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Synthesis, Magnetic, and Spectral Studies of Some Mixed-Ligand Complexes of Copper(II) Involving Diphenic Acid and Pyridine or Aniline Derivatives

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ABSTRACT

New mixed-ligand hexa-coordinated diphenato complexes of copper(II) having the general formula $[Cu(DPA)(L)_2]$, where DPAH₂ = diphenic acid and L = nicotinamide (NICA), 2-cyanopyridine (2-CPY), 3-cyanopyridine (3-CPY) and 4-cyanopyridine (4-CPY) or aniline derivatives, such as, *o*-toluidine (*o*-TD), *m*-toluidine (*m*-TD) or *o*-phenetidine (*o*-PD), have been prepared by the interaction of an aqueous solution of cupric chloride and ethanolic solutions of diphenic acid and the corresponding ligand L, in the mole ratio of 1:1:2. The resulting products have been characterized on the basis of analytical data, molar

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conductances, magnetic measurements, infrared, electronic and electron spin resonance spectral studies. All of the complexes are thermally stable and behave as non-electrolytes. A square-planar geometry has been suggested for these complexes.

Key Words: Diphenic acid; Mixed-ligand complexes; (4+2) Cu(II) compounds.

INTRODUCTION

Diphenic acid has been used as an analytical reagent^[1] and as a bidentate ligand in the formation of complexes with transition metal ions.^[2] Studies on some mixed-ligand complexes of cobalt(II), nickel(II), copper(II), palladiu-m(II), platinum(II), manganese(II), zinc(II), iron(II) and iron(III) with diphenic acid as primary and some heterocyclic bases as secondary ligand are available in the literature.^[1,3-6] However, there is no report on mixed-ligand complexes of copper(II) involving diphenic acid and pyridine or aniline derivatives. It was, therefore, thought worthwhile to synthesize and characterize some mixed-ligand copper(II) diphenates with pyridine derivatives, *viz.*, nicotinamide (NICA), 2-cyanopyridine (2-CPY), 3-cyanopyridine (3-CPY) and 4-cyanopyridine (4-CPY) or aniline derivatives, such as, *o*-toluidine (*o*-TD). *m*-toluidine (*m*-TD) and *o*-phenetidine (*o*-PD). The present paper describes the results at such a study. The structures of diphenic acid and the other ligands used in the present investigation are shown in Figure 1.

EXPERIMENTAL

Materials

Nicotinamide (Sisco Chem. Industries, Bombay), 2-, 3- and 4cyanopyridines (Nepera, New-York), *o*-toluidine, *m*-toluidine and cupric chloride dihydrate (B.D.H. Chemicals, Bombay), *o*-phenetidine (Aldrich Chemical Company, U.S.A.) and diphenic acid (E. Merck, India), were used as supplied.

Synthesis at Mixed-Ligand Complexes

An aqueous solution (10 mL) of cupric chloride dihydrate (1.70 g, 10 mmol) was added to the ethanolic solutions (20 mL) of diphenic acid



Figure 1. Structures of ligands.

(2.42 g, 10 mmol) and the corresponding pyridine/aniline derivative (20 mmol) in the mole ratio 1:1:2. The resulting mixture was then refluxed at 80 $^{\circ}$ C over a hot plate with magnetic stirrer, for the duration given below in each case:

Ligand	Duration, h
NICA	1.45
2-CPY	1.5
3-CPY	1.5
4-CPY	1.5
o-TD	2.0
<i>m</i> -TD	2.0
o-PD	2.5



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During this time a coloured mass separated out. It was filtered by suction, washed 4 to 5 times with ethanol and dried in a desiccator over anhydrous $CaCl_2$ at room temperature.

Analyses

Carbon, hydrogen and nitrogen were determined microanalytically on a Carlo Erba 1108 elemental analyzer at the Central Drug Research Institute, Lucknow, India. The copper content in the complexes was determined by the standard method.^[7]

Physical Methods

The IR spectra were recorded $(4000-400 \text{ cm}^{-1})$ as Nujol mulls on a Perkin-Elmer model 1620 FT-IR spectrophotometer, Electronic spectra were recorded in 10^{-3} M DMF solutions on a Shimadzu model UV-160 spectrophotometer; EPR spectra were recorded at 298 K on a Bruker spectrometer at the microwave frequency 9.45 GHz and magnetic field around 3000 G. Room temperature molar conductances in 10^{-3} M DMF solutions were measured on a Toshniwal conductivity bridge fitted with a dip-type cell (cell constant 1.3 cm⁻¹). Decomposition temperatures of the complexes were determined using an electrothermal apparatus having the capacity to record temperatures up to 360 °C. Room temperature magnetic measurements were performed by Gouy's method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant.

