observed is in the distortion of the cation framework. Any contribution from the disorder of the propionate groups is secondary to this but not necessarily negligible. The actual distortions present have been shown to be compatible with the regular distortions present in the related DSP structure, though the actual magnitude is much less (approximately one third as large). This result provides substantial confirmation of the hypothesis of Glazer *et al.* (1981). Earlier Monte Carlo experiments to investigate whether the short-range ordering could be caused directly by the interaction between neighbouring propionate groups gave no support to that hypothesis and we must conclude that any mechanism must be related more directly to the cation framework.

I am grateful to Dr A. M. Glazer for suggesting this problem to me and for the use of the diffuse scattering data shown in Fig. 4, and to Dr J. Epstein with whom I have had fruitful discussions.

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Structure of Piperidinium Tris(pyrocatecholato)ferrate(III) Sesquihydrate

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(*Received* 21 *October* 1981; *accepted* 8 *February* 1982)

Abstract

The structure of $(C_5H_{12}N)_3[Fe(C_6H_4O_2)_3].1\cdot5H_2O$ (M_r = 665·64) is reported. Crystals are monoclinic, space group $C2/c$ with a = 27·887 (4), b = 11·747 (1), c = 23·999 (3) Å, β = 118·19 (1)°, Z = 8, V = 6929·3 Å^3, $F(000)$ = 2848. Full-matrix least-squares refinement, with fixed H atoms, converged with R = 0·052 (3422 independent reflections). The anion is propeller shaped, with trigonally distorted octahedral coordination of the metal ion, and the piperidinium cations exhibit the chair conformation. The structure is extensively hydrogen bonded in sheets approximately perpendicular to [100]. It includes a large hydrophobic pocket which contains the 'half' water molecule and can accept small organic molecules giving rise to variable measured densities.

Introduction

Many of the iron-transport complexes known as siderophores exploit pyrocatechol (1,2-dihydroxybenzene) as the chelating group for binding Fe^{III} (Neilands, 1974). Interest in these complexes has stimulated several studies of the Fe^{III}–pyrocatechol system by a variety of techniques including crystallography (Raymond, Isied, Brown, Fronczek & Nibert, 1975; Anderson, Buckingham, Robertson, Webb, Murray & Clark, 1976). Elsewhere we have reported the structure of a dimeric complex, piperidinium μ-acetato-di-μ-pyrocatecholato-bis[(pyrocatecholato)ferrate(III)], $(C_5H_{12}N)_3[(CH_3COO)\{Fe(C_6H_4O_2)_2\}_2]$, isolated from the Fe–pyrocatechol system under conditions of low base (Anderson, Webb, Buckingham & Robertson, 1982). In the present paper we report the structure of

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0567-7408/82/071927-05$01.00

the monomeric species piperidinium tris(pyrocatecholato)ferrate(III) sesquihydrate which is obtained from the Fe^{III}–pyrocatechol system with excess piperidine base. The structure of this readily prepared air-stable Fe^{III} complex is of significance to the Fe^{III} siderophores and to the intradiol dioxygenases, pyrocatechase and protocatechuate-3,4-dioxygenase (Nozaki, 1970; Que & Heistand, 1979). The structures of the analogous potassium salts $K_3[M(C_6H_4O_2)_3].1{\cdot}5\ H_2O$ (M = Fe^{III}, Cr^{III}) have been reported by Raymond *et al.* (1975) and a preliminary account of the present work has appeared elsewhere (Anderson *et al.*, 1976).

Structure analysis

Well formed, deep-burgundy-coloured crystals were obtained from the reaction mixture of basic ferric acetate, pyrocatechol and excess piperidine. Air was not excluded from the reaction vessel.

Crystals are monoclinic with systematic absences (hkl for $h + k = 2n + 1$, $h0l$ for $l = 2n + 1$) consistent with either of the space groups Cc or $C2/c$. The centrosymmetric group ($C2/c$) was confirmed by the structure analysis.

