View Article Online / Journal Homepage / Table of Contents for this issue

Crystal forms of highly "dynamic" 18-crown[6] complexes with $M[HSO_4]$ and $M[H_2PO_4]$ ($M^+ = NH_4^+, Rb^+, Cs^+$): thermal behaviour and solid-state preparation†

Dario Braga, Enrico Modena, Marco Polito,* Katia Rubini and Fabrizia Grepioni*

Received (in Montpellier, France) 27th March 2008, Accepted 15th May 2008
First published as an Advance Article on the web 8th July 2008
DOI: 10.1039/b805203d

Downloaded by University of Belgrade on 01 January 2013
Published on 08 July 2008 on http://pubs.rsc.org | doi:10.1039/B805203D

The hydrated complexes 18-crown[6]·$[NH_4][H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot H_2O$ (**1**), 18-crown[6]·$Rb[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ (**2**), 18-crown[6]·$Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ (**3**) and 18-crown[6]·$Cs[HSO_4]\cdot 2H_2O$ (**4**) have been quantitatively prepared by the mechanical mixing of crystalline 18-crown[6], and $M[H_2PO_4]$ and/or $M[HSO_4]$ inorganic salts. The structures of the four complexes have been determined from single crystals, obtained by recrystallization of the products from water. On heating the complexes to *ca.* 70 °C, water loss takes place. The dehydration processes have been investigated by DSC, TGA and variable temperature X-ray powder diffraction; in all of the compounds, water loss leads to the formation of their corresponding anhydrous phases. On further heating of complexes **1** and **2** to 120 °C, decomplexation is observed, with formation of liquid crown ether and H_3PO_4, as well as crystalline $[NH_4]_2[SO_4]$ and $Rb_2[SO_4]$, while on heating compound **3** to 140 °C, decomplexation is observed, with formation of liquid crown ether and crystalline $Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}$. On heating complex **4**, the loss of water is followed by a reversible phase transition, that is very likely to be associated with the onset of a solid-state dynamic process, followed at 145 °C by the extrusion of the crown ether from the complex, with formation of crystalline $Cs[HSO_4]$.

Introduction

The number of investigations and applications involving crown ethers[1] is enormous. The popularity of these relatively simple organic molecules depends not only on their ability to coordinate to alkali and various metal ions,[2] but also on their widespread utilization in the construction of complex supramolecular structures.[3]

Recently, we have begun to explore "non-solution" methods of preparing novel supramolecular materials[4] as a development of our crystal engineering endeavours.[5] We have shown, *inter alia*, that manual grinding of solid 18-crown[6] in air with solid hydrogen sulfate salts of alkali metals,[6] dihydrogen phosphate salts[7] of alkali metals, and hydrogen sulfate salts[8] of Cd^{2+}, Mn^{2+} and Pb^{2+} leads to the formation of hydrated crown ether complexes; the water molecules being taken up from the ambient humidity during grinding.

The motivation for this study stems not only from fundamental research curiosity, but also from the quest for new materials that could find applications as solid electrolytes in fuel cell technology.[9]

The hydrogen sulfate and dihydrogen phosphate crown ether complex salts[6,7] showed very different behaviours upon heating: while thermal dehydration of the hydrogen sulfates led to the formation of their corresponding anhydrous salts, which underwent a reversible order–disorder phase transition upon further heating, the dihydrogen phosphate salts expelled the crown ether molecules to reconstruct the initial inorganic phase. The observation of relevant differences between the two types of salt, which may also have consequences on the possible practical utilization of these materials, prompted us to investigate the behaviour of mixed hydrogen sulfate/dihydrogen phosphate salts.

Results and discussion

In this paper we report the preparation and structural characterization of three such mixed inorganic salts, namely the hydrated complexes 18-crown[6]·$[NH_4][H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot H_2O$ (**1**), 18-crown[6]·$Rb[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ (**2**) and 18-crown[6]·$Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ (**3**), and our investigation of their behaviour under thermal treatment. We also report the preparation, structural features and thermal behaviour of the complex 18-crown[6]·$Cs[HSO_4]\cdot 2H_2O$ (**4**), which contains only the hydrogen sulfate anion, while the pure dihydrogenphosphate analogue was studied previously by us.[7] All complexes were obtained by the mechanical grinding of crystalline 18-crown[6], and anhydrous crystalline $M[H_2PO_4]$ and $M[HSO_4]$ ($M^+ = NH_4^+, Rb^+, Cs^+$). The polycrystalline samples were obviously unsuitable for a single crystal analysis. The structures of the complexes were therefore determined from crystals grown at room temperature by the slow evaporation of an aqueous solution of 18-crown[6], $M[H_2PO_4]$ and $M[HSO_4]$ first brought to boiling point. Comparisons between the powder diffraction patterns measured for the polycrystalline samples and those computed on the basis of

---

Dipartimento di Chimica G. Ciamician, Università di Bologna, Via Selmi 2, 40126 Bologna, Italy. E-mail: fabrizia.grepioni@unibo.it

† CCDC 688380–688383. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b805203d

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2008

Published on 08 July 2008 on http://pubs.rsc.org | doi:10.1039/B805203D
Downloaded by University of Belgrade on 01 January 2013

the single crystal structures were instrumental to the identification of the structures of the bulk materials.

Structural features and thermal behaviour of crystalline 1, 2 and 3

The three compounds, **1**, **2** and **3**, share the following features:

(i) The crown ether molecule forms conventional complexes with the cations; in **1**, the coordination sphere of the $[NH_4]^+$ cation is filled with one oxygen atom from the anions, while in **2** and **3**, two water molecules are also close to the alkali cation (see the structures of the three assemblies in Fig. 1).

