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Modified Metal Dibenzoylmethanates and their Clathrates. Part I. Clathration Ability of dipyridinebis(dibenzoylmethanato)nickel(II), a Novel Metal-Complex Host [1]

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The title complex, [NiPy$_2$(DBM)$_2$] (DBM = $C_6H_5COCHCOC_6H_5$, dibenzoylmethanate), entraps solvent molecules upon crystallization. Six clathrates of four structural types have been studied by single-crystal X-ray diffraction (guest, host:guest molar ratio, crystal system, space group, formula units per unit cell): (I) carbon tetrachloride, 1:2, orthorhombic, $P2_12_12_1$, Z = 4; (II) pyridine, 1:2, monoclinic, *C2/c*, Z = 8; (III) benzene, 1:1, monoclinic, *C2/c*, Z = 8; (IV) chlorobenzene, 1:1, monoclinic, *C2/c*, Z = 8; (V) chloroform, 1:2, monoclinic, $P2_1/n$, Z = 2; (VI) tetrahydrofuran, 1:2, monoclinic, $P2_1/n$, Z = 2. A non-clathrate form of the complex (VII) was obtained from acetone; it is triclinic, $P\bar{1}$, Z = 1. The compounds I–VII are consistent with van der Waals type of packing. The complex unit is formed by octahedral coordination to nickel of four oxygen and two nitrogen atoms from two chelate DBM and two pyridine molecules, respectively. In all seven compounds the host complex is *trans*-configured. Complexes of similar composition but with Zn (VIII) and Cd (IX) replacing Ni have been also studied for comparison: they are monoclinic, $P2_1$, Z = 2, with a *cis*-configured complex unit, and they do not form inclusion compounds with above guests.

Keywords: Novel host, nickel complex, dibenzoylmethanate

INTRODUCTION

In spite of the desire to design and synthesize novel types of host-guest systems, no dominant design strategy has emerged as a source of new materials. In this work we attempt to construct new molecular metal-complex hosts containing a rigid planar unit formed by coordination to a metal cation of acetylacetonate derivatives. The advantages of such bischelate hosts include their relative chemical and thermal stability as well as their versatility, as there are many possibilities for modification by the introduction of substituents into the chelating ligand or by additional apical coordination to the metal cation. Also, since the building block is neutral, there is no need to incorporate anions into the structure. A few clathrates of tris-acetylacetonate complexes have been reported [2]. However, based on the molecular organization, the title host is more akin to Werner hosts [3] and to porphyrin-based

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complexes [4]. There is also a structural analogy to some complexes of nickel xanthates with amines, as these complexes are also able to include solvent molecules [5].

EXPERIMENTAL SECTION

Preparations

Dipyridine-bis(dibenzoylmethanato)-nickel(II), [NiPy$_2$(DBM)$_2$]

The complex was prepared in three steps (Eqs. 1–3). (1) $Ni(NO_3)_2 * 6H_2O$ (1.45 g; 5 mmol) was dissolved with slight heating in a mixture of acetone (20 mL) and concentrated aqueous ammonia (30 mL). This violet solution was then added to a solution of dibenzoylmethane, H-DBM = $C_6H_5COCH_2COC_6H_5$, (2.24 g; 10 mmol) in acetone (80 mL). This warm green mixture, containing some precipitate, was stirred for 30 min and then for 15 min. more after the addition of excess water (100 mL). Light-green crystalline precipitate was separated, rinsed first with water, then ethanol, and air-dried.

$$Ni(NO_3)_2 * 6H_2O + 2(H - DBM) + 4NH_4OH \xrightarrow{NH_4OH,\ acetone} [Ni(NH_3)_2(DBM)_2] + 2NH_4NO_3 + 10H_2O \quad (1)$$

$$[Ni(NH_3)_2(DBM)_2] \longrightarrow [Ni(DBM)_2] + 2NH_3\uparrow \quad (2)$$

$$[Ni(DBM)_2] + 2Py \longrightarrow [NiPy_2(DBM)_2] \quad (3)$$

(2) This ammonium complex was decomposed for 1 hour at 150°C to give green-yellow bis(dibenzoylmethanato)-nickel(II); a mass loss of 6.4–6.7% corresponds to a value of 6.32% calculated for Eq. (2). (3) The product was dissolved in 0.2 M solution of pyridine in methylene chloride (60 mL; 12 mmol of pyridine). Evaporation, followed by drying of the solid in vacuum gave the final fine pale-green product with a near-quantitative yield. On heating (150°C), the complex loses 24.0% of mass that is consistent with a calculated value of 23.9% for loss of 2 moles of pyridine (Eq. (4)).

$$[NiPy_2(DBM)_2] \xrightarrow{150^\circ} [Ni(DBM)_2] + 2Py\uparrow \quad (4)$$

Crystals of [NiPy$_2$(DBM)$_2$] and its Inclusions

Clathrates of the complex with carbon tetrachloride (**I**), pyridine (**II**), benzene (**III**) and chlorobenzene (**IV**) were prepared by slow evaporation of solutions of the complex in the neat guests; those with chloroform (**V**) and tetrahydrofuran (**VI**), by recrystallization. Very often the bulky products did not have the stoichiometry obtained from X-ray crystallography as they contained some quantity of the non-clathrate phase of the complex (this was revealed in the course of checking several crystals taken randomly from the same batch of product). The pure, non-clathrate form of the complex (**VII**) was prepared by evaporation of its acetone solution. The color of the crystals, depending on their size, varied from green-yellow to dark-green. The shape of the crystals varied from compact blocks to prisms or needles and depended on crystallization conditions.

Dipyridine-bis(dibenzoylmethanato)-zinc(II), [ZnPy$_2$(DBM)$_2$], and -cadmium(II), [CdPy$_2$(DBM)$_2$]

The complexes (**VIII** and **IX**, respectively) were prepared in a similar way as the nickel compound as colorless, fine crystalline products. As was the case with the Ni-complex, these lost 2 moles of pyridine on heating. The complexes did not entrap solvent molecules upon crystallization from solvents which formed clathrates with [NiPy$_2$(DBM)$_2$].

