Thermochimica Acta, 186 (1991) 293–302
Elsevier Science Publishers B.V., Amsterdam

Preparation, structural characterisation, and thermal and electrical studies of complexes of cobalt, nickel and zinc with 2,3-pyrazinedicarboxamide

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(Received 24th January 1991)

Abstract

Compounds of 2,3-pyrazinedicarboxamide with cobalt, nickel and zinc were prepared and isolated from aqueous solution. Spectral and magnetic studies showed that the cobalt and nickel compounds have octahedral structures while the zinc compound has a tetrahedral structure. The thermal behaviour of these compounds was studied by thermogravimetry and differential thermal analysis. The compounds are hydrated and they decompose thermally by losing water, followed by organic ligand, to give the metal oxide.

Room temperature electrical conductivity measurements give results in the range 8.2×10^{-8} Ω^{-1} m^{-1} to 1.3×10^{-7} Ω^{-1} m^{-1} for the prepared compounds. A correlation between structure and electrical properties is apparent because the two complexes in which the metal environment is octahedral (i.e. the cobalt and nickel complexes) exhibit a polarity effect not observed for the zinc complex (in which the metal environment is tetrahedral). The effect is an increase in conductivity on reversal of the applied polarity but the increased conductivity remains on reinstatement of the initial polarity. The temperature dependence of the conductivity was obtained for each compound and used to infer an approximate activation energy for conduction.

INTRODUCTION

Compounds formed by the reaction of 2,3-pyrazinedicarboxamide with metal salts of cobalt, nickel and copper in acid solution and non-aqueous solvents have been reported in the literature [1,2]. In these compounds the 2,3-pyrazinedicarboxamide acts as a non-bridging chelate even though the metal-bridging properties of pyrazines are well documented. In this paper we report some novel compounds of cobalt, nickel and zinc with 2,3-pyrazinedicarboxamide. Spectral and magnetic measurements were used to characterise each of the metal complexes and to interpret the type of coordination which takes place with the metal ion. The thermal decomposition of the complexes and their electrical conductivities were studied.

EXPERIMENTAL

Preparation of the metal complexes

2,3-Pyrazinedicarboxamide (0.014 mol) was added to 75 cm^3 of water and refluxed. The metal chloride (0.007 mol) was dissolved in a minimum of water and added to the ligand solution. After 16 h of refluxing the solution was reduced in volume and the compounds isolated by filtration. The compounds were dried in an oven at 50 ° C.

Apparatus and measurement

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

The IR spectra were recorded using KBr discs over the wavenumber range 4000–600 cm^{-1} and using polyethylene discs over the range 600–200 cm^{-1} on a Perkin–Elmer IR spectrophotometer model 598.

Electronic spectra were recorded as solid diffuse reflectance spectra using a Beckmann Acta MIV spectrophotometer.

Measurements of magnetic moments were made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant.

Thermal analysis measurements were made on a Stanton Redcroft Model STA 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 ° C min^{-1} in static air. The 20–800 ° C temperature range was studied in all cases.

Electrical conductivity measurements were carried out on the complexes using the method previously described [3]. Powdered compounds were compressed using a hydraulic press set to apply a force of 100 kN to form discs of diameter 13 mm and thickness in the range 0.8–1.4 mm. Conducting silver paint electrodes 4.9 mm in diameter were applied concentrically on the flat faces of each disc. The d.c. characteristics of current (I) against voltage (V) were obtained at room temperature for each compound. A Keithley 610C electrometer was used to measure the current and a digital voltmeter was used to obtain corresponding voltages. The voltmeter was connected so that it did not interfere with the current measured by the electrometer. Readings were obtained under the following conditions: increasing voltage, decreasing voltage in the same polarity, increasing and then decreasing in the reverse polarity. The maximum voltage applied to all discs of the prepared compounds was 30 V.

Measurements were made of the temperature dependence of the conductivity by placing each disc in an oven and monitoring the current during heating whilst a constant voltage of 10 V was applied across the disc electrodes. The maximum temperature obtained during measurements was

350 K and additional current measurements were taken during the cooling cycle. The disc temperature was found from the e.m.f. of a calibrated copper–constantan thermocouple (44 SWG) with its hot junction in contact with the disc and its cold junction in melting ice.

