COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II) WITH THE BENZENEDICARBOXYLIC ACIDS. THERMAL PROPERTIES

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ABSTRACT

The thermal properties of the complexes of phthalic, isophthalic and terephthalic acid with cobalt(II), nickel(II) and copper(II) are determined by thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC).

The thermal stability of the anhydrous compounds gives, for the metal ions, a sequence Co > Ni > Cu.

The thermal stability series as a function of the ligand for each metal is terephthalate > isophthalate > phthalate.
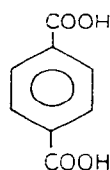
INTRODUCTION

In our research series on the behaviour of compounds obtained by the reaction between metal ions and organic ligands [1—9], the complexes of phthalic, isophthalic and terephthalic acids with the divalent metal ions cobalt(II), nickel(II) and copper(II) are studied.
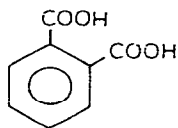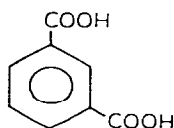
Phthalic acid   Isophthalic acid   Terephthalic acid

EXPERIMENTAL

Instrumentation

The TG, DTG and DSC curves of the solid complexes were obtained using a Du Pont Model 990 DSC Cell and console and a Model 951 thermobalance. The heating rate used was 10°C min^{-1} on samples whose mass ranged from 1 to 10 mg. The furnace atmosphere consisted of either dry nitrogen or air, at flow rates of 50—100 ml min^{-1}. All temperatures were corrected for the non-linearity of the thermocouples and are, of course, procedural temperatures.

TABLE 1

Metal contents of cobalt, nickel and copper phthalates

Compound	Metal %	
	Found	Theor.
Co phthalate	26.8	26.90
Ni phthalate	27.0	26.86
Cu phthalate	28.3	28.41
Cu isophthalate	28.5	28.41
Cu terephthalate	28.2	28.41

Preparation of compounds

The complexes of phthalic acid were prepared as reported by Ekeley and Banta [10]. The complexes of terephthalic and isophthalic acid were prepared in the same way but only the copper(II) complexes were also obtained quite pure by means of other procedures.

If precipitation of solid compounds did not occur from aqueous solution, the medium was suitably adjusted by adding absolute ethanol and diethyl ether until precipitation was obtained.

Each compound obtained was dried in vacuo for 48 h at room temperature.

Thermogravimetry was used to determine the water content and residual metal oxide; the metal content was also established by complexometric titration of the anhydrous compound (Table 1).

RESULTS

The activation energies for the first decomposition step have been calculated from the TG curves and the values obtained are summarized in Table 2.

The calculation method for the activation energy was discussed previously [9]. In all the compounds, the metal—ligand ratio appeared to be 1 : 1.

TABLE 2

Activation energies of cobalt, nickel and copper phtalates

Compound	Activation energy (kcal mole^{-1})
Co phthalate	43.4 ± 5.2
Ni phthalate	50.1 ± 4.1
Cu phthalate	54.4 ± 3.9
Cu isophthalate	35.7 ± 4.0
Cu terephthalate	24.0 ± 1.2

Cobalt(II) phthalate

The TG in air (Fig. 1) and N_2 (Fig. 2) and DSC curves (Fig. 2) of cobalt(II) phthalate (Co phthal · 2 H_2O) show that the compound loses water molecules in just one step (13.8% found; 13.90% calc.), then the anhydrous complex decomposes via two unidentified steps to give the oxide CoO (31.8% found; 32.03% calc.). The DSC curve in nitrogen reveals a single endothermic peak for the dehydration followed by one endothermic peak for the decomposition.

Nickel(II) phthalate

The TG in air (Fig. 1) and in N_2 (Fig. 3) and DSC curves (Fig. 3) of nickel-(II) phthalate (Ni phthal · 2 H_2O) are reported. The compound evolves water of hydration over the temperature range 50—210°C (13.7% found; 13.91% calc.), then the anhydrous complex decomposes via two identified steps to give the oxide NiO (28.8% found; 28.87% calc.). The DSC curve in nitrogen reveals an endothermic peak for the decomposition.

