Thermochimica Acta, 13 (1975) 461–466

COMPLEXES OF NICKEL(II), COPPER(II) AND ZINC(II) WITH THE AMINOBENZENEMONOCARBOXYLIC ACIDS

THERMAL PROPERTIES

G. D'ASCENZO, A. D. MAGRI, E. CARDARELLI AND G. DE ANGELIS
Istituto di Chimica Analitica, Università degli Studi di Roma, 00185 Rome (Italy)
(Received 23 June 1975)

ABSTRACT

The thermal properties of the complexes of *ortho-*, *meta-* and *para*-aminobenzenemonocarboxylic acids with nickel(II), copper(II), and zinc(II) are determined by TG and DTA. The activation energy values for the first decomposition step of the anhydrous compounds are also calculated. The thermal data are then examined and correlated with the structure of the compounds.

INTRODUCTION

In this paper the thermal behaviour of the complexes obtained by reaction between the *ortho-*, *meta-* and *para*-aminobenzenecarboxylic acids with the metal ions nickel(II), copper(II) and zinc(II) is studied.

The pdt's and the activation energy values are examined and correlated with the structure of the complexes.

EXPERIMENTAL

Instrumentation

Du Pont 951 thermobalance. Du Pont 990 thermal differential analyser. Radiometer PHM 22r potentiometer.

A heating rate of 10°C min^{-1} was employed. Atmosphere: air or nitrogen. All the temperatures referred to are the procedural decomposition temperatures (pdt's) at the employed heating rate.

Preparation of compounds

The complexes of *ortho-* and *meta*-aminobenzenecarboxylic acids were obtained by mixing the boiling 0.1M solution of the acid and of the metal chloride until an initial ligand–metal molar ratio of 4:1 was obtained, at a pH sufficiently low to prevent hydrolysis phenomena.

By this method it was impossible to obtain the complexes of the *para*-aminobenzenecarboxylic acid.

They were prepared by mixing the solid compounds, 2 mmoles of *para*-aminobenzenecarboxylic acid and 0.5 mmoles of metal chloride, adding 0.5 ml absolute ethanol and then heating in a steam-bath until the ethanol has completely evaporated. The obtained solid mixture is then treated with successive portions of ethyl ether until complete removal of the free acid, soluble in ethyl ether, when the complex is just slightly soluble.

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

Thermogravimetry was used to determine the water content and the residual metal oxide; the metal content was also established by compleximetric titration of the anhydrous compound.

RESULTS

TG and DTA curves in air and in nitrogen were obtained, only the TG curves in nitrogen of the copper compounds are reported in Figs. 1–3 as an example.

