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THERMAL–STRUCTURAL CORRELATIONS IN COPPER(II) CARBOXYLATE COMPLEXES

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ABSTRACT

The thermal behaviour of some hydrated copper(II) carboxylate complexes has been studied. It has been found that, when hydrogen-bonded to each other, coordinated and uncoordinated water molecules are not distinguished by their thermogravimetric curves. In addition, the dehydration temperatures are dependent on a variety of factors, the metal–O (water) distance being only of minor importance. Instead, when water-to-water contacts are absent, the water molecules are lost in separate steps and a direct correlation between the dehydration temperature and the metal–water distance has been found within a series of structurally similar complexes.

INTRODUCTION

The presence of metal-bound water molecules in coordination compounds is often inferred only on the basis of thermal measurements. Namely, coordinated water molecules are believed to be released at temperatures substantially higher than those for the uncoordinated or crystallization water.

Less usually, thermal results are checked on the grounds of known structural parameters and this questions the reliability of thermal measurements as a tool for distinguishing coordinated from uncoordinated water.

Being interested in furnishing experimental support for thermal–structural relationships concerning metal complexes we are investigating the thermal behaviour of compounds whose structural features are known on the basis of X-ray diffraction analysis [1,2].

The present paper describes the thermal properties of hydrated monomeric and dimeric copper(II) complexes formed by simple carboxylic acids to point out the variety of factors which can influence the thermal release of water molecules bound to metal ions.

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All the compounds investigated contain both coordinated and uncoordinated water molecules with the exception of $[Cu(DHB)_2(H_2O)_2]$ * and the dimeric copper(II) acetate monohydrate-like complexes. The main structural

TABLE 1

Structural data for the complexes studied

Compound	Cu–O (water) (Å)	O · · · O hydrogen-bonds (Å)		Ref.
		Coord. water	Uncoord. water	
$[Cu(DHB)_2(H_2O)_2]$	1.947(3) [a]	2.666(4) [c] 2.755(4) [d]		3
$[Cu(Sal)_2(H_2O)_2]\cdot 2\ H_2O$	1.92 [a] 2.8 [b]	2.56 [c] 2.67 [c]	2.56 [f] 2.76 [d]	4,5
$[Cu(Acetu)_2(H_2O)_2]\cdot 2\ H_2O$	1.947(3) [a]	2.633(4) [e] 2.718(5) [c]	2.633(4) [f] 2.773(5) [g] 2.811(3) [g]	6
$[Cu(His)(Asn)(H_2O)]\cdot 3\ H_2O$	2.642(7) [b]	2.772(10) [e] 2.687(9) [c] 2.806(10) [i]	2.687(9)–3.080(11) [h]	7
$[Cu(Hippu)_2(H_2O)_2]_2\cdot 4\ H_2O$	2.00(2)	[j]	[j]	8
$[Cu(H_2O)_6](DHB)_2\cdot 2\ H_2O$ [k]		2.734(2) [c] 2.661(2) [c] 2.753(2) [d] 2.737(2) [d] 2.835(2) [e] 2.980(2) [e]	2.835(2) [f] 2.980(2) [f]	3
$[Cu(His)(Ala)(H_2O)]\cdot 3\ H_2O$	2.512(9) [b]	2.749(14) [c] 2.910(13) [c]	2.108(108)–3.021(53) [l]	9
$[Cu(BBz)_2(H_2O)]_2$	2.17(2) [b]	2.89(3) [c]		10
$[Cu(Ac)_2(H_2O)]_2$	2.162(1) [b]	2.823(2) [c] 2.927(2) [c]		11
$[Cu(DMB)_2(H_2O)]_2$	2.133(4) [b]	2.918(5) [c] 2.927(2) [c]		12
$[Cu(Acetu)_2(H_2O)]_2$	2.108(3) [b]	2.748(4) [g]		13

[a] Equatorial.

[b] Axial.

[c] To carboxylic group.

[d] To phenolic group.

[e] To uncoordinated water.

[f] To coordinated water.

[g] To peptidic oxygen.

[h] To carboxylate, amide and water oxygens, and to amino, amide and imidazole nitrogens.

[i] To imidazole nitrogen.

