Metal-Containing Rigid Concave Surfaces: An Entry to the Confinement of Globular Molecules

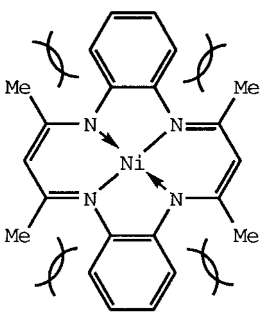
Philip C. Andrews, Jerry L. Atwood, Leonard J. Barbour, Peter J. Nichols, and Colin L. Raston*

Abstract: The nickel macrocycle 5,7,12,14-tetramethyldibenzo[*b*,*i*]-[1,4,8,11]tetraazacyclotetradecinenickel(II), which possesses two divergent concave surfaces, is a versatile receptor molecule for the formation of supramolecular arrays with globular molecules. This is demonstrated for three disparate main group cage molecules C_{60}, 1,2-dicarbadodecaborane(12) and P_4S_3: the macrocycle interacts with two cages, or one cage perched in each cavity, or self-associates as a dimeric divergent receptor with a cage perched in the available cavity of each macrocycle.

Keywords: cage compounds · fullerene · host–guest chemistry · macrocycles · nickel · supramolecular chemistry

Introduction

The self-assembly of globular molecules is important for the formation of complex inclusion nanostructures, in their crystal engineering, and in their purification.[1–4] A major challenge in the formation of supermolecules that involve clusters of this type is to gain control over the inherently weak host–guest interactions. Some advances have recently been made in fullerene[1,3–11] and carborane[2,11] host–guest complexation which use container molecules, such as calixarenes,[1,3–8] cyclotriveratrylene[7,9,10] and cyclodextrins.[11,12] We now report on the nickel(II) macrocycle 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclo-tetradecinenickel(II), [Ni(TMTAA)] (**1**), which has two divergent concave surfaces[13] and is a versatile receptor molecule. It can act as a divergent heterotopic receptor, or in its self-associated dimeric form, as a divergent homotopic receptor. Complexation with three disparate classes of globular main-group cage molecules, namely C_{60}, 1,2-dicarbadodecaborane(12), and the phosphorus chalcogenide P_4S_3, results in either a bent sandwich supermolecule in which two macrocycles shroud a single cage, or a polymeric structure containing cage–cage interactions. The P_4S_3 complex is particularly noteworthy as it is, to our knowledge, the first authenticated inclusion complex of a Group 15 chalcogenide cage species. This new approach offers a wide applicability for the confinement of globular species in general, and the ability to form an inclusion complex with a chalcogenide species is particularly significant for a possible use of such molecules with rigid curved surfaces in the regulation and stabilisation of nanoparticles of binary compounds that exhibit size-dependent functionality.[14]



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The two divergent concave surfaces of [Ni(TMTAA)], Figure 1, arise from otherwise unfavourable non-bonding interactions between the methyl groups and the hydrogen atoms on the aromatic rings *ortho* to the N atoms. The binding of globular cage molecules that have a complementary curvature to these shallow saddle-shaped voids is favoured entropically over the binding of solvent molecules, and importantly, no energy is required for the pre-organisation of the rigid macrocycle prior to complexation with such species. Fullerene C_{60}, 1,2-dicarbadodecaborane(12) (o-$C_2B_{10}H_{12}$), and P_4S_3 are cage molecules that have a comparable surface complementarity with [Ni(TMTAA)].

Results and Discussion

Slow evaporation of toluene solutions of the macrocycle and these clusters affords discrete crystalline complexes; either as a 1:1 complex, [(C_{60})Ni(TMTAA)], or as a 1:2 complex, [X{Ni(TMTAA)}$_2$], (where $X = o$-$C_2B_{10}H_{12}$ or P_4S_3)

