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First Examples of Type I Clathrate Hydrates of Strong Acids: Polyhydrates of Hexafluorophosphoric, Tetrafluoroboric, and Perchloric Acid[1-3]

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Abstract: The new acid polyhydrates $HPF_6 \cdot 7.67H_2O$ and $HBF_4 \cdot 5.75H_2O$ and the known $HClO_4 \cdot 5.5H_2O$ were obtained by crystallization at reduced temperatures and studied by difference thermal analysis and X-ray diffraction. The compounds were identified as the first examples of hydrates of strong acids possessing the type I or cubic 12-Å crystal structure of the polyhedral clathrate hydrates. The dimensions a of the cubic unit cells are 11.774 (5) Å for $HPF_6 \cdot 7.67H_2O$ at −162 °C, 11.744 (5) Å for $HBF_4 \cdot 5.75H_2O$ at −165 °C, and 11.861 (3) Å for $HClO_4 \cdot 5.5H_2O$ at −80 °C. A reversible phase transition of higher order was detected for the $HClO_4$ hydrate at −110 °C. Due to disorder in the crystals an accurate structure determination (from Mo Kα diffractometer data) was successful only for the HPF_6 hydrate (space group $Pm\bar{3}n$, $Z = 6$, unweighted $R = 0.035$ for 522 observed independent reflections with $\theta \leq 32.5°$). The smaller pentagonal dodecahedral or $[5^{12}]$ voids of the hydrogen-bonded type I host structure $2[5^{12}] \cdot 6[5^{12}6^2] \cdot 46H_2O$ were found vacant. The larger tetrakaidecahedral $[5^{12}6^2]$ voids are centered by octahedral PF_6^- species as anionic guests, which are twofold orientationally disordered around an F–P–F axis perpendicular to the hexagonal faces. Disorder is also present in the cationic host structure, where the H atoms are distributed over two half occupied positions on every polyhedron edge, and statistical H_2O/HF substitution toward the ideal composition $HPF_6 \cdot 6.67H_2O \cdot HF$ must be assumed to account for the positive charge. Dimensional aspects of the clathration in all three structures and possible modes for the higher disorder in the HBF_4 and $HClO_4$ hydrates are discussed.

The clathrate hydrates or polyhedral hydrate inclusion compounds, equally distinctive and widespread, usually have hydrogen-bonded host structures which are neutral or anionic and correspondingly neutral or cationic guest species. This is typified by the gas and alkylamine hydrates on one hand and the peralkylonium salt hydrates on the other.[4] So far, only the isotypic strong acid hydrates $HEF_6 \cdot 5H_2O \cdot HF$ with E = P, As, Sb have been reported as clathrate hydrates with a *cationic* host structure (a solitary body-centered cubic structure, called type VII[4a] and incorporating hydrogen fluoride as well as the protons of the acid) and an anionic, i.e., deprotonated, guest species.[5]

Further clathrate hydrates of strong acids have now been found and identified. Of these, $HPF_6 \cdot 7.67H_2O$, $HBF_4 \cdot 5.75H_2O$, and $HClO_4 \cdot 5.5H_2O$ are the first examples possessing the prominent type I or cubic 12-Å structure and are dealt with in this paper. Two more compounds, $HAsF_6 \cdot 6H_2O$ and $HSbF_6 \cdot 6H_2O$, which are related to the hypothetical hexagonal type IV[4a] host structure, will be described elsewhere.[6]

Table I. Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å^2) for $HPF_6 \cdot 7.67H_2O$

atom[a]	Wyckoff position	x	y	z	B^b
P	6d	$^1/_4$	$^1/_2$	0	1.20 (1)
F(1)	12h	0.1141 (1)	$^1/_2$	0	2.53 (4)
F(2)	48l	0.2501 (2)	0.3696 (1)	0.0268 (5)	5.5 (2)
O(1)	6c	$^1/_4$	0	$^1/_2$	2.95 (6)
O(2)	16i	0.18371 (8)	x	x	2.04 (1)
O(3)	24k	0	0.3051 (1)	0.1247 (1)	2.25 (3)
H(13)	24k	0	0.440	0.209	4.0
H(22)	16i	0.230	x	x	4.0
H(23)	48l	0.122	0.229	0.162	4.0
H(31)	24k	0	0.367	0.165	4.0
H(32)	48l	0.074	0.260	0.155	4.0
H(33)	24k	0	0.319	0.067	4.0

