# Nickel(II) and Zinc(II) Dibenzoylmethanates: Molecular and Crystal Structure, Polymorphism, and Guest- or Temperature-Induced Oligomerization†

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Four forms of nickel(II) and two of zinc(II) dibenzoylmethanates have been isolated and characterized with powder and single-crystal X-ray diffraction analyses, differential scanning calorimetry, magnetic susceptibility measurements, and solid-state $^{13}C$ cross-polarization/magic angle spinning NMR. Nickel dibenzoylmethanate, $Ni(DBM)_2$ ($DBM = PhCOCHCOPh^-$), forms three polymorphic forms (light-green, brown, and green) and a fourth clathrate form with guest benzene included. The light-green polymorph is metastable. Substituted benzenes induce recrystallization of the polymorph into a stable brown form ($C_{30}H_{22}NiO_4$; $a = 26.502(3)$ Å, $b = 5.774(1)$ Å, $c = 16.456(2)$ Å, $\beta = 116.03(1)°$; monoclinic, $C2/c$; $Z = 4$). Unlike the other forms, the brown form is diamagnetic and is comprised of monomers of the low-spin $[Ni(DBM)_2]$ complex. The Ni(II) is chelated by two DBM ligands in a square planar environment by four donor oxygen atoms. When heated, the brown form transforms to a green form which is stable above 202 °C ($C_{90}H_{66}Ni_3O_{12}$; $a = 13.819(2)$ Å, $b = 16.252(2)$ Å, $c = 17.358(2)$ Å, $\beta = 108.28(1)°$; monoclinic, $P2_1/n$; $Z = 2$). This polymorph is formed by van der Waals packing of trimers $[Ni_3(DBM)_6]$ containing linear $Ni_3$ clusters with an Ni−Ni distance of 2.81 Å. The cluster is surrounded by six DBM ligands, providing a distorted octahedral environment about each Ni by six oxygen atoms. Benzene stabilizes the trimeric structure at room temperature, forming a $[Ni_3(DBM)_6]\cdot 2(\text{benzene})$ inclusion compound (Ni−Ni distance of 2.83 Å) with guest benzene molecules located in channels ($C_{90}H_{66}Ni_3O_{12} + 2(C_6H_6)$; $a = 17.670(2)$ Å, $b = 20.945(3)$ Å, $c$=11.209(2) Å, $\beta = 102.57(1)°$; monoclinic, $P2_1/c$; $Z = 2$). Zinc dibenzoylmethanate has been prepared in two polymorphic forms. The monomeric form contains $[Zn(DBM)_2]$ molecules with the zinc center in a distorted tetrahedral environment of four oxygens from the two chelated DBMs ($C_{30}H_{22}O_4Zn$; $a = 10.288(2)$ Å, $b = 10.716(2)$ Å, $c = 12.243(2)$ Å, $\alpha = 89.19(1)°$, $\beta = 75.39(1)°$, $\gamma = 64.18(1)°$; triclinic, $P\bar{1}$; $Z = 2$). Another, dimeric form contains $[Zn_2(DBM)_4]$ species, with two zinc atoms separated by a distance of 3.14 Å and each zinc coordinated by five oxygen atoms ($C_{60}H_{44}O_8Zn_2$; $a = 25.792(3)$ Å, $b = 7.274(1)$ Å, $c = 24.307(2)$ Å, $\beta = 90.58(1)°$; monoclinic, $C2/c$; $Z = 4$). The polymorphic variety of the title complexes and the peculiarities of the Ni(II) and Zn(II) coordination environments are discussed in the context of using the complexes as precursors for new metal complex hosts.

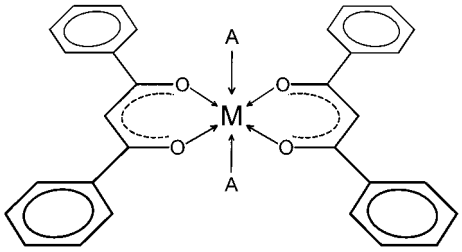
## Introduction

Nickel(II) DBM (DBM = dibenzoylmethanate, $PhCOCHCOPh^-$) gives rise to a family of metal complex hosts produced by apical coordination of a variety of pyridine-type ligands (A) to the basic metal bischelate unit (Chart 1).[1,2]

The $[NiPy_2(DBM)_2]$ complex was shown to be *trans* configured, both in six clathrates belonging to four structural types, and in its dense, nonclathrate phase.[1] In contrast, the analogous Zn complex (as well as the Cd complex) is *cis* configured and therefore probably is unable to include guests.[1] The electronic structure of a metal center thus controls the clathratogenic ability of this host type.[3] Packing and molecular features of the unmodified metal DBMs could shed some light on what part of the *trans*-$[MA_2(DBM)_2]$ molecule is the most important in maintaining the host properties.

