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4-Vinylpyridine-Modified Nickel and Cobalt Dibenzoylmethanates as New Hosts: Inclusions with Carbon Tetrachloride and Chlorobenzene*†

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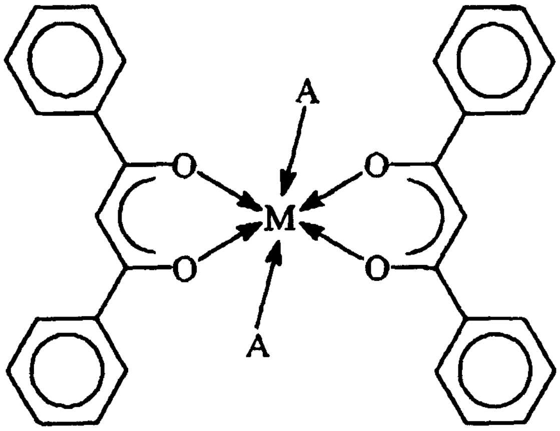
Bis(4-vinylpyridine)bis(dibenzoylmethanato)metal(II), $[M(ViPy)_2(DBM)_2]$ (M = Ni(II), Co(II); ViPy = 4-Vinylpyridine; DBM = $C_6H_5COCHCOC_6H_5^-$, dibenzoylmethanate) is a new metal-complex host. Its inclusions with carbon tetrachloride (host:guest = 1:2; triclinic, $P\bar{1}$, $Z=1$) and chlorobenzene (host:guest = 1:1; monoclinic, $P2_1/c$, $Z=4$) are consistent with the van der Waals packing of neutral complex (host) and solvent (guest) molecules. In the host unit, four oxygens from two chelate DBM-units provide a square-planar environment around the metal center that is extended to octahedral coordination by two apical nitrogens from two vinylpyridine moieties in the *trans*-position. In the carbon tetrachloride inclusions, the host traps two guest molecules in large prolate spheroidal cavities. In the chlorobenzene inclusions, guest species are located inside 8-shaped serpentine channels along the *y*-axis. The nickel and cobalt versions of the inclusion compounds were found to be very similar.

Keywords: Dibenzoylmethanate host, nickel complex, cobalt complex

INTRODUCTION

This contribution continues our investigation of the utilization of bis-chelate complex units as building blocks for the construction of porous solids. [1,2] The electrically neutral metal(II) dibenzoylmethanate as modified with two coordinating amine moieties (A) can be expected to support a new type of metal-complex host[1] in analogy with the versatile Werner [3] clathrates and the recently reported porphyrin-based [4] guest-host materials.



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Our previous work has revealed that nickel dibenzoylmethanate, as modified with pyridine and its derivatives as A-ligand, form numerous clathrate architectures capable of trapping a wide range of organic solvents. Here we report two new structures constructed from 4-vinylpyridine-modified nickel and cobalt dibenzoylmethanate hosts. We illustrate for the first time the use of 4-vinylpyridine as A-ligand and cobalt as the metal center.

EXPERIMENTAL SECTION

Bis(4-vinylpyridine)-bis(dibenzoylmethanato)-nicke(II), *[Ni(4-ViPy)$_2$(DBM)$_2$]* and its *cobalt(II)* counterpart were prepared in a similar way as the pyridine-containing nickel analog. [1] Crystals of inclusions were prepared by evaporation of saturated solutions of the complexes in neat guest liquids.

To prevent compounds from decomposing and to reduce the thermal motion of the guest molecules, crystals were taken from their respective mother liquors and frozen to –100°C; all further experiments were performed at this temperature. Data were collected using the ω scan mode over the 2θ range of 3–58° on a Siemens SMART CCD X-ray diffractometer with graphite-monochromated MoK_α radiation (λ=0.7107 Å). An empirical absorption correction utilized the SADABS routine. The final unit cell parameters were obtained using the entire data set. A summary of the crystal data and experimental parameters are given in Table I.

The structures were solved with the SHELXS system of programs [5] by using direct methods. Structural refinement (anisotropic for non-hydrogen atoms) on F^2 was performed with SHELXL [6] using all data with positive intensities. The geometry of disordered guest molecules in the minor orientations was fixed to be the same as that for the main orientations. Site occupancy factors for different orientations were refined independently; in the last cycles their sums were fixed to give ideal stoichiometry as observed deviations were not significant (see Table I). Hydrogen atoms were included in calculated positions as 'riding' on the corresponding carbon atoms and were refined isotropically with thermal factors 1.2 or 1.5 times greater than those for the adjacent carbon atoms.

