C-Donor lariat ether 'scorpionates'

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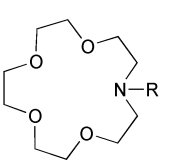
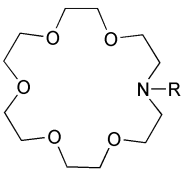
Structural studies on a range of Ag^+ and Pb^{2+} complexes of *N*-allyl and *N*-butenyl lariat ethers are reported. In the case of smaller ligands with allyl side arms (L = *N*-allylaza-15-crown-5 and *N*-azaallyl-18-crown-6), coordination polymers of type $[Ag(L)]^+_\infty$ exhibiting $Ag^+\cdots\pi$ interactions are observed. Increasing the length of the side arm to *N*-butenylaza-18-crown-6 gives a monomeric 'scorpionate' species in which the Ag^+ ion is simultaneously bound to the macrocyclic portion and side arm of a single ligand. NMR titration results indicate that the $Ag^+\cdots\pi$ interactions persist in solution. In the case of Pb^{2+} complexes no side arm involvement is observed in any case. The novel protonated complex (H_3O)(*N*-allylaza-18-crown-6)$[Cu_2I_3]$ is also reported.

Cation-π interactions, particularly those involving alkali metal cations, are of particular biological significance and a great deal of recent interest has centred around producing model systems that demonstrate the extent of hard and soft cation coordination by alkenes, alkyes, arenes and aromatic heterocycles.[1–3] Our own structural work on Ag(I) complexes of the non-complimentary macrocycles 15-crown-5 and benzo-15-crown-5 has shown that in each case the Ag^+ ion adopts a sandwich structure, perching on one pentadentate 15-crown-5 ligand while the exposed surface of the cation is capped by a further bidentate macrocycle.[4] Similarly, the $AgSbF_6$ complex of aza-15-crown-5, $[Ag(\text{aza-15-crown-5})_2][SbF_6]$, exhibits an unsymmetrical sandwich geometry with one pentadentate ligand and one N-bound unidenate cap.[5] It appears likely that this bidentate 'capping' ligand could be replaced by a variety of other functional groups, including π-systems, given the propensity of Ag(I) to engage in a variety of cation-π interactions.[6–11] Mak *et al.* have recently shown the utility of the "$Ag(15\text{-crown-5})^+$" unit as a synthon in the construction of large polymetallic cages that include C_2^{2-}.[12] Work by Gokel, Echegoyen *et al.*[13] has shown that the stability of Ag(I) complexes of aryl and allyl lariat ethers[14,15] such as *N*-allylaza-15-crown-5 (**2**), *N*-allylaza-18-crown-6 (**4**) and their *N*-benzyl analogues show a markedly linear dependence on the donor properties of the alkenic side arm. On the other hand, the binding of the 'hard' Na^+ and K^+ ions is less predictably influenced. It was suggested that this is related to the basicity of the macrocycle nitrogen atom, itself influenced in turn by the electron donor properties of the N-substituent. Much more recently, Gokel *et al.* have shown that in the solid state, however, a range of phenyl, alkenyl and alkynyl lariat ethers are fully capable of binding alkali metal cations such as Na^+ and K^+ *via* cation-π interactions.[1–3,16] This observation is of considerable biochemical relevance[17] although generally evidence of alkali metal cation-π interactions is rare.[18] These interactions are known to persist in solution in the case of lariat ethers containing indole-derived side arms.[19]

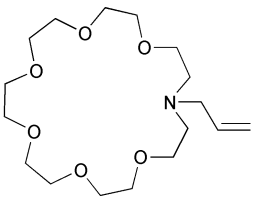
As a consequence of the non-complimentary nature of the Ag^+–ether oxygen interaction, solution binding constants for



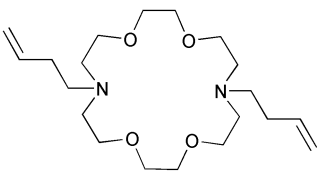
(**1**) R = H
(**2**) R = $CH_2CH{=}CH_2$



(**3**) R = H
(**4**) R = $CH_2CH{=}CH_2$
(**5**) R = $CH_2CH_2CH{=}CH_2$



(**6**)



(**7**)

Ag^+ crown ether complexes in the absence of lariat side arms are relatively small. However, we reasoned that the strong influence of the alkenic side arm in the Ag(I) complexes of **2** and **4** may contain a contribution from a more direct $Ag\cdots\pi$ interaction. This is partially corroborated by preliminary work showing that in the solid state $AgSbF_6$ forms an infinite organometallic coordination polymer of formula $\{[Ag(N\text{-allylaza-15-crown-5})][SbF_6]\}_\infty$ (**8a**) in which the crown-perching Ag^+ ion is capped by the allyl side arm of an adjacent ligand.[5] There is also a significant body of evidence supporting general $Ag^+\cdots\pi$ interactions.[10,11,20,21] We now report the full results of our investigations into C-donor lariat ether effects in these and related systems and contrast the observed $Ag\cdots\pi$ interactions with analogous complexes of Pb^{2+} and alkali metal cations. Investigations into the persistence of these interactions in solution are also presented.

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Results and discussion

Structural studies

Previously we demonstrated that reaction of the Ag(I) salt of a non-coordinating anion (SbF_6^-) with aza-15-crown-5 (**1**) in a 1 : 1 molar ratio resulted in the formation of a 1 : 2 solid [Ag(aza-15-crown-5)$_2$][SbF_6] in which the Ag^+ ion adopts a perching geometry, coordinating to all five donor atoms of one ligand and the nitrogen atom only of a second, capping aza-crown, Fig. 1.[5] Incorporation of an additional donor group in the form of *N*-allylaza-15-crown-5 (**2**) results in a 1 : 1 complex in which the capping azacrown is replaced by the C=C functionality of an adjacent ligand to give an infinite organometallic coordination polymer.[5] The generality of this result has been examined by the analogous reactions with $AgBF_4$, KPF_6 and $Pb(NO_3)_2$. In the case of the soft Ag^+ a closely analogous structure, {[Ag(*N*-allylaza-15-crown-5)][BF_4]}$_\infty$ (**8b**) is produced, again with the Ag^+ ion perching on the crown ether portion of the ligand while being capped by the C=C moiety from an allyl group of an adjacent ligand, Fig. 2 (crystallographic data are given in Table 1). As with **8a**, Ag–C distances are indicative of a strong coordination. Despite the expected preference of the soft Ag(I) ion for the nitrogen atom,[20] the Ag–N and Ag–O distances represent a compromise between intramolecular electronic preferences and the overall polymeric crystal packing scheme (shortest Ag–O distance 2.397 Å, Ag–N 2.483 Å, *cf.* **8a** 2.400 and 2.515 Å). In contrast, the complexes with K^+ and Pb^{2+} exhibit no interactions whatsoever with the C=C functionality. In the case of K^+ even the 'non-coordinating' PF_6^- anion ligates the metal ion in preference to the C-donor side arm, to give a hexafluorophosphate bridged dimer, {[K(PF_6)(*N*-allylaza-15-crown-5)]}$_2$ (**9**), Fig. 3. Again, a perching geometry is noted for the metal ion, highlighting the similar ionic radii of K^+ and Ag^+. The structure is particularly remarkable for the existence of a range of CH···F interactions as short as 2.471(19) Å, well within the sum of the van der Waals radii of H and F, although crystallographic evidence for intramolecular CH···F distances as low as 2.02 Å in an organic compound has been reported.[22] These weak hydrogen bonds apparently stabilise the dimer. This is consistent with the recent work of Gokel *et al.* who found that the allyl side arm is too short to give simultaneous coordination of the crown ring and alkene side arm to alkali metal cations.[2]