(ii) Complexes **2** and **3** are isomorphous.

(iii) In all three complexes, the dihydrogen phosphate and hydrogen sulfate monoanions are indistinguishable, given that they are affected by a 50 : 50 positional disorder of the P and S atoms. Because of the disorder, no attribution can be applied to the OH or O^- groups of these anions.

In all cases, the anions form hydrogen bonded dimers connecting two 18-crown[6]·M^+ units. The dimers are linked to one another *via* O(H)···O hydrogen bonds with the water molecules (see Fig. 1 and Table 1).

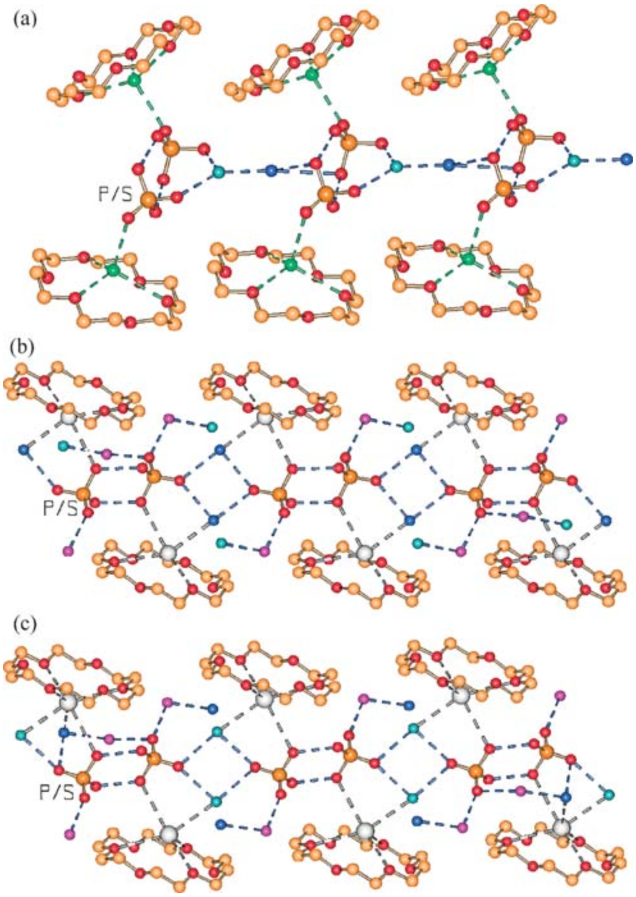


Fig. 1 The supramolecular arrangement in crystalline (a) **1** (both oxygen atoms belonging to the water molecules lie on a symmetry element), (b) **2** and (c) **3**. The label P/S indicates that, in all three complexes, the dihydrogen phosphate and hydrogen sulfate monoanions are indistinguishable, given that they are affected by a 50 : 50 positional disorder of the P and S atoms. The relevant hydrogen bonds are listed in Table 1.

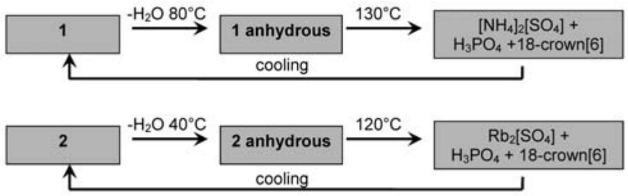
Table 1 Hydrogen bonding interactions (O···O and N···O below 3 Å, distances in Å) involving the anions and water molecules in crystalline **1**, **2** and **3**

Interaction	1	2	3
$O_{anion}\cdots O_{anion}$	2.504(8)	2.504(9) 2.53(2)	2.45(1)
$O_{anion}\cdots O_{water}$	2.63(1)	2.83(1) 2.801(9) 2.69(1) 2.74(2) 2.86(2) 2.67(1)	2.97(2) 2.73(1) 2.85(2)
$O_{water}\cdots O_{water}$	2.58 (2)	2.780(8) 2.884(9)	2.77(2) 2.87(1)
$N\cdots O_{anion}$	2.778(8)		
$N\cdots O_{crown}$	2.897(7) 2.895(8) 2.930(7)		

We shall now discuss the thermal behaviour of the four systems, starting with mixed anion salts **1** and **2**, which show similar behaviour.

18-Crown[6]·$[NH_4][H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot H_2O$ (1) and 18-crown[6]·$Rb[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ (2). Variable temperature X-ray powder diffraction (VT-XRPD) measurements show that, upon heating to *ca.* 80 °C and 40 °C, respectively, crystalline **1** and **2** lose their water molecules. The process leads to the formation of an anhydrous phase; on further heating to 130 °C in the case of **1** and 120 °C in the case of **2**, extrusion of the crown ether from the lattice is observed. Simultaneously, an acid–base reaction between the two anions, $H_2PO_4^-$ and HSO_4^-, takes place, in which the dihydrogen phosphate anion acts as a base and the hydrogen sulfate acts as an acid. The whole process results in the formation of crystalline $[NH_4]_2[SO_4]$ or $Rb_2[SO_4]$, and a mixture of liquid H_3PO_4 (m.p. 42 °C) and liquid 18-crown[6] (m.p. 40 °C). Furthermore, the whole process is fully reversible: after the mixture of crown ether, inorganic salt and H_3PO_4 has been cooled down to room temperature in air and subsequently ground (to accelerate the process), the crystalline materials **1** and **2** are reconstructed. The whole process is depicted in Scheme 1.

The reversible solid-state process described below, taking the Rb-adduct as an example, has also been investigated with differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The behaviour of **1** is analogous to that of **2**.



