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THERMAL ANALYSIS OF SOME COMPLEXES OF DIVALENT METAL IONS WITH PICROLONIC ACID

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ABSTRACT

A series of complexes of divalent transition metal ions with picrolonic acid have been studied using TG and DSC analysis and the metal oxides found as the final residue have been analysed by X-ray techniques. The thermal stability order of the series of these complexes was examined and discussed.

INTRODUCTION

In recent years, some Italian researchers have prepared and characterized many complexes, in the solid state, of metal ions and picrolonic acid [1]. However, satisfactory thermal stability data for these compounds are not yet

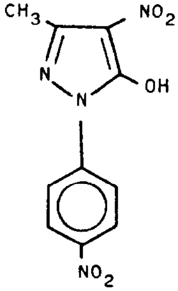

Fig. 1. Picrolonic acid.

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available. In this paper, thermoanalytical data (TG and DSC) are reported for picrolonates of some divalent transition metals, with the general formula Me(pic)$_2 \cdot n H_2O$, where Me = Mn(II), Fe(II), Cd(II), Ni(II), Cu(II) and Zn(II), pic = picrolonate ligand (see Fig. 1) and n can assume values from 1 to 2.

EXPERIMENTAL

The metal–picrolonate complexes studied were prepared as reported by Lorenzotti et al. [1]. Chemical characterization by elemental analysis, IR and NMR has been determined by the same authors [1]. TG, DTG and DSC curves of the solid complexes were obtained using a Du Pont model 951

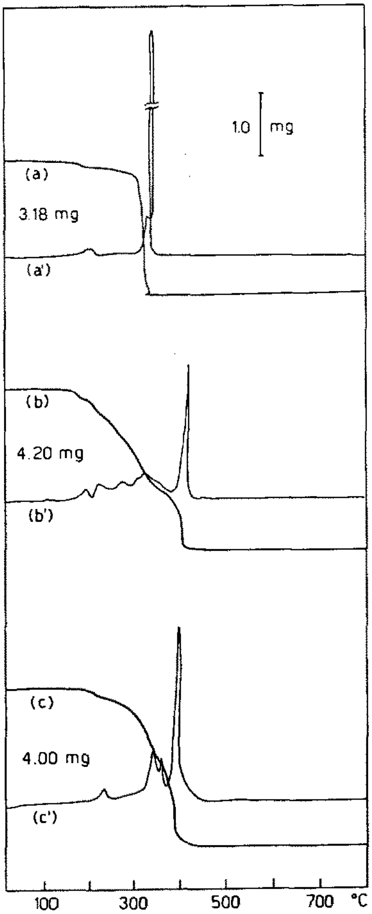

Fig. 2. TG and DTG curves of picrolonate complexes with (a) Mn(II), (b) Fe(II) and (c) Co(II), in static air with heating rate 10 °C min^{-1}.

thermobalance and model 990 DSC cell and console. The heating rate used was 10 °C min^{-1}, on samples of mass ranging from 3 to 5 mg. The furnace atmosphere was static air. All temperatures were corrected for thermocouple non-linearity and are, of course, procedural temperatures (pdt).

The X-ray powder spectra were recorded by an Isodebyeflex IIIA Seifert apparatus, employing Cu $K\alpha$ radiation ($\lambda = 1.5405$ Å). The samples were analysed under vacuum, for 10 h, using the Debye–Scherrer method.

RESULTS AND DISCUSSION

Figures 2 and 3 show the TG and DTG curves in static air and at a heating rate of 10 °C min^{-1} for complexes of Mn(II), Fe(II), Cd(II), Ni(II),

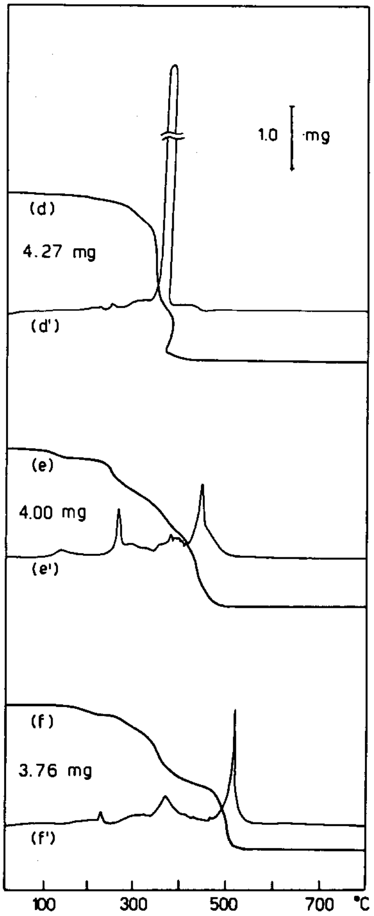

Fig. 3. TG and DTG curves of picrolonate complexes with (d) Ni(II), (e) Cu(II) and (f) Zn(II), in static air with heating rate 10 °C min^{-1}.

