

Inclusion Potential, Polymorphism, and Molecular Isomerism of Metal Dibenzoylmethanates Coordinated with 2-Methylpyridine[†]

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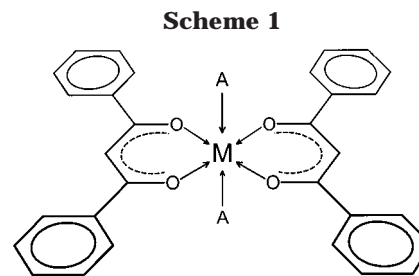
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In this study, new complexes of metal(II) (Ni, Zn, Cd) dibenzoylmethanates (DBMs) coordinated with 2-methylpyridine (2-MePy) were prepared and studied for host properties as a function of their structure and molecular isomerism. The novel [Ni(2-MePy)₂(DBM)₂] complex host exists as the trans isomer in five structurally distinct phases comprising two guest-free polymorphs as well as inclusion compounds with benzene, carbon tetrachloride, chlorobenzene, and toluene. All architectures arise from van der Waals packing, the host materials having guest species located in channels or cages. The stability of inclusions correlates with the shape of the cavity space. For zinc dibenzoylmethanate only one 2-MePy unit coordinates to give the [Zn(2-MePy)(DBM)₂] complex that does not exhibit inclusion properties. With cadmium dibenzoylmethanate, two polymorphic forms of the composition [Cd(2-MePy)₂(DBM)₂] were isolated. A metastable form contains complex molecules in the trans isomeric state, while a stable form contains cis isomers. As earlier, the ability to form clathrates was attributed only to trans-configured molecules of this type; the presence of a more stable cis form, with a trans-to-cis phase conversion enthalpy gain of as much as 17.2(6) kJ/mol, explains the failure to isolate any inclusion compounds of the Cd complex. The precedent of isolating both cis and trans isomers for the same complex of metal dibenzoylmethanate host is discussed in the context of designing novel materials where the potential for inclusion may be switched through molecular-level control of the isomeric state.

Introduction

Modified metal dibenzoylmethanates (Scheme 1) have a high potential for acting as host materials as both the metal center and the neutral ligand (A) may be changed without the complexes losing their ability to include guests.^{1–3} Each host, composed strictly of neutral molecular species, is capable of displaying a variety of architectures in order to accommodate guest species of various sizes, shapes, and polarities in cages or channels of various topologies. It is to be expected that this type of bis-chelate complex will form the basis of a vast family of molecular hosts on par with the versatile Werner⁴ clathrates and the porphyrin-based⁵ host-guest materials. Some structurally analogous chelates^{6,7}



and macrocyclic⁸ metal complexes have been reported as molecular hosts, those not maintaining host properties upon extensive modification.

[†] This is part 4 of the series "Modified metal dibenzoylmethanates and their clathrates"; for the three previous parts, see, in consecutive order, refs 1–3.

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Table 1. Melting Parameters of the Complexes Studied

complex	T_{melt} , °C and type (visual obsn)	T_{melt} , °C (from DSC)	ΔH_{melt} , kJ/mol (from DSC)
[Ni(2-MePy) ₂ (DBM) ₂], stable form	170–172, incongruent; 178–180, liquidus	180	51.0(5) ^a
[Zn(2-MePy)(DBM) ₂]	156–158, congruent	158	40.0(6)
[Cd(2-MePy) ₂ (DBM) ₂], cis (stable) form	132–133, congruent	133	66.2(5)
[Cd(2-MePy) ₂ (DBM) ₂], trans (metastable) form	112–113, congruent ^b	113	49.0(4)

^a Total effect. ^b Melting was observed only in the course of fast experiments (3 °C/min) if started at ~105 °C and usually followed by formation of a stable solid phase.

Table 2. Experimental Guest:Host Molar Ratios of Studied Inclusion Compounds

ideal (structural) formula	TGA	single-crystal XRD (refined)	isopiestic experiment
[Ni(2-MePy) ₂ (DBM) ₂] ^{4/3} benzene	1.38	1.34(1)	1.28(1)
[Ni(2-MePy) ₂ (DBM) ₂] ₂ CCl ₄	2.02		2.04(3)
[Ni(2-MePy) ₂ (DBM) ₂] ₂ chlorobenzene	0.99	1.00(1)	no or slow reaction
[Ni(2-MePy) ₂ (DBM) ₂] ₂ toluene	0.99		no or slow reaction

Earlier, we reported in detail on complexes with unsubstituted pyridine¹ and vinylpyridine^{2,3} as ligand A. The present contribution extends our studies and introduces 2-methylpyridine (2-MePy) into the basic M(DBM)₂ unit with Ni, Zn, and Cd as M. According to our studies so far, only trans-configured complexes (as depicted in Scheme 1) possess the desired ability to form supramolecular architectures. For nearly 30 inclusion compounds of five structural types the [M(4-ViPy)₂(DBM)₂] hosts (M = Ni, Co; 4-ViPy = 4-vinylpyridine) were found to be exclusively trans.^{2,3} The [NiPy₂(DBM)₂] complex appears as a trans isomer in six clathrates of four structural types and in its dense, nonclathrate form.¹ Analogous [MPy₂(DBM)₂] complexes of Zn and Cd form dense phases comprising cis complex species that do not show any inclusion properties. The nature of the metal center thus controls the isomeric state and, therefore, the ability to act as hosts for this series of complexes, a property already apparent in the complex precursors.⁹ One goal of our continuing research is to seek systems where both cis and trans forms of the host complex exist and possess similar energies. This would allow the creation of a new generation of “smart” sorbents whose main functionality could be switched on a molecular level simply by applying certain external stimuli such as temperature, pressure, guests, or catalysts. Our recent results on a related square complex (showing another type of isomerism) inspired substan-

tial optimism.^{10–13} A few other reports on host complexes able to isomerize also support this idea.¹⁴

From steric considerations, the methyl group in 2-MePy may facilitate the formation of the trans isomer, though at the expense of decreasing the overall stability of the [MA₂(DBM)₂] complex. The aims of this study are to investigate (1) if complexes with 2-MePy are stable enough to be isolated and utilized as host materials, (2) if the minimal change in molecular geometry due to the methyl group results in inclusions of new structural types, and (3) if the effect of the methyl group is enough to switch the Cd and Zn complexes over to the trans isomeric state.

Experimental Section

Preparations. General Information. Crude metal (Ni,⁹ Zn,⁹ Cd¹) DBMs were prepared as reported earlier. 2-MePy was from Aldrich (98% pure). Guest liquids and other solvents were of reagent grade quality or better. Crystallizations were done with 5–10 mL volumes, either by cooling hot solutions or by evaporating them at room temperature. Small quantities (2 drops or more) of 2-MePy were added to prevent dissociation of the complexes. The salient characteristics and analytical results of the new isolated compounds are given in Tables 1–4, Figures 1–4, and in the following text.

[Ni(2-MePy)₂(DBM)₂], *Stable Form.* Light-green Ni(DBM)₂ (1.0 g, 2 mmol) and an excess of 2-MePy (0.84 g, 9 mmol) were dissolved in warm chloroform (10 mL). The solution was filtered through a heated funnel. Hot hexane (40 mL) was immediately added to the solution with vigorous stirring. Green crystalline product started to precipitate after half a minute. The mixture was allowed to cool and the product was separated, rinsed twice with hexane, and air-dried (yield, 1.1 g, 75%). By TGA the product showed a mass loss of 26.7% (below 250 °C; 26.9% was expected for 2-MePy in [Ni(2-MePy)₂(DBM)₂]). The composition was also confirmed by a single-crystal X-ray diffraction experiment and comparison of the calculated powder diffractogram with that for the bulk product. The complex decomposes at 170 °C (incongruent melting). This stable polymorph of the complex crystallizes from a number of noninclusion solvents (see the Results section).

[Ni(2-MePy)₂(DBM)₂], *Metastable Form.* The only crystal of this polymorph appeared as a large (7 mm) green prism when an acetone solution of the complex evaporated at room temperature. After cutting off a fragment for X-ray analysis, the rest of the crystal was transformed into the stable polymorph, and subsequent attempts to reproduce the original crystallization were unsuccessful.

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Table 3. Crystal Data and X-ray Experiment Details for Studied Compounds