Scheme 1 A schematic representation of the thermal behaviour of complexes **1** and **2**, as observed in VT-XRPD measurements. The process consists of two main steps: (1) water loss and formation of the anhydrous phase; (2) extrusion of the crown ether from the lattice with a simultaneous acid–base reaction and formation of the inorganic salt; $[NH_4]_2[SO_4]$ in the case of **1**and $Rb_2[SO_4]$ in the case of **2**.

View Article Online

Downloaded by University of Belgrade on 01 January 2013
Published on 08 July 2008 on http://pubs.rsc.org | doi:10.1039/B805203D

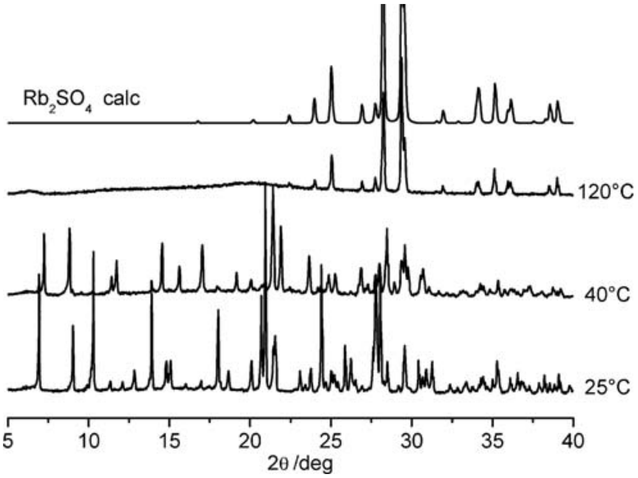


Fig. 2 The VT-XRPD of **2**: when the sample obtained from the crystallization process is heated to 40 °C, the diffraction pattern changes, with the formation of an anhydrous crystalline phase; on further heating to 120 °C, extrusion of liquid crown ether from the lattice is observed. Simultaneously, an acid–base reaction between the two anions, $H_2PO_4^-$ and HSO_4^-, takes place, in which the dihydrogen phosphate anion acts as a base and the hydrogen sulfate acts as an acid. The whole process results in the formation of crystalline $Rb_2[SO_4]$, and a mixture of liquid H_3PO_4 (m.p. 42 °C) and liquid 18-crown[6] (m.p. 40 °C).

Fig. 2 shows the results of the VT-XRPD experiments; when the sample obtained from the crystallization process is heated to *ca.* 40 °C, the diffraction pattern changes, with the formation of an anhydrous crystalline phase (as confirmed by TGA and DSC (see below). When the sample is heated to 120 °C, the formation of an amorphous phase superimposed over a new crystalline phase is observed. The crystalline phase has been unambiguously identified as anhydrous $Rb_2[SO_4]$ (ICSD[10] code 01-084-2124, year 1997).

When cooled to room temperature, the mixture retains the diffraction pattern observed at high temperature, *viz.* the solid mixture is composed of amorphous crown ether and crystalline $Rb_2[SO_4]$. Fig. 3 shows how the diffraction pattern of the starting material, namely **2**, is again present after the mixture has been left in air for a few hours and then gently ground.

The thermogram of **2** in the temperature range 40–100 °C shows a weight loss of *ca.* 4.7%, in agreement with the presence of 1.5 instead of 3 water molecules. The discordance with the water content observed from single crystal data is probably due to the fact that the compound starts losing water below 40 °C, *i.e.* below the minimum temperature value that can be reached in a TGA measurement. Upon further heating, evaporation of the crown ether and decomposition of the phosphoric acid are both observed at *ca.* 200 °C.

The same process was followed by DSC and TGA. Fig. 4 shows the DSC trace of a sample of **2** when heated. The broad shoulder that starts between 30 and 40 °C and the broad peak that follows after 60 °C can be attributed to the loss of water molecules, and to the transition process to the anhydrous phase, while the second peak (onset 121 °C) corresponds to the extrusion of the crown ether from the lattice and simultaneous recombination of the inorganic phase.

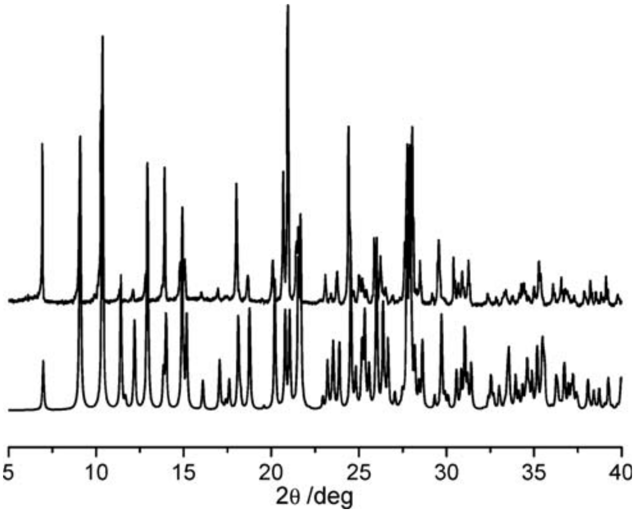


Fig. 3 The diffraction pattern of the starting material, namely **2**, is reconstructed after a few hours in air, followed by gentle grinding: comparison of the diffractogram of the product obtained from the ground material (top) and that calculated from the single crystal structure of product **2** (bottom).

