Inclusion Ability of 4-Phenylpyridine-Extended Nickel(II) Dibenzoylmethanate, a New Metal−Complex Host†

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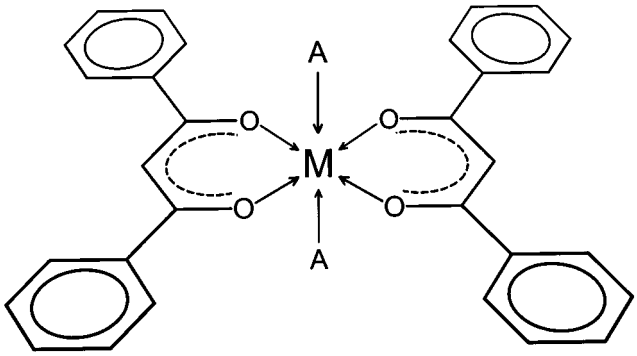
A new host complex, $[Ni(4\text{-}PhPy)_2(DBM)_2]$, has been prepared by modification of nickel dibenzoylmethanate ($Ni(DBM)_2$; DBM = $C_6H_5COCHCOC_6H_5^-$) with 4-phenylpyridine (4-PhPy). Of 17 organic solvents that were tested as guest candidates, 6 inclusion compounds were isolated, mostly as bulk products. All compounds were characterized with XRD methods. With benzene, fluoro-, chloro-, and bromobenzenes, toluene, and *o*-xylene, 1:1 inclusions form; they are all green, relatively stable, and isostructural (triclinic, $P\bar{1}$, $Z = 2$). The guest species accommodate flattened cages formed upon van der Waals packing of host molecules. The guest inclusion influences the distortion in the bischelate fragment of the host molecule, as the dihedral angle between two chelate rings ranges up to 12°. This distortion is probably responsible for the green color of these phases. The series of inclusions exhibits an order of thermal stability opposite to that which would be expected from the volativity of the neat guests; the order indicates strong preference of the inclusion matrix to benzenes with smaller substituents. With benzene, one more inclusion phase was isolated as a metastable product, with a host-to-guest ratio of 1:4; it is brown and of a distinct structural type (triclinic, $P\bar{1}$, $Z = 1$). The guest species are found in alternating layers of closely packed host molecules. The guest-free host phase is brown; its crystal structure (triclinic, $P\bar{1}$, $Z = 1$) is different from the inclusion compounds. In all the materials studied the host molecule is a trans-configured octahedral complex with two DBMs chelating the nickel(II) center in an equatorial plane and two 4-PhPy ligands coordinating axially.

Introduction

In the preceding parts of this series,[1−4] we demonstrated that modified metal dibenzoylmethanates (metal DBMs) constitute a new class of metal−complex hosts with the general formula shown in Scheme 1. Both the metal center M and the neutral ligand A may be changed to generate a variety of host materials with the ability to enclathrate a wide range of organic guests.

Of the numerous known "building elements" used to produce supramolecular architectures, only a few have been known to allow extensive modification. Among metal complexes that yield van der Waals type architectures, only Werner-type[5−7] and the porphyrin-based[8−10] hosts have been extensively studied after discovery; modified xanthates[11−13] and some other chelated[14−20] or macrocyclic[21−25] complexes might be of

Scheme 1



† This is part 5 of the Series "Modified Metal Dibenzoylmethanates and Their Clathrates"; for the four previous parts see, in consecutive order, refs 1−4.

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interest as well but these have not yet been fully explored.

Previously reported metal DBM hosts embrace complexes with Ni(II)[1−4] and Co(II)[2,3] as metal center M and unsubstituted pyridine (Py),[1] 4-vinylpyridine (4-ViPy),[2,3] 2-methylpyridine (2-MePy),[4] and some other pyridines[1] as ligand A. Every host studied so far was found to enclathrate a number of guests producing three to five distinct inclusion architectures, not including guest-free polymorphs. An important fundamental question with respect to the whole family of metal DBM hosts relates to the definition of the limits for their modification and the exploration of all possibilities. It has been demonstrated that changing the metal center to Zn and Cd switches the trans isomeric state of the unit to the cis isomer, thus producing nonincluding complexes. It is still not entirely clear how extensive the modification of the ligand A of the basic unit shown in Scheme 1 can be without losing the ability to form supramolecular architectures. The present study introduces the largest pyridine used so far as an A-ligand, 4-phenylpyridine (4-PhPy), and demonstrates that even such dramatic modification does result in a versatile host with its specific inclusion properties.

Experimental Section

[Ni(4-PhPy)$_2$(DBM)$_2$]. Light-green Ni(DBM)$_2$ (1.0 g, 2 mmol) prepared as reported elsewhere [26] and a slight excess of 4-PhPy (0.65 g, 4.2 mmol) from Aldrich, 97%, were dissolved in warm chloroform (20 mL). Into the filtered solution warm hexane (40 mL) was added immediately with vigorous stirring. A brown, fine-crystalline precipitate started to form in a few seconds. The mixture was allowed to cool; the product was separated, rinsed twice with hexane, and air-dried (yield: 1.5 g, 90% for nickel DBM). Elemental analysis (%). Calcd for [Ni(4-PhPy)$_2$(DBM)$_2$] ($C_{52}H_{40}N_2NiO_4$): C, 76.6; H, 4.9; N, 3.4. Found: C, 76.7; H, 5.0; N, 3.2. A powder XRD pattern identified the bulk product as the guest-free form of the complex studied by single-crystal XRD (Figure 1). Upon heating (TGA conditions) the complex lost most of the 4-phenylpyridine, producing, by 300 °C, a contaminated green form of nickel dibenzoylmethanate [26] (as confirmed by powder XRD).

