Thermochimica Acta, 13 (1975) 333–339

THE THERMAL PROPERTIES OF COBALT(II), NICKEL(II) AND COPPER(II) IMINODIACETATES

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(Received 1 July 1975)

ABSTRACT

The thermal properties of the Cu(II), Ni(II) and Co(II) complexes of iminodiacetic acid (H_2IMDA) were determined using TG, DTG and DSC techniques. The complexes, of general formula, $MIMDA \cdot 2H_2O$ evolved water of hydration from 50 to 150°C which was followed by the decomposition of the anhydrous complex in the 250 to 400°C temperature range. The thermal stability, as determined by procedural decomposition temperatures, was: Ni(II)>Co(II)>Cu(II). The thermal stability is discussed in terms of IR spectra, ΔH, and ΔS, as well as thermal data.

INTRODUCTION

The solid complexes obtained by the reaction between iminodiacetic acid (H_2IMDA) and many metal ions have been studied in detail by a number of authors[1–5]. Contrary to previous studies, little is known about the thermal properties of this interesting series of metal complexes. It is the purpose of this paper to present the thermal properties, as determined by thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC), of the iminodiacetic complexes of cobalt(II), nickel(II) and copper(II).

EXPERIMENTAL PART

Instrumentation

The TG, DTG, and DSC curves of the solid complexes were obtained using a DuPont 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 thermocouple non-linearity and are, of course, procedural temperatures.

Preparation of complexes

The iminodiacetic acid used was Fisher Chemical Co. highest purity. The other chemicals employed were all of reagent grade quality.

The complexes were prepared by mixing a 0.1 M hot solution of the acid (prepared by weighing out the acid and then adding sodium hydroxide in sufficient quantity to dissolve it) and of the metal chloride until an initial ligand–metal molar ratio of 1:1 was obtained. This solution was concentrated on a steam-bath and then passed through an Al_2O_3 chromatographic column using as elutant a 1:1 mixture of ethanol:water. The fraction corresponding to the purified compound was collected and evaporated on a steam-bath until a moist solid was obtained, which was then placed under vacuo to obtain the crystalline solid compound.

Thermogravimetry was used to determine the water content and the residual metal oxide of the compounds; the metal contents were also determined by compleximetric titration.

RESULTS AND DISCUSSION

Cobalt(II) iminodiacetate

The TG, DTG and DSC curves of cobalt(II) complex, CoIMDA·$2H_2O$, are shown in Figs. 1 and 2.

