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#### Key indicators

Single-crystal X-ray study  
 $T = 183$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.051  
 $wR$  factor = 0.130  
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

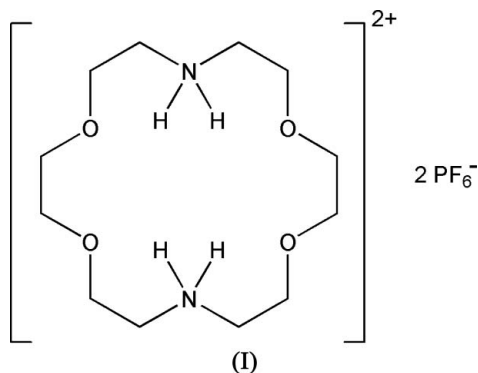
## 1,4,10,13-Tetraoxa-7,16-diazoniacyclooctadecane bis(hexafluorophosphate): $\text{PF}_6^-$ acting as a pseudohalide

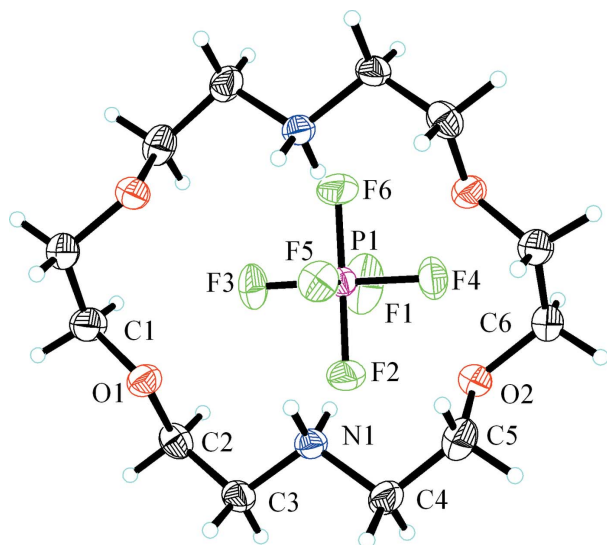
In the crystal structure of the title compound,  $\text{C}_{12}\text{H}_{28}\text{N}_2\text{O}_4^{2+} \cdot 2\text{PF}_6^-$ , the center of the diprotonated macrocycle  $18\text{N}_2\text{O}_4 \cdot 2\text{H}^{2+}$  ( $18\text{N}_2\text{O}_4 \cdot 2\text{H}^{2+}$  is the 1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane dication) coincides with a crystallographic inversion center. The structure displays  $\text{N}-\text{H} \cdots \text{F}$  interactions between H atoms of the cationic N atoms of the macrocycle and the F atoms of the  $\text{PF}_6^-$  anions. The  $\text{H} \cdots \text{F}$  distances are in the range 2.15 (3)–2.42 (4) Å. The structure is nearly isostructural with the previously determined iodide salt, with  $\text{PF}_6^-$  acting as a pseudohalide anion.

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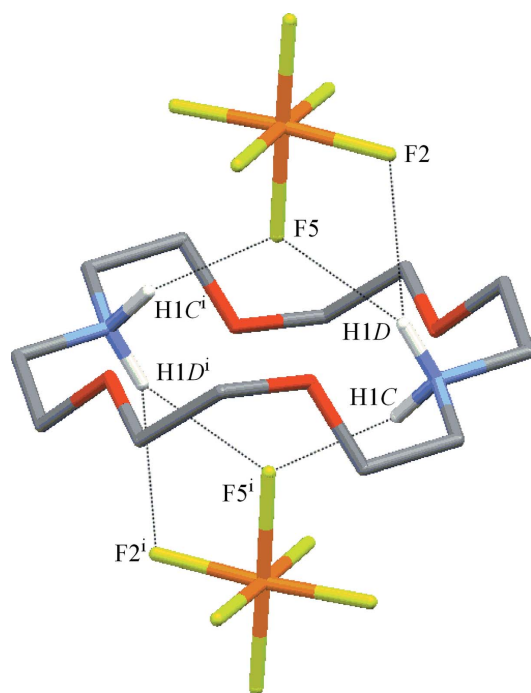
#### Comment

A number of salts of the diprotonated macrocycle  $18\text{N}_2\text{O}_4 \cdot 2\text{H}^{2+}$  ( $18\text{N}_2\text{O}_4 \cdot 2\text{H}^{2+}$  is the 1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane dication) have been structurally characterized [61 structures in a recent search of the Cambridge Structural Database (CSD; Version 5.27 of November 2005; Allen, 2002). Salts of this dication with simple inorganic anions, transition metal complex anions, lanthanide and actinide complex anions, and organic anions of various types have been reported. Most of these salts incorporate water solvent molecules. Hydrogen-bonding interactions between the ammonium H atoms of the cation and water and other acceptor atoms from anions, including oxygen and nitrogen, are common in these structures. Only a few of these structures exhibit hydrogen bonding with halogen atoms when halogens are the only acceptors present [CSD refcodes YOGZAV and YOGYUO (Chekhlov & Yurtanov, 1994), WUCGEU (Gel'mbol'dt, Ganin *et al.*, 1996), TECYUV (Gel'mbol'dt, Simonov *et al.*, 1996) and JUHGAU (Chekhlov *et al.*, 1991)]. The structure we report here, namely 1,4,10,13-tetraoxa-7,16-diazoniacyclooctadecane bis(hexafluorophosphate), (I), displays  $\text{N}-\text{H} \cdots \text{F}$  hydrogen bonding between the protonated macrocycle dication and the hexafluorophosphate anions.



