

“Macrocyclic Leaflets”

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Integration of macrocyclic ligands into a polymeric matrix leads to a relatively new class of compounds with a wide range of applications (e.g., efficient and economical industrial separations, ion transportation, isotope extraction, anion activation, sensing and switching, liquid crystalline properties, catalysis, etc.).^{1–4} Recently, we and others have shown that macrocyclic ligands can be imbedded into rigid layered frameworks of zirconium phosphates through exocyclic phosphorylation of crown ethers.^{5,6} Our efforts to further investigate the supramolecular assemblies based on exocyclic functional groups of crown ethers resulted in unprecedented “leaflet” (or “branch”) structures as shown in Figure 1a. In this communication, we report the synthesis and structural features of two supramolecular macrocyclic leaflets, which are stabilized by hydrogen bonding and coordination bonding networks.

It has been known that metal(IV) phosphates/phosphonates (e.g., $Zr(O_3P-R/O_3P-OR)_2$) form predictable layered structures when the size of the R groups is less than the free area around the metal atoms, 0.24 nm², in the layer.^{6a,7} However, the poor solubility and low crystallinity of these materials make their structural characterization a difficult task.^{5–7} On the other hand, metal(II) phosphonates are relatively more soluble and often form single crystals.^{6a,7} For these reasons, we have decided to study the metal(II) complexes of phosphonated crown ethers to understand the selectivity, conformational rigidity, and other important structural properties of polymeric crown ether assemblies in the solid state.

Monoaza-18-crown-6 was phosphonomethylated by reacting it with phosphorous acid and formaldehyde in the presence of concentrated HCl. Isolation and purification of *N*-(phosphonomethyl)-aza-18-crown-6, **1H₂N**, was achieved by treating the reaction mixture with an ion exchange column followed by recrystallization in ethanol (Scheme 1).^{5,8,9} An ethanolic solution (10 mL) of crown ether **1H₂N** (0.036 g, 0.1 mmol) was layered with metal salts $Co(ClO_4)_2 \cdot 6H_2O$ (0.037 g, 0.1 mmol, 15 mL)

(1) For an excellent overview on various aspects of crown ether chemistry by several distinguished scientists of this field see volumes 1 and 10 of the multiple volume series: *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Lehn, J.-M., Eds.; Pergamon: Oxford, 1996.

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(9) In general, *N*-(phosphonomethyl)-aza-crown ethers exist as zwitter ions and one of the two acid protons transfers to the amine moiety.

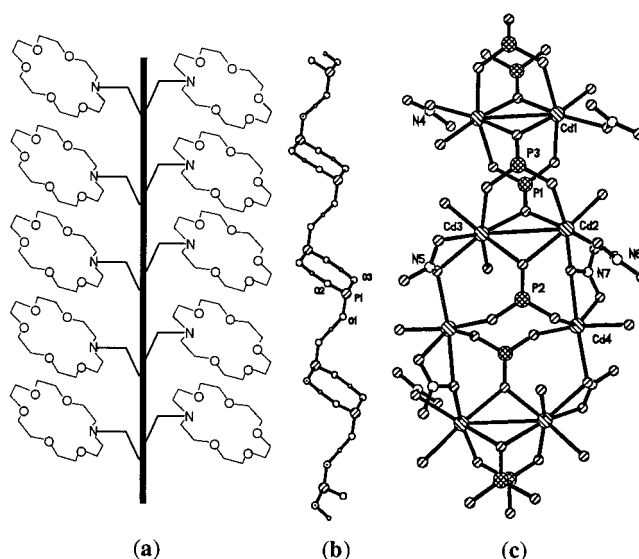
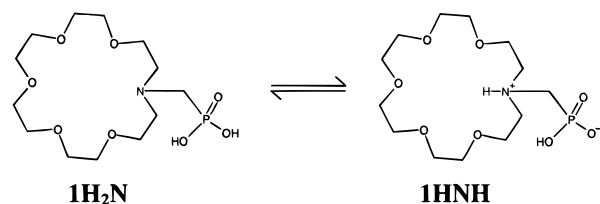


Figure 1. (a) A schematic representation of “macrocyclic leaflets” formed by self-assembly of *N*-(phosphonomethyl)-aza-18-crown-6 ethers. PLUTO diagram of the leaflet’s backbone formed through hydrogen bonds (b) and coordination bonds (c). The crown ether moieties are omitted and O atoms in the coordination network are not earmarked for the sake of clarity.

