

THERMAL PROPERTIES OF COBALT(II), NICKEL(II) AND COPPER(II) GLYCINATES AND IMINODIACETATES. CRITICAL COMPARISON

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ABSTRACT

The thermal properties of the Co(II), Ni(II) and Cu(II) complexes of iminodiacetic acid (H_2IDA) and of glycine were determined using TG, DTG and DSC techniques. The thermal properties of the two series were compared and discussed in terms of IR spectra, ΔH , ΔG and ΔS for the formation of the complexes in aqueous solutions, as well as the thermal data.

INTRODUCTION

The solid complexes obtained on the reaction between iminodiacetic acid (H_2IDA) or glycine (Gly) and many metal ions have been studied in detail by a number of authors [1-12]. The purpose of this paper is to compare and discuss the thermal properties, as determined by thermogravimetry (TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC), of the two series obtained on the reaction of cobalt(II), nickel(II) and copper(II), respectively, with iminodiacetic acid and glycine.

The thermal properties are discussed in terms of IR spectra, and ΔH , ΔG and ΔS values for the formation of the complexes in aqueous solution, as well as the thermal data.

EXPERIMENTAL

Instrumentation

The TG, DTG and DSC curves of the solid complexes were obtained using a Perkin-Elmer differential scanning calorimeter (model DSC-2b) equipped with a data-station and a Perkin-Elmer thermobalance (model

TGS-2). The heating rates ranged between 2.5 and 10°C min⁻¹ using 1–10-mg samples. The furnace atmosphere consisted of either dry, 99.999% purity 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 and glycine were obtained from Sigma Chemical Co. All the other chemicals employed were obtained from Merck. The nickel(II) and copper(II) glycinates were prepared by the procedure suggested by Sen et al. [7], while cobalt(II) glycinate was prepared as described by Petru and Jursik [8]. Each compound was crystallized from water three times, washed with ice-cold water, then dried in a vacuum desiccator at room temperature. The iminodiacetic acid complexes were prepared by mixing a 0.1 M hot solution of the acid (prepared by dissolving the appropriate weight of the acid in a sufficient quantity of sodium hydroxide) and a 0.1 M solution of the metal chloride, until an initial ligand–metal molar ratio of 1:1 was obtained. This solution was concentrated over a steam bath and passed through an Al₂O₃ chromatographic column using, for the elution, a 1:1 (v/v) 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 placed under vacuo to obtain the crystalline solid compound. Thermogravimetry was used to determine the water and the residual metal oxide contents of the compounds, the metal contents were determined by compleximetric titration.

RESULTS AND DISCUSSION

TG, DTG and DSC curves in air atmosphere of the two series of the Me(II)–iminodiacetic and Me(II)–glycine complexes are given in Figs. 1–3 and 4–6, respectively, while the DSC curves in nitrogen atmosphere are given in Figs. 7 and 8. The formulae of compounds fitting the TG curves and the data obtained by TG are collected in Table 1.

General

The procedural thermal stability order of the complexes within the two series is Ni(II) > Co(II) > Cu(II), and, comparing the same cation for the two series, the thermal stability order is Me(II)IDA > Me(II)(Gly)₂. As discussed earlier [13] this behaviour can be explained on the basis that the intermolecular bonds of the solid lattice of the complexes, having strong

