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Nitrile functionalised pendant-arm derivatives of [9]aneN_3 as new multidentate ligands for inorganic crystal engineering ([9]aneN_3 = 1,4,7-triazacyclononane)

Lorenzo Tei, Vito Lippolis, Alexander J. Blake, Paul A. Cooke and Martin Schröder*

School of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD.
E-mail: m.schroder@nottingham.ac.uk

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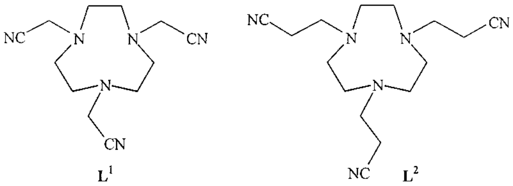
Functionalised pendant-arm derivatives of [9]aneN_3 have been used as building blocks for the synthesis of inorganic multi-dimensional networks in the presence of Ag^I.

Crystal engineering and the design of solid-state architectures have become areas of increasing interest over recent years.[1–4] Initially, attention was focused mainly upon the use of supramolecular contacts (particularly hydrogen bonding and π–π interactions) between suitable organic molecules to generate multi-dimensional arrays and networks.[1–3] More recently, the design of three-dimensional inorganic coordination polymers has become a rapidly expanding area[4,5] with transition metal ions such as Cu^I and Ag^I and multidentate ligands derived from 4,4′-bipy being used as building blocks for different network topologies and structural motifs.[6–8] Although subtle factors such as π–π interactions between ligand units and/or the nature of the anion may have profound effects on the topology of the cationic coordination array, the design and synthesis of new multidentate ligands that can be used as building blocks for the construction of desired solid-state architecture is still the major target.

Functionalised pendant arm derivatives of aza-crown ether macrocycles have long been used as ligands for producing complexes of low nuclearity and of high kinetic and thermodynamic stability, with the coordinated transition-metal ion(s) adopting specific coordination and redox properties which make them relevant as models for metallobiosites or catalytic reagents.[9,10] The pendant groups are carefully chosen and are often attached to the macrocyclic framework to give endocyclic complexes. However, functionalised pendant arms have not been previously intentionally attached onto aza-crown ether rings for the purpose of assembling a multidentate ligand to be used in the construction of three-dimensional exocyclic solid-state architectures.

We report herein the synthesis† and coordination properties of the new ligands L^1 and L^2 with Ag^I. We argued that nitrile functionalised pendant arms would prevent these polydentate ligands from encapsulating tetrahedral metal centres (Ag^I, Cu^I) or forming sandwich complexes with them, but would promote the formation of multinuclear or polymeric compounds.



L^1 L^2

Reaction of L^1 with 1 molar equivalent of $AgPF_6$ in MeCN at room temperature gives colourless plate crystals following partial removal of the solvent and diffusion of Et_2O vapour into the remaining solution. A single crystal X-ray determination‡ confirms the product to be a three-dimensional polymer, $\{[Ag(L^1)](PF_6)\}_\infty$ **1**. Each Ag^I ion is coordinated to six N-donors in a distorted octahedral coordination geometry, with one face taken up by the three N-donors of the triaza ring [Ag–N 2.523(4)–2.547(4) Å]. The remaining three positions are occupied by the N-donors of nitrile groups belonging to three different molecules of $[Ag(L^1)]^+$ [Ag–N 2.311(4)–2.486(4) Å] (Figs. 1 and 2). A three-dimensional inorganic network is therefore formed in which each molecule of L^1 is a node linked to four different Ag^I centres (Fig. 2) and each Ag^I ion represents a six-connected junction *via* NCH_2CN linkers to six other Ag^I ions in the overall 3D single network. Six-connected single networks at Ag^I consisting of a cationic frame linked by molecular rods are very rare in the literature, the only reported example being the complex $[Ag(pyz)_3]SbF_6$ which is topologically related to the structures of ReO_3 or Prussian blue.[7c]

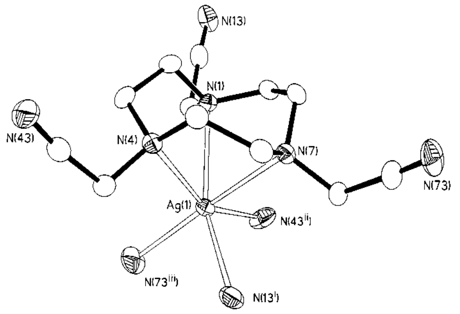


Fig. 1 View of the coordination sphere around the Ag^I ion in the $[Ag(L^1)]^+$ cation with numbering scheme adopted. The nitrogen atoms $N(13^i)$, $N(43^{ii})$ and $N(73^{iii})$ belong to three different symmetry related molecules of L^1 [i = $x + 1/2, -y + 3/2, z-1/2$; ii = $x-1/2, -y+3/2, z-1/2$; iii = $-x+1/2, y+1/2, -z+1/2$]. Hydrogen atoms are omitted for clarity and displacement parameters are drawn at 50% probability.

