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Metallohosts with a Heart of Carbon

Edwin C. Constable,* Guoqi Zhang, Daniel Häussinger, Catherine E. Housecroft,* and Jennifer A. Zampese

Department of Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland

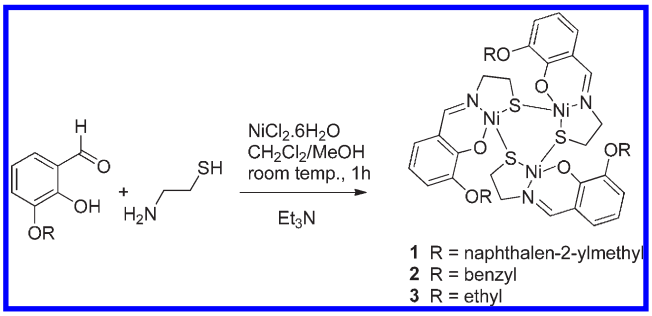
Supporting Information

ABSTRACT: Single-crystal X-ray diffraction studies have confirmed that Ni_3S_3-based molecular bowls prepared in one-pot reactions capture either CH_2Cl_2 or C_{60}. The nature of the pendant substituents (naphthalen-2-ylmethyl, benzyl, or ethyl) around the rim of the bowl dictates the formation of a 1:1 (bowl host−C_{60} guest) or 2:1 (capsule host−C_{60} guest) architecture. In $CDCl_3$, the trimeric complexes were found to be in equilibrium with dimeric analogues. For the naphthalen-2-ylmethyl-substituted host, NMR spectroscopic titration data confirmed a 1:1 host−C_{60} guest complex in 1,2-$Cl_2C_6D_4$ solution.

The assembly of metallomolecular containers allows the creation of beautiful architectures tailored to facilite specific reactions or catalytic processes.[1−7] The cavity size, shape, and ability to engage in noncovalent supramolecular interactions are of paramount importance for tuning the host−guest chemistry. Calixarene containers[7] are suited to hosting fullerenes,[8] and the selective complexation and purification of C_{60} and C_{70} is a major achievement in this area.[9] Fullerene separations have been achieved using cyclotriveratrylenes with pyrimidinone substituents capable of self-recognition through hydrogen bonding.[10] Other capsules that host fullerenes include those assembled from porphyrins,[11−13] concave aggregates of aromatic rings,[14,15] Cu-based molecular squares,[16] and Ni(II) complexes of tetraazaannulenes.[17] Fujita has engineered a coordination network that undergoes single-crystal fullerene inclusion.[18] We now report the assembly of Ni_3S_3-based bowls that capture a C_{60} molecule as either a 1:1 (bowl host−C_{60} guest) or 2:1 (capsule host−C_{60} guest) species.

The reaction of 2-hydroxy-3-(naphthalen-2-ylmethoxy)-benzaldehyde, 2-aminoethanethiol, and $NiCl_2 \cdot 6H_2O$ resulted in the formation of brown crystals. Structural analysis[19] revealed the assembly of the [3 + 3] complex **1** (Scheme 1 and Figure 1a). This crystallizes as $2(\mathbf{1}) \cdot CH_2Cl_2$ in the rhombohedral space group $R\bar{3}$ with one-third of the complex in the asymmetric unit. The latter contains one-sixth of a molecule of CH_2Cl_2, which is disordered about the $\bar{3}$ position (0,0,0), Wyckoff position *a*. The assembly of **1** and the chair conformation of the central Ni_3S_3 core mimic observations on related systems.[20−24] Each O,N,S-donor set of the ligand binds in a tridentate mode to a square-planar Ni^{2+} ion, and the S atom bridges two Ni centers. The bond lengths in the nickel coordination sphere are Ni1−O1 = 1.851(2) Å, Ni1−N1 = 1.887(3) Å, Ni1−S1 = 2.1870(10) Å, and Ni1−$S1^{ii}$ = 2.2141(10) Å. Molecule **1** has a bowl shape with the Ni_3S_3 unit as its base, and the CH_2Cl_2 molecule is encapsulated between two host molecules of **1** (Figure 1b).

