On the existence of hydronium hydrates $H_9O_4^+$ and $H_{15}O_7^+$ in minerals

By JAN KUBISZ

Dept. of Mineralogy and Petrology, Academy of Mining and Metallurgy, Cracow, Poland

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Summary. Properties and possible structures of hydronium trihydrate $H_9O_4^+$ and hexahydrate $H_{15}O_7^+$ are considered. From the 2330 minerals listed in Strunz's mineralogical tables nineteen were selected that appear to contain $H^+.4H_2O$ or $H^+.7H_2O$, and the possibility of discrete $H_9O_4^+$ or $H_{15}O_7^+$ groupings existing in their crystal lattice is discussed. From a crystallochemical point of view the most probable examples of hydronium hydrate compounds are layer lattice minerals like H-montmorillonite, H-vermiculite, troegerite, H-meta-autunite, sabugalite, and hewettite.

THE existence of the individual H_3O^+ pyramidal complex, called the hydronium ion, or sometimes the hydroxonium or oxonium[1] ion, in crystalline substances is a well-established fact. The best examined examples of hydronium compounds are 'hydrates' of strong inorganic acids. These compounds contain oxygens associated with three nearly equidistant protons forming H_3O^+ ions, as has been proven directly by means of nuclear magnetic resonance (Richards and Smith, 1951), Raman (Taylor and Vidale, 1956), infra-red spectroscopy (Bethell and Sheppard, 1953), X-ray diffraction (Luzzati, 1951), and neutron scattering (Janik, 1964).[2] Several authors have also indirectly demonstrated the occurrence of the hydronium ion in minerals (see, for instance, Shishkin, 1951; Halla and van Tassel, 1956; Smith, Gruner, and Lipscomb, 1957; Kubisz, 1961*a*, *b*, and 1964; White and Burns, 1963; Brophy and Sheridan, 1965; Ross and Evans, 1965).

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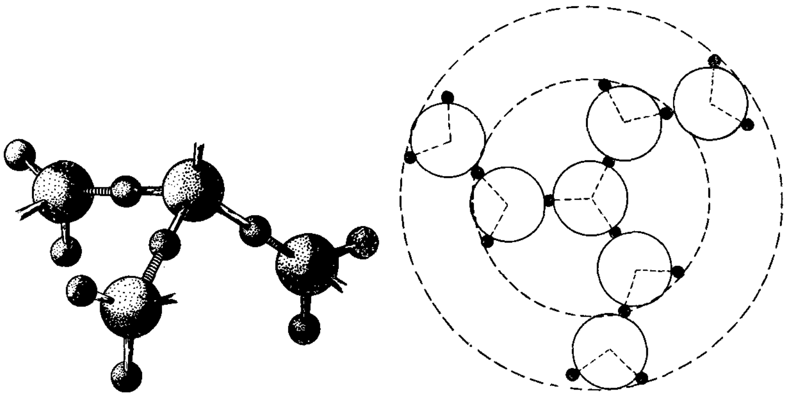
[1] The author prefers the name 'hydronium', which is consistent with the nomenclature introduced in the Encyclopedia of Chemical Technology (New York, 1952) where the ending 'onium' is used for cations that are co-ordination complexes of nonmetallic atoms (e.g., R_3O^+, R_3S^+, R_4N^+, where $R = H$ or an organic group). The name 'hydroxo' is used to designate OH ligands in co-ordination compounds, while 'oxonium' compounds are co-ordination compounds, commonly of certain oxygen-containing organic substances.

[2] For other references concerning more recent works on this subject see, for instance, Savoie and Giguère (1964).

