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Confinement of C_{60} in an extended saddle shaped nickel(II) macrocycle

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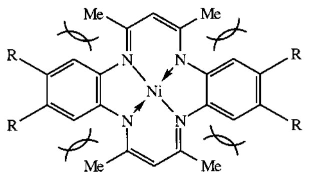
Saddle shaped (5,14-dihydro-2,3,6,8,11,12,15,17-octamethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine)nickel(II), Ni(OMTAA), acts as a divergent receptor molecule with C_{60} forming a 1 : 1 complex in solution and in the solid state, isolated as $[Ni(OMTAA)C_{60}]\cdot 2CS_2$. The extended supramolecular array is based on linear chains of close contact C_{60} molecules [fullerene ··· fullerene centroids 10.03(1) and 10.04(1) Å], and linear chains of π-stacked alternating molecules of C_{60} and Ni(OMTAA) with adjacent chains running in opposite directions.

Introduction

Host–guest chemistry of globular molecules including fullerenes,[1–19] carboranes,[20] and P_4E_3, E = S, Se,[1,21] has recently gained prominence in forming inclusion nano-structures, 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 per 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, guest–host and guest–guest interactions is important in determining the structure of the resulting supramolecular array. This is particularly evident in fullerene chemistry where inter-fullerene interactions play a major role in the structures of inclusion complexes.[5–16] The interactions of solvent with all species and crystal packing forces provide additional variables. Recently, we reported that Ni(TMTAA) (see below, R = H), acts as a divergent heterotopic receptor with C_{60}, 1,2-dicarbadodecaborane and the chalcogenides P_4S_3 and P_4Se_3;[1,21] the saddle shape for the host arises from otherwise unfavourable interactions between the $\{NC(Me)\}_2CH$ methyl groups and the hydrogen atoms on the aromatic rings.

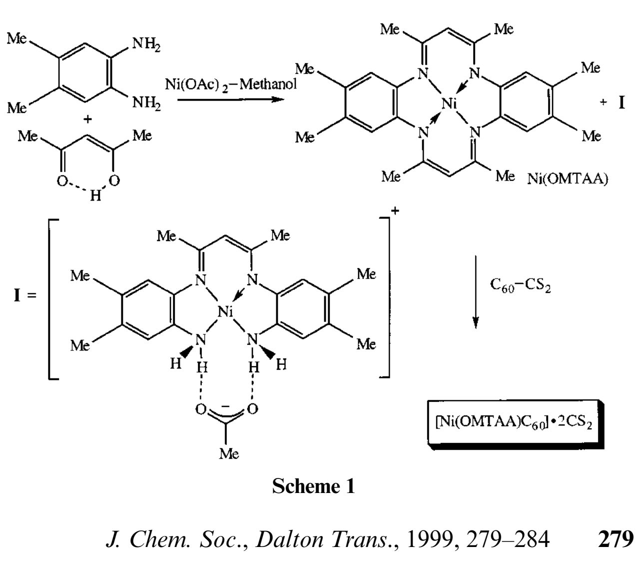
Herein we report the preparation and structural elucidation of a divergent receptor nickel(II) macrocycle which has an extended concave surface, Ni(OMTAA), (see above, R = Me) together with the structural elucidation and UV/vis studies of its supramolecular complex with C_{60}. The larger area of contact of the host with the surface of the fullerene should in principle lead to a complex with diminished fullerene–fullerene interactions per fullerene,[6,7,12] and indeed this was found to be the case. In contrast to $[Ni(TMTAA)C_{60}]$ which has a corrugated two dimensional sheet of close contact fullerenes, Ni(OMTAA) forms linear, single column chains of close contact C_{60} molecules in its 1 : 1 complex with the fullerene, $[Ni(OMTAA)C_{60}]\cdot 2CS_2$. This columnar motif of inter-fullerene contacts is unusual and has few precedents; Sugawara and Crane have prepared inclusion complexes of C_{60} with redox active hosts with a view to preparing molecular conduction devices, these complexes containing columnar stacks of C_{60} molecules.[17–19] Related to these are the zig-zag chains of C_{60} molecules surrounded by a sheath of bowl shaped cyclotriveratrylene (CTV) molecules in $[(CTV)C_{60}]$.[11]



