organic papers

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cyclo-Bis(paraquat-m-terphenylene) tetrakis(hexafluorophosphate) tetrahydrate

In the title compound, $C_{60}H_{48}N_4^{4+}\cdot 4PF_6^-\cdot 4H_2O$, the tetracation as a whole assumes a chair-like conformation, as seen by joining the centroids of the bridging terphenylene moieties with the four methylene C atoms. Two inversion-related hexafluorophophate anions are inserted into the cavity of the centrosymmetric tetracation, whereas the other two anions are situated away from the cavity. The size of the cavity is approximately 13.23×12.86 Å^2. The four water molecules are partly inserted into the cavity. In the crystal, the cations, anions and water molecules are held together by O—H$\cdots$O, O—H$\cdots$F, C—H$\cdots$F and C—H$\cdots$O intermolecular hydrogen bonds.

Comment

4,4′-Bipyridinium-based tetracationic cyclophanes are found to be versatile macrocycles for constructing rotaxanes and catenanes (Amabilino & Stoddart, 1995). They have potential uses in resolving racemic substrates containing π-electron-rich aromatic rings (Asakawa et al., 1996) and function as non-sequence-specific DNA photo-cleaving agents (Lorente et al., 1999). cyclo-Bis(paraquat-m-terphenylene) is such a tetracationic cyclophane, synthesized by refluxing an equimolar mixture of m-terphenyldibromide (Hart & Rajakumar, 1995) and 4,4′-bipyridine in acetonitrile for 48 h, followed by column chromatography and counter-ion exchange with NH_4PF_6. We report here the structure of the tetracation as its tetrakis-(hexafluorophosphate) tetrahydrate, (I).

(I)
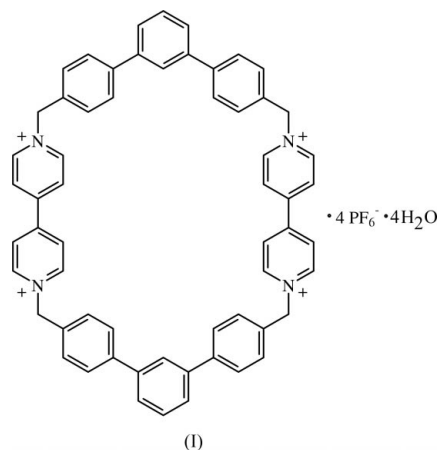
The asymmetric unit of (I) consists of one-half of the $(C_{60}H_{48}N_4)^{4+}$ tetracation, two PF_6^- anions and two water molecules. The other half of the tetracation is generated by a crystallographic inversion centre, as shown in Fig. 1. The centrosymmetric macrocyclic tetracation as a whole assumes a chair-like conformation, as seen by joining the centroids of the
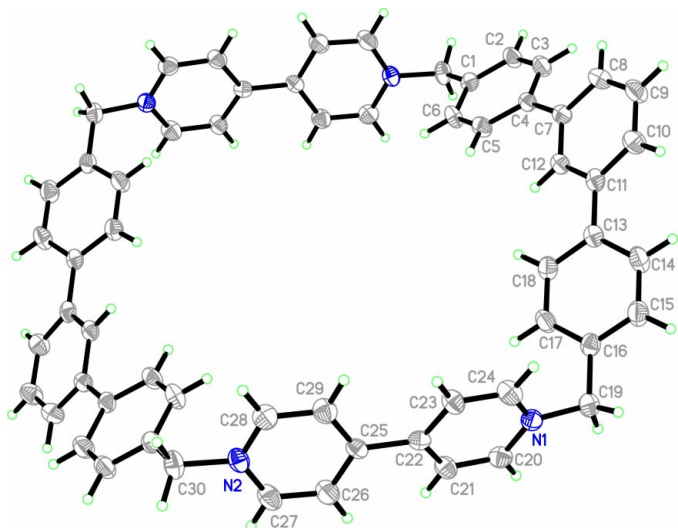
Figure 1
The structure of the macrocyclic tetracation in the title compound. Displacement ellipsoids are drawn at the 50% probability level. Only atoms of the asymmetric unit have been numbered.

