(6,17-Dimethyl-8,15-diphenyldibenzo[*b,i*][1,4,8,11]-tetra-aza[14]annulenato)nickel(II) in Solids: Two Guest-Free Polymorphs and Inclusion Compounds with Methylene Chloride and Fullerene (C_{60})−Carbon Disulfide

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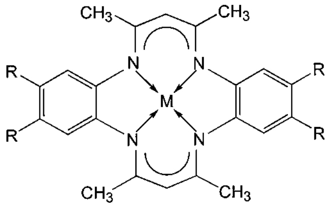
Two guest-free polymorphs and two inclusion compounds of the macrocyclic title complex [NiL] have been isolated and characterized with single-crystal and/or powder XRD, solid-state ^{13}C NMR, and other methods. The inclusion compound with methylene chloride, [NiL]*(CH_2Cl_2), is stable in air and thermally stable up to ∼128 °C. Its crystal structure is consistent with van der Waals packing of the host [NiL] and guest CH_2Cl_2 molecules. The host complex has square-planar coordination of the nickel(II) center with four nitrogen atoms of the macrocycle with an average Ni−N distance of 1.86 Å. The molecule has a saddle-shaped conformation with the guest molecule located between one phenylene and two phenyl rings of the host molecule. Isostructural compounds with chloroform and 2-chloropropane form only as mixtures along with a guest-free host polymorph. The inclusion compound with C_{60} has a composition 3[NiL]*(C_{60})*2(CS_2) and here also the crystal structure is consistent with a van der Waals type of packing. Three crystallographically inequivalent [NiL] molecules have geometries similar to that in the inclusion compound with methylene chloride. The concave surfaces of the complex molecules form a spherical cavity for the C_{60} molecule. At −100 °C the C_{60} molecule is disordered over two orientations centered at the same site. ^{13}C NMR studies at room temperature show that the C_{60} molecule is undergoing rapid pseudo-isotropic rotation. The stability and other properties of the title and related complexes are discussed.

Introduction

Macrocyclic metal dibenzotetraaza[14]annulenates have stimulated continuing interest in a wide range of areas.[1,2] These complexes have a distinctive saddle-shaped geometry with conformational rigidity and thus have the potential of forming porous architectures. The complexes [M(TMTAA)] and [M(OMTAA)] (Scheme 1), studied recently, are versatile hosts forming inclusion compounds with inorganic and organic species, not only in the solid but also in solution.[3−7] Because of their concave surfaces, these host molecules may be selective toward large globular molecules such as fullerenes; both C_{60}[3−5] and C_{70}[6] have been confined as guests in solid inclusions. A few other dibenzotetraaza[14]annulene complexes with the same ligands have been reported to entrap solvent molecules upon crystallization.[8−10]

Scheme 1



[M(TMTAA)] (R = H)
[M(OMTAA)] (R = CH$_3$)

The potential of tetraazaannulenates as host materials therefore needs to be more widely explored, the more so as two extensive classes of structurally related host complexes have been developed. Porphyrin-based complexes form inclusion compounds numbering in the hundreds, with many variations due to the wide range of metals, porphyrins and guests which have been utilized.[11−17] Metal bischelates with acetylacetonate-type ligands make up another class of related complexes, which may be considered as tetraaza[14]annulene precursors. We have

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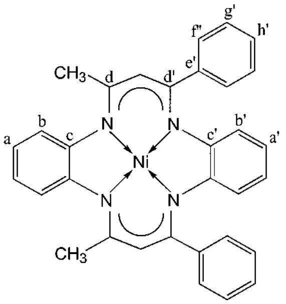
Scheme 2



[NiL]

discovered recently that metal dibenzoylmethanates, when modified with appropriate axial ligands, reveal remarkable inclusion properties.[18−32]

The present study characterizes solid forms of [NiL] (Scheme 2) which is an extension of its maternal analogue by two phenyls. The complex and its H_2L macrocycle were first reported in 1980 [33] but it was studied only recently by single-crystal XRD as a solvate with chloroform.[34] Difficulties in preparing suitable crystals, because of twinning and small size, led to a limited structural solution for the host only, with some centers representing disordered guest.[35] The present study elucidates the existence of two guest-free polymorphic forms of the complex, and characterizes two inclusion compounds of the complex, with methylene chloride and fullerene (C_{60})−carbon disulfide.

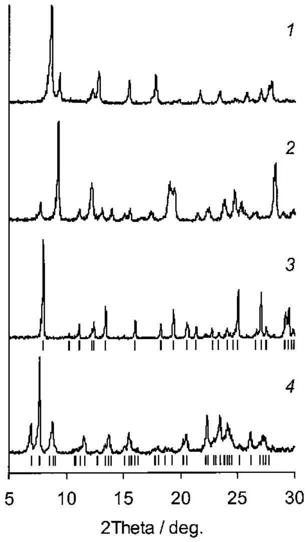


Figure 1. Powder X-ray diffractograms of isolated solids: (1) [NiL], low form; (2) [NiL], high form; (3) [NiL]*(CH_2Cl_2); (4) 3[NiL]*(C_{60})*2(CS_2). The vertical bars show the positions of the most intense reflections (>5% of the strongest peak) theoretically predicted from the single-crystal data (using room-temperature unit cell dimensions). Radiation: Co Kα, $\lambda = 1.7902$ Å.

