O(3)—H(1)···O(4) and O(12)—H(2)···O(7) (see Table 3). In particular, the donor–acceptor distance O(12)—O(7) is remarkably short, at 2·448 Å. The corresponding distance in the Mn analogue is 2·500 Å, whereas the shortest distance reported in hydrates, as studied by neutron diffraction, is 2·546 Å (Chiari & Ferraris, 1982). However, shorter distances have been observed in the compounds $K_3Cu_2H(P_2O_7)_2$ (Effenberger, 1987) and $Na_5Cu_3H(PO_4)_4$ (Effenberger, 1985) where symmetric P—O···H···O—P bonds lead to donor–acceptor distances of 2·437 and 2·388 Å respectively.

Our attempts to prepare a purely divalent iron analogue of $Mn_7(PO_4)_2(HPO_4)_4$ led to the formation of dark green–grey crystals, perhaps indicative of some degree of oxidation, though not as far as $Fe_7(PO_4)_6$ itself. Single-crystal X-ray analysis of this phase (Lightfoot & Cheetham, 1986) does indeed suggest some degree of mixed-valence character, an approximate composition $Fe_6^{II}Fe^{III}(PO_4)_3(HPO_4)_3$ being deduced on the basis of bond-length bond-strength calculations. It was apparent from this experiment that Fe^{III} showed a marked preference for the *M*(2) and *M*(4) sites, which are found to be fully occupied by Fe^{III} in $Fe_7(PO_4)_6$ (Gorbunov *et al.*, 1980).

It is possible that a solid solution $Fe_7(PO_4)_2(HPO_4)_4$–$Fe_7(PO_4)_6$ may exist, with subtle control of experimental conditions governing the degree of oxidation. Mössbauer spectroscopy would clearly be of great value in studying this possibility in detail. Our own studies in these systems have now been extended to the solid solutions $(Mn,Fe)_7(PO_4)_6$ and $(Co,Fe)_7(PO_4)_6$, results of which will be presented in a forthcoming publication.

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References

ANDERSON, J. B., KOSTINER, E. & RUSZALA, F. A. (1976). *Inorg. Chem.* **15**, 2744–2748.

BROWN, I. D. & SHANNON, R. D. (1973). *Acta Cryst.* A**29**, 266–282.

CARRUTHERS, J. R. & WATKIN, D. J. (1979). *Acta Cryst.* A**35**, 698–699.

CHIARI, G. & FERRARIS, G. (1982). *Acta Cryst.* B**38**, 2331–2341.

CUDENNEC, Y., RIOU, A. & GERAULT, Y. (1986). *C. R. Acad. Sci. Sér.* II, **302**, 1149–1154.

EFFENBERGER, H. (1985). *Z. Kristallogr.* **172**, 97–104.

EFFENBERGER, H. (1987). *Acta Cryst.* C**43**, 1237–1239.

GORBUNOV, YU. A., MAKSIMOV, B. A., KABALOV, YU. K., IVASCHENKO, A. N., MEL'NIKOV, O. K. & BELOV, N. V. (1980). *Dokl. Akad. Nauk SSSR*, **254**, 873–877.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

KRISHAMACHARI, N. & CALVO, C. (1972). *Acta Cryst.* B**28**, 2883–2885.

LIGHTFOOT, P. & CHEETHAM, A. K. (1986). Abstr. IIIrd Eur. Conf. Solid State Chemistry, Regensburg, Federal Republic of Germany. Vol. II, p. 410.

NORD, A. G. (1974). *Acta Chem. Scand.* A**28**, 150–152.

RIOU, A., CUDENNEC, Y. & GERAULT, Y. (1987). *Acta Cryst.* C**43**, 821–823.

WATKIN, D. J., CARRUTHERS, J. R. & BETTERIDGE, P. W. (1985). *CRYSTALS User Guide.* Chemical Crystallography Laboratory, Univ. of Oxford, England.

