

# A previously unrecognised hydronium di-cation in the crystal structure of a cucurbituril derivative

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Examination of the crystal structure of the adduct of hydronium tetrachloroferrate dichloride with cucurbituril resulted in the discovery that the hydronium cation present therein is not the well known  $\text{H}_3\text{O}_3^+$  species; rather, it is an unprecedented cyclic species of composition  $(\text{H}_{14}\text{O}_6)^{2+}$ , templated by the formation of five hydrogen bonds to cucurbituril.

The organic cavitand cucurbituril was discovered in 1981 by Freeman *et al.*,<sup>1</sup> reproducing the synthesis of Behrend *et al.* in 1905.<sup>2</sup> The cucurbit[6]uril molecule is a rather intriguing, highly symmetrical entity (essentially  $D_{6h}$ ), resembling a pumpkin (*cucurbitaceae* is Latin for pumpkin) or a napkin holder, and containing urea fragments linked by  $-\text{CH}-$  and  $-\text{CH}_2-$  bridges in a very elegant arrangement. Intrigued by the molecule, and lacking a proper three-dimensional visualisation of either it or its packing environment in a crystal structure, two of us (IB and UM) decided to create suitable graphics to examine both of these facets, based on the reported crystal structure of a cucurbituril adduct of a hydronium tetrachloroferrate(III) dichloride complex.<sup>3</sup> Much to our surprise, the graphics we generated showed the hydronium cation to be that shown in Fig. 1 and Fig. 2, some of the hydrogen bonding interactions having previously been overlooked. The  $(\text{H}_{14}\text{O}_6)^{2+}$  cyclic cluster consists of six water molecules, two of which lie opposite to each other in the ring and are protonated. Within the ring there are six covalent  $\text{O}-\text{H}$  bonds and six  $\text{O}\cdots\text{H}$  hydrogen bonds. A further five  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds link the cluster to a cucurbituril molecule (Fig. 3). Within the cyclic cation cluster the  $\text{H}-\text{O}-\text{H}$ ,  $\text{H}-\text{O}\cdots\text{H}$  and  $\text{H}\cdots\text{O}\cdots\text{H}$  angles range from  $98$ – $119^\circ$  (for the purpose of characterising hydrogen bond geometry, all refined  $\text{O}-\text{H}$  bonds have been normalised to a

length of  $1.0 \text{ \AA}$ , while retaining the observed bond direction). A summary of the geometry of the  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds is given in Table 1.

Given the surprising discovery of this cationic species, we went back to the original raw data set and solved the structure anew and independently in the space groups  $Cmca$  and  $C22_1$ .<sup>4</sup> The results

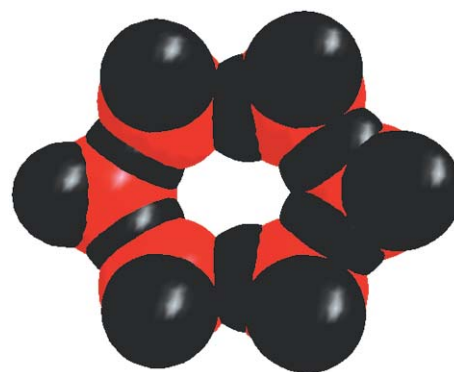


Fig. 2 Space filling view of the cluster cation.

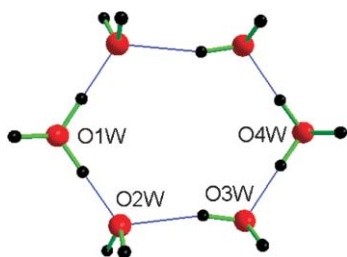


Fig. 1 The hydrogen bonded  $(\text{H}_{14}\text{O}_6)^{2+}$  cluster cation.

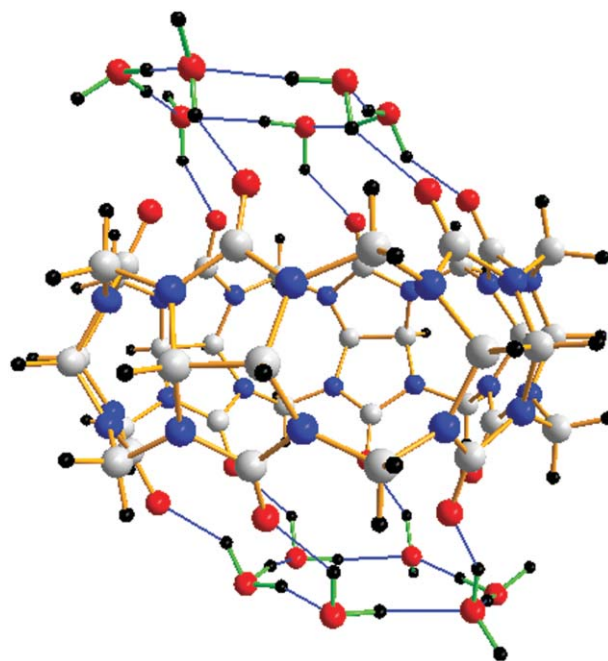


Fig. 3 The templating of two cluster cations by hydrogen bonding to the cucurbituril molecule.

