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Adenine Coordination around a Cu_6I_6 Core

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S Supporting Information

ABSTRACT: This Communication describes the synthesis and crystallographic investigation of copper(I) and silver(I) complexes of a modified adenine analogue, bearing a thiocyanate pendant arm at the N9 position. A novel adenine-containing hexagonal prismatic cuprous iodide aggregate was obtained with Cu^+, while Ag^+ interaction afforded interconnected two- and four-membered metallacycles.

Heterocyclic nucleobases have fascinated coordination chemists because of not only their biological relevance but also the presence of ring and exocyclic nitrogens that offer sites for metal-ion coordination. Prior knowledge of nucleobase–metal ion interactions and various binding patterns allows for the construction of complex hierarchical structures.[1] Adenine, in particular, has been a subject of intense scrutiny in terms of its coordination behavior and the possibility of catalyzing selected reactions by its metal complexes.[2]

Our sustained efforts in the area of adenine–metal ion interactions have explored interesting architectures, where subtle structural modifications were shown to influence the overall coordination pattern, particularly for the generation of metallacyclic frameworks.[3] In one such instance, the interaction of Cu^{II} ions with a modified adenine ligand was shown to reveal a one-dimensional coordination polymer to a discrete decanuclear motif, with interesting catalytic and magnetic properties.[3m] In another case, Cu^{I} ions were shown to interact with a N9-allyl substituent to afford a stable π complex.[3d]

Copper(I) halides are known to exhibit zero-dimensional and chainlike one-dimensional systems and three-dimensional frameworks. Consequently, topologies ranging from rhomboidal dimers, to cuboid tetramers, to hexagonal grids are achieved by invoking various coordination geometries and motifs.[4] As a specific example, a hexagonal prism-shaped Cu_6I_6 cluster could be constructed from a combination of two six-membered Cu_3I_3 units. In this motif, a 12-membered Cu_6I_6 puckered-crown feature is observed, where the iodido ligands serve as intervening bridges between cuprous ions in a μ-coordination mode. In addition, polynuclear d^{10} cuprous halide clusters are also important because of their interesting photochemical and photophysical properties, with potential applications as light-emitting diodes, luminescent probes, and photovoltaics.[5]

In the present work, we decided to explore a N9 appendage bearing a thiocyanate group to improve the ligand denticity and to exploit the sulfur center for possible metal-ion interaction.[6] 9-(2-Thiocyanatoethyl)adenine (**1**) was synthesized, and the site of alkylation was ascertained by crystallization from its acidic solution (Figure 1a).

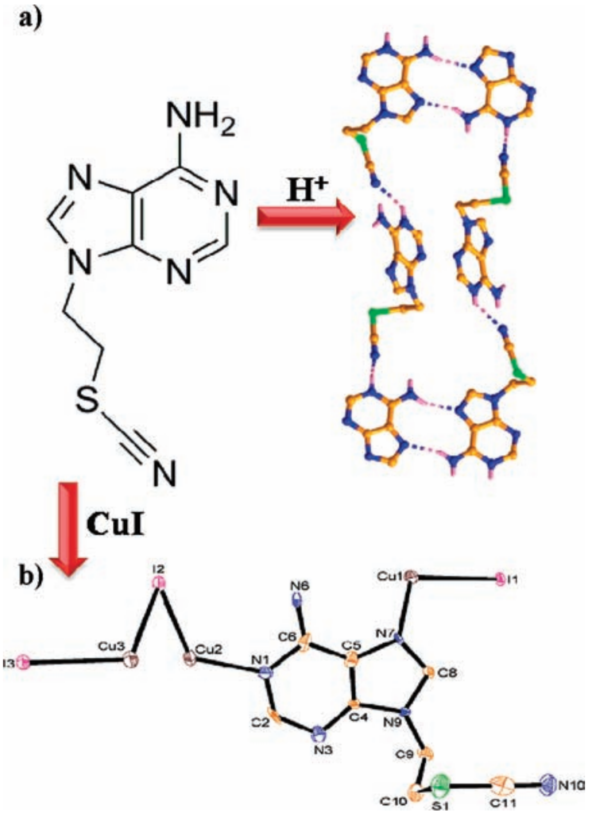

Figure 1. (a) Molecular and crystal structure of N1-protonated ligand **1** showing a hydrogen-bonded hexamer (perchlorate counteranions are omitted for clarity). (b) ORTEP rendering of the asymmetric unit of the cuprous complex **2** drawn at 50% probability level (hydrogen atoms are omitted for clarity).

The protonated ligand crystallized from its methanolic solution, acidified with $HClO_4$, and the X-ray studies suggested that the crystals belonged to the monoclinic space group $P2_1/c$. The cyclic hexamer was found to be stabilized by intermolecular hydrogen bonding, with length scales ranging from 2.11(2) to 2.23(3) Å (Figure 1a).

