Asian Journal of Chemistry Vol. 4, No. 1 (1992), 71-76

Physico-Chemical Investigations on the Complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) with N-(5-bromosalicylidene)-5-bromoanthranilic Acid

K. P. REMA, S. LALY AND GEETHA PARAMESWARAN*

Department of Chemistry
University of Calicut, Kerala, 673 635, India

Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) complexes of N-(5-bromosalicylidene)-5-bromoanthranilic acid have been synthesized and characterized on the basis of analytical data, IR and electronic spectral, magnetic measuremets and thermal studies. Thermal decomposition data of Co(II), Ni(II) and Cu(II) chelates have been analysed to obtain the energy and entropy of activation based on Coats-Redfern and Horowitz-Metzger equation. Thermal stabilities of the chelates under examination can be given as

$$[CoL(H_2O)_3] \approx [NiL(H_2O)_3] < [Cu_2L_2]$$

INTRODUCTION

Transition metal complexes of Schiff bases have important technical applications. In recent years the importance of salicylaldehyde Schiff base ligands and their metal chelates with transition metals have been emphasized. In continuation of earlier work from our laboratory on transition metal complexes of Schiff base ligands[1-4], we report in this paper the preparation and characterization of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Cd(II) complexes of N-(5-bromosalicylidene)-5-bromoanthranilic acid.

EXPERIMENTAL

Synthesis of the Ligand

The starting materials used for the preparation of N-(5-bromosalicylidene)-5-bromoanthranilic acid were anthranilic acid, salicylaldehyde and liquid bromine. Salicylaldehyde was purified by distillation and anthranilic acid by recrystallisation from water. N-(5-bromosalicylidene)-5-bromoanthranilic acid was prepared by standard method according to West[5]. The fine shining orange crystal of the ligand obtained was further purified by recrystallisation from ethanol.

General Method for Preparing the Complexes

An ethanolic solution of metal ion was added dropwise to a refluxing solution of ligand in ethanol (1 : 1 ratio). Sodium acetate was added to the mixture. The coloured metal complexes separated were filtered, washed with ethanol and dried in vacuum over anhydrous calcium chloride.

RESULTS AND DISCUSSION

Elemental analysis shows that Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Cd(II) form 1 : 1 complexes with the ligand. Analytical, molar conductance and magnetic data of the complexes are presented in Table 1.

TABLE 1

ANALYTICAL DATA, MOLAR CONDUCTANCE AND MAGNETIC MOMENTS

Chelate	Metal %	Bromine %	Molar conductance	Magnetic Moment B.M.
$[MnL(H_2O)_3]$	11.8 (12.7)	30 (31.5)	8.4	5.9
$[FeL(H_2O)_3]$	16.22 (17.9)	29.8 (31.5)	7.9	5.6
$[CoL(H_2O)_3]$	14.78 (15.74)	30.5 (31.3)	7.7	4.77
$[NiL(H_2O)_3]$	11.68 (11.71)	30.8 (31.3)	9	3.1
$[Cu_2L_2]$	13.38 (13.7)	16.1 (17.3)	1.4	1.89
$[CdL(H_2O)]$	18.2 (19.9)	29.7 (30.3)	1.05	Diamag.

The complexes exhibit molar conductance in the range 1–9 ohm^{-1} mol^{-1} cm^2 in methanol. The very low values indicate that complexes are non-electrolytes and are neutral in nature.

Room temperature magnetic moment of Fe(II) complex (5.6 B.M.) is consistent with spin free octahedral geometry around metal ion[6]. A magnetic moment of 4.77 B.M. for cobalt(II) complex is suggestive of an octahedral geometry. The magnetic moment of the nickel(II) complex 3.1 B.M.) is very close to the spin only value of octahedral nickel(II) complexes[7]. The copper(II) chelate displays anomalous behaviour. It exhibits a magnetic moment of 1.89 B.M. Based on similar observations on the parent compound, a nonplanar dimeric structure has been assigned to the complex[8]. The insolubility of the complex in common noncoordinating organic solvents and water, the decomposition temperature of the complex (> 160°C) without melting also supports this fact. The cadmium(II) complex is diamagnetic as expected for d^{10} configuration.