Geometric parameters for the structures studied are given in Tables II, III and IV. For the atom numbering schemes see Figure 1. The rest of the structural information has been deposited with the Cambridge Crystallographic Data Centre (CCDC): No. 136940 (compound **I**), No. 136941 (**II**), No. 136942 (**III**), and No. 136943 (**IV**) (see Table I for notations).

TABLE I Crystal data and experimental details

	Compound			
	I	*II*	*III*	*IV*
Host component	[Ni(ViPy)$_2$(DBM)$_2$]	[Co(ViPy)$_2$(DBM)$_2$]	[Ni(ViPy)$_2$(DBM)$_2$]	[Co(ViPy)$_2$(DBM)$_2$]
Guest component	carbon tetrachloride	carbon tetrachloride	chlorobenzene	chlorobenzene
Guest per host ratio:				
structural	2	2	1	1
refined	1.96(4)	1.94(4)	1.00(1)	0.99(1)
Empirical formula	$C_{46}H_{36}Cl_8N_2NiO_4$	$C_{46}H_{36}Cl_8N_2CoO_4$	$C_{50}H_{41}ClN_2NiO_4$	$C_{50}H_{41}ClN_2CoO_4$
Formula unit mass	1023.1	1023.3	828.0	828.2
Crystal parameters:				
color	dark-yellow	orange	green	red
habit	oblique block	shapeless	prism	prism
sizes, mm	0.2 0.2 0.2	0.2 0.2 0.2	0.3 0.3 0.4	0.3 0.3 0.5

	Compound			
	I	*II*	*III*	*IV*
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$ (No2)	$P\bar{1}$ (No2)	$P2_1/c$ (No14)	$P2_1/c$ (No14)
Unit cell parameters:				
a, Å	10.151(2)	10.214(2)	11.875(2)	11.887(2)
b, Å	11.080(2)	11.070(2)	20.553(3)	20.562(3)
c, Å	11.316(2)	11.293(2)	17.299(3)	17.368(3)
α, °	107.88(1)	107.59(1)	90	90
β, °	90.80(1)	90.87(1)	98.14(1)	98.21(1)
γ, °	107.64(1)	107.49(1)	90	90
V, $Å^3$	1146.3(4)	1153.0(4)	4180(1)	4202(1)
Z	1	1	4	4
D_{calc}, g cm^{-3}	1.482	1.474	1.316	1.309
Temperature, °C	–100	–100	–100	–100
$\mu(MoK_\alpha)$, cm^{-1}	9.35	8.81	5.76	5.20
Number of data:				
collected (R_{int})	13637 (0.019)	13241 (0.038)	47299 (0.035)	48224 (0.051)
unique (I>0)	5879	5910	10814	10863
unique (I>2σ(I))	4905	4826	8217	7310
Refined parameters	323	323	587	587
R^* (data with I>2σ(I))	0.031	0.040	0.036	0.039
R_w^{2**} (k;m) (I>2σ(I))	0.082 (0.0445;0.25)	0.108 (0.0528;0.37)	0.091 (0.0468;0.97)	0.097 (0.0564;0.00)

TABLE II Selected bond distances (Å) and angles (°) for $[M(ViPy)_2(DBM)_2]^*2(CCl_4)$ clathrates (**I**, M=Ni; **II**, M=Co)

	I, M=Ni	*II, M=Co*
Host		
M-O(1)	2.014(1)	2.035(1)
M-O(3)	2.015(1)	2.029(1)
M-N(7)	2.116(1)	2.176(2)
C(1)-O(1)	1.266(2)	1.265(2)
C(1)-C(2)	1.408(2)	1.405(2)
C(1)-C(11)	1.499(2)	1.501(2)
C(2)-C(3)	1.397(2)	1.397(2)
C(3)-O(3)	1.268(2)	1.275(2)
C(3)-C(31)	1.506(2)	1.505(2)
N(7)-C(71)	1.338(2)	1.334(2)
N(7)-C(75)	1.337(2)	1.336(2)
C(71)-C(72)	1.381(2)	1.387(3)
C(72)-C(73)	1.393(2)	1.390(3)
C(73)-C(74)	1.384(2)	1.377(3)
C(73)-C(76)	1.482(3)	1.488(3)
C(74)-C(75)	1.382(3)	1.390(3)
C(76)-C(77)	1.291(3)	1.283(4)
O(1)-M-O(1)A	180	180
O(1)-M-O(3)	91.12(4)	89.40(5)
O(1)-M-O(3)A	88.88(4)	90.60(5)
O(3)-M-O(3)A	180	180