Results and discussion

Synthesis of (5,14-dihydro-2,3,6,8,11,12,15,17-octamethyldibenzo[*b*,*i*][1,4,8,11]tetracyclotetradecine)nickel(II), Ni(OMTAA) and [*N*,*N′*-bis(2-amino-4,5-dimethylphenyl)pentanediiminato] nickel(II) acetate, I, and $[Ni(OMTAA)C_{60}]\cdot 2CS_2$

The synthesis of Ni(OMTAA) is a modification of an existing preparation.[22] Two equivalents of 1,2-diamino-4,5-dimethylbenzene were condensed with two equivalents of acetylacetone and one equivalent of nickel(II) acetate tetrahydrate as a highly concentrated mixture in anhydrous, anoxic methanol. The Ni(OMTAA) precipitates from solution and is isolated in 76% yield which is considerably higher than that obtained in the original preparation, 45%, Scheme 1. The reaction requires a high concentration of reagents for optimum yield and careful exclusion of air due to the oxygen sensitive nature of the "three-quarter complex" intermediate **I** which has been isolated and structurally characterised, Scheme 1. This was achieved when



Scheme 1

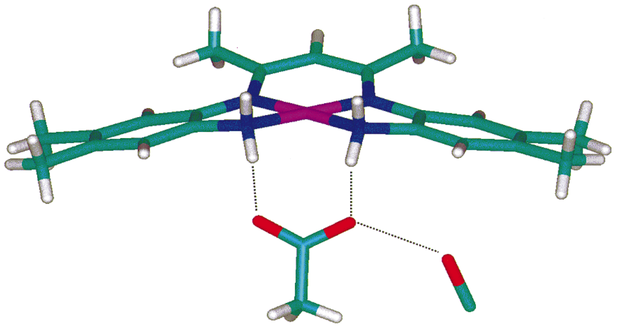


Fig. 1 Structure of **I** showing the cation/anion hydrogen bonding interplay.

the reaction mixture was more dilute and filtered hot to remove a small amount of Ni(OMTAA) and on cooling gave **I** in 12% yield. This intermediate complex is indefinitely air stable in the solid state but once in solution, decomposes rapidly in the presence of oxygen to an as yet unknown product. A related intermediate has been isolated, but not structurally authenticated, from the preparation of Ni(TMTAA).[23] [Ni(OMTAA)C_{60}]·$2CS_2$ was prepared by the slow evaporation of CS_2 solutions of C_{60} and excess Ni(OMTAA).

Structure of I·CH_3OH

The asymmetric unit consists of one molecule of the cation/anion complex which has the nickel atom in a square planar environment, as expected. The tetradentate ligand has a saddle shape with respect to the two phenyl groups, and has a shallow pitch, 159.4(3)°, defined as the dihedral angle between the planes of the two aromatic rings, Fig. 1. This is much shallower than in the closed macrocycle itself, Ni(OMTAA), pitch angle 137.9(3)°, and the related macrocycle Ni(TMTAA), pitch angle 128.3(3)–135.4(3)° (see below).[24–27] The shallower pitch is due to the presence of only one pair of $CH_3\cdots H\text{–}C_{aromatic}$ repulsions, compared to two pairs in Ni(TMTAA) and Ni(OMTAA). To a lesser extent it may be associated with longer Ni–N distances for the two terminal amine centres, and thus a more open side of the cation. The Ni–N bond lengths in the {NC(Me)}$_2$CH section of the complex are shorter [1.88(1) and 1.88(1) Å] than in the amine portion [1.91(1) and 1.92(1) Å], in accordance with the difference in valency of the N centres, sp^2 *versus* sp^3. The angle between the least-squares planes through the four nitrogen atoms and the least-squares planes through the phenyl rings is 169.3(3)° while the angle between the least-squares planes through the four nitrogen atoms and the least-squares planes through the {NC(Me)}$_2$CH section is 161.3(3)°.