[a] Statistical occupancy factors different from 1.0: 0.5 for F(2) and all H atoms. [b] For the non-H atoms calculated from the anisotropic B_{ij} by $(^1/_3)(B_{11} \cdot a^{*2} \cdot a^2 + ... + B_{23} \cdot b^* \cdot c^* \cdot b \cdot c \cdot \cos\alpha)$.

Table II. Interatomic Distances[a] (Å) and Angles[b] (deg) in the Host Structure of $HPF_6 \cdot 7.67H_2O$

O(1)...O(3)	2.729	O(2)...O(2)	2.704
O(2)...O(3)	2.684	O(3)...O(3)	2.936
$O(3)^c$...O(1)...$O(3)^d$	107.01	$O(3)^c$...O(1)...$O(3)^e$	114.52
O(2)...O(2)...O(3)	107.91	O(3)...O(2)...O(3)	111.99
O(1)...O(3)...O(2)	107.92	O(1)...O(3)...O(3)	122.74
O(2)...O(3)...O(2)	107.40	O(2)...O(3)...O(3)	105.01

[a] esd's: 0.001–0.002 Å. [b] esd's: 0.03–0.05°. [c] z, x, y. [d] $0.5 - z, 0.5 - y, 0.5 + x$. [e] $z, x, 1 - y$.

Results

Phase Relations and Unit Cells. From crystallization experiments at reduced temperatures a new polyhydrate was obtained of both hexafluorophosphoric and tetrafluoroboric acid. The compositions are $HPF_6 \cdot 7.67H_2O$ and $HBF_4 \cdot 5.75H_2O$, with melting points somewhat below room temperature and at −66 °C, respectively. By using low-temperature difference thermal analysis (DTA), the HBF_4 hydrate was further characterized as a stable hydrate phase in addition to others in the respective acid–water system. The result (Figure 1), at variance with previous work,[7] is largely paralleled by the system perchloric acid–water,[8] in particular by its polyhydrate phase $HClO_4 \cdot 5.5H_2O$ of similar composition, homogeneity range, and melting behavior. The melting point of this hydrate was confirmed within close limits as −45 °C. In addition a reversible higher order phase transition

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(1) This is paper 14 of our series Fluorides and Fluoro Acids and paper 24 of our series Crystal Structures of Acid Hydrates and Oxonium Salts.

(2) For papers 13 and 23, see: Mootz, D.; Wiebcke, M. *Z. Anorg. Allg. Chem.*, in press. Mootz, D.; Wiebcke, M. *Inorg. Chem.* **1986**, *25*, 3095–3097.

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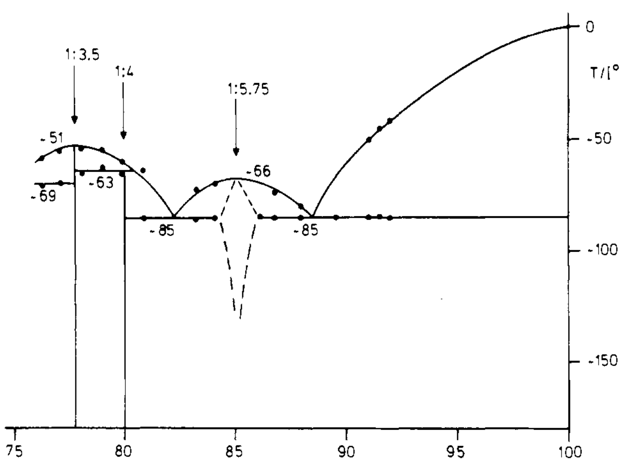

Figure 1. Melting diagram of the system HBF_4–H_2O in the water-rich range, showing the existence and stability ranges of three crystalline hydrates $HBF_4 \cdot nH_2O$ (n = 3.5, 4, 5.75).

was observed at −110 °C, which was not noticeable on temperature-dependent X-ray powder photographs and leaves single crystals undestroyed.