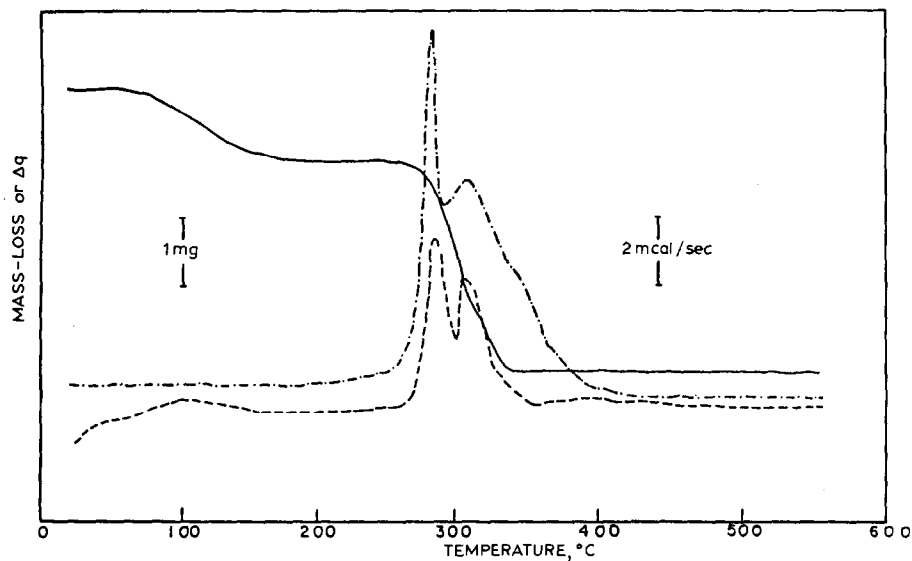


Fig. 1. TG (—), DTG (---), and DSC (·-·-·) curves of $\text{Co(IDA)} \cdot 2 \text{H}_2\text{O}$ in an air atmosphere.

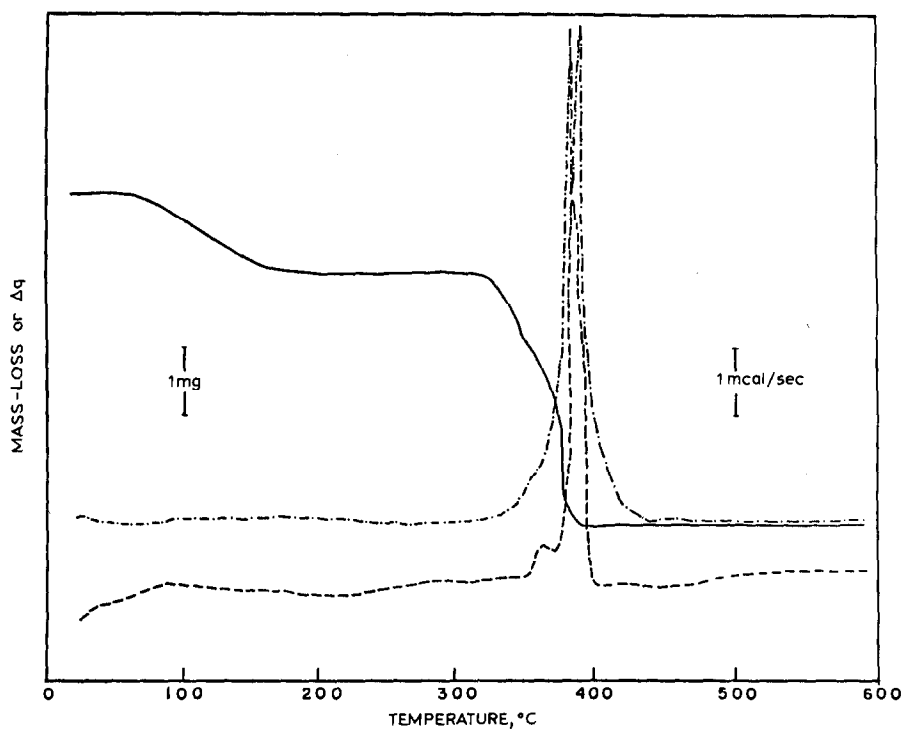


Fig. 2. TG (—), DTG (---), and DSC (·-·-·) curves of $\text{Ni(IDA)} \cdot 2 \text{H}_2\text{O}$ in an air atmosphere.