Experimental Section

(6,17-Dimethyl-8,15-diphenyldibenzo[b,i][1,4,8,11]-tetra-aza[14]-annulenato)nickel(II), [NiL]. The complex was prepared as described earlier,[33] by refluxing under nitrogen for 30 min a mixture of *o*-phenylenediamine (10.8 g, 0.10 mol) and nickel acetate tetrahydrate (12.4 g, 0.05 mol) in anhydrous butanol (200 mL), and then for a further 12 h after the addition of benzoylacetone (16.2 g, 0.10 mol). The green crude product was filtered off, washed with butanol and methanol, dried under nitrogen, and recrystallized from butanol. ^1H NMR (CD_2Cl_2) (δ, ppm): 2.24 (6H, $-CH_3$), 5.06 (2H, >C−H), 5.61 and 5.96 (2H+2H, aromatic a′ and b′), 6.70 and 6.89 (2H + 2H, aromatic a and b), 7.37 (10H, phenyls). Recrystallization of the product from a range of solvents resulted in one of two solid forms, or their mixture. Both forms exhibited the same ^1H NMR spectra after dissolving, which makes it possible to assign them as two polymorphic modifications of the complex.[36] Powder X-ray diffractograms (PXRD) of the two pure polymorphs are shown in Figure 1. Solid state ^{13}C NMR spectra are discussed in the next section.

[NiL]*(CH_2Cl_2). This inclusion compound formed as a dark green crystalline product in the course of fast evaporation (several hours) of a solution of the complex in methylene chloride. By TGA the product showed a mass loss of 13.9% in the 128−138 °C temperature range, cf. calculated 13.9% for methylene chloride content in [NiL]*(CH_2Cl_2). The composition of the bulk product was also confirmed by solid state ^{13}C NMR and by comparing the experimental PXRD pattern with that calculated from single-crystal X-ray analysis (Figure 1).

3[NiL]*(C_{60})*2(CS_2). The fullerene C_{60} (144 mg, 0.20 mmol) was dissolved with gentle heating in carbon disulfide (50 mL). [NiL] (315 mg, 0.60 mmol) was then added, and the resulting solution left to evaporate to dryness. The ^{13}C NMR spectra are discussed in the next section, and experimental and calculated PXRD patterns can be compared in Figure 1.

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Powder XRD. Powder patterns were recorded on a Rigaku Geigerflex diffractometer (CoKα radiation, $\lambda = 1.7902$ Å) over a 5−30° 2θ range, 0.02° step scan with 1 or 2 s per step. Theoretical diffractograms were calculated using atomic coordinates from the single-crystal XRD analyses, but with unit cell dimensions determined at room temperature.[37]

Single-Crystal XRD. Single crystals of the two inclusion compounds studied, in the form of dark-green plates, were picked out of the bulk products. Unit cell dimensions were measured both at room temperature[37] and at −100 °C, using the same crystals. Full XRD data sets were collected at −100 °C.

A Siemens SMART CCD X-ray diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) was used to collect the diffraction data. An empirical absorption correction utilized the SADABS routine associated with the diffractometer. The final unit cell parameters were obtained using the entire data set.

The structures were solved and refined using the SIR92[38] and SHELXTL[39] packages, by direct methods followed by differential Fourier syntheses. The structural refinement was performed on F^2 using all data with positive intensities. Non-hydrogen atoms were refined anisotropically. Isotropic approximations and geometric constraints were applied for the minor orientation of the CH_2Cl_2 molecule. Minor orientations of the disordered CS_2 group were constrained to have the same geometry as in the main orientation. Hydrogen atoms were refined isotropically with thermal factors 1.2 or 1.5 times greater than those for the adjacent carbon atoms. Site occupancy factors for guest orientations were refined independently; in the last cycles their sums were fixed to give the ideal stoichiometry as observed deviations were not significant.[40] The largest residual extrema on the final difference map were located about guest Cl or S atoms.

Analysis of the packing was accomplished using the XP[39] and CLAT[41] program packages. The following van der Waals radii were applied:[42,43] C, 1.71; H, 1.16; Cl, 1.90; N, 1.52; Ni, 1.63; S, 1.84 Å.

A summary of the crystal data and experimental parameters is given in Table 1. Complete data can be found in the Supporting Information.

NMR Spectroscopy. ^{1}H NMR Spectra were obtained for solutions of the polymorphs in deuterated methylene chloride with a Bruker DRX-400 instrument. Assignments were based on data reported earlier.[33,44] Stoichiometry ratios derived by integration of bands with the XWIN NMR 2.0 program package corresponded to the expected integral numbers within the experimental error of 5%.

Solid state ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra with ^{1}H decoupling were obtained at 75.48 MHz at room temperature on a Bruker AMX300 spectrometer equipped with a Doty Scientific 5 mm CP/MAS probe. A standard CP pulse program was used with fixed amplitude ^{1}H decoupling during signal acquisition. ^{1}H 90° pulse lengths were 2.7 μs, CP times were 3 ms, except for the C_{60} compound, and recycle times were 4−17s, depending on the sample. Dipolar dephased spectra[45] were obtained by interrupting the ^{1}H decoupling for 40 μs immediately after the CP sequence and before starting the data acquisition. CP spectra for the C_{60} complex were obtained with CP times 1, 5, 10 and 20 ms, and some spectra were also obtained without CP but with ^{1}H decoupling, using recycle times up to 5 min. Chemical shifts were measured relative to external solid hexamethylbenzene and then corrected to the TMS scale. Spinning speeds were set in the range 6.06−6.5 kHz to avoid overlap of spinning sidebands with isotropically shifted lines.