Figure 2
The structure of the title compound, showing the arrangement of anions and water molecules.

bridging terphenylene moieties with the four methylene C atoms. The mean planes through the terphenylene rings and through the bipyridinium ring are inclined at angles of 132.85 (3) and 97.45 (4)°, respectively, to the methylene plane. In the terphenylene system, the two outer rings are twisted from the central ring by 24.7 (1) and 18.9 (1)°. The dihedral angle between the two connected pyridinium rings is 15.2 (1)°. The macrocyclic valence angles at the methylene C atoms, C19 [110.9 (2)°] and C30 [111.8 (2)°], agree with the values reported for the pyridine-bridged phanes of 4,4′-bipyridine (Scheytza *et al.*, 1999), but these values are larger than those reported for *cyclo*-bis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate) (Odell *et al.*, 1988). The overall dimensions of the macrocyclic tetracation are 13.23 Å between the centroids of the bonds connecting pyridinium rings and 12.86 Å between C12 and C12^i [symmetry code: (i) $-x, 1 - y, -z$].

In the solid state, two inversion-related hexafluorophosphate anions are inserted into the cavity of the centrosymmetric tetracation. The two P atoms, P1 and its centrosymmetric equivalent at ($-x, 1 - y, -z$), lie on opposite sides of the methylene plane, at 0.874 (1) Å, and the distances separating them from the centroids of the bonds connecting pyridinium rings are each 3.975 Å. The other two anions lie on opposite sides of the methylene plane at 5.133 (1) Å. The water O atoms, O1*W* and O2*W*, are located 2.125 (3) and 1.989 (3) Å from the methylene plane. The four anions and the four water molecules are linked together by O—H···O and O—H···F hydrogen bonds to form discrete centrosymmetric units, as shown in Fig. 2. These units are linked to the macrocyclic tetracations through C—H···F hydrogen bonds (Table 2), to form a network structure. Two short intermolecular C···F contacts, C21···F4 [2.889 (3) Å] and C27···F6($-x, \frac{1}{2} + y, \frac{1}{2} - z$) [2.933 (4) Å], are observed in the structure. However, they are not indicative of C—H···F
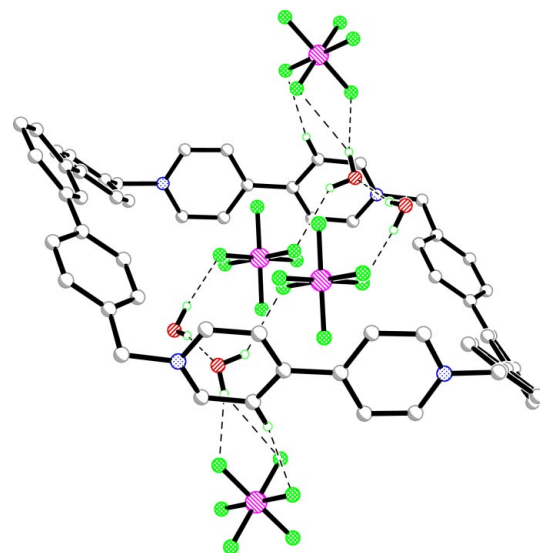
hydrogen bonding as the H21···F4 and H27···F6 distances are longer than the sum of the van der Waals radii.

Experimental

Crystal data

$C_{60}H_{48}N_4^{4+}$·4PF$_6^-$·4H$_2$O	$D_x = 1.569$ Mg m^{-3}
$M_r = 1476.97$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8192
$a = 11.7669$ (1) Å	reflections
$b = 16.0300$ (2) Å	$\theta = 2.5–28.3°$
$c = 18.4544$ (2) Å	$\mu = 0.24$ mm^{-1}
$\beta = 116.089$ (1)°	$T = 183$ (2) K
$V = 3126.27$ (6) Å^3	Slab, yellow
$Z = 2$	$0.46 \times 0.30 \times 0.26$ mm

Data collection

Siemens SMART CCD area-detector diffractometer	7566 independent reflections
ω scans	4043 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.114$
	$\theta_{max} = 28.4°$
$T_{min} = 0.896$, $T_{max} = 0.939$	$h = -15 \rightarrow 15$
18437 measured reflections	$k = -21 \rightarrow 9$
	$l = -22 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0121P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.149$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.91$	$\Delta\rho_{max} = 0.47$ e Å^{-3}
7565 reflections	$\Delta\rho_{min} = -0.58$ e Å^{-3}
446 parameters	Extinction correction: *SHELXTL*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0050 (6)

Table 1
Selected geometric parameters (Å, °).