Crystallography

To prevent the compounds from decomposing, and to reduce thermal motion of the molecules, all crystals were taken directly from under their respective mother liquors and frozen to −100°C; all further experiments including the unit cell search and the data collection were performed at this temperature. The experiments were carried on a Siemens SMART CCD diffractometer equipped with graphite-monochromated MoK_α radiation ($\lambda = 0.7107$ Å). The data collected were corrected for Lorentz and polarization effects and an empirical absorption correction (SADABS) was applied. The final unit cell parameters were obtained using all massif. A summary of the crystal data and experimental parameters are given in Table I.

The structures were solved with NRCVAX [6] (compounds **I, III, V, VII, VIII** and **IX**) or the SHELXS-86 [7] (compound **II, IV, VI**) program set, by using direct methods. Structure refinement was performed using SHELXTL [8] with full-matrix least squares on all data with positive intensities. Anisotropic thermal parameters were used for the non-hydrogen atoms. Hydrogen atoms were included in calculated positions as 'riding' on the corresponding carbon atoms and were refined isotropically with thermal factors 1.2 times greater than those for the parent carbon atoms. The largest residual extrema on the final difference map were located about the heavy atoms (Cl, Cd, Ni). Site occupancy factors for the guest molecules were treated as variables but were fixed in the final steps of the structure refinement as no significant deviations from the claimed stoichiometry were revealed.

The range of coordination bonds and angles is given in Table II, the conformational characteristics of the $[NiPy_2(DBM)_2]$ molecule in Table III. Atom numbering is shown in Figures 1 and 7a. Supplementary material deposited comprises all atomic coordinates and thermal parameters, bond distances and angles tables, and structure factor amplitudes.

Cross-sections of the structures were drawn with the program "SECTION" [9] using the atomic coordinates and the Zefirov-Zorkij's system of van der Waals radii [10].

RESULTS AND DISCUSSION

General Features

The main result of our study is that the $[NiPy_2(DBM)_2]$ complex acts as a host component to give a variety of clathrate structures (Tab. I, compounds **I**–**VI**). Four structural types were observed for inclusions with the six guests tested. The inclusion with carbon tetrachloride is orthorhombic while the rest are monoclinic. The triclinic, non-clathrate phase of the complex crystallizes from acetone (compound **VII**). All seven compounds show strictly molecular packing without intermolecular contacts shorter than the sum of the van der Waals radii of the respective atoms. At the same time, factors other than the guest geometry seem to be responsible for the structure of the resulting clathrate, as inclusions with pyridine and benzene are essentially different, whereas inclusions with chloroform and tetrahydrofuran are isostructural.

In contrast to the $[NiPy_2(DBM)_2]$ complex, its Zn- and Cd-analogues do not form inclusions with the guests tested and they crystallize in a monoclinic non-clathrate structure.

Structural Peculiarities of the $[NiPy_2(DBM)_2]$ Molecule

In all compounds studied, the $[NiPy_2(DBM)_2]$ molecule is *trans*-configured A distorted octahedral environment of the nickel cation is formed by the four oxygens of two chelating dibenzoylmethanate fragments located in the equatorial plane and two nitrogens of the two pyridine ligands in axial positions (Fig. 1). The range for the Ni—O distances of 2.01–2.04 Å is shorter than the 2.09–2.12 Å distances for the Ni—N

TABLE I Crystal data and experimental details

	Compound I	II	III
Host component	[Ni(DBM)$_2$Py$_2$]	[Ni(DBM)$_2$Py$_2$]	[Ni(DBM)$_2$Py$_2$]
Guest component	carbon tetrachloride	pyridine	benzene
Host : Guest ratio	1 : 2	1 : 2	1 : 1
Empirical formula	$C_{42}H_{32}Cl_8N_2NiO_4$	$C_{50}H_{42}N_4NiO_4$	$C_{46}H_{38}N_2NiO_4$
Formula unit mass	971.0	821.6	741.5
Crystal habit/sizes, mm	needle/0.1 0.1 0.05	prism/0.5 0.3 0.2	prism/0.5 0.1 0.1
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$ (N 19)	$C2/c$ (N 15)	$C2/c$ (N 15)
Unit cell:	9.436(2)	22.979(2)	21.502(2)
a, Å b, Å	21.309(4)	18.378(2)	13.031(1)
c, Å	21.637(4)	20.763(2)	26.954(3)
α, °	90	90	90
β, °	90	107.94(1)	103.05(1)
γ, °	90	90	90
V, Å^3	4351(2)	8342(1)	7357(1)
Z	4	8	8
$D_{calc.}$, g cm^{-3}	1.482	1.308	1.339
Temperature, °C	−100	−100	−100
μ(MoK$_\alpha$), cm^{-1}	9.81	5.16	5.75
$2\theta_{max}$, °	50	60	60
Data: collected (R_{int})	31902 (0.054)	47370 (0.033)	36627 (0.043)
unique ($I>0$)	7315	10057	9534
unique ($I>2\sigma(I)$)	5682	8134	7074
Refined parameters	528	629	478
R* (data with $I>2\sigma(I)$)	0.060	0.046	0.047
R_w^2** (k;m) ($I>2\sigma(I)$)	0.128 (0.0644 ; 2.92)	0.101 (0.0440 ; 8.10)	0.105 (0.0485 ; 6.62)
Absolute structure par-r	0.00(2)		
Res.density, e Å^{-3}	+0.56/−0.46	+0.36/−0.29	+0.42/−0.45