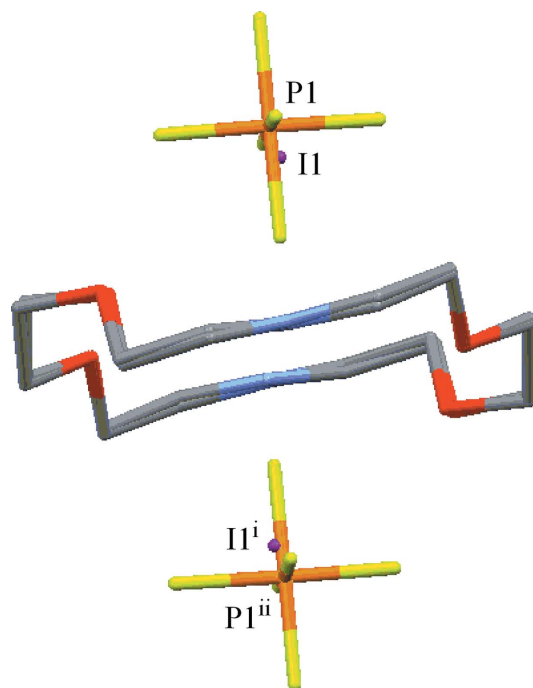
**Figure 1**

A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabeled atoms are related to labeled atoms by the symmetry operator  $(1 - x, -y, -z)$ .

**Figure 2**

A view of the structure of (I), showing the intermolecular N—H...F interactions (dashed lines). Only H atoms participating in N—H...F interactions are shown. Atoms are labeled with symmetry codes identifying the location relative to the dication asymmetric unit. [Symmetry code: (i)  $1 - x, -y, -z$ ]

The structure of (I) is presented in Fig. 1. The asymmetric unit consists of half of one 1,4,10,13-tetraoxa-7,16-diazonia-cyclooctadecane dication and one hexafluorophosphate anion. Atoms C1–C6, N1, O1 and O2 lie on general positions. The other half of the macrocycle is related by the inversion center at  $(\frac{1}{2}, 0, 0)$ . The atoms of the hexafluorophosphate anion lie on

**Figure 3**

Least-squares overlay of (I) with the iodide salt (CSD refcode YOGZAV; Chekhlov & Yurtanov, 1994). [Symmetry codes: (i)  $1 - x, -y, -z$ ; (ii)  $-x, -y, -z$ ]

general positions. No solvent molecules are present in the structure.

The ions of (I) show intermolecular N—H...F interactions between the H atoms attached to the N atoms of the macrocycle dication and the F atoms of the  $\text{PF}_6^-$  anion (Table 1). Fig. 2 shows a view of these interactions. Each complete diprotonated macrocycle participates in four N—H...F interactions with two different  $\text{PF}_6^-$  anions. Atom H1C has one short contact with F5. Atom H1D has two short contacts, one with F5 and another with F2. There are only 15 other examples in the CSD of organic structures that exhibit charge-assisted hydrogen bonding between a quaternary ammonium H atom and a  $\text{PF}_6^-$  anion.

The intermolecular hydrogen-bonding motif observed in (I) [graph-set descriptor  $R_4^2(8)$ ; Bernstein *et al.*, 1995] is also present for structures of the  $18\text{N}_2\text{O}_4$  diprotonated dication with  $\text{Cl}^-$  (JUHGAU),  $\text{Br}^-$  (YOGYUO) and  $\text{I}^-$  (YOGZAV) anions. The hydrogen bonding in each of these structures consists of an acceptor atom above and below the pocket of the macrocycle, with two NH donor groups, one from each N atom of the macrocycle. The difference between the hydrogen bonding of (I) and that of the other halide anion structures is one additional N—H...F interaction per  $\text{PF}_6^-$  [graph-set descriptor  $R_1^2(4)$ ], made possible by an additional F acceptor atom of  $\text{PF}_6^-$ . In the two other structures reported with N—H...F interactions in the absence of other acceptors (TECYUV and WUCGEU), the hydrogen-bonding patterns are more complicated as the anion also contains hydrogen-bond donor groups.

