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# Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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# Synthesis and Characterization of Copper(II) Complexes with Diphenylpyraline Hydrochloride

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# SYNTH. REACT. INORG. MET.-ORG. CHEM., 28(2), 263-274 (1998)

# SYNTHESIS AND CHARACTERIZATION OF COPPER(II) COMPLEXES WITH DIPHENYLPYRALINE HYDROCHLORIDE

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## ABSTRACT

A new series of copper complexes formed through the reaction of diphenylpyraline hydrochloride (DP.HCl) with copper(II) salts were synthesized. The solid complexes isolated were characterized by conductivity measurements, elemental analyses and magnetic susceptibility studies. The molecular structure of the  $Cu(C_{19}H_{23}ON)_2Cl_2$  complex was investigated by X-ray diffraction.

## **INTRODUCTION**

Diphenylpyraline hydrochloride (DP.HCl) has wide applications as pharmaceutical agent<sup>1-7</sup>, as antioxidant<sup>8</sup> and in industry<sup>9</sup>. It is found to exhibit antifungal activity<sup>10,11</sup>. DP.HCl has the following structure (Fig. 1).

Recently, we have reported the biological activity of its chelates with cobalt(II)<sup>12</sup>. The aim of the present work is to synthesize and characterise four new complexes of copper(II) with diphenylpyraline hydrochloride. The



Fig. 1. Structure of Diphenylpyraline Hydrochloride (DP.HCI)

complexes were investigated by elemental analyses, conductivity measurements, magnetic moments, TGA as well as spectroscopic techniques.

# **EXPERIMENTAL**

All compounds used were AnalaR grade. Solvents were used after distillation. Diphenylpyraline hydrochloride (DP.HCl), received as a gift sample from Smith Kline Beecham Ltd., Bangalore (India), was used directly without further purification (m.p. 205° C).

# **Physical Measurements**

IR spectra of the ligand and its complexes were recorded on a Hitachi Model 297 spectrophotometer in the 4000-250 cm<sup>-1</sup> region as Nujol mulls. Electronic spectra of 10<sup>-4</sup> M solutions of the complexes in chloroform were recorded on a JASCO Model UVIDEC-610 spectrophotometer. Molar conductances of the complexes in chloroform (10<sup>-4</sup> M) were measured at room temperature (305 K) using a Philips Model PR 9500 conductometer.

#### COPPER(II) COMPLEXES OF DIPHENYLPYRALINE

Magnetic susceptibilities of the complexes were measured at room temperature (305 K) with a Gouy balance using Hg[Co(SCN)<sub>4</sub>] as calibrant. A Dupont 9900 computer/thermal analyser with a 951TG module thermobalance was used for recording TG and DTA curves in an atmosphere of air at a heating rate of 6° C min<sup>-1</sup> with a chart speed of 5 mm min<sup>-1</sup>. The melting points were determined using a Thomas Hoover Capillary melting point apparatus. The X-ray data were recorded on a DE-CER P12 X-ray machine with a diffractogram. The diffraction pattern was recorded with a chart speed of 4°(20) min<sup>-1</sup> at 10-80°(20) using the scale  $1^{\circ} = 1$  cm.

## Preparation of the Complexes

A quantity of 5 mmol (0.564 g) of diphenylpyraline hydrochloride in 50 mL ethyl alcohol was slowly added to 50 mL of an ethanolic solution of copper(II) salt 2.5 mmol (0.17-0.24 g) (chloride/nitrate/acetate/ perchlorate) with continuous stirring<sup>13</sup>. The ligand to metal ratio in the reaction mixture was 2:1. The solution was warmed on a water bath (60-70°C) for about 0.5-1.0 h. On cooling, green solid copper(II) complexes separated which were filtered, washed with cold ethanol and then with ether and dried over fused CaCl<sub>2</sub>. The yield of the copper(II) complexes in these reactions was found to be in the range 57-82%.

# Elemental Analyses

Elemental analyses were done by conventional methods. The analysis of chloride in the complexes was carried out by fusing a known amount of complex in a mixture of Na<sub>2</sub>CO<sub>3</sub> and KNO<sub>3</sub> (4:3 w/w), followed by extraction with deionised water. After acidification with nitric acid, the chloride content was determined gravimetrically as AgCl<sup>14</sup>, Perchlorate was determined by fusion with sodium nitrite and the reduced chloride ion was determined gravimetrically as AgCl<sup>15</sup>. The copper content in the complexes was determined by decomposing the complexes with concentrated nitric acid as copper salicylaldoxime<sup>14</sup>. Nitrogen in the complexes was determined by Dumas' method.

#### **RESULTS AND DISCUSSION**

DP.HCl reacts with copper(II) chloride/nitrate/acetate/perchlorate to yield coloured complexes.

