# Crown Ethers and their Alkali Metal Ion Complexes as Assembler Groups in Uranyl–Organic Coordination Polymers with *cis*-1,3-, *cis*-1,2- and *trans*-1,2-Cyclohexanedicarboxylates

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## Supporting Information

### Crystallography

Complex **1**. The cyclohexane ring of one dicarboxylate ligand is disordered over two positions sharing one carbon atom, which were refined with occupancy parameters constrained to sum to unity. Restraints on bond lengths, angles and/or displacement parameters were applied for the disordered ligand, some atoms of the other dicarboxylate ligand, and the crown ether molecule, the last two parts being affected by unresolved disorder (that of the crown ether moiety in particular could not be solved and refined in a satisfying manner, and only one average position was retained). The highest residual electron density peaks are located near the crown ether molecule, as a result of the unresolved disorder.

Complex **2**. Four carbon atoms in one crown ether molecule are disordered over two positions each, which were refined with occupancy parameters constrained to sum to unity. Restraints on bond lengths, angles and/or displacement parameters were applied for atoms in the disordered parts, as well as for

some other carbon atoms in the crown ethers and the oxo atom O2. Twinning was detected with TwinRotMat (PLATON[1]) and taken into account in the refinement (HKLF 5, BASF 0.27).

Complex **3**. Atom K2 is disordered over two positions which were refined with occupancy parameters constrained to sum to unity. Atom K3 has been given an occupancy factor of 0.5 both for charge equilibrium and to retain an acceptable displacement parameter. The crown ether bound to K2 is very badly resolved and it could only be refined with severe restraints on several bond lengths, angles and displacement parameters, so that the environment of K2A and K2B is somewhat uncertain. Twinning was detected with TwinRotMat (PLATON[1]) and taken into account in the refinement (HKLF 5, BASF 0.15).

Complex **4**. Atom K5 is disordered over two positions which were refined with occupancy parameters constrained to sum to unity. Restraints on displacement parameters and some bond lengths were applied for atoms in the crown ethers. For charge equilibrium and also because only one hydrogen atom has been found to be bound to it, O84 has been assumed to correspond to a hydroxide ion. However, considering the U–O bond lengths, it appears that hydroxide and water are possibly disordered over the two sites O82 and O84, which are hydrogen bonded to one another.

Compound **5**. Atom K3 is disordered over two positions, both close to an inversion centre, which were refined with occupancy parameters of 0.5. O42 corresponds to 50:50 water/hydroxide anion, one of its hydrogen atoms (H42B), which has been given an occupancy parameter of 0.5, being hydrogen bonded to the image of O42 through an inversion centre. Restraints on bond lengths and/or displacement parameters were applied for some badly behaving atoms, particularly in one cyclohexyl ring.

Complex **6**. Atom K1 is disordered over two positions which were refined with occupancy parameters constrained to sum to unity; the minor component K1B is probably associated with a disordered position

of the crown ether molecule (as indicated by several too short contacts), which could not be resolved due to low data quality. Atom K2 has been given an occupancy parameter of 0.5 in order to account for a too close contact with its image by inversion. The water molecules (O38 and O39) associated with K1B were given occupancy parameters of 0.5 in order to retain acceptable displacement parameters. Restraints for some bond lengths and displacement parameters were applied, particularly in the crown ethers.

1. Spek, A. L. Structure Validation in Chemical Crystallography. *Acta Crystallogr., Sect. D* **2009**, *65*, 148–155.