Oxonium Ions from Aqua Regia: Isolation by Hydrogen Bonding to Crown Ethers

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The preparation and structures of a variety of oxonium ion tetrachloroaurate(III) salts isolated from aqua regia are reported. The new compounds are $[(H_5O_2)_2(12\text{-crown-}4)_2][AuCl_4]_2$ (**1**), $[(H_7O_3)(15\text{-crown-}5)][AuCl_4]$ (**2**), $[(H_5O_2)(\text{benzo-15-crown-5})_2][AuCl_4]$ (**3**), $[(H_3O)(18\text{-crown-}6)][AuCl_4]$ (**4**), $[(H_5O_2)(\text{dibenzo-24-crown-8})][AuCl_4]$ (**5**), $[(H_5O_2)(\text{4-nitrobenzo-15-crown-5})_2][AuCl_4]$ (**6**), $[(H_3O)(\text{4-nitrobenzo-18-crown-6})][AuCl_4]$ (**7**), $[(H_{11}O_5)(\text{tetrachlorodibenzo-18-crown-6})_2][AuCl_4]$ (**8**), and $[(H_7O_3)(\text{dinitrodibenzo-30-crown-10})][AuCl_4]$ (**9**). A significant correlation between the degree of proton hydration and crown ether size is observed. Aryl crown ethers are nitrated in concentrated aqua regia, but nonnitrated products may be obtained in a dilute solution of aqua regia by reaction with aqueous $HAuCl_4$.

Introduction

The crown ethers are noted for their ubiquitous alkali metal cation binding properties. In the solid state, remarkable geometries are observed in $M^+ \subset$crown ether complexes, particularly in cases for which there is a mismatch between the crown ether cavity and the metal ionic radius.[1] We have recently shown that in many cases metal cation complexation is either aided by or in competition with other supramolecular interactions, particularly hydrogen bonds.[1−4] As a general rule, the solid-state structure of crown ether inclusion complexes represents a compromise, optimizing the geometry and hence interaction energy of as many supramolecular interactions as possible, ranging from metal ion−dipole interactions to strong[5] and weak[6−9] hydrogen bonds. These general rules also apply to crown ether complexes with guests other than metal cations. In particular, a significant amount of work on crown ether complexes of the hydrated proton[10−21] (oxonium ion, $H(H_2O)_n^+$, $n = 1$ to ca. 20) has shown that crown ethers act as excellent acceptors for strong, charge-assisted hydrogen bonds found in oxonium ions and, most interestingly, the choice of crown ether and counteranion has a decisive influence on the identity of the oxonium ion formed in the crystal and on its bonding. Crown ethers thus represent an excellent way of "trapping" particular oxonium ion species; in effect, the problem of isolation of a particular oxonium ion becomes an exercise in crystal engineering.[8,9,22−24] For example, the ubiquitous 18-crown-6 has been shown in numerous examples to be almost entirely selective for the simplest oxonium ion, H_3O^+, because of the size and symmetry match of H_3O^+ and the crown ether cavity in its common D_{3d} conformation, allowing the formation of three strong, bifurcated $O-H^+\cdots O_{crown}$ interactions.[11] The effect is analogous to the use of crown ethers to stabilize reactive species such as $[(H_2O)_5FeOFe(H_2O)_5]^{4+}$.[25,26] From a crystal engineering perspective, it is also noteworthy that strong hydrogen-bonding interactions may have a significant effect on molecular structure, particularly the geometry of covalent bonds to hydrogen as well as other malleable interactions.[27] Thus, there exists a great deal of scope for a systematic study of solid-state oxonium ion complexes of the crown ethers, and the results of our studies in

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Table 1. Preparation of New Complexes

medium[a]	crown ether	oxonium ion	product
a, c	12-crown-4	$H_5O_2^+$	$[(H_5O_2)_2(12\text{-crown-4})_2][AuCl_4]_2$, **1**
a, b	15-crown-5	$H_7O_3^+$	$[(H_7O_3)(15\text{-crown-5})][AuCl_4]$, **2**
a	benzo-15-crown-5	$H_5O_2^+$	$[(H_5O_2)(\text{benzo-15-crown-5})_2][AuCl_4]$, **3**
b	benzo-15-crown-5	$H_5O_2^+$	$[(H_5O_2)(\text{4-nitrobenzo-15-crown-5})_2][AuCl_4]$, **6**
b	18-crown-6	H_3O^+	$[(H_3O)(18\text{-crown-6})][AuCl_4]$, **4**, form I
a	18-crown-6	H_3O^+	$[(H_3O)(18\text{-crown-6})][AuCl_4]$, **4**, form II
b	benzo-18-crown-6	H_3O^+	$[(H_3O)(\text{4-nitrobenzo-18-crown-6})][AuCl_4]$, **7**
b	dibenzo-18-crown-6	$H_{11}O_5^+$	$[(H_{11}O_5)(\text{tetrachlorodibenzo-18-crown-6})_2][AuCl_4]$, **8**
a, c	dibenzo-24-crown-8	$H_5O_2^+$	$[(H_5O_2)(\text{dibenzo-24-crown-8})][AuCl_4]$, **5**
b	dibenzo-30-crown-10	$H_7O_3^+$	$[(H_7O_3)(\text{dinitrodibenzo-30-crown-10})][AuCl_4]$, **9**

[a] a is dilute aqua regia, b is concentrated aqua regia, and c is aqueous $HAuCl_4$.

this area are reported herein, along with the extension of these solid-state results to the solution phase. Part of this work has been the subject of a preliminary communication.[28]

Results and Discussion

The structures of oxonium ion complexes of the crown ethers have been shown to depend on the identity of both the crown ether and the counteranion (and hence acid medium),[10−18,20,21,29−32] so in order to make meaningful and reproducible comparisons, it is necessary to employ the same counteranion in every structure. Moreover, it is desirable that this anion should be (i) sterically nondemanding and (ii) a poor hydrogen-bond acceptor in comparison to the crown ethers. For these reasons, we chose to study crown ether complexes crystallized from the unusual medium of an aqua regia solution of metallic gold (gold dissolved in a 4:1 mixture of hydrochloric and nitric acids), a mixture believed by Roger Bacon to be the “Elixir of Life”! Aqua regia is an oxidizing acidic solvent and has been known since the middle ages as the only reagent capable of dissolving metallic gold (its invention has been attributed to the alchemist Gerber, the “father of modern chemistry”, who died in 803 C.E.). Under these conditions, the gold is oxidized to Au(III), and thus, oxonium ion crown ether complexes are isolated as their tetrachloroaurate(III) ($[AuCl_4]^-$) salts.