Table 1. Summary of Low-Temperature Single-Crystal XRD Experiments

compound	[NiL]*(CH_2Cl_2)	3[NiL]*(C_{60})*2(CS_2)
chemical formula	$C_{32}H_{26}N_4Ni$, CH_2Cl_2	3($C_{32}H_{26}N_4Ni$), C_{60}, 2(CS_2)
formula weight	610.2	2448.6
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.742(2)	13.492(2)
b, Å	11.615(2)	15.701(2)
c, Å	14.189(2)	27.557(3)
α, Å	66.84(1)	74.16(1)
β, Å	73.27(1)	88.84(1)
γ, Å	75.06(1)	76.09(1)
V, Å^3	1394.5(4)	5445(1)
Z	2	2
D_{calcd}, g cm^{-3}	1.453	1.494
μ(Mo Kα), cm^{-1}	9.18	6.59
T, °C	−100	−100
λ, Å	0.7107	0.7107
R1 (F)[a]	0.030	0.054
wR2 (F_o^2)[b]	0.082	0.111

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\{\sum[w(F_o^2)^2]\}^{1/2}$.

The initial spectra of the C_{60} compound were obtained using a 1 or 2 s recycle time, and it was found that these short intervals ultimately resulted in gradual decomposition of the sample. This resulted in an increasing noise level in each scan, presumably due to the formation of charred, slightly conducting material. When the sample spinner was opened following this episode there was also a strong smell of H_2S, indicating reduction of CS_2. To circumvent this problem, recycle times of 10s or longer were used subsequently.

Other Methods. TGA and DSC measurements were made using a 2050 Thermogravimetric Analyzer and a 2920 Modulated Differential Scanning Calorimeter (TA Instruments), respectively. The heating rate was 5° per minute in both methods. Isopiestic measurements were performed with ∼100 mg samples of the high-temperature polymorph (high form) of the complex; the samples were placed in the vapor of the potential guest. More details on using the three techniques for similar host−guest systems are given elsewhere.[20,28,29,30,46]

Results and Discussion

Solid Forms of [NiL]. Four solid phases containing the complex [NiL] have been isolated and characterized in this work: two guest-free polymorphs of the complex, an inclusion compound with methylene chloride, [NiL]*(CH_2Cl_2), and a double inclusion compound with C_{60} and CS_2, 3[NiL]*(C_{60})*2(CS_2). Powder diffractograms of all four phases are compared in Figure 1, and are quite distinct.

The low-temperature polymorph (low form) was obtained upon crystallization from warm chloroform or pyridine. DSC analysis of this low form showed a weak (∼5 kJ/mol), diffuse, endothermal effect in the 130−160 °C temperature range, likely due to transformation into the high form.

The high form polymorph was reproducibly prepared by placing the low form in an oven at 135 °C for 1 h. It also was prepared directly in the course of crystallization from many solvents, including benzene, *n*-butanol, chloroform, 2-chloropropane, pyridine, acetone and tetrahydrofuran. Fine-crystalline or powder products were isolated from these solvents. If the solutions were evaporated slowly, the final products were badly contaminated with impurities, indicating decomposition of the complex itself with time. The high form exhibited no guest sorption or any other change in an atmosphere of *n*-heptane, benzene or 2-chlorobutane (isopiestic experiments). The DSC

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(37) At room temperature the unit cell dimensions were as follows. [NiL]*(CH_2Cl_2) (359 reflections): $a = 9.805(2)$, $b = 11.754(2)$, $c = 14.280(4)$ Å, $\alpha = 67.22(2)$, $\beta = 72.99(2)$, $\gamma = 74.80(2)$°, $V = 1430.1(6)$ Å^3. 3[NiL]*(C_{60})*2(CS_2) (310 reflections): $a = 13.565(3)$, $b = 15.836(4)$, $c = 27.743(7)$ Å, $\alpha = 74.11(2)$, $\beta = 88.62(2)$, $\gamma = 75.88(2)$°, $V = 5553(2)$ Å^3.

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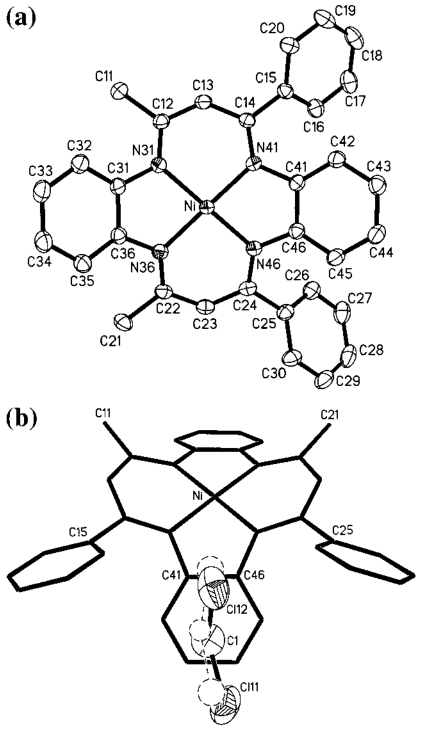

Figure 2. ORTEP drawings (50% probability level) of the host (a) and guest (b) molecules in [NiL]*(CH_2Cl_2). The guest molecule is shown as it is located with respect to the host. Minor orientation is depicted by dashes. In this and subsequent Figures H atoms are omitted.

thermogram of the high form exhibited a series of exotherms higher than 150 °C indicating irreversible degradation of the complex.

