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Coordination-Driven Self-Assembly of a Discrete Molecular Cage and an Infinite Chain of Coordination Cages Based on *ortho*-Linked Oxacalix[2]benzene[2]pyrazine and Oxacalix[2]arene[2]pyrazine

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Coordination-driven self-assembly has been widely used in the construction of nanosized supramolecular objects.[1] By encoding specific information in the molecular subunits, highly symmetrical species,[2] as well as assemblies of low symmetry,[3] can be formed via metal-mediated self-assembly. Calixarenes and resorcinarenes, due to their well-defined conformational structures, have been used as the most important classes of macrocyclic host molecules in supramolecular chemistry.[4,5] Various sized calix[4]arene- and resorcinarene-based nanoscale coordination cages[6,7] as well as linear and tubular calix[4]arene coordination networks[8] have been prepared via metal-mediated self-assembly. Heteracalixarenes,[9] in which the methylene linkage between the aromatic units are replaced by heteroatoms, have attracted considerable interest due to their synthetic availability and tunable cavity structures. Recently, several research groups succeeded in introducing nitrogen-containing heterocyclic rings into the heteracalixarene systems.[10] Thus the systems are even more attractive for the study of metal-directed self-assembly. Herein, we report on silver-mediated self-assembly of a discrete molecular cage based on ortho-linked oxacalix[2]benzene[2]pyrazine (**1**), as well as an infinite chain of coordination cages based on oxacalix[2]arene[2]pyrazine (**2**) (Figure 1). One crucial feature for this metal-mediated self-assembly is that the two rigidly arranged pyrazinyl units in compounds **1** and **2** predetermine the optimum geometry in the formation of molecular cages.

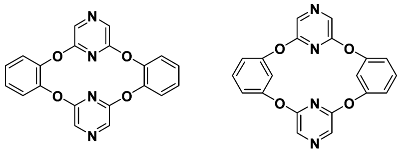

Figure 1. Molecular structures of compounds **1** (left) and **2** (right).

Previous reports confirmed that both compounds **1** and **2** adopt 1,3-alternate conformations with the two pyrazine rings arranged in face-to-face orientations, with the two *upper rim* nitrogen atoms directing outward from their central cavity (Figures S1 and S2).[10c,f] This geometrical arrangement thus makes them ideal molecular scaffolds for generation of supramolecular cages by capping two ligand molecules *via* the participation of their two *upper rim* nitrogen atoms in metal-mediated self-assembly.

Discrete molecular cage **3** (Figure 2) and polymeric coordination cages **4** (Figure 3) were prepared by stirring equal molar amounts of $\mathrm{AgBF_4}$ and their corresponding ligands **1** and **2** in a mixed solvent of benzene and acetonitrile under heat until complete dissolution of the starting materials. Single crystals of the resulting complexes **3** and **4** suitable for X-ray analysis were obtained after evaporation of the solvent at ambient temperature. ^{1}H NMR studies revealed that cages **3** and **4** do not survive in coordinating solvents like DMSO. However, the pyrazinyl H2 and H6 signals of **3** shifted slightly downfield in $\mathrm{CD_3NO_2}$, which implies that the $[\mathrm{Ag_2}(\mathbf{1})_2]^{2+}$ cage, or other related species such as a 1:1 complex $[\mathrm{Ag}(\mathbf{1})]^{1+}$, may be present in $\mathrm{CD_3NO_2}$ or that these species could be exchanging rapidly in the solvent. The ^{1}H NMR spectrum of **4** in $\mathrm{CD_3NO_2}$ shows a significant broadening of pyrazinyl H2 and H6 signals, suggesting formation of solution phase complex species, such as $[\mathrm{Ag}(\mathbf{2})]^{1+}$, $[\mathrm{Ag_2}(\mathbf{2})_2]^{2+}$, or related polymeric complexes $[\mathrm{Ag_2}(\mathbf{2})_2]_n^{2n+}$, which are under fast equilibration on the NMR time scale (Supporting Information). ESI-MS results demonstrate the presence of 1:1 complexes $[\mathrm{Ag}(\mathbf{1})]^{1+}$ and $[\mathrm{Ag}(\mathbf{2})]^{1+}$ in acetonitrile (Supporting Information), similar to the case of silver coordinated pyridinyl based cyclotriveratrylene ligand in solution.[12] These ESI-MS results suggest that 1:1 complex $[\mathrm{Ag}(\mathbf{1})]^{1+}$ dimerizes upon crystallization to generate cage **3**, while 1:1 complex $[\mathrm{Ag}(\mathbf{2})]^{1+}$ polymerizes in the crystallization process to form an infinite chain of coordination cages **4**.

Single crystal X-ray diffraction analysis unambiguously established the discrete structure of **3**. The structure revealed the formation of a rhomboidal molecular cage by two Ag^+ cation complexes in the equatorial region, connecting the two cyclophane ligands (Figure 2). Each Ag(I) ion adopts a distorted trigonal pyramidal arrangement, in which the metal center is occupied by three nitrogen atoms (Ag−N distances, 2.20−2.31 Å) and a fluorine atom (Ag−F distances, 2.38 Å and 2.78 Å) from the weakly coordinated $\mathrm{BF_4}^-$ anion in the apical position.[11] As a result, the three Ag−N bonds form a trigonal plane, and the coordinated acetonitrile is pointing outward from the metal-containing cage [two Ag−Ag−N(acetonitrile) angles: 176.2° and 176.3°]. The two $\mathrm{BF_4}^-$ anions are positioned outside the cage and reside on the opposite side of the equatorial plane (Figure S3). A small difference between the two N(pyrazinyl)−Ag−N(pyrazinyl) bond angles (117.0° and 122.3°) indicates a slight distortion of the rhomboidal cage. Within the cage, the two Ag^+ cations are separated by 7.867 Å, and a methyl group of an acetonitrile bonded to a neighboring cage

