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Silver–Adenine Metallamacrocyclic Hexamer

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Beneficial carboxylate–silver interactions afford facile coordination of five silver ions to a modified adenine ligand, leading to the formation of a hexameric cyclic structure in the solid state.

Specificity of recognition in nucleic acids is manifested by hydrogen-bonded base pairs, while the stability of ensuing nucleic acid structures is derived from base stacking and van der Waals forces and by metal ion or small cation coordination in certain cases. The constituent heterocyclic nucleobases in nucleic acids are bestowed with suitably predisposed metal ion binding sites; thus, it is not surprising that nucleobases serve as versatile platforms for the construction of supramolecular ensembles and for control of the self-association of functional materials.[1]

Metal ion coordination to nucleobases opens up exciting opportunities of structural and functional consequences and crystal engineering.[2] An interesting and specific application of nucleobase–metal ion coordination concerns the formation of metal-tethered base pairs, where classical nucleic acid base pairs are replaced by metal-mediated base pairs.[3] In addition to the formation of base triplets, quartets and higher hydrogen-bonded structures are often invoked for the stabilization of interesting topological features in oligonucleotides,[4] and, consequently, the construction of metal-mediated base triads and tetrads has been reported.[5] However, there are limited examples concerning the occurrence of base pentads, hexads, and heptads in oligonucleotides.[6] This Communication reports the formation of a metal-mediated hexameric nucleobase framework, as a part of a larger 3D crystal lattice structure, entirely composed of 9-(carboxypropyl)adenine and Ag^+ as a single intervening metal ion, without any supporting ligand. It is known that 9-substituted adenine offers three main N-coordination sites, of which N1 and N7 are predominantly used for metal ion complexation, with several reports also describing the possibility of N3 coordination.[7] Adenine analogues have been explored extensively for imino N coordination, with N1 and N7 being primarily invoked for transition-metal coordination via mono- and bidentate coordination modes. However, several examples involving the coordination mode that employs all three nitrogen atoms in adenine analogues are also reported,[8] including several examples from our group.[9] A report has also described the μ-N3,N7,N9-coordination mode of an adeninate ion.[10]

Previous reports from our group have described the formation of metallaquartet structures via the coordination of N9-substituted adenine to silver ions, involving all three ring

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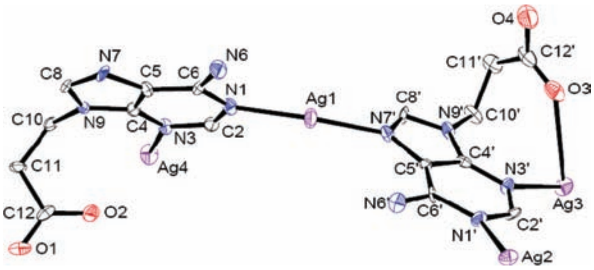

Figure 1. Part of the asymmetric unit of **1** as an ORTEP diagram with 50% ellipsoid probability (hydrogen atoms, solvent molecules, and perchlorate anions are omitted for clarity).

nitrogen atoms of the purine nucleobase.[9] In a continuation of our studies with N9-alkyl-substituted adenines, we decided to introduce a carboxylic group at the N9 position in order to explore the possibility of using a carboxylate group for silver interaction, thus gaining access to hierarchical structure(s) of increased complexity.

Beneficial carboxylate−silver interactions have been previously used for crystal engineering, in particular for the construction of coordination frameworks.[11] Interestingly, silver(I)−carboxylate interaction is believed to mimic the replacement of carboxylic acid protons with a monovalent cation, which permits further coordination, thus leading to the possibility of constructing neutral coordination networks.[12]

The colorless crystals of **1** (9-CA/silver complex) were grown from an aqueous solution of 9-CA and silver carbonate (1:1) in the presence of perchloric acid by slow evaporation. The refinement of data suggested that the silver-mediated adenine complex crystallized in the trigonal space group *R*3. The 9-CA/silver complex **1**, $C_{48}H_{48}N_{30}O_{12}Ag_{12}\cdot 6ClO_4\cdot 10O$ (isolated oxygen atoms represent water molecules), consisted of 12 silver ions neutralized by 6 perchlorate anions and 6 9-CA anions, along with water molecules (Figure 1).

Careful inspection of the crystal structure revealed that all three ring nitrogen atoms and the carboxylate oxygen atoms are coordinated to Ag^+ ions, to afford an unprecedented adenine−silver hexamer where six modified adenines were coordinated to six intervening silver ions (Figure 2a). All six exocyclic amino groups of adenine are projected inward with a maximum separation of 11.1 Å, whereas the N9 substituent and N3-coordinated silver ions are projected toward the outer periphery of the hexameric structure (Figure 2a). Interestingly, N3-coordinated silver ions can be visualized in a chair-like conformation with alternating ∠Ag−Ag−Ag angles of 105.02° and 106.58°, as shown in Figure 2b. It is notable that this hexameric framework is composed of two sets of ∠N1−Ag−N7 interactions [158.4(3)° and 165.1(3)° for alternating sets], and N1−Ag, N3−Ag, and N7−Ag bond lengths are in the range of 2.17−2.22 Å (Table S2 in the Supporting Information).

