Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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**To cite this Article** Prince, Paul D. and Steed, Jonathan W.(1998) 'Weak Interactions in Silver Complexes of 15-Crown-5', Supramolecular Chemistry, 10: 1, 155 — 158

**To link to this Article: DOI:** 10.1080/10610279808055407

**URL:** http://dx.doi.org/10.1080/10610279808055407

*SUPRAMOLECULAR CHEMISTRY*, Vol. 10, pp. 155–158
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Printed in Malaysia.

# Weak Interactions in Silver Complexes of 15-Crown-5

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*(Received 30 July 1998; In final form 11 August 1998)*

**The X-ray crystal structures of two closely related Ag(I) complexes of 15-crown-5 and benzo-15-crown-5 are reported. In the case of $[Ag(15\text{-crown-}5)_2][SbF_6]$ 1, pointing one of its oxygen atoms away from the $Ag^+$ cation enables one of the crown ligands to take part in an intermolecular C—H···O hydrogen bond. The analogous benzo-15-crown-5 species, $[Ag(benzo\text{-}15\text{-crown-}5)_2][SbF_6]$ 2, is too rigid to attain the necessary conformation. Crystal data for 1: $P2_1/c$, $a = 8.4481(3)$, $b = 25.5813(9)$, $c = 13.2773(4)$ Å, $\beta = 101.354(2)°$. $Z = 4$, unique data: 5187 $R_1$ $[F^2 > 2\sigma(F^2)]$ 0.0259. Compound 2: $P\bar{1}$, $a = 8.6511(15)$ Å, $b = 10.2322(18)$ Å, $c = 19.291(3)$ Å, $\alpha = 103.704(2)°$, $\beta = 101.274(2)°$, $\gamma = 95.952(2)°$, $Z = 2$, unique data: 5803 $R_1$ $[F^2 > 2\sigma(F^2)]$ 0.0931.**

*Keywords:* Supramolecular, Silver, 15-Crown-5, Hydrogen Bond

One of the most overwhelmingly important themes in supramolecular chemistry is the idea of complementarity, be it the steric match of host and guest (*e.g.*, recognition of alkali metals by crown ethers and cryptands) [1–3] or the electronic compatibility of hydrogen bond donors and acceptors (*e.g.*, self-replicating amide systems and the design of molecular capsules) [4, 5]. This idea underlies the whole lock and key principle of Fischer [3, 6]. In attempting to synthesise mutually complementary components, however, it is often the case that ideas which work well on paper or as models, are less than successful when experimental selectivities or complementarities are actually measured. This kind of difficulty is explicable in general terms by the important roles played by weak, but summative or even multiplicative intra- and intermolecular interactions, solvation, chelate and macrocyclic ring size, conformational preferences and the interplay between steric and electronic preferences. The possibility of gaining some kind of understanding of these subtle factors, which can have remarkable effects on molecular structure [3, 7], has recently led us to embark upon a programme of structural characterisation of hosts and guests (or, more generally, 'supramolecular synthons') which are not mutually complementary. An excellent example of what may be learned by such studies may be found in the series $[X^- \subset$ *bis*-tren-$6H^+]$ ($X = N_3$, F, Cl, Br)[8] in which the cylindrical *bis*-tren cryptand is found to be selective for the linear $N_3^-$ but is able to distort to a very large degree in order to encapsulate $F^-$ in a tetrahedral fashion or the larger halides in distorted octahedral environments. Previously we have examined systems which are either

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*Corresponding author. Tel.: 0171 873 2117, Fax: 0171 873 2810, e-mail: jon.steed@kcl.ac.uk sterically or symmetry mismatched, resulting in subtle, unsymmetrical hydrogen bonding patterns [9, 10]. In this work we report initial investigations into electronically incompatible host-guest chemistry by examination of the interaction of a 'soft' metal ion, Ag(I), with 'hard', oxygen donor crown ethers.

Generally, the affinity of crown ethers for Ag(I) increases dramatically as oxygen donor atoms are replaced by softer RR'NH or thioether moieties [2, 7]. Only a few examples of $Ag^+$ with solely oxygen donor crown ethers have been structurally characterised [11 - 13]. With the small 12-crown-4 the eight co-ordinate metal cation is sandwiched symmetrically between two crown ligands [12]. We find that reaction of $Ag[SbF_6]$ with larger crown ether ligands $L$ results in the ready isolation of further 1 : 2 complexes $[AgL_2][SbF_6]$ ($L$ = 15-crown-5, **1**; benzo-15-crown-5, **2**) in essentially quantitative yield [14].

