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Solution and Solid-State Preparation of 18-Crown[6] Complexes with $M[HSO_4]_n$ Salts ($M = NH_4^+, K^+, Sr^{2+}$ and $n = 1, 2$) and an Investigation of Solvation/Desolvation Processes and Crystal Polymorphism

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Abstract: 18-Crown[6] ether has been used to prepare a new class of organic–inorganic complexes of general formula 18-crown[6]·$M[HSO_4]_n$ (where $M = NH_4^+, K^+, Sr^{2+}$ and $n = 1, 2$) by reacting directly in solution or in the solid state the crown ether 18-crown[6] with inorganic salts such as $[NH_4][HSO_4]$, $K[HSO_4]$, and $Sr[HSO_4]_2$. The structures of 18-crown[6]·$[NH_4][HSO_4]$·2 H_2O (**1**·2 H_2O), 18-crown[6]·$[NH_4][HSO_4]$ (**1**), 18-crown[6]·$K[HSO_4]$·2 H_2O (**2**·2 H_2O), 18-crown[6]·$K[HSO_4]$ (**2**), and 18-crown[6]·$Sr[HSO_4]_2$ (**3**) have been characterized by single-crystal X-ray diffraction. The reversible water loss in compounds **1**·2 H_2O and **2**·2 H_2O leads to formation of the corresponding anhydrous phases 18-crown[6]·$[NH_4][HSO_4]$ (**1**), and 18-crown[6]·$K[HSO_4]$ (**2**), which undergo, on further heating, enantiotropic solid-solid transitions very likely associated with the on-set of a solid state dynamical process. Similar high-temperature behavior is shown by 18-crown[6]·$Sr[HSO_4]_2$ (**3**). The dehydration and phase-transition processes have been investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and variable temperature X-ray powder diffraction.

Keywords: crown compounds · crystal polymorphism · desolvation · phase transitions · X-ray diffraction

Introduction

Crown ethers are one of the symbols of supramolecular chemistry.[1] This is not only because of their extensive utilization in supramolecular chemistry and crystal engineering for the construction of complex superstructures,[2] but also because crown ethers are able to form stable complexes with alkali and transition-metal ions and hydrogenate cations via hydrogen bonding.[3]

We have recently communicated that crown ethers can take part in solid–solid and solid–liquid processes to capture alkali metal cations and the ammonium cation in extended hydrogen-bonded networks formed by inorganic acid anions, such as the hydrogensulfate.[4] In particular, we have shown that manual grinding of solid 18-crown[6] and solid $[NH_4][HSO_4]$ in the air leads to formation of the crown ether complex 18-crown[6]·$[NH_4][HSO_4]$·2 H_2O, the water molecules being taken up from ambient humidity during grinding. The crown ether 15-crown[5], which is a liquid at room temperature, has been otherwise kneaded with solid ammonium hydrate sulfate to produce the complex $(15\text{-crown}[5])_3\cdot[NH_4]_2[HSO_4]_3\cdot H_2O$.

Beside the interest in the solid–solid complexation[5] by means of the crown ethers, another reason to investigate hydrogen sulfate salts is the possibility that the hydrogen-bond chains of inorganic anions[6] allow proton transfer when the dynamical reorientational state is reached upon heating. As a matter of fact, solid acid salts such as $CsHSO_4$, $Rb_3H[SeO_4]_2$ have found applications in a number of devices such as H_2 and H_2O sensors, fuel and steam cells and high energy density batteries.[7] Fuel cell systems operating at relatively low temperatures, such as those using Nafion, require water in order to facilitate proton conduction. Hence, loss of water immediately results in loss of conductivity. For the same reason, another requirement is that the temperature of operation does not exceed 100 °C. Based on this premise, it is clear that beside high conductivity, chemical and thermal stability, anhydrous proton conducting materials are highly

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desirable for fuel cells working at temperatures above 100 °C. Recently, the use of crown ether based polymers has been reviewed.[8]

In this paper we report that 18-crown[6] ether has been used to prepare a new class of organic–inorganic complexes of general formula 18-crown[6]·M[HSO_4]$_n$ (where M = NH_4^+, K^+, Sr^{2+} and n = 1, 2) by reacting directly in solution or in the solid state the crown ether 18-crown[6] with inorganic salts such as [NH_4][HSO_4], K[HSO_4], and Sr[HSO_4]$_2$. The structures of 18-crown[6]·[NH_4][HSO_4]·2 H_2O (**1**·2 H_2O), 18-crown[6]·[NH_4][HSO_4] (**1**), 18-crown[6]·K[HSO_4]·2 H_2O (**2**·2 H_2O), 18-crown[6]·K[HSO_4] (**2**), and 18-crown[6]·Sr[HSO_4]$_2$ (**3**), have been characterized by single-crystal X-ray diffraction on crystals grown from aqueous solutions prepared by dissolving the polycrystalline reaction products in water. The reversible water loss in compounds **1**·2 H_2O and **2**·2 H_2O leads to formation of the corresponding anhydrous phases of the respective compounds. On further heating, compounds **1** and **2** undergo enantiotropic solid–solid transitions very likely associated with the on-set of a solid state dynamical process. Similar high-temperature behavior is shown by **3**. The dehydration and phase-transition processes have been investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and variable temperature X-ray powder diffraction. In particular, we are interested in investigating the loss/uptake of water of crystallization and the stability of the anhydrous phases as well as the existence of order–disorder phase transitions. These issues are relevant for a potential exploitation of these salts in fuel cell applications and are of interest in the investigation of crystal polymorphism[9] and crystal design.[10]

