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Crystal structure of 7^2,7^3,7^5,7^6-tetrafluoro-2^5,4^4-dimethyl-3^1,3^3,3^6,3^8-tetraoxo-3^1,3^2,3^3,3^6,3^7,3^8-hexahydro-3(2,7)-benzo[*lmn*][3,8]phenanthrolina-1,5(4,1)-dipyridin-1-iuma-2,4(1,2),7(1,4)-tribenzenacyclooctaphane-1^1,5^1-diium hexafluoridophosphate, $[C_{46}H_{28}F_4N_4O_4][PF_6]_2$, a dicationic cyclophane

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Abstract

$C_{46}H_{28}F_{16}N_4O_4P_2$, monoclinic, $P2_1/n$ (no. 14), a = 9.3041(2) Å, b = 22.4679(5) Å, c = 19.9446(3) Å, β = 98.154(2)°, V = 4,127.14(14) Å^3, Z = 4, $R_{gt}(F)$ = 0.0478, $wR_{ref}(F^2)$ = 0.1411, T = 173(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of materials

Bis(4-methyl-2-(4-pyridyl)phenyl)-naphthalenediimide (156 mg, 0.26 mmol) and 1,4-bis(bromomethyl)tetrafluorobenzene (87 mg, 0.26 mmol) were stirred in acetonitrile at 60 °C for 4 h under nitrogen protection. The yellow precipitate was collected by vacuum filtration and dissolved in water. When a saturated aqueous solution of ammonium hexafluorophosphate was added to the reaction mixture, the resulting precipitate was filtered off and then washed with deionized water. The precipitate was dried to afford yellowish solids. Single crystals were grown by slow diffusion of diethyl ether into an acetonitrile solution over 7 days of 7^2,7^3,7^5,7^6-tetrafluoro-

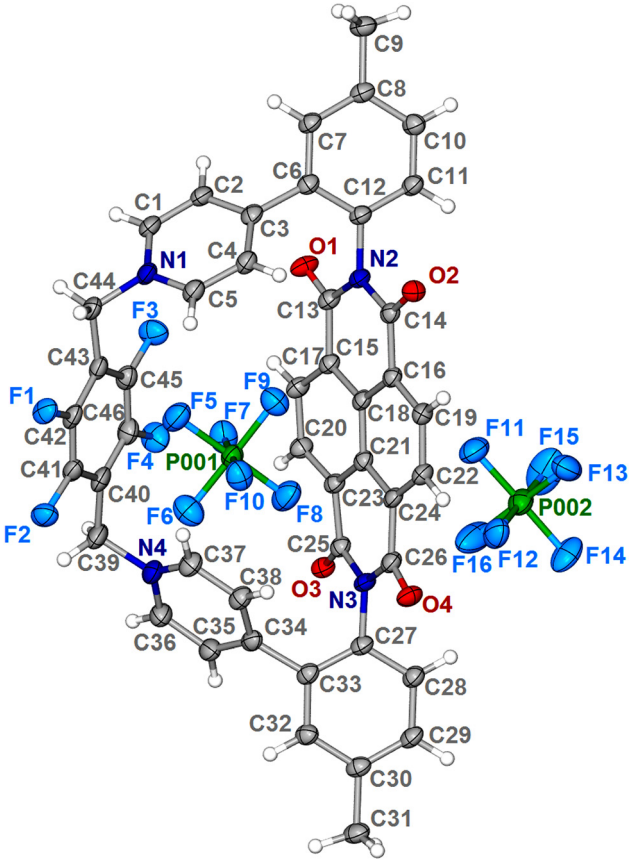

Table 1: Data collection and handling.

Crystal:	Colorless prism
Size:	0.26 × 0.21 × 0.20 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	2.11 mm^{-1}
Diffractometer, scan mode:	RIGAKU XtaLAB P200, φ and ω
θ_{max}, completeness:	73.9°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	24,672, 8,169, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6,826
$N(param)_{refined}$:	651
Programs:	Bruker,[1] SHELX,[2,3] Olex2[4]