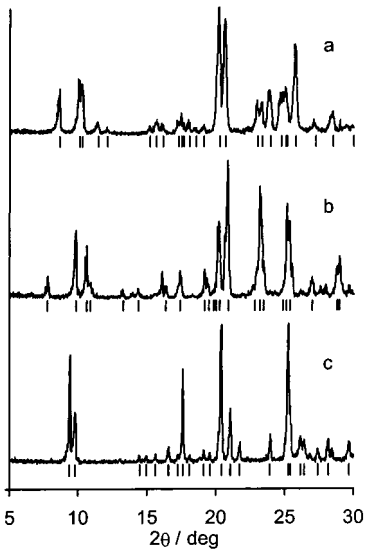

Figure 1. Selected powder diffractograms: (a) brown [Ni(4-PhPy)$_2$(DBM)$_2$]*4(benzene); (b) green [Ni(4-PhPy)$_2$(DBM)$_2$]*(benzene); (c) brown [Ni(4-PhPy)$_2$(DBM)$_2$] (host phase). The vertical bars mark positions of the main reflections (>5% of the strongest reflection intensity) calculated from single-crystal XRD results using room temperature unit cell dimensions. Radiation: Co Kα, λ = 1.7902 Å.

Guest-Free Form and Inclusion Compounds by Crystallization. The solvents were of reagent grade or better (greater than 98% purity). An excess of host complex was stirred with 7−15 mL of solvent at the required temperature; the resulting solutions were filtered and left either to evaporate at room temperature (benzene, chlorobenzene, methylene chloride, chloroform, and tetrahydrofuran) or to cool to room temperature (all other solvents). At least two crystallizations were completed for each solvent. From methylene chloride, chloroform, and tetrahydrofuran only a fine powdered material precipitated; from other solvents monophase crystalline products formed in most cases; the materials were analyzed with powder and/or single-crystal XRD methods. From 11 solvents the guest-free form of the complex was obtained. From 6 solvents inclusion compounds were obtained; they were kept under their mother solutions.

Thermogravimetric Analysis. Crystals of the inclusion compounds were taken from the corresponding mother solutions, crushed, and pressed to dryness between two pieces of blotter paper. In addition, the green compounds were dried in air (up to an hour, until no solvent odor was detectable). Thermogravimetric analysis of the prepared samples (15−25 mg) was carried out in a linear heating mode under a nitrogen purge. The temperature for the maximum decomposition rate of the samples did not depend (within ±1.5 °C) on the amount of sample (total mass) or particle size distribution that was present.

Single-Crystal XRD. Single-crystal diffraction experiments were performed on crystals taken from under their respective mother liquors and cooled immediately to −100 °C. A Siemens SMART CCD X-ray diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) was used to collect diffraction data. Full data sets were collected using the ω scan mode over the 2θ range of 3−58°. The coverage of the unique sets was over 99%. An empirical absorption correction was utilized. The unit cell parameters were obtained using the entire data sets. Crystal data and experimental details are listed in Table 1.

The structures were solved (direct methods) and refined (difference Fourier synthesis) using the SIR92[27] and

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Table 1. Details of Low-Temperature Single-Crystal XRD Experiments and Summary of Crystallographic Parameters

compound	[Ni(4-PhPy)$_2$(DBM)$_2$], guest-free form	[Ni(4-PhPy)$_2$(DBM)$_2$]* 4(benzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (benzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (fluorobenzene)
host:guest ratio (refined)		1:4.017(6)	1:1.003(1)	1:1.017(8)
formula	$C_{52}H_{40}N_2NiO_4$	($C_{52}H_{40}N_2NiO_4$), 4(C_6H_6)	($C_{52}H_{40}N_2NiO_4$), (C_6H_6)	($C_{52}H_{40}N_2NiO_4$), (C_6H_5F)
formula unit mass	815.6	1128.0	893.7	911.7
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	8.031(1)	11.565(2)	11.278(2)	11.278(2)
b, Å	12.155(2)	12.354(2)	13.630(2)	13.634(2)
c, Å	12.471(2)	13.205(2)	16.378(2)	16.407(3)
α, deg	61.53(1)	110.34(1)	80.81(1)	80.87(1)
β, deg	79.66(1)	94.32(1)	70.94(1)	70.76(1)
γ, deg	76.57(1)	117.73(1)	74.38(1)	74.65(1)
V, Å^3	1037.5(3)	1500.6(4)	2284.6(6)	2289.9(7)
Z	1	1	2	2
D_{calc}, g cm^{-1}	1.305	1.248	1.299	1.322
μ(Mo Kα), cm^{-1}	5.17	3.77	4.76	4.79
T, °C	−100	−100	−100	−100
crystal color and habit	brown block	brown block	green block	green plate
crystal size, mm	0.3 0.4 0.4	0.1 0.2 0.3	0.1 0.2 0.2	0.05 0.2 0.2
reflns collected	12322	18011	28934	27398
unique obs reflns ($I > 2\sigma(I)$)	4879	5583	8900	6491
refined parameters	268	379	586	597
R1/wR2 (observed data)	0.031/0.083	0.039/0.090	0.045/0.101	0.052/0.102
GOF on F^2	1.057	1.020	1.035	0.873
res. density, e Å^{-3}	+0.31/−0.54	+0.26/−0.37	+0.37/−0.30	+0.54/−0.60

