Asian Journal of Chemistry Vol. 16, Nos. 3–4 (2004), 1791–1795

Synthesis and Characterisation of Cobalt(II), Nickel(II), Copper(II), Zinc(II) and Cadmium(II) complexes of N,N′-propylene-bis (3-carboxypropenamide)

N. BABU
Department of Chemistry, Sree Narayana College for Women, Kollam-691 001, India

Five complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with a polydentate ligand N,N′-propylene-bis(3-carboxypropenamide) ($PBCPH_2$) have been synthesized and characterized by elemental analysis, conductance and magnetic measurements, infrared spectral, NMR, electronic spectra, X-ray diffraction and thermal analysis. Composition of the complexes other than Cu(II) is [ML] and for Cu(II) it is $[CuL]\cdot 2H_2O$, where L = $[PBCP]_2$. In these complexes the ligand acts as a tetradentate.

Key Words: Synthesis, Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II), Complexes, N,N′-propylene-bis (3-carboxypropenamide).

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 1,3-diaminopropane. The metal complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with this ligand were prepared and characterized by various physico-chemical methods.

EXPERIMENTAL

Preparation of N,N′-propylene-bis(3-carboxypropenamide) ($PBCPH_2$)

Maleic anhydride (9.8 g, 0.1 mmol) was dissolved in glacial acetic acid and to this 1,3-diaminopropane (4.2 mL, 0.05 mmol) was added dropwise with constant stirring while cooling in ice. The white solid formed 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. 163°C and yield 85%).

Preparation of the complexes

The complexes with the ligand were prepared by the following general procedure. The respective metal nitrate or acetate (0.1 mmol) was dissolved in methanol. To this a suspension of $PBCPH_2$ (0.1 mmol) in the same solvent was added slowly and refluxed for 2–3 h. The solid complexes formed were filtered, washed with water and acetone and dried *in vacuo*.

The TG, DTG and DTA curves of the complexes were recorded on a thermal analyzer in air in the temperature range 28–1200°C. Indepentant 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 contents of the complexes were obtained by analytical methods[1]. The molar conductivities of the complexes in methanol were measured at room temperature. The IR spectra of the ligands and complexes were recorded in potassium bromide pellets in the range 4000–400 cm^{-1} on a Perkin-Elmer FT-IR spectrophotometer. 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 DISCUSSION

All the complexes were non-hygroscopic crystalline solids, insoluble in benzene, petroleum ether and chloroform, but sparingly soluble in acetonitrile, methanol and nitrobenzene. The analytical data are given in Table-1. The molar conductivity values of the complexes in methanol were in the range corresponding to those of non-electrolytes.

ANALYTICAL, MAGNETIC AND MOLAR CONDUCTIVITY DATA OF THE COMPOUNDS

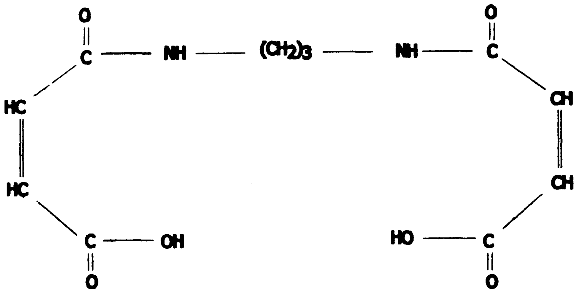
Compound	Analysis: Found (Calcd.) (%)				μ_{eff} (B.M.)	λ_m*
	C	H	N	M		
[$PBCPH_2$]	47.48 (48.88)	4.96 (5.18)	10.16 (10.37)	—	—	—
[Ni(PBCP)]	38.40 (40.20)	3.42 (3.53)	8.32 (8.47)	17.67 (17.87)	Diamag	28.1
[Co(PBCP)]	39.12 (40.36)	3.44 (3.66)	8.42 (8.56)	17.72 (18.06)	4.79	22.2
[Cu(PBCP)]$\cdot 2H_2O$	34.22 (35.91)	3.94 (4.12)	7.28 (7.42)	16.84 (17.92)	1.89	18.4
[Zn(PBCP)]	37.82 (39.54)	3.46 (3.59)	8.12 (8.39)	18.96 (19.61)	Diamag	27.3
[Cd(PBCP)]	32.32 (34.60)	3.41 (3.54)	7.58 (7.36)	28.12 (29.54)	Diamag	24.5

*λ_m in $ohm^{-1}\ cm^2\ mol^{-1}$.

