Reversible solid-state reaction between 18-Crown[6] and M[H₂PO₄] (M = K, Rb, Cs) and an investigation of the decomplexation process†

Dario Braga,* Marco Polito, Elena Dichiarante, Katia Rubini and Fabrizia Grepioni*

On heating the hydrated complexes 18-Crown[6]·M[H₂PO₄]·xH₂O (x = 2 for M = K, Rb; x = 1.5 for M = Cs), quantitatively prepared by mechanical mixing of crystalline 18-Crown[6] and M[H₂PO₄], to *ca.* 60 °C, water loss takes place, accompanied by the *extrusion* of the crown ether from the crystalline complex and followed by reconstruction of the inorganic phase M[H₂PO₄] (M = K, Rb, Cs); the resulting solid mixture reverts to 18-Crown[6]·M[H₂PO₄]·xH₂O (x = 2 for M = K, Rb; x = 1.5 for M = Cs) upon grinding in air.

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 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 to prepare novel supramolecular materials[4] as a development of our crystal engineering endeavour.[5] We have shown, *inter alia*, that manual grinding of solid 18-Crown[6] and solid [NH₄][HSO₄] in air leads to formation of the hydrated crown ether complex 18-Crown[6]·[NH₄][HSO₄]·2H₂O, the water molecules being taken up from ambient humidity during grinding.[6]

In this communication we report preparation‡§ and characterization of the hydrated complexes 18-Crown[6]·K[H₂PO₄]·2H₂O (**1**), 18-Crown[6]·Rb[H₂PO₄]·2H₂O (**2**) and 18-Crown[6]·Cs-[H₂PO₄]·1.5H₂O (**3**) obtained by mechanical grinding of crystalline 18-Crown[6] and anhydrous crystalline M[H₂PO₄] (M = K, Rb, Cs). The structures of the complexes¶ were determined from crystals grown at room temperature by slow evaporation of an aqueous solution of 18-Crown[6] and M[H₂PO₄] first brought to the boiling point. The three compounds **1**, **2** and **3** share the following features: (i) the crown ether forms conventional complexes with the alkali cations, the coordination spheres being filled with one (in the cases of M = Cs and Rb) or two (M = K) water molecules, respectively (see Fig. 1); in the case of the Cs complex the coordinated water molecule, which is located on a symmetry element, is also bound to a second caesium ion (not shown in the figure); (ii) the di-hydrogen phosphate monoanions form hydrogen bonded dimers connected into chains *via* inter-anion O–H···O hydrogen bridges; (iii) the water molecules also act as hydrogen bridges between the dihydrogen phosphate chains.

The behaviour of the crystalline materials upon heating is surprising and, to the best of the authors' knowledge, unprecedented. When crystalline **1**, **2** or **3** is heated up to *ca.* 60 °C, the expected loss of water molecules is accompanied by (i) alkali metal decomplexation, (ii) extrusion of the crown ether molecules from the crystals and (iii) reconstruction of the crystals of the starting anhydrous inorganic reactants M[H₂PO₄]. What is more, 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, the crystalline material **1**, **2** or **3** is reconstructed within hours. The whole process is schematically depicted in Scheme 1. It is noteworthy that the three inorganic salts M[H₂PO₄] (M = K, Rb, Cs) are not isostructural, and that the crown ether is in the liquid state (18-Crown[6] m.p. 42–45 °C) at the temperature of decomplexation.

The process has been investigated by a combination of solid-state techniques. It is described in detail below for the Cs-adduct, taken as the example of choice.

Variable temperature X-ray powder diffraction‖ has been particularly useful. Fig. 2 shows that when a polycrystalline sample of **3** (obtained by mechanical mixing of CsH₂PO₄ and 18-Crown[6]) is heated to 60 °C, the diffraction pattern changes abruptly, with formation of an amorphous phase superimposed on
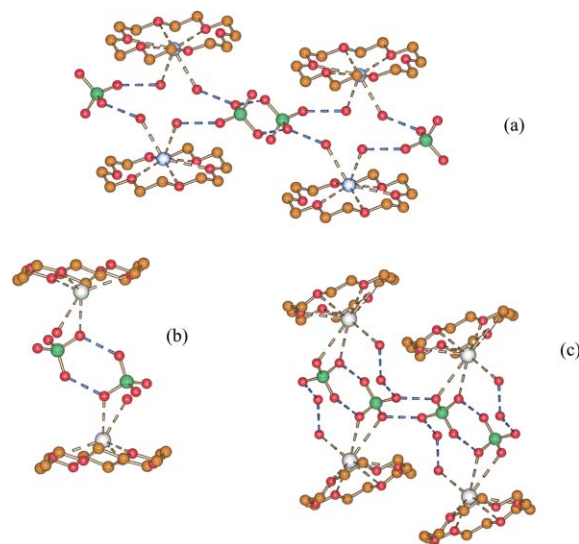

