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Synthesis and structural analysis of an infinite linear coordination network formed by the self-assembly of tetracyanocalix[4]arene ligands and silver cations

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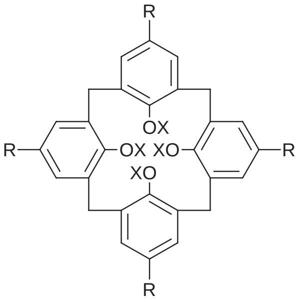
Using the O-alkylation of the lower rim of the calix[4]arene to impose the 1,3-alternate conformation and the functionalisation of the upper rim to set-up four nitrile groups pointing in a divergent fashion, an *exo*-ligand capable of forming linear coordination networks was obtained; upon self-assembly of the latter and silver cation, a linear coordination polymer was obtained and structurally analysed in the solid state by an X-ray study.

Due to their foreseeable wide scope of applications, coordination polymers which may also be described as molecular networks are currently attracting much attention.[1] In these assemblies, metals in addition to their structural role might also display functional features. The dimensionality (1-, 2- or 3-D networks) as well as the topology (linear, helical) of coordination polymers may be tuned through the interplay between the metal (coordination requirements, *i.e.* coordination number and coordination geometry) and the *exo*-ligand (number of coordination sites and their location, steric control). Many examples of coordination polymers based on bis-monodentate[1,2] bis-bidentate[3,4] and bis-tridentate ligands[5] have been reported. Here we report the synthesis of an *exo*-ligand of the calix[4]arene type bearing four nitrile groups as coordination sites as well as the structural analysis of the free ligand and of its linear Ag^I-coordination polymer.

For the formation of molecular networks, the design of *exo*-ligands in which the coordination sites are oriented in a divergent fashion is crucial. Molecular units possessing four coordination sites occupying the apices of a pseudo-tetrahedron may be of interest for construction of linear coordination polymers using metals requiring a tetrahedral coordination geometry. The design of such a ligand may be based on a preorganised backbone offering the possibility of anchoring four coordination sites in an alternating mode below and above its main plane. This aspect was previously demonstrated in the case of mercaptocalix[4]arene derivatives for which in the lower rim the OH groups were replaced by SH moieties.[6] Another design may be based on the use of both the upper and lower rims. Indeed, one may impose the needed 1,3-alternate conformation by proper transformation of all four hydroxy groups, and on the other hand, using *para* positions one may set-up, in a controlled manner, coordination sites. This has been demonstrated in the case of catechol units as the coordination sites.[7] Again, using this strategy, we designed the *exo*-ligand **1** containing four nitrile groups as a building block for the formation of linear coordination polymers. It is worth noting that for ligand **1**, due to the donor effect of oxygen atoms, the binding ability of nitriles is considerably enhanced.



1 R = CN, X = $CH_2CH_2OCH_3$
2 R = $C(CH_3)_3$, X = H
3 R = H, X = H
4 R = H, X = $CH_2CH_2OCH_3$
5 R = Br, X = $CH_2CH_2OCH_3$

The synthesis of **1** was achieved as follows. The starting material was the *p-tert*-butylcalix[4]arene **2**[8] which after dealkylation in toluene in the presence of phenol and $AlCl_3$ afforded **3** as a mixture of conformers.[9] The O-alkylation of the latter using 2-methoxyethyltosylate in DMF in the presence of Cs_2CO_3 afforded **4** which, after recrystallisation, was shown to adopt the 1,3-alternate conformation.[10] The desired tetracyano compound **1** was obtained after bromination of **4** using NBS in butanone leading to the tetrabromo compound **5** and followed by treatment of the latter by CuCN in *N*-methylpyrrolidone.[11] The structural assignment of **1** was achieved by classical NMR studies as well as by X-ray diffraction† which indeed confirmed the 1,3-alternate conformation (Fig. 1).

The metal cation, Ag^I, which is already extensively used for the formation of coordination networks,[12] was chosen because it forms kinetically labile complexes. Furthermore, coordination networks based on the binding of silver by bis-,[13a] tris-[13b] and tetrakis-nitrile[13c] based ligands have been reported. However, Ag^I may adopt a wide range of coordination geometries. We have observed linear,[14] trigonal[15] and tetrahedral[4] coordination geometries using pyridine, benzonitrile and bipyridine based ligands respectively.

In principle, for the combination of the ligand **1** and Ag^I, one may envisage two types of linear coordination polymers (Fig. 2). The difference between the two possibilities resides in the difference in the coordination geometry around the silver cation. Whereas for the di-coordinated Ag adopting a linear coordination geometry, a 1 : 2 ligand : metal stoichiometry would be obtained, in the case of tetrahedral coordination geometry, a 1 : 1 metal : ligand ratio would be expected.

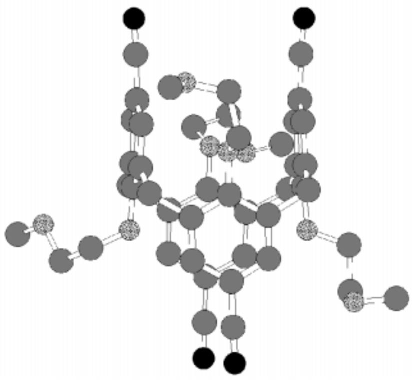


Fig. 1 X-Ray structure of the free ligand **1** adopting the 1,3-alternate conformation. H atoms are not presented for sake of clarity.