The hydronium ion H_3O^+ has many interesting properties. Because of a very high partial electrostatic charge on its protons, as compared with that on water protons (see below) it can form unusually strong hydrogen bonds with electronegative atoms. In aqueous environment the hydronium ion builds up one or two hydration shells (Wicke, Eigen, and Ackermann, 1954) depending on temperature and the amount of water. Of course, further hydration shells are possible but they would be very weakly bonded. The first or inner hydration shell (fig. 1), consisting of three water molecules,[1] is very stable up to 160° C. The second or outer shell (fig. 2), containing at normal temperatures about three water molecules (3·7 at 0° C), is less well-defined and less stable. This gives two hydration forms of the proton stable under normal conditions: $H_9O_4^+$ or $H_3O^+.3H_2O$ and approximately $H_{15}O_7^+$ or $H_3O^+.6H_2O$, called in this article 'hydronium trihydrate' and 'hydronium hexahydrate' respectively. It must be remembered that in aqueous media hydration is a matter of the length of time of contact of certain water molecules with H_3O^+ (Samoilov, 1957). The 'extra' proton is supposed to change its position inside both complexes freely by the tunnel effect, jumping along the hydrogen bonds from H_3O^+ to the adjacent H_2O molecules (Wicke *et al.*, 1954).



FIGS. 1 and 2: FIG. 1 (left). Hydronium trihydrate $H_9O_4^+$. FIG. 2 (right). Hydration shells of H_3O^+ ion. ○, oxygens; ●, hydrogens.

The question arises whether $H_9O_4^+$ and $H_{15}O_7^+$ ions can exist as true species similar to the hydronium ion in minerals. This problem requires

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[1] On account of the repulsion force of the three hydronium protons the probability of binding a fourth water molecule in a non-planar complex by the lone-pair electrons of the hydronium oxygen is very small.

thorough studies by appropriate methods. Nevertheless, there are certain minerals whose chemical composition and structure points to the possibility of the occurrence of hydronium hydrates in their crystal lattices.

Properties and structure of hydronium hydrates. The $H_9O_4^+$ ion is much more stable than the $H_{15}O_7^+$ ion. The energy of hydrogen bonds between protons of H_3O^+ and water oxygens of its first hydration shell is comparable with that of ordinary chemical bonds in water (110 kcal/mol for O—H bond), while the hydrogen bonds formed by H_2O molecules of the second shell are only 20–40 % stronger than H bonds in liquid water (Grahn, 1962; Coulson, 1959):

	H_3O^+ free	H_3O^+ in $H_9O_4^+$	Outer H_2O in $H_9O_4^+$	H_2O free
Electrostatic charge on H	+0·464	+0·461	+0·212	+0·176
Electrostatic charge on O	−0·391	−0·384	−0·424	−0·352
Energy per H-bond (Kcal/mole)	—	44 to 49	7·2 to 9·0	~ 6

Therefore the building in of $H_9O_4^+$ complexes in the crystal lattice is more probable than that of $H_{15}O_7^+$.

The exact steric configuration of $H_9O_4^+$ and $H_{15}O_7^+$ is not known. No experimental values of the H—O—H angle ω and rotation angle α of the H_2O molecules in either complex are available at present. Wicke *et al.* (1954) assume the free $H_9O_4^+$ ion to be pyramidal like the hydronium ion, with $\omega < 120°$. But, according to Grahn (1961, 1962), a planar configuration, with $\omega = 120°$, is equally probable, here and in the case of H_3O^+. The $H_{15}O_7^+$ ion has most probably a structure similar to that of $H_9O_4^+$. Although there are no exact data, it is obvious that because of the ionic character of the bonds in hydronium hydrates (~ 80–90 %, Grahn, 1962), both ω and α angles must depend strongly on crystal field forces.

Comparatively weak forces will cause a considerable change of both angles. This fact facilitates the fitting in of these ions in the places available in the crystal lattice. The most advantageous structure allowing the occurrence of $H_9O_4^+$ or $H_{15}O_7^+$ ions is probably a layer lattice with balanced or nearly balanced oxygens forming the surface of the layers.

On the other hand, salts of strong acids would form the most favourable chemical environment, and it may be expected that such compounds will be completely dissociated in the crystalline state. For example, Rudolph and Zimmermann (1964) found from H-bond shifts of infra-red vibrational-mode frequencies that $HBr.4H_2O$ was the hydronium trihydrate compound $H_9O_4^+Br^-$. But the presence of strongly polarizing cations in the structure will most certainly detach the hydration shell of $H_9O_4^+$.

