Stabilization of Guest-Free Forms of Metal Dibenzoylmethanate Host Type Through Self-Inclusion of a Ligand Fragment Into the Intramolecular Pocket[†]

D.V. Soldatov,[a,b,]* G.D. Enright,[a] A.S. Zanina[c] and I.E. Sokolov[c]

[a]*Steacie Institute for Molecular Sciences, National Research Council, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6 Canada*
[b]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Lavrent'ev Avenue 3, Novosibirsk, 630090 Russia*
[c]*Institute of Chemical Kinetics and Combustion, Siberian Branch of the Russian Academy of Sciences, Institutskaya Street 3, Novosibirsk, 630090 Russia*

Abstract—A derivative of the metal dibenzoylmethanate (DBM) host type, accomplished through the chemical modification of the DBM ligand, is reported for the first time. The new ligand, (1-naphthoyl)benzoylmethanate (NBM) differs from the parent DBM by an additional phenylene ring. Three new complexes $[NiA_2(NBM)_2]$, with pyridine (Py), 4-methylpyridine (4-MePy) and 4-phenyl-pyridine (4-PhPy) is A, were synthesized and studied for host properties. Complexes with Py and 4-MePy were isolated as solvent-free forms and did not show any ability to form inclusion compounds with ten solvents tested. Single-crystal XRD study revealed van der Waals type of crystal structure of the complexes. The nickel atom is octahedrally coordinated by two chelating NBMs in the equatorial plane and two terminal pyridines. Naphthyl ligands turn almost perpendicular to the equatorial plane of the complex filling the pocket space which usually accommodates guest species in metal DBM analogues. This 'self-inclusion' of its own fragment, that the molecule demonstrates, explains the inability of the complexes to entrap guest solvents. The complex with 4-PhPy forms inclusion compounds with chloroform, benzene, tetrahydrofuran and acetone, the compounds have 1:2 host to guest ratio and are isostructural. A possible explanation of such a difference is the larger size of the pocket which now cannot be completely filled with the naphthyl fragment.
© 2003 Elsevier Ltd. All rights reserved.

Introduction

Self-assembly[1–3] is governed by several factors of which the structure of the molecular building unit is the most important. Some types of molecules exhibit diverse ability to assemble into supramolecular structures providing cavity space for a second, guest component. Understanding the properties leading to such an ability is a key problem in rational design of host molecular receptors,[4–10] microporous solids,[11–22] and a wide range of functional materials.[23–37]

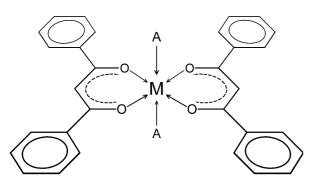Crystal structure is programmed on the molecular level. The statement seems evident. Nevertheless crystal structure prediction still remains a problem.[38–43] One of the reasons complicating crystal structure prediction is the flexibility of the building units themselves on a conformational and other levels.[31] Even for purely molecular crystals, the cumulative contribution of weak van der Waals interactions can appreciably affect the parameters that describe the structure of the molecular building units in the solid phase. This 'feedback', that is, the way crystal packing may affect molecular unit is a difficult subject which researchers are just beginning to explore. A clear example of such a feedback is 'contact stabilization', the phenomenon when a complex molecule can exist only in certain supramolecular matrices while decomposing upon removal of the guest template.[44–51] Stabilization in supramolecular solids of certain isomeric[31,52–54] or oligo-meric[31,55,56] molecules, metal–metal short contacts,[57,58] unusual oxidation states[59] and specific coordination environments,[60] and oxonium and other moieties of bio-logical significance[61–64] have been reported. Realization of different conformations for the same molecule in a single phase ('contact conformational isomerism')[65] or

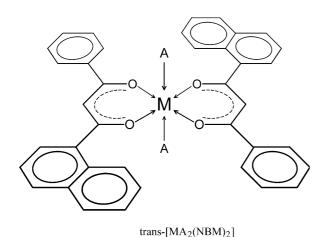in different phases (conformational isomerism induced by guest template)[66–70] has been reported as well.

The subject of this study addresses the problem of the versatile clathration ability of modified metal dibenzoylmethanates (DBMs) (Scheme 1).[71–77] These metal complexes constitute a new class of host molecules which entrap a wide range of organic guests in a cavity space of molecular crystal framework. The interest in this new family is that the complexes maintain their host properties upon extensive modification. In our previous work both metal center M and pyridine-type ligand A were replaced. The clathration ability of the complexes was attributed to shallow pockets located between dibenzoylmethanate and pyridyl fragments. In the observed crystal packing, part of these pockets is filled with fragments from neighboring complexes, while the residual pockets take part in constructing a cavity space for guest species.

This study introduces, for the first time, a new bis-chelate ligand, (1-naphthoyl)benzoylmethanate (NBM) to give complexes analogous to complexes with DBM. The NBM complexes (Scheme 2) may be considered as derivatives of metal DBMs with modification in the DBM chelating ligand. The difference is in an additional phenylene ring (cf. Schemes 1 and 2). The initial concept of using the larger NBM ligand was to enhance the clathration ability of the parent metal DBMs by enlarging the size of the pockets around the molecule. However, the introduction of the NBM ligand resulted in disappearance, or a notable decrease, of the clathration ability of the complexes. This situation seemed interesting as it could shed light on which part of the parent metal DBM complexes is responsible for host properties. To answer this question and to elucidate the properties and crystal structure of the new complexes, the present study was undertaken.