compound	[Ni(2-MePy) ₂ (DBM) ₂], stable form	[Ni(2-MePy) ₂ (DBM) ₂], metastable form	[Ni(2-MePy) ₂ (DBM) ₂] ^a / ₃ benzene	[Ni(2-MePy) ₂ (DBM) ₂] ^a - chlorobenzene
host:guest ratio (refined)			1:1.34(1)	1:1.00(1)
formula	C ₄₂ H ₃₆ N ₂ NiO ₄	C ₄₂ H ₃₆ N ₂ NiO ₄	C ₄₂ H ₃₆ N ₂ NiO ₄ (C ₆ H ₆) _{1.33}	C ₄₂ H ₃₆ N ₂ NiO ₄ ·C ₆ H ₅ Cl
formula unit mass	691.4	691.4	795.6	804.0
crystal system	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> $\bar{1}$ (No. 2)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> , Å	11.302(2)	8.768(1)	11.765(2)	8.234(1)
<i>b</i> , Å	12.505(2)	35.910(5)	12.861(2)	9.595(2)
<i>c</i> , Å	13.007(2)	12.000(2)	21.378(3)	13.214(2)
α , Å	80.78(1)	90	98.92(1)	79.51(1)
β , Å	76.67(1)	110.97(1)	99.23(1)	77.00(1)
γ , Å	86.51(1)	90	100.29(1)	82.23(1)
<i>V</i> , Å ³	1765.1(5)	3528(1)	3085(1)	995.4(3)
<i>Z</i>	2	4	3	1
<i>D</i> _{calc} , g cm ⁻³	1.301	1.302	1.285	1.341
μ (Mo K α), cm ⁻¹	5.94	5.95	5.19	6.02
<i>T</i> , °C	-100	-100	-100	-100
crystal color and habit	green block	green block	green block	green plate
crystal size, mm	0.2 × 0.3 × 0.5	0.2 × 0.4 × 0.4	0.2 × 0.3 × 0.3	0.2 × 0.2 × 0.4
reflns collected	20 906	41 746	36 830	11 864
unique obs reflns (<i>I</i> > 2 σ (<i>I</i>))	6823	7106	9222	4327
refined parameters	597	574	860	280
R1/wR2 (observed data)	0.042/0.118	0.034/0.082	0.040/0.080	0.038/0.102
GOF on <i>F</i> ²	1.063	1.033	0.877	1.059
res density, e Å ⁻³	+0.66/-0.45	+0.23/-0.35	+0.40/-0.47	+0.46/-0.54
CCDC deposition number	157436	157437	157438	157439
compound	[Zn(2-MePy) ₂ (DBM) ₂]	[Cd(2-MePy) ₂ (DBM) ₂], cis form ^a	[Cd(2-MePy) ₂ (DBM) ₂], trans form	
formula	C ₃₆ H ₂₉ NO ₄ Zn	C ₄₂ H ₃₆ CdN ₂ O ₄	C ₄₂ H ₃₆ CdN ₂ O ₄	
formula unit mass	605.0	745.1	745.1	
crystal system	orthorhombic	monoclinic	orthorhombic	
space group	<i>Fdd</i> 2 (No. 43)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ 2 ₁ 2 (No. 19)	
<i>a</i> , Å	21.189(3)	13.953(2)	11.516(2)	
<i>b</i> , Å	28.212(4)	15.902(3)	16.417(2)	
<i>c</i> , Å	10.050(2)	16.000(3)	18.622(3)	
α , Å	90	90	90	
β , Å	90	102.73(1)	90	
γ , Å	90	90	90	
<i>V</i> , Å ³	6008(2)	3463(1)	3521(1)	
<i>Z</i>	8	4	4	
<i>D</i> _{calc} , g cm ⁻³	1.338	1.429	1.406	
μ (Mo K α), cm ⁻¹	8.58	6.76	6.65	
<i>T</i> , °C	-100	-100	-100	
crystal color and habit	white prism	white, shapeless	white block	
crystal size, mm	0.3 × 0.3 × 0.5	0.1 × 0.1 × 0.2	0.2 × 0.3 × 0.5	
reflns collected	17 502	40 921	41 724	
unique obs reflns (<i>I</i> > 2 σ (<i>I</i>))	3697	29 045	8693	
refined parameters	197	445	468	
R1/wR2 (observed data)	0.025/0.066	0.036/0.075	0.017/0.043	
GOF on <i>F</i> ²	1.039	0.917	1.021	
res density, e Å ⁻³	+0.28/-0.33	+0.59/-0.52	+0.25/-0.33	
abs structure parameter	0.011(8)		0.000(9)	
CCDC deposition number	157440	157441	157442	

^a For twinning refinement, the equivalent reflections were not merged. Refined fraction of minor twin component was 0.1409(3).

Table 4. Assignments of ¹³C NMR Resonances in Complexes Studied^a

	>C-H	C-O	ipso (quat)	o/m	p	1(Py) (quat)	2(Py)	3(Py)	4(Py)	5(Py)	CH ₃
[Zn(2-MePy)(DBM) ₂]	90.2	184.8sh (1) 186.4(3)	139.2 140.8	126.9-130.7	~132	157.7	underneath 126.9	139.5 (after substr.)	123.0	147.6	24.0
[Cd(2-MePy) ₂ (DBM) ₂], cis (stable) form	90.6	183.5(1) 185.1(2) 186.5(1)	142.5	125.5-128.6	130.4	157.7 159.6	125.5 ?	137.8(2)	120.1	146.2 150.9	22.7
[Cd(2-MePy) ₂ (DBM) ₂], trans (metastable) form	91.8	181.7 184.0 186.5 189.8	141.0 143.4	125.0-132.8	131.5 132.8	158.7 159.9	125.0 ?	138.1 140.0	119.5 122.6	147.9 150.7	23.2
[Cd(DBM) ₂], crude	94.8	184.0 188.1	139.6	125-130 region	~130.4						
2-MePy, DMSO soln ^b						157.7	122.9	136.0	120.6	148.7	23.9

^a Numbering of pyridine ring starts with a quaternary carbon adjacent to methyl group. ^b Data from ref 30.

Inclusion Compounds of [Ni(2-MePy)₂(DBM)₂]. These compounds were prepared by one of two methods. The first involved crystallization of the host complex from neat guest

liquid. The crystals were kept under their mother solutions; if necessary, they were taken and dried with blotter paper. The second (isopiestic) method was performed by exposing the

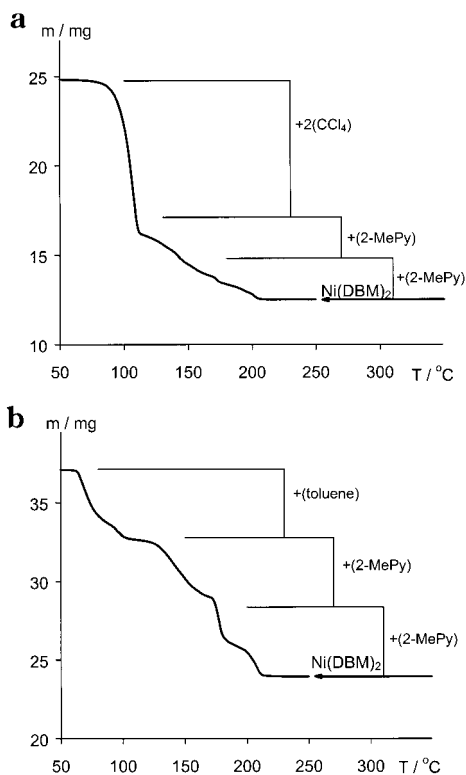


Figure 1. TGA thermograms of inclusion compounds of $[\text{Ni}(\text{2-MePy})_2(\text{DBM})_2]$ with carbon tetrachloride (a) and toluene (b). Calculated masses were obtained assuming the final product is $\text{Ni}(\text{DBM})_2$. Heating rate: $5\text{ }^\circ\text{C}/\text{min}$.

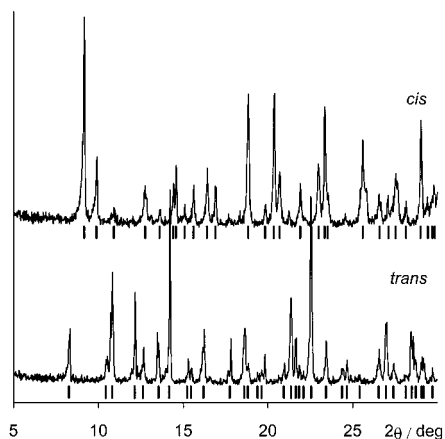


Figure 2. Powder X-ray diffractograms of cis (top) and trans (bottom) forms of $[\text{Cd}(\text{2-MePy})_2(\text{DBM})_2]$. The vertical bars show the positions of the main reflections ($>5\%$ of the strongest reflection intensity) calculated from the single-crystal data (using room-temperature unit cell dimensions). Radiation: $\text{Co K}\alpha$, $\lambda = 1.7902\text{ \AA}$.

solid host ($\sim 100\text{ mg}$) to guest vapor. The signature of a successful reaction was a mass increase with time to a plateau and a complete change of the powder diffraction pattern of the sample. Reactions were deemed to be absent if no changes were detected over 2 weeks. More details of this technique have been reported elsewhere.^{3,10,11}

$[\text{Zn}(\text{2-MePy})(\text{DBM})_2]$. Following the procedure for $[\text{Ni}(\text{2-MePy})_2(\text{DBM})_2]$, a colorless crystalline $[\text{Zn}(\text{2-MePy})(\text{DBM})_2]$ complex was prepared (yield, 0.87 g , 72%). Mass loss (observed below $180\text{ }^\circ\text{C}$) by TGA was 15.3% (15.4% expected for the loss of 1 mol of 2-MePy). The composition of the complex was confirmed by both X-ray diffraction and ^{13}C NMR experiments. The complex recrystallizes from many solvents including neat 2-MePy .

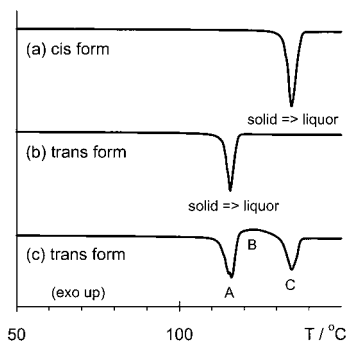


Figure 3. DSC thermograms of cis and trans forms of $[\text{Cd}(\text{2-MePy})_2(\text{DBM})_2]$ shown as heat flow (arbitrary units) vs temperature ($^\circ\text{C}$). (a) The cis form melts at $133\text{ }^\circ\text{C}$. (b) The trans form melts at $113\text{ }^\circ\text{C}$. (c) Another variant of the thermogram for the trans form, showing two endotherms (A and C) and an exotherm (B), the latter being due to intermediate formation of the stable cis form. Heating rate, $5\text{ }^\circ\text{C}/\text{min}$; sample mass, (a) 11.18 mg , (b) 9.90 mg , (c) 10.87 mg .

