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Synthesis of Open and Closed Metallacages Using Novel Tripodal Ligands: Unusually Stable Silver(I) Inclusion Compound

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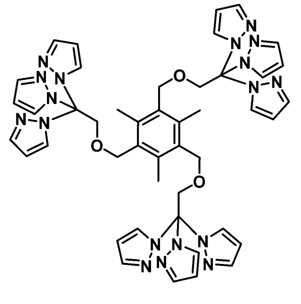
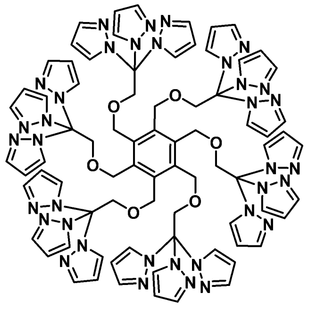
The tripodal ligand $1,3,5\text{-}(CH_3)_3C_6[CH_2OCH_2C(pz)_3]_3$ (**L1**, pz = pyrazolyl ring) reacts with $AgBF_4$ to yield $\{[\mathbf{L1}_2Ag_3(CH_3CN)](BF_4)_3\}\cdot(CH_3CN)_4$, an inclusion complex in which the encapsulated acetonitrile cannot escape the triangular cage unit in either the solid or solution phase. The analogous hexatopic ligand $C_6[CH_2OCH_2C(pz)_3]_6$ forms a 2-dimensional polymer composed of similar triangular cage units, again with the encapsulation of one acetonitrile molecule, linked by the additional tris(pyrazolyl)methane units. In contrast, the complex formed with **L1** and Cd^{2+} has a double, open cage structure holding two diethyl ether molecules.

The self-assembly of discrete molecular architectures based on metal–ligand interactions is a current topic of research, driven by the fact that such architectures can play a role in catalysis or molecular recognition or can act as molecular containers, molecular sensors, and sieves.[1,2] We have prepared a series of new multitopic ligands based on linking bis- and tris(pyrazolyl)methane units designed to promote specific extended structures.[3] Most of these new ligands are designed to be semiflexible in order to promote structures that will maximize both the covalent and noncovalent forces. Reported here are (1) the synthesis of two new tripodal ligands of this class with nine (**L1**) and eighteen (**L2**) potential donor atoms; (2) the use of these ligands to prepare both open and closed metallacage complexes; (3) the high thermal stability in the solid state (ca. 200 °C) and remarkable thermodynamic stability in solution of the closed metallacage inclusion complex formed from **L1** and silver(I); and (4) based on **L2**, the formation of the first infinite 2D covalent array incorporating M_3L_2-like cages.



L1



L2

The new ligand $(CH_3)_3C_6[CH_2OCH_2C(pz)_3]_3$ (**L1**, pz = pyrazolyl ring) has been prepared by the reaction of $1,3,5\text{-}(BrCH_2)_3C_6(CH_3)_3$ and tris-2,2,2-(1-pyrazolyl)ethanol, $HOCH_2C(pz)_3$, under basic (NaH) conditions.[4] **L1** reacts with $[Cd_2(thf)_5](BF_4)_4$ [4] to yield a white solid that after crystallization by vapor phase diffusion of diethyl ether into an

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(2) For recent papers on catalytic activity and guest encapsulation see: (a) Kusukawa, T.; Nakai, T.; Okano, T.; Fujita, M. *Chem. Lett.* **2003**, *32*, 284–285. (b) Yoshizawa, M.; Takeyama, Y.; Okano, T.; Fujita, M. *J. Am. Chem. Soc.* **2003**, *125*, 3243–3247. (c) Kusukawa, T.; Fujita, M. *J. Am. Chem. Soc.* **2002**, *124*, 13576-13582. (d) Biradha, K.; Fujita, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3392–3395. (e) Paul, R. L.; Bell, Z. R.; Jeffery, J. C.; Harding, L. P.; McCleverty, J. A.; Ward, M. D. *Polyhedron* **2003**, *22*, 781–787. (f) Paul, R. L.; Bell, Z. R.; Fleming, J. S.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Heteroat. Chem.* **2002**, *13*, 567–573. (g) Bell, Z. R.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 2515–2518. (h) Dolomanov, O. V.; Blake, A. J.; Champness, N. R.; Schröder, M.; Wilson C. *Chem. Commun.* **2003**, 682–683. (i) Hiraoka, S.; Yi, T.; Shiro, M.; Shionoya, M. *J. Am. Chem. Soc.* **2002**, *124*, 14510–14511. (j) Bourgeois, J.-P.; Fujita, M.; Kawano, M.; Sakamoto, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **2003**, *125*, 9260–9261.