[j] Details of hydrogen-bonding not given.

[k] The structural parameters are those of the isostructural Zn compound.

[l] To uncoordinated water and carboxylic group.

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* Abbreviations used: DHB = 2,6-dihydroxybenzoate; Sal = salicylate; Acetu = *N*-acetylglycinate; Hippu = *N*-benzoylglycinate; His = L-histidinate; Asn = L-asparaginate; Ala = L-alaninate; BBz = 2-bromobenzoate; Ac = acetate; and DMB = 2,6-dimethoxybenzoate.

features of the compounds are listed in Table 1 and summarized as follows.
$[Cu(DHB)_2(H_2O)_2]$. The water molecules are in the metal plane and form hydrogen-bonds with carboxylate and phenolic oxygen atoms of the ligand.
$[Cu(Sal)_2(H_2O)_2] \cdot 2\ H_2O$. The coordinated water takes part in hydrogen-bonding to the carboxylate group and to the uncoordinated water which is also linked to the phenolic oxygen atom. The metal-bound water is responsible for axial interaction to an adjacent copper atom.
$[Cu(Acetu)_2(H_2O)_2] \cdot 2\ H_2O$. Here too, the metal-bound water molecules interact with the carboxylate groups and the uncoordinated water. The latter is also hydrogen-bonded to the peptidic oxygen atom.
$[Cu(His)(Asn)(H_2O)] \cdot 3\ H_2O$. The coordinated water is hydrogen-bonded to the carboxylate group of asparagine, to another water molecule and to the imidazole nitrogen atom, whereas the three remaining molecules form contacts between one another and interact with the oxygen and nitrogen atoms of the amino acids.
$[Cu(Hippu)_2(H_2O)_2]_2 \cdot 4\ H_2O$. The complex adopts a dimeric structure in which the copper ions are bridged by single carboxylic oxygens. Each metal atom is surrounded by two *trans* water molecules and three carboxylic oxygen atoms.
$[Cu(H_2O)_6](DHB)_2 \cdot 2\ H_2O$. The metal surrounding is octahedral and involves six water molecules. Four of these are hydrogen-bonded to the crystallization water and two are engaged in contacts with the phenolic and carboxylic atoms.
$[Cu(His)(Ala)(H_2O)] \cdot 3\ H_2O$. The coordinated water is hydrogen-bonded to the carboxylate group of histidine, whereas the remaining water molecules, distributed randomly in the structure, form contacts with the amino and carboxylato groups as well as with one another.

The remaining complexes are dimeric compounds of the copper(II) acetate monohydrate-type.

EXPERIMENTAL

Materials

The compounds were prepared according to published procedures [3,4,7–10,12–14]. Analytical and spectral data compared well with those reported in the original references. Very pure, reagent grade cupric acetate monohydrate was obtained from Merck.

Thermal analyses

Thermogravimetric analyses were carried out by using a Perkin-Elmer TGS-2 apparatus. The temperature calibration was checked with calcium oxalate monohydrate. The thermal measurements were performed at the scanning rate of 2°C min^{-1} in nitrogen atmosphere (flow rate: 20 ml min^{-1}). The results are summarized in Table 2.

RESULTS

First of all it is noteworthy to compare the thermal behaviour of $[Cu(DHB)_2(H_2O)_2]$, $[Cu(Acetu)_2(H_2O)_2]\cdot 2\ H_2O$ and $[Cu(Sal)_2(H_2O)_2]\cdot 2\ H_2O$. Nevertheless, having very similar coordination sets around the metal ion (bonded to two carboxylic and two water oxygen atoms in the plane, and subjected to weak axial interactions) these complexes exhibit remarkably different dehydration temperatures (Fig. 1).

In particular, the water molecules of $[Cu(DHB)_2(H_2O)_2]$ are so strongly held that their removal is observed at temperatures high as 150–180°C. This finding could be accounted for by either the short Cu–O (water) distance or by the involvement of water in strong intramolecular (to the carboxylic groups) and intermolecular (to the phenolic groups) bonds, the former giving rise to six-membered rings.