Hydrogen atoms were placed in calculated positions and refined, except for those on the methanol molecule which were not included. Hydrogen bonding was deduced by inspection of the inter-atomic distances and the geometries of interacting species. The acetate moiety is hydrogen-bonded to the amine groups, the N···O distances being 2.78(1) and 2.95(1) Å, with associated N–H···O distances, 1.83(1) and 2.10(1) Å. The acetate oxygen associated with the longer N–H···O hydrogen bond is also involved in hydrogen bonding to a molecule of methanol, O···O 2.67(2) Å although the hydrogen atom on the methanolic oxygen atom was not located in the analysis of the X-ray diffraction data. The methanol molecule is also within hydrogen bonding distance [O···N 2.91(2) Å, N–H···O 2.00(1) Å] of the amine nitrogen participating in the shorter hydrogen bond to acetate.

Structure of Ni(OMTAA)

Despite the synthesis of and the use of Ni(OMTAA) as a precursor for metal ion complexes of $OMTAA^{2-}$,[22,28–30] and the crystal structure of the protonated metal-ion free ligand having been described,[31,32] the structure of Ni(OMTAA) has not previously been reported. The asymmetric unit consists of one molecule of Ni(OMTAA) which adopts a saddle-like conformation due to steric interactions between the 2,3,6,8-methyl groups ({NC(Me)}$_2$CH) and the hydrogen atoms on the aromatic rings, as observed for Ni(TMTAA)[24,27] and H_2(OMTAA).[31,32] Molecules of Ni(OMTAA) are assembled into dimers but the nature of the dimeric motif differs considerably from that observed for Ni(TMTAA). Ni(TMTAA) has been structurally characterised in three crystalline forms, as monomeric,[26] dimeric[24] and tetrameric units.[25] The tetrameric form of Ni(TMTAA), isostructural with Cu(TMTAA), self assembles around a central dimer in which the Ni(TMTAA) macrocycles interlock at 90°, driven by complementarity of curvature of the components as well as by Ni···H interactions, with the nickel atom of one macrocycle residing below a phenyl ring of the other. Additional interlocking of the dimers occurs through the ({NC(Me)}$_2$CH)$_2$Ni concave surfaces to two other Ni(TMTAA) molecules through the same surfaces.[25] Similarly, in dimeric Ni(TMTAA), the self assembly is driven by favourable complementarity of curvature of the interlocking components and favourable interactions between the {NC(Me)}$_2$CH moieties.[24]

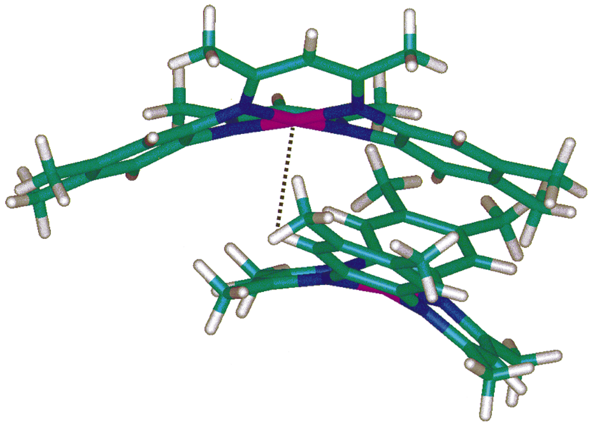


Fig. 2 Projection of the self associated dimers of Ni(OMTAA); the dotted line represents the close Ni···H–C contact.

Saddle shaped Ni(OMTAA) possesses two divergent concave surfaces, one face of which is comprised of the NiN_4 plane and the phenyl groups while the NiN_4 plane and the {NC(Me)}$_2$CH moieties and metal centres make up the opposing surface, Fig. 2.[1,21,24–28] The angles between the least-squares planes through the four nitrogen atoms and the least-squares planes through the phenyl rings are 158.6(3) and 159.4(3)°, while the angles between the least-squares planes through the four nitrogen atoms and the least-squares planes through the {NC(Me)}$_2$CH moieties are 156.0(3) and 155.3(3)°. The overall pitch angle between the least-squares planes of the phenyl rings is 137.9(3)° which is comparable to that observed for H_2(OMTAA) [139.2(3)°] and the Ni(TMTAA) dimer [135.4(3) and 134.4(3)°] but somewhat less than that observed for the Ni(TMTAA) momomer [128.3(3)°]. There is a slight decrease in the pitch angle for the ({NC(Me)}$_2$CH)$_2$ face in Ni(OMTAA), the least-squares planes intersecting at 131.3(3)° while in dimeric Ni(TMTAA) the same planes intersect at 130.5(3)°.[24,26,31–34]