Preparations. Standard dilute (a) and concentrated (b) aqua regia solutions of $HAuCl_4$ were prepared and mixed with stoichiometric quantities of crown ethers as shown in Table 1, which also shows the formulas of the resulting products. In many cases, crystalline precipitates were formed immediately, while for 12-crown-4 in particular, crystals were (reproducibly) isolated only after periods of months. In essentially every reaction attempted, yellow-orange crystalline products were formed, although many of the products exhibited a strong propensity for crystal twinning and disorder. It was found that, in the case of benzo crown ethers, concentrated aqua regia was a sufficiently good source of NO_2^+ to result in nitration of the aryl ring (as has been observed previously[17]) and, in the case of **8**, chlorination. As an alternative, it was found that use of aqueous $HAuCl_4$ gave unnitrated products. For non-benzenoid crown ethers, aqueous $HAuCl_4$ generally gave the same products as the same reaction in aqua regia.

Structures. The X-ray crystal structure of $[(H_5O_2)_2(12\text{-crown-4})_2][AuCl_4]_2$ (**1**) is shown in Figure 1. The compound is monoclinic but with a β angle very close to 90° (90.295°), frustrating initial attempts at structure determination using poor quality crystals prepared from dilute aqua regia. Much better quality crystals were obtained in essentially quantitative yield using aqueous $HAuCl_4$, although crystallization took over 3 months. The 12-crown-4 acceptor is too small to accommodate even H_3O^+ (which is approximately the same size as K^+ [16]), and as a consequence, a sandwich structure is adopted in which an $H_5O_2^+$ cation (O(3) and its symmetry equivalent) is situated between facing pairs of 12-crown-4 molecules, hydrogen bonding to two ether oxygen atoms on each crown. The remaining ether oxygen atoms interact with a second $H_5O_2^+$ cation which bridges between two “$H_5O_2^+ \subset (12\text{-crown-4})_2$” pairs (O(4) and its symmetry equivalent). Hydrogen atoms could not be located; however, the O···O distances of 2.419 and 2.452 Å are typical of the strong hydrogen bonding in $H_5O_2^+$, and both independent oxygen atoms are pyramidal, although O(4) deviates much more significantly from the mean plane of acceptor atoms.[5,10,15,29] Hydrogen bonds to ether oxygen atoms are short at 2.576 and 2.674 Å. The $[AuCl_4]^-$ anions adopt the usual square-planar geometry. The two independent $[AuCl_4]^-$ units are mutually perpendicular and chloro ligand Cl(1) attached to Au(1) interacts with Au(2) at a distance of 3.845 Å to give an infinite anionic chain. The Au(1)−Cl(1) distance of 2.2915(16) Å is significantly longer than the distance to Cl(2) of 2.2747(16) Å, presumably as a consequence of this interaction. The Au(2)−Cl bonds which do not show such long-range interactions are much more even in length, 2.2854(18) and 2.2881(17) Å.

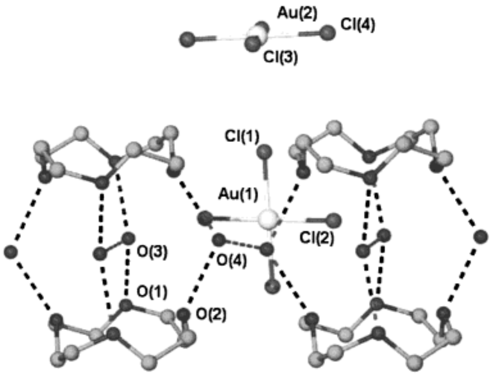

Figure 1. X-ray crystal structure of $[(H_5O_2)_2(12\text{-crown-4})_2][AuCl_4]_2$ (**1**) showing the two independent $H_5O_2^+$ units.

Addition of 15-crown-5 to both dilute and concentrated aqua regia gave the $H_7O_3^+$-containing complex $[(H_7O_3)(15\text{-crown-5})][AuCl_4]$ (**2**). While the oxonium ion/crown stoichiometry is similar to **1**, the structure is very different, consisting of an infinite alternating chain of $H_7O_3^+$ cations and 15-crown-5 acceptors. The crown ether adopts the usual conformation described by a torsion angle sequence (g$^+$)aa(g$^-$)aa(g$^+$)aa(g$^-$)ag$^-$(g$^-$)aa with O−C−C−O torsion angles alternating plus or minus gauche (generally ±60°) except for two that must retain

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the same sign as a consequence of molecular symmetry.[33] The $H_7O_3^+$ ion exhibits an uneven geometry with the O(1)−O(2) distance of 2.432(7) Å comparable to that found in $H_5O_2^+$ systems, such as compound **1** and others.[19,29,32] The O(2)−O(3) interaction is longer at 2.563(7) Å; the O(1)−O(2)−O(3) angle of 120(1)° suggests some contribution from an $H_5O_2^+{\cdot}H_2O$ resonance form. While $H_7O_3^+$ is relatively uncommon, other examples include $[H_7O_3][H_9O_4]Br_2{\cdot}H_2O$ in which the interoxygen separations are similar at 2.465 and 2.498 Å,[34] whereas the hydrogen-bonded $H_5O_2^+{\cdots}H_2O$ pair exhibits very different distances of 2.424 and 2.721 Å.[18] Oxonium ion to crown ether oxygen atom hydrogen bonds are to O(1a) and O(3a); O···O distances are 2.649(7) and 2.650(7) Å, respectively. The opposite end of the $H_7O_3^+$ unit interacts with an adjacent crown via longer hydrogen bonds; O(3)···O(2a) distance is 2.758(8) Å, and O(3)···O(4a) distance is 2.775(8) Å; all of these are in contrast to the short interactions in **1**. This presumably results from the conflicting steric requirements of the $AuCl_4^-$ anion and the oxonium cation and an additional 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) (3.318(6) Å). Chloride ligands are known to be reasonable hydrogen-bond acceptors.[35] The gold(III) ion exhibits a square-planar coordination geometry with Au−Cl distances again falling into two groups; Au−Cl(1) and Au−Cl(4) distances are 2.286(2) Å on average, and Au−Cl(2) and Au−Cl(3) distances are 2.273(2) Å on average (cf. compound **1**). Interestingly, the Au(III) ions also exhibit very long axial interactions with crown oxygen atoms O(5a) (which does not take part in a hydrogen bond) and O(3a); Au−O(3a) distance is 3.339(4) Å and Au−O(5a) distance is 3.373(4) Å, resulting in a cross-linked polymeric structure, as shown in Figure 2.

