Thermal studies on cobalt(II), nickel(II) and copper(II) complexes of Schiff base derived from salicylaldehyde and glycine

Mala Nath

Department of Chemistry, University of Roorkee, Roorkee 247667 (India)

(Received 8 October 1990)

Abstract

The thermal studies of $ML \cdot nH_2O$ (where M = Co or Ni, $n = 2$; M = Cu, $n = 1$; L = dianion of Schiff base derived from salicylaldehyde and glycine, abbreviated as Sal:gly) have been carried out in the temperature range 27–500°C using TG, DTG and DTA techniques. The decomposition of the complexes occurs in more than one step between 102 and 390°C. The dehydration takes place in the temperature range 102–133, 160–221 and 169–254°C for the cobalt, nickel and copper complex, respectively, two moles of water being lost in the cobalt and nickel complex, whereas one mole is lost in the copper complex. Dehydration is immediately followed by the decomposition of the ligand moiety attached to the metal ion giving the metal oxide end product. The kinetic data of the dehydration reaction have also been evaluated. The end product in each case has been identified by both far-IR and X-ray analysis.

INTRODUCTION

Imines (Schiff bases derived from amino acids) have frequently been suggested as intermediates in the reaction between pyridoxal vitamin B_6 aldehydes and various amino acids [1]. Furthermore, metal ions demonstrate a catalytic effect upon transamination involving vitamin B_6 [2,3]. These concurrent observations seem to indicate that the metal complexes of Schiff bases derived from amino acids are found as intermediates in the transamination reaction with vitamin B_6 [4]. For this reason, a plethora of references describing the metal complexes of such biologically important Schiff bases have appeared in the literature during the past few decades [5–13]. However, nothing is known about the thermal behaviour of such complexes. In view of our continuing interest in the thermal behaviour of metal chelates of Schiff bases [14,15], we decided to study the thermal decomposition of cobalt, nickel and copper chelates of Schiff base derived from salicylaldehyde and glycine, with special interest in investigation of the kinetics of dehydration of the complexes.

EXPERIMENTAL

Chemicals

Salicylaldehyde (from HPC) and glycine (from E. Merck) were used without further purification. Metal acetates of B.D.H. and AnalaR grade were used as supplied.

Preparation of metal complexes of Schiff base derived from salicylaldehyde and glycine

Cobalt(II), nickel(II) and copper(II) complexes of the above stated Schiff base were prepared as described elsewhere [7–9]. The ligand employed in the present investigation was prepared in situ by refluxing an aqueous solution of glycine (0.01 mol, 0.75 g) and an alcoholic solution of salicylaldehyde (0.01 mol, 1.047 ml) for 2 h at 50°C. To this solution an aqueous solution of metal acetate (0.01 mol) was added with constant stirring. The mixture was refluxed for 1 h and the volume of the solution was reduced. The products, which separated on cooling either immediately or when the reaction mixture was set aside for some hours, were filtered, washed with alcohol and ether and dried in vacuo over P_2O_5 (yields 70–80%).

Analytical procedures

Microanalyses for carbon, hydrogen and nitrogen were performed using an elementary analyser (CHN-rapid) at the Indian Institute of Technology, New Delhi. Cobalt, nickel and copper were determined by atomic absorption spectrometer (IL-751) at USIC, University of Roorkee. Analytical data of the complexes and their decomposition products are given in Table 1.

Thermal measurements

Thermal measurements were carried out using a Stanton Redcroft thermal analyser (STA-780 series), which simultaneously records DTA, DTG and TG curves. The samples of 7.8–8.1 mg were heated at a rate of 5°C min^{-1} in a platinum crucible to a temperature of approx. 550°C in static air. Alumina was used as a standard reference material. A thermobalance with 0.01 mg sensitivity was used and the chart speed was maintained at 20 cm h^{-1}.

IR spectra

IR spectra of the complexes and decomposition products at different temperatures were recorded in a KBr matrix on a Beckman IR 20 spectrophotometer in the region 4000–200 cm^{-1}.

TABLE 1

Analytical data of ML·nH_2O complexes and their decomposition products

Sample	Complex [a]/decomposition product [empirical formula]	Colour	mp (°C)	Elemental analysis: observed (calcd.)			
				C	H	N	M
1	CuL·H_2O [$C_9H_9NO_4Cu$]	Green	> 270	40.65 (41.78)	3.71 (3.50)	5.45 (5.41)	24.37 (24.55)
2	CuL (I) [b] [$C_9H_7NO_3Cu$]	–	–	44.21 (44.91)	2.80 (2.93)	5.72 (5.81)	26.50 (26.39)
3	CuO [c]	Black	–	–	–	–	79.78 (79.88)
4	NiL·$2H_2O$ [$C_9H_{11}NO_5Ni$]	Light green	> 300	38.50 (39.75)	4.00 (4.08)	5.25 (5.15)	22.67 (21.59)
5	NiL (I) [b] [$C_9H_7NO_3$...]	Yellow	–	47.00 (45.82)	2.95 (3.00)	5.72 (5.93)	24.75 (24.89)
6	NiO [c]	Black	–	–	–	–	78.60 (78.58)
7	CoL·$2H_2O$ [$C_9H_{11}NO_5Co$]	Brown	> 300	39.60 (39.72)	4.00 (4.07)	5.21 (5.14)	22.66 (21.65)
8	CoL (I) [b]	Grey	> 270	46.20 (45.78)	2.98 (2.99)	5.70 (5.93)	24.70 (24.96)
9	Co_2O_3 [c]	Black	–	–	–	–	78.70 (78.64)

[a] L is dianion of Schiff base Sal:gly.

