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

G. D'ASCENZO

Istituto di Chimica Analitica, Universita degli studi di Roma, 00185 Roma (Italy)

W. W. WENDLANDT

Department of Chemistry, University of Houston, Houston, Texas 77004 (U.S.A.)
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ABSTRACT

The thermal properties of the Ni(II), Co(II) and Cu(II) complexes of glycine were determined using TG, DTG and DSC techniques. The complexes, $MGly_2 \cdot nH_2O$ ($n = 1, 2$), dehydrated in the temperature range of 75 to 200°C, followed by the decomposition of the anhydrous compounds in the temperature range of 200 to 400°C. The thermal stability of the complexes, as determined by procedural decomposition temperatures, was: Ni(II) > Co(II) > Cu(II).

INTRODUCTION

The glycine complexes of the first transition series metals, especially those of cobalt(II), nickel(II), and copper(II), have been the subject of numerous investigations[1–7]. Perhaps the least studied property of these complexes are those pertaining to their thermal stability under various experimental conditions. 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 glycine 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 glycine used was obtained from the Fisher Chemical Co. All of the other chemicals employed were of reagent grade quality.

The nickel(II) and copper(II) glycinates were prepared by the procedure described by Sen et al.[2], while the procedure used to prepare the cobalt(II) glycinate was suggested by Frantisek and Frantisek[3]. Each compound was crystallized from water three times, washed with ice-cold water, then dried in a vacuum desiccator at room temperature. Thermogravimetry was used to determine the water content and the residual metal oxide of the compounds.

Reflectance spectra

The diffuse reflectance spectra of the complexes were obtained using a Beckman Model DK-2A spectroreflectometer.

RESULTS AND DISCUSSION

Cobalt(II) glycinate

The TG, DTG and DSC curves of cobalt(II) glycinate, $CoGly_2 \cdot 2H_2O$, are given in Figs. 1 and 2.

All of the thermal analysis curves show that the water of hydration is evolved in two steps from 140 to 190°C (14.7% found; 14.81% calc.). The resulting anhydrous

