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Inclusion compounds of alkaline-earth metal *O*,*O′*-dibenzoyl tartrates: structure and thermal stability

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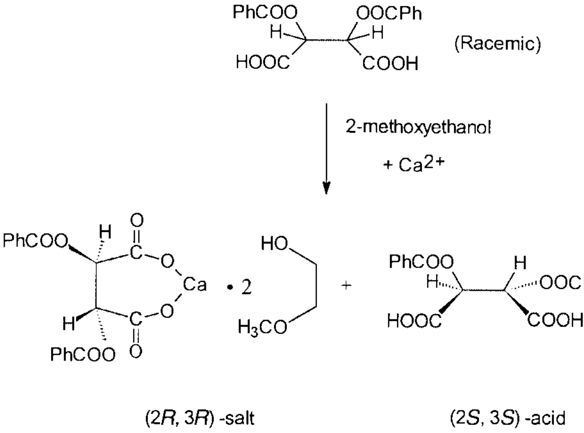
The structures of the magnesium, calcium and strontium salts of *O*,*O′*-dibenzoyl tartaric acid, formed in the presence of 2-methoxymethanol and ethanol, have been elucidated. Their thermal characteristics have been measured by TG, DSC and evolved gas analysis methods. The kinetics of thermal decomposition of the calcium salt has been studied, yielding an activation energy of 133(6) kJ mol^{-1}.

Introduction

This study arose from a report by Mravik *et al.*[1] that a simple resolution of *O*,*O′*-dibenzoyl tartaric acid can be achieved by the preferential crystallisation of its calcium salt with 2-methoxyethanol. They formulated the reaction as shown in Scheme 1.



Scheme 1

Their procedure required dissolution of the racemic acid in a mixture of ethanol and 2-methoxyethanol, adding calcium oxide, which was dissolved by heating, and allowing the crystallisation of the enantiomeric salt. The latter was induced by seeding with small quantities of the corresponding complex.

We have carried out extensive studies of inclusion compounds, their structures and thermal stabilities. Our studies have recently concentrated on organic systems, and we have employed bulky organic hosts to carry out the separation of close isomers by selective enclathration.[2,3] We have also studied the kinetics of desolvation and formation of inclusion compounds and monitored the phase changes that occur in the course of such reactions.[4,5]

Relatively little work, however, has been carried out on the structures of inclusion compounds containing alkaline-earth metals. The structures of selected Grignard reagents have been elucidated,[6–8] and the inclusion compounds of nitrogen base adducts of Group 2 salts, which contain substituted pyridines as guest molecules, have been described.[9] The co-ordination geometry of the carbazoles of Ca, Sr and Ba has been studied,[10] while the structural relations between alkoxides and aryl oxides of Ca and Ba have been studied.[11]

In this work we present the structural analysis and the results of thermal analysis of three related compounds: magnesium (2*R*,3*R*)-(−)-di-*O*-benzoyl tartrate–2-methoxyethanol-ethanol–water (1/1/3) **1**, calcium (2*R*,3*R*)-(−)-di-*O*-benzoyl tartrate–di-(2-methoxyethanol)–water (1/2/1) **2** and strontium (2*R*,3*R*)-(−)-di-*O*-benzoyl tartrate–di-(2-methoxyethanol)–water (1/2/1) **3**.

Experimental

The three compounds were prepared following the procedure described above except that we used the resolved form of the acid, *viz.* (2*R*,3*R*)-(−)-di-*O*-benzoyl tartaric acid. Suitable single crystals were obtained by slow evaporation of the mixed solvents. Preliminary cell parameters and space groups were determined photographically and subsequently refined by standard procedures on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation at 273 K. The important crystal and experimental data are given in Table 1. All the three structures were solved by direct methods using SHELX 86[12] and refined employing full-matrix least squares with SHELXL 93,[13] refining F^2.

