Thermochimica Acta, 77 (1984) 67–75
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INTERACTION OF METAL IONS WITH HUMIC-LIKE MODELS. PART 3. THERMAL BEHAVIOUR OF AQUO-BRIDGED POLYMERIC COMPLEXES OF 2,6-DIMETHOXYBENZOIC ACID WITH DIVALENT METAL IONS

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(Received 10 January 1984)

ABSTRACT

The thermal behaviour of some metal complexes of 2,6-dimethoxybenzoic acid has been investigated by means of thermogravimetry (TG) and differential scanning calorimetry (DSC). The intermediates formed at various stages have been studied using a variety of analytical and spectroscopic methods.

A mechanism of decomposition leading to 1 : 1 metal/ligand complexes of 2-hydroxy-*o*-anisic acid plus methyl 2,6-dihydroxybenzoate in the first stage and to binary oxides as final products is demonstrated.

INTRODUCTION

The thermal behaviour of outer-sphere complexes formed by 2,6-dihydroxybenzoic acid with some divalent metal ions has been described in a recent report [1]. It has been found that the decomposition of the complexes proceeds through solid-state deprotonation of the phenolic groups and formation of chelate complexes involving both carboxylate and phenolate oxygen atoms in the metal coordination environment. 2,6-Dihydroxybenzoic acid is formed in this stage and released as volatile product.

Metal complexes of 2,6-dimethoxybenzoic acid (HDMB), with formula $M(DMB)_2 \cdot 4\ H_2O$ ($M = Mn$, Co, Ni and Zn), have now been prepared.

0040-6031/84/$03.00

Single-crystal X-ray diffraction analysis shows the complexes to be polymeric [2]. The metal ions are octahedrally surrounded by two *trans*-related monodentate carboxylate groups with two water molecules in the plane, and bridging water molecules in the axial, positions to form linear chains. The fourth water molecule is hydrogen-bonded to the rest of the structure.

The results of a thermoanalytical study carried out on these complexes are reported here and compared with those obtained for the 2,6-dihydroxybenzoate complexes.

EXPERIMENTAL

Preparation of compounds

2,6-Dimethoxybenzoic acid (Merck) was twice recrystallized from aqueous ethanol and dried in vacuo. Commercially very pure metal salts were used without further purification. The complexes were prepared as described elsewhere [2].

Instrumentation

TG curves were obtained using a Perkin-Elmer TGS-2 apparatus in nitrogen or air atmosphere. A scanning rate of 2°C min^{-1} was employed. The temperature calibration was checked with calcium oxalate monohydrate. DSC measurements were performed on a Perkin-Elmer DSC-4 instrument in nitrogen atmosphere using aluminium sample pans and a scanning rate of 2°C min^{-1}. Chemical analyses for C and H were performed on a Perkin-Elmer 240 B elemental analyser. IR spectra were recorded on a Perkin-Elmer 683 B spectrophotometer. Electronic diffuse reflectance spectra were obtained on a Beckman Acta M IV spectrophotometer using $BaSO_4$ as reference sample. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer. Mass spectral data were obtained on a Finnigan 1020 GC/MS system. Magnetic susceptibilities were measured using a Brüker B-MB4 Faraday system equipped with a Cahn 1000 electrobalance.

Analytical data for I and II

Methyl-2,6-dimethoxybenzoate (***I***). White crystals, m.p. 88–89°C [3]. Anal. Calcd.: C, 61.22; H, 6.16. Found: C, 61.40; H, 6.21. NMR ($CDCl_3$), δ 7.28 (1 H, t), 6.55 (2 H, d), 3.90 (3 H, s), 3.81 (6 H, s). MS, m/z 196 (51, M^+), 165 (100), 150 (35), 135 (17), 122 (16), 107 (42), 92 (11), 77 (22).

