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Evidence for the Zundel-like character of oxoethylidenediphosphonic acid hydrate

Ivan V. Ananyev,[a] Petr Yu. Barzilovich[a,b] and Konstantin A. Lyssenko*[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5085; e-mail: kostya@xrlab.ineos.ac.ru*
[b] *Institute of Problems of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation*

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Based on the XRD investigations of ^{1}H and ^{2}H oxoethylidenediphosphonic acid crystalline hydrate and the statistical analysis of CSD, the nature of $H_2O\cdots H\cdots OP$ interaction was rationalized. The general character of the Zundel-like associate for phosphoric acid hydrates was proposed.

The cation···anion and ion···water hydrogen bonds play a crucial role in charge transfer from the anion to the cation.[1] Among the most representative examples are sulfo acid hydrates, which are considered appropriate models of proton conductive materials.[1(*a*)–(*c*)] Another class of compounds that are worth studying in this respect are phosphorus acids. It is well known that phosphorus acids form short strong H-bonds (SSHBs) with high energy,[2] which make these systems very suitable for the investigation of a hydrogen bond phenomenon and its role in hydrogen transfer.[3]

To expand the trends found for sulfo acids, we have performed the high-resolution X-ray diffraction investigation of hydroxyethylidenebisphosphonic acid monohydrate (OedpH). In its crystal, there is a SSHB between the water molecule and the P–O–H group with the O···O distance of 2.437(2) Å according to neutron diffraction (ND) data at 298 K.[4] The choice of OedpH as a test system was due to the accurate positions of hydrogen atoms available and the high reflective power of its crystals.

Note that such a strong $P–O–H\cdots OH_2$ hydrogen bond as in OedpH is rather unusual for this class of compounds. Indeed, the statistical analysis of Cambridge Structural Database (CSD)[5] has revealed that the H-bonds between water molecules and phosphorus acid species are usually moderate or weak. For 655 organic crystalline hydrates with PX_3O fragments (X = O, C, N or H), we have found 1924 hydrogen bonds $P–O\cdots H_2O$ with the O···O separation from 2.51 to 3.0 Å, and for only 55 H-bonds this value varied from 2.378 to 2.509 Å, in most cases (37 entries) corresponding to the $P–O–H\cdots OH_2$ bonding. In the case of onium salts of the compounds containing the same PX_3O fragment, only 24 structures were found with at least one of the H-bonds within the low-limit range observed for hydrates.

For comparison, in crystals containing an XSO_3 fragment, the $S–O–H\cdots OH_2$ bonds were observed only for HSO_4^- ions (13 structures) with the O···O separation exceeding 2.473 Å. In the case of onium salts with an $XSO_3\cdots HOH_2$ bond, the O···O separation with the only one exception (WEPVIV structure, O···O 2.485 Å) is larger than 2.5 Å. At the same time, for carbon acids and alcohols (more than 1000 H-bonds), there are 22 H-bonds with the O···O distances of 2.429–2.504 Å, and in only two structures [one of which is bis(methanol)hydrogen tetrafluoroborate MEHTB10 with the O···O separation of 2.394 Å] this value was less than 2.5 Å.

Based on this statistical analysis, one can propose that these shortened H-bonds with water molecules, which are unusual for the hydrates of phosphorus, sulfo and carboxylic acids, can be attributed to the formation of a Zundel-like associate, its general feature being such strong H-bond.[6,7] For instance, such associates are known for HCl acid solutions.[8] At the same time, we also cannot exclude that the position of hydrogen atom at 298 K is characterized by some systematic error due to the superposition of the oxonium ion and the neutral water molecule; however, the latter does not exclude the Zundel-like character of this associate.

