Thermochimica Acta, 116 (1987) 275–284
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL STUDIES ON PYRIDINE-2,3-DICARBOXYLIC ACID COMPOUNDS OF MANGANESE(II), IRON(II), COBALT(II) AND NICKEL(II)

J.R. ALLAN, M. BARRON and A.R. WERNINCK

Department of Applied Chemical Sciences, Napier College, Edinburgh (Gt. Britain)

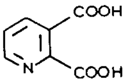
(Received 12 December 1986)

ABSTRACT

Some new compounds of pyridine-2,3-dicarboxylic acid with manganese(II), iron(II), cobalt(II) and nickel(II) have been prepared in aqueous solution. The thermal behaviour of these compounds has been studied by thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques. The compounds are all hydrated. Thermal decomposition studies show that these compounds lose water followed by organic ligand to give the metal oxide.

INTRODUCTION

This work is a continuation and extension of previous studies on pyridine monocarboxylic acids and the first row transition elements [1,2]. Pyridine-2,3-dicarboxylic acid has two different donor sites: the oxygen atoms of the carboxylic acid groups and the nitrogen atom in the aromatic ring.



Pyridine-2,3-dicarboxylic acid (2,3H_2dpc)

This paper reports the thermal analysis studies of pyridine-2,3-dicarboxylic acid together with the complexes formed by the acid and the transition metals manganese(II), iron(II), cobalt(II) and nickel(II). Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place to the metal ion. A study of the thermal stability of pyridine-2,3-dicarboxylic acid complexes has been carried out. The compound bis(pyridine-2,3-dicarboxylato) cobalt(II) dihydrate has been reported in the literature [3]. In the present investigation a different method of preparation was used and the compound bis(pyridine-2,3-dicarboxylato) cobalt(II) trihydrate has been prepared.

0040-6031/87/$03.50

EXPERIMENTAL

Preparation of compounds

The compounds were prepared by dissolving the metal carbonate in a hot aqueous solution of pyridine-2,3-dicarboxylic acid. The excess carbonate was removed by filtration. The compound was precipitated by concentrating the solution on a steam bath.

The anhydrous compounds were obtained by heating the hydrated compounds on the thermobalance at a fixed temperature until a constant weight was obtained.

Apparatus

The infrared spectra were obtained using KBr discs (4000–600 cm^{-1}) and polyethylene discs (600–200 cm^{-1}) on a Perkin-Elmer infrared spectrophotometer (Model 598).

The electronic spectra were obtained on a Beckmann Acta M IV spectrophotometer as solid diffuse reflectance spectra.

Magnetic measurements were carried out by the Gouy method using $Hg(Co(SCN)_4)$ as calibrant. Each magnetic moment has been corrected for diamagnetism using Pascal's constants [4].

The thermal analysis studies were carried out on a Stanton-Redcroft (Model STA 781) thermobalance and a Mettler differential scanning calorimeter (DSC TA 3000). Thermogravimetric curves were obtained at a heating rate of 6 °C min^{-1} in static air. In all cases, the 20–500 °C temperature range was studied. DSC curves were obtained at a heating rate of 10 °C min^{-1} in a stable atmosphere of air in the 30–400 °C range.

The concentration of the metal ion was obtained using a Perkin-Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses were carried out using a Carlo Erba elemental analyser.

RESULTS AND DISCUSSION

The compounds prepared (Table 1) have stoichiometry $M(2,3dpc) \cdot xH_2O$, where $x = 2$ for manganese and $x = 3$ for iron, cobalt and nickel.

The electronic spectra (Table 2) and the magnetic measurements (Table 1) would suggest that for the cobalt and nickel compounds the metal ion is in an octahedral environment [2,5]; the values for Dq are in agreement with this suggestion [6]. The values for β show a degree of ionic character in the metal–ligand bonds. The band in the electronic spectrum of the iron compound at 19950 cm^{-1} is typical of a charge transfer band found in six-coordinate iron(II) compounds. [7]. The iron compound has a magnetic