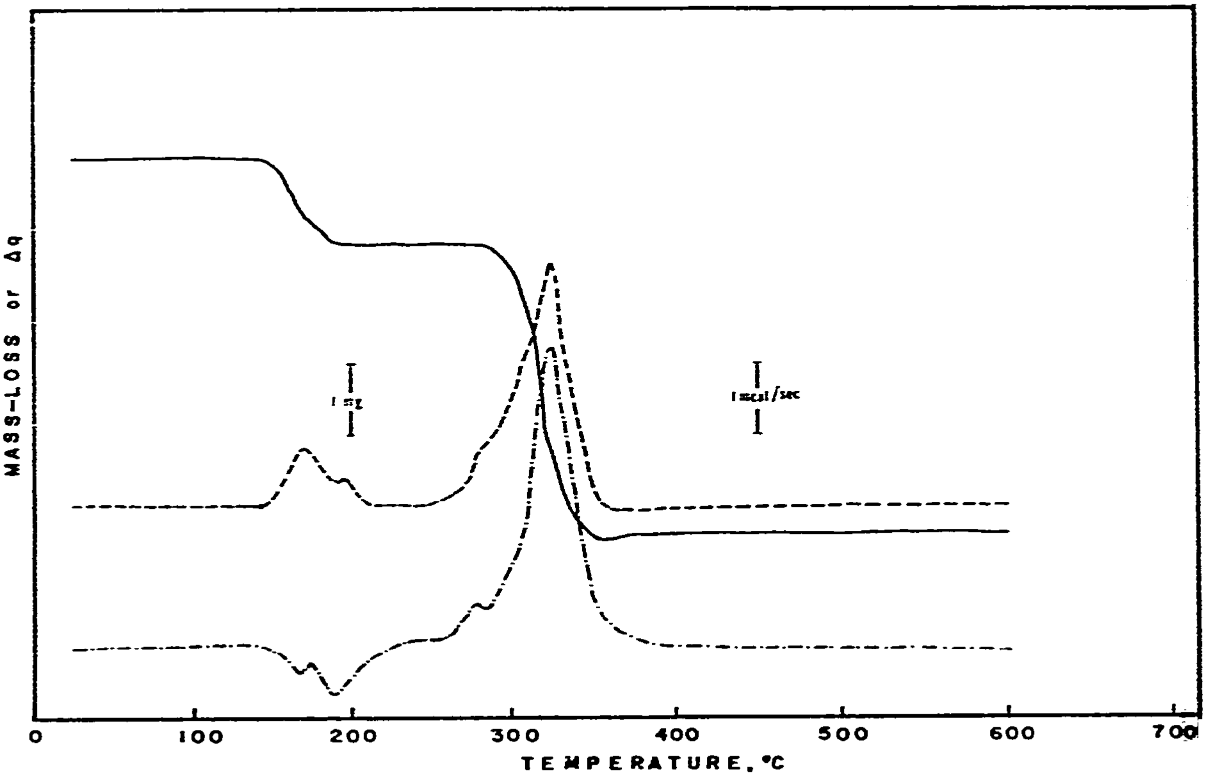

Fig. 1. TG, DTG and DSC curves of $CoGly_2 \cdot 2H_2O$ in an air atmosphere. TG ———; DTG – – –; and DSC —·—·.