compound	[Ni(4-PhPy)$_2$(DBM)$_2$]* (chlorobenzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (bromobenzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (toluene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (*o*-xylene)
host:guest ratio (refined)	1:1.005(5)	1:0.993(3)	1:1.023(8)	1:1.014(5)
formula	($C_{52}H_{40}N_2NiO_4$), (C_6H_5Cl)	($C_{52}H_{40}N_2NiO_4$), (C_6H_5Br)	($C_{52}H_{40}N_2NiO_4$), (C_7H_8)	($C_{52}H_{40}N_2NiO_4$), (C_8H_{10})
formula unit mass	928.1	972.6	907.7	921.7
crystal system	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	11.318(2)	11.333(2)	11.295(2)	11.321(2)
b, Å	13.694(3)	13.738(2)	13.770(2)	13.989(2)
c, Å	16.430(3)	16.409(3)	16.376(3)	16.460(3)
α, deg	81.43(1)	82.14(1)	81.27(1)	80.95(1)
β, deg	70.09(1)	69.93(1)	69.95(1)	68.68(1)
γ, deg	75.73(1)	76.75(1)	75.40(1)	75.90(1)
V, Å^3	2314.5(8)	2331.8(7)	2309.4(7)	2348.4(7)
Z	2	2	2	2
D_{calc}, g cm^{-1}	1.332	1.386	1.305	1.304
μ(Mo Kα), cm^{-1}	5.28	13.24	4.72	4.65
T, °C	−100	−100	−100	−100
crystal color and habit	green block	green block	green plate	green block
crystal size, mm	0.05 0.1 0.1	0.1 0.2 0.3	0.05 0.15 0.15	0.1 0.2 0.3
reflns collected	27869	27843	27414	27982
unique obs reflns ($I > 2\sigma(I)$)	6228	8941	7114	8457
refined parameters	597	597	601	608
R1/wR2 (observed data)	0.052/0.094	0.044/0.114	0.055/0.116	0.042/0.096
GOF on F^2	0.878	1.078	0.914	1.017
res. density, e Å^{-3}	+0.42/−0.29	+0.70/−0.69	+0.72/−0.73	+0.58/−0.33

SHELXTL[28] packages. The structural refinement was performed on F^2 using all data with positive intensities. Nonhydrogen atoms of host and nondisordered guest molecules were refined anisotropically. In the five inclusions with substituted benzenes the guest molecule was disordered. Four (three for *o*-xylene) orientations were refined with variable occupancies; guest geometry was fixed to ideal and the carbons of the phenyl rings were refined isotropically with a common thermal parameter. Side atoms were refined anisotropically with some restrictions on thermal parameters. Hydrogen atoms were refined isotropically with thermal factors 1.2 or 1.5 times greater than those for the adjacent carbon atoms. The guest occupancy was refined in all cases, with the refined occupancy of all orientations for disordered guests listed in the Supporting Information. Total refined guest:host ratios are given in Table 1. The largest residual extrema on the final difference map were about the heavy atoms. A series of extrema were observed about the Ni ion for inclusions with fluorobenzene, toluene, and *o*-xylene. These extrema evidently arise from inadequate absorption corrections as the crystals of these inclusions were of poor quality. Residual peaks were also observed near the disordered guest in inclusion with bromobenzene, evidently originating from unresolved disordered bromine atoms.

For all the compounds studied the room temperature unit cell dimensions were also measured (Table 2). To accomplish this, several dozens of reflections were found randomly using 120 or more frame ω scans, 0.3° wide, starting at three different ϕ positions. The crystal of the brown 1:4 inclusion with benzene was preserved by a coating prepared by dissolving foam plastic in benzene. Other compounds were stable at ambient conditions.

Powder XRD. Powder diffraction patterns were obtained with a Rigaku Geigerflex diffractometer (Co Kα radiation, λ = 1.7902 Å) in a 5−30° 2θ range, 0.02° step scan, 1 s/step. Samples of inclusion compounds were studied under vapor of the corresponding solvent. Theoretical diffractograms were

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Table 2. Room Temperature Unit Cell Parameters from Single-Crystal XRD Experiments

compound	[Ni(4-PhPy)$_2$(DBM)$_2$], guest-free form	[Ni(4-PhPy)$_2$(DBM)$_2$]* 4(benzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (benzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (fluorobenzene)
a, Å	8.093(2)	11.662(3)	11.361(3)	11.383(2)
b, Å	12.289(3)	12.537(3)	13.756(4)	13.756(3)
c, Å	12.597(3)	13.334(4)	16.444(5)	16.539(5)
α, deg	60.45(1)	111.37(1)	80.97(1)	80.95(1)
β, deg	80.56(1)	93.72(1)	71.01(1)	70.76(1)
γ, deg	76.98(1)	117.42(1)	74.22(1)	74.50(1)
V, Å^3	1059.8(4)	1546.4(7)	2332(1)	2349(1)
Z	1	1	2	2
D_{calc}, g cm^{-1}	1.278	1.211	1.273	1.289
no. of used reflns	151	215	244	283
compound	[Ni(4-PhPy)$_2$(DBM)$_2$]* (chlorobenzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (bromobenzene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (toluene)	[Ni(4-PhPy)$_2$(DBM)$_2$]* (*o*-xylene)
a, Å	11.426(4)	11.459(3)	11.420(3)	11.418(2)
b, Å	13.837(3)	13.837(4)	13.910(4)	14.127(3)
c, Å	16.544(4)	16.600(4)	16.544(3)	16.567(5)
α, deg	81.34(1)	81.72(2)	80.91(1)	80.80(1)
β, deg	70.03(1)	69.71(1)	69.73(1)	68.68(1)
γ, deg	75.41(1)	76.18(1)	74.76(1)	75.58(1)
V, Å^3	2373(1)	2392(1)	2372(1)	2404(1)
Z	2	2	2	2
D_{calc}, g cm^{-1}	1.299	1.350	1.271	1.273
no. of used reflns	238	263	234	277

calculated from single-crystal data but unit cell dimensions measured at room temperature were employed (Table 2).

Results and Discussion

Crystallization Products. Three types of solids were obtained and characterized in this work: a brown guest-free form of the host complex, green isostructural inclusions with 1:1 host-to-guest ratios, and a brown inclusion with a 1:4 host-to-guest ratio. The three materials exhibited characteristic powder patterns as shown in Figure 1 (the Supporting Information includes the complete set of diffractograms). All materials isolated were of one of these types or their mixtures.

The brown, guest-free form of the host was obtained from methylene chloride, chloroform, tetrahydrofuran, iodobenzene (as determined by powder XRD), ethyl acetate, *m*-xylene, *p*-xylene, *tert*-butylbenzene, mesitylene, acetonitrile, and nitromethane (as determined by single-crystal XRD).