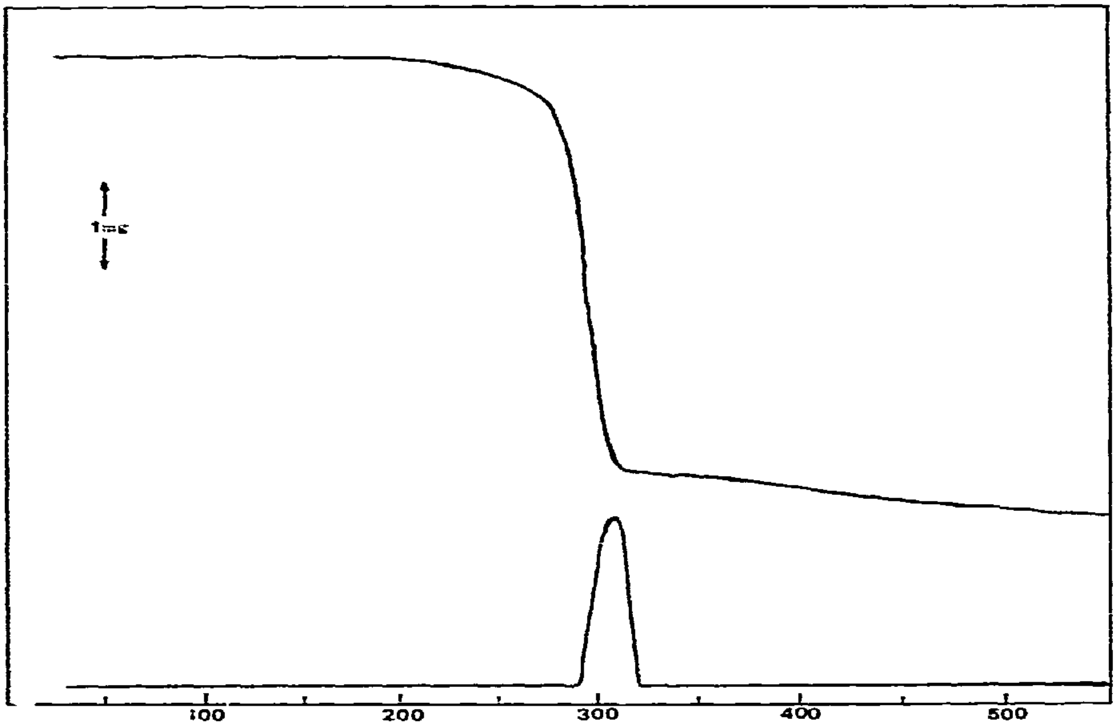

Fig. 1. TG and DTG curves of copper–*ortho*-aminobenzenecarboxylate. Heating rate 10°C min^{-1}; nitrogen atmosphere.

The pdt's of the first decomposition step are summarized in Table 1. In all the compounds the metal–ligand molar ratio appeared to be 1:2 and the found percentage of oxide agrees well with the calculated value. The decomposition process in air and in nitrogen, according to Erdey[1,2], appeared to be a single step for nickel(II) and copper(II) compounds, while for the zinc(II) complexes the decomposition proceeds in a two-step process giving first the carbonate and then the oxide.

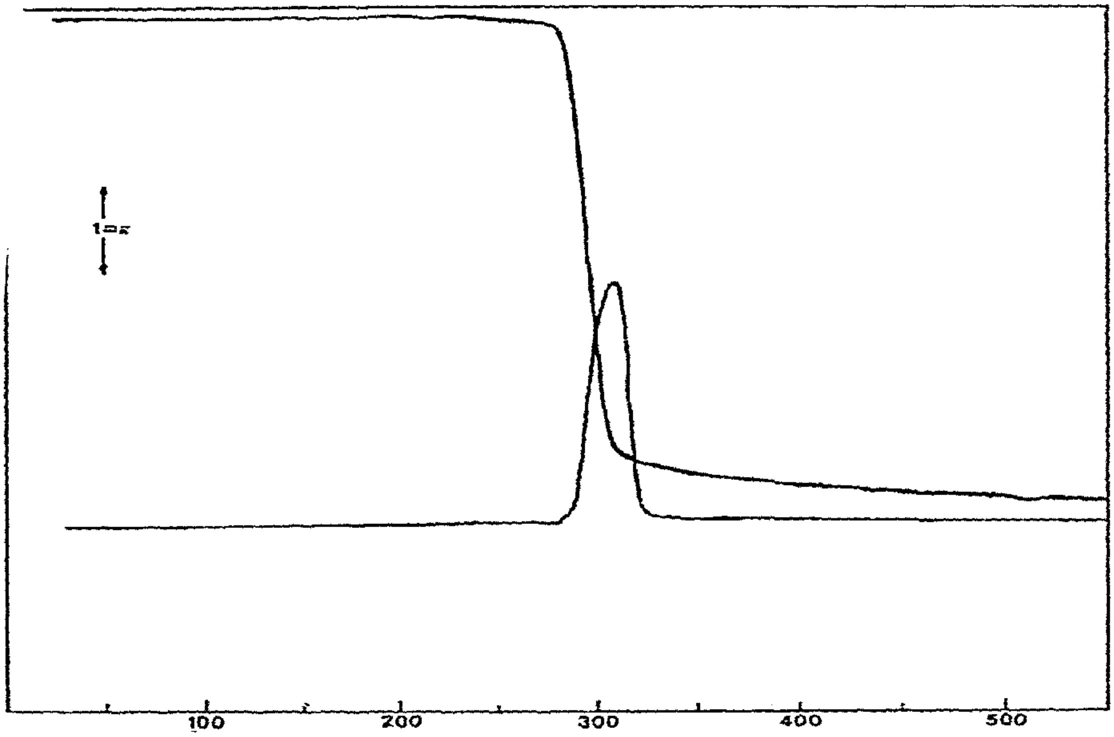

Fig. 2. TG and DTG curves of copper-*meta*-aminobenzenecarboxylate. Heating rate 10 °C min^{-1}; nitrogen atmosphere.