The electronic spectral bands and their tentative assignments are given in Table 2. The data was found to agree with conclusions arrived from magnetic susceptibility measurements. The electronic spectrum of the manganese(II) complex contained a band at 24,800 which was taken as evidence to support the presence of manganese(II) in an octahedral environment[9]. A weak shoulder observed at 16,129 may be attributed

TABLE 2

ELECTRONIC SPECTRAL BANDS OF THE METAL COMPLEXES

Complex	Absorption maxima cm^{-1}	Tentative assignments
$[MnL(H_2O)_3]$	48780 41666	Electronic transitions within the ligand
	34482 29700	Ligand → metal charge transfer d-d transition
	24800	” ” ” ”
$[FeL(H_2O)_2]$	48780 39215	Electronic transitions within the ligand
	29411 16129	Ligand to metal charge transfer $^5T_{2g} \rightarrow {}^5E_g$
$[CoL(H_2O)_3]$	47169 40000	Electronic transitions within the ligand
	30303 22721	Ligand → metal charge transfer d-d transition
	19417	” ” ” ”
	17241	” ” ” ”
$[NiL(H_2O)_3]$	45454 41666	Electronic transitions within the ligand
	31250 25000	Ligand → metal charge transfer d-d transition
	16129	” ” ” ”
	11764	” ” ” ”
$[Cu_2L_2]$	48780 40816	Electronic transitions within the ligand
	23809	Ligand → metal charge transfer d-d transition
	14686	

to $^5T_{2g} \rightarrow {}^5E_g$ transition, characteristic of octahedral stereochemistry around iron(III) metal ion[10]. The spectrum of cobalt(II) complex gave three d-d transition bands at 19,417, 22,721 and 17,241 cm^{-1}. The first two bands may be assigned to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively[11]. Nickel(II) complex shows three bands in the electronic spectrum. These can be attributed to spin allowed d-d transitions, 25,000; 16,129; 11,764 cm^{-1} assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively[10]. Copper(II) complex shows two bands with peaks at 23,809 and 14,686 cm^{-1}, the first being the stronger. The band at 14,686 cm^{-1} is assigned to d-d transition. The other band is attributed to the charge transfer transition[8]. For Cd(II), d-d transitions are not possible and hence no band in the visible region of spectrum was obtained for the complex.

The infrared spectrum of ligand shows a band of medium intensity at about 1640 cm^{-1} and a strong band 1560 cm^{-1}. The first band may be attributed to the carbonyl stretching frequency of the carbonyl group. A shift of this band to lower frequencies (*ca.* 1600 cm^{-1}) indicates chelation of the ligand to the metal atom through carbonyl oxygen. The sharp band at 1540 cm^{-1} in infrared spectrum of the ligand assignable to $\nu(C{=}N)$ of Schiff's base residue, shifts to lower frequencies at *ca.* 1520 cm^{-1} in the complexes indicating a reduction of electron density in the azomethine linkage as the nitrogen coordinates to the metal ion.

In the present complexes the asymmetric and symmetric stretching vibrations of the carboxylate group occur at 1580–1600 cm^{-1} and 1410–1430 cm^{-1} respectively with a $\Delta\nu$ of 170–190 cm^{-1}. A monodentate carboxylate group has a much closer difference. Monodentate carboxylate groups are therefore indicated in the chelates[12–14].

A broad band appearing in the region 3400 cm^{-1} assignable to the intermolecular hydrogen bonded phenolic –OH stretching frequency, disappears in the metal complexes showing deprotonation of –OH group and coordination of the phenolic oxygen atom. The sharp band at 1275 cm^{-1} in the infrared spectrum of the ligand due to phenolic $\nu(CO)$ vibration shifts to higher wave numbers. Thus coordination of ligand to the metal atom through phenolic oxygen after deprotonation is further confirmed[15].

In the cobalt(II), nickel(II), manganese(II), iron(II) and cadmium(II) complexes the presence of coordinated water is confirmed by the observation of a broad hump around 3300 and 3100 cm^{-1}. The coordinated nature of water molecule is further supported by the appearance of a rocking mode of medium intensity at 860 cm^{-1}.

However, conclusive evidences regarding the bonding of nitrogen and oxygen have been provided by occurrence of $\nu(M{-}N)$ and $\nu(M{-}O)$ in the regions 460–540 cm^{-1} and 350–440 cm^{-1} respectively in the spectra of the metal complexes. The infrared data suggest that N-(5-bromosalicylidene)-5-bromoanthranilic acid behaves as tridentate chelating agents for the metal ions, coordinating through phenolic oxygen, nitrogen atom of C=N group and carbonyl oxygen of carboxyl group.

The thermal decomposition studies of cobalt(II), nickel(II) and copper(II) chelates have been carried out. The TG traces exhibit a two stage decomposition pattern. The mass loss data at the end of the first stage of decomposition corresponds to the removal of three molecules of water and bromine atoms and the second stage corresponds to the loss of ligand molecule in the case of cobalt(II) and nickel(II). The studies indicate that the first stage commences around 150°C in the complexes. This evidence supports the assignment that the water present is the coordinated water. In the case of copper(II) complex the first step corresponds to the loss of two bromine atoms and the second step corresponds to the loss of the ligand. The first decomposition step in the TG curves of the three complexes were steep and hence introduced considerable difficulty in the mathematical analysis of this part. It was found to be impracticable to subject the very steep TG curve to a mathematical analysis; hence the first step was not studied further. Hence the second step which forms the main decomposition step was subjected to kinetic study. The mass loss data after the complete decomposition of the complexes show that the residue left behind are oxides. The observed mass loss agrees fairly well with the value calculated from pyrolytic experiments.