Synthesis and characterization

Preparation and thermal behavior of crystalline 18-crown[6]·[NH_4][HSO_4]: Compound **1** has been obtained by water elimination from the hydrate **1**·2 H_2O. Single crystals of **1** have been obtained by recrystallization from anhydrous acetone (see Experimental Section). The starting material **1**·2 H_2O has been prepared as previously reported.[4]

The structure of **1**·2 H_2O is characterized by the presence of chains of HSO_4^- anions linked by hydrogen bonds via the water molecules, while the ammonium cation interacts via N-H···O hydrogen bonds with the crown ether oxygen atoms (see Figure 1a).[4] Water removal yields the anhydrous phase **1**. Figure 1b shows the close structural relationship between the hydrated and the anhydrous forms. Water removal is accompanied by a small reorganization of the crown ethers and of the anions and by the formation of hydrogen bonded anion pairs.

A DSC measurement (Figure 2, top) shows that, after the first transition associated with water removal (at ca. 60 °C), a second phase transition occurs at 123 ± 1 °C (onset temperature). The water removal is shown also by TGA (see Figure 2, bottom), which also allows to appreciate that no decomposition occurs up to 200 °C.

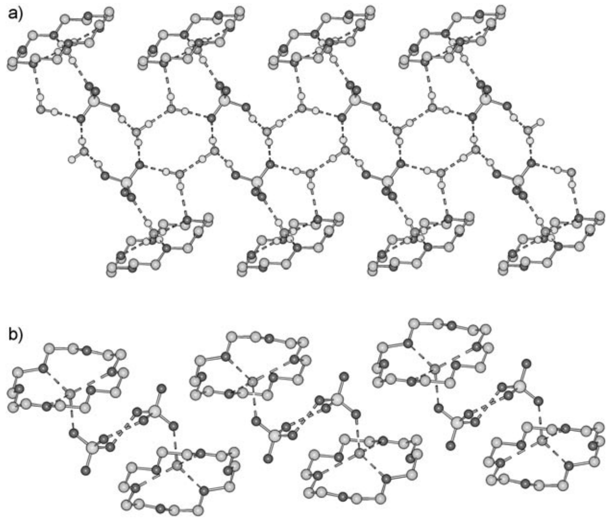


Figure 1. Crown ethers and ions organization in a) **1**·2 H_2O and b) the anhydrous phase **1**. Note the formation of hydrogen bonded anion pairs in **1** after water removal ($H_{OH,NH}$ atoms not shown for clarity in **1**).

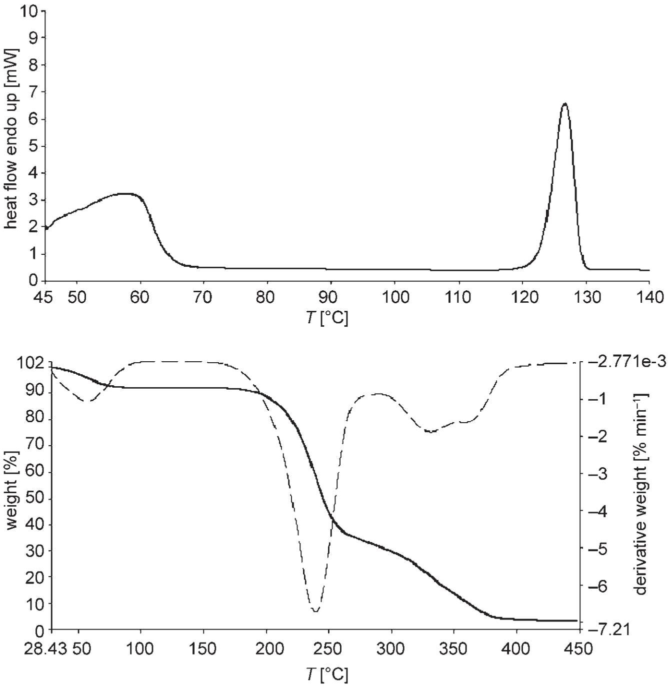


Figure 2. DSC trace (heating cycle, top) for compound **1**·2 H_2O, showing the transition associated with formation of **1** and a high temperature transition at 123 ± 1 °C (onset temperature). The loss of water is also visible in the thermogravimetric analysis (bottom).