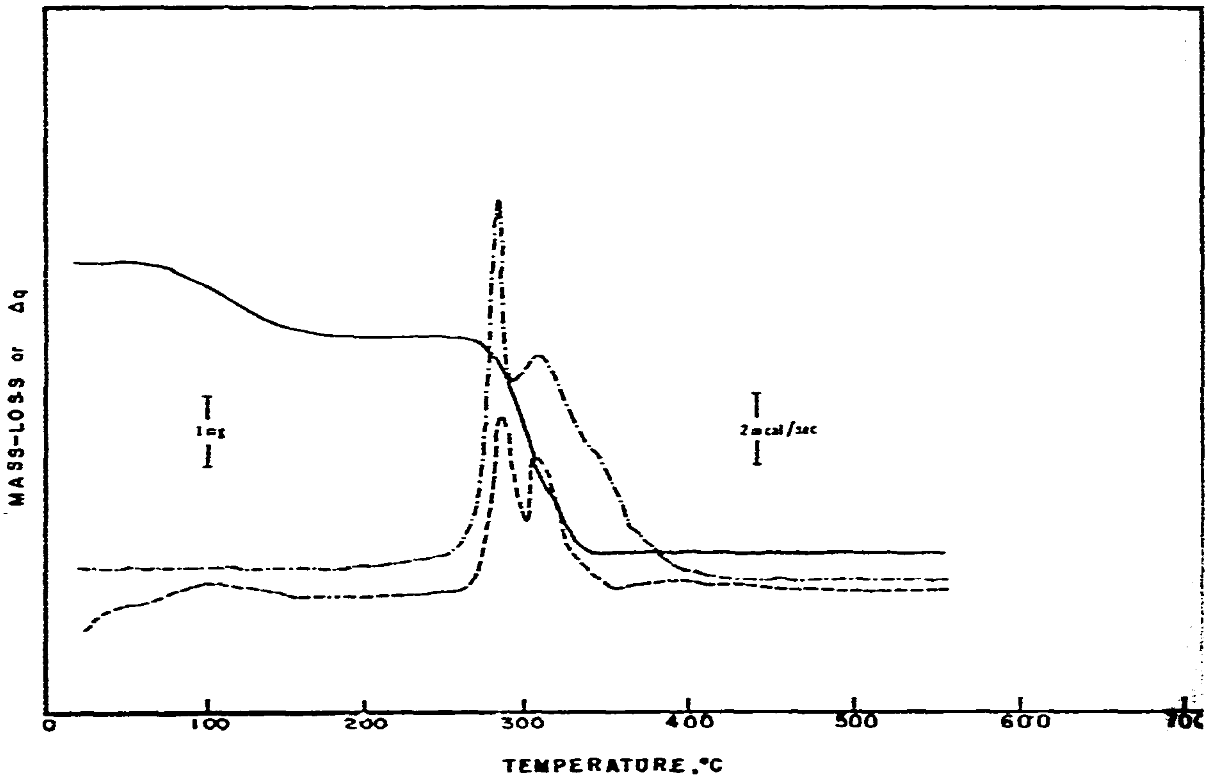

Fig. 1. TG, DTG, and DSC curves of CoIMDA·$2H_2O$. TG ———; DTG – – –; and DSC —·—· curves in an air atmosphere.

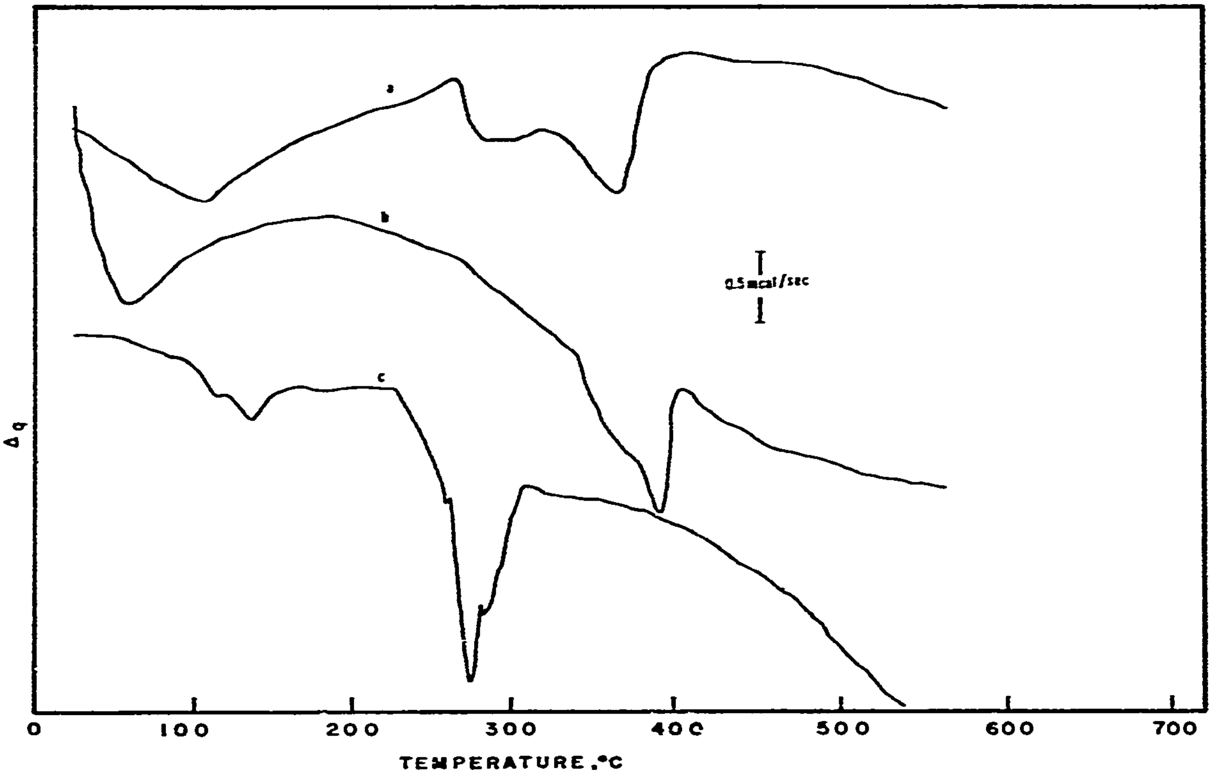

Fig. 2. DSC curves of complexes in a nitrogen atmosphere. (A) Cobalt(II) iminodiacetate; (B) nickel(II) iminodiacetate; (C) copper(II) iminodiacetate.

