First example of a dumbbell-like architecture containing M_3L_2 cages and terephthalate anions

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Letter

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A novel complex $[Ag_3(titmb)_2]_2[1,4\text{-}C_6H_4(COO)_2]_3\cdot 23\ H_2O$ [titmb = 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene] contains two M_3L_2 cages and three terephthalate anions, one of which is embedded in the two cages to form a dumbbell-like architecture and shows photoluminescence in the solid state when the titmb reacts with $[Ag(NH_3)_2]NO_3$, an individual M_3L_2 cage $[Ag_3(titmb)_2][NO_3]_3\cdot 5\ H_2O$ without luminescent properties was obtained.

Supramolecular frameworks with specific topologies such as closed three-dimensional (3D) molecular cages present a large range of applications in material science, medicine and chemical technology.[1] During the past decade, a variety of such architectures have been synthesized by assembly of organic ligands and transition metal salts.[2–6] From these studies, tripodal ligands with an arene core were found to be one of the most useful building blocks in construction of cage-like architectures. For example, ten-component M_6L_4 cage-like complexes were obtained by assembly of 2,4,6-tris(4-pyridyl)-1,3,5-triazine and 1,3,5-tris(pyrazol-1-ylmethyl)-2,4,6-triethylbenzene ligands with $Pd(en)(NO_3)_2$ (en = ethylenediamine) and $PdCl_2$, respectively.[2] We are investigating the effect of anion functionality in the construction of cage-like architectures based on imidazole-containing tripodal ligands,[7] and report here a unique dumbbell-like architecture with three terephthalate anions and two M_3L_2 cages.

The complex $[Ag_3(titmb)_2]_2[1,4\text{-}C_6H_4(COO)_2]_3\cdot 23\ H_2O$ (**1**) was obtained as colorless needle crystals by the layering method. The complex $[Ag_3(titmb)_2][NO_3]_3\cdot 5\ H_2O$ (**2**) was prepared analogously to **1** by using $[Ag(NH_3)_2]NO_3$ instead of $[Ag(NH_3)_2]_2[1,4\text{-}C_6H_4(COO)_2]$. Both **1** and **2** were isolated in high yield (larger than 50%) and they were found to be insoluble in common polar and non-polar solvents.

X-Ray crystallography evidenced that **1** contains two M_3L_2 type cages, three terephthalate anions and 23 molecules of water. As illustrated in Fig. 1(a), each Ag(I) ion is coordinated by two N atoms, each belonging to the imidazolyl group of a different titmb, in an essentially linear arrangement with N–Ag–N angles ranging from 168.1(2)° to 173.05(18)°. The two titmb ligands with a *cis,cis,cis* conformation take a face-to-face orientation and are joined together by three silver(I) ions through coordination bonds to give individual three-dimensional M_3L_2 type cages. In the cage with Ag1, Ag2, Ag3, the distance between the two central benzene rings with a dihedral angle of 2.6° is 10.73 Å and the intermetallic Ag$\cdots$Ag distances range from 6.66 to 7.03 Å, while in the cage with Ag4, Ag5 and Ag6, the distance between two central benzene rings with a dihedral angle of 1.8° is 10.62 Å and Ag$\cdots$Ag separations vary from 6.86 to 7.23 Å, which are compatible to those in the previously reported cages, $[Ag_3(titmb)_2](ClO_4)_3$ (**3**) and $[Ag_3(titmb)_2](ClO_4)_3\cdot 4\ CH_3CN$ (**4**).[7] In addition, a distance of 2.504(4) Å indicates the occurrence of a weak interaction between Ag1 and O9.[8]

The most striking structural feature of **1** is that two M_3L_2 type cages encapsulate one terephthalate anion to form a dumbbell-like architecture. Unlike the discrete cage-like architectures of **3** and **4** mentioned above, two cages in **1** are joined together by a terephthalate anion through four C–H$\cdots$O hydrogen bonds [$r_{\text{C132-O1}} = 3.250(10)$ Å; $r_{\text{C32-O2}} = 3.179(10)$ Å; $r_{\text{C352-O3}} = 3.140(9)$ Å; $r_{\text{C252-O4}} = 3.332(9)$ Å; Fig. 1(a)]. This terephthalate anion embeds in the "windows" of two cages with the benzene ring plane of the terephthalate oriented perpendicularly to the central benzene ring planes of titmb due to a steric effect. The dihedral angles between the benzene ring plane of the terephthalate and the benzene ring planes of the titmb range from 95.1° to 103.0°. We believe this structural motif to be unique among the dumbbell-like architectures. It is reminiscent of the 1-bromoadamantane that was encapsulated by two cyclodextrins.[9]

