

INTERACTION OF METAL IONS WITH HUMIC-LIKE MODELS. PART 2. THERMAL PROPERTIES OF HEXAAQUAMETAL(II) BIS(2,6-DIHYDROXYBENZOATE) DIHYDRATE COMPLEXES

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ABSTRACT

Compounds of formula $M(2,6\text{-DHB})_2 \cdot 8 \text{H}_2\text{O}$ [$M = \text{Mn(II)}$, Fe(II) , Co(II) , Ni(II) , Cu(II) , Zn(II) , and 2,6-DHB = 2,6-dihydroxybenzoate anion), whose structure consists of hexaaquametal(II) cations and uncoordinated 2,6-DHB molecules, have been investigated by means of thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), diffuse reflectance, and electron spin resonance (ESR). On heating, the outer-sphere arrangement is destroyed and $M(2,6\text{-DHB})_2$ complexes are formed, those of Ni, Co and Cu exhibiting hexacoordination at the metal ions.

It is shown that the first decomposition step of the anhydrous complexes involves the release of 2,6-dihydroxybenzoic acid and solid-state deprotonation of phenolic groups of the remaining DHB molecules to give, in certain cases, well-defined 1:1 M/L complexes [$L = \text{C}_6\text{H}_3(\text{OH})(\text{O}^-)\text{COO}^-$].

INTRODUCTION

Compounds of general formula $M(2,6\text{-DHB})_2 \cdot 8 \text{H}_2\text{O}$ have been obtained by reaction of 2,6-dihydroxybenzoic acid with salts of divalent metal ions (Mn, Fe, Co, Ni, Cu and Zn) [1]. X-Ray diffraction analysis [1] indicates that the 2,6-DHB molecules are not coordinated to the ions which are octahedrally surrounded by six water molecules. As such compounds contain a rather uncommon isostructural series of solid aquocations, it appeared of interest both to compare the thermal stability of the hexaaquametal(II) complexes and to establish the coordination changes taking place after dehydration of outer-sphere complexes involving a salicylic-like ligand. Results obtained from a thermoanalytical and spectroscopic study are reported here.

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EXPERIMENTAL

Preparation of compounds

2,6-Dihydroxybenzoic acid (Merck, 97%) was twice crystallized from water and dried in vacuo. Commercially very pure metal salts were used without further purification. All the complexes were prepared as described elsewhere [1].

Instrumentation

TG curves were obtained using a Perkin-Elmer TGS-2 thermogravimetric apparatus under either nitrogen or air atmosphere. A heating rate of $5^{\circ}\text{C min}^{-1}$ was employed. The temperature calibration was checked with calcium oxalate monohydrate. DSC measurements were performed on a Mettler TA 3000 system under air atmosphere. A heating rate of $5^{\circ}\text{C min}^{-1}$ was employed. Spectroscopic analysis was carried out as described in ref. 1.

RESULTS

Thermograms for the complexes either in air or nitrogen atmosphere are given in Figs. 1–5. The first weight losses observed in the TG curves are due

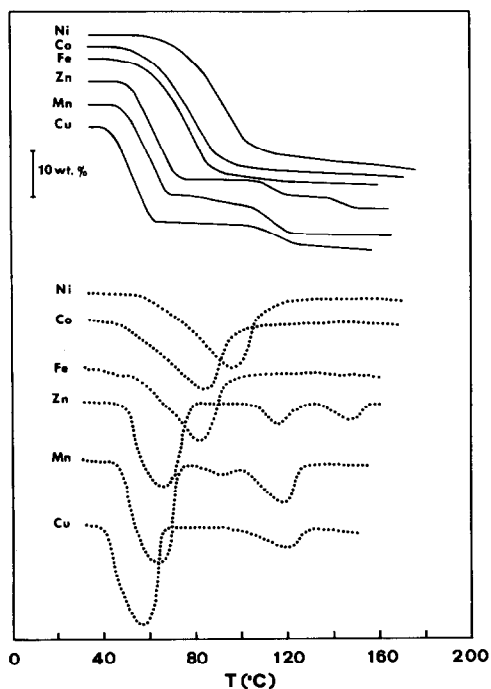


Fig. 1. TG (—) and DTG (·····) curves of hexaaquaM(II) bis(2,6-dihydroxybenzoate) dihydrate complexes in nitrogen atmosphere.