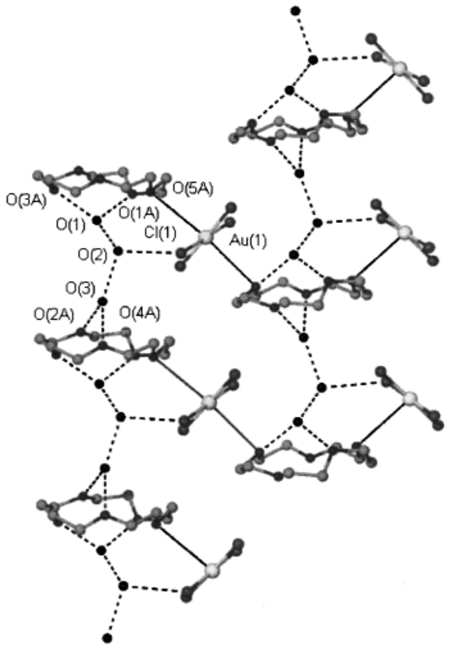

Figure 2. Packing in $[(H_7O_3)(15\text{-crown-}5)][AuCl_4]$ (**2**) showing the hydrogen-bonded chain structure and long-range interactions to the $[AuCl_4]^-$ anions.

Unlike 15-crown-5 itself, the reaction of benzo-15-crown-5 with $HAuCl_4$ gave different products in dilute and concentrated aqua regia. In dilute solution, the 1:2 sandwich complex $[(H_5O_2)(\text{benzo-15-crown-5})_2][AuCl_4]$ (**3**) was produced, as shown in Figure 3, whereas in concentrated acid, attack by NO_2^+ resulted in nitration of the benzo ring[17] to give 4-nitrobenzo-15-crown-5 which also crystallized as a sandwich complex, $[(H_5O_2)(4\text{-nitrobenzo-15-crown-5})_2][AuCl_4]$ (**6**), broadly similar to complex **3**. Compound **6** formed extremely poor quality crystals, and a complete structure determination could not be accomplished. However, examination of the unit cell parameters reveals close similarities to compound **3** (Table 2), and a partial structure solution shows clearly the sandwiched $[(H_5O_2)(4\text{-nitrobenzo-15-crown-5})_2]^+$ cation. Further evidence for the nitration of the aryl ring comes from the ^1H NMR spectrum of crystalline **6**, which is consistent with a 1,2,4-trisubstituted aryl ring, and elemental analysis (see Experimental Section). In contrast, the X-ray structure of compound **3** was of high precision, and hydrogen atoms were located in the final difference Fourier map and refined freely. The central proton lies on a crystallographic inversion center and appears to be equally shared between the two oxygen atoms of the $H_5O_2^+$ cation, although slight disorder of this proton about the inversion center cannot be ruled out. The O···O distance of 2.420(6) Å is consistent with the formulation, although longer than distances that have been previously observed, which may be as short as 2.34−2.37 Å.[14,32] Hydrogen bonds to the crown ether are typical at 2.642(6) and 2.715(6) Å. The formation of a 1:2 complex in both **3** and **6** is likely to be a consequence of the steric bulk of the benzo-derived crown ethers, preventing formation of infinite chains as observed for **2**. In particular, long-range Au···O interactions would not be feasible in **3** and **6**.

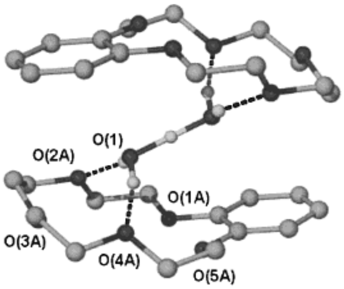

Figure 3. The discrete $[(H_5O_2)(\text{benzo-15-crown-5})_2]^+$ unit in complex **3**.

It is well-established that the reaction of 18-crown-6 with a variety of acidic media gives the $[H_3O{\subset}18\text{-crown-}6]^+$ cation. The macrocycle is highly selective for H_3O^+ because of the size and symmetry match between them, allowing near-planar inclusion of the oxonium ion with the formation of three bifurcated hydrogen bonds.[16] The present study confirms these results, and a complex of formula $[(H_3O)(18\text{-crown-}6)][AuCl_4]$ (**4**) is isolated from both dilute and concentrated aqua regia. Interestingly, however, the complex exists in two polymorphic forms. The two forms have very similar densities and closely related packing modes and may well be very similar in energy. The highly crystalline form I is isolated from concentrated aqua regia (solution b), whereas long needles of less crystalline form II are produced in the dilute medium a (see Experimental Section). The close similarity between the two forms may be observed in the *b* and *c* unit cell dimensions in forms I and II, respectively, which are almost identical. This corresponds to the width of the $[(H_3O)(18\text{-crown-}6)][AuCl_4]$ layer with the

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Table 2. Crystallographic Data for New Complexes

	1	**2**	**3**	**4**(I)	**4**(II)
formula	$C_8H_{21}AuCl_4O_6$	$C_{10}H_{27}AuCl_4O_8$	$C_{28}H_{45}AuCl_4O_{12}$	$C_{12}H_{27}AuCl_4O_7$	$C_{12}H_{27}AuCl_4O_7$
fw (g mol^{-1})	522.01	614.08	912.41	622.10	622.10
temp (°C)	−173(2)	−150(2)	−150(2)	−173(2)	−150(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P2/m$	$P2_1/n$	$P\bar{1}$	$Pbam$	$P2/m$
a (Å)	8.2616(7)	7.9485(3)	9.2950(6)	8.710(3)	13.4509(8)
b (Å)	12.2727(10)	18.7082(7)	10.2293(11)	10.2103(4)	12.0398(7)
c (Å)	8.2855(6)	13.9930(6)	11.6412(11)	12.0284(5)	20.2750(11)
α (deg)	90	90	64.767(1)	90	90
β (deg)	90.295(4)	104.341(1)	88.627(1)	90	100.084(1)
γ (deg)	90	90	66.994(1)	90	90
V (Å^3)	840.07(12)	2015.95(14)	907.99(14)	1069.7(4)	3232.7(3)
Z	2	4	1	2	6
D_c (g cm^{-3})	2.182	2.023	1.539	1.931	1.917
μ (mm^{-1})	9.407	7.858	4.400	7.403	7.349
final R1^a ($I > 2\sigma(I)$)	0.0364	0.0517	0.0279	0.0220	0.0871
wR2^a (all data)	0.0858	0.1459	0.0643	0.0492	0.2632

