

Confinement of C₇₀ in an extended saddle shaped nickel(II) macrocycle

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Saddle shaped {2,3,6,8,11,12,15,17-octamethyldibenzo-[b,i]1,4,8,11-tetraaza(1,4)annulene}nickel(II), Ni(OMTAA), acts as a heterotropic divergent receptor molecule with C₇₀ forming a 1 : 1 complex in the solid state, where the extended supramolecular array consists of zigzag alternating C₇₀-Ni(OMTAA) chains and corrugated sheets of close contact C₇₀ molecules.

Host-guest chemistry of globular molecules including fullerenes,¹⁻¹⁸ carboranes,¹⁹ and P₄E₃ (E = S, Se),^{1,20} has recently gained prominence in forming inclusion nanostructures, crystal engineering, and in their purification. A major challenge in forming supermolecules involving such molecules is gaining control over the inherently weak host-guest interactions. Complementarity of curvature and maximising the number of points/area of van der Waals contact are important factors in the formation of stable host-guest complexes, at least in the absence of hydrogen bonding, and electrostatic and coordination interactions. Competition between the host-host, host-guest and guest-guest interactions is important in determining the structure of the resulting supramolecular array. This is particularly evident in fullerene chemistry where interfullerene interactions play a major role in the structures of inclusion complexes.⁵⁻¹⁵ The interactions of solvent with all species and crystal packing forces provide additional variables.

Recently we reported that Ni(TMTAA), Fig. 1 (R = H), acts as a divergent heterotropic receptor with C₆₀, 1,2-dicarbododecaborane and the chalcogenides P₄S₃ and P₄Se₃;^{1,20} the saddle shape of the host arises from otherwise unfavourable interactions between the -{NC(Me)}₂CH- methyl groups and the hydrogen atoms on the aromatic rings. Here we report the structure of a 1 : 1 inclusion complex of C₇₀ in an extended nickel(II) macrocycle, Ni(OMTAA) (Fig. 1, R = Me). It is noteworthy that there is only one structurally authenticated inclusion complex of C₇₀, a 2 : 1 complex with calix[6]arene.⁵

[Ni(OMTAA)C₇₀] crystallised from a 2 : 1 toluene solution of the two constituents with the host in excess.[†] The X-ray structure determination[‡] revealed that a 1 : 1 complex formed, a molecule of each component comprising the asymmetric unit. Surprisingly it is isostructural to that complex formed between Ni(TMTAA) and C₆₀. It appears that the larger macrocycle and fullerene allows for a similar packing to that of the smaller macrocycle and fullerene. However, the interplay between the fullerene and the host is, in the present structure, complicated somewhat by the long axis present in C₇₀. There are close contacts between the two supramolecular synthons involving the nickel centre, Ni...C 3.20(1) and 3.22(1) Å for the phenylene and {NC(Me)}₂CH- lined faces respectively. The extended structure has each fullerene in each saddle in a zigzag motif, Fig. 2. A third macrocycle-fullerene interaction is

observed between a pseudo-cavity, defined by the backside face of a phenyl ring and one methyl group from each of the {NC(Me)}₂CH- moieties, and a third fullerene residing with its long axis running within the long pseudo-mirror-plane of the Ni(OMTAA) molecule, Fig. 2(a). The interaction is comprised of a π...π stacking of a five membered ring of the fullerene and the phenyl of the host, ring centroid-ring centroid distance 3.30(1) Å; methyl groups in close contact with the fullerene have C...C distances at 3.44(1) and 3.20(1) Å respectively for

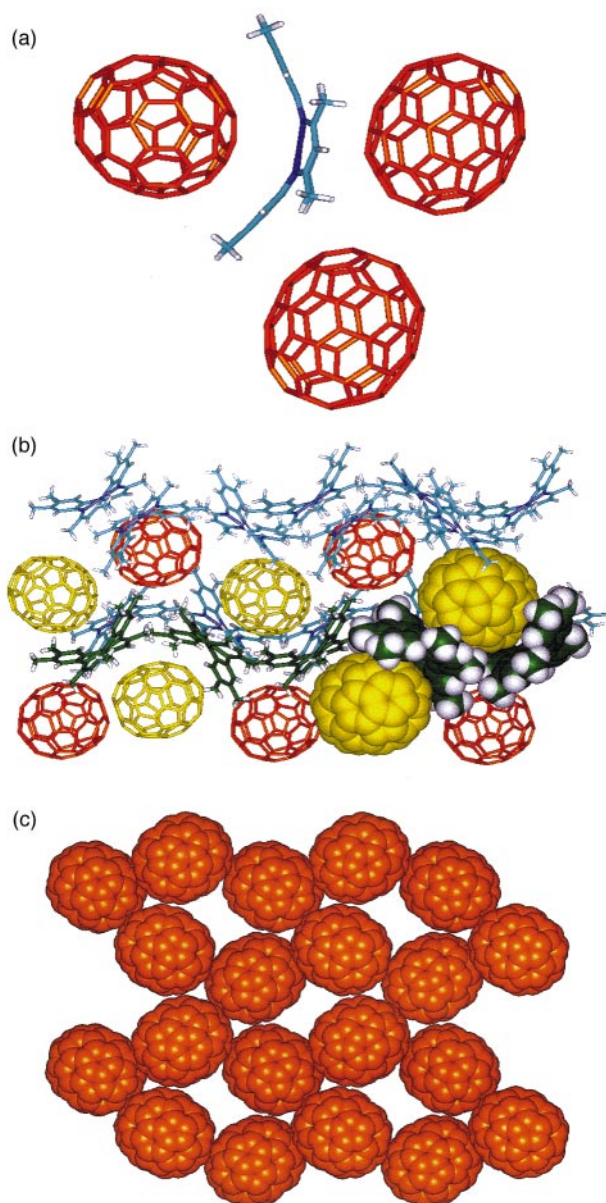


Fig. 2 Structure of [Ni(OMTAA)C₇₀] showing (a) three guest interactions for each macrocycle. (b) The alternating sheets of close-contact fullerenes and Ni(OMTAA) molecules respectively. (c) The corrugated sheet of close contact fullerenes in [Ni(OMTAA)C₇₀].

