Supramolecular complexes

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Anion-Directed Self-Assembly of Flexible Ligands into Anion-Specific and Highly Symmetrical Organic Solids**

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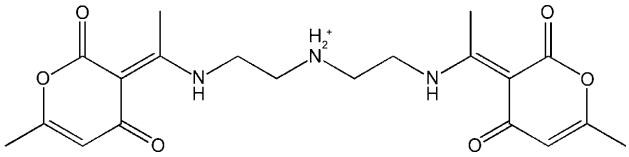
Template-induced association of molecular species represents one of the main approaches in the control of supramolecular assembling.[1] This strategy can be used in the design of porous materials of importance for inclusion (host–guest) chemistry and coordination polymers,[2] in which the tunable size and nature of pores is a great advantage over their inorganic analogues. Most numerous in this class of compounds are the MOFs[3] (metal–organic frameworks) and, to a minor extent, COFs[4] (covalent organic frameworks). Porous organic architectures, in which the tectons are linked through non-covalent interactions, are very rare and still represent an undeveloped area of research.[5]

Both neutral and cationic templates have been known for a long time and are widely used in different fields of synthetic chemistry.[6] However, anionic templates are rarely used in supramolecular chemistry because of the properties of anions, such as low charge to radius ratio, various geometries, high solvation energies, and pH-dependent charge.[7] Template-directed processes that are anion specific can lead us to the always challenging development of new selective systems with industrial, ecological, and biomedical applications. Systems that show great oxoanion selectivity are of special interest in the area of nuclear and toxic waste management.[8]

Herein we report a solid-state study of two supramolecular complexes assembled by an anion-templated reaction of a flexible ligand L[9] (Scheme 1) and anions with trigonal planar (NO_3^-, **1**; Figure 1), and tetrahedral geometry (SO_4^{2-}; **2**) in methanol. The anion organizes folding of three podands to achieve hydrogen bond saturation, resulting in formation of a pseudomacrocyclic host PMH (Figure 2). The PMH assembly is highly anion specific, and the occurrence of the above-mentioned complexes in systems with high concentrations of competing anions has been explored. Expansion of **1** and **2** through hydrogen bonds leads to a highly symmetrical organic solid with voids and channels habited by counterions and more than 300 disordered solvent molecules per unit cell of complex. The role of solvent in structure stabilization is also examined.



Scheme 1. Structure of HL^+. L (*N*,*N*′-3-azapentane-1,5-bis[3-(1-aminoethylidene)-6-methyl-3*H*-pyran-2,4-dione]) belongs to the group of podands, acyclic receptors with three potential binding sites for anions.