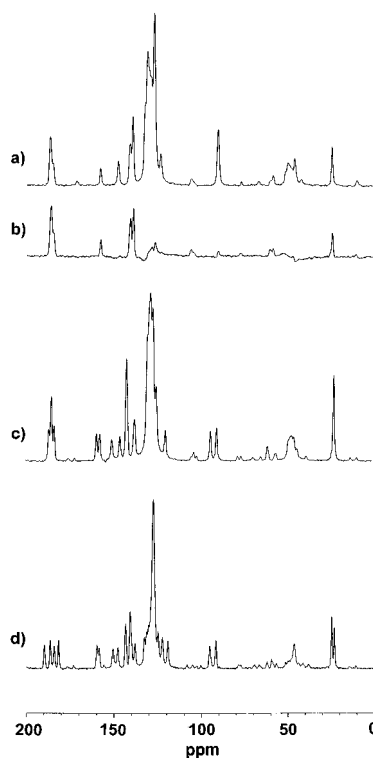


Figure 4. Solid-state ^{13}C CP/MAS NMR spectra of (a) $[\text{Zn}(\text{2-MePy})(\text{DBM})_2]$; (b) $[\text{Zn}(\text{2-MePy})(\text{DBM})_2]$ with dipolar dephasing; (c) $[\text{Cd}(\text{2-MePy})_2(\text{DBM})_2]$, cis form; (d) $[\text{Cd}(\text{2-MePy})_2(\text{DBM})_2]$, trans form.

$[\text{Cd}(\text{2-MePy})_2(\text{DBM})_2]$, *Stable (Cis) Form*. Light-yellow $\text{Cd}(\text{DBM})_2$ (1.6 g , 2.9 mmol) was immersed in a warm mixture of 2-MePy (2 mL , 23 mmol) and ethanol (2 mL) and stirred for 30 min . The pale-yellow crystalline product was filtered and dried on a sintered disk (yield, 2.1 g , 98%). Its composition was confirmed with TGA (24.8% mass loss was observed vs 25.0% calculated for 2-MePy content) and by X-ray diffraction and ^{13}C NMR experiments. Phase purity of the product was confirmed by the two latter methods (see Figures 2 and 4, Table 4, and the Results section). A single crystal for the X-ray experiment was taken from the bulk product as it was not possible to recrystallize this polymorph from any of the solvents employed.¹⁵

$[\text{Cd}(\text{2-MePy})_2(\text{DBM})_2]$, *Metastable (Trans) Form*. This polymorph formed as large colorless crystals during the course of evaporating saturated solutions of the complex in 2-MePy at room temperature. This form was prepared first and proved

to be metastable; many experiments were performed before a more stable modification was obtained. Subsequently, the transformation of the metastable form into the stable form was observed in many instances, as reported for other systems,¹⁶ but we still were able to reproduce the trans form preparation. The composition of the separated crystals was confirmed by TGA (24.5% observed mass loss was vs 25.0% calculated for 2-MePy content) and by X-ray diffraction and ¹³C NMR experiments. The phase purity of the product was ascertained unequivocally (see Figures 2 and 4, Table 4, and the Results section). This form exhibited a significantly lower melting temperature and melting enthalpy than the cis form (Table 1).

Measurements. *Isopiestic and Thermogravimetric Analyses.* In addition to its preparative use, the isopiestic method served also for analytical purposes, as the mass gain indicated the quantities of volatile component added. Guest:host molar ratios (x) of the resulting inclusion compounds were calculated from the formula $x = (\Delta m/m_0)(M_H/M_C)$, where Δm and m_0 are the mass increase and the starting sample mass and M_H and M_C are host and guest molecular masses, respectively. Three independent determinations were made. For the trans form of [Cd(2-MePy)₂(DBM)₂] complex placed in an atmosphere of various solvents, no mass increase was observed, but the powder diffraction patterns changed to that of the cis form, thus indicating a phase transition between polymorphs.

TGA was used to determine composition of both complexes and inclusion compounds. A 2050 Thermogravimetric Analyzer (TA Instruments) was utilized. Samples were 20–40 mg. According to our earlier investigations,⁹ metal DBMs reveal thermal stability up to ~330 °C (Ni) or ~220 °C (Zn, Cd). All compounds studied in this work lost all of their 2-MePy (as well as guest organics) far before reaching these temperatures, so that plateaus corresponding to metal DBM were clearly observed in the TGA thermograms (Figure 1). For the complexes, the mass decrease corresponded directly to escaping 2-MePy, from which its content was calculated. For inclusion compounds of [Ni(2-MePy)₂(DBM)₂], the steps due to loss of guest and loss of 2-MePy were not fully resolved, so the guest content was calculated by subtracting the expected contribution from 2 mol of 2-MePy. Figure 1 exemplifies TGA thermograms of inclusions with carbon tetrachloride and toluene. The steps on the curves did not necessarily indicate the formation of monophasic intermediate solids (e.g. due to melting) but the final product, as attested by powder XRD, always was the green form of the Ni(DBM)₂.⁹ The total decrease was well-reproducible for every compound and confirmed the proposed stoichiometries.

X-ray Crystallography. Phase analyses were performed on powder samples with a Rigaku Geigerflex diffractometer (Co K α radiation, $\lambda = 1.7902$ Å) in a 5–30° 2 θ range, with a 0.02° step scan with 1 or 2 s per step. Samples recovered after isopiestic experiments were studied in an atmosphere of the corresponding guest. For theoretical powder diffractograms, the low-temperature single-crystal analysis results were used from unit cell dimensions determined at room temperature.¹⁷

Single-crystal diffraction experiments were performed with crystals, or chips cut therefrom, taken from under their respective mother liquors and cooled immediately to –100 °C. A Siemens SMART CCD X-ray diffractometer with graphite-

monochromated Mo K α radiation ($\lambda = 0.7107$ Å) was used to collect diffraction data. Preliminary unit cell parameters were determined using 60 or more frame ω scans, 0.3° wide, starting at three different ϕ positions. Full data sets were collected using the ω scan mode over the 2 θ range of 3–58°. Coverage of the unique sets was over 99%. 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 SIR92¹⁸ and SHELXTL¹⁹ 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 in some cases for minor orientations of disordered fragments. 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 (see Table 2). The largest residual extrema on the final difference map were located about the heavy atoms (Cl, Ni, Zn, Cd). The most difficult problems were faced solving the [Ni(2-MePy)₂(DBM)₂] (stable form)²⁰ and [Cd(2-MePy)₂(DBM)₂] (cis form) structures.²¹

Analysis of packing was accomplished using XP¹⁹ and CLAT²² program packages. The following van der Waals radii (Å) were applied:²³ C, 1.71; H, 1.16; Cl, 1.90; N, 1.52; O, 1.29; Ni, 1.63; Cd, 1.5; Zn, 1.39.

A summary of the crystal data and experimental parameters is given in Table 3. Further crystallographic information for seven structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) and allocated the deposition numbers from 157436 to 157442, the numbers given in Table 3.

DSC Measurements. These were performed using a 2920 Modulated Differential Scanning Calorimeter (TA Instruments). Samples of ~10 mg were pressed into aluminum pans and the DSC curves were recorded at a 5°/min heating rate. Two determinations were made for Ni and Zn compounds and four for each polymorph of the Cd complex.

NMR Spectroscopy. ¹³C Cross-polarization/magic angle spinning (CP/MAS) NMR spectra of diamagnetic complexes 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 ¹H decoupling during signal acquisition. ¹H

(18) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Gualardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

(19) Sheldrick, G. M. *SHELXTL PC, Ver. 4.1. An Integrated System for Solving, Refining and Displaying Crystal Structure from Diffraction Data*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(20) The structure of [Ni(2-MePy)₂(DBM)₂] (stable form) was first solved with two independent molecules. As nickel centers were located on inversion centers, two halves represented the asymmetric unit of the structure. An R -value of 0.063 was reached at this stage. An unreasonable geometry, unacceptable thermal parameters, and large residual extrema (+1.64 and –1.79 e/Å³) suggested displacement of a fragment of molecule C (including nickel, oxygen atoms, and 2-MePy) from that imposed by the inversion center. It was thus set to be disordered across the inversion center. Refinement with additional 85 parameters dropped the R -value to 0.042 and left residual extrema of +0.66 and –0.44 e/Å³.

(21) An initial structure solution of [Cd(2-MePy)₂(DBM)₂] (cis form) led to reasonable molecular geometry and packing features. However, the solution left large residual extrema (+1.67 and –2.25 e/Å³) about Cd with an R -value of 0.085 (for 6885 merged data and 444 parameters). The problem was recognized as due to twinning. Further refinement with TWIN 1 0 0 0 –1 0 –0.5 0 –1 instruction without merging reflections resulted in a solution with $R = 0.036$ (for 29045 data and 445 parameters) and residual extrema of +0.59 and –0.52 e/Å³. The refined value for the minor fraction of twin components was 0.1409(3).

(22) Grachev, E. V.; Dyadin, Yu. A.; Lipkowski, J. *J. Struct. Chem.* **1995**, *36*, 876–879.

(23) (a) Zefirov, Yu. V.; Zorkii, P. M. *Russ. Chem. Rev.* **1995**, *64*, 415–428. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451.

(15) Evaporating solutions of the complex in methylene chloride, chloroform, tetrahydrofuran, chlorobenzene, or toluene produced powder products; the same precipitated during cooling of hot solutions. The only good crystals of the complex grew from solution in 2-MePy, but they were of the metastable (trans) form.

(16) Dunitz, J. D.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193–200.

