Thermochimica Acta, 48 (1981) 253—262
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

THERMAL PROPERTIES AND SPECTROSCOPIC CHARACTERISTICS OF THE COMPLEXES OF PYRAZINE-2,3-DICARBOXYLIC ACID WITH DIVALENT METAL IONS *

A.L. MAGRÌ, A.D. MAGRÌ, F. BALESTRIERI, E. CARDARELLI, G. D'ASCENZO

Istituto di Chimica Analitica dell'Università di Roma, Rome (Italy)

A. PANZANELLI

Istituto di Chimica Analitica e Spettroscopia della Università di Sassari, Sassari (Italy)

(Received 19 December 1980)

ABSTRACT

Depending on the experimental conditions, two series of solid compounds are obtained by the reaction of pyrazine-2,3-dicarboxylic acid with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II), in keeping with the simplest formulae $(C_6H_2N_2O_4)Me(II) \cdot n\ H_2O$ and $(C_6H_3N_2O_4)_2Me(II) \cdot n\ H_2O$.

The spectroscopic characteristics (IR and diffuse reflectance), the thermal properties (TG and DSC) and the thermal stability order are reported and discussed; the structures of the compounds are also hypothesized.

INTRODUCTION

Pyrazine carboxylic acids can act as chelating agents and, depending on experimental conditions, they react with metal transition ions giving soluble and/or solid, mononuclear and/or polynuclear complexes, as shown by data reported in the international literature [1—22].

In previous papers, we have reported in detail the reaction of pyrazine-2-carboxylic (2-HL) and pyrazine-2,3-dicarboxylic (2,3-H_2L) acids with chromium(III) [20], that of 2-HL with nickel(II) and iron(II) [21] and, recently, extensive information on the synthesis, thermal properties and spectroscopic characteristics of the solid compounds obtained by the direct reaction of 2-HL with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) [22].

Following on from the last study, in this paper we report the thermoanalytical and spectroscopic behaviour of the pyrazine-2,3-dicarboxylato derivatives of the same divalent metal ions. Only partial data concerning these compounds have previously been discussed [7,10—12,19].

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* This work was supported by the National Research Council of Italy (C.N.R.).

EXPERIMENTAL

Apparatus

The physical measurement were carried out as described in a previous paper [22].

Reagents

Pyrazine-2,3-dicarboxylic acid was a purum grade product of Fluka purified by crystallization from water; its purity was checked as previously reported [20]. The metal ions were in the form of perchlorate hexahydrate (Alfa). All other chemicals were analytically pure.

Preparation of the solid compounds

Depending on the selected experimental conditions (acidity of the solution, initial ligand/metal ion molar ratio), two series of compounds were obtained.

(A) (Pyrazine-2,3-dicarboxylato)Me(II). 50 ml of 0.1 M aqueous solution of the ligand at pH 5 (adjusted by NaOH) were added with stirring to 3.6 g of $Me(ClO_4)_2 \cdot 6\ H_2O$ in 50 ml of water ($C_M/C_L = 2$).

(B) Bis(pyrazine-2,3-dicarboxylato)Me(II). 50 ml of 0.15 M aqueous solution of the ligand at pH 1.5 (adjusted by $HClO_4$) were added with stirring to 1.5 g of $Me(ClO_4) \cdot 6\ H_2O$ in 50 ml of water ($C_L/C_M = 2$).

The subsequent steps (precipitation, washing, and storage of the compounds) were carried out as previous described [22].

RESULTS

The analytical data of the A series are summarized in Tables 1 and 2 and those of the B series in Tables 3 and 4.

Because the spectroscopic characteristics and the thermal behaviour of the different compounds within each series are similar, we give below, as an example, only a brief discussion of the related studies of the two compounds obtained by the reaction of the iron(II) with the proposed ligand.

(Pyrazine-2,3-dicarboxylato)iron(II)

This red-violet compound precipitates slowly from aqueous solution. Elemental analysis for $Fe(C_6H_2N_2O_4) \cdot 2\ H_2O$ is calcd.: C 27.93%, H 2.34%, N 10.86%, Fe 21.65%, O 37.21%; found: C 27.8%, H 2.3%, N 10.9%, Fe 21.5% (by TG in air), O 37.5% (by difference).