Experimental

Preparations

3-Anilino-1-(1-naphthyl)-3-phenylpropen-2-on-1. A mixture of 1-(1-naphthyl)-3-phenylpropin-2-on-1 (12.6 g, 0.05 mol; synthesis was reported earlier[90]), aniline (4.7 g, 0.05 mol) and amyl alcohol (20 mL) was refluxed for 8 h. After cooling and adding pentane (10 mL), a precipitated product was separated and recrystallized from ethanol/octane (1:1 v/v). Yellow sheets. Yield 12 g (69%). M.p. 164-165 °C. Anal.: found (%): C, 85.97; H, 5.60; N, 4.06. Calcd for $C_{25}H_{19}NO$ (%): C, 85.93; H, 5.48; N, 4.01.

(1-Naphthoyl)benzoylmethane (HNBM). This 1,3-diketone was prepared by hydrolysis of the above amine using general method described earlier.[91] A mixture of 3-anilino-1-(1-naphthyl)-3-phenylpropen-2-on-1 (5 g, 14.3 mmol), methanol (40 mL) and aqueous HCl (1:1 v/v; 5 mL) was stirred for 2 h at 65 °C. Organic phase was extracted with benzene (total volume of 200 mL), rinsed with water and dried with anhydrous sodium sulfate. After removing benzene (rotor evaporator), a final product (4 g) was obtained as a viscous yellow liquid (the liquid remained as such for 3 years and solidified (crystallized) on fourth year). ^1H NMR (CDCl$_3$) (δ, ppm): 8.57 (1H; arom.), 8.02 (3H; arom.), 7.94 (1H, arom.), 7.87 (1H, arom.), 7.65–7.50 (6H, arom.), 6.75 (s, 1H; enol C-H). An extra single peak at 7.40 ppm indicated the presence of benzene (less than 10%). The product was not purified and was used as such in further preparations

[Ni(NBM)$_2$]. The complex was prepared by the same method used for nickel(II) DBM.[71] Ni(NO$_3$)$_2$*6H$_2$O (1.45 g, 5 mmol) was dissolved in a warm mixture of aqueous ammonium hydroxide (30 mL) and acetone (20 mL). HNBM (2.74 g, 10 mmol) was dissolved in warm acetone (80 mL). The solutions were added together and stirred vigorously. With a short delay (~2 min) a light green product started to precipitate from the green solution. The mixture was stirred with heating for 30 min and then, after adding hot water (100 mL), for one more hour till it completely cooled down. The precipitate was separated, washed with 50% aqueous ethanol and air-dried. The product, presumably [Ni(NH$_3$)$_2$(NBM)$_2$], was allowed to decompose at 130 °C till constant weight was achieved (~3 h), the observed weight loss of 5.28% corresponded to calculated mass percentage of 5.33% for ammonia in the diammino-complex. The final [Ni(NBM)$_2$] was a yellowish-green powder. Yield: 2.62 g (87%).

trans-[MA$_2$(DBM)$_2$]

Scheme 1.

trans-[MA$_2$(NBM)$_2$]

Scheme 2.

[NiPy$_2$(NBM)$_2$] and [Ni(4-MePy)$_2$(NBM)$_2$]. [Ni(NBM)$_2$] (0.605 g, 1 mmol) was dissolved in a warm solution of pyridine (0.24 g, 3 mmol) or 4-methylpyridine (0.28 g, 3 mmol) in chloroform (5 mL). Into this green transparent solution warm anhydrous ethanol was added, stirred, and left to cool. Green (Py-complex) or green-brown (4-MePy-complex) fine-crystalline precipitate was separated and air-dried. Yield: 0.69 g (90%) for Py-complex and 0.72 g (90%) for 4-MePy-complex. Crystals suitable for single-crystal XRD analysis were obtained from nitromethane (Py-complex) and ethylacetate (4-MePy-complex). Experimental powder patterns of the bulk products corresponded to patterns calculated from single-crystal XRD analysis.

[Ni(4-PhPy)$_2$(NBM)$_2$] and its inclusion compounds. [Ni(NBM)$_2$] (0.605 g, 1 mmol) was equilibrated in a warm solution of 4-phenylpyridine (0.47 g, 3 mmol) in chloroform (5 mL) for 1 h. A green powder precipitate was separated, rinsed with ethanol and air-dried. TGA of this product showed weight loss of 20.3% (30–140 °C) followed by a plateau (140–180 °C) and further weight loss (> 180 °C) with melting and irreversible decomposition. The data were interpreted as decomposition of inclusion compound with chloroform (1:2), [Ni(4-PhPy)$_2$(NBM)$_2$]*2(CHCl$_3$) (calculated chloroform content: 20.7%). Therefore, the solvent-free complex [Ni(4-PhPy)$_2$(NBM)$_2$] was prepared by decomposition of the inclusion product in oven (100 °C) until constant weight was achieved (1 h). In an atmosphere of chloroform, benzene, tetrahydrofuran and acetone the complex absorbed ∼2 mol of each solvent, and powder XRD pattern indicated that all four inclusion compounds were isostructural but structurally different from the solvent-free complex. Because of the insolubility of the complex in all applied solvents, no products suitable for single-crystal XRD analysis were obtained.