In the present structure the phenyl group of one Ni(OMTAA) molecule sits over the phenyl of another in a skewed π-stacked arrangement with the two rings separated by 3.52(1) to 3.71(1) Å (Fig. 2). This distortion from a conventional offset π-stacked arrangement is due to otherwise unfavourable Me_{phenyl}–Me_{phenyl} and Me_{phenyl}–{NC(Me)}$_2$CH interactions and results in an *o*-aromatic proton residing unusually close to the nickel atom, Ni···H 2.81(1) Å (Fig. 2).

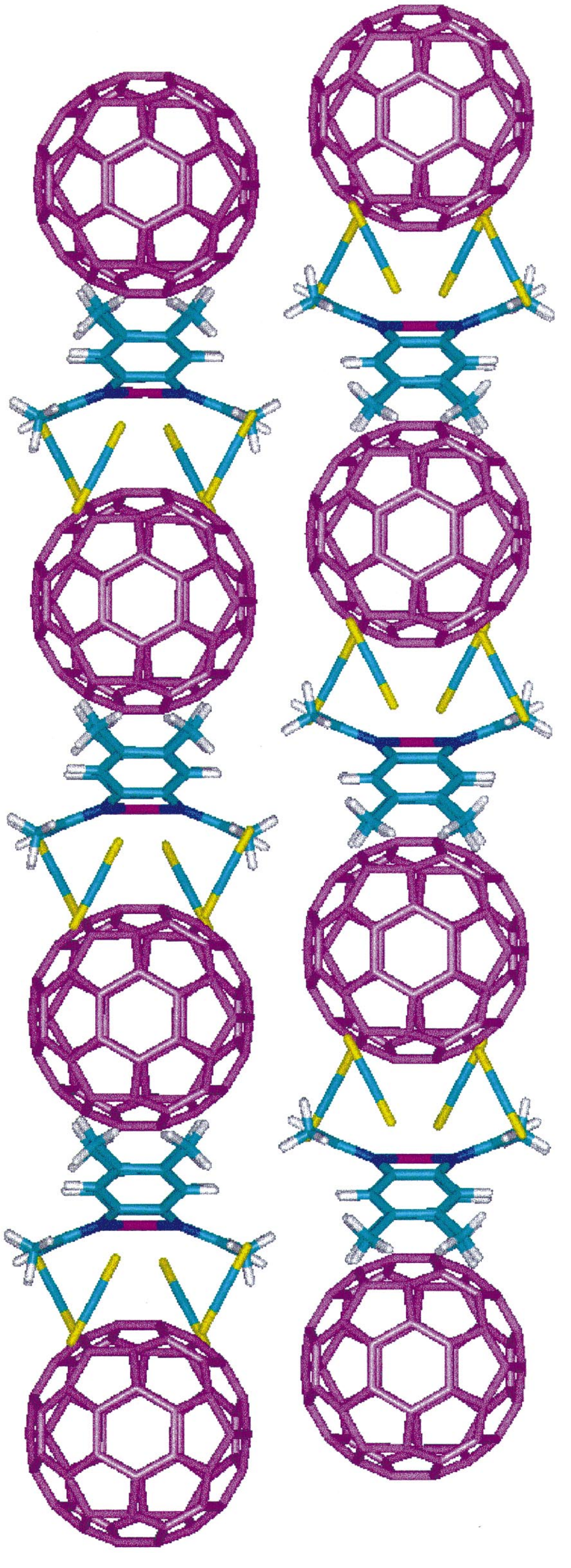


Fig. 3 Host–guest–host–guest · · · interplay in the structure of [Ni(OMTAA)C_{60}]·$2CS_2$.