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Thermal analyses were carried out on a Perkin-Elmer PC7 series system. All samples were dried in air and lightly crushed before analysis. The samples were placed in an open platinum pan for thermogravimetry (TG) and in vented aluminium sample pans for differential scanning calorimetry (DSC). Sample masses in each case were 2–8 mg, and the samples were purged by a stream of nitrogen flowing at 40 ml min^{-1}. Evolved Gas Analysis (EGA) was carried out with a Perkin-Elmer Series 7 TG-FTIR interface.

Results and discussion

The inclusion compound of the magnesium salt, **1**, crystallises in space group $P2_1$, with $Z = 2$. The asymmetric unit in Fig. 1 shows the numbering scheme, which is consistent with those of **2** and **3**. The crystal structure of **1** is shown as a projection viewed along [010] in Fig. 2. The magnesium ion is surrounded by six oxygen atoms (shown in Figs. 1 and 2 as dashed lines): two from water molecules, two from the methoxyethanol, one from ethanol and one from the ionised carboxyl group of a neighbouring host molecule. The oxygens form an irregular octahedron, shown in Fig. 3, and the salient Mg–O bond lengths are given in Table 2. The structure exhibits considerable hydrogen bonding (given in Table 3).

The structures of the calcium and strontium salts, **2** and **3**, are isomorphous, and both crystallise in the space group $C222_1$, with $Z = 4$, requiring the molecule to lie on a diad at Wyckoff position *b*. The metal ion is surrounded by seven oxygen atoms (shown in Fig. 4 as dashed lines) and is best described as having

Table 1 Crystal data, experimental and refinement parameters for compounds **1**–**3**

	1	**2**	**3**
Molecular formula	$C_{18}H_{12}MgO_8{\cdot}C_3H_8O_2{\cdot}C_2H_5OH{\cdot}3H_2O$	$C_{18}H_{12}CaO_8{\cdot}2C_3H_8O_2{\cdot}H_2O$	$C_{18}H_{12}O_8Sr{\cdot}2C_3H_8O_2{\cdot}H_2O$
Host : guest ratio	1 : 1 : 1 : 3	1 : 2 : 1	1 : 2 : 1
M	556.80	566.56	614.10
Crystal symmetry	monoclinic	orthorhombic	orthorhombic
Space group	$P2_1$	$C222_1$	$C222_1$
a/Å	10.906(1)	9.186(1)	9.223(1)
b/Å	11.486(1)	14.020(1)	14.287(1)
c/Å	11.369(1)	20.864(1)	20.905(1)
β/°	105.09(3)		
Z	2	4	4
V/Å^3	1375.0(9)	2687.0(4)	2754.6(4)
μ(Mo-Kα)/mm^{-1}	0.13	0.30	2.02
No. reflections collected	7977	14031	17070
No. unique reflections	2962	1559	1596
R(int)	0.033	0.028	0.099
Data/restraints/parameters	2944/9/396	1554/3/194	1589/3/185
Final R ($I > 2\sigma I$)	0.0405	0.029	0.049
(all data)	0.0505	0.037	0.070

Table 2 Mg–O bond lengths [Å] for compound **1**

Mg(1)–O(1)	2.012(2)	Mg(1)–O(1w)	2.032(2)
Mg(1)–O(2w)	2.037(2)	Mg(1)–O(1g)	2.055(2)
Mg(1)–O(3g)	2.059(3)	Mg(1)–O(2g)	2.191(3)

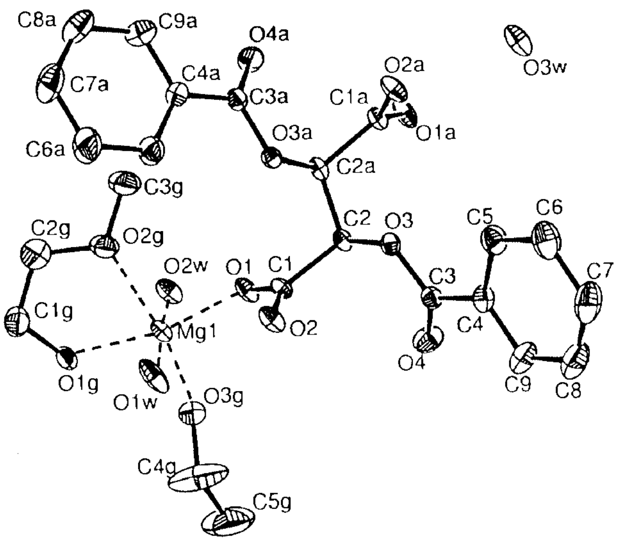

Fig. 1 An ORTEP[14] plot of the asymmetric unit of complex **1** showing the atomic labelling scheme used. Hydrogens have been omitted for clarity.