The overall mass loss as shown by the TG curves is 85.8% for $[CoL(H_2O)_3]$, 86.7% for $[(NiL(H_2O)_3]$ and 84% for $[Cu_2L_2]$ while the calculated percentage mass losses are shown below.

Reaction	Mass loss %
$[CoL(H_2O)_3] \rightarrow Co_3O_4$	84.26
$[NiL(H_2O)_3] \rightarrow NiO$	85.4
$[Cu_2L_2] \rightarrow CuO$	82.8

The kinetic parameters obtained from application of the Coats Redfern equation[16]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \ln\left[\frac{AR}{\phi E}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{1}$$

and Horowitz-Metzger equation[17]

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\frac{ART_s^2}{\phi E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \tag{2}$$

are given in Table 3.

TABLE 3

KINETIC DATA

Chelate	Parameter	From Coats-Redfern equation	From Horowitz-Metzger equation
	E^* (kJ mol^{-1})	102.5	102.1
$[CoL(H_2O)_3]$	z (S^{-1})	2.5×10^4	1.4×10^4
	ΔS^* (JK^{-1} mol^{-1})	−168.4	−173.3
	E^* (kJ mol^{-1})	96.6	99.2
$[NiL(H_2O)_3]$	z (S^{-1})	2.4×10^3	2.8×10^3
	ΔS^* (JK^{-1} mol^{-1})	−188.6	−187.1
	E^* (kJ mol^{-1})	114.6	122.6
$[Cu_2L_2]$	z (S^{-1})	1.09×10^6	5.4×10^5
	ΔS^* (JK^{-1} mol^{-1})	−136	−141

The left hand side of the equation (1) was plotted against reciprocal absolute temperature (I/T) and against θ, $(T - T_s)$ for equation (2).

The values obtained for cobalt(II) and nickel(II) complexes are comparable. Because of their similar structures, both the complexes show similar thermal behaviour, as evidenced from their peak temperature and comparable values of activation energy. The negative values for entropy of activation indicates that the activated complexes have a more ordered structure than the reactants and the reactions are slower than normal. On the basis of the experimental findings in the present course of studies the relative thermal stabilities of N-(5-bromosalicylidene)-5-bromoanthranilic acid chelates are in the order

$$[(CoL(H_2O)_3] \approx [NiL(H_2O)_3] < [Cu_2L_2].$$

REFERENCES

1. V. Indira and G. Parameswaran, *Thermochim. Acta*, **101**, 145 (1986).
2. J. Chacko and G. Parameswaran, *J. Thermal Anal.*, **29**, 3 (1984).
3. V. Indira and G. Parameswaran, *J. Thermal Anal.*, **32**, 1151 (1987).
4. J. Chacko and G. Parameswaran, *Indian J. Chem.*, **28(A)**, 77 (1989).
5. B. O. West, *J. Chem. Soc.*, 4977 (1960).
6. B. N. Figgis and J. Lewis, *Prog. Inorg. Chem.*, 197 (1964).
7. ———, The Magnetochemistry of Complex Compounds in Modern Coordination Chemistry, Ed. J. Lewis and R. G. Wilkins, Interscience, New York (1969).
8. R. K. Mehta, V. C. Singhi and S. L. Pania, *Talanta*, **19**, 687 (1972).
9. S. N. Poddar, K. Dey, J. Haldar and S. C. Nathsarkar, *J. Indian Chem. Soc.*, **47**, 743 (1970).
10. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, London (1968).
11. C. K. Jϕrgensen, *Acta Chem. Scand.*, **10**, 887 (1956).
12. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley, New York (1966).
13. N. F. Curtius, *J. Chem. Soc.*, 7(A), 1579 (1968).
14. K. Dey and K. C. Ray, *J. Indian Chem. Soc.*, **50**, 66 (1973).
15. K. Ueno and A. E. Martell, *J. Phys. Chem.*, **60**, 1270 (1956).
16. A. W. Coats and J. P. Redfern, *Nature*, **68**, 201 (1964).
17. H. H. Horowitz and G. Metzger, *Anal.*, **35**, 1464 (1963).

[*Received*: 23 December 1989; *Accepted*: 5 October 1990] AJC–231