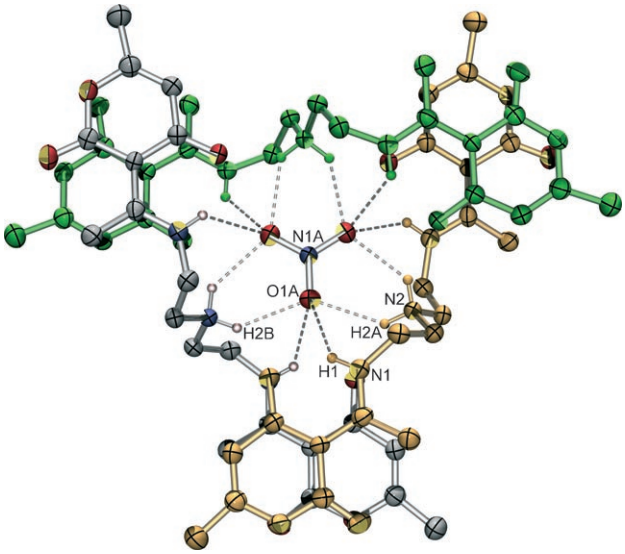


Figure 1. ORTEP[12]/POV-Ray[13] rendered view of the C_3-symmetrical supramolecular complex $[(HL)_3NO_3]^{2+}$ in **1**. Thermal ellipsoids are scaled to the 50% probability level. H atoms not involved in hydrogen bonding are omitted for clarity. C gray, N blue, O red, H pink; two symmetry related molecules are colored green and yellow; dashed lines indicate hydrogen bonds. Key bond parameters for **1**: N1–H1···O1A (N1–H1 0.88 Å, H1···O1A 2.52 Å, N1···O1A 3.190(6) Å, N1–H1···O1A 133°); N2–H2A or –H2B···O1A (N2–H2A(B) 0.92 Å, H2A(B)···O1A 2.20 Å, N2···O1A 2.930(5) Å, N2–H2A(B)···O1A 133°) and **2**: N1–H1···O1A (N1–H1 0.88 Å, H1···O1A 2.40 Å, N1···O1A 3.084 (4) Å, D–H···A 135°); N2–H2A or H2B···O1A (N2–H2A(B) 0.92 Å, H2A(B)···O1A 2.22 Å, N2···O1A 2.930(5) Å, N2–H2A(B)···O1A 133°). The structure is projected almost down the threefold axis.

In both cases, crystals were obtained by addition of the methanolic solution of the corresponding acid to L dissolved in methanol. The crystals are insoluble in a number of organic solvents but are fairly soluble in water. In the methanolic solution or methanol vapor, crystals of **1** and **2** are stable for

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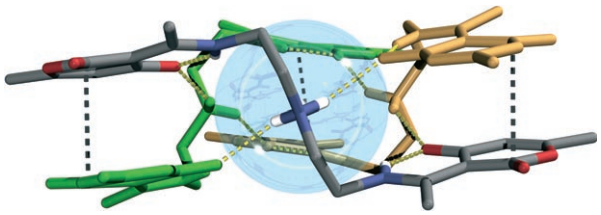

Figure 2. ORTEP/POV-Ray rendered side view of PMH. Most H atoms have been removed for clarity. C gray, N blue, O red, H white, other molecules are colored by symmetry equivalence; inter- and intraligand interactions are indicated with dashed lines (hydrogen bonds in yellow, π–π interactions in black). Interior sphere radius is approximately 3 Å. Key interaction parameters for **1**: intra N1–H1···O3 (N1–H1 0.88 Å, H1···O3 1.85 Å, N1···O3 2.583(7) Å, N1–H1···O3 140°); double inter N2–H2A···O3 (N2-H2A 0.92 Å, H2A···O3 2.08 Å, N2···O3 2.857(7) Å, N2–H2A···O3 141°), π–π (Cg1···Cg2^{i} 3.740(3) Å, $i = x-1/4, 1-y, z+1/4$); and **2**: intra N1–H1···O3 (N1–H1 0.88 Å, H1···O3 1.87 Å, N1···O3 2.585(5) Å, N1–H1···O3 138°); double inter N2–H2A···O3 (N2–H2A 0.92 Å, H2A···O3 2.11 Å, N2···O3 2.864(4) Å, N2–H2A···O3 139°), π–π (Cg1···Cg2^{i} 3.781(2) Å, $i = x-1/4, 2-y, z+1/4$).

months, but upon exposure to air decomposition takes place within seconds.[10] Complexes **1** and **2** are isomorphous and crystallize in the rare cubic space group $Fd\bar{3}c$ (see Figure S2 in the Supporting Information) with unit cell parameters comparable to those found in macromolecules ($a \approx 42$ Å).[11]