to the dehydration process. Both the number of steps and the temperature ranges corresponding to the release of water molecules are markedly dependent on the nature of the metal ion (see Fig. 1 and Table 1). The Mn, Cu and Zn complexes clearly show separate dehydration steps, the first accounting for six water molecules. In contrast, for the Fe complex all the water molecules are apparently lost in only one step. Exceptions are represented by both Ni and Co complexes which, when dehydrated in nitrogen atmosphere, show only one step, whereas in air at least two stages are observed (Figs. 4 and 5). However, the asymmetric shape of the derivative curves indicates that for all the complexes the dehydration occurs through consecutive stages which, in some cases, are partially overlapped. By comparing the dehydra-

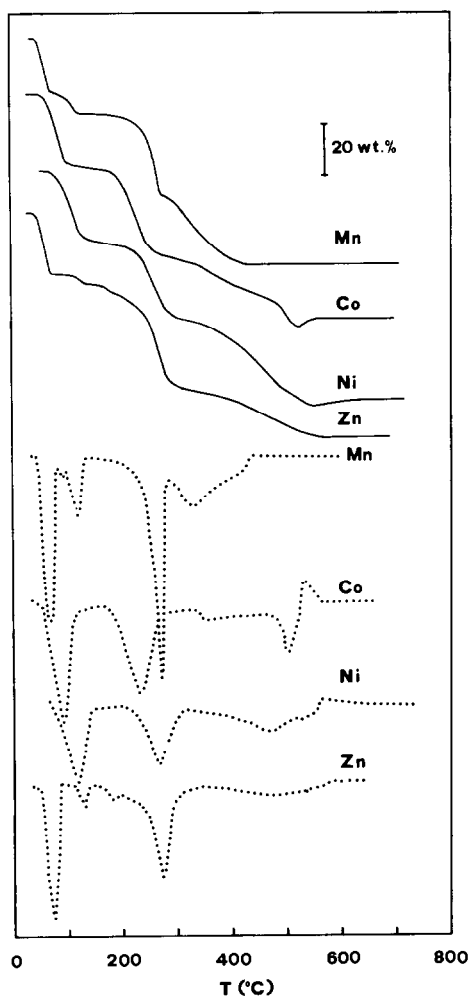


Fig. 2. TG (—) and DTG (·····) curves of hexaaquaM(II) bis(2,6-dihydroxybenzoate) dihydrate complexes in nitrogen atmosphere.

TABLE I

Decomposition temperatures and TG analytical data of hexaaquametal(II) bis(2,6-dihydroxybenzoate) dihydrate complexes in nitrogen atmosphere

| Compound | H ₂ O (I) | | | | H ₂ O (II) | | | |
|---|----------------------|---|----------|---------|-----------------------|-----------------------------|----------|---------|
| | Loss | Temp. (°C) | % Calcd. | % Found | Loss | Temp. (°C) | % Calcd. | % Found |
| Mn(2,6-DHB) ₂ · 8 H ₂ O | 6 H ₂ O | ^{64^a} 43 - 75 ^b | 21.37 | 20.8 | 0.5 H ₂ O | ⁹² 80 - 98 | 1.78 | 1.8 |
| Fe(2,6-DHB) ₂ · 8 H ₂ O | 8 H ₂ O | ⁸⁰ 40 - 150 | 28.44 | 27.7 | | | | |
| Co(2,6-DHB) ₂ · 8 H ₂ O | 8 H ₂ O | ⁸⁵ 45 - 135 | 28.27 | 28.0 | | | | |
| Ni(2,6-DHB) ₂ · 8 H ₂ O | 8 H ₂ O | ⁹⁸ 60 - 150 | 28.28 | 28.2 | | | | |
| Cu(2,6-DHB) ₂ · 8 H ₂ O | 6 H ₂ O | ⁵⁸ 40 - 70 | 21.01 | 21.0 | 2 H ₂ O | ¹²⁰ 95 - 135 | 7.00 | 6.9 |
| Zn(2,6-DHB) ₂ · 8 H ₂ O | 6 H ₂ O | ⁶⁸ 47 - 80 | 20.94 | 21.5 | 1 H ₂ O | ¹¹⁸ 105 - 130 | 3.49 | 3.7 |

^a Maximum rate.

^b Temperatures at the beginning and end of the reaction.

tion temperatures (maximum rate of the first dehydration step) the stability order Ni > Co > Fe > Zn > Mn > Cu is obtained.