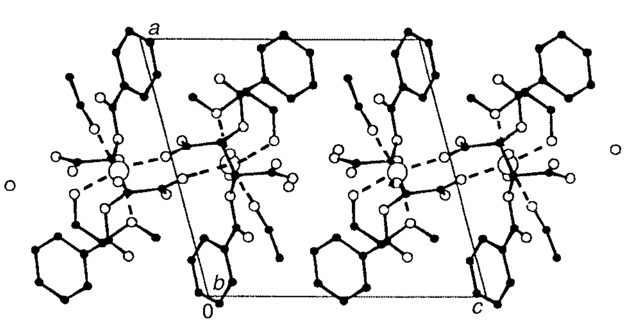

Fig. 2 Packing diagram of complex **1** viewed along [010]. Carbons are shown as filled circles and oxygens as open circles. Hydrogens have been omitted for clarity.

the geometry of a capped trigonal prism. The metal ion is bonded to four oxygens of the two methoxyethanol guests, one water molecule which lies in the diad and two oxygens from the ionised carboxyl moieties derived from adjacent host molecules.

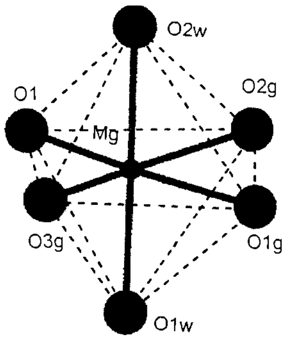

Fig. 3 Coordination geometry of Mg in **1**.

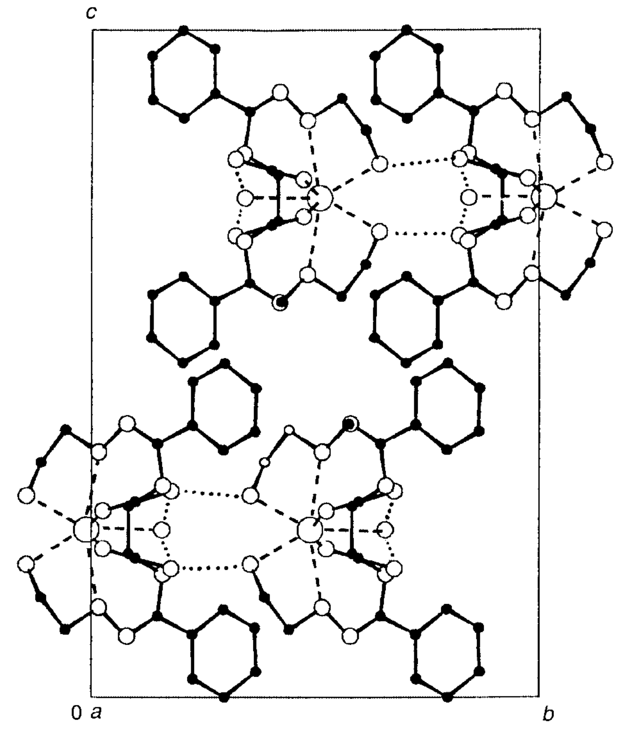

Fig. 4 Packing diagram of complex **2** viewed along [100]. Details as in Fig. 2.

The hydrogen bonding, shown in Fig. 4 as dotted lines, links adjacent molecules in the [010] direction.

