Formation of an organometallic coordination polymer from the reaction of silver(I) with a non-complimentary lariat ether

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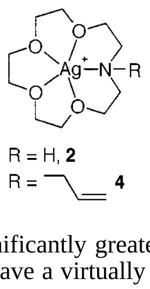
The 'Ag^I(15-crown-5)' core moiety is a versatile supramolecular synthon, which is able to satisfy its coordination requirements using a variety of capping ligands; in the presence of the lariat ether *N*-allylaza-15-crown-5 an infinite organometallic coordination polymer is formed.

The design of supramolecular hosts for metal cations is based upon the proposition that the more complementary a host is to the guest the stronger the binding will be.[1–3] This is especially true in cases where the host is rigidly preorganised for guest complexation, as in the case of the spherands.[4] It follows from this well established fact that the majority of synthetic effort is geared towards the matching of host and guest electronic, steric and topological properties in order to maximise their mutual affinity. Clearly therefore, a successful host serves to confirm the rationality of its design. An interesting caveat of this line of reasoning is that potentially much information on host design may be gained by examination of cases in which the host is *not* complementary to the guest. In such cases the host–guest system is necessarily forced to distort in order to accommodate the conflicting requirements of each partner, with consequent diminution of affinity. The degree of distortion should furnish useful information about the tolerances on what may, and may not be termed 'complementary'.

Recently we have looked at a number of sterically and electronically non-complementary systems.[5–10] As part of these studies we reported the reaction of 'hard' oxygen donor ligands with the soft Ag^I cation to give complexes [Ag(L)][SbF$_6$] (L = 15-crown-5, **1a**; benzo-15-crown-5, **1b**).[7] In contrast to the usual linear or tetrahedral geometries of Ag^I[11] this results in the formation of two unusual seven-coordinate systems in which the 'Ag(15-crown-5)$^+$' core is capped by interactions with two oxygen atoms of the second macrocycle. The non-complementary nature of the hard base–soft acid interaction is exemplified in the long Ag–O bonding distances which ranged from 2.512(2) to 2.633(2) Å, compared with typical Ag–N$_{\rm amine}$ distances of *ca.* 2.2–2.4 Å.[12] Similar weak Ag–O$_{\rm ether}$ interactions have been noted recently in a range of β-diketonato glyme derivatives, which are of interest as CVD precursors.[13] This unsymmetrical sandwich geometry suggests that the Ag(15-crown-5)$^+$ core may be relatively stable and that the more loosely bound bidentate macrocycle could be readily replaced by other ligands, particularly those which are *more* complementary for the soft metal cation.

With this in mind we examined the reaction of Ag[SbF$_6$] with aza-15-crown-5 **2** since binding constant measurements demonstrate that Ag$^+$ has a significantly greater affinity for *N*-donor ligands.[14] This reaction gave a virtually quantitative yield of a further 1 : 2 complex of formula [Ag(aza-15-crown-5)$_2$][SbF$_6$] **3**. The X-ray crystal structure of this material (Fig. 1)† proved to be approximately isomorphous with complex **1**. The key difference between the more complementary azacrown and its O-donor analogues is that in complex **3** the 'Ag(aza-15-crown-5)$^+$' core is capped by the nitrogen atom of a monodentate azacrown ligand, as opposed to two oxygen atoms in compounds **1**. It is likely that this is a direct result of the greater affinity of Ag^I for nitrogen, resulting in Ag–N distances of 2.304(2) and 2.2759(19) Å (core and cap respectively), compared to Ag–O distances in the range 2.6807(16)–2.7199(16) Å. Indeed the conformation of the capping crown ligand is entirely different because the driving force directing *two* donor atoms at the metal ion is no longer present. Interestingly this results in a significant offset to the crystal packing, which is dominated by C–H···O hydrogen bonding interactions to the non-coordinated oxygen atoms of the capping crown.[7] For compound **1a** this weak hydrogen bond results in an offset of the sandwich cation pairs giving a long crystallographic *a* axis (the direction of intermolecular chain propagation; 8.448 *vs.* 8.263 Å) and a larger monoclinic angle *β*. For compound **3** the weakly hydrogen bonded cation pairs are more directly on top of one another, reducing *β* from 101.4 to 98.8°. It is particularly noteworthy that it is the pairwise C–H···O interactions, of distances C···O 3.398(2) and 3.568(2) Å, H···O 2.58 and 2.62 Å (C–H normalised to 0.99 Å), which dominate the inter-cation packing, and not interactions to the more polar N–H moiety, which forms a long *intramolecular*