Scheme 1. One-Pot Synthesis of Compounds 1−3



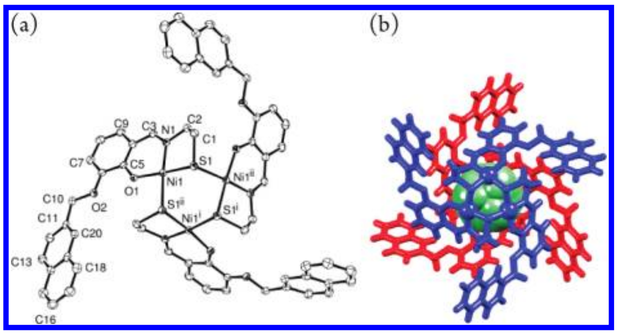


Figure 1. (a) Structure of **1** in $2(\mathbf{1}) \cdot CH_2Cl_2$ with ellipsoids plotted at the 30% probability level and H atoms omitted. Symmetry codes: (i) $2 - y, 1 + x - y, z$; (ii) $1 - x + y, 2 - x, z$. (b) Hosting of CH_2Cl_2 in the capsule formed by two molecules of **1** in $2(\mathbf{1}) \cdot CH_2Cl_2$.

The manner in which $2(\mathbf{1}) \cdot CH_2Cl_2$ assembles and the diameter of the capsule (~8.5 Å for the central cavity) suggested that **1** may host C_{60} (diameter ≈ 7 Å). A search of the Cambridge Structural Database (version 5.31 with August 2010 updates)[25] gave 23 structures with C_{60} in a bowl-shaped host or molecular capsule. Among these, calixarene[26] and functionalized macrocyclic metal complexes[27] predominate. In addition, there are structures with less well-defined molecular containers (e.g., porphyrins that by virtue of a twisted conformation or pendant substituents act as shallow vessels for C_{60} guests[28]).

Crystalline $2(\mathbf{1}) \cdot CH_2Cl_2$ was dissolved in 1,2-$Cl_2C_6H_4$/CH_2Cl_2 (4:1 by volume), and 1 equiv of C_{60} was added. After sonication and filtration, Et_2O was diffused into the filtrate, and crystals of $\mathbf{1} \cdot C_{60} \cdot 0.5(1,2\text{-}Cl_2C_6H_4) \cdot Et_2O$ grew in 3 days. Structural analysis[19] revealed that bowl-shaped **1** hosts a C_{60} molecule (Figure 2). The closest separations between the host and guest

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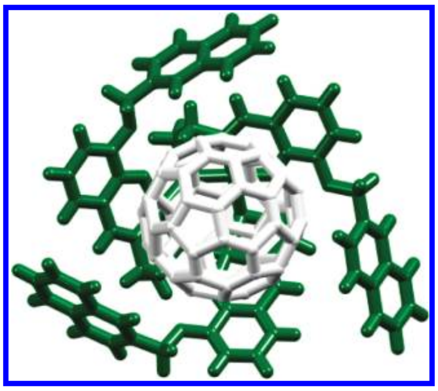

Figure 2. Bowl host **1**−C_{60} guest assembly in **1**·C_{60}·0.5(1,2-$Cl_2C_6H_4$)·Et_2O.

involve Ni···$C_{fullerene}$ [3.24(1)−3.54(1) Å] and N_{imine}···$C_{fullerene}$ [3.22(1)−3.41(2) Å] contacts. The naphthalene domains of **1** do not engage in face-to-face interactions with the C_{60} guest. Rather, the former are twisted in such a way that weak $CH_{naphthalene}\cdots\pi_{fullerene}$ interactions develop. However, these are not optimal, with the shortest contact between a CH and the centroid of a fullerene C_6 ring being 3.04 Å.