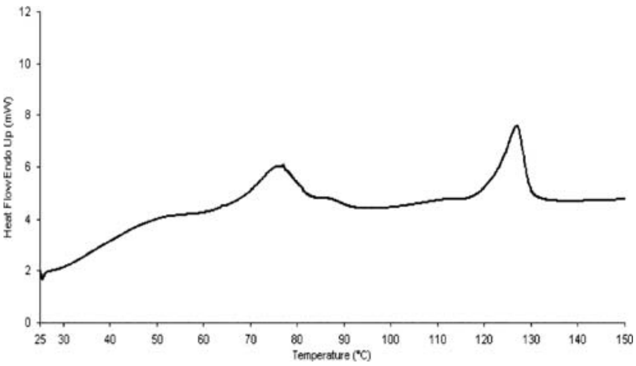


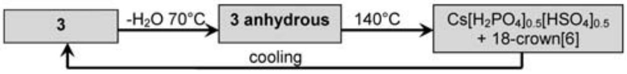
Fig. 4 The DSC trace of **2** (heating cycle).

18-Crown[6]·Cs[H$_2$PO$_4$]$_{0.5}$[HSO$_4$]$_{0.5}$·3H$_2$O (3). Compounds **2** and **3** are isomorphous and the behaviour upon heating crystalline compound **3** is very similar to that of **2**. Compound **3** loses its three water molecules at *ca.* 70 °C; the process is accompanied by a phase transition to an anhydrous phase that is stable up to 140 °C, when extrusion of liquid crown ether from the lattice and the formation of crystalline $Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}$ takes place (inorganic phase identified by comparison with ICSD[10] code 00-054-0294, year 2000, pattern taken at 145 °C). As in the cases of **1** and **2**, the process is fully reversible: after the mixture of crown ether and inorganic salt has been cooled down to room temperature and ground in air, crystalline **3** is reconstructed. The whole process is depicted in Scheme 2. Fig. 5 shows the process monitored by VT-XRPD.

Structural features and thermal behaviour of crystalline 4

In crystalline **4**, contrary to what is observed for compounds **1–3**, no direct interaction is found between the hydrogen sulfate anions. Each anion interacts with two Cs^+ cations, so that the structure can be seen as being constituted of large

Downloaded by University of Belgrade on 01 January 2013
Published on 08 July 2008 on http://pubs.rsc.org | doi:10.1039/B805203D



Scheme 2 Thermal behaviour of complex **3**. The process consists of two main steps: (1) water loss with formation of the anhydrous phase; (2) decomplexation and acid–base reaction to form the liquid crown ether and crystalline $Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}$.

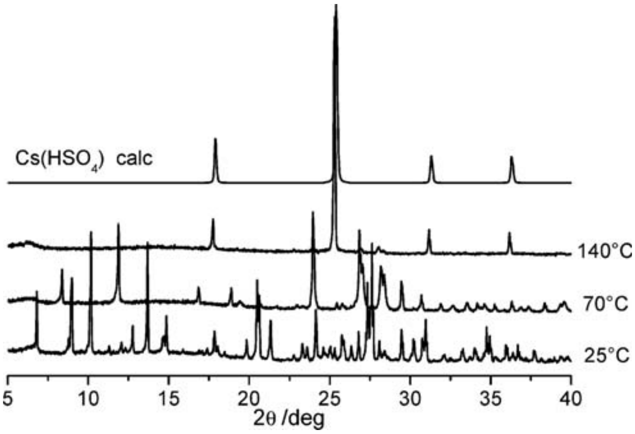


Fig. 5 The VT-XRPD pattern of crystalline **3**: when the sample obtained from the crystallization process is heated to 70 °C, the diffraction pattern changes, with the formation of an anhydrous crystalline phase. On further heating to 140 °C, extrusion of the crown ether from the lattice and reconstruction of the inorganic phase $Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}$ are observed.

“supermolecules”, in which two anions are sandwiched in between two 18-crown[6]·Cs^+ units (see Fig. 6). These large supermolecules are linked together in an extended ribbon *via* hydrogen bonds with the water molecules [$O_{anion}\cdots O_{water}$ 2.727(5), 2.640(7), 2.656(8), 2.73(3) and 2.80(2) Å; $O_{water}\cdots O_{water}$ 2.733(5) Å].

Compound **4** displays behaviour similar to that of 18-crown[6]·$K[HSO_4]\cdot 2H_2O$, previously studied by us.[6] Crystalline **4** loses both water molecules at *ca*. 60 °C with formation of an anhydrous phase, which at *ca*. 90 °C undergoes a phase transition to a second crystalline anhydrous phase. This second phase is stable up to 140 °C, at which point extrusion of the crown ether from the crystalline lattice and formation of the inorganic $Cs[HSO_4]$ phase takes place.

The thermal behaviour of compound **4** has been investigated by VT-XRPD, DSC and TGA.

Fig. 7 shows the results of the VT-XRPD experiments on **4**. When the sample is heated to 60 °C, the diffraction pattern changes abruptly, with the formation of an anhydrous crystalline phase (as confirmed by the TGA and DSC experiments). On further heating to 100 °C, compound **4** undergoes a phase transition to a second crystalline anhydrous phase that is stable up to 145 °C, at which point extrusion of the crown ether from the crystalline lattice and formation of the inorganic $Cs[HSO_4]$ phase take place. The whole process is fully reversible: after the mixture of crown ether and inorganic salt has been cooled down to room temperature and ground in air, crystalline **4** is completely reconstructed. The whole process is depicted in Scheme 3.

