Metallosupramolecular Complexes

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An Extensive Class of Solids Full of Holes Large Enough To Enclose over 200 Molecules of H_2O**

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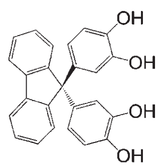

LH_4 (I)

Multifunctional ligands bearing metal-chelating sites derived from catechol have been much used in supramolecular chemistry.[1] Here, we describe some unusual metal derivatives of the ligand LH_4 (**I**), in which two catechol units are attached to the central carbon atom of a fluorene unit. Complexes of this previously unreported ligand are unknown, however, paramagnetic zinc complexes of a related fluorene-derived ligand containing *tert*-butyl-substituted orthosemiquinone radical components have been reported.[2] Reported below are various metal derivatives of **I** showing unusual structural features which appear to be determined by the propensity of the hydrophobic fluorene components to cluster together in symmetrical groups of 12, somewhat like the hexaphenyl embrace described by Dance et al.[3] but on a grander scale. A direct consequence of the clustering is the generation of large voids repeated throughout the structure, much like the holes in the Swiss Emmental cheese. Essentially the same structure is seen for a wide range of combinations of L^{4-}, coordinated metal, and co-cation, pointing to the structure-determining role of the association of fluorene units into groups of 12.

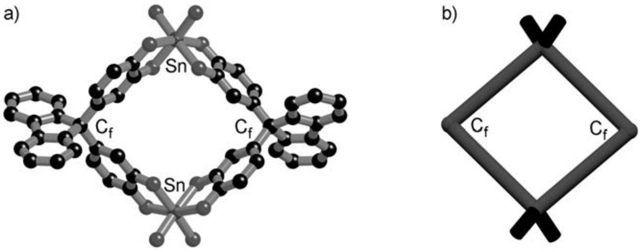

Figure 1. a) The chiral $[L_2\{Sn(OH)_2\}_2]^{4-}$ macrocycle. b) Schematic representation of the macrocycle in which the corners represent the tetrahedral fluorene carbon atoms, C_f, and the dihydroxytin centers.

Reaction of LH_4 in basic aqueous medium with Sn^{IV} in the presence of NMe_4^+ affords hydrated crystals of composition $(NMe_4)_{4/3}Na_{8/3}[L_2\{Sn(OH)_2\}_2]$ suitable for single-crystal X-ray diffraction studies.[4a] The crystals are cubic with the chiral space group $F432$ ($a = 38.502(2)$ Å). Ligand L^{4-} is present as a component of a 2:2 macrocyclic anion of composition $[L_2\{Sn(OH)_2\}_2]^{4-}$ (Figure 1). Numerous examples of related metallosupramolecular aggregates have been reported.[5] The macrocycle as a whole is chiral, with its two *cis* dihydroxotin centers having the same absolute configuration. A twofold axis passes through the tin centers, another passes through the two central fluorene carbon centers (C_f, see Figure 1 a), and a third passes through the center of the macrocycle, perpendicular to the $Sn_2(C_f)_2$ plane. All macrocycles in the crystal have the same absolute configuration.

A dominant feature of the structure is the presence of almost spherical clusters of hydrophobic fluorene units, one from each of 12 separate macrocycles (Figure 2 a and b). The centers of the (fluorene)$_{12}$ clusters are disposed in the face centered cubic (fcc) manner shown in Figure 2 c. A direct consequence of this clustering of fluorene units in groups of 12 is the generation of large enclosures surrounded by 12 "face on" macrocycles, as explained immediately below. Figure 3 a shows four clusters with their centers located in the *ab* plane and four associated macrocycles, whose centers are also in the *ab* plane. These four macrocycles are "face on" to the enclosure, the center of which is located at the mid-point of the vertical cell edge in Figure 3 a. Eight other macrocycles (omitted for clarity from Figure 3 a) are also "face on" to this enclosure,: the centers of four of these lie parallel to the *ac* plane and the centers of the other four lie in the *bc* plane. The clustering of the fluorene units leads directly, in this way, to the formation of large enclosures each surrounded by 12 "face on" macrocycles, all of which are equivalent and whose centers are located at the corners of a cuboctahedron (Figure 3 b). The centers of the enclosures are located at the "octahedral sites" of the fcc array of (fluorene)$_{12}$ clusters (i.e. at the mid-points of the cell edges and at the centers of the fcc cells).