In this paper we report on the structure and relevant properties of the nickel(II) DBM as well as of its zinc(II) counterpart,

**Chart 1**




elucidating fundamental questions related to the entire family of metal DBM hosts. A structural comparison has been made to reveal whether the tendency of the $[Ni(DBM)_2]$ unit to adopt a planar bischelate configuration appears on the level of the precursor. Up to the present, structures for Pd(II), Cu(II), and Sn(II) DBMs have been reported,[4−6] but these metal centers

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differ too much from Ni(II) and Zn(II) to allow sound comparisons. A key problem for the present study was the preparation of single crystals of nickel DBM suitable for single-crystal X-ray analysis. The compound has low solubility in neutral organics, while contact with solvents containing oxygen or nitrogen donor atoms results in bonding of the solvents to the coordinatively unsaturated [Ni(DBM)$_2$] unit. The problem has been overcome by heating the powdered solid under a layer of aromatic solvent, a procedure initially developed to grow crystalline inclusion compounds from mutually insoluble mixtures.[7]

## Experimental Section

**Nickel(II) DBM, Light-Green Form.** This form of the complex salt was prepared in two steps (eqs 1 and 2). A solution of dibenzoylmethane, $C_6H_5COCH_2COC_6H_5$, (Aldrich, 98%; 4.49 g, 20 mmol) in 90% ethanol (150 mL) was added to a hot solution of nickel acetate tetrahydrate (2.49 g, 10 mmol) in 90% ethanol (150 mL). The mixture was allowed to cool while being stirred for at least 1 h. The light-green crystalline precipitate was separated, rinsed with 90% ethanol, and air-dried to give ca. 5.1 g (95%) of diaqua complex. This was dehydrated for 2 h at 130 °C to give the light-green final product; a mass loss of 7.0−7.3% was observed, compared to 6.7% calculated from eq 2 for Ni. Anal. Found: C, 70.9; H, 4.33. Calcd for "Ni(DBM)$_2$" ($C_{30}H_{22}NiO_4$): C, 71.3; H, 4.39.

$$Ni(CH_3COO)_2{*}4H_2O + 2(\text{H-DBM}) \xrightarrow{\text{ethanol/water}} [Ni(H_2O)_2(DBM)_2]\downarrow + 2CH_3COOH + 2H_2O \quad (1)$$

$$[M(H_2O)_2(DBM)_2] \xrightarrow{t} \text{“M(DBM)}_2\text{”} + 2H_2O\uparrow \ (M = Ni, Zn) \quad (2)$$

**Nickel(II) DBM, Brown Form.** A sample of the light-green form of the complex was placed under a layer of dried warm (70 °C) solvent (xylenes, toluene, or chlorobenzene) for 30 min or until the light-green powder completely transformed to brown prismatic crystals. These were separated from the warm supernatant fluid (drybox), rinsed with solvent, and dried. Anal. Found: C, 71.3; H, 4.35. Calcd for [Ni(DBM)$_2$] ($C_{30}H_{22}NiO_4$): C, 71.3; H, 4.39. A single crystal for X-ray study was obtained from chlorobenzene.

**Nickel(II) DBM, Green Form.** A sample of the brown form of the complex was placed in the oven (215 °C) for 30 min or until the brown prismatic crystals quantitatively transformed into green powder. Anal. Found: C, 71.7; H, 4.50. Calcd for [Ni$_3$(DBM)$_6$] ($C_{90}H_{66}Ni_3O_{12}$): C, 71.3; H, 4.39. Single crystals for X-ray study were prepared as follows: A ∼1 g sample of the brown form and ∼10 mL of 1,3,5-triisopropylbenzene (Aldrich, 97%) were sealed in an ampule which was first heated for a short time to 230 °C. At this point a small quantity of the powdered green form under a pale-green solution was observed. Then, upon slow cooling of the ampule to room temperature at a rate of 10 deg/h, green blocks grew. The separated crystals showed no signs of decay in air at room temperature over several weeks.

**Nickel(II) DBM−Benzene Inclusion, 1:$^2/_3$.** A sample of the brown form of the complex was placed under dried warm (70 °C) benzene (sealed ampule) for several days until the brown prisms completely recrystallized into green plate crystals of the inclusion compound. The product was separated and kept in a tightly closed container to avoid escape of the benzene guest. Anal. Found: C, 73.3; H, 4.70. Calcd for [Ni$_3$(DBM)$_6$]·2(benzene) ($C_{102}H_{78}Ni_3O_{12}$): C, 73.3; H, 4.70.

**Zinc(II) DBM, Monomeric Form.** The method was very similar to that for the nickel analogue (light-green form). Starting from zinc acetate dihydrate (2.20 g, 10 mmol), 3.6 g (65%) of pale pearly diaqua complex was prepared; its dehydration (mass loss of 6.9% compared to 6.6% calculated from eq 2 for Zn) yielded the white final product. Anal. Found: C, 70.2; H, 4.30. Calcd for [Zn(DBM)$_2$] ($C_{30}H_{22}O_4Zn$): C, 70.4; H, 4.33. The compound was recrystallized from chlorobenzene.

**Zinc(II) DBM, Dimeric Form.** The polymorph of the complex was prepared as large (up to 5 mm) isometric blocks by slow evaporation of a solution of the monomeric form in benzene at 70 °C. The crystals were separated and rinsed with the solvent. Anal. Found: C, 70.8; H, 4.33. Calcd for [Zn$_2$(DBM)$_4$] ($C_{60}H_{44}O_8Zn_2$): C, 70.4; H, 4.33.