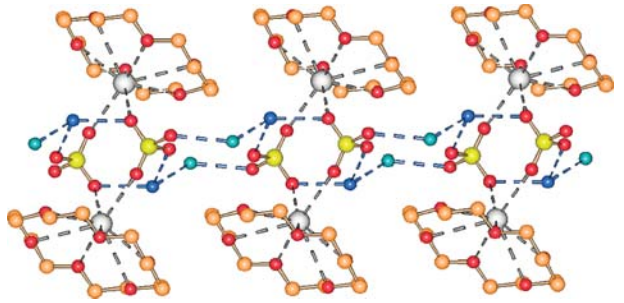


Fig. 6 Packing features in crystalline **4**, showing the large supermolecules, in which two anions are sandwiched in between two 18-crown[6]·Cs^+ units. These large supermolecules are linked together *via* hydrogen bonds with the water molecules [$O_{anion}\cdots O_{water}$ 2.727(5), 2.640(7), 2.656(8), 2.73(3) and 2.80(2) Å; $O_{water}\cdots O_{water}$ 2.733(5) Å].

As shown by the TGA trace, the weight loss of 6.7% in the range 40–110 °C is consistent with the loss of two water molecules per formula unit. The DSC analysis (Fig. 8) shows three endothermic peaks: the first is related to the loss of water and the consequent transition to the anhydrous phase (onset 60.3 °C); the second (onset 83.4 °C), as demonstrated by the VT-XRPD experiments, is related to the phase transition to a second anhydrous phase; the third (onset 132.5 °C) is related to the extrusion of the crown ether from the crystalline lattice and the formation of the inorganic $Cs[HSO_4]$ phase.

Conclusions

In this paper, we have reported new examples of compounds belonging to the family of hydrogen-bonded acid oxo-anion salts with crown ether-complexed cations. In particular, we have prepared and structurally investigated the mixed anion salts, 18-crown[6]·$[NH_4][H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot H_2O$ (**1**), 18-crown[6]·$Rb[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ (**2**) and 18-crown[6]·$Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ (**3**), containing both the

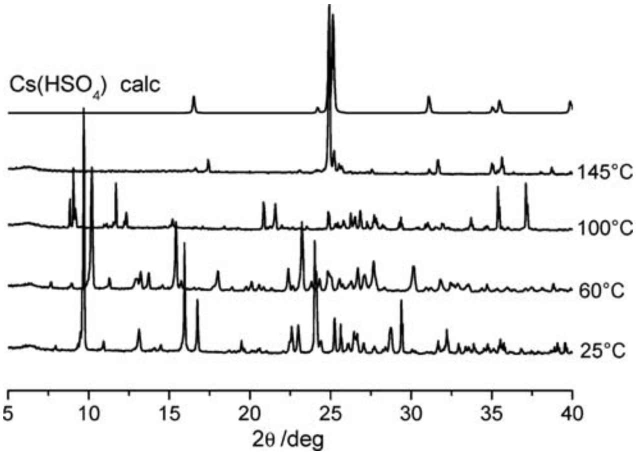
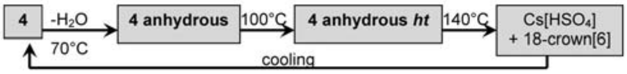


Fig. 7 The VT-XRPD pattern of compound **4**: when the sample is heated to 60 °C, the diffraction pattern changes abruptly, with the formation of an anhydrous crystalline phase. On further heating to 100 °C, compound **4** undergoes a phase transition to a second crystalline anhydrous phase that is stable up to 145 °C, at which point extrusion of the crown ether from the crystalline lattice and formation of the inorganic $Cs[HSO_4]$ phase take place.

Published on 08 July 2008 on http://pubs.rsc.org | doi:10.1039/B805203D
Downloaded by University of Belgrade on 01 January 2013



Scheme 3 Thermal behaviour of complex **4**. The process consists of two main steps: (1) water loss, with formation of the anhydrous phase; (2) decomplexation and acid–base reaction to form the liquid crown ether and crystalline Cs[HSO_4].

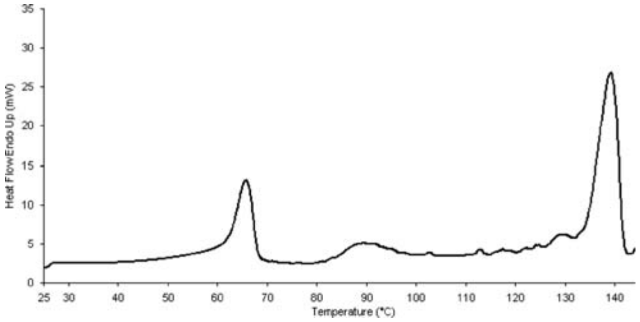


Fig. 8 The DSC trace of compound **4**: the DSC analysis shows three endothermic peaks: the first is related to the loss of water and the consequent transition to the anhydrous phase (onset 60.3 °C); the second (onset 83.4 °C), as demonstrated by the VT-XRPD experiments, is related to the phase transition to a second anhydrous phase; the third (onset 132.5 °C) indicates extrusion of the crown ether from the crystalline lattice and formation of the inorganic Cs[HSO_4] phase.

hydrogen sulfate and dihydrogen phosphate anions. We were prompted to make this choice by the intriguing difference in behaviour of the crystals of 18-crown[6]·M[HSO_4]·$x$$H_2O$ (M^+ = NH_4^+, K^+) and 18-crown[6]·M[H_2PO_4]·$x$$H_2O$ (M^+ = NH_4^+, K^+, Rb^+, Cs^+) upon heating: while the former lose water and undergo enantiotropic solid–solid phase transitions,[6,8] which are very likely to be associated with the onset of dynamic reorientational motions in the crystal structure, the latter show the phenomenon of demixing, *i.e.* the crown ether is decomplexed from the alkali cations, "extruded" as a liquid phase and the inorganic crystal reformed.[7] The hydrogen sulfate salt 18-crown[6]·Cs[HSO_4]·2H_2O (**4**) has also been investigated.