Scheme 1



and $Cd(NO_3)_2 \cdot 4H_2O$ (0.031 g, 0.1 mmol, 15 mL) dissolved in EtOH to obtain single crystals of the complexes, **2** [$(1H_{1.5}NH \cdot H_2O)_2 \cdot (ClO_4)$] and **3** [$Cd_4(1NH \cdot H_2O)_3 \cdot (H_2O)_5(NO_3)_4[NO_3]$]. These crystals were subjected to X-ray crystallographic studies using a Bruker-AXS CCD diffractometer.¹⁰

Interestingly, Co(II) does not form a complex with acid **1H₂N**, rather the ClO_4 anions enter into the crystal lattice of complex **2** for balancing the charge as the phosphonic acid anion is only half deprotonated and the amine is fully protonated ($1H_{1.5}NH$).⁹ In other words, the azacrown ether moiety bears a net charge of +0.5 and two positively charged azacrown ethers together balance the charge of every ClO_4^- anion. The phosphonic acids self-assemble through hydrogen-bonded dimers and symmetrical hydrogen bonds using 1.5 acidic protons to form a unique polyphosphonate chain flanked by crown ethers such as a leaflet ($O \cdots O$, 2.415(2) Å, 2.501(3) Å, Figures 1b and 2a). Water molecules occupy the molecular cavities of the crown ethers and

(10) **Crystal Data:** **2**, $C_{26}H_{61}N_2O_{22}P_2Cl$, $M = 851.6$, triclinic, $P\bar{1}$, $a = 7.418(1)$ Å, $b = 11.056(2)$ Å, $c = 12.630(2)$ Å, $\alpha = 87.225(4)^\circ$, $\beta = 74.044(3)^\circ$, $\gamma = 85.097(3)^\circ$, $V = 992.0(3)$ Å³, $Z = 1$, $D_c = 1.425$ Mg m⁻³, GOF = 1.08. 2835 absorption collected reflections out of 4570 reflections measured on convergence gave final values of $R = 0.050$, $R_w = 0.132$. **3**, $C_{30}H_{97}N_8O_{47}P_3Cd_4$, $M = 1967.60$, monoclinic, space group $P2_1/c$, $a = 17.136(2)$ Å, $b = 20.818(3)$ Å, $c = 20.858(3)$ Å, $\beta = 104.937(2)^\circ$, $V = 7189.4(2)$ Å³, $Z = 4$, $D_c = 1.8050(4)$ Mg m⁻³, GOF = 0.72. 16905 absorption collected reflections out of 45693 reflections measured on convergence gave final values of $R = 0.068$, $R_w = 0.133$. Data on **2** and **3** were collected at 110 K with a CCD area detector ($4 < \theta < 56$). H atoms of methylenes in **2** and **3** were calculated ($d_{C-H} = 0.95$ Å) and protons of water molecules in **2** only were found via difference maps. All non-H atoms were anisotropically refined and H atoms were fixed with thermal parameters based upon the C atoms to which they are bonded.

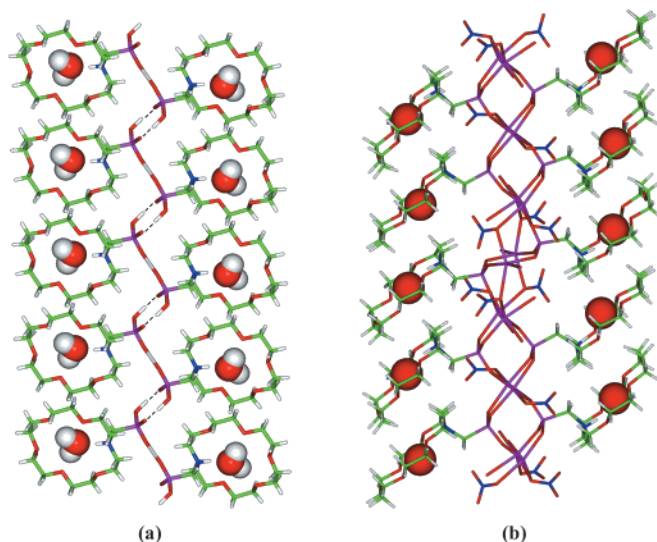


Figure 2. The macrocyclic leaflets of **2** (a) and **3** (b). Water molecules encapsulated in the crown ethers are highlighted (H atoms are not shown for **3**). Note the subtle differences in the alignment of crown ethers in **2** and **3**.

hydrogen bond with ethereal O atoms and the N–H proton (five O···O contacts in the range of 2.9–3.0 Å, N···O 2.686(3) Å).¹¹