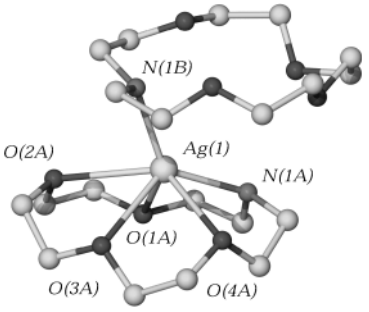

Fig. 1 X-Ray crystal structure of the 1 : 2 complex [Ag(aza-15-crown-5)$_2$][SbF_6] showing the unidentate N-coordination of the 'capping' crown ether.[5] Selected bond distances: Ag(1)–N(1B) 2.2759(19), Ag(1)–N(1A) 2.304(2), Ag(1)–O(3A) 2.6807(16), Ag(1)–O(1A) 2.7193(15), Ag(1)–O(4A) 2.7199(16), Ag(1)–O(2A) 2.7449(16) Å.

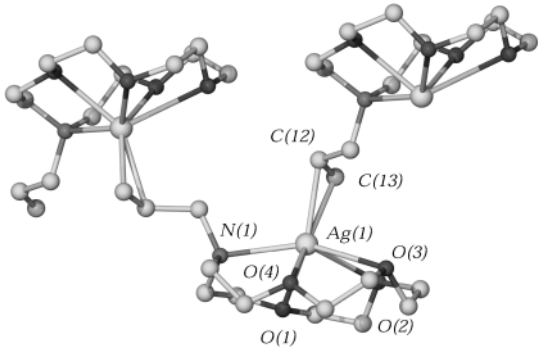

Fig. 2 An infinite coordination polymer {[Ag(*N*-allylaza-15-crown-5)][BF_4]}$_\infty$ (**8b**) analogous to **8a** results from the reaction of the soft Ag^+ with the mixed donor ligand **2**. Selected bond distances: Ag(1)–C(13) 2.363(3), Ag(1)–C(12) 2.422(3), Ag(1)–O(4) 2.397(2), Ag(1)–N(1) 2.483(3), Ag(1)–O(1) 2.525(2), Ag(1)–O(2) 2.692(2), Ag(1)–O(3) 2.788(2) Å.

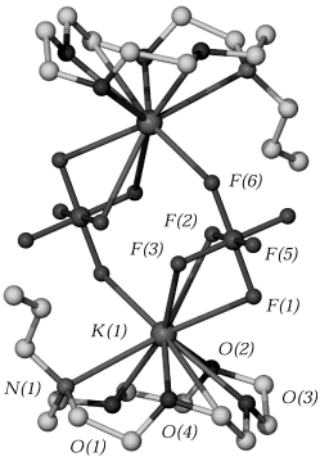

Fig. 3 Dimeric structure of {[K(PF_6)(*N*-allylaza-15-crown-5)]}$_2$ (**9**) showing K$^+$···F_6P bonds and no K$^+$···π interactions. Selected bond distances: K(1)–O(4) 2.7426(12), K(1)–F(6) 2.7437(12), K(1)–O(3) 2.7976(12), K(1)–O(1) 2.8619(12), K(1)–O(2) 2.8682(12), K(1)–F(2) 2.9029(13), K(1)–F(1) 2.9649(13), K(1)–F(3) 2.9821(12), K(1)–N(1) 3.0237(13) Å.

As with **9**, Pb(II) also exhibits no interaction with the allyl side arm. Instead, the perching metal ion is capped by the nitrato anions to give [Pb(NO_3)$_2$(*N*-allylaza-15-crown-5)] (**10**) or the closely related mixed crystal [Pb(η^2-NO_3)$_2$(*N*-allylaza-15-crown-5)]$_2$·[Pb(η^2-NO_3)(η^1-NO_3)(H_2O)(*N*-allylaza-15-crown-5)]·H_2O (**11**), Fig. 4, depending on conditions. In both complexes there appears to be little preference for N- or O-donor atoms, with Pb–N distances falling in the middle of the range of Pb–O bond lengths. Again, it is likely that overall crystal packing constraints, rather than intramolecular electronic preferences for N or O, dominate the molecular geometry. In both cases the Pb^{2+} ion is nine coordinate. The formation of **11**, which contains two independent molecules, one disordered (50 : 50 η^2-NO_3 and η^1-NO_3, H_2O), apparently results from aquation of the bis(bidentate) nitrato complex upon prolonged exposure to atmospheric moisture.

Clearly the electronic (soft/hard)[23] nature of the metal cation is responsible for the gross coordination preferences observed in comparing complexes **8**–**11** and indeed Ag···π interactions are commonly observed, whereas they are much less common for the other metals.[7–10,20] Furthermore, the structural work makes it plain that while Ag···π interactions may be observed in the solid state to give a coordination polymer, it is unlikely that such an intermolecular aggregation would be maintained in solution. Much more feasible is the notion that a unimolecular 'scorpion-type' structure, in which the C-donor lariat ether side arm wraps around and coordinates to the metal ion held within its own cavity, might persist in both the solid and solution phases. However, the small size of the 15-crown-5 ring and short –CH_2– spacer in the side arm of **2** suggests that such a