The green 1:1 inclusion compounds were obtained from fluorobenzene, chlorobenzene, toluene, and *o*-xylene. The powder patterns of the isolated bulk products corresponded to those calculated from the results of single-crystal XRD analyses of the inclusion compounds. From bromobenzene, either only green inclusion formed or a mixture of the coexisting green inclusion and brown guest-free host crystals formed. All the green inclusions appeared stable in air.

From benzene, a brown inclusion with a 1:4 host-to-guest ratio formed reproducibly (five crystallizations). This inclusion lost guest benzene in air, transforming into the guest-free host form. Under a layer of mother solution the brown 1:4 inclusion eventually regrew into the green 1:1 inclusion. For deliberately prepared mixtures of brown and green inclusion crystals the process was complete in several days. These observations give direct evidence that the green 1:1 inclusion is thermodynamically more stable than the brown 1:4 inclusion (under benzene). An explanation of this observation may be given in terms of packing. Taking unit cell volumes and *Z* values from Table 2 and assuming that the host molecule occupies approximately the same volume in all phases, the volume per guest benzene molecule is 106 Å^3 in the green and 122 Å^3 in the brown clathrate.[29] The overall packing is thus more effective in green clathrate, providing improved van der Waals contacts.

Thermal Stability of Inclusion Compounds. All inclusion compounds reported in this paper lost the guest upon heating, producing the guest-free form of the host [Ni(4-PhPy)$_2$(DBM)$_2$]. The host complex was stable up to about 200 °C, though some mass loss was observable at lower temperatures.

The thermal stability of the inclusion compounds is closely related to their structure. As shown below, the brown 1:4 inclusion has pseudo-layer packing, where the guest species are relatively free to leave, a process that likely triggers the collapse of the host matrix. On the other hand, the green 1:1 compounds have guests entrapped in cages so guest removal must follow the destruction of the whole host matrix. This principal difference is illustrated by the decomposition of brown and green clathrates included with the same guest—benzene (Figure 2). The layered brown compound starts to decompose already at room temperature and by 70 °C produces a guest-free host (temperature at maximum decomposition rate T_{max} = 60 °C). The green cage compound exhibits a remarkable thermal stability; no decomposition is observed up to 120 °C, much higher than the boiling point of neat benzene. Kinetic control over the difference is also evident from the fact that decomposition of the brown compound does not produce the green inclusion, which should be a thermodynamic product (transformation of one clathrate into another was observed earlier in pseudo-equilibrium[30,31] and conventional[32,33] TGA).

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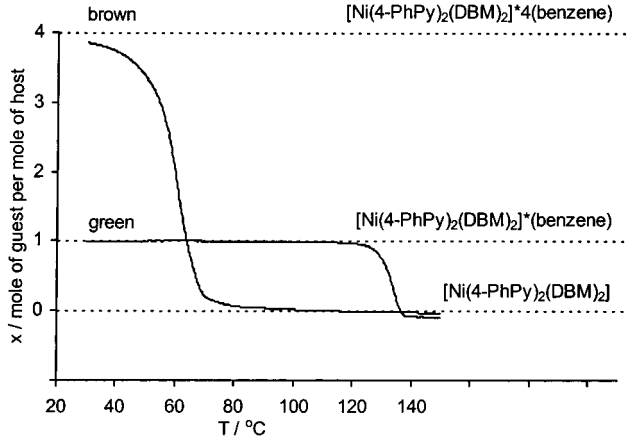

Figure 2. TGA thermograms of green and brown inclusion compounds of $[Ni(4\text{-}PhPy)_2(DBM)_2]$ with benzene. For easier comparison, mass change is expressed in moles of guest benzene per mole of host. Heating rate: 5 °C/min. Sample masses: 16.25 mg (brown) and 14.11 mg (green).

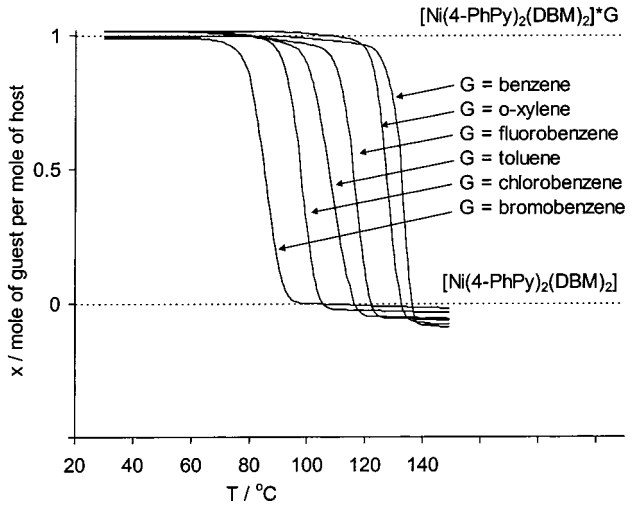

Figure 3. TGA thermograms of green isostructural inclusion compounds $[Ni(4\text{-}PhPy)_2(DBM)_2]$*G (G = guest). For easier comparison, mass change is expressed in moles of guest per mole of host. Heating rate: 5 °C/min. Sample masses: 14.11 mg (inclusion with benzene), 18.50 mg (*o*-xylene), 22.04 mg (fluorobenzene), 27.07 mg (toluene), 25.25 (chlorobenzene), and 18.96 mg (bromobenzene).