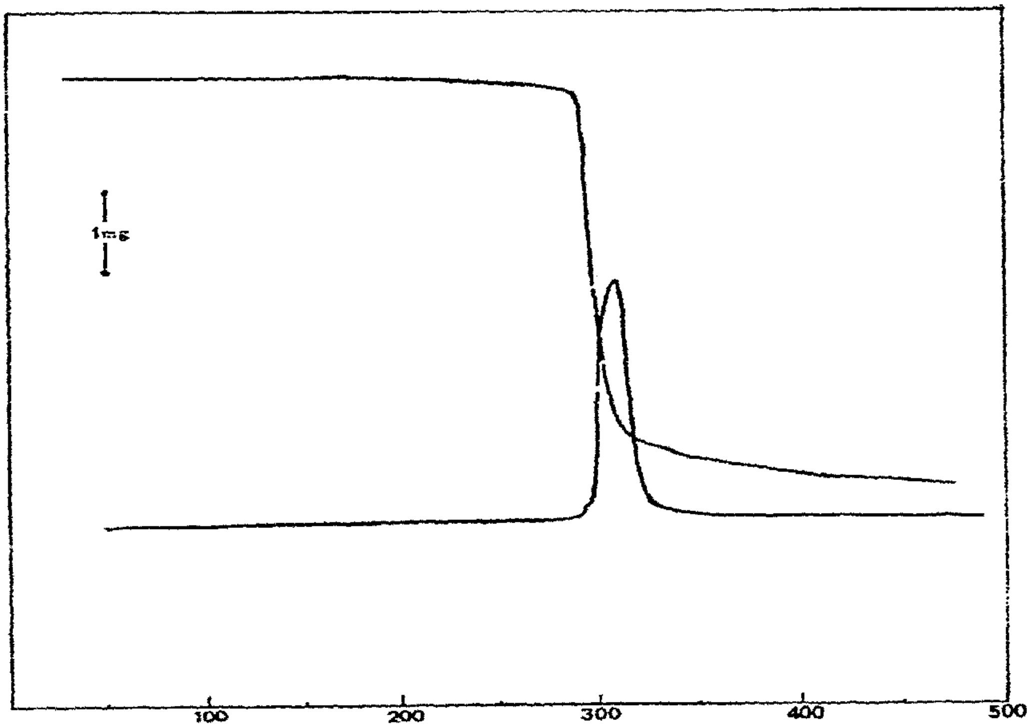

Fig. 3. TG and DTG curves of copper-*para*-aminobenzenecarboxylate. Heating rate 10 °C min^{-1}; nitrogen atmosphere.

TABLE 1

PDT'S IN C OF THE FIRST DECOMPOSITION STEP OF THE ANHYDROUS COMPOUND

Nitrogen atmosphere, 20 l h^{-1}; heating rate, 10 °C min^{-1}.

	ortho-Aminobenzene-carboxylic acid	*meta-Aminobenzene-carboxylic acid*	*para-Aminobenzene-carboxylic acid*
Nickel	420	435	440
Copper	300	310	310
Zinc	370	360	340

DTA curves confirm this and give only endothermic peaks in nitrogen while in air the decomposition peaks become strongly exothermi.

The TG curves were also used to calculate the conditional activation energy values for the first decomposition process.

To minimize the errors and to standardize the process, the TG curves were obtained by using a platinum cylindrical sample holder 10 mm diameter, 3 mm depth with a 1 mm sample layer. The sample particles sizes ranged between 100 and 120 mesh.

The purge gas was very pure (99.99%) nitrogen at 20 l h^{-1}.

The activation energy values were obtained by a Univac 1108 computer, by a program properly implemented as referred to before[3].

The activation energy values are summarized in Table 2.

