Electronic Supplementary Information (ESI)

(12 pages)

Reversible Solid-State Reaction between 18-Crown[6] and M[H₂PO₄] (M = K, Rb, Cs) and an Investigation of the Decomplexation Process

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Packing patterns, DSC and TGA measurements, and X-ray powder patterns for the complexes 18-Crown[6]·K[H₂PO₄]·2H₂O (1), 18-Crown[6]·Rb[H₂PO₄]·2H₂O (2) and 18-Crown[6]·Cs[H₂PO₄]·1.5H₂O (3).
Figure ESI-1. Dihydrogen phosphate anions and water molecules form two-dimensional networks in the crystals of the (a) potassium, (b) rubidium and (c) caesium complexes; the water molecules act as bridges between the dihydrogen phosphate chains (H$_{OH}$ atoms not observed in the rubidium and caesium complexes).
18-Crown[6]·K[H_2PO_4]·2H_2O (1)

**Figure ESI-2.** DSC trace (heating cycle) for compound 1.

**Figure ESI-3.** TGA measurement for compound 1.
**Figure ESI-4.** Comparison between the experimental (top) and calculated (bottom) X-ray powder diffraction patterns for compound 1.

**Figure ESI-5.** Comparison between (a) the experimental X-ray powder diffraction pattern of complex 1 at 70°C and (b) the calculated pattern of K[H₂PO₄].
Figure ESI-6. Comparison between the diffractogram of 1 (ground material) after treatment at 70°C (a) and the calculated pattern for the starting material 1 (b).
18-Crown[6]-Rb[H₂PO₄]-2H₂O (2)

**Figure ESI-7.** DSC trace (heating cycle) for compound 2.

**Figure ESI-8.** TGA trace for compound 2.
**Figure ESI-9.** Comparison between experimental (top) and calculated (bottom) X-ray powder diffraction patterns for compound 2.

**Figure ESI-10.** Comparison between (top) the experimental X-ray powder diffraction pattern of 2 at 70°C and (bottom) the calculated pattern of Rb[H₂PO₄].
Figure ESI-11. Comparison between the diffractogram of the starting material 2 (a) and the diffractogram of the ground material after treatment at 70°C (b).
18-Crown[6]·Cs[H₂PO₄] ·1.5H₂O (3)

Figure ESI-12. The DSC trace of a sample of 3 (heating cycle). Note the single, though asymmetric, endothermic peak (onset at 56.4°C, ΔH = 79.2 J g⁻¹) due to loss of water, extrusion of crown ether from the crystalline complex and reconstruction of crystalline Cs[H₂PO₄].

Figure ESI-13. The TGA trace of 3 shows a weight loss of ca. 5.2% in the interval 40°-100°C, in agreement with a loss of 1.5 moles of water. Further heating shows evaporation of the crown ether at ca. 200 °C.
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Figure ESI-14. Comparison between the diffraction pattern measured on a polycrystalline sample of 3 and that calculated on the basis of the single crystal structure.

Figure ESI-15. Heating the complex 3 to 60°C leads to a mixture of an amorphous phase superimposed to a crystalline phase, which has been identified as anhydrous Cs[H₂PO₄].
Figure ESI-16. Comparison between the diffractogram of the starting material 3 (a) and the diffractogram of the ground material after treatment at 60°C (b).

N.B.: Thermal treatment on compounds 1, 2 and 3, in the variable temperature X-ray powder diffraction experiments, was performed at the minimum temperature required for the decomplexation process to occur, i.e. at 70°C for 1 and 2, and at 60°C for 3.