Structure of [Ni(OMTAA)C_{60}]·$2CS_2$

The compound crystallises in the space group *C2*/*c* with the asymmetric unit comprised of half a molecule of the two supramolecular synthons and a molecule of CS_2. The fullerene is in the larger saddle of one Ni(OMTAA) molecule, *i.e.* the saddle built up by the phenyl groups, and in the opposite smaller saddle of another Ni(OMTAA) molecule. The overall host–guest contacts form a continuous linear chain parallel to the *b* axis within which the host molecules are aligned unidirectionally, Fig. 3. There are no significant interactions between hosts, the closest host · · · host distances being greater than 4.0 Å. The closest fullerene contact to the nickel centre in the phenyl lined face of the host is to the midpoint of an edge shared by two C_6 rings which lies "parallel" to Ni(OMTAA), Ni · · · C_{60} 3.23(1) Å (C_2—mid point). Although the Ni · · · C_{60} distance is similar on the other face there is not such a clear geometrical alignment. Despite this apparent preference of C_{60} for the phenyl face of the host, the subtle interplay between the guest and host manifests itself in the tendency for the fullerene to bind to both faces of Ni(OMTAA). In the presence of excess host, this array still forms despite the apparent advantage of C_{60} binding to the larger surface area of the phenyl containing face, and thus greater potential van der Waals interactions. Contiguous chains are slightly offset to achieve efficient packing within the array, Fig. 3, and run in opposite directions, thus effectively cancelling dipoles.

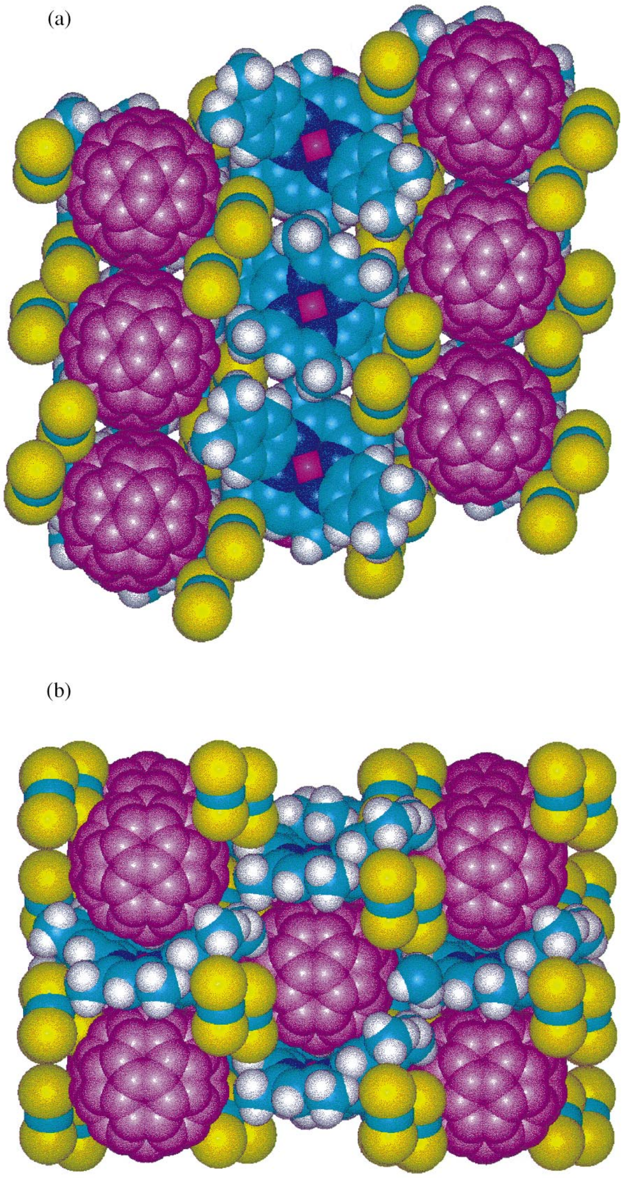


Fig. 4 Inter-fullerene contacts in [Ni(OMTAA)C_{60}]·$2CS_2$ showing the linear chains of fullerenes along the *c* axis in the (a) *ac* and (b) *ab* planes.