The diffuse reflectance spectrum shows a first broad absorption band which is clearly split into two components at 9400—11 000 cm^{-1} ($^5T_{2g} \rightarrow {}^5E_g$) and a second band centered at 19 000 cm^{-1} ($t_{2g} \rightarrow \pi$C.T.) which suggest the

TABLE 1

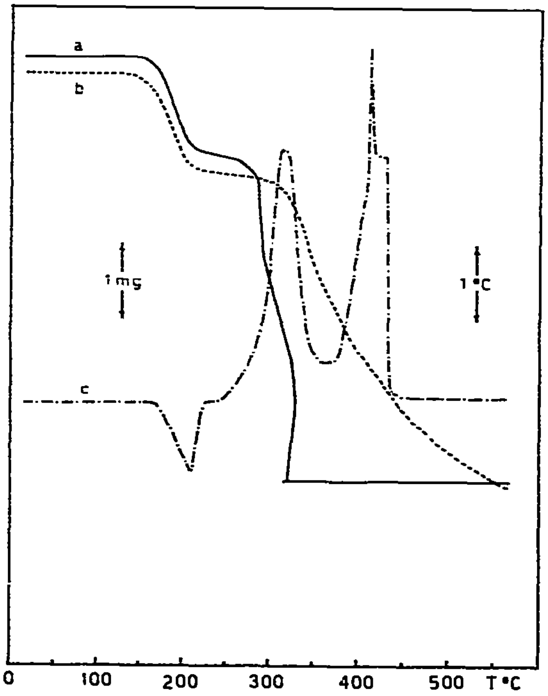
Decomposition temperatures and TG and DSC analytical data of (pyrazine-2,3-dicarboxylato) metal (II) compounds

Compound	Atmosphere	TG						DSC	
		H_2O loss			Decomp. temp. (°C)	Residual oxide		H_2O loss temp. (°C)	Decomp. temp. (°C)
		Temp. (°C)	% calcd.	% found		% calcd.	% found		
$[Mn(C_6H_2N_2O_4)2\ H_2O]_n$	N_2	90 50—120			310 →				
	Air	120 70—130	14.00	14.1	370 310—380	29.67	29.8	120 70—135	375 335—430
$[Fe(C_6H_2N_2O_4)2\ H_2O]_n$	N_2	180 120—230			260 →				
	Air	200 150—220	13.96	14.3	300 220—315	30.95	30.7	210 150—225	315—410 240—440
$[Co(C_6H_2N_2O_4)2\ H_2O]_n$	N_2	190 140—220			230 →				
	Air	205 150—230	13.79	13.7	345 230—355	28.70	28.5	210 150—230	365—415 230—430
$[Ni(C_6H_2N_2O_4)2\ H_2O]_n$	N_2	210 140—230			230 →				
	Air	230 140—250	13.80	13.9	355 250—355	28.64	28.6	240 140—255	380—415 255—425
$[Cu(C_6H_2N_2O_4)H_2O]_n$	N_2	70 30— 90			240 →				
	Air	70 30— 95	7.27	7.5	295 230—305	32.12	32.3	65 30— 90	285—305—325 235—380
$[Zn(C_6H_2N_2O_4)2\ H_2O]_n$	N_2	200 110—250			245 →				
	Air	165 120—250	13.46	13.6	330—420 250—460	30.42	30.7	180 110—225	335—465 275—490

TABLE 2

Diffuse-reflectance and IR spectroscopic data of (pyrazine-2,3-dicarboxylato) metal (II) compounds

Compound	Colour	Diffuse-reflectance absorption maxima (cm^{-1})	IR frequencies (cm^{-1})	
			$\nu_{C=O}$	ν_{C-O}
$C_6H_4N_2O_4$	White		1700	1260
$[Mn(C_6H_2N_2O_4) \cdot 2\ H_2O]_n$	Pale yellow	16 100—17 800 26 700	1640	1360
$[Fe(C_6H_2N_2O_4) \cdot 2\ H_2O]_n$	Red-violet	11 000 19 000	1620	1360
$[Co(C_6H_2N_2O_4) \cdot 2\ H_2O]_n$	Pink	8 300 20 000—21 700	1630	1360
$[Ni(C_6H_2N_2O_4) \cdot 2\ H_2O]_n$	Light blue	9 250 13 500—15 300 26 500	1640	1360
$[Cu(C_6H_2N_2O_4) \cdot H_2O]_n$	Green	16 000 24 400	1650	1330
$[Zn(C_6H_2N_2O_4) \cdot 2\ H_2O]_n$	White		1630	1360



