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3D silver-dabco coordination polymers with zeolitic
or 3-connected topology

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ABSTRACT The simple linear linking ligand diazabicyclo[2.2.2]octane (dabco) combines with silver(I) to form 3D coordination polymers which have either a zeolitic mtn topology structure or a (10,3)-bths network according to the counter-anion used. The tetrahedral anions BF$_4^-$ or ReO$_4^-$ promote formation of [Ag(dabco)$_2$]·X which has a 3D four-connected mtn framework of fused 5$_{12}^4$ and 6$_4^4$$_{512}^4$ cages, and the material shows modest absorption of iodine. The bulky anion [Co(C$_2$B$_9$H$_{11}$)$_2$]$^-$ promotes and an excess of dabco promote formation of complex [Ag$_2$(dabco)$_3$(CH$_3$CN)$_2$]·2[Co(C$_2$B$_9$H$_{11}$)$_2$] with a three-connected (10,3)-b network, while use of one equivalent of dabco gives a previously reported [Ag(dabco)]·[Co(C$_2$B$_9$H$_{11}$)$_2$] which has a 1D coordination chain structure.

The study of crystalline polymeric metal-ligand assemblies, termed metal-organic frameworks or coordination polymers, has been an active area of research for several decades. Using bridging functionality and stereochemistry as design principles, complexes with regular 2-D and 3-D
network structures can be assembled, often with inherent porosity. These have potential zeolitic applications such as catalysis, separations and extractions, and gas storage. Diazabicyclo[2.2.2]octane (dabco) is one of the simplest linear bridging ligands that is used for coordination polymers. While there are a number of examples of dabco-containing coordination polymers, the majority of these also involve another type of bridging ligand or anion, and it is surprising that the chemistry of simpler M-dabco systems remains relatively unexplored. Examples where dabco is the sole linking ligand are unusual and include 1D coordination chains, a 2D hexagonal network of topology of \([\text{Ag(dabco)}_3(H_2O)](3\text{-fluorobenzenecarboxylate})\), and a series of networks where dabco ligands bridge between \(\text{M}_2\text{I}_2\) dimers or between \(\text{Cu}_4\text{X}_4\) or higher ordered metal clusters where \(\text{X} = \text{I} \) or \(\text{Cl}\). The latter feature 3D coordination polymer structures with an extraordinary range of topologies. Recently, a luminescent \([\text{Cu}_4\text{I}_4(\text{dabco})_2]\) coordination polymer was reported with a zeolitic mtn type structure, and very large pores. This is a spectacular and rare network topology in coordination polymer chemistry. We report herein a much simpler route to the zeolitic mtn structure in complex \([\text{Ag(dabco)}_2]\cdot\text{X}\) where \(\text{X} = \text{BF}_4^{-}\) or \(\text{ReO}_4^{-}\). The use of 3-8 molar equivalents of dabco per \(\text{Ag(I)}\) salt exclusively gives the mtn framework in the case of both silver salts, however use of fewer equivalents of dabco leads to the formation of needle-like crystals of the same composition but with a 1-D coordination polymer whose crystal structure could not be properly resolved. Mass spectrometry was performed in acetonitrile, but only a \(\text{Ag(DABCO)}_2^{+}\) fragment could be identified as a building tecton, and this could give rise to either of the observed networks. Therefore we believe that these polymers are purely a phenomenon of the solid-state and their assembly cannot be monitored in solution. Use of the larger weakly coordinating counter-anion cobalticarborane, gave rise to both a \([\text{Ag(dabco)}_2(\text{CH}_3\text{CN})]^{+}\) coordination polymer
with a network of $10^3$ ths topology, commonly referred to as the (10,3)-b net, or a previously reported 1D polymer with composition $[\text{Ag(dabco)}]^+$, *Scheme 1*.

![Scheme 1](image)

**Scheme 1.** Ag-dabco complexes reported here and previously.$^4$

Colorless single crystals of $[\text{Ag(dabco)}_2] \cdot X \cdot n(\text{solvent}), X= \text{BF}_4^-$ (1a) or $\text{ReO}_4^-$ (1b) were grown by standing an acetonitrile solution of $\text{AgX}$ and an excess of $\text{dabco}$. Crystals appear in as little as 30 minutes from mixing, and complexes were obtained in yields of 50-56%. The complexes were isomorphic with cubic unit cell length $a > 45 \, \text{Å}$, and their structure solved in the space group $Fd\overline{3}$m.$^\dagger$ The structure of $[\text{Ag(dabco)}_2] \cdot (\text{BF}_4) \cdot 5(\text{CH}_3\text{CN}) \cdot (\text{H}_2\text{O})$ 1a is shown in Figure 1, although the location of $\text{BF}_4^-$ counter-ions and any solvent could not be established due to disorder. In the isomorphic complex $[\text{Ag(dabco)}_2] \cdot (\text{ReO}_4) \cdot 4(\text{CH}_3\text{CN})$ 1b only the Re positions of perrhenate counter-ions could be established.
Figure 1. From the crystal structure of [Ag(dabco)]\textsuperscript{+}BF\textsubscript{4} \textbf{1a}. (a) extended diagram of the [Ag(dabco)]\textsuperscript{+} mtn network with hydrogen atoms excluded; (b) detail showing the two types of
cage, smaller $5^{12}$ and larger $6^45^{12}$ in space-filling mode; (c) framework diagram showing only the Ag positions that make up the mtn network, $6^45^{12}$ cages are shown in red, while $5^{12}$ cages are shown in grey.