	I, M=Ni	*II, M=Co*
O(1)-M-N(7)	90.88(5)	90.79(6)
O(3)-M-N(7)	89.88(5)	90.01(6)
O(1)-M-N(7)A	89.12(5)	89.21(6)
O(3)-M-N(7)A	90.12(5)	89.99(6)
N(7)-M-N(7)A	180	180
M-O(1)-C(1)	125.11(9)	125.9(1)
O(1)-C(1)-C(11)	115.4(1)	115.4(2)
O(1)-C(1)-C(2)	126.0(1)	125.9(2)
C(11)-C(1)-C(2)	118.5(1)	118.7(2)
C(1)-C(2)-C(3)	125.9(1)	125.8(2)
M-O(3)-C(3)	125.36(9)	126.2(1)
O(3)-C(3)-C(31)	114.8(1)	114.9(1)
O(3)-C(3)-C(2)	125.0(1)	124.6(2)
C(31)-C(3)-C(2)	120.2(1)	120.4(2)
M-N(7)-C(71)	121.3(1)	121.9(1)
M-N(7)-C(75)	121.6(1)	121.4(1)
C(71)-N(7)-C(75)	116.9(1)	116.4(2)
N(7)-C(71)-C(72)	123.5(2)	123.8(2)
C(71)-C(72)-C(73)	119.6(2)	119.4(2)
C(72)-C(73)-C(74)	116.7(2)	116.9(2)
C(73)-C(74)-C(75)	120.2(2)	120.0(2)
C(74)-C(75)-N(7)	123.1(2)	123.4(2)
C(72)-C(73)-C(76)	123.3(2)	123.5(2)
C(74)-C(73)-C(76)	120.0(2)	119.6(2)
C(73)-C(76)-C(77)	126.3(2)	125.9(3)
Guest		
All C-Cl	~1.755	~1.755
All Cl-C-Cl	~109	~109

Symmetry transformation A: -x, -y, -z

TABLE III Selected bond distances (Å) and angles (°) for $[M(ViPy)_2(DBM)_2]^*(C_6H_5Cl)$ clathrates (**III**, M=Ni; **IV**, M=Co)

	II, M=Ni	**IV**, M=Co
Host		
M-O(1)	2.023(1)	2.042(1)
M-O(3)	2.030(1)	2.041(1)
M-O(4)	2.042(1)	2.056(1)
M-O(6)	2.024(1)	2.046(1)
M-N(7)	2.104(1)	2.164(1)
M-N(8)	2.117(1)	2.180(2)
C(11)-C(1)	1.502(2)	1.502(2)
O(1)-C(1)	1.268(2)	1.266(2)
C(1)-C(2)	1.406(2)	1.405(2)
C(2)-C(3)	1.402(2)	1.401(2)
O(3)-C(3)	1.271(2)	1.271(2)
C(3)-C(31)	1.505(2)	1.502(2)
C(41)-C(4)	1.505(2)	1.505(2)
O(4)-C(4)	1.274(2)	1.270(2)
C(4)-C(5)	1.399(2)	1.401(2)
C(5)-C(6)	1.410(2)	1.404(2)

O(6)-C(6)	1.269(2)	1.273(2)
C(6)-C(61)	1.496(2)	1.495(2)
N(7)-C(71)	1.337(2)	1.335(2)
C(71)-C(72)	1.381(2)	1.383(2)
C(72)-C(73)	1.393(2)	1.391(2)
C(73)-C(74)	1.395(2)	1.393(2)
C(74)-C(75)	1.376(2)	1.378(2)
C(75)-N(7)	1.350(2)	1.349(2)
C(73)-C(76)	1.472(3)	1.473(3)
C(76)-C(77)	1.306(3)	1.307(3)
N(8)-C(81)	1.344(2)	1.342(2)
C(81)-C(82)	1.371(2)	1.372(2)
C(82)-C(83)	1.392(2)	1.390(3)
C(83)-C(84)	1.392(3)	1.393(3)
C(84)-C(85)	1.379(3)	1.377(3)
C(85)-N(8)	1.342(2)	1.339(2)
C(83)-C(86)	1.472(3)	1.470(3)
C(86)-C(87)	1.307(3)	1.309(3)
O(1)-M-O(3)	91.06(4)	89.37(5)
O(1)-M-O(4)	174.81(4)	173.79(5)
O(1)-M-O(6)	87.12(4)	88.37(4)
O(3)-M-O(4)	91.32(4)	93.64(5)
O(3)-M-O(6)	177.98(4)	177.62(4)
O(4)-M-O(6)	90.42(4)	88.53(4)
O(1)-M-N(7)	94.55(5)	95.10(5)
O(3)-M-N(7)	90.04(5)	90.16(5)
O(4)-M-N(7)	90.06(5)	90.32(5)
O(6)-M-N(7)	90.98(5)	90.79(5)
O(1)-M-N(8)	89.25(5)	88.87(5)
O(3)-M-N(8)	88.46(5)	88.58(5)
O(4)-M-N(8)	86.21(5)	85.79(5)
O(6)-M-N(8)	90.64(5)	90.61(5)
N(7)-M-N(8)	175.94(5)	175.82(5)
M-O(1)-C(1)	124.2(1)	125.0(1)
M-O(3)-C(3)	124.3(1)	125.4(1)
M-O(4)-C(4)	123.3(1)	124.4(1)
M-O(6)-C(6)	124.52(9)	125.4(1)
M-N(7)-C(71)	120.7(1)	120.6(1)
M-N(7)-C(75)	122.6(1)	122.6(1)
C(71)-N(7)-C(75)	116.5(1)	116.6(2)
N(7)-C(71) -C(72)	123.6(2)	123.6(2)
C(71)-C(72)-C(73)	119.9(2)	119.8(2)
C(72)-C(73)-C(74)	116.5(2)	116.8(2)
C(73)-C(74)-C(75)	120.1(2)	119.9(2)
C(74)-C(75)-N(7)	123.3(2)	123.3(2)
C(72)-C(73)-C(76)	120.1(2)	119.9(2)
C(74)-C(73)-C(76)	123.5(2)	123.4(2)
C(73)-C(76)-C(77)	127.0(2)	126.9(2)
M-N(8)-C(81)	119.3(1)	119.5(1)
M-N(8)-C(85)	123.4(1)	123.7(1)
C(81)-N(8)-C(85)	117.2(2)	116.6(2)
N(8)-C(81)-C(82)	123.3(2)	123.9(2)
C(81)-C(82)-C(83)	120.1(2)	119.6(2)

