Thermochimica Acta, 124 (1988) 345–357
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL AND ELECTRICAL STUDIES ON PYRAZINE-2,3-DICARBOXYLIC ACID COMPOUNDS OF MANGANESE(II), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II)

J.R. ALLAN and A.D. PATON

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

K. TURVEY

Department of Physics, Napier College, Edinburgh (Gt. Britain)

H.J. BOWLEY and D.L. GERRARD

British Petroleum Research Centre, Sunbury, Middlesex (Gt. Britain)

(Received 20 May 1987)

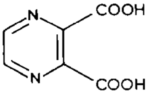
ABSTRACT

Some new compounds of pyrazine-2,3-dicarboxylic acid with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) have been prepared in aqueous solution. The thermal behaviour of these compounds has been studied by thermogravimetry (TG), 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. Electrical conductivity measurements were made at room temperature. Ohmic and space charge limited conduction is observed. A current component opposing the applied voltage is observed in the compounds, with the exception of the copper compound.

INTRODUCTION

This work is a continuation and extension of previously reported studies on pyrazine compounds and the first row transition elements [1,2]. Pyrazine-2,3-dicarboxylic acid has two different donor sites: the oxygen atoms of the carboxylic acid groups and the nitrogen atoms in the aromatic ring.

This paper reports the thermal analysis studies of pyrazine-2,3-dicarboxylic acid together with the complexes formed by the acid and the transition



Pyrazine-2,3-dicarboxylic acid (2,3-H_2dpyc).

0040-6031/88/$03.50

metals manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II). Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place with the metal ion. The results of electrical conductivity studies on the complexes at room temperature are also reported.

EXPERIMENTAL

Preparation of compounds

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

Apparatus

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

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 MIV 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 [3].

The thermal analysis studies were carried out on a Stanton Redcroft model STA 781 thermobalance and a Mettler differential scanning calorimeter (DSC TA 3000). Thermogravimetry 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 30–500 °C range.

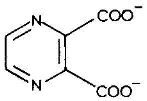
Room temperature electrical properties were investigated by obtaining the current (I) vs. voltage (V) characteristics on discs of the compounds. These discs, of diameter 13 mm and thickness in the range 0.6–1.1 mm, were prepared by compressing powder in a hydraulic press set to apply a force of 100 kN. A silver-based conducting paint was used to form circular electrodes of diameter 5.9 mm on each side of the discs. The current through each disc was measured for a series of applied voltages in the range 0–300 V using a Keithley 610C electrometer in a d.c. circuit. Further measurements were taken with reversed polarity and it was found that the current for any

TABLE 1

Analyses of compounds and magnetic moments

Compound	Theory (%)				Experimental (%)				μ (B.M.)
	Metal	Carbon	Hydrogen	Nitrogen	Metal	Carbon	Hydrogen	Nitrogen	
Mn(2,3-dpyc)·$3H_2O$	19.82	25.98	3.64	10.10	19.61	25.22	2.98	9.51	5.68
Co(2,3-dpyc)·$2H_2O$	22.87	27.47	3.05	10.68	22.24	26.66	2.77	10.02	4.81
Ni(2,3-dpyc)·$2H_2O$	22.50	27.60	3.06	10.73	22.12	26.95	3.01	10.41	3.32
Cu(2,3-dpyc)·H_2O	25.64	29.07	1.61	11.30	24.81	28.22	0.98	11.01	1.91
Zn(2,3-dpyc)·$2H_2O$	24.43	26.71	2.99	10.46	24.01	26.13	2.09	9.81	–

2,3-dpyc =



given voltage agreed to within 10%, indicating that the contacts were not blocking. The thickness of each disc was measured using a micrometer.

RESULTS AND DISCUSSION

The compounds prepared (see Table 1) have stoichiometry M(2,3-dpyc)·xH_2O where for cobalt, nickel and zinc $x = 2$; copper $x = 1$; manganese $x = 3$.

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 [4]. No information is available on the stereochemistry of the manganese compound since no *d–d* bands were observed in the electronic spectrum. The magnetic moment for the compound corresponds to five unpaired electrons suggesting either a tetrahedral or octahedral structure. The position of the band in the electronic spectrum of the copper compound would indicate that the metal ion is in a octahedral environment [5]. The magnetic moment for this compound is similar to the spin-only value.

