Vogel, A. I. A Textbook of Quantitative Inorganic Analysis; ELBS and Longman: London, 1978.