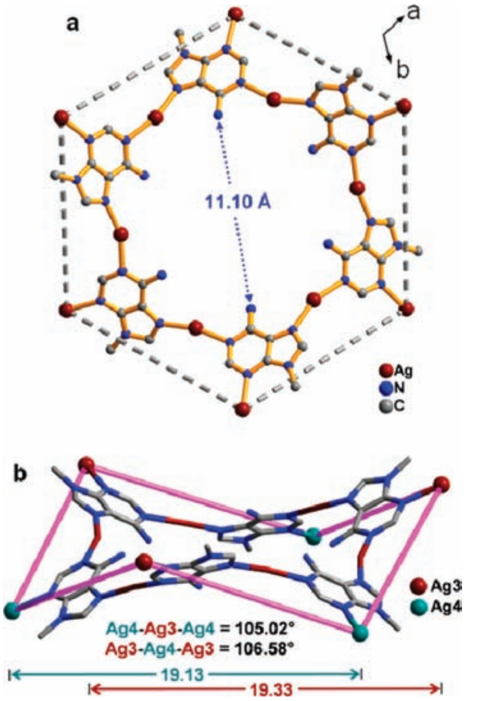

Figure 2. (a) Silver-mediated adenine hexameric framework of **1** (hydrogen atoms and the solvent, counteranion, and N9 substitutent are removed for clarity). (b) Another representation of the hexameric structure showing a chairlike arrangement of Ag^+ ions at the outer periphery of the hexameric structure (Ag3 and Ag4 indicate two different N3-coordinated silver ions) with Ag−Ag distances (in angstroms) and Ag−Ag−Ag angles (in degrees).

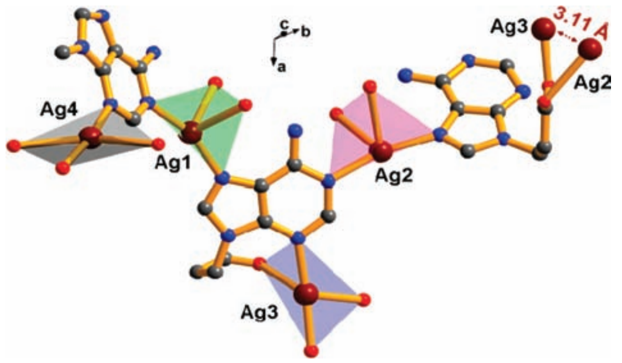

Figure 3. Four crystallographically unique Ag^+ ions are highlighted by colored polyhedra, and an Ag−Ag short contact is also identified.

Notably, the crystal lattice is composed of four crystallographically unique silver ions, namely, Ag1, Ag2, Ag3, and Ag4, as represented by polyhedra of four different colors: the former two are located within the hexamer ring (pink and green), while the other two are located at the outer periphery and are coordinated to N3 (gray and blue) (Figure 3). Interestingly, there also is the possibility of a Ag−Ag short contact, with a separation of 3.11 Å, between two Ag^+ ions coordinated to the carboxylate group at the N9 position (Figure 3).

The coordination environment of two silver ions Ag1 and Ag2 (green and pink polyhedra, respectively) consists of two N1 and N7 imino nitrogen atoms from two different adenine ligands and two oxygen atoms. One oxygen atom belongs to the carboxylate group of a third adenine ligand, while the other oxygen atom comes from either an aqua ligand or a perchlorate anion (Figure 4). The coordination sphere of the other two

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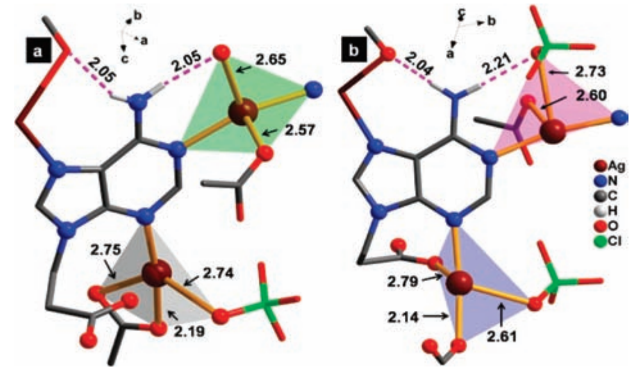

Figure 4. Values of various Ag−O distances (black arrow) and hydrogen bonding (pink dotted bonds) observed for the four different silver centers: (a) for Ag1 (green polyhedron) and Ag4 (gray polyhedron); (b) for Ag2 (pink polyhedron) and Ag3 (blue polyhedron) (distances are in angstroms).