	5	**6**	**7**	**8**	**9**
formula	$C_{24}H_{37}AuCl_4O_{10}$	$C_{28}H_{43}AuCl_4N_2O_{16}$	$C_{16}H_{26}AuCl_4NO_9$	$C_{40}H_{51}AuCl_{12}O_{17}$	$C_{28}H_{45}AuCl_4N_2O_{17}$
fw (g mol^{-1})	824.30	1002.469	715.14	1426.17	1020.43
temp (°C)	−150(2)	−173(2)	−150(2)	−173(2)	−173(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Cc	$P2_1/n$
a (Å)	7.7268(3)	9.1537(8)	7.1538(7)	20.490(2)	11.4366(9)
b (Å)	8.5254(4)	21.3073(25)	11.2743(11)	12.3900(10)	13.6666(15)
c (Å)	11.6999(6)	22.4196(24)	15.4753(11)	21.171(2)	24.949(3)
α (deg)	85.438(1)	63.044(6)	77.395(6)	90	90
β (deg)	88.430(1)	87.590(7)	79.995(6)	91.536(6)	90.487(6)
γ (deg)	73.801(1)	82.973(7)	82.499(5)	90	90
V (Å^3)	737.77(6)	3868(1)	1193.9(4)	5372.6(9)	3899.3(7)
Z	1	4	2	4	4
D_c (g cm^{-3})	1.855		1.989	1.763	1.738
μ (mm^{-1})	5.400		6.655	3.401	4.119
final R1^a ($I > 2\sigma(I)$)	0.0435		0.0544	0.0671	0.0927
wR2^a (all data)	0.1149		0.1109	0.1361	0.1893

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

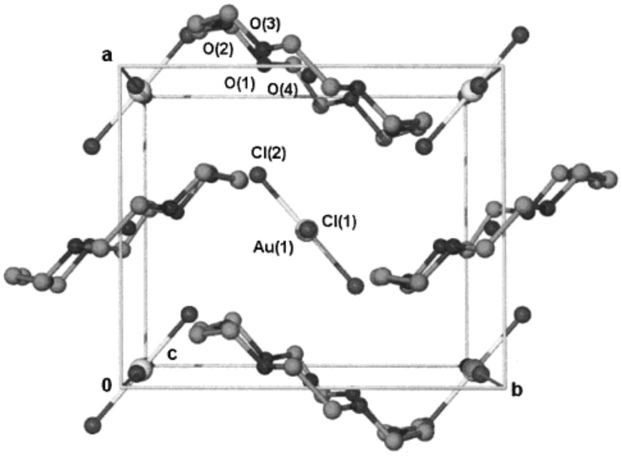

Figure 4. Herringbone packing in [(H_3O)(18-crown-6)][$AuCl_4$] (**4**), form I. The polymorphic form II is almost identical.

crown ether edge-on. In both structures, the crown ethers pack in a herringbone arrangement based on a tetragonal arrangement of crown ethers surrounding an [$AuCl_4$]$^-$ anion, as shown in Figure 4. The only key difference is that form II exhibits extensive disorder of the tetrachloroaurate moiety and of the oxonium ions, whereas form I is ordered. It proved to be difficult to derive a chemically sensible model for the disorder in form II, and as a result, some significant electron density is still unaccounted for. In form I, as with most [$H_3O{\subset}$18-crown-6]$^+$ cations, the crown ether adopts near-perfect D_{3d} symmetry, although it is situated on a crystallographic 2-fold axis. The oxonium ion is apparently planar, although examination of anisotropic displacement parameters suggests that it may in fact exhibit slight pyramidal disorder across the crystallographic symmetry element. This disorder is more pronounced in form II, and we were able to partially resolve it, and hence, this may be the fundamental root of the polymorphic behavior. The oxonium ion forms the expected three bifurcated hydrogen bonds to the six crown ether oxygen atoms with O···O distances of 2.72−2.79 Å. The [$AuCl_4$]$^-$ anions do not interact with one another or with crown ether oxygen atoms as in previous structures.

The reactions of benzo-18-crown-6 and dibenzo-18-crown-6 with aqua regia were also attempted; however, characterizable crystalline products were only obtained from the concentrated solution b. In the case of benzo-18-crown-6, nitration of the aryl ring was observed as for **6** to give [(H_3O)(4-nitrobenzo-18-crown-6)][$AuCl_4$] (**7**). Solution ^{1}H NMR data confirmed the ring substitution pattern, and the nitrated ligand was also observed by FAB-MS (see Experimental Section). The X-ray crystal structure of this material proved to be extensively disordered, the disorder taking the form of two alternative sets of positions for the entire crown ether and corresponding to the fact that the nitro group may be on either side of the pseudo mirror plane of the rest of the ligand. A satisfactory model was developed, however, and a good refinement was obtained. Unlike the D_{3d} conformation in **4**, the 18-crown-6 ring adopts a dome-shaped geometry with the pyramidal H_3O^+ ion perched on top. The protons of the oxonium ion were located, and their positions, along with O···O distances, suggest the formation of

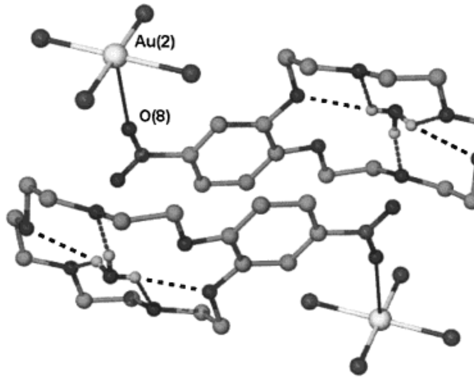

Figure 5. The $[H_3O\subset \text{nitrobenzo-18-crown-6}]^+$ complex in **7** showing the π-stacked overlap and nitro−gold interactions, $NO_2\cdots Au$ distance of 3.109(11) Å.

two bifurcated interactions and one short, nonbifurcated hydrogen bond, as shown in Figure 5. The shortest distances (to the major disordered component) are 2.597(8) and 2.635(16) Å, comparable to those found in **1**. The doming apparently arises to accommodate a direct face-to-face π-stacking interaction involving the nitroaryl groups (Figure 5). The intercentroid distance is 3.45 Å, consistent with previously observed systems,[36,37] with the electron-rich alkoxy substituents overlapping the nitro group on the adjacent molecule. The π-stacking continues infinitely throughout the crystal. The doming also accommodates a rather short "long-range" interaction from the NO_2 group to both axial faces of one of the two independent $[AuCl_4]^-$ anions, making it pseudooctahedral, as in **2**. The $NO_2\cdots Au$ distance is shorter than **2**, however, at 3.109(11) Å (cf. 3.373 Å in **2**).