**Powder Diffraction Measurements.** Powder patterns were recorded on a Rigaku Geigerflex diffractometer (Co Kα radiation, $\lambda = 1.7902$ Å) in a 5−30° $2\theta$ range, 0.02° step scan, 1 s per step. The observed diffraction patterns were compared with those calculated from single-crystal diffraction measurements (using room-temperature unit cell dimensions).

**Differential Scanning Calorimetry (DSC) Measurements.** Samples of 5−10 mg were pressed inside aluminum pans, and the DSC curves were recorded at a 5 deg/min heating rate using a 2920 modulated differential scanning calorimeter (TA Instruments). Samples of each polymorph were used from two independent syntheses.

**Magnetic Susceptibility Measurements.** Magnetic susceptibilities ($\chi_M$) were determined using samples of 70−150 mg, on an Evans balance.[8] Two or three determinations were made, and the experimental data were corrected for the ligand diamagnetism and the temperature-independent paramagnetism ($N_\alpha = 230 \times 10^{-6}$ cm$^3$/mol per Ni atom). Magnetic moments were obtained from the relation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

**NMR Spectroscopy.** $^{13}$C cross-polarization/magic angle spinning (CP/MAS) NMR spectra 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 $^1$H decoupling during signal acquisition. $^1$H 90° pulse lengths were 2.7 μs, CP times were 1−3 ms, and recycle times were 2−60 s, depending on the sample. Dipolar dephased spectra[9] were obtained by interrupting the $^1$H decoupling for 40 μs 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 6.1−6.6 kHz to avoid overlap of spinning sidebands with any of the isotropically shifted lines.

**Single-Crystal Diffraction Analysis.** Single crystals were cooled rapidly to −100 °C, at which temperature full X-ray diffraction experiments were performed. A Siemens SMART CCD X-ray diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) was used. Full data sets were collected using the $\omega$ scan mode over the $2\theta$ range of 3−58°. An empirical absorption correction utilized the SADABS routine associated with the Siemens diffractometer. The final unit cell parameters were obtained using the entire data set.

The structures were solved and refined using the SHELXTL package.[10] Solution was accomplished by using direct methods followed by differential Fourier syntheses. Structural refinement was performed on $F^2$ using all data with positive intensities. Non-hydrogen atoms were refined anisotropically except for the atoms of the minor orientation of the benzene guest molecule. Hydrogen atoms were refined isotropically with thermal factors 1.2 or 1.5 times greater than those for the adjacent carbon atoms. The hydrogen atoms of the minor benzene orientation in [Ni$_3$(DBM)$_6$]·2(benzene) were fixed in calculated positions as "riding" on the corresponding carbon atoms. For this structure, two guest benzene orientations were refined with complementary occupancy.

A summary of the crystal data and experimental parameters is given in Table 1. For the atom numbering schemes see the figures. Complete results can be found in the Supporting Information.

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**Table 1.** Summary of Low-Temperature Single-Crystal X-ray Experiments

| compound | $[Ni(DBM)_2]$ (brown form) | $[Ni_3(DBM)_6]$ (green form) | $[Ni_3(DBM)_6]$·2(benzene) | $[Zn(DBM)_2]$ | $[Zn_2(DBM)_4]$ |
|---|---|---|---|---|---|
| empirical formula | $C_{30}H_{22}NiO_4$ | $C_{90}H_{66}Ni_3O_{12}$ | $C_{102}H_{78}Ni_3O_{12}$ | $C_{30}H_{22}O_4Zn$ | $C_{60}H_{44}O_8Zn_2$ |
| fw | 505.2 | 1515.6 | 1671.8 | 511.9 | 1023.7 |
| space group | *C*2/*c* (no. 15) | $P2_1/n$ (no. 14) | $P2_1/c$ (no. 14) | $P\bar{1}$ (no. 2) | *C*2/*c* (no. 15) |
| *a*, Å | 26.502(3) | 13.819(2) | 17.670(2) | 10.288(2) | 25.792(3) |
| *b*, Å | 5.774(1) | 16.252(2) | 20.945(3) | 10.716(2) | 7.274(1) |
| *c*, Å | 16.456(2) | 17.358(2) | 11.209(2) | 12.243(2) | 24.307(2) |
| α, deg | | | | 89.19(1) | |
| *β*, deg | 116.03(1) | 108.28(1) | 102.57(1) | 75.39(1) | 90.58(1) |
| *γ*, deg | | | | 64.18(1) | |
| *V*, Å$^3$ | 2262.7(5) | 3701.6(8) | 4049(1) | 1168.6(4) | 4560(1) |
| *Z* | 4 | 2 | 2 | 2 | 4 |
| $\rho_{calcd}$, g cm$^{-1}$ | 1.483 | 1.360 | 1.371 | 1.455 | 1.491 |
| $\mu$, cm$^{-1}$ | 8.94 | 8.20 | 7.57 | 10.87 | 11.14 |
| *T*, °C | 100 | 100 | 100 | 100 | 100 |
| R1(*F*)[a] | 0.025 | 0.026 | 0.027 | 0.028 | 0.024 |
| wR2($F_o^2$)[b] | 0.066 | 0.067 | 0.069 | 0.066 | 0.062 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\{\sum[w(F_o^2)^2]\}^{1/2}$.