RESULTS AND DISCUSSION

The compounds isolated from aqueous solution are listed in Table 1. It is evident from the elemental analyses that nitrogen has been lost from the ligand on complexation with the metal. It is postulated that one of the amide groups has been hydrolysed to the corresponding carboxylate group. Some experimental evidence for this conversion was obtained by refluxing a 2 : 1 molar ratio of 2,3-pyrazinedicarboxamide with the metal salt in water, then distilling and collecting the initial condensate. The condensate was found to have a $pH > 8$ due to the evolution of ammonia. The condensate was specifically tested for ammonia using Nessler's reagent [4]. A positive result was obtained for ammonia.

The electronic spectra and magnetic measurements (see Table 2) suggest that the cobalt and nickel ions are in an octahedral environment [5]. No information is available about the stereochemistry of the zinc compound

TABLE 1

Analyses of compounds (%)

Compound		Metal	Carbon	Nitrogen	Hydrogen
$Co(C_6H_4N_3O_3)_2 \cdot 4H_2O$	Theory	12.73	31.11	18.15	3.47
	Found	12.61	30.90	18.11	3.47
$Ni(C_6H_4N_3O_3)_2 \cdot 4H_2O$	Theory	12.68	31.12	18.15	3.46
	Found	12.57	30.96	18.09	3.41
$Zn(C_6H_4N_3O_3)_2 \cdot 3H_2O$	Theory	14.48	31.90	18.61	3.10
	Found	14.39	31.75	18.59	3.06

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Co(C_6H_4N_3O_3)_2 \cdot 4H_2O$	9060	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.92
	14814	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	20021(sh) [a]	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_6H_4N_3O_3)_2 \cdot 4H_2O$	6920	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.41
	16940	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
	26986	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	

[a] sh, shoulder.

TABLE 3

IR spectra (4000–200 cm^{-1}) [a]

Compound	$\nu_{O-H}(H_2O)$	$\nu_{N-H}(NH_2)$	Ring vibrations	$\nu_{C=O}(CONH_2)$	$\nu(COO^-)$	$\nu(M-O)$	$\nu(M-N)$
$C_6H_6N_4O_2$		3432(s) 3311(s)	1560(s) 621(s)	1699(s)			
$Co(C_6H_4N_3O_3)_2 \cdot 4H_2O$	3480–2850(br,s)	3550(s)	1576(s) 656(s)	1677(s)	1463(s)	316(m) Co–OH_2 292(m)	236(vw)
$Ni(C_6H_4N_3O_3)_2 \cdot 4H_2O$	3660–2760(br,s)	3444(s)	1572(s) 661(s)	1651(s)	1465(s)	319(m) Ni–OH_2 294(m)	232(vw)
$Zn(C_6H_4N_3O_3)_2 \cdot 3H_2O$	3550–2980(br,s)	3502(s)	1571(s) 656(s)	1649(s)	1466(s)	350(m)	238(vw)

[a] br, broad; s, strong; m, medium; vw, very weak.

from the electronic spectrum because the zinc ion has a d^{10} electronic configuration.

The main bands in the IR spectra of the compounds are reported in Table 3. All the compounds show a strong absorption band in the region 3660–2760 cm^{-1}, ν(OH), and in the region 1630–1580 cm^{-1}, δ(OH), indicating the presence of water which is not coordinated to the metal. The presence of coordinated water in the cobalt and nickel compounds is shown by bands at 315 and 372 cm^{-1}. These bands have been assigned to the M–OH_2 vibration [6]. In each of the compounds it is observed that the ν(C=O) and ν(N–H) bands for the amide move to lower and higher wavenumbers respectively on complexation. We thus conclude that the oxygen atom of the C=O group has bonded to a metal atom, while the nitrogen atom of the amide group has not bonded to a metal atom [7,8]. On complexation, positive shifts of the bands due to the skeletal modes of the pyrazine ring are observed, indicating coordination via one or both ring nitrogen atoms [8]. The band at around 1465 cm^{-1} in the metal complexes has been assigned to the $\nu(COO^-)$ vibration [9]. Metal–nitrogen and metal–oxygen bands have also been assigned in Table 3. The metal–oxygen bands show that the cobalt and nickel compounds have octahedral structures, in agreement with their electronic spectra, while the zinc compound has a tetrahedral structure [10].