Fig. 1 The supramolecular arrangement in crystalline **1** (top), **2** (bottom left) and **3** (bottom right; only one of the two crown ether disorder images is shown for clarity). Note how the alkali metal interacts with the oxygen atoms of the crown ether molecule and with the water molecules, which are, in turn, hydrogen bonded to the hydrogen phosphate mono-anions.

Department of Chemistry G. Ciamician, Via F. Selmi 2, 40126 Bologna, Italy. E-mail: dario.braga@unibo.it; Fax: (39)051-2099456

K/Rb/Cs(H₂PO₄)

Heating −H₂O
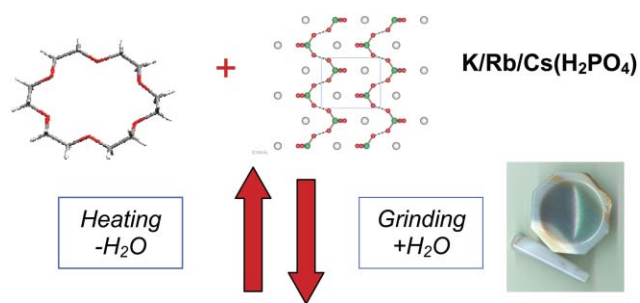
Grinding +H₂O

18-Crown[6]M(H₂PO₄)·xH₂O (M= K, Rb, x=2, Cs x=1.5)

Scheme 1 A schematic representation of the reversible complexation/decomplexation processes obtained by co-grinding of solid 18-Crown[6] and M[H₂PO₄] (M = K, Rb, Cs) and by thermal desorption of water accompanied by 18-Crown[6] *extrusion*.

a new crystalline phase (Fig. 2b). The crystalline phase has been unambiguously identified as anhydrous Cs[H₂PO₄].[7] When cooled down to room temperature, the mixture retains the diffraction pattern observed at high temperature, *viz.* amorphous crown ether and crystalline Cs[H₂PO₄] (Fig. 2c). The diffraction pattern of the starting material, **3**, is then reconstructed when the sample is ground and left for a few hours in air (Fig. 2d). Bulk product and single crystal (Fig. 2e) possess exactly the same powder pattern, thus the same solid state structure.

The same process could be followed by differential scanning calorimetry and thermogravimetry** (see Electronic Supplementary Information). The DSC trace, on heating, shows a single endothermic peak (onset at 56.4 °C) corresponding to the simultaneous, or very nearly so, loss of water and *extrusion* of crown ether from the crystalline complex. Clearly, the enthalpic balance ($\Delta H = 79.2$ J g^{-1}) includes the reconstruction of the inorganic phase Cs[H₂PO₄]. A second DSC cycle repeated on a sample after processing yielded a $\Delta H = 78.1$ J g^{-1}, and an onset temperature of 56.5 °C.
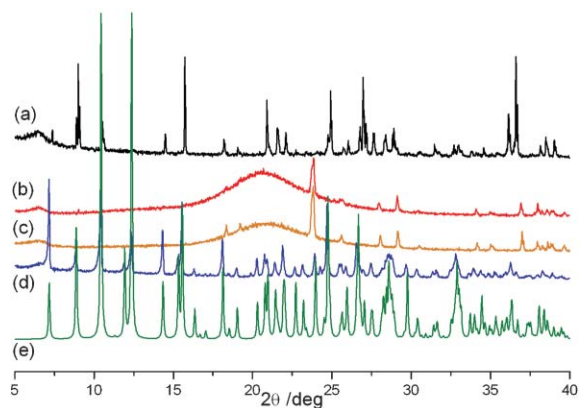

Fig. 2 Comparison between the diffraction patterns measured on **3**. (a) Starting diffractogram of **3**. (b) Diffractogram after heating the complex **3** to 60 °C; note the mixture of an amorphous phase superimposed on a crystalline phase, identified as anhydrous Cs[H₂PO₄]. (c) The mixture of amorphous organic and crystalline inorganic phases is stable when cooled to room temperature. (d) The diffraction pattern of the starting material is reconstructed after a few hours in the air and gentle mixing. (e) Diffraction pattern of **3** calculated on the basis of the single crystal structure.