Methods

Single-crystal XRD analysis

Single-crystal diffraction experiments were performed at −100 °C. A Bruker SMART CCD X-ray diffractometer with graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.7107$) was used to collect the diffraction data. Full spheres were collected using the ω scan mode over the 2θ range of 2–58°. The coverage of the unique sets was over 99%. An empirical absorption correction SADABS[92] was applied. The final unit cell parameters were obtained using the entire data sets. Crystal data and experimental details of the low-temperature experiments are listed in Table 1.

The structures were solved by direct methods followed by differential Fourier synthesis, using the SIR92[93] and SHELXTL[92] packages. The structural refinement was performed on F^2 using all data with positive intensities. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically with thermal factors 1.2 (aromatic) or 1.5 (methyl) times greater than

Table 1. Low-temperature single-crystal XRD analysis: experimental parameters and crystallographic data

Formula	[NiPy$_2$(NBM)$_2$]	[Ni(4-MePy)$_2$(NBM)$_2$]
Gross formula	C$_{48}$H$_{36}$N$_2$NiO$_4$	C$_{50}$H$_{40}$N$_2$NiO$_4$
Formula unit mass	763.5	791.6
Temperature (°C)	−100	−100
Crystal system	Monoclinic	Monoclinic
Space group	P2$_1$ (#4)	P2$_1$/n (#14)
Unit cell dimensions:		
a (Å)	7.327(1)	7.732(1)
b (Å)	27.724(3)	21.730(3)
c (Å)	9.361(2)	12.171(2)
β (deg.)	96.34(1)	94.78(1)
V (Å^3)	1889.9(5)	2037.8(5)
Z	2	2
Calculated density (g cm^{-3})	1.342	1.290
Crystal color and habit	Green sheet	Brown prism
Crystal dimensions (mm)	0.5 0.3 0.02	0.5 0.2 0.2
Reflections collected	22666	23864
Unique (I > 2σ(I))	15691	4438
Refined parameters	497	260
Goodness of fit on F^2	0.947	1.028
R1 (data with I > 2σ(I))	0.071	0.032
wR2 (data with I > 2σ(I))	0.169	0.075
Max residual peak (e Å^{-3})	+ 0.75	+ 0.26
Absolute structure ('Flack') parameter	0.51(1)	
CCDC deposition number	194608	194610

those for the adjacent carbon atoms. Large residual extrema on the final difference map for the [NiPy$_2$(NBM)$_2$] structure were located about nickel atom; they apparently arose from inadequate absorption corrections as the crystal sample was a very thin sheet.

For calculating powder diffractograms, the room temperature unit cell dimensions were also measured.[94] To accomplish this, the same crystal samples as for the low-temperature experiment were used; several dozen reflections were found randomly using 90 frame ω scans, 0.3° wide, starting at three different φ positions.

Powder XRD analysis

Phase analyses were performed with a Rigaku Geigerflex diffractometer (Co$K\alpha$ radiation, $\lambda = 1.7902$ Å) in a 5–30° 2θ range, with a 0.02° step scan with 1 s per step. Inclusion compounds with volatile guest were recorded in an atmosphere of correspondent guest solvent. For theoretical powder diffractograms, the low-temperature single-crystal analysis results were used with unit cell dimensions determined at room temperature.[94]

Thermogravimetric analysis

A 2050 thermogravimetric analyzer (TA Instruments) was utilized in a linear heating mode (5° per min) under a nitrogen purge.

NMR spectroscopy

A ^{1}H NMR spectrum was obtained for a solution in deuterated chloroform with a Bruker DRX-400 instrument. Integration of bands was performed with the XWIN-NMR 2.0 program package.

Results and discussion

Clathration ability of isolated complexes

Three new complexes were isolated in this work: [NiPy$_2$(NBM)$_2$], [Ni(4-MePy)$_2$(NBM)$_2$] and [Ni(4-PhPy)$_2$(NBM)$_2$]. They differ in the size of the axial pyridine ligand. The complexes with unsubstituted pyridine and 4-methylpyridine were isolated as solvent-free forms upon crystallization from benzene, chlorobenzene, chloroform, tetrahydrofuran, nitromethane, acetone and ethylacetate. They also did not change upon contact with pentane, cyclohexane and ethanol. From these observations we conclude that the complexes do not possess the versatile inclusion ability inherent in previously studied metal DBMs.[71–76] The complex with 4-phenylpyridine was isolated both as a solvent-free form and as 1:2 inclusion compounds with chloroform, benzene, tetrahydrofuran and acetone, the four inclusion compounds being isostructural.