The capped trigonal prism co-ordination is shown in Fig. 5, while details of the metal–oxygen bond lengths and of the hydrogen bonding are given in Tables 4 and 5 respectively. The

Table 3 Hydrogen bonds for compound **1**

O–H···O	*d*(O–H)/Å	*d*(O···H)/Å	DHO/°	*d*(O···O)/Å
O1w–H1w1···O2	0.97(3)	1.907(4)	137(4)	2.695(3)
O1w–H1w2···O1a	0.96(3)	1.79(3)	170(4)	2.746(3)
O2w–H2w1···O2	0.95(3)	1.80(3)	176(4)	2.747(3)
O2w–H2w2···O1g	0.98(3)	2.27(12)	123(10)	2.921(3)
O2w–H2w2···O2g	0.98(3)	2.28(13)	123(11)	2.924(4)
O3w–H3w1···O2a	0.93(3)	1.89(3)	169(4)	2.802(3)
O3w–H3w1···O3a	0.93(3)	2.65(4)	117(6)	3.178(3)
O3w–H3w2···O1a	0.93(3)	1.85(3)	170(3)	2.773(3)
O1g–H1g···O2a	0.95(3)	1.65(3)	163(6)	2.569(3)
O3g–H3g···O3w	0.98(3)	1.85(4)	152(6)	2.754(4)

Table 4 Metal–oxygen (M–O) bond lengths (Å) for compounds **2** and **3**

Compound	M–O1	M–O1g	M–O2g	M–O1w
2 (Ca)	2.335(1)	2.427(2)	2.521(2)	2.354(2)
3 (Sr)	2.458(4)	2.559(5)	2.631(5)	2.513(7)

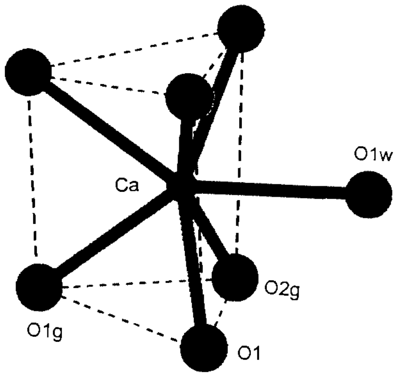

Fig. 5 Coordination geometry of Ca in **2**.

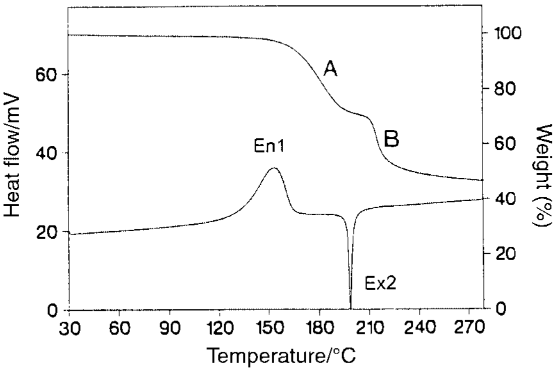

Fig. 6 TG and DSC curves for complex **2**.

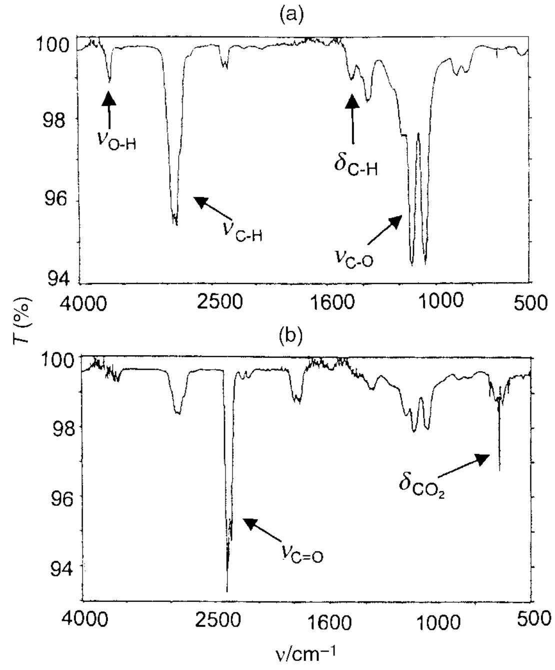

Fig. 7 IR spectra obtained from decomposition steps A and B.

bond lengths of the carboxylate groups are of interest, and range from 1.233(8) to 1.256(8) Å, thus falling between the typical C=O value of 1.21 Å and C–OH value of 1.31 Å,[15] which is consistent with the delocalisation of the negative charge over the CO_2 moieties. The Ca^{2+}–O bond lengths vary from 2.335(1) to 2.521(2) Å, similar to those found in the structure of *O*,*O*′-dibenzoyl tartrate with Ca^{2+} and tetrahydrofuran carboxylate.[16] In the latter structure, however, the Ca^{2+} ion is described as exhibiting pentagonal bipyramidal co-ordination geometry.