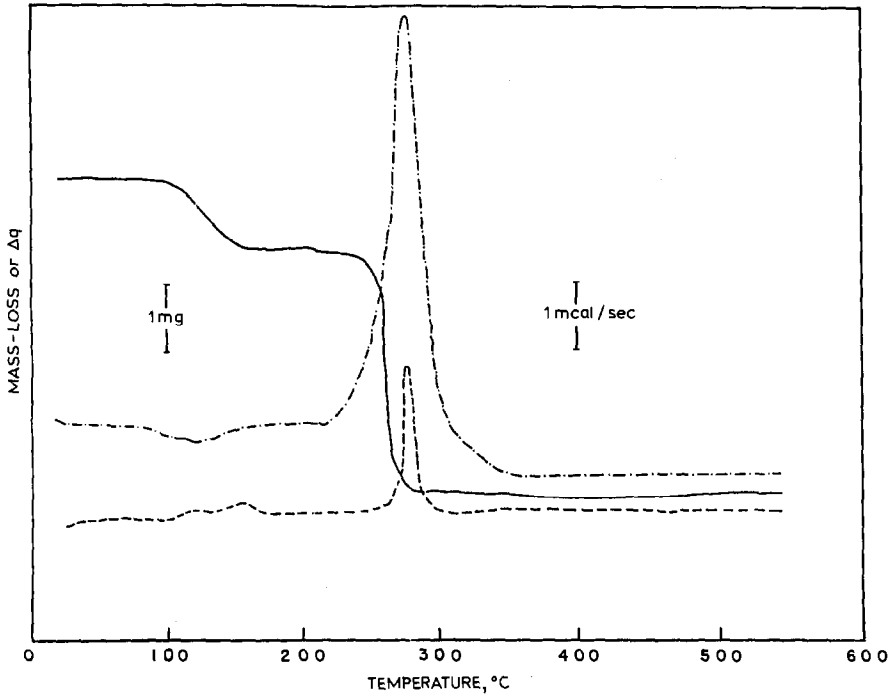


Fig. 3. TG (—), DTG (---), and DSC (·-·-·) curves of $\text{Cu(IDA)} \cdot \text{H}_2\text{O}$ in an air atmosphere.

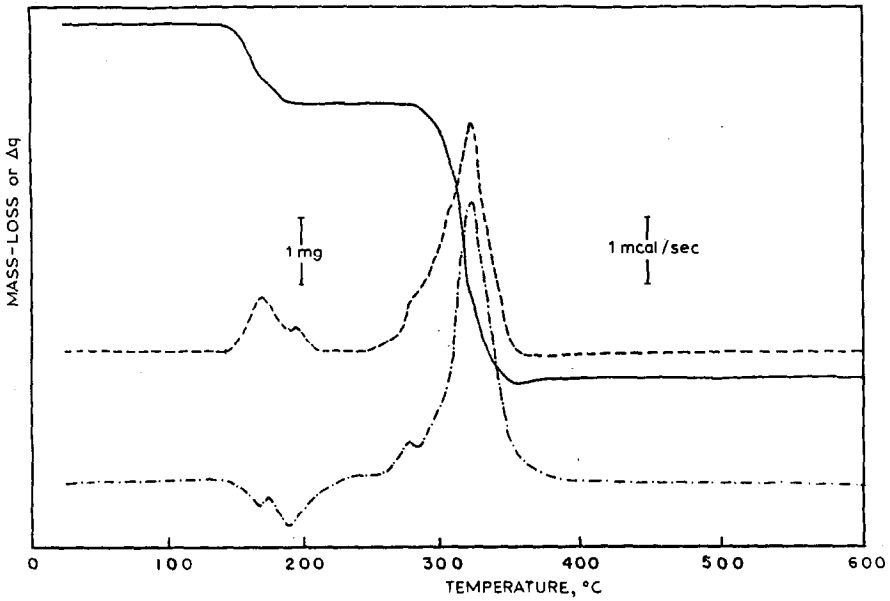


Fig. 4. TG (—), DTG (---), and DSC (·-·-·) curves of $\text{Co(Gly)}_2 \cdot 2 \text{H}_2\text{O}$ in an air atmosphere.

