

Novel clay-like and helical superstructures generated using arene–arene interactions

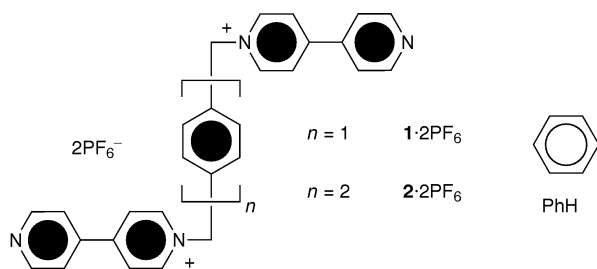
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Two novel supramolecular arrays are reported, which rely upon the noncovalent linking of cationic 4,4'-pyridylpyridinium units by enclathrated benzene (PhH) molecules through aromatic π - π interactions. Dicationic clathrands, consisting of two 4,4'-pyridylpyridinium units connected *via* arylidimethylene spacers, are cocrystallized with PhH to generate clathrated supramolecular arrays. A *p*-xylyl-spaced dicationic clathrand crystallizes with PhH to produce a layered solid, in which π -stacked dication-PhH layers are separated by bands containing PF_6^- anions and PhH molecules to form a superstructure that is reminiscent of an organic clay. On the other hand, its *p,p'*-bitolyl-spaced congener cocrystallizes with PhH to create a novel helical supramolecular array.

The noncovalent synthesis of clathrates¹ is a field of supramolecular chemistry² that is still captivating scientists' imaginations,³ even though clathrated systems have been known since the beginning of the nineteenth century. Indeed, their importance in present-day chemistry is highlighted by their incorporation into several significant industrial processes¹ involving, for example, recognition, transport and catalysis. In furtherance of our studies on crystal engineering⁴ utilizing π - π stacking and $[\text{C}-\text{H}\cdots\pi]$ interactions,^{5, 6} we have crystallized the dicationic bis(hexafluorophosphate) salts $1 \cdot 2\text{PF}_6$ ⁷ and $2 \cdot 2\text{PF}_6$ ⁸ in the presence of benzene (PhH). The formation of novel clathrated supramolecular arrays, which are held together primarily by arene–arene interactions,⁹ has been revealed. In this article, we discuss the self-assembly¹⁰ of these polymeric supramolecular architectures¹¹ in the solid state, as determined by single crystal X-ray analyses.



Results and Discussion

The X-ray analysis of a single crystal, formed by liquid diffusion of PhH into a MeNO_2 solution of $1 \cdot 2\text{PF}_6$, reveals a unit cell that contains a single dication and three PhH molecules positioned about the crystallographic symmetry centers, together with two PF_6^- anions. The dications adopt an *anti* geometry and pack to form (Fig. 1) staircase-like arrays with the near-planar 4,4'-pyridylpyridinium rings of one dication being π -stacked with those of the next with a mean interplanar separation of 3.39 Å. Adjacent stacks in the crystallo-

graphic *a* direction are arranged so as to create a box-like cavity between lattice-translated 4,4'-pyridylpyridinium units, within which one of the three crystallographically-independent PhH solvent molecules is trapped. The principal host–guest interaction is a face-to-face π - π stacking interaction, the mean interplanar separation between the PhH molecule and the sandwiching 4,4'-pyridylpyridinium units being 3.42 Å.¹² The adjacent π -stacked host–guest sheets within the crystal are essentially planar and are separated by *ca.* 9 Å. The interstitial region of the clathrated structure is occupied by the PF_6^- anions and the remaining two crystallographically independent PhH solvent molecules to produce (Fig. 2) an intercalated¹³ 'organic clay'-like¹⁴ structure. In view of the disorder of the PF_6^- anions, we have not carried out an analysis of any potential $[\text{C}-\text{H}\cdots\text{F}]$ interactions.

