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Synthesis and studies on metal coordination with a novel carboxyamide ligand

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Abstract

Novel complexes of Co(II), Ni(II), Cu(II) and Pd(II) with the new ligand [*N*,*N*′-bis(2-carboxy-1-oxo-phenelenyl)ethylenediamine] (H_2L) have been synthesized and characterized on the basis of elemental analyses, magnetic susceptibility, thermal, infrared, electronic, ^1H NMR and EPR spectral studies. Infrared and ^1H NMR spectra show that H_2L acts as a binegative tetradentate ligand. Coordination occurs through deprotonated carboxylate oxygens and nondeprotonated amido nitrogens in all the complexes. Electronic spectral studies and magnetic moment values suggest N_2O_2 coordination around each metal centre with strong field square planar chromophores. The probable structures of the complexes have been assigned on the basis of spectral studies. The complex formation between M(II) [M(II) = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] and (L^{2-}) has also been studied potentiometrically in 75% aqueous DMF at 25 °C in 0.1 M $NaClO_4$. The stability constants were found to follow the order: Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carboxyamides; Stability constants; EPR; Solid complexes

1. Introduction

Metal ion interaction with ligands containing amide group plays a vital role in a vast number of widely differing biological processes [1,2]. Ligands containing 3-carboxyamide chain and their metal chelates have been stated to have noteworthy pharmacological activities [1–4]. Literature survey clearly shows that research interest is centered on the stability and structure of metal ion complexes of amides and related ligands; of special interest are the deprotonation processes and the species thereby formed [5–8]. In view of the biological significance and diverse coordinating behaviour of amide group, it was considered worthwhile to prepare and study some of these complexes. In the present manuscript, we report the preparation and study of Co(II), Ni(II), Cu(II) and Pd(II) complexes of the new ligand *N*,*N*′-bis(2-carboxy-1-oxo-phenelenyl)ethylenediamine (H_2L).

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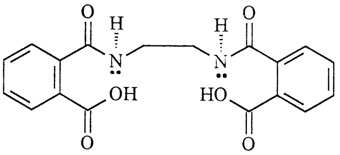

Fig. 1. *N*,*N*′-bis(2-Carboxy-1-oxo-phenelenyl)ethylenediamine (H_2L).

2. Experimental

The details of experimental techniques have been described elsewhere [6–8].

2.1. Synthesis of ligand

The ligand H_2L (Fig. 1) was prepared by direct mixing of warm anhydrous THF solutions of ethylinediamine and phthalic anhydride in 1:2 molar ratio. The ligand was purified by dissolving it in sodium carbonate solution and regenerating it by acidification followed by repeated washings with hot water and finally with Et_2O.

2.2. Synthesis of complexes

The ligand (0.02 mol) was suspended in 50 cm^3 of water and a calculated volume of standard Na_2CO_3 solution (0.02 mol) was added to it and the mixture was stirred constantly. A clear solution of ligand thus obtained, was mixed with a solution of metal salts (0.02 mol) in water (40 cm^3). A coloured metal complex immediately precipitated. The complex was filtered by suction, washed with warm dilute Na_2CO_3 solution followed by warm water and dried in vacuo over P_4O_{10} (yield ~ 60–80%).

3. Results and discussion

All the complexes were found to be high melting (m.p. not less than 528 K) and microcrystalline or powders, stable in atmospheric conditions, insoluble in most of the organic solvents and water. They are slightly soluble in DMF and DMSO. Colours, yields, decomposition temperature range, activation energy and analytical data of complexes are given in Table 1.

3.1. Vibrational spectra

A comparison of the IR spectra of the ligand H_2L and its complexes revealed that the ligand is coordinated through the deprotonated carboxylic oxygen and nitrogen of the amide group (Table 2). The IR band due to ν_{NH} mode observed in the ligand at 3300 cm^{-1} shifts to a lower frequency by 50–70 cm^{-1} in complexes indicating that the nitrogen of the amide group is coordinating [9,10]. The strong $\nu_{C=O}$ band of the amide group is observed in the ligand at 1625 cm^{-1} has not shown observable shift. The free ligand exhibits $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ at ca. 1540 and ca. 1430 cm^{-1}, respectively. The corresponding frequencies in the complexes occur at ca. 1560 and 1380 cm^{-1} indicating an enhancement in $\Delta\nu$ value upon complexation, whereas $\Delta\nu$ is the difference between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$. This fact suggests that the carboxylate moiety of the present ligand system coordinates to the metal centre in monodentate fashion [11]. The stabilization of such seven membered chelate rings, though unusual, is not unknown [12].