	IV	V	VI
Host component	[Ni(DBM)$_2$Py$_2$]	[Zn(DBM)$_2$Py$_2$]	[Ni(DBM)$_2$Py$_2$]
Guest component	chlorobenzene	chloroform	tetrahydrofuran
Host : Guest ratio	1 : 1	1 : 2	1 : 2
Empirical formula	$C_{46}H_{37}ClN_2NiO_4$	$C_{42}H_{34}Cl_6N_2NiO_4$	$C_{48}H_{48}N_2NiO_6$
Formula unit mass	775.9	902.1	807.6
Crystal habit/sizes, mm	block/0.2 0.2 0.2	block/0.4 0.3 0.2	block/0.4 0.4 0.4
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$ (N 15)	$P2_1/n$ (N 14)	$P2_1/n$ (N 14)
Unit cell:	21.598(3)	14.998(2)	14.431(2)
a, Å b, Å	13.021(2)	8.763(1)	9.350(1)
c, Å	27.345(3)	16.110(2)	15.411(2)
α, °	90	90	90
β, °	103.18(1)	94.67(1)	92.73(1)
γ, °	90	90	90

V, Å^3	7488(2)	2110.3(5)	2077.0(5)
Z	8	2	2
$D_{calc.}$, g cm^{-3}	1.377	1.420	1.291
Temperature, °C	−100	−100	−100
μ(MoK$_\alpha$), cm^{-1}	6.38	8.82	5.19
$2\theta_{max}$, °	60	60	60
Data: collected (R_{int})	39696 (0.030)	20743 (0.025)	23104 (0.026)
unique (I > 0)	9684	5269	5376
unique (I > 2σ(I))	7173	4818	4629
Refined parameters	580	250	259
R* (data with I > 2σ(I))	0.041	0.037	0.043
R_w^2** (k;m) (I > 2σ(I))	0.104 (0.0585; 3.80)	0.097 (0.0514; 1.03)	0.112 (0.057; 1.17)
Res.density, e Å^{-3}	+0.43/−0.38	+0.56/−0.54	+0.44/−0.33

	VII	VIII	IX
Host component	[Ni(DBM)$_2$Py$_2$]	[Zn(DBM)$_2$Py$_2$]	[Ni(DBM)$_2$Py$_2$]
Guest component	no	no	no
Host : Guest ratio	–	–	–
Empirical formula	$C_{40}H_{32}N_2NiO_4$	$C_{40}H_{32}N_2O_4Zn$	$C_{40}H_{32}CdN_2O_4$
Formula unit mass	663.4	670.1	717.1
Crystal habit/sizes, mm	prism/0.4 0.2 0.1	prism/0.4 0.2 0.2	block/0.2 0.2 0.2
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$(N2)	$P2_1$ (N 4)	$P2_1$ (N 4)
Unit cell:	8.121(1)	10.360(1)	10.699(1)
a, Å b, Å	10.293(1)	9.421(1)	9.383(1)
c, Å	11.387(1)	17.385(2)	17.311(2)
α, °	102.61(1)	90	90
β, °	105.14(1)	102.95(1)	103.44(1)
γ, °	107.82(1)	90	90
V, Å^3	827.4(2)	1653.6(3)	1690.2(3)
Z	1	2	2
$D_{calc.}$, g cm^{-3}	1.331	1.346	1.409
Temperature, °C	−100	−100	−100
μ(MoK$_\alpha$), cm^{-1}	6.31	7.87	6.90
$2\theta_{max}$, °	60	60	60
Data: collected (R_{int})	9682 (0.023)	19361 (0.043)	19922 (0.023)
unique (I > 0)	4235	8471	8613
unique (I > 2σ(I))	3958	7886	8328
Refined parameters	214	423	423
R* (data with I > 2σ(I))	0.035	0.029	0.025
R_w^2** (k;m) (I > 2σ(I))	0.090 (0.0467; 0.36)	0.066 (0.0249; 0.00)	0.061 (0.0289; 0.38)
Absolute structure par-r		0.00(1)	0.00(2)
Res.density, e Å^{-3}	+0.41/−0.32	+0.31/−0.25	+0.55/−0.23

* $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$.

** $R_w^2 = \Sigma[w(F_o^2 - F_c^2)^2] / \sqrt{\Sigma[w(F_o^2)^2]}$; $w = 1/[\sigma^2(F_o^2) + (kP)^2 + mP]$, where $P = (\max(F_o^2) + 2F_c^2)/3$.

TABLE II Geometry of the coordination polyhedra of the [$MPy_2(DBM)_2$] unit in the compounds studied

Compound	I	II	III	IV	V	VI	VII	VIII	IX
M	Ni	Ni	Ni	Ni	Ni	Ni	Ni	Zn	Cd
Guest	CCl_4	Py	C_6H_6	C_6H_5Cl	$CHCl_3$	C_4H_8O	no	no	no
Polyhedron:									
symmetry*	dist.Oh	dist.Oh	dist.Oh	dist.Oh	dist.Oh	dist.Oh	dist.Oh	v.dist.Oh	v.dist.Oh
composition	[O_4N_2]	[O_4N_2]	[O_4N_2]	[O_4N_2]	[O_4N_2]	[O_4N_2]	[O_4N_2]	[O_4N_2]	[O_4N_2]
configuration	*trans*	*trans*	*trans*	*trans*	*trans*	*trans*	*trans*	*cis*	*cis*
Bond lengths (Å):									
M—O (DBM)	2.02-2.04	2.02-2.04	2.02-2.04	2.02-2.04	2.02-2.03	2.03	2.01-2.04	2.06-2.09	2.24-2.26
M—N (Py)	2.09-2.11	2.09-2.10	2.09-2.12	2.09-2.11	2.10	2.10	2.11	2.22-2.23	2.37-2.38
Angles (°) (see Figs. 1 and 7a):									
O1—M—O3	91.8(1)	91.21(5)	89.90(5)	89.39(5)	90.80(4)	91.88(5)	91.00(4)	87.77(4)	81.92(5)
O4—M—O6	91.4(1)	90.97(5)	89.71(5)	89.96(5)				86.86(4)	81.03(5)
O3—M—O4($O1^{\#}$)**	91.6(1)	88.48(5)	92.09(5)	92.47(5)	89.20(4)	88.12(5)	89.00(4)	92.35(5)	95.25(6)
O1—M—O6	85.2(1)	89.36(5)	88.24(5)	88.14(5)				176.13(5)	176.32(6)
O—M—N7	87.8-90.8	88.0-91.3	90.1-92.3	90.0-91.8	88.1-92.0	88.9-9.11	88.4-91.6		
O—M—N8	87.5-92.6	88.3-90.9	88.0-89.9	88.1-89.8					
N7—M—N8($N7^{\#}$)**	178.3(2)	178.11(6)	179.15(6)	179.53(6)	180	180	180	87.65(5)	87.50(6)
O1—M—O4	176.5(1)	178.47(5)						94.26(5)	98.03(6)
O3—M—O6	176.6(2)	178.93(5)						95.90(5)	101.69(6)