The enclosures are unusually large, the distance from the center of a macrocycle to the one diametrically opposed being approximately 27 Å. These roughly spherical enclosures are occupied by large numbers of highly disordered water molecules. We estimate the volume of the cavity defined by the van der Waals surfaces of the surrounding matrix to be of the order of 6000 Å^3, a space capable of enclosing no less than 200 water molecules if the collection has the density of liquid water. This estimate of roughly 200 water molecules per enclosure is also indicated by the residual electron density[6]

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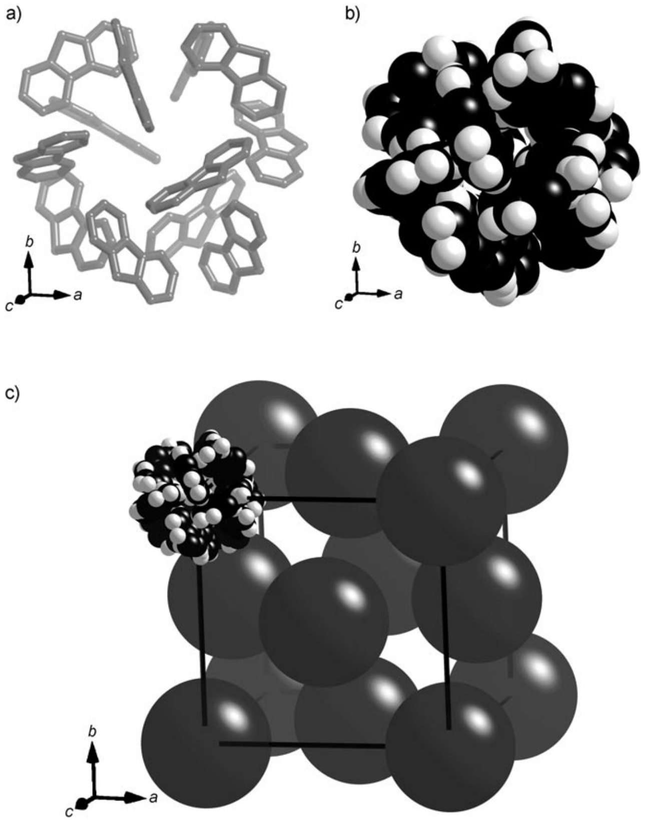

Figure 2. a) A framework representation of the clustering of the fluorene units from 12 separate macrocycles. b) A space-filling representation of the (fluorene)$_{12}$ cluster showing individual $C_{13}H_8$ units. c) The fcc arrangement of the (fluorene)$_{12}$ clusters. A space-filling representation of all the atoms in only one cluster is shown here, the other clusters being represented, for clarity, as spheres.

associated with the disordered contents of the cavities. An imaginary slice through the structure would reveal a surface pitted with holes reminiscent of Swiss Emmental cheese.

Whilst the octahedral sites of the fcc array of (fluorene)$_{12}$ clusters are where the large enclosures are centered, the tetrahedral sites are occupied by NMe_4^+ and Na^+ cations. As can be seen in Figure 4, the tetrahedral sites are surrounded by 12 hydroxo groups provided by six macrocycles disposed "edge-on" to the site. The oxygen centers of the 12 hydroxo groups are equidistant from the center of the tetrahedral site. Not surprisingly, the NMe_4^+ and Na^+ cations required to balance the charge on the $[L_2\{Sn(OH)_2\}_2]^{4-}$ units, together with associated water molecules, are found in the general vicinity of these 12 hydroxo groups.

