Controlling the confinement of fullerene C_{60} molecules using a saddle shape Ni(II) macrocycle†‡

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A saddle-shaped Ni-macrocycle bearing flexible benzyl arms, Ni(TBTAA), **1**, has been prepared and structurally authenticated in the solid state as a toluene adduct, with the toluene residing in the extended cavity of the macrocycle, close to two of benzylic substituents. The Ni-macrocycle forms a crystalline inclusion complex with fullerene C_{60}, $\{C_{60}\cap(\mathbf{1})_2\}\cdot(\text{toluene})_5$, **2**, which has each fullerene encapsulated by two macrocycles involving $\pi\cdots\pi$ interactions to the phenyl lined face of the macrocycles, as well as $CH\cdots\pi$ from the benzyl groups and toluene molecules closing up the fullerene surface. The $CH\cdots\pi$ for the benzyl groups effectively increases the steric demands of the macrocycle over the surface of the fullerene, circumventing any fullerene$\cdots$fullerene interactions. The nature of the interactions in the fullerene complex has been probed using Hirshfeld surface analysis.

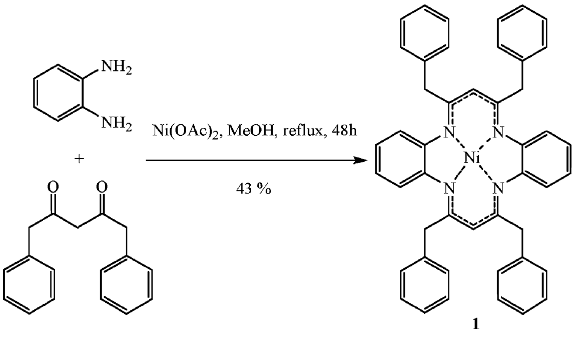
Introduction

Understanding and controlling the host–guest interactions involving inherently weak interactions is a prime challenge of supramolecular chemistry,[1] requiring design characteristics of the host molecule to optimize its interplay with specific guest molecules to enhance the likelihood of forming stable complexes.[2] Fullerene C_{60} is a spheroidal molecule which is an attractive guest molecule in designing effective molecules for its supramolecular confinement. This is important in separation technology of the fullerene and changing its properties.[3]

Fullerene C_{60} readily forms host–guest complexes with a variety of compounds, such as porphyrins,[4] calixarenes,[5] cyclodextrins,[6] cyclotriveratrylenes (CTV),[7] and concave polyarenes.[8] A starting point in design principles is the use of a concave host molecules having complimentary of curvature, then to optimise the non-covalent interactions between the C_{60} and the host molecule(s).[9] Besides a plethora of host molecules possessing cavities as in CTV and polyarenes, suitable concave surfaces are also found in metal macrocycles such as Ni(TMTAA),[10] which exhibits a unique saddle shape, caused by intra-molecular non-bonding interactions.[11] The original solid-state studies on complexation behaviour between Ni(TMTAA) and C_{60} showed that the fullerene resides in both of the shallow cavities of the macrocycle, giving rise to a 1 : 1 complex where the fullerenes are arranged in a corrugated sheet with five nearest neighbour fullerenes, *i.e.* each fullerene has five other fullerenes at the van der Waals limit.[12] Incorporating methyl groups on the aromatic rings of the macrocycle also affords a 1 : 1 complex, but the interplay of fullerenes is dramatically changed, with a linear arrangement of fullerenes, each fullerene having two fullerene$\cdots$fullerene interactions.[13] Ripmeester and co-workers have partially introduced rigid phenyl substituents onto the nickel macrocycle thereby extending the walls of the shallow cavity resulting in limited interactions between fullerene molecules.[14]

While Ni(TMTAA) and its derivatives mentioned above demonstrate that the nickel macrocycle is effective in forming complexes with fullerene C_{60}, as well as fullerene C_{70},[15] there is limited work on incorporating design principles into the macrocycle to effectively stabilize the ultimate host–guest complex where fullerene$\cdots$fullerene interplay is sterically inaccessible. This is the research objective herein, where we report the synthesis and structural characterisation of a novel nickel macrocycle, Ni(TBTAA), **1** (Scheme 1).