In all of the compounds, water loss leads to the formation of the corresponding anhydrous phases. In crystalline **3**, the crown ether extrusion is accompanied by reconstruction of the inorganic Cs[H_2PO_4]$_{0.5}$[HSO_4]$_{0.5}$ phase, while in complexes **1** and **2**, the decomplexation process results in the formation of a liquid mixture of crown ether and phosphoric acid, as well as the inorganic crystalline phases [NH_4]$_2$[SO_4] and Rb_2[SO_4]. On the other hand, complex **4** undergoes a reversible phase transition that is very likely to be associated with the onset of a solid-state dynamic process, followed at 145 °C by extrusion of the liquid crown ether and the formation of crystalline Cs[HSO_4].

Demixing of crystalline phases is a well established phenomenon in liquid crystal and polymer science, and is also known to occur in the cases of solid solutions and mixed inorganic systems.[11]

The cases discussed herein, however, are quite different: in the first place, the supramolecular adducts are prepared easily by mechanical mixing of the solid reactants, a well established method[12] that is also being actively explored in the field of crystal engineering.[13] More importantly though, the reactions that lead to the formation of the crown ether adducts are reversible in the solid-state if the product of the decomplexation is ground, again in the presence of moisture in order to permit water uptake.

The reverse process, namely the reformation of 18-crown[6]·M[H_2PO_4]$_{0.5}$[HSO_4]$_{0.5}$·$x$$H_2O$ from the inorganic salt, can be seen as a special kind of solvation by the crown ether "solid solvent". As far as the solid-state complexation reaction is concerned, the formation of the adducts by means of mechanical grinding recalls the reaction that was observed when the neutral organometallic zwitterion [(η^5-C_5H_4COOH)(η^5-C_5H_4COO)Co^{III}] was ground with alkali metal salts such as KBr, CsI *etc.*, leading to solid-state complexation of the alkali metal cation and formation of the supramolecular salts [Co^{III}(η^5-C_5H_4COOH)(η^5-C_5H_4COO)]$_2$·M^+X^- (M^+ = K^+, Rb^+, Cs^+, NH_4^+; X^- = Cl^-, Br^-, I^-, PF_6^-).[14]

Clearly, processes of this kind can only be understood on the basis of a model of extreme molecular and ionic mobility, which must accompany the uptake and release of *both* water and crown ether molecules. High molecular mobility has been shown to often be the prerequisite for the occurrence of many solid-state processes.[15]

With the new findings reported in this paper, we have a broad picture of the behaviour with temperature of a class of relatively simple, inexpensive and easy to make crown ether complexes that show remarkable differences upon thermal treatment. The hydration–dehydration processes are crucial: the room temperature phases all appear to require water of complexation/crystallization to attain stability and cohesion. When the water is removed, two different processes are observed: (i) water loss and formation of stable high temperature phases that undergo dynamic reversible polymorphic transitions upon heating, (ii) water loss and extrusion of the crown ether molecules in a liquid state, and reconstruction of the inorganic phases. The occurrence of either process is not strictly dependent on the type of anion, as inorganic phase reconstruction is observed with both hydrogen sulfates, dihydrogen phosphates and mixed anion salts when the cation is a heavy alkali metal.

It remains to be understood which energetic factors dominate the choice, and also whether doping of either type of crystal may lead to materials with tuneable intermediate behaviour. These aspects are now under investigation.

Experimental section

Synthesis

All starting materials were purchased from Aldrich. Reagent grade solvents and twice-distilled water were used.

18-Crown[6][NH_4][HSO_4]$_{0.5}$[H_2PO_4])$_{0.5}$·H_2O (1). 18-Crown[6] (0.528 g, 2 mmol), [NH_4][HSO_4] (0.115 g, 1 mmol) and [NH_4][H_2PO_4] (0.115 g, 1 mmol) were dissolved in 6 mL of water. The solution was refluxed for 1 h. Single crystals of **1** were obtained by slow evaporation of the solution.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2008

Downloaded by University of Belgrade on 01 January 2013
Published on 08 July 2008 on http://pubs.rsc.org | doi:10.1039/B805203D

Table 2 Crystal data and details of measurements for compounds **1–4**

	1	**2**	**3**	**4**
Formula	$C_{12}H_{31.5}NO_{11}P_{0.5}S_{0.5}$	$C_{12}H_{31.5}O_{13}P_{0.5}RbS_{0.5}$	$C_{12}H_{31.5}O_{13}P_{0.5}CsS_{0.5}$	$C_{24}H_{58}O_{24}Cs_2S_2$
M_r	397.40	500.86	548.30	1060.64
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*F2dd*	*C2/c*	*C2/c*	*P*2$_1$/*n*
a/Å	8.710(5)	19.802(4)	19.840(7)	11.064(4)
b/Å	28.868(7)	8.447(4)	8.460(4)	8.655(3)
c/Å	31.206(6)	25.777(7)	26.190(2)	22.644(8)
α (°)	90	90	90	90
β (°)	90	101.00(2)	101.14(6)	100.907(6)
γ (°)	90	90	90	90
V/Å^3	7846(5)	4232(2)	4313(4)	3188(1)
Z	16	8	8	2
μ(Mo-K$_\alpha$)/mm^{-1}	0.205	2.486	1.861	1.890
$2\theta_{max}$ (°)	50	44	54	56
Reflections measured	1830	2583	3288	16927
Unique reflections	1830	2583	3196	4733
R_{int}	0.0474	0.0385	0.0411	0.0427
Reference parameters	227	271	244	262
GOF on F^2	1.044	0.998	1.040	0.871
$R1$ [on F, $I > 2\sigma(I)$]	0.0598	0.0390	0.0661	0.0333
w$R2$ [on F^2, all data]	0.1875	0.1124	0.2168	0.0835

18-Crown[6]·Rb[HSO_4]$_{0.5}$[H_2PO_4]$_{0.5}$·3H_2O (2). 18-Crown[6] (0.264 g, 1 mmol), Rb[HSO_4] (0.091 g, 0.5 mmol) and Rb[H_2PO_4] (0.091 g, 0.5 mmol) were dissolved in 4 mL of water. The solution was refluxed for 1 h. Single crystals of **2** were obtained by slow evaporation of the solution.

