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Solid-state caging of 1,10-phenanthroline π–π stacked dimers by calix[4]arene dihydroxyphosphonic acid

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The calix[4]arene dihydroxyphosphonic acid–1,10-phenanthroline complex shows caging of the guest molecules as a π–π stacked dimer in a cavity formed by intermolecular hydrogen bonds and aromatic walls formed by the calixarene.

In the solid-state structure of 1,10-phenanthroline with calix[4]arene dihydroxyphosphonic acid, a face-to-face aromatic stacked dimer of 1,10-phenanthroline is held within a cage of eight hydrogen bonded calix[4]arene dihydroxyphosphonic acid molecules by face-to-face and CH–C interactions and hydrogen bonding between the mono-protonated 1,10-phenanthroline and the single deprotonated phosphonic acid.

There exists increasing interest in the use of calix[4]arenes in the construction of solid-state systems. The work of Atwood[1] and Raston[2] on the structural motifs of *para*-sulfonato-calix[4]arene and of Hosseini on calix[4]arene tectons[3,4] has demonstrated the structural diversity present in the solid-state structure of calixarenes. Recent work, by ourselves, on organic amine complexes with calix[4]arene dihydroxyphosphonic acid, **1**, Fig. 1, has shown that the self-included dimeric building block characteristic of this molecule can generate novel structural motifs. The complex of **1** with hexanediamine shows encapsulation of the dimer within a cage of diammonium cations,[5] whereas with propanediamine a complex hexameric assembly of dimers generates an aqua-channel.[6]

In this paper we describe the solid-state structure of **1** with 1,10-phenanthroline. Here the structural motif is composed of an intermolecular hydrogen bonded cage of eight molecules of **1** within which π–π stacked, mono-protonated 1,10-phenanthroline dimers show face-to-face interactions and CH–C interactions[7] with different molecules of **1**.

Crystallisation of **1** with 1,10-phenanthroline from aqueous methanol generated crystals of a 1:1 trihydrate complex.†

The characteristic dimeric motif of **1** formed from symmetry-related molecules is present with a shallow interpenetration of the molecules, an angle of 159° is formed by the *para*-carbon atoms describing the interpenetration, Fig. 2. This angle is similar to that observed in the uncomplexed dimer (158.8°).[8]

Intramolecular hydrogen bonding between the unsubstituted and substituted phenolic groups (2.92 and 2.87 Å) rigidifies the cone conformation of **1**. A water molecule (W1) is a donor in a hydrogen bond (2.70 Å) to a phosphonic acid oxygen and forms a weak bifurcated hydrogen bond with one substituted phenolic oxygen and with a phosphonic acid hydroxyl group (3.50 and 3.43 Å, respectively).

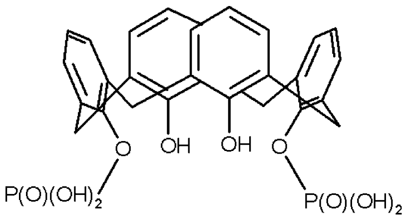

Fig. 1 Schematic structure of the calix[4]arene dihydroxyphosphonic acid molecule, **1**.

The crystal packing shows planes of dimers of **1** perpendicular to the *a* crystal axis, Fig. 3. These planes are held together by different networks of hydrogen bonds.

- Facing phosphonic acid groups form strong intermolecular hydrogen bonds (2.52 Å).
- A second water molecule (W2) acts as both a hydrogen donor (2.74 and 2.80 Å) or acceptor (2.60 Å) bridging the phosphonic groups.
- A third water molecule (W3) acts as a hydrogen acceptor from a phosphonic acid group (2.43 Å) and as a donor to another phosponic acid group lying in the same plane and to W1 (2.57 and 2.54 Å).

Eight molecules of **1** together with the series of three independent water molecules generate a cage within which is included the face-to-face aromatic stacked 1,10-phenanthroline dimer.

Two crowns of hydrogen bonds are crosslinked by 14 other hydrogen bonds (Fig. 4), generating the hydrophilic part of the cage. This cage is closed by two hydrophobic regions formed by aromatic rings of three molecules of **1** (Fig. 5).

The trapped 1,10-phenanthroline is involved in a hydrogen bond *via* its protonated nitrogen atom and the deprotonated hydroxyl of the phosphonic acid (2.75 Å).

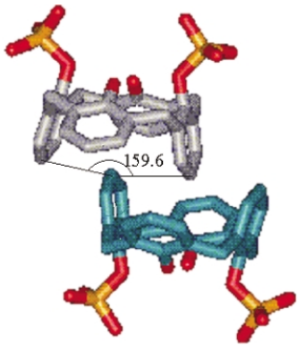

Fig. 2 Dimeric structural motif of **1** formed from symmetry-related molecules showing the interpenetration angle.

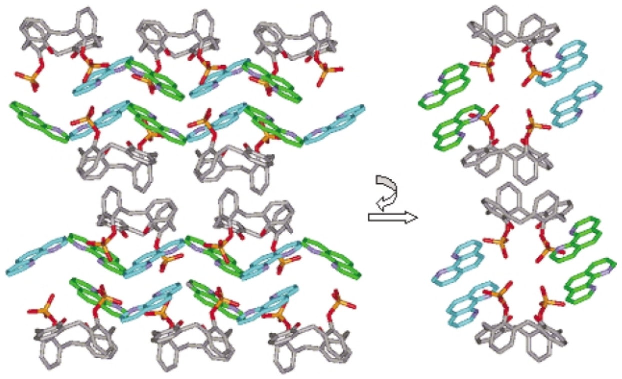

Fig. 3 View of the molecular packing along the *c* axis (at the left) and along the *b* axis (on the right).