Single crystals of the compounds could not be isolated from aqueous solution. Therefore, without X-ray analysis, no definite structures can be described. However, the spectroscopic and magnetic data suggest that for the cobalt and and nickel compounds the metal is coordinated octahedrally by two nitrogen atoms (from different pyrazine molecules) and four oxygen atoms, one of which belongs to the carboxylate group, another of which belongs to the oxygen atom of the amide group and two of which belong to coordinated water molecules. The remaining water molecules are attached by hydrogen bonding. The proposed stereochemistry for $M(C_6H_4N_3O_3)_2 \cdot 4H_2O$ is shown in Fig. 1. In the zinc compound the metal atom is coordinated tetrahedrally by two nitrogen atoms (from different pyrazines) and two oxygen atoms, one of which is from the oxygen atom of the amide group of one pyrazine molecule and the other from an oxygen atom of the carboxylate group of a different pyrazine molecule.

The TG and DTA curves for 2,3-pyrazinedicarboxamide show that it is thermally stable in the temperature range 20–235 °C. Its pyrolytic decomposition starts at 235 °C and finishes at 572 °C with the total elimination of the sample. The DTA curve for 2,3-pyrazinedicarboxamide (Fig. 2) shows an endothermic peak at 248 °C corresponding to fusion, with a specific fusion enthalpy of 20 kJ mol^{-1}. Liquid 2,3-pyrazinedicarboxamide decomposes immediately with an exothermic peak at 528 °C. The TG and DTA curves for compounds formed between 2,3-pyrazinedicarboxamide and cobalt, nickel and zinc are shown in Figs. 3–5. The dehydration of the metal complexes takes place in one step. The observed weight losses for these

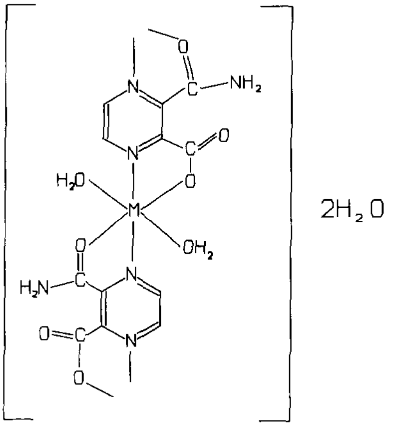

Fig. 1. Proposed structure (not to scale) for $M(C_6H_4N_3O_3)_2 \cdot 4H_2O$, where M is Co or Ni.

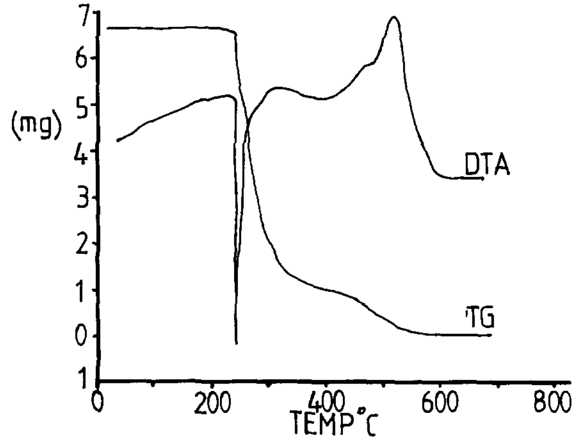

Fig. 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for 2,3-pyrazinedicarboxamide; initial sample mass, 6.70 mg.

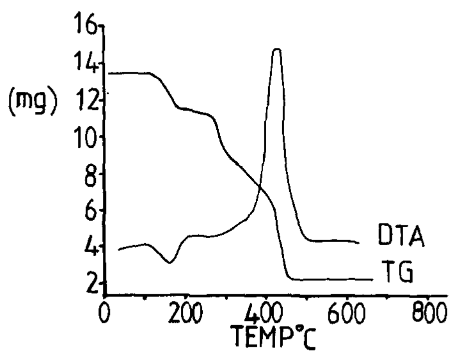

Fig. 3. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for $Co(C_6H_4N_3O_3)_2 \cdot 4H_2O$; initial sample mass, 13.45 mg.

