Response to steric constraint by d^{10} cations: an ‘A-frame’ disilver cryptate

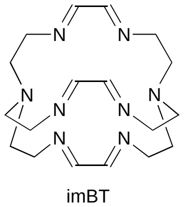
Joanne L. Coyle,[a,b] Vickie McKee*[a]† and Jane Nelson*[a,b]†

[a] *School of Chemistry, Queens University, Belfast, UK BT9 5AG*
[b] *Chemistry Department, Open University, Milton Keynes, UK MK7 6AA*

A pair of silver(I) cations is accommodated within a small azacryptand which adopts an A-frame conformation, allowing both intra- and inter-cryptate bonding of silver cations.

In recent years we have successfully used the strategy of constraining copper ions within small azacryptand hosts in coordination geometry appropriate to overlap of d_{z^2} bonding orbitals, to generate, *via* one-electron oxidation of the dicopper(I) cryptates, metal–metal bonded dicopper cryptates of average-valence $Cu^{1.5}$ redox state.[1] This unprecedented copper–copper bond has unusual and possibly applicable spectroscopic and electrochemical properties.[1,2] The isomorphism observed between copper(I) and silver(I) cryptates elsewhere in our azacryptate series[3] encouraged us to examine the silver(I) analogues of the dicopper(I) precursors to see if similarly enforced proximity would generate delocalized metal–metal bonding in the disilver(I) pair on oxidation. This is of interest not just from the point of view of metal–metal bonding theory, but because higher redox states of silver may be of interest as replacements for chlorine-based oxidants for some specialist purposes. However, as the coordination geometry preferences of silver and copper are known to be different, a necessary first step was the structural characterisation of any disilver(I) cryptate isolated. Treatment of the free ligand imBT with silver perchlorate in either 1:2 or 1:1 stoichiometry resulted in the isolation of a pale yellow microcrystalline product $[Ag_2(imBT)][ClO_4]_2$ **2** which could be recrystallised from acetonitrile to generate X-ray quality crystals.

When copper(I) cations coordinate the tren-derived N_4 caps within the small azacryptand host imBT, steric constraint brings this pair of cations to within 2.45 Å[1] of each other, within the internuclear distance of *ca.* 2.56 Å in elemental copper. In the average-valence dicopper(1.5) state, this distance reduces only slightly, to 2.38 Å,[4] whereas within the larger (trispropylene capped) cryptate host, imbistrpn, the contraction in going from the dicopper(I) state to the average-valence $Cu^{1.5}{}_2$ state is sizeable (>0.5 Å).[4] The lack of significant increase of internuclear distance on going to the dicopper(I) state within the imBT host suggests that the 2.45 Å separation is near the maximum achievable when the cryptand caps are used as coordination sites. As 2.45 Å would represent an improbably short Ag^I–Ag^I internuclear distance, isomorphism of polycrystalline $[Cu_2(imBT)][ClO_4]_2$ **1** and $[Ag_2(imBT)][ClO_4]_2$ **2** did not appear likely and was not, indeed, observed. Although, unexpectedly, CD_3CN solution ^1H NMR spectra of **1** and **2** show a good deal of similarity,[5] their solid state MAS NMR spectra[6] are quite different. The ^{13}C solid state NMR for **1** is simple, consistent with high symmetry of the cryptand conformation while for the disilver(I) analogue **2** it is complex, indicating lower symmetry for the cryptand host. The structure obtained by X-ray crystallography reveals the reason for these differences; the silver(I) cations have not chosen the ‘pre-organised’ N_4 site used by copper in its imBT, amBT and imbistrpn cryptates and adopted also in other, less constrained, disilver(I) cryptates.[7]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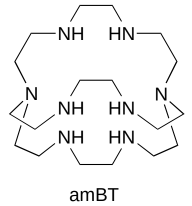
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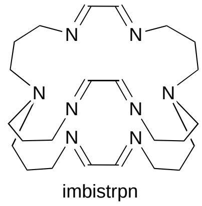
imbistrpn