Treatment of dibenzo-18-crown-6 with concentrated aqua regia/$HAuCl_4$ solution b also resulted in chemical modification of the crown ether itself, although the results were surprising. The reaction was carried out a number of times, and in each case, an orange-yellow crystalline product was isolated with elemental analysis showing varying quantities of nitrogen. As with many of the compounds reported herein, crystals were readily obtained but were invariably of poor quality as a result of multiple twinning and needle morphology. Only one data set (of four collected) was solved, and this very surprisingly gave the structure as $[(H_{11}O_5)(\text{tetrachlorodibenzo-18-crown-6})_2]$-$[AuCl_4]$ (**8**), as shown in Figure 6. It seems likely that varying amounts of nitrated and chlorinated product are formed during the reaction, and indeed, nitro compounds may be precursors to chlorination. The structure is striking from the point of view of the oxonium ion species present, $H_{11}O_5^+$. The acidic proton appears to be located predominantly on O(3) situated in the center of the crown ether O(1A)−O(6A). Although hydrogen atoms could not be located, this oxygen atom forms four short contacts (2.5−2.6 Å) to the ether acceptors as well as two longer ones (2.7−2.8 Å). Contacts to the water oxygen atoms O(2) and O(4) are also apparently very short at 2.22 and 2.34 Å, although the former distance is likely to be shortened by unresolved disorder in O(2). This atom appears to "rattle" around the cavity formed by the stacking of the two crown ethers, which resemble two hands held mutually perpendicularly, back-to-palm. The terminal oxygen atom, O(1), more resembles a water molecule than part of an oxonium ion with O(1)$\cdots$O(2) distance of 2.561 Å and all contacts to crown ether oxygen atoms O(1B)−O(6B) greater than 3.0 Å. The apparent O(4)$\cdots$O(5) distance is also unreasonably short at 2.22 Å, and again, unresolved disorder is likely, although none of our attempts to model this were successful. Clearly, however, in this case, the propensity of 18-crown-6 derivatives to select H_3O^+ is not operating. The pronounced "cup"-shaped conformation of the crown ether (cf. **7**) is a possible cause, encouraging greater exposure of the included oxonium ions.

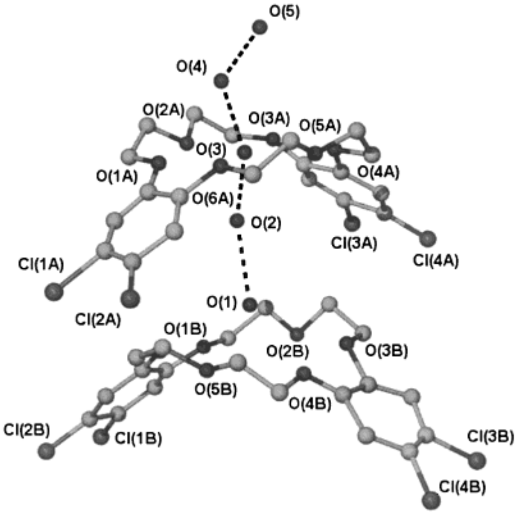

Figure 6. The stacked channel-like arrangement in the tetrachlorodibenzo-18-crown-6 derivative **8** showing the $H_{11}O_5^+$ ion threaded through the crown ethers. Hydrogen bonds to crown ethers are omitted for clarity.

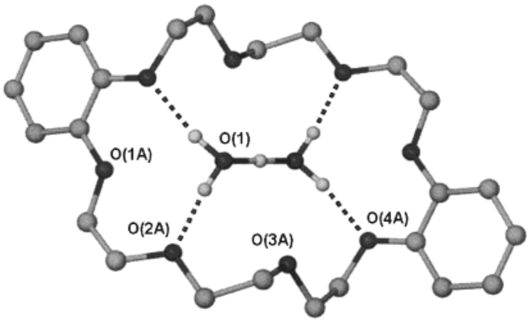

Figure 7. Excellent match between $H_5O_2^+$ and dibenzo-24-crown-8 in complex **5**.

Despite the high reactivity of benzo crown ethers toward nitration and other covalent modification, we were able to prepare an unmodified complex with dibenzo-24-crown-8 through use of dilute aqua regia solution a and aqueous $H[AuCl_4]$ (solution c), namely, $[(H_5O_2)(\text{dibenzo-24-crown-8})]$-$[AuCl_4]$ (**5**). In the case of larger crown ethers such as 21-crown-7 and dibenzo-30-crown-10, it has been shown that the former is an excellent match for $H_5O_2^+$ while the latter accommodates two isolated H_3O^+ ions.[30] Dibenzo-24-crown-8 is also of the correct size to neatly accommodate $H_5O_2^+$ which forms strong hydrogen bonds with four crown ether oxygen atoms, as shown in Figure 7. As in compound **3**, the $H_5O_2^+$ cation is situated over an inversion center and the central proton (located on the final difference Fourier map) is located on the symmetry position and is thus equally shared between the two oxygen atoms. The O$\cdots$O distance of 2.422 Å is consistent with other structures described above. Hydrogen-bonded O$\cdots$O distances to the crown ether are long on average at 2.645 and 2.809 Å, consistent with the large size of the macrocycle. The $[AuCl_4]^-$ anion does not form any short intermolecular contacts,

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(36) Aspley, C. J.; Boxwell, C.; Buil, M. L.; Higgitt, C. L.; Long, C.; Perutz, R. N. *Chem. Commun.* **1999**, 1027.

(37) Nichols, P. J.; Raston, C. L.; Steed, J. W. *Chem. Commun.* **2001**, 1062−1063.

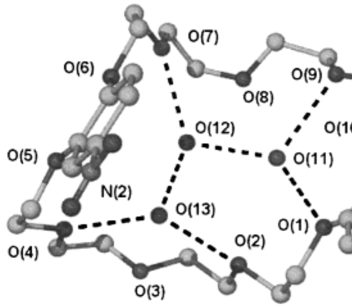

Figure 8. The $H_7O_3^+$ ion deeply embedded in the U-shaped dinitrodibenzo-30-crown-10 in complex **9**.

and the two independent Au−Cl bond lengths are very similar to one another.