In order to investigate whether the assembly of the host−guest complex also occurs in solution, compound **1** was dissolved in 1,2-$Cl_2C_6D_4$. In this solvent, there was no evidence for the presence of a dimeric species (see below); no exchange peaks were observed in an NMR excitation spectroscopy (EXSY) spectrum. A series of NMR samples was prepared [see the Supporting Information (SI)] in which the number of molar equivalents of C_{60} with respect to **1** ranged from 0 to 7.5. A comparison of the ^{1}H NMR spectra for the samples (Table S1 in the SI) showed that the resonance assigned to the imine proton of **1** undergoes the greatest perturbation ($\Delta\delta_{imine}$) upon addition of C_{60} to the solution of **1**. This is in keeping with the proximity of the imine CH protons to the fullerene in the solid state (see above). The data in Table S1 also indicate that in solution, three of the naphthalene protons (H^{B1}, H^{B7}, and H^{B8}) sense the presence of the C_{60} molecule. In the titration curve for addition of C_{60} to 1 equiv of **1** (Figure S3 in the SI), the observed chemical shift difference $\Delta\delta_{imine}$ approaches the hypothetical value of 0.299 calculated for a 1:1 host−guest complex (see the SI). The Job's plot shown in Figure S4 also confirms the formation of a 1:1 complex. The dissociation constant for **1**·C_{60} is K_d = 2.1 mmol dm^{-3} (see the SI).

We investigated the effect of changing the substituent from naphthalen-2-ylmethyl to benzyl. Complex **2** (Scheme 1) was prepared in a manner analogous to that for **1** starting from 3-(benzyloxy)-2-hydroxybenzaldehyde. Crystals of **2**·CH_2Cl_2 were grown by evaporation of a CH_2Cl_2/MeOH solution of **2**, and the structure determination confirmed the presence of a [3 + 3] complex (Figure S1). Unlike **1**, **2** does not host a CH_2Cl_2 molecule in a dimeric capsule but instead forms centrosymmetric dimers by π stacking (separation of 3.50 Å) of the NiNCCCO chelate ring and adjacent arene rings (Figure 3a). Solid **2** was dissolved in 1,2-$Cl_2C_6H_4$/CH_2Cl_2 (4:1 by volume), and ~0.5 equiv of C_{60} was added. After sonication and filtration, Et_2O was diffused into the filtrate. Structural analysis of the black plates that grew confirmed a formulation of 2(**2**)·C_{60}·1,2-$Cl_2C_6H_4$·0.25H_2O and the assembly of molecular capsules hosting C_{60}. The compound crystallizes in the $P\bar{1}$ space group, and the asymmetric unit contains two independent molecules of **2** and two half-C_{60} molecules. Operation through inversion centers completes two independent 2(**2**)·C_{60} capsules (Figure 3b). In one capsule, a benzyl group is disordered and was modeled over two sites. The most important host−guest interactions involve (i) short Ni···C contacts [3.380(7)−3.672(13) Å] and (ii) face-to-face π interactions between the fullerene and the central arene rings in **2**. In one of the independent molecules, there is an edge-to-face contact (2.54 Å) between a $CH_{benzyl\text{-}ring}$ unit and a six-membered ring of the fullerene.

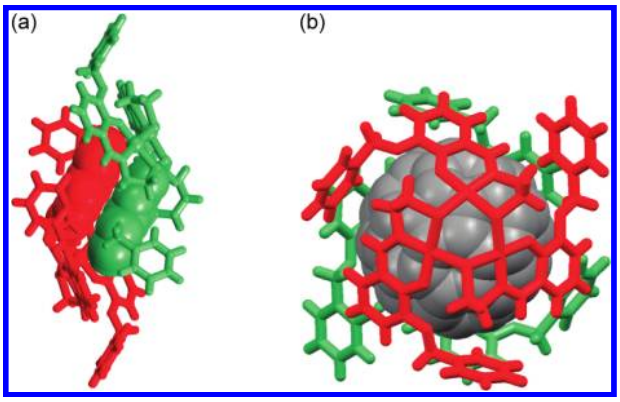

Figure 3. (a) Centrosymmetric dimers of **2** supported by π stacking. (b) One of two independent 2(**2**)·C_{60} molecular capsules in 2(**2**)·C_{60}·1,2-$Cl_2C_6H_4$·0.25H_2O.

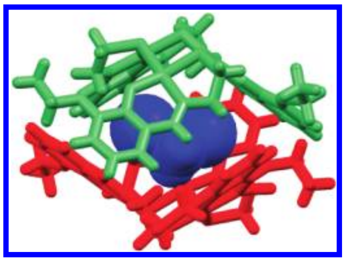

Figure 4. Hosting of CH_2Cl_2 in the capsule formed by two independent molecules of **3** in 2(**3**)·CH_2Cl_2.