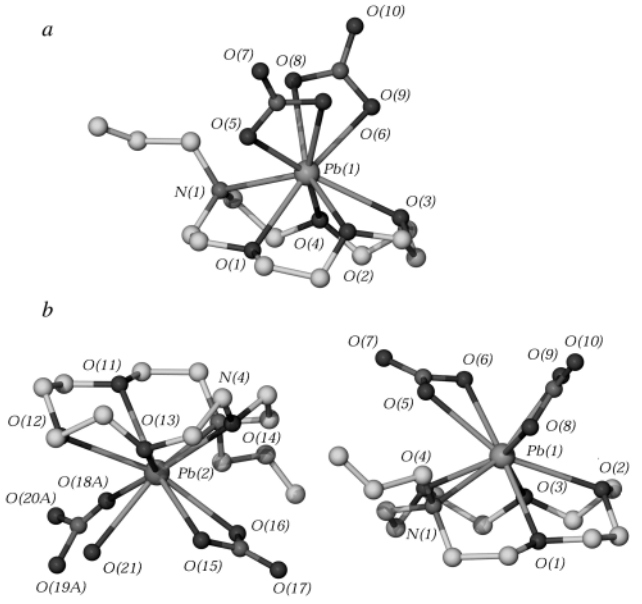

Fig. 4 Structures of (a) $[Pb(NO_3)_2(N\text{-allylaza-15-crown-5})]$ (**10**) and (b) the mixed crystal $[Pb(\eta^2\text{-}NO_3)_2(N\text{-allylaza-15-crown-5})]\cdot[Pb(\eta^2\text{-}NO_3)(\eta^1\text{-}NO_3)(H_2O)(N\text{-allylaza-15-crown-5})]$ (**11**) showing the hydrated Pb(II) complex. In both cases no interactions to the allyl sidearm are observed. Selected bond lengths for compound **10**: Pb(1)–O(5) 2.594(3), Pb(1)–O(1) 2.630(2), Pb(1)–O(8) 2.632(3), Pb(1)–O(4) 2.661(3), Pb(1)–N(1) 2.697(3), Pb(1)–O(9) 2.701(3), Pb(1)–O(2) 2.742(2), Pb(1)–O(6) 2.747(3), Pb(1)–O(3) 2.748(3) Å and for compound **11**: Pb(1)–O(5) 2.628(8), Pb(1)–O(8) 2.634(9), Pb(1)–O(4) 2.634(9), Pb(1)–N(1) 2.646(9), Pb(1)–O(1) 2.654(8), Pb(1)–O(9) 2.753(10), Pb(1)–O(6) 2.755(8), Pb(1)–O(3) 2.805(8), Pb(1)–O(2) 2.819(8), Pb(2)–O(14) 2.610(9), Pb(2)–O(16) 2.659(8), Pb(2)–O(15) 2.700(10), Pb(2)–O(11) 2.711(8), Pb(2)–O(13) 2.715(8), Pb(2)–O(18) 2.72(2), Pb(2)–O(18A) 2.72(3), Pb(2)–N(4) 2.728(11), Pb(2)–O(21) 2.73(2), Pb(2)–O(19) 2.80(2), Pb(2)–O(12) 2.819(8) Å.

complexation mode is sterically unfeasible in this instance. In order to attempt to observe 'scorpionate'-type lariat ether behaviour, we adopted two strategies for the introduction of additional flexibility, namely increase of the size of the crown ether ring to give *N*-allylaza-18-crown-6 (**4**) and *N*-allylaza-21-crown-7 (**6**), and concurrent lengthening of the lariat side arm to give *N*-butenylaza-18-crown-6 (**5**).

As expected, reaction of the enlarged ligand **4** with $Pb(NO_3)_2$ gave $[Pb(NO_3)_2(N\text{-allylaza-18-crown-6})]\cdot H_2O$ (**12**), which exhibits no Pb–C interaction (analogous to **10** and **11**). However, unlike **10** and **11** the two nitrato ligands are situated on opposite faces of the macrocycle, reflecting the better fit of the Pb^{2+} ion into the larger ring, resulting in less exposed metal surface on a given face. The metal ion is still somewhat 'cupped' by the ligand, however, resulting in significantly shorter bonds to the nitrato ligand on the more exposed (less hindered) face, Fig. 5. Metal–heteroatom distances within the crown ether display no obvious preference for N or O.

In contrast, the analogous reaction of **4** with $AgBF_4$, results in a remarkable stacked coordination polymer that clearly demonstrates the scorpionate concept. The resulting product, $\{[Ag(N\text{-allylaza-18-crown-6})][BF_4]\}_\infty$ (**13**), shows a marked distortion of the tertiary amine nitrogen atom out of the mean plane of the crown ether, allowing the allyl side arm to reach directly over the Ag^+ cation. The larger size of the 18-membered crown ether ring allows the Ag^+ ion to drop much more deeply into the macrocyclic cavity, however, and as a result the system still does not exhibit sufficient flexibility to allow *intramolecular* Ag···π coordination. Intramolecular Ag–C distances are long at 3.325 and 3.613 Å, whereas a much shorter bond (analogous to that observed for **8a** and **8b**) is found to the Ag^+ ion in the molecule directly above the allyl

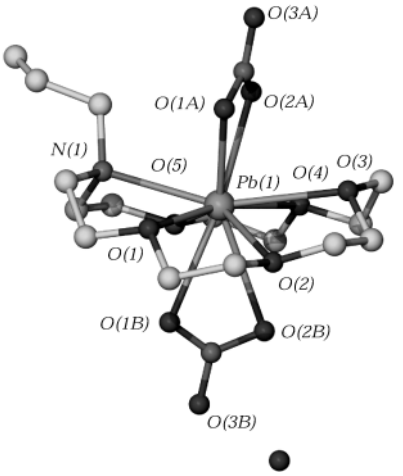

Fig. 5 Structure of $[Pb(NO_3)_2(N\text{-allylaza-18-crown-6})]\cdot H_2O$ (**12**). Selected bond lengths: Pb(1)–O(1A) 2.571(4), Pb(1)–O(2A) 2.646(4), Pb(1)–O(1) 2.649(3), Pb(1)–N(1) 2.673(5), Pb(1)–O(5) 2.684(3), Pb(1)–O(2) 2.762(3), Pb(1)–O(1B) 2.787(4), Pb(1)–O(4) 2.815(3), Pb(1)–O(3) 2.857(4), Pb(1)–O(2B) 3.026(4) Å.

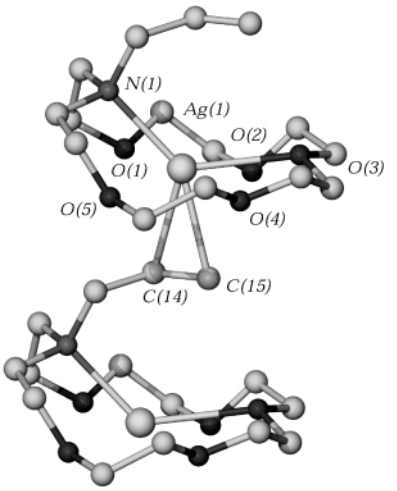

Fig. 6 Coordination polymeric stack based on Ag–C interactions in the product $\{[Ag(N\text{-allylaza-18-crown-6})][BF_4]\}_\infty$ (**13**). Selected bond distances: Ag(1)–N(1) 2.3590(19), Ag(1)–C(15) 2.515(2), Ag(1)–C(14) 2.566(2), Ag(1)–O(3) 2.5921(17), Ag(1)–O(4) 2.6843(16), Ag(1)–O(5) 2.7475(17), Ag(1)–O(1) 2.7840(17), Ag(1)–O(2) 3.1020(17) Å

side arm (2.515 and 2.566 Å), to give an organometallic coordination polymeric stack, Fig. 6. Silver–heteroatom distances suggest a much stronger interaction to the tertiary amine nitrogen atom (2.359 Å) compared to the ether oxygen atoms (2.592–3.102 Å), consistent with electronic arguments. It was anticipated that incorporation of slightly more flexibility into the ligand system should result in an intramolecular equivalent of these Ag···π interactions.