C(82)-C(83)-C(84)	116.5(2)	116.7(2)
C(83)-C(84)-C(85)	120.2(2)	120.1(2)
C(84)-C(85)-N(8)	122.7(2)	123.1(2)
C(82)-C(83)-C(86)	122.5(2)	122.5(2)
C(84)-C(83)-C(86)	120.9(2)	120.9(2)
C(83)-C(86)-C(87)	125.4(2)	125.4(2)
C(11)-C(1)-O(1)	115.8(1)	116.2(1)
C(11)-C(1)-C(2)	118.3(1)	118.3(1)
O(1)-C(1)-C(2)	125.9(1)	125.6(2)
C(1)-C(2)-C(3)	126.1(2)	126.1(2)
C(31)-C(3)-O(3)	115.8(1)	115.9(1)
C(31)-C(3)-C(2)	118.5(1)	119.0(1)
O(3)-C(3)-C(2)	125.7(1)	125.0(2)
C(41)-C(4)-O(4)	115.9(1)	116.2(1)
C(41)-C(4)-C(5)	118.2(1)	118.4(2)
O(4)-C(4)-C(5)	125.8(1)	125.5(1)
C(4)-C(5)-C(6)	125.9(1)	125.7(2)
C(61)-C(6)-O(6)	116.0(1)	115.8(1)
C(61)-C(6)-C(5)	118.5(1)	119.0(1)
O(6)-C(6)-C(5)	125.4(1)	125.1(1)
Guest		
All C-Cl	~1.732	~1.730
All C-C	~1.370	~1.370
All angles	~120	~120

RESULTS AND DISCUSSION

General features

The main result of this study is that the replacement of pyridine in the original [NiPy$_2$(DBM)$_2$] host [1] with 4-vinylpyridine does give a new complex host. Incorporating cobalt(II) instead of a nickel(II) center also gives a new host. Both of these results demonstrate the potential of the metal complexes as versatile dibenzoylmethanate hosts with many possible variations. The modification with 4-vinylpyridine leads to architecturally new phases whereas substitution of Co for Ni does not affect the structural type formed. All inclusions studied show molecular packing without intermolecular contacts shorter than the sum of the van der Waals radii of the respective atoms. Different structural types were observed for inclusions with carbon tetrachloride and chlorobenzene guests. The former is a cage-type inclusion whereas the latter is a channel-type.

Structure and conformations of the [M(ViPy)$_2$(DBM)$_2$] molecule

In all compounds studied, the [M(ViPy)$_2$(DBM)$_2$] molecule is *trans*-configured. Four oxygens of two chelating dibenzoylmethanate fragments in the equatorial plane and two nitrogens of two pyridine ligands in axial positions form the distorted octahedral environment around the metal center (Figure 1, Tables II and III). The M-O distances of 2.01–2.06 Å are shorter than the 2.10–2.18 Å distances observed for the M-N bond lengths, and the bonds around Co are slightly longer. Most of the coordination angles lie between 88–92°.