However, on examining $[Cu(Acetu)_2(H_2O)_2]\cdot 2\ H_2O$ and $[Cu(Sal)_2(H_2O)_2]\cdot 2\ H_2O$, it can be observed that, in spite of the shorter Cu–O (water) bonds, the water molecules are released at lower temperatures and below 100°C for the salicylate complex. In addition, it appears that the removal of coordinated and uncoordinated water occurs in only one step.

TABLE 2

Thermogravimetric data for copper(II) complexes

Complex	Loss	*T* (°C) [a]	% Calcd.	% Found
$[Cu(DHB)_2(H_2O)_2]$	2 H_2O	143–187(170)	8.87	9.2
$[Cu(Acetu)_2(H_2O)_2]\cdot 2\ H_2O$	4 H_2O	81–130(117)	19.59	18.5
$[Cu(Sal)_2(H_2O)_2]\cdot 2\ H_2O$	4 H_2O	53–91(67)	17.58	17.0
$[Cu(His)(Asn)(H_2O)]\cdot 3\ H_2O$	4 H_2O	38–70(61)	17.11	16.7
$[Cu(Hippu)_2(H_2O)_2]_2\cdot 4\ H_2O$	8 H_2O	53–105(88)	14.64	14.0
$[Cu(H_2O)_6](DHB)_2\cdot 2\ H_2O$	6 H_2O	40–70(58)	21.01	21.0
	2 H_2O	95–135(120)	7.00	6.9
$[Cu(His)(Ala)(H_2O)]\cdot 3\ H_2O$	1 H_2O	27–58(46)	4.76	3.5
	1 H_2O	58–82(71)	4.76	6.0
	2 H_2O	88–148(136)	8.52	8.5
$[Cu(BBz)_2(H_2O)]_2$	2 H_2O	100–134(120)	3.74	4.0
$[Cu(Ac)_2(H_2O)]_2$	2 H_2O	103–144(128)	9.01	9.5
$[Cu(DMB)_2(H_2O)]_2$	2 H_2O	120–152(137)	5.96	6.5
$[Cu(Acetu)_2(H_2O)]_2$	2 H_2O	170 →	5.74	

[a] Range gives temperatures at the beginning and end of the loss; maximum rate in parentheses.

Inspection of the structures of $[Cu(Acetu)_2(H_2O)_2] \cdot 2\ H_2O$ and $[Cu(Sal)_2(H_2O)_2] \cdot 2\ H_2O$ shows that in both the cases the coordinated and uncoordinated water molecules are hydrogen-bonded each to other and suggests that such a bonding could be responsible for the simultaneous weight losses observed in the thermogravimetric curves. If so, it is expected that the dehydration temperatures should depend on the whole bond constraint involving both types of water molecules, the metal-to-oxygen bond length playing only a minor role.

In effect, in $[Cu(Acetu)_2(H_2O)_2] \cdot 2\ H_2O$, where dehydration occurs at higher temperatures, the uncoordinated water seems to be more strongly anchored to the ligand (as judged from the detection of two bonds to the peptidic oxygens) than in $[Cu(Sal)_2(H_2O)_2] \cdot 2\ H_2O$ (one hydrogen-bond to the phenolic oxygen).

To lend confirmation to such an observation, other representative copper(II) complexes have been examined (Fig. 2), the experimental results being in accord with the expectations.

In fact, both $[Cu(His)(Asn)(H_2O)] \cdot 3\ H_2O$ and $[Cu(Hippu)_2(H_2O)_2]_2 \cdot 4\ H_2O$, where the coordinated and uncoordinated water molecules are hydrogen-bonded one to another (although details are not given for the latter complex [8]), still display a single weight loss. On the other hand, only four