RESULTS AND DISCUSSION

The mixed-ligand complexes of copper(II) were prepared according to the following equation:

$$CuCl_2 \cdot 2H_2O + DPAH_2 + 2L \xrightarrow[Reflux(80 \ ^\circ C)]{} [Cu(DPA)(L)_2] + 2HCl + 2H_2O$$

Where L = NICA (1), 2-CPY (2), 3-CPY (3), 4-CPY (4), o-TD (5), m-TD (6) and o-PD (7) and DPAH₂ = diphenic acid.

All of the compounds are air-stable, non-hygroscopic, coloured solids (see Table 1 for colors). The analytical data and some physical properties of the complexes are also given in Table 1. The solubilities of these

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	Table 1. Analytica	l data and sc	ome physica	ll properties	of the synthe	ssized complexes.		
	Comulex		Found (calc.), %			Decom	Vield
Sr. no	(empirical formula) (mol. wt.)	С	Н	N	Cu	Color	temp. (°C)	(%)
(1)	[Cu(DPA)(NICA) ₂]	56.27	4.08	10.48	11.85	Aquamarine	243	52
	$(C_{26}H_{20}CuN_4O_6)$ (547.54)	(56.98)	(3.65)	(10.22)	(11.60)			
(2)	$[Cu(DPA)(2-CPY)_2]$	60.35	3.17	10.53	12.72	Sky blue	252	50
	$(C_{26}H_{16}CuN_4O_4)$ (511.54)	(60.09)	(3.12)	(10.94)	(12.42)			
(3)	$[Cu(DPA)(3-CPY)_2]$	60.52	3.25	10.28	12.18	Aquamarine	251	54
	$(C_{26}H_{16}CuN_4O_4)$ (511.54)	(60.09)	(3.12)	(10.94)	(12.42)			
(4)	$[Cu(DPA)(4-CPY)_2]$	60.35	3.25	10.73	12.21	Bright green	251	55
	$(C_{26}H_{16}CuN_4O_4)$ (511.54)	(60.09)	(3.12)	(10.94)	(12.42)			
(5)	$[Cu(DPA)(o-TD)_2]$	64.77	5.17	5.52	12.38	Black	246	38
	$(C_{28}H_{26}CuN_2O_4)$ (517.54)	(64.92)	(5.02)	(5.41)	(12.27)			
(9)	$[Cu(DPA)(m-TD)_2]$	64.31	5.16	5.20	12.13	Black	234	38
	(C ₂₈ H ₂₆ CuN ₂ O ₄) (517.54)	(64.92)	(5.02)	(5.41)	(12.27)			
6	$[Cu(DPA)(o-PD)_2]$	62.48	5.27	4.32	10.59	Grey	240	40
	$(C_{30}H_{30}CuN_2O_6)$ (577.54)	(62.33)	(5.19)	(4.84)	(11.00)			

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Sr. no.	Compound	Acetone	$CC1_4$	CHCl ₃	DMF	Ethanol	Methanol	Ethyl acetate
(1)	[Cu(DPA)(NICA) ₂]	IS	IS	IS	S	IS	Sd	IS
(2)	$[Cu(DPA)(2-CPY)_2]$	PS	IS	IS	S	PS	PS	IS
(3)	$[Cu(DPA)(3-CPY)_2]$	PS	IS	IS	S	PS	PS	IS
(4)	$[Cu(DPA)(4-CPY)_2]$	PS	IS	IS	S	PS	PS	IS
(2)	$[Cu(DPA)(o-TD)_2]$	IS	IS	IS	S	PS	PS	IS
(9)	$[Cu(DPA)(m-TD)_2]$	IS	IS	IS	S	PS	IS	IS
(1)	$[Cu(DPA)(o-PD)_2]$	Sd	IS	IS	S	PS	IS	
Abbreviati 100 mg of	on: $S = $ soluble (80–100%) each of the compounds in	(b); PS = parti 5 mL of the s	ally soluble solvent.	$(\sim 50\%);$ IS	= insoluble	e (5–10%). So	lubility was test	ed by dissolving

Table 2. Solubility of the synthesized compounds in various solvents.