In compounds with the carbon tetrachloride guest the host molecule is centrosymmetric (Figure 1, top). The bis-chelate fragment is planar and the coordinating environment of the metal is close to that of a right octahedron. The phenyl rings are turned out of the equatorial plane by ca. 20° (Table IV). The whole dibenzoylmethanate

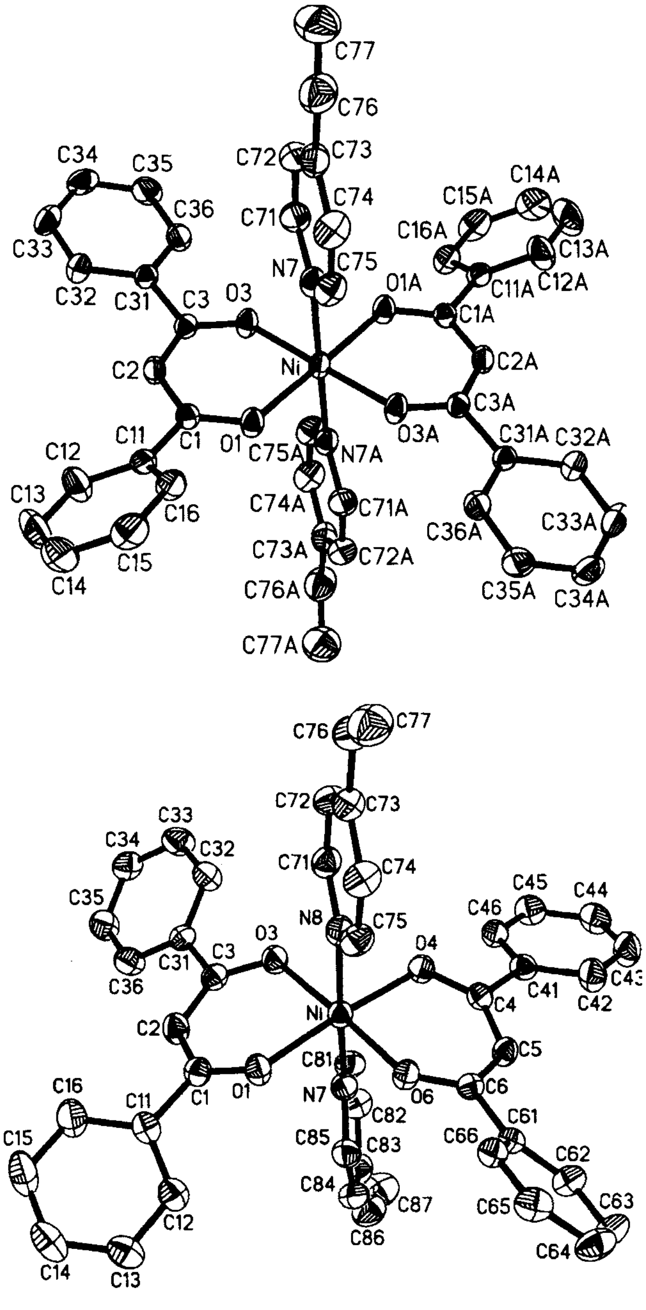


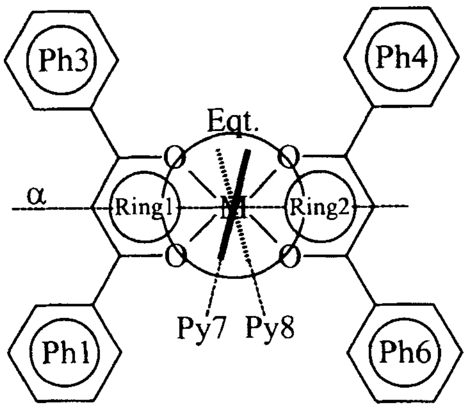
FIGURE 1 The [Ni(ViPy)$_2$(DBM)$_2$] host molecule as it is found in the clathrate with carbon tetrachloride **I** (Top) and with chlorobenzene **III** (Bottom). The A-marked atoms are generated by centrosymmetry

unit thus has the shape of a lozenge. The vinylpyridine moieties are attached perpendicularly to the unit, being located near the plane that divides the bischelate fragment into two chelate parts.