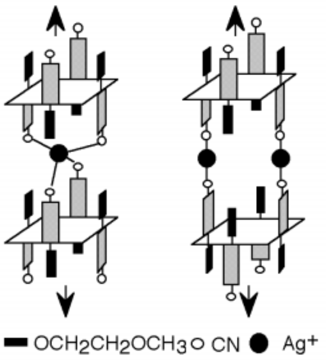


Fig. 2 Schematic representation of two types of linear coordination networks which may be envisaged for the self-assembly of the ligand **1** and Ag^I cation adopting tetrahedral- (left) or linear- (right) coordination geometries.

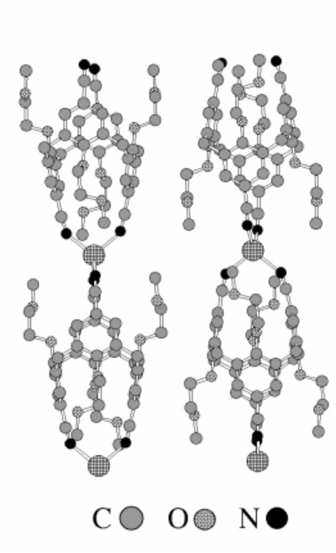


Fig. 3 A portion of the X-ray structure showing fragments of two parallel cationic linear coordination networks obtained by mutual bridging of Ag^I cations and ligands **1** (projection down the polymer axis). H atoms, solvent molecules and anions are not presented for sake of clarity.

Upon slow diffusion of a CH_2Cl_2 (1 ml) solution of ligand **1** (5 mg, 6.6×10^{-6} mol) into an EtOH (2 ml) solution of $AgAsF_6$ (20 mg, 6.7×10^{-4} mol) in large excess, a colourless crystalline material was obtained. The analysis of monocrystals by X-ray crystallography‡ revealed the presence of disordered H_2O and EtOH molecules in the lattice. In addition to the solvent molecules the crystal (tetragonal, space group $P4/nnc$) was composed of linear coordination polymers and disordered AsF_6 anions. The ligand **1**, as in the absence of Ag^I cation (Fig. 1), adopted a 1,3-alternate conformation (Fig. 3). The ether fragments adopted a *gauche* conformation with an OCCO dihedral angle of 73.8°. In order to bind two Ag^I cations in the tetrahedral mode of coordination, the calix unit was slightly pinched at the upper rim, *i.e.*, the N···N and O···O distances between nitrogen and oxygen atoms located within the same side of the calix unit were 3.533 and 5.670 Å respectively. The nitrile groups were almost linear with a CCN angle of 176.8° and CN distance of 1.104 Å. The cationic network was formed by mutual bridging between ligands **1** and Ag^I cations (Fig. 3). The silver cations were tetrahedrally coordinated to four nitrile groups with the NAgN angle varying from 100.9 to 121.9° (average 106.2°), CNAg angle of *ca.* 144.0° and AgN distance of *ca.* 2.292 Å. The packing of the cationic and anionic components (Fig. 4) showed parallel strands of linear coordination polymers with columns of disordered AsF_6^- anions separated by water molecules.

In conclusion, employing the self-assembly strategy, the formation of a silver coordination network using an *exo*-ligand based on calix[4]arene in the 1,3-alternate conformation and bearing at the upper rim four nitrile groups was achieved. The structure of the infinite network was established by single-crystal X-ray analysis.

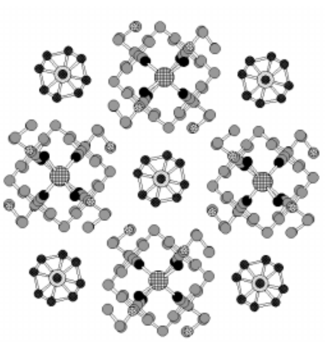


Fig. 4 A portion of the structure showing the packing of the cationic linear coordination networks and AsF_6^- anions (projection normal to the polymer axis). The AsF_6^- anions were found to be disordered. H atoms and solvent molecules (H_2O and EtOH) are not presented for sake of clarity.

Notes and references

† (Colorless, 173 K), $C_{44}H_{44}N_4O_8$, M = 1756.86, orthorhombic, a = 14.8980(3), b = 35.729(1), c = 14.9520(3) Å, U = 7958.8(5) Å^3, Z = 8, space group $Pbca$, D_c = 1.26 g cm^{-3}, Nonius CCD, Mo-Kα, μ = 0.088 mm^{-1}, 3543 data with $I > 3\sigma(I)$, R = 0.045, Rw = 0.056.

‡ (Colorless, 173 K), $C_{44}H_{44}N_4O_8Ag{\cdot}AsF_6{\cdot}2H_2O{\cdot}CH_3CH_2OH$, M = 1135.75, tetragonal, $a = b$ = 14.4450(7), c = 27.129(1) Å, U = 5660.7(7) Å^3, Z = 4, space group $P4/nnc$, D_c = 1.33 g cm^{-3}, Nonius CCD, Mo-Kα, μ = 1.001 mm^{-1}, 1078 data with $I > 3\sigma(I)$, R = 0.081, Rw = 0.119. CCDC 182/1062.

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