Acta Cryst. (1988). C**44**, 1334–1337

Structures of (I) Hexafluoroaluminic Acid Hexahydrate and (II) Pentafluoroaluminic Acid Pentahydrate*

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Abstract. (I) $H_3AlF_6.6H_2O$, $M_r = 252{\cdot}08$, hexagonal, $R\bar{3}c$, $a = 9{\cdot}861$ (5), $c = 17{\cdot}497$ (2) Å, $V = 1473{\cdot}4$ Å^3, $Z = 6$, $D_x = 1{\cdot}71$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}292$ mm^{-1}, $F(000) = 780$, $T = 183$ K, $R = 0{\cdot}036$ for 471 unique observed reflections. (II) $H_2AlF_5.5H_2O$, $M_r = 214{\cdot}06$. Previously reported [Trunov, Efremov, Konstantinova, Velikodnyi & Golota (1980). *Sov. Phys. Dokl.* **25**, 508–509] structural data [monoclinic, *Pc*, $a = 7{\cdot}926$ (2), $b = 3{\cdot}651$ (2), $c = 13{\cdot}776$ (5) Å, $\beta = 108{\cdot}27$ (3)°, $Z = 2$] are newly interpreted in the centrosymmetric supergroup *P*2/*c* with the crystallographic axes unchanged. The crystalline compounds are oxonium salts, $(H_5O_2)_3AlF_6$ and $(H_5O_2)_2$-

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* Part 22 of the series *Fluorides and Fluoro Acids* and 29 of the series *Crystal Structures of Acid Hydrates and Oxonium Salts*. For parts 21 and 28 see Mootz & Merschenz-Quack (1988, 1987), respectively.

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$AlF_5.H_2O$, respectively. All $H_5O_2^+$ cations have a very short central hydrogen bond. In (I) the cations are further hydrogen-bonded to discrete AlF_6^{3-} anions of nearly perfect octahedral geometry in a three-dimensional network. In (II) the cations donate hydrogen bonds to neutral water molecules and/or infinite chain-like polyanions $[AlF_4F_{2/2}^{2-}]_n$ with distorted octahedral coordination at the Al atoms and the bridging F atoms in *trans* positions.

Introduction. In the course of our studies of hydrates of fluoro acids we have carried out an X-ray structure analysis of $H_3AlF_6.6H_2O$ (I). The results are reported below, along with a space-group reassignment and new interpretation of the structure of the related phase $H_2AlF_5.5H_2O$ (II), which had been determined previously from single-crystal X-ray data (Trunov, Eframov, Konstantinova, Velikoduyi & Golota, 1980).

Experimental. Crystals of (I) were obtained from the reaction of Al cuttings with an equimolar mixture of HF and H_2O. The composition was checked by chemical analysis. Low-temperature DTA and X-ray powder studies, also of some mixtures of (I) with H_2O, were performed as described elsewhere (Mootz & Poll, 1984), and yielded a congruent melting point for (I) of 309 K and a simple eutectic behavior of the system (I)—H_2O with the eutectic point at 250 K and *ca* 95 mol % H_2O.

Crystal growth for the structure determination was performed on a Syntex $P2_1$ diffractometer equipped with a low-temperature device. A liquid sample of (I) was sealed in polyethylene tubing (approximate diameter 0·4 mm inside and 0·8 mm outside), which for mechanical fixation was enclosed in a thin-walled glass capillary. A miniature zone-melting procedure using focused heat radiation was applied (Brodalla, Mootz, Boese & Osswald, 1985).