From X-ray powder photographs as well as single-crystal diffractometry, the three hydrates were found to be cubic with Laue group $m\bar{3}m$ and very similar values of the lattice constant a as given in the abstract. Oscillation photographs of the low-temperature form of the $HClO_4$ hydrate show an intricate pattern of relatively weak reflections in addition to strong ones characteristic of the high-temperature form and suggest a superstructure with possibly the same Laue group and a sixfold lattice constant.

Crystal Structures. The crystal data and powder line intensities clearly indicated the three hydrates to be clathrate hydrates or polyhedral hydrate inclusion compounds[4] with the type I (cubic 12-Å type) crystal structure. This was further substantiated for the HPF_6 hydrate by the results of a complete single-crystal X-ray structure analysis.

The hydrate crystallizes with the space group $Pm\bar{3}n$ and Z = 6 formula units per unit cell. The atomic parameters are summarized in Table I, the distances and angles between hydrogen-bonded O atoms in Table II. In the hydrogen bonds the H atoms are twofold disordered with observed ranges of 0.70–1.08 Å for bond lengths O–H, 1.61–2.26 Å for distances H···O, 103–116° for bond angles H–O–H, and 163–180° for hydrogen bonding angles O–H···O.

The pentagonal dodecahedral or $[5^{12}]$ void and the tetrakaidecahedral $[5^{12}6^2]$ void of the clathrate hydrate type I host structure of the unit cell formula $2[5^{12}] \cdot 6[5^{12}6^2] \cdot 46H_2O$ are shown in Figure 2. The smaller void is vacant in this crystal structure. The larger one is fully occupied by an octahedral PF_6^- anion. The compensation of the negative charge of the guest species by the host structure is dealt with in the Discussion.

The PF_6^- anion shows twofold orientational disorder around an F–P–F axis and across two crystallographic mirror planes perpendicular to the hexagonal faces. The angle between the two orientations is 23.3 (2)°. The two independent bonds P–F(1) and P–F(2) have lengths of 1.601 (2) and 1.568 (2) Å, respectively, not corrected for thermal motion. None of the F–P–F bond angles of the anion deviates significantly from the ideal values of 90 and 180°.

The distance between two F(1) atoms of adjacent anions on both sides of the hexagonal polyhedral face is 2.686 (2) Å. The shortest guest–host distances are 2.969 (4) Å for F···O and 2.59 (2) Å for F···H.

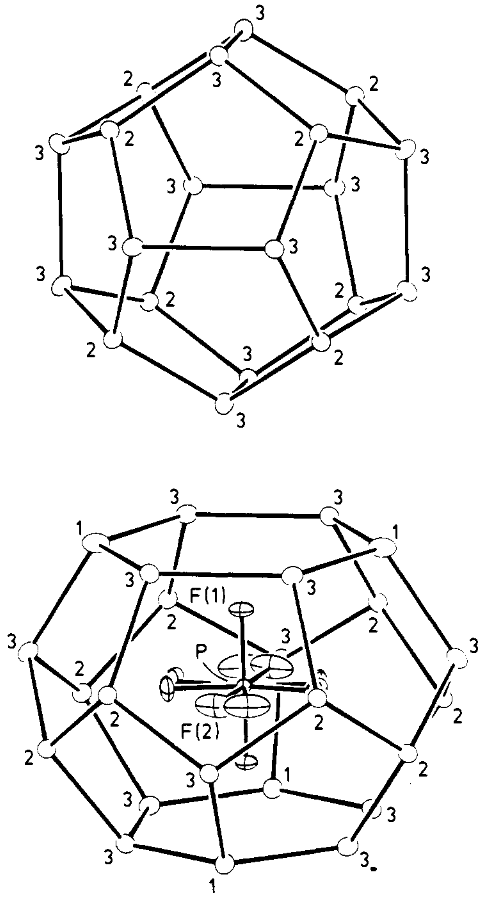

Figure 2. The $[5^{12}]$ (above) and the $[5^{12}6^2]$ void (below) in crystalline $HPF_6 \cdot 7.67H_2O$. Host structure O atoms designated by numbers only, disordered H atoms omitted for clarity, and thermal vibration ellipsoids having 30% probability.