(17) At room temperature the unit cell dimensions were as follows (the same crystals as for the low-temperature experiments were used): [Ni(2-MePy)₂(DBM)₂] (stable form (213 reflections), $a = 11.430(3)$ Å, $b = 12.543(5)$ Å, $c = 13.125(6)$ Å, $\alpha = 80.71(2)^\circ$, $\beta = 77.03(4)^\circ$, $\gamma = 86.84(3)^\circ$); [Zn(2-MePy)₂(DBM)₂] (230 reflections), $a = 21.355(7)$ Å, $b = 29.100(8)$ Å, $c = 9.941(3)$ Å; [Cd(2-MePy)₂(DBM)₂] (cis form (219 reflections), $a = 13.995(5)$ Å, $b = 16.042(5)$ Å, $c = 16.116(6)$ Å, $\beta = 102.50(3)^\circ$); [Cd(2-MePy)₂(DBM)₂] (trans form (599 reflections), $a = 11.593(2)$ Å, $b = 16.628(4)$ Å, $c = 18.675(4)$ Å).

90° pulse lengths were 2.7 μ s, CP times were 2 ms, and recycle times were 3–30 s, depending on the sample. Dipolar dephased spectra²⁴ were obtained by interrupting the ¹H decoupling for 40 μ s immediately after the CP sequence and before starting the data acquisition. Chemical shifts were measured relative to external solid hexamethylbenzene and then corrected to the TMS scale. Spinning speeds were set in the range 6.09–6.14 kHz to avoid overlap of spinning sidebands with isotropically shifted lines.

Results

Polymorphs and Inclusions of [Ni(2-MePy)₂(DBM)₂]. All isolated compounds were green. Upon heating, all compounds decomposed to Ni(DBM)₂ (see Figure 1). The stability of inclusions in air were ranked in the order carbon tetrachloride < benzene < toluene, chlorobenzene, correlating directly with the shape of the available cavity space; the first decomposed in several hours, whereas the last was stable for weeks. Guest: host ratios derived from three independent methods are summarized in Table 2. Some essential properties and structural parameters of the compounds are listed in Tables 1 and 3.

A stable polymorph of [Ni(2-MePy)₂(DBM)₂] forms upon the interaction of nickel DBM with 2-MePy in chloroform/hexane as well as after crystallization of the product from methylene chloride, chloroform, acetone, tetrahydrofuran, or nitromethane. The crystal structure is triclinic, *P* $\bar{1}$, with two molecules per unit cell (A and C), each located about a symmetry center.

Molecule A is centrosymmetric (Figure 5a) and reveals principal features common to all structures. This is a trans-configured octahedral complex. Nickel(II) is chelated by two DBMs in the equatorial plane with Ni–O distances 1.99–2.03 Å and coordination angles 89.7°–90.3°. The overall geometry of the bis-chelate unit is as usually observed for metal bis-acetylacetonate and related complexes.²⁵ 2-MePy ligands coordinate to the nickel axially with Ni–N distances of 2.11(2) Å for main and 2.30(1) Å for minor orientations. The disordering of 2-MePy is shown in Figure 5a (major orientation occupied by 54.8(5)%). This type of disordering is observed in most structures of the complex. There is a significant steric repulsion as the methyl group approaches oxygen atoms of two DBMs in the equatorial plane. The 2-MePy ligand tilts over due to this repulsion. The Ni–N bond therefore deviates from the axial position, forming an angle of 83°–87° with respect to the equatorial plane. This geometry weakens the coordination bond, the observed distances in this and other structures being longer compared to complexes of unsubstituted¹ or 4-substituted^{2,3} pyridines. With specified exceptions, the general structural and conformational features of the molecule are similar to those of other metal DBM hosts (Tables 5 and 6). The phenyl rings rotate slightly from the equatorial plane to avoid repulsion with the methanate hydrogen, and a 2-MePy ring locates close to a plane dividing the bis-chelate fragment on two chelate rings.

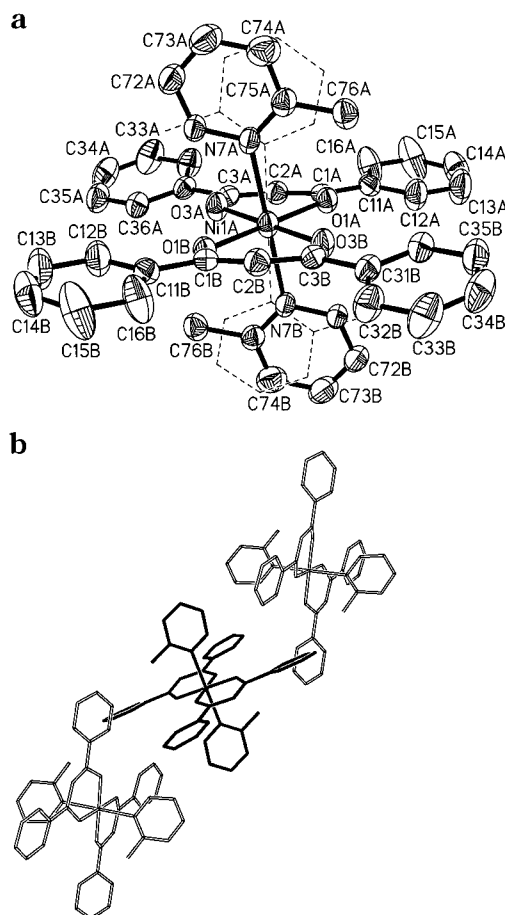


Figure 5. Structure of [Ni(2-MePy)₂(DBM)₂], stable form. (a) Molecule A, an ORTEP drawing with atom numbering scheme. Atoms labeled B are generated by centrosymmetry. The minor orientation of the 2-MePy ligand is shown by dashes. (b) Fragment of packing showing a chain of alternating A (heavy line) and C (open line) molecules. H atoms are omitted.

Molecule C is pseudocentrosymmetric. Nickel is displaced from the center by 0.324 Å, and oxygens and atoms of the 2-MePy ligands are shifted accordingly, while the rest of the molecule is centrosymmetric. The dihedral angle between two chelates is therefore ~15°. Other features of the molecule are qualitatively similar to those of others (Tables 5 and 6).

As for all the other compounds studied, the crystal structure of the stable form of [Ni(2-MePy)₂(DBM)₂] is controlled by van der Waals packing. Chains of alternating A and C molecules stretch parallel to each other approximately along the normal to the (111) plane. Neighboring molecules in the chain interdigitate as shown in Figure 5b, with an angle of ~62° between their equatorial planes. This mode of packing allows nickel centers to approach each other to within 9.2–9.5 Å, resulting in more effective packing in this direction while the shortest distances between nickel atoms in different chains are greater than 10 Å. A similar packing motif was found before in the triclinic form of [Co(4-ViPy)₂(DBM)₂] complex.³ In previous papers of this series^{1–3} we used a simple model to explain the crystal packing of metal DBM hosts and the stoichiometry of their inclusions. Each molecule of a complex (e.g. as shown in Figure 5a) has four pockets formed by the 2-MePy and DBM fragments. In accordance with the principle of close packing,²⁶ these pockets should be

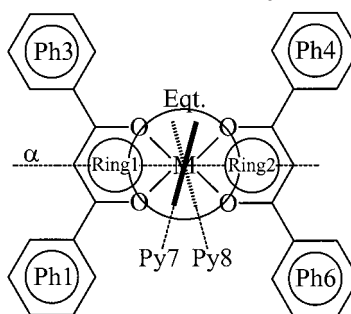
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(25) (a) Fackler, J. P. *Progr. Inorg. Chem.* **1966**, *7*, 361–425. (b) Lingafelter, E. C. *Coord. Chem. Rev.* **1966**, *1*, 151–155. (c) Joshi, K. C.; Pathak, V. N. *Coord. Chem. Rev.* **1977**, *22*, 37–122. (d) Kawaguchi, S. *Coord. Chem. Rev.* **1986**, *70*, 51–84.

Table 5. Selected Structural Parameters of [M(2-MePy)₂(DBM)₂] Molecules in Phases Studied^{a,b}

	Ni						Cd	
	stable form		metastable form	benzene clathrate		chlorobenzene clathrate	cis form	trans form
	mol A	mol C		mol A	mol B			
distances (Å)								
M–O1	2.027(1)	2.009(5)	1.997(1)	2.011(1)	1.995(1)	2.018(1)	2.272(1)	2.238(1)
M–O3	1.994(1)	1.996(5)	2.030(1)	2.004(1)	2.011(1)	2.018(1)	2.272(1)	2.280(1)
M–O4		2.015(5)	2.019(1)	2.027(1)			2.270(1)	2.268(1)
M–O6		1.995(5)	2.012(1)	1.991(1)			2.218(1)	2.239(1)
M–N7	2.30(1)	2.283(5)	2.206(2)	2.189(2)	2.189(3)	2.193(1)	2.368(1)	2.403(2)
	[2.11(2)]		[2.168(5)]		[2.31(2)]			[2.31(2)]
M–N8		2.215(4)	2.147(4)	2.204(2)			2.400(1)	2.433(1)
			[2.28(2)]					
valent angles (deg)								
O1–M–O3	89.65(5)	90.5(2)	89.40(4)	89.23(4)	89.90(5)	89.82(4)	79.53(4)	80.99(4)
O4–M–O6		90.5(2)	89.14(4)	90.76(5)			81.40(3)	82.83(3)
line–plane angles (deg)								
(M–N7) (eqt) ^c	83.3	85.0	82.9	86.8	86.8	86.7	–	88.8
	[87.0]		[80.1]		[82.8]			[76.5]
(M–N8) (eqt) ^c		86.6	85.2	86.9			–	85.6
			[82.2]					

^a Atom numbering in the table follows schemes given in Figures 5, 6, 10, and 11 but without the letter labels. ^b Values for minor orientations of disordered fragments are inscribed in square brackets. ^c eqt is an equatorial plane traced through M and adjacent oxygens.