The methyl-lined face of the parent macrocycle Ni(TMTAA) has been extended through the incorporation of benzyl-substituents, and its ability to act as a host towards fullerene C_{60} is reported. Such a change was expected to lead to increased surface area contact between the macrocycle and C_{60},[14] and consequently enhance complex formation, at the



Scheme 1 Synthesis of Ni(TBTAA), **1**.

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same time minimizing the ability of the fullerene to be involved in fullerene···fullerene interactions. This refers to the 1 : 2 complex with the fullerene bound by two macrocycles, with the extended arms involved in π···π and/or CH···π interactions. We note that the binding of two macrocycles to fullerene C_{60} is documented, for example in the binding of *p*-phenyl- and *p*-benzyl-calix[5]arenes,[16,17] where the complexes are dominated by π···π and C–H···π interactions respectively for the two macrocycles. The *p*-benzylcalix[5]arene complex is particularly relevant to the present study in that the substituents are also flexible benzyl groups.[17] We also report the Hirshfeld surfaces of the fullerene complex as a probe in mapping out the interaction between the components in the crystals. The structure of the parent Ni-macrocycle could not be analysed using this approach because of disorder associated with some of the benzyl groups.

Results and discussion

The Ni-macrocycle **1** was readily synthesized through condensation of *o*-phenylenediamine, 1,5-diphenyl-pentane-2,4-dione and nickel(II) acetate tetrahydrate in methanol, as a 'one pot' condensation of equimolar amounts of each reagent. Dissolution of **1** in toluene, followed by slow evaporation afforded crystals suitable for X-ray crystallography.§ The asymmetric unit contains one molecule of **1**, which adopts the expected saddle shape previously observed in related compounds,[11] and one toluene molecule. The four benzyl groups are all directed upwards on the same side of the plane of the central core of the macrocycle, thereby forming "walls" to the phenyl-lined cavity. In the extended packing the macrocycles line up in stacked rows with Ni···Ni distance at 7.975 Å and a toluene molecule residing in the groove formed by four benzyl groups, two from the individual macrocycles, Fig. 1. The toluene molecule is held in place with intricate edge-to-face interactions involving the phenylene and the benzyl substituents, and CH···π interactions to the benzyl group from neighbouring stacked molecule with H···ring centroid short contacts distances of 2.179 and 3.152 Å. Two benzyl groups of each macrocycle are directed edge on towards the metal centre on a neighbouring macrocycle, with Ni···H–Ar short contacts distances of 3.283 and 2.956 Å.

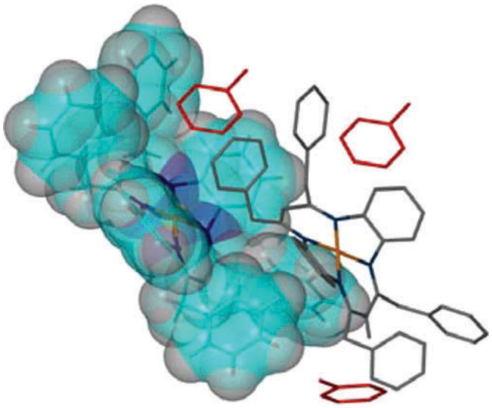

Fig. 1 Stacked arrangement adopted by saddle-shaped molecules of Ni(TBTAA), **1** (toluene molecules shown in red).

The overall packing in **1** consists of four columns of stacked macrocycles running orthogonal to each other, involving extensive CH···π interactions with toluene filling the interstitial space. Stacked rows are arranged in a tetrameric motif, consisting of antiparallel columns, involving mutual phenyl embraces, with CH···π short contact distances at 2.656 Å, 2.880 Å and 2.91 Å, Fig. 2.