TABLE 1

Analyses of compounds and magnetic moments

Compound	Theory (%)				Experiment (%)				μ (B.M.)
	M	C	H	N	M	C	H	N	
Mn(2,3dpc)·$2H_2O$	21.46	32.82	2.73	5.47	20.66	31.94	1.92	4.51	5.96
Mn(2,3dpc)	24.97	38.19	1.36	6.36	23.81	37.02	1.03	5.11	
Fe(2,3dpc)·$3H_2O$	20.32	30.56	2.54	5.09	20.46	29.84	2.02	4.11	4.24
Fe(2,3dpc)	25.28	38.06	1.35	6.33	25.10	37.62	1.05	6.02	
Co(2,3dpc)·$3H_2O$	21.20	30.24	3.23	5.03	20.72	29.42	2.95	4.62	4.58
Co(2,3dpc)	26.31	37.51	1.33	6.25	25.14	36.82	0.96	5.66	
Ni(2,3dpc)·$3H_2O$	21.14	30.27	3.24	5.04	20.42	29.32	3.14	4.66	3.01
Ni(2,3dpc)	26.24	37.55	1.34	6.25	26.04	35.94	0.94	5.82	

TABLE 2

Electronic spectral details of the prepared compounds

Compound	Peak positions (cm^{-1})	*Dq*	*B*	β
Fe(2,3dpc)·$3H_2O$	$\nu_1 = 19950$ sh			
Co(2,3dpc)·$3H_2O$	$\nu_1 = 8511$ $\nu_3 = 19910$	966	836	0.80
Ni(2,3dpc)·$3H_2O$	$\nu_1 = 6756$ $\nu_2 = 10860$ $\nu_3 = 18870$	675	813	0.83

sh, Shoulder.

moment of 4.24 B.M. No information is available on the stereochemistry of the manganese compound from the electronic spectrum and the magnetic moment since no *d–d* bands were observed in the electronic spectrum and the magnetic moment is similar to the spin-only value.

Table 3 lists the main bands in the infrared spectrum of the compounds. The infrared spectra of the compounds show a strong broad absorption band in the region 3510–3100 cm^{-1}, ν_{O-H} indicating the presence of water

TABLE 3

Infrared spectra (4000–200 cm^{-1}) for the isolated compounds

Compounds	$\nu_{O-H}(H_2O)$ (cm^{-1})	ν_{COOH} (cm^{-1})	ν_{COO^-} (cm^{-1})	Ring vibrations (cm^{-1})	ν_{C-O} (cm^{-1})	ν_{M-O} (cm^{-1})
2,3 H_2dpc		1701 m		1579 m 1459 m	1440 s	
Mn(2,3 dpc)·$2H_2O$	3500–3150 br,s		1610 m	1582 m 1462 m	1382 s	290 w, 250 w
Fe(2,3 dpc)·$3H_2O$	3500–3100 br,s		1626 m	1581 m 1462 m	1376 s	260 w
Co(2,3 dpc)·$3H_2O$	3500–3100 br,s		1615 m	1581 m 1461 m	1370 s	265 w
Ni(2,3 dpc)·$3H_2O$	3510–3100 br,s		1628 m	1582 m 1461 m	1378 s	270 w

br, Broad; m, medium; s, strong; w, weak.