TABLE IV Conformational data for the *trans*-[M(ViPy)$_2$(DBM)$_2$] molecule

Compound	*I*	*II*	*III*	*IV*
M	Ni	Co	Ni	Co
Guest	CCl_4	CCl_4	C_6H_5Cl	C_6H_5Cl
Dihedral angles* (deg.):				
Ring1-Ring2	0	0	24.2	26.0
Eqt.-Ph1	22.6	21.4	22.6	21.5
Eqt.-Ph3	18.5	19.2	36.1	36.1
Eqt.-Ph4	−22.6	−21.4	14.9	14.3
Eqt.-Ph6	−18.5	−19.2	45.6	46.2
α-Py7	76.2	74.5	69.6	68.3
α-Py8	−76.2	−74.5	−85.9	−85.6

*Least-squares planes are designated as follows (*see* the scheme and Figure 1):



Ring1	the chelate ring:	(M,O1,C1,C2,C3,O3);
Ring2	the chelate ring:	(M,O1A,C1A,C2A,C3A,O3A) for I and II, (M,O4,C4,C5,C6,O6) for III and IV;
Eqt.	equatorial plane:	(M,O1,O3,O1A,O3A) for I and II, (M,O1,O3,O4,O6) for III and IV;
Ph1	the phenyl ring:	(C11,C12,C13,C14,C15,C16);
Ph3	the phenyl ring:	(C31,C32,C33,C34,C35,C36);
Ph4	the phenyl ring:	(C11A,C12A,C13A,C14A,C15A,C16A) for I and II, (C41,C42,C43,C44,C45,C46) for III and IV;
Ph6	the phenyl ring:	(C31A,C32A,C33A,C34A,C35A,C36A) for I and II, (C61,C62,C63,C64,C65,C66) for III and IV;
α	the plane	(M,C2,C2A,N7,N7A) for I and II, (M,C2,C5,N7,N8) for III and IV;
Py7	the pyridyl ring	(N7,C71,C72,C73,C74,C75);
Py8	the pyridyl ring	(N7A,C71A,C72A,C73A,C74A,C75A) for I and II, (N8,C81,C82,C83,C84,C85) for III and IV

In compounds with chlorobenzene the host unit is asymmetric and the coordinating environment of the metal center is more distorted. These changes are responsible for the green color of the Ni-compound, whereas the Ni inclusion with carbon tetrachloride is dark-yellow; analogous observations have been observed for the Co-compounds (Table I). This exemplifies the influence of van der Waals forces on the electronic structure of a complex molecule: the adjustment of the molecule to specific packing with a given guest may affect the electronic structure to such an extent that the result is quite obvious upon visual inspection. [7] The bis-chelate fragment in the chlorobenzene inclusions is bent at ~25° (Table IV) with the phenyl rings turned out of the plane at 15–45°. With these changes, the conformation of the host molecule is qualitatively similar for both structural types and is quite similar to that observed for $[NiPy_2(DBM)_2]$ in the seven structures studied previously [1].

The $[M(ViPy)_2(DBM)_2]^*2CCl_4$ inclusions (I, M=Ni; II, M=Co)

These isostructural inclusions are triclinic with one host and two guest molecules per unit cell. We will consider only the Ni-compound as no differences of note were observed for the Co counterpart. Figure 2 demonstrates the packing of the host molecules within a layer extending along the (101) plane. This 2-D packing motif resembles that of the $[NiPy_2(DBM)_2]$ host in its channel inclusion with pyridine [1]. However, small changes in the mutual arrangement of the molecules, the presence of the vinyl moiety and a relative shift of adjacent layers results in a completely different shape of the void space in the title compounds. Centered in the unit cell (Figure 3) is a cage in the shape of a prolate spheroid with dimensions of at least 7×15 Å. This allows not only the incorporation of two carbon tetrachloride guest molecules but also their positional disordering. The cage walls are formed by portions of host molecules located at the corners of the unit cell. The guest species do not have the possibility of moving from one cavity to another.