The HBF_4 hydrate and the high-temperature form of the $HClO_4$ hydrate, which were also subjected to structure analysis, gave unsatisfactory results, which are not listed. This is probably due to a much higher degree of disorder in these crystals (see Discussion). As a consequence, even their compositions, taken initially from the maxima of the liquidus lines of the respective melting diagrams, were not certainly reconciled with the computations. Still the general features of the clathrate hydrate type I structure were confirmed for these hydrates, too, with the BF_4^- and ClO_4^- anions, respectively, probably in both the smaller and larger voids of the host structures.

Discussion

The compounds $HPF_6 \cdot 7.67H_2O$, $HBF_4 \cdot 5.75H_2O$, and $HClO_4 \cdot 5.5H_2O$, identified in this work as polyhedral type I clathrate hydrates, are the first examples of polyhydrates of strong inorganic Brønsted acids with this crystal structure. Differing from the polyhedral gas and alkylamine as well as peralkylonium salt hydrates,[4] the guest species are anionic, formed by deprotonation of the acid molecules. Consequently the host structures are cationic, i.e., protonated.

Protonation of the host structure, while maintaining a four-connected three-dimensional net of hydrogen-bonded water molecules with just the balanced and saturated 2:1 ratio of H to non-H atoms, can be achieved only with some additional structural change. Two possibilities are the following: (i) the removal of water molecules, thus creating vacancies in the host structure (at least one for every two excess protons to be accommodated), and (ii) the replacement, for every acid proton, of a water by a hydrogen fluoride molecule. The latter possibility with statistical distribution of the O and F host structure atoms, which is effective in the type VII clathrate hydrates $HEF_6 \cdot 5H_2O \cdot HF$ with E = P, As, Sb[5], is also assumed for the HPF_6 hydrate of this work. Its ideal composition, then, would be $HPF_6 \cdot 6.67H_2O \cdot HF$, which is not precluded by the way of its crystallization (see the Experimental Section).

The vacancy model, on the other hand, appears to be pertinent to the hydrogen fluoride-free HBF_4 and $HClO_4$ clathrate hydrates. In addition, vacancies in the host structures may enable the BF_4^- and ClO_4^- anions to better fit into the smaller besides the larger

Table III. Crystal Data and Parameters Related to Diffractometry and Refinement for $HPF_6 \cdot 7.67H_2O$

cryst syst	cubic
space group; Z	$Pm\bar{3}n$; 6
a, Å	11.774 (5)
V, Å^3	1632 (1)
temp, °C	−162
density (calcd), g·cm^{-3}	1.74
scan mode	variable ω scan
radiation	monochromatized Mo Kα
wavelength, Å	0.71073
μ(Mo Kα), cm^{-1}	3.6
range of θ, deg	1.5–32.5
octants collcd	$+h,+k,+l$
no. of total reflcns	3308
no. of indep reflcns all/obsd ($I > 1.96\sigma_I$)	560/522
R (all/obsd)	0.038/0.035
R_w (all/obsd)	0.048/0.048

voids. It is also conceivable, and known from other clathrate hydrate structures,[9] that vacant sites of the host structures are occupied by F or O atoms of the guests. This would lead to significantly off-centered additional modes of enclosure of the anions. All these possibilities and some more, e.g., partial occupation of the smaller voids also by molecules of the atmosphere and increased orientational freedom of the tetrahedral anions in the larger voids, probably contribute to the much higher degree of disorder actually observed for these hydrates when compared to the HPF_6 hydrate.

The PF_6^- anion as the biggest of the three anions has a largest van der Waals diameter of about 5.9 Å. It is noteworthy that neutral molecules of similar size, e.g., SF_6, are known to form gas hydrates of the *type II* structure,[10] in which they occupy the more spacious [$5^{12}6^4$] hexakaidecahedra.