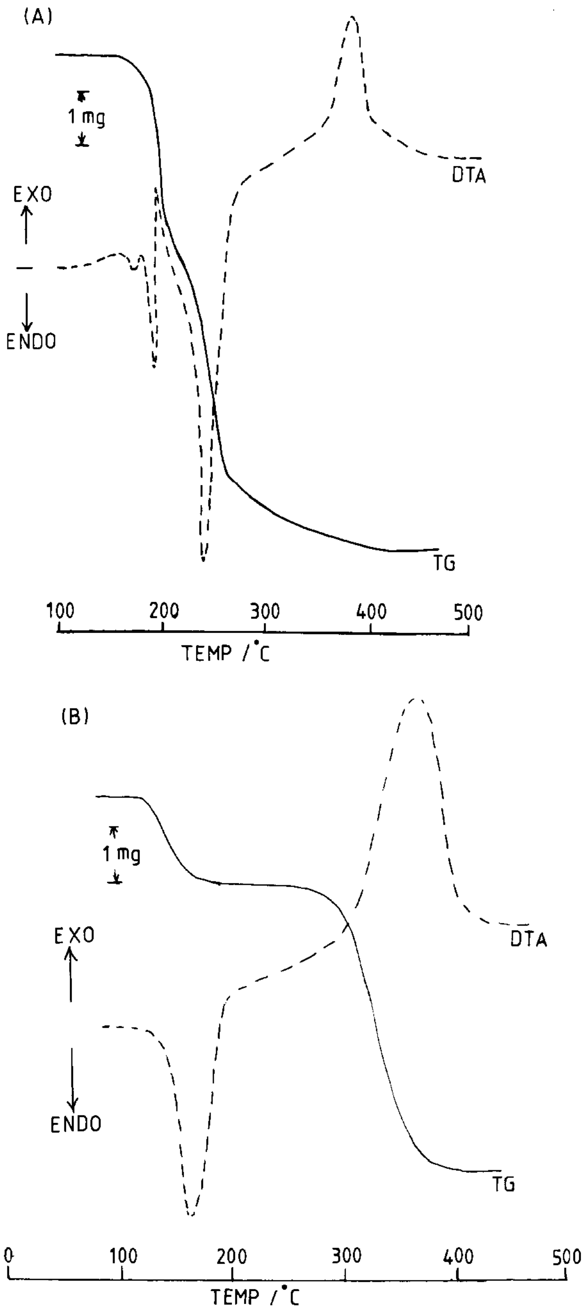


Fig. 1. Thermogravimetric and differential thermal analysis curves for (A) pyridine-2,3-dicarboxylic acid, sample weight 9.20 mg; (B) Mn(2,3dpc)·$2H_2O$, sample weight 9.60 mg; (C) Fe(2,3dpc)·$3H_2O$, sample weight 9.80 mg; (D) Co(2,3dpc)·$3H_2O$, sample weight 8.54 mg; (E) Ni(2,3dpc), sample weight 9.09 mg.

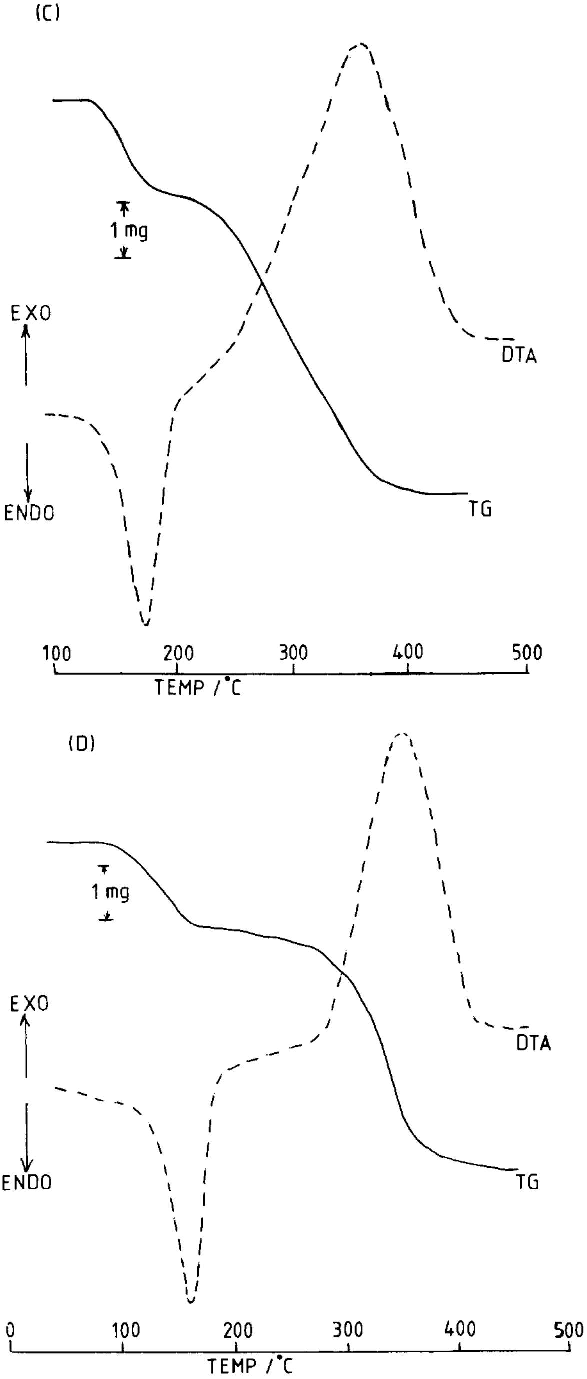


Fig. 1 (continued).