A more detailed view of the behavior with temperature of **1**·2 H_2O and its anhydrous form **1** is obtained by variable temperature powder diffraction experiments (VTXPD). Figure 3 provides clear indication of the transition **1**·2 H_2O → **1**, associated with water removal, which is then followed by a second change in the diffraction trace (measured at 130 °C) with formation of the phase $\mathbf{1}_{ht}$ where the subscript

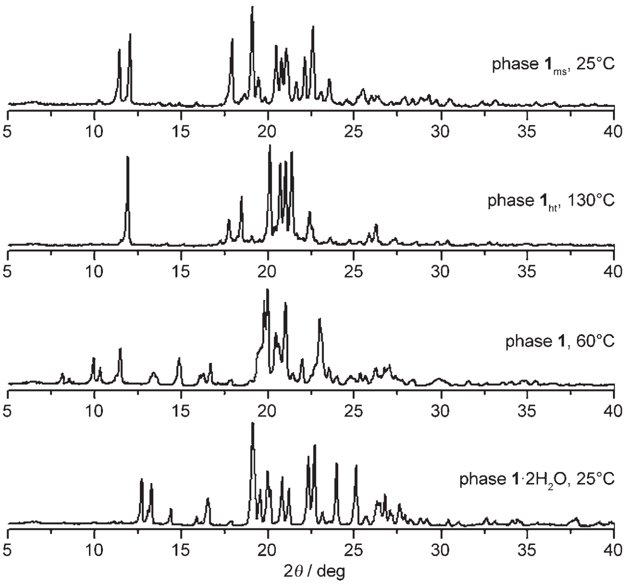


Figure 3. Variable temperature powder diffraction experiments on compound **1** showing the XRPD patterns for the process **1**·2 H_2O → **1** → $\mathbf{1}_{ht}$ → $\mathbf{1}_{ms}$.

"ht" stands for high temperature (see below). On cooling, however, phase $\mathbf{1}_{ht}$ does not revert to anhydrous phase **1** directly, but passes through a metastable phase ($\mathbf{1}_{ms}$) which slowly converts into phase **1**. The comparison between the XRPD patterns measured on the samples **1** and **1**·2 H_2O and those computed on the basis of the single crystal structures (see Figures 4 and 5) confirms the exact nature of the polycrystalline materials. No single-crystal X-ray data are available for the high temperature phases, $\mathbf{1}_{ht}$ and $\mathbf{1}_{ms}$.

The diffraction, thermogravimetric and calorimetric measurements allow to construct a simple model for the phase-transition behavior of **1**, starting from the hydrated form **1**·2 H_2O (see Scheme 1).

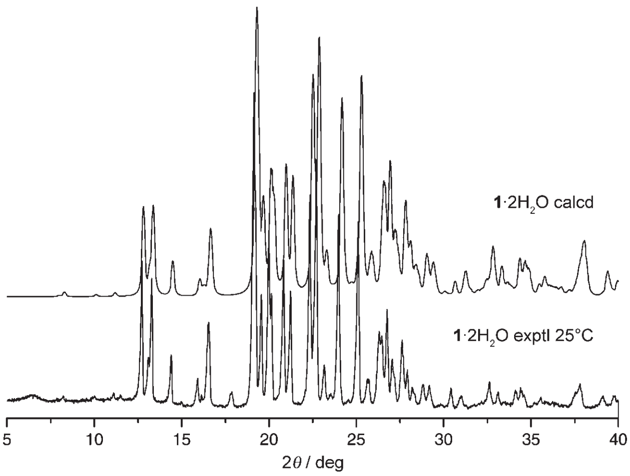


Figure 4. Comparison between the XRPD pattern measured on polycrystalline **1**·2 H_2O and that computed on the basis of the single crystal structure.

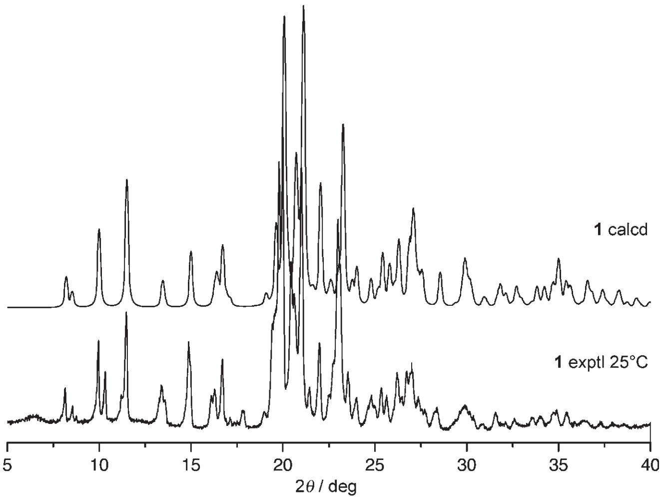
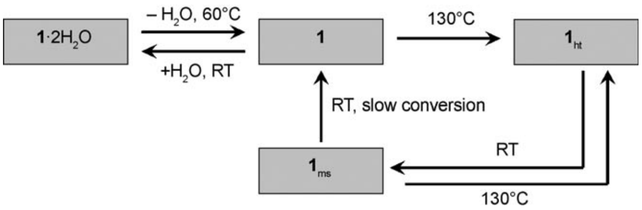


Figure 5. Comparison between the XRPD pattern measured on polycrystalline **1** and that computed on the basis of the single crystal structure.