Table 6. Conformational Characteristics for the *trans*-[M(2-MePy)₂(DBM)₂] Molecule Found in Different Phases^a

M, phase	point sym	dihedral angles (deg) ^b									
		ring1–ring2	eqt–Ph1	eqt–Ph3	eqt–Ph4	eqt–Ph6	eqt–Py7	eqt–Py8	α–Py7	α–Py8	2-MePy
Ni, stable form											
molecule A	–1	0	6	–10	–6	10	84	84	86	–86	disordered
molecule C	(–1)	15	8	25	7	25	88	80	83	–83	opposite
Ni, metastable form	1	2	6	12	1	54	80	83	87	85	disordered
Ni, benzene clathrate											
molecule A	1	7	7	–2	28	–30	83	85	83	–87	one side
molecule B	–1	0	11	–5	–11	5	87	87	87	–87	disordered
Ni, chlorobenzene clathrate	1	0	25	–14	–25	14	87	87	86	–86	opposite
Cd, trans form	1	13	7	–14	–33	–5	87	89	90	84	one side

^a Values for molecules in main orientations only are given. ^b Least-squares planes are designated as shown in the drawing above. For example, the planes for the molecule shown in Figure 11a are as follows: ring1 (Cd, O1, C1, C2, C3, O3); ring2 (Cd, O4, C4, C5, C6, O6); eqt (Cd, O1, O3, O4, O6); Ph1 (C11–C16); Ph3 (C31–C36); Ph4 (C41–C46); Ph6 (C61–C66); α (Cd, C2, C5, N7, N8); Py7 (N7, C71–C75); Py8 (N8, C81–C85).

filled. In these terms, four pockets of the molecule are filled partially by four phenyls and two pyridine moieties from two adjacent molecules in the chain (Figure 5b) and partially by fragments from neighboring chains.

A metastable polymorph obtained from acetone is monoclinic, space group $P2_1/n$, with four *trans* [Ni(2-MePy)₂(DBM)₂] molecules per unit cell. One complex molecule forms the asymmetric unit of the structure (Figure 6a). Its overall geometry is similar to that described above for the stable form (Tables 5 and 6).

Both 2-MePy ligands are disordered, but unlike the stable form, the major orientations of 2-MePy [67.2(3)% for N7–C76 and 83.0(3)% for N8–C86] are turned in a similar fashion. In the crystal structure, chains of molecules stretch along the *x* direction parallel to each other. Equatorial and other planes of neighboring molecules in the chain are parallel as they are pinned by translation (Figure 6b). The packing along the chain is very effective. The distance between nickel atoms is 8.8 Å within the chain, compared to >10.1 Å between nickels of neighboring chains. Two pockets of a molecule are filled with 2-MePy moieties of closest neighbors, while the other two pockets point out of the chain and are shared by four phenyls from three molecules belong-

(26) Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultant's Bureau: New York, 1961. (English translation of the Russian original published by Press of the Academy of Sciences of the USSR, Moscow, 1955).

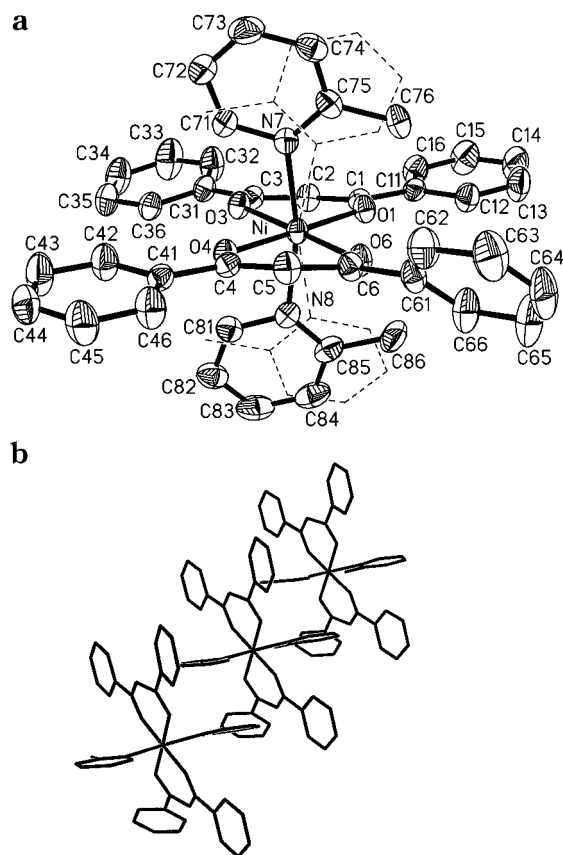


Figure 6. Structure of $[\text{Ni}(\text{2-MePy})_2(\text{DBM})_2]$, metastable form. (a) Molecule of the complex, an ORTEP drawing with atom numeration scheme. Minor orientations of 2-MePy ligand are shown by dashes. (b) Fragment of packing showing a chain of molecules stretching along the x axis. H atoms are omitted.

ing to parallel chains. Despite the different structural organization of this polymorph, the resulting density is practically the same as for the stable form (one molecule occupies $\sim 882 \text{ \AA}^3$).

With benzene, both upon recrystallization and through gas-phase contact (the latter process takes several hours), an inclusion compound with fractional stoichiometry forms (Table 2), $[\text{Ni}(\text{2-MePy})_2(\text{DBM})_2]^{4/3}\text{benzene}$. The results of single-crystal analysis give justification for the formula. The structure is triclinic, space group $P\bar{1}$. There are three host and four guest molecules per unit cell that result in $Z = 3$ and a guest:host molar ratio of 4/3. Two equivalent host molecules (A) are asymmetric and the third one (B) is centrosymmetric. The structures and conformations of the molecules are within the range observed in other structures (Tables 5 and 6). Molecule A has its bis-chelate fragment bent by 7° , and the 2-MePy ligands are turned in the same direction (analogous to that shown in Figure 6a). In molecule B, the 2-MePy group is disordered with the major orientation occupied by 82.4(4)%; due to the inversion center, the ligands are turned in opposite directions.

The crystal architecture of this clathrate is complicated. The shortest nickel–nickel distances of 9.6 Å were found between neighboring A and B molecules interdigitating in a similar fashion as in the stable host form, with $\sim 61^\circ$ dihedral angle between their equatorial planes. This results, however, in A–B–A packing units (Figure 7a) rather than in endless chains. These units

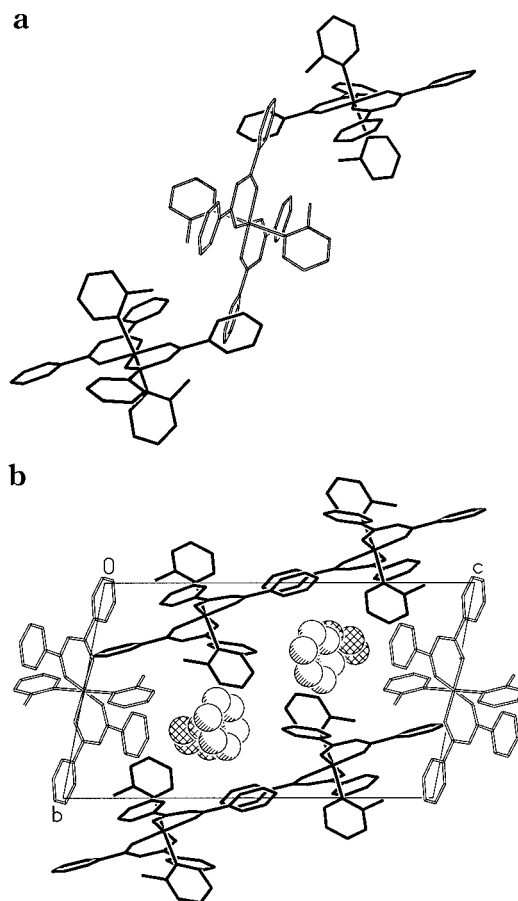


Figure 7. Structure of the $[\text{Ni}(\text{2-MePy})_2(\text{DBM})_2]^{4/3}\text{benzene}$ inclusion compound. (a) Fragment of the crystal structure showing three interdigitated host molecules. Molecules A are shown in heavy lines, and molecule B is shown with double lines. (b) Unit cell content projected along x . For clarity, the host is outlined by sticks while the guest is shown by balls. Guest molecules locating at $x \sim 0$ are crosshatched and those at $x \sim 0.5$ are clear. H atoms are omitted.

translate along x to form channels in the x direction (Figure 7b). Two adjacent channels go through the unit cell. Within one translation period the channels are formed cooperatively by vacant pockets of six surrounding molecules from four A–B–A associates. The channels possess two types of widenings. At $x \sim 0$ the cross-section of a channel may be approximated by a $4 \times 8 \text{ \AA}$ ellipse; this widening is filled by a guest molecule disordered in a way assuming its rotation. A minor orientation occupied by 45(2)% arises from the main one by rotating $\sim 30^\circ$ about the 6-fold axis. At $x \sim 0.5$, the $6.5 \times 8 \text{ \AA}$ widening is occupied by another guest molecule; at this level two adjacent channels almost merge. The restrictions of $4 \times 5 \text{ \AA}$ located at $x \sim 0.25$ and 0.75 in effect form barriers that lock the guests in place. This explains the moderate stability of the clathrate, even though it is of the channel type.

With carbon tetrachloride the $[\text{Ni}(\text{2-MePy})_2(\text{DBM})_2] \cdot 2\text{CCl}_4$ inclusion forms (Table 2). The process proceeds well not only upon crystallization but also upon interacting the solid host with the guest vapor. From a preliminary single crystal study,²⁷ there are four host (two independent) and eight guest molecules (four independent) per unit cell. The host molecules are asymmetric and trans-configured. The guest molecules appear to have strong thermal motions and/or disorder.