Copper(II) phthalate

The TG in air (Fig. 1) and in N_2 (Fig. 4) and DSC curve in N_2 (Fig. 4) show that the compound (Cu phthal · H_2O) evolves its water at about 200°C
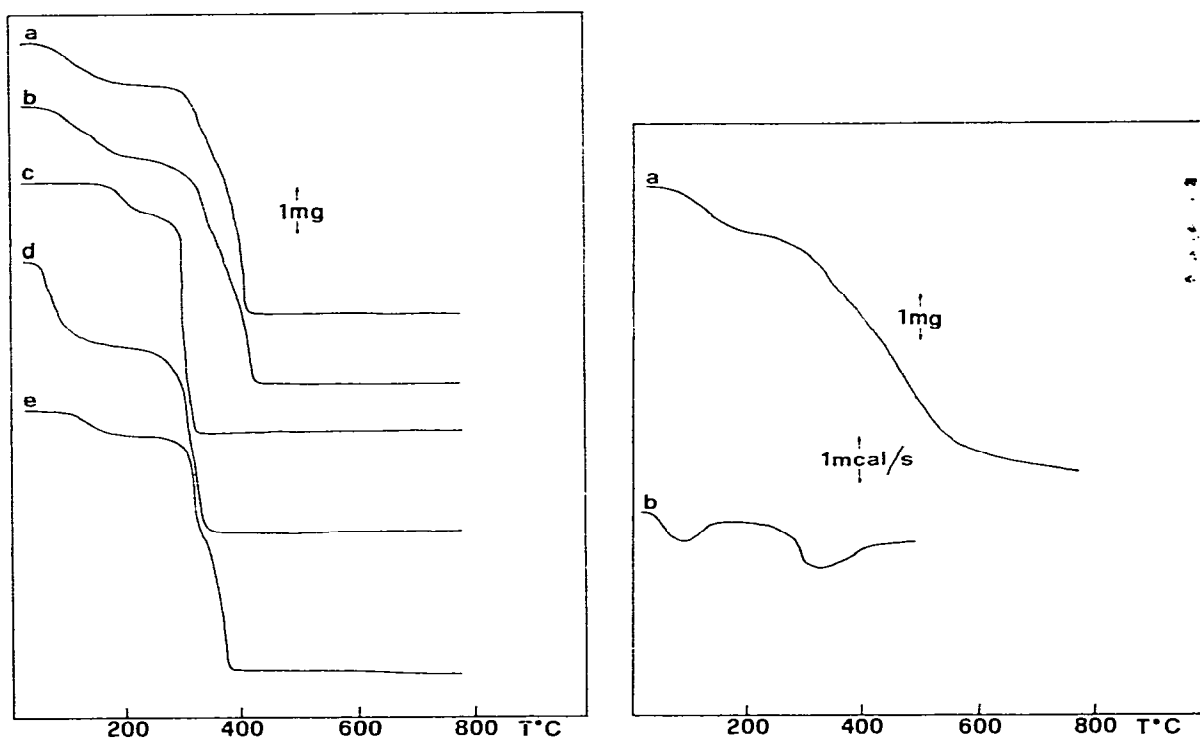

Fig. 1. TG in air. (a) Cobalt phthalate; (b) nickel phthalate; (c) copper phthalate; (d) copper isophthalate; (e) copper terephthalate.

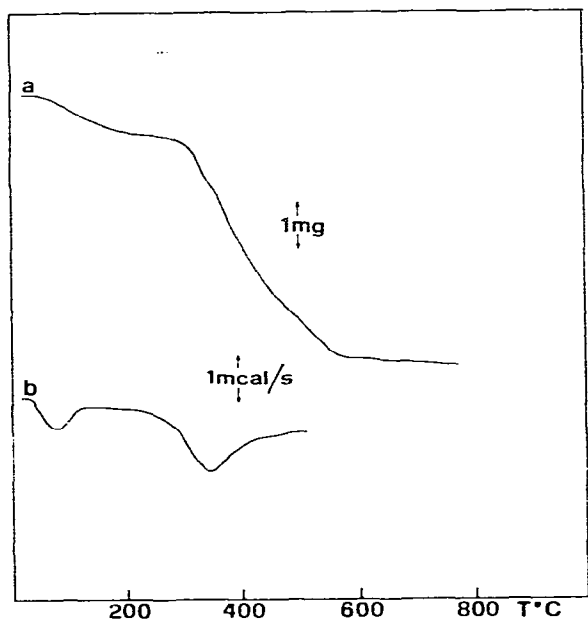Fig. 2. Cobalt phthalate. (a) TG in nitrogen; (b) DSC in nitrogen.