As may be expected, in acetone solution the $^1H$ NMR spectra of **1** and **2** are consistent with rapid exchange between bound and unbound $Ag^+$. In the solid state however, the X-ray crystal structures [15] of both species demonstrate a highly unsymmetrical binding mode, Figures 1 and 2. In both cases the $Ag^+$ cation exhibits a seven co-ordinate geometry with all five oxygen atoms of one crown ether ligand coordinated to one face of the metal with Ag—O distances in the range 2.537(2) - 2.633(2) Å for **1**. Notably, for the more sterically restricted **2**, the analogous Ag—O bond lengths are all significantly longer; 2.597(7) - 2.751(7) Å. These distances compare with values of 2.56 - 2.59 Å[12] for the symmetrical $[Ag(12\text{-crown-}4)_2]^+$ suggesting that the distances found in **1** are optimal while those in **2** are elongated as a result of unfavourable O-aromatic ring steric interactions between one crown ether and another. This is particularly marked in the O(3B)—C(10A) distance of only 3.15 Å. The analogous distance in **1** is 3.72 Å. The Ag—O distances in $[Ag(dibenzo\text{-}18\text{-crown-}6]^+$ and $[Ag(cryptand[2.2.2])]^+$ are much longer (2.63 - 2.85 Å) suggesting poor fit between $Ag^+$ and the larger crown [11, 13]. The second crown ether ring in both **1** and **2** is bound to the metal centre by only two oxygen atoms with a particularly short Ag—O(2B) distance of 2.512(2) Å in **1**. Again, distances in **2** are markedly longer (see figure captions). For comparison, Na—O distances in $Na^+$ complexes of 15-crown-5 typically fall in the range 2.14 - 2.56 Å [16]. Interestingly the inter-crown repulsion in **2** (which results in more space around the $Ag^+$ ion) apparently allows a *closer* approach of the 'non-bonded' atoms of the second crown ring. In the case of **1**, non-bonded Ag—O distances range from 3.86 - 4.86 Å. In **2** all of the three 'non-bonded' oxygen atoms are between 3.01 - 3.38 Å

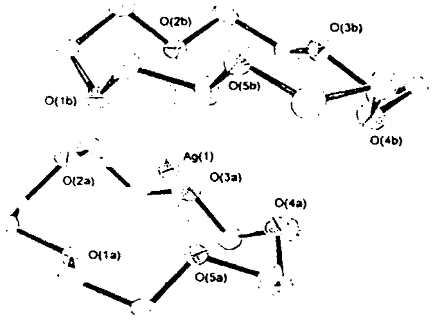

FIGURE 1 The $[Ag(15\text{-crown-}5)_2]^+$ cation in **1**. Selected bond lengths: Ag(1)—O(1A) 2.633(2), Ag(1)—O(2A) 2.625(2), Ag(1)—O(3A) 2.601(2), Ag(1)—O(4A) 2.5380(19), Ag(1)—O(5A) 2.537(2), Ag(1)—O(1B), 2.5788(19), Ag(1)—O(2B) 2.512(2) Å.

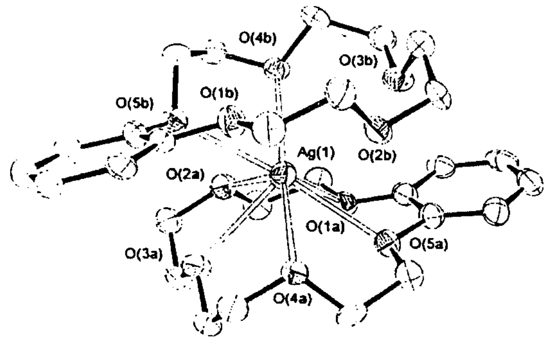

FIGURE 2 The $[Ag(benzo\text{-}15\text{-crown-}5)_2]^+$ cation in **2**. Selected bond lengths: Ag(1)—O(1A) 2.693(7), Ag(1)—O(2A) 2.751(7), Ag(1)—O(3A) 2.662(7), Ag(1)—O(4A) 2.705(7), Ag(1)—O(5A) 2.597(7), Ag(1)—O(4B) 2.665(7), Ag(1)—O(5B) 2.545(6) Å.

away from the metal, suggesting a significant residual ion – dipole attraction, perhaps compensating for the longer 'bonded' distances.

Clearly, these large differences between complexes **1** and **2** result from very different crown conformations, and it may be seen from Figures 1 and 3 that in the case of **1** two non-bonded crown oxygen atoms [O(3B) and O(5B)] are directed away from the metal centre. The ether function O(5B), in particular, is highly exposed and since it is unable to interact with the $Ag^+$ cation, it is in a position to form a C—H···O hydrogen bond [17, 18] with a methylene group on an adjacent molecule, resulting in a pair-wise association of cations, Figure 3. The C···O distance of 3.349(3) Å is well within the tolerances established for such interactions [17] and, more importantly, the hydrogen atom (idealised position) is directed along the C···O vector (C—H···O angle 143°). The H···O distance, without correction for librational shortening, is 2.51 Å.