*2-Hydroxy-*o*-anisic acid* (***II***). White crystals, m.p. 136–137°C [4]. Anal. Calcd.: C, 57.14; H, 4.80. Found: C, 57.49; H, 4.85. NMR ($CDCl_3$), δ 12.16 (1 H, s), 11.34 (1 H, s), 7.41 (1 H, t), 6.72 (1 H, m), 6.49 (1 H, m), 4.07 (3 H, s). MS, m/z 168 (25, M^+), 150 (100), 149 (52), 122 (30), 107 (56).

RESULTS AND DISCUSSION

Thermogravimetric data (Fig. 1 and Table 1) show the water molecules to be released between 35 and 140°C and both the number of steps and the temperature ranges to be markedly dependent on the metal ion. Dehydration of the Co and Ni complexes occurs in three separate steps: one molecule is released in each of the first two steps, while two molecules are simultaneously lost in the final stage. On the other hand, all the water molecules of the Zn and Mn compounds are apparently removed in a single step.

However, dehydration begins at about 35°C for all the complexes which could be due to the release of the uncoordinated water molecule. Instead, the metal-bound molecules are lost at temperatures which depend on the metal ion. Furthermore, the behaviour of Co and Ni indicates that the bridging water is more weakly held than the equatorially-bound molecules, as equivalent molecules are removed only in the final stage. Thus, the dehydration appears to follow the sequence

$$[M(DMB)_2(H_2O)_3]\cdot H_2O \rightarrow [M(DMB)_2(H_2O)_3] \rightarrow [M(DMB)_2(H_2O)_2] \rightarrow [M(DMB)_2]$$

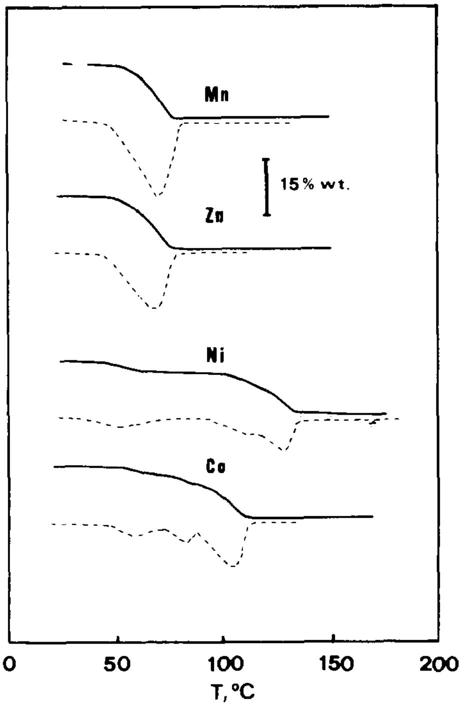


Fig. 1. TG (————) and DTG (······) curves of $[M(DMB)_2(H_2O)_3]\cdot H_2O$ complexes in nitrogen atmosphere.

TABLE 1

TG analytical data and decomposition temperatures for $[M(2,6\text{-DMB})_2(H_2O)_3]\cdot H_2O$ complexes in nitrogen atmosphere

M	H_2O(I)				H_2O(II)				H_2O(III)				Decomposition temp. (°C)
	Loss	Temp. [a] (°C)	% Calcd.	% Found	Loss	Temp. [a] (°C)	% Calcd.	% Found	Loss	Temp. [a] (°C)	% Calcd.	% Found	
Mn	4 H_2O	37–80 (71)	14.73	14.3									255 →
Co	1 H_2O	44–77 (61)	3.65	~ 3	1 H_2O	77–91 (85)	3.65	~ 3	2 H_2O	91–115 (108)	7.30	~ 8.5	185 →
Ni	1 H_2O	38–74 (54)	3.65	~ 3	1 H_2O	85–119 (111)	3.65	~ 4.5	2 H_2O	119–137 (128)	7.30	~ 7.0	195 →
Zn	4 H_2O	37–81 (69)	14.42	14.3									230 →

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

The above results are in accordance with the DSC measurements (Fig. 2) displaying endothermic peaks for the loss of water. Resolved effects connected with three separate losses of water are also observed for the Zn complex when sealed sample pans are used.