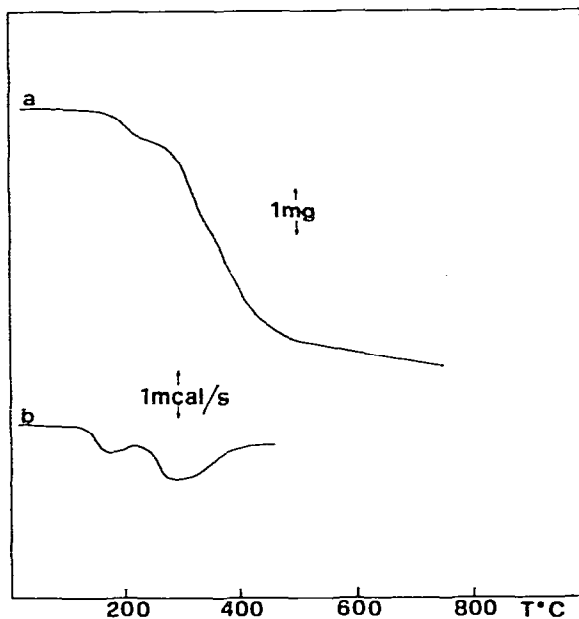Fig. 3. Nickel phthalate. (a) TG in nitrogen; (b) DSC in nitrogen.

Fig. 4. Copper phthalate. (a) TG in nitrogen; (b) DSC in nitrogen.

(7.2% found; 7.33% calc.), then the anhydrous complex decomposes abruptly to give the oxide CuO (32.6% found; 32.40% calc.). The DSC curve in nitrogen shows only one endothermic peak for the decomposition.
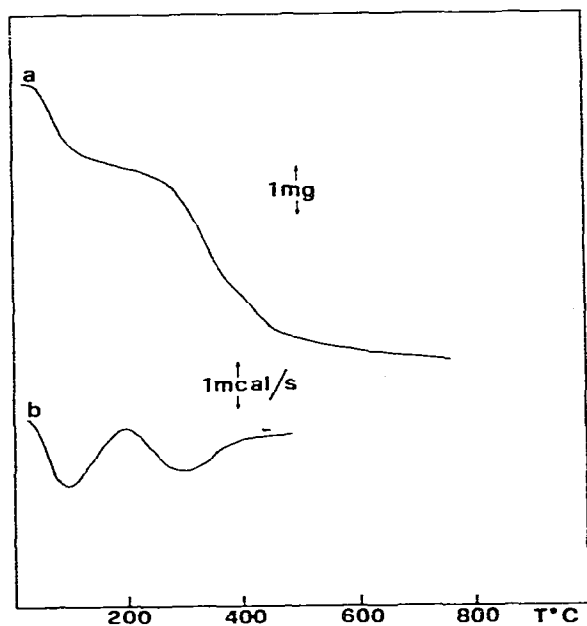

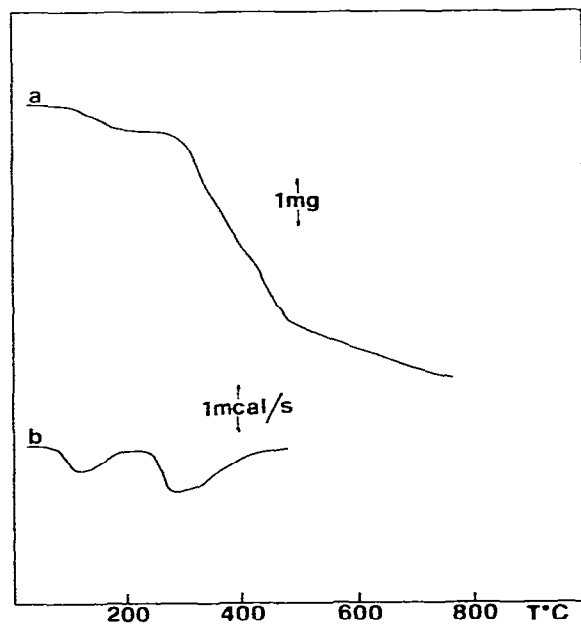Fig. 5. Copper isophthalate. (a) TG in nitrogen; (b) DSC in nitrogen.

Fig. 6. Copper terephthalate. (a) TG in nitrogen; (b) DSC in nitrogen.

Copper(II) isophthalate

The TG in air (Fig. 1) and in N_2 (Fig. 5) and DSC curve in N_2 (Fig. 5) are reported. The compound (Cu isophthal · 4 H_2O) evolves all the four water molecules in one step (14.1% found; 13.92% calc.), then the anhydrous complex decomposes via two unidentified steps to give the oxide CuO (26.4% found; 26.56% calc.). The DSC curve in nitrogen shows a large endothermic peak for the dehydration and only one endothermic peak for the decomposition of the anhydrous complex.

Copper(II) terephthalate

The compound (Cu terephthal · H_2O) evolves the water in one step (7.2% found; 7.33% calc.), as shown from the TG in air (Fig. 1) and in N_2 (Fig. 6) and DSC in N_2 (Fig. 6), then the anhydrous complex decomposes via two unidentified steps to give the oxide CuO (31.5% found; 31.15% calc.). The DSC curve in nitrogen shows one endothermic peak for the dehydration and one endothermic peak for the decomposition.