The [NiL]*(CH_2Cl_2) inclusion compound formed as a bulk monophase product upon fast evaporation of the solution of the complex in methylene chloride. Other solvents, as mentioned above, yielded guest-free forms. Crystallizations with addition of [NiL]*(CH_2Cl_2) as nucleation agent yielded mixtures of the high form of [NiL] and the inclusion form with chloroform or 2-chloropropane (as determined from PXRD and TGA results). CH_2Cl_2 is therefore the only one of all the potential guests which were tried which transforms the complex into the inclusion form quantitatively. The TGA thermogram of [NiL]*(CH_2Cl_2) (see Supporting Information) shows a surprisingly high thermal stability, which implies that the guest molecules are tightly confined inside the structure.

The 3[NiL]*(C_{60})*2(CS_2) inclusion compound formed reproducibly as a bulk product from carbon disulfide solution containing stoichiometric quantities of the host complex and fullerene. Because of the high solubility of the host, most solvents washed out the host complex producing a solid residue of C_{60}.

Structure of [NiL]*(CH_2Cl_2). This inclusion compound is triclinic, $P\bar{1}$, with two formula units per unit cell. One entire host molecule and one guest molecule form the asymmetric unit of the structure. The CH_2Cl_2 molecule is disordered over two orientations in a 9:1 occupancy ratio. Van der Waals contacts dominate the packing in the structure everywhere.

The Ni atom of the host molecule (Figure 2a) has a square planar coordination defined by the four N atoms of the macrocycle, and the deviation of the Ni atom from this equatorial plane is less than 0.02 Å. The Ni−N distances vary between 1.862(1) and 1.868(1) Å. The N−Ni−N coordination angles are ~85° and ~95° in the five- and six-membered rings, respectively. All the N−C bonds of the six-membered rings are very similar (1.330(2) to 1.340(2) Å), and likewise for the C−C bonds (1.393(2) to 1.410(2) Å), indicating strong conjugation within these fragments. The whole molecule has a typical saddle-shaped conformation governed by strong repulsive intramolecular interactions (Figure 2b). With the sum of the carbon van der Waals radii of $1.71 \times 2 = 3.42$ Å, the shortest contacts (Figure 2b) between phenylenes and methyl carbons C32...C11 and C35...C21 are both 2.98 Å, and those between phenylenes and phenyls C42...C16 and C45...C26 are 3.11 and 3.28 Å, respectively.[47] An overlap between ortho hydrogens of phenyl and phenylene rings is avoided due to phenyls rotating out of the plane of the six-membered rings by 46° (C15...C20) and 41° (C25...C30), the resulting H···H contacts of 2.34 Å. The degrees of curvature of the molecule may be judged from two dihedral angles: the angle between the two NCCCN semi-rings is 136° and the angle between the two phenylene rings is 116°. For a planar unit both these angles would be 180°.

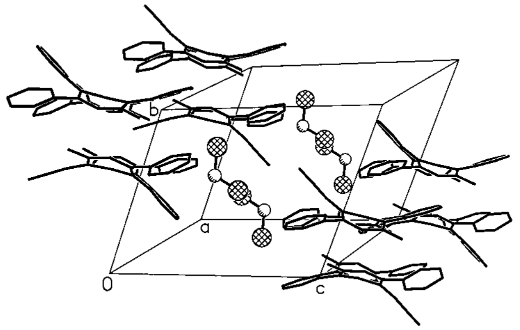

Figure 3. Fragment of crystal packing in [NiL]*(CH_2Cl_2) comprising two cavities with two guests in each and showing stacking of host molecules.

The CH_2Cl_2 guest molecule has large thermal parameters and is disordered over two orientations (Figure 2b) (the main orientation is occupied by 90.4(4) %). It sits in a pocket formed by two phenyls and one phenylene of the host molecule. The short distance of 2.74 Å from one of the guest hydrogens to the center of the C41−C46 aromatic ring may be indicative of weak C−H...π interactions. Two adjacent pockets form a centrosymmetric cavity with the center at (0,0.5,0.5). This cavity is built up of exclusively hydrocarbon parts of the host, i.e., neither Ni nor N atoms are accessible from inside. The cavity is closed so that the guest cannot move through the structure, which is consistent with the stability of the compound in air.

Figure 3 shows a fragment of the crystal packing comprising two cavities with centers at (0,0.5,0.5) and (1,0.5,0.5). Each host molecule stacks up over a neighbor related by centrosymmetry, with 5.18 Å between the Ni centers; four such pairs are shown in Figure 3. Another neighbor host molecule is located on the opposite side of the molecule, but with a longer Ni−Ni distance of 7.27 Å.