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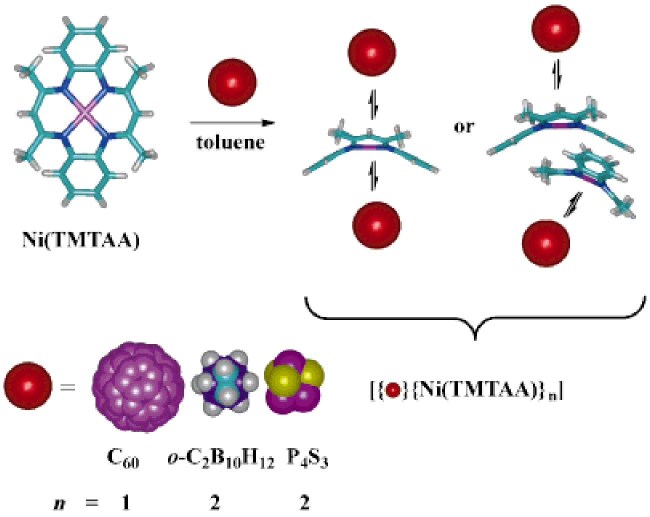

Figure 1. Synthesis of $[(C_{60})Ni(TMTAA)]$, and $[X\{Ni(TMTAA)\}_2]$, X = o-$C_2B_{10}H_{12}$ or P_4S_3.

(Figure 1). In all three solid state structures the cage molecules reside, at the van der Waals limit, in the saddle of two [Ni(TMTAA)] molecules to produce bent, sandwich-like supermolecules with the two host molecules adjacent to each other.[15] The dihedral angle subtended by the two nickel centres and the centroid of the clusters is significantly less than 180°, that is 83.4, 109.2 and 102.3°, respectively, for encapsulated C_{60}, o-$C_2B_{10}H_{12}$ and P_4S_3. The interplay of the supermolecules in the extended structures differs for the 1:1 and 1:2 complexes. In the 1:1 complexes, the asymmetric unit is $[(C_{60})Ni(TMTAA)]$ such that crystallographic symmetry places the fullerene in the saddle of one [Ni(TMTAA)] molecule with the methyl groups directed towards it and in the opposite saddle of another [Ni(TMTAA)] molecule so that the overall host–guest contacts form a continuous zigzag array (Figure 2 top). Molecular mechanics[16] show that for the 1:1 complex, and indeed, for the 1:2 complexes (see below), there is sufficient space on the surface of the cluster to bind a third [Ni(TMTAA)] macrocycle. However, only a phenyl ring of a third [Ni(TMTAA)] molecule is at the van der Waals limit, and it is nearly coplanar with a C_5 ring of C_{60}; the ring centroids are separated by 3.50 Å. The remaining space around each fullerene is associated with inter-fullerene interactions. Each fullerene has contacts to five other fullerenes, with centroid–centroid distances of 9.98–10.07 Å (Figure 2 bottom). There is a sixth fullerene at a distance of 12.81 Å, which, together with the corrugated rather than planar structure of the fullerene sheets, is a departure from the hexagonal close packing of the fullerenes. The structure embodies a balance between host–cage interactions, utilising both concave surfaces and cage–cage interactions, as found in cyclotriveratrylene[9, 10] and calix[6]arene[4] complexes of C_{60}. It is the first structurally authenticated metal–macrocycle complex of C_{60} in which the metal centre is not directly bound to the fullerene. Interestingly, the use of a supported porphyrin–zinc(II) complex for the separation of endohedral metallofullerenes has been reported.[17]