The TGA measurement indicates a weight loss of *ca.* 5.2% in the interval 40–100 °C, which is in agreement with a loss of 1.5 moles of water. Further heating shows evaporation of the crown ether at *ca.* 200 °C.

The behaviour of the potassium and rubidium complexes is very similar (see Electronic Supplementary Information).

Demixing of crystalline phases is a well established phenomenon in liquid crystal and polymer science and is also known to occur in the case of solid solutions and mixed inorganic systems.[8] 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[9] that is being actively explored also in the field of crystal engineering.[10] More importantly though, the reactions that lead to 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 whole process ought to be described as a heterogeneous complexation equilibrium, with components participating as solids and vapour.

M[H₂PO₄] (s) + 18-Crown[6] (s) + H₂O (vap) ⇆ 18-Crown[6]·M[H₂PO₄]·xH₂O (x = 2 for M = K, Rb, x = 1.5 for M = Cs)

In conclusion, we have come across an unprecedented case of solid-state complexation (by mechanical means) and decomplexation (by heating) reversible processes. Clearly a process 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 molecules and crown ether molecules. Indeed, high molecular mobility has been shown by Kaupp to be the prerequisite for the occurrence of many solid-state processes.[11] In the cases of the supramolecular complexes 18-Crown[6]·M[H₂PO₄]·xH₂O, however, there is an intriguing thermodynamic balance to consider, because water leaves as a vapour and the crown ether is in the liquid phase as it exits the crystalline complex, while the resulting mixture (solid amorphous crown and inorganic salt) is evidently *metastable* with respect to water uptake and re-formation of the complex.

Notes and references

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

§ *Preparation of 18-Crown[6]·K[H₂PO₄]·2H₂O* (**1**), *18-Crown[6]·Rb-[H₂PO₄]·2H₂O* (**2**) *and 18-Crown[6]·Cs[H₂PO₄]·1.5H₂O* (**3**): 18-Crown[6] (265 mg, 1 mmol) and M[H₂PO₄] (138 mg, 1 mmol for M = K; 180 mg, 1 mmol for M = Rb; 230 mg, 1 mmol for M = Cs) were manually ground in an agate mortar for ten minutes. Single crystals of **1**, **2** or **3** were obtained by slow evaporation at RT of a solution obtained by dissolving the ground material in 5 mL of hot water.

¶ *Crystal structure determination*. Single crystal data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å), monochromator graphite. **1**: C₁₂H₃₀KO₁₂P, $Mr = 436.43$; monoclinic $C2/c$, $a = 20.281(4)$, $b = 8.350(3)$, $c = 24.411(6)$ Å, $\beta = 92.69(2)°$, $V = 4129(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.404$ g cm^{-3}, R_1 (wR_2) 0.0467 (0.1361) for 3582 observed independent reflections, 2θ range = 6.0–50.0. **2**: C₁₂H₃₀O₁₂PRb, $Mr = 482.80$; monoclinic $C2/c$, $a = 25.266(6)$, $b = 8.590(5)$, $c = 19.394(6)$ Å, $\beta = 103.47(2)°$, $V = 4093(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.567$ g cm^{-3}, R_1 (wR_2) 0.0433 (0.1283) for 3579 observed independent reflections, 2θ range = 6.0–50.0. **3**: C₂₄H₅₆Cs₂O₂₃P₂, $Mr = 1040.45$; monoclinic $C2/c$, $a = 25.042(5)$, $b = 8.248(3)$, $c = 20.208(3)$ Å, $\beta = 99.66(2)°$, $V = 4115(3)$ Å^3, $Z = 4$ (as the compound is dimeric, with the linking water oxygen lying on a two-fold axis), $\rho_{calcd} = 1.680$ g cm^{-3}, R_1 (wR_2) 0.0354 (0.1032) for 3592 observed

independent reflections, 2θ range = 6.0–50.0. The crown ether in the caesium complex was found disordered over two equivalent positions around the moiety axis. Anion H_{OH} atoms found, and refined, only for **1**; only two out of four hydrogen atoms found, and not refined, for the two water molecules in **1**. All H_{CH} atoms were added in calculated positions and refined riding on their respective C atoms. All non-H atoms refined anisotropically. SHELXL97[12a] used for structure solution and refinement on F^2 and SCHAKAL99[12b] for the molecular graphics. See Supporting Information for X-ray powder patterns, TGA and DSC measurements for the potassium and rubidium complexes. 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. CCDC 633143–633145. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702301d

|| *Powder data* 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[12c] was used for calculation of the X-ray powder patterns.