Unfortunately, no crystals were forthcoming of Ag(I) complexes of the larger lariat ether **6** despite repeated attempts. Crystals of the $AgPF_6$ complex of the longer *N*-butenylaza-18-crown-6 (**5**) were isolated, however, and this species, $[Ag(N\text{-butenylaza-18-crown-6})][PF_6]$ (**14**), demonstrated conclusively an *intramolecular* scorpionate Ag···π interaction with the butenyl side arm reaching readily over the crown ether mean plane to give a three-dimensional lariat ether encapsulation of the Ag^+ ion, Fig. 7. The presence of some molecular strain is demonstrated by the Ag–C bond distances (2.580 and 2.612 Å), somewhat longer than for the less strained situation encountered in complexes **8** and **13**. It is clear that this represents a true covalent interaction however, since this is

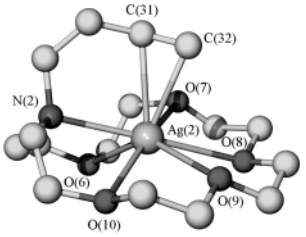

Fig. 7 X-Ray crystal structure of the mononuclear C-lariat 'scorpionate' [Ag(*N*-3-butenylaza-18-crown-6)][PF_6] (**14**). Selected bond lengths: Ag(2)–N(2) 2.485(8), Ag(2)–C(32) 2.580(14), Ag(2)–O(9) 2.606(7), Ag(2)–C(31) 2.612(14), Ag(2)–O(10) 2.677(8), Ag(2)–O(8) 2.683(6), Ag(2)–O(6) 2.701(9), Ag(2)–O(7) 2.793(7) Å [the other independent molecule based on Ag(1) is disordered].

much shorter than the distances in excess of 3 Å observed for alkali metal complexation.[1,2] Silver to nitrogen bond lengths are slightly shorter than silver–oxygen distances, consistent with the softer nature of the N-donor atom. The crown as a whole is significantly distorted from the usual D_{3d} conformation of 18-crown-6 in a fashion analogous to **13**, apparently in order to facilitate the 3D encapsulation of the Ag^+ ion both by the lariat side arm above the mean plane of the macrocycle and by one ether oxygen atom below it. Indeed, the NCH_2CH_2-$CH{=}CH_2$–Ag ring forms a near optimal 5/6-membered chelate. In contrast to **9**, the PF_6^- counter anions are located *ca.* 6.5 Å from the metal centre and play no part in the primary coordination sphere.

Reaction of *N*-allylaza-18-crown-6 was also attempted with CuI in anticipation of observing similar Cu(I)···π interactions. In this case, however, some disproportionation to Cu(II) and Cu metal occurred during the course of the crystal growth such that the only Cu(I) product isolated contained the unusual polymeric $[Cu_2I_3]^-$ anion acting as a non-coordinating counter ion to the protonated lariat ether. The source of H^+ appears to be the Lewis acidic Cu^{2+} also present in the reaction medium or residual HI. The X-ray crystal structure of this material, (H_3O)(*N*-allylaza-18-crown-6)[Cu_2I_3] (**15**), shows that the acidic proton resides on the nitrogen atom of the azacrown moiety, and hydrogen bonds strongly to a water molecule included within the macrocyclic cavity. The presence of this interaction leads to the allyl side arm being pulled up almost perpendicular to the plane of the macrocyclic ring [Fig. 8(a)] but it is not situated above the macrocyclic cavity as in **13**. The $[Cu_2I_3]^-$ anion [Fig. 8(b)] comprises an infinite Cu···Cu···Cu chain with Cu···Cu distances of 2.509 and 2.662 Å, suggesting a metal–metal interaction and resulting in extremely acute Cu–I–Cu angles for the bridging iodo ligands of 52.4–57.1°. This edge- and face-sharing structure deviates markedly from the known $Cu_2X_3^-$ anions (X = Cl, Br, I).[24] The unusual polymeric $[Cu_2I_3]^-$ anion has been observed previously[24] from direct combination of quaternary ammonium triiodide salts with copper metal. The X-ray crystal structure of R[Cu_2I_3] (R = NMe_4 or $Me_2N{=}CH{-}N{=}CHNMe_2$) shows a similar geometry of the anion to that found in **13** with Cu···Cu distances of 2.49/2.51 and 2.69/2.68 Å (depending on the counter anion).

Very recently the synthesis of *N*,*N*′-bis(3-butenyl)-4,13-diaza-18-crown-6 (**7**) has been reported by Gokel *et al*. This ligand binds to Na^+ *via* short Na–O bonds, longer Na–N interactions and Na–C bonds to both side arms (Na–C: 3.10–3.15 Å).[2] Attempts were made to crystallise this ligand with both $Pb(NO_3)_2$ and $AgBF_4$ but only the former reaction yielded X-ray quality crystals. In contrast to the $NaPF_6$ complex reported by Gokel *et al*., reaction of **7** with $Pb(NO_3)_2$ gives [$Pb(NO_3)_2${*N*,*N*′-bis(3-butenyl)-4,13-diaza-18-crown-6}] (**16**) in which the Pb^{2+} ion does not coordinate to the butenyl side arms. The lead ion sits in a U-shaped pocket defined at its base