Scheme 1. Schematic representation of the hydration/dehydration and phase-transition behavior of compound **1**.

Preparation and thermal behavior of crystalline 18-crown[6]·K[HSO$_4$]: The second example of crown ether hydrogen sulfate salt material is provided by the anhydrous complex salt **2**, obtained by dehydration of the complex **2**·2 H_2O. Analogously to what observed for **1**, crystallization from water or co-grinding of solid 18-crown[6] and K[HSO$_4$] generates first the dihydrated compound **2**·2 H_2O (see Experimental Section). At variance with the preparation of **1**·2 H_2O, in the case of the potassium compound it is necessary to boil the solution for a few minutes. Once anhydrous **2** is obtained as a polycrystalline material by dehydration of **2**·2 H_2O, crystals of **2** can be grown from anhydrous acetone. The structures of both **2**·2 H_2O and **2** have been determined by single crystal X-ray diffraction and are sketched in Figure 6. It can be appreciated that between **2**·2 H_2O and **2** exists the same structural relationship as that between **1**·2 H_2O and **1**, that is, water removal generates pairs of hydrogen bonded [HSO$_4$]$^-$ anions that form supramolecular dimers with two crown ether molecules and two [HSO$_4$]$^-$ anions.

The DSC trace (heating cycle) in Figure 7 (top) shows two transitions as in the case of **1**. The dehydration takes place at about 55 °C, immediately followed by the transformation into the anhydrous phase **2** at 65 °C, while the peak at 114 ± 1 °C (onset temperature) corresponds to an enantiotropic transition. The TGA trace (Figure 7, bottom) clearly shows that decomposition takes place above 200 °C.

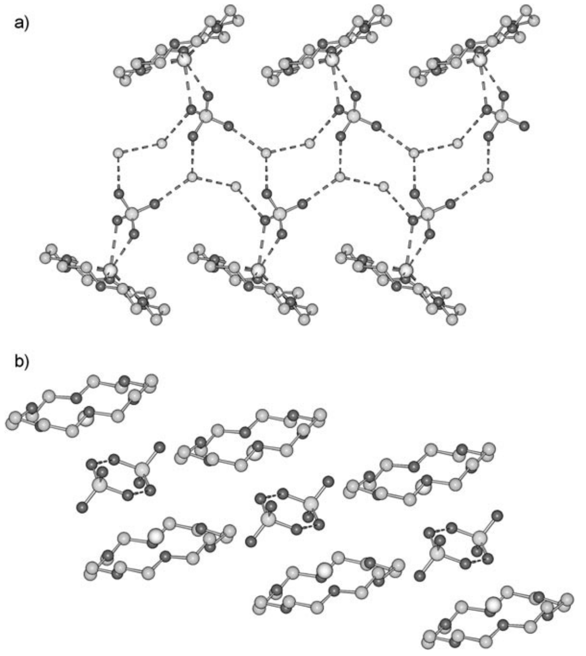


Figure 6. Crown ether and ion organization in a) $\mathbf{2}\cdot 2H_2O$ and b) anhydrous **2**.

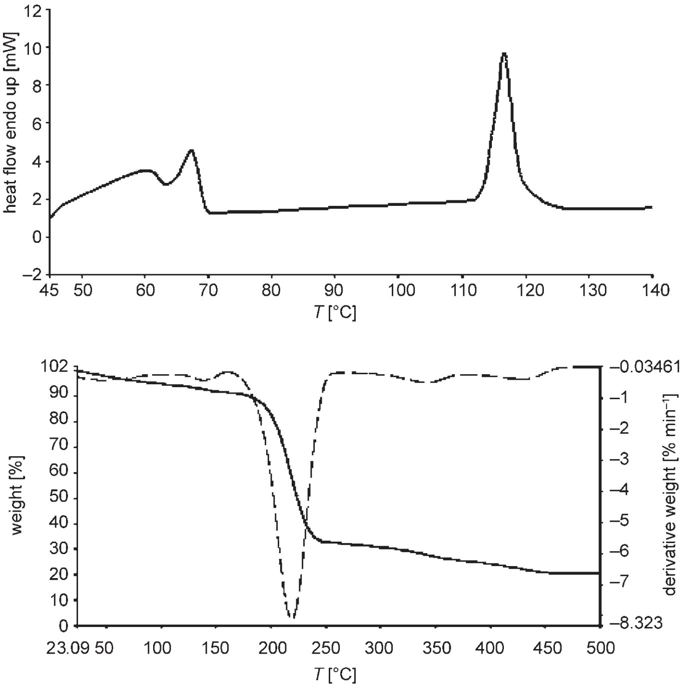


Figure 7. DSC (heating cycle, top) and TGA (bottom) traces for compound $\mathbf{2}\cdot 2H_2O$.

