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Synthesis and Characterization of Zinc(II) and Cadmium(II) Complexes of N,N′-ethylene-bis(3-carboxypropenamide)

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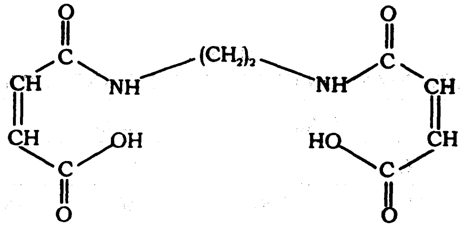
Complexes of Zn(II) and Cd(II) with a tetradentate ligand N,N′-etyhlene-bis(3-carboxypropenamide) ($EBCPH_2$) have been synthesized and characterized by elemental analysis, conductance, thermal, magnetic, infrared and X-ray powder diffraction studies. The complexes have been assigned the formula $[M(EBCP)(H_2O)_2]$ where M = Zn or Cd. These complexes have octahedral geometry.

Key Words: Synthesis, Zn(II) and Cd(II) complexes, N,N′-ethylene-bis(3-carboxypropenamide).

INTRODUCTION

Studies of metal complexes of amide group containing ligands have been reported[1, 2]. The present communication reports the preparation and characterization of the complexes of zinc(II) and cadmium(II) with N,N′-ethylenebis(3-carboxypropenamide) [$EBCPH_2$] (I).



(I)

Fig. 1. N,N′-Ethylene-bis(3-carboxypropenamide)

EXPERIMENTAL

All the chemicals used were of AR grade. The solvents were distilled before use.

Preparation of N,N′-ethylene-bis(3-carboxypropenamide) ($EBCPH_2$)

Maleic anhydride (9.8 g) was dissolved in glacial acetic acid (50 mL). To this, 3.05 g of ethylenediamine was added dropwise with constant stirring while cooling in ice. The white solid separated was filtered, washed thoroughly with acetone and dried in air. It was purified by dissolving in sodium carbonate solution (5%) and reprecipitated by the addition of dilute hydrochloric acid in cold. Melting point 197°C, yield (92%).

Preparation of complexes

The Zn(II) and Cd(II) complexes with this ligand were prepared by the following general procedure. The respective metal nitrate (0.001 mol) was dissolved in methanol. To this, a suspension of $EBCPH_2$ (0.001 mol) was added slowly and refluxed for 2–3 h. The solid complexes formed were filtered, washed with water and acetone and finally dried *in vacuo*.

Both the complexes were analyzed for the metal, carbon, hydrogen and nitrogen contents. The molar conductivities of the complexes in acetonitrile, methanol, DMF and nitrobenzene solutions were measured at room temperature ($28 \pm 2°C$). The molar masses of the complexes were determined by Rast method[3]. The infrared spectra of the ligand and the complexes were recorded in the range 4000–400 cm^{-1} by using KBr disc technique. The X-ray powder patterns were recorded using Philips diffractometer (model PW 1710) for the Zn(II) and Cd(II) complexes. The TG and DTG curves of the complexes were recorded on a thermal analyzer in air in the temperature range 25–850°C. Independent pyrolysis experiments in air were also carried out for both of the complexes studied and loss of mass determined in each case was compared with that obtained from TG.

RESULTS AND DISCUSSION

Both the complexes are non-hygroscopic crystalline solids. They are insoluble in benzene, petroleum ether and chloroform, but are sparingly soluble in acetonitrile, methanol and nitrobenzene. The analytical data are given in Tables 1 and 2. The analytical results indicate a 1 : 1 (M : L) stoichiometry for the complexes.