**Table 2.** Room-Temperature Unit Cell Parameters from Single-Crystal X-ray Experiments

| compound | $[Ni(DBM)_2]$ (brown form) | $[Ni_3(DBM)_6]$ (green form) | $[Ni_3(DBM)_6]$·2(benzene) | $[Zn(DBM)_2]$ | $[Zn_2(DBM)_4]$ |
|---|---|---|---|---|---|
| *a*, Å | 26.741(8) | 13.928(3) | 17.930(3) | 10.307(3) | 25.908(4) |
| *b*, Å | 5.791(1) | 16.404(3) | 21.077(4) | 10.719(4) | 7.397(1) |
| *c*, Å | 16.703(4) | 17.422(5) | 11.284(2) | 12.480(6) | 24.367(3) |
| α, deg | | | | 88.32(2) | |
| *β*, deg | 116.64(1) | 108.44(1) | 102.27(1) | 75.71(1) | 90.47(1) |
| *γ*, deg | | | | 63.94(1) | |
| *V*, Å$^3$ | 2312(1) | 3776(2) | 4167(1) | 1195.3(8) | 4670(1) |
| Z | 4 | 2 | 2 | 2 | 4 |
| $\rho_{calcd}$, g cm$^{-1}$ | 1.451 | 1.333 | 1.332 | 1.422 | 1.456 |
| no. of used reflns | 196 | 574 | 373 | 220 | 601 |

**Table 3.** List of the Forms of Nickel(II) and Zinc(II) DBMs Isolated

| compound | molecular formula | stability[a] | color | $\mu_{eff}$ ($\mu_B$) per metal atom |
|---|---|---|---|---|
| nickel(II) DBM | $Ni(DBM)_2$ | metastable | light green | 3.1(1) |
| nickel(II) DBM | $[Ni(DBM)_2]$ | stable <202 °C | brown | diamagnetic |
| nickel(II) DBM | $[Ni_3(DBM)_6]$ | stable >202 °C | green | 3.22(5) |
| nickel(II) DBM, clathrate with benzene | $[Ni_3(DBM)_6]$·2(benzene) | stable in dry benzene | green | 3.25(5) |
| zinc(II) DBM | $[Zn(DBM)_2]$ | stable >140 °C | colorless | diamagnetic |
| zinc(II) DBM | $[Zn_2(DBM)_4]$ | stable <140 °C | colorless | diamagnetic |

[a] Note: This is the thermodynamic stability; all of the compounds exist at room temperature in air for kinetic reasons.

For compatibility with the X-ray powder diffractograms and comparisons with other structures, unit cell parameters of the single crystals were measured as well at room temperature, using several dozen frame $\omega$ scans. The parameters are listed in Table 2.

## Results and Discussion

**Isolation and Stability of Individual Compounds.** A list of isolated polymorphs of nickel and zinc DBMs is given in Table 3. The gross compositions of the compounds follow from the mass changes observed during the preparation and/or from elemental analysis. In each case the composition, along with the structural properties, is consistent with the single-crystal X-ray study (five compounds; molecular formulas derived therefrom are given) and $^{13}C$ NMR results (for three diamagnetic compounds). The phase purity of the isolated products is demonstrated by comparison of their powder patterns with those calculated from single-crystal X-ray diffraction data (Figure 1). Qualitatively, the chemical identity of each polymorph can be seen from properties such as color, magnetic properties, and relative stability. Although all the compounds have been isolated and can exist at room temperature in air, some of them are not thermodynamically stable under these conditions and may undergo transformation to stable forms catalyzed by humidity or organic solvents, or induced by heating. Besides pure polymorphs, nickel DBM forms an inclusion compound with benzene; its characteristics are also given in Table 3.

Crude nickel and zinc DBMs are prepared by dehydration of their diaqua complexes, $[M(H_2O)_2(DBM)_2]$,[11,12] the latter most probably possessing molecular structure similar to that of $[M(H_2O)_2(acac)_2]$ (acac = acetylacetonate).[13] According to the powder X-ray patterns, the diaqua complexes of nickel and zinc DBMs are isostructural (Figure 1, patterns 1 and 6). The dehydrated powder products correspond to stoichiometry $M(DBM)_2$ and show crystallinity (Figure 1, patterns 2 and 7) but differ from each other. Both are metastable. The formation of stable forms apparently requires recrystallization. During the dehydration process the hydrophobicity and thermal stability of the compounds inhibit the formation of a liquid interphase boundary layer that would facilitate recrystallization.

