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

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ABSTRACT

The spectroscopic characteristics (IR and diffuse reflectance) and thermal properties (TG, DSC) of the solid compounds obtained by the direct reaction of pyrazine-2-carboxylic acid with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) are reported and discussed. The stoichiometry and thermal stability order of the compounds obtained are determined and their structures hypothesized.

INTRODUCTION

Several data are reported in the literature on the reaction of transition metal ions and pyrazine derivatives [1—20]. In a previous paper [20], we reported the donor behaviour of pyrazine-2-carboxylic acid towards nickel(II) and iron(II). Few data are available in the literature on the complexes of cobalt(II), zinc(II) [9] and copper(II) [7] with the same ligand.

In the present paper extensive information on the syntheses, thermal properties [as determined by thermogravimetry (TG) and differential scanning calorimetry (DSC)] and spectroscopic characteristics (IR and diffuse reflectance) of the solid compounds obtained by the direct reaction of pyrazine-2-carboxylic acid with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) are reported.

EXPERIMENTAL

Apparatus

The DSC and TG curves were obtained using a "Du Pont" Model 990 DSC cell and a Model 951 thermobalance; the heating rate used was 10°C min^{-1}

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on samples of 1—10 mg; the furnace atmosphere consisted of air or dry pure nitrogen at flow rates of 50—100 ml min^{-1}; all temperatures were corrected for thermocouple non-linearity and are, of course, procedural decomposition temperatures. The reflectance spectra were recorded using a "Beckman" DBG spectroreflectometer; the IR spectra were recorded using a "Perkin-Elmer" 125 grating IR spectrophotometer. The acidity of the solutions was checked with an "Amel" 333 potentiometer equipped with an "Ingold" type 201 glass electrode and an "Ingold" type 303 calomel reference electrode.

Reagents

Pyrazine-2-carboxylic acid was a pure grade product of "Fluka" purified as reported previously [19]. The metal ions were in the form of perchlorate hexahydrate ("Alfa"). All other chemicals used were analytically pure.

Preparation of the solid compounds

The following general procedure [20] was applied: 50 ml of 0.15 M aqueous solution of the ligand at pH $\simeq$ 5 (adjusted by NaOH) were added to 1.5 g of $M(ClO_4)_2 \cdot 6\,H_2O$ ($C_L/C_M \simeq 2$); the resulting solution was maintained at room temperature for at least 2 h (scratching the wall of the beaker with a glass stick if necessary). The precipitate was filtered off, washed with water and dried in vacuo over silica gel for at least 48 h.

RESULTS

The results obtained are summarized in Tables 1 and 2, while the thermal behaviour is reported in Figs. 1—3. The single compounds, in particular, have the properties reported below.

Bis(pyrazine-2-carboxylato) manganese(II)

A lemon-yellow compound precipitates from aqueous solution. The simplest formula is $Mn(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$, which agrees with elemental and thermogravimetric analysis [calc. (%): C 35.62, H 2.99, N 16.62, Mn 16.29, O 28.47; found (%): C 35.2, H 3.0, N 16.5, Mn 16.6 (by TG in air), O 28.7 (by difference)]. The IR spectrum shows very intense carboxylate absorption bands at 1630 and 1370 cm^{-1}; these are characteristic of a covalently bound —COO group [7,21]. The diffuse-reflectance spectrum shows bands at 11750, 17500 and 25000 cm^{-1} assigned to metal ion $d \leftrightarrow d$ transitions and which are characteristic of an octahedral coordination [22]. According to thermogravimetry in air, this compound loses its water molecules in one step (calc.: 10.68%. found: 10.5%). The anhydrous compound is stable up to 360°C and then decomposes, through several unresolved successive steps, leading to the oxide Mn_3O_4 at 520°C (calc.: 22.62%; found 23.0%); the TG in N_2 shows the same decomposition temperature at

TABLE 1

Decomposition temperature (°C) and analytical data from TG and DSC curves of bis(pyrazine-2-carboxylate) metal(II) compounds