Slowly cooling a toluene solution of fullerene C_{60} and **1** afforded crystals suitable for X-ray diffraction studies.§ Despite a 1 : 1 ratio of the two components in solution, the favoured complex in the solid state is the complex with a 1 : 2 ratio, along with five molecules of toluene per fullerene. The asymmetric unit of the structure contains two Ni-macrocycles, one C_{60} and five toluene molecules, with the C_{60} encapsulated between the two phenyl-lined faces of the Ni-macrocycles, Fig. 3.

No guest is included in the benzyl-lined cavity, contrary to previously reported structures containing a shallower methyl-lined cavity, which does include guests.[12,13] The host molecules are not symmetrically placed over the surface of the fullerene, with the Ni···fullerene centroid···Ni angle at 153.05°. This skewed arrangement is associated with slightly different closest

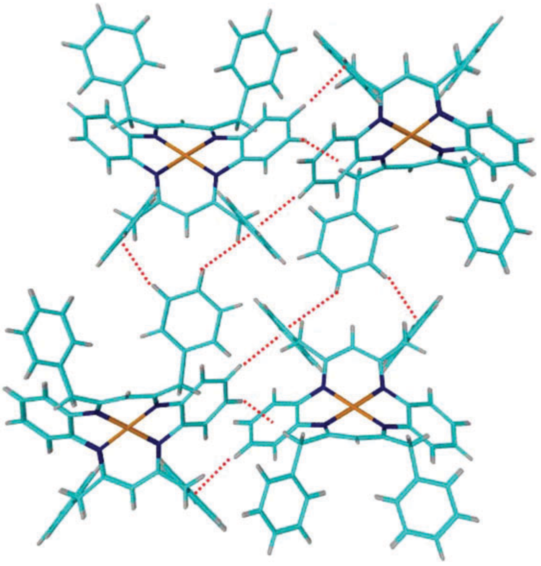

Fig. 2 Partial packing diagram of Ni(TBTAA) along the *a* axis showing edge-to-face and CH···π interactions in the tetrameric arrangement of the columns (toluene solvent molecules removed for clarity and dashed red lines depict CH···π interactions).

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§ ***Crystal data and refinement details*** **for 1·toluene:** $C_{53}H_{46}N_4Ni$, M = 797.65, $F(000)$ = 1680 e, monoclinic, $P2_1/n$ (no. 14), Z = 4, T = 100(2) K, a = 7.9746(16), b = 24.528(7), c = 20.765(4) Å, β = 92.928(16)°, V = 4056.4(16) Å^3; D_c = 1.306 g cm^{-3}; μ_{Mo} = 0.521 mm^{-1}; $\sin(\theta/\lambda)_{max}$ = 0.6462; N(unique) = 7367 (merged from 20 594, R_{int} = 0.0408, R_{sig} = 0.1052), N_o ($I > 2\sigma(I)$) = 4113; R = 0.0721, $wR2$ = 0.1934 (A, B = 0.14, 0), GOF = 1.001; $|\Delta\rho_{max}|$ = 1.22(9) e Å^{-3}. CCDC reference number 656080.

Crystal data and refinement details **for 2: $\{C_{60}\cap(1)_2\}\cdot(toluene)_5$:** $C_{187}H_{116}N_8Ni_2$, M = 2592.30, $F(000)$ = 2700 e, monoclinic, Pn (no. 7), Z = 2, T = 100(2) K, a = 13.7015(8), b = 14.3052(15), c = 32.130(4) Å, β = 95.576(8)°, V = 6267.8(11) Å^3; D_c = 1.374 g cm^{-3}; μ_{Mo} = 0.368 mm^{-1}; $\sin(\theta/\lambda_{max})$ = 0.5396; N(unique) = 8193 (merged from 41 816, R_{int} = 0.0855, R_{sig} = 0.1144), N_o ($I > 2\sigma(I)$) = 4864; R = 0.0671, $wR2$ = 0.1531 (A, B = 0.15, 6.17), GOF = 1.042; $|\Delta\rho_{max}|$ = 0.88(8) e Å^{-3}. CCDC reference number 656079.

