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Synthesis and Characterization of Manganese(II), Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Cadmium(II) Complexes of a Polydentate Ligand

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A few complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with a polydentate ligand, N,N'-diethyleneamine-bis(3-carboxy propenamide) ($DBCPH_2$) have been synthesized and characterized by elemental analysis, conductance, thermal, magnetic, IR, electronic spectra and X-ray diffraction methods.

Key-words: Synthesis, Metal complexes, Polydentate ligand.

INTRODUCTION

As a part of our studies on coordination characteristics of amide group containing ligands, we have synthesized a polydentate ligand using maleic anhydride and diethylenetriamine. Further, Co(II), Ni(II), Cu(II) Mn(II), Zn(II) and Cd(II) complexes with this ligand were prepared and characterized by various physicochemical methods. From the literature it is found that the coordination of the amide type ligand derived from maleic anhydride and diethylenetriamine towards transition metal ions has not been studied so far.

EXPERIMENTAL

All the chemicals used were of AR grade.

Preparation of N,N'-diethyleneamine-bis(3-carboxy propenamide) ($DBCPH_2$): Maleic anhydride (9.8 g, 0.1 mmol) was dissolved in glacial acetic acid and to this, diethylenetriamine (5.4 mL, 0.05 mmol) was added dropwise with constant stirring while cooling in ice. The white solid separated was filtered, washed thoroughly with acetone and dried. It was purified by dissolving in sodium carbonate solution (5%) and reprecipitated by the addition of dilute hydrochloric acid in cold. m.p. 193°C and yield 85%.

Preparation of the complexes: The complexes with the ligand were prepared by the following general procédure. The respective metal acetate or chloride (0.1 mmol) was dissolved in methanol. To this a suspension of $DBCPH_2$ (0.1 mmol) was added slowly and refluxed for 2-3 h. The solid complexes formed were filtered, washed with water and acetone and dried *in vacuo*.

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The TG and DTG curves of the complexes were recorded on a thermal analyzer in air at temperature range 25–800° C. Independent pyrolysis experiment in air was also carried out for each of the complexes studied and loss of mass determined in each case was compared with that obtained from TG.

The metal content of the complexes was obtained by analytical methods[1]. The molar conductivities of the complexes in acetonitrile, methanol and introbenzene were measured at room temperature. The IR spectra of the ligand and complexes were recorded in the range 4000–400 cm^{-1}. Molecular masses of the complexes were determined by Rast method using biphenyl as the solvent[2]. The elemental analysis was carried out by microanalytical method. Magnetic susceptibility at room temperature was measured by Gouy method[3,4].

RESULTS AND DISCUSSIONS

All 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 the Tables 1 and 2.

Molar conductivity values of the complexes in methanol, acetonitrile and nitrobenzene were in the range corresponding to those of non-electryolytes.

TABLE-1
CHARACTERIZATION OF THE LIGAND AND COMPLEXES

S. No.	Compound	% Analysis: Found (Calcd.)				
		C	H	N	M	μ_{eff} (B.M.)
1.	$DBCPH_2$	46.12 (48.16)	5.46 (5.68)	12.82 (14.04)		
2.	[Ni(DBCP)]	38.64 (40.48)	4.11 (4.21)	10.96 (11.81)	15.48 (16.50)	3.01 (2.83)
3.	[Co(DBCP)]	39.12 (40.44)	4.02 (4.21)	11.02 (11.79)	16.12 (16.57)	4.82 (3.9)
4.	[Mn(DBCP)]	38.86 (40.9)	3.98 (4.26)	11.12 (11.43)	14.95 (15.62)	5.79 (5.9)
5.	$[Cu_2(DBCP)(OH)_2(H_2O)_2]$	28.64 (29.1)	4.02 (4.25)	7.98 (8.50)	25.12 (25.70)	1.89 (1.73)
6.	[Zn(DBCP)]	38.76 (39.73)	4.08 (4.13)	11.02 (11.58)	17.82 (18.03)	Dia.
7.	[Cd(DBCP)]	35.02 (35.17)	3.32 (3.66)	9.86 (10.25)	27.09 (27.45)	Dia.

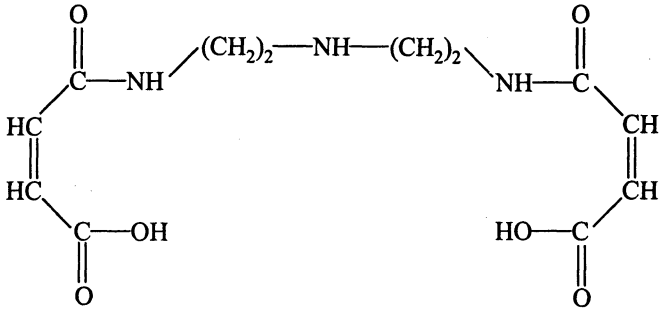
TABLE-2
MOLAR CONDUCTANCE IN $ohm^{-1}\ cm^2\ mol^{-1}$

S. No.	Complex	Methanol	Nitrobenzene	Acetonitrile
1.	[Ni(DBCP)]	41.2	14.1	48.1
2.	[Co(DBCP)]	38.3	12.2	47.2
3.	[Mn(DBCP)]	26.1	11.0	36.0
4.	$[Cu_2(DBCP)(OH)_2(H_2O)_2]$	28.4	16.1	32.2
5.	[Zn(DBCP)]	32.0	12.5	32.1
6.	[Cd(DBCP)]	29.2	13.0	34.0

The IR spectrum of the ligand exhibits a stretching frequency of amide[5] —NH at 3300 cm^{-1}, a band at 3100 cm^{-1} which is assigned ν(OH) of COOH which is hydrogen bonded with carbonyl group of amide[6], another band at 1700 cm^{-1} due to νCO of COOH group, amide-1 [ν(C=O)] at 1626 cm^{-1} and amide-II [$\nu(CN^+)\delta(NH)$] at 1500 cm^{-1} and another band at 3320 cm^{-1} due to ν(NH) of secondary amino group[5].