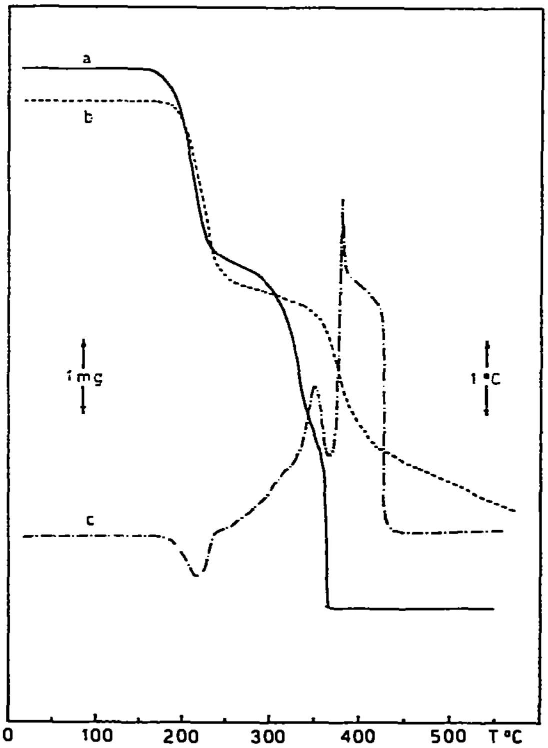


Fig. 1. TG curves of the (pyrazine-2,3-dicarboxylato)iron(II) complex (a) in air, (b) in nitrogen and (c) DSC curve in air.

Fig. 2. TG curves of the bis(pyrazine-2,3-dicarboxylato)iron(II) complex (a) in air, (b) in nitrogen and (c) DSC curve in air.

N—Fe—O sequence of the bonds, by analogy with spectrochemical series of the frequencies [23], and an octahedral coordination of this complex [24]. In its IR spectrum, the presence of very intense absorption bands at 1620 and 1360 cm^{-1}, characteristic of the covalently bonded —COO group [7,25] and the absence of the free carboxylic group centered near 1700 cm^{-1} and just below 1300 cm^{-1} [7,10], suggests that both acid groups of the ligand are employed in metal ion complexation. This hypothesis is confirmed by the thermal decomposition trend of the complex (TG in air; Fig. 1, curve a) which shows only two steps: the former agrees with the loss of two water molecules (calcd.: 13.96%; found: 1[illegible].3%) and the latter, in the temperature range 230—315°C, agrees with the oxidative decomposition process of the anhydrous compound that leads to the oxide Fe_2O_3 (calcd.: 30.95%; found: 30.7%). A free carboxylic group, thermally unstable [26], should be eliminated, as CO_2, at a lower temperature than that of the complete decomposition of the complex, but it did not occur. The TG in N_2 (Fig. 1, curve b) shows the same decomposition trend and that is also confirmed by DSC in air (Fig. 1, curve c) by an endothermic peak for the loss of water and by exothermic unresolved peaks for the oxidative decomposition of the complex (240—440°C).

Bis(pyrazine-2,3-dicarboxylato)iron(II)

The compound precipitates from aqueous solution as a dark violet crystalline solid. The simplest formula is $Fe(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$ according to the elemental and thermogravimetric analysis [calcd.: C 33.82%, H 2.36%, N 13.15%, Fe 13.11%, O 37.55%; found: C, 33.9%, H 2.3%, N 13.0%, Fe 13.0% (by TG in air), O 37.8% (by difference)]. As with the compound previously described, the iron(II) ion is chelated by nitrogen oxygen donor atoms, giving a very stable five-membered ring [27] and the complex assumes an octahedral configuration. This hypothesis is supported by spectroscopic and thermal analysis. In fact, the free carboxylic group bonds (1700—1230 cm^{-1}) and those of the covalently bonded —COO group (1640—1360 cm^{-1}) are both present in the IR spectrum. The TG curve in air (Fig. 2, curve a) shows a weight loss at 160°C that agrees with the simultaneous evolution of two water molecules plus two CO_2 molecules (calcd. 29.10%; found 28.9%) and this process, as well as the successive oxidative decomposition of the complex leading to the oxide Fe_2O_3 (calcd. 18.74%; found 18.6%) at 365°C, is confirmed by the DSC curve (Fig. 2, curve c) which shows an endothermic peak at 160°C and exothermic unresolved peaks in the temperature range 240—440°C. In N_2 atmosphere, the initial decomposition temperature is higher (280°C) and the residue does not reach constant weight (Fig. 2, curve b).

Other compounds

The following complexes complete the A series.