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
P001	0.69407 (7)	0.51807 (3)	0.38952 (3)	0.03046 (15)
F1	0.49150 (17)	0.68605 (6)	0.43832 (7)	0.0375 (3)
O1	0.48231 (18)	0.54505 (7)	0.07785 (9)	0.0340 (4)
N1	0.5653 (2)	0.68551 (8)	0.24132 (10)	0.0285 (4)
C1	0.5183 (3)	0.70573 (9)	0.17805 (12)	0.0290 (5)
H1	0.4431	0.7346	0.1711	0.035*
P002	0.51806 (8)	0.22304 (3)	0.14149 (4)	0.03846 (17)
F2	0.31869 (18)	0.60855 (7)	0.48862 (7)	0.0408 (4)
O2	0.94359 (18)	0.48221 (7)	0.15257 (8)	0.0297 (3)
N2	0.7131 (2)	0.51324 (8)	0.11432 (9)	0.0250 (4)
C2	0.5789 (3)	0.68465 (9)	0.12392 (12)	0.0284 (5)
H2	0.5466	0.6994	0.0797	0.034*
F3	0.31345 (18)	0.62016 (7)	0.21714 (7)	0.0424 (4)
O3	0.20501 (17)	0.32481 (7)	0.27488 (8)	0.0287 (3)
N3	0.4352 (2)	0.30320 (8)	0.32486 (9)	0.0258 (4)
C3	0.6885 (2)	0.64132 (9)	0.13371 (11)	0.0267 (5)
F4	0.14714 (18)	0.54069 (7)	0.26835 (8)	0.0456 (4)
O4	0.66646 (19)	0.27980 (7)	0.37181 (9)	0.0332 (4)
N4	0.1738 (2)	0.46717 (8)	0.41146 (10)	0.0319 (4)
C4	0.7369 (3)	0.62307 (10)	0.19998 (12)	0.0300 (5)
H4	0.8134	0.5949	0.2085	0.036*
F5	0.6962 (2)	0.58933 (7)	0.39752 (8)	0.0524 (4)
C5	0.6742 (3)	0.64571 (10)	0.25282 (12)	0.0306 (5)
H5	0.7079	0.6332	0.2978	0.037*
F6	0.59622 (19)	0.51433 (8)	0.44920 (8)	0.0502 (4)
C6	0.7491 (2)	0.61629 (10)	0.07547 (11)	0.0259 (4)
F7	0.55357 (18)	0.52266 (8)	0.33482 (8)	0.0493 (4)
C7	0.7873 (3)	0.65436 (10)	0.02536 (11)	0.0279 (5)
H7	0.7712	0.6959	0.0290	0.034*
F8	0.6942 (2)	0.44807 (7)	0.38362 (9)	0.0564 (5)
C8	0.8482 (3)	0.63282 (10)	−0.02959 (11)	0.0287 (5)
F9	0.79308 (18)	0.52315 (8)	0.33052 (8)	0.0468 (4)
C9	0.8902 (3)	0.67474 (11)	−0.08247 (12)	0.0347 (5)
H9A	0.8041	0.6965	−0.1035	0.052*
H9B	0.9310	0.6520	−0.1172	0.052*
H9C	0.9629	0.7030	−0.0611	0.052*
F10	0.83624 (18)	0.51497 (7)	0.44573 (8)	0.0459 (4)
C10	0.8703 (3)	0.57155 (10)	−0.03398 (11)	0.0293 (5)
H10	0.9155	0.5561	−0.0701	0.035*
F11	0.51311 (19)	0.29313 (7)	0.12781 (9)	0.0504 (4)
C11	0.8271 (3)	0.53295 (10)	0.01367 (11)	0.0281 (5)
H11	0.8390	0.4913	0.0088	0.034*
F12	0.5986 (2)	0.23415 (7)	0.21726 (8)	0.0533 (4)
C12	0.7669 (2)	0.55476 (9)	0.06795 (11)	0.0253 (4)
F13	0.6737 (2)	0.21884 (8)	0.11739 (9)	0.0540 (4)
C13	0.5612 (3)	0.51196 (9)	0.11421 (11)	0.0270 (5)
F14	0.5245 (2)	0.15311 (7)	0.15714 (11)	0.0583 (5)
C14	0.8136 (2)	0.47653 (9)	0.15412 (11)	0.0250 (4)
F15	0.4402 (3)	0.21142 (10)	0.06742 (12)	0.0871 (8)
C15	0.5059 (2)	0.46879 (9)	0.16051 (11)	0.0248 (4)
F16	0.3675 (2)	0.22751 (9)	0.16927 (14)	0.0770 (7)
C16	0.7540 (2)	0.43153 (9)	0.19700 (11)	0.0247 (4)
C17	0.3600 (3)	0.46748 (10)	0.16541 (12)	0.0283 (5)
H17	0.2969	0.4963	0.1421	0.034*
C18	0.6026 (2)	0.42906 (9)	0.19868 (11)	0.0242 (4)
C19	0.8461 (3)	0.39324 (10)	0.23634 (12)	0.0283 (5)
H19	0.9475	0.3947	0.2345	0.034*
C20	0.3039 (3)	0.42366 (10)	0.20470 (12)	0.0282 (5)
H20	0.2025	0.4220	0.2065	0.034*
C21	0.5469 (2)	0.38675 (9)	0.24040 (11)	0.0243 (4)
C22	0.7911 (3)	0.35226 (10)	0.27901 (12)	0.0282 (5)
H22	0.8555	0.3265	0.3065	0.034*
C23	0.3952 (2)	0.38313 (9)	0.24066 (11)	0.0250 (4)
C24	0.6437 (2)	0.34906 (9)	0.28139 (11)	0.0252 (4)
C25	0.3353 (2)	0.33521 (9)	0.27957 (11)	0.0252 (4)
C26	0.5878 (3)	0.30767 (9)	0.32944 (11)	0.0279 (5)
C27	0.3787 (3)	0.26335 (9)	0.37213 (11)	0.0266 (4)
C28	0.4056 (3)	0.20286 (10)	0.36826 (12)	0.0290 (5)
H28	0.4575	0.1878	0.3342	0.035*
C29	0.3562 (3)	0.16432 (10)	0.41463 (12)	0.0301 (5)
H29	0.3757	0.1229	0.4121	0.036*
C30	0.2788 (3)	0.18515 (10)	0.46448 (11)	0.0292 (5)
C31	0.2286 (3)	0.14348 (11)	0.51588 (12)	0.0351 (5)
H31A	0.1629	0.1136	0.4925	0.053*
H31B	0.1774	0.1662	0.5471	0.053*
H31C	0.3128	0.1236	0.5414	0.053*
C32	0.2480 (3)	0.24585 (10)	0.46598 (11)	0.0288 (5)
H32	0.1918	0.2606	0.4986	0.035*
C33	0.2982 (3)	0.28547 (9)	0.42051 (11)	0.0272 (5)
C34	0.2578 (3)	0.34945 (10)	0.42200 (11)	0.0282 (5)
C35	0.1137 (3)	0.36595 (10)	0.42211 (12)	0.0319 (5)
H35	0.0426	0.3363	0.4262	0.038*
C36	0.0736 (3)	0.42476 (11)	0.41634 (13)	0.0344 (5)
H36	−0.0253	0.4355	0.4158	0.041*
C37	0.3140 (3)	0.45294 (10)	0.41483 (13)	0.0331 (5)
H37	0.3837	0.4836	0.4133	0.040*
C38	0.3595 (3)	0.39452 (10)	0.42043 (12)	0.0313 (5)
H38	0.4597	0.3851	0.4232	0.038*
C39	0.1246 (3)	0.53109 (10)	0.40713 (15)	0.0377 (6)
H39A	0.0298	0.5335	0.3776	0.045*
H39B	0.1100	0.5448	0.4529	0.045*
C40	0.2295 (3)	0.57166 (10)	0.38012 (13)	0.0329 (5)
C41	0.3190 (3)	0.61012 (10)	0.42123 (11)	0.0306 (5)
C42	0.4063 (3)	0.65059 (9)	0.39512 (11)	0.0300 (5)
C43	0.4077 (3)	0.65662 (9)	0.32627 (12)	0.0285 (5)
C44	0.4927 (3)	0.70561 (10)	0.29904 (12)	0.0320 (5)
H44A	0.4265	0.7390	0.2841	0.038*
H44B	0.5670	0.7204	0.3357	0.038*
C45	0.3177 (3)	0.61765 (10)	0.28505 (12)	0.0315 (5)
C46	0.2329 (3)	0.57637 (10)	0.31106 (13)	0.0337 (5)