2 DP.HCI + CuX<sub>2</sub>  $\longrightarrow$  Cu(DP)<sub>2</sub>X<sub>2</sub> + 2 HCI

The elemental analyses indicate that the experimental values of the amount of metal, chloride and nitrogen obtained for the complexes are in close agreement with those calculated on the basis of the molecular formulae given in Table 1.

# **Conductivity**

The molar conductivity values calculated from the conductivities measured on 10<sup>-4</sup> M solutions of copper(II) complexes in chloroform lie in the range 20.1 - 32.4 Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating them to be non-ionic.

## Magnetic and Electronic Spectral Studies

The magnetic moment values ( $\mu_{eff}$ ) were calculated for the metal complexes from the measured magnetic susceptibilities at room temperature (305 K). These values (1.87 - 2.07 BM) of the new complexes

Table I

Analytical and Physical Data of the Complexes

		4								
Compound	Empirical	Formula	Yield	M.P	Foun	d (Calculi	ated)%	مربع مربع	$\mu_{\rm eff}$	Electronid
	Formula	Weight	%	(°C)	z	σ	S	cm <sup>2</sup> mol <sup>-1</sup>	BM	(cm <sup>-1</sup> )
Cu(DP) <sub>2</sub> Cl <sub>2</sub>	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> O <sub>2</sub> Cl <sub>2</sub> Cu	697	80	160-63	4.00	10.14	9.40	27.6	1.87	25025
					(4.02)	(10.17)	(9.11)	. 1		35460
				:						37650
	-									
Cu(DP) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	C <sub>3</sub> H <sub>4</sub> N <sub>4</sub> O <sub>5</sub> Cu	750	82	150-54	7.50	ı	8.10	32.4	1.82	25278
	-				(7.47)		(8.48)			35161
										38580
	-									
Cu(DP) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub>	C <sub>w</sub> H <sub>w</sub> N <sub>2</sub> O <sub>6</sub> Cu	744	57	167-70	3.63	ı	8.10	16.2	2.07	25100
					(3.77)		(8.55)			36161
										38700
Cu(DP) <sub>2</sub> (CIO <sub>4</sub> ) <sub>2</sub>	C <sub>3</sub> H <sub>4</sub> N <sub>2</sub> O <sub>10</sub> Cl <sub>2</sub> Cu	825	74	175-78	3.26	8.40	7.56	20.1	1.94	25050
	-				(3.39)	(8.60)	7.70	•		38580
					1.1					41186
	· · · · · · · · · · · · · · · · · · ·									

# COPPER(II) COMPLEXES OF DIPHENYLPYRALINE

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indicate that these complexes are paramagnetic and confirm the +2 oxidation state of copper (Table I).

The electronic spectra (Fig. 2) of the four copper(II) complexes display a strong absorption band at 24390 - 25640 cm<sup>-1</sup> which can be attributed to a combination of  ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$  plus charge transfer transition<sup>16-18</sup>. The other strong bands obtained in the regions ~35,088 and ~41,150 cm<sup>-1</sup> are charge transfer transitions. The magnetic moment values and electronic spectra of these new complexes support the square-planar geometry for these complexes.

#### IR Spectra

The IR data are presented in Table II. Diphenylpyraline hydrochloride, like many other organic compounds with a heterocyclic nitrogen atom attached to an alkyl group combined with halogen gives rise to a broad band<sup>19</sup> generally between 2250-2700 cm<sup>-1</sup>. The broad band at 2300-2700 cm<sup>-1</sup> in the DP.HCI ligand corresponds to a tertiary nitrogen atom attached to an alkyl group combined with chloride. The band at 1060-1150 cm<sup>-1</sup> in the IR spectrum of the ligand is due to a C-O-C symmetric vibration (ethers)<sup>19</sup>. In the IR spectra of the copper(II) complexes the band at 2300-2700 cm<sup>-1</sup> has totally disappeared, thereby indicating that the tertiary nitrogen atom in the ligand is the site of coordination. The bands at 1060-1150 cm<sup>-1</sup> appeared in the ligand and also in the complexes, indicating that the oxygen atom in the ligand is not involved in bonding with the metal ion. The new bands appearing in the far IR region at 460-485 and 390-400 cm<sup>-1</sup> may be assigned to v(Cu-N) and v(Cu-X), respectively<sup>20</sup>.



Fig. 2. Electronic Spectra of 1. Cu(DP)<sub>2</sub>Cl<sub>2</sub>, 2. Cu(DP)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, 3. Cu(DP)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>, 4. Cu(DP)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>

# Thermogravimetric Study

On heating, diphenylpyraline hydrochloride was found to be melting around 205° C and decomposing around 250° C. On the basis of the percentage loss in weight, the thermal decomposition for the complexes can be formulated as shown below.