Fig. 1 illustrates the alternative site selected by Ag^I. The asymmetric unit contains two independent cations and four perchlorate anions. The cations are very similar to one another, differing only in the minor details of conformation in the cryptand strands. The Ag–Ag distances are 2.8314(8) and 2.8545(8) for Ag(1a)–Ag(2a) and Ag(1d)–Ag(2d) respectively. Two of the three strands act as bidentate diimine donors to a silver ion, while the third strand bridges the two silver ions. The bridgehead nitrogen atoms are not coordinated (Fig. 2) and the overall $N_{br}\cdots N_{br}$ distance is 6.05 Å, *vs.* 5.88 Å in **1**. The three

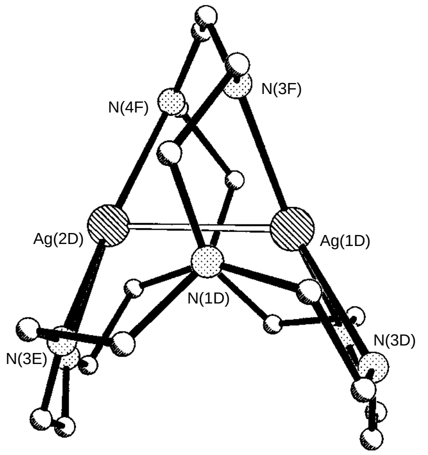

Fig. 1 View of the disilver(I) cryptate looking down the $N_{bridgehead}$ axis

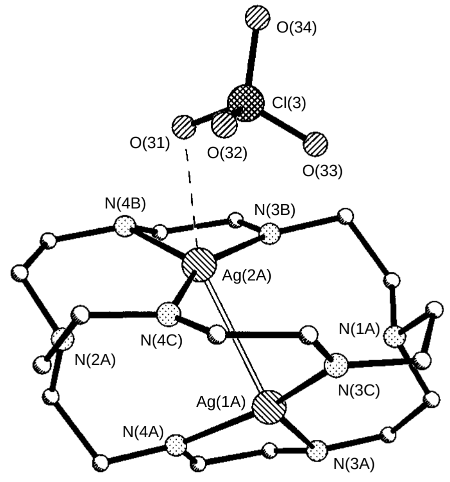

Fig. 2 View of the disilver cryptate looking sideways on to the $N_{bridgehead}$ axis. (One of the two very similar cations existing independently in the unit cell.)

imine donors take up an irregular trigonal geometry with the silver ion close to the mean plane of the nitrogen donors. The chelating diimine groups are necessarily restricted to a bite angle of *ca*. 72°. They are also asymmetric: one of the Ag–N distances is long (mean 2.405 Å) and the second is considerably shorter (mean 2.283 Å). The more tightly bound imine of the chelating imine group makes a large N–Ag–N angle [mean 158.6(2)°] with the third nitrogen donor, reflecting the preference of silver(I) for linear-based coordination.

The exposed position of the silver ions: on the outer surface of the ligand cage rather than cryptated along the main axis, allows interaction with the perchlorate anions. Ag(2a) and Ag(2d) form Ag–OClO$_3$ bonds of 2.681(6) and 2.731(5) Å, respectively while there are longer interactions with the remaining silver ions [Ag(1a)–O(22) 3.335, Ag(1d)–O(34) 3.087, Ag(2a)–O(33) 3.319 Å]. These interactions link the disilver cations in zigzag perchlorate-bridged chains, using two of the four independent perchlorate anions.

Viewed along the bridgehead–bridgehead vector the cations show A-frame geometry (Fig. 1). The top (hinge) angle is provided by the bridging diimine strand and requires a large torsion angle [46(1)° for N(3c)–C(3c)–C(4c)–N(4c) and 45(1)° for N(3f)–C(3f)–C(4f)–N(4f)]. The equivalent torsion angles for the bidentate diimine strands are in the range 28–31°.