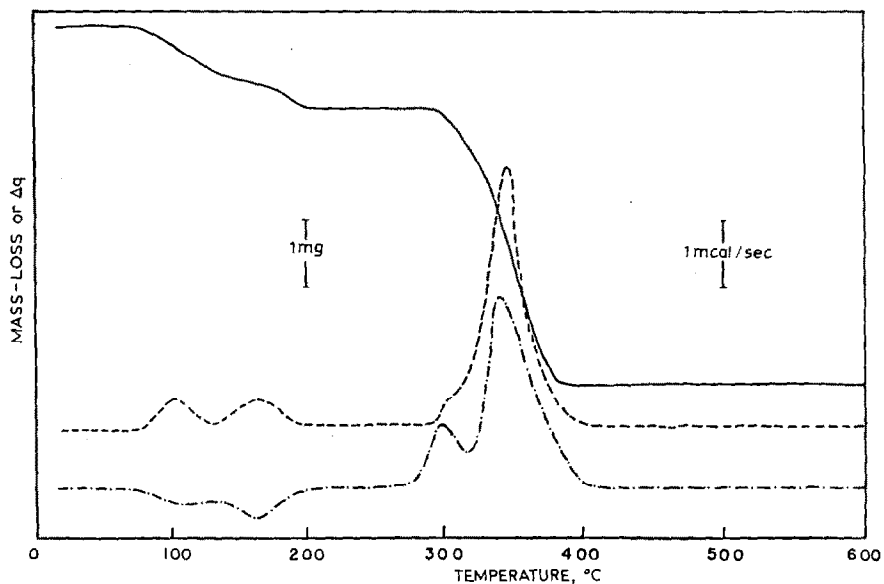


Fig. 5. TG (—), DTG (---), and DSC (·-·-·) curves of $\text{Ni}(\text{Gly})_2 \cdot 2 \text{H}_2\text{O}$ in an air atmosphere.

covalent metal–ligand bonds, are weaker than those existing when the metal–ligand bonds have an ionic character.

From the thermodynamic data for the formation of the two series of

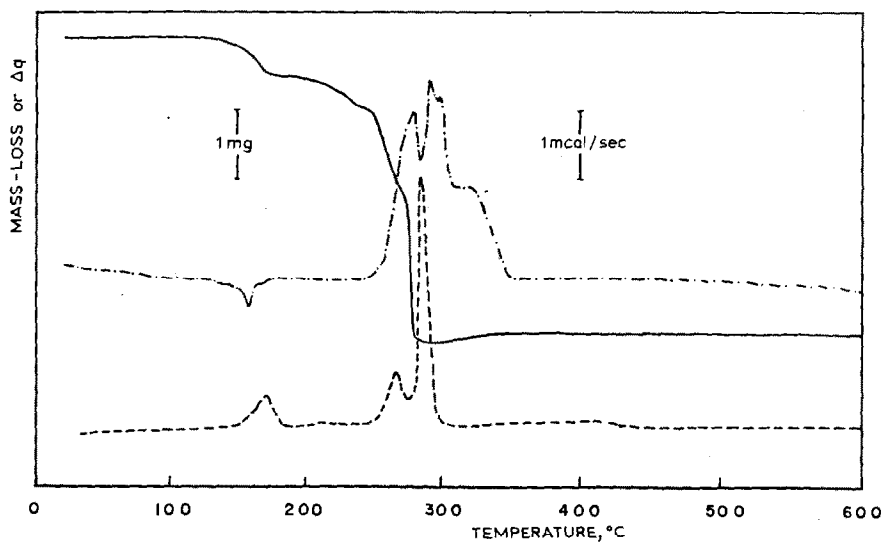


Fig. 6. TG (—), DTG (---), and DSC (·-·-·) curves of $\text{Cu}(\text{Gly})_2 \cdot 2 \text{H}_2\text{O}$ in an air atmosphere.