It can be seen from the crystal packing diagram of **1** [Fig. 1(b)] that the benzene ring plane of one terephthalate anion is sandwiched between two benzene ring planes from two different cages with a centroid-centroid distance of 3.60 Å. This implies that there are π-π interactions in **1**. Furthermore, a distance Ag5$\cdots$Ag5$(1-x,\ y,\ -0.5-z)$ of 3.3268(10) Å indicates that there are very weak ligand-unsupported Ag$\cdots$Ag interactions in **1** between two adjacent cages.[10–12]

The structure of **2** with nitrate anions contrasts markedly with that of **1** with the terephthalate anions. The single-crystal X-ray structure of **2** revealed a different and comparatively simple structure based on a discrete M_3L_2 cage [Fig. 2(a)]. The distance between two central benzene rings with a dihedral angle of 0.5° is 10.93 Å and the intermetallic Ag$\cdots$Ag distances range from 6.42 to 6.55 Å. It is noteworthy that there are two water molecules inside the cage (Fig. 2), held there through six C–H$\cdots$O hydrogen bonds, while three nitrate anions are all outside the cage. In the case of **3** with perchlorate anions, one of the three perchlorate anions was located inside the cage and no water molecules were found.[7]

There are 23 and 5 lattice water molecules in **1** and **2**, respectively, although **1**, **2** and **3** were prepared by a similar method and the structures were all determined at 200 K. Thermogravimetric analysis (TGA) showed a weight loss of 13.8% centered at 95 °C for **1** and 6.8% centered at 93 °C for **2**,

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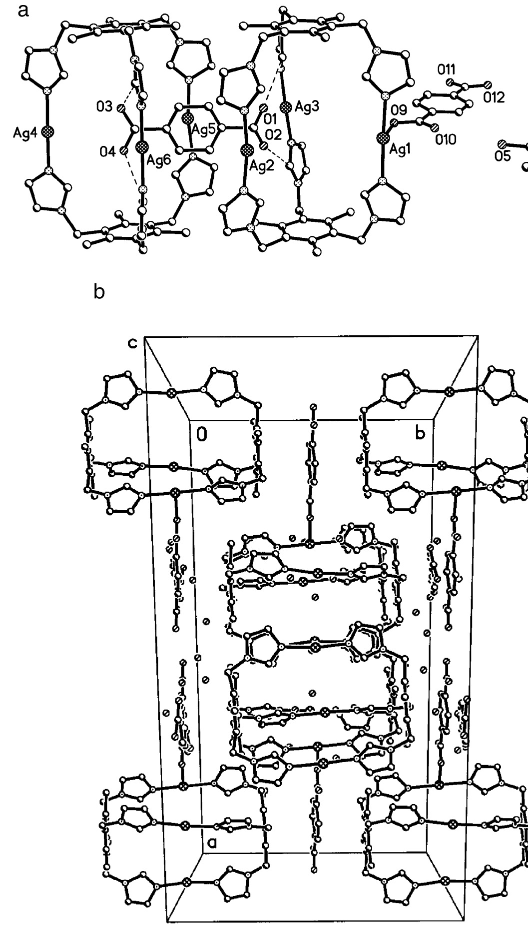

Fig. 1 (a) Crystal structure of the dumbbell-like complex **1**, in which one of the three terephthalate ions embeds in the "windows" of the two cages through C–H···O hydrogen bonds indicated by dashed lines. Selected bond lengths (Å) and angles (°): Ag1–N12 = 2.146(5), Ag1–N112 = 2.150(5), Ag1–O9 = 2.504(4), Ag2–N152 = 2.078(5), Ag2–N52 = 2.089(5), Ag3–N132 = 2.098(5), Ag3–N32 = 2.112(5), Ag4–N212 = 2.103(5), Ag4–N312 = 2.106(5), Ag5–N332 = 2.102(5), Ag5–N232 = 2.109(5), Ag6–N252 = 2.102(5), Ag6–N352 = 2.104(5); N12–Ag1–N112 = 173.05(18), N12–Ag1–O9 = 95.85(16), N112–Ag1–O9 = 90.26(15), N152–Ag2–N52 = 171.3(2), N132–Ag3–N32 = 168.1(2), N212–Ag4–N312 = 171.78(19), N332–Ag5–N232 = 171.1(2), N252–Ag6–N352 = 172.3(2). (b) Crystal packing diagram of **1** in the *ab* plane.

corresponding to the loss of these water molecules. Except for the above mentioned C–H···O hydrogen bonds, there are many O(water)–H···O(water or nitrate anion) hydrogen bonds with O···O distances ranging from 2.71 to 2.91 Å for **1** and from 2.87 to 2.95 Å for **2**.