Table 1
Physical and analytical data for ligand and complexes

Complex	Colour	Decomposition range (K)	Activation energy (E_a) (kJ mol^{-1})	Elemental analysis: found (Calc.)			
				C	H	N	M
LH_2	Shiny white	503–523	–	60.86 (60.89)	4.43 (4.46)	7.80 (7.82)	–
CoL	Pale brown	578–833	33.68	52.51 (52.53)	3.29 (3.37)	6.58 (6.74)	14.17 (14.21)
NiL	Pale green	558–813	28.52	52.36 (52.56)	3.18 (3.37)	6.72 (6.75)	14.12 (14.15)
$[CuL]_2 \cdot 2H_2O$	Pale blue	528–596	23.25	49.80 (49.82)	4.08 (4.11)	6.28 (6.39)	14.33 (14.52)
PdL	Pale yellow	588–813	42.60	47.12 (47.14)	2.89 (3.02)	6.02 (6.05)	22.92 (23.01)

Table 2
Diagnostic IR bands (cm^{-1}) of the ligand and complexes

Tentative assignment	LH_2	CoL	NiL	$[CuL]_2 \cdot 2H_2O$	PdL
ν_{N-H} amide	3300	3250 m	3240 m	3230 m	3230 m
$\nu_{C=O}$[a]	1625 s	1625 s	1620 s	1620 s	1620 s
$\nu_{(COO-)\ asym}$	1540 s	1570 s	1560 s	1550 s	1565 s
$\nu_{(COO-)\ symm}$	1430 s	1390 s	1380 s	1360 s	1380 s
$\nu_{C-N}+\delta_{N-H}$[b]	1470 m	1460 m	1450 m	1440 m	1460 m
ν_{M-N}	–	520 w	510 m	520 m	540 w
ν_{M-O}	–	380	400	390	400

s, strong; m, medium; w, weak.

[a] Amide-I.

[b] Amide-II.

3.2. Electronic spectra and magnetic moments

The electronic spectra of Co(II) complex possess band around 10400, 22840 and 27150 cm^{-1} suggesting low spin four coordinate complex [13] and μ_{eff} value is 2.40 B.M. (Table 3). Square planar Co(II) chelates have magnetic moments in the region 2.2 and 2.7 B.M. at room temperature [14] and exhibit absorption maxima at different energies [13]. However, it should be noted that very few four coordinate low spin planar Co(II) complexes have been reported.

Ni(II) complex is found to be diamagnetic and has shown only two electronic spectral bands around 22280 and 28260 cm^{-1}. Square planar Ni(II) complexes are expected to show three d–d bands, i.e. $^1B_{1g} \leftarrow {}^1A_{1g}$, $^1A_{2g} \leftarrow {}^1A_{1g}$ and $^1E_g \leftarrow {}^1A_{1g}$. But only one or two bands are usually observed [15]. In the present case higher energy band is assigned for charge transfer and the single d–d band is assigned to $^1B_{1g} \leftarrow {}^1A_{1g}$. This reveals that Ni(II) is present in square planar environment.

The electronic spectrum of Cu(II) complex shows two bands at 19320 and 27800 cm^{-1}. The lower energy band is assigned to $^2E_g \leftarrow {}^2B_{1g}$ transition assuming square planar geometry around central atom. A strong band observed at 27800 cm^{-1} is assigned to M←L charge transfer transitions from 'O' atom of ligand to Cu(II) in binuclear copper complexes [16,17]. The magnetic moment value of Cu(II) complex in the present case is around 1.50 B.M., which also suggests a binuclear structure. Variable temperature magnetic moment studies over temperature range 300–100 K shows variation from 1.50 to 0.61 B.M. A graph was plotted between χ_M^{corr} versus T(K). Diamagnetic corrections were determined by Pascals method and subtracted from the measured values of the total susceptibility. The best fit for the complex was obtained for a $2J$ value equal to -278 cm^{-1} which indicates a relatively strong magnetic interaction between the two copper ions. This assumption was further supported by EPR spectral data and thermal behaviour of the complex. From the diamagnetic behaviour of Pd(II) complex and from the electronic spectral data, a square-planar geometry has been proposed for the Pd(II) [18] as suggested for Ni(II).

3.3. Thermal analysis

The thermal decomposition of complexes was studied using mainly thermogravimetry (TG) and differential thermal analysis (DTA).