The thermal analysis of these compounds yielded interesting results. A typical TG and DSC result, that of the calcium salt, is given in Fig. 6. The TG shows a two step decomposition, and the percentage mass loss of the first step corresponds to the first endotherm, En1, of the DSC curve, and is associated with the loss of the 2-methoxylethanol and water guests. The second decomposition step, however, shows a concomitant exotherm, Ex2, in the DSC, and could not, at first, be interpreted. We therefore carried out EGA, and recorded the IR spectrum of the gases evolved during the first decomposition step, A, shown in Fig. 7(a), and that corresponding with the second step B, shown in Fig. 7(b). The first spectrum clearly shows all the features of the 2-methoxylethanol guest, in that the stretching modes, ν(O–H), ν(C–H) and ν(C–O), as well as the bending δ(C–H) are clearly present.[17] In the second spectrum, the bands for the CO_2 stretch and CO_2 bend are clearly identified,[18] showing that CO_2 is a decomposition product of the host. This explains the presence of the exotherm on the DSC, and the percentage mass loss of the second step.

We have carried out a kinetic study of the guest desolvation of the calcium salt. We recorded nine isothermal decomposition mass loss curves in the temperature range 95 to 135 °C. Plots of the extent of reaction, a, *versus* time showed the desolvation process to be deceleratory, and the data were best fitted by eqn. (1) corresponding to the contracting volume mechanism.[19]

$$1 - (1 - a)^{1/3} = kt \qquad (1)$$

A plot of ln k *vs.* $1/T$ is shown in Fig. 8 and this yields an activation energy of 133(6) kJ mol^{-1} over an a range of 0.1 to 0.9 and a pre-exponential factor ln $A = 35.9(2)$.

Table 5 Hydrogen bonds for compounds **2** and **3**

Compound	Donor · · · acceptor	d(O–H)/Å	d(O · · · H)/Å	DHO/°	d(O · · · O)/Å
2	O1w · · · O2	0.92(2)	1.96(2)	144(3)	2.762(2)
	O1g · · · O2	0.94(3)	1.79(3)	158(3)	2.692(2)
3	O1w · · · O2	0.94(3)	2.01(7)	132(8)	2.821(5)
	O1g · · · O2	0.97(3)	1.78(5)	148(6)	2.660(7)

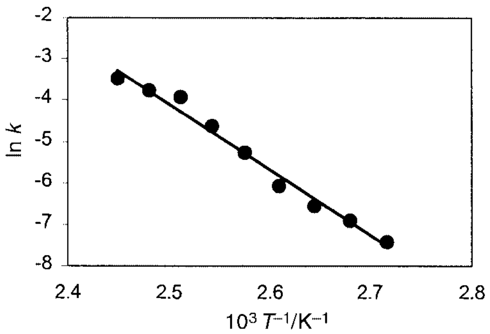

Fig. 8 Arrhenius plot of ln k *vs.* $1/T$ for the desolvation of complex **2**.

The application of the Arrhenius equation (2) to heterogeneous reactions is controversial, but Galway and Brown[20,21] have discussed this topic and give a theoretical justification for its use.

$$k = Ae^{-E_a/RT} \qquad (2)$$

Conclusion

Thermal methods of analysis are important for understanding the stabilities of inclusion compounds and relating these to their structures. Evolved gas analysis is particularly useful in cases where desolvation is accompanied by decomposition. Reliable activation energies for the desolvation reaction can be obtained by isothermal kinetic methods.

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