The TG curve indicates that water of hydration is evolved in a single step from 50 to about 175°C (15.8% found; 15.94% calc.) and this is followed by the decomposition of the anhydrous complex from about 250 to 350°C. Decomposition of the latter apparently takes place in several steps, as revealed by the shoulder peak on the DTG curve. Total mass-loss to the oxide, Co_3O_4, was 35.05%, compared to a calculated value of 35.52%. The DSC curve in nitrogen revealed only a single endothermic peak for the dehydration reaction which was followed by a doublet endothermic peak for the decomposition reaction. In air, the decomposition reaction resulted in a large exothermic doublet peak.

Nickel(II) iminodiacetate

The TG, DTG, and DSC curves of this compound, whose composition corresponded to the formula, $NiIMDA \cdot 2H_2O$, are given in Figs. 2 and 3

The TG curve was similar to that for the cobalt(II) compound in that water of hydration was evolved from 50 to 175°C (16.1% found; 15.97% calc.) followed by the decomposition of the anhydrous compound from 315 to 400°C. The latter decomposition reaction is also a multi-stage process whose mass-loss to the oxide, NiO, corresponded to 32.9% found compared to 33.07% for the calculated value. The DSC curve in nitrogen revealed a single endothermic peak for the dehydration

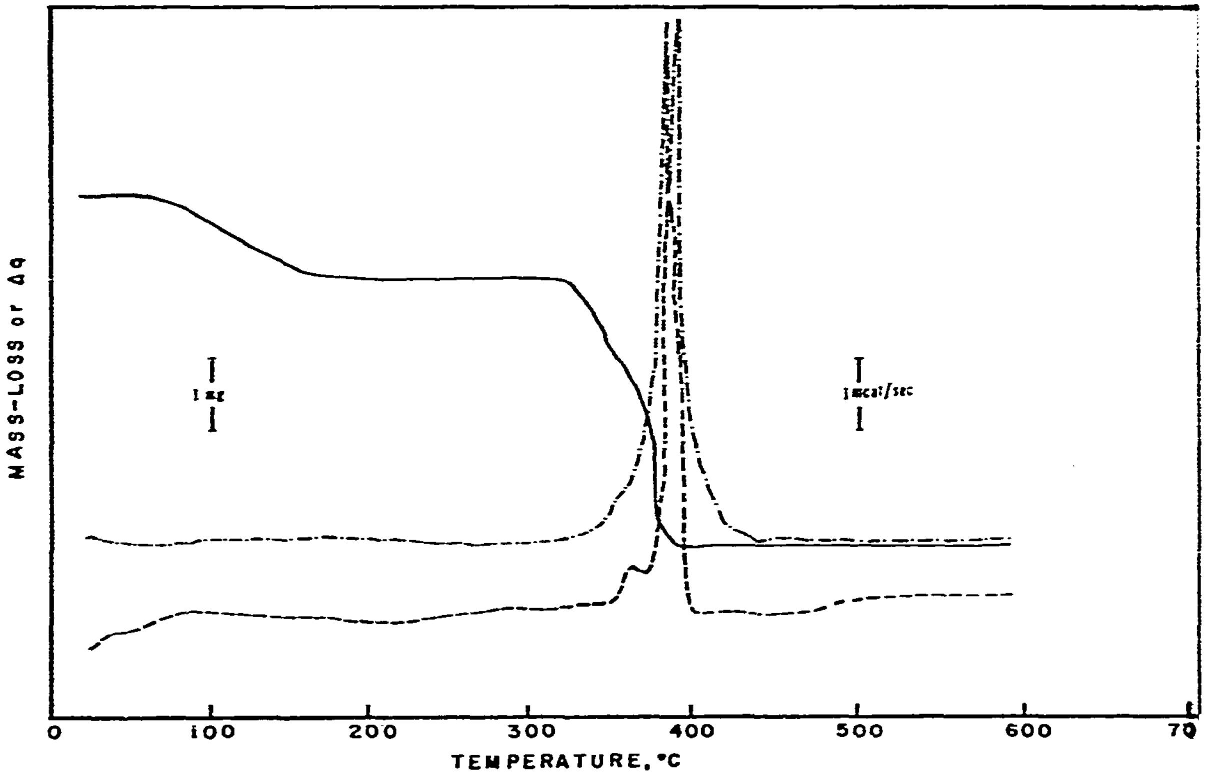

Fig. 3. TG, DTG, and DSC curves of NiIMDA·$2H_2O$. TG ———; DTG – – –; and DSC —·—· curves in an air atmosphere.