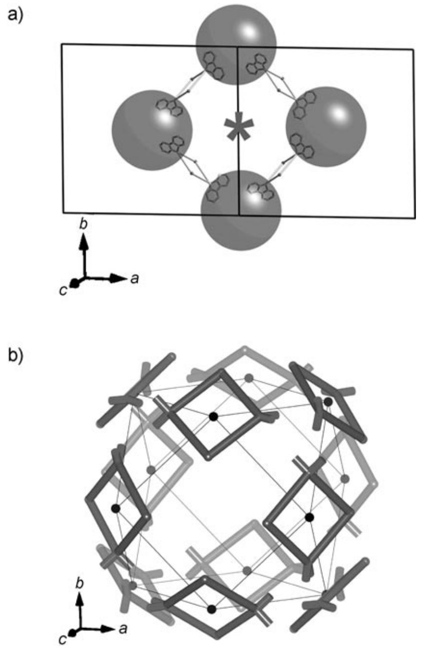

Figure 3. a) Representation of four near-neighbor (fluorene)$_{12}$ clusters, two at the corners of the fcc cell and two others (those on the left and right here) at the face centers. The mid-point of the vertical cell edge, shown here by an asterisk, represents the center of one enclosure. In addition to the four clusters and the four associated macrocycles shown here (which are centered in the *ab* plane), there are eight other macrocycles (not shown for clarity) that are "face-on" to the enclosure, four centered in the *ac* plane and four centered in the *bc* plane. b) Arrangement of 12 macrocycles surrounding an enclosure, with their centers, shown here as small spheres, located at the corners of a cuboctahedron.

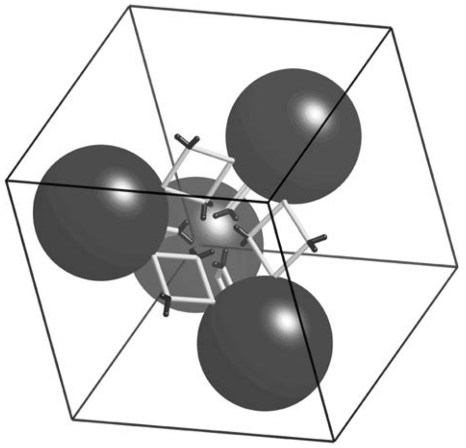

Figure 4. View of four (fluorene)$_{12}$ clusters and six associated macrocycles, showing a tetrahedral site surrounded by 12 equivalent hydroxo groups. The edges of the fcc cell are shown, with the four clusters shown being located in the left, back, and bottom faces, and at the remote corner of the cell. Seven other equivalent sites are present within the cell shown.

The unusual structural features described above are not limited to just one isolated case. For example, reaction of LH_4 with either sodium molybdate or sodium tungstate in aqueous methanol yields solvated crystals suitable for single-crystal X-ray crystallography of composition $(NMe_4)_{4/3}Na_{8/3}[L_2(MO_2)_2]$ ($M = Mo$ or W).[4b] These compounds have cubic unit cells [$a = 37.4755(11)$ Å (Mo) and 37.3271(3) Å (W), space group $Pa\bar{3}$] and essentially identical structures. Chiral, macrocyclic $[L_2(MO_2)_2]^{4-}$ ($M = Mo$, W) anions, very similar to the $[L_2\{Sn(OH)_2\}_2]^{4-}$ macrocycles described above, are present. In their gross structural features, the Sn, Mo, and W compounds are very similar in that in all three cases (fluorene)$_{12}$ clusters are disposed in a fcc manner with very large voids at the octahedral sites and with collections of Na^+, NMe_4^+ cations, and solvent molecules at the tetrahedral sites.

The Mo and W compounds, however, do show significant structural differences from the Sn compound as outlined below. Whereas all the macrocycles in the Sn compound have the same absolute configuration, the (fluorene)$_{12}$ clusters in the Mo and W compounds contain equal numbers of fluorene units from macrocycles of opposite hand as shown in Figure 5.

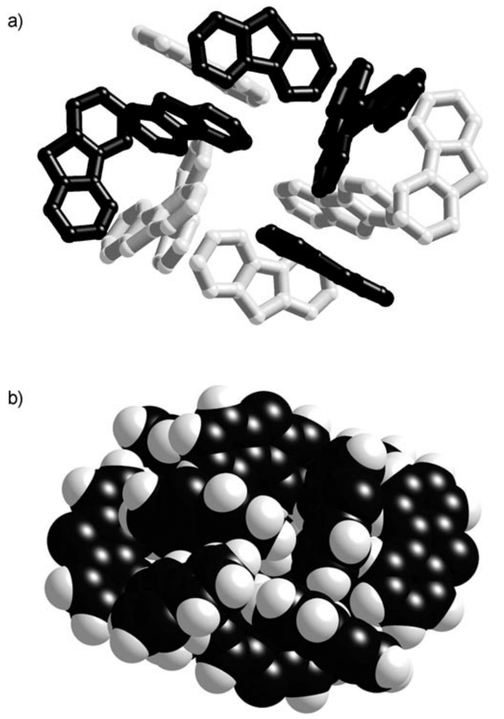

Figure 5. a) Arrangement of the fluorene units in solvated $(NMe_4)_{4/3}Na_{8/3}[L_2(MO_2)_2]$ (M = Mo or W). Fluorene units from macrocycles of different hand are indicated as dark and pale. b) A space-filling representation of the (fluorene)$_{12}$ cluster. The oblate spheroidal shape of the cluster is apparent.