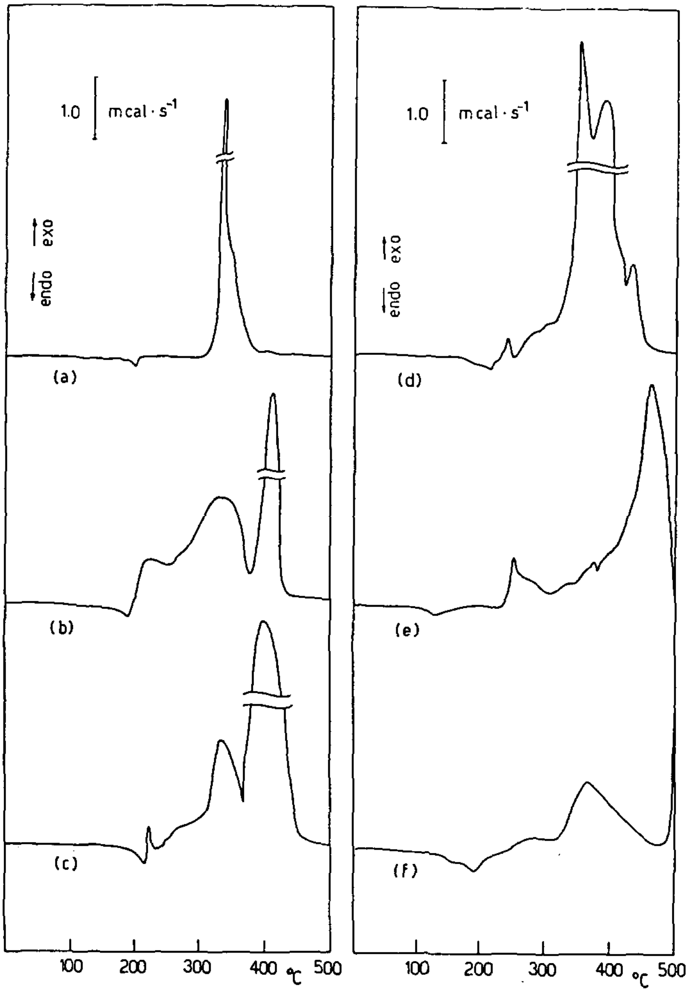

Fig. 4. DSC curves of picrolonate complexes with (a) Mn(II), (b) Fe(II), (c) Co(II), (d) Ni(II), (e) Cu(II) and (f) Zn(II), in static air with heating rate 10 ° C $\min^{-1}$.

Cu(II) and Zn(II) with picrolonic acid, in the operational temperature range 25–750 ° C. Figure 4 shows the DSC curves of these complexes obtained under the same experimental conditions in the temperature range 25–500 ° C. All the thermal data are summarized in Table 1. It can be seen that loss of water is completed at different but generally high temperatures for all the complexes, indicating that the water is most probably crystallization water.

The decomposition process of the anhydrous compounds generally occurs in two principal exothermic steps, the second of which is generally fast. However, in the case of Mn(II) picrolonate only, a single very fast exothermic process occurs, practically a deflagration, as other researchers have observed for some analogous compounds [1].

TABLE 1

TG of $Me(II)(pic)_2 \cdot nH_2O$ complexes, where Me(II) = divalent transition metal ion, pic = picrolonate anion and n = number of molecules of crystallization water

Metal ion	H_2O loss		1st step		2nd step		Metal oxides found in the TG residue (800 ° C) by X-ray analysis
	% Loss found	Pdt	% Loss found	Pdt	% Loss found	Pdt	
Mn(II)	4.9	135	88.9	270		–	Mn_3O_4
		200		330			
		215		355			
Fe(II)	5.6	100	51.4	200	29.9	370	Fe_2O_3
		180		310		410	
		190		370		440	
Co(II)	4.8	160	34.3	245	46.7	360	Co_3O_4
		220		330		385	
		240		360		450	
Ni(II)	3.7	110	59.6	225	24.8	370	NiO
		210		345		390	
		220		370		440	
Cu(II)	4.9	80	44.1	210	38.2	395	CuO
		120		250		430	
		180		395		520	
Zn(II)	5.2	130	43.8	240	37.5	445	ZnO
		215		360		505	
		230		445		550	

Results were obtained in static air, at a heating rate of 10 ° C min^{-1}. Weights are referred to the residue at the end of each step and are expressed as the fraction of the initial amount. Pdt = procedural decomposition temperatures. The reported percent mass losses are expressed as the fraction of the initial amount.