Variable temperature XRPD measurements for compound **2** are shown in Figure 8. As in the case of the ammonium derivative there is perfect agreement with the behavior ascertained by TGA and DSC. It can be seen that $\mathbf{2}\cdot 2H_2O$ converts into **2** at about 65 °C and that **2** converts into $\mathbf{2}_{ht}$ at about 120 °C. Contrary to $\mathbf{1}_{ht}$, however, there is no evidence for the formation of an intermediate metastable phase and, on cooling, $\mathbf{2}_{ht}$ reverts to **2**. A comparison between the XRPD patterns measured on compounds **2** and $\mathbf{2}\cdot 2H_2O$ and those computed on the basis of the single crystal structures (see Figures 9 and 10) confirms the exact nature of the polycrystalline materials. No single-crystal X-ray data are available for the high-temperature phase $\mathbf{2}_{ht}$.

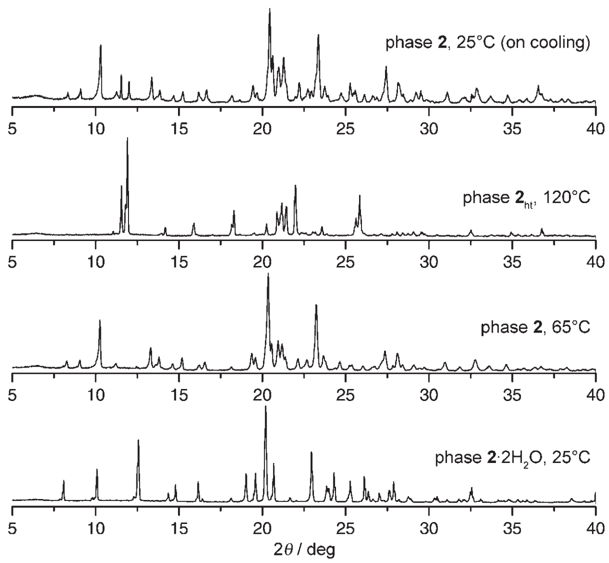


Figure 8. Variable temperature X-ray powder diffraction experiments on compound **2** for the process $\mathbf{2}\cdot 2H_2O \rightarrow \mathbf{2} \rightarrow \mathbf{2}_{ht} \rightarrow \mathbf{2}$.

In summary, the phase-transitional behavior of **2** is slightly less complicated than that described for **1**, as the anhydrous phase **2** converts into the high-temperature phase $\mathbf{2}_{ht}$ upon heating above 120 °C via a fully reversible process, as summarized in Scheme 2.

Preparation and thermal behavior of crystalline 18-crown[6]·Sr[HSO$_4$]$_2$: The behavior of **3** is necessarily differ-

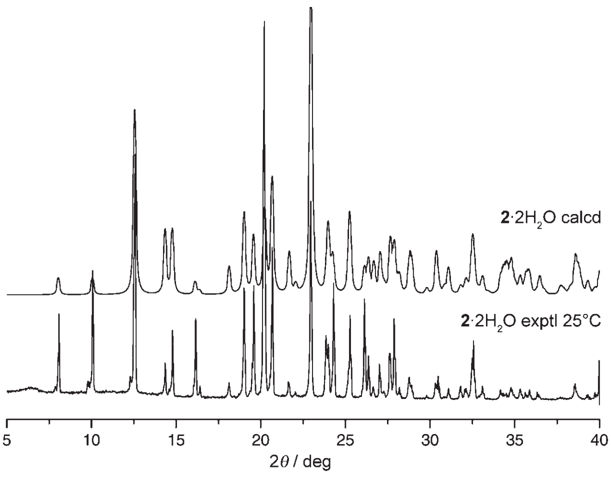


Figure 9. Comparison between the XRPD pattern measured on polycrystalline $\mathbf{2}\cdot 2H_2O$ and that computed on the basis of the single crystal structure.