Compound	Atmo-sphere	TG						DSC	
		t (°C)H_2O loss	% Calc.	% Found	t (°C) decomp.	% Calc.	% Found	t (°C)H_2O loss	t (°C) decomp.
$Mn(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	N_2	160 140—180			360 →				
	Air	160 150—180	10.68	10.5	425 360—520	22.62	23.0	160 150—175	420—485 345—510
$Fe(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	N_2	180 140—250			320 →				
	Air	220 155—230	10.65	10.4	310—350 280—370	23.62	23.6	205 155—250	320—380 260—465
$Co(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	N_2	205 160—220			315 →				
	Air	205 170—220	10.55	10.8	340—390 300—410	21.96	22.3	225 170—240	340—390 300—480
$Ni(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	N_2	200 150—220			310 →				
	Air	225 185—235	10.56	10.9	370 310—390	21.91	21.8	235 185—250	385—400 290—475
$Cu(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	N_2	100 85—110			275 →				
	Air	110 90—120	10.41	10.1	315 275—320	23.00	22.8	100 90—115	320—335 290—420
$Zn(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	N_2	180 140—200			285 →				
	Air	180 140—195	10.36	10.1	285—485 275—515	23.41	23.8	185 140—205	300 →

TABLE 2

Spectroscopic data from diffuse-reflectance and IR spectra of bis(pyrazine-2-carboxylate)metal(II) compounds

Compound	Colour	Diffuse-reflectance absorption maxima (cm^{-1})	IR frequencies (cm^{-1})	
			$\nu_{C=O}$	ν_{C-O}
$C_5H_4N_2O_2$	White	—	1700	1280
$Mn(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	Lemon-yellow	11 750—17 500—25 000	1630	1370
$Fe(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	Dark red-violet	13 700—21 300	1650	1350
$Co(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	Yellow-orange	9 100—20 400	1630	1350
$Ni(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	Pale light-blue	11 000—16 100—17 000—26 700	1630	1360
$Cu(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	Light-blue	15 100—25 600	1640	1350
$Zn(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$	White	—	1630	1360

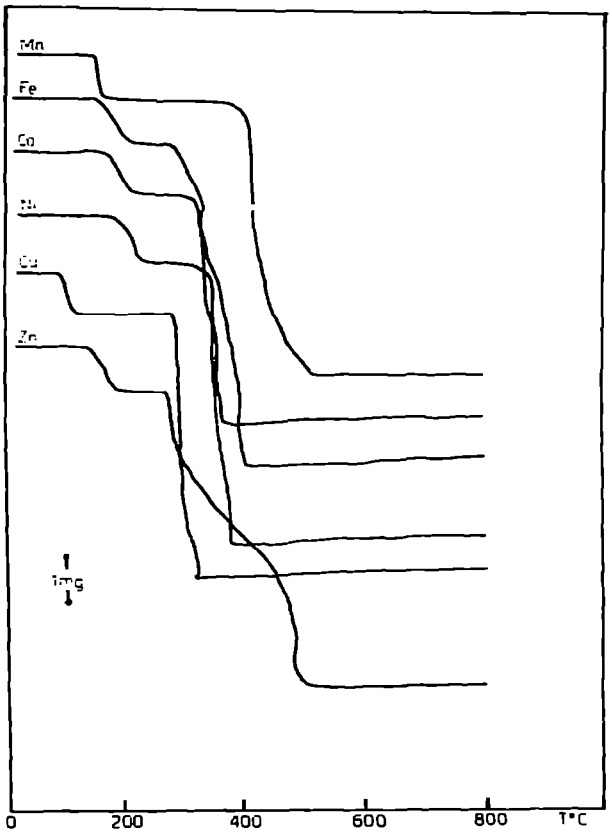


Fig. 1. TG of bis(pyrazine-2-carboxylate)metal(II) compounds in air.

360°C. The DSC curve in an atmosphere of air shows only one endothermic peak for the water loss, while an exothermic peak appears up to 345°C for the decomposition process.