Since it was difficult to assess the importance of the pendant aromatic substituents in facilitating the assembly of the host−guest complexes, we prepared **3** (Scheme 1) having ethyl groups as the substituents. The method of preparation was as for **1** and **2**, starting from 3-ethoxy-2-hydroxybenzaldehyde, and structural characterization[19] of brown crystals of **3** confirmed the formation of a [3 + 3] complex (Figure S2). The compound crystallizes as 2(**3**)·CH_2Cl_2, with two independent molecules of **3** forming a capsule around a CH_2Cl_2 molecule (Figure 4). The bond lengths in the coordination sphere of atom Ni1a [Ni1a−O1a = 1.843(2) Å, Ni1a−N1a = 1.881(3) Å, Ni1a−S1a = 2.1896(10) Å, Ni1a−S2a = 2.2265(10) Å] are representative of those for each independent Ni. The CH_2Cl_2 molecule is disordered over two positions, with the two Cl sites in common. The six closest Ni···Cl host···guest contacts lie in the range 3.6623(17)−3.8634(17) Å.

Crystalline 2(**3**)·CH_2Cl_2 was dissolved in 1,2-$Cl_2C_6H_4$/CH_2Cl_2, and 1 equiv of C_{60} was added. Following sonication, the mixture was filtered, and Et_2O was allowed to diffuse into the fitrate, yielding crystals of 2(**3**)·C_{60}·CH_2Cl_2 within a few days. Structural analysis[19] revealed that **3** hosts either a C_{60} or CH_2Cl_2

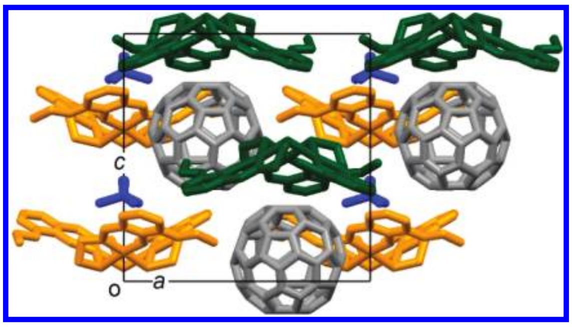

Figure 5. Partial packing diagram for $2(\mathbf{3})\cdot C_{60}\cdot CH_2Cl_2$.

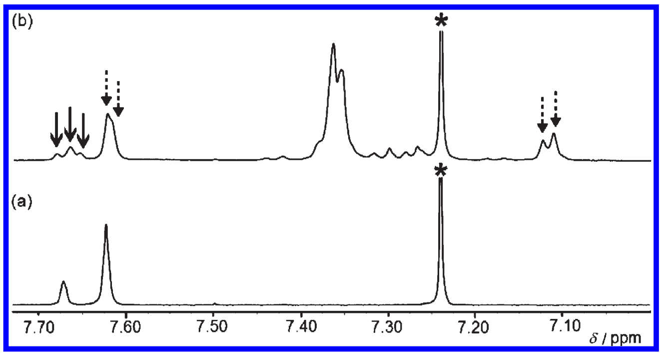

Figure 6. Part of the 400 MHz ^{1}H NMR spectra ($CDCl_3$) of **3** (a) alone and (b) after addition of **2**. Signals from the N=CH protons are marked as follows: trimers, hashed arrows; dimers, solid arrows. * indicates residual $CHCl_3$.

molecule (Figure 5). The bowl host−C_{60} guest assembly is similar to that observed for $\mathbf{1}\cdot C_{60}\cdot 0.5(1,2\text{-}Cl_2C_6H_4)\cdot Et_2O$ but contrasts with the 2:1 (capsule host−C_{60} guest) species observed in $2(\mathbf{2})\cdot C_{60}\cdot 1,2\text{-}Cl_2C_6H_4\cdot 0.25H_2O$. $2(\mathbf{3})\cdot C_{60}\cdot CH_2Cl_2$ crystallizes in the trigonal $P31c$ space group, and the asymmetric unit contains one-third of each of the two independent molecules of **3** and one-third of both CH_2Cl_2 and C_{60}. Each complete molecule is generated by rotation about the threefold axis passing through the center of each Ni_3S_3 unit (which causes threefold disorder of the CH_2Cl_2). The $\mathbf{3}\cdot CH_2Cl_2$ domains stack parallel to the *c* axis, with the Cl atoms of the guest molecule facing into the cavity of **3** [closest Ni···Cl contact = 3.275(3) Å]; the CH_2Cl_2 H atoms interact with S atoms of the adjacent bowl (shortest S···H contact = 2.95 Å). The fullerene nestles into the bowl with shortest Ni···C contacts of 3.674(10) and 3.544(7) Å.