The changes of the metal coordination environment taking place upon dehydration of the Co and Ni complexes have been followed by means of reflectance spectroscopy (Fig. 3). The starting complexes display *d–d* absorption bands typical of nearly regular octahedral O_6 coordination at the metal ions [5]. A six-coordinate structure, although more severely distorted, is still consistent for the anhydrous Ni complex. On the contrary, $[Co(DMB)_2]$ has tetrahedral coordination at the metal ion, as supported by the electronic spectrum and the magnetic moment value (4.54 BM at 298 K).

Structural differences inside the series of anhydrous complexes are also

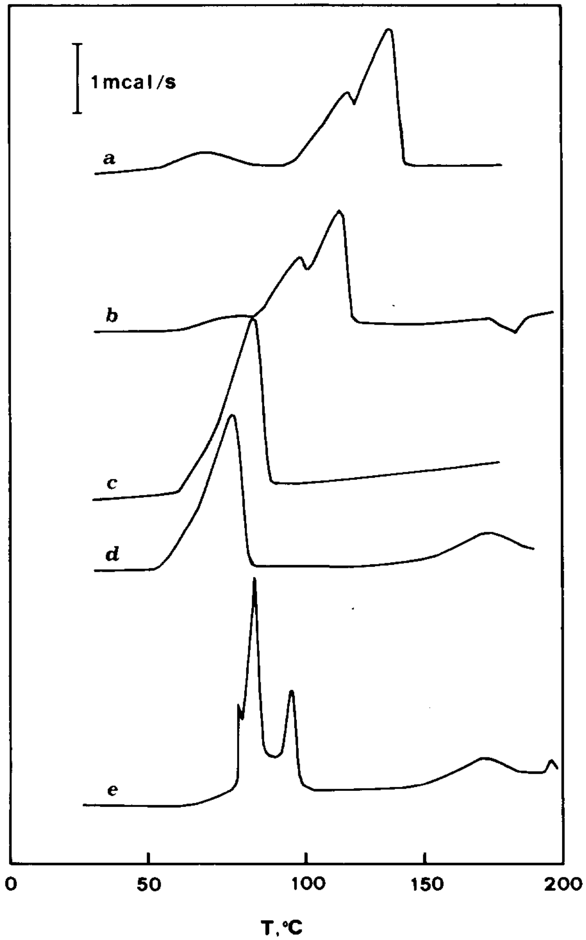


Fig. 2. DSC curves (nitrogen atmosphere) of $[M(DMB)_2(H_2O)_3]\cdot H_2O$ complexes. M = Ni (a), Co (b), Mn (c) and Zn (d and e). The thermogram e is obtained using sealed sample pans.