In Table 3 the main bands in the infrared spectra of the compounds are listed. The infrared spectra of the compounds show a strong absorption band in the region 3700–2650 cm^{-1}, ν_{O-H} indicating the presence of water of crystallisation. The compounds show an absorption band around 1635 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 C–O stretching vibration [6–8]. The bands due to the ring vibrations of the pyrazine molecule [9] are found to move to higher frequency in the compounds suggesting that coordination is taking place through the nitrogen atoms of the aromatic ring and the metal atom [4]. Metal–oxygen bands are also reported for each of the compounds and would suggest that the metal ions are in a six-coordinate environment [2,10]. The insolubility of the

TABLE 2

Electronic spectral details of prepared compounds

Compound	Peak positions (cm^{-1})	d–d Transition
Co(2,3-dpyc)·$2H_2O$	8000	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	20000	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
Ni(2,3-dpyc)·$2H_2O$	9259	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	13698	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	26666	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
Cu(2,3-dpyc)·H_2O	15748	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$

TABLE 3

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

Compounds	$\nu_{O-H}(H_2O)$	ν_{COOH}	ν_{COO^-}	Ring vibrations	ν_{C-O}	ν_{M-O}
2,3-H_2dpyc		1752 (s)		1442 (m) 1017(m)	1400 (m)	
Mn(2,3-dpyc)·$3H_2O$	3700–2744 (br,s)		1635 (s)	1457 (m) 1030 (m)	1390 (m)	255 (w)
Co(2,3-dpyc)·$2H_2O$	3700–2730 (br,s)		1625 (s)	1450 (m) 1020 (m)	1392 (m)	260 (w)
Ni(2,3-dpyc)·$2H_2O$	3700–2680 (br,s)		1642 (s)	1450 (m) 1026 (m)	1392 (m)	258 (w)
Cu(2,3-dpyc)·H_2O	3600–2660 (br,s)		1642 (s)	1422 (m) 1019 (m)	1390 (m)	267 (w)
Zn(2,3-dpyc)·$2H_2O$	3600–2650 (br,s)		1630 (s)	1450 (m) 1036 (m)	1392 (m)	261 (w)

Symbols: br, broad; m, medium; s, strong;, w, weak.

compounds in both polar and non-polar solvents is indicative of polymeric structures [4].

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 in the compounds the metal ions are in an octahedral environment. It is suggested that in these compounds, for each molecule of pyrazine-2,3-dicarboxylic acid two ring nitrogen atoms and the two oxygen atoms of each carboxyl group are used in forming coordinate bonds with the metal atom. A ring nitrogen atom and one of the oxygen atoms of the carboxyl group is coordinated to a metal atom to give a planar arrangement while the remaining oxygen atom of each carboxyl group is coordinated to an equivalent nearby metal atom in a neighbouring unit to give a polymeric structure. This means that each metal atom has a coordination number of six and is in an octahedral environment. The water molecules are attached by hydrogen bonding.

The TG and DSC curves for pyrazine-2,3-dicarboxylic acid show that the acid is thermally stable in the temperature range 20–138 °C. Its pyrolytic decomposition begins at 138 °C and finishes at 400 °C with the total elimination of the sample. The DSC curve of pyrazine-2,3-dicarboxylic acid shows an endothermic peak at 189.4 °C due to melting. The acid then decomposes immediately producing an exothermic peak at 194.5 °C and an endothermic peak at 229 °C.

The TG and DSC curves for the complexes are given in Figs. 1, 3 and 4. 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 these compounds has been observed in their DSC curves. The dehydration enthalpies have been calculated and are given in Table 4. The decomposition of the anhydrous complexes follows immediately after the dehydration process and the residual weights are in good agreement with the values obtained for the metallic oxides. In the DSC curves, these decomposition processes correspond to exothermic effects for the manganese, copper and zinc compounds; endothermic and exothermic effects for the cobalt and nickel compounds.

The I–V characteristic for Cu(2,3-dpyc) · H_2O is linear and passes through the origin. Assuming the current density vector to be normal to the electrodes, the conductivity at 290 K as determined from the gradient of the characteristic is $3.5 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$.