Crystallographic and spectroscopic studies[14] reveal that only the central amino group of L is protonated, whereas the side amino groups, involved in a resonance-assisted hydrogen bond, remain unprotonated but participate in bonding as hydrogen-bond donors. Three HL^+ molecules in the C_3-symmetrical complex accommodate the nitrate/sulfate ion by which they are selectively templated: the protonated amino groups are placed in the plane defined by the nitrate oxygen atoms or the sulfate off-axial oxygen atoms,[15] resulting in a total of 12 receptor–anion hydrogen bonds (Figure 1). It was not possible to obtain PMH without an encapsulated anion. In the case of the sulfate anion, we are aware of only one example in which 12 hydrogen bonds are involved in receptor–anion binding,[16] whereas other studies had shown that the maximum number of hydrogen bonds for sulfate was eight.[17] Hay's theoretical studies suggested that the ideal coordination number for the nitrate was six.[18] The fact that the nitrate accommodates 12 hydrogen bonds was, to the best of our knowledge, not yet observed either in synthetic or natural hosts.[19] The oxygen atom as a tetrafurcated hydrogen-bond acceptor is not unusual in protein binding sites,[20] but it is not often observed in the chemistry of small molecules.

Complexes **1** and **2** are further stabilized through the network of interligand hydrogen bonds between the -NH_2 protons and oxygen atoms that point into the PMH cavity and through π–π stacking of the 2-pyrone moieties (Figure 2). In both supramolecular complexes, independently of the geometry and charge of the anion, the PMH:anion stoichiometry is 1:1 and this complex moiety remains positively charged. Elemental analysis[10] revealed that the net charge is balanced by nitrate/sulfate anions located in the crystal structure voids.

The quantitative yields obtained for the products show that assembly of the complexes is very favorable. PMH is similar to C_3-symmetric receptors for trigonal and tetrahedral anions synthesized earlier,[21] with difference that, in this case, the anion led its assembly. Complexes are stabilized by directional hydrogen bonds, which induce rigidity in the formed pseudomacrocycle[22] and serve as the foundation for selective crystallization of desired products. Guided by this principle, we tested the selectivity of HL^+ for nitrate or sulfate in an experiment of competitive crystallization. High yields of **1** and **2** were found even in the presence of high concentrations of competitive anions (Table S1 in the Supporting Information).[23] The ligand expressed high affinity for nitrate versus Cl^-, AcO^-, $C_2O_4^{2-}$, BO_3^{3-}, CO_3^{2-}, BF_4^-, $TsSO_3^-$, and PO_4^{3-}, and the formation of PMH:nitrate is observed in 92–100% yield, even in 6:1 ratios of competitive anions. Slightly poorer affinity was observed for sulfate in the presence of halides or phosphate, whereas in the sulfate/nitrate system, no significant affinity was observed for either anion.

Symmetry expansion of **1** and **2** results in a 3D network provided by weak hydrogen-bonding interactions of the C–H···O type and T-shaped C–H···π interactions between 2-pyrone moieties of discrete supramolecules[25] (Figure 3). As a consequence of this arrangement, approximately 40% of the cell volume is accessible to the counterions and solvent molecules[26] (Figure S2 in the Supporting Information), which occupy two interpenetrating diamondoid networks. Each network consists of voids ($d \approx 12.5$ Å, Figures S3–5 in the Supporting Information) that are connected through channels ($d \approx 5$ Å) parallel to the face-diagonal directions. Since the networks are independent, one guest molecule cannot get into the other network without leaving the crystal.

It was not possible to determine the position of the counterions, which indicates that they are disordered. Lower-

