Letter

Single crystal neutron and X-ray diffraction studies of $(H_7O_3)[AuCl_4]\cdot$15-crown-5

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The single crystal neutron diffraction structure at 80 K of $(H_7O_3)[AuCl_4]\cdot$15-crown-5 is presented. The $H_7O_3^+$ ion is unsymmetrical with the positive charge lying predominantly at one end of the chain. The oxonium ion is stabilised by hydrogen bonding to the crown ethers to form an infinite hydrogen-bonded polymer, and also by a bifurcated interaction with the $[AuCl_4]^-$ anion. The OH bond distances and H atom thermal ellipsoids indicate a profound influence of the hydrogen bonding network on the oxonium ion structure. Improved X-ray data are also reported.

An understanding of the way in which water aggregates and associates with adjacent ionic and neutral species is crucial to many aspects of biological chemistry as well as solvation, acid–base equilibria and sensing.[1–6] One of the simplest of such associations is the interaction of water with protons to form oxonium ions.[1,2] Oxonium ion chemistry in the solid, solution and gas phases has continued to intrigue chemists for many years. Recent results have shown that the crown ethers[7,8] may be used to systematically isolate particular oxonium ions from aqueous acidic solutions. Thus, 18-crown-6 invariably includes H_3O^+ (which exhibits both a size and symmetry match for the common D_{3d} crown conformation)[9–13] while larger crown ethers such as 21-crown-7 and dibenzo-24-crown-8 include $H_5O_2^+$.[7,8] The ability of 18-crown-6 derivatives to include H_3O^+ has been used as the basis for an oxoacid luminescent sensor.[14] Dibenzo-30-crown-10 is capable of including two H_3O^+ ions,[7] however, its dinitro analogue gives a $H_7O_3^+$ containing species from $HAuCl_4$ in *aqua regia*.[8] Smaller crown ethers give less predictable products. In the case of the $HAuCl_4$ system, both benzo-15-crown-5 and 12-crown-4 stabilise $H_5O_2^+$ as sandwich compounds. Conversely, 15-crown-5 forms a hydrogen-bonded polymer of formula $(H_7O_3)[AuCl_4]\cdot$15-crown-5 (**1**), containing the less common $H_7O_3^+$ ion.[8] The formation of these complexes illustrates the highly useful crystal engineering properties of the crown ethers as excellent "hard" hydrogen bond acceptors that possess little hydrogen bond donor capability (the crown ethers form only soft CH···O hydrogen bonds as donors, which may contribute to their high degree of crystallinity[15]).

Both H_3O^+ and $H_5O_2^+$ have been extensively characterised by X-ray and neutron diffraction.[1,2,9–13,16] The larger members of the oxonium ion series such as $H_7O_3^+$ are less predictable, however.[16–20] A single crystal neutron structure has been reported for *o*-sulfobenzoic acid trihydrate, which shows the isolated $H_7O_3^+$ unit to be appropriately described as $H_5O_2^+\cdot H_2O$.[21] We now report a single crystal neutron structure determination of complex **1** undertaken using the D19 instrument[22] at the Institut Laue Langevin (ILL). Compound **1** is particularly appropriate for this type of study since the oxonium ion is not located on any crystallographic symmetry element. Of particular interest to us was not only the structure of $H_7O_3^+$ itself, but also the way in which the oxonium ion interacts with the crown ether and tetrachloroaurate(III) anion, and whether there is evidence of any cooperativity between the strong (intra-oxonium), medium (oxonium···crown) and weak (CH···O) hydrogen bonding interactions.[23–25]

We have previously reported a low temperature (120 K) X-ray crystal structure of **1** of limited precision in which it proved impossible to locate the oxonium ion hydrogen atoms reliably.[8] The X-ray structure of this material has now been redetermined to higher precision at 100 K. The original data indicated a significant number of observed reflections of type $h+l\neq 2n$ on $(h0l)$ and as a result the space group was assigned as acentric $P2_1$.[26] The present X-ray and neutron re-determinations indicate that $h+l\neq 2n$ is, in fact, an absence on $(h0l)$ and the space group is therefore $P2_1/n$. A minor reversible phase change is observed at 60 K, resulting in significant peak broadening, but this does not result in a change of space group. See the Experimental section for a full discussion.