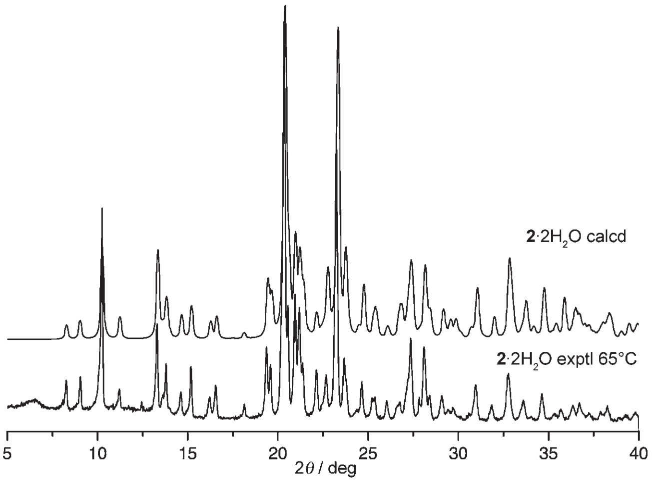
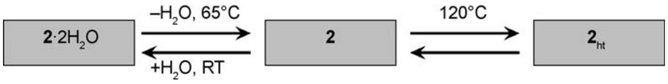


Figure 10. Comparison between the XRPD pattern measured on polycrystalline **2** and that computed on the basis of the single crystal structure.



Scheme 2. Schematic representation of the hydration/dehydration and phase-transition behavior of compound **2**.

ent from those of **1** and **2** because the phase that precipitates out from solution is anhydrous. The structure of compound **3** as determined by single crystal X-ray diffraction is shown in Figure 11. The close structural relationship between the structure of **3** and those of anhydrous **1** and **2** can easily be appreciated.

Figure 12 (top) shows that compound **3** undergoes a phase transition around 60 °C, while the TGA measurement (Figure 12, bottom) confirms the stability of the compound up to 150 °C.

The variable temperature X-ray powder diffraction measurements on compound **3** are in agreement with the general picture described above. Figure 13 shows that the XRPD pattern remains essentially the same up to 60 °C, even though some reflections change in shape and broaden, suggesting an order–disorder phase transition, with retention of long-range order (the position of the anions and of the complexes) and loss of short-range order (possibly because of the onset of reorientational motion of the crown ethers and of the hydrogen sulfate anions). A comparison between the XRPD patterns measured on polycrystalline **3** and that com-

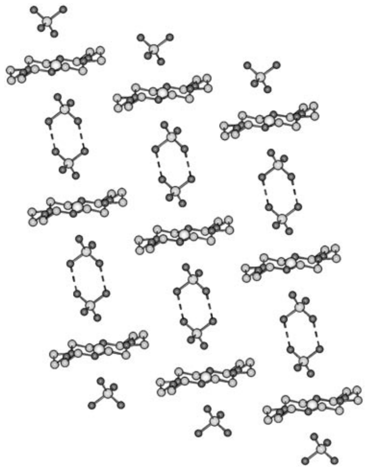


Figure 11. Crystal structure of anhydrous **3** as determined at room temperature.

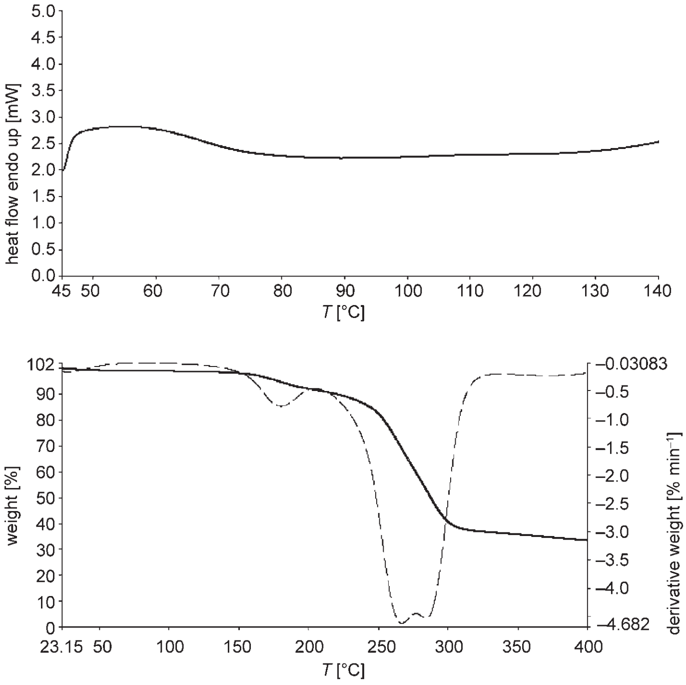


Figure 12. DSC (heating cycle, top) and TGA (bottom) traces for compound **3**.