The complexes with pyridine and 4-methylpyridine were studied by single-crystal XRD method as described below.
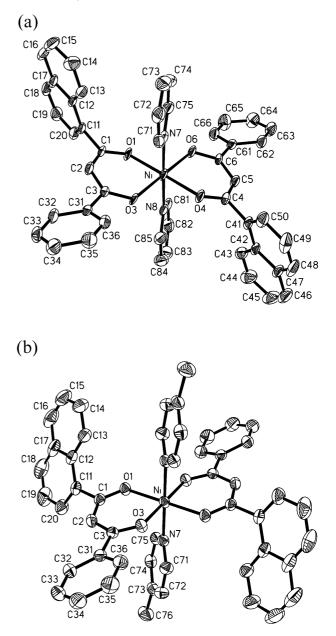
Molecular structure of [NiPy$_2$(NBM)$_2$] and [Ni(4-MePy)$_2$(NBM)$_2$]

The [NiPy$_2$(NBM)$_2$] complex crystallizes in a monoclinic system, sp. gr. P2$_1$, with two formula units per unit cell.[95] One whole complex molecule forms the asymmetric unit of the structure. The molecule is pseudo-centrosymmetric (Fig. 1a). The nickel atom is chelated with two NBM anionic ligands in the equatorial plane. Two pyridine ligands coordinated axially complete coordination environment of the central atom to *trans*-octahedral. The Ni–O bonds range within 2.02–2.05 Å, and Ni–N bonds are slightly longer at 2.11 Å. Coordination angles deviate from ideal by not more than 3°. Chelating OCCCO semi-rings are planar within 0.03 Å and Ni atom deviates from their planes by 0.45 Å.

With respect to the equatorial plane of the complex, NiO$_4$, naphthyl fragments are close to a perpendicular position, with dihedral angles of 83.2° (C11) and 82.4° (C41). Phenyl fragments are closer to a coplanar position with the equatorial plane, with dihedral angles of 17.8° (C31) and 15.0° (C61). Pyridine rings are close to a plane dividing the bis-chelate fragment into two NBMs, deviating from the plane by 2.2° (N7) and 4.0° (N8).

The [Ni(4-MePy)$_2$(NBM)$_2$] complex also crystallizes in a monoclinic system, sp. gr. P2$_1$/n, with two formula units per unit cell. The asymmetric unit is formed by half a complex, and the whole molecule is completed across the inversion center located on the nickel atom (Fig. 1b). Molecular structure is very similar to that for Py-complex. The Ni–O bonds range within 2.01–2.03 Å, and the Ni–N bond is longer at 2.09 Å. Coordination angles deviate from ideal by less than 2°. Chelating OCCCO semi-rings are planar within 0.02 Å and Ni atoms deviate from their planes by 0.30 Å.

Again, the naphthyl fragment is closer to a perpendicular positioning with respect to the equatorial plane,

Figure 1. The molecular structure of the [NiPy$_2$(NBM)$_2$] (a) and [Ni(4-MePy)$_2$(NBM)$_2$] (b) complexes with atom numbering. H-atoms are omitted; ellipsoids are drawn at the 50% probability level.

with a dihedral angle of 69.7°, while the phenyl is closer to a coplanar positioning deviating from the equatorial plane by 23.8°. The pyridyl ring of the 4-MePy ligand is close to a plane dividing the bis–chelate fragment into two NBMs, deviating from the plane by 3.5°.

Crystal packing in studied complexes

In both structures, crystal packing is governed by van der Waals interactions of the neutral complex molecules. The molecules are aggregated in parallel chains stretching along the a direction (Fig. 2). The packing along the chain is very effective. The distances between nickel centers of the chain neighbors match the a translation, 7.33 and 7.73 Å for the pyridine and 4-methylpyridine complexes, respectively; the distances between nickel centers from
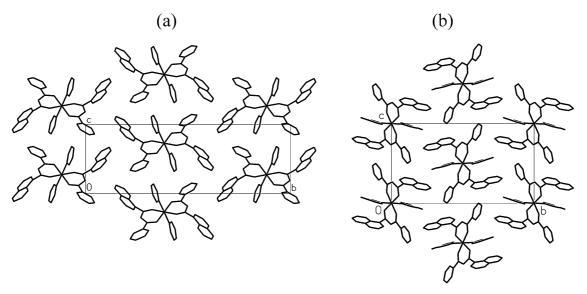
(a)   (b)

Figure 2. Crystal packing in the [NiPy$_2$(NBM)$_2$] (a) and [Ni(4-MePy)$_2$(NBM)$_2$] (b) complexes, viewed along a.

different chains are 9.36 and 12.17 Å. Equatorial and other planes of neighboring molecules are parallel. The angles between the equatorial plane and the chain direction are 38.3 and 40.8° for the pyridine and 4-methylpyridine complexes, respectively. Figure 3 illustrates the packing of the [Ni(4-MePy)$_2$(NBM)$_2$] molecules in the chain. The molecules interdigitate in such a way that 4-methylpyridine ligands approach the equatorial planes of adjacent molecules between two NBMs. Two pockets of each molecule are filled with naphthyl fragments from its own NBMs while the other two are partially filled with phenyl fragments of two adjacent molecules.

In the [NiPy$_2$(NBM)$_2$] structure the chains are closer to each other in the c direction (Fig. 2a) and the molecules from different chains lie on the same level along a. The molecules partially insert their pyridine fragments into
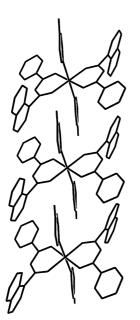
the pockets of neighbors in the c direction. In the [Ni(4-MePy)$_2$(NBM)$_2$] structure the chain going through the center of the unit cell is shifted by half and a translation with respect to the chain going through the origin.