In conclusion, the malleable nature of the Ag—O interactions result in a sequence of cause and effect interactions which conspire to make an oxygen atom available for weak intermolecular hydrogen bonding in **1** simply because there is no other accessible source of positive charge or dipole for it to interact with. In the case of **2** unfavourable inter-crown steric interactions expose the $Ag^+$ cation allowing long range Ag—O attractions and disfavouring weak intermolecular interactions. Finally, it is noteworthy that in both structure the fluorine atoms of the $SbF_6^-$ anion engage in a complex network of C—H···F interactions with C···F distances as short as 3.12 Å.

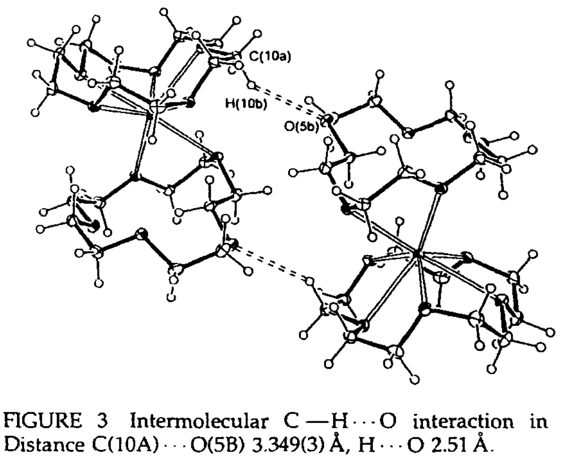

FIGURE 3 Intermolecular C—H···O interaction in **1**. Distance C(10A)···O(5B) 3.349(3) Å, H···O 2.51 Å.

## *Acknowledgements*

We thank the EPSRC the King's College London for funding of the diffractometer system. Grateful acknowledgement is also given to the EPSRC Chemical Database Service at Daresbury and to the Nuffield Foundation for the provision of computing equipment.

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[14] $Ag[SbF_6]$ (0.052 g, 0.15 mmol) was dissolved in methanol (1 $cm^3$). To this was added 15-crown-5 (0.085 g, 0.39 mmol) resulting in the formation of an immediate white precipitate. This was dissolved by addition of further methanol (2 $cm^3$) to give a colourless solution and the mixture allowed to stand in air for 24 hours resulting in the deposition of the product, $[Ag(15\text{-crown-}5)_2][SbF_6]$ **1**, as large, colourless blocks. Complex **2** was prepared similarly from a 2:1 mixture of benzo-15-crown-5 and $Ag[SbF_6]$ using a 1:1 v/v mixture of acetone and methanol. Analytical data were consistent with the proposed formulations.

[15] Crystal data for 1: $C_{20}H_{40}AgF_6O_{10}Sb$, $M$ 784.14 g mol$^{-1}$, monoclinic, space group $P2_1/c$, $a = 8.4481(3)$, $b = 25.5813(9)$, $c = 13.2773(4)$ Å, $\beta = 101.354(2)°$. $U = 2813.25(16)$ Å$^3$, $Z = 4$, $\mu = 17.44$ cm$^{-1}$, $T = 100$ K, Reflections measured: 22 073, unique data: 5187 ($R_{\text{int}} = 0.038$), parameters: 344, $R_1$ [$F^2 > 2\sigma(F^2)$] 0.0259, $wR_2$ (all data) 0.0638. CCDC reference number 186/XXX. Compound 2: $C_{28}H_{40}AgF_6O_{10}Sb$, $M$ 880.22 g mol$^{-1}$, triclinic, space group $P\bar{1}$, $a = 8.6511(15)$ Å, $b = 10.2322(18)$ Å, $c = 19.291(3)$ Å, $\alpha = 103.704(2)°$, $\beta = 101.274(2)°$, $\gamma = 95.952(2)°$. $U = 1606.8(4)$ Å$^3$, $Z = 2$, $\mu = 15.39$ cm$^{-1}$, $T = 100$ K, Reflections measured: 11 923, unique data: 5803 ($R_{\text{int}} = 0.089$), parameters: 418, $R_1$ [$F^2 > 2\sigma(F^2)$] 0.0931, $wR_2$ (all data) 0.2440. CCDC reference number XXX. Crystals were mounted using silicon grease on the end of a glass fibre and cooled to 100 K on the diffractometer using an Oxford Cryostream. All crystallographic measurements were carried out with a Nonius KappaCCD diffractometer equipped with graphite monochromated Mo$-K_\alpha$ radiation using $\phi$ rotations with 2° frames and a detector to crystal distance of 25 mm. Unit cell determination and integration was carried out by the program DENZO-SMN [19]. Data sets were corrected for Lorentz and polarization effects and for the effects of absorption using the program Scalepack [19]. Structures were solved using the direct methods option of SHELXS-97 [20] and developed using conventional alternating cycles of least squares refinement and difference Fourier synthesis (SHELXL-97 [20]) with the aid of RES2INS [21]. All non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were fixed in idealized positions and allowed to ride. Hydrogen atom thermal parameters were tied to those of the atom to which they were attached. In the case of 2 unresolved, incommensurate crystal twinning was responsible for the relatively poor overall refinement.

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