Oxonium-ion crown ether complexes from *aqua regia*

Karin Johnson and Jonathan W. Steed*†

Department of Chemistry, King's College London, Stand, London, UK WC2R 2LS

Reaction of an *aqua regia* solution of gold metal with 15-crown-5 and its derivatives results in the formation of the hydrogen bonded aggregates [H_7O_3][$AuCl_4$]·15-crown-5 1 and [H_5O_2][$AuCl_4$]·(benzo-15-crown-5)$_2$ 2; complex 1 exhibits a complex, cross-linked structure in which the $H_7O_3^+$ unit hydrogen bonds to two adjacent crown ethers and a chloride ligand of the anion; the Au^{III} centre also engages in long-range interactions wtih the crown oxygen atoms.

Recent work in acidic liquid clathrate[1,2] media has indicated that the selective crystallisation of various forms of the hydrated proton (H_3O^+, $H_5O_2^+$, *etc.*) may sometimes be achieved by isolation in the presence of a crown ether of the complementary dimensions to the desired oxonium species. A good fit is observed for 18-crown-6 with H_3O^+,[3,4] whereas larger crown ethers such as 21-crown-7 select $H_5O_2^+$.[5,6] Dibenzo-30-crown-10 is able to encapsulate two H_3O^+ ions.[5] In the case of the smaller crown ethers the nature of the oxonium species is variable, and depends considerably on the counter anion.[7] Indeed, [$H_{13}O_6$][$PtCl_5(H_2O)$]·H_2O·(18-crown-6)$_2$ shows that the oxonium ion species isolated by larger crown ethers may be strikingly influenced by the nature of the anion.[8] For protonated derivatives of 2,6-pyrido-21-crown-7 a water molecule is included within the cavity, while the analogous 2,6-pyrido-24-crown-8 complex encapsulates two water molecules with hydrogen bonding interactions to the protonated nitrogen.[9] We have recently begun a programme of research into host–guest species which exhibit a symmetry or steric mismatch.[10] As an extension of this work we now report the results of our investigations into oxonium ion complexes of tetrachloroaurate(III) containing small and intermediate-sized crown ethers.

Aqua regia [HCl–HNO_3 (3 : 1)] has been known since the thirteenth century as the only reagent capable of dissolving metallic gold.[11] A stock solution containing gold in *aqua regia* was prepared, resulting in oxidation of the gold to H[$AuCl_4$]. To aliquots of this solution were added equimolar amounts (relative to Au) of 15-crown-5 and benzo-15-crown-5 in aqueous ethanol. This resulted in the very rapid formation of bright orange–yellow crystalline products from each solution over periods of 1–4 h in good yields. The products were subjected to analysis by X-ray crystallography at −150 °C,‡ which gave the formulations [H_7O_3][$AuCl_4$]·15-crown-5 **1** and [H_5O_2][$AuCl_4$]·(benzo-15-crown-5)$_2$ **2**. The $H_7O_3^+$ ion in particular is relatively uncommon, though it has been observed in hydrogen bromide tetrahydrate.[12]

Complex **1** consists of an unusual, infinite hydrogen bonded chain containing alternating oxonium ion···crown pairs separated by $AuCl_4^-$ anions. The structure of the repeating unit of the infinite $H_7O_3^+$·15-crown-5 chain is shown in Fig. 1, while the overall crystal packing arrangement is illustrated in Fig. 2.

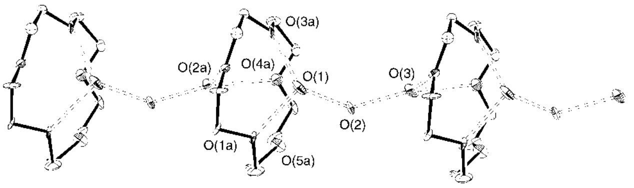

Fig. 1 Structure of the infinite $H_7O_3^+$·15-crown-5 chain repeating unit in **1**