The structure is isomorphous with the $[\text{NiPy}_2(\text{DBM})_2] \cdot 2\text{pyridine}$ clathrate described in our introductory paper.¹ In both cases, well-packed layers of host molecules extend perpendicular to the z axis, at $z \sim 0.25$ and 0.75 for CCl_4 clathrate and at $z \sim 0$ and 0.5 for pyridine clathrate. From these layers some phenyl ligands protrude into the interlayer space, creating parallel isolated channels running along the y direction in the CCl_4 clathrate and along the x direction in the pyridine clathrate. The translation period in the former is approximately half that found in the latter.

Inclusion compounds of a third type were obtained with chlorobenzene and toluene with 1:1 stoichiometry that formed only during crystallization²⁸ (Table 2). From a single crystal study, $[\text{Ni}(2\text{-MePy})_2(\text{DBM})_2] \cdot \text{chlorobenzene}$ clathrate is triclinic, space group $P\bar{1}$, with one centrosymmetric host molecule and one guest molecule per unit cell. Chains of interdigitating molecules extend along the x axis (Figure 8a), with 8.2 Å between the centers of adjacent molecules. The chains are different from those found in the stable and metastable host forms. Two pockets of every molecule of the chain take part in building cages for the guests. The cage is formed mainly by two pockets from two molecules of neighboring chains. This fragment is shown in Figure 8b; similar fragments have been found previously in clathrates of $[\text{NiPy}_2(\text{DBM})_2]$ with benzene and chlorobenzene¹ and of $[\text{M}(4\text{-ViPy})_2(\text{DBM})_2]$ ($\text{M} = \text{Ni}, \text{Co}$) with benzene.² All four have the same stoichiometry though different overall architectures. The cage has the shape of an oblate spheroid with approximate dimensions $3.6 \times 7.1 \times 8.5$ Å and is centrosymmetric. The guest molecule is therefore restricted to lie in a plane but is disordered due to the center of symmetry, and two nonequivalent orientations exist: the minor one, populated by 38.4-(3)%, may be obtained from the main one by rotation in the plane of the molecule by $\sim 60^\circ$. The toluene clathrate showed a similar composition (Table 2) and unit cell dimensions²⁹ and was thus found to be isostructural.

$[\text{Zn}(2\text{-MePy})_2(\text{DBM})_2]$. The complex with only one coordinated 2-MePy ligand crystallizes even from neat 2-MePy liquid. The complex does not form inclusion compounds with methylene chloride, chloroform, acetone, tetrahydrofuran, benzene, and chlorobenzene (as concluded from powder diffractograms of crystalline materials obtained from these solvents). A single crystal study elucidates the structural features of the complex that are essentially different from the those of metal DBM hosts. The structure is orthorhombic, space group $Fdd2$. There are eight molecules per unit cell but only half a molecule in the asymmetric unit. The molecule is located on a 2-fold axis running through the Zn–N(2-MePy) bond parallel to the z axis. The coordination environment of the zinc is trigonal bipyramidal (Figure

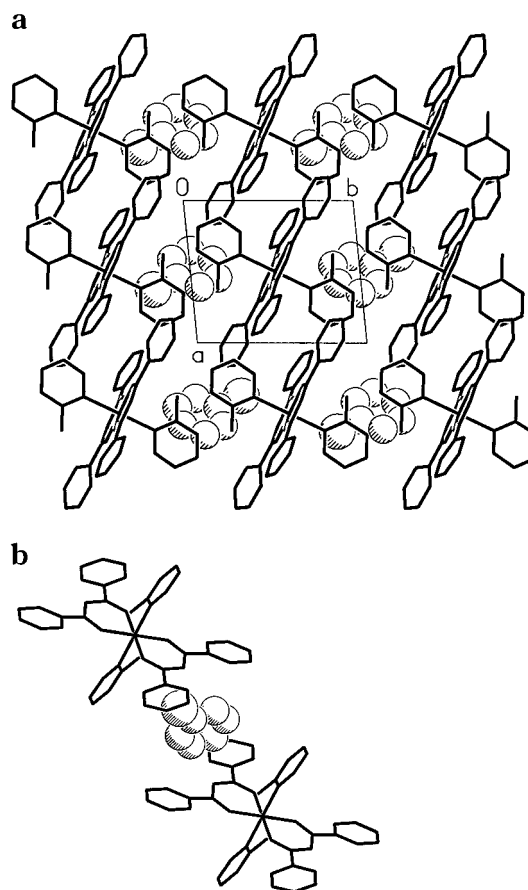


Figure 8. Structure of the $[\text{Ni}(2\text{-MePy})_2(\text{DBM})_2] \cdot \text{chlorobenzene}$ inclusion compound. (a) Projection of the structure along z . For clarity, the host is outlined in sticks with the guest as balls. Guest disorder about symmetry centers is suppressed so that only one guest orientation is shown in each location. (b) Fragment of the structure showing guest molecule trapped between two host molecules. H atoms are omitted.

9a). The axial distances from Zn to O3 and O3A are 2.065(1) Å. The nitrogen atom from 2-MePy, O1, and O1A form a coordination triangle in the equatorial plane with Zn–N of 2.040(2) Å and Zn–O of 1.980(1) Å. The N4–Zn–O1 angle is 122.23(4)°, O1–Zn–O1A is 115.55-(8)°, and the angles between Zn–O3 and the equatorial bonds are within 88°–92°. The chelate fragment (O1, C1, C2, C3, O3) as usual is planar (within 0.01 Å), while Zn deviates from the plane by 0.68 Å. The phenyls rotate from the plane by 21.4° (C11–C16) and 2.8° (C31–C36). The 2-MePy is necessarily disordered because of the 2-fold axis, so the methyl group points out either at O3 or O3A.

The ¹³C NMR spectra (Figure 4a,b) provide some valuable complementary analytical and structural information. Chemical shift assignments (see Table 4) were based on previous work on DBM complexes⁹ and on dipolar dephased spectra to identify carbons without attached H and C–H atoms that have dynamics. 2-MePy shifts were assigned with the aid of previously published data for the pure 2-MePy in DMSO³⁰ (Table 4) and dipolar dephased spectra.

The intensities of the 2-MePy resonances (relative to those of DBM) confirm that there is only one of these ligands in the Zn complex.

Because of spatial averaging, the X-ray structure shows one DBM and half a disordered 2-MePy in the

(27) Due to the poor quality of the available crystals, only a preliminary structure solution was obtained for $[\text{Ni}(2\text{-MePy})_2(\text{DBM})_2] \cdot 2\text{CCl}_4$. The structure was solved in the monoclinic space group $P2_1$ (No 4) with (–100 °C) $a = 17.567(3)$ Å, $b = 11.849(2)$ Å, $c = 21.991(3)$ Å, $\beta = 96.90(1)^\circ$, $V = 4544(1)$ Å³; for $\text{C}_{44}\text{H}_{36}\text{Cl}_8\text{N}_2\text{NiO}_4$ and $Z = 4$: $M = 999.1$, $d_{\text{calc}} = 1.460$, $\mu(\text{Mo K}\alpha) = 9.41$ cm^{–1}. The CCDC deposition number is 157443.

(28) No mass changes or powder diffractogram changes were observed for host samples placed in atmospheres of these solvents for 2 weeks.

(29) Approximate unit cell dimensions for $[\text{Ni}(2\text{-MePy})_2(\text{DBM})_2] \cdot \text{toluene}$ (–100 °C): $a \sim 8.24$ Å, $b \sim 9.67$ Å, $c \sim 13.12$ Å, $\alpha \sim 80.44^\circ$, $\beta \sim 77.31^\circ$, $\gamma \sim 82.43^\circ$, $V \sim 1000$ Å³.

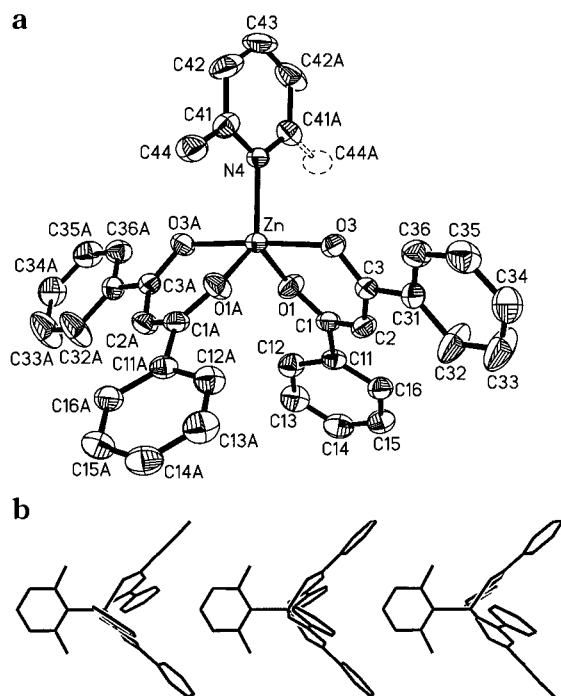


Figure 9. Structure of $[\text{Zn}(2\text{-MePy})(\text{DBM})_2]$. (a) ORTEP drawing and atom numbering scheme for the complex molecule. Atoms labeled A are generated by the 2-fold axis stretching through the Zn–N4 bond. The second possible position for the C44 atom (C44A) is contoured by dashes. (b) The fragment of the crystal structure showing packing of molecules in a column going along the z axis (in the figure, the z axis goes from left to right). H atoms are omitted.

asymmetric unit. The 2-MePy ring carbons in the 2,6 and 3,5 positions overlap under the average 2-fold symmetry (these correspond to C41/C41A and C42/C42A, respectively, in the X-ray solution). However, the carbons involved are still chemically distinct, and the ^{13}C NMR shows them as separate resonances. The dipolar dephased spectrum (Figure 4b) shows that the methyl is rotating, as is usually the case for CH_3 attached to aromatic rings, but the complete disappearance of signals from the proton-bearing carbons of the 2-MePy indicates that the group is static. Consequently, although on space averaging over the crystal there is 2-fold symmetry, in reality the symmetry is not present in each individual complex, and this is also seen in the NMR spectra: Under 2-fold symmetry a doublet (intensities 2:2) would be expected for the C=O resonances of the DBM units, and this would be achieved if the 2-MePy had dynamic disorder. However, the observed C=O resonances show as an overlapped doublet with 3:1 intensity ratio (at 186.4/184.8 ppm), which again indicates that the 2-MePy disorder is static and the methyl group is in close proximity to only one of the four C=O groups. None of the other DBM resonances show any effect of the lowered local symmetry, presumably because of greater distances from the perturbing methyl group.