Further analysis of the structures indicates other weak interactions that may play an important role in stabilizing observed mode of packing. The molecules contain several aromatic systems located on the periphery. A geometry favorable for π–π interaction[96] was found in the 4-methylpyridine complex. The distance between centers of naphthyl phenylene (containing C11) and a pyridine ring belonging to adjacent molecule is 4.07 Å, with the angles between the line connecting the centers and planes of the aromatic fragments being 10.1 and 35.3°, respectively. Also, in many cases a geometry for π-hydrogen bonding[97] was observed. In the absence of strong hydrogen bond acceptors,[98] hydrogen bonding to the π-system of aromatic rings can play an important role in the packing of crystals. Selected geometrical parameters of such possible interactions are listed in Table 2. Some distances between hydrogen atoms and centers of aromatic rings, down to as short as 2.6 Å, imply that significant interaction may occur.

General conclusions

As it was expected, the basic molecular structure of metal NBMs studied in this work is similar to the structure usually observed for metal DBMs.[71–77] Some conformational features are also similar: Pyridyl rings are close to a plane dividing the bis–chelate fragment into two chelated rings. Phenyl rings show a tendency to be coplanar with the equatorial plane of the complex. The tendency was unequivocally observed for all metal DBM hosts previously studied[71–76] and can be understood in terms of the interaction between aromatic systems of phenyl and metal-chelated fragments. These conformational features result in shallow pockets which build up a cavity space in metal DBMs. Figure 4a illustrates a typical location of guest molecules in two of four pockets on a metal DBM

Figure 3. Molecules of [Ni(4-MePy)$_2$(NBM)$_2$] interdigitating along the a direction.

Table 2. Possible π-hydrogen bonding in the studied structures: selected parameters of the X...H–C contacts (X represents a center of an aromatic system)

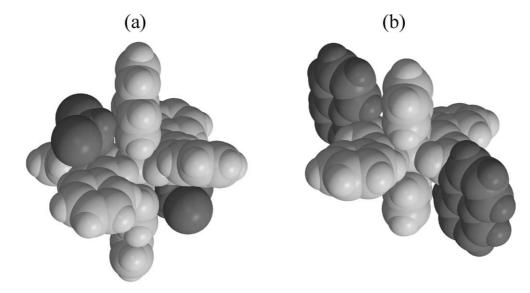| Compound	Atoms of the aromatic system	C–H (neighboring molecule)	X...H distance (Å)	X...H–C angle (deg.)
[NiPy$_2$(NBM)$_2$]	C11, C12, C17-C20 (naphthyl)	C45-H45 (naphthyl)	3.04	129.9
	C12-C17 (naphthyl)	C34-H34 (phenyl)	2.81	146.6
	C41, C42, C47-C50 (naphthyl)	C16-H16 (naphthyl)	2.64	156.1
	C42-C47 (naphthyl)	C64-H64 (phenyl)	2.81	144.7
	C31-C36 (phenyl)	C20-H20 (naphthyl)	2.95	146.4
	C61-C66 (phenyl)	C50-H50 (naphthyl)	2.83	145.1
	N7, C71-C75 (pyridine)	C66-H66 (phenyl)	3.06	134.7
	N8, C81-C85 (pyridine)	C36-H36 (phenyl)	3.11	130.1
[Ni(4-MePy)$_2$(NBM)$_2$]	C11, C12, C17-C20 (naphthyl)	C34-H34 (phenyl)	2.93	132.4
	C12-C17 (naphthyl)	C72-H72 (pyridyl)	3.07	137.7

Figure 4. Filling of the pockets with guest molecules in [Ni(4-vinylpyridine)$_2$(DBM)$_2$]*2(CH$_2$Cl$_2$)[73] (a) and filling of the pockets with naphthyl fragments in [NiPy$_2$(NBM)$_2$] (b). All molecules are shown in their van der Waals size; guest molecules and naphthyl fragments are drawn darker for clarity.

molecule (the other two are filled with fragments of adjacent host complexes). Introduction of naphthyl instead of some phenyls in the chelating ligand could enlarge the size of the pocket, thereby enhancing clathration ability of the complex.

Nevertheless, naphthyl ligands rotate almost perpendicular to the equatorial plane to fill the pocket and to provide effective packing without help of a guest. This conformational mode is observed in both structures of this work and is likely to be the reason why the NBM complexes do not entrap guest solvents. Crystal structures result from many interactions, both intra- and intermolecular. In this particular case, destabilization due to perpendicularity between chelate and naphthyl aromatic systems seems to be compensated by favorable non-valent interactions, such as van der Waals contacts, which can result in more effective packing.[38,39]

Figure 4b illustrates how the naphthyl fragment of the molecule occupies the space which in metal DBMs is usually available for guests. The molecule adopts a conformation that eliminates potential empty space in the crystal packing. In the case of metal DBM host the molecule is not able to do this effectively and thus requires a guest component to provide effective packing.

It should be noted that a similar observation of a versatile Hoffmann host complex losing clathration ability stepwise upon certain successive modifications has been discussed before.[48,99] The present study elucidates that planar shape of metal bis-chelate unit is a key part of metal DBM host and distortion of its geometry may result in losing clathration ability. In contrast, a modification of the axial ligand with a wide range of substituted pyridines did not have this effect,[71–76] apparently because the substituents in pyridine are unable to fill the pockets due to steric limitations.