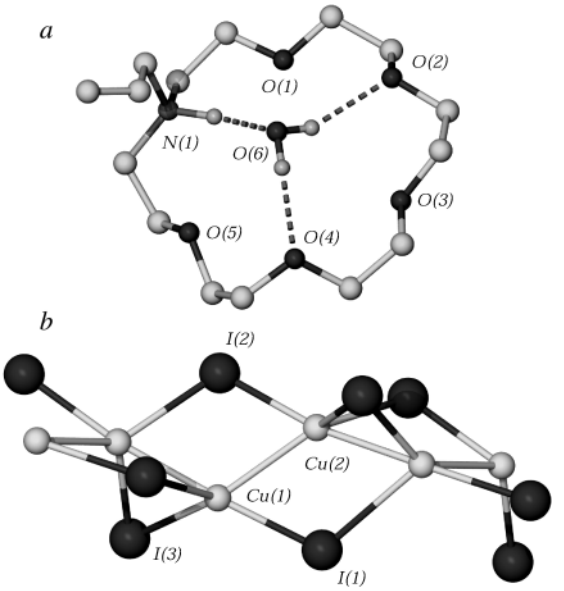

Fig. 8 (a) Structure of the protonated *N*-allylaza-18-crown-6 in **15** formed from CuI, (b) the $[Cu_2I_3]^-$ coordination polymeric anion in **15**. Selected bond lengths: I(1)–Cu(1) 2.5584(14), I(1)–Cu(1)#1 2.7664(14), I(2)–Cu(2) 2.5548(14), I(2)–Cu(1) 2.6943(13), I(3)–Cu(1) 2.6207(12), I(3)–Cu(2)#2 2.6282(13), Cu(1)–Cu(2)#2 2.5090(16), Cu(1)–Cu(2) 2.6619(17), Cu(1)–I(1)#2 2.7664(13), Cu(2)–I(3)#1 2.6282(13) Å. Symmetry transformations used to generate equivalent atoms: #1 x, $-y+{}^3/_2$, $z-{}^1/_2$, #2 x, $-y+{}^3/_2$, $z+{}^1/_2$. Hydrogen bonds: N(1)···O(6) 2.786(9), O(6)···O(2) 2.986(9), O(6)···O(4) 3.064(8) Å.

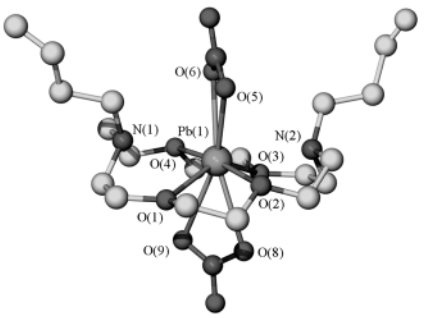

Fig. 9 Structure of [$Pb(NO_3)_2${*N*,*N*′-bis(3-butenyl)-4,13-diaza-18-crown-6}] (**16**). Selected bond lengths: Pb(1)–O(5) 2.652(8), Pb(1)–O(1) 2.670(8), Pb(1)–O(3) 2.695(8), Pb(1)–O(6) 2.712(8), Pb(1)–O(2) 2.717(7), Pb(1)–O(4) 2.785(8), Pb(1)–O(8) 2.795(8), Pb(1)–O(9) 2.816(8) Å.

by the four near co-planar ether oxygen atoms, while the two crown nitrogen atoms both point out of the plane and coordinate to the Pb(II) ion, Fig. 9. The average Pb–N distance of 2.836 Å is slightly longer than the average Pb–O bond, 2.717 Å. The ten-coordinate geometry about the lead ion is completed by two bidentate axial nitrato ligands. These ligands are bound to opposite sides of the metal ion and Pb–O_2NO distances to O(8) and O(9) are longer than observed in compounds **10** and **11** as a result of the doming of the metal ion towards O(5) and O(6).

Solution studies

The solid state results reported herein and by others[2] strongly suggest that while Ag^+ coordination to alkenic lariat side arms is common, harder metal ions such as Pb^{2+}, Na^+ and K^+ form π-complexes less readily. If such results are to be transferable

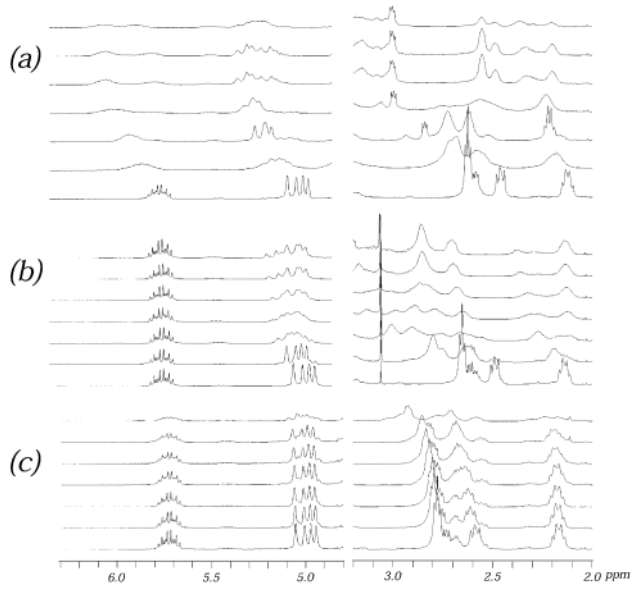

Fig. 10 Partial ^{1}H NMR titrations for the interaction of *N*-3-butenyl-aza-18-crown-6 (**5**) with (a) Ag^+, (b) Pb^{2+} and (c) K^+. Successive spectra represent addition of 0, 0.1, 0.2 0.3, 0.4, 0.5 and 1.0 equiv. of cation (D_2O solution, 20 °C).

to biological systems, however, it is clearly of interest to assess the extent of π-system participation in cation binding in aqueous solution. Gokel *et al.* have shown by NMR titration[1] that in acetone solution a bis(indolylethyl)-sidearmed 18-crown-6 derivative shows a significant shift in the pyrrolo CH proton of the side arm. In general, however, solution studies, particularly in aqueous media, are lacking. In the present work this has been addressed by ^{1}H NMR titration of $AgBF_4$, $Pb(NO_3)_2$ and KPF_6 with ligands **4**, **5** and **7** in D_2O. In such a competitive medium binding constants are likely to be small, however, the most significant problem encountered was precipitation. White precipitates were formed in all nine titration experiments between the addition of 0.5–1.0 equiv of the metal cation to the host solution. Despite this setback, which precludes the calculation of accurate binding constants, a great deal of qualitative information is afforded by the early parts (low M : L ratio) of the titration data. Fig. 10 shows stacked plots for titration of *N*-(3-butenyl)aza-18-crown-6 (**5**) with Ag^+, Pb^{2+} and K^+. In each case there are marked changes in the region of 2.5–3.5 ppm, corresponding to the resonances for the macrocycle backbone, indicative of a conformational change upon binding the metal cation within the macrocyclic cavity. However, in the case of both Pb^{2+} and K^+ essentially no changes are observed in the region of 5.0–6.0 ppm, corresponding to the resonances assigned to the alkenic protons. Only in the case of Ag^+ are marked changes observed in the alkenic protons, with the resonances assigned to the terminal $=CH_2$ and internal CH alkenic protons shifting systematically by 0.3 ppm [Fig. 10(a)] following addition of 0.5 equiv of Ag^+. Further changes are masked by precipitation. In the case of the ligands *N*-allylaza-18-crown-6 (**4**) and *N*,*N*′-bis(3-butenyl)-4,13-diaza-18-crown-6 (**7**), similar behaviour is observed with systematic shifts throughout the spectrum for Ag^+ while essentially no change is observed in the 5.0–6.0 ppm region for K^+. In the case of Pb^{2+}, interaction with **7** gave similar behaviour to **5**, consistent with the structure of **16**. However, binding of Pb^{2+} by the allyl derivative **4** resulted in significant (0.3 ppm) shifts of one of the terminal alkenic protons but *not* the internal –CH= group. This may be a consequence of conformational changes occurring on binding the tertiary amine nitrogen atom to the Pb^{2+} ion but some π-coordination cannot be ruled out.