Although the solid-state structures of **1**, **2** and **3** all feature a trimeric nickel(II) complex, the electrospray ionization mass spectrometry (ESI-MS) data and NMR spectra in $CDCl_3$ solution are consistent with more than one solution species in each case. The ^{1}H and ^{13}C NMR spectra of dissolved crystals of $2(\mathbf{3})\cdot CH_2Cl_2$ show two sets of signals (Figure 6a; also see the SI). The subspectra of the two components are very similar (e.g., for the imine H, singlets appear at 7.67 and 7.62 ppm in a reproducible ratio of 1:3). Similarly, NMR spectra of $CDCl_3$ solutions of **1** or $\mathbf{2}\cdot CH_2Cl_2$ showed two sets of signals in a ratio of 1:4, the latter being concentration-dependent. These results are consistent with those observed for a related Ni_3S_3 system for which the minor component has been proposed to be dimeric.[21] Using pulsed-gradient spin-echo (PGSE) diffusion NMR spectroscopy, we confirmed that the minor species in a $CDCl_3$ solution of **3** is smaller in size than the major component. Diffusion coefficients (D) of 8.38×10^{-10} and 9.46×10^{-10} $m^2\ s^{-1}$ were determined for the major and minor components (Figure S5). The relative sizes of the species follow from the Stokes−Einstein equation. The ratio of the D values is 0.885, which leads to a ratio of molecular masses for the two species of 0.693, in reasonable agreement with a calculated value of 0.667 for M(dimer)/M(trimer). EXSY spectra were recorded for a $CDCl_3$ solution of **3** with mixing times of 250 ms, 500 ms, 1 s, and 2 s, and with the approximation of initial rates, the rate constants k_f and k_b in eq 1 were determined to be 0.0254 and 0.0577 s^{-1}, respectively.

$$2[\mathrm{NiL}]_3 \underset{k_b}{\overset{k_f}{\rightleftarrows}} 3[\mathrm{NiL}]_2 \qquad (1)$$

Attempts to separate the two species by chromatography resulted in only one brown fraction, the ^{1}H NMR spectrum of which was identical to the original spectrum of the bulk sample. The ESI-MS spectra of dissolved crystalline $\mathbf{2}\cdot CH_2Cl_2$ and $2(\mathbf{3})\cdot CH_2Cl_2$ revealed peak envelopes corresponding to $[Ni_2L_2 + Na]^+$, $[Ni_3L_3 + Na]^+$, and $[Ni_4L_4 + Na]^+$. We propose that the latter is better formulated as $[2\{Ni_2L_2\} + Na]^+$ rather than as a single tetrameric complex. The matrix-assisted laser desorption ionization−time of flight (MALDI−TOF) mass spectra also indicated the presence of trinuclear and dinuclear complexes.

The presence of a dynamic equilibrium was also tested by adding benzyl derivative **2** to a $CDCl_3$ solution of **3**. Figure 6a shows the imine resonances of the trinuclear and dinuclear species of **3**. Upon addition of **2**, seven imine signals were observed (Figure 6b), consistent with an equilibrium mixture of homo- and heteroleptic ethoxy and benzyloxy di- and trinuclear species.

In summary, we have shown that Ni_3S_3-based bowls prepared in one-pot syntheses can capture either CH_2Cl_2 or C_{60}. Although numerous examples of host−fullerene guest complexes have previously been structurally characterized, this report is a rare example in which the size and shape of the cavity of the metallohost complements that of the C_{60} molecule. The formation of 1:1 (bowl host) or 2:1 (capsule host) assemblies with the fullerene depend upon the pendant substituents. NMR spectroscopic titration data and a Job's plot confirmed the formation of a 1:1 host−guest complex $\mathbf{1}\cdot C_{60}$ in $1,2\text{-}Cl_2C_6D_4$ solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details, full characterization data for all new compounds, Figures S1−S5, Table S1, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

edwin.constable@unibas.ch; catherine.housecroft@unibas.ch

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