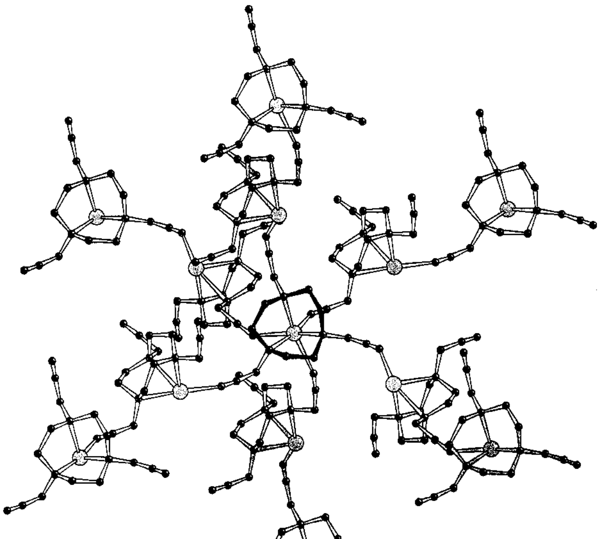


Fig. 2 View of part of the $\{[Ag(L^1)]^+\}_\infty$ three-dimensional polymer. Counter-anions are omitted for clarity and chains running through the structure are distinguished by the colour of their bonds.

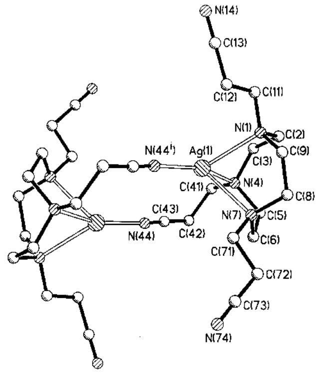


Fig. 3 View of the $[Ag_2(L^2)_2]^{2+}$ dinuclear cation with numbering scheme adopted. Hydrogen atoms are omitted for clarity. Symmetry operation i = $-x+1$, $-y+1$, $-z$.

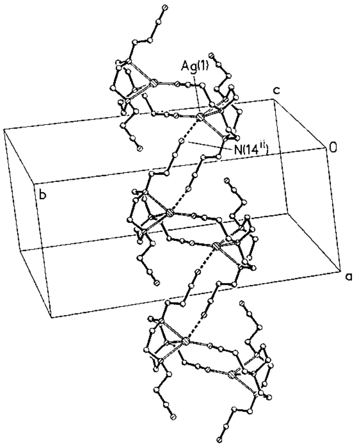


Fig. 4 Packing diagram for the $\{[Ag_2(L^2)_2]^{2+}\}_\infty$ polymeric chain. Counter-anions are omitted for clarity. Symmetry operation ii = $-x+2$, $-y+1$, $-z$.