* Dist.Oh, distorted octahedron; v.dist.Oh, very distorted octahedron.

** Symmetry operation ($^{\#}$) is due to centrosymmetricity of the unit in compounds V, VI and VII.

TABLE III Conformational features of the *trans*-[$NiPy_2(DBM)_2$] molecule in the compounds studied

Compound	I	II	III	IV	V	VI	VII
Guest	CCl_4	Py	C_6H_6	C_6H_5Cl	$CHCl_3$	C_4H_8O	no
Dihedral angles* (deg.):							
Ring1-Ring2	5.8	9.0	27.5	26.6	(0)	(0)	(0)
Eqt.-Ph1	20.7	16.9	21.8	24.2	− 26.7	− 39.5	55.8
Eqt.-Ph3	40.0	− 41.3	− 17.5	− 14.0	14.0	− 19.5	− 7.3
Eqt.-Ph4	− 20.2	− 20.0	14.3	12.1	(26.7)	(39.5)	(− 55.8)
Eqt.-Ph6	− 10.8	− 41.6	− 21.3	− 20.5	(− 14.0)	(19.5)	(7.3)
α-Py7	84.4	− 87.4	78.4	83.5	79.6	− 88.5	75.7
α-Py8	− 86.0	− 89.0	− 85.5	− 86.3	(− 79.6)	(88.5)	(− 75.7)

* Least-squares planes are designated as follows (see Fig. 1):; Ring1 first chelate ring, (Ni, O1, C1, C2, C3, O3); Ring2 second chelate ring, (Ni, O4, C4, C5, C6, O6); Eqt. equatorial plane, (Ni, O1, O3, O4, O6); Ph1 phenyl ring (C11, C12, C13, C14, C15, C16); Ph3 phenyl ring (C31, C32, C33, C34, C35, C36); Ph4 phenyl ring (C41, C42, C43, C44, C45, C46); Ph6 phenyl ring (C61, C62, C63, C64, C65, C66); α plane (Ni, C2, C5, N7, N8); Py7 pyridine ring (N7, C71, C72, C73, C74, C75); Py8 pyridine ring (N8, C81, C82, C83, C84, C85).

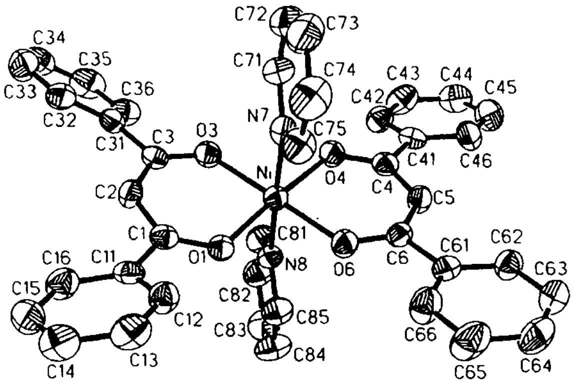

FIGURE 1 Structure of the [$NiPy_2(DBM)_2$] host molecule as is found in the clathrate with carbon tetrachloride (compound I). H-atoms are omitted; ellipsoids are drawn at 50% probability level.

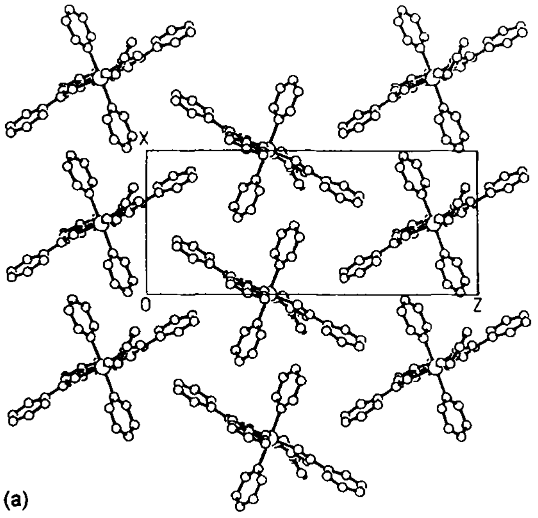

FIGURE 2 Crystal packing in [$NiPy_2(DBM)_2$] * $2CCl_4$ (compound I): (a) host molecules layer at $y \sim 0$; (b) guest molecules layer at $y \sim 0.25$; (c) cross-section of the structure cut with the (040) plane (van der Waals radii; guest species are designated with the black contour).

bond lengths; the coordination angles mainly lie between 88 – 92° (Tab. II).

The complex molecule is either asymmetric (compounds I – IV) or centrosymmetric (compounds V – VII). Qualitatively, the molecule keeps its geometry from compound to compound (Tab. III). The bischelate fragment (Fig. 1) is more or less planar except in inclusions with benzene and chlorobenzene, where the angle between two chelate rings is about 27°. The phenyl rings are turned, adjusting to packing restrictions within the structure, often by about 10 – 25° out of the equatorial plane. Within this restriction different situations are observed concerning the mutual positions of the ring planes, including the sign of the turning angles. The pyridine compound rings are perpendicular to the equatorial plane and located near to the plane which divides the bischelate fragment into two chelate parts.

