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Synthesis and Characterization of Cu(II) Complexes Derived from Phenylene Diamines and 3-Carboxaldehyde.

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Schiff Bases synthesized by the reaction of pyridine-3-carboxaldehyde with *o*-phenylene diamine (COPDE) and *m*-phenylene diamine (CMPDE) form monomeric and dimeric complexes with divalent Cu^{2+} ions. Structure of the complexes have been assigned on the basis of elemental analysis, molar conductance, molecular wt. determination, IR, UV, magnetic moment values and ESR spectral data.

INTRODUCTION

Metallic and polymetallic complexes of divalent metal ions containing multidentate ligands have drawn considerable interest in recent years[1–4] due to variable structural and magnetic properties. The present paper reports the preparation of two new Schiff Bases derived from phenylene diamimes and 3-carboxaldehyde and its complexes with Cu(II) ions.

EXPERIMENTAL

o-Phenylene diamine, *m*-phenylene diamine (Koch Light, U.K.); pyridine-3-aldehyde (Sigma, U.S.A) were used as received. Metal salts and solvents used were of either B.D.H. or Sarabhai Merck.

Pyridine-3-aldehyde-*o*-phenylenediamine (COPDE) and pyridine 3-aldehyde-*m*-phenylenediamine (COMPDE).

An alcoholic solution of *o*-phenylene diamine or *m*-phenylene diamine and pyridine-3-carboxaldehyde were mixed in 1 : 1 mole ratio. The solution mixture was stirred and was refluxed for 2 h at 30–40°C. It was kept in refrigerator for overnight. A green precipitate was obtained after recrystallization from acetone and dried over anhydrous $CaCl_2$ (COPDE m.p. 45°C. and COMPDE, m.p. 55°C)

Synthesis of metal complexes

An alcoholic solution of the respective ligands were prepared separately in dioxane and mixed separately with ethanolic/aqueous solution of the metal salt with constant stirring in 2 : 1 mole ratio. The reaction mixture was kept over water bath for about 1–2 h. After cooling and stirring the metal chelates separated out. These were filtered washed with ethanol, ether and dried in *vacuo*.

RESULTS AND DISCUSSION

Most of compounds are partially soluble in common organic solvents, but are soluble in DMF to larger extent. Some of compounds are amorphous in nature and possess high decomposition/melting temperature. The analytical data of the compounds are shown in Table 1. Molar conductance values of the complexes from (1) to (4) in DMF at 10^{-3}M were observed in the range 124–128 ohm^{-1} cm^2 $mole^{-1}$ indicating that these complexes behave as 1 : 2 electrolytes. Molar conductance value (18–20 ohm^{-1} cm^2 $mole^{-1}$) of complexes from (5) to (8) are indicative of their non-electrolytic nature.

TABLE 1
ANALYTICAL DATA OF COPPER(II) COMPLEXES.

S.No	Complexes/Colour	M.p./Decomp. (°C)	% Analysis Found (Calcd)			
			M	C	H	N
1.	$Cu(COPDE)_2Cl_2$ (Dark Brown)	210	11.52 (12.02)	53.96 (54.48)	3.96 (4.16)	15.16 (15.89)
2.	$Cu(CMPDE)_2Cl_2$ (Deep Brown)	212	11.62 (12.02)	54.00 (54.48)	4.00 (4.16)	15.25 (15.89)
3.	$Cu(COPDE)_2SO_4$ (Greyish)	236	6.28 (6.68)	13.78 (14.19)	4.45 (4.91)	18.34 (18.76)
4.	$Cu(CMPDE)_2SO_4$ (Greenish)	240	6.34 (6.68)	13.58 (14.19)	4.40 (4.91)	18.50 (18.76)
5.	$Cu_2(COPDE)_4(NO_3)_2$ (Brown)	218	11.89 (12.23)	55.23 (55.43)	3.74 (4.23)	16.00 (16.18)
6.	$Cu_2(CMPDE)_4(NO_3)_2$ (Brown)	217	12.00 (12.23)	55.01 (55.43)	3.84 (4.23)	15.81 (16.18)
7.	$Cu(COPDE)_2(CH_3COO)_2$ (Green)	305	71.30 (71.55)	4.28 (4.68)	4.08 (4.68)	14.48 (14.59)
8.	$Cu(CMPDE)_2(CH_3COO)_2$ (Dark Green)	306	71.15 (71.55)	4.19 (4.68)	3.95 (4.68)	14.28 (14.59)

A perusal of the infrared spectra of the Schiff base ligands show bands at 3300 cm^{-1} and 3100 cm^{-1} characteristic of asymmetric and symmetric stretching vibrations of νNH_2 group[5]. However a strong band at 1540 and 1630 cm^{-1} indicates the presence of ν(pyridine)[6] and ν(C=N) groups[7] respectively. In the spectra of all the complexes no shifting was observed in νNH_2 band frequency; ruling out the possibility of coordination through nitrogen. However downward shift of about 40 and 30 cm^{-1} in ν(C=N) and ν(pyridine) frequency which was observed at 1600 and 1500 cm^{-1} indicating coordination through ν(C=N) and of nitrogen of pyridine ring. It was further confirmed by the appearance of ν(M–N) band at 510–540 cm^{-1}, $[Cu_2L_4(NO_3)_2]$ complexes show additional bands at 1490, 1385 and 810 cm^{-1}. The difference of 105 cm^{-1} between 1490 and 1385 cm^{-1} bands, the two components of ν_3 band of nitrate ion suggests unidentate coordination of nitrates in these complexes[7]. $[CuL_2(CH_3COO)_2]$ complexes also exhibit additional bands at 1510, 1445, 1340 and 710 cm^{-1} which can be assigned to $\nu_{as}(COO)$, $\nu_s(COO)$, $\delta(CH_3)$ and $\delta(OCO)$ vibrations respectively indicating the presence of acetate ion in the coordination sphere[8].