To try to isolate large oxonium ions in a controlled fashion, reactions were also attempted with dibenzo-21-crown-7 and dibenzo-30-crown-10. Crystalline products were obtained in both cases, and elemental analysis data indicated that both crown ethers had been nitrated. In the case of dibenzo-21-crown-7, however, we were unable to solve the crystallographic data (unit cell dimensions: 8.167(12), 13.60(3), 14.66(2) Å, 86.75(11)°, 101.02(10)°, 93.30(9)°, triclinic) and the elemental analysis is *not* consistent with a straightforward formulation of $[(H_5O_2)$(dinitrodibenzo-21-crown-7)]$[AuCl_4]$ (cf. compound **5**), and hence, this material remains uncharacterized. The product from the reaction with dibenzo-30-crown-10, namely, $[(H_7O_3)$(dinitrodibenzo-30-crown-10)]$[AuCl_4]$ (**9**) proved to be highly interesting, however. The crown ether adopts a "U-shaped" conformation reminiscent of the inclusion complexes of dibenzo-30-crown-10 with aromatic guests such as $[Pt(NH_3)_2(2,2'\text{-bipyridyl})]^{2+}$ and diquat.[38,39] This enables it to envelop an $H_7O_3^+$ cation, which is buried deeply within the macrocycle cavity, as seen in Figure 8. The O···O distances within the $H_7O_3^+$ ion of 2.436 and 2.529 Å resemble those found in **2,** and the cation forms a total of five nonbifurcated hydrogen bonds with the crown ether with distances ranging from 2.636 to 2.880 Å, with the shortest interaction being to the central oxygen atom of the $H_7O_3^+$ unit. The crystal examined proved to be a mixture of 4,4′- and 4,5′-dinitrodibenzo-30-crown-10 isomers, confirmed by the ^1H NMR spectrum of the sample, again resulting in some disorder of the nitro groups. In the solid state, complexes pack into mutually interpenetrating dimers (see Supporting Information) resulting in the formation of an infinite π-stacked chain running throughout the crystal. In this conformation, the large crown ether appears to be well-suited toward selectivity for $H_7O_3^+$, and it may be that the additional stabilization arising from π-stacking of the nitroaryl units selects this conformation over the more planar $[(H_3O)_2(\text{dibenzo-30-crown-10})]^{2+}$.[30] There is thus a "qualified" series of size selectivity running from 18- to 21-/24- to 30-membered crown ethers allowing the isolation of H_3O^+, $H_5O_2^+$, and $H_7O_3^+$, respectively. The chemistry of the smaller crown ethers is rather less predictable.

Solution Studies. All of the tetrachloroaurate(III) salts reported above proved to be soluble in chloroform solution, and it proved to be possible to observe ^1H NMR peaks corresponding to the oxonium ion species in the region of 3−5 ppm. In particular, signals for compounds **4** and **7**, which have very similar structure, were both observed at 4.25 ppm at 0.007 M concentration using the same batch of solvent. Clearly, in solution, there will be a number of competing equilibria such as those shown in eqs 1−3, among others. These equilibria will

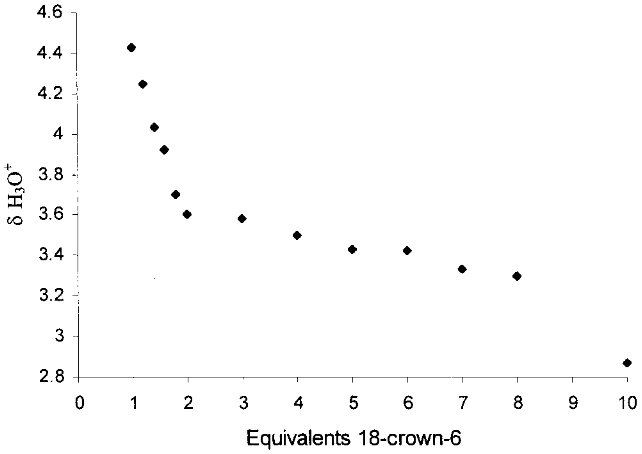

Figure 9. ^1H NMR titration curve for the oxonium ion signal upon gradual addition of 18-crown-6 under dry, constant concentration conditions.

$$H(H_2O)_n + \text{crown} = [\{H(H_2O)_n\}\subset\text{crown}]^+ \tag{1}$$

$$H(H_2O)_n = H(H_2O)_{n-1} + H_2O \tag{2}$$

$$H(H_2O)_n + H_2O = H(H_2O)_{n+1} \tag{3}$$

result in a marked concentration dependence of the oxonium ion chemical shift and a very significant effect of adventitious water.

In general, we found that oxonium ion peak integrals were 20−50% higher than those anticipated from the molecular formula, even using dried $CDCl_3$. The tendency of the solid materials to absorb atmospheric moisture is likely to be a significant factor, and because no separate signal was observed for free water (or HDO), it may be inferred that the equilibria represented by eqs 2 and 3 are fast on the NMR time scale. This was confirmed by deliberate addition of 1 drop of water to ^1H NMR samples of **4** and **7**, which resulted in large shifts (from 4.25 to 2.26 and 1.60 ppm, respectively) coupled with an approximate trebling of peak intensity.

Clearly, it is desirable to assess the equilibrium shown in eq 1, the equilibrium constant of which corresponds to the conventional binding constant for the system. Accordingly, an ^1H NMR titration experiment was carried out using dried $CDCl_3$ in which dry 18-crown-6 was titrated into samples of a solution of complex **4** of constant concentration (see Experimental Section). In this way, we could be sure that the ratio of H^+ to $[AuCl_4]^-$ was always exactly 1:1 and that the amount of adventitious water was small and constant. The resulting binding curve is shown in Figure 9. The steep slope in the early region of the graph is clearly indicative of strong binding; however, we were unable to obtain a convincing fit to a simple 1:1 binding model, and it is questionable whether a meaningful binding constant can be extracted from this kind of simple experiment.

Conclusion

This study has demonstrated that crown ethers are excellent hosts for oxonium ions in the solid and solution phases. With suitable choice of noninteracting counteranion, it is possible to discern the factors governing the mutual selectivity of various crown ethers for particular oxonium ions although, as for alkali

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metal cation binding, these factors are not entirely trivial. To achieve a greater degree of predictability as to what particular macrocyclic ligands will select from solution equilibria, it will probably be necessary to move toward more rigidly preorganized ligands, and a future study of this type along with an examination of larger crown ethers and poly(ethylene glycol) is planned.