A clear TG plateau is reached for all the complexes, except Cu(II) complex, up to 558–533 K with simple degradation mechanisms as revealed by appearance of single DTA peak. Mass loss calculations shows that the final residues were metal oxides. Exothermic peaks in DTA suggests that conformational changes occurred in the amide chelate rings [19,20]. The TG curve for $(CuL)_2 \cdot 2H_2O$ shows a first mass loss between 348 and 373 K, which corresponds very well to the release of whole water content; the relatively low temperature for the water loss shows that this is

Table 3
Magnetic moments and electronic spectral data of complexes

Complex	μ_{eff}	Electronic spectral bands (cm^{-1}), λ_{max}	Tentative assignments	Comments
CoL	2.40	10 400,		Characteristic of low spin Co(II)
		22 840,		
		27 150		
NiL	Diamagnetic	22 280,	$^1B_{1g} \leftarrow {}^1A_{1g}$,	10 $D_q = 22280$,
		28 260	$M \leftarrow L$ (C.T.)	Square-planar Ni(II)
$[CuL]_2 \cdot 2H_2O$	1.50	19 320,	$^2E_g \leftarrow {}^2B_{1g}$	Square-planar Cu(II) dimeric nature
		27 800	,$M \leftarrow L$ (C.T.)	
PdL	Diamagnetic	22 355,	$^1B_{1g} \leftarrow {}^1A_{1g}$,	Square-planar Pd(II)
		26 786,	$^1E_g \leftarrow {}^1A_{1g}$,	
		35 710	$M \leftarrow L$ (C.T.)	

C.T., charge transfer.

lattice held. Relatively low thermal stability of Cu(II) complex may be due to its dimeric nature.

From TG curves, the order (n) and activation energy (E_a) for thermal reactions, of the complexes have been elucidiated by the linearlisation method of Coats and Redfern [21]. Lower activation energies (E_a's) of the thermal reaction of the complexes (23.25–42.60 kJ mol^{-1}) reveals that the ligand crystal field strength is a border line case and may be slightly higher than that is required for producing low spin complexes. The lowest value of E_a for the Cu(II) complex indicates that it may be dimeric, which is also supported by jerks present in DTA and by other spectral evidences.

3.4. ^{1}H NHR spectra

^{1}H NMR spectrum could be recorded only for Pd(II) complex because it is sufficiently soluble in DMSO-d_6. The NMR spectrum of H_2L shows (value in δ scale) a resonance signal due to NH proton at 6.50 ppm which is not observed in its Pd(II) at 6.50 ppm in the range studied (0–20 ppm) implying a large down field shift in this proton and suggesting that the amide group nitrogen participates in coordination. Deprotonation of amide proton has been ruled out on the basis of IR spectra of the complex which has clearly shown ν_{NH} stretching band around 3230 cm^{-1}. In addition to it, a signal at 9.90 ppm (2H) in the ligand spectrum assignable to carboxylic protons disappears in the spectrum of the complex indicating deprotonation of carboxylic group and the involvement of oxygen of carboxylate ion in chelation.

3.5. EPR spectra

The EPR spectrum of Cu(II) complex was recorded in the solid state at room temperature (RT) and liquid nitrogen temperature (LNT). The spectrum consists of a moderately strong absorption at 480 G, an absorption of moderate intensity at 3050 G, strong absorption at 4675 G and weak absorption at 6100 G. The intensities of the other three absorptions decreased at LNT leaving the absorption at 3050 G virtually unchanged. The absorption at 3050 G with g_{av} value of 2.22 ($g_{||}$, 2.40; $g_{\perp}$, 2.13) has, therefore, been assigned to a small percentage of monomeric impurity [22]. It is clear that in such systems, intermolecular interactions are responsible for the exchange broadening apparent in the spectra which provides little definitive structural information. It is noticeable that the line widths of the triplet (binuclear) absorptions differ (Fig. 2). The line width of the high and low field absorptions is approximately three times that of the absorption at 4675 G. All these features of the present complex are similar to those observed in the case of Cu(II) complexes of unsaturated carboxylic acids [23], dicarboxylic acids and acid amides [24] for which a dimeric structure was proposed. Based on this, the present