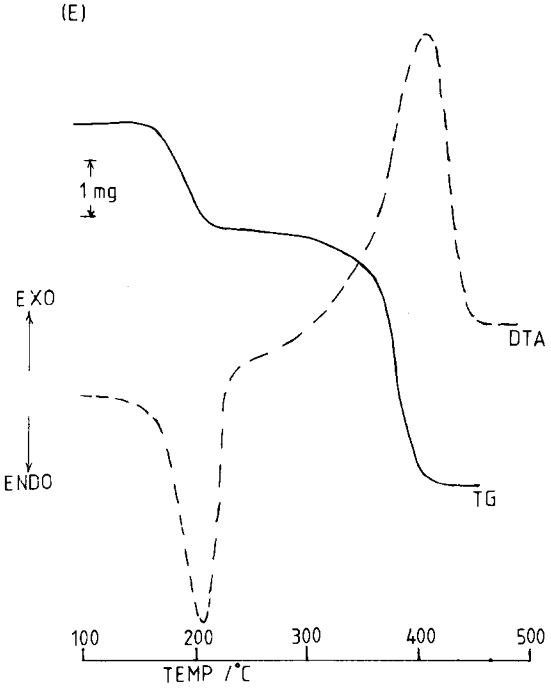


Fig. 1 (continued).

of crystallisation. The compounds show an absorption band around 1620 cm^{-1} due to the stretching vibration of the carboxylate groups linked to the metal ions. An increase in carboxylate resonance causes single-bond character in the carbonyl group which is observed by a lowering of the frequency of the C=O stretching vibration [8–10]. A change to higher frequency of the bands due to the ring vibrations of the pyridine ring is also observed, suggesting that coordination takes place through the nitrogen atom of the pyridine ring and the metal atom [1,2]. Metal–oxygen bands are also reported for each of the compounds. The metal–oxygen bands for the manganese compound would suggest a six-coordinate environment for the manganese atom [11].

The insolubility of the compounds in both polar and non-polar solvents is indicative of polymeric structures [2].

The fact that the compounds were isolated as powders and not as single crystals means that no complete structure determination can be made. However, spectroscopic and magnetic data enable us to predict that the metal ions are in an octahedral environment in the compounds. The compounds are considered to have a planar arrangement formed between two molecules of the dicarboxylate and the metal ion. The ring nitrogen atom and an oxygen atom of one of the carboxyl groups for the carboxylate ion are considered to be involved in coordination to the metal. An oxygen atom of the remaining carboxyl group is considered to be coordinated to an equivalent nearby metal atom in a neighbouring unit to give a polymeric structure. It is further suggested that the water molecules are attached to the structure by hydrogen bonding.

The TG, DTA and DSC curves for pyridine-2,3-dicarboxylic acid show that the acid is thermally stable in the temperature range 20–170 °C. Its pyrolytic decomposition begins at 170 °C and finishes at 456 °C with the total elimination of the sample. The DSC curve of pyridine-2,3-dicarboxylic acid shows an endothermic peak at 170 °C due to melting. The acid then