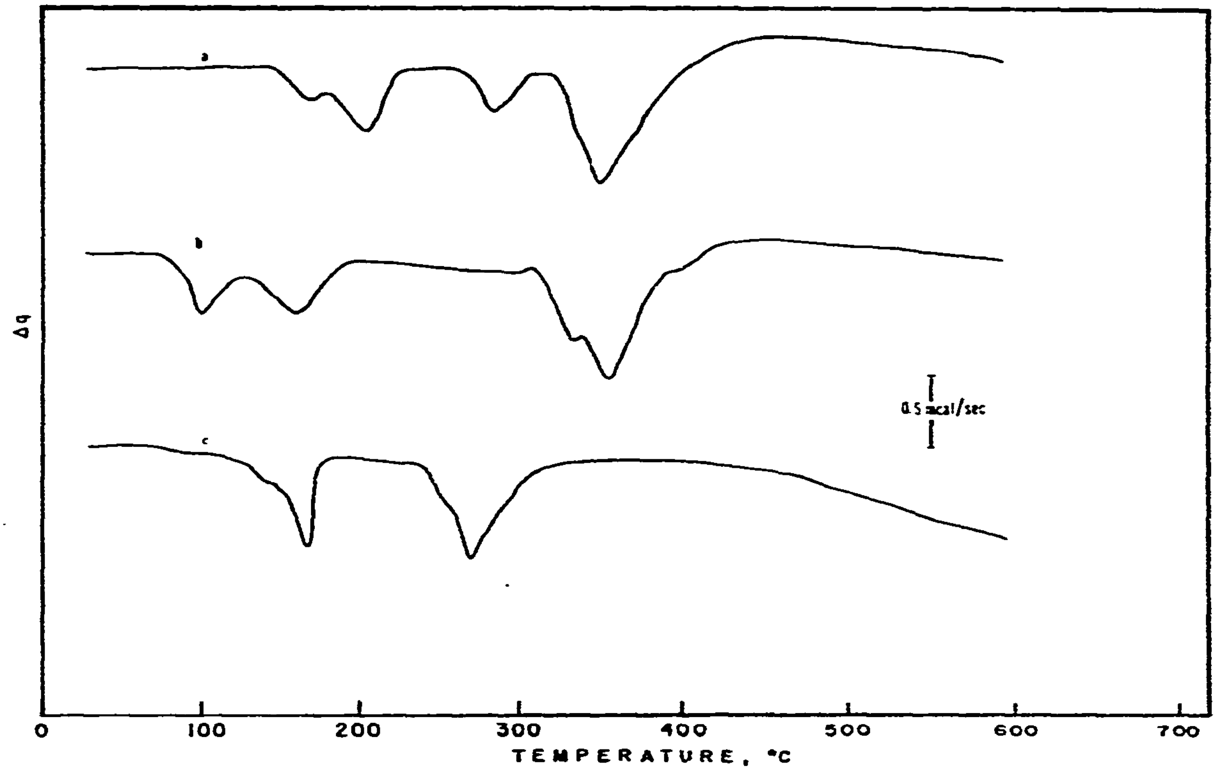

Fig. 2. DSC curves of metal glycinates in a nitrogen atmosphere. (A) cobalt(II) glycinate; (B) nickel-(II) glycinate; (C) copper(II) glycinate.

complex then dissociates between 290 and 360 °C to give a residue of the metal oxide, Co_3O_4 (33.2% found; 33.01% calc.). In air, the latter reaction is exothermic, while in nitrogen it is endothermic. The DSC curve in nitrogen contains two well-defined peaks for the decomposition reaction, however, not enough data are given to interpret the origin of the two curve peaks. In air, the first reaction for the decomposition shows up as a shoulder peak rather than a completely resolved peak.

Nickel(II) glycinate

The TG, DTG and DSC curves of $NiGly_2 \cdot 2H_2O$ are shown in Figs. 2 and 3.

The blue colored crystals evolved water of hydration over a fairly large temperature interval, 75 to 200°C (14.9% found; 14.82% calc.), and indicate the presence of an intermediate hydrate. The pale green colored anhydrous compound, $NiGly_2$, dissociates in the temperature range of 290 to 400 °C to give the metal oxide, NiO (31.2% found; 30.76% calc.). There is evidence for a multi-step decomposition reaction as indicated by shoulder peaks on the DSC curve peaks in both air and nitrogen. However, the curve peaks are not resolved as was the case with the cobalt(II) complex.

