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Design, synthesis and structural investigation of a 2-D coordination network based on the self-assembly of the tetracarboxylate derivative of tetrathiacalix[4]arene and silver cation

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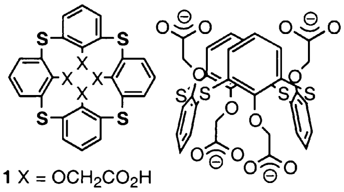
The fully deprotonated tetrathiacalix[4]arene 1^{4-} in 1,3-alternate conformation and bearing four carboxylate units was shown to act as a tecton leading, in the presence of Ag^+ cation, to a 2-D coordination network in the crystalline phase which can be described as discrete binuclear $[1^{4-}, (Ag^+)_2]^{2-}$ complexes interconnected by Ag^+ cations.

Molecular networks are defined as infinite architectures possessing translational symmetry of assembling nodes (interaction patterns) and are obtained under self-assembly conditions from molecular components capable of reversible and mutual interactions. Coordination networks, based on exo-ligands and metal cations, form a subclass of molecular networks and are currently under active investigation.[1] The majority of coordination networks reported to date are based on two component systems composed of an organic exo-ligand bearing coordination sites oriented in a divergent manner and a metal cation. Furthermore, the ligands employed so far are mainly of the bis-monodentate,[2] bis-bidentate,[3] tetrakis monodentate[4] or bis-tridentate[5] types bearing almost exclusively nitrogen atoms as coordination sites.

For the design of coordination networks, instead of considering a two component system for which both the metal centre and the free exo-ligand act as tectons, a further conceptually new design principle may be based on the use of a metal complex acting as a metallatecton and a metal cation. The design of such a system may be based on a ligand bearing multiple coordination sites allowing, on one hand, the formation of a endomolecular complex with a metal cation M, and on the other, the interconnection of the latter complex into a coordination network using either the same metal cation M or another metallic centre M′. A similar strategy, based on the simultaneous use of coordination and hydrogen bonds has already been investigated with success.[6]

In the present contribution we report, to the best of our knowledge, the first example of a 2-D coordination network based on the use of the above mentioned strategy.

Compound **1**,[7] a tetrathiacalix[4]arene derivative in 1,3-alternate conformation and bearing four carboxylic acid groups, presents several interesting features (Scheme 1). In its fully deprotonated form, $\mathbf{1}^{4-}$ possesses a total of 16 heteroatoms (12 O and 4 S atoms) which may participate in the coordination of metal cations. Its 1,3-alternate conformation[7] allows the positioning of two coordination poles (one may define a coordination pole as a set of coordination sites located in close proximity and capable of coordinating to metal centres) below and above the main plane of the backbone with a 90° angle between them. Each coordination pole is composed of two carboxyl units and two ether junctions. Importantly, owing to the connection of the carboxyl groups to O atoms of the calix by a CH_2 unit, the ether O atom and one of the two oxygen atoms of the carboxyl group may adopt a *syn* conformation leading to a chelate of the glycol type capable of binding metal cations. Thus, within each coordination pole, two such units may bind a metal cation leading to a discrete binuclear metal complex (Fig. 1). This type of coordination mode has been previously observed and structurally proven for the dipotassium salt of a calix[4]arene derivative in 1,3-alternate conformation and bearing amide groups[8] and for the sodium salt of a calix[4]diquinone derivative which was also found to form a 1-D network.[9] It is worth noting that upon formation of the binuclear complex, the remaining O atoms on carboxylate groups would be blocked and oriented in a divergent fashion. Thus, for the formation of coordination networks, the discrete binuclear complex mentioned above which may act as a tetrakis monodentate metallatecton, may be interconnected using metal cations through the remaining O atoms (Fig. 2). The dimensionality of the coordination networks which may be formed using ligand **1** depends on the coordination requirements (coordination number and geometry) of the metal cation used. In principle, either 2- or 3-D networks may be expected.