2^5,4^4-dimethyl-3^1,3^3,3^6,3^8-tetraoxo-3^1,3^2,3^3,3^6,3^7,3^8-hexahydro-3(2,7)-benzo[*lmn*][3,8]phenanthrolina-1,5(4,1)-dipyridin-1-iuma-2,4(1,2),7(1,4)-tribenzenacyclooctaphane-1^1,5^1-diium hexafluoridophosphate.

2 Experimental details

The crystal structure was determined using the Shelxt program[2] and subsequently underwent refinement via the Shelxl tools[3] available in the Olex2 suite.[4] The hydrogen atoms were placed in idealized positions and allowed to ride on the relevant carbon atoms.

3 Comment

Macrocyclic hosts with cavities are the major workhorses in supramolecular chemistry,[5] and they can play a central role in molecular recognition[6] and be used to construct complex systems such as molecular machines[7] and other 'smart' materials.[8] Despite many recent advances in the development of new macrocyclic hosts,[9] their rational design remains a great challenge, due to low yields and tedious purifications. It is known that structural preorganization of building blocks facilitates the ring-closure process for constructing macrocyclic structures.[10] Herein, an syn-atropisomer based on naphthalene diimide (NDI) can be employed as a preorganized precursor to rationally construct a dicationic organic macrocycle, and the crystallographic structure of this macrocycle in the form of hexafluorophosphate salt has been elucidated.

The title compound crystallizes in the monoclinic space group $P2_1/n$ with one whole macrocycle molecule in the asymmetric unit (see the figure). As depicted in the graphical representation, this macrocycle is composed of an NDI skeleton, a tetrafluorobenzene linker and two lateral pyridinium groups, exhibiting an anticipated trapezoid-shape box-like structure. The centroid–centroid separation of the parallel NDI and phenyl units is ~6.1 Å, which is sufficient to accommodate planar molecules via face-to-face π–π stacking.[11–13] The crystal lattice also contains two counter anions hexafluorophosphate. Bond lengths and angles are all in the normal range, and are very similar to those given in the literature.[12–14] In addition, the hexafluorophosphate ions interact with the electron-deficient NDI and tetrafluorobenzene rings via anion-p interactions, wherein the distances between *F* and centroid are 3.0322(1), 3.0537(1) and 3.0799(1) Å, which are all typical for anion-π interactions.[15]

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