The asymmetric unit of complex **3** contains four Cd(II) cations, three phosphonate anions, **1NH**, five nitrate anions, and eight water molecules. Interestingly, **3** also forms a leaflet structure like **2**, but has a complicated polymeric coordination network as the backbone, in which Cd(II) cations adopt octahedral geometry and form two unique Cd···Cd metal contacts (3.288(3) and 3.470(2) Å, Figures 1c and 2b).¹² The phosphonate anions not only bridge the metal cations that make short contacts but also interconnect them further to form a 1D polymeric network (Cd–O distances range from 2.21 to 2.40 Å). Each metal cation is coordinated with at least one nitrate anion and a water molecule and two of the four metal coordinated nitrate anions additionally bridge the adjacent metal cations. In effect, the polymeric chain is positively charged and the free nitrate anions balance the charge. The crown ethers of the leaflet structure encapsulate water molecules such as **1** and form multiple hydrogen bonds. There are five O···O contacts in the range of 2.75–3.0 Å in each of the three crystallographically distinct crown ethers along with N–H···O hydrogen bonds (N···O 2.734(15), 2.708(16), and 2.722(16) Å).

The crown ethers in the polymeric matrix of complex **2** are coplanar and stack at an interplanar distance of ca. 3.8 Å, while in **3** the crown ethers are inclined at angles 4.7° and 5.4° and

(11) 18-Crown-6 ethers are known to accommodate water molecules and hydronium cations in their molecular cavities. For example, see: Atwood, J. L.; Bott, S. G.; Means, M.; Coleman, A. W.; Zhang, H.; May, M. T. *Inorg. Chem.* **1990**, *29*, 467–470.

(12) A survey of the Cambridge Structural Database (CSD) for short Cd···Cd contacts resulted in five compounds for which the Refcodes are, JOZCAC, 3.461 Å, 3.503 Å; KUVŞAV, 2.979 Å; REXHOR, 3.473 Å; TUBZIZ, 3.348 Å; WEFJUM, 3.091 Å.

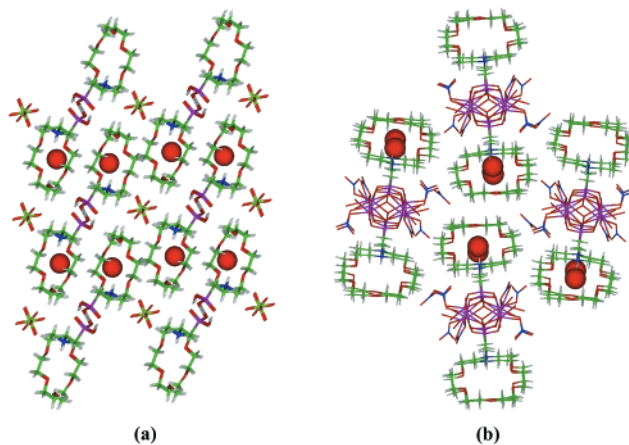


Figure 3. Packing diagram of the “macrocyclic leaflets”. Note the formation of continuous channels in **2** (a) and **3** (b). Such an arrangement of crown ethers may facilitate ion transportation. Perchlorate anions in **2** are disordered.

stack with interplanar distances of ca. 3.5 and 3.6 Å. The packing diagram of **2** and **3** reveals the continuous open channels formed through stacking of crown ether moieties (Figure 3).⁴

The structural features of complexes **2** and **3** are of great interest for their exquisite aesthetic appeal and for the following reasons: (i) Crystal structures of **2** and **3** suggest novel supramolecular routes for grafting crown ethers into a polymeric matrix. (ii) Deprotonation of organophosphonic acids leads to the formation of hydrogen-bonded polyphosphonate chains. (iii) The polymeric assemblies of crown ethers formed through self-assembly of exocyclic functional groups may exhibit distinct selectivity as compared to simple crown ethers in the solution or the solid state because the polymeric assemblies can either encapsulate or sandwich the metal cations in their molecular cavities. Further, the cooperative effects of metal cation insertion and relative orientation of crown ethers with respect to each other may influence the metal binding properties. These factors may be of significant importance in the separation of metal ion isotopes. (iv) The stacking arrangement of macrocycles in **2** and **3** provides new models for the design of macrocyclic tubular channels for transporting ionic species and discotic liquid crystals.^{4,13}

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Supporting Information Available: Crystallographic data of **2–3** (crystallographic information, atomic coordinates, bond lengths and angles, and temperature factors) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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