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**Table 1** Hydrogen bond geometry (distances in Å and angles in °). D and A are donor and acceptor atoms respectively, O(cuc) are the oxygen atoms of the cucurbituril molecule, and O1W–O4W are the oxygen atoms of the cluster cation

D	A	H...A	D–H...A	D...A
O1W	O2W	1.47	180	2.465
O4W	O2W	1.90	166	2.885
O3W	O4W	1.54	162	2.506
O2W	O(cuc)	1.70	151	2.620
O3W	O(cuc)	1.86	137	2.676
O4W	O(cuc)	1.69	147	2.589

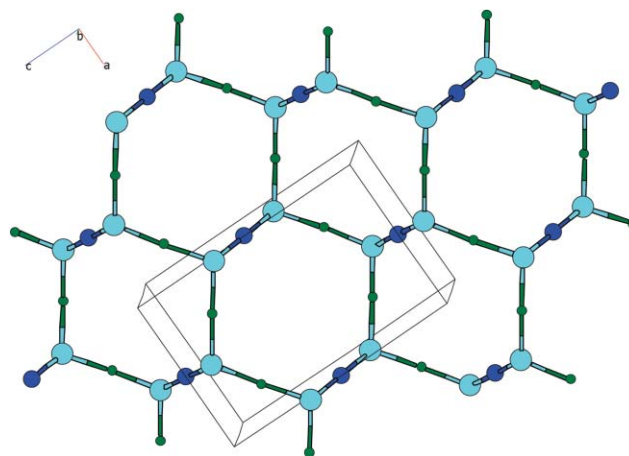
were essentially the same; namely, the cyclic species of composition  $(\text{H}_{14}\text{O}_6)^{2+}$  was invariably found. Therefore, the dimeric nature of the di-hydronium species was not an artefact due to a false symmetry operation by a space group of higher symmetry than that observed in reality. Given that the *R*-factors were virtually identical for the two refinements, while there were twice as many refined parameters in  $C222_1$ , we believe that the correct space group is the original one,  $Cmca$ .<sup>3</sup> This argument is further strengthened by the fact that the Flack absolute structure parameter<sup>5</sup> in  $C222_1$  gives a value essentially equal to 0.5. This indicates the presence of inversion in the structure, while PLATON<sup>4</sup> suggests a missing inversion centre in the results from this refinement.

A notable aspect of this cyclic di-hydronium di-cation is its geometry: the six oxygen atoms of the cluster are nearly coplanar (rms deviation is 0.077 Å, all the oxygen atoms except for O1W are coplanar with an rms deviation of 0.008 Å, O1W lies 0.335 Å out of this mean plane). Almost all the hydrogen atoms lie on one side of the mean plane of the oxygen atoms (the top—towards the viewer in Fig. 1 and Fig. 2). Therefore the di-cation differs markedly from the geometry found in hexameric, neutral water rings—which are almost classical examples of chair conformations.<sup>6,7</sup> This essentially planar conformation is a direct result of the set of five hydrogen bonds between the di-hydronium cluster (providing five donors) and the  $\text{O}_6$  portal of cucurbituril (providing five acceptors, the sixth potential O–H...O hydrogen bond being geometrically unfavourable). Thus cucurbituril acts here as a rigid template for the assembly of one di-cation on each of its two portals (Fig. 3).

The corresponding tetrachlorogallate(III) complex is isostructural (except for two-fold disorder of the anion that does not affect the interaction between cucurbituril and the di-cation) and contains the same di-hydronium cluster.<sup>8</sup>

The cluster cation also forms hydrogen bonds with the chloride anions in the crystal structure. Topological analysis of the hydrogen bonding<sup>4</sup> shows that the cluster cations, chloride anions and cucurbituril molecules form corrugated honeycomb nets, perpendicular to the crystallographic *b* axis (Fig. 4). The Schläfli symbol<sup>9</sup> of the net is  $\{12^3\}2\{12\}3$  and the coordination sequences are (3 3 6 6 12 9 15) for  $(\text{H}_{14}\text{O}_6)^{2+}$ , (2 4 4 8 8 14 10) for cucurbituril and (2 4 4 8 8 14 10) for  $\text{Cl}^-$ .

The cluster cation reported here is unprecedented, its novel features being its essentially planar cyclic nature and +2 charge. Recently, cucurbit[*n*]urils, where *n* = 5, 7, 8 and 10, have been prepared and structurally characterised.<sup>10</sup> It is possible that some of them may fulfil a similar template role for the formation of even larger hydronium–water cluster cations.



**Fig. 4** The honeycomb net formed by hydrogen bonding of the cluster cations (represented by light blue balls), cucurbituril molecules (dark blue) and chloride anions (green).

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- A notation, devised by Ludwig Schläfli, a pupil of Euler, which describes the number of edges of each polygon meeting at a vertex of a regular or semi-regular tiling or solid. For a Platonic solid it is written  $\{p, q\}$ , where *p* is the number of sides each face has, and *q* is the number of faces that touch at each vertex. See <http://www.davidarling.info/encyclopedia/S/schlaefli-symbol.html>.
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