[b] Decomposition product (I).

[c] End product.

X-ray diffraction

The X-ray diffraction patterns of the end products were taken with a Phillips diffractometer using Cu Kα radiation and a nickel filter at 35 kV.

RESULTS AND DISCUSSION

Stoichiometry and stereochemistry

The composition and structure of the complexes ML·nH_2O given in Fig. 1(A) and (B) were confirmed using the methods reported in the literature [7–9]. The elemental analysis revealed (Table 1) 1:1 metal to ligand stoichiometry for all three complexes which are insoluble in common organic solvents such as benzene, acetone, acetonitrile and chloroform, but soluble in coordinating solvents such as dimethylformamide (DMF) and dimethyl-sulfoxide (DMSO). The analysis also indicated that the cobalt and nickel complexes contain two molecules of water whereas the copper complex has
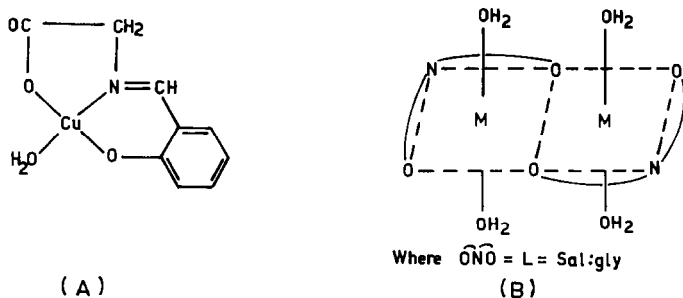
14

Fig. 1. Structure of CuL·H₂O and dimeric ML·2H₂O complexes (where L = dianion of Sal:gly; M = Co or Ni).

only one. The appearance of IR bands at 3400, 925 ± 5, and 740 ± 10 cm^{-1} indicates the presence of coordinated water [11]. The bands are assigned to the νO–H, rocking and wagging modes of the coordinated water [11]. The δOH at ≈ 1600 cm^{-1} has also been assigned but it overlapped with the ν_{as}COO at the same frequency. This is further confirmed by thermal decomposition data (Figs. 2–5).

The complexes lose their water molecules in one step which is immediately followed by a single- or two-stage decomposition of the ligand to give the end product. Figures 3–5 show the TG, DTG and DTA curves of cobalt, nickel, and copper complexes, respectively. The various stages are discussed below.
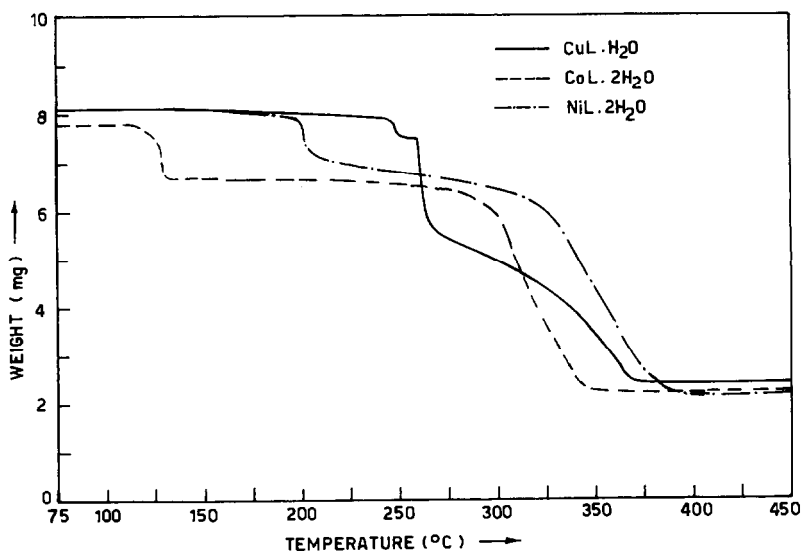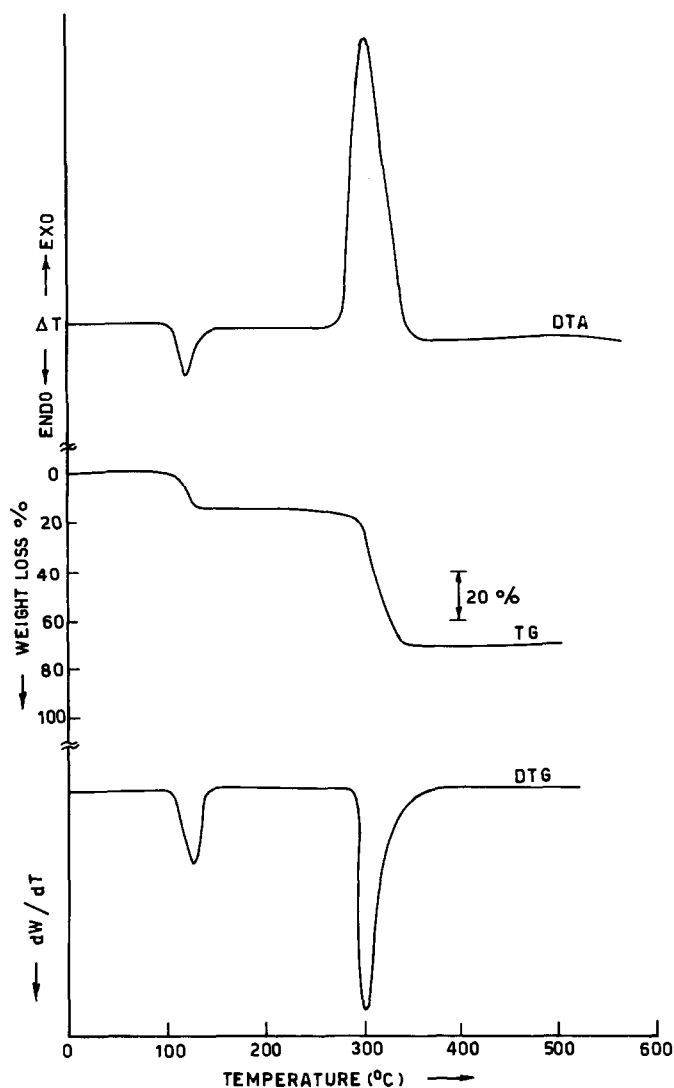