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(4) See Supporting Information for further details.

10.1021/ic035192o CCC: $25.00

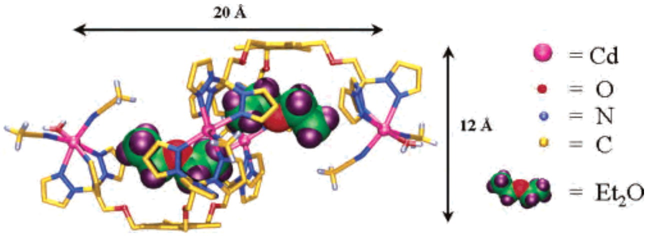

Figure 1. Structure of [$\mathbf{L1}_2$Cd$_4$(CH$_3$CN)$_6$(H$_2$O)$_2$(Et$_2$O)$_2$]$^{8+}$.

acetonitrile solution afforded crystals containing the {[$\mathbf{L1}_2$Cd$_4$(CH$_3$CN)$_6$ (H$_2$O)$_2$(Et$_2$O)$_2$]$^{8+}$ cation (**1**). The solid-state structure consists of a double, open cage (Figure 1) with each of the two tritopic ligands having two tris(pyrazolyl)methane units coordinated to two bridging cadmium(II) cations with the third each coordinated to an additional metal center.

Each of the bridging cadmium centers is κ^3-bonded to one tris(pyrazolyl)methane unit and κ^2-bonded to the other, with an acetonitrile molecule occupying the remaining octahedral coordination site. The terminal cadmiums are κ^3-bonded to the remaining tris(pyrazolyl)methane unit in each ligand with the other coordination sites filled with two acetonitrile and one water molecules. Two ether molecules reside inside the cavities of the "cages," held in place by C−H···π interactions, involving the methyl and methylene groups as donors and the central arene ring and two of the pyrazolyl rings acting as acceptors.

The cage height, measured between the planes of the two central arene rings, is 12 Å. The bridging Cd···Cd distance is 10.8 Å, and the distance between the two terminal cadmium centers is 20 Å.

The reaction of **L1** with AgBF$_4$ in thf afforded a white precipitate that analyzed for a compound with the formula $\mathbf{L1}_2$Ag$_3$(BF$_4$)$_3$ (the same product is formed in reactions where the metal to ligand molar ratio is varied), indicating the formation of a closed cage complex. ES/MS showed peaks corresponding to [$\mathbf{L1}_2$Ag$_3$(BF$_4$)$_2$]$^+$. Crystallization of the white powder from acetonitrile afforded {[$\mathbf{L1}_2$Ag$_3$(CH$_3$CN)](BF$_4$)$_3$}·(CH$_3$CN)$_4$ (**2**).[4] The solid-state structure of the cationic unit (Figure 2a) consists of closed, trigonal prismatic cages constructed by two ligands with their sidearms on the same side of the central arene ring and a face-to-face orientation, each κ^2-bonded to three bridging silver centers. The central arene rings are parallel and in an almost perfect eclipsed position.

Each cage encapsulates one CH$_3$CN guest molecule, disordered over two sites by the operation of a 2-fold axis. The cage height, measured between the two central arene rings, is 12.3 Å, and the distance between two adjacent silver atoms is ca. 10 Å. However, the dimensions of the triangular cage, if measured between the 4th carbon atoms from the pyrazolyl rings that are on the outsides of the cages, are much larger, ca. 15 Å. The cages are stacked along the *a* axis of the unit cell organized by $\pi-\pi$ interactions with several C···C distances being in the range 3.6−3.7 Å. The stacked cages are organized in close packed rows, Figure 2b, with the top of the cages in one row aligned with the middle of the cages in the next row.