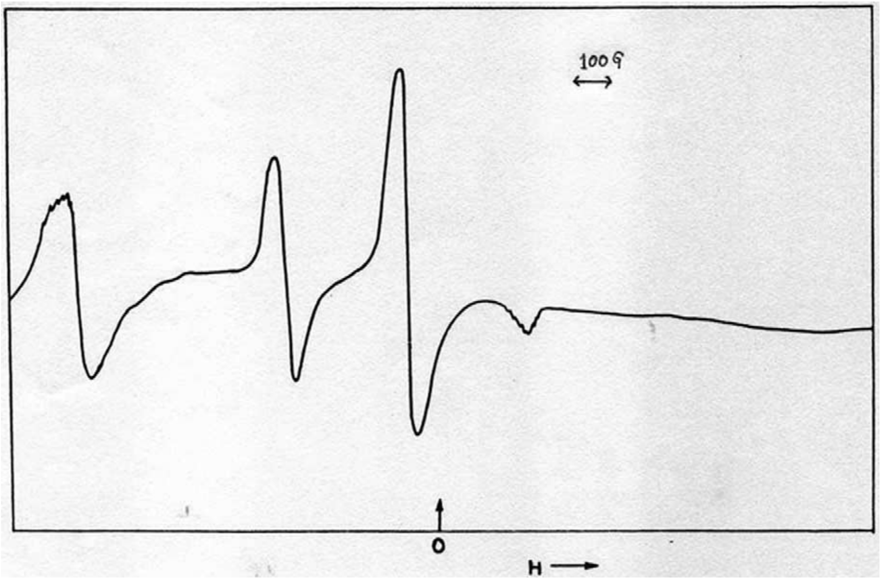

Fig. 2. X-band EPR spectrra of $[CuL]_2{\cdot}2H_2O$ at LNT.

complex is assigned a dimeric structure with a small monomeric impurity.

In the light of above facts and arguments, tentative structures assigned to the complexes are shown in Fig. 3.

3.6. Potentiometric study of the M(II)–H_2L system-stability constants determination

The acid base equilibria were determined by potentiometric titration of 0.1 M of H_2L at 25 ± 0.5 °C and $I = 0.1$ M $NaClO_4$. The pH values, were plotted against the volume of TMAH for the titrations. The protonation constants and the stability constants of its complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) are reported in Table 4. The extraordinarily good σ_{fit} provides assurance that the experimental refinement is as complete as can be expected. The values for the logarithms of the stepwise protonation constants of the carboxylate groups of L^{2-} are within the range observed for β-(electronegative group) substituted carboxylic acids [25]. The very weak acidity of the amides makes difficult to determine the deprotonation constants involving N–H amide groups by potentiometry. Because it requires a very basic medium, a few values appear in literature [3]. The complex forming ability of H_2L with regard to Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) has been investigated in the pH range 3.0–10.5. Potentiometric studies at greater pH values could not be carried out because of the precipitation of complexes. The values of the stability constants for ML complexes are of the magnitude as those for 1:1 and 1:2 (M: carboxyamide ligand) complexes

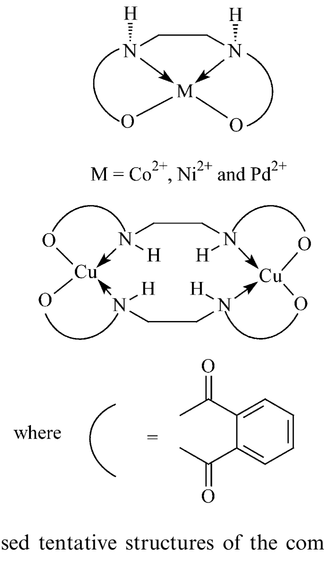

Fig. 3. Proposed tentative structures of the complexes.

Table 4
Stability constants of bivalent metal complexes of (H_2L) in 75% aqueous DMF at 25 °C in 0.1 M $NaClO_4$

Constant	(H_2L)	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
Log K_1^H	7.75	–	–	–	–	–
Log K_2^H	5.23	–	–	–	–	–
Log K_1	–	3.60	4.00	4.90	6.65	5.57
Log K_2	–	3.20	3.30	4.05	4.15	3.90
Log β_2	12.99	6.80	7.30	8.95	10.80	9.47
σ_{fit}	0.0000	0.03545	0.05842	0.04048	0.06203	0.06761

in which the carboxylate acts as a monodentate ligand [25].

Therefore, L most probably coordinates to M(II) through its carboxylate groups to yield mononuclear ML and ML_2 species. The stability constant of the Cu(II) complex ($\log\beta = 10.80$) is somewhat greater than that of the corresponding Mn(II) complexes, as expected according to higher stability of Cu(II) complexes. The values of the stability constant follows the order Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II) which fairly correlates with the Irving–Williams series [26]. These values are higher than the literature values and reveal the chelating character of ligand (L^{2-}).

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