Reflection intensities were recorded on a Picker FACS-1 diffractometer in θ–2θ continuous scan mode [scan velocity 2° min^{-1} 2θ, 2 × 10 s background counts at extremes, $3 < 2\theta < 125°$, Cu $K\alpha$ radiation, graphite monochromator (λ = 1·5418 Å), T = 293 ± 1 K, reflection forms recorded $h,k,\pm l$]. Unit-cell dimensions and the crystal-orientation matrix were determined by least squares from observed setting angles for twelve high-angle well dispersed reflections ($63 < 2\theta < 81°$, λ = 1·54051 Å). Crystal dimensions in the **a**, **b** and **c*** directions, respectively, were 0·016 × 0·028 × 0·011 cm. Developed faces were (101), (011), (01$\bar{1}$), (1$\bar{1}$0) and ($\bar{2}\bar{1}$0).

Intensities of three standard reflections (2,0,16, 22,0,$\overline{12}$, 080) were monitored at intervals of fifty reflections. No significant intensity variations were observed. Including standards, 6320 reflections were measured. Reflection data with $I < 3\sigma(I)$ or with background imbalance $\Delta/\sigma \geq 3$ were rejected. The remainder were reduced to $|F_o|$ and $\sigma(F_o)$ values with instrumental uncertainty constant p^2 = 0·002 (Busing & Levy, 1957; Corfield, Doedens & Ibers, 1967). Data were not corrected for absorption (μ = 39·98 cm^{-1}) or for extinction. R_s for the terminal data set (Robertson & Whimp, 1975) was 0·032 (3422 unique data).

The structure was solved using *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). Space group Cc was assumed and the largest 400 normalized structure amplitudes were employed. The second E map examined (ABS FOM = 0·89, R_k = 30·2) allowed two Fe and 42 lighter atoms to be identified. Subsequent difference syntheses located all remaining non-hydrogen atoms, except the half waters, in each of two complete formula units. The derived coordinates confirmed the presence of inversion symmetry and, hence, space group $C2/c$. Coordinates were transformed accordingly and refinement continued in $C2/c$. Atom scattering factors were taken from Cromer & Waber (1965) with the anomalous-scattering corrections for Fe taken from Cromer (1965). Stewart, Davidson & Simpson (1965) scattering factors were used for H. Scattering contributions from water molecule H atoms (three) were at no stage included in the refinement. Contributions from all other H atoms [48, located by calculation, d(C—H) = 0·95, d(N—H) = 0·85 Å] were included but not refined. Refinement was continued using large-block least-squares analysis with isotropic thermal parameters specified for H atoms [$B_H = 1{\cdot}1 \times (\bar{B}_C, B_N)$], anisotropic parameters for the remainder, and only one water molecule included in the scattering model. Analytical data are consistent with 1·5 water molecules per formula unit (D_c = 1·276 g cm^{-3}) but measured densities (>1·285 g cm^{-3}, flotation in organic media) appeared to indicate two water molecules. However, subsequent difference syntheses showed the sesquihydrate formulation to be correct, with the O of the remaining half water occupying the special fourfold position at 0,½,½ (site symmetry $\bar{1}$). Vibration amplitudes for this O are very large, consistent with the low electron density in the difference peak (*ca* 1·7 e Å^{-3}), but the (refined) occupancy parameter does not differ significantly from unity. Refinement was completed by full-matrix least-squares analysis. At convergence R = 0·052, R_w = 0·092 and $s = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ = 1·31. Except for OX(2) (Δ/σ max. = 0·92) final shift to e.s.d. ratios were all less than 0·5. The most prominent feature in the final difference map was a peak of 0·9 e Å^{-3} located 2·1 Å from OX(2). A peak of 0·4 e Å^{-3} (at 0·262, 0·162, 0·180) located 0·9 Å from OX(1) and 1·8 Å from O(12) can be attributed reliably to the H-bonding H atom on water O atom OX(1) (O—H···O = 164°). Two other small peaks [both at 0·9 Å from OX(1)] are each possible sites for the second H with the calculated H—O—H and H—O···H angles favouring the higher peak at 0·305, 0·121, 0·233 (96°, 117°, 0·3 e Å^{-3}, *cf.* 89°, 76°, 0·2 e Å^{-3}). Neither site is sterically inhibited and neither can be involved in H bonding. Remaining features in the map were all less than ±0·5 e Å^{-3} in height.