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							Λ_{M_1}	
Sr. no	Complex	v _{as} (C=O)	v _s (C-O)	$\Delta = [v(C=0)-v(C=0)]$	v(C=N)	Pyridine ring breathing mode	$(Ohm^{-1}cm^{2}, mole^{-1})$	μ _{eff} (B.M.)
(1)	[Cu(DPA)(NICA) ₂]	1604 s	1378 s	226	Merged with v.c.(C=O)	1021 m	12.2	1.92
(5)	$[Cu(DPA)(2-CPY)_2]$	1601 s	1376 s	225) I	1048 m	14.4	1.97
(3)	$[Cu(DPA)(3-CPY)_2]$	1600 s	1376 s	224	I	1034 m	14.0	2.01
(4)	$[Cu(DPA)(4-CPY)_2]$	1612 s	1383 s	229	I	1026 m	13.2	1.87
(2)	$[Cu(DPA)(o-TD)_2]$	1590 s	1377 s	213	I	3380, 3100 ^a w 1623 ^b	11.8	2.05
(9)	$[Cu(DPA)(m-TD)_2]$	1589 s	1398 s	191	I	1032 III 3385, 3200 ^a w 1632 ^b m	13.4	1.98
6	[Cu(DPA)(o-PD) ₂]	1588 s	1402 s	186	I	3331, 3200 ^a w 1632 ^b m	12.8	1.89
a = v(N)	(HI).							

 $b = \delta$ (NH2).

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complexes in different solvents are recorded in Table 2. The resulting compounds were characterized on the basis of the following studies.

Conductance Measurements

The observed molar conductances of these mixed-ligand complexes are given in Table 3, and are consistent with the non-electrolytic^[8] nature of the complexes.

Magnetic Measurements

Copper(II) has a d^[9] electronic configuration and its complexes contain one unpaired electron in the 3d shell. The majority of the complexes are formed by involvement of d-orbitals and they are square-planar or distorted-octahedral. Jahn Tellar distortions play a major role in the distortions of the geometry of the complexes. The formation of tetrahedral complexes of copper(II), with no involvement of d-orbitals has also been reported.^[9] In cases where the copper(II) complexes display magnetic moments values equivalent to one unpaired electron, the complexes are referred to as magnetically dilute. In such complexes the paramagnetic metal centres are situated apart and the metal ions are surrounded by ligand molecules in such a way that the unpaired spins of neighbouring metal ions remains unaffected. In the case of tetrahedral or distortedoctahedral copper(II) complexes, the room temperature magnetic moment values are usually observed in range of 1.8-2.2 B.M., which are not affected appreciably by the temperature and the magnetic field. In the case of planar, dimeric or polynuclear species, the complexes display subnormal magnetic moments. In practice, compounds whose geometry approaches octahedral, usually exhibit magnetic moments which are at the lower end, while those approaching tetrahedral geometry are at the higher end. Reports are also available where square-planar^[10,11] complexes have magnetic moment in the range 1.8-2.2 B.M.

The magnetic moments of the present complexes (Table 3) fall within the 1.87–2.05 B.M. range, usually reported for copper(II) complexes irrespective of the stereochemistry.^[12] The magnetic moments are, therefore, structurally non-diagnostic. These values also rule out any copper–copper interactions.^[13]

Electronic Spectra

Square-planar complexes commonly exhibit a broad structured band from about 18,000 to 21,000 cm⁻¹ (555–475 nm)^[14] while distorted-octahedral copper(II) complexes usually show a broad d–d band in the

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Figure 2. Electronic spectrum of [Cu(DPA)(NICA)₂] (1).

range^[15] 11,000–17,000 cm⁻¹ (900–580 nm). The electronic spectra of the present complexes show a broad d–d band with an absorption maximum located at 540–580 nm (18,518–17,241 cm⁻¹). These data suggest that the present complexes represent a border line case of square-planar and distorted octahedral complexes. The additional band of relatively high intensity at 285–300 nm in these complexes is assigned as ligand \rightarrow metal charge transfer transition. The electronic spectrum of a representative compound, [Cu(DPA)(NICA)₂], is given in Figure 2.

Electron Spin Resonance Spectra

The room temperature X-band EPR spectrum of one representative compound, $[Cu(DPA)(o-PD)_2]$, was recorded on a powdered sample using the microwave frequency 9.45 GHz. Both parallel and perpendicular features of ⁶³Cu are not resolved in the spectrum of this compound. The observed 'g' value of 2.067 which is less than 2.3, suggests the covalent nature^[16] of metal-ligand bonds in this complex. The ESR spectrum of this compound is shown in Figure 3.