Fig. 2. TG curves of ML·nH₂O complexes.

Fig. 3. DTA, TG (% weight loss) and DTG curves of $CoL \cdot 2H_2O$.

Dehydration

It is evident from the TG curves (Figs. 2–5) that the cobalt complex is stable up to 102°C, whereas nickel and copper complexes are stable up to 160 and 169°C, respectively. The dehydration extends up to 133°C for cobalt, 211°C for nickel and 254°C for the copper complex, and corresponds to the loss of two water molecules per cobalt or nickel ion and one water molecule per copper ion. The observed weight losses are 13.84, 13.58 and 7.4%, compared with the calculated values of 13.24, 13.25 and 6.96% for the cobalt, nickel, and copper complexes, respectively. This is observed in
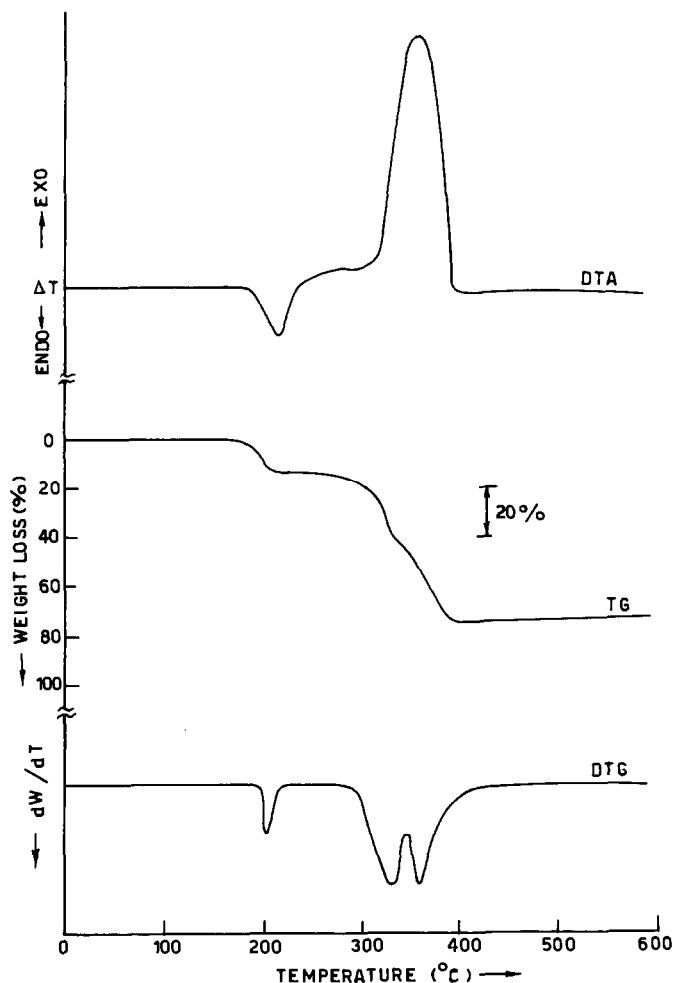
Fig. 4. DTA, TG (% weight loss) and DTG curves of NiL·2H$_2$O.

the DTA (endothermic peak) and DTG curves as peaks at 120, 127°C, respectively, for the cobalt complex (Fig. 3); 215 and 204°C, for the nickel complex (Fig. 4); and 254 and 264°C, for the copper complex (Fig. 5); giving ML as an intermediate (I).