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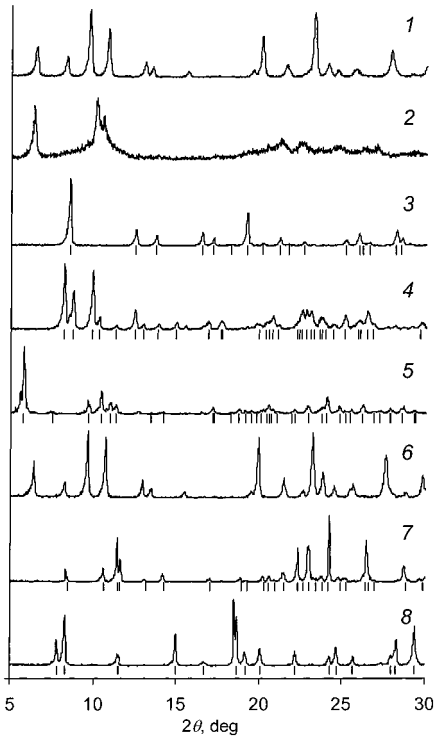
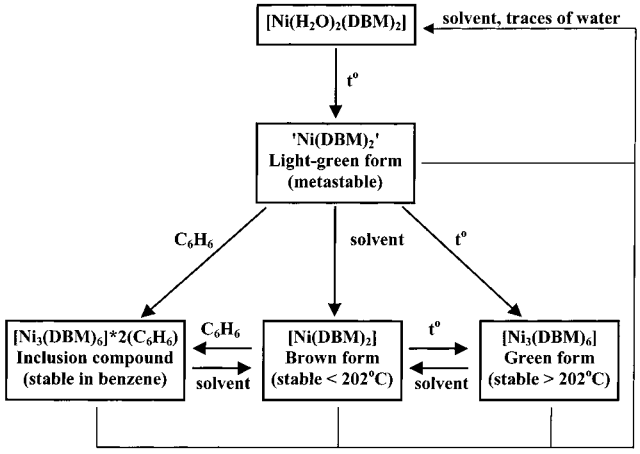



**Figure 1.** Powder X-ray diffractograms of (1) $[Ni(H_2O)_2(DBM)_2]$, (2) $Ni(DBM)_2$ (light-green form), (3) $[Ni(DBM)_2]$ (brown form), (4) $[Ni_3(DBM)_6]$ (green form), (5) $[Ni_3(DBM)_6]\cdot 2(benzene)$, (6) $[Zn(H_2O)_2(DBM)_2]$, (7) $[Zn(DBM)_2]$, and (8) $[Zn_2(DBM)_4]$. The vertical bars show the positions of the main reflections (>5% of the strongest reflection intensity) calculated from the single-crystal data (where available). Radiation: Co *K*α, $\lambda = 1.7902$ Å.

**Scheme 1**




Phase interconversions for nickel DBM are depicted in Scheme 1. Although the dehydration product is thermodynamically metastable and shows some dispersity (Figure 1, pattern 2), it is stable in air and nonhygroscopic. In organic solvents (chlorobenzene, toluene, xylenes) the light-green powder quickly transforms into brown prisms of a stable polymorph containing monomeric $[Ni(DBM)_2]$ complexes. If left under solvent in air, the crystals eventually convert back to the diaqua complex. Organic solvents thus catalyze both polymorphous and hydration processes, apparently through recrystallization.

Figure 2 shows the DSC thermogram for the brown form: it is stable up to 202 °C, at which temperature it transforms into a green form with an enthalpy of the polymorphous transformation at this temperature of 9.6(3) kJ/mol (of monomer). The

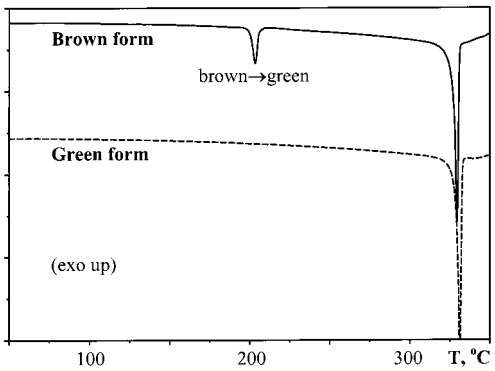



**Figure 2.** DSC thermograms of the brown and green forms of nickel DBM shown as heat flow (arbitrary units) versus temperature (°C). The brown-to-green polymorph transformation occurs at 202 °C, and melting of the green form at 330 °C. Sample mass: 6.50 and 7.56 mg for the brown and green forms, respectively.

rest of the thermogram is similar to that of the pure green form (Figure 2b), showing melting at ~330 °C. The green form contains trimers, with linear $Ni_3$ clusters surrounded by bridging and/or chelating DBM ligands. The back conversion of the green form to the brown form is hindered kinetically and occurs readily only under a layer of warm solvent.

Unlike substituted benzenes, benzene itself, acting as a template, is capable of redirecting the whole process into an essentially new product, $[Ni_3(DBM)_6]\cdot 2(benzene)$. This inclusion compound contains trimers similar to those found in the green form. The trimers thus can form a room-temperature stable phase with the help of an included guest.

Crude zinc DBM contains monomeric $[Zn(DBM)_2]$ units; the crystals of this compound were obtained from chlorobenzene. From benzene a dimeric form containing $[Zn_2(DBM)_4]$ molecules was isolated. The crystalline monomeric form shows no change until 222 °C, at which temperature a strong endotherm of 36.3(2) kJ/mol (DSC) indicates melting followed by an irreversible (exothermal) change above 240 °C. DSC of the dimeric form shows a small endotherm of irregular shape in the 140−175 °C range, with the rest of the thermogram identical to that of the monomeric form. From these observations it is seen that the dimeric form is thermodynamically stable below 140 °C while the monomeric form is stable at higher temperatures.