The pitch of the phenyl groups in Ni(OMTAA) decreases upon complexation with the fullerene, the unique angle between the least-squares planes through the four nitrogen atoms and the least-squares plane through the phenyl ring is 148.5(3)°, a decrease of 10.1(3)–10.9(3)°; the corresponding angle between the phenyl groups (pitch angle) is 116.9(3)°. In contrast, the angle between the least-squares plane through the four nitrogen atoms and the least-squares plane through the $\{NC(Me)\}_2CH$, 156.9(3)°, moieties remains virtually unchanged relative to uncomplexed Ni(OMTAA). The corresponding pitch angle between the two $\{NC(Me)\}_2CH$ moieties is 135.8(3)°. A similar change is observed on complexation of C_{60} with Ni(TMTAA). The least-squares planes through the phenyl rings of the Ni(TMTAA) dimer intersect at 135.4(3), 134.4(3)° and decrease to 127.9(3)° upon complexation to C_{60}.[1]

Importantly, fullerene–fullerene interactions are now restricted to one dimensional chains, with fullerene at the van der Waals limit, centroid $\cdots$ fullerene centroid distances 10.03(1) and 10.04(1) Å; the chains of fullerenes run parallel to the *c* axis and are associated with a sheath of Ni(OMTAA) and CS_2 molecules, Fig. 4. Each fullerene makes intimate contact, $C\cdots C$ 3.45(1) to 3.84(1) Å, with another by typical offset π–π interactions involving six membered rings of adjacent fullerenes. This is in contrast to $[Ni(TMTAA)C_{60}]$ which crystallises as two dimensional corrugated sheets of interacting fullerenes with the sheets separated by Ni(TMTAA) molecules.[1] Here the dihedral angle defined by the two nickel centres and the C_{60} centroid is not linear but is markedly stepped at 83.4° whereas in the present structure it is 180°. For $[Ni(TMTAA)C_{60}]$ the host is small enough to skew from linearity without disrupting the host–guest interactions or engaging in destabilising host–host interactions, while allowing the fullerene a suitable surface for inter-fullerene interactions. A difference in this angle is expected because of the larger contact surface area of the Ni(OMTAA) with C_{60} for the phenyl lined face relative to the same face for Ni(TMTAA), especially given that the two host molecules associated with each fullerene in the Ni(TMTAA) are already at the van der Waals limit with respect to each other. However, the magnitude of the change is larger than expected just on steric considerations alone, and most certainly arises from the interplay of the CS_2 molecules and the overall cohesion of the supramolecular array.

The Ni(OMTAA) molecules occupy opposite longitudinal poles of the fullerene, intra-chain C_{60} molecules occupy opposite latitudinal poles, while CS_2 molecules and phenyl–methyl groups from adjacent chains complete the sphere of van der Waals contacts to each C_{60}. The CS_2 molecules occupy voids created by the face of the phenyl rings not involved in host–guest binding and make contact with both C_{60} and Ni(OMTAA). The closest $CS_2\cdots C_{60}$ contact involves the central carbon of the carbon disulfide [$C\cdots C$ 3.41(1) Å] while the sulfur atoms interact with the underside of the Ni(OMTAA) phenyl face [$C\cdots S$ 3.48(1) Å] and the $\{NC(Me)\}_2$CH methyl groups [$C\cdots S$ 3.69(1) Å], Figs. 3 and 4.

Ni(OMTAA)–C_{60} Solution studies

The UV/vis spectra indicate the formation of a 1:1 association of C_{60} and Ni(OMTAA) in solution. Carbon disulfide solutions were prepared with Ni(OMTAA) and C_{60} in ratios varying from 10:2 to 10:30 whilst keeping the concentration of Ni(OMTAA) constant (1×10^{-4} mol dm^{-3}). The C_{60} concentration in the fullerene deficient solutions was increased incrementally and showed the presence of three isosbestic points at 467, 562 and 619 nm, indicating the presence of one host–guest species, Fig. 5. Further, prior to stoichiometric equality, the addition of C_{60} led to a linear *decrease* in the intensity of the nickel d–d transition as well as a slight shift to longer wavelength (λ_{max} 595 to 600 nm). A similar perturbation was observed with the ligand to metal charge transfer band (λ_{max} 447 to 456 nm). Once the C_{60} was in stoichiometric excess absorbance at these wavelengths *increased* markedly. This linear relationship between the concentration of C_{60} and the change in absorbance prior to stoichiometric equality, indicates the presence of a tightly bound 1:1 host–guest species with an association constant in excess of 10^5 mol^{-1} dm^3.