Ligand decomposition

The decomposition of the ligand takes place immediately after the dehydration, in two steps for the copper complex and in a single step for the cobalt and nickel complexes. The first step in the ligand decomposition of the copper complex takes place at 259–266°C and corresponds to the loss of two moles of carbon monoxide and one mole of hydrogen to give an intermediate (II), having tentative composition CuC$_7$H$_5$NO. The observed
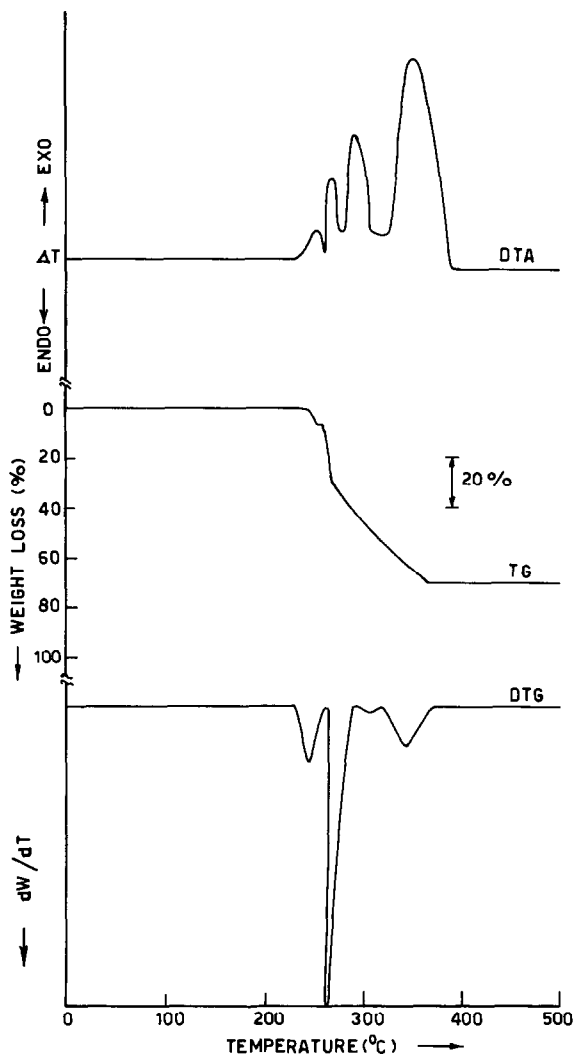
Fig. 5. DTA, TG (% weight loss) and DTG curves of CuL·2H₂O.

weight loss is 23.28% compared with the calculated value of 21.99%. Both DTA and DTG show peaks at 269 (exothermic) and 264° C respectively, as is evident in Fig. 5. The second stage occurs between 266–371°C and involves the loss of organic (C_7H_5) moiety and one half-mole of nitrogen to give CuO as an end product. The further weight loss of 39.88% is observed against the calculated value of 39.86% along with the exothermic DTA and DTG peaks at 294, 350°C and 346°C, respectively.

The decomposition of the ligand in the cases of cobalt and nickel complexes occurs in the 211–346 and 258–389°C ranges, respectively, corresponding to the loss of all ligand moiety to give Co_2O_3 and NiO as the end products. The observed weight losses are 57.31% and 59.25% compared

TABLE 2

IR frequencies (cm^{-1}) for $ML \cdot nH_2O$ and the decomposition products

Sample number	Complex/decomposition products	νC=N	ν_{as}COO/ Phenylring	ν_sCOO	νO–H	δH_2O rocking	δH_2O wagging	νM–O	νM–N
1	$CuL \cdot 2H_2O$	1660vs	1615vs	1400m	3523br,s	938w	770w	546w	480w
2	CuL (I)	1640s	1600m,sh	1405w	–	–	–	520m 525w	480w
3	CuO	–	–	–	–	–	–	500s,br	–
4	$NiL \cdot 2H_2O$	1665s	1615vs 1684d	1400m	3400s	900w	750w	538w	477w
5	NiL (I)	1630s	1595vs 1580d	1395m	–	–	–	530w	480w
6	NiO	–	–	–	–	–	–	510w	–
7	$CoL \cdot 2H_2O$	1670vs	1605s	1405m	3420s	920w	730w	533w	500m
8	CoL (I)	1630s	1595vs	1405w	–	–	–	530w	485w
9	Co_2O_3	–	–	–	–	–	–	538vs 542vs	–