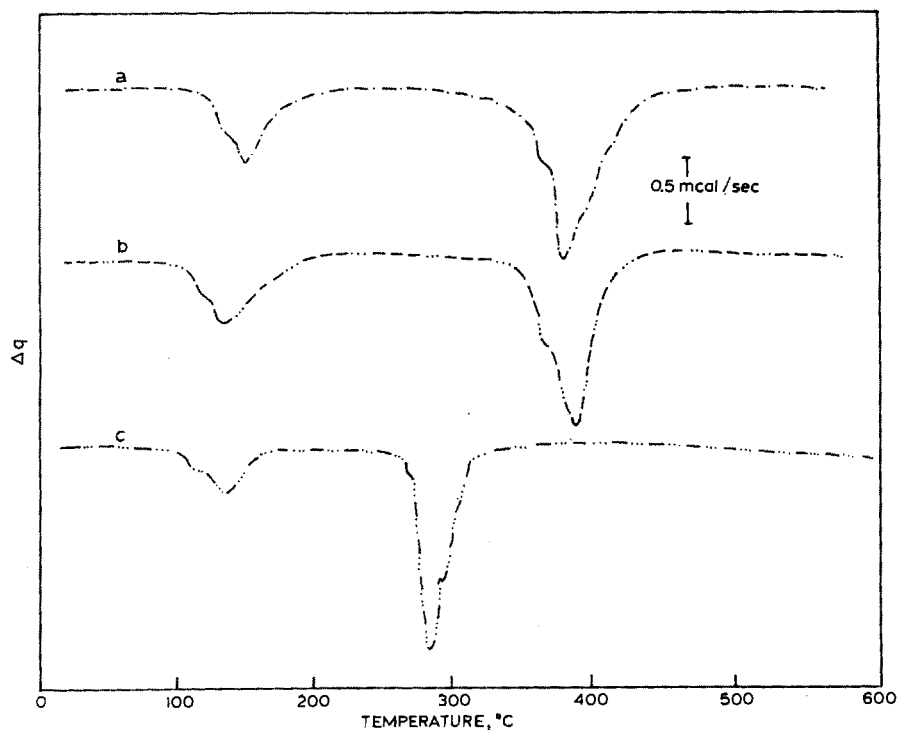


Fig. 7. DSC curves of complexes in a nitrogen atmosphere. (a) Cobalt(II) iminodiacetate; (b) nickel(II) iminodiacetate; (c) copper(II) iminodiacetate.

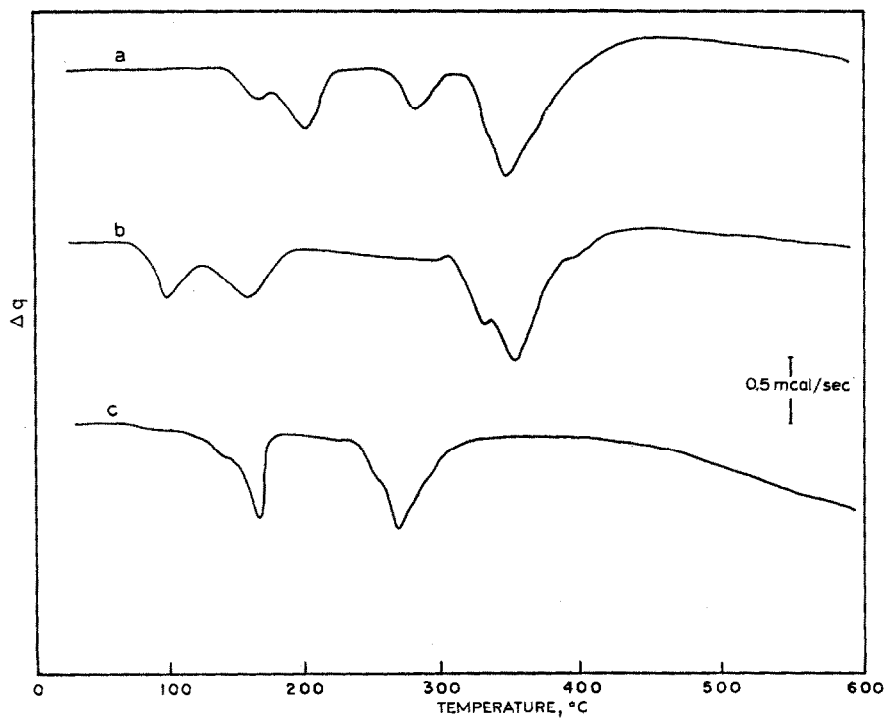


Fig. 8. DSC curves of metal glycinate complexes in a nitrogen atmosphere. (a) Cobalt(II) glycinate; (b) nickel(II) glycinate; (c) copper(II) glycinate.

TABLE 1

Water and metal oxide data: theoretical and TG data for water and metal oxide of the Me(II) IDA and Me(II) Gly compounds

Formulae	Water (%)		Metal oxide	
	Found	Theor.	Formula	Theor.
Co(IDA)·2 H ₂ O	15.7	15.92	Co ₃ O ₄	35.51
Ni(IDA)·2 H ₂ O	16.1	15.94	NiO	33.08
Cu(IDA)·2 H ₂ O	15.8	16.61	CuO	34.49
Co(Gly) ₂ ·2 H ₂ O	14.8	14.81	Co ₃ O ₄	33.02
Ni(Gly) ₂ ·2 H ₂ O	14.7	14.82	NiO	30.76
Cu(Gly) ₂ ·H ₂ O	8.0	7.84	CuO	34.64

TABLE 2

Thermodynamic data for the formation of iminodiacetate (IDA; ligand/metal ratio, 1 : 1) and glycinate (Gly; ligand/metal ratio, 2 : 1) complexes in aqueous solutions