The X-ray analysis of a single crystal, obtained when a MeNO_2 solution of $2 \cdot 2\text{PF}_6$ was layered with PhH, reveals

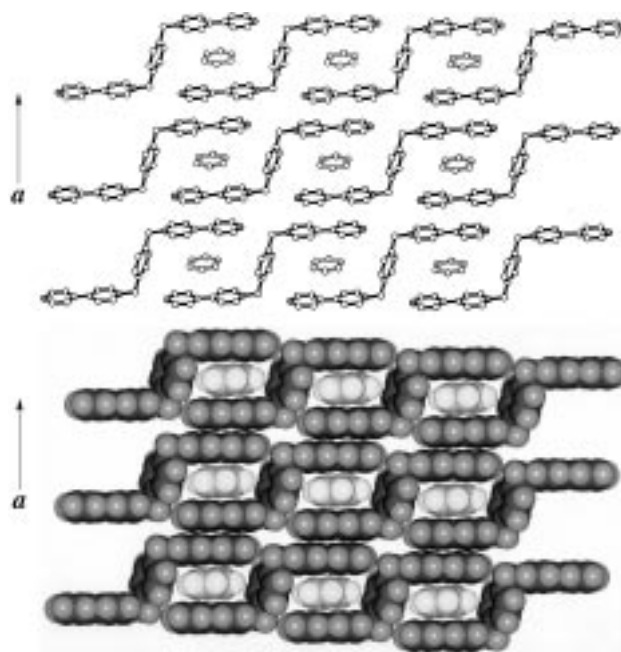


Fig. 1 Views of the π -stacked $[(1 \cdot \text{PhH})^{2+}]_n$ sheets. Top: ball-and-stick representation. Bottom: space-filling representation

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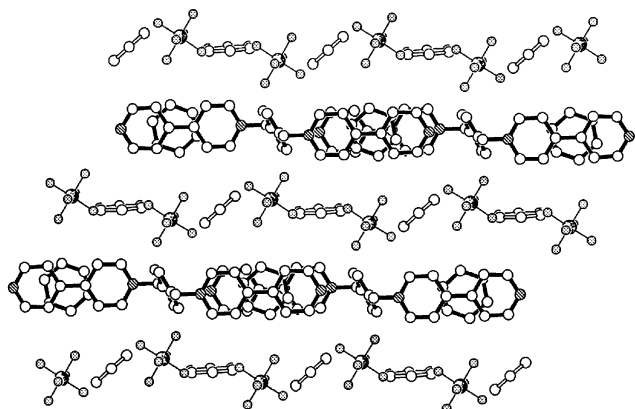


Fig. 2 Ball-and-stick representation depicting the alternating $[(1 \cdot \text{PhH})^{2+}]_n$ and $[(\text{PF}_6)_2 \cdot (\text{PhH})_2]^{2-}_n$ layers of the 'organic clay'

the formation of a 1 : 2 complex $[2 \cdot 2\text{PF}_6 \cdot (\text{PhH})_2]$, wherein the dication sustains a distinctly different conformation from its *p*-xylyl-spaced analog, *viz.*, 1^{2+} . Once again, the dication adopts a semi-extended geometry, although, in this case, with a skewed conformation: the $\text{N} \cdots \text{CH}_2 \cdots \text{CH}_2 \cdots \text{N}$ 'molecular torsion angle' (where the N atoms are the terminal pyridyl N atoms) is *ca.* 118° [*cf.* 180° for 1^{2+} (*vide supra*)]. Inspection of the packing of the complex's constituents reveals (Fig. 3) the formation of a helical superstructure^{15,16} in which one of the two included PhH molecules is sandwiched between the pyridinium ring of one dication and the pyridyl ring of its screw-related neighbor in the crystallographic *c* direction. The mean interplanar separations between the PhH guest and the pyridyl and pyridinium rings of the dicationic host are 3.58 and 3.51 Å, respectively, consistent with a π -stacked arrangement. There is a weak edge-to-face interaction (centroid-centroid separation 5.43 Å) between the PhH molecule and