The X-ray measurements were performed after lowering the temperature of the cold gas stream. Graphite monochromator. Lattice constants from setting angles of 15 strong reflections with $35 < 2\theta < 44°$. Intensities by variable ω-scan technique. Three standard reflections every 100 reflections showed only small random variations. 2947 reflections were measured up to $(\sin\theta)/\lambda = 0{\cdot}704$ Å^{-1} in the hemisphere $0 \le h \le 11$, $-11 \le k \le 11$, $-11 \le l \le 11$, using a rhombohedral setting with $a = 8{\cdot}150\,(3)$ Å and $\alpha = 74{\cdot}45\,(3)°$. 52 reflections with too large intensities discarded. Transformation to hexagonal axes. 472 unique reflections after merging equivalent reflections, $R_{\rm int} = 0{\cdot}038$. Criterion for observed reflections $I > 1{\cdot}96\sigma(I)$, only one unobserved reflection.

Direct methods. Full-matrix least-squares refinement, function minimized $\sum w(\Delta F)^2$, observed reflections only, weighted according to $w = 1/\sigma^2(F)$. H atoms located by difference-Fourier method. In final refinement 33 parameters varied: one scale factor, coordinates of all atoms, anisotropic and isotropic thermal parameters for non-H atoms and H atoms, respectively; $wR = 0{\cdot}030$, $S = 3{\cdot}176$, all Δ/σ in last cycle 0·00. $\Delta\rho_{\rm min}$ and $\Delta\rho_{\rm max}$ in final difference Fourier synthesis −0·64 and +0·48 e Å^{-3}, respectively. Complex atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final atomic parameters of (I) are listed in Table 1.*

Table 1. *Atomic coordinates and* (*equivalent*) *isotropic thermal parameters* (Å^2) *for* (I) *with e.s.d.'s in parentheses*

	x	y	z	$U_{\rm eq}$*
Al	0·0	0·0	0·0	0·0194 (2)
F	−0·02566 (7)	0·13628 (7)	0·05901 (2)	0·0262 (2)
O	−0·24455 (10)	0·20262 (10)	0·02865 (3)	0·0314 (3)
H1	−0·1799 (21)	0·1726 (20)	0·0349 (7)	0·040 (4)
H2	−0·2792 (30)	0·1873 (27)	−0·0173 (10)	0·054 (5)
H3†	−0·3055 (43)	0·1873 (40)	0·0675 (15)	0·042 (9)

* For the non-H atoms calculated with $U_{\rm eq} = (1/3)(U_{11}a^{*2}a^2 + U_{12}a^*b^*ab\cos\gamma + \ldots)$.

† Occupancy factor 0·5, owing to disorder.

Table 2. *Atomic coordinates for* (II) *after conversion to P*2/*c*

	x	y	z	Derived from*
Al	0·0	−0·0182	0·25	Al
F1	0·1547	−0·0250	0·3773	F1, F3
F2	−0·1831	−0·0219	0·3006	F2, F4
F3	0·0	0·4804	0·25	F5
O1	0·4597	−0·3287	0·4193	O1, O3
O2	−0·1471	0·3656	−0·0318	O2, O4
O3	−0·5	−0·6621	0·25	O5
H11	0·352	−0·28	0·413	H11, H31
H12	0·472	−0·44	0·368	H12, H32
H13†	0·490	−0·44	0·472	H13
H21	−0·167	0·21	0·007	H21, H41
H22	−0·163	0·26	−0·086	H22, H42
H23†	−0·034	0·43	−0·006	H23
H3	−0·417	−0·78	0·265	H51, H52

* Atomic symbols as used by Trunov *et al.* (1980).

† Occupancy factor 0·5, owing to disorder.

The atomic coordinates of (II) (Trunov *et al.*, 1980) were found to conform very well to a higher-symmetry space group than reported, *i.e.* to *P*2/*c* instead of *Pc* only. New values derived for the smaller asymmetric unit in *P*2/*c* are listed in Table 2. They were obtained by an origin shift of 0·25 along **c**, pairwise merging of atoms related by the twofold axis, and assigning special positions to atoms where appropriate. The new positions of the non-H and the H atoms are within 0·035 and 0·38 Å, respectively, of the old ones.