Key: vs, very strong; s, strong; m, medium; w, weak; br, broad; sh, shoulder; d, doublet.
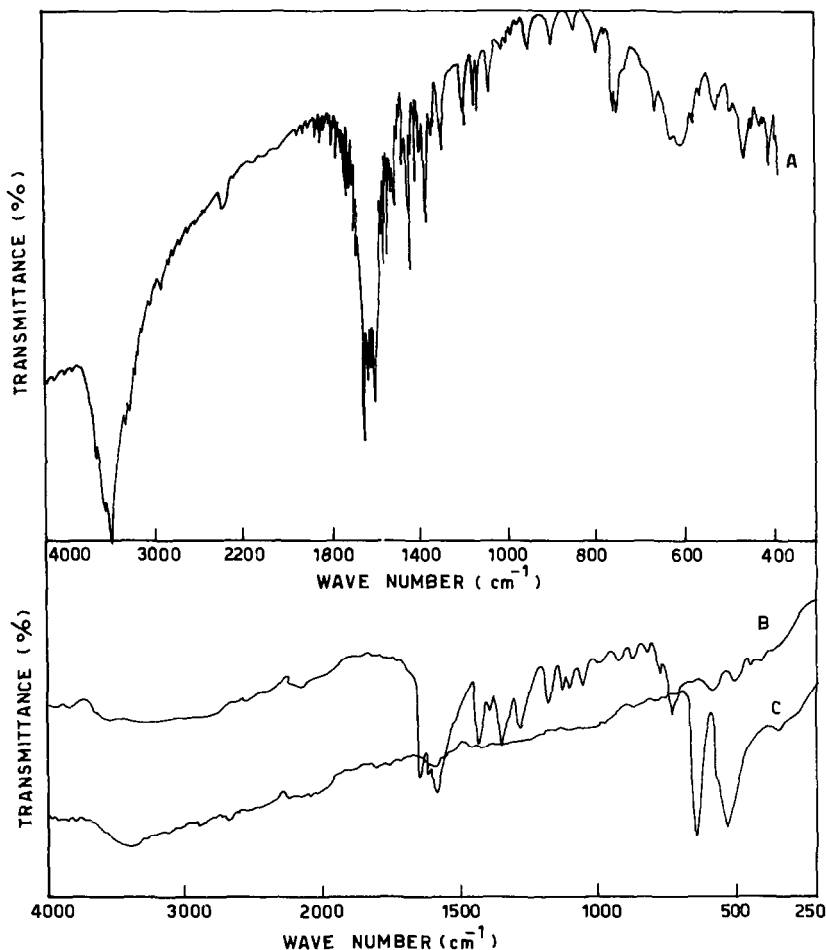
Fig. 6. IR spectra of CoL·2H$_2$O, (A); CoL·2H$_2$O heated to 140°C, (B); CoL·2H$_2$O heated to 350°C, (C).

with the calculated values of 56.28% and 59.27% for the cobalt and nickel complex, respectively. These are evident (Figs. 3 and 4) in the DTA and DTG curves as peaks, at 307 (exothermic) and 302°C for the cobalt complex, and at 365 (exothermic) and 336, 352°C for the nickel complex, respectively. In the case of the nickel complex an unidentified inflection occurs at 350°C.

Characterization of the decomposition products

The compositions assigned to the intermediates are well supported by the results of elemental analyses and IR spectra (Tables 1 and 2) of the samples obtained by heating ML · nH$_2$O isothermally at 140, 350°C (Fig. 6, curves B and C), 225, 390°C (Fig. 7, curves B and C) and 255, 375°C (Fig. 8, curves
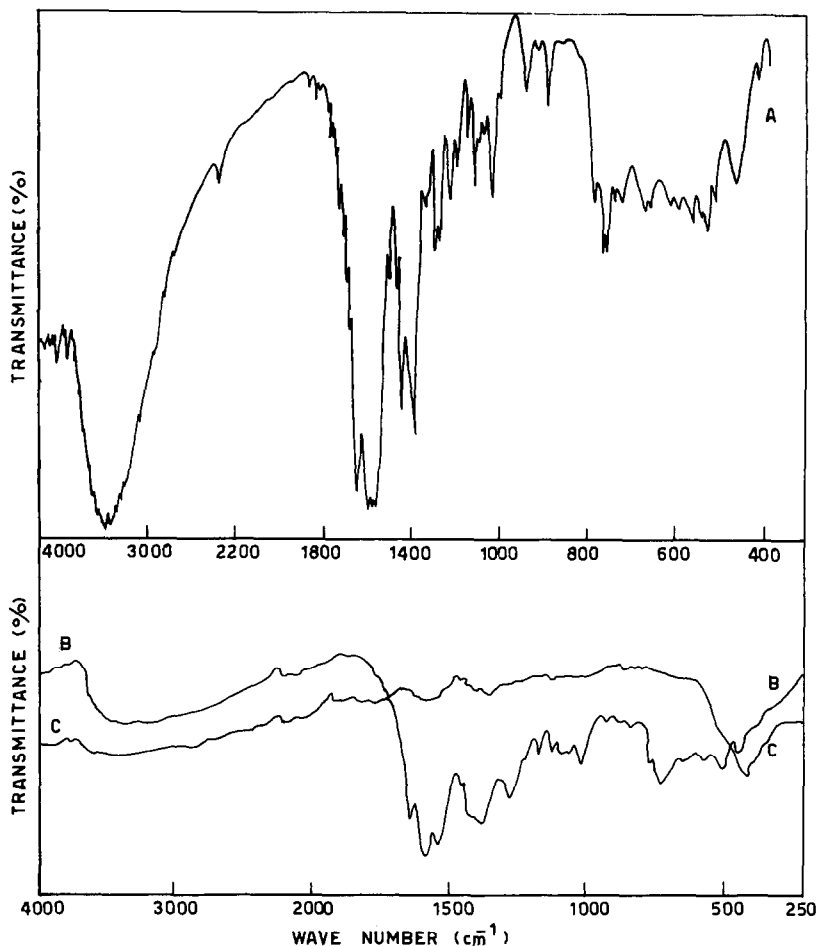
Fig. 7. IR spectra of NiL·2H$_2$O, (A); NiL·2H$_2$O heated to 225°C, (B); NiL·2H$_2$O heated to 390°C, (C).