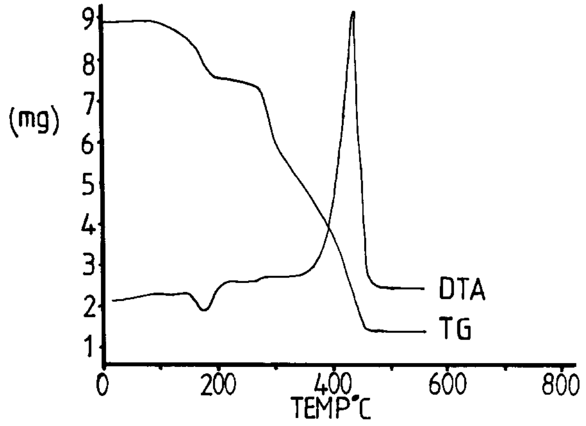

Fig. 4. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for $Ni(C_6H_4N_3O_3)_2 \cdot 4H_2O$; initial sample mass, 8.93 mg.

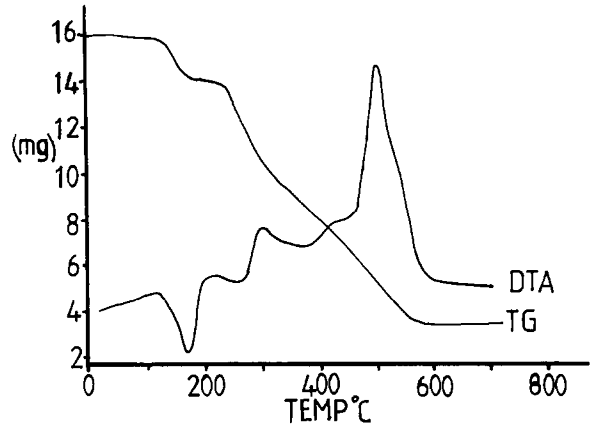

Fig. 5. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for $Zn(C_6H_4N_3O_3)_2 \cdot 3H_2O$; initial sample mass, 15.89 mg.

TABLE 4

Dehydration processes of the metal complexes

Process	Peak temp. (°C)	Thermal nature of transformation	% Weight loss		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(C_6H_4N_3O_3)_2 \cdot 4H_2O \rightarrow Co(C_6H_4N_3O_3)_2$	157	Endo	15.55	15.29	253
$Ni(C_6H_4N_3O_3)_2 \cdot 4H_2O \rightarrow Ni(C_6H_4N_3O_3)_2$	183	Endo	15.56	14.72	235
$Zn(C_6H_4N_3O_3)_2 \cdot 3H_2O \rightarrow Zn(C_6H_4N_3O_3)_2$	165	Endo	11.96	12.07	150

TABLE 5

Decomposition processes of 2,3-pyrazinedicarboxamide and its metal complexes

Process	Temp. range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_6H_6N_4O_2 \rightarrow$ pyrolytic process		Exo	–	–
$Co(C_6H_4N_3O_3)_2 \rightarrow Co_3O_4$	220–462	Exo	16.18	16.35
$Ni(C_6H_4N_3O_3)_2 \rightarrow NiO$	225–483	Exo	16.14	15.78
$Zn(C_6H_4N_3O_3)_2 \rightarrow ZnO$	200–596	Exo	18.01	19.63

processes compare favourably with the theoretical values (see Table 4). The expected endothermic peak for the dehydration processes associated with these compounds was observed in the DTA curve. The dehydration enthalpies were obtained from the curve and are listed in Table 4. The decomposition of the anhydrous compounds follows immediately after the dehydration process and the residual weights are in good agreement with the values required for the metallic oxides (Table 5). In the DTA curves these decomposition processes correspond to exothermic peaks.

The room temperature current (*I*)–voltage (*V*) characteristics, obtained under the two different polarity conditions, for a disc of nickel complex are shown in Fig. 6. Both *I*–*V* characteristics are linear except for a small curvature in the range 0–3 V. However, the magnitude of the current during reverse polarity measurements is approximately 50% greater than the current obtained from the initial polarity measurements. The effect of blocking

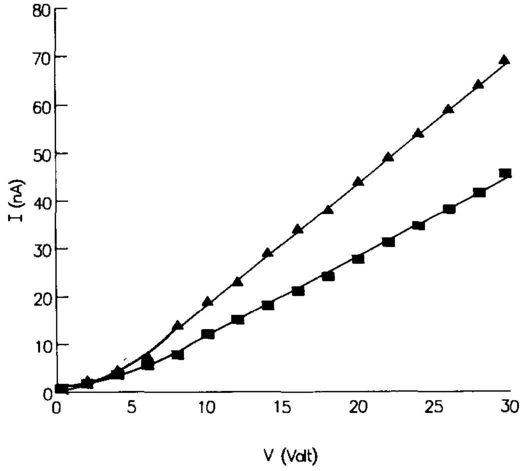

Fig. 6. Current (*I*) as a function of voltage (*V*) for a disc of $Ni(C_6H_4N_3O_3)_2 \cdot 4H_2O$ at room temperature (19 °C): data obtained under initial polarity, ■; data obtained under reversed polarity, ▲.