In the neutron study a total of 4176 unique reflections were measured on the D19[22] instrument at ILL at 80 K. A data-to-parameters ratio of 9.3 : 1 was obtained, resulting in good overall precision. The sample crystallises with one independent oxonium ion, crown ether and tetrachloroaurate(III) anion in the asymmetric unit. The X-ray data suggests that the $H_7O_3^+$ ion is unsymmetrical, possessing a significant contribution from an $H_5O_2^+\cdot H_2O$ "resonance form". This is confirmed by the neutron structure, which gives one short O···O distance of 2.437 Å and one longer one of 2.574 Å (Table 1), in agreement with the X-ray experiment (2.430 and 2.559 Å). Notably, the longer O···O separation is markedly shorter than in the *o*-sulfobenzoic acid trihydrate in which the highly unsymmetrical $H_5O_2^+\cdot H_2O$ unit exhibits O···O distances of 2.414 and 2.721 Å.[21] All seven acidic hydrogen atoms were readily located on the initial difference Fourier map and, along with the CH hydrogen atoms, were refined freely and anisotropically (Fig. 1). The neutron result shows that one proton, H(1), is situated asymmetrically along a line joining the closest pair of oxygen atoms: ∠O(6)–H(1)···O(7) = 178.5°. The two O–H(1) bond distances (1.120 and 1.317 Å) are significantly longer than those found in isolated OH bonds (generally *ca.* 0.95 Å), and imply the kind of three-centre two-electron OHO bond typical of $H_5O_2^+$.[7,12] The anisotropic displacement parameters relating to H(1) are also somewhat elongated along the O(6)···O(7) axis, even at 80 K, indicating that the proton interacts strongly with both centres. Interestingly, however,

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Table 1 Hydrogen bonds in **1** (in Å and °)[a]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
(a) Within the $H_7O_3^+$ unit				
O(6)–H(1)···O(7)	1.120(3)	1.317(3)	2.4374(19)	178.5(3)
O(7)–H(4)···O(8)	0.996(3)	1.579(3)	2.574(2)	177.9(3)
(b) Oxonium···crown ether				
O(6)–H(2)···O(2)	0.996(3)	1.666(3)	2.6475(18)	167.4(3)
O(8)–H(7)···O(4)′	0.960(3)	1.809(3)	2.7670(19)	174.8(3)
O(6)–H(3)···O(5)	0.998(3)	1.662(3)	2.6562(18)	173.8(3)
O(8)–H(6)···O(1)′	0.966(3)	1.792(3)	2.7509(19)	171.4(3)
(c) Oxonium···$[AuCl_4]^-$				
O(7)–H(5)···Cl(3)	0.960(3)	2.490(3)	3.3087(16)	143.1(3)
O(7)–H(5)···Cl(2)	0.960(3)	2.688(4)	3.4555(16)	137.2(3)

[a] Symmetry transformation used to generate primed atoms: $x-1$, y, z.

H(1) is not situated symmetrically between O(6) and O(7) and, in fact, lies closest to O(6), the terminal oxygen atom of the O(6)–H···O(7)–H···O(8) hydrogen-bonded chain. This suggests that the positive charge of the oxonium ion is stabilised by interactions with the crown ether. These O(6)–H···O$_{\mathrm{crown}}$ interactions (Fig. 2) are typical of moderate strength electrostatic hydrogen bonds with the protons located close to the donor O(6) atom (Table 1). The hydrogen bond linking the central oxygen atom O(7) to O(8) is of intermediate length between the values expected for strong and moderate interactions,[27] however the O(7)–H(4) distance, 0.996 Å, is similar to that found for the covalent OH distances for O(6) and O(8), involved in moderate strength hydrogen bonds. The H(4)···O(8) distance is clearly much longer at 1.579 Å. This is consistent with a description of H(6)–O(8)–H(7) as a very strongly hydrogen-bonded water molecule, rather than part of the oxonium ion. This water molecule in turn interacts with the crown ether to form two additional moderate strength hydrogen bonds (Table 1). Interestingly, however, the bond lengths from O(8) to H(6) and H(7) (the protons involved in moderate hydrogen bonds to the crown ether), each 0.96 Å in length, are significantly shorter than the analogous O(6)–H(2) and O(6)–H(3) distances (0.99 Å), suggesting charge assistance in the hydrogen bonding in the latter case and repulsion of H(2) and H(3) by H(1).