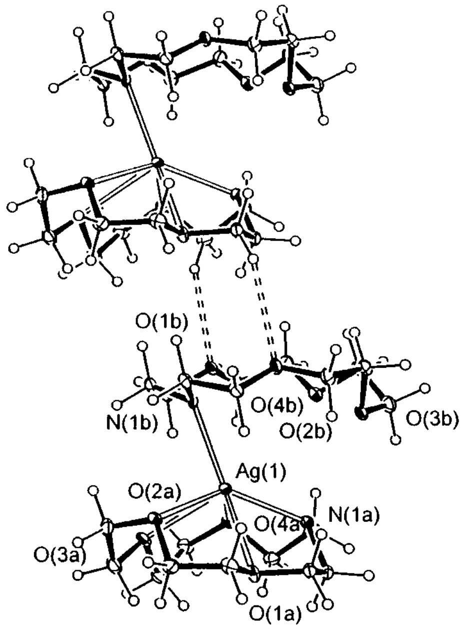


Fig. 1 Intermolecular interactions in [Ag(aza-15-crown-5$_2$][SbF$_6$] **3**. Selected bond distances (Å): Ag(I)–O(1A) 2.7193(15), Ag(1)–O(2A) 2.7449(16), Ag(1)–O(3A) 2.6807(16), Ag(1)–O(4A) 2.7199(16), Ag(1)–N(1A) 2.304(2), Ag(1)–N(1B) 2.2759(19).

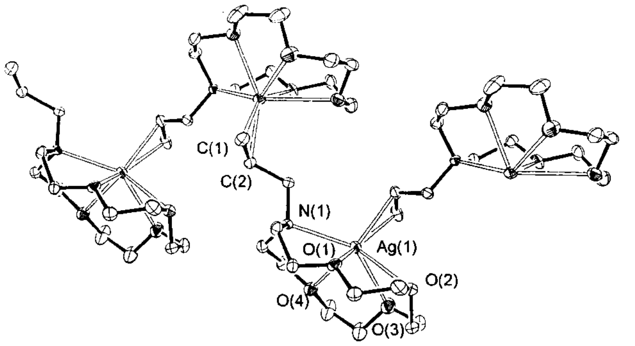


Fig. 2 The coordination polymer $\{[\mathrm{Ag}(N\text{-allylaza-15-crown-5})]\}_\infty$ **5**. Selected bond distances (Å): Ag(1)–C(1)′ 2.363(4), Ag(1)–C(2)′ 2.393(4), Ag(1)–O(1) 2.400(2), Ag(1)–O(2) 2.711(3), Ag(1)–O(3) 2.773(3), Ag(1)–O(4) 2.485(3), Ag(1)–N(1) 2.515(4) Å.

hydrogen bond to the distal oxygen atom of the capping azacrown, N(1A)···O(3B) 3.034(2) Å. The proton attached to N(1B) forms a bifurcated hydrogen bond to the oxygen atoms of the same crown ring, N···O 2.698(2) and 2.712(2) Å. Again, these do not affect the crystal packing because they are entirely intramolecular. The packing is however, further supported by C–H···F interactions[15–17] to the $\mathrm{SbF_6}^-$ anions, with shortest H···F distances 2.51–2.57 Å.