Coordinates of non-H atoms are listed in Table 1.* Atom nomenclature for the complex anion is defined in Fig. 1. Piperidinium atoms P(nm) (n = 1–3, m = 1–6) are numbered consecutively in each ring with carbons

* Tables of anisotropic thermal parameters, H-atom coordinates and observed and calculated structure factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36784 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)†
Fe(1)	0·2421 (1)	−0·0009 (1)	0·0671 (1)	2·56
O(1)	0·1621 (1)	−0·0448 (2)	0·0178 (1)	2·88
O(2)	0·2113 (1)	0·1161 (2)	0·1013 (1)	2·79
O(3)	0·2591 (1)	−0·1133 (2)	0·0155 (1)	2·75
O(4)	0·2432 (1)	0·1090 (2)	0·0037 (1)	2·61
O(5)	0·2584 (1)	−0·1151 (2)	0·1375 (1)	2·87
O(6)	0·3190 (1)	0·0475 (2)	0·1292 (1)	3·00
C(1)	0·1303 (2)	0·0316 (3)	0·0259 (2)	2·80
C(2)	0·0737 (1)	0·0309 (3)	−0·0058 (2)	3·45
C(3)	0·0444 (2)	0·1123 (4)	0·0069 (2)	4·21
C(4)	0·0701 (2)	0·1952 (4)	0·0516 (2)	4·06
C(5)	0·1267 (2)	0·1984 (3)	0·0841 (2)	3·43
C(6)	0·1568 (1)	0·1185 (3)	0·0718 (2)	2·64
C(7)	0·2629 (1)	−0·0619 (3)	−0·0322 (2)	2·61
C(8)	0·2718 (2)	−0·1202 (3)	−0·0774 (2)	3·45
C(9)	0·2767 (2)	−0·0617 (4)	−0·1242 (2)	4·15
C(10)	0·2726 (2)	0·0573 (4)	−0·1271 (2)	3·97
C(11)	0·2616 (2)	0·1155 (3)	−0·0844 (2)	3·25
C(12)	0·2555 (1)	0·0577 (3)	−0·0378 (2)	2·59
C(13)	0·3093 (1)	−0·1050 (3)	0·1855 (2)	2·82
C(14)	0·3307 (2)	−0·1777 (4)	0·2373 (2)	4·43
C(15)	0·3837 (2)	−0·1615 (5)	0·2848 (2)	6·15
C(16)	0·4146 (2)	−0·0766 (5)	0·2808 (2)	6·03
C(17)	0·3941 (2)	−0·0042 (4)	0·2291 (2)	4·47
C(18)	0·3415 (1)	−0·0180 (3)	0·1808 (2)	2·79
P(11)	0·3439 (1)	0·2354 (3)	0·0777 (1)	3·19
P(12)	0·3715 (2)	0·3349 (3)	0·1186 (2)	4·18
P(13)	0·4246 (2)	0·2989 (4)	0·1735 (2)	4·56
P(14)	0·4610 (2)	0·2407 (5)	0·1523 (2)	5·28
P(15)	0·4320 (2)	0·1412 (4)	0·1092 (2)	4·54
P(16)	0·3788 (2)	0·1806 (4)	0·0546 (2)	3·94
P(21)	0·1873 (1)	−0·1494 (3)	0·1820 (2)	4·13
P(22)	0·1343 (2)	−0·1906 (4)	0·1307 (2)	4·43
P(23)	0·0918 (2)	−0·1914 (5)	0·1521 (2)	5·33
P(24)	0·0857 (2)	−0·0757 (5)	0·1754 (3)	6·43
P(25)	0·1398 (2)	−0·0364 (5)	0·2273 (2)	5·75
P(26)	0·1830 (2)	−0·0361 (4)	0·2066 (2)	4·89
P(31)	0·3480 (1)	−0·2711 (3)	0·0616 (1)	3·40
P(32)	0·3853 (2)	−0·1770 (4)	0·0643 (2)	4·33
P(33)	0·4431 (2)	−0·2182 (4)	0·0945 (2)	5·12
P(34)	0·4610 (2)	−0·2685 (5)	0·1585 (2)	6·01
P(35)	0·4222 (2)	−0·3625 (4)	0·1542 (2)	5·12
P(36)	0·3642 (2)	−0·3206 (4)	0·1246 (2)	4·12
OX(1)	0·2816 (1)	0·1784 (3)	0·2231 (1)	5·19
OX(2)	0·0	0·5	0·5	41·07