Thus, the conformational nature of the molecule is not very flexible except for the peripheral phenyl rings that are capable of turning without significant steric barriers. The molecule has four holes, or shallow pockets, each located between

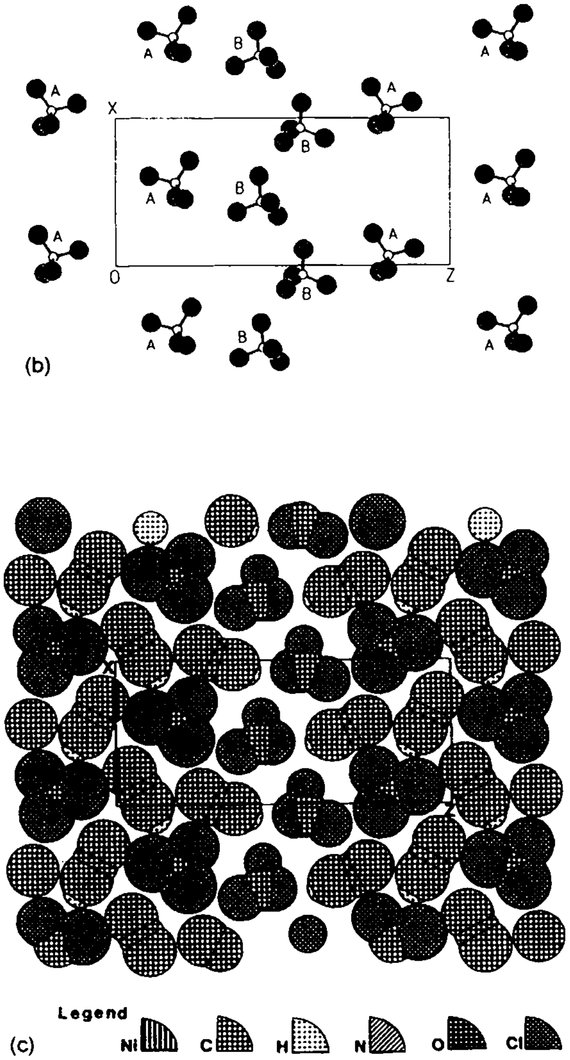

FIGURE 2 (Continued).

the pyridine and dibenzoylmethanate fragments. The holes have a tendency to contain phenyl and pyridine fragments of neighboring molecules. In three of four clathrate types (compounds **I**, **II**, **V** and **VI**) such hole-filling results in rather dense-packed host layers with the remaining phenyl moieties (two from each molecule) sticking out of the layer. Alternatively, although one hole is too shallow, two neighboring host units are able to form a cavity suitable for accommodating one guest molecule (see Fig. 4a).

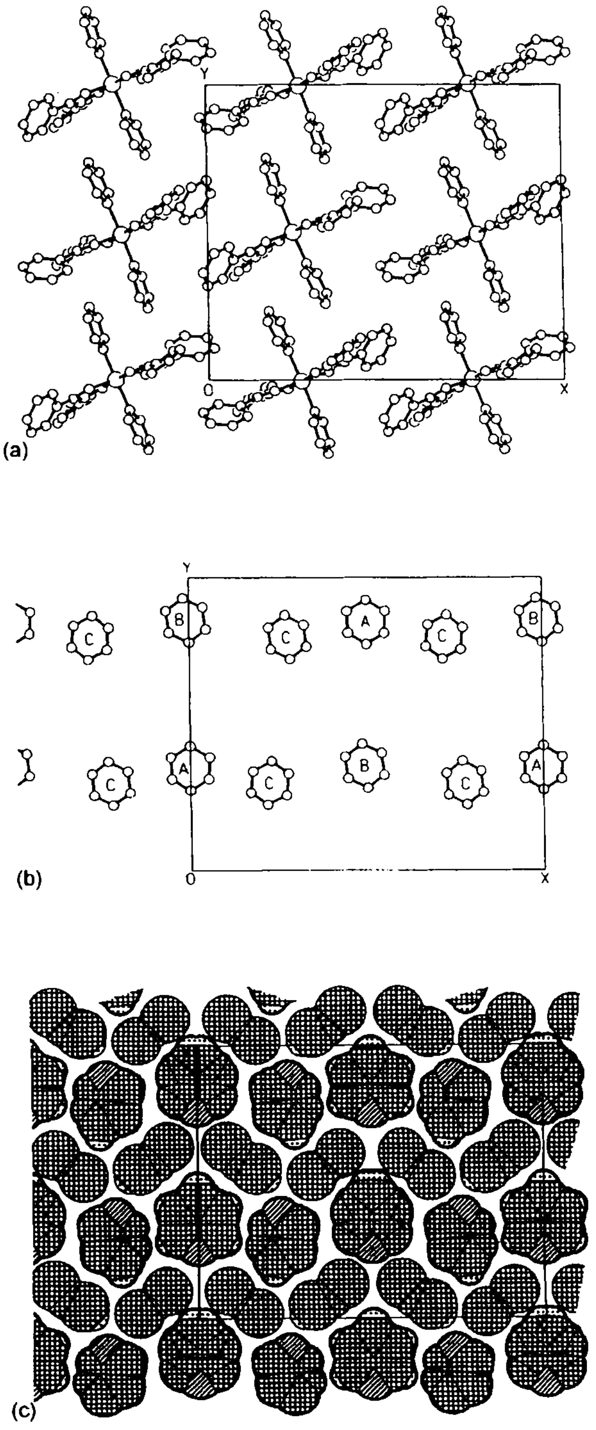

FIGURE 3 Crystal packing in $[NiPy_2(DBM)_2]*2Py$ (compound **II**): (a) host molecules layer at $z \sim 0$; (b) guest molecules located at $z \sim 0.25$; (c) cross-section of the structure cut with the (040) plane (van der Waals radii; guest species are designated with the black contour).