B and C) for the cobalt, nickel, and copper complexes, respectively. The intermediate (I) in all three complexes does not show peaks of coordinated OH at 3400, 925 ± 10, and 740 ± 10 cm^{-1}, indicating the loss of coordinated water molecules to form an anhydrous complex (Fig. 6, curve B, Fig. 7, curve B and Fig. 8, curve B). This is further confirmation of dehydration.

Elemental analyses also correspond to the proposed formula of the intermediate (I) in all three complexes. The IR spectrum of the intermediate (II) formed in the decomposition of the copper complex could not provide any information on stoichiometry and the stereochemistry of the product. This is probably due to the lack of a clear-cut horizon in the TG curve at this temperature.

The end product in each case is a metal oxide which is characterized by X-ray analysis and metal determination. All *d* values together with their
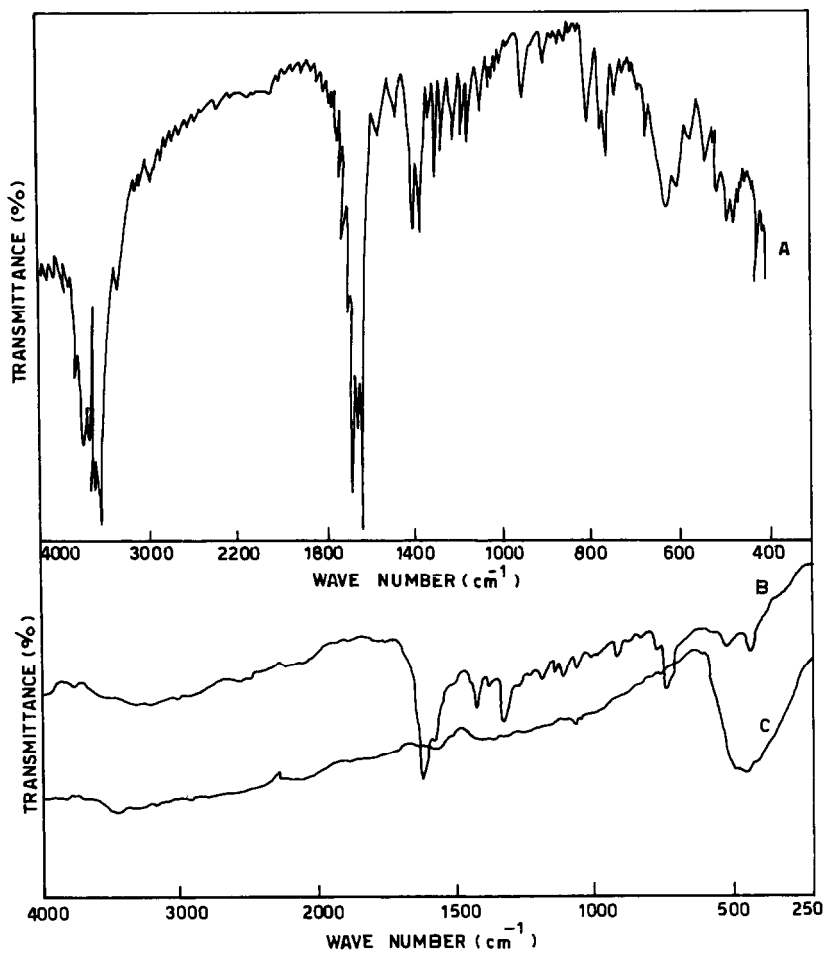
Fig. 8. IR spectra of CuL·2H$_2$O, (A); CuL·2H$_2$O heated to 255°C, (B); CuL·2H$_2$O heated to 375°C, (C).