Experimental Section

Instrumentation. Mass spectra were run at King's College London on a JEOL AX505W spectrometer in FAB mode in a thioglycerol matrix. NMR spectra were recorded on a Bruker ARX-360 spectrometer operating at 360.1 MHz. IR spectra were recorded on a PE Paragon 100 FTIR spectrometer as Nujol mulls. Microanalyses were performed at University College London. All reactions were carried out in air, and the products showed no oxygen sensitivity although many solid products readily absorbed atmospheric moisture. Conditions were optimized to produce X-ray diffraction quality crystals; however, yields were generally near-quantitative.

Preparation of Standard Solutions. Standard $HAuCl_4$/Aqua Regia Solution a. A gold slug (1.00 g) was treated with HCl/HNO_3 solution (20 cm^3, 4:1 v/v), and the mixture was stirred at room temperature overnight. The resulting orange solution was diluted with water (30 cm^3) to minimize the risk of nitration of aryl crown ethers and used without further purification.

Standard $HAuCl_4$/Aqua Regia Solution b. A gold slug (1.00 g) was treated with HCl/HNO_3 solution (100 cm^3, 4:1 v/v), and the mixture was stirred at room temperature overnight. The resulting orange solution was used without further purification.

Standard $HAuCl_4$ Solution c. Chloroauric acid (1.00 g) was dissolved in distilled water (32 cm^3) to give immediately an orange-yellow solution that was used without further purification.

Preparations. $[(H_5O_2)_2(12\text{-crown-}4)_2][AuCl_4]_2$ (1). Method 1. A methanolic solution (2 cm^3) of 12-crown-4 (0.05 g, 0.30 mmol) was added to gold solution c (2 cm^3, 0.30 mmol of Au) resulting in the deposition of large yellow needle-shaped crystals after ca. 3 months. Anal. Calcd for $C_{12}H_{27}O_7Cl_4Au$: C, 17.41; H, 3.83. Found: C, 17.41; H, 3.85.

Complex 1. Method 2. An identical product was produced by addition of a methanolic solution of 12-crown-4 (0.17 g, 1.0 mmol) to gold solution a (10 cm^3, 1.0 mmol of Au). The product formed over a period of ca. 3 months as orange crystals.

$[(H_7O_3)(15\text{-crown-}5)][AuCl_4]$ (2). Method 1. An aqueous solution (2 cm^3) of 15-crown-5 (0.11 g, 0.50 mmol) was added to gold solution b (10 cm^3, 0.50 mmol Au) resulting in the deposition of orange crystals after ca. 30 days. Anal. Calcd for $C_{10}H_{27}O_8Cl_4Au$: C, 19.56; H, 4.43. Found: C, 19.57; H, 4.04. ^1H NMR ($CDCl_3$, 0.007 M, 20 °C): δ 3.81 (s, crown), 3.34 (s, br, $H_7O_3^+$) ppm. Integral intensities suggest that the oxonium ion peak is averaged with the signal arising from adventitious water.

Complex 2. Method 2. An identical product was produced by addition of a methanolic solution of 15-crown-5 (0.23 g, 1.0 mmol) to gold solution a (10 cm^3, 1.0 mmol of Au). The product formed immediately as a yellow precipitate. X-ray quality crystals were grown by recrystallization from ethanol.

$[(H_5O_2)(\text{benzo-15-crown-}5)_2][AuCl_4]$ (3). An aqueous/methanolic solution (15 cm^3, 2:1) of benzo-15-crown-5 (0.27 g, 1.0 mmol) was added to dilute gold solution a (10 cm^3, 1.0 mmol of Au) resulting in the immediate deposition of the product as orange crystals. Anal. Calcd for $C_{28}H_{45}O_{12}Cl_4Au$: C, 36.86; H, 4.97. Reliable elemental analysis could not be obtained because of the hygroscopic nature of the product.

$[(H_3O)(18\text{-crown-}6)][AuCl_4]$ (4). Method 1. An aqueous solution (2 cm^3) of 18-crown-6 (0.13 g, 0.50 mmol) was added to gold solution b (10 cm^3, 0.50 mmol of Au) resulting in the deposition of yellow needle-shaped crystals after 30 days, identified crystallographically as form I. Anal. Calcd for $C_{12}H_{27}O_7Cl_4Au$: C, 23.17; H, 4.37. Found: C, 23.36; H, 4.26. ^1H NMR ($CDCl_3$, 0.007 M, 20 °C): δ 4.26 (s, br, H_3O^+), 3.79 (s, crown) ppm. Integral intensities suggest that the oxonium ion peak is averaged with the signal arising from adventitious water.

Complex 4. Method 2. The compound was prepared as a polymorph, form II, by addition of 18-crown-6 (0.13 g, 0.5 mmol) to gold solution a (5 cm^3, 0.5 mmol of Au). The product formed overnight as orange crystals.

$[(H_5O_2)(\text{dibenzo-24-crown-}8)][AuCl_4]$ (5). Method 1. A chloroform solution (2 cm^3) of dibenzo-24-crown-8 (0.18 g, 0.40 mmol) was added to gold solution c (5 cm^3, 0.40 mmol of Au) resulting in the deposition of large orange block-shaped crystals after 1 day. Anal. Calcd for $C_{24}H_{37}O_{10}Cl_4Au$: C, 34.97; H, 4.52. Found: C, 36.01; H, 4.56. ^1H NMR ($CDCl_3$, 0.007 M, 20 °C): δ 6.89 (m, 8H, ArH), 5.11 (s, br, $H_5O_2^+$), 4.18 (s, br, 8H crown), 3.93 (s, br, 8H crown), 3.80 (s, 8H crown) ppm. Integral intensities suggest that the oxonium ion peak is averaged with the signal arising from adventitious water.

Complex 5. Method 2. An identical product was produced by addition of a methanolic solution of dibenzo-24-crown-8 (0.05 g, 0.1 mmol) to gold solution a (1 cm^3, 0.1 mmol of Au). The product formed immediately as orange crystals.

$[(H_5O_2)(\text{4-nitrobenzo-15-crown-}5)_2][AuCl_4]$ (6). An aqueous solution (9 cm^3) of benzo-15-crown-5 (0.13 g, 0.50 mmol) was added to gold solution b (10 cm^3, 0.50 mmol of Au) resulting in the deposition of orange needle-shaped crystals after ca. 30 days. Anal. Calcd for $C_{28}H_{43}N_2O_{16}Cl_4Au$: C, 33.55; H, 4.32; N, 2.79. Found: C, 33.92; H, 4.25; N, 2.54. ^1H NMR ($CDCl_3$, 0.007 M, 20 °C): δ 7.91 (dd, 1H, $^3J = 8.9$ Hz, $^4J = 2.5$ Hz, ArH), 7.70 (d, 1H, $^4J = 2.5$ Hz, ArH), 6.92 (d, 1H, $^3J = 8.9$ Hz, ArH), 4.22 (m, 4H, CH_2), 4.06 (s, br, H_3O^+), 3.96 (m, 4H, CH_2), 3.76 (m, 8H, CH_2) ppm. Integral intensities suggest that the oxonium ion peak is averaged with the signal arising from adventitious water.