In all cases, between 350 and 550 ° C, thermal decomposition ends, giving the oxides. To identify each oxide, each residue obtained at the end of the TG processes (about 800 ° C) was analysed from its X-ray powder spectrum. Experimental d_{hkl} values are reported in Table 2 and compared with the standard ASTM values [2].

The formulae of the oxides are shown in the last column of Table 1. These oxides are the same oxides, found as TG residues from other complexes [3] which have the same central ions, under the same operating conditions.

Considering the thermal stability order for the divalent metal complexes examined, experimental TG data show the sequence

$$Mn(II) > Co(II) \geqslant Zn(II) > Ni(II) > Cu(II) > Fe(II)$$

It can be noted that, except in the case of Fe(II) picrolonate, whose stability value is very much lower than that expected, the thermal stability sequence determined in this study is the same as that found by other researchers in earlier works [3,4], and is practically the reverse of the general

TABLE 2

X-ray powder spectra of TG final residues (at about 800 ° C) from the examined picrolonate complexes

(a) d_{hkl}	(a′) d_{hkl}	(b) d_{hkl}	(b′) d_{hkl}	(c) d_{hkl}	(c′) d_{hkl}
4.92	4.93	3.66	3.61	2.86	2.86
3.09	3.09	2.69	2.69	2.44	2.43
2.77	2.77	2.51	2.51	2.02	2.01
2.49	2.48	2.20	2.20	1.56	1.55
1.80	1.80	1.84	1.84	1.43	1.43
1.58	1.57	1.69	1.69	1.05	1.05
1.54	1.54	1.48	1.48		
		1.45	1.45		

(d) d_{hkl}	(d′) d_{hkl}	(e) d_{hkl}	(e′) d_{hkl}	(f) d_{hkl}	(f′) d_{hkl}
2.41	2.41	2.53	2.53	2.82	2.82
2.09	2.09	2.32	2.33	2.60	2.60
1.48	1.48	1.87	1.87	2.48	2.48
1.26	1.26	1.51	1.51	1.91	1.91
1.21	1.21	1.41	1.41	1.63	1.63
		1.38	1.38	1.48	1.48
				1.38	1.38
				1.36	1.36

Reported in the literature [2] for (a) Mn_3O_4, (b) Fe_2O_3, (c) Co_3O_4, (d) NiO, (e) CuO and (f) ZnO.

Determined from the TG residue of (a′) $Mn(pic)_2$, (b′) $Fe(pic)_2$, (c′) $Co(pic)_2$, (d′) $Ni(pic)_2$, (e′) $Cu(pic)_2$ and (f′) $Zn(pic)_2$.

series, found by Irving and Williams, for the stability of complexes in solution [5] which was explained in terms of inter- and intra-molecular bonds and of the covalent or ionic nature of the metal–ligand bonds (6–8).

The low stability of the iron complex is an exception that was not usually observed in other experiments and can, therefore, not be easily explained.

In a previous work [7], in which we studied metal derivatives of azoles, but with ligands slightly different from picrolonic acid, the accepted order of expected thermal stability was not verified. This was explained in terms of a structural hypothesis. However, the fact that in this case only the iron complex did not obey the expected thermal sequence, made such an explanation rather dubious. Other interpretations can nevertheless be advanced and are related either to a certain degree of polymerization, which was observed in some of these complexes [1], or to the oxidation state of the iron complex with picrolonic acid, which, according to the literature [1], should be present as a divalent ion. It is observed, however, that in Fe_2O_3 the iron is surely trivalent. The oxidation state can even be checked by heating in the presence of air. However, if it were not so, a different oxidation state of the central ion of the iron complex (with respect to the other picrolonic complexes examined) could play a not negligible role, in regard to either the degree of polymerization of the complex or the conformational structure and, consequently, in the thermal stability.

Besides, it is well known that in general the stability constants of iron (III) compounds are higher than those of iron (II) with the same ligands [9] and that consequently [6–8], the thermal stabilities of iron (II) complexes are higher than those of iron (III) complexes with the same ligands.

Although these hypotheses cannot be sufficiently supported by the experimental data, they could explain the anomalous behaviour in the thermal stability order which was observed only in the case of the iron complex and not in the other picrolonates examined.

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