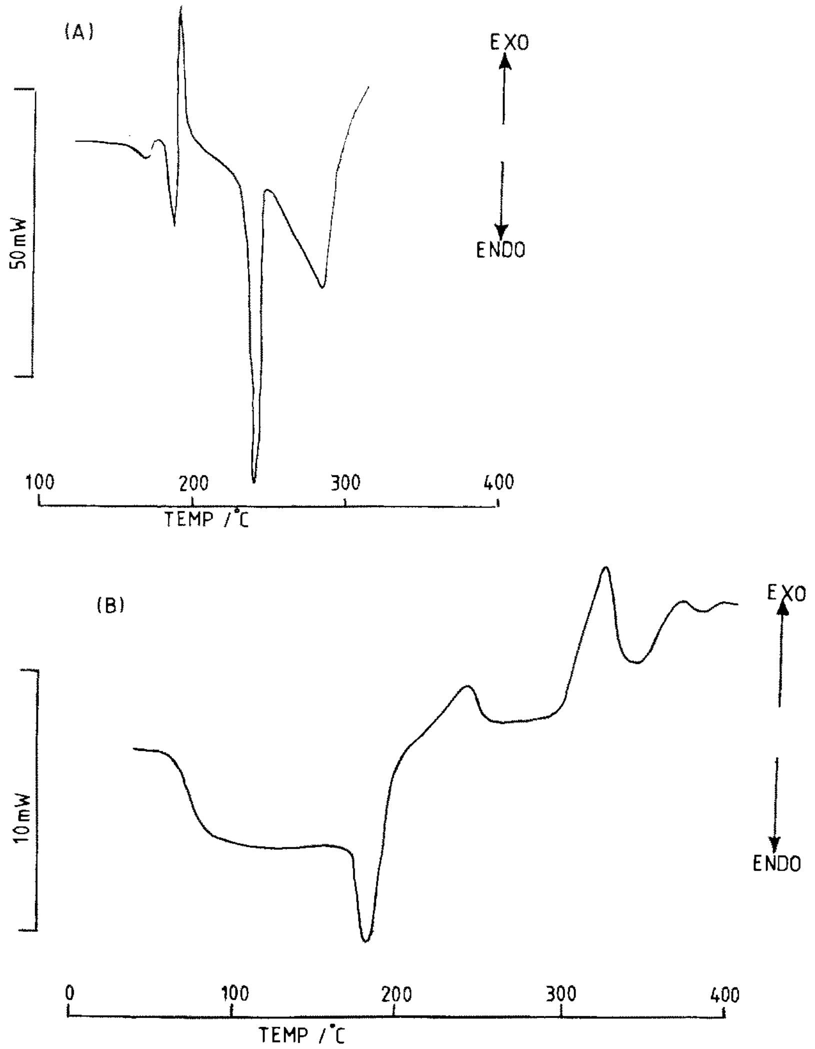


Fig. 2. DSC curves for (A) pyridine-2,3-dicarboxylic acid, (B) Mn(2,3dpc)·$2H_2O$, (C) Fe(2,3dpc)·$3H_2O$, (D) Co(2,3dpc)·$3H_2O$, (E) Ni(2,3dpc)·$3H_2O$.

decomposes immediately producing an exothermic peak at 184°C and an endothermic peak at 236°C. The TG/DTA and DSC curves for the complexes formed between pyridine-2,3-dicarboxylic acid and manganese(II), iron(II), cobalt(II) and nickel(II) are given in Figs. 1 and 2. The TG/DTA and DSC curves for the complexes are similar. The dehydration of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values (Table 4). The expected endothermic peak for the dehydration processes associated with

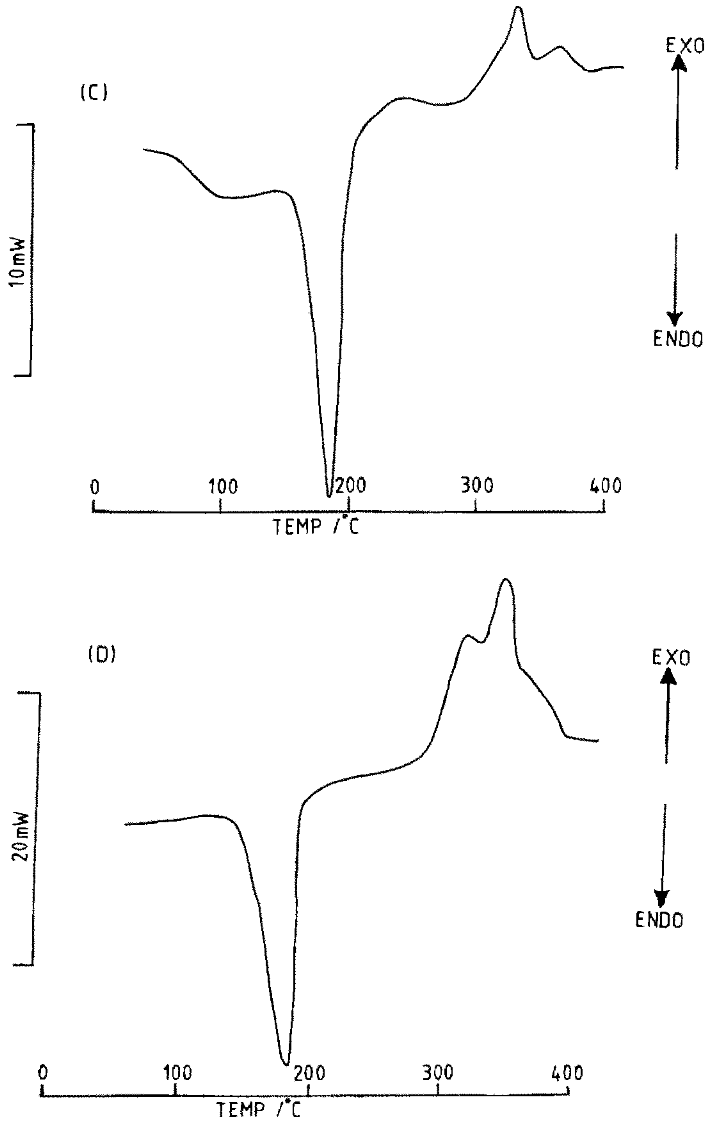


Fig. 2 (continued).

