Inter-anion O–H⋯O interactions are classical hydrogen bonds

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Inter-anion O–H⋯O interactions have consequences on the covalent bonding of the donor and acceptor moieties that are typical for strong hydrogen bonding; in contrast to published views, they are classified as strong hydrogen bonds, with bond orders of H⋯O of the magnitude 0.25 valence units.

Of all types of hydrogen bonds, O–H⋯O is by far the best investigated.[1] At H⋯O distances larger than about 1.6 Å, hydrogen bonds are primarily electrostatic interactions with only a relatively small charge transfer contribution. With reducing distance, the interaction gradually gains a quasi-covalent nature.[2] The extreme case of the centred hydrogen bond, O⋯H⋯O, in which the proton is equally shared between two O-atoms, can be considered as two half covalent bonds.[3] Intermolecular O–H⋯O hydrogen bonds can be formed between uncharged molecules, but can involve also ions, in particular O–H⋯O⁻, +O–H⋯O, +O–H⋯O⁻, −O–H⋯O and −O–H⋯O⁻. Inter-anion hydrogen bonds are frequently observed between ions like HSO_4^-, $H_2PO_4^-$, HPO_4^{2-}, related inorganic anions, and numerous hydrogen carboxylates like hydrogen oxalate, hydrogen fumarate and so on. On the basis of structural and IR spectroscopic data, they are usually considered as strong. An example of a well-studied system is the hydrogen sulfates, which have been extensively investigated by X-ray diffraction and vibrational spectroscopy.[4]

Recently, the usual interpretation of inter-anion O–H⋯O interactions as hydrogen bonds has been seriously challenged.[5] For the O–H⋯O interaction in potassium hydrogen oxalate, $K^+[HC_2O_4]^-$, it has been argued that it does not represent a hydrogen bond despite the short O⋯O distance of 2.52 Å and the linearity of the geometry. As the reason, it is stated that the electrostatic inter-anion repulsion would prevent a stable anion–anion bond. On the basis of *in vacuo* computations on hydrogen oxalate dimers, it is stated that contacts between hydrogen oxalate ions are destabilizing in all geometries, and the geometry found in the crystal is adopted because it is the least destabilizing one. In this view, the O–H⋯O interaction does not 'link' the ions, but still organises them in space because the anions adopt the 'least destabilizing' mutual arrangement. Because this theoretical paper challenges a large part of the hydrogen bond literature, in particular of the literature on strong hydrogen bonds, a close look at the experimental data is appropriate.

The crystal structure of potassium hydrogen oxalate **1** has been determined by X-ray[6,7] and neutron[8] diffraction. The structure is layered, as shown in Fig. 1(*a*) for the neutron diffraction data. The anions are arranged in infinite chains, and the chains are linked by potassium ions coordinated to the O-atoms. The O–H group of each anion is oriented at a carboxylate O-atom of the next anion in the chain. The published IR absorption spectrum shows the typical features of a strong hydrogen bond (not commented upon in ref. 5).[6] The covalent bonding is quantitatively described by the bond distances given in Fig. 1(*a*). The O–H bond is elongated almost 0.09 Å compared to the typical gas-phase values of monomeric carboxylic acids [0.972(5) Å in formic acid,[9] 0.971(2) Å in acetic acid[10]]. Such a lengthening is inherent to strong hydrogen bonds,[2,3] and is a consequence of weakening of the covalent O–H bond by the bonding H⋯O interaction. A further indication

of the bonding nature of H⋯O is found in the bond lengths of the carboxylate group. The O–H⋯O interaction is directed at the O-atom that is *cis* with respect to O–H of the accepting molecule. The corresponding C–O bond is 0.017 Å longer than the C–O bond of the O-atom that does not accept an O–H⋯O interaction. This means that the acceptor C–O bond is weakened by the O–H⋯O interaction, as it must be in a strong hydrogen bond.

A second hydrogen oxalate crystal structure has been determined by neutron diffraction, and is very informative here. In dimethylammonium hydrogen oxalate **2**, the anions also form infinite chains linked by short O–H⋯O interactions [Fig. 1(*b*)].[11] The geometry of the O–H⋯O contact is very similar to that in **1**, with the covalent O–H bond even being slightly longer, and H⋯O slightly shorter. Unlike **1**, the interaction is directed at the carboxylate O-atom that is *trans* with respect to O–H of the accepting molecule. Again, the C–O bond of the accepting O-atom is longer than that of the other carboxylate O-atom. The main difference of **1** and **2** is in the interaction pattern of the cations. In a layer of **1**, each K⁺ ion coordinates to O-atoms of three anions, two of which are successive in a chain. This could support an argument (implicitly made in ref. 5) that the strong O⋯K⁺⋯O interaction pulls together the anions within the chains, forcing them to make a short contact that they would otherwise avoid. In **2**, on the other hand, each cation
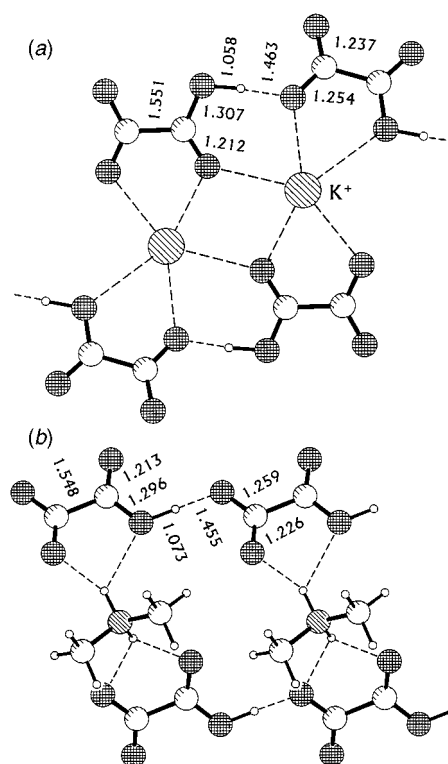