	Co ²⁺	Ni ²⁺	Cu ²⁺
ΔH_{IDA}	-2.14	-5.05	-4.5
ΔH_{Gly}	-6.37	-9.6	-13.18
ΔG_{IDA}	-9.35	-10.98	-14.25
ΔG_{Gly}	-11.71	-15.35	-21.37
ΔS_{IDA}	24.6	20.0	33.3
ΔS_{Gly}	20.0	19.5	27.5

TABLE 3

 ΔH and ΔS values for [Me(II)(en)]²⁺ complexes in aqueous solution

	Co ²⁺	Ni ²⁺	Cu ²⁺
ΔH	-6.90	-8.90	-13.00
ΔS	4.0	5.5	5.4

complexes [14–17], collected in Table 2 and plotted in Fig. 9, it is evident that the changes in entropy are

$$\Delta S_{\text{Cu}(\text{Gly})_2 \cdot 2 \text{H}_2\text{O}} > \Delta S_{\text{Co}(\text{Gly})_2 \cdot 2 \text{H}_2\text{O}} > \Delta S_{\text{Ni}(\text{Gly})_2 \cdot 2 \text{H}_2\text{O}}$$

and

$$\Delta S_{\text{Cu}(\text{IDA}) \cdot \text{H}_2\text{O}} > \Delta S_{\text{Co}(\text{IDA}) \cdot 2 \text{H}_2\text{O}} > \Delta S_{\text{Ni}(\text{IDA}) \cdot 2 \text{H}_2\text{O}}$$

Comparing the two series the entropy change for the formation of Me(II)–iminodiacetic complexes is, considering the same cation, always higher than that of Me(II)–glycine complexes.

From the entropy changes for the formation of Me(II)–ethylenediamine [18] complexes it is evident that they are in the region of 5 e.u., or ~ 2 –3 e.u. per amino group, whilst the entropy changes for the Me(II)–glycine complexes lie between 20 and 28 e.u. (Table 3). Therefore, the contribution of a

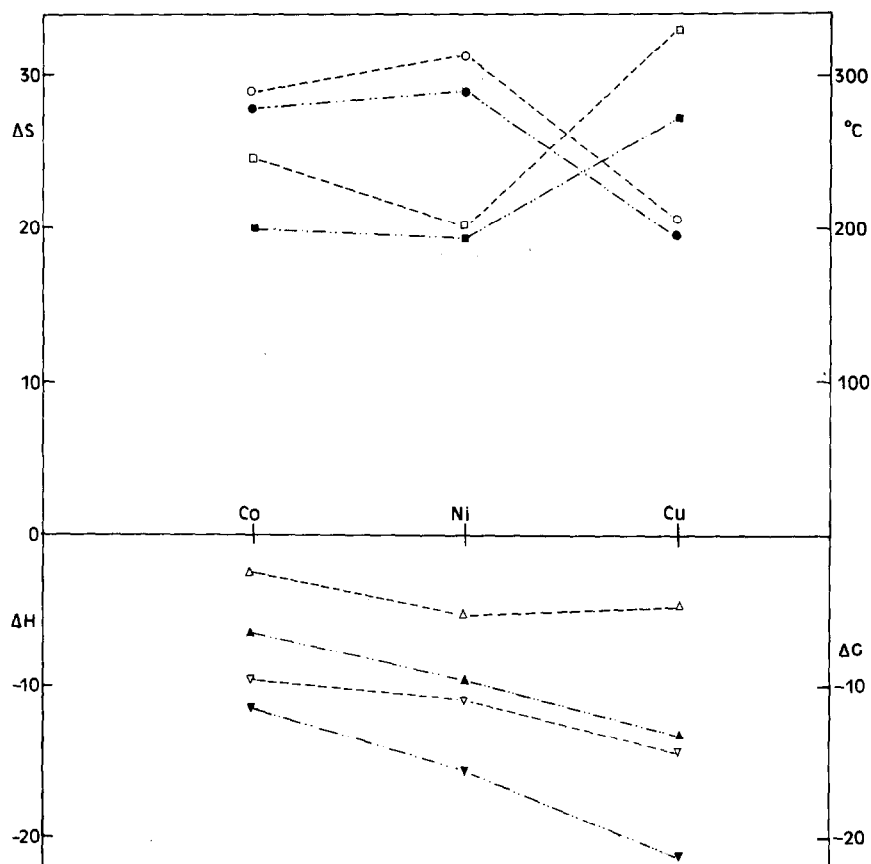


Fig. 9. PDT's (procedural decomposition temperatures) and thermodynamic data for the formation of Me(II)IDA and Me(II)Gly₂ complexes in aqueous solutions: Me(II)IDA: PDT (○); ΔS (□); ΔH (Δ); and ΔG (▽); Me(II)Gly₂: PDT (●); ΔS (■); ΔH (▲); and ΔG (▼).