When heated in nitrogen atmosphere, the Co, Ni, Zn and Mn complexes decompose in a well-defined two-step process (Fig. 2), the former always

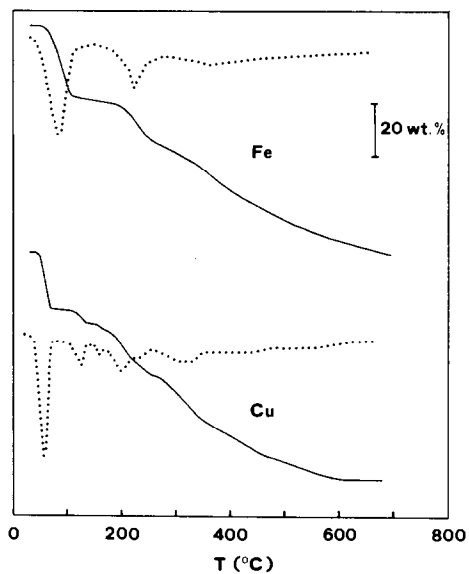


Fig. 3. TG (—) and DTG (·····) curves of hexaaquaM(II) bis(2,6-dihydroxybenzoate) dihydrate complexes in nitrogen atmosphere.

| H ₂ O (III) | | | | Decomprn. (I) | (Decomprn. (II)) |
|------------------------|------------|----------|---------|---------------|------------------|
| Loss | Temp. (°C) | % Calcd. | % Found | Temp. (°C) | Temp. (°C) |
| 1.5 H ₂ O | 102 – 135 | 5.34 | 6.0 | 190 – 295 | 300 → |
| | | | | | 175 → |
| | | | | 175 – 300 | 345 → |
| | | | | 200 – 310 | 325 → |
| 1 H ₂ O | 135 – 155 | 3.49 | 3.3 | 200 – 350 | 375 → |
| | | | | | 150 → |

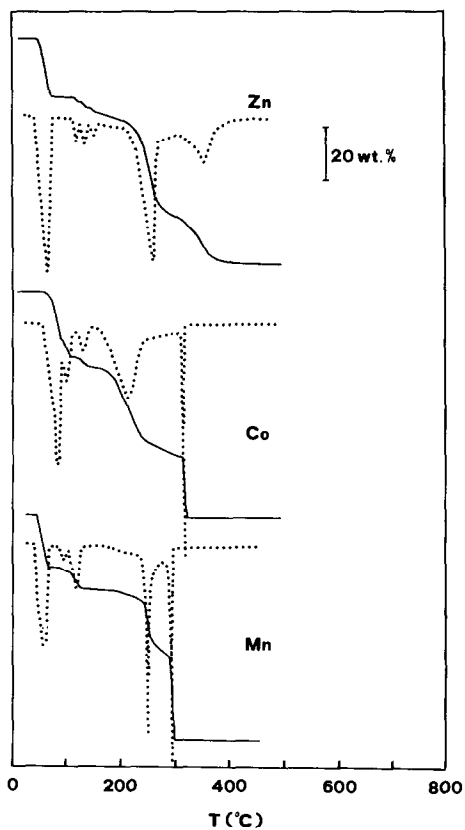


Fig. 4. TG (—) and DTG (· · · · ·) curves of hexaaquaM(II) bis(2,6-dihydroxybenzoate) dihydrate complexes in air atmosphere.

corresponding to the release of one 2,6-dihydroxybenzoic acid molecule (~ 30 wt.%). IR analysis of the product evolved upon heating confirms such a hypothesis; thus, a 1 : 1 M/L complex seems to be formed in the decomposition process. Based on the temperature of maximum rate for the release of the ligand molecule, the order of thermal stability $Zn \geq Mn > Ni > Co$ is deduced for the above series of anhydrous complexes. In contrast, the decomposition pattern of Cu and Fe complexes (Fig. 3) appears to involve the release of ligand molecules, but in a rather not well-defined multi-step process. In any case, for all the complexes, the last decomposition step leads to formation of the metal binary oxide (see Table 1).

Regarding the decomposition pathway in air atmosphere (Figs. 4 and 5), it must be observed that:

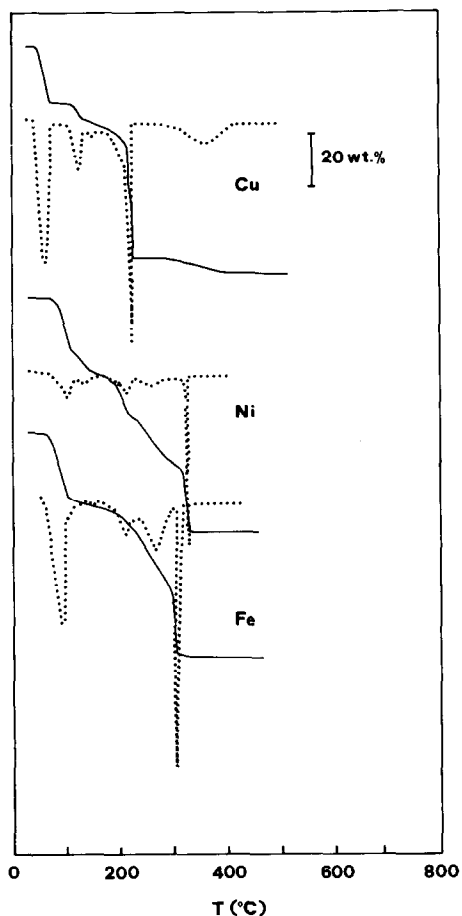


Fig. 5. TG (—) and DTG (·····) curves of hexaaquaM(II) bis(2,6-dihydroxybenzoate) dihydrate complexes in air atmosphere.

(i) two well-defined stages, the former accounting for a molecule of acid, the latter corresponding to the oxidative decomposition of the 1 : 1 complex to give the final oxide, were observed for Co and Zn;

(ii) the above mechanism seems valid also for Cu and Mn, but the two stages appear to be partially overlapped. The Cu complex in the final stage yields first the basic carbonate (theoret. 21.5, exptl. \sim 21 wt.%) and then the oxide CuO;

(iii) a less defined trend involving several consecutive stages quite similar to that described for the decomposition of Cu and Fe complexes in nitrogen atmosphere is observed for Ni and Fe.

Again, by comparing the temperature accounting for the release of the first ligand molecule, when well-defined decomposition patterns are observed, the order $Zn \approx Mn > Co \approx Cu$ is obtained.

DSC measurements, carried out in air atmosphere (see, for example, Fig. 6), show for all the complexes:

(i) consecutive endothermic steps corresponding to the release of water molecules;

(ii) an endothermic peak corresponding to the breakdown of the anhydrous compound and evolution of a molecule of acid;

(iii) diffuse exothermic effects connected with the oxidative decomposition of the 1 : 1 complex to give the final oxide.

Spectroscopic analysis

Detailed results obtained by IR, ESR and electronic absorption spectra have been reported elsewhere [1]. Here, attention will be paid to the

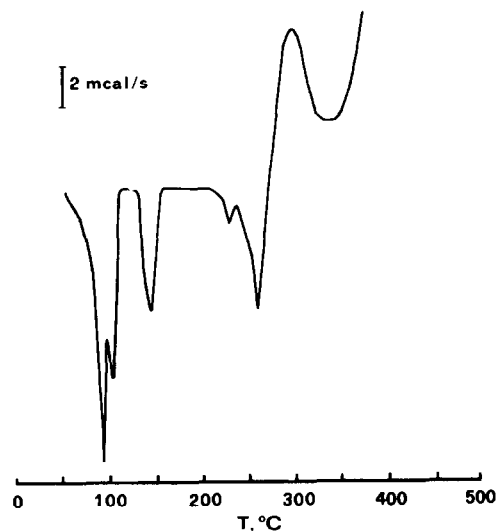


Fig. 6. DSC curve (air) of hexaaquazinc(II) bis(2,6-dihydroxybenzoate) dihydrate.

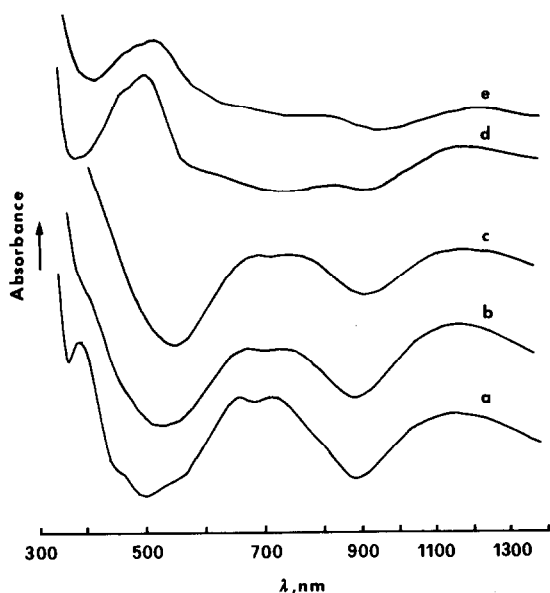


Fig. 7. Diffuse reflectance spectra of (a) $\text{Ni}(\text{2,6-DHB})_2 \cdot 8 \text{H}_2\text{O}$; (b) $\text{Ni}(\text{2,6-DHB})_2 \cdot \sim 4 \text{H}_2\text{O}$; (c) $\text{Ni}(\text{2,6-DHB})_2$; (d) $\text{Co}(\text{2,6-DHB})_2 \cdot 8 \text{H}_2\text{O}$; and (e) $\text{Co}(\text{2,6-DHB})_2$.

coordinative changes taking place after dehydration of the complexes.