The conformation observed for the 18N<sub>2</sub>O<sub>4</sub> diprotonated dication is also similar to that observed in the halide structures. The similarity of the macrocycle conformation of (I) with the halide salt structures is seen in the comparison of the r.m.s. distance differences in the atomic positions of the diprotonated macrocycle dication non-H atoms of (I) with each of the halide salt structures [I<sup>-</sup> 0.099, Br<sup>-</sup> 0.231, Cl<sup>-</sup> 0.279; calculated with *MERCURY* (Bruno *et al.*, 2002)]. Fig. 3 shows a least-squares overlay of the iodide salt and the structure of (I). In fact, the differences in the conformation of (I) compared with the halogens can be described as mainly changes in the macrocycle pocket. The macrocycle pocket size is strongly influenced by the hydrogen-bond acceptor anion. The intramolecular transannular N···N distance varies by almost 0.8 Å across this series [Cl<sup>-</sup> 4.17 Å, Br<sup>-</sup> 4.27 Å, I<sup>-</sup> 4.69 Å, and PF<sub>6</sub><sup>-</sup> 4.853 (4) Å]. For comparison, in the structure of the unprotonated 18N<sub>2</sub>O<sub>4</sub> with no solvent present, the intramolecular N···N distance is 5.80 Å (CSD refcode TOAZOC03; Dokurno *et al.*, 1997). These changes in transannular N···N distances illustrate how the macrocycle ring may be compressed due to the effects of anion hydrogen bonding.

## Experimental

1,4,10,13-Tetraoxa-7,16-diazoniacyclooctadecane bis(hexafluorophosphate) was synthesized by the following procedure. HgSO<sub>4</sub> (0.0606 g, 0.204 mmol) was heated at reflux for 1 h with 18N<sub>2</sub>O<sub>4</sub> (0.0631 g, 0.241 mmol) in an H<sub>2</sub>O–CH<sub>3</sub>OH mixture (1:1 v/v, 87 ml). Excess NH<sub>4</sub>PF<sub>6</sub> (0.130 g, 0.797 mmol) was added and the solution was cooled overnight. No precipitate formed, so the solvent was completely removed by rotary evaporation to yield 106 mg of a white solid. As much of the solid as possible was redissolved in CH<sub>3</sub>NO<sub>2</sub>. Slow diffusion of diethyl ether into this solution gave colorless crystals. <sup>1</sup>H NMR (CD<sub>3</sub>NO<sub>2</sub>, δ, p.p.m.): 6.37 [*v br s*, 4 H (NH)], 3.84 (*m*, 8 H), 3.72 (*s*, 8 H), 3.54 (*m*, 8 H); <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>NO<sub>2</sub>, δ, p.p.m.): 71.08 (4 C), 66.25 (4 C), 50.00 (4 C). Calculated for C<sub>12</sub>H<sub>28</sub>F<sub>12</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C 26.00, H 5.09, N 5.05%; found: C 26.30, H 5.15, N 5.19%.

### Crystal data

C<sub>12</sub>H<sub>28</sub>N<sub>2</sub>O<sub>4</sub><sup>2+</sup>·2F<sub>6</sub>P<sup>-</sup>  
*M<sub>r</sub>* = 554.30  
 Monoclinic, *P*<sub>2</sub><sub>1</sub>/*n*  
*a* = 9.269 (2) Å  
*b* = 10.333 (2) Å  
*c* = 12.264 (3) Å  
 β = 110.647 (7)°  
*V* = 1099.2 (4) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 1.675 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 7032 reflections  
 θ = 2.4–26.0°  
 μ = 0.32 mm<sup>-1</sup>  
*T* = 183 (2) K  
 Block, colorless  
 0.43 × 0.43 × 0.22 mm

### Data collection

Rigaku AFC7R CCD diffractometer  
 ω scans  
 Absorption correction: multi-scan (*CRYSTALCLEAR*; Rigaku, 2000)  
*T<sub>min</sub>* = 0.874, *T<sub>max</sub>* = 0.933  
 9148 measured reflections  
 1948 independent reflections  
 1785 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.024  
 θ<sub>max</sub> = 25.1°  
*h* = -11 → 11  
*k* = -12 → 12  
*l* = -14 → 14

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.051  
*wR*(*F*<sup>2</sup>) = 0.130  
*S* = 1.05  
 1948 reflections  
 153 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0685*P*)<sup>2</sup> + 1.4259*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.52 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.40 e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1C···F5	0.90 (4)	2.23 (3)	2.983 (3)	141 (3)
N1–H1D···F5 <sup>i</sup>	0.82 (3)	2.15 (3)	2.922 (3)	156 (3)
N1–H1C···F2	0.90 (4)	2.42 (4)	3.249 (3)	154 (3)

Symmetry code: (i) -*x* + 1, -*y*, -*z*.

All H atoms bonded to C atoms were placed in ideal positions and constrained to ride on their parent atoms, with C–H distances of 0.99 Å and *U*<sub>iso</sub>(H) values of 1.2*U*<sub>eq</sub>(C). The H atoms bonded to N atoms were refined with isotropic displacement parameters.

Data collection: *CRYSTALCLEAR* (Rigaku, 2000); cell refinement: *CRYSTALCLEAR*; data reduction: *CRYSTALCLEAR*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Version 1.4; Bruno *et al.*, 2002); software used to prepare material for publication: *MERCURY*.

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