Structure of 3[NiL]*(C_{60})*2(CS_2). This inclusion compound is triclinic, $P\bar{1}$. The asymmetric unit is formed by three crystallographically different [NiL] molecules (A, B and C), one C_{60} disordered over two positions, and two CS_2 molecules, one of which is also disordered. This results in 177 crystallographically independent non-hydrogen atoms and, due to guest disorder, in as many as 2171 refined parameters. A symmetry center produces the other half of the unit cell contents, thus

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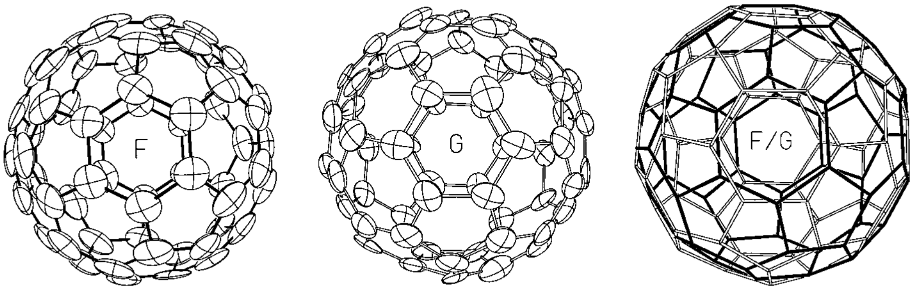

Figure 4. Guest fullerene molecule in 3[NiL]*(C_{60})*2(CS_2). Shown are F (63%) and G (37%) orientations (ORTEP, 50% probability level), and their superposition. G and F are related by a rotation of ~30° around the 6-fold axis of the molecule which is almost perpendicular to the plane of the Figure.

resulting in six [NiL], two C_{60}, and four CS_2 molecules per unit cell. The intermolecular contacts are consistent with van der Waals packing.

The molecular structure is roughly the same for all three [NiL] molecules, and similar to that for the CH_2Cl_2 inclusion compound. The Ni−N distances vary between 1.847(1) and 1.883(2) Å, with an average of 1.862(3) Å for 12 bonds in three molecules. The saddle-shaped conformation changes little from molecule to molecule: The dihedral angles between the two NCCCN semi-rings in each [NiL] are 135°, 136°, and 132°, and those between the two phenylene rings are 128, 120 and 120° (A, B and C molecules, respectively). The phenyl (C15...C20) is rotated from its adjacent six-membered ring by 52, 44 and 53°, and the phenyl (C25...C30) is rotated by 56°, 45°, and 52° (A, B and C molecules, respectively). The shortest contacts are 2.99−3.02 Å (C32...C11), 3.00−3.02 Å (C35...C21), 3.16−3.31 Å (C42...C16), and 3.07−3.27 Å (C45...C26).

The C_{60} molecule occupies a general position in the structure. High thermal atomic parameters in tangent directions (Figure 4) indicate the presence of rotation of the molecule, predominantly around one of its 6-fold axes, approximately parallel to the c direction. The molecule is disordered over two orientations (Figure 4), and the minor orientation G (37.1(1) %) is related to the main orientation F through a rotation around the 6-fold axis by ~30°. The centroids of the two orientations are displaced from each other by only 0.14 Å. It should be emphasized that this crystal structure was studied at −100 °C and the minor orientation was impartially observed from difference Fourier synthesis. As evident from MAS ^{13}C NMR spectra, the molecule is rotating rapidly at room temperature (see below).

The C_{60} molecule is surrounded principally by five [NiL] molecules (Figure 5). Three of them (A, B′, and C′ in Figure 5) contribute their large concavities (that is, concavities formed by the six-membered rings) whereas the other two ("B and C" in Figure 5) donate their minor concavities (concavities formed by five-membered and phenylene rings). Many other inclusion compounds with C_{60} as a guest are already known,[3−5,7,48−57] but none display this kind of fit between the convex surface of the C_{60} and the concave surfaces of several host molecules. The surroundings are completed by other guest molecules, including CS_2 and another C_{60} molecule approaching the first at a C−C distance of 3.90 Å. This shortest C_{60}−C_{60} contact takes place across the symmetry center at (0,0,0.5). The distance between centroids of the adjoining fullerene molecules is 10.8 Å.

The interplay of host and guest molecules is shown in Figure 6. The molecules B of the complex (black) donate both of their concavities to create sockets for C_{60} molecules, resulting in alternating [NiL] and C_{60} molecules along the a direction. An analogous motif was previously found for the related material [Ni(OMTAA)]*(C_{60})*2(CS_2).[4] In the layer parallel to the (*ab*) plane the sockets are completed with [NiL] (C) and CS_2 (D) molecules. These layers alternate with inverted ones along the *c* direction. In the layer parallel to the (*ac*) plane the A molecules contribute their large concavities to the sockets and stack by their minor concavities as in the CH_2Cl_2 compound (with 7.01 Å between Ni centers). As a whole, the architecture is surprisingly complex and entirely different from what has been observed before for analogous host complexes.[3−10]

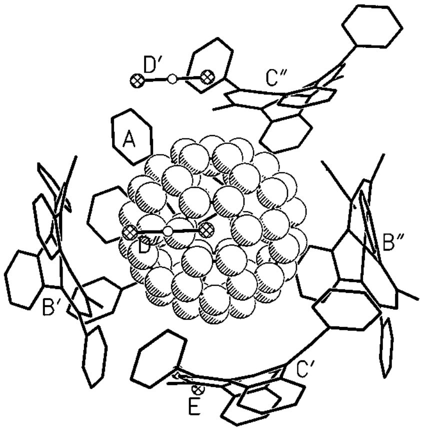

Figure 5. One C_{60} molecule (large balls) surrounded by the host (black sticks) and carbon disulfide (ball-and-stick) molecules in 3[NiL]*(C_{60})*2(CS_2). The projection axis is the same as in Figure 4.