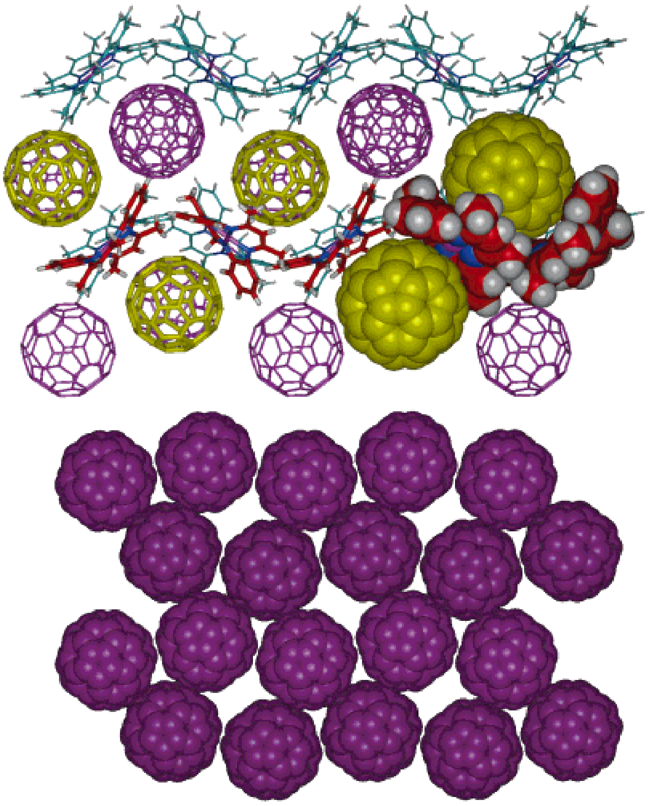

Figure 2. Projections of the structure of $[(C_{60})Ni(TMTAA)]$ showing the supramolecular arrays based on host–guest interactions (top), and cage–cage interactions (bottom).

The 1:2 complexes, $[X\{Ni(TMTAA)\}_2]$, X = o-$C_2B_{10}H_{12}$ or P_4S_3, are isostructural, crystallising in the same space group, *Pnma*, and have similar cell dimensions. The sandwich supermolecules form extended structures by the locking together of pendant phenyl rings of adjacent [Ni(TMTAA)] supermolecules; the methyl groups are all directed towards the cage (Figure 3). The open surfaces of the clusters in the 1:2 supermolecules now involve van der Waals contacts with the hydrogen atoms of four [Ni(TMTAA)] moieties and are without contacts to other cages (Figure 3). Alternatively, the structures can be viewed as two associated [Ni(TMTAA)] molecules which act as a receptor for two cage molecules (see below).

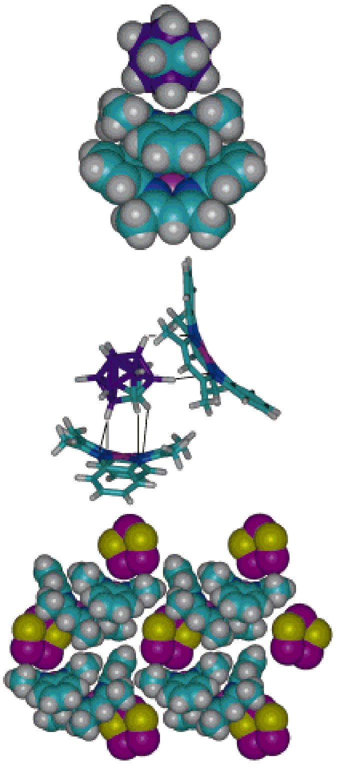

Figure 3. Projection of the supramolecular arrays found in $[X\{Ni(TMTAA)\}_2]$, (top) and (center) X = o-$C_2B_{10}H_{12}$ and (bottom) X = P_4S_3.

The carborane is disordered with about 70 and 30 % occupancy of two sites. The dominant orientation is shown in Figures 3 top and 3 center. Hydrogen atoms were not located and are not included in the structure calculations. However, if the H atoms are placed in idealised positions, the distances C–H$\cdots$N $\approx$ 3.0 Å and B–H$\cdots$N = 2.7 Å (equidistant to two N atoms) for a single triangular face of the cluster to one N_4 plane, and B–H$\cdots$N $\approx$ 2.9 and 3.4 Å (each equidistant to two N atoms) for an edge of the cage to the N_4 plane of the other macrocycle. These distances are significantly longer than those for H atoms of o-$C_2B_{10}H_{12}$ interacting with N and O donors of a crown ether as hydrogen bonds: BH$\cdots$N = 2.34 Å, CH$\cdots$O = 2.36 and 2.49 Å.[18]