The proton NMR spectrum of $DBCPH_2$ recorded in DMSO shows signals at 4.5 (8H, CH_2), 8.4 (2H, amide NH), 5-8-6.1 (doublet 4H, CH=CH), 5.1 (singlet 1H, *sec.* amino group) and a sharp singlet at 9.1 (2H, COOH) ppm[5].

The mass spectrum of the ligand exhibits molecular ion peak at 299 and a base peak at m/z = 183 due to $[C_8N_3O_2H_{13}]^+$ ion. From these data the following structure has been assigned to the ligand.



Structure of N,N′-diethyleneamine-bis(3-carboxypropenamide)-$DBCPH_2$

The IR spectrum of the complexes exhibits characteristic absorption of all the fundamental groups of the ligand but a shifted position in the case of coordinated groups. The amide —NH stretching frequency of the ligand observed at 3300 cm^{-1} in the spectrum of the ligand is lower frequency around 3260 cm^{-1}. The characteristic carboxyl group absorption disappears and two bands at 1620–1570 and 1400–1320 cm^{-1} were observed which can be assigned to asymmetric and symmetric stretching frequencies of coordinated carboxyl group[7]. The large separation between these two bands confirms the unidentate nature of carboxylate ion[7]. The amide carbonyl group stretching frequency remains unaltered indicating its non-participation in bonding to the metal ion. The Cu(II) complex exhibits an absorption band at 3398 and 3542 cm^{-1} which were

assigned to ν(OH) of coordinated hydroxyl group and water molecule respectively. Moreover, the presence of absorption bands 836 and 640 cm^{-1} supports the presence of water molecule[7]. These bands are due to rocking $\rho_r(H_2O)$ and wagging $\rho_w(H_2O)$ of coordinated water molecule. The band at 1120 cm^{-1} in copper complex is assigned to bending mode of M—O—H moiety. These bands are not found in other complexes indicating the absence of coordinated water molecule and hydroxyl group.

The band at 3320 cm^{-1} in the IR spectrum of the ligand due to ν(NH) of *sec.* amino group is shifted to 3290 cm^{-1} in all complexes except that of Cu(II). In addition to these absorption bands, two new bands around 450 and 540 cm^{-1} are assigned to ν(M—O) and ν(M—N) respectively.

The Ni(II) complex showed a magnetic moment of 3.01 BM which is expected for octahedral geometry. The high value may be due to the spin orbit coupling at higher state mixing with ground state. For Co(II) complex the magnetic moment is found to be 4.82 BM which is consistent with the reported value of high spin octahedral geometry. The magnetic moment of Mn(II) complex (5.79 BM) indicates high spin octahedral environment. The Cu(II) complex exhibits a magnetic moment of 1.89 BM, which comes in the range of squre-planar geometry. Zn(II) and Cd(II) complexes are diamagnetic since they posses d^{10} configuration.

The electronic spectra of octahedral complex of Ni(II) showed bands at 25030, 16130 and 11360 cm^{-1} which correspond to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$. The Co(II) comples showed an intense band at 17530 cm^{-1} which is due to $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition and the other bands are out of range.

The X-band ESR spectrum of Cu(II) complex with $DBCPH_2$ gave $g_{\|}$ and $g_{\perp}$ values 2.215 and 2.158 respectively. The trend $g_{\|} > g_{\perp} > g_e$ (free ion value) shows that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectrum is characteristic of axial symmetry[8].

The X–ray powder patterns of Cu(II) and Ni(II) complexes were analyzed to determine their structure[9]. The lattice constants for Cu(II) complex are 0.0029, 0.0046 and 0.0032 with edge lengths 14.304, 11.284 and 13.61 Å respectively. For Ni(II) complex the lattice constants are 0.00636, 0.00242 and 0.00424 and edge lengths are 9.568, 15.658 and 11.829 Å respectively. The values correspond to orthrhombic system having two molecules per unit cell.

The thermal studies were conducted on the complexes of $DBCPH_2$. For the complex [Ni(DBCP)], the TG curve shows three stage decomposition. The three stages of decomposition are attributed to the stepwise removal of ligand from the complex. A residue of 20.2% is due to metal oxide. This is in conformity with the mass loss data obtained from independent pyrolysis (78.9%) and theoretical value (79.02%). The TG curve of [Co(DBCP)] shows that it also undergoes three stage decomposition resulting in a total mass loss of 78.2%. The final product is cobalt oxide.

The [Cd(DBCP)] complex undergoes a two stage decomposition in which the ligand is lost leaving behind a residue of 32% which is due to metal oxide at 733 K. This is in conformity with mass loss data obtained from independent pyrolysis (68.14%) and theoretical value (68.1%).

For the Mn(II) and Zn(II) complexes the decomposition is a three step process leaving behind the metal oxide as the final product. The Cu(II) complex undergoes three stage decomposition. The first stage of decomposition at a temperature 421 K with a mass loss of 7.3% (calcd. 7.28%) indicates the presence of two coordinated water molecules. Final mass corresponds to the metal oxide. The presence of water molecules is confirmed from TG analysis. According to Nikolaev *et al.*[10], water eliminated above 150° C may be due to coordinated molecules.

Conclusion

In these complexes (except Cu(II)) the ligand acts as pentadentate and the sixth coordination is satisfied through a weak interaction between metal ion and carbonyl group of neighbouring ligand. For Cu(II) complex the analytical data suggest a square-planar geometry.

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