**Magnetic Properties.** All the green Ni compounds are paramagnetic, with the value of $\mu_{eff}$ indicating two unpaired electrons per Ni atom (Table 3). This is consistent with a high-spin-state Ni center coordinated octahedrally. This presumes sharing of DBM ligands between two or more Ni centers, thus implying polymerization of coordination units. Indeed, in two compounds (Table 3) the existence of trimeric units has been demonstrated. At the same time, the brown form of nickel DBM is diamagnetic, which indicates a low-spin-state Ni center characteristic of square planar complexes of Ni(II).

**Structure of Brown $[Ni(DBM)_2]$.** The structure is monoclinic, *C*2/*c*. Electrically neutral molecules of $[Ni(DBM)_2]$ are assembled with only van der Waals interactions, with four molecules per unit cell. Features of the crystal packing are very similar to those in the isostructural[14] Pd(II) and Cu(II) complexes (reported in refs 4 and 5, respectively) and are not described here. The nickel atom resides on an inversion center and has a

(14) The $[Pd(DBM)_2]$ and $[Cu(DBM)_2]$ were solved in the *I*2/*c* space group. The primitive unit cell for $[Ni(DBM)_2]$ (at room temperature, $a = 5.767$ Å, $b = 13.567$ Å, $c = 16.232$ Å; $\alpha = 108.95°$, $\beta = 100.22°$, $\gamma = 102.21°$) may be transformed both to monoclinic *C* ($a = 26.521$ Å,

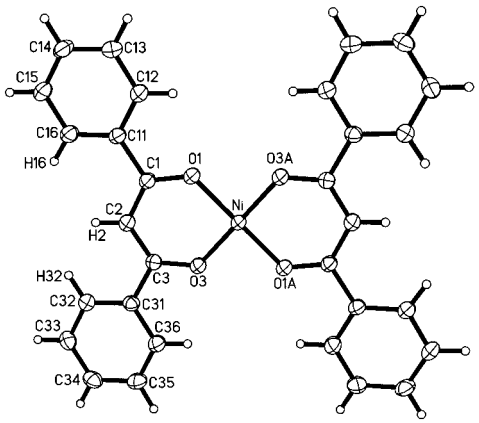



**Figure 3.** ORTEP drawing of the [Ni(DBM)$_2$] molecule in the brown form of nickel DBM.

square planar environment defined by four oxygen atoms from the chelating DBM ligands (Figure 3). The absence of apical coordination and shortened Ni−O bonds (1.845 Å to O1 and 1.836 Å to O3)[15] are consistent with the observed low-spin state of the nickel center arising from tetragonal distortion characteristic of $d^8$ and $d^9$ cations.

The bischelate fragment is planar; the bond lengths for C−O (1.28 Å) and C−C (1.40 Å) imply strong conjugation in the chelate rings. The C−C distance for bonds joining chelate and phenyl rings (<1.50 Å) is close to a value for the bond between aryl systems in biphenyls.[16] The whole molecule is nearly planar, with average and maximal deviations of atoms from the least-squares plane of 0.09 and 0.3 Å, respectively. Due to steric problems the molecule cannot adopt ideal planarity (there would be an overlap of the chelate ring hydrogen with the *ortho* hydrogens of the phenyl rings). This is avoided partially by a slight turning of the phenyls; the C11−C16 ring bends by 3.6° and the C31−C36 ring rotates by 9.0° with respect to the bischelate fragment. This results in H2−H16 and H2−H32 contacts of 2.09 and 2.13 Å, respectively, which are slightly shorter than the sum of hydrogen van der Waals radii (2.32 Å).[17] The tendency of the molecule to planarity may be explained by applying a geometry favoring delocalization of electron density over the local aromatic systems.

The observed features are observed also in the crystal structure of dibenzoylmethane (H-DBM) itself, the molecule appearing in the enol form in two polymorphic modifications of the protonated ligand.[18,19] Although neither C−O nor C−C bonds of the chelate ring are equivalent, the conjugation seems apparent, both from the bond lengths and from the planarity of the whole fragment clamped by the enol hydrogen. The phenyl rings again reveal the tendency to go into the chelate plane, turning by 4° and 17° (in the stable polymorph) or 8° and 24° (in the metastable polymorph) to overcome $H_{Ph}$–$H_{chelate}$–$H_{Ph}$ repulsion.