TABLE-1
CHARACTERIZATION OF THE LIGAND AND COMPLEXES

Complex	% Analysis: Found (Calculated)				Molar mass
	C	H	N	M	
$[Zn(EBCP)(H_2O)_2]$	33.12 (33.76)	3.84 (3.93)	7.56 (7.88)	18.12 (18.39)	342.1 (355.37)
$[Cd(EBCP)(H_2O)_2]$	28.98 (29.85)	3.32 (3.48)	6.90 (6.96)	27.56 (27.86)	390.8 (402.4)

TABLE-2
MOLAR CONDUCTANCE DATA FOR THE COMPLEXES IN DIFFERENT SOLVENTS

Complex	Molar conductance, ohm^{-1} cm^2 mol^{-1}			
	In acetonitrile	In nitrobenzene	In DMF	In methanol
$[Zn(EBCP)(H_2O)_2]$	4.2	1.1	3.1	7.4
$[Cd(EBCP)(H_2O)_2]$	4.8	1.4	3.2	10.2

The molar conductivity values of the complexes in acetonitrile, nitrobenzene, DMF and methanol were in the range corresponding to those of non-electrolytes.

The infrared spectrum of the ligand exhibits a stretching frequency of amide[4] >NH at 3300 cm^{-1}, a medium band at 3100 cm^{-1} which is assigned ν(OH) of COOH[5] which is hydrogen bonded with carbonyl group of amide, another band at 1700 cm^{-1} due to ν(CO) of COOH group, amide-I [ν(C=O)] at 1624 cm^{-1} and amide-II [ν(C—N) + δ(NH)] at 1482 cm^{-1}. The mass spectrum of the ligand exhibits the molecular ion peak at 256 and a base peak at M/Z = 114, which is due to $[C_4H_4O_3N]^+$. The proton NMR spectrum of $EBCPH_2$ recorded in d_6-DMSO shows signals at 4.3–4.7 (4H, CH_2), 8.4 (2H, NH), 5.8–6.1 (doublet of doublet, 4H, CH=CH) and a sharp singlet at 9.1 (2H, —COOH) ppm.

The infrared spectrum of the complexes shows characteristic absorption of all the fundamental groups of the ligand but at a shifted position in the case of coordinated groups. The amide >NH stretching frequency[4, 6] observed at 3300 cm^{-1} in the infrared spectrum of the ligand is shifted to 3260–3250 cm^{-1} in the spectra of the complexes indicating the involvement of amide nitrogen in coordination. The amide carbonyl frequency observed at 1624 cm^{-1} remains unaltered indicating its non-participation in coordinate bond formation with the metal ion. The disappearance of the band at 3100 cm^{-1} due to ν(O—H) of the carboxylic acid indicates the deprotonation of carboxyl group and coordination through the oxygen atom. This is further supported by the disappearance of the strong band[8] at 1700 cm^{-1} which is due to the stretching frequency of C=O of carboxylic acid and the appearance of two new bands at 1565–1540 cm^{-1} and 1385–1365 cm^{-1}. These two new bands may be assigned to the asymmetric and symmetric stretching frequencies of coordinated carboxylate group. The spectra of the complexes exhibit an absorption band at 3500 cm^{-1} which was assigned to ν(OH) of coordinated water molecule. Moreover, the presence of absorption bands at 836 and 640 cm^{-1} supports the presence of coordinated water molecule[9]. These bands were assigned to rocking $\rho_r(H_2O)$ and wagging $\rho_w(H_2O)$ of coordinated water molecule. In addition to these, two new bands are observed at 520 and 465 cm^{-1} which may be due to ν(M—N) and ν(M—O) respectively.