Bis(pyrazine-2-carboxylato) iron(II)

A dark red-violet compound precipitates from aqueous solution. The simplest formula is $Fe(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$, which agrees with elemental and thermogravimetric analysis [calc. (%). C 35.53, H 2.98, N 16.57, Fe 16.52, O 28.40; found (%): C 35.4, H 3.0, N 16.6, Fe 16.5 (by TG in air), O 28.5 (by difference)]. Its IR spectrum is similar to that of the manganese(II) complex described earlier, and shows ν_{COO} absorption bands at 1650—1350 cm^{-1}. Octahedral coordination of this complex is postulated from diffuse-reflectance data which show characteristic bands at 13700 cm^{-1} ($1A_{1g} \rightarrow 1T_{1g}$) and 21300 cm^{-1} ($T_{2g} \rightarrow \pi^*$ C.T.) [22]. The thermogravimetry and DSC in air show that the two molecules of water are evolved between 155 and 230°C (in only one endothermic process) (calc.: 10.65%; found: 10.4%). The anhydrous compound starts to decompose rapidly at 280°C, and leads to the oxide Fe_2O_3 (calc.: 23.62%; found: 23.6%) through an exothermic process; in an atmosphere of N_2 the initial decomposition temperature is delayed (320°C) and the residue does not reach constant weight.

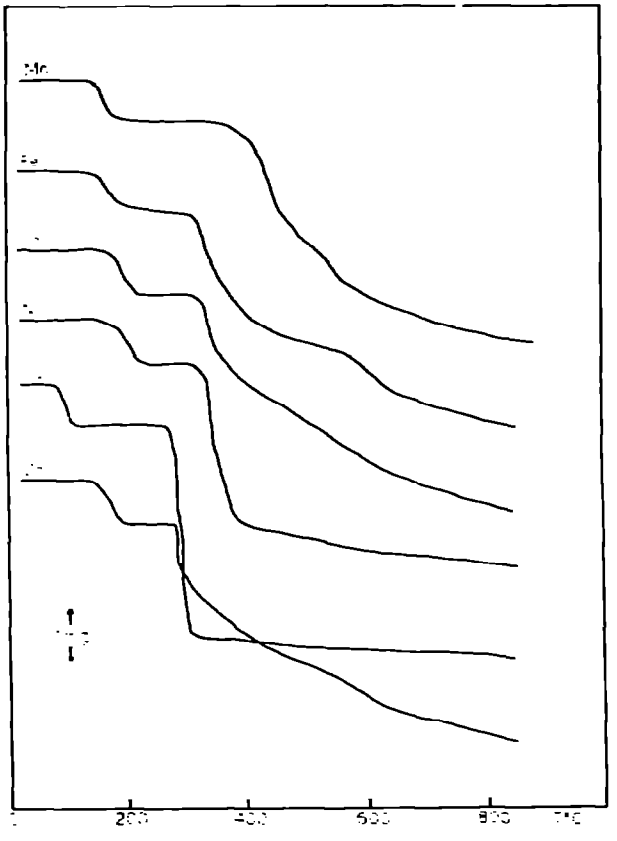


Fig. 2. TG of bis(pyrazine-2-carboxylate)metal(II) compounds in nitrogen.

Bis(pyrazine-2-carboxylato) cobalt(II)

A yellow-orange compound precipitates from aqueous solution with the simplest formula $Co(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$ [calc. (%): C 35.20, H 2.95, N 16.42, Co 17.27, O 28.14; found (%): C 35.7, H 2.9, N 15.9, Co 17.5 (by TG in air), O. 28.0 (by difference)]. The absorption bands at 1630—1350 cm^{-1} in the IR spectrum, and at 9100 cm^{-1} ($^4T_{1g} \rightarrow {}^4T_{2g}$)—20400 cm^{-1} [$^4T_{1g} \rightarrow {}^4T_{1g}(P)$] shown in the diffuse-reflectance spectrum allows the hypothesis of a covalently bound cobalt(II)-carboxylic group and an octahedral coordination [22]. Also in this complex, the two molecules of water are evolved in one step [calc.: 10.55%; found: 10.8% (by TG in air)] between 170—220°C, while the decomposition process takes place in the temperature range 300—410°C (315°C → in an atmosphere of N_2), giving the oxide CoO (calc.: 21.96%; found: 22.3%). The thermal decomposition trend is confirmed by the DSC curve.