For Mn(2,3-dpyc) · $3H_2O$ the I–V characteristic (Fig. 5) shows that a current flows at zero voltage and current is in opposition to the applied field until $V = 130$ V. For $V > 200$ V the characteristic becomes linear and the conductivity obtained from the gradient in this region is $8.5 \times 10^{-11}\ \Omega^{-1}\ m^{-1}$. The negative current was reproducible and was also observed in all other discs of the same compound. Bässler et al. [11] have observed a current

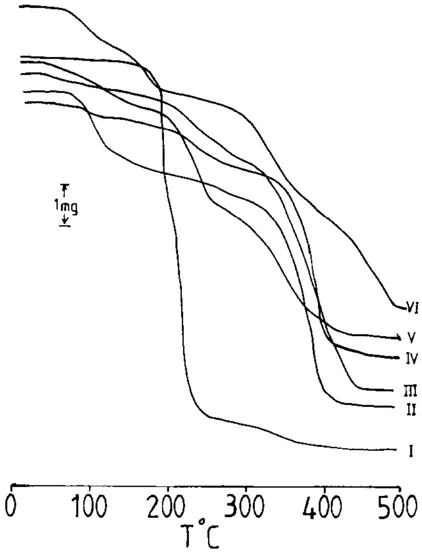


Fig. 1. I, thermogravimetric analysis curve for pyrazine-2,3-dicarboxylic acid, sample weight 9.30 mg; II, thermogravimetric analysis curve for Mn(2,3-dpyc)·$3H_2O$, sample weight 10.20 mg; III, thermogravimetric analysis curve for Co(2,3-dpyc)·$2H_2O$, sample weight 9.87 mg; IV, thermogravimetric analysis curve for Ni(2,3-dpyc)·$2H_2O$, sample weight 9.18 mg; V, thermogravimetric analysis curve for Cu(2,3-dpyc)·H_2O, sample weight 10.01 mg; VI, thermogravimetric analysis curve for Zn(2,3-dpyc)·$2H_2O$, sample weight 9.75 mg.

at zero voltage in anthracene crystals to which a voltage had previously been applied and they attributed this current to thermal release of electrons from a spatially asymmetric trap distribution. However, in the present work the disc had not previously been under applied voltage and also the current at

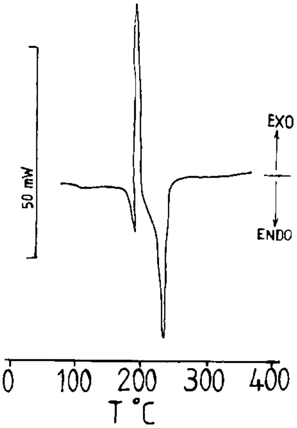


Fig. 2. DSC curve for pyrazine-2,3-dicarboxylic acid.

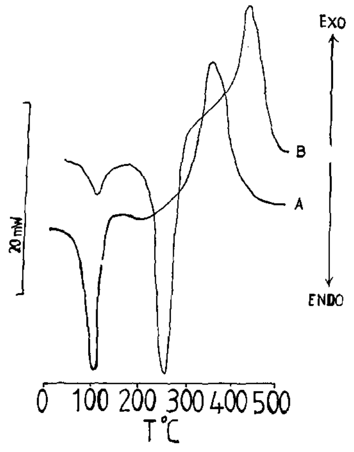


Fig. 3. A, DSC curve for Mn(2,3-dpyc)·$3H_2O$; B, DSC curve for Ni(2,3-dpyc)·$2H_2O$.

zero voltage showed no change when the disc was heated to 340 K in a stream of warm air. It is therefore concluded that a different mechanism operates. A further test showed that with strong illumination of the disc the zero-voltage current was unaffected, indicating that optical release of electrons is not operative. The current remained steady when observed for several minutes also indicating that traps played no role. With the same experimental arrangement and with discs of other organometallic compounds having approximately the same conductivity, the negative current was not observed [1,2].

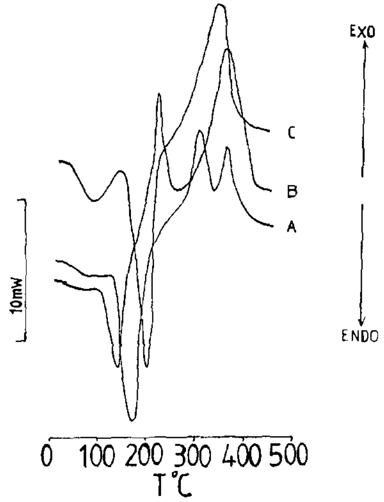


Fig. 4. A, DSC curve for Zn(2,3-dpyc)·$2H_2O$; B, DSC curve for Cu(2,3-dpyc)·H_2O; C, DSC curve for Co(2,3-dpyc)·$2H_2O$.