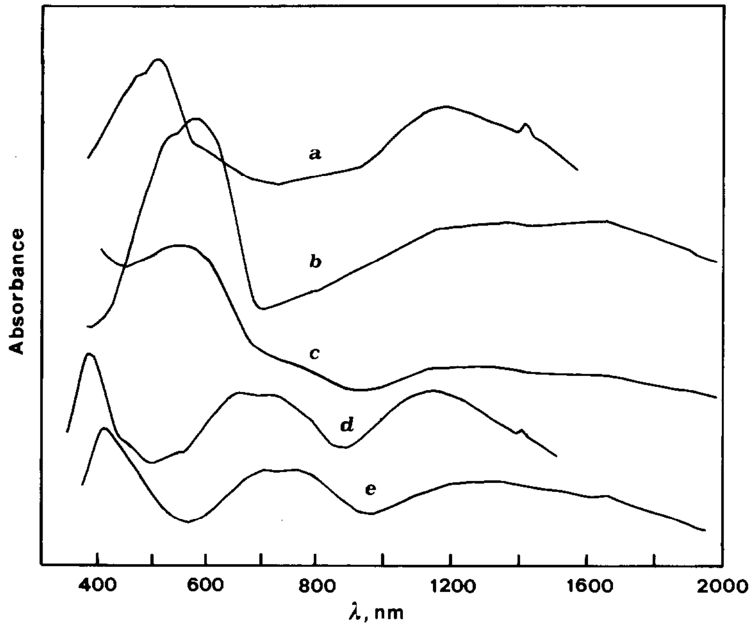


Fig. 3. Diffuse reflectance spectra of (a) $[Co(DMB)_2(H_2O)_3]\cdot H_2O$, (b) $[Co(DMB)_2]$, (c) Co residue after complete evolution of **I**, (d) $[Ni(DMB)_2(H_2O)_3]\cdot H_2O$, and (e) $[Ni(DMB)_2]$.

suggested by the IR spectra. Particularly, in the case of Ni and Mn, the carboxylate bands, while remaining grossly indicative of monodentate coordination, are considerably broader than for the hydrated complexes. This could be suggestive of carboxylate groups coordinating in different ways. On the contrary, narrow absorptions are observed for the Co and Zn complexes, the $\Delta(\nu_{as}(COO)-\nu_s(COO))$ value of ca. 128 cm^{-1} being supportive of bidentate coordination of the carboxylate group. Carboxylate-bridged dinuclear structures can be ruled out by comparison with the IR data for the tetrakis-μ-(2,6-dimethoxybenzoato)-diaqua-dicopper(II) complex [6] and by the magnetic moment value of the Co complex which falls in the range expected for monomeric species. Also the involvement of oxygen atoms from methoxyl groups in the metal coordination is ruled out for all the complexes on the basis of the IR results.

Thus, distorted octahedral geometry is achieved by Ni and Mn through intermolecular binding, while tetrahedral O_4 (from two carboxylate groups) donor sets can be suggested for Co and, probably, Zn in the anhydrous complexes.

The octahedral → tetrahedral transition of the Co complex is irreversible provided the compound is heated up to ca. 180°C as, contrary to the behaviour of the remaining complexes, $[Co(DMB)_2]$ does not revert back to $Co(DMB)_2\cdot 4\ H_2O$ even after prolonged exposure to air. An exothermic effect is observed around this temperature in the DSC thermogram of Co

(Fig. 2) which could be indicative of structural rearrangement taking place in the whole molecule, favouring stable anhydrous tetrahedral species.

Based on the TG curves in either nitrogen or air atmosphere (Fig. 4), the decomposition of the anhydrous complexes appears as a multi-step process involving overlapping weight-losses. Binary oxides are always found as final products. In all cases, a volatile product, evolved during the first decomposition steps, is deposited on the sides of the TG tube. After having been collected, the compound is identified as methyl-2,6-dimethoxybenzoate (**I**) on the basis of elemental, IR, ^{1}H NMR and mass-spectrometry analyses (see Experimental).