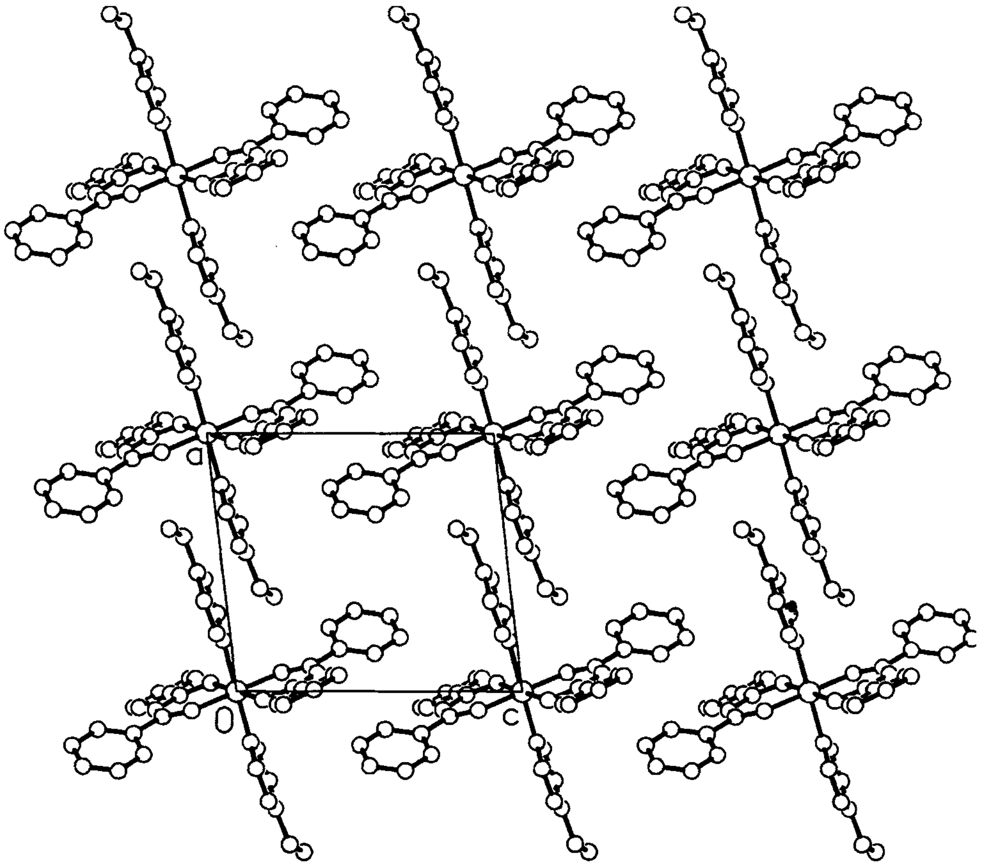


FIGURE 2 Layer of host molecules at y~0 for $[Ni(ViPy)_2(DBM)_2]^*2(CCl_4)$

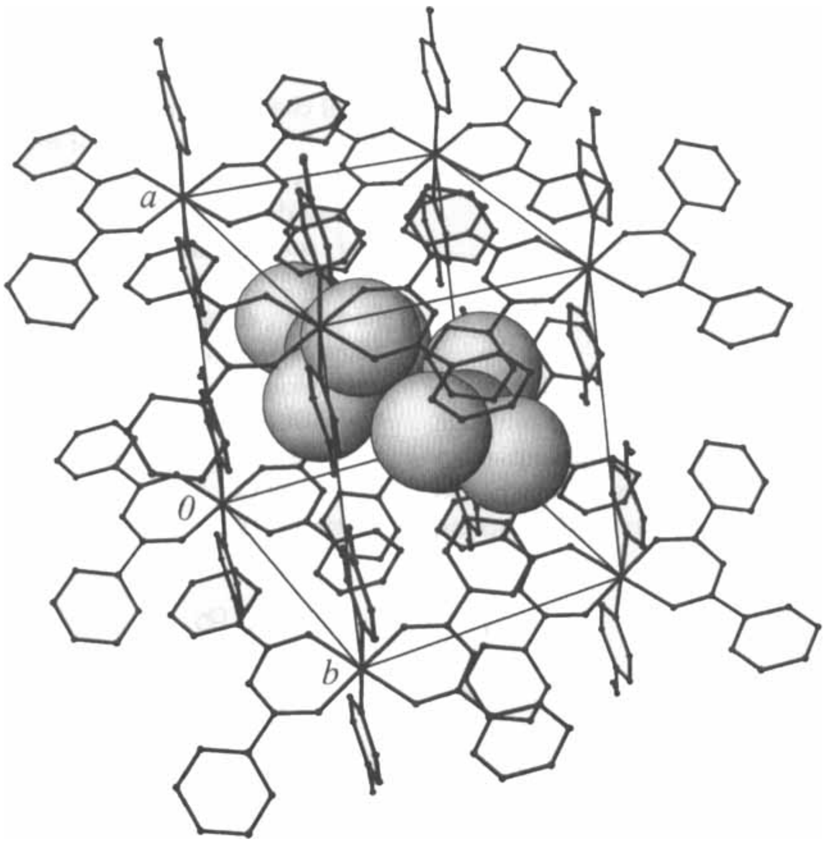


FIGURE 3 Unit cell contents for $[Ni(ViPy)_2(DBM)_2]^*2(CCl_4)$: a pair of guest molecules occupying the prolate spheroidal cage. The van der Waals dimensions for the guest are outlined

On the whole, the structural nature of the $[M(ViPy)_2(DBM)_2]^*2(CCl_4)$ is essentially different from all known forms of $[NiPy_2(DBM)_2]$. The only feature in common with some of these is the ability of host units to pack well within layers but not so well in three dimensions.