TABLE 3

Decomposition temperature and TG and DSC analytical data of bis(pyrazine-2,3-dicarboxylato)metal(II) compounds

Compound	Atmosphere	TG						DSC	
		$H_2O + CO_2$ loss			Decomp. temp. (°C)	Residual oxide		$H_2O + CO_2$ loss temp. (°C)	Decomp. temp. (°C)
		Temp. (°C)	% calcd.	% found		% calcd.	% found		
$Mn(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	N_2	230			300 →				
		170—300							
	Air	225	29.17	29.0	315—385	17.94	17.9	220	410
		185—280			280—410			185—265	290—440
$Fe(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	N_2	240			280 →				
		160—280							
	Air	220	29.10	28.9	310—355	18.74	18.6	215	350—375
		160—250			250—365			160—235	240—440
$Co(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	N_2	240			275 →				
		150—275							
	Air	285	28.89	29.0	345—370	17.46	17.7	215	315—360—390
		180—300			300—385			180—240	290—465
$Ni(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	N_2	225			270 →				
		180—280							

	N_2 [b]	80–140 255 195–265			265 →				
	Air [a]	105 70–125	8.30	8.4	295–330–380 265–385	18.34	18.3	105 70–125	295–355–400
	Air [b]	255 195–265	20.29	20.3				225 195–245	245–445
$Zn(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	N_2	230 160–250			270 →				
	Air	225 175–260	28.47	28.5	290–485 260–485	18.68	18.7	225 175–240	480–510 275–520

[a] H_2O loss.
[b] CO_2 loss.

TABLE 4

Diffuse-reflectance and IR spectroscopic data of bis(pyrazine-2,3-dicarboxylato)metal(II) compounds

Compound	Colour	Diffuse-reflectance absorption maxima (cm^{-1})	IR frequencies (cm^{-1})	
			$\nu_{C=O}$	ν_{C-O}
$C_6H_4N_2O_4$	White		1700	1260
$Mn(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	Yellow	11 600 16 300 25 000	1700–1630	1230–1360
$Fe(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	Dark violet	10 000 19 250	1700–1640	1230–1360
$Co(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	Yellow-orange	9 400 20 400	1700–1635	1250–1360
$Ni(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	Light blue	11 000 16 100–17 100 26 500	1700–1630	1260–1360
$Cu(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	Turquoise	15 900 26 600	1700–1650	1230–1320
$Zn(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$	White		1700–1630	1230–1300

(Pyrazine-2,3-dicarboxylato)manganese(II)
$Mn(C_6H_2N_2O_4) \cdot 2\,H_2O$, calcd.: C 28.03%, H 2.35%, N 10.90%, Mn 21.37%, O 37.34%; found: C 28.0%, H 2.31%, N 10.8%, Mn 21.5% (by TG in air), O 37.4% (by difference).

(Pyrazine-2,3-dicarboxylato)cobalt(II)
$Co(C_6H_2N_2O_4) \cdot 2\,H_2O$, calcd.: C 27.60%, H 2.32%, N 10.73%, Co 22.57%, O 36.77%; found: C 27.5%, H 2.3%, N, 10.8%, Co 22.4% (by TG in air), O 37.0% (by difference).

(Pyrazine-2,3-dicarboxylato)nickel(II)
$Ni(C_6H_2N_2O_4) \cdot 2\,H_2O$, calcd.: C 27.62%, H 2.32%, N 10.74%, Ni 22.51%, O 36.80%; found: C 27.5%, H 2.3%, N 10.8%, Ni 22.5% (by TG in air), O 36.9% (by difference).

(Pyrazine-2,3-dicarboxylato)copper(II)
$Cu(C_6H_2N_2O_4) \cdot H_2O$, calcd.: C 29.10%, H 1.63%, N 11.31%, Cu 25.66%, O 32.30%; found: C 29.0%, H 1.6%, Ni 11.3%, Cu 25.8% (by TG in air), O 32.3% (by difference).

(Pyrazine-2,3-dicarboxylato)zinc(II)
$Zn(C_6H_2N_2O_4) \cdot 2\,H_2O$, calcd.: C 26.94%, H 2.26%, N 10.47%, Zn 24.44%, O 35.89%; found: C 26.9%, H 2.2%, N 10.4%, Zn 24.7% (by TG in air), O 35.8% (by difference).

In addition to bis(pyrazine-2,3-dicarboxylato)iron(II), the B series includes the following complexes.

Bis(pyrzine-2,3-dicarboxylato)manganese(II)
$Mn(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$, calcd.: C 33.90%, H 2.37%, N 13.18%, Mn 12.92%, O 37.63%; found: C 33.8%, H 2.4%, N 13.1%, Mn 12.9% (by TG in air), O 37.8% (by difference).