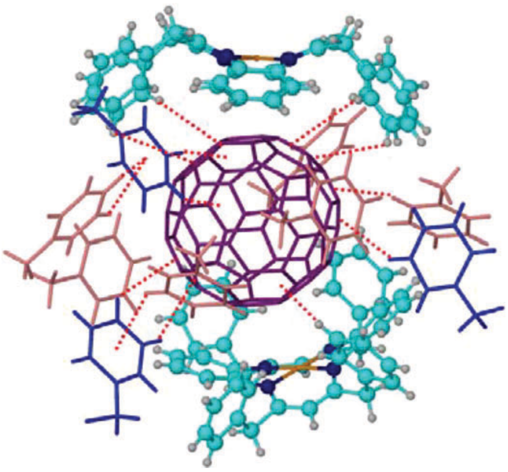

Fig. 3 Projection of complex **2**, $\{C_{60}\cap(\mathbf{1})_2\}\cdot(\text{toluene})_5$, showing host–guest interactions and confinement of the C_{60} within the benzyl-lined concave domain of the macrocycle along with intermolecular interactions from moieties of neighbouring macrocycles (red: dashed line represent CH···π contacts, blue: fragment of neighbouring molecules, pink: toluene solvent molecules).

contact distances between the Ni centres of the macrocycle and the fullerene, at 3.253 and 3.085 Å, respectively for the two macrocycles. The closest contact between C_{60} and the macrocycles is a face-to-face π···π interaction of 3.094 Å, measured from a 6:6 ring junction to an arene in a phenyl-lined cavity. There are extensive CH···π interactions from the benzyl groups to the six-membered ring of the fullerene. Analysis of the extended structure reveals that each fullerene is completely isolated from neighbouring fullerenes being shrouded by two macrocycles and toluene molecules, with the closest centroid···centroid fullerene distance being 13.701 Å. This distance is the closest contact within a distorted hexagonal 2D array of encapsulated fullerene molecules, Fig. 4. The closest distance between fullerenes from adjacent hexagonal sheets is 17.671 Å. Previous studies on related complexes of saddle-shaped Ni-macrocycles and C_{60} have revealed different structural motifs relating to the fullerenes, such as corrugated sheets,[3] and linear chains.[3] The results herein present the first report of a saddle shape Ni-macrocycle forming an encapsulated fullerene complex (1 : 2 complex) at the expense of a 1 : 1 complex which would allow fullerene···fullerene interactions.

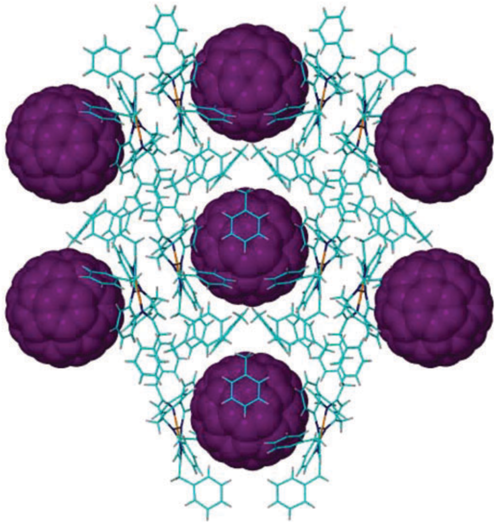

Fig. 4 Packing diagram projection down the *a* axis of complex **2** showing the C_{60} fullerenes dispersed within the molecular crystal with intricate intermolecular interactions between the macrocycle moieties.

Unlike the columnar tetrameric organisation of the macrocycle in **1**, the macrocycles in the fullerene complex **2** are arranged in layers where the macrocyles are in a back-to-back fashion with the benzyl extended cavities directed outwards for interplay with fullerene C_{60}, Fig. 5. The back-to-back mode of association of the macrocycles relates to the associated shallow cavities with Ni···Ni separation at 5.085 Å. Within the layer, the back-to-back dimmers are associated with interdigitation involving CH···π interactions from the benzyl groups to the phenylene aromatic ring with a short contact of 2.770 Å.