It is well known that the Zundel ion $H_5O_2^+$ is formed by a low-barrier hydrogen bond (LBHB) with the hydrogen atom position changing from quasi-symmetrical (the hydrogen atom shuttles between two oxygens over the barrier) to asymmetrical (double-well potential) depending on the crystal surrounding.[7] From a structural point of view, one can probe the type of the H-bonds potential by the replacement of protium with deuterium – by the so-called Ubbelohde effect.[9] In the case of a double-well potential, this substitution will lead to an increase in the O···O separation, while for a very strong single-well H-bond it will lead to its decrease. For this purpose, we analyzed the structure of OedpH and its deuterated analogue (OedpD) at the same temperature (85 K). The crystals of OedpH were obtained by the recrystallization of the commercial compound; OedpD was obtained from water-free OedpH (p = 10^{-2} Torr, T = 80 °C, 6 h) by double recrystallization from heavy water (99.8% D). Unfortunately, the presence of multiple strong H-bonds almost excludes the use of vibrational spectroscopy for the analysis of H-bonding in a crystal; thus, we focused on its structural aspect.

We have found that, upon cooling, the H(1WA) atom (Figure 1), which was located at PO group at 298 K, has moved towards the water molecule.[†] Indeed, the analysis of Fourier electron density synthesis has revealed the presence of three maxima of almost the same height located around the O(1W) atom at distances of ~1 Å. The least-squares refinement has resulted in some increase in the O(1W)–H(1WA) distance. However, it remains smaller than the H(1WA)–O(5) distance [1.06(3) *vs.* 1.40(3) Å and 0.97(3) *vs.* 1.52(3) Å for ^{1}H and ^{2}H analogues, respectively]. Although the shortening of the P(2)–O(5) bond upon cooling [1.5264(9) (^{1}H), 1.5231(9) Å (^{2}H) at 85 K *vs.* 1.534(2) Å (^{1}H) at 298 K[4]] is also in line with the proton transfer, the difference in bond lengths is small to unambiguously detect the oxonium moiety at 85 K.

[†] CCDC 875360 and 875361 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2012.

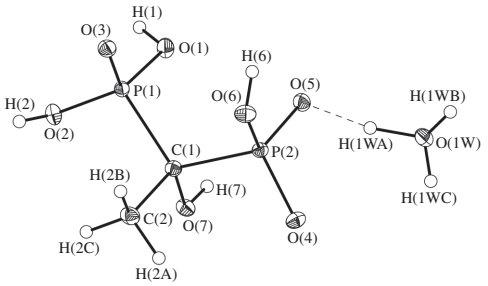

Figure 1 General view of OedpH with the representation of non-hydrogen atoms by anisotropic ellipsoids of thermal vibrations (p = 50%).

More information was extracted from the crystal packing analysis (Figure 2). It is reasonable to propose that, in the case of the oxonium moiety, all hydrogen bonds formed by H(1WB) and H(1WC) atoms will in general be shorter than those with the water molecule. Indeed, the comparison of the crystal patterns of OedpH at two different temperatures (85 and 298 K) clearly shows that the differences in the O···O distances for H-bonds interlinking two acid species are almost equal with the maximum elongation of 0.05 Å for the weakest bond O(7)–H(7)···O(4).

In contrast, the H-bonds formed by the H(1WB) and H(1WC) atoms for O(1W) atom of the onium type are 0.09–0.2 Å shorter than those for a water type moiety at 85 and 298 K, respectively. Note that the degree to which the O···O distance changes upon variation of temperature can be explained by the strengths of H-bonds, given that the O(1W)–H(1WB)···O(7) bond is characterized by the O···O distance that is even smaller than that for O(7)–H(7)···O(4) at 85 K. Thus, the formal charge redistribution upon hydrogen transfer leads to the drastic variation of H-bond strengths, although it does almost not disturb the O(5)···H(1WA)··· O(1W) interaction [2.437(2) *vs*. 2.456(1) Å], clearly indicating its special character inherent to a Zundel-like associate.

The comparison of the O···O separation for OedpH and OedpD shows that all short H-bonds are characterized by the double-well potential (basing on the Ubbelohde effect) as it