Using the same synthetic procedure as for **1**, colourless crystals were obtained from the reaction of L^2 with $AgBF_4$ in 1:1 molar ratio in MeCN. Although analytical and mass spectroscopic data for the product were consistent with the stoichiometry $[Ag(L^2)]BF_4$, a single crystal structure determination was undertaken to ascertain the ligation and nuclearity of the complex. The structure confirms the product to be a one-dimensional zigzag polymer, $\{[Ag_2(L^2)_2](BF_4)_2\}_\infty$ **2** in which the repeating unit is the binuclear complex cation $[Ag_2(L^2)_2]^{2+}$ which lies across a crystallographic inversion centre (Fig. 3). Each Ag^I ion in the binuclear fragment is coordinated to four N-donors in a distorted tetrahedral geometry with N–Ag–N angles ranging from 74.0(2) [N(4)–Ag(1)–N(7)] to 159.1(2)° [N(4)–Ag(1)–N(44^i), i = $-x+1$, $-y+1$, $-z$] and Ag–N bond distances from 2.192(6) [Ag(1)–N(44^i)] to 2.504(5) Å [Ag(1)–N(7)]. Three out of four N-donors are provided by the [9]aneN_3 framework of a molecule of L^2 and the fourth, which completes the coordination sphere around the metal centre, belongs to the nitrile group of a pendant arm of the symmetry related $[Ag(L^2)]^+$ unit (Fig. 3). One of the remaining two pendant arms of L^2 interacts with a Ag^I centre of an inversion-related $[Ag_2(L^2)_2]^{2+}$ binuclear fragment [Ag(1)–N(14^{ii}) 2.779(7) Å, ii = $-x+2$, $-y+1$, $-z$] to give an infinite zigzag polymer along the *a* axis (Fig. 4). Thus, simply altering the pendant arm length, from C_2 in L^1 to C_3 in L^2, affords a different network motif for the resultant coordination polymer.

The work described herein represents the first attempt to use properly designed functionalised pendant-arm derivatives of aza crown ethers as building blocks for the synthesis of extended inorganic architectures. We have also shown that the potential of this type of ligand can be increased further by the fine-control over the nature of the resulting inorganic network offered by varying the length of the pendant arms.

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Notes and References

† The ligands L^1 and L^2 were prepared in 53 and 95% yield, respectively, starting from [9]aneN_3·3HBr and [9]aneN_3, respectively, according to procedures adapted from the literature.[11] L^1: Found (calc. for $C_{12}H_{18}N_6$): C, 58.2 (58.5); H, 7.6 (7.4); N, 34.0 (34.1%); ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz), δ 2.85 (12H, s), 3.59 (6H, s); ^{13}C NMR ($CDCl_3$, 298 K, 75 MHz), δ 54.12, 46.49, 116.14. L^2: Found (calc. for $C_{15}H_{24}N_6$): C, 61.80 (62.50); H, 8.22 (8.33); N, 28.88 (29.17%); ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz), δ 2.44 (6H, t, *J* 6.67 Hz, CH_2CN), 2.79 (12H, s), 2.86 (6H, t, *J* 6.62 Hz, NCH_2CH_2CN); ^{13}C NMR ($CDCl_3$, 298 K, 75 MHz), δ 17.06, 54.06, 55.71, 119.26.

‡ Stoe Stadi-4 four-circle diffractometer, Mo-Kα radiation, ω–θ scans, θ_{max} = 25°. Both structures were solved using direct methods[12] and all non-H atoms were located using subsequent difference Fourier methods.[13] Hydrogen atoms were placed in calculated positions and thereafter allowed to ride on their parent atoms.

Crystal data: $\{[AgL^1](PF_6)\}_\infty$ **1**: $C_{12}H_{18}AgF_6N_6P$, *M* = 499.16, monoclinic, space group $P2_1/n$ (no. 14), a = 10.652(9), b = 15.400(9), c = 10.924(6)Å, β = 92.14(6)°, U = 1791(2)Å^3, T = 150(2) K, Z = 4, D_c = 1.851 g cm^{-3}, μ(Mo-Kα) = 1.283 mm^{-1}. At final convergence R_1 [$I \geqslant 2\sigma(I)$] = 0.0364, wR_2 (all data) = 0.0976 for 247 refined parameters, S = 1.08, $(\Delta/\sigma)_{max}$ = 0.025, $\Delta\rho_{max,\,min}$ = 0.97, −1.02 e Å^{-3}.

$\{[Ag_2(L^2)_2](BF_4)_2\}_\infty$ **2**: $C_{15}H_{24}AgBF_4N_6$, *M* = 483.08, monoclinic, space group $P2_1/n$ (no. 14), a = 9.7157(7), b = 22.949(2), c = 10.1326(6)Å, β = 116.892(6)°, U = 2014.9(3)Å^3, T = 298(2) K, Z = 4, D_c = 1.592 g cm^{-3}, μ(Mo-Kα) = 1.048 mm^{-1}. At final convergent R_1[$I \geqslant 2\sigma(I)$] = 0.0546, wR_2 (all data) = 0.1246 for 261 refined parameters, S = 1.17, $(\Delta/\sigma)_{max}$ = 0.070, $\Delta\rho_{max,\,min}$ = 0.79, −0.56 e Å^{-3}. CCDC 182/1054.

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