TABLE 6

Electrical properties of the compounds

Compound	Conductivity at room temperature [a] (Ω^{-1} m^{-1})	ΔE [b] (eV)	
		Heating	Cooling
$Co(C_6H_4N_3O_3)_2 \cdot 4H_2O$	1.3×10^{-7}	0.90	1.32
$Ni(C_6H_4N_3O_3)_2 \cdot 4H_2O$	9.1×10^{-8}	1.09	1.42
$Zn(C_6H_4N_3O_3)_2 \cdot 3H_2O$	8.2×10^{-8}	0.97	1.51

[a] Values calculated from final polarity used.

[b] ΔE is the activation energy in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$.

electrode contacts, which would inhibit current flow in one direction, is not considered plausible as further current measurements, taken when the polarity was changed back to the initial polarity, displayed the same higher values.

Similar room temperature I–V characteristics were observed for a disc of the cobalt complex. In this case the magnitude of the current when measured in the reverse polarity showed a 30% increase over the initial measurements.

For a disc of the zinc compound there was no evidence of an increase in conductivity on reversal of the polarity. The room temperature conductivities, as determined for the final polarity used, are given in Table 6.

A similar phenomenon of increasing conductivity with changing polarity was observed and reported by this laboratory for transition metal complexes of 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline [11]. In that study the occurrence of the higher conductivity values under changing polarity conditions was attributed to distortions of the ligand molecules under an applied electric field. For the present work it is of interest to note that the cobalt and nickel compounds which exhibit this polarity effect have octahedral structures, whilst the zinc compound has a tetrahedral structure and shows no polarity effect.

The temperature dependence of conductivity σ is shown in Fig. 7 for the cobalt compound as a graph of ln σ v. 10^{-3} T^{-1} where T is the absolute temperature. Linearity of such plots would show the validity of the expression $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ where σ_0 and ΔE are constants for a given compound. Possible interpretations for ΔE if the band model is assumed are that it represents the energy barrier for electron release from the valence to the conduction bands [12] or the ionisation energy for donor or acceptor centres [12].

As can be seen from Fig. 7, the experimental data obtained for the cobalt compound can only be poorly represented by a straight line and the data for the cooling part of the cycle does not reproduce the data for heating. Thermal decomposition is not the cause of the poor agreement between

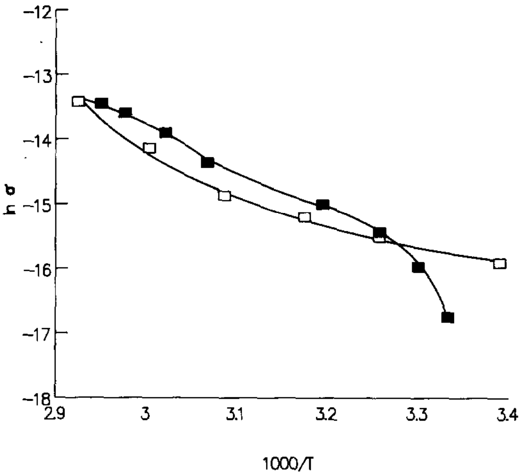

Fig. 7. Arrhenius plot (in the form of ln σ vs. $10^3/T$, where σ is the conductivity in units of Ω^{-1} m^{-1} and T is the absolute temperature) for a disc of $Co(C_6H_4N_3O_3)_2 \cdot 4H_2O$; □, points obtained during heating; ■, points obtained during cooling.

heating and cooling data because the maximum temperature reached was only 342 K which is far below that already found for the onset of decomposition. The nickel and zinc complexes exhibit a temperature dependence of conductivity similar to that described for the cobalt compound.

Values of ΔE, as calculated from the gradients of the best-fitting line using least-squares regression, are listed in Table 6. Separate ΔE values are given for the conditions of rising temperature and decreasing temperature.

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