carboxylate group to the entropy change lies in the region 8–12 e.u. The entropic change for the Me(II)–iminodiacetic acid lies between 20 and 33 e.u., corresponding to 9–15 e.u. per carboxylate group. For the copper complexes the values are at the upper limit, and the differential between the values in the two series are the highest, while for the nickel complexes the differentials are the lowest and the values are at the minimum limit.

The order of ΔH values for these complexes is, for the glycine series

$$\Delta H_{\text{Co(II)}} > \Delta H_{\text{Ni(II)}} > \Delta H_{\text{Cu(II)}}$$

while for the iminodiacetic acid series the order is

$$\Delta H_{\text{Co(II)}} > \Delta H_{\text{Cu(II)}} > \Delta H_{\text{Ni(II)}}$$

From the ΔH values for the ethylenediamine complexes and glycine complexes [19,20] it is evident that the ΔH values for glycine, with both one amino and one carboxylate group, are about half the corresponding values for ethylenediamine (Table 3). Therefore, the contribution to the total enthalpy by the carboxylate group is apparently very small, accounting for the much lower ΔH values of the iminodiacetic acid complexes. Moreover, the differentials between the ΔH values for corresponding complexes of the two series are quite high.

Considering in particular the copper(II) complexes, it is evident that, according to Sharma et al. [21] and Nancollas [22], the ΔH value for the Cu(II) complex with glycine is more negative than that for complexes of other metals. This behaviour can be explained in terms of the unique electronic configuration of the Cu(II) ion (d^9), which is subject to the Jahn–Teller effect [23]. Therefore, a tetragonal distortion of the octahedral symmetry would lead to four short bonds in the xy plane and two long bonds along the z axis. Consequently, the covalent character of the Cu–N bond increases with the negativity of ΔH , producing a more effective neutralization of cationic and anionic charges, by reducing the distances between them. Decreasing the residual metal-ion field will, therefore, have a lower influence on water dipoles with an additional gain of entropy.

The exception of the Cu(II)–IDA complex can probably be explained, as proposed by Laitinen and Nortia [4], by considering that the complexes have a bicyclic chelate structure where the nitrogen and both carboxylate groups of the ligand are coordinated to the metal.

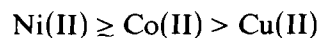
The radius of the central ion must also affect the degree of distortion of the bond, because the metal ion in solution is particularly closely associated with six molecules of water, each of which can separately assume an optimum position for both minimizing the energy of the system and maximizing the strength of the bonding. In a bicyclic chelate structure the atoms available for coordination have lower degrees of freedom, and not all of the atoms are in optimum positions in relation to the central ion, therefore,

influencing the distances between the oxygen atoms in the different carboxyl groups between which there is a repulsion.

Glycine is obviously intermediately situated between the aquo-complexes and the iminodiacetic complexes. However, in the same series, the large, positive ΔS values contribute continually to the thermal stability scale, but comparing the two series the large difference between the enthalpic values plays an important role and justifies the higher thermal stability of the iminodiacetic acid complexes. An examination of the IR spectra supports this hypothesis; the peaks in the 3- μm region [4,7,8] can be assigned to the N-H stretching vibration and the shift of the N-H band, which is a measure of the Me-N bond strength, is, for each series, higher for copper(II) while it is about the same order of magnitude for nickel(II) and cobalt(II). It is higher for the glycine series than for the iminodiacetic acid series.

The N-H stretching vibration frequency changes on the formation of an Me-N bond, if the bond is essentially covalent.

Simultaneously, the absorptions in the 1600 cm^{-1} region indicate that the resonance in the carboxylate ion (resulting in equivalent carbon-oxygen bonds) is preserved in the complexes. The oxygen-metal bonds in these complexes must, therefore, essentially be electrostatic, and the contribution of the electrostatic bond is, within one series, of the following type



while for the two series



according to the thermal behaviour within and between the series.

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