Another interesting comparison is given by polyhydrates of strong *dibasic* acids with likewise octahedral and tetrahedral anions. A series of such structures has recently been determined, e.g., for $H_2SiF_6 \cdot 6H_2O$, $H_2SiF_6 \cdot 9.5H_2O$,[11] $H_2SO_4 \cdot 6.5H_2O$, and $H_2SO_4 \cdot 8H_2O$.[12] Although in most of them the water-to-acid ratio is even higher than in the hydrates of this work, the ratio of acid protons to water molecules and the hydrogen-bonding acceptor strength of the doubly charged anions are increased for all of them. As a consequence, the hydrogen-bonded cationic water structures are no longer polyhedral, and the anions are fully ordered. The crystal structures of most of the lower, nonclathrate hydrates of HBF_4[13] and $HClO_4$[14] have also been studied and found to be ionic.

Experimental Section

Materials. A solution with the approximate composition $HBF_4 \cdot 2H_2O$ was prepared by reacting HBO_2 with HF and was used as one of the components for the phase studies in the system HBF_4–H_2O. Single-crystal growth for the structure determinations was started from the following materials: a solution of about 11.7 mol % of HPF_6, prepared by adding H_2O to $HPF_6 \cdot 5H_2O \cdot HF$, which in turn was obtained from commercial 60–65% HPF_6[5a] (Ventron); a solution of 14.3 mol % HBF_4, prepared from $HBF_4 \cdot 2H_2O$ (see above); and a solution of 15.4 mol % $HClO_4$, prepared from 70% $HClO_4$ (Ferak, pa). Almost anhydrous HF was obtained by rectifying technical grade hydrofluoric acid (Riedel-de Häen, 71–75%). Compositions were checked by their acid equivalent and fluorine content. PTFE or polyethylene systems were used where necessary.

Phase Studies. For DTA the solutions were enclosed in PTFE or glass ampoules, as suitable. Samples for X-ray powder studies were prepared in the same way as those for the crystal growth experiments. The apparatus used and more experimental detail are described and referred to elsewhere.[15]

Crystal Growth. The starting materials were sealed in thin-walled glass capillaries or polyethylene tubings. The latter were also placed inside glass capillaries for mechanical fixation. Single crystals were grown on a Syntex $P2_1$ four-circle diffractometer equipped with a modified LT-1 low-temperature device. A miniature zone-melting technique using focused heat radiation[16] was applied while the samples were kept in an adjustable gas stream at temperatures somewhat below their melting points.

Structure Determinations. All X-ray measurements of single crystals were performed on the diffractometer with graphite-monochromatized Mo Kα radiation. The reflection intensities were not corrected for absorption. Crystallographic data and some experimental and computational figures for $HPF_6 \cdot 7.67H_2O$ are assembled in Table III.

A starting model was given by the structural relationship to the type I structure of the clathrate hydrates as recognized and completed and refined in the usual way. Half H atoms were located in a difference Fourier map of the electron density and treated in the refinement with fixed coordinates and thermal parameters. The function minimized was $\sum w(|F_o| - |F_c|)^2$. Reflections were weighted according to $w = 1/[\sigma_F^2 + (0.005F_o)^2]$. The scattering factors used were those of the neutral atoms with anomalous dispersion coefficients for the P atom.[17] All non-H atoms of the host structure were treated as O atoms, after initial refinement had shown no evidence of an ordered O/F substitution. A final difference Fourier map showed no significant electron density in the center of the pentagonal dodecahedral void.

Intensity measurements and structure computations were also performed on the HBF_4 and high-temperature $HClO_4$ hydrates. Various models of disorder were tried for these structures without definite solutions.

The computations were done with the E-XTL[18] program system on a Data General Eclipse S/200 computer. Figure 2 was generated by using the program ORTEP II[19] on a Telefunken TR 445 computer.

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Supplementary Material Available: Listings for $HPF_6 \cdot 7.67H_2O$ of anisotropic thermal parameters, distances and angles involving H atoms, and angles in the PF_6^- anion (2 pages); and a listing of structure factors (2 pages). Ordering information is given on any current masthead page.

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