Conclusions

This work firmly established that Ag^+ exhibits a strong preference for coordination of alkenes both in the solid state and in aqueous solution. With appropriate molecular design this may be an intramolecular 'scorpionate'-type bonding involving simultaneous coordination of the macrocyclic ring and lariat ether side arm to the same metal cation. π-Coordination of harder cations is also possible[1,2] and may be favoured by optimal ligand design, particularly in the absence of strongly competing anions. The present study suggests that this does not persist in aqueous solution in these simple model compounds.

Experimental

Instrumental

Mass spectra were run at King's College London on a Jeol AX505W spectrometer in FAB mode in a thioglycerol or NBA 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 the University of North London. All reactions were carried out in air and the products showed no oxygen sensitivity, although aluminium foil was used to protect all Ag(I) complexes from light. Many solid products readily absorbed atmospheric moisture. Conditions were optimised to produce X-ray diffraction quality crystals and hence measured yields were highly variable.

Ligand syntheses

Azacrown ethers **1** and **3** were prepared by literature methods.[25,26]

***N*-Allylaza-15-crown-5 (2).** A solution of allyl bromide (1.04 mL, 12 mmol) in dry diethyl ether (10 mL) was added dropwise, *via* cannula, to a stirred solution of aza-15-crown-5 (2.63 g, 12 mmol) and triethylamine (1.84 mL, 13.2 mmol) in dry diethyl ether (25 mL) at room temperature under nitrogen. The mixture was stirred for 24 h to ensure complete precipitation of triethylamine hydrochloride. Solvent was removed *in vacuo* and sodium-dried pentane (25 mL) was added to the residue. The mixture was stirred vigorously for 2 h whereupon the solution was removed through a cannula wire fitted with a filter. This extraction step was repeated with a further wash of sodium-dried pentane (25 mL), the solutions were combined, and solvent removed. The pale green oil that resulted was purified by distillation in a Kugelrohr apparatus at 118–20 °C and 0.25 mm Hg to yield a colourless oil (2.51 g, 9.8 mmol, 82%). ^{1}H NMR ($CDCl_3$, δ, J/Hz): 5.69 (m, 1H, NCH_2CHCH_2), 4.98 (m, 2H, NCH_2CHCH_2, $^3J_{HHtrans} = 14.3$, $^2J_{HH} = 1.3$), 3.55 (m, 16H, OCH_2CH_2O), 2.95 (d, 2H, NCH_2CHCH_2), 2.62 (t, 4H, CH_2NCH_2). MS(FAB): 259 (M^+). IR (thin film, cm^{-1}): 2880 $\nu(CH_2)$, 1650 $\nu(C{=}C)$, 1460 $\nu(CH_2)$, 1300 $\nu(C–N)$, 1130 $\nu(C–O–C)$. Anal. calcd. for $C_{13}H_{25}NO_4 \cdot 0.25\ H_2O$: C, 59.18; H, 9.74; N, 5.31. Found: C, 59.26; H, 10.26; N, 5.46%. Ligand **2** is hydroscopic, as evidenced by the elemental analysis, however, its properties are identical to samples prepared by an alternative method.[26]

***N*-Allylaza-18-crown-6 (4).** *N*-Allylbis(2-hydroxyethyl)-amine[27] (3.63 g, 25 mmol) was dissolved in dry THF (25 mL). Sodium hydride (1.68 g, 67 mmol) was added to this solution and the resulting grey suspension stirred at room temperature for 1 h. Tetraethylene glycol ditosylate[28] (12.57 g, 25 mmol) was dissolved in dry THF (50 mL) and added dropwise to the hydride suspension. The mixture was refluxed for 48 h. The

suspension was allowed to cool to room temperature and excess hydride quenched with water. The solution was evaporated to dryness under reduced pressure, the resulting solid was taken up in dichloromethane (60 mL) and filtered on a celite pad. Water (50 mL) was added to the filtrate, which was acidified with 2 M HCl to pH 2. The water layer was washed with chloroform (50 mL), made alkaline with 6 M NaOH to pH 12 and washed with chloroform (50 mL). The combined organic extracts were dried over magnesium sulfate and evaporated under reduced pressure to yield the crude product. This was purified using column chromatography (Al_2O_3, CH_2Cl_2) to afford a yellow oil (1.21 g, 4 mmol, 16%). ^{1}H NMR ($CDCl_3$, δ, J/Hz): 5.88 (m, 1H, NCH_2CHCH_2), 5.19 (m, 2H, NCH_2CHCH_2), 3.68 (m, 20H, OCH_2CH_2O), 3.17 (d, 2H, NCH_2CHCH_2, 6.5), 2.78 (t, 4H, CH_2NCH_2, 5.85). MS(FAB): 303 (M^+). IR (thin film, cm^{-1}): 2857 ν(CH_2), 1642 ν(C=C), 1250 ν(C–N), 1114 ν(C–O–C). Anal. calcd. for $C_{15}H_{29}N_1O_5$: C, 59.38; H, 9.63; N, 4.62. Found: C, 59.25; H, 9.78; N, 4.76%.

***N*-Butenylaza-18-crown-6 (5).** Aza-18-crown-6 (0.5 g, 1.90 mmol) was dissolved in acetonitrile (20 mL). To this were added potassium carbonate (4.2 g, 40 mmol) and potassium iodide (0.06 g, 0.4 mmol). A solution of 4-bromo-1-propene (0.26 g, 1.9 mmol) in acetonitrile (5 mL) was added dropwise and the resulting mixture refluxed for 24 h. The solution was cooled, filtered and evaporated under reduced pressure to an oil. The oil was dissolved in dichloromethane (20 mL), washed with water (35 mL), brine (15 mL) and once more with water (15 mL). The combined organic layers were dried over magnesium sulfate and the solvent evaporated to afford an orange oil (0.18 g, 0.55 mmol, 29%). ^{1}H NMR ($CDCl_3$, δ, J/Hz): 5.78 (m, 1H, $NCH_2CH_2CHCH_2$), 5.07 (m, 2H, $NCH_2CH_2CHCH_2$, $^3J_{HHcis} = 6.6$, $^3J_{HHtrans} = 15.3$, $^2J_{HH} = 1.8$), 3.68 (m, 20H, OCH_2CH_2O), 2.80 (t, 4H, CH_2NCH_2, 5.9), 2.60 (t, 4H, $NCH_2CH_2CHCH_2$, 7.8), 2.21 (dt, 2H, $NCH_2CH_2CHCH_2$, $^3J_{HH} = 7.9$, 7.1). MS(FAB): 318 (M^+). IR (thin film, cm^{-1}): 2864 ν(CH_2), 1672 ν(C=C), 1455 δ(CH_2), 1297 ν(C–N), 1197 ν(C–O–C). Anal. calcd. for $C_6H_{31}NO_5$: C, 60.54; H, 9.84; N, 4.41. Found: C, 60.56; H, 9.76; N, 4.34%.