Whether some degree of metal–metal bonding is to be implied from the observation of Ag–Ag internuclear distances shorter than those (2.89 Å) in elemental silver is a matter of debate. The rationale for the close approach of d^{10} ions observed in many systems[8] has remained a longstanding puzzle in bonding theory. To quote Hoffman[9] 'One has difficulty in seeing why two or more d^{10} ions should come near each other; after all they are filled shells'. His explanation of this behaviour relies on hybridisation of 4d with higher energy 5s and 5p orbitals which converts the closed shell repulsions into weak attractive interactions. In the case of Au^I, relativistic effects reduce the d–s energy gap to allow Au–Au interaction[10] of around 6–8 kcal mol^{-1} (cal = 4.184 J), but this mechanism cannot be invoked for Ag^I. Oxidation of the d^{10} cation should however allow stronger interaction, of the order of a one-electron bond. Preliminary electrochemical study[11] of **2** reveals a pair of overlapped and poorly reversible waves in the range 1.0–1.5 V *vs*. Ag/AgCl indicating that this disilver cryptate can be oxidised at accessible potential, apparently generating Ag^IAg^{II} and $Ag^{II}Ag^{II}$ products, at least in solution. Should cryptates of these redox states be isolable, the comparison of the weak $d^{10}d^{10}$ interaction with that existing in d^9d^{10}, or d^9d^9 where formal metal–metal bonding is theoretically possible, will assist understanding of the $d^{10}d^{10}$ situation.

The significance of the novel and unusual conformation adopted in this cryptate is that linkage of metal–metal intra-cryptate bonded entities becomes possible, *via* bridging donors coordinated at the vacant axial positions on the face of the A. Such a possibility, illustrated by the perchlorate bridging of Fig. 3, could be exploited by the use of efficient bridging ligands. In this way, cryptand-enforced metal–metal bonds could be linked together *via* unsaturated bridging groups such as CN$^-$ to generate potentially exploitable oligomeric or continuous solid materials. These would still incorporate the valuable properties of the cryptand host such as steric constraint and cryptand cavity protection, while enabling propagation of bulk electronic properties such as conductivity or magnetism through the extended structure.

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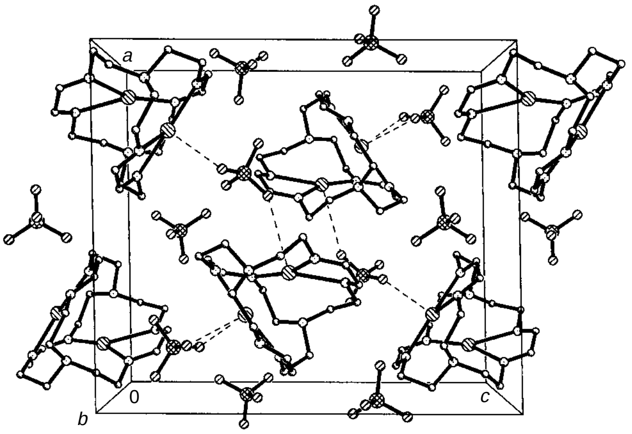

Fig. 3 Linkage of cryptate units *via* anion (perchlorate) bridging

Notes and References

† E-mail: v.mckee@qub.ac.uk, m.j.nelson@open.ac.uk

‡ *Crystal data*: [Ag$_2$(imBT)][ClO$_4$]$_2$, C$_{18}$H$_{30}$Ag$_2$Cl$_2$N$_8$O$_8$, pale yellow lath, dimensions 0.80 × 0.37 × 0.17 mm, monoclinic, space group $P2_1/n$, a = 14.467(2), b = 11.194(1), c = 16.555(2) Å, β = 91.29(1)°, U = 2682.0(5) Å^{-3}, space group $P2_1$, Z = 4, μ = 1.718 mm^{-1}, $F(000)$ = 1544. Using Mo-Kα radiation, (λ = 0.71073 Å) at 153(2) K, a total of 7680 reflections was collected in the range $4 < 2\theta < 52°$. Data were corrected for a 2% drop in intensity as well as for Lorentz and polarisation effects and an empirical absorption correction was applied. The structure was solved by direct methods (TREF[12]) and refined by full-matrix least squares on F^2, using all 5608 independent reflections (R_{int} = 0.0365). All the non-hydrogen atoms were refined with anisotropic atomic displacement parameters and hydrogen atoms were inserted at calculated positions. Refinement of 685 parameters, converged with wR_2 = 0.0706, GOF = 1.065 (all data) and conventional R_1 = 0.0300 (2σ data). There were no significant residual peaks in the electron density map. All programs used in the structure refinement are contained in the SHELXL-97 package.[13] CCDC 182/780.

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