TABLE 2

ACTIVATION ENERGY VALUES (kcal mol^{-1}) OF THE ANHYDROUS COMPLEXES REFERRED TO A FIRST DECOMPOSITION STEP

Nitrogen atmosphere, 20 l h^{-1}; heating rate, 10 °C min^{-1}.

	ortho-Aminobenzene-carboxylic acid	*meta-Aminobenzene-carboxylic acid*	*para-Aminobenzene-carboxylic acid*
Nickel	65±3	56±3	61±3
Copper	154±9	74±3	125±8
Zinc	67±3	111±5	539±23

DISCUSSION

Looking at the conditional activation energy values obtained for the *ortho*-aminobenzenecarboxylic acid complexes it is possible to see the following sequence

$$E^*_{\mathrm{Cu^{II}}} > E^*_{\mathrm{Zn^{II}}} \simeq E^*_{\mathrm{Ni^{II}}}$$

This sequence agrees with that of the stability constants of these complexes in solution found by Young and Sweet[4] and with that of the ΔG sequence for the formation of the same complexes, proposed by Thompson[5] (Fig. 2).

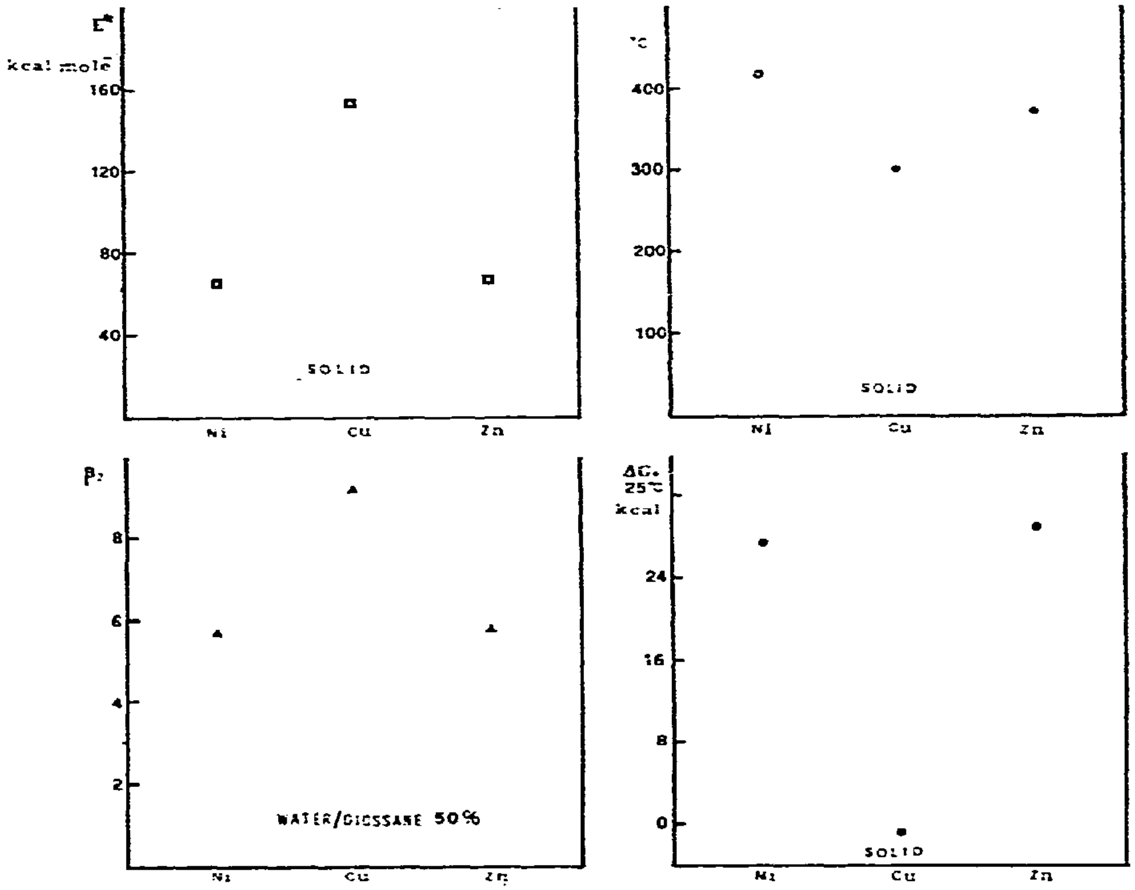

Fig. 4. Graphic representation of the parameters: E^* (a), pdt's (b), β (c) and ΔG (d) for the copper complexes of the *ortho*-aminobenzenecarboxylic acid.