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* Lists of structure factors and anisotropic thermal parameters for (I) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44924 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

All calculations were performed with the Nicolet (1983) *SHELXTL* program system on a Data General Eclipse S/140 computer. Illustrations were generated with the program *ORTEP*II (Johnson, 1976) on a Telefunken TR 445 computer.

Discussion. Crystalline (I) and (II) are oxonium salts with the structural formulae $(H_5O_2)_3AlF_6$ and $(H_5O_2)_2AlF_5.H_2O$, respectively, the latter being at variance with that of the previous work, $(H_3O)_2AlF_5.(H_2O)_3$ (Trunov *et al.*, 1980).

In the crystal structure of (I) the $H_5O_2^+$ cations are linked *via* hydrogen bonds to F atoms of the AlF_6^{3-} anions into infinite puckered ribbons of fused rings with two cations and two F atoms each. Part of a ribbon is illustrated in Fig. 1. The centrosymmetric six-membered rings have chair conformations and are *cis*-linked. The cations have point symmetry 2; the anions have a nearly perfect octahedral geometry (point symmetry $\bar{3}$). The ribbons run in three directions and are cross-linked by the anions (see Fig. 2). Interatomic distances and angles of (I) are listed in Table 3. The values are not corrected for thermal motion or for the systematic error of X-ray methods to produce O–H (and H···F) distances which are shorter (and longer) than the internuclear separations.

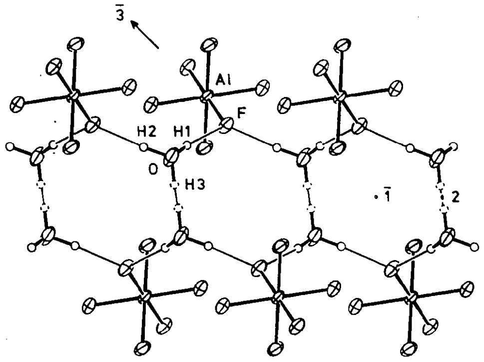

Fig. 1. Part of a ribbon of hydrogen-bonded atoms in the structure of (I). Thermal ellipsoids correspond to the 50% probability level. H atoms with arbitrary size, half-occupied positions with dotted circles.

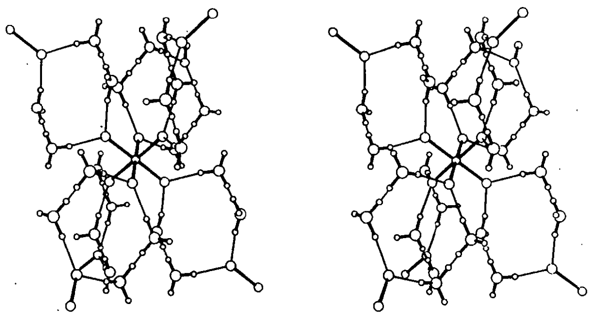

Fig. 2. The cross-linking function of the anion in (I), stereoscopic view.

Table 3. *Interatomic distances* (Å) *and angles* (°) *for* (I) *with e.s.d.'s in parentheses*

Al–F	1·810 (1)	O–H1	0·83 (2)
O–H2	0·86 (2)	O–H3	0·87 (3)
O···O^{i}	2·442 (2)	O···F	2·604 (2)
O···F^{ii}	2·590 (1)	H1···F	1·78 (2)
H2···F^{ii}	1·74 (2)	H3···O^{i}	1·59 (3)
F–Al–F^{iii}	89·3 (1)	F–Al–F^{iv}	90·7 (1)
F–Al–F^{v}	180·0	H1–O–H2	112 (2)
H1–O–H3	115 (3)	H2–O–H3	122 (3)
O–H1···F	172 (2)	O–H2···F^{ii}	169 (3)
O–H3···O^{i}	165 (4)		

Symmetry code: (i) $-\frac{2}{3}-x, -\frac{1}{3}-x+y, \frac{1}{6}-z$; (ii) $-\frac{1}{3}+x, \frac{1}{3}+x-y, -\frac{1}{6}+z$; (iii) $y, y-x, -z$; (iv) $-y, x-y, z$; (v) $-x, -y, -z$.