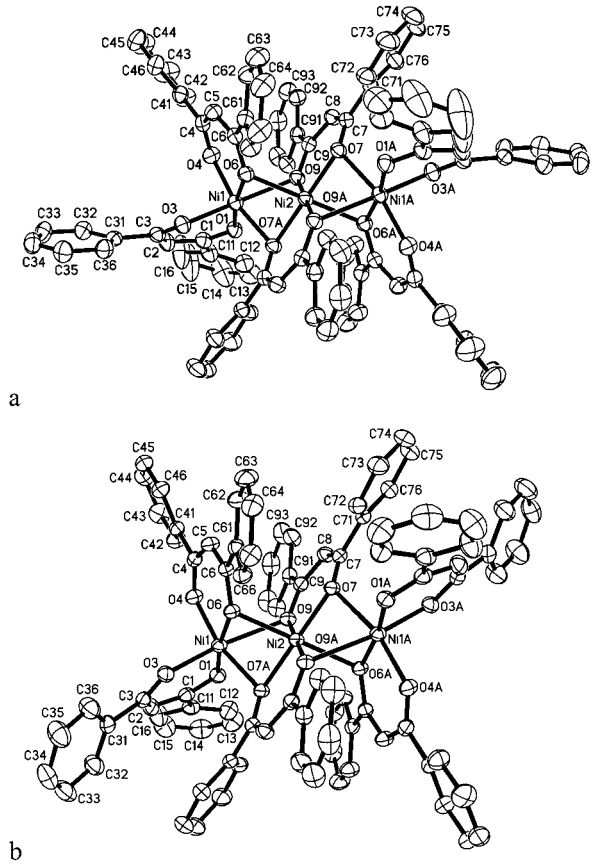



**Figure 4.** ORTEP drawing of the [Ni$_3$(DBM)$_6$] molecules found in the green form of nickel DBM (a) and in its benzene clathrate (b). H atoms are omitted.

In the structure of [Ni(DBM)$_2$] it is the nickel cation that clamps the ring and closes the delocalized $\pi$-system of the fragment through the nickel orbitals and allows merging of the two DBM systems to give a common state embracing the entire molecule. In addition to the isostructural Pd(II)[4] and Cu(II)[5] DBMs other complexes with substituted DBMs of Ni(II), Pd(II),[20] and Cu(II)[21] exhibit similar tendencies in that the bischelate fragments are planar and the phenyl rings deviate by no more than 20° from the plane. Sn(II) DBM is a non-transition-metal analogue that is essentially nonplanar.[6]

**Structure of Green [Ni$_3$(DBM)$_6$].** The structure is monoclinic and has been solved in the $P2_1/n$ space group. This form of nickel DBM differs dramatically from the brown polymorph not only in its crystal structure but also in its molecular organization. There is molecular packing of trimeric nickel DBM molecules, [Ni$_3$(DBM)$_6$], with two trimers per unit cell.

The trimer is centrosymmetric (Figure 4a) with a linear Ni$_3$ cluster (Ni−Ni distance of 2.811 Å) surrounded by chelato-bridging DBM ligands. Each nickel is in a distorted octahedral environment of six oxygens from four DBM ligands. The Ni−O distances vary from 1.95 to 2.25 Å; the coordination angles vary from 76° to 98°. Despite these distortions, the total energy gain

$b$ = 5.768 Å, $c$ = 16.474 Å, $\beta$ = 116.09°) and to monoclinic $I$ ($a$ = 24.298 Å, $b$ = 5.768 Å, $c$ = 16.474 Å, $\beta$ = 101.42°). With the latter choice the isostructural relationship to the Pd and Cu compounds becomes apparent.

(15) Here, and in the remainder of the text, the derived numerical values are given with estimated errors less than the last meaningful figure.

(16) *CRC Handbook of Chemistry and Physics*; Lide, D. R., Ed.; Frederikse, H. P. R., Assoc. Ed.; CRC Press: New York, 1997; Section 9-1.

(17) The following system of van der Waals radii (Å) has been used: C, 1.71; H, 1.16; O, 1.29 (a); Ni, 1.63; Zn, 1.39 (b). (a) Zefirov, Yu. V.; Zorkii, P. M. *Russ. Chem. Rev.* **1995**, *64*, 415−428 and refs 3−6 therein. (b) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441−451.

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upon formation of these six bonds compared to four bonds in the brown form must favor the cluster formation.

More than 300 structures with direct chemical Ni−Ni interactions have been reported. These comprise $Ni_2$ clusters,[22] $Ni_3$ bent clusters,[23] and triangular,[24] square,[25] pentagonal,[26] hexagonal,[27] tetrahedral,[28] octahedral,[29] cubic,[30] and pentagonal prismatic or antiprismatic clusters,[31] with the Ni−Ni distance varying from 2.3 to 3.3 Å. In organometallic compounds incorporating Ni(0) clusters the length for the Ni−Ni single bond is typically between 2.3 and 2.6 Å. In Ni(II) complexes the nickel clusters are surrounded by polydentate-bridging ligands; the Ni−Ni distance varies continuously up to the sum of the atomic van der Waals radii,[17] 3.3 Å, at which point the chemical interaction may be considered to be insignificant. Using special polydentate ligands, complexes comprising linear $Ni_4$,[32] $Ni_5$,[33,34] and $Ni_7$[34] and cyclic $Ni_{12}$ clusters[35] were recently prepared, with the Ni−Ni distance varying between 2.3 and 3.1 Å. Linear $Ni_3$ trimers have been found for nickel complexes with acetylacetonate,[36] its 3-substituted derivatives,[37] and some other ligands,[38] the Ni−Ni distance varying between 2.4 and 3.1 Å. The trimerization may be explained as a means of achieving octahedral coordination, as the trimer is the smallest polymeric unit in which octahedral coordination of all the nickel atoms can be accomplished provided there is no intermolecular sharing of oxygen atoms. Bulky substituents were shown to suppress trimerization of nickel acetylacetonate derivatives due to steric hindrance.[39,40] Moreover, when passing from the molecular level to 3D packing, the trimer molecule yields to simpler units to satisfy packing requirements. This is probably the main reason only a few trimeric nickel complexes of this type have been found so far in the solid state.