18-Crown[6]Cs[HSO_4]$_{0.5}$[H_2PO_4]$_{0.5}$·3H_2O (3). 18-Crown[6]·Cs[HSO_4]·2H_2O (0.530 g, 1 mmol) and 18-crown[6]·Cs[H_2PO_4]·H_2O (0.521 g, 1 mmol) were dissolved in 4 mL of water. The solution was refluxed for 1 h. Single crystals of **3** were obtained by slow evaporation of the solution.

18-Crown[6]Cs[HSO_4]·2H_2O (4). 18-Crown[6] (0.264 g, 1 mmol), $Cs_2[SO_4]$ (0.181 g, 0.5 mmol), and H_2SO_4 (0.049 g, 0.5 mmol) were dissolved in 4 mL of water. The solution was refluxed for 1 h. Single crystals of **4** were obtained by slow evaporation of the solution.

Solid-state synthesis. All solid-state syntheses were performed in air at room temperature. In a typical experiment, 100 mg of 18-crown[6] was manually ground in an agate mortar for 15 min with a stoichiometric amount of the appropriate inorganic salts ([NH_4][H_2PO_4] and [NH_4][HSO_4] in a 1 : 1 ratio for compound **1**; Rb[H_2PO_4] and Rb[HSO_4] in a 1 : 1 ratio for compound **2**; Cs[H_2PO_4] and Cs[HSO_4] in a 1 : 1 ratio for compound **3**; Cs[HSO_4] for compound **4**).

Crystal structure determination. Single crystal data of compounds **1**, **2** and **3** were collected on a NONIUS CAD-4 diffractometer. Crystal data of compound **4** were collected on a Bruker Smart ApexII CCD diffractometer. Crystal data and details of measurements are summarised in Table 2. Common to all compounds: Mo-K$_\alpha$ radiation, λ = 0.71073 Å, graphite monochromator, T = 293(2) K. The program SHELXL97[16a] was used for structure solution and refinement on F^2; the programs PLATON[16b] and SCHAKAL[16c] were used for hydrogen-bonding analysis and molecular graphics. All non H-atoms were refined anisotropically.† The identities of the bulk materials obtained *via* solid-state processes and the structures obtained by single crystals were verified by comparing calculated and observed powder diffraction patterns.

P and S atoms belonging to the dihydrogen phosphate and hydrogen sulfate monoanions in complexes **1**, **2** and **3** are positionally disordered in the structures, and were refined with a 0.5 occupancy factor. Because of the disorder, the hydrogen atoms belonging to the anions could not be attributed with confidence and were not added to the model. In addition to this, the position of the whole dihydrogen phosphate/hydrogen sulfate monoanions is disordered around one of the P/S–O axes (occupancy ratio 60 : 40). In **1**, two oxygen atoms belonging to water molecules were found in the structure, both lying on a symmetry element. Heavy decay in complex **2** prevented the data collection from being extended further than 22° of 2θ.

X-Ray powder diffraction. XRPD measurements were collected using a Panalytical X'Pert Pro (Cu-K$_\alpha$ radiation, graphite monochromator) equipped with an X'Celerator detector and a TK 450 Anton Paar variable temperature camera. The program Mercury 1.5[16d] was used for the calculation of X-ray powder patterns.

Calorimetric analysis. TGA was performed using a Perkin-Elmer TGA-7 thermogravimetric analyzer. Heating was performed in a nitrogen flow (20 cm^3 min^{-1}) using a platinum crucible at a rate of 5 °C min^{-1} up to decomposition. The samples' weights were in the range 5–10 mg.

Calorimetric measurements were performed using a Perkin-Elmer Pyris Diamond DSC equipped with a model ULSP 90 intra-cooler. The instrument was calibrated with high purity standards (indium and cyclohexane) at 5 °C min^{-1}. The samples (3–5 mg) were placed in open aluminium pans. Heating was carried out at 5 °C min^{-1} in the temperature range 40 to 180 °C.

Published on 08 July 2008 on http://pubs.rsc.org | doi:10.1039/B805203D
Downloaded by University of Belgrade on 01 January 2013

Acknowledgements

We acknowledge financial support from the University of Bologna (postdoc. fellowship GP) and from MiUR (PRIN2006).

References

1 (*a*) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017; (*b*) J. Pedersen, *Science*, 1988, **241**, 536.

2 C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 16.

3 (*a*) M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (*b*) J. L. Atwood, K. T. Holman and J. W. Steed, *Chem. Commun.*, 1996, 1401; (*c*) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley & Sons, Chichester, UK, 2000; (*d*) J. W. Steed, *Coord. Chem. Rev.*, 2001, **215**, 171; (*e*) P. C. Junk, B. J. McCool, B. Moubaraki, K. S. Murray, L. Spiccia, J. D. Cashion and J. W. Steed, *J. Chem. Soc., Dalton Trans.*, 2002, **6**, 1024; (*f*) M. Calleja, S. A. Mason, P. D. Prince, J. W. Steed and C. Wilkinson, *New J. Chem.*, 2003, **27**, 28; (*g*) J. M. Harrington, S. B. Jones, P. H. White and R. D. Hancock, *Inorg. Chem.*, 2004, **43**, 4456; (*h*) J. M. Dou, X. K. Gao, F. Y. Dong, D. C. Li and D. Q. Wang, *Dalton Trans.*, 2004, **18**, 2918; (*i*) D. R. Turner, S. N. Pek and S. R. Batten, *New J. Chem.*, 2008, **32**, 719; (*j*) P. C. Junk, *New J. Chem.*, 2008, **32**, 762; (*k*) K. M. Fromm and R. D. Bergougnant, *Solid State Sci.*, 2008, **9**, 580.