Furthermore, the intermediate decomposition residues dissolved in aque-

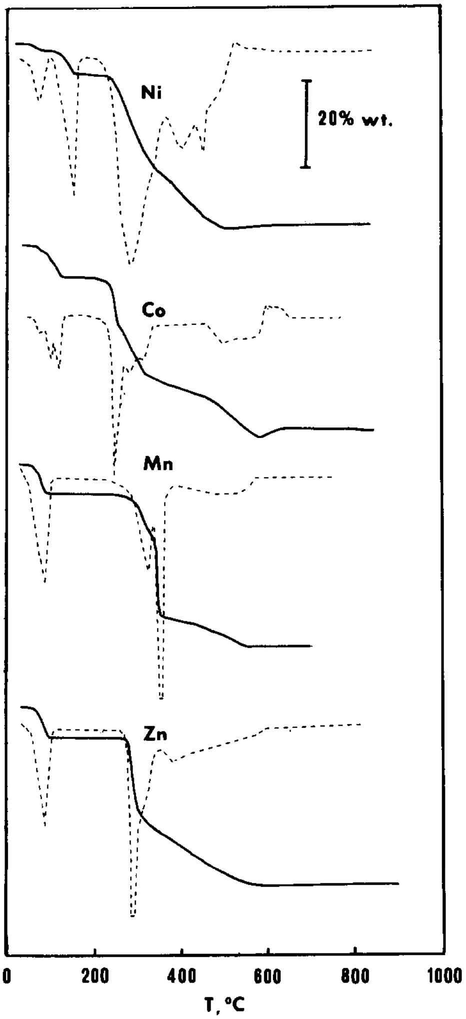
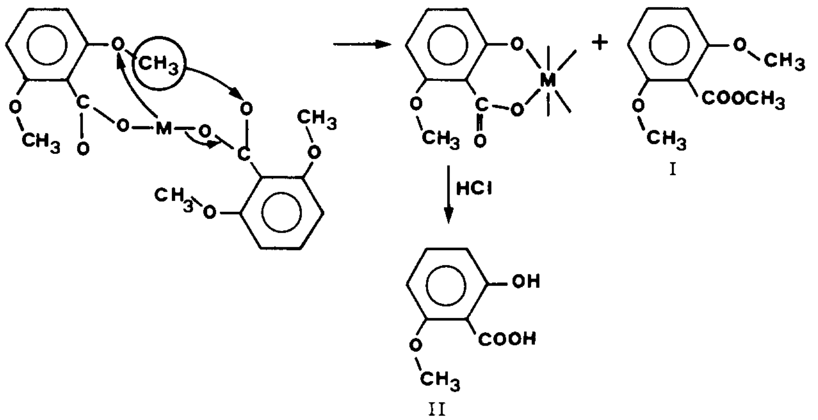


Fig. 4. TG (————) and DTG (······) curves of $[M(DMB)_2(H_2O)_3]\cdot H_2O$ complexes in nitrogen atmosphere.



Scheme 1

ous HCl yield another solid compound which is analysed as 2-hydroxy-*o*-anisic acid (**II**) by the above methods (see Experimental).

On the whole, the results can be interpreted according to a mechanism involving the migration of a methyl group from a DMB molecule to the carboxylate group of the second ligand to give the volatile ester (**I**).

Chelate complexes of **II**, provided with 1 : 1 metal/ligand ratios, involving *O*(phenolate) and *O*(carboxylate) coordination, are simultaneously formed. These species have, probably, polymeric structures and, as suggested by the electronic spectrum of the Co residue after complete evolution of **I** (Fig. 3), irregular six-coordination at the metal ion.

The last decomposition step leads to the formation of metal binary oxides.

CONCLUSION

This study provides further information on the coordination behaviour of carboxylic acids of phenolic derivatives and on the thermal properties of the resulting complexes.

Methoxyl substitutions hinder the participation of phenolic oxygen atoms in hydrogen bonding and lead to metal complexes having different structures with respect to those of 2,6-dihydroxybenzoates.

In fact, outer-sphere arrangements held by hydrogen bonding do not take place in the DMB complexes, where the carboxylate groups are directly bound to the metal ions. On heating, unstable bis(carboxylato)diaquaM(II) complexes and, subsequently, anhydrous compounds are formed. The methyl substitutions at the phenolic groups allow the anhydrous complexes to be stable over an extended temperature range and to decompose at temperatures which are substantially higher than for the analogous 2,6-dihydroxybenzoate complexes. However, due to the tendency of metal ions to form chelate complexes involving coordination of *ortho*-phenolate and carboxylate groups, unexpected reactivity of the OCH_3 groups is thermally-induced. Thus, on the analogy of the 2,6-dihydroxybenzoate systems, where deprotonation of phenolic groups was observed, displacement of a methyl group from a ligand molecule takes places in the DMB complexes to allow phenolate coordination. These findings suggest that the participation of phenolate groups might represent a general trend in thermally-induced reactions of metal complexes formed by phenolic derivatives.

ACKNOWLEDGEMENTS

The authors are grateful to Mr. A. Canu for technical assistance. This research was supported by the Consiglio Nazionale delle Ricerche (CNR, Rome).

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