***N*-Allylaza-21-crown-7 (6).** *N*-Allylbis(2-hydroxyethyl)amine (1.45 g, 10 mmol) was dissolved in dry THF (25 mL). Potassium hydride (0.8 g, 20 mmol) was added and the resulting grey suspension stirred at room temperature for 1 h. Pentaethylene glycol ditosylate (5.47 g, 10 mmol) was dissolved in dry THF (50 mL) and added dropwise to the hydride suspension. The brown mixture was refluxed for 48 h whereupon the suspension was allowed to cool to room temperature and excess hydride quenched with water. The solution was evaporated to dryness under reduced pressure, the resulting solid was taken up in dichloromethane (50 mL) and filtered on a celite pad. Water (50 mL) was added to the filtrate, which was acidified with 2 M HCl to pH 2. The water layer was washed with chloroform (50 mL), made alkaline with 6 M NaOH to pH 12 and washed with chloroform (50 mL). The combined organic layers were dried over magnesium sulfate and evaporated under reduced pressure to yield the crude product. This was purified using column chromatography (SiO_2: 9 : 1 $CHCl_3$–MeOH) to yield a yellow oil (0.034 g, 1%). ^{1}H NMR ($CDCl_3$, δ, J/Hz): 5.87 (m, 1H, NCH_2CHCH_2), 5.23 (m, 2H, NCH_2CHCH_2), 3.70 (m, 24H, OCH_2CH_2O), 3.29 (d, 4H, NCH_2CHCH_2, $J = 6.59$), 2.76 (t, 4H, CH_2NCH_2, $J = 5.29$). MS(FAB): 349 (M^+).

***N*,*N*′-Bis(3-butenyl)-4,13-diaza-18-crown-6 (7).** Diaza-18-crown-6[29] (0.5 g, 1.9 mmol) was dissolved in acteonitrile (40 mL) with sodium carbonate (8.46 g, 80 mmol) and potassium iodide (0.06 g, 0.04 mmol). A solution of 4-bromobut-1-ene (0.566 g, 4.2 mmol) dissolved in acetonitrile (10 mL) was added dropwise. The mixture was then refluxed for 24 h, cooled to room temperature, filtered through a celite pad and the filtrate evaporated under reduced pressure. The resulting oil was dissolved in dichloromethane (20 mL), washed with water (35 mL), brine (15 mL), and water (15 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure to yield an orange oil (0.24 g, 0.66 mmol, 35%). ^{1}H NMR ($CDCl_3$, δ, JHz): 5.78 (m, 2H, $NCH_2CH_2CHCH_2$), 5.07 (m, 4H, $NCH_2CH_2CHCH_2$, $^3J_{HHcis} = 6.5$, $^3J_{HHtrans} = 15.5$, $^2J_{HH} = 1.6$), 3.62 (m, 16H, OCH_2CH_2O), 2.80 (t, 8H, CH_2NCH_2, 5.9), 2.60 (t, 4H, $NCH_2CH_2CHCH_2$, $J_{HH} = 7.7$), 2.21 (dt, 4H, $NCH_2CH_2CHCH_2$, $^3J_{HH} = 6.9$). MS(FAB): 371 (M^+). This ligand was recently reported independently by Gokel *et al.*[2]

Preparation of complexes

{[Ag(*N*-allylaza-15-crown-5)][BF_4]}$_\infty$ (8b). $AgBF_4$ (0.049 g, 0.25 mmol) was dissolved in methanol (1 mL). To this was added *N*-allylaza-15-crown-5 (0.05 g, 0.19 mmol). The resulting solution was left to stand for 2 weeks, resulting in the deposition of the product as colourless crystals suitable for X-ray crystallography. Yield (0.07 g, 0.15 mmol, 38%). Anal. calcd. for $C_{15}H_{29}O_5NBF_4$: C, 34.39; H, 5.55; N, 3.09. Found: C, 34.41; H, 5.64; N 2.99%.

{[K(PF_6)(*N*-allylaza-15-crown-5)]}$_2$ (9). A solution of *N*-allylaza-15-crown-5 (0.13 g, 0.50 mmol) in boiling methanol (1 mL) was added to KPF_6 (0.18 g, 0.98 mmol) in boiling methanol (1 mL) to give a colourless mixture that was allowed to cool in air for 48 h, resulting in the deposition of the product as colourless plates [m.p. 120–122 °C (from methanol)]. Anal. calcd. for **9**·H_2O ($C_{13}H_{27}F_6KNO_5P$): C; 33.84, H; 5.90, N; 3.04. Found: C; 33.56, H; 5.55, N; 2.89%.

[Pb(NO_3)$_2$(*N*-allylaza-15-crown-5)] (10). $Pb(NO_3)_2 \cdot H_2O$ (0.051 g, 0.15 mmol) was dissolved in water (1 mL). To this was added *N*-allylaza-15-crown-5 (0.050 g, 0.19 mmol). The resulting solution was left to stand for 2 weeks, resulting in the deposition of the product as colourless crystals suitable for X-ray crystallography. Microanalytical data indicated that **10** absorbs atmospheric moisture to give **11** on standing (see below).

[Pb(η^2-NO_3)$_2$(*N*-allylaza-15-crown-5)]$_2$·[Pb(η^2-NO_3)(η^1-NO_3)(H_2O)(*N*-allylaza-15-crown-5)]·H_2O (11). $Pb(NO_3)_2 \cdot 6H_2O$ (0.051 g, 0.15 mmol) was dissolved in water (1 mL). To this was added *N*-allylaza-15-crown-5 (0.050 g, 0.19 mmol). The resulting solution was left to stand for 2 weeks, resulting in the deposition of the product as colourless crystals suitable for X-ray crystallography. Yield (0.03 g, 0.05 mmol, 14%). Anal. calcd. for $C_{13}H_{27}N_3O_{11}Pb$: C, 25.66; H, 4.47; N, 7.02. Found: C, 25.77; H, 4.53; N, 7.03%.

General procedure for compounds 12–16. The lariat ether (0.10 g, 0.33 mmol) was weighed into a sample tube and dissolved in distilled water (1.0 mL). The appropriate metal salt was dissolved in distilled water (1.0 mL) and added to the original solution. The sample tubes were then wrapped in foil, covered with a perforated lid and left to evaporate in a dark cupboard. The procedure was designed to yield X-ray quality crystals and hence yields are artificially low.