DISCUSSION

The thermal stability order of the phthalate compounds shown by the experimental data is Co > Ni > Cu. This scale is the reverse of that corresponding to the stability constants of those systems in aqueous solutions [11,12]. Looking at the stability constant increment from metal to metal (using all the values corrected at $\mu = 0$) (Fig. 7) it is possible to see that there is not a regular increase, while the thermal stability decreases monotonically.

A hypothesis to justify this behaviour is that the complexes in solution are obtained by replacement of the water by a more polarisable molecule in the coordination sphere of the metal ions. Considering the two parameters which essentially guide the extent of the electrostatic and covalent interaction, viz. the reciprocal of the ionic radius and the second ionization potential, both increase monotonically in our series from cobalt to copper.
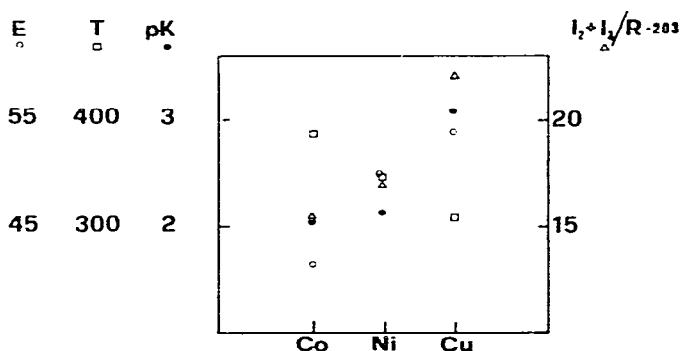
Fig. 7. Activation energies (kcal mole^{-1}), decomposition temperatures (°C), stability constants, and ionic radii of cobalt, nickel and copper phthalates.

The interaction with a ligand having an electron-donor power higher than that of water will increase monotonically the stability constants through covalent bonding, as the replacing of the water by a ligand with a formal negative charge will increase the stability constants through pure electrostatic forces as a monotonic function of the decreasing of the ionic radius. Looking now at the scale of the activation energies, it is possible to see that there is a monotonic increase in the values obtained.

Now the discrepancies between the behaviour of the stability constants and the behaviour of the other examined parameters could be explained by considering that the enthalpies of formation of the metal dicarboxylate complexes involving phthalate ions are endothermic [12]. In spite of this unfavourable enthalpy change the complexes are stabilized by a process of water molecule liberation, due to the ligand—metal interaction, with a corresponding large positive entropy change. With the copper ion, whose thermodynamic data are not given in the literature, an additional stabilization is possible due to the Jahn—Teller effect. The resulting tetragonal distortion of the octahedral symmetry causes (a) shortening of the four bonds in the xy plane and the elongation of the two bonds in the z direction with a consequent increase in the covalent nature of the bonds in the xy plane resulting in a less endothermic enthalpy of formation, (b) higher electrostatic interaction between the copper ion and the charged ligand resulting in a higher positive entropy of formation, (c) the limiting possibility of a change of coordination, from six in the aqua-complex to four in the phthalate complex, with a consequently more positive entropy of formation reflecting the breaking of the two metal—water bonds. The additional stabilization discussed can account for the irregular increase in the stability constants when the pdt's and the activation energy values, measured for the anhydrous complexes, and then without any water interaction, change regularly as a monotonic function from metal to metal.

Considering now the series of copper(II) complexes with phthalic, isophthalic and terephthalic acids, the thermal stability scale obtained is terephthalic > isophthalic > phthalic. The lower thermal stability of the phthalate complex can be justified by considering that the two carboxylate groups of the phthalate both interact with the same metal ion giving a chelate seven membered ring that stabilizes the complex, increasing the intramolecular and decreasing the intermolecular bonds with a consequent decrease in the thermal stability, which agrees with values on the activation energy scale (Table 2).

The terephthalate and isophthalate complexes cannot give chelation effects and the interaction of two carboxylate groups with the metal ions occurs through two carboxylates from two different molecules giving a polymeric structure that strongly stabilizes the intermolecular bonds which accounts for the higher thermal stability with respect to the phthalate complex.

The tere- and isophthalate complexes show a similar thermal stability because both give a polymerization, the acid strength is nearly the same (pK_{ortho} = 2.95; pK_{meta} = 3.62; pK_{para} = 3.52) [13] and the residual charge on the molecule is very close for both complexes.

The data obtained for the activation energy of the copper(II) iso- and tere-

phthalate complexes are very close, confirming that the bond strengths are very similar for both these complexes.

ACKNOWLEDGEMENT

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