$[(H_3O)(\text{4-nitrobenzo-18-crown-}6)][AuCl_4]$ (7). An aqueous solution (3 cm^3) of benzo-18-crown-6 (0.16 g, 0.50 mmol) was added to gold solution b (10 cm^3, 0.50 mmol of Au) resulting in the deposition of orange needle-shaped crystals after ca. 30 days. Anal. Calcd for $C_{16}H_{26}NO_9Cl_4Au$: C, 26.87; H, 3.66; N, 1.96. Found: C, 27.90; H, 3.63; N, 1.88. ^1H NMR ($CDCl_3$, 0.007 M, 20 °C): δ 7.91 (d, 1H, $^3J = 8.9$ Hz, ArH), 7.72 (d, 1H, $^4J = 2.4$ Hz, ArH), 6.96 (d, 1H, $^3J = 8.9$ Hz, ArH), 4.30 (m, 12H, CH_2), 4.10 (m, 4H, CH_2), 3.87 (m, 4H, CH_2), 3.76 (s, br, H_3O^+) ppm. Integral intensities suggest that the oxonium ion peak is averaged with the signal arising from adventitious water. FAB-MS: 358 (crown + H^+).

$[(H_{11}O_5)(4,5,4',5'\text{-tetrachlorodibenzo-18-crown-}6)_2][AuCl_4]$ (8). An ethanolic solution (12 cm^3) of dibenzo-18-crown-6 (0.09 g, 0.25 mmol) was added to gold solution b (5 cm^3, 0.25 mmol of Au) resulting in the deposition of golden needle-shaped crystals after ca. 30 days. Four separate crystals were examined, and all proved to have the same structure; however, elemental analysis data suggest significant contamination by nitrated products, and no clean samples could be obtained.

$[(H_7O_3)(\text{dinitrodibenzo-30-crown-}10)][AuCl_4]$ (9). An ethanolic solution (1 cm^3) of dibenzo-30-crown-10 (0.11 g, 0.20 mmol) was added to gold solution b (4 cm^3, 0.20 mmol of Au) resulting in the deposition of orange crystals after 1 day. Anal. Calcd for $C_{28}H_{43}N_2O_{16}Cl_4Au$: C, 32.96; H, 4.44; N, 2.75. Found: C, 34.21; H, 4.53; N, 2.00. ^1H NMR ($CDCl_3$, 0.007 M, 20 °C): δ 7.84 (m, 2H, ArH), 7.65 (s, 2H, ArH), 6.88 (m, 2H, ArH), 4.87 (s, br, $H_7O_3^+$), 4.22 (m, 8H, CH_2), 4.10 (m, 4H, CH_2), 3.92 (m, 8H, CH_2), 3.71 (m, 12H, CH_2) ppm. Integral intensities suggest that the oxonium ion peak is averaged with the signal arising from adventitious water. The compound exists as an unequal mixture of 4,4′- and 4,5′-dinitro isomers.

NMR Titration. A standard 0.0050 M solution of $[(H_3O)(18\text{-crown-}6)][AuCl_4]$ (**4**) in $CDCl_3$ was prepared and divided equally between 15 NMR tubes in 0.500 cm^3 aliquots. To each tube were added varying amounts of a standard solution of 18-crown-6 (0.0500 M). The volume in each tube was then topped off to 1.000 cm^3 with $CDCl_3$, and the mixture was mixed thoroughly.

Crystallography. Crystal data and data collection parameters are summarized in Table 2. Crystals were mounted on a thin glass fiber using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low-temperature attachment. Oscillation frames each of width 1°−2° in either ϕ or ω and of 10−60 s deg^{-1} exposure time were recorded using a Nonius ^{Kappa}CCD diffractometer, with a detector-to-crystal distance of 30 mm. Crystals were indexed from five preliminary frames each of 2° width in ϕ using the Nonius Collect package.[40] Final unit cell dimensions and positional data were refined on the entire data set along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack[41]) resulted in a data set corrected for Lorentz and polarization effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved by direct methods (SHELXS-97[42]) and developed via alternating least-squares cycles and difference Fourier synthesis (SHELXL-97[43]) with the aid of the XSeed interface.[44] All non-hydrogen atoms were modeled anisotropically. Hydrogen atoms were placed in calculated positions and allowed to ride on the atoms to which they were attached with an isotropic thermal parameter 1.2 times that of the parent atom. Oxonium ion protons were located experimentally and treated likewise if refinement proved unfeasible. All calculations were carried out either on a Silicon Graphics Indy workstation or on an IBM-PC compatible personal computer. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, issue no. 1. Disorder of one oxonium ion oxygen atom was observed for compound **1** which was modeled satisfactorily in terms of two alternative positions of occupancy constrained to sum to unity. Extensive disorder was observed in the case of compound **4** (form II) apparently taking the form of various orientations for the $[AuCl_4]^-$ anions. This was modeled in terms of a number of alternative chloro ligand positions, essentially at right angles to one another. Despite this chemically reasonable model, significant electron density remained unaccounted for. Complex **7** exhibited a further severe disorder taking the form of two alternative sets of positions for the vast majority of the atoms in the crown ether ligand. This was modeled extremely satisfactorily in terms of a 70:30 occupancy distribution, and a good final refinement was achieved. The $[AuCl_4]^-$ and oxonium ions were ordered. Complex **9** also exhibited a similar disorder of the crown ether ligand, primarily centered on one of the aryl rings, and this was treated similarly, although data quality did not result in such a satisfactory refinement. In general, the majority of the complexes reported herein (particularly nitro derivatives) proved to be particularly prone to crystal twinning, and this is reflected in some high residuals and large residual difference Fourier peaks. This is despite the collection of as many as four low-temperature data sets on some recalcitrant samples.

Acknowledgment. We thank the EPSRC and King's College London for funding of the diffractometer system. Grateful acknowledgment is also given to the Nuffield Foundation for the provision of computing equipment.

Supporting Information Available: Figure S1 showing the pairing in complex **9** via π-stacking and nine X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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