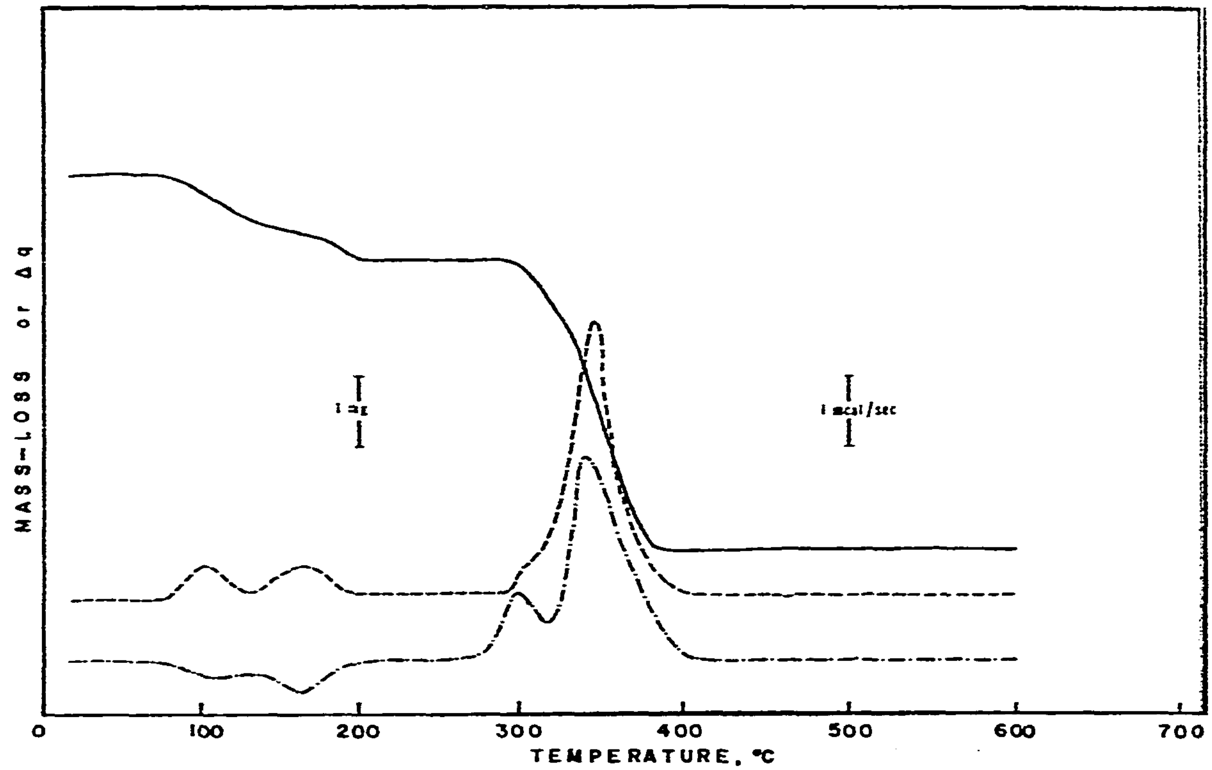

Fig. 3. TG, DTG and DSC curves of $NiGly_2 \cdot 2H_2O$ in an air atmosphere. TG ———; DTG – – –; DSC –·–·–.

Copper(II) glycinate

The TG, DTG and DSC curves of $CuGly_2 \cdot H_2O$ are given in Figs. 2 and 4.

The TG curve for this compound shows that the water of hydration is evolved in the temperature range from 125 to 180°C (8.0% found; 7.84% calc.). Contrary to the other compounds, the copper(II) complex is the 1-hydrate rather than the 2-hydrate. The anhydrous compound, $CuGly_2$, decomposes in the temperature range from 200 to 300°C, yielding the metal oxide, CuO (31.9% found; 32.12% calc.). Again, there is evidence in the DSC curves, both in air and in nitrogen, of a multi-step dissociation process, the exact nature of which is not known. It is also difficult to determine at what temperature the dissociation reaction begins due to the gradual mass-loss at the early stages of the reaction.

General

The procedural thermal stability order of the complexes is:

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

As discussed earlier[8], this behavior 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