The decomposition of the six green clathrates is compared in Figure 3. All the clathrates have the same host:guest ratio and the same structure; the processing conditions are similar and the final product is essentially the same for all the series. Therefore, the observed difference is determined by two parameters: volatility of guest components and complementarity of the guest molecule to the available cavities.[34] As evident from Figure 3 and Table 3, the observed stability

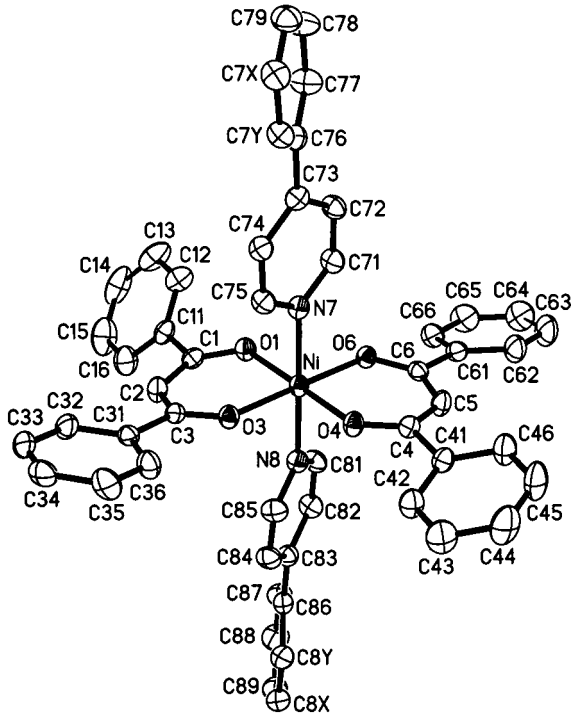

Figure 4. Structure of the $[Ni(4\text{-}PhPy)_2(DBM)_2]$ molecule found in the green 1:1 clathrate of the complex with benzene. H atoms are omitted; ellipsoids are drawn at 50% probability level.

Table 3. Temperatures at Maximal Rate of Decomposition in a TGA Experiment of $[Ni(4\text{-}PhPy)_2(DBM)_2]$*G Clathrates ($T_{max}$) and Boiling Points of Neat Guests (bp)

G	T_{max} (°C)	bp (°C)	G	T_{max} (°C)	bp (°C)
benzene	133	80	toluene	108	111
o-xylene	126	145	chlorobenzene	98	132
fluorobenzene	116	85	bromobenzene	85	156

sequence does not follow to what would be expected from the volatilities of neat guests.[37] Thermal stability is maximal for an inclusion compound with benzene and drops dramatically in the series: benzene >fluorobenzene > chlorobenzene > bromobenzene. The effect is remarkable, indicating a strong preference of the inclusion matrix to benzenes with smaller substituents. The matrix itself expands in the series by 2.5% (Table 2) to include the larger guests. This expansion clearly indicates that the original cage, which is suitable for benzene, needs to be enlarged to include the other guest molecules. Presumably, the expansion decreases the effectiveness of crystal packing, consequently decreasing the stability of the clathrate phase. This is in accordance with the observation that from bromobenzene, in some cases mixtures of the clathrate and host phases formed, and from iodobenzene only the host phase formed.

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(34) Because of the similarity of the reactions and experimental conditions, the order of thermal stability must follow the order of thermodynamic stability of these inclusion compounds. In terms of thermodynamics, the guest volatility is determined by the enthalpy of evaporation of a neat guest, and the host−guest complementarity is determined by the enthalpy of guest sorption into a host matrix. Other factors contributing to the total formation (dissociation) enthalpy of the inclusion compounds are very similar in this case. For further details on the subject see refs 35 and 36.

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(36) Lipkowski, J.; Starzewski, P.; Zielenkiewicz, W. *Thermochim. Acta* **1981**, *49*, 269−279.

(37) A negative correlation between guest volatility and thermal stability of inclusion compounds is evident from numerous reported results. For example, Casellato and Casu reported the following orders of thermal stability in isostructural clathrates (only guests are listed): benzene < toluene < ethylbenzene; fluoro- < chloro- < bromo- for halobenzenes, *p*-halotoluenes, and *p*-dihalobenzenes. Casellato, F.; Casu, B. *Erdol Kohle Erdgas Petrochem.* **1969**, *22*, 71−77.

Table 4. Selected Parameters of the [Ni(4-PhPy)$_2$(DBM)$_2$] Molecule in the Phases Studied[a−c]

guest		benzene	benzene	benzenes[d]
phase type (H:G)	guest-free form	(1:4)	(1:1)	average for six (1:1) phases
phase color	brown	brown	green	all green
point symmetry	−1	−1	1	1
distances (Å)				
Ni−O1	2.033(1)	2.015(1)	2.032(1)	2.031(2)
Ni−O3	2.019(1)	2.002(1)	2.014(1)	2.012(2)
Ni−O4			2.023(1)	2.024(2)
Ni−O6			2.015(1)	2.013(2)
Ni−N7	2.096(1)	2.122(1)	2.130(1)	2.130(2)
Ni−N8			2.120(2)	2.122(3)
valent angles (deg)				
O1−Ni−O3	90.32(4)	91.15(4)	90.64(5)	90.73(6)
O4−Ni−O6			91.22(5)	91.01(6)
O1−Ni−O6{O3′}	{89.68(4)}	{88.85(4)}	89.78(5)	89.56(6)
O3−Ni−O4{O1′}			88.37(5)	88.70(6)
line−plane angles (deg)				
(Ni−N7)−Eqt	88.3	89.4	88.6	88.6(1)
(Ni−N8)−Eqt			88.9	89.0(1)
plane−plane angles (deg)				
Ring1−Ring2	0	0	9.5	10.6(5)
Eqt−Ph1	+67.9	+9.3	+51.2	+50.7(6)
Eqt−Ph3	−16.3	+8.1	+10.8	+10.1(3)
Eqt−Ph4	{−67.9}	{−9.3}	−18.4	−16.1(8)
Eqt−Ph6	{+16.3}	{−8.1}	+13.3	+13.0(2)
Eqt−Py7	89.6	84.8	89.4	87.3(7)
Eqt−Py8	{89.6}	{84.8}	85.1	84.0(3)
α−Py7	+83.2	+71.7	+54.5	+55.3(3)
α−Ph7	+55.2	−68.8	+83.7	+83.6(5)
Py7−Ph7	28.2	39.6	29.4	28.4(4)
α−Py8	{−83.2}	{−71.7}	−71.8	−72.9(4)
α−Ph8	{−55.2}	{+68.8}	+81.2	+80.0(5)
Py8−Ph8	{28.2}	{39.6}	27.0	27.1(2)