† $B_{eq} = \frac{1}{3}\sum_i \sum_j \beta_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

P(n2) and P(n6) bonded to N atoms P(n1) *etc.* Figs. 2 and 3 were drawn with *ORTEP* (Johnson, 1976). Computations were performed on the Univac 1100-42 computer at the Australian National University Computing Centre using previously described programs (Robertson & Whimp, 1975). Bond distances and angles are given in Table 2.

Table 2. *Bond lengths* (Å) *and interbond angles* (°)

Fe—O(1)	2·037 (2)	C(13)—C(14)	1·389 (5)
Fe—O(2)	1·993 (2)	C(13)—C(18)	1·401 (5)
Fe—O(3)	2·014 (2)	C(14)—C(15)	1·389 (6)
Fe—O(4)	2·008 (2)	C(15)—C(16)	1·352 (7)
Fe—O(5)	2·033 (2)	C(16)—C(17)	1·384 (6)
Fe—O(6)	2·032 (2)	C(17)—C(18)	1·384 (5)
O(1)—C(1)	1·338 (4)	P(11)—P(12)	1·486 (5)
O(2)—C(6)	1·339 (4)	P(11)—P(16)	1·476 (5)
O(3)—C(7)	1·342 (4)	P(12)—P(13)	1·505 (5)
O(4)—C(12)	1·340 (4)	P(13)—P(14)	1·497 (7)
O(5)—C(13)	1·346 (4)	P(14)—P(15)	1·517 (6)
O(6)—C(18)	1·335 (4)	P(15)—P(16)	1·515 (5)
C(1)—C(2)	1·390 (5)	P(21)—P(22)	1·487 (5)
C(1)—C(6)	1·425 (5)	P(21)—P(26)	1·486 (6)
C(2)—C(3)	1·382 (5)	P(22)—P(23)	1·498 (6)
C(3)—C(4)	1·373 (6)	P(23)—P(24)	1·510 (7)
C(4)—C(5)	1·393 (5)	P(24)—P(25)	1·505 (7)
C(5)—C(6)	1·381 (5)	P(25)—P(26)	1·503 (7)
C(7)—C(8)	1·400 (5)	P(31)—P(32)	1·501 (5)
C(7)—C(12)	1·418 (5)	P(31)—P(36)	1·478 (5)
C(8)—C(9)	1·377 (5)	P(32)—P(33)	1·500 (6)
C(9)—C(10)	1·402 (6)	P(33)—P(34)	1·495 (7)
C(10)—C(11)	1·381 (5)	P(34)—P(35)	1·514 (6)
C(11)—C(12)	1·387 (5)	P(35)—P(36)	1·511 (6)
O(1)—Fe—O(2)	81·14 (10)	C(8)—C(9)—C(10)	120·1 (4)
O(1)—Fe—O(3)	89·37 (10)	C(9)—C(10)—C(11)	119·9 (4)
O(1)—Fe—O(4)	97·35 (10)	C(10)—C(11)—C(12)	120·7 (4)