** *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 in aluminium open pans. Heating was carried out at 5 °C min^{-1} in the temperature range 40 to 180 °C. *Thermogravimetric analysis* was performed using a Perkin Elmer TGA-7. Heating was performed in a nitrogen flow (20 cm^3 min^{-1}) using a platinum crucible at the rate of 5 °C min^{-1} up to decomposition. The sample weights were in the range 5–10 mg.

1 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
2 C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 16.
3 (*a*) J. W. Steed, *Coord. Chem. Rev.*, 2001, **215**, 171; (*b*) J. M. Harrington, S. B. Jones, P. H. White and R. D. Hancock, *Inorg. Chem.*, 2004, **43**, 4456; (*c*) J. M. Dou, X. K. Gao, F. Y. Dong, D. C. Li and D. Q. Wang, *Dalton Trans.*, 2004, **18**, 2918; (*d*) M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (*e*) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley & Sons, 2000; (*f*) see also for applications of crown ethers: M. Calleja, S. A. Mason, P. D. Prince, J. W. Steed and C. Wilkinson, *New J. Chem.*, 2003, **27**, 28; (*g*) 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; (*h*) J. L. Atwood, K. T. Holman and J. W. Steed, *Chem. Commun.*, 1996, 1401.
4 (*a*) D. Braga, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem.–Eur. J.*, 2004, **10**, 3261; (*b*) D. Braga, L. Maini, M. Polito, L. Mirolo and F. Grepioni, *Chem.–Eur. J.*, 2003, **9**, 4362; (*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, 2751; (*b*) D. Braga and F. Grepioni, *Chem. Commun.*, 2005, 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, L. Maini, S. L. Giaffreda, F. Grepioni, M. R. Chierotti and R. Gobetto, *Chem.–Eur. J.*, 2004, **10**, 3261; (*e*) D. Braga and F. Grepioni, *Angew. Chem., Int. Ed.*, 2004, **43**, 2.
6 D. Braga, M. Curzi, M. Lusi and F. Grepioni, *CrystEngComm*, 2005, **7**, 276.
7 ICSD code 79608, ICSD Database, version 2006-2.
8 See, for example: (*a*) J. C. Loudet and P. Poulin, *Top. Curr. Chem.*, 2003, **226**, 173; (*b*) W. B. Hu and D. Frenkel, *Adv. Polym. Sci.*, 2005, **191**, 1; (*c*) H. A. J. Oonk, *Pure Appl. Chem.*, 2001, **73**, 807.
9 (*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*) J. F. Fernandez-Bertran, *Pure Appl. Chem.*, 1999, **71**, 581; (*f*) J. Fernandez-Bertran, J. C. Alvarez and E. Reguera, *Solid State Ionics*, 1998, **106**, 129; (*g*) N. Shan, F. Toda and W. Jones, *Chem. Commun.*, 2002, 2372; (*h*) V. V. Boldyrev, *Solid State Ionics*, 1995, 537.
10 (*a*) M. C. Etter, *J. Phys. Chem.*, 1991, **95**, 4601; (*b*) M. C. Etter, S. M. Reutzel and C. G. Choo, *J. Am. Chem. Soc.*, 1993, **115**, 4411; (*c*) W. H. Ojala and M. C. Etter, *J. Am. Chem. Soc.*, 1992, **114**, 10228; (*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.
11 (*a*) G. Kaupp, *CrystEngComm*, 2003, **5**, 117; (*b*) G. Kaupp, in *Making Crystals by Design. Methods, techniques, Applications*, ed. D. Braga and F. Grepioni, John Wiley & Sons, Weinheim, 2006.
12 (*a*) G. M. Sheldrick, SHELXL97, *Program for Crystal Structure Determination*; University of Göttingen, Göttingen, Germany, 1997; (*b*) E. Keller, SCHAKAL99, *Graphical Representation of Molecular Models*; University of Freiburg, Germany, 1999; (*c*) PowderCell program by W. Kraus and G. Nolze (BAM Berlin)© subgroups derived by Ulrich Müller (Gh Kassel).