Table 4. *Interatomic distances* (Å) *and angles* (°) *for* (II) *after conversion to P*2/*c*

Al–F1	1·798	Al–F2	1·796
Al–F3	1·820	Al–F3^{i}	1·831
O1–H11	0·85	O1–H12	0·85
O1–H13	0·80	O2–H21	0·83
O2–H22	0·81	O2–H23	0·89
O3–H3	0·76	O1···F1	2·556
O1···O3^{ii}	2·737	O1···O1^{iii}	2·455
O2···F1^{iv}	2·578	O2···F2^{v}	2·564
O2···O2^{vi}	2·426	O3···F2^{i}	2·724
H11···F1	1·75	H12···O3^{ii}	1·89
H13···O1^{iii}	1·66	H21···F1^{iv}	1·79
H22···F2^{v}	1·75	H23···O2^{vi}	1·56
H3···F2^{i}	1·97		
F1–Al–F1^{iv}	180·0	F1–Al–F2	90·5
F1–Al–F2^{iv}	89·5	F1–Al–F3	90·8
F1–Al–F3^{i}	89·2	F2–Al–F2^{iv}	180·0
F2–Al–F3	90·4	F2–Al–F3^{i}	89·6
F3–Al–F3^{i}	180·0	H11–O1–H12	113
H11–O1–H13	102	H12–O1–H13	116
H21–O2–H22	105	H21–O2–H23	107
H22–O2–H23	110	H3–O3–H3^{vii}	111
O1–H11···F1	157	O1–H12···O3^{ii}	177
O1–H13···O1^{iii}	177	O2–H21···F1^{iv}	160
O2–H22···F2^{v}	176	O2–H23···O2^{vi}	167
O3–H3···F2	172		

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

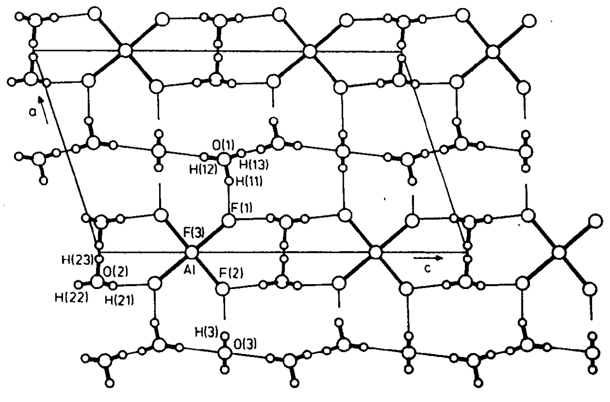

Fig. 3. Structure of (II) as projection on the *ac* plane. All atoms with arbitrary size. Interrupted lines indicate hydrogen bonds to atoms equivalent to and behind the ones shown.

The crystal structure of (II) with the newly assigned space-group symmetry *P*2/*c* is illustrated in Fig. 3. Infinite chain-like polyanions $[\mathrm{AlF_4F^{2-}_{2/2}}]_n$ with distorted octahedral coordination at the Al atoms and the bridging F atoms in *trans* positions (point symmetry 2 for both kinds of atoms) are extended parallel to the *b* axis. They are linked *via* hydrogen bonds with $\mathrm{H_5O_2^+}$ cations as well as chains of alternating $\mathrm{H_5O_2^+}$ cations and neutral water molecules (point symmetry 2) which run parallel to the *c* axis. The two independent cations lie on inversion centres of the space group. Interatomic distances and angles of (II) are listed in Table 4. They show a much better internal consistency than those of the reported *Pc* model of the structure (Trunov *et al.*, 1980), although in *P*2/*c* the atomic coordinates have not been further refined.