Hirshfeld surfaces and related graphical tools[18] provide a means of exploring the nature of the intermolecular interactions within supramolecular and host–guest systems.[19] Hirshfeld surfaces analysis was performed on complex **2** in order to ascertain the environment of C_{60} in forming a complex with Ni(TBTAA) and *vice versa.* Hirshfeld surfaces were mapped with d_e, and are shown in Fig. 6. They clearly show the regions

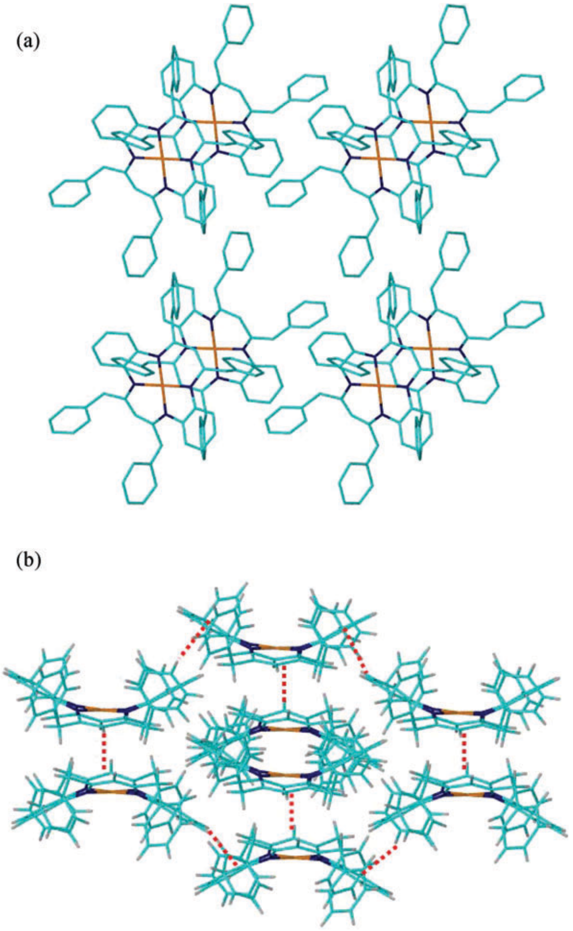

Fig. 5 Projections of an array of macrocycle in **2** showing the back-to-back arrangement of the core of the macrocycles, which form centrosymmetric dimmers associated with non-classical C–H···π interactions (shown in red).