It is interesting that the framework **1** shows photoluminescence with an emission maximum at 433 nm upon excitation at 329 nm in the solid state at room temperature, recorded on a Hitachi 850 fluorescence spectrophotometer with 4 nm resolution. However, no clear luminescent properties were observed for **2**. The observed luminescence of **1** is probably attributable to the terephthalate anion and/or the aggregation of M_3L_2 cages through the hydrogen bonds, π-π interactions and weak silver(I)-silver(I) interactions.

The present work demonstrates that the anion plays an important role in the self-assembly process of these architectures. Studies directed towards the assembly of related structures employing other aliphatic or aromatic diacids are currently in progress.

Experimental

All the procedures were carried out in the dark. A solution of 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb, 0.05 mmol, 18 mg) in methanol (5 ml) was carefully layered over an aqueous solution of $[Ag(NH_3)_2]_2[1,4\text{-}C_6H_4(COO)_2]$ (0.05 mmol ml^{-1}, 2 ml). Colorless crystalline **1** formed after several weeks. Complex **2** was prepared similarly to complex **1**. Anal. calcd for $C_{108}H_{154}N_{24}O_{35}Ag_6$, **1**: C, 43.30; H, 5.18; N, 11.22; found: C, 43.20; H, 5.19; N, 11.20%. Calcd for $C_{42}H_{58}N_{15}O_{14}Ag_3$, **2**: C, 38.20; H, 4.43; N, 15.91; found: C, 38.02; H, 4.68; N, 15.72%.

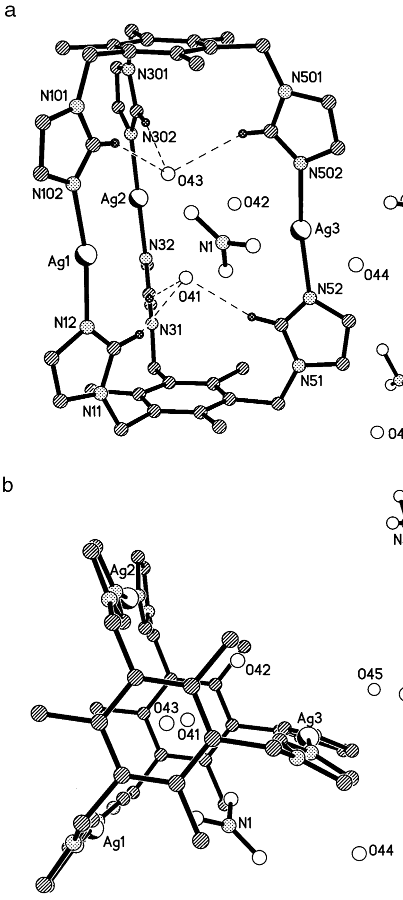

Fig. 2 (a) Crystal structure of the cylindrical cage of **2** showing encapsulated water molecules held through C–H···O hydrogen bonds indicated by dashed lines. (b) View along the axis of the cylinder.

X-Ray crystallography

Data collection (1.03 ⩽ θ ⩽ 27.48 for **1** and 1.59 ⩽ θ ⩽ 27.48 for **2**) was performed at 200 K on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo_{K_α} radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with SIR92,[13] and expanded using Fourier techniques.[14] All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method, giving for **1** final R_1 and wR_2 values of 0.0502 and 0.0972 for 1600 parameters and 10 208 observed reflections with $I > 2\sigma(I)$ and for **2** final R_1 and wR_2 values of 0.0742 and 0.2116 for 671 parameters and 7512 observed reflections with $I > 2\sigma(I)$. In spite of the low temperature data collection, one of the nitrate anions in **2** is disordered over two positions.

1: $C_{108}H_{154}N_{24}O_{35}Ag_6$, $M_w = 2995.77$, monoclinic, space group $C2/c$, $a = 35.8754(6)$ Å, $b = 17.6365(3)$ Å, $c = 43.1894(8)$ Å, $\beta = 113.5310(10)°$, $U = 25054.3(8)$ Å^3, $Z = 8$, $D_c = 1.588$ g cm^{-1}, $\mu = 1.006$ mm^{-1}. **2**: $C_{42}H_{58}N_{15}O_{14}Ag_3$, $M_w = 1320.64$, monoclinic, space group $P2_1/n$, $a = 14.6892(5)$ Å, $b = 21.5676(8)$ Å, $c = 16.0239(7)$ Å, $\beta = 94.3500(10)°$, $U = 5061.9(3)$ Å^3, $Z = 4$, $D_c = 1.733$ g cm^{-1}, $\mu = 1.229$ mm^{-1}.

CCDC reference numbers 168896–168897. See http://www.rsc.org/suppdata/nj/b1/b109141g/ for crystallographic data in CIF or other electronic format.

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