one of the biphenylene rings. However, there is a slightly stronger inter-dication $[\text{C}-\text{H} \cdots \pi]$ interaction between the pyridinium ring of one dication and the other biphenylene ring of the next (the ring centroid-centroid separation is 5.21 Å and the $[\text{H} \cdots \pi]$ distance 2.95 Å). There are no significant interactions involving the other included PhH molecule. Enantiomeric helices pack with the pyridyl ring of the 4,4'-pyridylpyridinium unit—which is not involved in the face-to-face and edge-to-face interactions described above—of one helix lying parallel to, and overlying one of, the faces of the biphenylene ring system of the next: the mean interplanar separation is *ca.* 3.60 Å. As was observed in the previous crystal structure, the PF_6^- anions exhibit rotational disorder; hence, we have not attempted an analysis of possible anion-cation interactions.

Conclusions

We have demonstrated that the dicationic salts $1 \cdot 2\text{PF}_6$ and $2 \cdot 2\text{PF}_6$ form¹⁷ clathrated supramolecular arrays with PhH that are held together principally as a result of arene-arene interactions.⁹ In both of the examples described in this article, only *one* PhH guest molecule is incorporated into the cavities defined by the dicationic clathrands. Presumably, this preference for the enclathration of only a single guest molecule within the hosts' cavities dictates the formation of the helical $[(2 \cdot \text{PhH})^{2+}]_n$ superstructure—and not a sheet-like architecture analogous to the $[(1 \cdot \text{PhH})^{2+}]_n$ system—when $2 \cdot 2\text{PF}_6$ is cocrystallized with PhH. These results were not readily predictable and were only discovered empirically. Indeed, it is only through meticulous experimentation and analysis of intermolecular interactions, like the ones displayed here, that we may eventually be able to design⁴ solid state supramolecular architectures rationally, using noncovalent bonding interactions, with the level of control and precision that the synthetic chemist relies upon to fabricate complex *molecular* species using covalent bonds.

Experimental

Preparation of clathrands and X-ray quality single crystals

The syntheses of the dicationic clathrands $1 \cdot 2\text{PF}_6$ ⁷ and $2 \cdot 2\text{PF}_6$ ⁸ have already been described in the literature. Crystal growing techniques resembled those described by Jones.¹⁸ PhH was carefully layered on top of a solution of the dicationic salts (*ca.* 15 mg) in MeNO_2 (0.35 mL) in an NMR tube (5×200 mm). Single crystals, suitable for the X-ray analyses, were obtained after several days, when the PhH had diffused totally into the MeNO_2 layer.

X-Ray crystallographic analyses for $1 \cdot 2\text{PF}_6 \cdot 3\text{PhH}$ and $2 \cdot 2\text{PF}_6 \cdot 2\text{PhH}$

For $1 \cdot 2\text{PF}_6$, $\text{C}_{28}\text{H}_{24}\text{N}_4 \cdot 2\text{PF}_6 \cdot 3\text{PhH}$, $M = 940.8$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.298(3)$, $b = 10.671(3)$, $c = 11.046(3)$ Å, $\alpha = 64.63(2)$, $\beta = 87.60(2)$, $\gamma = 86.29(2)^\circ$, $V = 1094.4(5)$ Å³, $Z = 1$ (the superstructure has crystallographic C_i symmetry), $D_c = 1.43$ g cm⁻³, $\mu = 17.0$ cm⁻¹, $F(000) = 484$. For $2 \cdot 2\text{PF}_6$, $\text{C}_{34}\text{H}_{28}\text{N}_4 \cdot 2\text{PF}_6 \cdot 2\text{PhH}$, $M = 938.8$, orthorhombic, space group $Pna2_1$ (no. 33), $a = 25.690(2)$, $b = 15.520(1)$, $c = 11.416(1)$ Å, $V = 4551.6(7)$ Å³, $Z = 4$, $D_c = 1.37$ g cm⁻³, $\mu = 16.3$ cm⁻¹, $F(000) = 1928$. Data for both structures were measured at 293 K on a Siemens P4/PC diffractometer with Cu-K α radiation (graphite monochromator) using ω -scans. For $1 \cdot 2\text{PF}_6$ and $2 \cdot 2\text{PF}_6$, 3445 and 3581 independent reflections, respectively, were measured ($2\theta \leq 124^\circ$ for $1 \cdot 2\text{PF}_6$ and 120° for $2 \cdot 2\text{PF}_6$). Of these, 2993 and 2580, in turn, had $|F_0| > 4\sigma(|F_0|)$, and were considered to be observed. The data were corrected for Lorentz