The X-ray powder patterns were recorded for zinc(II) and cadmium(II) complexes. The diffraction patterns were indexed by using the method developed by Hesse[10] and Lipson[11, 12]. Both the complexes are found to be orthorhombic. The cell parameters have been calculated by using the equation

$$\sin^2\theta\,(hkl) = Ah^2 + Bk^2 + Cl^2$$

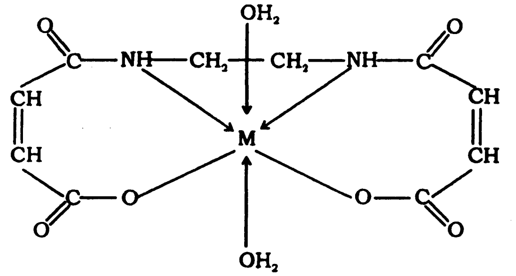
where $$A = \frac{\lambda^2}{4a^2};\quad B = \frac{\lambda^2}{4b^2}\quad \text{and}\quad C = \frac{\lambda^2}{4c^2}$$

The lattice constants for zinc(II) complexes are A = 0.0042, B = 0.0094 and C = 0.0796. Hence, a = 17.9812 Å, b = 15.2084 Å and c = 10.6986 Å. The cell volume of the complex is given as $V = abc = 2.925 \times 10^{-21}$ cm^3 and its density is 0.8183 g/cm^3 and molar mass is 355.37. This gives n as equal to $\frac{dN_0V}{M} = 4.05 \approx 4$. Therefore, the number of molecules per unit cell is 4. For cadmium(II) complexes the unit cell dimensions are A = 0.004938, B = 0.0113 and C = 0.0945. Hence, a = 21.002 Å, b = 18.318 Å and c = 12.7012 Å. Thus, for cadmium(II) complex the cell volume is V = abc = 4.886 × 10^{-21} cm^3. Its density is 0.5701 g/cm^3 and the molar mass is 402.4. This gave n as equal to 4.16 ≈ 4. Thus, the number of molecules per unit cell is 4. The densities of the complexes were determined with specific gravity bottle using petroleum ether as the displacing liquid.

The thermal studies were conducted on the complexes. For both these complexes, the TG curve shows three stage decomposition. The first stage of decomposition of the zinc(II) complex at a temperatrue of 451 K with a mass loss of 10.28% (calculated 10.13%) indicates the presence of two water molecules. The TG analysis confirms the presence of water molecules. According to Nikolaev *et al.*[13] and Singh *et al.*[14] water eliminated above 150°C can be because of coordinated water. The second stage of decomposition causes a mass loss of 47%. This is due to the loss of two —CO—CH=CH—CO fragments of the ligand which corresponds to a theoretical loss of mass equal to 46.1%. The third stage of decomposition is accompanied by a mass loss of 16.5% which is due to the loss of the —NH—CH_2—CH_2—NH part of the ligand which would theoretically produce a mass loss of 16.32%. The decomposition attains stability around 960 K. The residual mass of 23.2% corresponds to zinc oxide. This is in conformity with the data of independent pyrolysis (23.41%) and the theoretical value (22.89%).

The thermal decomposition of cadmium(II) complex also occurs in three stages. The first stage of decomposition takes place in the range 430–460 K with a mass loss of 9.1% (calculated 8.95%) corresponds to two molecules of coordinated water[13, 14]. The second stage of decomposition causes a mass loss of 39.89% which is due to the loss of two —CO—CH=CH—CO— fragments of the ligand which would theoretically produce a mass loss of 40.75%. This is in agreement with the observed value. In the third stage, there is a mass loss of 14.8% which can be because of the loss of the —NH—CH_2—CH_2—NH— fragment of the ligand. This would theoretically produce a mass loss of 14.42% which is very close to the experimental value. The decomposition attains stability at about 980 K leaving behind a residue of 32.8% which is due to the oxide of the metal. This is in agreement with the mass of the residue obtained in independent pyrolysis (32.4%) and the theoretical value (31.9%).

Based on the above results, it is concluded that the ligand $EBCPH_2$ is tetradentate, the coordination sites being two oxygen and two nitrogen atoms. Both the complexes contain two molecules of coordinated water also. The structure of the complex may be represented as:



M= Zn or Cd

Thus, the complexes [$Zn(EBCP)(H_2O)_2$] and [$Cd(EBCP)(H_2O)_2$] have octahedral geometries.

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