Each of the three independent $\mathrm{H_5O_2^+}$ cations [one in (I) and two in (II)] has a very short central hydrogen bond O—H···O, in which the H atom is disordered between two positions. In its four outer hydrogen bonds, to O and/or F atoms, each cation, in compliance with its positive charge, acts as the donor only, never as an acceptor, of the respective H atom. The behavior described is characteristic of this kind of cationic water species, which also occurs in many other hydrates of strong acids (Lundgren & Olovsson, 1976; Ratcliffe & Irish, 1986).

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References

BRODALLA, D., MOOTZ, D., BOESE, R. & OSSWALD, W. (1985). *J. Appl. Cryst.* **18**, 316–319.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

LUNDGREN, J.-O. & OLOVSSON, I. (1976). *The Hydrogen Bond*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, Vol. II. Amsterdam: North-Holland.

MOOTZ, D. & MERSCHENZ-QUACK, A. (1987). *Z. Naturforsch. Teil B*, **42**, 1231–1236.

MOOTZ, D. & MERSCHENZ-QUACK, A. (1988). *Acta Cryst.* C**44**, 924–925.

MOOTZ, D. & POLL, W. (1984). *Z. Naturforsch. Teil B*, **39**, 1300–1305.

Nicolet (1983). *SHELXTL Structure Determination System – Revision* 4.1. Nicolet XRD Corp., Madison, Wisconsin, USA.

RATCLIFFE, C. I. & IRISH, D. E. (1986). *Water Science Reviews, An Annual Journal*, edited by F. FRANKS, Vol. 2. Cambridge Univ. Press.

TRUNOV, V. K., EFREMOV, V. A., KONSTANTINOVA, L. I., VELIKODNYI, Y. A. & GOLOTA, A. F. (1980). *Sov. Phys. Dokl.* **25**, 508–509.

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Structure of Silyl Iodide at 116 K

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Abstract. $\mathrm{SiH_3I}$, $M_r = 158{\cdot}01$, monoclinic, $P2_1/c$, $a = 4{\cdot}564\,(5)$, $b = 8{\cdot}3878\,(21)$, $c = 10{\cdot}5086\,(21)$ Å, $\beta = 103{\cdot}13\,(7)°$, $U = 391{\cdot}8$ Å^3, $Z = 4$, $D_x = 2{\cdot}678$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71073$ Å, $\mu = 8{\cdot}282$ mm^{-1}, $F(000) = 280$, $T = 116$ K, $R = 0{\cdot}0238$ for 661 unique observed reflections. Molecules of silyl iodide are linked by short, 3·8030 (13) Å, I···Si intermolecular contacts into infinite zigzag chains characterized by Si—I···Si and I···Si—I angles of 84·14 (4) and 178·13 (5)° respectively. At 2·4533 (13) Å, the Si—I bond is significantly longer than the gas-phase value of 2·4384 (6) Å. Comparisons are drawn between the intermolecular geometries of the simple silyl halides $\mathrm{SiH_3}X$ (X = F, Cl, Br, I) and with the intramolecular geometries of the disilyl chalcogenides $(\mathrm{SiH_3})_2E$ (E = O, S, Se, Te).

Introduction. As part of our continuing programme of work on the solid-state structures of low-melting silyl compounds, we undertook a study of the simple silyl halides $\mathrm{SiH_3}X$ (X = F, Cl, Br, I). Of these four compounds, only the last presented no serious difficulties: the fluoride has no well defined liquid phase at ambient pressure and both the chloride and the bromide exhibit phase transformations near their freezing points which prevent the growth, stabilization or transfer of single crystals. Nevertheless, we were able to obtain a single crystal of $\mathrm{SiH_3F}$ and to determine its structure (Blake, Ebsworth, Henderson & Welch, 1985). Here we describe low-temperature X-ray powder diffraction studies which have established the gross structures of $\mathrm{SiH_3Cl}$ and $\mathrm{SiH_3Br}$ and a low-temperature single-crystal diffraction study of $\mathrm{SiH_3I}$.

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