Magnetic moment values for 1 and 2 complexes were found to be 2.11 B.M. and 2.13 B.M. respectively at room temperature after applying diamagnetic corrections. This is due to large orbital contribution to magnetic moment values, which is an evidence for tetrahedral Cu(II) complexes[9, 10]. The large value obtained for the present Cu(II) complexes suggest tetrahedral orientation of the ligand around Cu(II). The electronic spectra of these complexes exhibit bands at 7,200–7,300 ($\varepsilon = 88$) and 10,500–10,550 ($\varepsilon = 95$) cm^{-1} respectively. Although tetrahedral Cu(II) complexes generally exhibit one or three bands. The presence of two bands at low energy indicate a pseudo-tetrahedral geometry around the Cu(II) centre[11]. The distortion of geometry is not surprising in view of the bulkiness of the ligand. Complexes 3 and 4 were found to be diamagnetic. The diamagnetic behaviour of these complexes indicate strong metal-metal interaction giving rise to square planar structure[12, 13]. The electronic spectra of these complexes show an intense band *ca.* 23000 cm^{-1} ($\varepsilon = 35$) is assigned to charge transfer from ligand to metal. The other two bands at *ca.* 17250 cm^{-1} ($\varepsilon = 40$) and *ca.* 15510 cm^{-1} ($\varepsilon = 30$) may be due to d–d transfers. These bands suggest a square planar geometry[14]. The magnetic moment values of 5 and 6 complexes have been observed in the range 1.12–1.14 B.M. The subnormal magnetic moment value of the present Cu(II) complexes indicate metal-metal interaction in a polymeric structure. The UV spectra of these complexes were in the range 15950–16000 cm^{-1} ($\varepsilon = 13.4$) (broad) is indicative of its distorted octahedral structure. The magnetic moment values of 7 and 8 complexes were obtained in the range 1.82 B.M. corresponding to one unpaired electron. These value correspond to the distorted octahedral structure[15]. The spectra of these complexes were observed at 15800–16000 ($\varepsilon = 15$) cm^{-1} is also indicative of distorted octahedral or tetragonal structure. As it is known that tetragonal Cu(II) complexes involve three transitions *viz.*, $^2B_{1g} \rightarrow {}^2B_{2g}$, $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2A_{1g}$ but bands due to these transitions usually overlap to give one broad absorption band[16].

ESR spectra of complexes were recorded in D.M.F. ESR spectra of $[CuL_2]SO_4$ and $[CuL_2]Cl_2$ complexes show no $M_s = \pm 2$ transition at half field; indicating the absence of intramolecular and intermolecular antiferromagnetic interactions. The magnitude of $g_{11} = 2.07$ and $g_1 = 2.01$ is indicative of square planar environment[17] around metal ion in $[CuL_2]SO_4$ complexes.

However, DMF solution of $[CuL_2]Cl_2$ complexes do not show any hyperfine splitting. There are examples of pseudotetrahedral complexes of Cu(II) which did not show any hyperfine ESR spectra in solution[18–20]. This absence of hyperfine splitting is attributed to dipolar line broadnening and to the much reduced nuclear hyperfine coupling constant for pseudotetrahedral Cu(II) complexes A_{10} values for $[CuL_2]Cl_2$ complexes are of the order ~ 87×10^{-4} cm^{-1} indicative of pseudo-tetrahedral structure[21]. Band corresponding to $M_s = \pm 2$ transition at half field was not observed in ESR spectra of $[Cu_2L_4(NO_3)_2]$ and $CuL_2(CH_3OO)_2]$ complexes indicating the absence of intramolecular and intermolecular antiferromagnetic interaction.

The magnetic parameters (Table 2) deduced from the spectra show the trend $g_{11} > g_1 > g_e$ (2.0023 free electron spin) indicating the presence of unpaired electron in $d_{x^2-y^2}$ orbital[22] of Cu(II). The considerable deviations of g_{11} and g_1 values of complexes from the free ion values and closeness of those values to those reported for distorted octahedral complexes suggest distorted octahedral geometry[24-24] for the complexes. The σ-bonding parameters α^2 comes out be 0.58 and 0.60 for $Cu_2L_4(NO_3)_2$ and $CuL_2(CH_3COO)_2$ respectively suggesting a predominantly covalent nature of metal ligand bond.

TABLE 2

MAGNETIC PARAMETERS OF Cu(II) COMPLEXES.

	$Cu_2L_4(NO_3)_2$	$CuL_2(CH_3COO)_2$
g_{11}	2.149	2.181
g_1	2.0248	2.0399
g_{av}	2.0763	2.0843
A_{11}(G)	162.8	162.8
A_1(G)	14.3	13.8
A_{av}(G)	65.3	66.3
	0.58	0.60

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