reaction followed by a larger endothermic peak for the decomposition reaction. There is evidence, due to the shoulder peaks, of the multi-stage process observed in the TG curve.

Copper(II) iminodiacetate

The TG, DTG, and DSC curves of this compound, whose composition was also that of the 2-hydrate, CuIMDA·$2H_2O$, are given in Figs. 2 and 4.

The first mass-loss observed in the TG curve corresponded to that for the dehydration reaction (15.8% found; 15.97% calc.) which occurred over the temperature range from 100 to 150°C. The DSC curve in nitrogen shows two small, unresolved endothermic peaks which suggests a two-stage dehydration reaction—this was not observed on any of the other complexes, however. The anhydrous complex undergoes thermal decomposition in the temperature range from 205 to 290°C to give the oxide, CuO, as the residue (34.2% found; 34.50% calc.). The DSC curves in an air atmosphere, for the decomposition reaction indicate only a single exothermic peak, while in a nitrogen atmosphere, several shoulder peaks were observed on an endothermic peak.

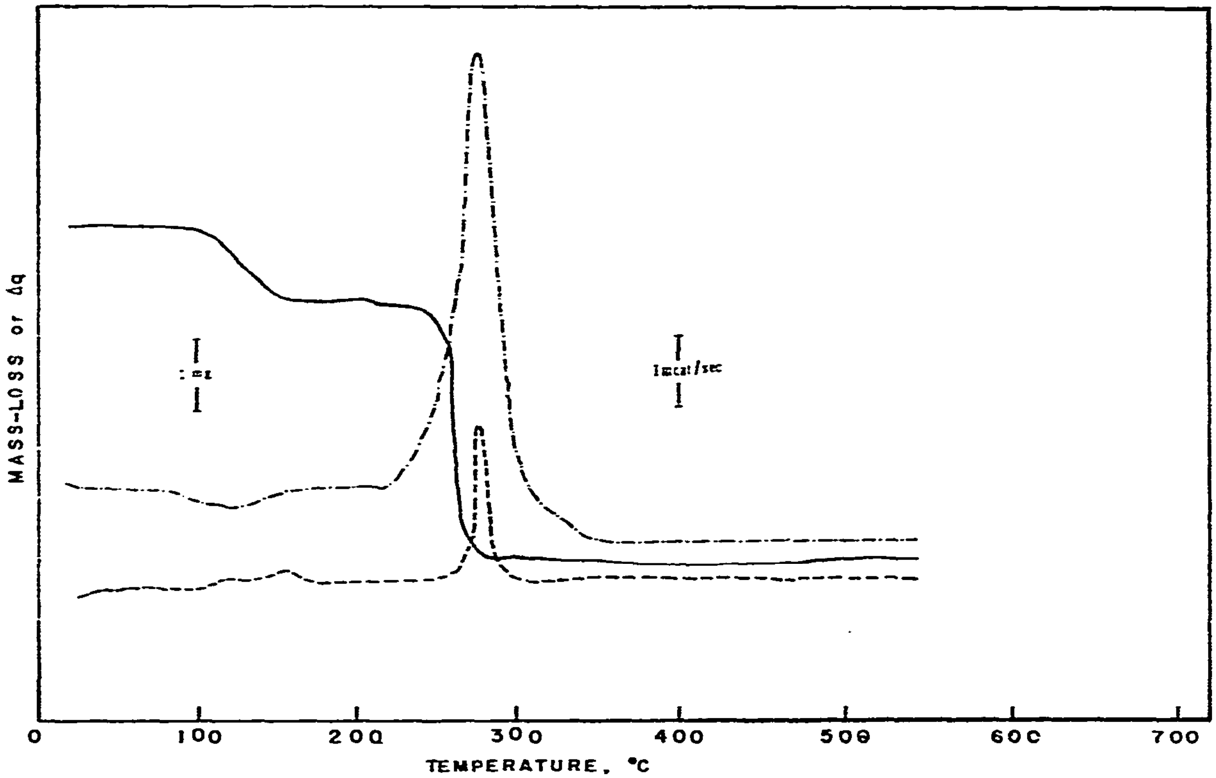

Fig. 4. TG, DTG, and DSC curves of CuIMDA·$2H_2O$. TG ———; DTG – – –; and DSC —·—· curves in an air atmosphere.