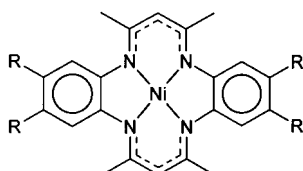


Fig. 1 Ni(TMTAA), R = H, and Ni(OMTAA), R = CH₃.

{NC(Me)}₂CH– and 3.17(1) and 2.93(1) Å for the phenyl methyls.

Rather than lie flat across the phenylene face of Ni(OMTAA), the C₅ axis of C₇₀ intersects with NiN₄ plane at 33.1(1)° along the valley formed by the phenyl rings, and at 15.1(1)° across the valley, and lies almost flat against the {NC(Me)}₂CH– face, corresponding angle 15.4(1)°. The elliptical fullerene makes close contact with five other fullerenes forming a two-dimensional corrugated sheet consisting of slightly offset fullerene chains, Fig. 2(b). Within each ridge or trough, the C₅ axes of each C₇₀ are arranged in a zigzag fashion with a five-membered ring of one fullerene and a six-membered ring of another fullerene in the chain π -stacking, albeit with a slight deviation from coplanarity, making a point of closest contact at 3.14(1) Å. One of the poles of the fullerene, *i.e.* the five-membered ring through which the C₅ axis passes, forms a classical $\pi\cdots\pi$ stacking interaction with that of an adjacent fullerene such that one of the participating fullerenes is on a ridge, the other in a trough. The fourth and fifth close contact points to each fullerene run at right angles to the grain of the sheet, as defined by the ridges and troughs, and continue on to form a chain which has the C₅ axes aligned in a zigzag fashion and contiguous fullerenes alternating between ridge and trough positions. These points are those of closest contact to each fullerene, C \cdots C 3.05(1) Å. Interestingly, the C₅ axes of the C₇₀ in this structure and one of the C₅ axes of C₆₀ in the [Ni(OMTAA)C₆₀] structural analogue are aligned similarly within their respective supramolecular arrays despite the spherical nature of the C₆₀.

The pole of the fullerene not involved in the $\pi\cdots\pi$ interfullerene interaction, aligns itself with one of the {NC(Me)}₂CH– methyl groups making a C \cdots C point of close contact at 3.05(1) Å. Four other fullerene molecules make van der Waals contact with the phenylmethyl and {NC(Me)}₂CH– methyl groups of Ni(OMTAA). The phenylmethyl groups at one end of the Ni(OMTAA) molecule make two van der Waals contact points with those of an adjacent molecule of opposite curvature to form an S-shaped fragment –CH₃ \cdots CH₃ 2.88(1) Å. A second host–host interaction involves offset side-by-side molecules, again with opposing curvature, such that the central {NC(Me)}₂CH– proton aligns itself with the aromatic proton of its neighbour H \cdots H 2.91(1) Å. {NC(Me)}₂CH– methyl groups make close contact at 2.89(1) Å and crystallographic symmetry makes the third contact point identical to the first. Ni(OMTAA) makes van der Waals contact with two further host molecules through the methyl groups on both the phenyl and {NC(Me)}₂CH– moieties. Consequently, the supramolecular array consists of sheets of fullerene layered between intercalating sheets of Ni(OMTAA) [Fig. 2(c)].

The 1:1 complex [Ni(OMTAA)C₇₀] is isostructural with [Ni(OMAA)C₆₀] despite the difference in host shape and increased host–host interaction. This finding gives insight into now studying the supramolecular chemistry of higher fullerenes *via* extending the arms of the nickel macrocycle to accommodate the large fullerenes in an isostructural system.

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Notes and references

† [Ni(OMTAA)C₇₀] was obtained by mixing hot toluene solutions of the nickel(II) macrocycle (20 mg, 0.04 mmol) and C₇₀ (16 mg, 0.02 mmol) and cooling the resultant solution slowly whereupon black plate-like crystals of the complex were deposited. Cold toluene was added quickly to the cooled mixture and the crystals were removed by filtration and washed with

dichloromethane until the filtrate became colorless giving [Ni(OMTAA)C₇₀] (20 mg, 80% yield).

‡ *X-Ray crystallography*: [Ni(OMTAA)C₇₀]: data were collected on an Enraf Nonius CCD and were corrected for Lorentzian and polarisation but not absorption. The structure was solved using TEXSAN. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares refinement against *F*. Hydrogen atoms were included at calculated positions with a riding model. *Crystal data*. C₉₆H₃₀N₄Ni, *M* = 1298.02, monoclinic, space group *P*2₁/*n*, *a* = 14.9165(5), *b* = 18.8797(7), *c* = 19.5635(4) Å, β = 105.490(1)°, *U* = 5309.3(3) Å³, *Z* = 4, *D*_c = 1.624 g cm^{−3}, Mo-K α radiation, λ = 0.71073 Å, *T* = 123 K, μ = 4.35, 4235 reflections observed, 910 parameters, *R* = 0.0649, *wR*₂ = 0.0474. CCDC 182/1105. See <http://www.rsc.org/suppdata/cc/1999/193/> for crystallographic files in .cif format.

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