TABLE 3

Kinetic parameters for the thermal dehydration of ML·nH$_2$O complexes

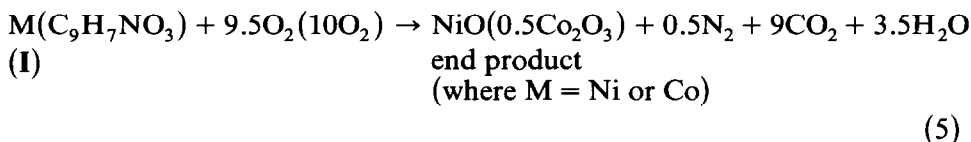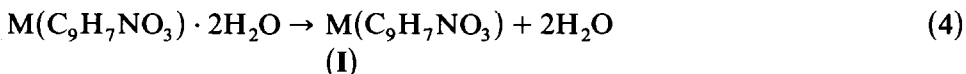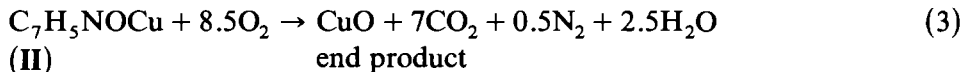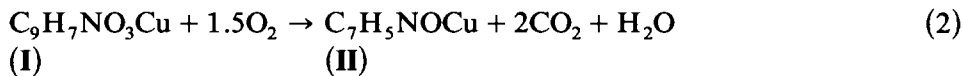| Sample number	Complex	T_i (K)	E^* (kJ mol^{-1})	S^* (J mol^{-1} K^{-1})	G^* (kJ mol^{-1})	H^* (kJ mol^{-1})	log Z (s^{-1})	log k_r (s^{-1})
1	CuL·H$_2$O	521	87.69	−128.86	150.49	83.34	6.30	−2.49
2	NiL·2H$_2$O	477	79.24	−129.70	137.27	75.39	6.22	−2.45
3	CoL·2H$_2$O	402	75.47	−104.26	114.01	72.13	7.47	−2.33

Key: E^*, energy of activation (kJ mol^{-1}); S^*, entropy of activation (J mol^{-1} K^{-1}); G^*, free energy of activation (kJ mol^{-1}); H^*, enthalpy of activation (kJ mol^{-1}); Z, frequency factor (s^{-1}); k_r, specific rate constant (s^{-1}).

intensities (measured by peak height) are in accordance with those reported [16]. The IR spectra of the end products do not show aromatic CH stretching and bending vibrations or other characteristic frequencies of the ligands (νC=N, νCOO etc.), but the characteristic νM–O at 500, 538, 642 and 510 cm^{-1} for the copper, cobalt and nickel oxide, respectively, are observed [17].

On the basis of the above mentioned results, the following tentative schemes are proposed for the thermal decomposition of ML$\cdot n$H$_2$O complexes

$$\text{(1)}$$
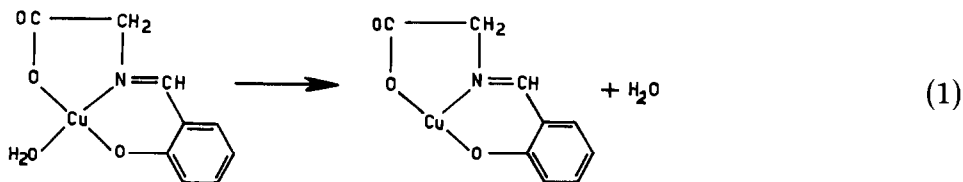
(I) (Empirical formula C$_9$H$_7$NO$_3$Cu)

$$C_9H_7NO_3Cu + 1.5O_2 \rightarrow C_7H_5NOCu + 2CO_2 + H_2O \tag{2}$$
(I) (II)

$$C_7H_5NOCu + 8.5O_2 \rightarrow CuO + 7CO_2 + 0.5N_2 + 2.5H_2O \tag{3}$$
(II) end product

$$M(C_9H_7NO_3)\cdot 2H_2O \rightarrow M(C_9H_7NO_3) + 2H_2O \tag{4}$$
(I)

$$M(C_9H_7NO_3) + 9.5O_2(10O_2) \rightarrow NiO(0.5Co_2O_3) + 0.5N_2 + 9CO_2 + 3.5H_2O$$
(I) end product
(where M = Ni or Co)

$$\text{(5)}$$

Kinetics of thermal dehydration

Using the TG curves (Fig. 2), a kinetic study has been made of the dehydration process. The methods of Horowitz and Metzger [18] and Fuoss et al. [19] were found to be suitable for this.

Various kinetic parameters for the thermal dehydration reaction have been evaluated and are presented in Table 3. The same table contains the log Z values.

Determination of reaction order

The Horowitz and Metzger equation $C_s = (n)^{1/1-n}$ [18], where C_s is the weight fraction of the substance present at the DTG peak temperature T_s, given by

$$C_s = (W_s - W_f)/(W_0 - W_f) \tag{6}$$

was used for determining the values of reaction order. Here W_s stands for the weight remaining at a given temperature T_s, i.e. the DTG peak temperature, W_0 and W_f are the initial and final weights of the substance, respectively. The order of the dehydration reaction of $ML \cdot nH_2O$ complexes is obtained by comparing the C_s value yielded by the above equation with the values given in the Horowitz and Metzger [18] table. The values of C_s for the copper, nickel, and cobalt complex are 0.366, 0.3636, and 0.37, respectively. Therefore, the calculated order in each case shows that the dehydration follows first-order kinetics.