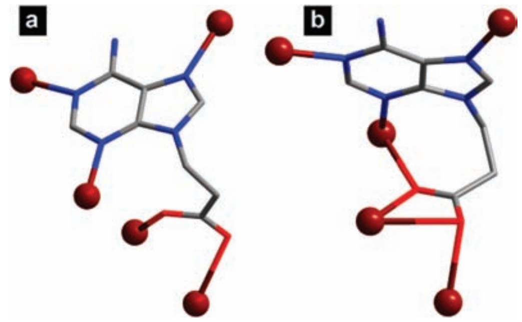

Figure 5. Two different types of carboxylate coordination modes in the crystal lattice: (a) binding in a bidentate mode (η^1:μ^2); (b) interaction with three Ag$^+$ ions (η^2:μ^3 mode).

silver ions, Ag3 and Ag4 (blue and gray polyhedra, respectively), comprises a N3 ring nitrogen atom and three oxygen atoms, where two oxygen atoms belong to the carboxylate group and the third one belongs to the perchlorate anion (Figure 4).

Interestingly, three tetracoordinated silver ions (Ag1, Ag2, and Ag3) exhibit distorted tetrahedral geometries. However, the coordination geometry for Ag4 is slightly different because the carboxylate oxygen atom of the 9-CA ligand and the other oxygen atom from the perchlorate anion additionally show long-range interactions with Ag···O distances of 3.24 and 3.02 Å, respectively. This geometry may be described as distorted square planar with a sum of in-plane angles of 359.37°, with further weak axial interactions from oxygen atoms. The various Ag−N and Ag−O distances are given in Table S2 in the Supporting Information. The latter ranges from 2.19 to 2.79 Å, where the Ag3−O separation of 2.79 Å in blue polyhedra is considerably less than the sum of the van der Walls radii (3.24 Å) of silver and oxygen, thus suggesting that this oxygen atom is perhaps weakly coordinated to Ag3. The exocyclic amino groups are involved in hydrogen bonding, with the oxygen atoms situated at the corners of the green and pink polyhedra.

Subtle variation in the coordination geometries results from two different types of silver−carboxylate interactions. In one case, two Ag$^+$ ions bind to carboxylate oxygen atoms in a bidentate η^1:μ^2 mode (Figure 5a), whereas the other interaction exhibits both chelating and bridging modes (η^2:μ^3) (Figure 5b). Thus, each modified adenine ligand is coordinated to five different silver ions, leading to a complex 3D network with an embedded hexameric framework.

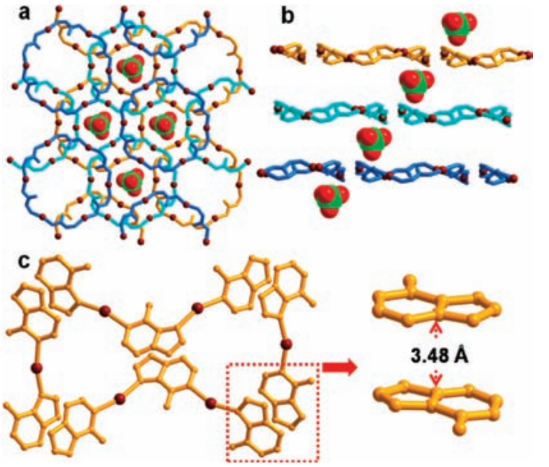

Figure 6. (a) Arrangements of different hexamer layers in the crystal lattice and the position of the perchlorate anions (viewed along the *c* axis). (b) ClO_4^- anions bridging different hexamer layers (viewed along the *a* axis). (c) $\pi-\pi$ stacking between adenine rings from adjacent hexamers.

Notably, three different nonintervening hexamer layers present in the crystal lattice give rise to a zeolite-like framework where a perchlorate anion sits in the apparent cavity (Figure 6a, b). The crystal lattice of **1** also exhibits $\pi-\pi$ stacking between adenine moieties present in one hexamer with adenines from another hexamer with a separation of 3.48 Å (Figure 6c).

Four types of perchlorate anions are also encountered in the lattice: one interacts with Ag2 in a η^1:μ^1 manner (pink polyhedra) (Figure 4b), a second one interacts with six silver ions in a η^3:μ^6 manner with Ag−O distances of 2.61 Å (for Ag3) and 2.74 Å (for Ag4) (see the Supporting Information), and two are involved in hydrogen bonding with C8−H.

Although there are some reports concerning metal-mediated polyads,[13] the structure presented here is an unprecedented example of a silver−adenine hexameric framework, without participation of any supporting ligand. We envisage that such metallacyclic adenine polyads, where the exocyclic amino groups are projected inward, may provide a suitable opportunity for host−guest interactions in the solid state. +

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Supporting Information Available: Characterization of the compound, additional pictures, crystal structure refinement parameters, bond lengths and bond angles as a table, and X-ray crystallographic data in CIF format. CCDC contains the supplementary crystallographic data for this paper ;with a deposition number of CCDC 720508. Copies of this information can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB21EZ, U.K. (fax +44−1223/336-033; e-mail deposit@ccdc.cam.ac.uk). This material is available free of charge via the Internet at http://pubs.acs.org.

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