O(1)—Fe—O(5)	93·97 (10)	O(4)—C(12)—C(7)	116·9 (4)
O(1)—Fe—O(6)	169·84 (10)	O(4)—C(12)—C(11)	123·5 (4)
O(2)—Fe—O(3)	168·08 (9)	C(7)—C(12)—C(11)	119·6 (4)
O(2)—Fe—O(4)	91·87 (10)	O(5)—C(13)—C(14)	123·0 (3)
O(2)—Fe—O(5)	94·79 (10)	O(5)—C(13)—C(18)	117·0 (3)
O(2)—Fe—O(6)	90·94 (10)	C(14)—C(13)—C(18)	120·0 (3)
O(3)—Fe—O(4)	82·14 (9)	C(13)—C(14)—C(15)	119·5 (4)
O(3)—Fe—O(5)	93·06 (10)	C(14)—C(15)—C(16)	120·6 (4)
O(3)—Fe—O(6)	99·24 (10)	C(15)—C(16)—C(17)	120·7 (4)
O(4)—Fe—O(5)	167·64 (10)	C(16)—C(17)—C(18)	120·3 (4)
O(4)—Fe—O(6)	89·22 (10)	O(6)—C(18)—C(13)	117·2 (3)
O(5)—Fe—O(6)	80·27 (10)	O(6)—C(18)—C(17)	123·9 (3)
Fe—O(1)—C(1)	111·4 (2)	C(13)—C(18)—C(17)	118·9 (3)
Fe—O(2)—C(6)	113·5 (2)	P(12)—P(11)—P(16)	111·3 (3)
Fe—O(3)—C(7)	111·5 (2)	P(11)—P(12)—P(13)	110·2 (3)
Fe—O(4)—C(12)	112·0 (2)	P(12)—P(13)—P(14)	112·1 (4)
Fe—O(5)—C(13)	112·6 (2)	P(13)—P(14)—P(15)	110·8 (4)
Fe—O(6)—C(18)	112·9 (2)	P(14)—P(15)—P(16)	110·1 (4)
O(1)—C(1)—C(2)	125·1 (3)	P(15)—P(16)—P(11)	111·0 (3)
O(1)—C(1)—C(6)	117·0 (3)	P(22)—P(21)—P(26)	112·6 (3)
C(2)—C(1)—C(6)	117·8 (3)	P(21)—P(22)—P(23)	110·9 (4)
C(1)—C(2)—C(3)	120·7 (4)	P(22)—P(23)—P(24)	111·6 (4)
C(2)—C(3)—C(4)	121·3 (4)	P(23)—P(24)—P(25)	109·8 (4)
C(3)—C(4)—C(5)	119·3 (4)	P(24)—P(25)—P(26)	111·9 (4)
C(4)—C(5)—C(6)	120·3 (4)	P(25)—P(26)—P(21)	111·0 (4)
O(2)—C(6)—C(1)	116·0 (3)	P(32)—P(31)—P(36)	112·1 (3)
O(2)—C(6)—C(5)	123·6 (3)	P(31)—P(32)—P(33)	110·3 (4)
C(1)—C(6)—C(5)	120·4 (3)	P(32)—P(33)—P(34)	112·7 (4)
O(3)—C(7)—C(8)	123·7 (4)	P(33)—P(34)—P(35)	109·7 (4)
O(3)—C(7)—C(12)	117·4 (4)	P(34)—P(35)—P(36)	111·5 (4)
C(8)—C(7)—C(12)	118·8 (4)	P(35)—P(36)—P(31)	110·5 (3)
C(7)—C(8)—C(9)	120·7 (4)		