Remarkably, the [Ni(4-PhPy)$_2$(NBM)$_2$] complex does display clathration ability with a series of studied guest solvents. Although the structure of the inclusion compounds remains unknown, the difference between this 4-phenylpyridine host and the two other complexes of this study is quite understandable. 4-Phenylpyridine significantly increases the size of pockets on the molecule, and the naphthyl fragment is not large enough to fill the pocket effectively. The inclusion of guest components becomes favorable again and clathrates with most expected host:guest ratio of 1:2 form. The [Ni(4-PhPy)$_2$(NBM)$_2$] complex represents the first successful modification of the metal DBM host type accomplished by changing the chelating ligand.

Supporting information

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC deposition numbers are given in Table 1 and ref 94).

Acknowledgements

References and notes

1. Sauvage, J.-P., Hosseini, M. W., Eds. *Comprehensive Supramolecular Chemistry; Templating, Self-assembly, and Self-organization,* Vol. 9. Pergamon: Oxford, 1996.

2. Dinolfo, P. H.; Hupp, J. T. *Chem. Mater.* **2001**, *6*, 3113–3125.

3. Stoddart, J. F.; Tseng, H. R. *PNAS (Proceedings of the National Academy of Sciences of the U.S.A.)* **2002**, *99*, 4797–4800.

4. Vögtle, F., Ed. *Comprehensive Supramolecular Chemistry; Molecular Recognition: Receptors for Molecular Guests,* Vol. 2. Pergamon: Oxford, 1996.

5. Goldberg, I. *Chem. Eur. J.* **2000**, *6*, 3863–3870.

6. Kim, I.; Kwak, B.; Lah, M. S. *Inorg. Chim. Acta* **2001**, *317*, 12–20.

7. Nassimbeni, L. R.; Kilkenny, M. L. *J. Chem. Soc., Dalton Trans* **2001**, 1172–1175.

8. Gerasko, O. A.; Samsonenko, D. G.; Fedin, V. P. *Uspekhi Khimii (Russian Chemical Reviews)* **2002**, *71*, 840–861 (in Russian).

9. Potrzebowski, M. J.; Grossmann, G.; Ganicz, K.; Olejniczak, S.; Ciesielski, W.; Koziol, A. E.; Wawrzycka, I.; Bujacz, G.; Haeberlen, U.; Schmitt, H. *Chem. Eur. J.* **2002**, *8*, 2691–2699.

10. Campbell, K.; Kuehl, C. J.; Ferguson, M. J.; Stang, P. J.; Tykwinski, R. R. *J. Am. Chem. Soc.* **2002**, *124*, 7266–7267.

11. Ung, A. T.; Gizachew, D.; Bishop, R.; Scudder, M. L.; Dance, I. G.; Craig, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8745–8756.

12. Kitagawa, S.; Kondo, M. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739–1753.

13. Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148–1150.

14. Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2082–2084.

15. Sozzani, P.; Comotti, A.; Simonutti, R.; Meersmann, T.; Logan, J. W.; Pines, A. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 2695–2698.

16. Eddaoudi, M.; Li, H.; Yaghi, O. M. *J. Am. Chem. Soc.* **2000**, *122*, 1391–1397.

17. Kristiansson, O.; Tergenius, L.-E. *J. Chem. Soc., Dalton Trans.* **2001**, 1415–1420.

18. Lu, J. Y.; Babb, A. M. *Chem. Commun.* **2002**, 1340–1341.

19. Noro, S.; Kitaura, R.; Kondo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568–2583.

20. Seki, K. *Langmuir* **2002**, *18*, 2441–2443.

21. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469–472.

22. Soldatov, D. V.; Grachev, E. V.; Ripmeester, J. A. *Cryst. Growth Des.* **2002**, *2*, 401–408.

23. Tanaka, Y.; Kobuke, Y.; Sokabe, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 693–694.

24. Reinbold, J.; Cammann, K.; Weber, E.; Hens, T.; Reutel, C. *J. Prakt. Chem.* **1999**, *341*, 252–263.

25. Kondo, M.; Shimamura, M.; Noro, S.; Minakoshi, S.; Asami, A.; Seki, K.; Kitagawa, S. *Chem. Mater.* **2000**, *12*, 1288–1299.

26. Min, K. S.; Suh, M. P. *J. Am. Chem. Soc.* **2000**, *122*, 6834–6840.

27. Tabares, L. C.; Navarro, J. A. R.; Salas, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 383–387.

28. Fletcher, A. J.; Cassen, E. J.; Prior, T. J.; Rosseinsky, M. J.; Kepert, C. J.; Thomas, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 10001–10011.

29. Seki, K. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1968–1971.

30. Nossov, A. V.; Soldatov, D. V.; Ripmeester, J. A. *J. Am. Chem. Soc.* **2001**, *123*, 3563–3568.

31. Soldatov, D. V.; Ripmeester, J. A. *Stud. Surf. Sci. Catal.* **2002**, *141*, 353–362.

32. Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762–1765.

33. Moulton, B.; Zaworotko, M. J. *Curr. Opin. Solid State Sci.* **2002**, *6*, 117–123.

34. Dalrymple, S. A.; Shimizu, G. K. H. *Chem. Eur. J.* **2002**, *8*, 3010–3015.

35. Uemura, K.; Kitagawa, S.; Kondo, M.; Fukui, K.; Kitaura, R.; Chang, H.-C.; Mizutani, T. *Chem. Eur. J.* **2002**, *8*, 3586–3600.