In complex 1a there are three Ag(I) sites of site symmetry $m$, $3m$ or $-43m$. Each is approximately tetrahedrally coordinated by four dabco molecules with Ag-N distances ranging from 2.353(6) to 2.425(7) Å, and N-Ag-N angle 106.2(2) to 111.6(2)°. Dabco ligands bridge between Ag(I) centres to give a 3D coordination polymer with tetrahedral nodes and large cages and channels, Figure 1a. The mtn topology features pentagons and hexagons which form two types of cages within the network: the smaller $5^{12}$ cage with twelve pentagons, and the larger $6^45^{12}$ cage with four hexagons and twelve pentagons, Figure 1b. Each $6^45^{12}$ cage connects to four others through face-sharing of the hexagonal rings, Figure 1c, and to twelve $5^{12}$ cages through face-sharing of the pentagonal rings to form the overall network, Figure 1. The mtn topology is found in zeolites of framework code MTN, and there have been a small number of other examples involving coordination polymers. As well as the aforementioned cubic [Cu$_4$I$_4$(dabco)$_2$] with Cu$_4$I$_4$ cage clusters as the tetrahedral node, there is [Cd$_2$(H$_2$O)$_3$(hmta)], hmta = hexamethylenetetramine, where the hmta ligand is the connecting node. The metal-organic frameworks designated MIL-100, MIL-101, and related materials have augmented mtn networks where supertetrahedral clusters such as $\{\text{M}_3\text{O}_4\}$_4[btc]$_4$, btc = benzene-1,3,5-tricarboxylate, are vertex-linked into a mtn network. The internal volume of the cages in 1a and 1b are remarkably similar to those of [Cd$_2$(H$_2$O)$_3$(hmta)]. For the larger cage the closest cage centroid to cage wall contact is around 9.8 Å to a calculated hydrogen atom in 1a, and 10.0 Å to an aquo oxygen in [Cd$_2$(H$_2$O)$_3$(hmta)].
Taking aquo hydrogen atoms into account, the void spaces in 1a are slightly larger. Thermal gravimetric analysis (TGA) of complex 1a is consistent with ca. 5 CH$_3$CN and one water solvent molecules per formula unit, and the coordination polymer is not thermally stable above 200 °C (Figure S2 ESI). For complex 1b TGA was consistent with four molecules of CH$_3$CN per formula unit (Figure S4 ESI). These degrees of solvation are consistent with void calculations for the networks. Surprisingly, N$_2$ sorption measurements on evacuated [Ag(dabco)$_2$](BF$_4$)$_2$·n(solvent) 1a did not show significant gas up-take, with measured BET surface area of 0.066 ± 0.022 m$^2$/g, despite powder X-ray diffraction showing that bulk crystallinity is retained (Fig S1). However, long range order of the powders is lost over the data collection as low angle peaks, conferring information about the void spaces, reduce in intensity over the collection, suggesting slow decomposition of the material. Transmission Electron Microscopy (TEM) shows darker regions across the crystal surface that have high silver content. While some regions on the surface have definite ordering there is also surface decomposition apparent, Figure 2. Hence, while the material is macroscopically crystalline, nanoscale surface decomposition may be blocking access to the internal pores.
Interestingly, the complex 1a was able to bind molecular iodine to some degree. The binding of iodine into a solid state host is of interest in nuclear fuel reprocessing, and a handful of coordination polymers or metal-organic frameworks that bind I\(_2\) have been previously reported.\(^{14}\) Crystals of the zeolitic framework were evacuated in an H-tube, and gaseous iodine vapour was passed over the crystals until the entire sample showed a uniform color. An immediate orange/brown color-change was observed which gradually darkened with exposure for several
minutes. Optically microscopy confirmed that the morphology and quality of the crystals had not been compromised, Figure 3. Attempts to wash the iodine out of the material using various polar and non-polar solvents were unsuccessful. While the darkened I\(_2\)-exposed crystals of 1a diffracted as single crystals, there was no crystallographic evidence of molecular I\(_2\) within the crystal lattice. This suggests that the I\(_2\) uptake does not penetrate far into bulk of the crystals which is in keeping with the surface pore collapse noted above. EDX measurements are also supportive this, with observed iodine levels higher for single crystals than for a crushed up bulk sample (see Table S1, ESI).