[a] Atom numbering used in the table is illustrated in Figure 4. Definitions of most least-squares planes are shown in Scheme 2; for example, the planes for the molecule in Figure 4 are as follows: Ring1 (Ni,O1,C1,C2,C3,O3); Ring2 (Ni,O4,C4,C5,C6,O6); Eqt (Ni,O1,O3,O4,O6); Ph1 (C11−C16); Ph3 (C31−C36); α (Ni,C2,C5,N7,N8); Py7 (N7,C71,C72,C73,C74,C75); Ph7 (C76,C77,C78,C79,C7X,C7Y) and so on. [b] For line−plane and plane−plane angles estimated experimental errors do not exceed 0.1°. [c] Values for angles involving symmetry-generated atoms are given in figure brackets; for example, the angle O1−Ni−O3′, where O3′ arises from O3 by centrosymmetry, corresponds to O1−Ni−O6 in the asymmetric molecule. [d] Benzene, fluorobenzene, chlorobenzene, bromobenzene, toluene, and *o*-xylene. Conformational parameters of host molecule in phases with all the guests are presented in the Supporting Information.

Toluene also fits the observed tendency. *o*-Xylene is the only disubstituted guest and, as would be expected, deviates from the tendency.

Host Molecule: Structure and Conformations. Molecules of the host complex, [Ni(4-PhPy)$_2$(DBM)$_2$], appear in eight isolated solids belonging to three crystal structure types. In all cases they are trans configured (Figure 4) and exhibit, basically, the same structure. At the same time, the different colors of the solids indicate a significant influence of packing on the host complex geometry.

Table 4 lists selected geometrical parameters of the molecule in the three structural types (for more complete data see Supporting Information). The molecule is centrosymmetric in brown compounds and asymmetric in green clathrates. The nickel center (Figure 4) is chelated by two DBM units in the equatorial plane and axially coordinated by two 4-PhPy ligands. The overall geometry of the bis-chelate unit is as usually observed for metal bis-acetylacetonates and related complexes.[38−40] The coordination octahedra are slightly distorted due to deviations (up to 2°) in coordination angles and longer axial Ni−N (up to 0.1 Å) over equatorial Ni−O bonds.

The bischelate fragment is planar in brown compounds and is bent in green clathrates, the Ring1−Ring2 dihedral angle ranging from 9.2° in the fluorobenzene compound to 12.4° in the *o*-xylene compound. The phenyl rings of the DBM units reveal some preference for coplanarity with the chelate rings. The pyridyl rings of 4-PhPy ligands lie close to the plane bisecting the metal bischelate fragment into two chelate parts. These tendencies were discussed previously.[1−3]

As evident from Table 4, the most significant difference between molecules found in the brown and green solids is the shorter coordination bonds in brown compounds and significant bending of the bischelate fragment in green compounds. Such changes caused by specificity of crystal packing were shown to be sufficient to change the color of octahedral complexes.[41−43]

Similar to other metal DBM hosts, the molecule possesses four pockets located between DBM and pyridyl fragments, the pockets usually are responsible for the clathration ability of the complexes. The difference is in ∼23 Å axial size of the molecule, which is much greater than ≈14 Å for the original [NiPy$_2$(DBM)$_2$] complex.

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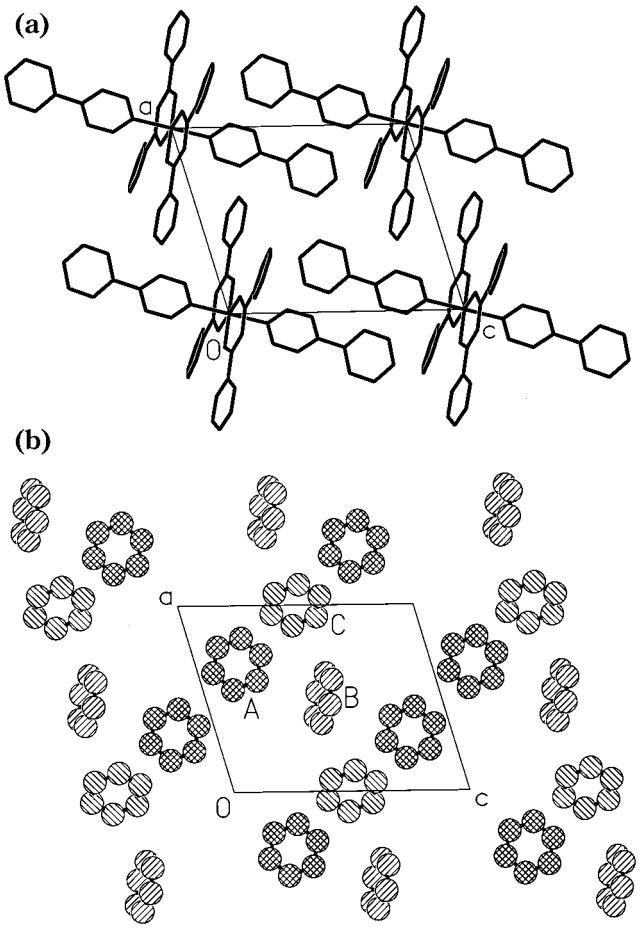


Figure 5. Crystal packing in the brown $[Ni(4\text{-}PhPy)_2(DBM)_2]$*4(benzene) clathrate. (a) Layer of host molecules at $y \sim 0$. (b) Layer of guest molecules at $y \sim 0.5$. The crystallographically different guest molecules are indicated with distinct hatching and labeled with capital letters A, B, and C. H atoms are omitted.