Of the total of five OH protons that are not involved in interactions *within* the $H_7O_3^+$ unit, only four are geometrically capable of interacting with crown ether oxygen atoms. The last remaining proton, H(5), is unable to reach the non-hydrogen-bonded crown ether oxygen atom O(3). As a result, H(5) forms a fascinating, nearly symmetrical bifurcated interaction with the chloro ligands of the $[AuCl_4]^-$ anion (Fig. 3), with H···Cl distances of 2.490 and 2.688 Å. Such hydrogen bonds to coordinated chloride have been observed previously,[28] although bifurcation is relatively uncommon and difficult to unambiguously identify (Atwood *et al.* have reported a bifurcated NH···Cl–M interaction characterised by X-ray work[29]). The clear position of H(5) in the present case allows the definitive characterisation of this class of interaction. The bifurcation is also evidenced in the anisotropic displacement parameters for H(5), which show significant elongation perpendicular to the H···Cl$_{\mathrm{centroid}}$ vector, and in the relatively small O–H···Cl angles (Table 1).

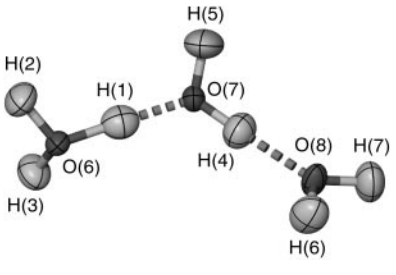

Fig. 1 Thermal ellipsoid plot (70% level) of the $H_7O_3^+$ ion in the neutron structure of **1**. Hydrogen bond lengths and angles are given in Table 1(a).

Regarding the CH hydrogen atoms, the shortest intermolecular contacts are in the range of 2.25–2.3 Å and are to other CH protons. The angular characteristics suggest that these are repulsive, enforced short contacts.[30]

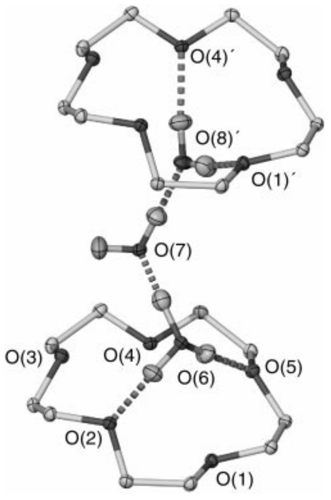

Fig. 2 Oxonium···crown ether hydrogen bonding interactions. For hydrogen bond distances and angles see Table 1(b).

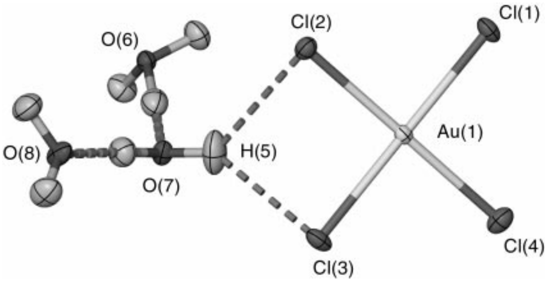

Fig. 3 The bifurcated oxonium ion···tetrachloroaurate(III) hydrogen bond. For distances and angles see Table 1(c). Tetrachloroaurate coordination geometry: Au(1)–Cl(4) 2.2739(13), Au(1)–Cl(1) 2.2797(12), Au(1)–Cl(3) 2.2883(12), Au(1)–Cl(2) 2.2906(12) Å.

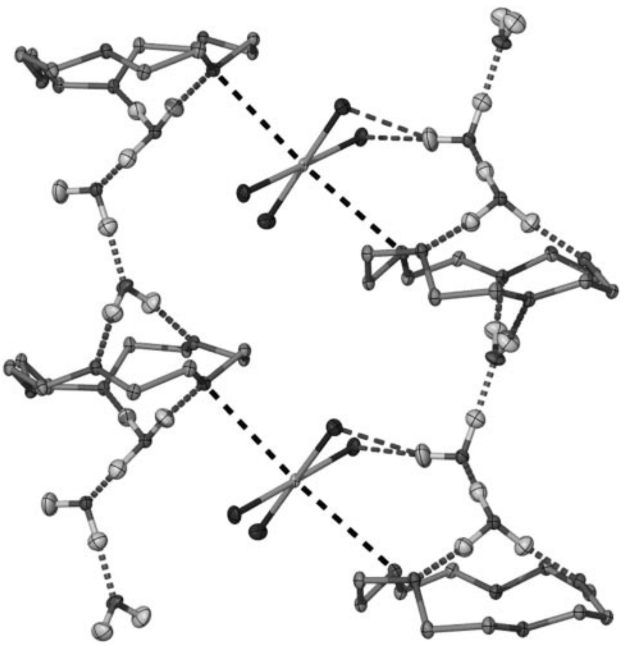

Fig. 4 The hydrogen-bonded chain structure in **1**. Hydrogen bond distances and angles are given in Table 1. Intermolecular distances: Au(1)···O(3) 3.351(1), Au(1)···O(5) 3.323(1) Å.