Hydronium hydrates in minerals. Table I lists minerals, selected from among 2330 in Mineralogische Tabellen (Strunz, 1966), that contain $H^+.4H_2O$ or $H^+.7H_2O$. Some of them may contain individual $H_9O_4^+$ or $H_{15}O_7^+$ complex ions in a slightly modified configuration as compared with that in the free state. Although the chemical formulae of all the minerals listed in table I permit the presence of hydronium hydrates in their lattice, only in a few of them could the $H_9O_4^+$ or $H_{15}O_7^+$ ions maintain their true identity. This is because most of these minerals contain strongly polarizing cations. The effect of contrapolarization (that is, weakening of the binding within the $H_9O_4^+$ or $H_{15}O_7^+$ complex) exerted by various cations increases with their polarizing power. Therefore it is probable that the hydronium ion could hold its hydration shells in K^+, Na^+, or Ca^{2+} minerals, and possibly in Mg^{2+}, Co^{2+}, and Ni^{2+} minerals too, but not, for example, in rhomboclase which contains Fe^{3+} cations. Only in the case of a mineral like sabugalite are there enough water molecules to screen the electric field of the Al^{3+} ion. In the case of acid phosphates and arsenates it should, first of all, be established whether these minerals are sufficiently dissociated to produce H_3O^+ ions at all.

The most probable examples of hydronium hydrate compounds are layer lattice minerals exhibiting the property of cation exchange: H-montmorillonite, troegerite, H-vermiculite H-meta-autunite, sabugalite, and hewettite. The structures of hewettite and sabugalite are not sufficiently known to establish the possible pattern of $H_9O_4^+$ arrangement, but in the crystal structure of sabugalite, which is most probably autunite-like, the large cavities might be occupied by Al^{3+} ions screened by six (or eight) coordination water molecules, and the smaller ones by $H_9O_4^+$; the latter ions are possibly arranged as in troegerite (compare discussion of autunite-like structures, Ross and Evans, 1965). In clay minerals, which have a pseudo-hexagonal array of SiO_4^{4-} tetrahedra, $H_9O_4^+$ or $H_{15}O_7^+$ ions may be easily fitted in a hexagonal net (fig. 3) similar to that proposed by Hendricks and Jefferson (*fide* Brown, 1961) for H_2O in montmorillonite, whereas in uranyl compounds like troegerite or H-meta-autunite with tetragonal arrangement of water positions (Ross and Evans, 1964) the steric configuration of $H_9O_4^+$ ion must be somewhat modified. In the uranyl minerals squares of four water molecules form double, superimposed sheets; every fourth H_2O is replaced