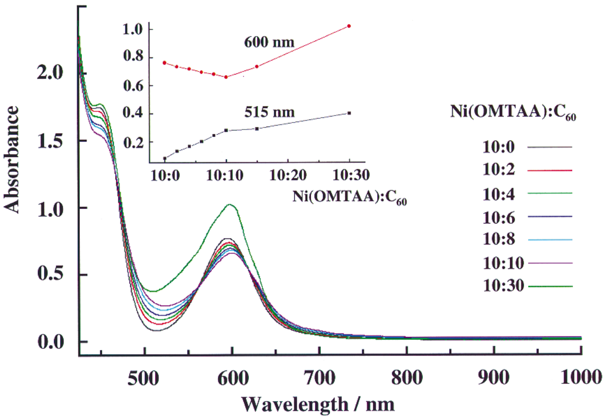


Fig. 5 UV/visible titration of Ni(OMTAA) with C_{60}.

It appears most likely that in solution the fullerene is interacting almost exclusively with the phenyl containing face due to the greater van der Waals forces involved/greater surface area contact. For an excess of C_{60} a dramatic change in absorbance at 600 nm is observed. This may be due to the formation of micelle like species,[4,10] involving clusters of fullerenes shrouded by a sheath of Ni(TMTAA) molecules.

Conclusion

In attempting to further understand the inclusion chemistry of the $[Ni(TMTAA)C_{60}]$ system we have prepared a C_{60} complex of Ni(OMTAA) as a CS_2 adduct. The effect of extending the phenyl arms of the macrocycle and the interplay of the CS_2 molecules gives a structure with infinite linear chains of host–guest–host– species. Further, and more importantly, this array manifests itself into linear chains of close contact fullerenes. In the context of generating arrays containing fullerenes, reducing the inter-fullerene interactions into a directional array is of fundamental importance, and metal-ion doping of such an array is an attractive endeavour,[17–19] as is changing the metal in the macrocycle with a view of forming reduced fullerenes *via* electron transfer.

Experimental

Measurements

Elemental analyses (C,H,N) were performed by the Campbell Microanalytical laboratory, University of Otago. Infrared spectra were recorded on a Perkin-Elmer FT 1600 spectrometer, UV/vis measurements were recorded on a Varian Cary 5 spectrophotometer, and NMR spectra on a Varian Mercury 300 MHz spectrometer.

Materials

All reagents used were purchased from Aldrich and used without further purification. Methanol was dried over magnesium methoxide and distilled immediately prior to use. Carbon disulfide was used without further purification.

Syntheses

(5,14-Dihydro-2,3,6,8,11,12,15,17-octamethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine)nickel(II), Ni(OMTAA) and I. Nickel acetate tetrahydrate (8.4 g, 0.034 mol), 1,2-diamino-4,5-dimethylbenzene (9.2 g, 0.068 mol), and acetylacetone (6.8 g, 0.068 mol) were combined and the mixture flushed with nitrogen. Dry methanol (50 mL) was added and the resulting mixture was then stirred and brought to the boil. After 48 hours at reflux, the green mixture was cooled and filtered to remove the product as a green precipitate (11.8 g, 76%). Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of carbon disulfide–hexane solutions. (Found: C, 68.12; H, 6.78; N, 11.96. $NiC_{26}H_{30}N_4$ requires C, 68.30; H, 6.61; N, 12.25%). ^1H NMR (solvent $CDCl_3$, standard $SiMe_4$): δ 2.05 (s, 12H), 2.06 (s, 12H), 4.78 (s, 2H), 6.48 (s, 4H). ^{13}C NMR (solvent $CDCl_3$, standard $CDCl_3$): δ 19.70, 22.13, 110.37, 121.92, 129.41, 145.19, 154.68. λ_{max} (ε) (CS_2): 595 (7180), 447 (16 500), 407 (20 300) nm ($dm^3\ mol^{-1}\ cm^{-1}$). *m*/*z* 456.2, 471.3, 489.2, 519.2, 912.4, 927.2, 975.2.