These results suggest that the interaction of derivatives of the $\mathrm{Ag(15\text{-}crown\text{-}5)}^+$ core with further ligands with more affinity for $\mathrm{Ag^I}$ than etheric oxygen may prove of interest. In particular the affinity of Ag^+ for C-donor ligands has been well established, with the cation typically interacting with olefins and individual double bonds of arenes to form complexes such as $[\mathrm{Ag}([2.2.2]\mathrm{paracyclophane})]^+$.[18] Furthermore Gokel and coworkers have noted a marked linearity between the electronic effect of the substituent on the aryl ring of the lariat and Ag^+ binding affinity in aryl lariat ethers[19] which is not reflected in the analogous interactions with Na^+ and K^+, which may arise from direct Ag–π interactions. Accordingly we examined the reaction of $\mathrm{Ag[SbF_6]}$ with the simple *N*-allyl lariat ether **4**.‡ This resulted in the formation of a polymeric complex $\{[\mathrm{Ag(allylaza\text{-}15\text{-}crown\text{-}5)}][\mathrm{SbF_6}]\}_\infty$ **5** again consisting of a substituted $\mathrm{Ag(aza\text{-}15\text{-}crown\text{-}5)}^+$ core unit analogous to compounds **1** and **3** with a pendant allyl side arm. This side arm, while too short to wrap around and coordinate to the same $\mathrm{Ag^I}$ centre, is able to take the role of the second crown ether in complexes **1** and **3** resulting in an organometallic coordination polymer, with Ag–C distances of 2.363(4) and 2.393(4) Å (Fig. 2). This compares to distances of 2.49–2.68 for a range of recently reported $\mathrm{Ag^I}$ complexes of polyaromatic hydrocarbons[20] and typical distances of 2.40–2.60 Å[2] and confirms a full coordination interaction. Also remarkable is the Ag–N distance of 2.515(4) Å, which is *longer* than the distances from the metal cation to the two oxygen atoms nearest to the *N*-allyl moiety, Ag–O(1) 2.400(2) and Ag–O(4) 2.483(3) Å (*cf.* compounds **1** and **3**). The distal Ag–O distances are in the region of 2.74 Å. This striking difference may be rationalised by the delocalisation of the tertiary nitrogen atom lone pair onto the olefinic susbstituent,[21] and on steric grounds in which the relatively plastic coordination environment of the $\mathrm{Ag^I}$ ion is placing itself spatially where it may most effectively bond to the ext unit in the polymeric chain. Further evidence in support of this latter suggestion comes from the fact that the shortest Ag–O distances in **3** are to the oxygen atoms farthest away from the nitrogen atom. Again, the crystal packing is supported by C–H···F interactions to the $\mathrm{SbF_6}^-$ anion (shortest 2.48 Å).

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Notes and references

† *Crystal data*: **3**: $\mathrm{C_{20}H_{42}AgF_6N_2O_8Sb}$, M = 782.18, monoclinic, space group $p2_1/n$, a = 8.2633(2), b = 13.7364(3), c = 25.8077(4) Å, β = 98.752(2)°, U = 2895.27(10) Å^3, Z = 4, μ = 16.92 cm^{-1}, T = 100 K, Refelections measured: 15 220, unique data: 6596 (R_{int} = 0.050), parameters: 352, R_1 [$F^2 > 2\sigma(F^2)$] = 0.0293, wR_2 (all data) = 0.0653.

5: $\mathrm{C_{13}H_{25}AgF_6NO_4Sb}$, M = 602.96, orthorhombic, space group $Pn2_1a$, a = 9.3842(4), b = 9.4558(2), c = 21.5735(9) Å, U = 1914.33(12) Å^3, Z = 4, μ = 25.08 cm^{-1}, T = 100 K, Reflections measured: 13 305, unique data: 3460 (R_{int} = 0.027), parameters: 236, R_1 [$F^2 > 2\sigma(F^2)$] = 0.0231, wR_2 (all data) 0.0598.

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‡ *N*-Allylaza-15-crown-5 was prepared through direct combination of aza 15-crown-5 and 3-bromoprop-1-ene in dry diethyl ether in the presence of triethylamine and was identical in all respects to that prepared by an alternative procedure.[22]

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