Infrared Spectra

The important IR spectral bands and their tentative assignments are presented in Table 3. The strong bands at 1700 and 1450 cm⁻¹ in the spectrum



Figure 3. EPR spectrum of [Cu(DPA)(o-PD)₂] (7).

of diphenic acid are assigned^[1,6] as $v_{as}(C=O)$ and $v_s(C-O)$. The shifting of these bands to lower wave numbers and appearing at 1588–1612 cm⁻¹ and 1376–1402 cm⁻¹ in the present complexes, suggests the coordination of diphenic acid through its carboxylate anions. It is notable here that Δ values [the difference between $v_{as}(C=O)$ and $v_s(C-O)$] in the solid state vary smoothly from 229–186 cm⁻¹ which fall within the range expected for a unidentate^[17,18] carboxylate ligand/group. The v(OH) band (observed at 3600–3450 cm⁻¹ as a broad band) for free diphenic acid disappears upon coordination, indicating that diphenic acid is a dibasic bidentate ligand coordinating through both carboxylate anions. For the convenience of interpretation, the present discussion of the IR data is divided into three parts.

NICA Complexes

The ligand NICA used in the present part of the discussion contains two potential donor sites: 1) the pyridine ring nitrogen, and 2) the amide oxygen. Significant IR spectral bands due to the amide group are v(NH), v(CO) and v(CN). In amides^[19] and other carbonyl donors,^[20] a significant shift to lower wave numbers of the v(CO) band takes place because of coordination through the carbonyl oxygen. The v(NH), v(CO) and v(CN) bands of free NICA remain almost unperturbed. These features clearly indicate that the amide group does not coordinate.

The characteristic ring vibration, v(C=N), of the free ligand at 1575 cm⁻¹ generally shows a significant shift to higher frequency in the complexes. But in the present case this band could not be distinguished because of overlapping with v(C=O) of the diphenic acid. However, the pyridine breathing mode occurring at 990 cm⁻¹ in the free ligand undergoes a significant shift to higher frequency and appears at 1021 cm⁻¹ in the complex. This observation indicates the coordination of NICA *via* the pyridine ring nitrogen^[21] only.

CPY Complexes

The ligands 2-CPY, 3-CPY and 4-CPY used in the present study possess two donor sites: 1) the pyridine ring nitrogen, and 2) the nitrile group. The nitrile group may be involved in coordination either through the nitrogen or the triple bond. Coordination through the nitrogen of the nitrile group^[22] invariably results in an increase in v(C=N) by at least 30 cm⁻¹. A decrease in v(C=N) is generally interpreted as resulting from the coordination of the cyano group through its triple bond.^[22] In the complexes of the cyanopyridines studied here, the v(CN) band of the free cyanopyridines (~2235 cm⁻¹) remains the almost unchanged, thereby suggesting that the cyano group of these ligands does not participate in coordination. However, the appearance of a ring breathing mode at 1026–1040 cm⁻¹ in the complexes (2)–(4), suggests the coordination of these ligands through the pyridine ring nitrogen.

o-TD, m-TD and o-PD Complexes

These three ligands possess only the amino nitrogen as donor site. The appearances of two broad bands at 3331–3385 and 3100–3200 cm⁻¹ assignable to $v_{as}(NH)$ and $v_{s}(NH)$ suggest the coordination of the amino nitrogen of these ligands to copper (Table 2).



Figure 4. Proposed square-planar structure of $[Cu(DPA)(L)_2]$ (L = NICA, 2-CPY, 3-CPY, 4-CPY, *o*-TD, *m*-TD or *o*-PD).



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CONCLUSION

Satisfactory analytical data and all of the above results suggest the formulation of these complexes as $[Cu(DPA)(L)_2]$, where L = NICA, 2-CPY, 3-CPY, 4-CPY, *o*-TD, *m*-TD or *o*-PD. Considering the unidentate coordination of each of the carboxylate group of the diphenic acid ligand, a square-planar structure, shown in Figure 4, is tentatively proposed for these complexes. However, the electronic spectral results of these complexes in dimethylformamide solutions (*vide supra*) probably suggest a tendency of copper(II) square-planar complexes behaving as distorted octahedral complexes (4 + 2 compounds) in solution.

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