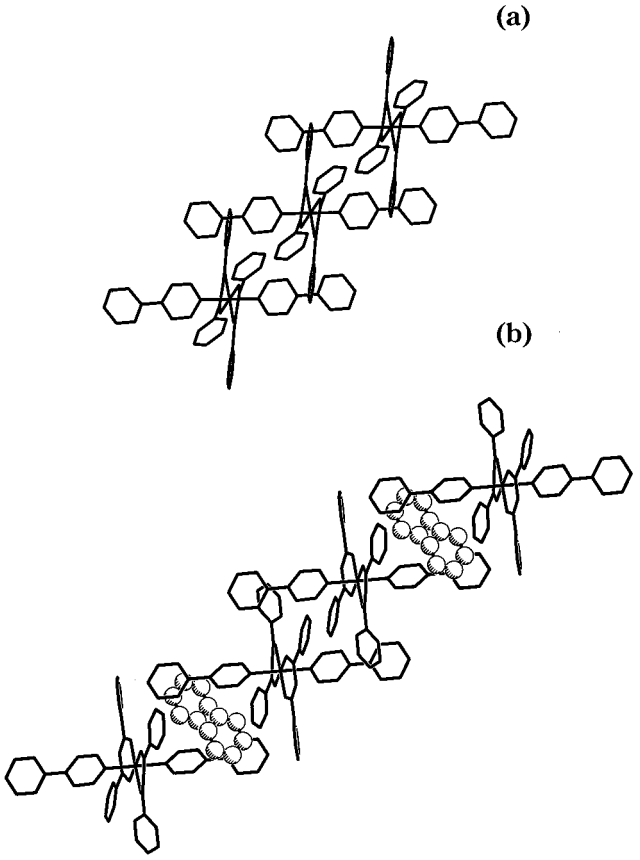


Figure 6. Chain packing motif of $[Ni(4\text{-}PhPy)_2(DBM)_2]$ molecules. (a) The guest-free form of the complex. The intervals between neighbors are equal. (b) The green 1:1 clathrate with benzene. The long and short intervals between host complexes alternate along the chain, with the long intervals providing spaces for guest molecules.

Brown $[Ni(4\text{-}PhPy)_2(DBM)_2]$*4(benzene). As in all the compounds studied, the structure is controlled by van der Waals forces. Despite this, the distinct packing anisotropy makes it possible to classify this clathrate as pseudo-layered. The host molecules effectively pack in the ac plane (Figure 5a) with the axial direction of the host complex directed ≈20° off the *c* axis, filling the layer with 4-PhPy and phenyl fragments (from the DBM ligands). Two DBM phenyls from every host molecule protrude up and down out of the layer. The shortest Ni···Ni distances are more than 11.6 Å as no interpenetration of host molecules is observed. All pockets that accommodate guest molecules are directed into the interlayer space. Each host molecule has four possible pockets and all are used by the guests, thus resulting in a 1:4 host:guest ratio—the maximal possible guest content within a "pocket" model. The interlayer space (at $y \sim 0.5$) is predominantly filled with guest benzene molecules (Figure 5b). There are three crystallographically distinct guest molecules: A, B, and C (Figure 5b). Molecule A is in a general position while molecules B and C reside on symmetry centers. The interlayer space is subdivided into channels going in two directions; along the diagonal between *a* and *c* crystallographic axes with AACAAC guest filling and along the *a* axis with BCBCBC guest filling. It seems evident that guest species can move easily through the intersecting channels within the layer and leave the structure and that the whole architecture could not exist without the guest.

Host Form and Green $[Ni(4\text{-}PhPy)_2(DBM)_2]$*G Inclusions. Both the host form and the green inclusions exhibit similar packing motifs. Both types contain tightly packed chains of host molecules rather than layers. In the host form the chain neighbors interpenetrate in such a way that a 4-PhPy fragment fits between phenyls of two DBMs belonging to the neighboring molecule (Figure 6a; for full packing stereodiagrams see Supporting Information). This allows nickel centers of adjacent molecules to approach each other at 8.0 Å while the shortest distance between nickel centers of different chains is 12.2 Å. The chains run parallel to the crystallographic direction and the molecular axis is inclined by ≈50° to the chain direction. The host molecule is surrounded symmetrically on both sides of the equatorial plane.

A similar motif exists in the green 1:1 clathrates (Figure 6b; for full packing stereodiagrams see Supporting Information). The distances between neighbors are different and each molecule has different surroundings on the two sides of the equatorial plane. The nearest molecules again have nickel centers at 8.0 Å with a similar interpenetration. These close pairs alternate with neighbors separated by 11.7 Å between nickel centers, although the mutual orientation remains approximately the same. This separation creates cavity space between the DBM phenyls of the neighboring

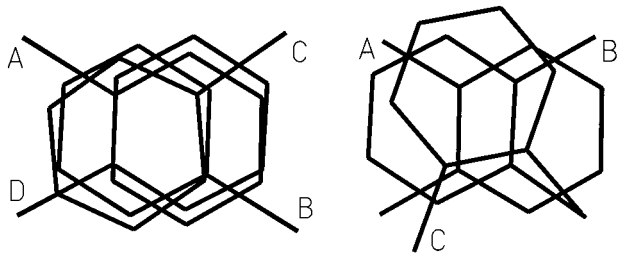
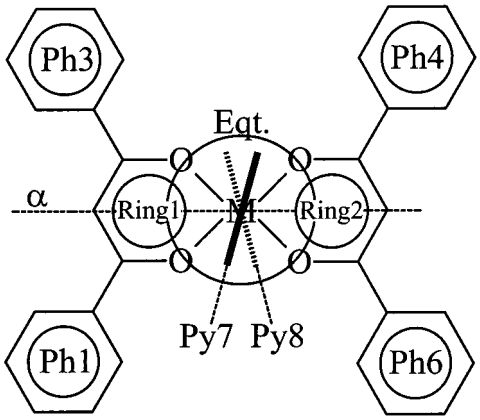


Figure 7. Typical disordering of guest molecules in green $[Ni(4\text{-}PhPy)_2(DBM)_2]$*G clathrates. (a) Chlorobenzene: A, 31.6%; B, 31.3%; C, 23.7%; D, 13.9%. (b) *o*-Xylene: A, 22.0%; B, 55.7%; C, 23.7%.