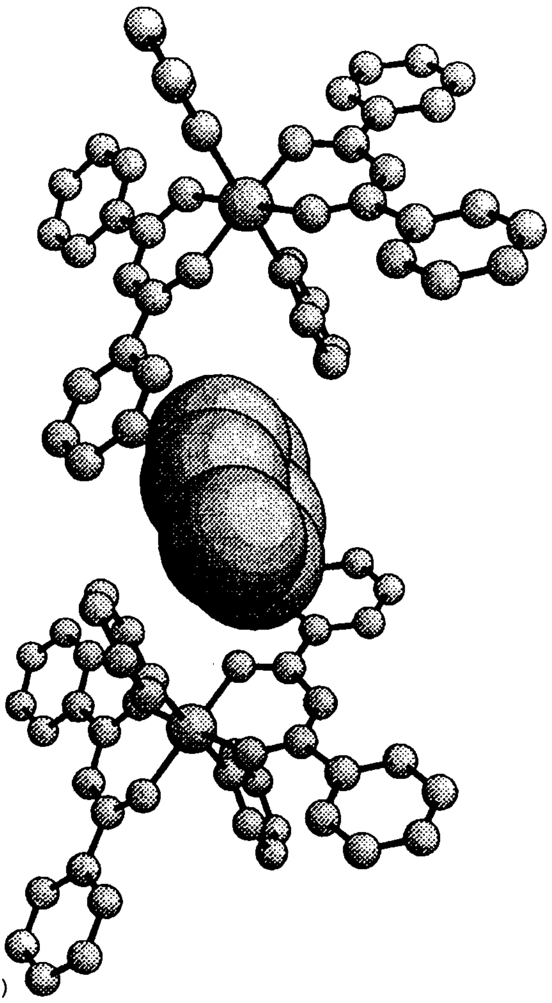

FIGURE 4 Crystal packing in [NiPy$_2$(DBM)$_2$] * C$_6$H$_6$ (compound III): (a) fragment showing guest molecule (van der Waals radii) entrapped between two host molecules; (b) structure viewed along the z-axis (guest atomic radii are enlarged for clarity; (c) cross-section of the structure cut with the (404) plane (van der Waals radii; guest species are designated with the black contour).

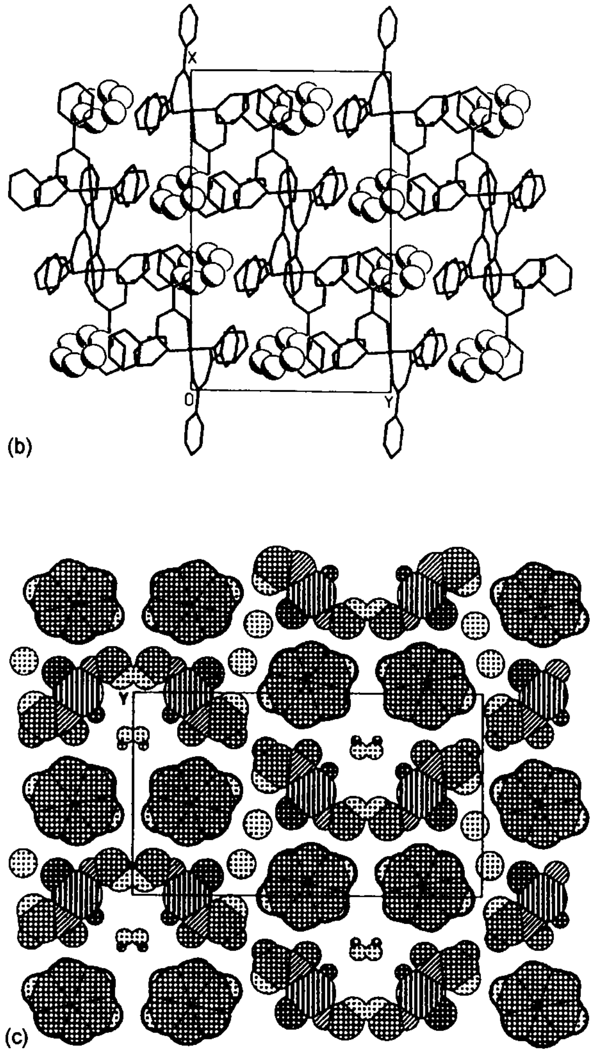

FIGURE 4 (Continued).

The [NiPy$_2$(DBM)$_2$] * 2CCl$_4$ Clathrate (I)

This clathrate has the highest Laue symmetry of the compounds studied in this work. It is orthorhombic, with four formula units per unit cell. One asymmetric host molecule and two guests (A and B) form crystallographically independent parts of the structure. The host complex molecules build up layers which are perpendicular to the *b* crystallographic direction and are located near the $y = 0$ and $y = 0.5$ levels (Fig. 1a). Each host molecule fills holes in the neighboring molecules in the layer with two phenyl and two pyridine moieties, whereas the remaining two phenyl rings point into the interlayer space. Guest CCl$_4$ species are arranged among these phenyls between host layers (Figs. 2b,c). There are zigzag channels within the interlayer space stretching along the *a* axis. Guest species "B" are located along the channel and have more freedom: they are