TABLE I. Minerals in which hydronium hydrate ions are possible

Mineral name	Strunz's formula	Alternative formula
Rhomboclase	$FeH[SO_4]_2.4H_2O$	$(H_9O_4)Fe[SO_4]_2$?
Ardealite	$Ca_2H[PO_4 \mid SO_4].4H_2O$	$(H_9O_4)Ca_2[PO_4 \mid SO_4]$?
Dittmarite	$(NH_4)Mg_3H_2[PO_4]_3.8H_2O$	$(H_9O_4)_2(NH_4)Mg_3[PO_4]_3$?
Stercorite	$(NH_4)NaH[PO_4].4H_2O$	$(H_9O_4)(NH_4)Na[PO_4]$?
Guerinite	$Ca_5H_2[AsO_4]_4.9H_2O$	$(H_9O_4)_2Ca_5[AsO_4]_4.H_2O$
Forbesite	$(Ni,Co)H[AsO_4].3-4H_2O$	$(H_9O_4)(Ni,Co)[AsO_4]$?
Picropharmacolite	$Ca_4(Mg,Co,Ni)H_2[AsO_4]_4.10H_2O$	$(H_9O_4)_2Ca_4(Mg,Co,Ni)[AsO_4]_4.2H_2O$
Chudobaite	$(Na,K)(Mg,Zn)_2H[AsO_4]_2.4H_2O$	$(H_9O_4)(Na,K)(Mg,Zn)_2[AsO_4]_2$
Thaumasite	$Ca_3H_2[CO_3 \mid SO_4 \mid SiO_4].13H_2O$	$(H_9O_4)_2Ca_3[CO_3 \mid SO_4 \mid SiO_4].5H_2O$
Pintadoite	$CaH[VO_4].4H_2O$	$(H_9O_4)Ca[VO_4]$?
Hewettite	$H_2Ca[V_6O_{17}].8H_2O$*	$(H_9O_4)_2Ca[V_6O_{17}]$
Natrium-Hewettite	$H_2(Na,K)_2[V_6O_{17}].8H_2O$*	$(H_9O_4)_2(Na,K)_2[V_6O_{17}]$
Sabugalite	$HAl[UO_2 \mid PO_4]_4.20H_2O$	$(H_9O_4)Al[UO_2 \mid PO_4]_4.16H_2O$
H-Meta-autunite	$(H_3O)_2[UO_2 \mid PO_4]_2.6H_2O$	$(H_9O_4)_2[UO_2 \mid PO_4]_2$
Trögerite	$(H_3O)_2[UO_2 \mid AsO_4]_2.6H_2O$	$(H_9O_4)_2[UO_2 \mid AsO_4]_2$
H-Vermiculite	$\left\{ Mg_3[(OH)_2 \mid Si_{4-n}Al_nO_{10}] \right.$	$\left\{ Mg_3[(OH)_2 \mid Si_{4-n}Al_nO_{10}] \right.$
(H-Saponite)	$\left. H_n(H_2O)_4 \right\}$	$\left. (H_9O_4)_n(H_2O)_{4(1-n)} \right\}$
H-Montmorillonite	$\left\{ Al_2[(OH)_2 \mid Si_{4-n}Al_nO_{10}] \right.$	$\left\{ Al_2[(OH)_2 \mid Si_{4-n}Al_nO_{10}] \right.$
(H-Beidellite)	$\left. H_n(H_2O)_4 \right\}$	$\left. (H_9O_4)_n(H_2O)_{4(1-n)} \right\}$
Phosphor-rösslerite	$MgH[PO_4].7H_2O$	$(H_{15}O_7)Mg[PO_4]$?
Rösslerite	$MgH(AsO_4].7H_2O$	$(H_{15}O_7)Mg[AsO_4]$?

* Old formula, analogous to that of anhydrous silver vanadate, $Ag_4[V_6O_{17}]$.

by H_3O^+, but the exact position of the protons is not known. Fig. 4*a*, *b* shows one of the possible arrangements of $H_9O_4^+$ that presumably may be found in troegerite at any arbitrary instant of time: two water molecules of one square and one molecule from the adjacent square constitute the hydration shell of the hydronium ion. One water proton of each square forms an H-bond with an adjacent square, three others with arsenate oxygens. The lone-pair electrons of hydronium oxygens are directed towards arsenate oxygens. In this case no direct H-bonds between H_3O^+ and AsO_4^{3-} exist, the charge on $\{UO_2AsO_4\}$ groupings being balanced by H_3O^+ indirectly, through water protons of its hydration shell. As can be seen from the figures given above, the charge on water protons of $H_9O_4^+$ is 20 % higher than on protons of free H_2O.

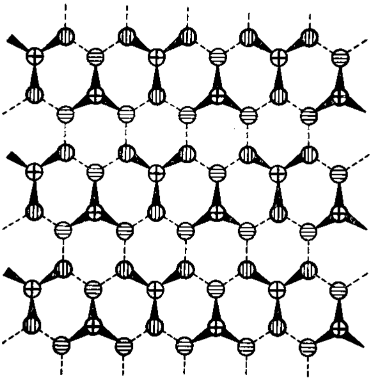

FIG. 3. Projection on (001) of a possible arrangement of hydronium trihydrate complexes in H-montmorillonite. ⊕, hydronium ions; ◍, water molecules of hydration.