The $H_7O_3^+$ ion exhibits an unsymmetrical conformation with a short O(1)···O(2) distance comparable to that found in $H_5O_2^+$ systems[6,13,14] and a longer O(2)···O(3) interaction, 2.43(2) *vs.* 2.536(18) Å, O(1)–O(2)–O(3) angle 121(2)°. In contrast, a somewhat more symmetrical example is found in [H_7O_3]-[H_9O_4]Br_2·H_2O in which the inter oxygen separations are 2.465 and 2.498 Å,[12] whereas the hydrogen bonded $H_5O_2^+$···H_2O pair exhibits very different distances of 2.424 and 2.721 Å.[15] In complex **1** the oxonium ion hydrogen bonds to the crown oxygen atoms O(1a) and O(3a); O···O 2.64(2) and 2.63(3) Å respectively. The opposite end of the $H_7O_3^+$ unit interacts with an adjacent crown *via* longer hydrogen bonds; O(3)···O(2a) 2.75(2), O(3)···O(4a) 2.820(18) Å. This presumably results from the conflicting steric requirements of the $AuCl_4^-$ anion and the oxonium cation, although it may also be influenced by an additional, albeit long hydrogen bond from the central atom of the oxonium ion to one of the chloride ligands of the tetrachloroaurate(III) anion, O(2)···Cl(1) 3.30(2) Å. The gold(III) ion exhibits a square-planar coordination geometry, with Au–Cl distances falling into two groups; Au–Cl(1), –Cl(4) 2.296(7) Å and Au–Cl(2), –Cl(3) 2.267(7) Å (average). Interestingly, the Au^{III} ions also exhibit very long axial interactions with crown oxygen atom O(5a) (which does not take part in a hydrogen bond) and O(3a); Au–O(3a) 3.342(16), Au–O(5a) 3.381(19) Å, resulting in a cross-linked polymeric structure.

Given the polymeric nature of **1**, the structure of the benzo-15-crown-5 derivative **2** is somewhat surprising. Complex **2** contains discrete $H_5O_2^+$·(benzo-15-crown-5)$_2$ units in which a pair of crowns sandwich the oxonium ion (Fig. 3). The syntheses of both **1** and **2** were carried out under identical conditions, in a 1 : 1 ratio of Au : crown. Examination of Fig. 2, however, suggests that the long range Au–O$_{crown}$ interactions seen for **1** as well as the hydrogen bond to O(2), would not be sterically feasible for an analogous benzo-15-crown-5 complex. Indeed, the closest axial approach to the $AuCl_4^-$ anions in **2** is

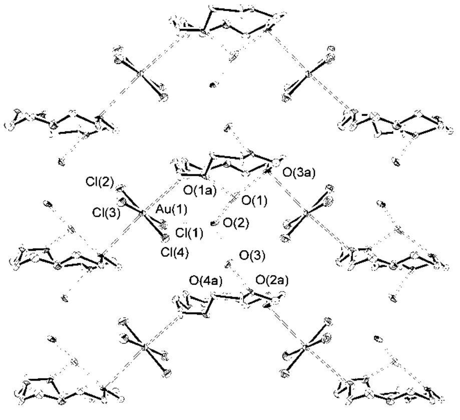

Fig. 2 Crystal packing arrangement in [$H_7O_3^+$][$AuCl_4$]·15-crown-5 **1** showing long-range axial interactions from the crown ether to the $AuCl_4^-$ anions. Au–Cl(1–4) 2.297(7), 2.268(8), 2.266(7), 2.295(7) Å; Au–O(3a) 3.342(16), Au–O(5a) 3.381(19) Å. Hydrogen bonds: O(1)–O(1a) 2.64(2), O(1)–O(3a) 2.63(3), O(3)–O(2a) 2.75(2), O(3)–O(4a) 2.820(18) Å. Oxonium ion: O(1)–O(2) 2.43(2), O(2)–O(3) 2.536(18) Å.

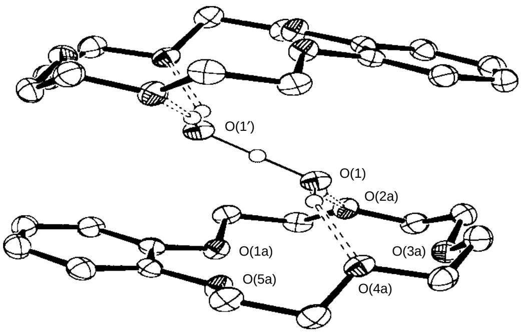

Fig. 3 The discrete H_2O_2'·(benzo-15-crown-5)$_2$ unit in **2**. Hydrogen bonds: O(1)–O(2a) 2.715(4), O(1)–O(4a) 2.642(4) Å. Oxonium ion: O(1)–O(1′) 2.420(6) Å.

by the hydrogen atoms of a crown ethylene moiety, and hence it seems likely that in the absence of these stabilisations a simple ion paired structure results.