36. Kitaura, R.; Fujimoto, K.; Noro, S.; Kondo, M.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 133–135.

37. Zaman, M. B.; Udachin, K.; Akhtaruzzaman, M.; Yamashita, Y.; Ripmeester, J. A. *Chem. Commun.* **2002**, 2322–2323.

38. 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.).

39. Brock, C. P.; Dunitz, J. D. *Chem. Mater.* **1994**, *6*, 1118–1127.

40. Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309–314.

41. Wolff, J. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2195–2197.

42. Fayos, J.; Cano, F. H. *Cryst. Growth Des.* **2002**, *2*, 591–599.

43. Abourahma, H.; Moulton, B.; Kravtsov, V.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 9990–9991.

44. Dyadin, Yu.A.; Kislykh, N. V. *Mendeleev Commun.* **1991**, 134–136.

45. Dyadin, Yu.A.; Kislykh, N. V. *Russ. J. Phys. Chem.* **1992**, *66* (1), 60–65.

46. Lipkowski, J.; Soldatov, D. V.; Kislykh, N. V.; Pervukhina, N. V.; Dyadin, Yu.A. *J. Inclusion Phenom.* **1995**, *23*, 23–33.

47. Dyadin, Yu.A. *Russ. J. Coord. Chem.* **1996**, *22*, 402–404.

48. Dyadin, Yu.A.; Soldatov, D. V.; Logvinenko, V. A.; Lipkowski, J. *J. Coord. Chem.* **1996**, *37*, 63–75.

49. Lipkowski, J.; Kislykh, N. V.; Dyadin, Yu.A.; Sheludyakova, L. A. *J. Struct. Chem.* **1999**, *40*, 772–780.

50. Ukraintseva, E. A.; Soldatov, D. V.; Dyadin, Yu.A.; Logvinenko, V. A.; Grachev, E. V. *Mendeleev Commun.* **1999**, 123–125.

51. Soldatov, D. V.; Ukraintseva, E. A.; Logvinenko, V. A.; Dyadin, Yu.A.; Grachev, E. V.; Manakov, A.Yu. *Supramol. Chem.* **2000**, *12*, 237–246.

52. Nassimbeni, L. R.; Niven, M. L.; Zemke, K. J. *Acta Crystallogr.* **1986**, *B42*, 453–461.

53. Adams, R. P.; Allen, H. C.; Rychlewska, U.; Hodgson, D. J. *Inorg. Chim. Acta* **1986**, *119*, 67–74.

54. Guilard, R.; Siri, O.; Tabard, A.; Broeker, G.; Richard,

P.; Nurco, D. J.; Smith, K. M. *J. Chem. Soc., Dalton Trans.* **1997**, 3459–3463.

55. Cariati, E.; Bu, X.; Ford, P. C. *Chem. Mater.* **2000**, *12*, 3385–3391.

56. Yang, C. T.; Moubaraki, B.; Murray, K. S.; Ranford, J. D.; Vittal, J. J. *Inorg. Chem.* **2001**, *40*, 5934–5941.

57. Soldatov, D. V.; Henegouwen, A. T.; Enright, G. D.; Ratcliffe, C. I.; Ripmeester, J. A. *Inorg. Chem.* **2001**, *40*, 1626–1636.

58. Mäkinen, S. K.; Melcer, N. J.; Parvez, M.; Shimizu, G. K. H. *Chem. Eur. J.* **2001**, *7*, 5176–5182.

59. Gerbeleu, N. V.; Simonov, Yu.A.; Arion, V. B.; Leovac, V. M.; Turta, K. I.; Indrichan, K. M.; Gradinaru, D. I.; Zavodnik, V. E.; Malinovskii, T. I. *Inorg. Chem.* **1992**, *31*, 3264–3268.

60. Burdukov, A. B.; Ovcharenko, V. I.; Reznikov, V. A.; Ikorskii, V. N.; Shvedenkov, Y. G.; Pervukhina, N. V. *Cryst. Engineering* **2000**, *3*, 41–61.

61. Atwood, J. L.; Bott, S. G.; Coleman, A. W.; Robinson, K. D.; Whetstone, S. B.; Means, C. M. *J. Am. Chem. Soc.* **1987**, *109*, 8100–8101.