Figure 3. Crystals of complex 1a (a) before; and (b) after exposure to I\(_2\) vapors.

While small tetrahedral counteranions give the mtn network, crystallisation in the presence of the large cobalticarborane anion, [Co(C\(_2\)B\(_9\)H\(_{11}\))\(_2\)]\(^-\), gives two different materials. Which compound is produced can be controlled through stoichiometry. Crystallisation from a MeCN solution containing Ag[Co(C\(_2\)B\(_9\)H\(_{11}\))\(_2\)] and 0.5 or 1.0 equivalent of dabco gives single crystals of [Ag(dabco)]\(^-\)[Co(C\(_2\)B\(_9\)H\(_{11}\))\(_2\)] with a needle-like morphology. We have previously reported the structure of this complex which features a linear 1D [Ag(dabco)]\(^+\) chain.\(^4\) Crystallisation from a
MeCN solution with Ag[Co(C₂B₉H₁₁)₂] and 2 or more equivalents of dabco gives crystals with prismatic morphology and composition [Ag₂(dabco)₃(CH₃CN)]₂·2[Co(C₂B₉H₁₁)₂] 2. The highest yield of 2 was obtained with 4 equivalents of dabco. The crystal structure of complex 2 was solved in space group P2₁/n. There are two crystallographically independent Ag(I) sites each on a general position. Both Ag(I) cations have approximately tetrahedral geometries each with three dabco ligands (Ag-N distances from 2.329(15) to 2.398(15) Å) and one acetonitrile ligand (Ag-N distances 2.382(18) and 2.44(3) Å). The dabco ligands bridge between two Ag(I) sites while the MeCN ligand is terminally coordinated, hence a 3-connected coordination polymer is formed, Figure 3. The coordination polymer has 3D connectivity forming 10 member rings, Figure 3b. The topology of the network is (10,3)-b or ths⁷ topology. There are substantial channels throughout the network however these are filled by the terminal acetonitrile ligands which are directed into the centre of the rectangular channels, Figure 3a, and by the bulky [Co(C₂B₉H₁₁)₂]⁻ counter-anions, (Figure S12, ESI). There are a number of close B-H...H-C distances between neighbouring [Co(C₂B₉H₁₁)₂]⁻ anions indicating the presence of dihydrogen bonding.¹⁵ The closest interactions are at separations 1.63, 1.89 and 1.94 Å, which are similar to those previously reported for dihydrogen interactions between [Co(C₂B₉H₁₁)₂]⁻ anions.¹⁶
Figure 3. From the crystal structure of $[\text{Ag(dabco)}_2(\text{CH}_3\text{CN})] \cdot [\text{Co}(\text{C}_2\text{B}_9\text{H}_{11})_2] \ 2$. (a) $[\text{Ag(dabco)}_2(\text{CH}_3\text{CN})]^+$ coordination polymer; (b) connectivity diagram with Ag(I) positions only showing the (10,3)-b type network.
In summary, despite being utilized as a bridging ligand for coordination polymer synthesis for many years, these are the first reports of dabco forming a 3D metal-dabco coordination polymer in the absence of some other linking anion or ligand. This includes a simple and high yielding route to coordination polymers with the spectacular mtn topology. It is notable that the 3D networks were isolated from solutions containing an excess of dabco, although this excess is not reflected in the M:L ratios in the resultant mtn or ths type networks. All of the networks show relatively high-stability in dark ambient conditions, however, long-term exposure of the crystals to visible light leads to reduction of silver, and decomposition of the networks. The crystals dissolve in water, however, the crystals do not seem to be sensitive to atmospheric water, even on exposure for several months. The mtn-topology structures (1a,b) are capable of binding molecular iodine, which could be exploited for nuclear fuel reprocessing applications, or as antimicrobial agents or materials due to the incorporation of high concentrations of silver into these structures.

ASSOCIATED CONTENT

Supporting Information includes experimental procedures, pXRD, TGA, SEM, TEM EDX analyses, details of crystal structure determinations with additional Figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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ABBREVIATIONS

DABCO Diazabicyclo[2.2.2]nonane.

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The simple linear linking ligand diazabicyclo[2.2.2]octane (dabco) combines with AgBF$_4$ or AgReO$_4$ to form a 3D coordination polymer with a zeolitic mtn topology structure, or combines with Ag[Co(C$_2$B$_9$H$_{11}$)$_2$] to give a 3D coordination polymer with a (10,3)-b ths network structure.