^{13}C NMR of Isolated Solids. ^{13}C CP/MAS NMR spectra of all four compounds are shown in Figure 7, and shifts and assignments are given in Table 2. As a whole, the data indicate that all of the solid phases contain [NiL] in a similar isomeric state and have the same basic geometry. The absence or presence of guests is also seen to be consistent with the claimed stoichiometries.

The spectra of the low and high forms of the host [NiL] complex, Figure 7a,b, have very similar maxima, but the low form shows line broadening. Since the PXRD pattern of the low form (Figure 1) shows it to be crystalline this broadening is most likely due to trace paramagnetic impurities. Probably both forms have the complex in a very similar conformation and may have similar packing motifs, resulting, however, in different crystal structures.

Examination of the spectra of the high form and [NiL]*(CH_2Cl_2), Figure 7b,c, d, reveal that these are similar to that for [NiL], although small differences in the shifts and splitting patterns are clear indicators of differences in the carbon environments. Doublets for $-CH_3$, bridging >C−H and the quaternary carbons on the phenyl groups (carbons e) in both materials indicate that there is more than half an L in the asymmetric unit. The quaternary carbons of the phenylene groups and those attached to N also show multiplicities that are incompatible with only half a molecule in the asymmetric unit. The intensity of the

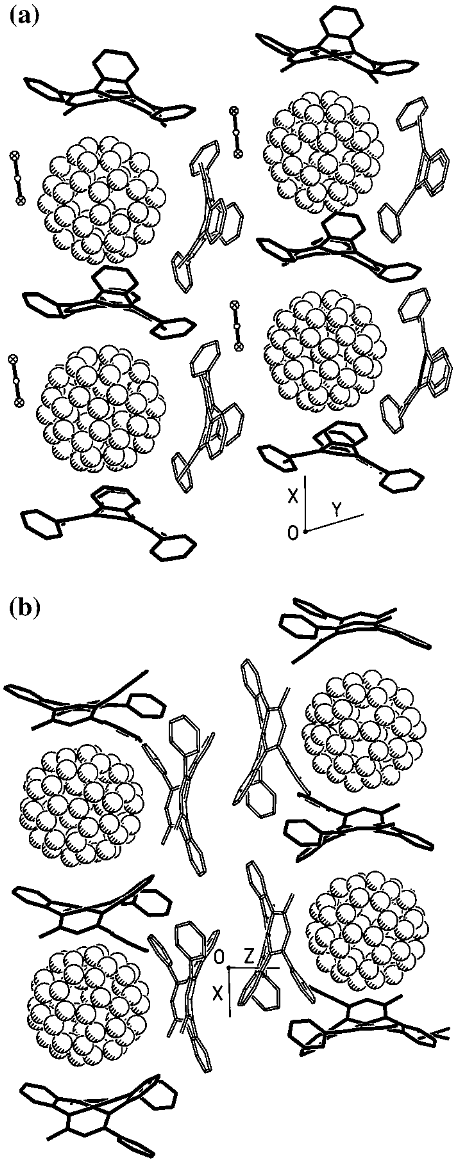

Figure 6. Views of the crystal packing in 3[NiL]*(C_{60})*2(CS_2). (a) A layer parallel to the (*ab*) plane (half thickness of the unit cell); host B and C molecules are outlined in black and white sticks, respectively. (b) A layer parallel to the (*ac*) plane (thickness of the unit cell); host A molecules are outlined in white sticks.

guest CH_2Cl_2 carbon indicates a ~1:1 host per guest ratio. This implies that the asymmetric unit contains either an asymmetric L molecule or 2 L molecules each with equivalent halves.

Figure 7d shows the dipolar dephased spectrum of [NiL]*(CH_2Cl_2), which is typical of the dephased spectra for all four compounds studied. The dipolar dephased spectra show only the quaternary carbons at full intensity, and any proton-bearing carbons undergoing motion at reduced intensity. Thus the methyl groups of the host and the CH_2Cl_2 guest show dynamics. Also, there is a small amount of residual intensity in the aromatic region due to a motion which is probably a partial reorientation of the phenyl groups about their 2-fold axes. The phenylene groups can be expected to be quite rigid, and any motion other than those about the 2-fold axis would imply motion of the whole complex.

The ^{13}C CP/MAS spectrum of 3[NiL]*(C_{60})*2(CS_2), Figure 7e, is more complex than those for the host polymorphs or the CH_2Cl_2 compound. In particular, several resonances show multiplets consistent with six-half [NiL] molecules in the asymmetric unit: CH_3 (1:2:1:1:1), bridging CH (3:2:1), and phenyl quaternaries (1:1:2:2). Experiments without CP but with ^1H decoupling indicate that the C_{60} atoms have a much shorter relaxation time than the other carbons, which probably reflects its dynamics (see below), but using a 5-minute recycle time the system appears to be fully relaxed, and the relative intensity of the C_{60} versus the other carbons is consistent with the unit cell content to within 15%. On the other hand, one can discriminate against the C_{60} signal by using a short CP time; there is a roughly 12-fold increase in intensity relative to the most intense lines of the [NiL] between CP = 1 ms and 20 ms. Also note that with increasing CP time the quaternary carbons of [NiL] gain intensity less rapidly than the proton-bearing carbons. For the C_{60} and the quaternaries of [NiL] the lack of attached ^1H's means that the CP is long range and ^{13}C