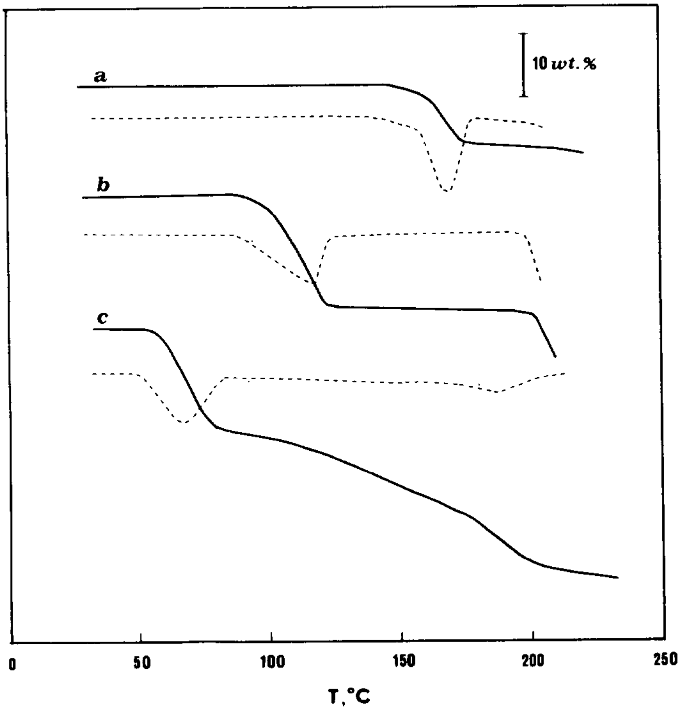

Fig. 1. TG (———) and DTG (- - - -) curves of $[Cu(DHB)_2(H_2O)_2]$ (a), $[Cu(Acetu)_2(H_2O)_2] \cdot 2\ H_2O$ (b) and $[Cu(Sal)_2(H_2O)_2] \cdot 2\ H_2O$ (c).

of the six metal-bound water molecules of $[Cu(H_2O)_6](DHB)_2 \cdot 2\ H_2O$ take part in hydrogen-bonding with the uncoordinated water. Accordingly, a loss of six molecules is observed at rather low temperatures whereas the metal-bound water interacting with carboxyl and phenolic groups is released at higher temperatures.

Resolved weight losses are observed in the case of $[Cu(His)(Ala)(H_2O)] \cdot 3\ H_2O$ where, based on the X-ray-determined structure, short contacts between coordinated and uncoordinated water molecules are absent. In particular, the loss of the metal-bound water, which occurs over the 58–82°C range, as suggested by electronic and ESR spectra, seems to be sufficiently separated from those corresponding to the crystallization water.

Finally, a series of binuclear copper(II) acetate monohydrate-like complexes has been examined. Based on the X-ray structural determinations, the metal–O (water) distance ranges from 2.108(3) to 2.17(2) Å (see Table 1). In all but one of the compounds the water molecule is involved in hydrogen-

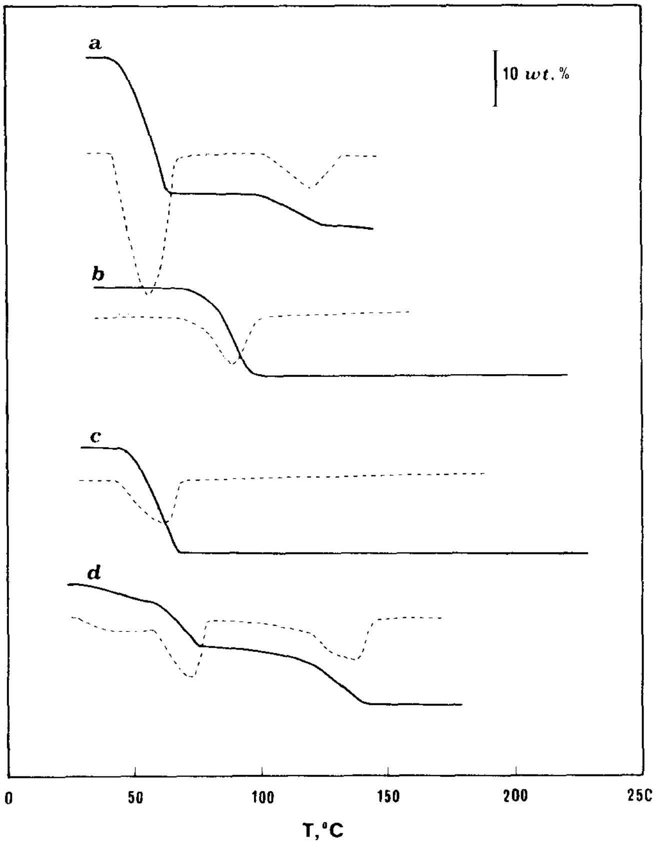

Fig. 2. TG (———) and DTG (- - - - -) curves of $[Cu(H_2O)_6](DHB)_2 \cdot 2\ H_2O$ (a), $[Cu(Hippu)_2(H_2O)_2]_2 \cdot 4\ H_2O$ (b), $[Cu(His)(Asn)(H_2O)] \cdot 3\ H_2O$ (c) and $[Cu(His)(Ala)(H_2O)] \cdot 3\ H_2O$ (d).