N1—C20	1.341 (3)	N2—C30	1.486 (3)
N1—C24	1.347 (3)	C4—C7	1.483 (4)
N1—C19	1.486 (3)	C11—C13	1.480 (4)
N2—C27	1.337 (3)	C22—C25	1.484 (4)
N2—C28	1.339 (3)		
N1—C19—C16	110.9 (2)	N2—C30—C1^i	111.8 (2)
C3—C4—C7—C8	24.0 (4)	C17—C16—C19—N1	−38.5 (4)
C5—C4—C7—C12	24.4 (4)	C23—C22—C25—C29	13.0 (4)
C12—C11—C13—C18	−19.1 (4)	C21—C22—C25—C26	13.9 (4)
C10—C11—C13—C14	−18.9 (4)	C27—N2—C30—C1^i	−75.0 (3)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W1$\cdots$O2W	0.84 (2)	1.96 (3)	2.782 (4)	166 (4)
O1W—H2W1$\cdots$F3	0.84 (1)	2.06 (4)	2.883 (4)	167 (4)
O2W—H1W2$\cdots$F7	0.83 (4)	2.49 (5)	3.222 (4)	147 (4)
O2W—H1W2$\cdots$F8	0.83 (4)	2.19 (4)	2.963 (4)	155 (5)
O2W—H2W2$\cdots$F2^i	0.83 (4)	2.20 (4)	2.890 (4)	141 (5)
C19—H19A$\cdots$F9^{ii}	0.97	2.32	3.051 (4)	131
C21—H21$\cdots$F7^{iii}	0.93	2.49	3.365 (4)	158
C24—H24$\cdots$O1W^{iv}	0.93	2.48	3.161 (5)	130
C27—H27$\cdots$O1W^{iii}	0.93	2.46	3.364 (5)	163
C28—H28$\cdots$F9^v	0.93	2.43	3.321 (3)	160
C29—H29$\cdots$F12^i	0.93	2.46	3.384 (4)	171
C30—H30B$\cdots$F4^{iii}	0.97	2.53	3.280 (4)	134

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1+x, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $x, 1+y, z$.

The H atoms of the tetracation were fixed geometrically and allowed to ride on the parent non-H atoms, with C—H distances of 0.93 or 0.96 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of the water molecules were located from a difference map and their positional parameters were refined with restraints on the O—H distances; the isotropic displacement parameters were set equal to $1.5U_{eq}(O)$. The reflection (132) was removed during refinement, as the observed and calculated structure factors showed a large disagreement. The R_{int} value is high (0.114), owing to the poor diffraction quality of the crystal.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 1990).

References

Amabilino, D. B. & Stoddart, J. F. (1995). Chem. Rev. 95, 2725–2828.
Asakawa, M., Brown, C. L., Pasini, D., Stoddart, J. F. & Wyatt, P. G. (1996). J. Org. Chem. 61, 7234–7235.
Hart, H. & Rajakumar, P. (1995). Tetrahedron, 51, 1313–1336.
Lorente, A., Fernandez-Saiz, M., Herraiz, F., Lehn, J. M. & Vigneron, J. P. (1999). Tetrahedron Lett. 40, 5901–5904.
Nardelli, M. (1995). J. Appl. Cryst. 28, 659.
Odell, B., Reddington, M. V., Slawin, A. M. Z., Spencer, N., Stoddart, J. F. & Williams, D. J. (1988). Angew. Chem. Int. Ed. Engl. 27, 1547–1550.
Rajakumar, P & Srinivasan, K. (2002). Eur. J. Org. Chem. Submitted.
Scheytza, H., Rademacher, O. & Reibig, H.-U. (1999). Eur. J. Org. Chem. pp. 2373–2381.
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (1997). SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). SMART and SAINT. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). Acta Cryst. A46, C-34.