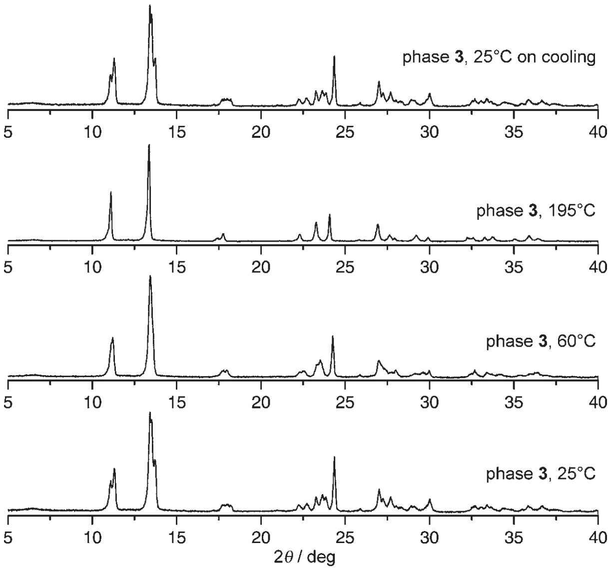


Figure 13. Variable temperature X-ray powder diffraction experiments on compound **3**.

puted on the basis of the single crystal structure (see Figure 14) confirms the exact nature of the polycrystalline material.

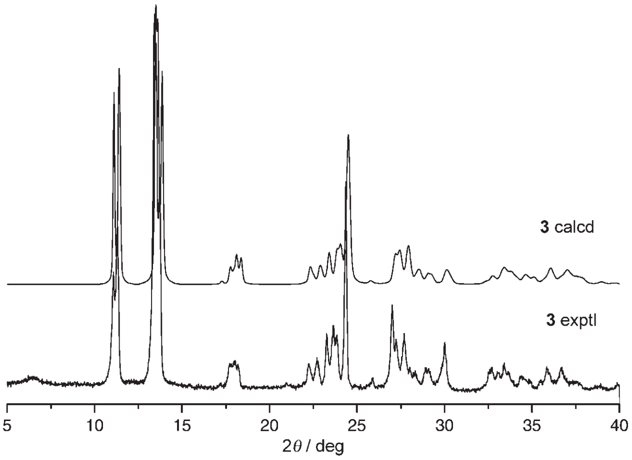


Figure 14. Comparison between the XRPD pattern measured on polycrystalline **3** and that computed on the basis of the single crystal structure.

Conclusion

We have discovered that 18-crown[6] ether complexes of alkali, alkaline earth and ammonium hydrogen sulfate salts show complex, and yet homogeneous, hydration and dehydration as well as phase-transition behavior with temperature. All compounds appear to transform into stable high temperature phases upon heating at a temperature in the range 110–150 °C. These high temperature phases have all been characterized by VTXRPD and calorimetric measurements. Essential points shown in this work can be summarized as follows:

i) The ammonium and potassium salts are obtained as dihydrate crystalline materials of formula 18-crown[6]·$[NH_4][HSO_4]\cdot 2H_2O$ and 18-crown[6]·$K[HSO_4]\cdot 2H_2O$, wherefrom the respective anhydrous phases 18-crown[6]·$[NH_4][HSO_4]$ and 18-crown·$K[HSO_4]$ can be obtained by thermal dehydration.
ii) Contrary to the ammonium and potassium salts, the strontium salt is obtained directly as the anhydrous form 18-crown[6]·$Sr[HSO_4]_2$.
iii) All compounds can be prepared either by evaporation of water solutions of the reactants or, more straightforwardly, by mechanical mixing of the reactants. Single crystals of all species have been grown from water solution, with the exception of the anhydrous species **1** and **2**, which have been obtained from acetone.
iv) The hydrate forms 18-crown[6]·$[NH_4][HSO_4]\cdot 2H_2O$ and 18-crown[6]·$K[HSO_4]\cdot 2H_2O$ are isostructural and are characterized by water bridges joining the HSO_4^- anions via hydrogen bonds of the O-H···O type.
v) Both crystalline materials can easily be dehydrated by heating the polycrystalline hydrated forms at about 60 °C. The dehydration/hydration processes are reversible.
vi) The anhydrous phases of 18-crown[6]·$[NH_4][HSO_4]$ and 18-crown[6]·$K[HSO_4]$ are almost isostructural with that of 18-crown[6]·$Sr[HSO_4]_2$; the three anhydrous phases share structural features and also possess the same behavior with temperature.
vi) All anhydrous → high-temperature transitions are reversible and the compounds can be cycled through several heating/cooling cycles without decomposition.

It seems possible to conclude that the crown ether complexes of general formula 18-crown[6]·$M[HSO_4]_n$ (where M = NH_4^+, K^+, Sr^{2+} and n = 1, 2) described in this work can be one of a plurality of different kinds of materials of general form $crown[X]_n\cdot M_m[HSO_4]_q$ or $crown[X]_n\cdot M_m[HSO_4]_q\cdot p\,H_2O$, where M can be one of a variety of cations and the crown ether can be of a size apt to cation complexation. The reversible water uptake/release as well as the phase-transition behavior, combined with the stability of the compounds and their ease of preparation, make this family of complexes interesting candidates for further studies, in particular for an exploration of the electrical properties, which is under way.