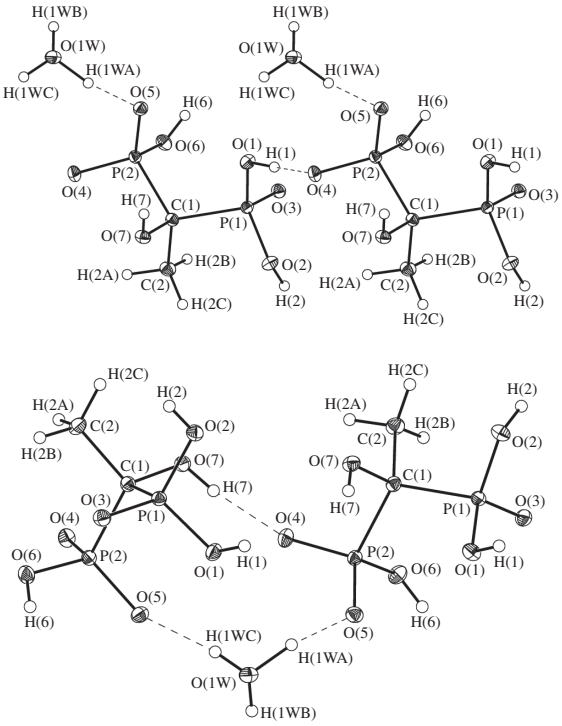

Figure 2 Fragments of the crystal packing of OedpH.

Table 1 O···O separations for H-bonds according to ND and XRD studies.

H-bonds[a]	ND[4] (^{1}H) 298 K	XRD (^{1}H) 85 K	XRD (^{2}H) 85 K
O(1W)–H(1WA)···O(5)	2.437(2)	2.4559(14)	2.4877(13)
O(1W)–H(1WB)···O(7)#1	2.697(2)	2.6014(14)	2.5834(14)
O(1W)–H(1WC)···O(5)#2	2.888(2)	2.6901(13)	2.6307(13)
O(1)–H(1)···O(4)#3	2.476(2)	2.4771(13)	2.4922(13)
O(2)–H(2)···O(3)#4	2.604(2)	2.5918(13)	2.5990(13)
O(6)–H(6)···O(3)#5	2.617(2)	2.6158(13)	2.6293(13)
O(7)–H(7)···O(4)#6	2.687(2)	2.6308(13)	2.6223(13)

[a] Symmetry transformations used to generate equivalent atoms: #1, $x+1$, y, z; #2, x, $-y+3/2$, $z-1/2$; #3, x, y, $z+1$; #4, $-x$, $-y+1$, $-z+1$; #5, $-x+1$, $-y+1$, $-z+1$; #6, x, $-y+3/2$, $z+1/2$.

follows from a 0.02–0.03 Å increase in the O···O separation upon the deuteration of the sample. Note that the O···O separation observed in OedpH is of the same order of magnitude as that recently found for benzoylacetone intramolecular H-bond, which corresponded to LBHB.[10]

In the case of all other H-bonds, which are of moderate strength, the exchange of ^{1}H by ^{2}H does not change or lead to a decrease in the O···O separation by 0.01–0.06 Å. Although the latter effect should be interpreted[11] as the indication of a single-well potential, a significant structural isotope observed for the O(1W)–H(1WC)···O(5) H-bond effect is unlikely for hydrogen bonds with O···O separations larger than 2.6 Å.[12] Therefore, it is reasonable to propose that this variation is solely the consequence of different charge accumulation on the onium moiety in a crystal due to an increase in the O(5)···O(1W) distance in OedpD with respect to OedpH.

Assuming that for such SSHB as in OedpH one can expect at least the protium atom to shuttle between the two oxygen atoms over the barrier and/or the tunneling to play a significant role upon hydrogen atom transfer along the O(1W)–H(1WA)···O(5) H-bond, for the correct analysis of charge density function in a crystal and the estimation of H-bond properties, it is necessary to fully prove the absence of a disorder in the structure. As the Hirshfeld rigid-bond criteria[13] for such systems might be insufficient to identify a disorder due to the proximity of P=O and P–OH bond lengths,[14,15] the extensive multi-temperature XRD investigation for both ^{1}H and ^{2}H compounds will be reported elsewhere.

Here, the XRD investigation of OedpH and OedpD at 85 K has revealed that the hydrate of oxoethylidenediphosphonic acid should be described as a Zundel-like associate with the hydrogen atom shifted upon cooling from the acid species towards the water molecule leading to a formally zwitterionic structure. Based on CSD data, we can propose that such a type of binding is a unique feature of phosphorus acids rather than sulfo acids. The position of the hydrogen atom within this associate and the barrier of H transfer depend on the crystal packing, and they can be governed by varying the temperature.

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