The $[M(ViPy)_2(DBM)_2]^*C_6H_5Cl$ inclusions (III, M=Ni; IV, M=Co)

These inclusions are isostructural as well and are very alike in all respects, being monoclinic with four formula units per unit cell. One host and one guest molecule form the independent part of the structure. As shown in Figure 4, the guest chlorobenzene is surrounded by phenyl and vinylpyridine moieties belonging to four host molecules. Within one unit cell, two such segments are connected; this results in the channel stretching along the y-axis. Two channels run through the unit cell, one near (x,z)=(0.5,0.25) and another near (x,z)=(0.5,0.75) (Figure 4), and these have a serpentine shape: in the (x,z)-projection, the axis of the channel follows a figure-eight shape 4 Å in height along *z* and 1.5 Å along *x*. The narrowest parts of the channel at y~0 and y~0.5 are approximately 2 Å in diameter although it is possible that these could be widened by small guest species by causing a slight rotation of the host phenyl moieties.

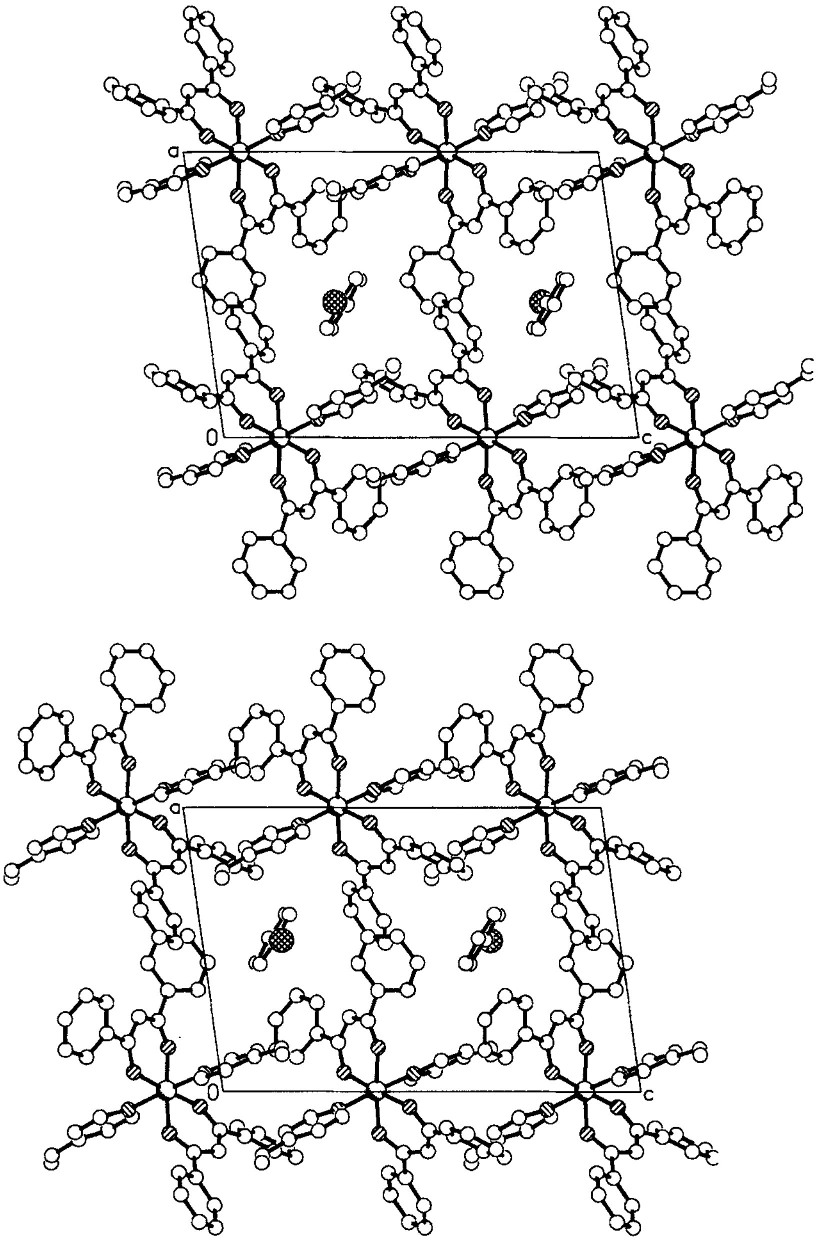


FIGURE 4 The unit cell contents for $[Ni(ViPy)_2(DBM)_2]^*(C_6H_5Cl)$ along the *y*-axis: $y = 0 \div 0.5$ (Top); $y = 0.5 \div 1$ (Bottom)

The structural type illustrated here is quite different from the dibenzoylmethanates studied before. In addition, our preliminary studies have suggested that architecture of the host may have the desirable property of remaining intact after guest removal (for instance, from the another $[Ni(ViPy)_2(DBM)_2]^*2(CH_2Cl_2)$ clathrate). This suggests zeolite-like behavior of the matrix [2,8], at least in the presence of small molecules.

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