Experimental Section

Crystal structure determination: Single crystal data were collected at room temperature on a NONIUS CAD-4 diffractometer, equipped with a graphite monochromator ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å), in the 2θ range 6–50°. All non-H atoms refined anisotropically. H_{OH} and H_{NH} atoms found only in compound **1** and not refined. SHELXL97[11a] used for structure solution and refinement on F^2, and SCHAKAL[11b] for molecular graphics. In the case of compound **1**, and to a minor extent in compound **3**, the quality of the single crystals obtained was not very good, as it can be seen from the $R1$ and $wR2$ values in Table 1. The identity between the bulk material obtained via the solid-state processes and the structures obtained by single crystals was verified by comparing calculated and observed powder diffraction patterns. Crystal data and details of measurements are listed in Table 1. CCDC-265481 (**1**·$2H_2O$),[4] -630364, -630365, -630366, -630367 (**1**, **2**·$2H_2O$, **2** and **3**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

XRPD measurements were collected with a Panalytical X'Pert Pro equipped with X'Celerator detector and a TK 450 Anton Paar variable temperature camera. A Cu anode was used as X-ray source at 40 kV and 40 mA. The program PowderCell 2.2[11c] was used for calculation of X-ray powder patterns.

Thermogravimetric and calorimetric analysis: Thermogravimetric analysis was performed using a Perkin Elmer TGA-7. Heating was performed in nitrogen flow (20 $cm^3 min^{-1}$) using platinum crucible at the 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 DSC-7 equipped with a model PII intracooler. Temperature and enthalpy calibrations were performed by using high purity standards (*n*-decane, benzene and indium). The samples (3–5 mg) were placed in aluminium open

Table 1. Crystal data and details of measurements for **1**, **2**·2 H_2O, **2** and **3**.

	1	**2**·2 H_2O	**2**	**3**
formula	$C_{12}H_{29}NO_{10}S$	$C_{12}H_{29}KO_{12}S$	$C_{12}H_{25}KO_{10}S$	$C_{12}H_{26}O_{14}S_2Sr$
M_W	379.42	436.51	400.48	546.07
system	monoclinic	monoclinic	monoclinic	triclinic
space group	$C2/c$	Cc	$P2_1/n$	$P\bar{1}$
a [Å]	26.32(1)	14.3162(5)	10.259(3)	8.238(4)
b [Å]	8.280(6)	17.5839(6)	8.463(5)	8.295(2)
c [Å]	21.623(9)	8.3317(3)	21.634(9)	8.429(3)
α [°]	–	–	–	103.43(2)
β [°]	125.09(3)	100.291(1)	99.38(3)	99.98(3)
γ [°]	–	–	–	103.69(3)
V [Å^3]	3856(4)	2063.6(1)	1853(1)	528.2(3)
Z	8	4	4	1
F(000)	1632	928	848	280
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.214	0.412	0.445	2.816
unique reflns	3386	3578	3246	1840
unique reflns with $I > 2\sigma(I)$	2554	3451	1346	847
parameters	218	236	217	170
GOF on F^2	1.061	0.993	1.008	0.860
$R1$ (on F [$I > 2\sigma(I)$])	0.1062	0.0620	0.0738	0.0599
$wR2$ (on F^2, all data)	0.3056	0.1678	0.2824	0.2334

pans. Heating was carried out at 5 °C min^{-1} in the temperature range from 40 to 180 °C.

Solid-state and solution syntheses: All starting materials were purchased from Aldrich. Reagent grade solvents and bi-distilled water were used.

18-Crown[6]·[NH_4][HSO_4] (1): Compound **1** was obtained by heating **1**·2 H_2O (prepared according to literature)[4] at 80 °C for 6 h in an oven. Single crystals of **1** were grown by slow evaporation at RT of a solution obtained by dissolving **1** (100 mg, 0.26 mmol) in boiling anhydrous acetone (7 mL).

18-Crown[6]·K[HSO_4]·2 H_2O (2·2 H_2O): 18-Crown[6] (265 mg, 1 mmol) and K[HSO_4] (136 mg, 1 mmol) were manually ground in an agate mortar for five minutes. Single crystals of **2**·2 H_2O were obtained by slow evaporation at RT of a solution obtained by dissolving the ground material in water (5 mL).

18-Crown[6]·K[HSO_4] (2): Compound **2** was obtained by heating **2**·2 H_2O at 80 °C for 6 h in an oven. Single crystals of **2** were grown by slow evaporation at RT of a solution obtained by dissolving **2** (100 mg, 0.26 mmol) in boiling anhydrous acetone (7 mL).

18-Crown[6]·Sr[HSO_4]$_2$ (3): 18-Crown[6] (520 mg, 2 mmol), Sr[SO_4] (368 mg, 2 mmol) and 98 % H_2SO_4 (0.1 mL, 2 mmol) were manually ground in an agate mortar for ten minutes. Single crystals of **3** were obtained by slow evaporation at RT of a filtered solution obtained dissolving the ground material in water (15 mL).

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