The TG and DTA curves indicate that these copper complexes are generally stable up to 170-190° C. At higher temperature the oxidation of the organic substance begins. It has been found that concurrent with

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Table II

IR Spectral Data of Ligand and its Complexes (cm<sup>-1</sup>)

Compound	v(C-H) <sup>a</sup>	v(C-N-H) <sup>b</sup>	v(c=c) <sup>c</sup>	v(c-o-c)	v(Cu-N)	v(Cu-X)
DP.HCI	2950-2850	2700-2300	1600 w	1100-1010	1	I
Cu(DP) <sub>2</sub> Cl <sub>2</sub>	2955-2840	<b>T</b>	1610 w	1100-1000	485-465	393-395
Cu(DP) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	2950-2850	•	1595 w	1080-1030	470-460	398-400
Cu(DP) <sub>2</sub> (CH <sub>3</sub> COO) <sub>2</sub>	2920-2845	•	1605 w	1095-1010	475-463	395-399
Cu(DP) <sub>2</sub> (CIO <sub>4</sub> ) <sub>2</sub>	2920-2810	١	1615 w	1070	472-461	390-394

<sup>a</sup>Piperidine ring, <sup>b</sup>Heterocyclic nitrogen atom attached to alkyl group combined with halogen, <sup>c</sup>Benzene ring, w = weak

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the decomposition and oxidation of organic substances and anhydrous intermediate compunds, some volatilization also takes place. The endproduct obtained in each thermogravimetric analysis was chemically analysed and found to be pure copper(II) oxide.

# X-ray Diffraction

The molecular structure of Cu(DP), Cl, was studied by X-ray diffraction and the data are presented in Table III. The complex has the cell dimensions, a = 7.474, b = 5.337 and c = 3.887 Å ( $\alpha = 87.439$ ,  $\beta$  = 86.929 and  $\gamma$  = 94.045),  $\rho$  = 3.0126 g cm<sup>-3</sup>, n = 1. The diffractogram recorded 17 reflections between 10 and 60° (20) with maxima at  $2\theta = 16.7^{\circ}$ , and 22° which correspond to d = 5.303 Å and 4.036 Å, respectively. The 20 values for prominent peaks are listed in Table III. The main peaks have been indexed<sup>22,23</sup> and their sin<sup>2</sup> 0 values compared with the calculated ones. A comparison of the values reveals good agreement between calculated and observed values of sin<sup>2</sup> 0. The unit cell has been calculated by the trial and error method<sup>23-25</sup>. The observed values fit well with a triclinic system to give a unit cell with the lattice constants a = 7.474, b = 5.337and c = 3.887 ( $\alpha$  = 87.439°,  $\beta$  = 86.929°,  $\gamma$  = 94.045°). Substituting of this cell volume primitive lattice (n = 1) for the complex Cu(DP)<sub>2</sub>Cl<sub>2</sub> gives the theoretical value of the density equal to 3.0126 g cm<sup>-3</sup>. The experimental value of the density of the complex has been found to be 3.0237 g cm<sup>-3</sup> which is in fairly good agreement within the limits of experiemental errors. The above observations suggest the square-planar structure in Fig. 3 for these complexes.

Peak No.	d Å	Observed sin²θ	Calculated sin <sup>2</sup> 0	(h.k.l)	Observed 2 θ	Calculated 2 θ
1.	7.429	0.0107	0.0106	100	11.900	11.828
2.	,				* · · ·	
3.						
4.	5.303	0.0210	0.0208	010	16.700	16.600
5.	4.036	0.0364	0.0392	001	22.000	22.850
6.	3.689	0.0432	0.0424	200	24.100	23.780
7.	3.335	0.0533	0.5200	101	26.700	26.370
8.		-				
9.	3.086	0.0623	0.0623	011	28.900	28.980
10.	2.736	0.0792	0.0733	.112	32.700	31.420
11.	2.619	0.0864	0.0832	020	34.200	33.540
12.	2.184	0.1244	0.1173	220	41.300	40.060
13.	2.153	0.1278	0.1276	021	41.900	41.860
14.	1.995	0.1489	0.1414	301	45.410	44.170
15.	1.864	0.1706	0.1699	400	48.800	48.680
16.	1.659	0.2154	0.2171	321	55.300	55.550
17.	1.606	0.2298	0.2298	212	57.300	57.300

Table III X-ray Data of the  $Cu(DP)_2Cl_2$  Complex



 $x = c_1, NO_3, CH_3 COO, CIO_4$ 

Fig. 3. Suggested Structure of Cu(DP)<sub>2</sub>X<sub>2</sub>

#### Screening for Antifungal and Antibacterial Activity

The antimicrobial activity of the free ligand and its copper(II) complexes clearly indicates that the compounds have both antibacterial and antifungal potency against all tested organsims.

The *in vitro* biocidal activities of the investigated compounds were screened against Alternaria alternata, Aspergillus flavus, Aspergillus niger and Alternaria tenius fungi. The compounds were also screened against Staphylococous aureus and Escherichia coli bacteria following the cup-diffusion technique. The antimicrobial activity of the complexes was found to be higher than that of the free ligand.

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