DISCUSSION

The order of procedural decomposition temperatures, as determined by the TG and DSC curves, is:

Ni(II) > Co(II) > Cu(II)

This order can be explained on the basis that the intermolecular bonds of the solid lattice of the complexes having strong covalent metal–ligand bonds are weaker than those existing in the case of the complexes in which the metal–ligand bond has a higher ionic character[6]. On the basis of an increase in the intramolecular bonds there is an increase in the stability of the complex and a decrease in the procedural decomposition temperatures.

Looking at the IR spectra of these compounds[4], it is possible to see that the N–H frequencies are lower for these complexes than for the sodium and potassium salts, indicating the presence of a metal–nitrogen bond. This bond weakens the N–H bond and the shift of this band is a measure of the Me–N bond strength. The band shift is largest for the copper(II) compound and smallest for the nickel(II) and cobalt(II) compounds. At the same time, the asymmetric vibration band, ν_a(COO), is situated at about 1700 cm^{-1} for the –COOH group and shifted to 1550–1620 cm^{-1} for the metal complexes. The metal–carboxylate bond is shifted to 1580–1590 cm^{-1} which is consistent with an ionic bond between the metal ion and carboxylate ion. The fact that the shift is practically the same for all the compounds accounts for similar bond strengths of the ionic bonds.

TABLE 1

THERMODYNAMIC DATA FOR THE FORMATION OF 1:1 METAL–IMINODIACETATE COMPLEXES IN AQUEOUS SOLUTIONS AT 20°C (ref. 7)

Function[a]	*Co(II)*	*Ni(II)*	*Cu(II)*
ΔH	−2.14	−5.05	−4.5
ΔG	−9.35	−10.98	−14.25
ΔS	24.6	20.0	33.3

[a] The usual units are used.

Looking now at the thermodynamic data of these complexes in Table 1, as given by Anderegg[7], it is possible to see that the change in entropy for the complex formation is:

$$\Delta S_{\mathrm{Cu}}\mathrm{II} > \Delta S_{\mathrm{Co}}\mathrm{II} > \Delta S_{\mathrm{Ni}}\mathrm{II}$$

This order agrees well with the thermal data. It is interesting to note that on plotting the ΔS values against the ionic radius, the curve obtained is quite different from that of Care and Staveley[8] who found that ΔS decreases as the radius of the cation increases. This order, as well as that found in the thermal data, is the reverse of the usual Irving and Williams[9] order for the stability of metal complexes in solution. Using the ΔH values, this change is given as:

$$\Delta H_{\mathrm{Co}}\mathrm{II} > \Delta H_{\mathrm{Cu}}\mathrm{II} > \Delta H_{\mathrm{Ni}}\mathrm{II}$$

which disagrees with the data of Sharma et al.[10] who found that for the complexes of the amino acid anions, the ΔH_1 and ΔH_2 values are generally more negative than for the complexes of other metals. This difference can probably be explained considering that the complexes have, as proposed by Laitinen and Nortia[4], a bicyclic chelate structure where the nitrogen and both the carboxylate groups of the ligand are coordinated to the metal. The metal ion in solution is particularly closely associated with six water molecules, each one of which can separately take a better position to minimize the energy of the system and to maximize the strength of the bonding. Contrarily, in a bicyclic chelate structure, the atoms available for the coordination have lower degrees of freedom and not all of the atoms are in an optimum position in relation to the central metal ion. Then the radius of the central metal ion must affect the degree of distortion of the bonds and this will also influence the distances between the oxygen atoms in the different carboxyl groups, between which there is a repulsion. However, the ΔS values, which are large and positive, contribute in a prevailing manner to the complexes stability.

ACKNOWLEDGMENTS

The partial financial support of this work by the CNR (Italy) and the Robert A. Welch Foundation (Houston, Texas) are gratefully acknowledged.

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