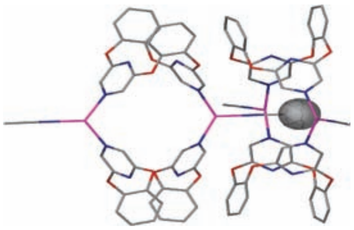

Figure 2. Crystal structure of **3** showing a methyl group of a bonded acetonitrile from one molecule of **3** occupies the void of a neighboring molecule. $\mathrm{BF_4}^-$ and hydrogen atoms have been omitted for clarity. Color code: Ag (purple), O (red), N (blue), and C (gray).

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occupies the cage void. To accommodate the coordination geometry adopted by the Ag^+ cations, the dihedral angle between two pyrazine rings in the cyclophane was changed to 57.9° (27.2° for free ligand), and the angle between the two phenyl planes also changed (from 28.6° to 17.1°). No solvent molecules were found included in the cavity of the cyclophane.

The crystal structure of **4**, determined at 173 K, revealed a one-dimensional cationic chain of coordination cages formed by the bridging of consecutive cyclic units by Ag^+ cations (Figure 3). The Ag^+ cation coordination sphere is composed of four nitrogen atoms (from four pyrazine rings) with the four Ag−N bonds (2.422 Å) forming a tetragonal plane (square-planar metal complex), and the two sets of N−Ag−N angles (86.95° and 91.83°) indicate a slight distortion of the square-planar geometry of the Ag center. As expected, the 1,3-alternate conformation of the cyclophanes (**2**) was preserved upon silver coordination, and the dihedral angle between the two pyrazinyl rings is changed to 120.1° (74.4° for free ligand) to accommodate the Ag^+ coordination geometry. The two phenyl planes in each ligand are almost parallel (3.3°, 54.4° for free ligand). In each metal-containing cage, the two N−Ag−N bond angles are equal to 86.95° with the two silver atoms being separated by 12.669 Å, and the distances between the cross-section intra-annular protons at the two cage openings are 3.704 and 5.470 Å, respectively. One molecule of benzene was found to reside per opening of each metal-containing cage with a larger intra-annular proton distance (5.470 Å). The included benzene ring is positioned perpendicular to the two intra-annular C−H bonds with the two C−H...π distances equal 2.769 Å, indicating strong C−H...π interactions are present. The cavities of the cyclophane units remain unoccupied. The anionic BF_4^- is positioned between the cationic silver layers with a Ag−F distance >3.0 Å in the solid state.

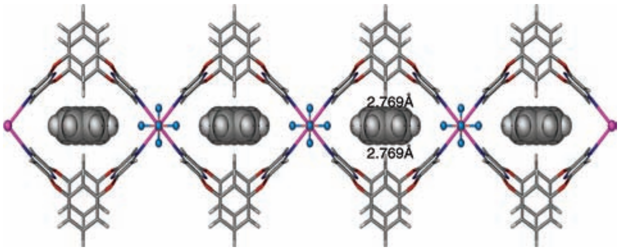

Figure 3. Crystal structure of **4** showing a molecule of benzene resides at the void of the metal-containing cage. Color code: Ag (purple), O (red), N (blue), C (gray), and BF_4^- (green).

As shown in Figures 2 and 3, the silver centers in **3** and **4** adopted different coordination geometries, with **3** in a tetrahedral geometry and **4** in a square-planar geometry. We reasoned that this was caused by the conformational rigidity differences of scaffolds **1** and **2**. Due to its conformational restriction, it would be very difficult to significantly enlarge the dihedral angle between the two pyrazine rings of the *ortho*-linked cyclophane **1** to accommodate the square-planar coordination geometry for Ag^+. However, as for tetrahedral coordination geometry, free ligand acetonitrile and BF_4^- could easily occupy the other two orbitals of the Ag^+ center accordingly. In cyclophane **2**, the *meta*-linkage is more flexible to afford a dihedral angle change between the two pyrazine rings to accommodate the square-planar coordination geometry for Ag^+ in the formation of complex **4**.

In summary, *ortho*-linked oxacalix[2]benzene[2]pyrazine (**1**) and oxacalix[2]arene[2]pyrazine (**2**) have been successfully employed in the construction of a discrete molecular cage **3** and an infinite chain of cages **4** *via* coordination-driven self-assembly. X-ray structure analysis revealed that both **3** and **4** were formed by bridging the consecutive cyclic units by Ag^+ cations. The Ag^+ ions in **3** adopted a tetrahedral geometry and in **4** adopted a square-planar one. The conformational rigidity difference between the two cyclophanes **1** and **2** is believed to be responsible for such a difference. The void of cage **3** was occupied by a methyl group of an acetonitrile bonded to a neighboring cage in the solid state, while one benzene ring was found to reside in the void of each cage of complex **4**. Studies on oxacalix[*n*]arene[*n*]hetarenes with larger cavities, as well as their coordination-driven self-assembly and guest inclusion, are currently ongoing in our laboratory; the results will be reported in due course.

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Supporting Information Available: Experimental details for the synthesis of compounds **1** and **2**, NMR spectra of all the reported compounds, ESI-MS results of **3** and **4**, molecular structures of **1** and **2**, single crystal X-ray data, molecular packing and CIF files for **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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