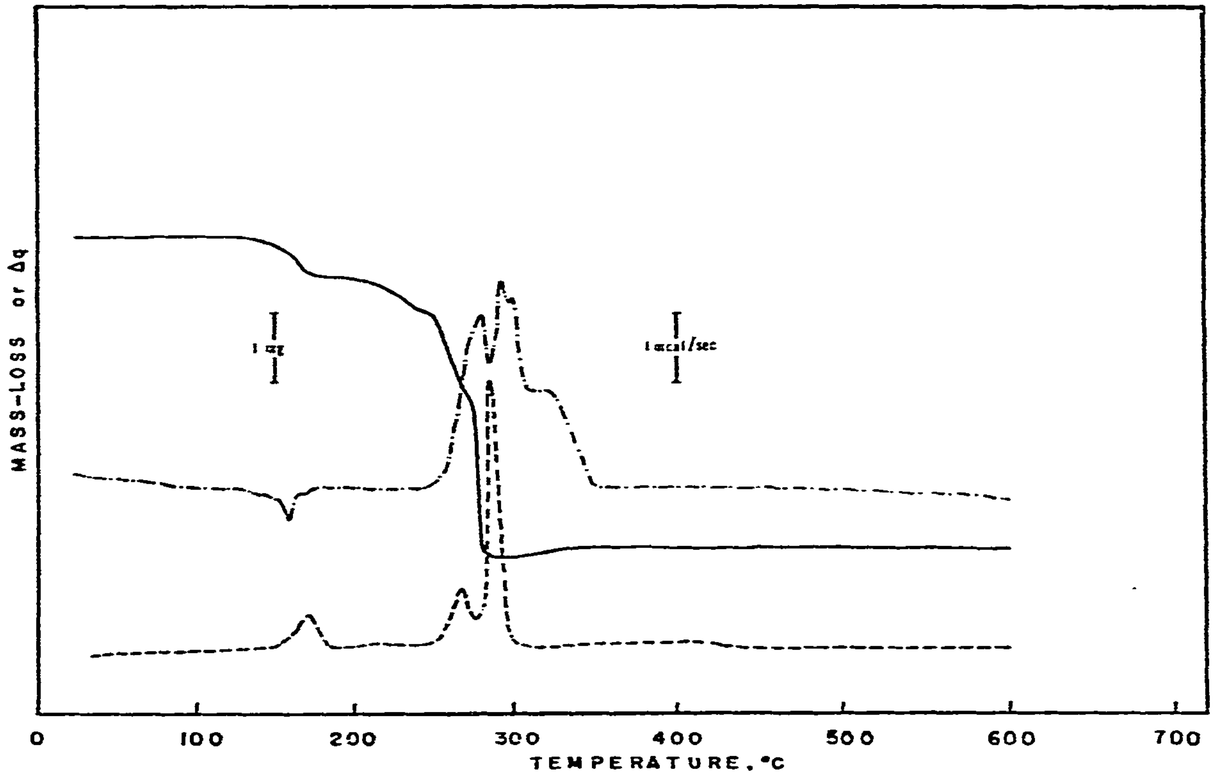

Fig. 4. TG, DTG and DSC curves of CuGly$_2$·2H$_2$O in an air atmosphere. TG ———; DTG – – –; DSC –·–·–·–.

metal–ligand bond has a higher ionic character. At the same time, when the strength of the intramolecular bonds increases and consequently the stability constants for the complexes also increase, the corresponding thermal stability temperature decreases.

The peaks of the IR spectra of these compounds in the 3μ region[2,3] can be assigned to the N–H stretching vibration and the shift of the N–H band, which is a measure of the M–N bond strength, is higher for copper(II), while the shift for cobalt(II) is just a little higher than that of the nickel(II) compound. The N–H stretching vibration frequency is changed on the formation of the M–N bond if the bond is essentially covalent. According to the thermal data, the Cu–N is the strongest covalent bond, while the Ni–N is the weakest. The ν_a(COO) asymmetric band situation at about 1700 cm^{-1} for the –COOH group is shifted in the 1600 cm^{-1} region and indicates that the resonance in the carboxylate ion is preserved in the complex and that the oxygen-to-metal bonds in these complexes are essentially electrostatic. This shift accounts for the highest ionic character for the nickel(II) compound and the least for the copper.

Looking at the thermodynamic data for the formation of these complexes[9–11] in Table 1, the change in entropy is

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

TABLE 1

THERMODYNAMIC DATA FOR THE FORMATION OF 1:2 METAL–GLYCINATE COMPLEXES IN AQUEOUS SOLUTION[1–11]

Function[a]	*Co(II)*	*Ni(II)*	*Cu(II)*
ΔH	−6.37	−9.60	−13.18
ΔG	−11.71	−15.35	−21.37
ΔS	20.0	19.5	27.5

[a] Expressed in the usual units.

but the difference between the ΔS_{Co}II and ΔS_{Ni}II is very small. As discussed for the same complexes with iminodiacetic acid[12], in plotting the ΔS values against the ionic radius, the resulting trend is different from that pointed out by Care and Staveley[13] who found that ΔS decreases as the ionic radius increases. Looking at the ΔH values for these complexes, the order is:

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

Sharma et al.[14] found that for the copper(II) complexes of the aminoacids anions,