TABLE 4

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

Process	Peak temperature (° C)	Thermal nature of transformation	% Weight loss		Enthalpy (kJ mol^{-1})
			Calc.	Found	
2,3-H_2dpyc (s) → 2,3-H_2dpyc (l)	189	Endo	–	–	3.97
Mn(2,3-dpyc)·$2H_2O$ → Mn(2,3-dpyc)	121	Endo	19.49	19.60	93.29
Co(2,3-dpyc)·$2H_2O$ → Co(2,3-dpyc)	95	Endo	13.73	14.89	22.89
Ni(2,3-dpyc)·$2H_2O$ → Ni(2,3-dpyc)	100	Endo	13.80	10.75	10.07
Cu(2,3-dpyc)·H_2O → Cu(2,3-dpyc)	145	Endo	7.21	8.59	40.90
Zn(2,3-dpyc)·$2H_2O$ → Zn(2,3-dpyc)	178	Endo	13.44	15.89	73.66

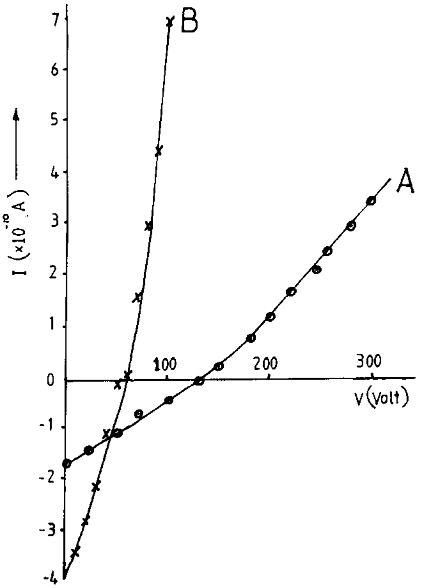


Fig. 5. Room temperature $I-V$ characteristics for Mn(2,3-dpyc)·$3H_2O$, (A) and Ni(2,3-dpyc) ·$2H_2O$, (B). Disc thicknesses 1.12 mm and 1.10 mm, respectively.

Ni(2,3-dpyc) · $2H_2O$ (Fig. 5) exhibits similar behaviour to that described for the manganese compound. The current for zero voltage was not time dependent, nor was it altered by heating or illumination.

The $I-V$ characteristic for Co(2,3-dpyc) · $2H_2O$ (Fig. 6) shows a back current which remains constant until V exceeds 60 V. When the part of the

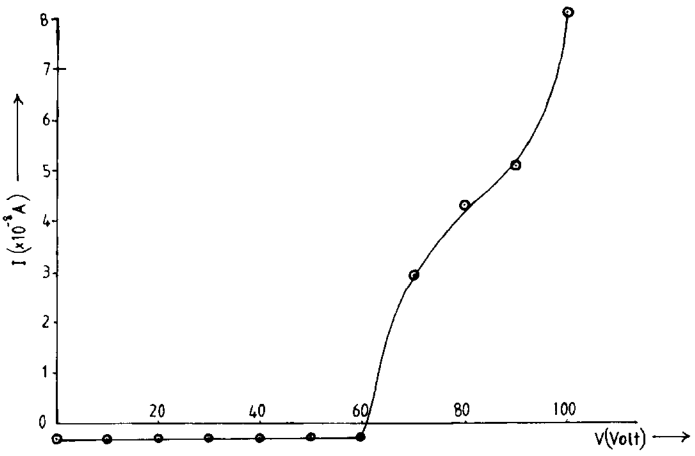


Fig. 6. Room temperature $I-V$ characteristics for Co(2,3-dpyc)·$2H_2O$. Disc thickness 0.88 mm.