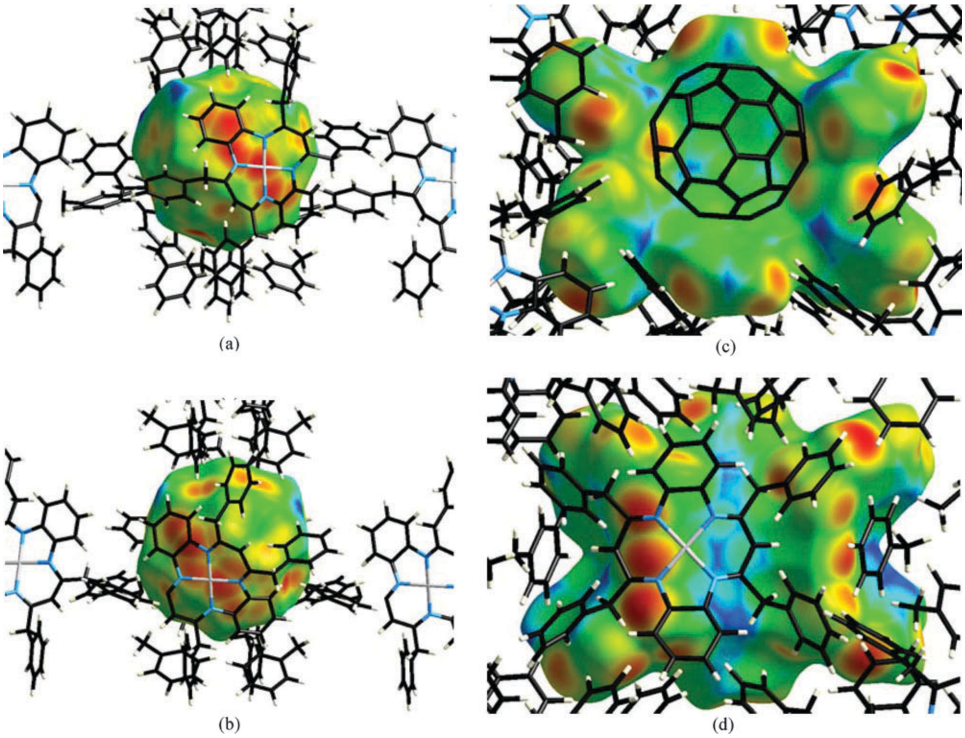

Fig. 6 Hirshfeld surfaces for **2**: $\{C_{60}\cap(\mathbf{1})_2\}$·toluene, with (a) and (b) focused on the fullerene, the two projections related by a rotation along a vertical axis of 180°, and similar for (c) and (d) for the macrocycle.

of strong interactions on the VDW surface where the red spots represent contacts shorter than the van der Waals limits. The distribution of interactions is associated with pairs of distances d_e and d_i and are accumulated in the form of fingerprints which are depicted in Fig. 7. The majority of close contacts are highlighted by the red area, with a limit of $d_e + d_i$ ranging from 2.8 to 3.0 Å for the Hirshfeld surface of C_{60}, Fig. 7(a), and one of the two independent Ni(TBTAA) macrocycle, Fig. 7(b).

The line of isolated fullerene molecules along the *a* axis in the crystal, Fig. 4, are interlocked between layers of the Ni-macrocycle. The intermolecular interactions between the macrocycles involve predominantly C–H···π acceptor interactions, 71.3%. For comparison, the inter-atomic contacts for C···C, C···N and C···Ni are 22.8, 4.1 and 1.8%, respectively. This feature is displayed with colour, as the yellow and red spots on Fig. 7(a).

The analysis of Ni(TBTAA) finger print plots reveals the character and number of interactions, and are remarkably similar for the two macrocycles in the asymmetric unit of the complex, with only that of one of them shown in Fig. 7(b). There are a number of yellow and red spots that can be associated with a major component of all interactions with H···H at 55.1 and 54.6% for molecules A and B, respectively. The C–H···π interactions are 15.9% donor and 19.2% acceptor, molecule A, and 15.8% donor and 19.8% acceptor for molecule B.

Experimental

All solvents and starting materials were purchased from commercial suppliers and used without further purification and the synthetic protocols described below. Crystals for compounds **1** were prepared by slow evaporation of a toluene solution of Ni(TBTAA) (10 mg ml^{-1}) while crystals for compounds **2** were prepared by slow evaporation of an equimolar toluene solution of Ni(TBTAA) and C_{60}, with crystals suitable for single-crystal diffraction studies forming over a week. Crystal uniformity of each sample was checked by determining unit cell dimensions on crystals from the same preparation and from different preparations.

Synthesis of (5,14-dihydro-6,8,15,17-tetrabenzyldibenzo[*b*,*i*][1,4,8,11]tetracyclodecine)nickel(II), (1)

A suspension of $Ni(OAc)_2{\cdot}4H_2O$ (1.48 g, 5.95 mmol) and *o*-phenylenediamine (1.29 g, 11.9 mmol) in dry degassed methanol (5 mL) was heated to reflux for 30 min, then 1,5-diphenylpentane-2,4-dione (3.00 g, 11.9 mmol) was added in