Description of the structure

The structure is comprised of infinite sheets of anions, cations and type 1 [OX(1)] water molecules interlinked *via* H bonding. Part of one such sheet, viewed parallel to **a**, is shown in Fig. 2 and some additional detail is shown schematically in Fig. 1. Sheets are not cross linked (by H bonding) and are apparently bound together only by normal van der Waals forces. The type

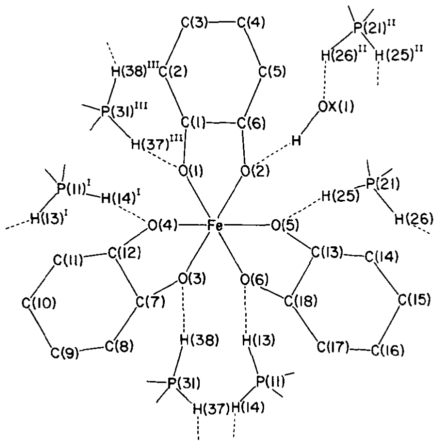

Fig. 1. Atom nomenclature for the complex anion.

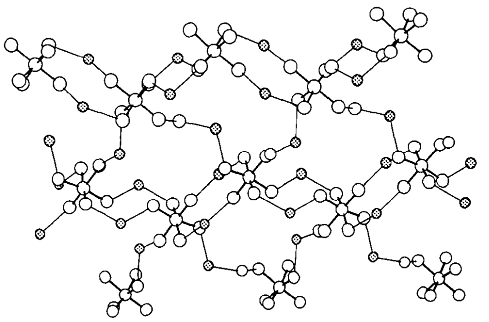

Fig. 2. Interconnecting H bonds in a single sheet of anions, cations and water molecules. C and H atoms have been omitted. Piperidinium N atoms are shown shaded.

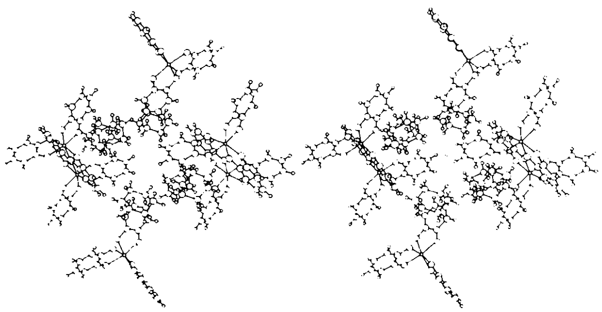

Fig. 3. Detail of the crystal packing around water molecule OX(2), showing the cavity centred on this atom.

2 [OX(2)] water molecule is not involved in the H-bond network but is located at the centre $(0,\frac{1}{2},\frac{1}{2})$ of a large cavity bounded by hydrophobic groups (Fig. 3).

The anion exhibits the expected propeller shape and has approximate D_3 symmetry. Metal–ligand distances range from 1·993 (2) to 2·037 (2) Å and the ligand bite angles range from 80·3 (1) to 82·1 (1)°. The trigonal twist angle is 46·5 (8)°, *cf.* 60° for regular octahedral and 0° for trigonal-prismatic coordination. Carbon skeletons in ligands (1) and (3) are planar within experimental error (Δ < 0·01 Å) while that in ligand (2) is marginally aplanar ($\Delta_{max} \simeq$ 0·03 Å). One or more O atoms in each ligand are significantly displaced from the phenyl-group planes (Δ_{max} = 0·08 Å) and Fe-atom displacements are also significant (0·18, 0·01 and 0·09 Å respectively). Corresponding dihedral angles between the ring and O–Fe–O planes are 7·4, 3·3 and 3·1° (7·6, 2·2 and 2·9° to the C_6O_2 planes). The interligand dihedral angles are 87·0 (1–2), 77·7 (1–3) and 98·0° (2–3).