Disorder was also evident in the P_4S_3 complex which was resolved into two components related by a mirror plane through a P–P bond perpendicular to the crystallographic mirror plane through the P(unique)–S bond. In the dominant orientation (Figure 3 bottom, 66% of clusters) a sulfur atom and the unique phosphorus are closest to the metal centre of one [Ni(TMTAA)] molecule at 3.22 and 3.77 Å, respectively. A phosphorus in the P_3 ring of P_4S_3 is 3.32 Å from the metal centre in the second [Ni(TMTAA)] molecule. The other two phosphorus atoms of the P_3 ring are 3.24 Å from the methyl hydrogen atoms of this second [Ni(TMTAA)] molecule. The third and fourth [Ni(TMTAA)] molecules have phenyl hydrogen atoms close to the two phosphorus atoms of the P_3 ring (3.57 Å) and the two adjacent sulfur atoms (3.43 Å), respectively. In the other orientation the positions of the unique phosphorus and the sulfur atom closest to the first [Ni(TMTAA)] are exchanged: the phosphorus atom closest to the second [Ni(TMTAA)] moves across the mirror plane and is replaced by two sulfur atoms. For comparison we note that the same cage molecule in [Ni(P_4S_3){tris(2-(diphenylphosphino)ethyl)amine)}] is in fact bound to the metal centre through the unique phosphorus of the cage molecule with Ni–P = 2.072(5) Å.[19] Other attempts to complex this cage resulted in cluster fragmentation.[20] Any metal-to-cage interaction in the present structure is weak, and the P_4S_3 cage-to-[Ni(TMTAA)] contacts are close to the van der Waals limit.

The self-assembly of two [Ni(TMTAA)] moieties at 90° to each other is interesting in its own right and is driven by the complementarity of curvature of the interlocking components, as well as by Ni$\cdots\pi$-arene interactions previously overlooked in the structure of [Cu(TMTAA)].[21] The Ni atom of one macrocycle sits below a phenyl ring of the other macrocycle. For [X{Ni(TMTAA)}$_2$], X = o-$C_2B_{10}H_{12}$ and P_4S_3, and [Cu(TMTAA)][21] Ni/Cu$\cdots$phenyl centroid = 3.55,3.51 and 3.49 Å with Ni/Cu$\cdots$C = 3.78–3.85, 3.73–3.84 and 3.67–3.83 Å, respectively. The second Ni atom sits above the π-imine system of the first macrocycle. For [X{Ni(TMTAA)}$_2$], X = o-$C_2B_{10}H_{12}$ and P_4S_3, and [Cu(TMTAA)][21] Ni/Cu$\cdots\pi$-imine geometric centre = 3.66, 3.60 and 3.29 Å; Ni/Cu$\cdots$C = 3.84–3.85, 3.76–3.77 and 3.23–3.53 Å and Ni/Cu$\cdots$N = 4.03, 4.01 and 3.83 Å, respectively.

Even for an excess of [Ni(TMTAA)], the 1:1 complex of C_{60} is formed, rapidly crystallising from solution as a result of its low solubility in toluene. This is consistent with the polarisation of the fullerene on host–guest formation in solution and results in the aggregation of the fullerene,[6, 7, 10] to give a solid-state structure containing both host–guest and fullerene–fullerene interactions. The 2:1 complexes of o-$C_2B_{10}H_{12}$ or P_4S_3 are favoured, even for an excess of the cage, and indeed these conditions are best for driving the precipitation of the complexes from solution, because the complexes are more soluble than [Ni(TMTAA)] itself.

Conclusion

[Ni(TMTAA)] is an adaptable molecule as it forms both 1:1 and 2:1 complexes with globular molecules. We note that C_{60} has curvature complementarity more closely matched to the phenyl face of the macrocycle and that for the smaller cages, o-$C_2B_{10}H_{12}$ and P_4S_3, curvature complementarity is closer for the methyl face (Figure 1). It may be that the 1:1 complex is formed for C_{60} because the favourable docking of a fullerene with the phenyl face of the macrocycle blocks the association of the macrocycles, which is favoured through this face. In contrast, any preferential binding of the smaller cages with the methyl face could leave the phenyl face free for association with another macrocycle.

The self-assembly of three types of cage molecules with [Ni(TMTAA)] demonstrates that this macrocycle is a versatile receptor molecule for globular species, and has the added concomitant capability of self-dimerisation. In establishing ground rules, the use of more easily oxidised metal(II) derivatives of TMTAA^{2-} offers a direct electron-transfer route to supramolecular arrays of reduced cages with the oxidised macrocycle as the counterion, M^{2+}(TMTAA) $\rightarrow$ [M^{2+n}(TMTAA)]$^{n+}$, and the prospect of generating materials with novel functions.