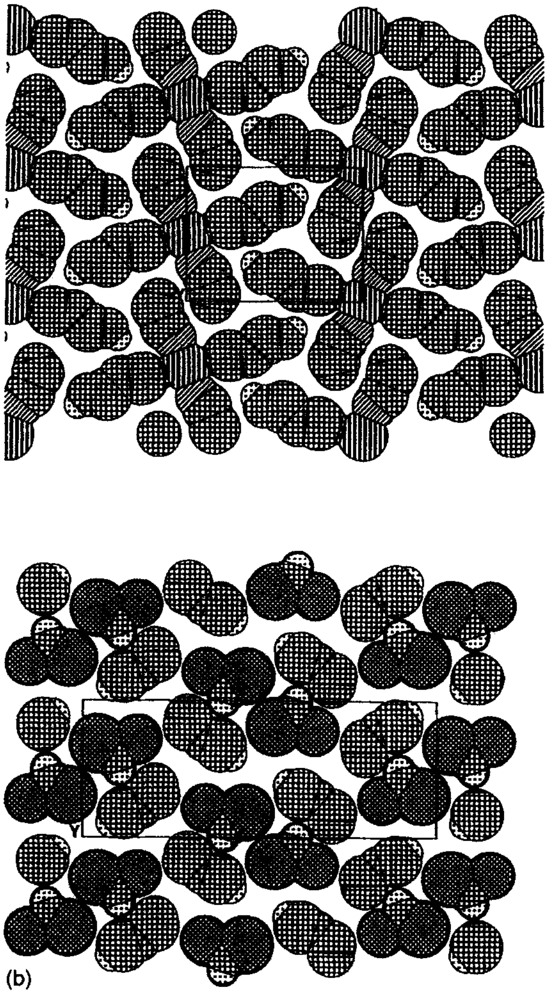

FIGURE 5 Crystal packing in [NiPy$_2$(DBM)$_2$] * 2CHCl$_3$ (compound **V**): (a) cross-section through the host layer (by the (202) plane); (b) cross-section through the cavities filled with guest (by the (101) plane) (van der Waals radii; guest species are designated with the black contour).

disordered and are characterized by significantly higher thermal parameters. Guest species "A" are located inside niches on both sides of the channel, and are packed more tightly.

The [NiPy$_2$(DBM)$_2$] * 2Py Clathrate (II)

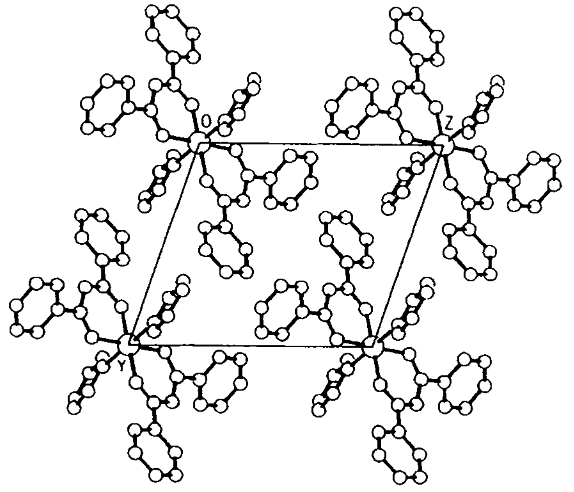

FIGURE 6 Crystal packing in the [NiPy$_2$(DBM)$_2$] non-clathrate phase (compound **VII**) viewed along the *x*-axis.

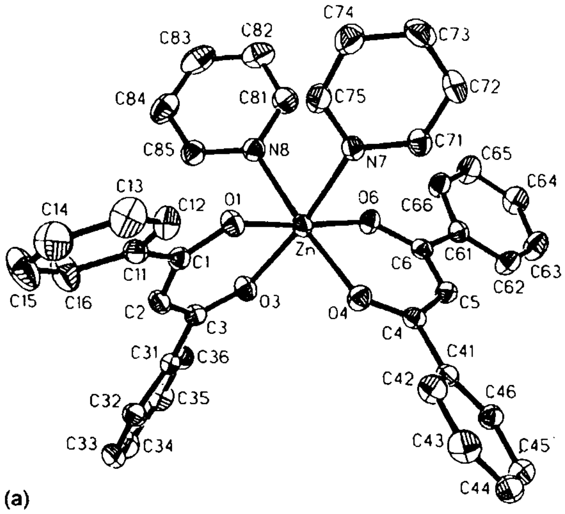

FIGURE 7 Structure of the [ZnPy$_2$(DBM)$_2$] (**VIII**): (a) complex molecule (H-atoms are omitted; ellipsoids are drawn at 50% probability level); (b) crystal packing along the *x*-axis.

This clathrate is monoclinic and has structural motifs similar to those in **I**. There are eight formula units per cell, as the value of parameter *b* is double that of *a* in **I** (*cf*. Figs. 2 and 3). The layers of the host molecules (Fig. 3a) stretch perpendicular to the *c* direction at the $z = 0$ and $z = 0.5$ levels. The holes of the host molecules are also filled with phenyl or pyridine moieties of adjacent molecules while the excess phenyls point out into the interlayer space, thus creating a channel for guests. However, as one can

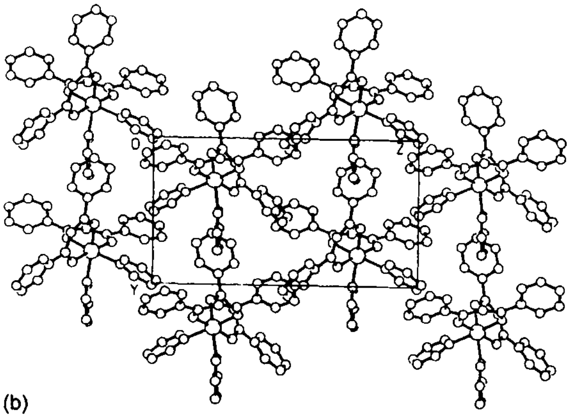

FIGURE 7 (Continued).

clearly see from Figures 2a and 3a there is a difference in the layer organization resulting in a different channel geometry; the channel in **II** is undulating and lacks the niches observed in **I**. The asymmetric unit of the structure contains one asymmetric host molecule and three crystallographically different guest pyridines, in a 0.5:0.5:1 ratio (A, B and C). They alternate along channels, as shown in Figure 3b,c. Guest A lies on double axis and guest B is disordered about it, as only the nitrogen atom is in a special position. Guest C is in a general position. The thermal parameters for all of the guest pyridines are similar and indicate low thermal motion. We note the low temperature of the diffraction experiment; at room temperature the crystals of the clathrate partially lose the guest without losing crystallinity, and this indicates that the guests are free to move along the channels.