The formation of a copper(I) complex was achieved by adding a methanolic solution of ligand **1** to the acetonitrile solution of cuprous iodide, which resulted in the immediate formation of a precipitate that dissolved on gentle shaking. The homogeneous mixture so obtained was stored undisturbed for slow evaporation, affording colorless crystals of **2** after 1 week. Careful refinement of the crystal data suggested that this crystal belonged to the

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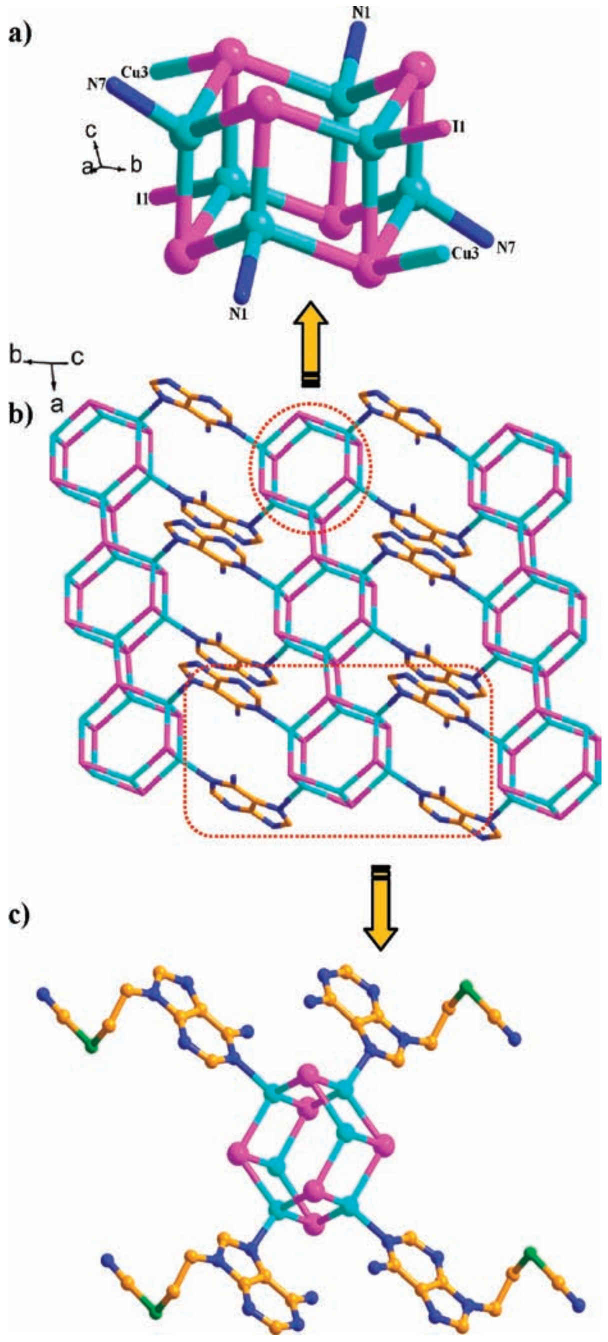

Figure 2. (a) Hexagonal prism-shaped Cu_6I_6 unit composed of two chair-shaped trinuclear Cu_3I_3 units. (b) Two-dimensional lattice containing Cu_6I_6 units in complex **2**. (c) Interaction of four adenine moieties with a single Cu_6I_6 unit.

triclinic space group $P\bar{1}$ and the asymmetric unit of **2** was composed of one ligand molecule, three cuprous ions, and three iodido ligands (Figure 1b).

Cu_6I_6 clusters were formed by a combination of two chair-shaped trinuclear Cu_3I_3, via mutually bonded six cuprous ions and six iodido ligands, and they exhibited a structure analogous to double six-membered, hexagonal prism-shaped rings in zeolites (Figure 2a). Such cuprous clusters are quite unique, with only some examples documented in the literature.[4] The crystal lattice in Figure 2b could be visualized in two ways: on the one hand, four adenine units are coordinated to a single Cu_6I_6 cluster (Figure 2c); on the other hand, a dimeric metallacycle could also form through the interaction of two Cu_6I_6 clusters and two adenine units (Figure 3).

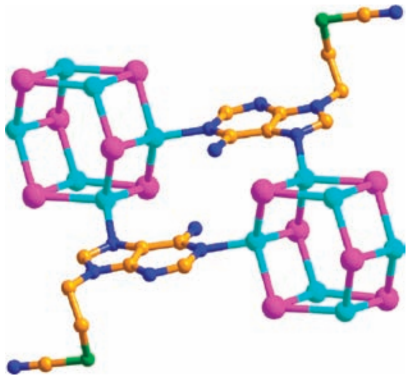

Figure 3. Coordinated metallacycle built with two modified adenine nucleobases and two Cu_6I_6 units.