Also, the $M_2(C_f)_2$ (M = Mo or W) systems are slightly deformed from planar. Whilst the C_f centers of the (fluorene)$_{12}$ clusters in the Sn compound are located on the surface of a sphere, those in the Mo and W compounds are located on the surface of an oblate spheroid (a sphere that has been flattened at the poles) as shown in Figure 5. The Na^+ and NMe_4^+ cations and associated solvent molecules in the Mo and W compounds are located, as in the Sn compound, generally in the vicinity of the tetrahedral sites of the cubic close-packed (ccp) array of (fluorene)$_{12}$ clusters, but the detailed arrangements of the cations differ significantly. Whilst the centers of the 12 "face-on" macrocycles surrounding the large cavities in the Sn compound are located on the surface of a sphere, those in the Mo and W compounds have the shape of a prolate spheroid (one elongated along its polar axis).

The above compounds are not isolated "freak" structures, but rather are part of a very extensive series afforded by the ligand **I**, all with essentially the same "Swiss cheese" like arrangement; we have now isolated and carried out preliminary structural studies on over 30 different derivatives of this type. The metallic macrocyclic components, $[Sn^{IV}(OH)_2]^{2+}$, $[Mo^{VI}O_2]^{2+}$, and $[W^{VI}O_2]^{2+}$ in the examples described above, all of which carry an overall 2+ charge, can be replaced by $[Co^{II}(H_2O)_2]^{2+}$, $[Zn^{II}(H_2O)_2]^{2+}$, and $[Cd^{II}(H_2O)_2]^{2+}$ (and probably by other divalent cations) and also by $[Nb^{V}(O)(OH)]^{2+}$ cations. The Na^+ components can be replaced by other alkali-metal cations. Various nitrogenous cations such as NEt_3Me^+, NMe_3Et^+, NEt_4^+, the choline cation, protonated dabco (dabco = 1,4-diazabicyclo[2.2.2]octane), *N*-methyldabco$^+$, and *N*-ethyldabco$^+$, and also PMe_4^+ and $OS(Me)_3^+$ can replace the NMe_4^+ component. This collection of 30 or so solids all have in common the following features: a) the presence of tetra-anionic, chiral, 2:2 macrocycles, b) the presence of a fcc array of (fluorene)$_{12}$ clusters, c) collections of counter cations at the tetrahedral sites of the fcc array, and d) large solvent-filled voids at the octahedral sites. It is remarkable that the same unusual overall structure is observed for such a wide range of compositions and, in particular, for such widely differing metallic components of the macrocycle. We have no doubt that the range of combinations of components giving rise to this structure could be extended beyond the current 30 or so examples. It does appear that hydrophobic interactions between the fluorene units favor the formation of clusters of 12 and that this is a dominant contributor to the preference for the unusual "Swiss cheese" like structure.

Experimental Section

Synthesis of ligand LH_4 (**I**): Concentrated hydrochloric acid (3 mL) was added to a molten mixture of catechol (8.8 g, 0.08 mol), mercaptobenzoic acid (100 mg, 0.6 mmol), and fluorenone (3.6 g, 0.02 mol). The reaction mixture was heated at reflux at 140 °C for 8–9 h, after which time the reaction mixture had solidified to a pale yellow gum. The solid was redissolved in methanol (20 mL) and then added to 500 mL of boiling aqueous methanol (30 % methanol by volume). The solid obtained after cooling was recrystallized from dioxane and dried under vacuum. The purified crystals were isolated as colorless rod-shaped crystals.

Preparation of $(NMe_4)_{4/3}Na_{8/3}[(Sn(OH)_2)L_2]\cdot 14H_2O$: A solution containing **I** (50 mg, 0.13 mmol) and a large excess of NMe_4OH (0.25 mg, 2.7 mmol) in water (3 mL) was added to a solution of $SnCl_4\cdot 5H_2O$ (45.6 mg 0.13 mmol) and NaCl (15.2 mg 0.26 mmol) in water (3 mL). Green crystals began to separate after 24 h. The crystals were filtered off after 48 h, washed with water, and dried in air. Yield: 48.1 mg (45 %). Elemental analysis (%) calcd: C 40.0, H 4.6, N 1.1; found: C 40.0, H 4.5, N 1.1.