The small amount of residual intensity in the region of the phenyl ring carbons in the dipolar dephased spectrum indicates some motion of the phenyl groups, presumably about their 2-fold axes.

The molecules pack in columns running along the z axis. Two DBMs form a bell-shaped hole wherein 2-MePy of the next molecule is inserted. The column is illustrated in Figure 9b.

Cis and Trans Forms of $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$. Each of the two isolated polymorphs of $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$ show distinctly different characteristics illustrated by all methods applied (see Tables 1, 3, and 4 and Figures 2–4). The difference originates at the molecular level, as the stable form contains cis isomers while the metastable form has trans species.³¹

The stability relations between the two forms become apparent from DSC (Figure 3). The cis form (trace a) shows no changes until 133 °C, at which point it experiences true melting, absorbing 66.2(5) kJ/mol. The trans form (trace b) also melts congruently but at 113 °C, absorbing 49.0(4) kJ/mol. As the postexperiment samples are essentially the same (both return to the cis form on cooling), the cis form is 17.2(6) kJ/mol more stable than the trans form.³² Trace c illustrates another result of heating the trans form (the samples of the trans form spontaneously displayed either b or c variants under the same experimental conditions). The first effect (endotherm A), which is due to melting, is followed by the sloping exotherm (B), corresponding to crystallizing cis form, which in this temperature range is more stable than the liquor. On further heating, the melting of this fresh-formed cis form is observed (endotherm C). Again the total of these three effects (A – B + C) equals ~49 kJ/mol, confirming that both cis and trans forms transform into the same product on melting.

The cis form does not form any inclusions, either upon wetting or upon placing under the vapor for 2 weeks, with methylene chloride, chloroform, carbon tetrachloride, *n*-hexane, tetrahydrofuran, ethyl acetate, benzene, fluorobenzene, and 2-MePy (as determined by powder XRD). Also, all of these solvents catalyze transformation of the trans form into the stable cis form. In atmospheres of the above solvents, the trans to cis conversions are usually complete in 2 h. The mechanism of this polymorphic transformation is not entirely clear. The whole process is complicated; as of necessity it involves two steps: the isomerization of the actual molecules and the integration of the new species into the new phase. It would seem necessary that the molecular isomerization has priority and that this is followed by the formation of a new phase. Whether the molecule “dissolves” in a solution formed locally at a surface in order to change its isomeric state or if this change might be accomplished some other way is the principal issue here. We have discussed this problem before,^{3,10,12} but it requires specific studies before more certain conclusions can be formulated.

The cis form of $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$ is monoclinic, space group $P2_1/c$, with four molecules per unit cell. One entire complex molecule forms the asymmetric unit of

(31) These two forms relate to each other both as isomers (the term describes state of molecules) and as polymorphs (the term describes features of phase or 3D packing). We follow, therefore, a widely accepted condition that two materials are polymorphs if they dissolve to give the same solution: McCrone, W. C. In *Physics and Chemistry of the Organic Solid State*; Fox, D., Labes, M. M., Weissberger, A., Eds.; Interscience: New York, 1965; Vol. 2, pp 725–767.

(32) It should be noted that this enthalpy difference refers to the temperature region where the forms melt; at room temperature the value may differ.

(30) Riand, J.; Chenon, M. Th.; Lumbruso-Bader, N. *J. Am. Chem. Soc.* **1977**, *99*, 6838–6845.

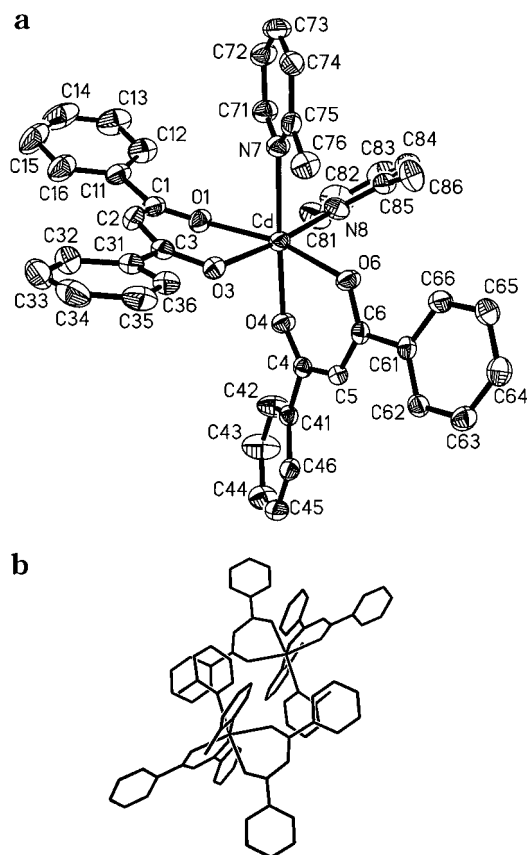


Figure 10. Structure of $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$, cis form. (a) ORTEP drawing and atom numbering scheme for a molecule of the complex. (b) Fragment of the crystal structure showing two interdigitated molecules. H atoms are omitted.

the structure. The cadmium center is chelated by two DBMs with Cd–O distances of 2.22–2.27 Å and by two 2-MePy with Cd–N of 2.37–2.40 Å in cis fashion (Figure 10a). The coordination angles experience considerable distortion, varying from 80° to 96° (O–Cd–O) and 84° to 104° (O–Cd–N). The chelate fragments (e.g. O1, C1, C2, C3, O3) are planar within 0.02 Å while Cd deviates from their planes by 0.50–0.67 Å. The angle between the planes is 81.3°. The phenyls rotate from the planes by +13.6° (C11–C16) and –9.1° (C31–C36) and by +28.6° (C41–C46) and –20.7° (C61–C66). The angle between the pyridine rings of two 2-MePy ligands is 64.0°. The cis configuration facilitates closer packing. The shortest distance between cadmium centers was found to be 7.6 Å (across an inversion center, Figure 10b). The volume per molecule is less than 866 Å³—substantially smaller than for phases formed by analogous nickel or cadmium trans species.

The trans form of $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$ is orthorhombic, space group $P2_12_12_1$, with four molecules per unit cell. The asymmetric unit is formed by one complex molecule. It reveals coordination and spatial features similar to trans metal DBM hosts (Figure 11a, Tables 5 and 6). Cd(II) is chelated by two DBMs in the equatorial plane with Cd–O distances 2.24–2.28 Å and coordination angles 81°–100°. The two 2-MePy ligands coordinate to the cadmium axially, with one (N7–C76) disordered in the same fashion as was shown in Figure 6a (minor orientation occupied by 9.2(3)%). The Cd–N distances are from 2.31 to 2.43 Å. Steric repulsion of the methyl group seems to be weaker because of the

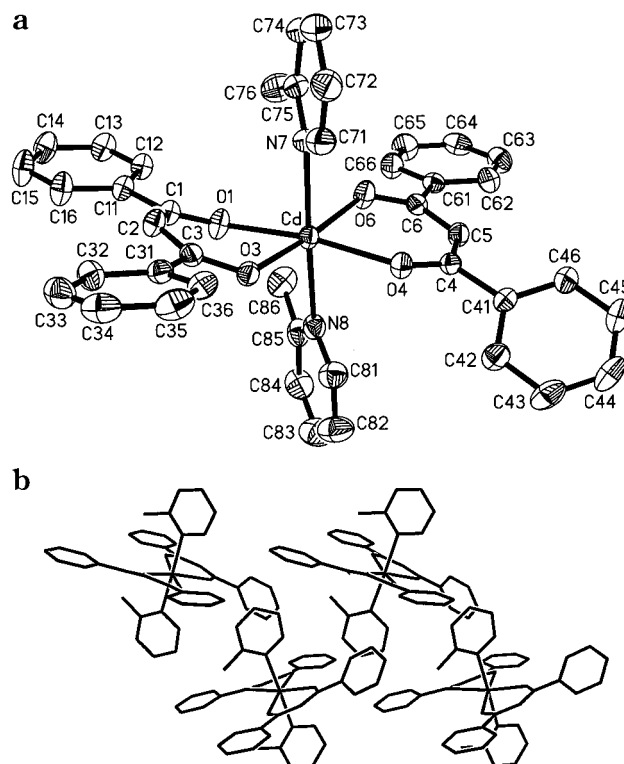


Figure 11. Structure of $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$, trans form. (a) ORTEP drawing and atom numbering scheme for a molecule of the complex. (b) Fragment of the crystal structure showing zigzag chain of molecules creeping around the double screw axis stretching parallel to x (in the figure, the x axis goes from right to left). H atoms are omitted.

longer coordination bonds: the Cd–N bond deviates from the axial position, forming 86°–89° angles to the equatorial plane (though for the minor orientation this angle is ~77°). As for other metal DBM hosts, the phenyl rings rotate from the equatorial plane to avoid overlapping with the chelate hydrogen, and the 2-MePy ring is located close to a plane dividing the bis-chelate fragment on two chelate rings (Table 6).