4 (*a*) D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem.–Eur. J.*, 2003, **9**, 4362; (*b*) D. Braga, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem.–Eur. J.*, 2004, **10**, 3261; (*c*) D. Braga, M. Curzi, F. Grepioni and M. Polito, *Chem. Commun.*, 2005, 2915; (*d*) D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini and F. Grepioni, *Angew. Chem., Int. Ed.*, 2006, **45**, 142.

5 (*a*) D. Braga, *Chem. Commun.*, 2003, **22**, 2751; (*b*) D. Braga and F. Grepioni, *Chem. Commun.*, 2005, **29**, 3635; (*c*) D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi and M. Polito, *Dalton Trans.*, 2006, **10**, 1249; (*d*) D. Braga and F. Grepioni, *Angew. Chem., Int. Ed.*, 2004, **43**, 2.

6 (*a*) D. Braga, M. Curzi, M. Lusi and F. Grepioni, *CrystEngComm*, 2005, **7**, 276; (*b*) D. Braga, M. Gandolfi, M. Lusi, D. Paolucci, M. Polito, K. Rubini and F. Grepioni, *Chem.–Eur. J.*, 2007, **13**, 5249.

7 D. Braga, M. Polito, E. Dichiarante, K. Rubini and F. Grepioni, *Chem. Commun.*, 2007, 1594.

8 D. Braga, M. Gandolfi, M. Lusi, M. Polito, K. Rubini and F. Grepioni, *Cryst. Growth Des.*, 2007, 919.

9 (*a*) J. Lipkowski, B. Baranowski and A. Lunden, *Pol. J. Chem.*, 1993, **67**, 1867; (*b*) S. M. Haile, *Mater. Res. Soc. Symp. Proc.*, 1999, **547**, 315; (*c*) C. R. I. Chisholm and S. M. Haile, *Solid State Ionics*, 2000, **229**, 136; (*d*) S. M. Haile, D. A. Boyens, C. R. I. Chisholm and R. B. Merie, *Nature*, 2001, **400**, 910; (*e*) P. G. Bruce, *Dalton Trans.*, 2006, 1365; (*f*) A. Abouimrane, P.-J. Alarco, Y. Abu-Lebdeh, I. Davidson and M. Armand, *J. Power Sources*, 2007, **174**, 1193.

10 *ICSD Database*, version 2005-2, FIZ Karlsruhe, Karlsruhe, Germany.

11 See, for example: (*a*) H. A. J. Oonk, *Pure Appl. Chem.*, 2001, **73**, 807; (*b*) J. C. Loudet and P. Poulin, *Top. Curr. Chem.*, 2003, **226**, 173; (*c*) W. B. Hu and D. Frenkel, *Adv. Polym. Sci.*, 2005, **191**, 1.

12 (*a*) R. P. Rastogi, P. S. Bassi and S. L. Chadha, *J. Phys. Chem.*, 1963, **67**, 2569; (*b*) R. P. Rastogi and N. B. Singh, *J. Phys. Chem.*, 1966, **70**, 3315; (*c*) R. P. Rastogi and N. B. Singh, *J. Phys. Chem.*, 1968, **72**, 4446; (*d*) A. O. Patil, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, 1984, **106**, 348; (*e*) N. Shan, F. Toda and W. Jones, *Chem. Commun.*, 2002, 2372; (*f*) V. V. Boldyrev, *Solid State Ionics*, 1995, **63–65**, 537; (*g*) J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, **71**, 581; (*h*) J. Fernandez-Bertran, J. C. Alvarez and E. Reguera, *Solid State Ionics*, 1998, **106**, 129.

13 (*a*) M. C. Etter, *J. Phys. Chem.*, 1991, **95**, 4601; (*b*) W. H. Ojala and M. C. Etter, *J. Am. Chem. Soc.*, 1992, **114**, 10228; (*c*) M. C. Etter, S. M. Reutzel and C. G. Choo, *J. Am. Chem. Soc.*, 1993, **115**, 4411; (*d*) V. R. Pedireddi, W. Jones, A. P. Chorlton and R. Docherty, *Chem. Commun.*, 1996, 987; (*e*) A. V. Trask, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, 2004, 890; (*f*) A. Pichon, A. Lazuen-Garay and S. L. James, *CrystEngComm*, 2006, **8**, 211; (*g*) A. V. Trask, D. A. Haynes, W. D. S. Motherwell and W. Jones, *Chem. Commun.*, 2006, 51.

14 D. Braga, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem.–Eur. J.*, 2004, **10**, 3261.

15 (*a*) G. Kaupp, *CrystEngComm*, 2003, **5**, 117; (*b*) G. Kaupp, in *Making Crystals by Design: Methods, Techniques and Applications*, ed. D. Braga and F. Grepioni, John Wiley & Sons, Weinheim, 2006, ch. 2, pp. 87–148.

16 (*a*) G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997; (*b*) E. Keller, *SCHAKAL99, Graphical Representation of Molecular Models*, University of Freiburg, Germany, 1999; (*c*) A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, C34; (*d*) W. Kraus and G. Nolze, *PowderCell*, BAM, Berlin, © subgroups derived by U. Müller (Universität Gh Kassel).

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2008