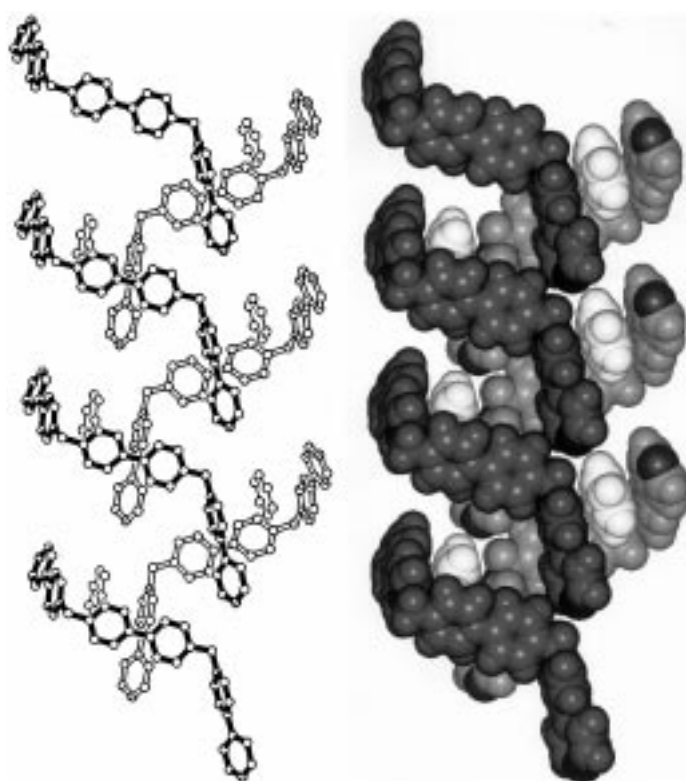


Fig. 3 Views of the helical $[(2 \cdot \text{PhH})^{2+}]_n$ supramolecular array, which is sustained by a combination of π - π and $[\text{C}-\text{H} \cdots \pi]$ interactions. Left: ball-and-stick portrayal. Right: space-filling representation

and polarization factors. The structures were solved by direct methods and all the major occupancy non-hydrogen atoms were refined anisotropically. In both structures, the PF_6^- anions and the included PhH solvent molecules were disordered. In each case, two discrete orientations were identified, the major occupancy orientation being refined anisotropically. The geometries of the PhH molecules were optimized. The positions of the hydrogen atoms were idealized, assigned isotropic thermal parameters [$U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$] and allowed to ride on their parent carbon atoms. Refinements were by full matrix least squares based on F^2 to give $R_1 = 0.094$, $wR_2 = 0.268$ ($1 \cdot 2\text{PF}_6$) and 0.068 , 0.187 ($2 \cdot 2\text{PF}_6$) for the observed data and 314 and 674 parameters, respectively. The maximum and minimum residual electron densities in the final ΔF maps for $1 \cdot 2\text{PF}_6$ and $2 \cdot 2\text{PF}_6$ were 0.59 , -0.63 , and 0.26 , -0.24 e \AA^{-3} , respectively. Computations were carried out using the SHELXTL PC program system.¹⁹ The polarity of $2 \cdot 2\text{PF}_6$ was determined unambiguously by employing the Flack parameter, which refined to a value of $0.04(17)$.

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