The $[NiPy_2(DBM)_2] * C_6H_6$ (III) and $[NiPy_2(DBM)_2] * C_6H_5Cl$ (IV) Clathrates

These clathrates are isostructural, crystallizing in the monoclinic system with eight formula units per cell. This structural type is essentially different from the others. The crystallographically independent part contains one host and one guest molecule, resulting in 1:1 host-to-guest molar ratio. The overall architecture of this structural type is rather complicated. Each guest molecule is located inside a cavity formed between two adjacent host units (Fig. 4a). Two such fragments aggregate together to give a large flat cage with two guest molecules inside (Fig. 4b,c). In the clathrate with chlorobenzene, the guest molecule is disordered over two orientations with the chlorine atoms in nearly opposite positions.

The $[NiPy_2(DBM)_2] * 2CHCl_3$ (V) and $[NiPy_2(DBM)_2] * 2C_4H_8O$ (VI) Clathrates

These isostructural clathrates represent a monoclinic variation of structure **I**. Half of a host molecule, which is centrosymmetric, and one guest molecule form the crystallographycally independent asymmetric unit, giving two formula units per cell and a 1:2 host-to-guest molar ratio. As in **I**, there are layers of host molecules (Fig. 4a); they extend between the direction *b* and the longer diagonal of the (*ac*)-plane. The phenyl moieties pointing inside the interlayer space create cavities, each containing two guest molecules (Fig. 4b). Note, that in this structural type the molecules are packed more effectively than in **I**, and the system of cavities does not have a distinct channel structure (*cf.* Figs. 2c and 4b). The difference between **V** and **VI** is that in the clathrate with the chloroform, the guest atoms have rather small thermal parameters while those in the tetrahydrofuran clathrate are significantly larger, indicating better complementarity of chloroform for this matrix type.

Non-clathrate Phase of the $[NiPy_2(DBM)_2]$ (VII)

The complex crystallizes in triclinic system with one molecule per unit cell (Fig. 6). The molecule is centrosymmetric; its overall geometry does not significantly change from that in inclusions **I**, **II**, **V** and **VI** except for the large rotation of two phenyls. Each molecule has six closest neighbors that partially fill molecular holes with phenyl and pyridine moieties. The packing is not so effective as that of the host layer in compounds **I**, **II**, **V** and **VI**, as four holes should be filled with six moieties (four phenyls and two pyridines).

The [ZnPy$_2$(DBM)$_2$] (VIII) and [CdPy$_2$(DBM)$_2$] (IX) Complexes

The structure of these complexes may be of crucial significance in order to understand the clathration ability of their Ni-counterparts. The complexes did not form any inclusions with the guests tested, although other features such as chemical composition, the preparation method, the mode of thermal decomposition and solubility in organic solvents did not show any serious distinctions from the properties of the Ni-complexes.

From X-ray studies, the complexes crystallize consistently with van der Waals, molecular type of packing, but the molecules are *cis*-configured (Fig. 7a). It should be remembered that the Ni-complex always was found as *trans*, both in its inclusions and in the non-clathrate modifications. Therefore, the electronic structure of the metal cation, through a switching of the complex isomerization, appears to control the clathration abilities of the resulting complex. In the Ni-complex the metal cation, having empty *d*-orbitals, is involved in a delocalized electron system of planar bischelate fragments stabilizing this isomer type. In Zn- and Cd-complexes, the metal cation has filled the outer *d*-level and cannot participate in the electron system of chelate fragments, so other spatial or packing factors determine which isomer forms. In this case, the *cis*-isomer appears to be favored in spite of serious deviations from octahedral coordination (Tab. II).

The complexes crystallize in the monoclinic system with two molecules per unit cell. The molecular packing is shown in Figure 7b. Although *trans*-to-*cis* change does not add flexibility to the molecule, the resulting geometry is more suitable to provide effective packing without solvent.

Prospects for Metal Dibenzoylmethanates as Hosts Materials

Of the known metal complex hosts, the [NiPy$_2$(DBM)$_2$] studied in this work are most closely related to Werner complexes [3]. These hosts are described by a general formula [MA$_4$X$_2$] with a metal(II) as the central atom M, a neutral pyridine-type base A, and a univalent acidogroup X. As a rule, the complexes are also *trans*-configured and have the related geometry. The variation of Werner complex substituents (especially of the A-ligand [11]) has resulted in a tremendous diversity of resulting hosts with a versatile ability to form clathrates, selectivity of clathration, guest capacity and structural stability. In the case of [NiPy$_2$(DBM)$_2$], the possibilities for modification could be even significantly higher. According to our preliminary studies, the analogous complex with 4-methylpyridine [Ni(4-MePy)$_2$(DBM)$_2$], does also form a number of clathrate structures and probably surpasses the title complex in clathration ability, forming two different structures with some of the guests studied. Several clathrates of the analogous complex with 4-benzylpyridine also were prepared. Note that the replacement of the neutral ligand is performed very easily and quantitatively. Variation of dibenzoylmethanate itself is more complicated but also may give very wide range of host modifications.

At the same time, as was shown in this work, replacement of the central atom can switch off clathration through *trans*-to-*cis* isomerization. It would be of great benefit if the energy of this transition were low enough to allow the design of hosts with the ability to switch their isomeric state through the addition of particular guest components. This would give effective control for clathrate formation processes at the molecular level. (So far, only one such complex is known among Werner hosts [12]). The kinetic barrier inherent in this isomerization could also add robustness to porous clathrate frameworks that would be stable after removal of the templating guest out of the structure.

Acknowledgments

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