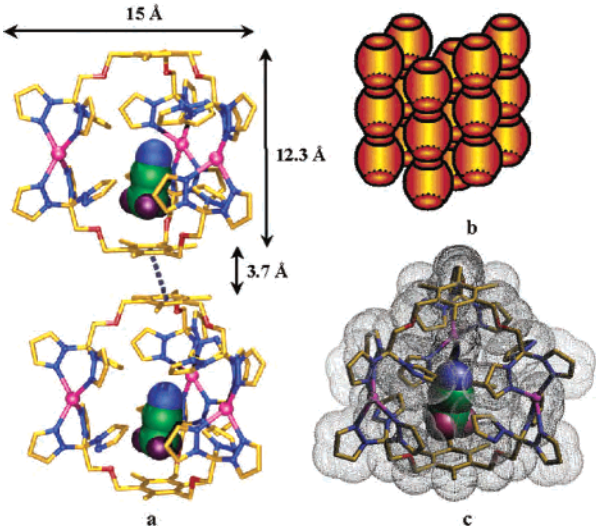

Figure 2. (a) The [$\mathbf{L1}_2$Ag$_3$(CH$_3$CN)]$^{3+}$ cage and the $\pi-\pi$ stacking between two cages. (b) Columnar packing of the cages. (c) Space-filling representation of [$\mathbf{L1}_2$Ag$_3$(CH$_3$CN)]$^{3+}$ showing the encapsulated acetonitrile molecule.

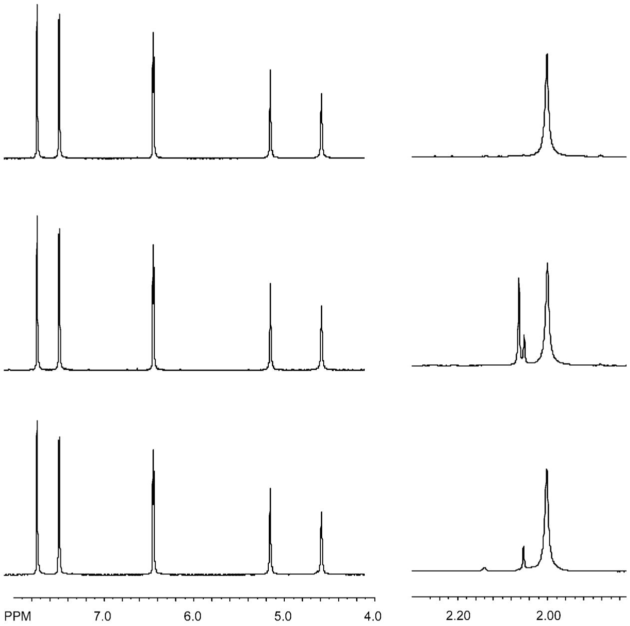

Figure 3. NMR study of the silver(I) complex with **L1**. Top: the white precipitate obtained after reaction in thf that contains no solvent molecules. Middle: spectrum of crystalline sample **2**; the two new resonances around 2.06 δ arise from the "free" and "caged" acetonitrile. Bottom: NMR spectrum of **2** after the TGA experiment showing the complete absence of the "free" acetonitrile.

The solution ^{1}H NMR spectrum of the powder sample that contains no solvent (see top of Figure 3) has resonances expected for the ligands of the cage complex: three resonances in the aromatic region for the three positions on the pyrazolyl rings, two around 5 δ for the CH$_2$ groups, and one at 2 δ for the CH$_3$ groups. In this spectrum (and those of the crystalline samples) the pyrazolyl rings are equivalent, presumably because of a fluxional process that equilibrates the free and coordinated rings fast on the NMR time scale. This fast exchange process is maintained even at low temperatures. As indicated by the formula of **2**, in addition to the encapsulated acetonitrile, the crystalline sample contains four acetonitrile molecules of solvation per cage

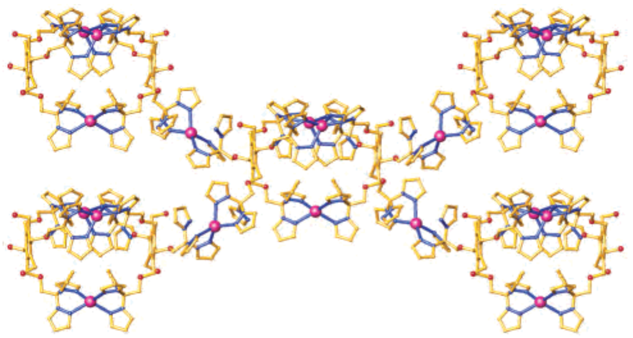

Figure 4. The connectivity of the $\{[C[CH_2OCH_2C(pz)_3]_6]_2Ag_5(CH_3CN)_3\}_n^{5+}$ coordination polymer, showing five metallacages, one acting as a bridge between the other four; the noncoordinated sidearms not shown.