Fig. 1 (*a*) Neutron crystal structure of potassium hydrogen oxalate, determined by Moore and Power (ref. 8). (*b*) Neutron crystal structure of dimethylammonium hydrogen oxalate, determined by Thomas (ref. 11). Distances are given in Å.
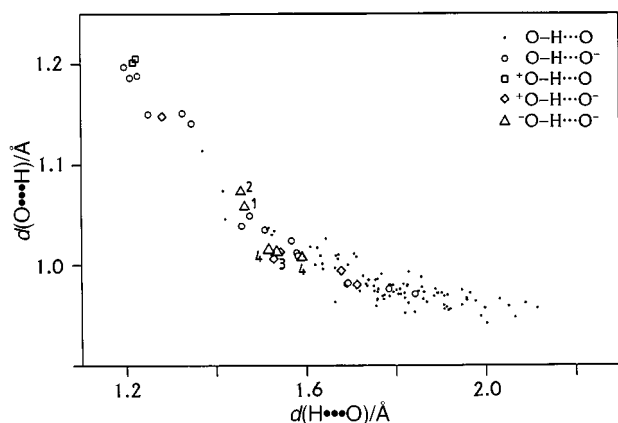
Fig. 2 Lengthening of the covalent O–H bond in O–H···O hydrogen bonds. Scatterplot of data from 125 hydrogen bonds in 66 ordered and error-free neutron crystal structures with $R < 0.06$ (CSD, update 5.16 with 190 307 entries). For the cases $^+$O–H···O, $^+$O–H···O$^-$ and $^-$O–H···O$^-$, R values up to 0.09 were allowed. In hydrogen bonds classified as $^-$O–H···X, the donor is part of an anion where the negative charge is either delocatized or formally very close to the O–H group. The symbols marked as **1**, **2**, **3** and **4** correspond to the compounds with the same identifiers mentioned in the text.
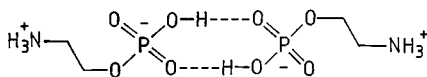

Fig. 3 Structure of 2-aminoethyl phosphate anion dimer.

forms N$^+$–H···O$^-$ hydrogen bonds with only two anions, which belong to different chains. There is no anion–cation–anion bridge that could pull the anions together along the chains.

It is of interest to compare the lengthening of the O–H bond in **1** and **2** with the related lengthening in undisputed O–H···O hydrogen bonds of various kinds. Fig. 2 shows the correlation of the O–H and H···O distances in 125 O–H···O interactions found in neutron diffraction crystal structures extracted from the Cambridge Structural Database[12] (details are given in the legend). The overall correlation is as repeatedly published.[2,3,13] It is of importance that the data for different kinds of hydrogen bonds [O–H···O, O–H···O$^-$, $^+$O–H···O, $^+$O–H···O$^-$] all obey a common function r(O–H) $= f$[d(H···O)].[3] The data for inter-anion O–H···O interactions, indicated by triangles, *obey this function too*. Four relevant neutron diffraction studies are available: the hydrogen oxalates **1** and **2**, 2-aminoethyl phosphate,[14] **3**, and putrescine diphosphate[15] **4**. The latter two structures are also very interesting. In **3**, the anions form dimers, as shown in Fig. 3, and in **4**, the dihydrogen phosphate ions even form a layer where the anions are connected by interionic O–H···O interactions.

Fig. 2 guides directly to the valence model of the hydrogen bond.[2,3] In this model, O–H and H···O are attributed bond orders or 'valences' s, which depend strictly on the interatomic distances. In hydrogen bonds, the sum of valences at the H-atom is conserved, *i.e.* $s_{O-H} + s_{H···O} = 1.0$. In hydrogen bonds with long H···O, $s_{H···O}$ is small so that s_{O-H} is only slightly reduced from unity, and O–H is only slightly elongated. If H···O is

short, however, $s_{H···O}$ becomes large, leading to a large reduction of s_{O-H} and a pronounced elongation of the O–H bond. According to Fig. 2, this is valid for inter-anion O–H···O interactions in the same way as for all other O–H···O hydrogen bonds. For various types of hydrogen bonds X–H···A, the distance dependence of s_{X-H} and $s_{H···A}$ has been parametrized by fitting model functions against structural data (ref. 16 and references therein). Using the most recent parametrization for the case O–H···O,[16] one obtains for the O–H···O interaction in **1** the bond orders $s_{O-H} = 0.73$ and $s_{H···O} = 0.26$. This means that the H-atom is bonded with about $\frac{3}{4}$ of a valence unit to one O-atom, and with $\frac{1}{4}$ to the other. The whole interaction O–H···O is, therefore, well inside the quasi-covalent regime of strong hydrogen bonds.[2]

The experimental data discussed above do not indicate any behaviour of inter-anion O–H···O interactions that would fundamentally differ from classical hydrogen bonds. On the contrary, the covalent bonding on the donor as well as on the acceptor sides shows the normal features of strong hydrogen bonding. The effects on the covalent geometries are strong, and indicate that the O–H···O interaction in **1** and related compounds is in the regime of quasi-covalent hydrogen bonds, in which the central hydrogen atom is involved in two bonds of essentially covalent nature.

Notes and references

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