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Multiple aromatic–aromatic interactions are present in the cage. The central ring of each 1,10-phenanthroline molecule undergoes face-to-face stacking with an aromatic ring of molecule **1** (3.74 Å). The molecules of 1,10-phenanthroline are displaced with face-to-face stacking between the central ring and the non-protonated heterocycle (3.55 Å).

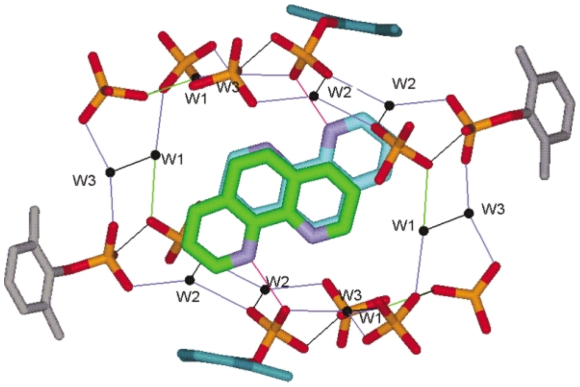

Fig. 4 View of the hydrophilic part of the cage containing the 1,10-phenanthroline dimer; the double crown of hydrogen bonds involving the phosphonic acid groups and water molecules (W1, W2, W3) is shown in blue, the four hydrogen bonds (2.54 Å) between W1 and W3 as well as the six POH···PO (2.52 Å) and POH···W2 (2.74 Å) hydrogen bonds are shown in black and the two NH···OP hydrogen bonds (2.75 Å) are shown in red. Four short but non-hydrogen bonded contacts exist between W2 and POH (2.85 Å) and are shown in green.

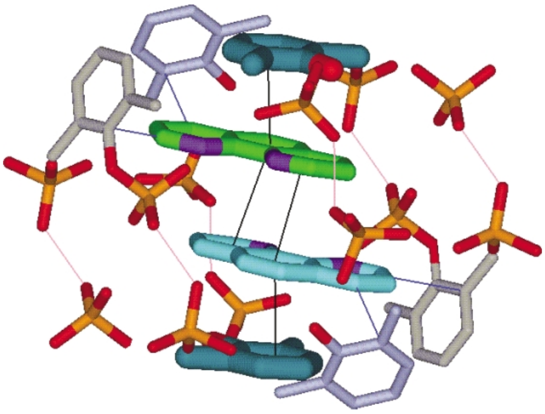

Fig. 5 View of the cage containing the π–π stacked 1,10-phenanthroline dimers showing face-to-face calix–1,10-phenanthroline interactions (3.70 Å) colored in black and short aromatic CH–C 1,10-phenanthroline–calix interactions (3.69 and 3.63 Å) colored in blue; the POH···OP hydrogen bonds are shown in red.

The protonated heterocyclic ring is involved in CH–C interactions with two aromatic rings of different molecules of **1** (3.63 and 3.69 Å).

Additionaly, a short contact occurs between the CH group, α to the protonated 1,10-phenanthroline nitrogen and a water molecule (3.47 Å).

The structure of calix[4]arene dihydroxyphosphonic acid with 1,10-phenanthroline shows an unexpected degree of complexity, aromatic–aromatic stacked 1,10-phenanthroline molecules being held within a hydrogen bonded cage by face-to-face and CH–C aromatic interactions as well as by strong and weak hydrogen bonds. Further work is in progress to crystallise other aromatic polyamines with calix[4]arene dihydroxyphosphonic acid.

Notes and references

† Crystallographic data: to a solution of 1,10-phenanthroline monohydrate (0.01 M) in water, a solution of calix[4]arene dihydroxyphosphonic acid (0.01 M) in methanol is added so as to form interfacial layers of the two solutions. Crystals were obtained by slow diffusion of the solvents at room temperature after several days.

Crystal data for $(C_{28}H_{26}O_{10}P_2).(C_{12}H_8N_2).3H_2O$: M = 818.7, colorless, 0.25 × 0.10 × 0.10 mm, monoclinic, space group $C2/c$, a = 36.833(7), b = 10.774(2), c = 22.352(5) Å, β = 120.82(3)°, V = 7618(4) Å^3, Z = 8, ρ_{calc} = 1.428 g cm^{-3}, $2\theta_{\max}$ = 49.4°, μ(Mo-Kα) = 0.19 mm^{-1}, 6435 independent reflections, 3052 with $I > 2\sigma(I)$. Intensity data were collected at 123 K on a Nonius KappaCCD diffractometer using Mo-Kα radiation (λ = 0.7107 Å). Lorentz and polarisation corrections were applied and diffracted data were not corrected for absorption. The structure was solved by direct methods and Fourier techniques (SHELXS-86) and refined, on $|F|^2$ using the program SHELX-97. Three water molecules were located. No disorder was observed. All hydrogen atoms were observed on Fourier difference maps. Water hydrogen atoms were fixed in observed positions and other ones in ideal positions. They were refined with isotropic thermal parameters based upon the corresponding bonding carbon atom [U(H) = 1.2 U_{eq}]. R_1 = 0.0740, wR_2 = 0.1783. GOF = 0.968 for all data. Residual electron density was between 0.46 and −0.47 eÅ^{-3}.

CCDC 230027. See http://www.rsc.org/suppdata/cc/b3/b315600c/ for crystallographic data in .cif or other electronic format.

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