Interaction of H[$AuCl_4$] with other crown ethers also results in the formation of oxonium ion–crown ether salts of tetrachloroaurate(III). In particular, reactions with larger crown ethers, namely 18-crown-6 and dibenzo-24-crown-8, give respectively the H_3O^+ and $H_5O_2^+$ containing species [H_5O][$AuCl_4$]·18-crown-6 and [H_5O_2][$AuCl_4$]·dibenzo-24-crown-8. Full details of this work will be reported separately.

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Notes and References

† E-mail: jon.steed@kcl.ac.uk

‡ *Crystal data* **1**: $C_{10}H_{27}AuCl_4O_8$, M = 614.08, monoclinic, space group $P2_1$, a = 7.9485(3), b = 18.7082(7), c = 13.9930(6) Å, β = 104.34(1)°, U = 2015.95(14) Å^3, Z = 4, 7868 unique data ($2\theta \leqslant 52°$), 406 parameters, R_1 [$F^2 > 2\sigma(F^2)$] = 0.058, wR_2 (all data) = 0.174. **2**: $C_{28}H_{45}AuCl_4O_{12}$, M = 912.41, triclinic, space group $P\bar{1}$, a = 9.2950(6), b = 10.2293(11), c = 11.6412(11) Å, α = 64.77(1), β = 88.63(1), γ = 66.99(1)°, U = 907.99(14) Å^3, Z = 1, 3321 unique data ($2\theta \leqslant 52°$), 214 parameters, R_t [$F^2 > 2\sigma(F^2)$] = 0.028, wR_2 (all data) = 0.064. Crystals were mounted using a fast setting epoxy resin on the end of a glass fibre and cooled on the diffractometer. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo-Kα radiation using ϕ rotations with 2° frames and a detector to crystal distance of 25 mm. Integration was carried out by the program DENZO-SMN.[16] Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program Scalepack.[16] Structures were solved using the direct methods option of SHELXS-97[17] and developed using conventional alternating cycles of least squares refinement and difference Fourier synthesis (SHELXL-97).[17] In general, all non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in idealized positions and allowed to ride on the atom to which they were attached. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. In the case of **2** oxonium ion protons were located experimentally and refined freely. Oxonium ion protons could not be located for **1**. All calculations were carried out either on a Silicon Graphics Indy workstation or an IBM-PC compatible personal computer. CCDC 182/889.

1 J. L. Atwood, in *Chemical Separations*, ed. C. J. King and J. D. Navratil, Litarvan, Denver, 1986.
2 J. L. Atwood, in *Separation Technology*, ed. N. N. Li and H. Strathmann, United Engineering Trustees, New York, 1988.
3 J. L. Atwood, S. G. Bott, A. W. Coleman, K. D. Robinson, S. B. Whetstone and C. M. Means, *J. Am. Chem. Soc.*, 1987, **109**, 8100.
4 J. L. Atwood, S. G. Bott, K. D. Robinson, E. J. Bishop and M. T. May, *J. Cryst. Spectrosc. Res.*, 1991, **21**, 459.
5 P. C. Junk and J. L. Atwood, *J. Chem. Soc., Dalton Trans.*, 1997, 4393.
6 P. C. Junk and J. L. Atwood, *J. Chem. Soc., Chem. Commun.*, 1995, 1551.
7 J. L. Atwood and P. C. Junk, *Chem. Commun.*, submitted.
8 D. Steinborn, O. Gravenhorst, H. Hartung and U. Baumeister, *Inorg. Chem.*, 1997, **36**, 2195.
9 P. D. J. Grootenhuis, J. W. H. M. Uiterwijk, D. N. Reinhoudt, C. J. van-Stavren, E. J. R. Sudhölter, M. Bos, J. van-Eerden, W. T. Klooster, L. Kruise and S. Harkema, *J. Am. Chem. Soc.*, 1986, **108**, 780.
10 J. W. Steed, H. Hassaballa and P. C. Junk, *Chem. Commun.*, 1998, 577.
11 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984.
12 J.-O. Lundgren and I. Olovsson, *J. Chem. Phys.*, 1968, **49**, 1068.
13 C. I. Ratcliffe and D. E. Irish, in *The Nature of the Hydrated Proton*, ed. F. Franks, Cambridge, 1986.
14 A. Bino and F. A. Cotton, *J. Am. Chem. Soc.*, 1979, **101**, 4150.
15 R. Attig and J. M. Williams, *Inorg. Chem.*, 1976, **15**, 3057.
16 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. C. W. Carter and R. M. Sweet, Academic Press, New York, 1996.
17 G. M. Sheldrick, in 'SHELX-97', University of Göttingen, 1997.

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