The piperidinium cations all have the chair conformation with each N linked to two O atoms (five pyrocatechol, one water) by N–H···O bonding (Fig. 1). Ring dimensions agree well with previously reported values (Dattagupta & Saha, 1975; Kashino, 1975; Fukuyama, Kashino & Haisa, 1975). Mean endocyclic bond angles range from 110·1 (6) (C–C–C) to 112·0 (4)° (C–N–C). The mean C–N distance is 1·486 (4) Å and the mean C–C distance is 1·506 (2) Å. The apparent contraction of the C–C distances from the standard value (1·542 Å) is larger than observed in previous studies and probably results from libration shortening. The small increase in the endocyclic angles from exact tetrahedral (109° 28′) is commonly observed and is almost certainly a result of distributed ring strain necessary to accommodate the hetero atom.

Discussion

The anion geometry differs only marginally from that observed in its potassium salt (Raymond *et al.*, 1975). The spread of metal–ligand distances is nearly identical in both salts and in the present instance [1·993 (2)–2·037 (2) Å] is certainly greater than can be attributed to experimental error. Trigonal twist angles are also in good agreement [46·5 (8)°, piperidinium (ppy^+) salt; 44·7 (10)°, K^+ salt] but dihedral angles between phenyl rings differ significantly [77·8, 86·3 and 98·9°, ppy^+; 68·6, 91·1 and 92·9°, K^+], reflecting the differences in crystal packing.

In the present structure the packing arrangement is such as to satisfy all of the H-bonding requirements of the ppy^+ cations (Table 3). Unusually, the H-bond requirement of water molecule OX(1) is only partially satisfied with just one H atom donated [to O(12)] and just one H atom accepted [from ppy^+ nitrogen P(21)]. Indeed, no other potential donor or acceptor atoms occur within 3·2 Å of OX(1).

Water molecule OX(2) at $0,\frac{1}{2},\frac{1}{2}$ is effectively encapsulated by hydrophobic groups and takes no part in H bonding. The encapsulating cavity has approximate dimensions 11 × 6·5 × 6·5 Å (Fig. 3) and can obviously include molecules larger than water. Its presence and the layered packing arrangement appear to be the factors which preclude sensible crystal-density measurements. Measured densities in apparently equili-

Table 3. *Hydrogen-bond parameters*

P(n1) are piperidinium N atoms.
H atoms, except on OX(1), were located by calculation.
Roman numerals denote symmetry operations to bring Y into contact with H: (I) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (II) $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z$; (III) $\frac{1}{2}-x, -\frac{1}{2}-y, -z$.

X—H···Y	X···Y (Å)	X—H (Å)	H···Y (Å)	∠X—H···Y (°)
OX(1)—H···O(2)	2·741 (3)	0·94	1·83	164
P(11)—H(13)···O(6)	2·774 (4)	0·88	1·92	163
P(11)—H(14)···O(4)$^{\mathrm{I}}$	2·929 (4)	0·88	2·14	150
P(21)—H(25)···O(5)	2·688 (4)	0·87	1·82	171
P(21)—H(26)···OX(1)$^{\mathrm{II}}$	2·858 (4)	0·88	1·99	173
P(31)—H(37)···O(1)$^{\mathrm{III}}$	2·808 (4)	0·88	1·94	168
P(31)—H(38)···O(3)	2·865 (4)	0·88	2·06	152

brated systems are uniformly greater than 1·285 g cm^{-3} (*cf.* D_c = 1·276 g cm^{-3}), and increase with immersion time to at least 1·35 g cm^{-3} consistent with progressive diffusion of density media into the cavity. In principle, dry crystal densities could be determined by extrapolating time-dependent measurements to $t = 0$, but we have not attempted such an experiment.

One author (JW) wishes to acknowledge the support of the Australian Research Grants Committee and a Murdoch University Special Research Grant.

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