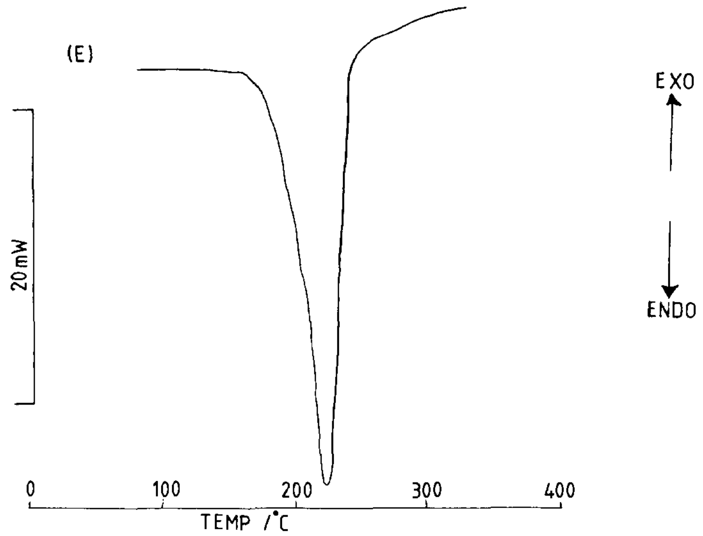


Fig. 2 (continued).

these compounds has been observed in their DSC and DTA curves. The dehydration enthalpies have been calculated and are given in Table 4. Decomposition of the anhydrous complexes follows immediately after the

TABLE 4

Dehydration processes of the pyridine-2,3-dicarboxylic acid metal complexes

Process	Initial temp. of decomposition (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
Mn(2,3dpc)·$2H_2O$ → Mn(2,3dpc)	102	endo	14.06	15.41	10.35
Fe(2,3dpc)·$3H_2O$ → Fe(2,3dpc)	128	endo	19.64	19.38	55.31
Co(2,3dpc)·$3H_2O$ → Co(2,3dpc)	94	endo	19.42	18.73	133.40
Ni(2,3dpc)·$3H_2O$ → Ni(2,3dpc)	141	endo	19.44	19.80	222.61

TABLE 5

Decomposition processes of the pyridine-2,3-dicarboxylic acid and the metal complexes

Process	Temp. range (°C)	Thermal nature of transformation	Residue weight loss (%)	
			Calc.	Found
2,3H_2dpc → pyrolytic process	170–456	endo/exo	–	–
Mn(2,3dpc) → Mn_3O_4	180–419	exo	29.79	28.12
Fe(2,3dpc) → Fe_2O_3	192–494	exo	30.12	28.57
Co(2,3dpc) → Co_3O_4	184–450	exo	28.84	29.74
Ni(2,3dpc) → NiO	236–414	exo	26.89	26.40

dehydration process and the residual weights are in good agreement with the values required for the metallic oxides. In the DSC and DTA curves, these decomposition processes correspond to exothermic effects for the complexes.

Thermogravimetric studies reported on the compound bis(pyridine-2,3-dicarboxylato) cobalt(II) dihydrate have shown that it dehydrates in one step beginning at 195 ° C followed by loss of organic ligand to give Co_3O_4 [3]. In the present investigation the compound bis(pyridine-2,3-dicarboxylato) cobalt(II) trihydrate dehydrates in one step beginning at 94 ° C followed by loss of the organic ligand to give Co_3O_4.

REFERENCES

1 J.R. Allan, G.M. Ballie and N.D. Baird, J. Coord. Chem., 10 (1980) 171.
2 J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79.
3 A. Tenhunen, Acta Chem. Scand., 26 (1972) 1291.
4 B.N. Figgis and J. Lewis, in J. Lewis and R.G. Wilkins (Eds.), Modern Coordination Chemistry, Interscience, New York, 1960, p. 403.
5 R.W. Matthews, A.D. Hamer, D.L. Hoof, D.C. Tisley and R.A. Walton, J. Chem. Soc., Dalton Trans., (1973) 1035.
6 A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, London, 1968, pp. 324 and 336.
7 K. Madija and E.T. Konig, J. Inorg. Nucl. Chem., 25 (1963) 377.
8 M.L. Morris and D.H. Bush, J. Am. Chem. Soc., 78 (1956) 5178.
9 R.C. Paul and S.L. Chadha, J. Inorg. Nucl. Chem., 31 (1969) 2753.
10 R.C. Paul and S.L. Chadha, Indian J. Chem., 8 (1970) 739.
11 R.H. Nuttall and G.A. Melson, J. Inorg. Nucl. Chem., 25 (1969) 2979.