*[Pb(NO_3)$_2$(N-allylaza-18-crown-6)] (**12**).* Yield (0.07 g, 0.13 mmol, 40%). MS(FAB): 573 (M^+), 510 ($M^+ - 2NO_3$), 302 ($M^+ - Pb(NO_3)_2$). IR (cm^{-1}): 1635 m ν(C=C). Anal. calcd. for $C_{25}H_{31}N_3O_{12}Pb$: C, 27.61; H, 4.79; N, 6.44. Found: C, 27.60; H, 4.89; N, 6.36%.

Table 1 Crystallographic data for new complexes

	8b	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Formula	$C_{13}H_{25}AgBF_4NO_4$	$C_{13}H_{25}F_6KNO_4P$	$C_{13}H_{25}N_3O_{10}Pb$	$C_{26}H_{52}N_6O_{21}Pb_2$	$C_{15}H_{31}N_3O_{12}Pb$	$C_{15}H_{29}AgBF_4NO_5$	$C_{16}H_{31}AgF_6NO_5P$	$C_{15}H_{32}Cu_2I_3NO_6$	$C_{20}H_{38}N_4O_{10}Pb$
Formula weight	454.02	443.41	590.55	1199.12	652.62	498.07	570.26	830.195	701.73
T/°C	−173(2)	−173(2)	−173(2)	−173(2)	−173(2)	−173(2)	−173(2)	−173(2)	23(2)
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1$	$P2_1/c$	$Pbca$
a/Å	9.0985(6)	10.8857(3)	9.2947(2)	7.6545(5)	8.4495(5)	13.3966(7)	10.589(2)	14.829(3)	13.894(3)
b/Å	9.3302(4)	16.4547(6)	13.6796(6)	12.0537(4)	9.4557(3)	5.8041(2)	8.5424(17)	19.689(4)	12.865(3)
c/Å	20.8800(12)	11.2887(4)	15.3903(4)	21.6309(4)	27.680(2)	24.5126(13)	23.835(5)	8.5073(17)	30.066(6)
α/°				90.671(5)					
β/°	96.591(3)	100.677(2)	96.365(2)	96.212(4)	95.563(3)	91.767(2)	90.300(3)	97.090(3)	
γ/°				96.610(4)					
U/Å^3	1760.81(17)	1987.03(11)	1944.78(11)	1970.28(15)	2201.1(2)	1905.08(16)	2156.0(7)	2464.8(9)	5374.2(19)
Z	4	4	4	2	4	4	4	4	8
μ/mm^{-1}	1.201	0.419	8.731	8.621	7.731	1.122	1.088	5.511	6.335
Reflections collected	14 323	16 968	11 619	20 988	13 197	12 844	9526	15 252	21 245
Independent reflections	3988	3890	4428	7646	4930	4315	7220	5618	5248
R_1 [$I > 2\sigma(I)$]	0.0363	0.0316	0.0279	0.0670	0.0404	0.0316	0.0521	0.0603	0.0783
wR_2 [$I > 2\sigma(I)$]	0.0776	0.0770	0.0649	0.1733	0.0728	0.0572	0.1189	0.1265	0.1156
R_1 (all data)	0.0466	0.0397	0.0338	0.0878	0.0650	0.0492	0.0620	0.0835	0.1388
wR_2 (all data)	0.0802	0.0812	0.0674	0.1892	0.0788	0.0610	0.1225	0.1360	0.1290

*{[Ag(N-allylaza-18-crown-6)][BF$_4$]}$_\infty$ (**13**)*. Yield (0.02 g, 0.04 mmol, 13%). MS(FAB): 410 ($M^+ - BF_4$), 304 ($M^+ - AgBF_4$). IR (cm^{-1}): 1641 m ν(C=C). Anal. calcd. for $C_{15}H_{29}O_5NBF_4$: C, 36.17; H, 5.89; N, 2.81. Found: C, 36.25; H, 5.84; N, 2.75%.

*[Ag(N-butenylaza-18-crown-6)][PF$_6$] (**14**)*. Yield (0.01 g, 0.02 mmol, 7%). MS(FAB): 426 ($M^+ - PF_6$), 318 ($M^+ - AgPF_6$). IR (cm^{-1}): 1652 m ν(C=C). Anal. calcd. for $C_{16}H_{31}NO_5AgPF_6$: C, 33.74; H, 5.49; N, 2.46. Found: C, 33.77; H, 5.58; N, 2.53%.

*(H$_3$O)(N-allylaza-18-crown-6)[Cu$_2$I$_3$] (**15**)*. MS(FAB): 304 (*N*-allylaza-18-crown-6).

*[Pb(N,N′-bis(3-butenyl)-4,13-diaza-18-crown-6)][NO$_3$]$_2$ (**16**)*. MS(FAB): 578 (M^+), 371 [$M^+ - Pb(NO_3)_2$]. Anal. calcd. for $C_{20}H_{38}N_2O_4Pb$: C, 34.23; H, 5.46; N, 7.98. Found: C, 34.33; H, 5.38; N, 7.89%.

NMR titrations

In each titration 0.500 mL of a 0.100 M solution of the appropriate lariat ether in D_2O was transferred to a single predried NMR tube. To this tube were added aliquots of a standard 1.000 M solution of the required metal salt and the tube shaken thoroughly after each addition. The ^{1}H NMR spectrum of the sample was recorded after each addition.

Crystallography

Crystal data and data collection parameters are summarised in Table 1. Crystals were mounted on a thin glass fibre 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 using Mo-Kα radiation ($\lambda = 0.7107$ Å), 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.[30] 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[31]) resulted in data set corrected for Lorentz and polarisation 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[32]) and developed *via* alternating least squares cycles and difference Fourier synthesis (SHELXL-97[33]) with the aid of the XSeed interface.[34] All non-hydrogen atoms were modelled 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 (1.5 times for CH_3 groups). Amine NH protons were located experimentally and treated likewise if refinement proved unfeasible. All calculations were carried out either on a Silicon Graphics Indy workstation or an IBM-PC compatible personal computer.

The structure of **14** proved to be significantly disordered with two sets of positions of equal occupancy for all of the ligand atoms of the ligand attached to Ag(1). This was modelled reasonably satisfactorily with all fractional atoms being located and refined initially with distance and thermal parameter restraints. Upon completion of the refinement distance restraints were removed although loose restraints were maintained on C, N and O displacement parameters. A related, less severe disorder was also apparent for the ligand attached to the second independent metal ion, Ag(2). This was modelled satisfactorily in terms of only a single set of positions. The disorder is apparent in the slightly enlarged anisotropic displacement parameters for O(6) onwards. Furthermore, the structure displayed orthorhombic pseudosymmetry with the monoclinic β angle being close to 90°. The structure was solved in space group $P2_12_12_1$ with a single unique molecule, however the resulting disorder proved impossible to model and it was concluded that the lower symmetry space group choice was correct.

CCDC reference numbers 180577–180585. See http://www.rsc.org/suppdata/nj/b1/b108522k/ for crystallographic data in CIF or other electronic format.

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