The $\text{M}(\text{2,6-DHB})_2 \cdot 8 \text{H}_2\text{O}$ complexes exhibit $d-d$ absorption bands (see, for example, Fig. 7) quite typical of a regular hexacoordination of water molecules at all the metal ions [2,3]. Hexacoordinated ions, although subjected to progressively increased tetragonal distortion, as suggested by the red shift of the absorption maxima, are also detected for lower hydrates and anhydrous complexes of Co and Ni (Fig. 7). On the other hand, a pronounced tetragonality is suggested for the copper ion in the dihydrate species (absorption maximum: 715 nm; ESR parameters: $g_{\parallel} = 2.335$ and $g_{\perp} = 2.082$). A more regular octahedral environment is further attained by copper after complete dehydration (absorption maximum: 770 nm). Moreover, it must be noticed that IR, ESR and electronic absorption spectra of the copper dihydrate complex formed upon dehydration are all consistent with those of $\text{Cu}(\text{2,6-DHB})_2 \cdot 2 \text{H}_2\text{O}$, whose structure is known [1].

DISCUSSION AND CONCLUSION

The results of this thermoanalytical study provide further evidence that $\text{M}(\text{2,6-DHB})_2 \cdot 8 \text{H}_2\text{O}$ compounds are isomorphous and isostructural. In fact, the dehydration behaviour observed for the complexes suggests that only differences related to the nature of the metal ions characterize the

thermal breakdown of the outer-sphere arrangement. The thermal stability order of the solid aquocations(II) is easily connected with the general relationship of the crystal field stabilization energy for high-spin divalent ions of the first transition series octahedrally coordinated by the same ligands. It is known that in such a case the extra stability which results from the splitting of the d orbitals imposes a characteristic variation of some structural and thermochemical properties which would otherwise exhibit a regular progression along the series [4]. This order, which is also connected with the dimensions of the ions, is just that observed for the dehydration of the 2,6-DHB complexes, confirming the presence of regular and similar octahedral coordination at each metal ion. An exception is $\text{Cu}(2,6\text{-DHB})_2 \cdot 8 \text{H}_2\text{O}$, but, as usual for this ion, it is explained by the tetragonal distortion due to Jahn–Teller effects, which cause two waters to be more weakly bonded and released at temperatures lower than for a strictly regular geometry.

Upon partial dehydration, the 2,6-DHB anion is forced to coordinate the metal ions giving rise to inner-sphere complexes. All the spectral data suggest that the dihydrate species of the copper complex has the structure observed for $\text{Cu}(2,6\text{-DHB})_2 \cdot 2 \text{H}_2\text{O}$ [1]. In such a case the ion is in elongated octahedral geometry with waters and carboxylate groups at the equatorial sites, two phenolic groups from neighbouring molecules being the axial donors. On the contrary, for lower hydrates of Ni and Co complexes, a more regular coordination involving at least carboxylate groups and water molecules is observed.

Finally, the binding of phenolic groups must be necessarily taken into account to explain the hexacoordination requirements of the ions in the anhydrous complexes. The decomposition of the anhydrous $\text{M}(2,6\text{-DHB})_2$ species proceeds through solid-state deprotonation of the phenolic groups and the release of a molecule of acid for each deprotonated OH in order to preserve the charge balance. Thus, in some instances, complexes provided with a well-defined 1 : 1 metal/ligand ratio are formed in the first decomposition stage. In other cases, depending upon either the ion or the heating conditions, intermediate products are formed. In such stages, complex and, likely, polymeric species ML_x ($x \neq 1$), whose stoichiometry depends on the number of ionized OH groups per ligand molecule, must be hypothesized.

With regard to the ligand behaviour of 2,6-dihydroxybenzoic acid, which can be considered as a useful model of the humic substances, further evidence is presented to show that the interaction of phenolic groups with some metal ions is unfavourable, unless substantial reduction of the water content (in the solid state) or OH-deprotonation (in the solid state or solution) occurs. Furthermore, the increase of temperature induces a sequence of solid-state reactions:



which is just the same as observed for copper(II) solutions with increasing pH values [5].

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