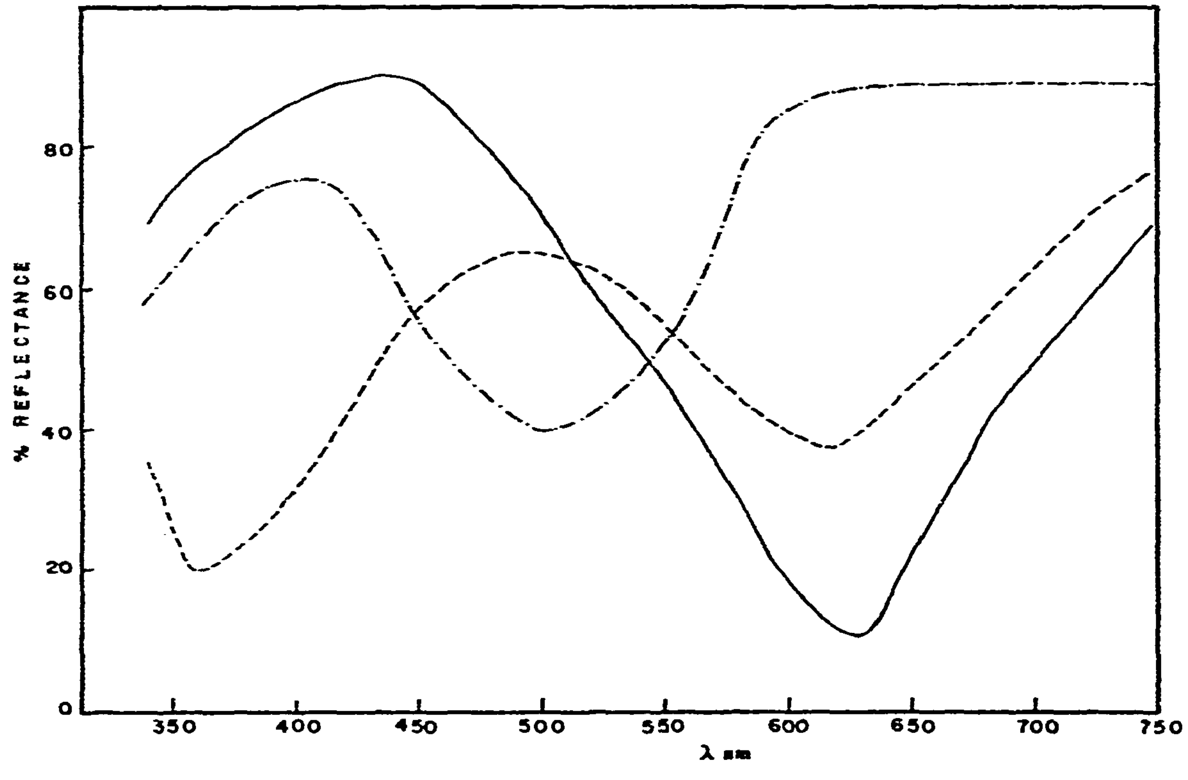

Fig. 5. Diffuse reflectance spectra of metal glycinates. Cobalt(II) glycinate –·–·–·; nickel(II) glycinate — — —; copper(II) glycinate ———.

the ΔH_1 and ΔH_2 values are generally more negative than those for the other metal complexes. It is possible to explain this behavior[14,15] for the copper(II) complexes, which have a planar structure. The more negative values of ΔH mean that the covalent character[2] of the Cu–N bond is increased and the cationic and anionic charges are more neutralized by reducing the distance between them. This means that the entropy change for the formation of copper(II) complexes is larger than for the other metals because of the residual metal ion field on water dipoles is diminished with an additional gain of entropy and with a consequent decrease in their thermal stability.

The diffuse reflectance spectra of the metal complexes are given in Fig. 5.

The copper(II) glycinate complex has a broad absorption band centered around 630 nm in accordance with its planar structure[16]. The reflectance spectrum of the nickel(II) compound shows two bands at 615 and 355 nm, respectively, which are the ν_2 and ν_3 bands[17]. These bands agree with these for an octahedral structure, according to the energy level diagram[18] and the color change from blue to pale green on dehydration. The spectrum of cobalt(II) glycinate shows only one band at 500 nm, while the octahedral complexes have two bands at 460 and 550 nm, respectively. The 500 nm band can probably be attributed to the ν_3 transition because it is possible to miss the ν_2 band because of the weak character of the $^4T_{1g}(F)$–$^4A_{2g}(P)$ transition.

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