unit. The NMR spectrum of this crystalline sample (see Figure 3 middle) shows the expected ligand resonances plus two additional resonances around 2.06 δ that correspond to the one acetonitrile molecule imprisoned in the cage and four acetonitrile molecules outside the cage. TGA analysis of the crystalline sample shows a mass loss between 30 and 90 °C that corresponds to four acetonitrile molecules. The only other significant mass loss starts above 200 °C, when decomposition of **2** occurs.[4] A similar experiment on another crystalline sample was conducted, but the heating was stopped at 190 °C. The sample had lost its crystallinity, but when analyzed by ^{1}H NMR spectroscopy (see Figure 3 bottom) it showed unchanged resonances for the ligands, but only the resonance that corresponds to the acetonitrile *imprisoned within the cage*. This spectrum did not change for a week. A small amount of acetonitrile-d_3 was added to this solution, and no exchange of the imprisoned acetonitrile was observed over a period of a month. These experiments show that the encapsulated acetonitrile *cannot escape the cage* in either the solid or solution phase, and demonstrate the *retention and stability of the cage structure in solution*. These results are particularly surprising for a metal of known lability such as silver(I).[2h]

The ligand $C_6[CH_2OCH_2C(pz)_3]_6$, **L2**, was synthesized and the silver(I) complex prepared as above, and crystals containing the $\{[C[CH_2OCH_2C(pz)_3]_6]_2Ag_5(CH_3CN)_3\}_n^{5+}$ (**3**) cation formed from an acetonitrile solution. The structure of this cation, Figure 4, is a 2D network built by linking $[\mathbf{L1}_2Ag_3(CH_3CN)]^{3+}$ like cages to four analogous cages using four of the other six ether-linked tris(pyrazolyl)methane units of two **L2** ligands to bond bridging silver cations that are not part of the cages. One sidearm of each **L2** is noncoordinated and not shown in the figure. As with **2**, all of the cages are filled with one acetonitrile molecule (not shown). In addition, there is another acetonitrile molecule situated within the "semi-closed" cage, formed from the two bridging and the free arms.[4] This structure appears to represent the first infinite 2D covalent array incorporating M_3L_2 cages and demonstrates the generality of the formation of the trigonal prismatic cage structural unit, filled with one acetonitrile.[5]

The synthetic strategy for the designed syntheses of metallacages used in the research reported here is a variation of the *symmetry-interaction approach*, that uses multibranched, highly directed bidentate-chelating ligands.[1f] We have used a more flexible linking group, and our approach differs from other studies using tritopic 1,3,5-substituted arene ligands to build M_3L_2 cages in that each of our sidearms is a bulky, potentially tridentate tris(pyrazolyl)methane unit.

To date, most of the M_xL_y cages were constructed using multitopic ligands in which each of the individual bonding units were monodentate, with the remaining (planar or tetrahedral) coordination sites of the metal occupied by additional ligands. In the silver(I) complexes reported here, all the coordination sites of the metals involved in the closed cages are occupied solely by the ligand. In the case of **2** these design features lead to an unusually stable, nonlabile inclusion compound. By using the potentially tridentate tris(pyrazolyl)methane units as the bonding groups, any exits from the trigonal prismatic cages are "blocked" (see Figure 2c), causing the central acetonitrile to be tightly held so that it does not exchange in solution with acetonitrile outside the cage even over a period of weeks or be driven off in the solid phase below 200 °C. *This strong retention of the inclusion molecule appears to be unique for metallacage complexes*. Complex **2** also represent a rare example of the formation of a cage without requiring the template effect of a central anion.[2f,h,i] The 2D structure of the silver complex with the hexatopic ligand **L2** supports the stability argument of the M_3L_2 trigonal prismatic cages that form with the encapsulated acetonitrile molecule and represent a new supramolecular motif, at the interface between the assembly of discrete M_xL_y supermolecules and of coordination polymers. Switching from silver(I), a metal that prefers low coordination numbers, to cadmium(II), a metal that strongly prefers octahedral coordination, changes the structure from the closed caged type arrangement observed with **2** and **3** to the open cage structure of **1**. These structural variations demonstrate that these semiflexible ligands provide the opportunity to adjust supramolecular architectures by changing the bonding preferences of the metal.

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Supporting Information Available: Synthetic procedures for **L1**, **L2**, **1**, **2**, and **3**, ESI-MS, NMR, and TGA curve for **2**, ORTEP representations of asymmetric units of **1**, **2,** and **3**, and CIFs for **1**, **2**, and **3** and extended structure of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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