Bis(pyrazine-2-carboxylato) nickel(II)

A pale light-blue compound precipitates from aqueous solution. The simplest formula is $Ni(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$ according to elemental and thermogravimetric analysis [calc. (%): C 35.23, H 2.96, N 16.43, Ni 17.22, O 28.16;

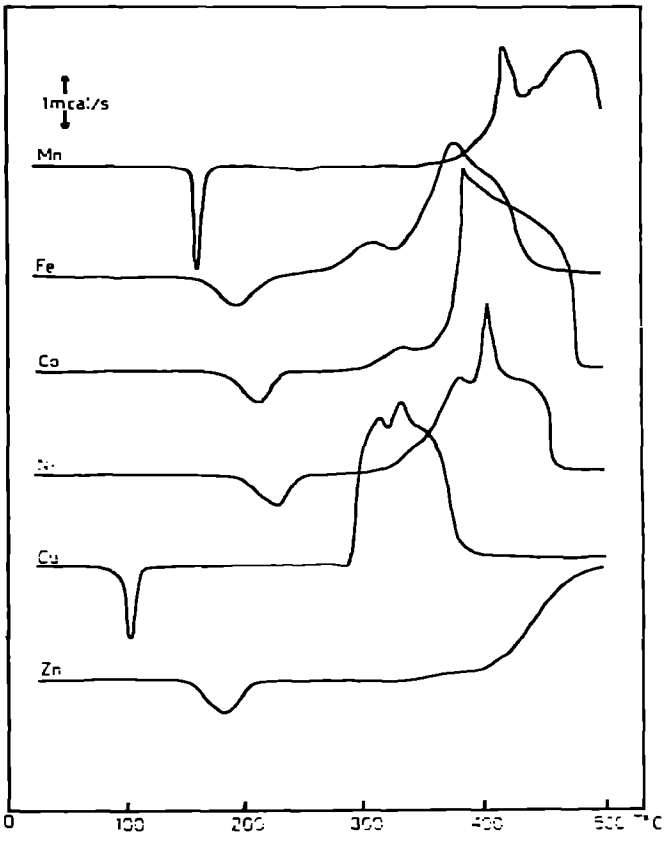


Fig. 3. DSC of bis(pyrazine-2-carboxylate)metal(II) compounds in air.

found (%): C 35.1, H 3.0, N 16.5, Ni 17.1 (by TG in air), O 28.3 (by difference)]. Its IR spectrum is virtually identical to the others described previously, suggesting the presence of a bridging carboxylate group (υ_{COO} at 1630—1360 cm^{-1}). The electronic spectrum of this complex exhibits absorption bands at 11000 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{2g}$), 16100—17000 cm^{-1} [$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)] and 26700 cm^{-1} [$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)], according to the data reported by Matthews et al. [23] for the octahedral nickel(II)-dipicolinate complex.

This compound loses its water molecules in a single step (cal.: 10.56%; found: 10.9%) in the range 185—235°C, as confirmed by the endothermic peak in the DSC curve. The anhydrous compound is stable up to 310°C, after which it decomposes through some unresolved steps leading to NiO (calc.: 21.91%; found: 21.8%) at 390°C (TG in air). This oxidative decomposition is proved by the exothermic peak that appears in the DSC curve. The TG in an atmosphere of N_2 shows an unchanged initial decomposition temperature (310°C).

Bis(pyrazine-2-carboxylato) copper(II)

A light-blue compound precipitates from aqueous solution with the simplest formula $Cu(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$) [calc. (%): C 34.74, H 2.91, N 16.20, Cu 18.38, O 27.77; found (%): C 35.0, H 2.9, N 16.0, Cu 18.2 (by TG in