Finally, the interesting observation of a close contact between the gold atom Au(1) and the non-hydrogen-bonded O(3) observed by X-ray is confirmed in the neutron data with Au(1)···O(3) equal to 3.351 Å (Fig. 4). On the other side the gold atom interacts with O(5) : Au(1)···O(5) = 3.323 Å.

This study has shown that there is a well-defined interplay between supramolecular and covalent interactions with O–H bond distances being modulated by the characteristics of the acceptor atom. In this instance the $H_7O_3{}^+$ ion may best be described as a very strong $H_5O_2{}^+ \cdot H_2O$ hydrogen-bonded unit with the asymmetry arising as a consequence of the better H bond acceptor properties of the crown ether over the softer $[AuCl_4]^-$ anion. An unusual bifurcated OH···ClAu interaction has also been fully characterised.

Experimental

X-Ray crystal data for **1**: $C_{10}H_{27}AuCl_4O_8$, M 614.08 g mol^{-1}, $P2_1/n$, $a = 7.9441(7)$, $b = 18.6964(16)$, $c = 13.9886(10)$ Å, $\beta = 104.347(3)°$, $U = 2012.9(3)$ Å^3, $T = 100$ K, 7727 data, 4598 unique, 237 parameters, $Z = 4$, R_1 $[F^2 > 2\sigma(F^2)]$ 0.0358, wR_2 (all data) 0.0830, Nonius KappaCCD, see ref. 8 for experimental description. Neutron crystal data for **1**: $C_{10}H_{27}AuCl_4O_8$, M 614.08 g mol^{-1}, $P2_1/n$, $a = 7.9346(4)$, $b = 18.6728(9)$, $c = 13.9672(7)$ Å, $\beta = 104.485(3)°$, $U = 2003.62(17)$ Å^3, $Z = 4$, R_1 $[F^2 > 2\sigma(F^2)]$ 0.0381, wR_2 (all data) 0.0851.

In the D19 experiment a yellow needle crystal ($6.0 \times 2.4 \times 2.0$ mm) was mounted using glass wool in quartz capillaries and cooled to 80 K using an Air Products 201 helium Displex[31] on the D19 instrument[22] at ILL equipped with both "banana" and square detectors. A total of 8681 reflections [4176 unique, $\theta < 66.55°$, $\lambda = 1.2316(3)$ Å] were collected on both detectors simultaneously using equatorial and normal beam geometry. Two standard reflections showed no change in intensity. Integration and geometric corrections were carried out using the "retreat" software.[32] Neutron scattering factors were taken from ref. 33. Some ambiguity was apparent in space group choice since some reflections of type $h + l \neq 2n$ on $(h0l)$ were observed up to the 20σ level. These reflections were rescanned slowly and were shown to be essentially absent at 80 K in all but one case, which was badly off-centre and presumably arises from the presence of a second crystallite or background scatter from the aluminium Displex can, for example. The X-ray data reported herein were taken as a starting point for structure refinement using conventional alternating cycles of least-squares refinement and difference Fourier synthesis (SHELXL-97).[34] The initial difference Fourier map showed clearly the positions of all acidic hydrogen atoms and these were incorporated into the model with full anisotropic refinement using a total of 451 parameters. Interestingly, below 60(1) K the crystal passed through a fully reversible phase change resulting in significant peak broadening, even at temperatures down to 16 K. Re-measurement of the unit cell dimensions and selected $(h0l)$ reflections at 16 K, however, revealed that there was no change in the space group nor significant change in unit cell dimensions [unit cell at 16 K: $a = 7.919(2)$, $b = 18.633(5)$, $c = 13.941(3)$ Å, $\beta = 104.6(1)°$]. The measurement temperature of 80 K was chosen to give the sharpest diffraction peaks.

CCDC reference numbers 173090–178091. See http://www.rsc.org/suppdata/nj/b1/b108935h/ for crystallographic data in CIF or other electronic format.

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