The IR spectrum of the ligand exhibits a stretching frequency of amide[5] ν(NH) 3300 cm^{-1}, ν(OH) of COOH group, which is hydrogen bonded with carbonyl group of amide at 3100 cm^{-1}, another band at 1700 cm^{-1} due to ν(CO) of COOH group, amide-I (ν(C=O)) at 1626 cm^{-1} and amide II (ν(CN) + δ(NH)) at 1500 cm^{-1} and a band at 1590 cm^{-1} due to ν(C=C) of olefinic linkage.

The NMR spectrum of the ligand recorded in DMSO shows signals at 9.1 (2H, COOH) and 3.6–4.3 (4H, CH_2) near to the secondary amide group. A quintet at 2.05 (2H, CH_2 in between the above protons), 8.2 (2H, amide NH) and 5.8–6.2 (doublet of doublet), (4H, CH=CH)[7] ppm.

The mass spectrum of the ligand exhibits molecular ion peak at m/z 270 and a base peak at m/z = 116 due to $[C_4H_4O_4]^+$ ion. The peak at m/z 72 is due to $[CH_2{=}CHCOOH]^+$ and one at m/z 45 is due to $[COOH]^+$. From these data the following structure has been assigned to the ligand.



Structure of N,N′-propylene-bis(3-carboxypropenamide) ($PBCPH_2$)

The infrared spectra of the complexes exhibit characteristic absorptions of all the fundamental groups of the ligand, but at shifted positions in the case of coordinated groups. The amide NH stretching frequency of the ligand at 3300 cm^{-1} in the spectrum of the ligand is shifted to lower frequency around 3260 cm^{-1}.The characteristic carboxyl absorption disappears and two bands in 1620–1570 and 1400–1320 cm^{-1} regions are obtained which can be assigned to asymmetric and symmetric stretching frequencies of coordinated carboxyl group. The large separation (*ca.* 200 cm^{-1}) between the two bands confirms the unidentate nature of carboxylate ion[5]. The amide carboxyl group stretching frequency remains unaltered indicating its non-participation in bonding to metal ion. The combined band due to amide-II (ν(CN) + δ(NH)) observed at 1500 cm^{-1} in the ligand undergoes a negative shift of 20 cm^{-1}. This also confirms that amide nitrogen is coordinated to metal ion. The Cu(II) complex exhibits a broad absorption band at 3550 cm^{-1} which may be assigned to ν(OH) of water molecule. Further, the absence of characteristic absorption bands around 800 cm^{-1} indicates that the water molecule is not coordinated[5] to the metal ion. The band at 1608 cm^{-1} assigned to δ(H_2O) also supports the presence of water of crystallization. In addition to the above absorption bands, two new bands observed in the far infrared region around *ca.* 450 and 540 cm^{-1} are assigned to ν(M—O) and ν(M—N) respectively.

The Ni(II) complex of $PBCPH_2$ is diamagnetic, suggesting a square-planar geometry. The Co(II) complex is found to have a magnetic moment of 4.79 B.M., suggesting a tetrahedral geometry. The Cu(II) complex has a magnetic moment of 1.89 B.M. which is the range for square-planar geometry. The Zn(II) and Cd(II) complexes are diamagnetic since they possess d^{10} configuration.

The electronic spectrum of four coordinated diamagnetic square-planar complex of Ni(II) shows bands at 16320 cm^{-1} due to the transition $^1A_{1g} \rightarrow {}^1B_{1g}$. The Co(II) complex shows a broad band with maximum at 14720 cm^{-1} and it is attributed to the transition $^1A_2 \rightarrow {}^1T_1(P)$. The other two transitions $^4A_2 \rightarrow {}^4T_2$; $^4A_2 \rightarrow {}^4T_1(F)$ occurring at very low energy regions are not observed. The pale blue Cu(II) complex shows an absorption at 13520 cm^{-1} which is due to $^2B_{1g} \rightarrow {}^2E_g$ transition characteristic of square-planar geometry. The Zn(II) and Cd(II) complexes show absorption bands around 26000 cm^{-1} and 24800 cm^{-1} which are attributed to intraligand and charge transfer transitions.