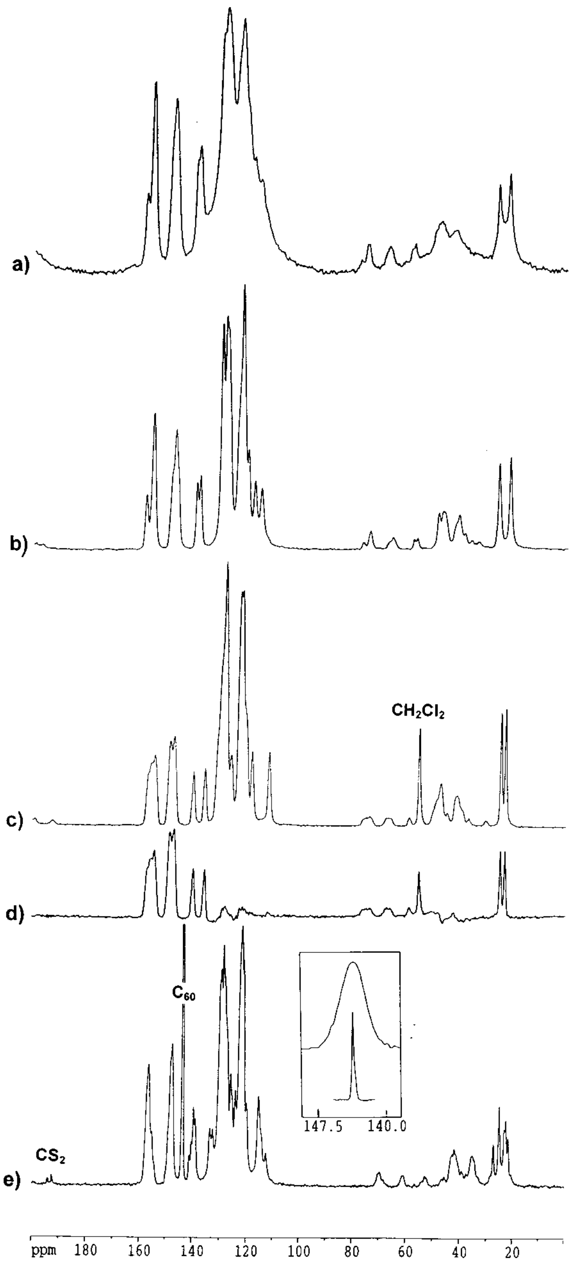

Figure 7. ^{13}C CP/MAS NMR spectra of solid [NiL] compounds: (a) Low polymorph; (b) High polymorph; (c) [NiL]*(CH_2Cl_2); (d) [NiL]*(CH_2Cl_2), dipolar dephased; (e) 3[NiL]*(C_{60})*2(CS_2), the inset shows the C_{60} line shape, static (top), MAS (below). The lines in the region 30−80 ppm are spinning sidebands from the aromatic region, with the exception of the CH_2Cl_2 resonance in (c) and (d).

Table 2. Assignments of ^{13}C NMR Chemical Shifts (ppm) of [NiL] Compounds (relative intensity in brackets)

	No.^{a}	[NiL], low form	[NiL], high form		[NiL]*(CH_2Cl_2)		3[NiL]*(C_{60})*2(CS_2)	
CH_3	2	21.7	21.7 (1)		23.1 (1)		21.7 (1)	
		25.8	25.9 (1)		24.9 (1)		22.7 (1)	
							23.2 (1)	
							25.2 (2)	
							27.4 (1)	
>C−H	2	~115	115.2 (1)		111.7 (1)		112.5 (1)	
		~117	117.7 (1)		118.1 (1)		114.3 sh (2)	
							115.4 (3)	
aromatic	18	120.4 sh	120.2	(8)	120.4 sh	(8)	120.1	(24)
(a,b,a′,b′,		122.3	122.3		122.1		121.2	
f′,g′,h′)^b		123.8 sh	123.7 sh		122.8		122.0	
							122.4 sh	
		127.1 sh	127.9 sh	(10)	126.1	(10)	124.3	
		128.3	128.5		128.4			
		~129	130.1		129.8 sh		125.4 sh	(30)
					131.1 sh		126.0	
							127.2 sh	
							127.6	
							128.2	
							128.9	
							129.6	
							130.2 sh	
							132.6	
							133.6	
quaternary e′	2	138.2	138.1 (1)		135.8 (1)		138.9 (2)	
		139.2 sh	139.4 (1)		140.1 (1)		139.6 (2)	
							140.3 (1)	
							141.1 (1)	
quaternary c and c′	4	146.4 sh	146.5 sh (1)		147.3 (2)		147.8 (5)	
		147.6	147.5 (2)		148.8 (2)		148.2 sh (4)	
		148.6 sh	148.6 sh (1)				149.2 sh (2)	
							149.9 sh (1)	
quaternary d and d′	4	155.7	155.7 (3)		154.6	(4)	154.5 sh (1)	
		158.1	158.2 (1)		156.1 sh		155.4 (2)	
					157.1 sh		156.7 (5)	
							157.4 sh (4)	
CH_2Cl_2	1				55.4 (1)^c			
C_{60}	20						143.8	
CS_2	2/3						192.6^c	
							194.1	

^{a} Number of carbons per NiL unit. ^{b} See Scheme 2 for letter designations. ^{c} Liquid CH_2Cl_2 at 54.4 ppm, liquid CS_2 at 193.1 ppm.[58]

magnetization takes longer to build up. There are two resonances for CS_2, again consistent with the asymmetric unit content. In this instance, prohibitively long experimental times would be required to obtain accurate relative intensities of the guest molecules relative to those of the host.