When nickel(II) actetate tetrahydrate (12.4 g, 0.05 mol), acetylacetone (10.1 g, 0.10 mol) and 1,2-diamino-4,5-dimethylbenzene (13.6 g, 0.10 mol) were reacted using 250 mL of methanol, Ni(OMTAA) was isolated in reduced yield (2.9 g, 13%) and purple crystals of **I** as the methanol solvate, formed on cooling (3.0 g, 12% based on 1,2-diamino-4,5-dimethylbenzene) (Found: C, 58.80; H, 7.15; N, 11.61. $NiC_{26}H_{30}N_4$ requires C, 59.41; H, 7.06; N, 11.55%). ^1H NMR (solvent $CDCl_3$, standard $SiMe_4$): δ 2.12 (s, 6H), 2.15 (s, 6H), 2.26 (s, 6H), 4.99 (s, 1H), 6.78 (s, 2H), 6.96 (s, 2H). ^{13}C NMR (solvent $CDCl_3$, standard $CDCl_3$): δ 19.18, 20.03, 23.43, 50.75, 62.39, 109.36, 122.07, 125.22, 131.35, 133.10, 133.82, 146.76, 156.48. *m*/*z* 393.2, 785.3.

[Ni(OMTAA)C_{60}]·2CS_2. To a purple solution of C_{60} (0.021 g, 3.0×10^{-5} mol) in carbon disulfide (3 mL) was added Ni(OMTAA) (0.030 g, 6.6×10^{-5} mol). The resulting green solution was evaporated to dryness depositing large black crystals. These were then washed with dichloromethane until the filtrate ran colourless (0.031 g, 78% yield) (Found: C, 78.82; H, 2.36; N, 4.48. $NiC_{88}H_{30}S_4N_4$ requires C, 79.46; H, 2.27; N, 4.21%). λ_{max} (ε) (CS_2): 600 (6 150), 456 sh (14 100), 409 (28 290) nm ($dm^3\ mol^{-1}\ cm^{-1}$).

X-Ray crystallography

Data were collected on an Enraf-Nonius CCD diffractometer at 123 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71013$ Å). Data were corrected for Lorentzian and polarisation but not absorption. The structure of Ni(OMTAA) was solved by direct methods using maXus,[35] whilst the structures for **I** and [Ni(OMTAA)C_{60}]·2CS_2 were solved using TEXSAN.[36] 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.

I. $C_{24}H_{34}N_4O_3Ni$. $M_r = 485.26$ monoclinic, $a = 7.9740(6)$, $b = 23.452(2)$, $c = 12.267(1)$ Å, $\beta = 90.911(5)°$, $U = 2293.8$ Å^3, space group $P2_1/c$, $Z = 4$, μ(Mo-Kα) = 8.70 mm^{-1}, 4917 reflections, 289 parameters, $R_1 = 0.0673$, $wR = 0.0810$.

Ni(OMTAA). $C_{26}H_{30}N_4Ni$. $M_r = 457.24$. monoclinic, $a = 20.2852(5)$, $b = 11.5462(4)$, $c = 19.0594(5)$ Å, $\beta = 94.8529$ (10)°, $U = 4447.8$ Å^3, space group $C2/c$, $Z = 8$, μ(Mo-Kα) = 8.935 mm^{-1}, 3164 reflections, 280 parameters, $R_1 = 0.042$, $wR = 0.046$.

[Ni(OMTAA)C_{60}]·2CS_2. $C_{88}H_{30}N_4S_4Ni$. $M_r = 1330.11$, monoclinic, $a = 21.8510(5)$, $b = 13.2492(4)$, $c = 19.6201(5)$ Å. $\beta = 105.7109(10)$, $U = 5468$ Å^3, space group $C2/c$, $Z = 3$, μ(Mo-Kα) = 6.20 mm^{-1}, 7032 reflections, 438 parameters, $R_1 = 0.088$, $wR = 0.089$.

CCDC reference number 186/1287.

See http://www.rsc.org/suppdata/dt/1999/279/ for crystallographic files in .cif format.

Acknowledgements

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