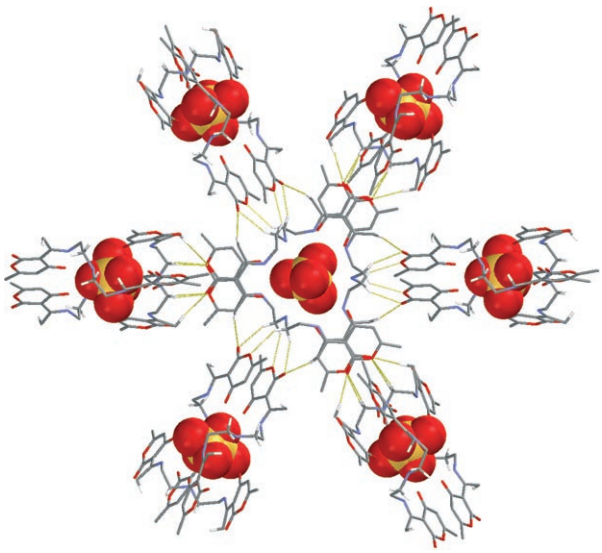

Figure 3. Mercury[24]/POV-Ray rendered view of $[(HL)_3SO_4]^+$ in **2** showing intermolecular contacts of the central supramolecular complex with the surrounding complex molecules. This pattern is repeated from each molecule to form a 3D network. Hydrogen bonds are represented with dashed yellow lines. The sulfate anion is statistically disordered over two orientations.

symmetry space groups were tested but no ordering could be found. We also tested the role of solvent in stabilizing the crystal structure. In aprotic solvents, such as acetonitrile and dichloromethane, we obtained, in the case of **1**, isomorphous products **1**-ACN and **1**-DCM (Figure S6 and Table S2 in the Supporting Information). Sulfate complexes exhibit poor solubility and thus it was not possible to obtain crystalline products from these solvents. Thermogravimetric measurements of **1** and **2** confirmed that there are only weak interactions involving the solvent molecules in the voids. These solvent molecules readily leave the crystals, even at room temperature (Figure S1 in the Supporting Information). This observation is also consistent with the rapid decomposition of the crystals upon exposure to air.

The mass fraction of solvent for both compounds amounts to 19%, which corresponds to more than 300 solvent molecules per unit cell. To examine the stability of the structures upon solvent loss, complexes **1** and **2** were subjected to different temperatures (room temperature, 65°C, and 105°C) for two hours; powder X-ray data were collected on the treated material and compared with data of the solvated complexes. The patterns of products exposed to higher temperatures exhibit broader peaks (quicker solvent removal induces stress on the crystals and consequently the crystallites are smaller); however, no significant change in the patterns was observed. In all cases, the structures remain conserved upon solvent removal (Figure S7 in the Supporting Information), suggesting that the solvent molecules do not represent crucial building blocks in the structures of **1** and **2**. Drying the complexes at low temperatures gives air-stable products (Figure S8 in the Supporting Information). Although the crystals remain transparent, we were unable to obtain single crystals of good size and quality to continue research.[27]

To conclude, the present findings provide evidence for anion-templated assembly of three acyclic molecules HL^+ to the C_3-symmetrical supramolecular complex. This is an example of a system in which a simple and flexible molecule adapts its conformation to respond to the demands of the anion. The architecture of the PMH cavity could serve as a model for building novel, highly selective receptors for nitrate or sulfate, which is indicated by impressive selectivity for these anions, even in highly competitive methanol environment. This conformational movement could prove to be significant in the field of anion sensing and signal transduction. Furthermore, the fact that the host structure remains conserved upon guest (solvent) loss makes these organic solids very desirable in the field of inclusion chemistry, where porous organic solids, consisting of noncovalently bounded tectons, are extremely rare. We are currently investigating the conformational adaptability of this and similar ligands in the presence of different anions.

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[11] a) According to the Cambridge Structural Database (Ver. 5.29), there are only 21 structures that crystallize in this space group (only two of them are metal-free). b) Crystal data for **1**: cubic, $Fd\bar{3}c$, $a = 41.775(3)$ Å, $V = 72900(10)$ Å^3, $R_1 = 0.1478$ [$I > 2\sigma(I)$] and $wR_2 = 0.4208$ (all data); **2**: cubic, $Fd\bar{3}c$, $a = 41.772(4)$ Å, $V = 72887(11)$ Å^3, $R_1 = 0.1229$ [$I > 2\sigma(I)$] and $wR_2 = 0.3750$. Close inspection of the Fourier difference map revealed positions of some methanol molecules in the crystal structures of **1** and **2**

(modeled and refined anisotropically without attached H atoms). For more details see Table S2 in the Supporting Information. CCDC 677195, 677196, 677197, and 677198 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.

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