62. Atwood, J. L.; Junk, P. C. *Chem. Commun.* **1995**, 1551–1552.

63. Shimizu, G. K. H.; Enright, G. D.; Rego, G. S.; Ripmeester, J. A. *Can. J. Chem.* **1999**, *77*, 313–318.

64. Atwood, J. L.; Barbour, L. J.; Jerga, A. *J. Am. Chem. Soc.* **2002**, *124*, 2122–2123.

65. Zorkii, P. M.; Razumaeva, A. E. *J. Struct. Chem.* **1979**, *20* (3), 390–393.

66. Nassimbeni, L. R.; Niven, M. L.; Taylor, M. W. *Inorg. Chim. Acta* **1987**, 67–73.

67. Nassimbeni, L. R.; Niven, M. L.; Taylor, M. W. *J. Chem. Soc., Dalton Trans.* **1989**, 119–125.

68. Soldatov, D. V.; Grachev, E. V.; Lipkowski, J. *J. Struct. Chem.* **1996**, *37*, 658–665.

69. Barbour, L. J.; Atwood, J. L. *Chem. Commun.* **2001**, 2020–2021.

70. Nakano, K.; Sada, K.; Kurosumi, Y.; Miyata, M. *Chem. Eur. J.* **2001**, *7*, 209–220.

71. Soldatov, D. V.; Enright, G. D.; Ripmeester, J. A. *Supramol. Chem.* **1999**, *11*, 35–47.

72. Soldatov, D. V.; Ripmeester, J. A. *Supramol. Chem.* **2001**, *12*, 357–368.

73. Soldatov, D. V.; Ripmeester, J. A. *Chem. Eur. J.* **2001**, *7*, 2979–2994.

74. Soldatov, D. V.; Enright, G. D.; Ratcliffe, C. I.; Henegouwen, A. T.; Ripmeester, J. A. *Chem. Mater.* **2001**, *13*, 4322–4334.

75. Soldatov, D. V.; Enright, G. D.; Ripmeester, J. A. *Chem. Mater.* **2002**, *14*, 348–356.

76. Soldatov, D. V., Tinnemans, P., Enright, G. D., Ratcliffe, C. I., Diamente, P. R., Ripmeester, J. A. (submitted for publication).

77. For synthesis, structure and properties of other metal dibenzoylmethanates see, for example, refs.[78–89]

78. Shugam, E. A.; Shkol'nikova, L. M.; Knyazeva, A. N. *Zh. Strukt. Khim.* **1968**, *9* (2), 222–227 (in Russian).

79. Knyazeva, A. N.; Shugam, E. A.; Shkol'nikova, L. M. *Zh. Strukt. Khim.* **1969**, *10* (1), 83–87 (in Russian).

80. Uchida, T.; Kozawa, K.; Obara, H. *Acta Crystallogr.* **1977**, *B33*, 3227–3229.

81. Cornwell, A. B.; Harrison, P. G. *Acta Crystallogr.* **1979**, *B35*, 1694–1696.

82. Kasumov, V. T.; Guseinova, M. K.; Medzhidov, A. A.; Mamedov, Kh.S. *Zh. Strukt. Khim.* **1981**, *22* (1), 90–97 (in Russian).

83. Baidina, I. A.; Stabnikov, P. A.; Igumenov, I. K.; Borisov, S. V. *Koord. Khim.* **1986**, *12* (2), 258–265 (in Russian).

84. Kradenov, K. V.; Kolesov, B. A.; Igumenov, I. K. *Koord. Khim.* **1987**, *13* (9), 1178–1187 (in Russian).

85. Logvinenko, V. A.; Fedotova, N. E.; Igumenov, I. K.; Gavrilova, G. V. *J. Therm. Anal.* **1988**, *34*, 259–268.

86. Zaitseva, E. G.; Baidina, I. A.; Stabnikov, P. A.; Borisov, S. V.; Igumenov, I. K. *Zh. Strukt. Khim.* **1990**, *31* (2), 184–189 (in Russian).

87. Kostyuk, N. N.; Dik, T. A.; Umreyko, D. S. *Zh. Prikl. Spektrosk.* **1993**, *58* (1–2), 178–183 (in Russian).

88. Müller, H.; Seidel, W.; Görls, H. *Z. Anorg. Allg. Chem.* **1997**, *623*, 155–158 (in German).

89. Aromi, G.; Knapp, M. J.; Claude, J. P.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1999**, *121*, 5489–5499.

90. Zanina, A. S.; Shergina, S. I.; Sokolov, I. E.; Kotlyarevskii, I. L. *Russ. Chem. Bull.* **1990**, *39* (11), 2307–2311 (*Izv. Akad. Nauk, Ser. Khim.* **1990**, *(11)*, 2551–2555, in Russian).

91. Zanina, A. S.; Shergina, S. I.; Sokolov, I. E.; Myasnikova, R. N. *Russ. Chem. Bull.* **1995**, *44* (4), 689–694 (*Izv. Akad. Nauk, Ser. Khim.* **1995**, *(4)*, 710–714, in Russian).

92. 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.

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

94. At room temperature: [NiPy$_2$(NBM)$_2$] is monoclinic, $a = 7.400(3)$, $b = 27.82(2)$, $c = 9.464(4)$ Å, $\beta = 97.10(4)°$, $V = 1933(2)$ Å^3, $D_{calc} = 1.311$ g cm^{-1} (for $Z = 2$), calculated from 79 reflections, CCDC deposition number: 194609. [Ni(4-MePy)$_2$(NBM)$_2$] is monoclinic, $a = 7.832(8)$, $b = 21.86(4)$, $c = 12.296(9)$ Å, $\beta = 95.66(5)°$, $V = 2095(5)$ Å^3, $D_{calc} = 1.255$ g cm^{-1} (for $Z = 2$), calculated from 100 reflections, CCDC deposition number: 194611.

95. The chiral space group was verified using a symmetry-checking program (Spek, A. L. *PLATON, A Multiple Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2001).

96. Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.

97. Subramanian, S.; Zaworotko, M. J. *Coord. Chem. Rev.* **1994**, *137*, 357–401.

98. Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120–126.

99. Iwamoto, T.; Nishikiori, S.; Dyadin, Yu.A.; Soldatov, D. V. *J. Struct. Chem.* **1999**, *40*, 750–756.