Evaluation of other kinetic parameters

The activation energy E^* and the frequency factor Z for the first order kinetics of dehydration have been calculated by the Fuoss Method [19], using the following equations:

$$E^* = -\left(\frac{RT_i^2}{W_i}\right)\left(\frac{dW}{dT}\right)_i \tag{7}$$

$$Z = -\left(\frac{a}{W_i}\right)\left(\frac{dW}{dT}\right)_i \exp(E^*/RT_i) \tag{8}$$

where R is the gas constant, T_i is the inflection temperature (measured in K), W_i is the weight at the point on the TG curve where it goes from concave-down to concave-up, $(dW/dT)_i$ is the rate of change of weight at the point of inflection i.e. corresponding inflection slope, and a is the heating rate.

Equations (9), (10) and (11) are employed for calculating the activation entropy S^*, the free energy of activation G^* and the specific reaction rate constant k_r [20], respectively.

$$S^* = 2.303\left(\log\frac{Zh}{kT}\right)R \tag{9}$$

$$G^* = H^* - T_iS^* \tag{10}$$

$$k_r = Z\exp(-E^*/RT_i) \tag{11}$$

where k and h are the Boltzmann and Planck constant, respectively. The kinetic parameters thus obtained are compiled in Table 3.

Perusal of Table 3 shows that the activation energies for the splitting of H_2O–Co, H_2O–Ni and H_2O–Cu bonds lie around 18.04, 18.94 and 20.96 kcal mol^{-1}, respectively, with an estimated uncertainty of ± 0.55 kcal mol^{-1}. These values are comparable to the generally accepted values of the activation energy of the dehydration reaction [21] and are also consistent with those reported by Khadikar [22].

The negative value of the activation entropy suggests that the thermal dehydration reaction is slower. This is clearly borne out from the shape of the corresponding TG curve.

Binding strength of the water molecules

The order of binding strength of the water molecules to the metal(II) ions is shown clearly from the temperature range over which these chelates are dehydrated. The dehydration temperatures are found in the order $Cu > Ni > Co$. It is also noteworthy that for dehydration of these complexes, more quantitative evidence for the binding strength of water molecules in the chelates is obtained from the corresponding values of activation energy, which are also found in the order given above.

REFERENCES

1 D.E. Metzler, J. Am. Chem. Soc., 79 (1957) 485.
2 D.E. Metzler and E.E. Snell, J. Am. Chem. Soc., 74 (1952) 979.
3 D.E. Metzler and E.E. Snell, J. Biol. Chem., 198 (1952) 353, 363.
4 G.L. Eichhorn and J.W. Dawes, J. Am. Chem. Soc., 76 (1954) 5663.
5 R.C. Burrows and J.C. Bailar, Jr., J. Am. Chem. Soc., 88 (1966) 4150.
6 G.N. Weinstein, M.J. O'Connor and R.H. Holm, Inorg. Chem., 9 (1970) 2104.
7 G.O. Carlisle and L.J. Theriot, J. Inorg. Nucl. Chem., 35 (1973) 2093.
8 L.J. Theriot, G.O. Carlisle and H.J. Hu, J. Inorg. Nucl. Chem., 31 (1969) 2841, 2891 and 3303.
9 T. Ueki, T. Ashida, Y. Sasada and M. Kakudo, Acta Crystallogr., 22 (1967) 870.
10 V.V. Ramanujam and B. Sivasankar, J. Indian Chem. Soc., 58 (1981) 1152; Ind. J. Chem., 20A (1981) 749.
11 M. Singh, Synth. React. Inorg. Met. Org. Chem., 15 (1985) 235.
12 N.S. Biradar, V.L. Roddabasanagoudar and T.M. Aminabhavi, Polyhedron, 3 (1984) 575.
13 T.M. Aminabhavi, N.S. Biradar, G.V. Karatagi and W.E. Rudzinski, Inorg. Chim. Acta, 91 (1984) 49.
14 M. Singh, Thermochim. Acta, 99 (1986) 253.
15 M. Nath, N. Sharma and C.L. Sharma, Thermochim. Acta, 149 (1989) 173.
16 Powder Diffraction File sets 1–10, Joint Committee on Powder Diffraction Standards, Philadelphia, PA, 1967, pp. 5–661, 02-770 and 04-835.
17 M. Singh, Synth. React. Inorg. Met. Org. Chem., 16 (1986) 915.
18 H.H. Horowitz and G. Metzger, J. Anal. Chem., 35 (1963) 1464.
19 R.M. Fuoss, I.O. Salyer and H.S. Wilson, J. Polym. Sci., Pt.A, 2 (1964) 3147.
20 S. Glasstone, Textbook of Physical Chemistry, 2nd edn., Macmillan, India, 1974, p. 1103.
21 I.S. Rossonskaya, Thermal Analysis, Vol. II, Academic Press, New York, NY, 1963.
22 P.V. Khadikar, Thermochim. Acta, 124 (1988) 371.