Preparation of $(NMe_4)_{4/3}Na_{8/3}[(WO_2)L_2]\cdot 10H_2O$: A solution of **I** (50 mg, 0.13 mmol) in MeOH (0.25 mL) was added to a solution of $Na_2WO_4\cdot 2H_2O$ (42.8 mg, 0.13 mmol) and NMe_4Cl (9.4 mg, 0.086 mmol) in water (10 mL). Yellow crystals began to separate after a few hours. The crystals were filtered off after 48 h, washed with water, and dried in air. Yield: 40.3 mg (40 %). Elemental analysis (%) calcd: C 43.1, H 4.2, N 1.2; found: C 43.1, H 4.2, N 1.5.

Preparation of $(NMe_4)_{4/3}Na_{8/3}[(MoO_2)L_2]\cdot 12H_2O$: A solution of **I** in MeOH(0.25 mL) was added to a solution of $Na_2MoO_4\cdot 2H_2O$ (31.5 mg, 0.13 mmol) and NMe_4Cl (9.4 mg, 0.086 mmol) in water (5 mL). Red crystals began to separate after a few hours. The crystals were filtered off after 48 h, washed with water, and dried in air. Yield:

38.2 mg (42 %). Elemental analysis (%) calcd: C 47.9, H 4.3, N 1.3; found: C 47.9, H 4.3, N 1.4.

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[4] a) Crystal data for $(NMe_4)_{4/3}Na_{8/3}[(Sn(OH)_2)_2L_2]\cdot 40\,H_2O$: $M_r = 1834.08$, cubic, $F432$, $a = 38.502(2)$ Å, $V = 57\,076(4)$ Å^3, $Z = 24$, $\theta_{max} = 27.48°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 130$ K, $\mu(Mo_{K\alpha}) = 0.629\ mm^{-1}$, 89 867 reflections measured, 5500 unique which were used in all calculations, 202 parameters, The structure was solved by direct methods (SHELX97[6]). $wR2 = 0.2317$ (all data) and $R1 = 0.0736$ ($I > 2\sigma(I)$), Flack parameter = 0.00(9). b) Crystal data for $(NMe_4)_{4/3}Na_{8/3}[(WO_2)_2L_2]\cdot 12\,MeOH\cdot 4\,H_2O$: $M_r = 1804.782$, cubic $Pa\bar{3}$, $a = 37.3271(3)$ Å, $V = 52\,008.3(7)$ Å^3, $Z = 24$; $\theta_{max} = 27.5°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 130$ K, $\mu(Mo_{K\alpha}) = 2.736\ mm^{-1}$, 323 865 reflections measured, 8659 unique which were used in all calculations, 349 parameters, The structure was solved by direct methods (SHELX97[6]). $wR2 = 0.3718$ (all data) and $R1 = 0.1137$ ($I > 2\sigma(I)$). c) Crystal data for $(NMe_4)_{4/3}Na_{8/3}[(MoO_2)_2L_2]\cdot 10\,MeOH\cdot 6\,H_2O$: $M_r = 1601.268$, cubic $Pa\bar{3}$, $a = 37.4755(11)$ Å, $V = 52\,631(3)$ Å^3, $Z = 24$; $\theta_{max} = 25°$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 130$ K, $\mu(Mo_{K\alpha}) = 0.367\ mm^{-1}$, 245 052 reflections measured, 5262 unique which were used in all calculations, 349 parameters, The structure was solved by direct methods (SHELX97[6]). $wR2 = 0.5124$ (all data) and $R1 = 0.1675$ ($I > 2\sigma(I)$).
CCDC-650911 ($(NMe_4)_{4/3}Na_{8/3}[(Sn(OH)_2)_2L_2]\cdot 40H_2O$), CCDC-650912 ($(NMe_4)_{4/3}Na_{8/3}[(WO_2)_2L_2]\cdot 12MeOH\cdot 4H_2O$), and CCDC-650910 ($(NMe_4)_{4/3}Na_{8/3}[(MoO_2)_2L_2]\cdot 10MeOH\cdot 6H_2O$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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