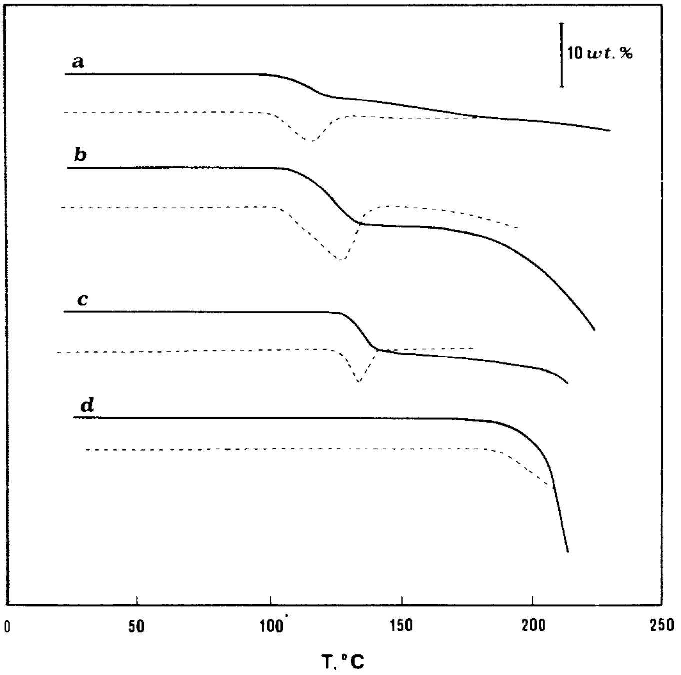

Fig. 3. TG (———) and DTG (- - - - -) curves of $[Cu(BBz)_2(H_2O)]_2$ (a), $[Cu(Ac)_2(H_2O)]_2$ (b), $[Cu(DMB)_2(H_2O)]_2$ (c) and $[Cu(Acetu)_2(H_2O)]_2$ (d).

bonding to carboxylate oxygen atoms, the O · · · O distances being similar. The one exception is $[Cu(Acetu)_2(H_2O)]_2$ which displays water–peptidic oxygen contacts.

All these complexes release water above 100°C, the dehydration temperature being particularly high for $[Cu(Acetu)_2(H_2O)]_2$ which decomposes immediately after the water loss (Fig. 3).

The comparative examination of the thermogravimetric curves shows that a direct correlation between the dehydration temperature and the metal–water bond length seems tenable in this case. In fact, the shorter the copper–water bond the higher is the dehydration temperature (Table 2), suggesting that the breaking of the metal–oxygen bond could be of primary importance in determining the thermal stability of the hydrated complexes. However, it is not possible to rule out a contribution of the short bonds between water and peptidic oxygens in determining the unexpected thermal stability of $[Cu(Acetu)_2(H_2O)]_2$.

CONCLUSIONS

The main results of this study suggest that the breaking of the metal–water bonds must not be considered of primary importance in determining the thermal behaviour of hydrated metal complexes. Instead, it has been observed that water molecules, either coordinated or not, hydrogen-bonded to one another can be released simultaneously and at remarkably low temperatures.

This seems to substantiate the concept that in order to explain the thermal stability of aquo-complexes, one must take into account all the interactions, structural and, possibly, electronic, involving both coordinated and uncoordinated water molecules. Thus, in the presence of water–metal, water–water and water–ligand bond contacts, any attempt to predict the thermal behaviour of metal-bound water may be outweighed.

On the other hand, when water-to-water contacts are absent, a direct correlation between the dehydration temperatures and the metal–water distance within a series of structurally similar complexes has been found.

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