1 X = OCH_2CO_2H
2 X = OCH_2CO_2Na

Scheme 1

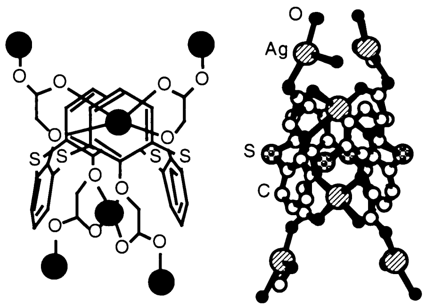


Fig. 1 Schematic representation of the binding mode of Ag^+ cations by ligand 1^{4-} (left) and a portion of the X-ray structure showing the two modes of coordination for the cations with H atoms omited for clarity. For distances and angles see text.

Dealing with the metal cation, as mentioned above, owing to the fact that the formation of coordination networks using the ligand $\mathbf{1}^{4-}$ requires two different binding modes, silver appeared to be the most suitable cation. Indeed, Ag^+ forms kinetically labile complexes and shows rather loose coordination requirements since it may tolerate bi-, tri- or tetra-dentate ligands with linear, trigonal or tetrahedral coordination geometries. The Ag^+ cation has been extensively used for the formation of coordination networks.[10] In our own studies, Ag^+

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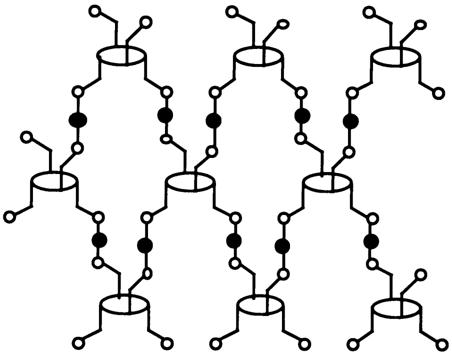

Fig. 2 Schematic representation of the 2-D network formed through interconnection of $[\mathbf{1}^{4-}, (\mathrm{Ag}^+)_2]^{2-}$ units by Ag^+ cations. For clarity, the Ag^+ cations forming the binuclear complex are not shown.

has been used to form metallamacrocycle,[11] linear,[4] helical[12] and tubular[4b,11b] coordination polymers.

Compound **1** was prepared[7] in four steps stating with *p-tert*-butyltetrathiacalix[4]arene[13] and its 1,3-alternate conformation was established by X-ray diffraction on a single crystal.[7] $[\mathbf{1}^{4-}, (\mathrm{Na}^+)_4]$ was generated upon treatment of **1** in MeOH by addition of 4 eq. of NaOH in H_2O. The removal of volatiles afforded a white solid which was dried in vacuum overnight. Upon slow diffusion at r.t. of a MeOH solution (1 ml) containing $[\mathbf{1}^{4-}, (\mathrm{Na}^+)_4]$ (10 mg) into an aqueous solution (1 ml) of $\mathrm{AgNO_3}$ (2 mg), colourless crystals were obtained after three days. An X-ray study† on a single crystal showed the following relevant features (Figs. 1–3): the crystal is composed of $\mathbf{1}^{4-}$, $4\mathrm{Ag}^+$, MeOH and H_2O solvent molecules. $\mathbf{1}^{4-}$ adopts the 1,3-alternate conformation thus presenting two carboxylate moieties on each face. The $\mathrm{OCH_2CO_2}^-$ fragments adopt a *syn* conformation (OCCO dihedral angles of 14.0 and 11.9° on one side and -9.2 and -11.6° on the other). For the carboxylate units the C–O distance varies between *ca.* 1.23 and 1.27 Å. Dealing with silver, among the four present, two types of Ag^+ cation are observed. For the first variety composed of two Ag^+ cations, both are coordinated, one on each face, to the ligand thus affording the binuclear $[\mathbf{1}^{4-}, (\mathrm{Ag}^+)_2]^{2-}$ complex. Both Ag^+ cations are tetracoordinated to four O atoms with two short (2.2–2.3 Å) and two long (2.6–2.9 Å) O–Ag distances and adopt a strongly distorted square planar coordination geometry (OAgO angles varying from *ca.* 63 to 171°). However, owing to the fact that on each side of the complex the Ag^+ cations are located in close proximity to two carbon atoms belonging to two opposite aromatic rings ($d_{\mathrm{C-Ag}}$ = 3.2–3.3 Å, with CAgC angle of 8.8°), one may describe the coordination geometry around the silver cation as distorted octahedral.