The mode of packing in the crystal structure is complex. The molecules are arranged in zigzag chains around a double screw axis, parallel to x . A fragment of the chain is shown in Figure 11b. The distance and angle in the zigzag sequence of cadmium centers are 8.7 Å and 82.6°. The angle between equatorial planes of neighboring molecules is ~32°. Every molecule inserts one of its phenyl rings into a pocket of one of its neighbors, and one of its 2-MePy is almost in the equatorial plane of another neighbor (between two DBM ligands). Other pockets are shared between phenyls and 2-MePy rings of molecules from adjacent chains. Despite the larger size of the molecule, the volume per molecule of 880.2(2) Å³ is slightly less than that for the nickel complex. At the same time, the packing is clearly not as effective as for the cis form.

The ¹³C NMR spectra for the cis and trans forms of the Cd complex are quite distinct (Figure 4c,d), reflecting the structural difference. In both cases one whole molecular complex $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$ forms the asymmetric unit of the crystal. The NMR results are entirely consistent with this: Both isomers show two distinct resonances due to the methanate C–H and four resonances for the C=O (four lines for trans and a 1:2:1

triplet for cis). Likewise, several of the 2-MePy resonances are split, indicating that there are two such distinct groups. The dipolar dephased spectra, just the same as for the Zn complex, indicate that the methyl groups are rotating, but that the 2-MePy groups as a whole are static and that there is some motion of the phenyl groups.

Discussion

Two new results can be derived from the present study. The first is the successful modification of a metal DBM, leading to a new host, $[\text{Ni}(2\text{-MePy})_2(\text{DBM})_2]$, whose versatility has been demonstrated by forming inclusion compounds of at least three structural types, two of which have not been observed previously. Second, for the first time, both cis and trans forms of the same complex of the metal DBM host type $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$ were prepared. Both forms were isolated as bulk products and characterized by a number of methods, thus giving strong support to the concept of creating new materials with properties controllable on the molecular level through molecular isomerization. These and other results are discussed below.

Despite the destabilizing effect of the methyl group at the 2 position, $[\text{Ni}(2\text{-MePy})_2(\text{DBM})_2]$ forms and exhibits stability. Five structurally distinct phases of the complex were isolated, including two guest-free polymorphs and three supramolecular architectures filled with guest organics. As with other metal DBM complexes displaying clathration ability,¹⁻³ the host molecule appears as a trans isomer. As may be seen from Tables 5 and 6, the structural and conformational features of the host molecule remain qualitatively similar through all structures. The coordination octahedron is distorted mainly due to the shorter Ni-O bonds (average distance is 2.009 Å for 18 independent bonds) as compared with the Ni-N bonds (average is 2.215 Å for 13 bonds). The bis-chelate fragment shows a tendency to be planar, though in some instances the bend may reach 13°–15°. The phenyl rings do not usually deviate from the equatorial plane by more than 30°, though no steric problems are encountered, which indicates the possibility of interaction between the aromatic systems of the phenyl rings and the pseudoaromatic systems of the chelate rings. 2-MePy is always displaced from the axial position by 3–10°, and its plane is close to that dividing the bis-chelate fragment on two chelate rings. This geometry minimizes repulsion between the methyl group and the DBM ligands. No preference for mutual orientation of 2-MePy ligands is observed.

In the present study we observe an intriguing contrast between the relative simplicity and stability of the host molecule geometry and the wide variety of packing motifs and architectures it forms. Analogous observations are valid for the metal DBM hosts studied earlier.¹⁻³ The observed polymorphism and inclusion properties are manifestations of the same phenomenon inherent to many hosts in general:³³ the inability of the

molecules to pack efficiently in three dimensions. In most structures close packing in one dimension is observed while 3D packing usually requires assistance by smaller species. The impact of the 2-methyl group on the overall geometry of the host molecule, although expected to be small, nevertheless is strong enough to give essentially new architectures as compared with the parent complex $[\text{NiPy}_2(\text{DBM})_2]$. This remarkable tendency to create a variety of frameworks, energetically close to each other, depending on guest parameters ranks the host type with some well-known classes of organic and inorganic hosts, like gossipol,³³ $[\text{MA}_4\text{X}_2]$ complexes,⁴ and water.³⁴

With Zn as the metal center, the complex of desired stoichiometry does not form at all. As was described for the Ni complex, the 2-methyl group causes the 2-MePy ligand to turn and move away from the metal center, thus weakening the M-N(2-MePy) coordination bond. The host complex still forms for nickel but not for zinc, as complexes of the latter, as a rule, are less stable. The $[\text{Zn}(2\text{-MePy})(\text{DBM})_2]$ complex, isolated instead, has a different molecular geometry that lacks the ability to form inclusion compounds. It should be noted that another class of host complexes, $[\text{MA}_4\text{X}_2]$, bearing nearly 40 substituted pyridines as ligand A, does not form complexes with 2-substituted A at all, as this would create strong repulsive interactions between the ligands around the metal center.⁴

For the cadmium complex steric problems are less significant due to the increased size of the cation. The complex $[\text{Cd}(2\text{-MePy})_2(\text{DBM})_2]$ appears as the cis isomer in its stable form. The complex does not exhibit any ability to include, in agreement with our observation that only the trans isomer can serve as a host. The comparison between the nickel complex, a versatile host, and the cadmium complex illustrates how the macro-property to include may be programmed at the molecular level: replacing the metal center switches the isomeric state and thereby the spatial parameters of the resulting molecule, thus dramatically changing the material.

There is however another form of the complex, isolated as a metastable polymorph containing the trans species. The packing problem (that is usually responsible for host properties) for the trans species becomes apparent as the volume per trans molecule (880.2 Å³) is ~1.7% larger than per cis molecule (865.7 Å³). As the geometry of the coordination bonding does not reveal clear advantages for the cis isomer, the higher stability of the cis form may be attributed to its tighter crystal packing. At the same time, the possibility to isolate the trans form, which is less stable by $\Delta H = 17.2(6)$ kJ/mol, reveals a significant kinetic barrier between the

(33) Examples of versatile organic hosts displaying polymorphism: Gossipol (7 guest-free polymorphs): (a) Ibragimov, B. T.; Talipov, S. A. *J. Incl. Phenom.* **1994**, *17*, 325–328. (b) Gdanec, M.; Ibragimov, B. T.; Talipov, S. A. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon:

Oxford, 1996; Vol. 6, pp 117–145, and refs 48, 68 therein. Hydroquinone (3 guest-free polymorphs): Mak, T. C. W.; Bracke, B. R. F. In *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6, pp 23–60, and refs 6, 13, 14 therein. 4,5-Bis(4-methoxyphenyl)-2-(4-nitrophenyl)-1H-imidazole (3 guest-free polymorphs): Sakaino, Y.; Fujii, R.; Fujiwara, T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2852–2854. Perhydrotriphenylene (2 guest-free polymorphs): Allegra, G.; Farina, M.; Immirzi, A.; Colombo, A.; Rossi, U.; Broggi, R.; Natta, G. *J. Chem. Soc. B* **1967**, 1020–1028.

(34) (a) Jeffrey, G. A. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: London, 1984; Vol. 1, pp 135–190. (b) Dyadin, Yu. A.; Bondaryuk, I. V.; Aladko, L. S. *J. Struct. Chem.* **1995**, *36*, 995–1045.

forms that is most probably due to the different isomeric configurations. As solvents can easily catalyze the trans to cis transition, the process can be controlled in this direction. To transform cis back to trans, the above ΔH must be overcome. Accomplishing this transformation through the clathration process would add to this energy another unfavorable term for transforming the dense trans form into a porous phase.^{35,36} The resulting energy to overcome would be $>17.2(6)$ kJ/mol. Typical values for polymorphic transitions from dense to open forms that may be compensated easily due to guest inclusion were reported before: 0.5(1) kJ/mol for the $\alpha \rightarrow \beta$ transformation of hydroquinone,³⁷ 3.5(1) kJ/mol for the [Ni-(4-MePy)₄(NCS)₂] host,³⁶ and 1.31(5) kJ/mol for [CuL₂],¹² where L = L⁻ = CF₃COCHCOC(CH₃)₂OCH₃ (this transition involves cis–trans isomerization). Finally, 11.3 kJ/mol reported in our preceding paper for transforma-

tion of stable [Ni(4-ViPy)₂(DBM)₂] into a preorganized “apohost” form is still surmountable. Compared to the above values, the polymorphic transition energy for [Cd-(2-MePy)₂(DBM)₂] is too high. The results obtained in this work, however, provide a precedent in that both isomeric forms for the same metal DBM type complex may have comparable energies and may be prepared as bulk products and that complexes of that kind may be generated by introducing certain groups in the pyridine ligand. This inspires optimism for creating new metal DBM type hosts able to serve as switchable sorbent materials.

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

Supporting Information Available: X-ray structural information on eight studied compounds (see Table 3 and ref 27) (PDF/CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(35) (a) Hart, H. J.; Smith, N. O. *J. Am. Chem. Soc.* **1962**, *84*, 1816–1819. (b) Lipkowski, J.; Starzewski, P.; Zielenkiewicz, W. *Thermochim. Acta* **1981**, *49*, 269–279.

(36) Lipkowski, J.; Chajm, J. *Rocz. Chem.* **1977**, *51*, 1443–1448.

(37) Evans, D. F.; Richards, R. E. *J. Chem. Soc.* **1952**, 3932–3936.