Scheme 2



molecules. The cavity is further expanded at the expense of a distortion of the bischelate fragments out of the equatorial plane. The change in color to green seems to be the consequence of this deviation and, therefore, of guest inclusion.

Including larger guests leads to further expansion of the cavity. Apparently, the packing within the chain is so effective that the expansion of the cavity occurs not only because of increasing the separation between neighboring host molecules but also because of the bending of the bischelate fragment, that is, increasing the distortion of the host molecule. For example, in the series of guests benzene, fluorobenzene, chlorobenzene, and bromobenzene the nickel−nickel distance changes in the order 11.7, 11.8, 11.9, and 12.0 Å, and the Ring1−Ring2 angle (Scheme 2) changes in the order 9.5, 9.2, 10.3, and 11.1°.

The cavity is a flat cage restricted mostly by phenyl fragments of the host molecules. In terms of a "pocket" model, each cage is formed by two pockets from two adjoining host molecules. The 1:1 stoichiometry arises from only two of four host pockets contributing to the building of a cavity while the other two are filled with phenyl fragments of another host molecule approaching from the opposite side of the equatorial plane. Two cages join across a symmetry center. The distance between centers of adjoining cages is ≈7 Å, and planes of the cages are displaced by ≈1 Å. Guest molecules of substituted benzenes are disordered inside the cavity. There are four positions for monosubstituted benzenes and three for *o*-xylene (Figure 7). The total occupancy for each guest was close to 100%. The disordering may be dynamic but there is no way for guest molecules to move through the structure.

General Discussion

The main result of the present study is that modification of the basic metal DBM unit with 4-phenylpyridine does result in a new host. It forms inclusion compounds of at least two different types and reveals preference to guest molecules of specific geometry. The host molecules demonstrate their ability to pack effectively in two dimensions forming a dense layer in the brown $[Ni(4\text{-}PhPy)_2(DBM)_2]$*4(benzene) compound while the stacking of the layers inevitably leaves extended cavity space available for guest species. Alternatively, the host molecules can create effective packing in one dimension, resulting in chains of interpenetrating molecules. The packing of the chains in the remaining two dimensions can result in a guest-free host form but in the presence of a suitable smaller molecule the compound transforms to a more effectively packed material that includes the guest species such as in $[Ni(4\text{-}PhPy)_2(DBM)_2]$*G. The inclusion occurs even to the detriment of a strong host molecule distortion that gives, as one of the consequences, the change in color from brown to green.

4-Phenylpyridine is one of the largest ligands previously used to produce other metal complex hosts. Werner complexes of general formula $[MA_4X_2]$ (M is a metal(II), A is a pyridine-type ligand, X is an anionic group) have been famous for their multiplicity by means of changing all three components.[5−7] This gives for every particular guest a product host complex highly selective to the particular guest, an idea well supported by extensive experimental studies.[44,45] A change in the pyridine-type ligand (A) has been employed as the main strategy to produce a variety of new $[MA_4X_2]$ host complexes.[46−56] 4-Phenylpyridine was successfully incorporated into this type of material and the resulting host complexes formed a variety of inclusion structures, with one to four guest moles per mole of host.[46,47,53−55] A host complex with mixed ligands, $[Ni(4\text{-}PhPy)_2(4\text{-}MePy)_2(NCS)_2]$, had a geometry resembling that of the complex of this work and revealed some similar features in crystal packing. An attempt to incorporate a longer ligand, 4-benzylpyridine, was not successful though, as only a guest-free form was isolated.[57] Nevertheless,

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other authors have reported inclusion compounds of $[CoA_4Cl_2]$ complexes with 4-benzylpyridine and even 4-(*p*-chlorobenzyl)pyridine. In addition, host complexes with quinoline[58] and 4-styrylpyridine[59] were recently reported. Incorporation of larger ligands is interesting not just from the viewpoint of exploring the possibility for modification; as a rule, complexes with heavy ligands display higher thermal stability that may be useful for some applications. It can be noted, for instance, that excessive thermal dissociation of complexes with such volatile ligands as 4-methylpyridine was the main problem for their utilization in gas chromatography.[60,61]

The results of this work make it possible to anticipate that the range of A ligands, which can be used for the design of new metal DBM hosts, may be much wider than previously suspected. There is now a significant area within which extensive research and, one hopes, rational design could be realized. The latter requires prediction of supramolecular architectures from molecular structure. Very fruitful approaches recently have been developed in the area of coordination polymers[62−64] and self-assembly by hydrogen bonding or other directional interactions.[65−69] For low-dimensional systems, though, only general principles of crystal packing are used,[70,71] and while for simple molecules some predictions could be made, the subject still remains *Terra Incognita*. A method by analogy and empirically derived models (like a "pocket" model) along with thorough analysis of available experimental data may assist in further design of new metal DBM-type materials.

Acknowledgment. D.V.S. is grateful for support in the form of a Visiting Fellowship.

Supporting Information Available: Figures comparing experimental and calculated powder diffractograms for green 1:1 inclusions with fluorobenzene, chlorobenzene, bromobenzene, toluene, and *o*-xylene. Figures showing packing stereodiagrams of $[Ni(4\text{-}PhPy)_2(DBM)_2]$ (guest-free form of the complex) and $[Ni(4\text{-}PhPy)_2(DBM)_2]$*(benzene). Table comparing structural and conformational parameters of host molecule in all eight studied compounds. Table comparing refined occupancy of disordered guest orientations in green 1:1 inclusions. Tables of crystal data and structural refinements, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom parameters for eight structures reported in this paper (listed in Table 1) (CIF/PDF). This material (7 figures and 34 tables) is available free of charge via the Internet at http://pubs.acs.org.

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