The inset of Figure 7e shows the C_{60} resonance with halfwidths of only 247 Hz (static) and ~18 Hz (MAS). Averaging of the chemical shift anisotropy (csa) to such a narrow line unequivocally indicates rapid pseudo-isotropic reorientation of the C_{60} molecule, as found in solid C_{60} itself at room temperature (the csa for the C atoms of a static C_{60} molecule has a span =180 ppm (=13 587 Hz at a field of 7T)).[59−66] This could be reorientation in such a manner that all of the C atoms exchange sites or it could be rotational diffusion over a sphere. The lattice site itself does not have high symmetry, and so in theory there could be residual anisotropy of the chemical shift, however this was not detectable within experimental limitations.

[NiL] vs Other Dibenzotetraaza[14]annulenates. As shown in this study, the [NiL] complex has certain attributes common to molecular hosts: in particular, a conformationally stable molecular structure, and variability of crystal packing.

The geometry of the [NiL] complex remains very similar for all four independent molecules found in the two inclusion complexes studied. This geometry is largely determined by the strained coordination environment of the metal center. The short Ni−N bonds are consistent with a low-spin state of the nickel center arising from the tetragonal distortion characteristic of d^8 and d^9 cations. The complex therefore is diamagnetic, in both the solid state and in solution. The restraints imposed by the narrow coordination cavity of the macrocycle prevent transformation of the complex into a high-spin state through the formation of two additional axial bonds. Even crystallizations from neat pyridines do not change the square-planar coordination environment of the nickel center. Another consequence of the narrow coordination cavity is the rigid saddle-shaped conformation of the molecule, as this conformation makes it possible to increase the dimensions of the cavity to some extent. The resulting overall geometry is therefore very similar to that of other, simpler complexes. For example, the average Ni−N distance and dihedral angle between two phenylenes equal to 1.860(4) Å (16 bonds) and 121(3)° (4 molecules) for [NiL] in the two structures of our work are quite similar to respective values of 1.868(1) Å (42 bonds) and 125(1)° (14 molecules) found in six inclusion compounds[3,5] and two guest-free forms[67,5] of the [Ni(TMTAA)] complex. Another comparison may be made with the guest-free structure of [CuL], reported earlier.[68] Longer coordination bonds with Cu−N (average distance of 1.923(3) Å for 8 bonds) result in greater distortion of the coordination unit and thus the dihedral angles between the phenylenes equal 136° and 133° for two [CuL] molecules. Overall, however, the [CuL] species has the same type of geometry as [NiL].

Crystal packing is a variable characteristic of the [NiL] complex since two guest-free and two inclusion forms have been

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(66) NMR of C_{60} pentane solvate: Aliev, A. E.; Harris, K. D. M.; Tegze, M.; Pekker, S. *J. Mater. Chem.* **1993**, *3*, 1091−1094.

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isolated. The host thus exhibits a general tendency as for many other systems conventional polymorphism[36] and the ability to include are found together.[69] Small guest species such as CH_2Cl_2 or $CHCl_3$ fill out the side pocket of the [NiL] molecule but the large concave surfaces of the host are still used ineffectively. Medium sized molecules of other solvents are not complementary to the host and thus remain indifferent to inclusion. Only a large globular molecule such as C_{60} is able to provide extended, and therefore effective, contact of two complementary surfaces. The inclusion with C_{60} is much denser (Table 1) than that with CH_2Cl_2, despite having lighter atoms. The [NiL] therefore may be selective to very specific kinds of potential guest candidates. This feature is inherent in simpler tetraazaannulenates, [M(TMTAA)] and [M(OMTAA)] (Scheme 1),[3−7] though it results in distinct supramolecular architectures.

The specific inclusion properties discussed above may be significant when it comes to designing other tetraazaannulenates bearing peripheral substituents. The overall stability of the final complex may be of crucial significance in such design though.[75] The [Ni(TMTAA)] complex is easily prepared by template condensation (using nickel(II) acetate) of *o*-phenylenediamine with acetylacetone, $CH_3COCH_2COCH_3$, in boiling ethanol (bp 78 °C).[44] The synthesis of [NiL] (with benzoylacetone, $PhCOCH_2COCH_3$) requires the higher temperature of boiling butanol (bp 118 °C) and the resulting complex shows a tendency to decompose in most solvents. As evident from intramolecular contacts in [NiL], the phenyl substituents do not create any greater strain in the molecule than the methyl groups. The destabilization may be due to the electronic properties of the phenyl group, or there may be an entropy effect as the macrocycle formation restricts transient rotation of the phenyls in the initial reagent. Remarkably, our attempts to perform the analogous synthesis with dibenzoylmethane ($PhCOCH_2COPh$) did not produce any condensation at all. Increasing the size of the macrocycle itself could increase the stability of these and new host tetraazaannulenates.

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Supporting Information Available: A figure showing the TGA thermogram of [NiL]*(CH_2Cl_2). Full data for the structure determination of [NiL]*(CH_2Cl_2) and 3[NiL]*(C_{60})*2(CS_2) inclusion compounds at −100 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(69) Examples of versatile organic hosts displaying polymorphism: Gossipol (7 guest-free polymorphs) (refs 70, 71); hydroquinone (3 guest-free polymorphs) (ref 72); 4,5-Bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1H-imidazole (3 guest-free polymorphs) (ref 73); perhydrotriphenylene (2 guest-free polymorphs) (ref 74).

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