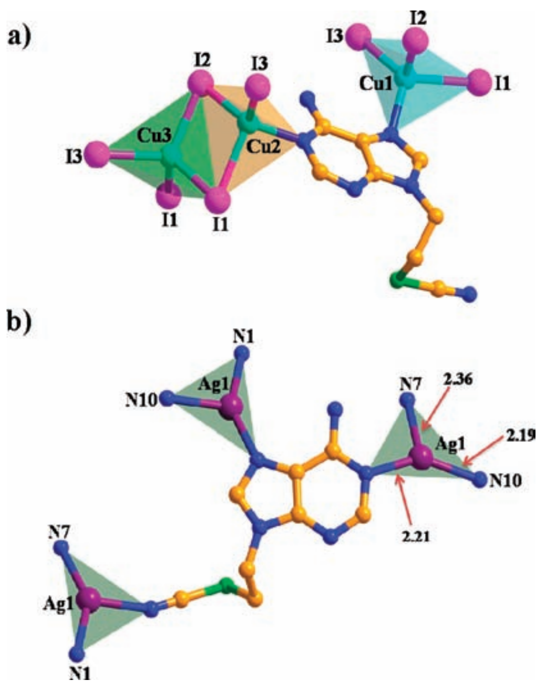

Figure 4. (a) Three crystallographically unique Cu^+ ions in **2** are highlighted by colored polyhedra. (b) Tridentate coordination mode of a Ag^+ ion and ligand in **3** (bond distances are in angstroms).

Three crystallographically unique cuprous ions (Cu1, Cu2, and Cu3), present in the Cu_6I_6 cluster, possess distorted tetrahedral geometry. Cu1 and Cu2 coordination spheres contain three crystallographically different iodido ligands (I1, I2, and I3), which act as a bridge between the three cuprous ions and one imino nitrogen (N1 or N7) from the adenine ligand. Cu3 only has iodido ligands in its coordination sphere, and it helps to connect neighboring Cu_6I_6 units to form an extended polymeric network (Figure 4a).

Ligand **1** was also subjected to interaction with silver ions, and complex **3** was prepared by mixing an aqueous solution of $AgClO_4$ with a methanolic solution of the ligand. The precipitate so formed was redissolved in acetonitrile and left undisturbed for

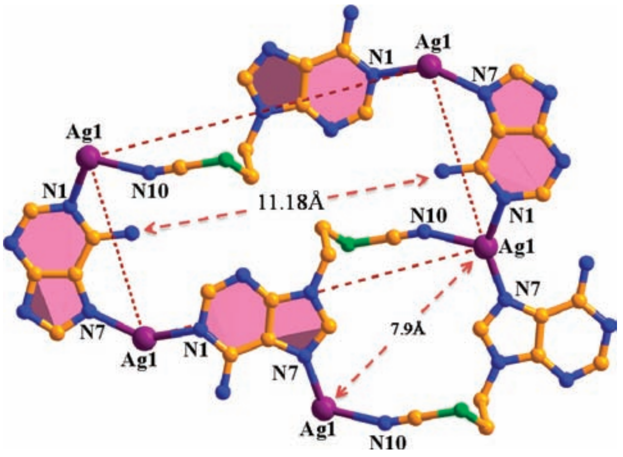

Figure 5. Interconnected two- and four-membered metallacycles in the silver complex, **3**.

slow evaporation. Colorless crystals suitable for X-ray diffraction were obtained over a period of 2 days, and evaluation of the crystal data suggested that it belonged to the monoclinic space group *C*2/*c*. The crystal lattice revealed a tridentate coordination mode for Ag^+ ions (Figure 4b). All silver ions were crystallographically identical and coplanar, leading to the formation of a two-dimensional sheetlike architecture (Figure S1 in the Supporting Information), with embedded two- and four-membered interconnected metallacycles (Figure 5).

Notably, four-membered metallacycles composed of four N1–Ag1 and two N7–Ag1 contacts, each with bond lengths 2.21(3) and 2.19(3) Å, respectively, and ring closure aided by two N10–Ag1 interactions of bond length 2.36(4) Å. N1–Ag–N7 and N1–Ag–N10 bond angles were found to be 144.40(1)° and 108.78(1)°, respectively. The interconnected dimeric metallacycles emerge via the interaction of N7–Ag1 and N10–Ag1, with an N7–Ag1–N10 bond angle of 105.71(1)°. Further analysis of the crystal lattice revealed the presence of $\pi-\pi$ stacking between six-membered rings of adenine moieties in adjacent layers having a separation of 3.55(1) Å and intermolecular hydrogen bonding between N6–H and perchlorate oxygen having a distance of 2.27(2) Å (Figures S2 and S3 in the Supporting Information).

In conclusion, we have investigated the coordination behavior of coinage metals copper(I) and silver(I), with a modified adenine analogue having a thiocyanate pendant arm at the N9 position. The formation of unusual adenine-containing, hexagonal prismatic cuprous iodide aggregates was observed, while the silver ions coordinated in a tridentate fashion to form a two-dimensional supramolecular architecture, composed of two- and four-membered metallacycles.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Characterization and crystal data and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. The supplementary crystallographic data for this paper with deposition numbers of CCDC 805169, 805170, and 805171 have also been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44-1223/336-033; e-mail deposit@ccdc.cam.ac.uk).

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