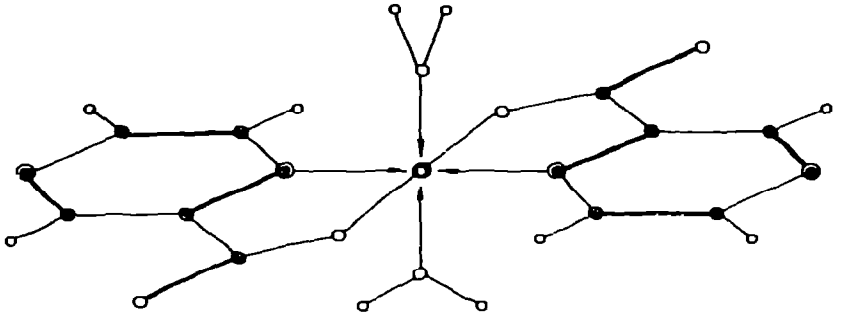
air), O 27.9 (by difference)]. Characteristic absorption bands appear in the IR sprectrum at 1640—1350 cm^{-1} (ν_{COO}) and in the diffuse-reflectance spectrum at 15100 cm^{-1} (metal ion $d \cdots d$ transition) and 25600 cm^{-1} ($e_g \rightarrow \pi^*$C.T. [22]. The TG in air shows one step corresponding to the loss of two water molecules (calc.: 10.41%; found: 10.1%) in the range 90—120°C and the oxidative decomposition process (285—320°C) leads to CuO (calc.: 23.00%; found: 22.8%); the beginning of the latter process in the TG curve, obtained in an atmosphere of N_2, is practically unchanged. The DSC curve confirms the thermal decomposition trend of the complex.

Bis(pyrazine-2-carboxylato) zinc(II)

A white compound precipitates from aqueous solution with the simplest formula $Zn(C_5H_3N_2O_2)_2 \cdot 2\,H_2O$ according to elemental and thermogravimetric analysis [calc. (%): C 34.55, H 2.90, N 16.12, Zn 18.81, O 27.62; found (%): C 34.8, H 3.0, N 15.9, Zn 19.1 (by TG in air), O 27.2 (by difference)]. Its IR spectrum is similar to the others described previously and shows ν_{COO} absorption bands at 1630—1360 cm^{-1}, while no absorption bands are present in the visible reflectance spectrum. The thermogravimetry and DSC in air show that the two water molecules are evolved in the range 140—195°C (calc.: 10.36%; found: 10.1%); the decomposition of the anhydrous compound starts at 275°C and the exothermic process leads to ZnO at 515°C (calc.: 23.41%; found: 23.8%); in an atmosphere of N_2 the initial decomposition temperature is delayed (285°C) and the residue does not reach constant weight.

CONCLUSION

Pyrazine-2-carboxylic acid, because of the carboxylic group in the α position, can act as chelating agent forming a very stable five-membered ring [24]. The spectroscopic data confirm this hypothesis showing the N—M—O sequence of the bond in all analysed compounds. In fact the IR spectrum of pyrazine-2-carboxylic acid shows very intense absorption bands centred around 1700 cm^{-1} and just below 1300 cm^{-1} which are characteristic of a free carboxylic group [21]; these absorption bands are shifted to a shorter wave-number (≤1650 cm^{-1}) and to a higher wave-number (≥1350 cm^{-1}), respectively, consistent with a covalently bound —COO group [7,21]. The



diffuse-reflectance spectra agree with our hypothesis by analogy with the spectrochemical series of the frequencies [25], and suggests an octahedral configuration about the metal ion, especially for the Mn(II), Fe(II), Co(II) and Ni(II) derivatives (21—23) which probably have a structure of the type shown above with the pyrazinoic groups in a *trans*-planar position. In the case of the copper(II) complex the water is more weakly bound and there is probably a tetragonal distortion along the copper—water axis.

The following thermal stability order for the examined divalent metal ions has been calculated by the experimental data of TG in an atmosphere of N_2 (initial decomposition temperature): (Mn(II) > Fe(II) > Co(II) ⩾ Ni(II) > Cu(II) < Zn(II); this is in agreement with the literature [26—28]. The general series found by Irving and Williams [29] for the stability of similar complexes in solution is practically the reverse of the above series for the thermal stability; this can be explained on the basis that the strength of intermolecular bonds plays a notable part in the thermal stability of the solid compounds [26].

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