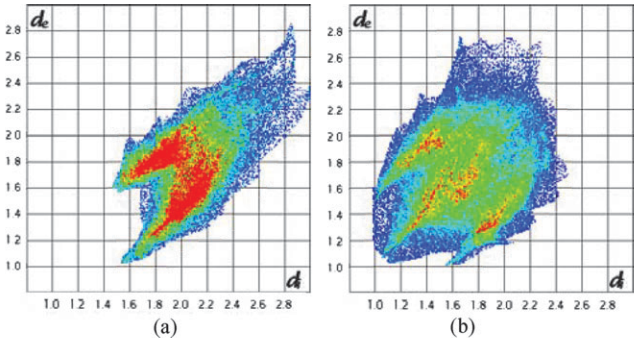

Fig. 7 2-D Histograms (fingerprint plots) of the relative frequency of points of contacts for C_{60} (a) and one of the two crystallographically independent Ni(TBTAA) macrocycles (b).

one portion and the reaction heated at reflux for 48 h. The resulting green suspension was cooled to RT, filtered, and the filtercake washed with methanol until washings were colourless. The solid was dried under reduced pressure to give **1** (1.81 g, 2.56 mmol, 43%) as a green solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ_H (ppm) 3.79 (s br, 8H), 4.75 (s br, 2H), 6.44 (dd, J = 6.1, 3.4, 4H), 6.61 (dd, J = 6.0, 3.6, 4H), 7.17 (d, J = 7.2, 8H), 7.20 (t, J = 7.2, 4H), 7.28 (t, J = 7.2, 8H). ^{13}C ($CDCl_3$, 75.5 MHz): δ_C (ppm) 39.1, 120.2, 122.7, 126.4, 128.7, 128.8, 138.7, 146.9, 157.1. FAB-MS (in CH_2Cl_2): m/z 704.24 $[M]^+$; Anal. Found: C, 78.44; H, 5.47; N, 8.01. Calc. for $C_{46}H_{38}N_4Ni$: C, 78.31; H, 5.43; N, 7.94%.

Preparation procedure of complex 2

To a solution of C_{60} (5 mg) in toluene (5 mL) was added **1** (5 mg) in toluene (2 mL). The mixture was heated to reflux, filtered, then allowed to stand for 16 h which resulted in formation of dark crystals of complex **2**. The solution was filtered and the crystals washed with hexane, yield: 4.5 mg, 45%.

X-Ray crystallography

The X-ray diffracted intensities were measured from single crystals at about 100 K on an Oxford Diffraction Xcalibur or Gemini-R Ultra CCD diffractometer using monochromatized Mo-Kα (λ = 0.71073 Å) radiation. Data were corrected for Lorentz and polarization effects and absorption correction applied using multiple symmetry equivalent reflections. The structures were solved by direct methods and refined on F^2 using the SHELX-97 crystallographic package[20] and the X-Seed interface.[21] A full matrix least-squares refinement procedure was used, minimizing $w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. Agreement factors ($R = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ and GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$ are cited, where n is the number of reflections and p the total number of parameters refined). Non-hydrogen atoms were refined anisotropically. In structure of **1**, the toluene solvent molecule and the two closest aromatic rings of the macrocycle are disordered between two positions with 0.5 : 0.5 ratio and refined isotropically. The positions of hydrogen atoms were calculated and their atomic parameters were constrained to the bonded atoms during the refinement.

CCDC reference number 656079 (**2**).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718937k

Conclusion

We have prepared a new saddle-shaped macrocycle and established its complexation with fullerene C_{60} in the solid state. By altering one concave surface of the parent divergent receptor molecule Ni(TMTAA), encapsulation of the globular fullerene molecule is possible. The flexible benzyl arms are effective in circumventing fullerene···fullerene interactions, and it would seem that the associated C–H···π interaction with the fullerene increases the steric demands of the macrocycle on the surface of the fullerene. This aside, the dispersed fullerenes form a distorted hexagonal array with the sheets stacked in an eclipsed fashion such that the centre of one fullerene in one sheet lies directly over a fullerene in next sheet. The Hirshfeld surface analysis of the fullerene complex clearly identifies the nature of interplay of the fullerene with its nearest neighbours and vice versa for the macrocycle. Inroads have been made in designing a molecule for controlling the organisation of fullerenes, in this case, isolated fullerenes. This has implications in materials science along with potential applications in photoelectrical devices, which is a trajectory we are currently pursuing.

Acknowledgements

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