The above conception is not contradictory in any way to Ross and Evans' (1964, 1965) conclusions. These authors are of the opinion that '. . . H_3O^+ ions may not exist as discrete groups' in structures of abernathyite–troegerite type. They put forward a supposition that probably H_3O^+ (protons), NH_4^+, and K^+ ions do not enter minerals like montmorillonite, vermiculite, or troegerite together with their hydration spheres, but may be randomly distributed over water molecule positions. It must be remembered, however, that the H_3O^+ ion and its hydrates have not a rigid structure. The 'extra' proton can change its position freely along H-bonds when H_3O^+ is surrounded by water molecules of hydration shells, whereas the K^+ ions cannot move in the crystal lattice as fast and freely as do the protons. In an equilibrium state, K^+ ions may be regarded, in comparison with protons, as practically fixed to a certain position. Therefore random distribution of ions like K^+ ion would mean 'statistical in space' and in the case of H_3O^+ (or protons) 'statistical in space and time'. There will be limited periods of time when a particular proton–oxygen steric configuration, e.g. $H_9O_4^+$, actually exists. The lower limit of time, when a proton remains associated with any four H_2O molecules forming $H_9O_4^+$, is set by the lowest infra-red frequency (vibrational or translational).

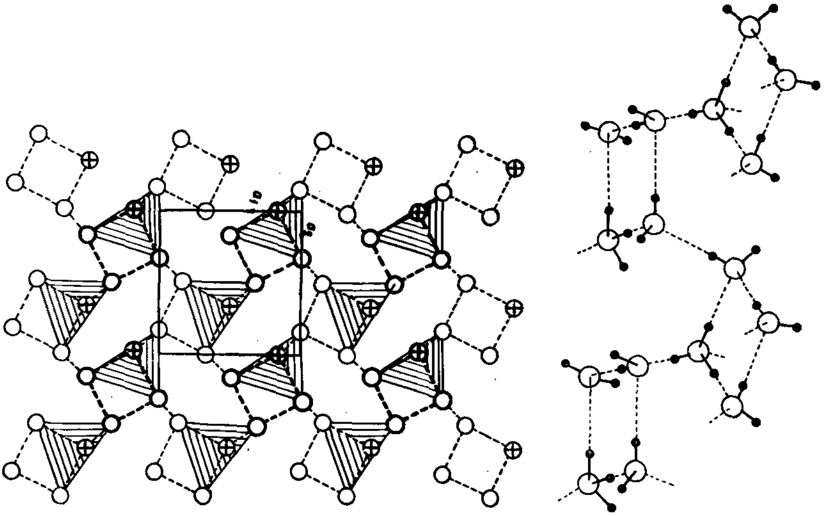

FIG. 4. Water-hydronium sheets in troegerite, showing one of the possible $H_9O_4^+$ configurations. Based on Ross and Evans' (1964) diagrams of abernathyite structure. *a*, left: Projection on (001). Hydronium ions denoted ⊕. *b*, right: Pictorial diagram with presumable positions of protons.

The hydronium ion cannot be compared with K^+ ion in its behaviour in H-bonded systems. Although similar in radius, both ions have entirely different migration ability and electric charge distribution around them. The high mobility of protons in solids and the H-bonding property and polarity of H_3O^+ determine the unusual character of its hydrates.

Conclusions

There are two interesting problems in the crystal chemistry of 'acid' and 'basic' hydrated salts: the problem of proton distribution, i.e. the dissociation equilibrium and formation of H_3O^+ ions in the crystalline state; and the problem of maintaining hydration spheres of these H_3O^+ ions in the crystal lattice of such compounds.

The first problem has been solved experimentally in many cases. It is to be expected that in anisodesmic, hydrated salts of oxy-acids, where $\frac{3}{2}$ or more of the charge on anion-oxygens is balanced by the central cation, as in sulphates, nitrates, or chlorates, the proton joins the H_2O molecule easily, which probably is not the case in arsenates, phosphates, and mesodesmic silicates. It must be kept in mind, however, that the structure type and presence of other than H^+ positive ions will influence the proton distribution equilibrium (the effect of contrapolarization).

The problem of building in hydronium hydrates in the crystal structure requires detailed neutron diffraction or infra-red absorption examinations. Nevertheless, general crystallochemical considerations allow one to select the most probable hydronium hydrate minerals for further investigations. The existence of hydration spheres around H_3O^+ ions depends on the chemistry and structure of a given mineral. A loose, balanced layer structure, and the absence of strong polarizing cations, constitute the most favourable crystallochemical environment.

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