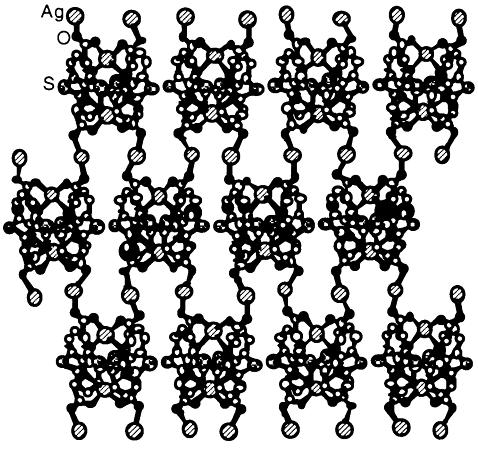

Fig. 3 A portion of the X-ray structure of the 2-D network formed between $\mathbf{1}^{4-}$ and Ag^+. H atoms and solvent molecules are not shown for clarity. For distances and angles see text.

The other type of Ag^+ cations serve to interconnect the dianionic binuclear $[\mathbf{1}^{4-}, (\mathrm{Ag}^+)_2]^{2-}$ complexes which act as tectons, thus leading to the formation of a 2-D coordination network (Fig. 2). The interconnection is achieved through Ag–O bonds ($d_{\mathrm{Ag-O}}$ varying between *ca.* 2.2 and 2.4 Å) engaging the remaining O atoms on the carboxylate units ($d_{\mathrm{C-O}}$ = 2.24–2.26 Å) (Fig. 3). The coordination sphere around the metal centres is composed of three O atoms among which one MeOH ($d_{\mathrm{Ag-O}}$ of *ca.* 2.40 Å) or one H_2O ($d_{\mathrm{Ag-O}}$ of *ca.* 2.39–2.69 Å) solvent molecules with distorted trigonal coordination geometry (OAgO angles of 89.4, 117.4 and 151.2° for Ag^+ coordinated to MeOH and 95.8, 124.0 and 140.0° for Ag^+ coordinated to H_2O).

In conclusion, using the tetraanionic form of the thiacalix-[4]arene bearing four carboxylate units and Ag^+ cation, a 2-D coordination network has been obtained and structurally characterised in the crystalline phase. The network was composed of discrete binuclear $[\mathbf{1}^{4-}, (\mathrm{Ag}^+)_2]^{2-}$ complexes acting as metallatectons interconnected by Ag^+ cations. The effect of the number of negative charge on the calix unit on the formation of coordination network, as well as the nature of the connecting cation are currently under investigations.

Notes and references

† *Crystal data* for **1**: colourless, 173 K, $\mathrm{C_{65}H_{45}Ag_8O_{26}S_8{\cdot}4CH_3OH{\cdot}4H_2O}$, M = 2561.77, monoclinic, a = 16.6647(6), b = 24.7585(5), c = 19.9024(7) Å, β = 91.224(5), U = 8209.7(8) Å^3, Z = 4, space group $P2/n$, D_C = 2.07 g cm^{-3}, Nonius Kappa CCD, Mo-Kα radiation (λ = 0.71073 Å), μ = 2.157 mm^{-1}, 6997 data with $I > 3\sigma(I)$, R = 0.059, R_w = 0.062. Structural determination was achieved using the Nonius OpenMolenN package.[14] CCDC 182/1802. See http://www.rsc.org/suppdata/cc/b0/b007761p/ for crystallographic files in .cif format.

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