Experimental Section

Synthesis of [(C_{60})Ni(TMTAA)] and [X{Ni(TMTAA)}$_2$] (X = o-$C_2B_{10}H_{12}$ or P_4S_3): Equimolar amounts of cage compound and [Ni(TMTAA)] were dissolved in warm (60 °C) toluene. The solutions were mixed, cooled to room temperature and allowed to evaporate slowly. The title compounds precipitated and were collected and washed with toluene or hexane. [(C_{60})Ni(TMTAA)] precipitated in the presence of excess [Ni(TMTAA)], whereas the other cage compounds are more soluble than [Ni(TMTAA)].
[(C_{60})Ni(TMTAA)]: M.p. > 400 °C; anal. calcd: C 87.79, H 1.98, N 5.00; found: C 88.16, H 1.62, N 5.35.

[(P_4S_3){Ni(TMTAA)}$_2$]: M.p. > 200 °C (decomp); anal. calcd: C 51.69, H 4.34, N 10.96; found: 51.76, H 4.39, N 11.00.

[(o-$C_2B_{10}H_{12}$){Ni(TMTAA)}$_2$]: M.p. 218 °C (decomp); anal. calcd: C 58.37, H 5.96, N 11.84; found: C 58.89, H 6.39, N 12.20.

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[15] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-100893. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
[(C_{60})Ni(TMTAA)]: (Siemens SMARTCCD diffractometer, $T = 173$ K): $M = 1121.75$ g mol^{-1}; crystal dimensions: $0.40 \times 0.20 \times 0.15$ mm; monoclinic, $P2(1)/n$, $a = 14.6328(9)$, $b = 17.5541(11)$, $c = 18.2846(11)$ Å, $\beta = 107.7090(10)^\circ$, $V = 4474.1(5)$ Å^3; $Z = 4$; $\rho = 1.665$ g cm^{-3} ; $F(000) = 2280$, $\mu_{\mathrm{Mo}} = 5.01$ cm^{-1}, $2\theta_{\mathrm{max}} = 50^\circ$; final R, $R_{\mathrm{w}} = 0.0855$, 0.1349 [statistical weights]; unique reflections = 25471, observed = 9723 ($I > 3\sigma(I)$).
[(o-$C_2B_{10}H_{12}$){Ni(TMTAA)}$_2$]: [Siemens SMART CCD, $T = 173$ K]: $M = 946.51$; crystal dimensions: $0.40 \times 0.25 \times 0.25$ mm; orthorhombic, $Pnma$, $a = 19.3677(10)$, $b = 17.3458(9)$, $c = 13.8163(7)$ Å, $V = 4641.6(4)$ Å^3; $Z = 4$; $\rho = 1.354$ g cm^{-3}; $F(000) = 1976$, $\mu_{\mathrm{Mo}} = 8.55$ cm^{-1}; $2\theta_{\mathrm{max}} = 50^\circ$; final R, $R_{\mathrm{w}} = 0.111$, 0.2079 [statistical weights]; unique reflections = 25886, observed = 5293 ($I > 3\sigma(I)$).
[(P_4S_3){Ni(TMTAA)}$_2$]: [Nicolet R3m/v diffractometer, $T = 173$ K]: $M = 1022.36$; crystal dimensions: $0.20 \times 0.15 \times 0.15$ mm; orthorhombic, $Pnma$, $a = 19.00(2)$, $b = 17.31(2)$, $c = 13.626(9)$ Å, $V = 4481(11)$ Å^3; $Z = 4$; $\rho = 1.52$ g cm^{-3} ; $F(000) = 2112$, $\mu_{\mathrm{Mo}} = 11.7$ cm^{-1}; $2\theta_{\mathrm{max}} = 45^\circ$; final R, $R_{\mathrm{w}} = 0.080$, 0.059 [statistical weights]; unique reflections = 3305, observed = 1394 ($I > 3\sigma(I)$).

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