The PMR spectra of diamagnetic Ni(II) and Zn(II) complexes have been recorded in DMSO. The methylene protons of the ligand resonate at 4.3–4.7 ppm and —CH=CH protons resonate at 5.8–6.2 ppm as a double doublet. Two amide —NH protons resonate at 8.9 ppm (singlet) with a downfield shift compared to that in free ligand (8.2 ppm) indicating coordination through amide nitrogen. The carboxylic protons, which exhibited a resonance signal at 9.1 ppm in the free ligand spectrum, disappeared on complexation, confirming the loss of these protons and coordination through carboxylate group.

The X-band ESR spectrum of Cu(II) complex with $PBCPH_2$ gave $g_{\|}$ and $g_{\perp}$ values 2.3038 and 2.142 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 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 0.0019, 0.0036 and 0.0028 with edge lengths 13.104, 10.138 and 12.618 Å respectively. For Ni(II) complexes the lattice constants are 0.0058, 0.00214 and 0.00434 and edge lengths 8.654, 16.432and 10.87 Å respectively. The values correspond to orthorhombic system. For Cu(II) and Ni(II) complexes the number of molecules per unit cell is found to be two in both cases.

The thermal studies were conducted on the complexes of $PBCPH_2$. In Cu(II) complex, the IR data suggest the presence of water molecule. It is further confirmed by TG analysis. According to Nikolaev *et al.*[10] and Singh *et al.*[11], water eliminated below 150°C can be considered as lattice water and that eliminated above 150°C can be due to coordinated water. The Cu(II) complex undergoes three stage decompositions. In the first stage the weight loss of Cu(II) complex at 110–160°C is 9.62% (calcd. 9.69%), corresponding to two molecules of lattice water. The decomposition attains stability around 700°C and the weight loss corresponds to the formation of the metal oxide. The other four complexes undergo two stage decompositions. There is no mass loss below 200°C indicating the absence of water molecule attached to the metal ions. In all cases the final decomposition is completed near 750°C, and the weight loss corresponds to the formation of the metal oxide. This is in conformity with the mass loss data obtained from independent pyrolysis in each case. The two stages of decomposition are attributed to the stepwise removal of ligand from the complexes. The order of stability of the complexes is Ni > Co > Cd > Zn > Cu. Activation energy and various thermodynamic parameters have been calculated using Coats-Redfern equation[12].

REFERENCES

1. Vogel's Text Book of Quantitative Chemical Analysis, 5th Edn., Addison Wesley-Longmans (1999).
2. W.G. Palmer, Experimental Physical Chemistry, University Press, Cambridge (1954).
3. P.W. Selwood, Magnetochemistry, 2nd Edn., Interscience, New York (1958).
4. A. Earnshaw, Introduction to Magnetochemistry, Academic Press, New York (1968).
5. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 3rd Edn., Wiley, New York (1978).
6. R.M. Silverstein, Spectroscopic Identification of Organic Compounds, Wiley, New York (1998).
7. W. Kemp, Organic Spectroscopy, Palgrave Publishers Ltd. (1991).
8. B.D. Goodman and J.B. Raynor, ESR of Transition Metal Compounds, 3rd Edn., Wiley, NewYork (1978).
9. H. Lipson and H. Steeple, Interpretation of X-ray Powder Diffraction Patterns, Macmillian, London (1979).
10. A.V. Nikolaev, V.A. Logvienk and L.I. Myachina, Thermal Analysis, Academic Press, New York, p. 779 (1969).
11. B. Singh, B.B. Agarvala, P.L. Moury and A.K. Dey, *J. Indian Chem. Soc.*, **59**, 1130 (1982).
12. W. Coats and J.P. Redfern, *Nature*, **201,** 68 (1964).

(*Received*: 4 March 2004; *Accepted*: 10 June 2004) AJC-3444