Bis(pyrazine-2,3-dicarboxylato)cobalt(II)
$Co(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$, calcd.: C 33.58%, H 2.35%, N 13.05%, Co 13.73%, O 37.28%; found: C 33.5%, H 2.4%, N 13.0%, Co 13.9% (by TG in air), O 37.2% (by difference).

Bis(pyrazine-2,3-dicarboxylato)nickel(II)
$Ni(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$, calcd.: C 33.60%, H 2.35%, N 13.06%, Ni 13.69%, O 37.30%; found: C 35.5%, H 2.4%, N 13.0%, Ni 13.6% (by TG in air), O 37.5% (by difference).

Bis(pyrazine-2,3-dicarboxylato)copper(II)
$Cu(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$, calcd.: C 33.23%, H 2.32%, N 12.92%, Cu 14.65%, O 36.89%; found: C, 33.1%, H 2.3%, N 13.0%, Cu 14.6% (by TG in air), O 37.0% (by difference).

Bis(pyrazine-2,3-dicarboxylato)zinc(II)

$Zn(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$, calcd.: C 33.08%, H 2.31%, N 12.86%, Zn 15.01%, O 36.73%; found: C 33.0%, H 2.3%, N 12.9%, Zn 15.0% (by TG in air), O 36.8% (by difference).

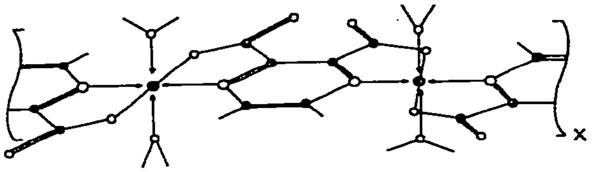
CONCLUSIONS

Because the complexation reaction of the metal ions with pyrazine-2,3-dicarboxylic acid occurs via release of protons [20] according to the equilibrium

$$M + n\,H_2L \rightleftharpoons MH_xL_n + (2n - x)\,H^+$$

and looking at the acidity constants of the ligand [20], it is possible to precipitate the solid compounds with the 1 : 1 metal : ligand molar ratio (series A) in excess of metal ion and at $pH_f \simeq 2.5$, while 1 : 2 complexes (series B) are obtained in excess of ligand and at $pH_f \simeq 1.2$, so that the 3-carboxylic group remains in the protonated form.

Spectroscopic analyses (Tables 2 and 4) prove that, in each complex, the metal ion is chelated through the pyrazinic nitrogen and an oxygen atom of the 2-carboxylate group, forming a very stable five-membered ring [27]. In fact, diffuse-reflectance spectrum of each compound shows the presence of the N—Me—O sequence of bonds [23] and the IR spectra show the shift of the stretching bands of the free carboxylic group (1700 cm^{-1} and 1260 cm^{-1}), one to shorter wave-number ($\leqslant$1650 cm^{-1}), the other to higher wave-number ($\geqslant$1320 cm^{-1}), characteristic of covalently bonded —COO group [7,25]. We must emphasize that, while in the 1 : 2 compounds only one carboxylic group of each ligand molecule is involved in coordination (Table 4), in the 1 : 1 compounds both carboxylic groups coordinate to the metal ion, suggesting the polymeric structure



in the A series of complexes. The primary coordination sphere is generally completed by two water molecules. The resulting hexacoordinated complexes contain the metal ion in pseudo-octahedral environments and their diffuse-reflectance absorption maxima may be assigned in the usual fashion [28]. On the other hand, the copper(II) complexes show a tetragonal distortion along the copper—water axis. The water molecules are more weakly bonded because they are not coordinated and so the 1 : 1 complex contains only one water molecule at room temperature. Thermal analysis confirms our hypotheses. TG in air (Fig. 1) of 1 : 1 complexes shows two steps, one corresponding to the dehydration process, the other to the oxidative decomposition of the complex that leads to the oxide (Table 1). But TG in air of

1 : 2 complexes (Fig. 2) exhibits a first weight loss corresponding to the evolution of two water molecules plus two carboxylic groups (Table 3) in accordance with the lower thermal stability of the free carboxylic group compared with that of the complex. In particular, thermal analysis of the $Cu(C_6H_3N_2O_4)_2 \cdot 2\,H_2O$ complex shows two separate steps for the loss of water (70—125°C) and CO_2 (195—265°C). This is possible because the water molecules are not coordinated so that their evolution occurs at a lower temperature. The thermal stability order, obtained by TG in N_2 atmosphere (initial decomposition temperature), is $Mn > Fe > Co > Ni > Cu < Zn$ which is the same as in the first (A) and second (B) series of the analysed complexes. It agrees with that reported in a previous paper [22] and in the international literature [28—31].

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