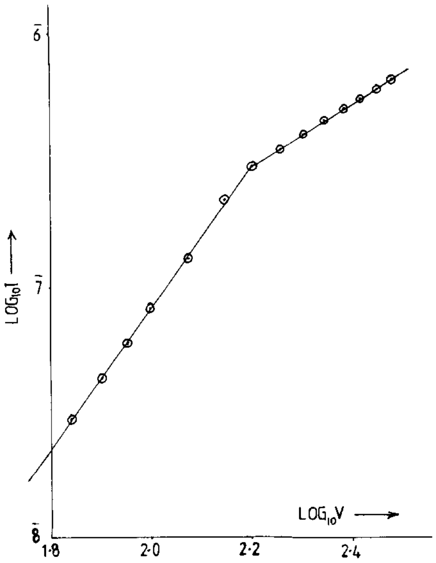


Fig. 7. Log–log plot of the room temperature I–V characteristic ($I > 0$) for Co(2,3-dpyc)·$2H_2O$, disc thickness 1.04 mm. I and V are respectively in units of amps and volts.

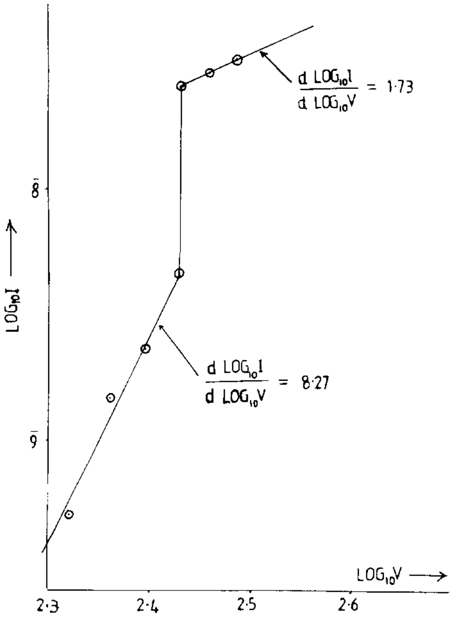


Fig. 8. Log–log plot of the room temperature I–V characteristic ($I > 0$) for Zn(2,3-dpyc)·$2H_2O$, disc thickness 1.02 mm. I and V are respectively in units of amps and volts.

TABLE 5

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

Process		Temperature range (°C)	Thermal nature of transformation	Residue % weight loss	
				Calc.	Found
2,3-H_2dpyc	→ pyrolytic process	138–400	Exo/endo	–	–
Mn(2,3-dpyc)	→ Mn_3O_4	150–436	Exo	28.51	27.45
Co(2,3-dpyc)	→ Co_3O_4	237–442	Endo/exo	30.62	29.68
Ni(2,3-dpyc)	→ NiO	248–442	Endo/exo	28.64	27.23
Cu(2,3-dpyc)	→ CuO	163–448	Exo	32.10	32.96
Zn(2,3-dpyc)	→ ZnO	198–503	Exo	29.74	30.42

characteristic covering positive I is replotted on a log–log scale (Fig. 7) the points fit to $I \propto V^{2.8}$ for $V < 160$ V and to $I \propto V^{1.3}$ for higher voltages. These results, in which an $I \propto V^m$ dependence with $m > 1$ precedes near ohmic behaviour as V is increased, suggests that in the former region the current is electrode limited [12].

The Zn(2,3-dpyc) · $2H_2O$ exhibits and I–V characteristic having a back current of 4.2×10^{-9} A for zero voltage and the current becomes positive for $V > 200$ V. The section of the characteristic for positive I when plotted on a log–log scale (Fig. 8) shows $I \propto V^{8.3}$ for $V < 270$ V, a discontinuity at $V = 270$ V and $I \propto V^{1.73}$ for $V > 270$ V. These results are consistent with space charge limited current in material having a trap distribution which varies exponentially with energy and where there is a gap between the trap distribution and the conduction or valance band edges. As the Fermi energy rises through the trap distribution there is a region in which $I \propto V^m$ with $m = 1 + T_c/T$ where T_c is a temperature characterising the distribution [13]. Putting $m = 8.3$ and $T = 290$ K yields $T_c = 2120$ K. The discontinuity in the I–V characteristic corresponds to the trap-filled limit. In the theory, beyond the trap-filled limit $I \propto V^2$ and this is close to the experimentally observed $I \propto V^{1.73}$ law.

Perhaps the most significant feature of the electrical properties of the compounds, with the exception of Cu(2,3-dpyc) · $2H_2O$, is the existence of a current component opposing the applied voltage. This property has not been observed in other organometallic compounds reported from these laboratories [1,2].

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