While the activation energy is an increasing function of the complex stability in a series having the same ligand, the initial pdt is a decreasing function. This behaviour can be explained on the basis that the strength of intermolecular bonds plays a notable part in the thermal stability of solid compound as seen before[6]. It seems probable that the intermolecular bonds of the solid lattice of complexes having strong covalent metal–ligand bonds are weaker than those existing in the case of complexes in which the metal–ligand bond has a higher ionic character. We can assume that the lower ΔH value[5] for the formation of the copper(II)-*ortho*-aminobenzenecarboxylate involves an increase of the covalent bond Cu–N as explained by Nancollas[7] for similar compounds bringing about a more effective neutralization of cationic and anionic charges by reducing the distance between them. The study of Hill and Curran[8] on the IR spectroscopy of the complexes of the *ortho*-aminobenzenecarboxylic acid supports this hypothesis.

This phenomenon justifies whether the higher stability constant of the copper complex, or the lower decomposition temperature is a consequence of the weaker intermolecular bonds.

Finally examining the activation energy values in a series having the same central ion, e.g., the copper(II) with the three aminobenzenecarboxylic acids, we have the sequence:

$$E^*_{ortho} > E^*_{para} > E^*_{meta}$$

This behaviour can be justified considering that in the case of the *ortho*-aminobenzenecarboxylic acid there is the intramolecular stabilization effect whether for the formation of a chelate, or for the electron donor effect of the amino group that implies a charge delocalisation along the ring with a localisation of a δ^- on the carboxylic group and following stabilization of the Cu–carboxylic oxygen bond.

The copper–carboxylic group interaction is further increased by the bond shortening[7] with more neutralisation of the anionic and cationic charges.

For the *para*-aminobenzenecarboxylic acid we can assume that as regards the steric effect the chelation is impossible and then the metal is bound to the carboxyl group. The amino group in *para* position to the carboxyl group implies a charge delocalisation along the ring with a δ^- localisation on the carboxyl group and then a bond stabilization.

For the *meta*-aminobenzenecarboxylic acid we can still assume that there is no chelation and that the metal is bound to the carboxyl group, but now the amino group effect in *meta* position is lower with consequently a weaker metal–ligand bond.

The pdt's for both compounds are higher than for the copper(II)-*ortho*-aminobenzenecarboxylate. Considering the *meta* and *para* acid complexes, the higher percentage of the ionic bond accounts for the differences in the pdt's and the E^* values.

The nickel compounds show a similar behaviour, while the behaviour of the zinc complexes is quite different.

The activation energy values increase from the *ortho* to the *para* compound as the pdt's decrease. The reaction order for the *ortho*-aminobenzenecarboxylic acid complex is 2, and also for the nickel and copper compounds, and changes to 3 for the *para* complex and to 0.66 for the *meta* complex.

This phenomenon probably accounts for the formation of polymers with a consequent increase in activation energy.

ACKNOWLEDGEMENT

This work has been supported by the National Research Council (CNR).

REFERENCES

1 L. Erdey and G. Liptay, *Periodica Polytech.*, 7 (1963) 185.
2 L. Erdey, P. Marik-Korda and G. Liptay, *Talanta*, 15 (1968) 149.
3 G. D'Ascenzo, U. Biader Ceipidor, E. Cardarelli and A. D. Magri, *Thermochim. Acta*, 13 (1975) 449.
4 A. Young and T. R. Sweet, *J. Am. Chem. Soc.*, 80 (1958) 800.
5 J. K. Thompson and C. L. Wilson, *Anal. Chim. Acta*, 17 (1957) 185.
6 G. D'Ascenzo, U. Biader Ceipidor and G. De Angelis, *Anal. Chim. Acta*, 58 (1972) 175.
7 G. H. Nancollas, *Interactions in Electrolyte Solutions*, Elsevier, Amsterdam, 1966.
8 A. G. Hill and C. Curran, *J. Phys. Chem.*, 64 (1960) 1519.