There are three types of DBM units in the trimer molecule (Figure 4a). The first (O1, O3, etc.) and second (O4, O6, etc.) chelate to the terminal nickels with Ni−O distances of 1.95−2.02 Å, while the second also bridges one donor oxygen (O6) to the central nickel (Ni2) at 2.11 Å. As these ligands coordinate in the *cis* mode, the chelate rings surrounding the nickel atom are not coplanar and cannot interact. The third type (O7, O9, etc.) coordinates to all three nickel atoms, chelating the central one at 1.97−1.99 Å and bridging the terminal atoms at 2.16 (Ni1A−O7) and 2.25 (Ni1−O9) Å. These ligands chelate to the central atom in the *trans* mode, so that their chelate rings are coplanar and may interact. Qualitatively the trimeric molecule is quite similar to trimeric nickel acetylacetonate,[36] except that in that molecule the Ni−Ni distance is longer, 2.86−2.88 Å. But, as compared with the $[Ni_3(acac)_6]$ trimer, the $[Ni_3(DBM)_6]$ molecule has greater conformational freedom; the phenyl rings rotate from the corresponding chelate rings (which are planar within 0.1−0.2 Å) by 29.7° (C11‴), 37.5° (C31‴), 28.2° (C41‴), 24.1° (C61‴), 30.7° (C71‴), and 21.5° (C91‴). This 22−38° range in the angles indicates the molecule's ability to respond to crystal packing requirements.

It should be noted that the green form is thermodynamically stable above 202 °C and the structure was studied at −100 °C. Although there should be no significant changes in molecular structure or packing mode, the metastable phase is more than 300° away from the conditions of its stability. Crystal packing of the trimers in the structure is shown in Figure 5a. The van


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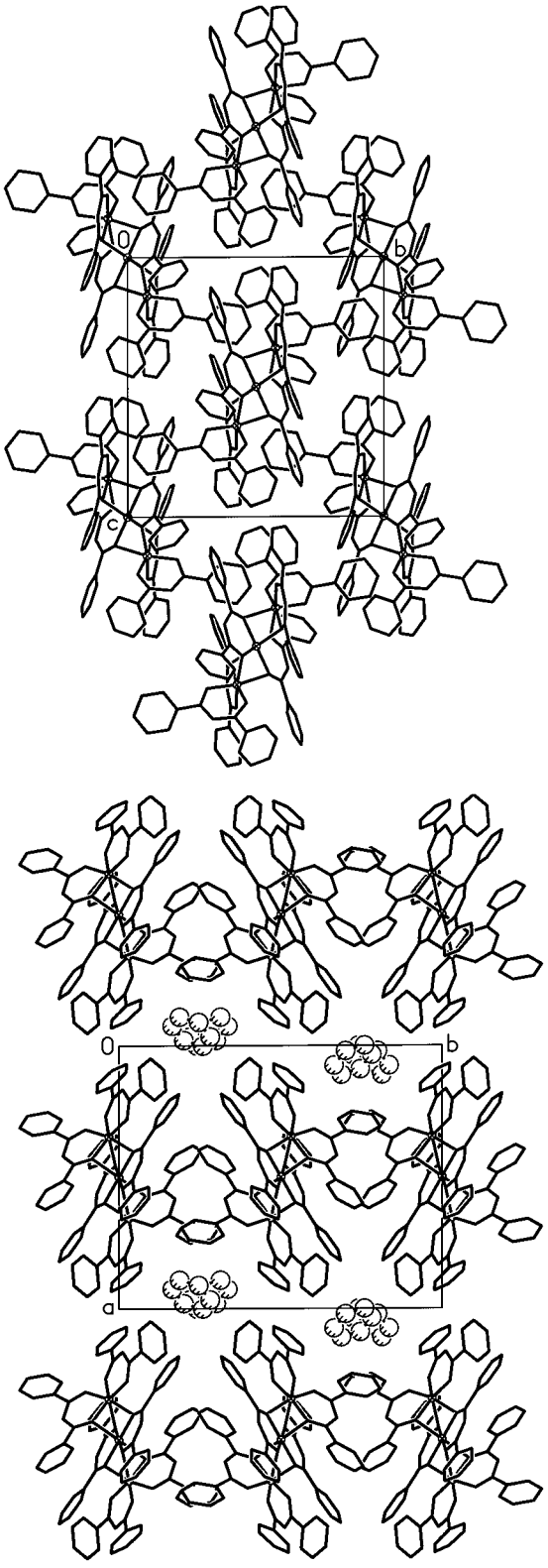


**Figure 5.** Two projections showing the dense packing of $[Ni_3(DBM)_6]$ molecules in the green form (a, top) and packing of the same molecules leaving channels in $[Ni_3(DBM)_6]\cdot 2$(benzene) (b, bottom). For clarity, guest atoms are enlarged and H atoms are omitted.

der Waals shape of the trimer may be roughly approximated as an ellipsoid with prominent phenyl substituents. In the projection along the *a* axis the staggered packing order of these bulky molecules is apparent.

**Structure of the $[Ni_3(DBM)_6]\cdot 2$(Benzene) Inclusion Compound.** The structure is monoclinic, $P2_1/c$. It shows molecular

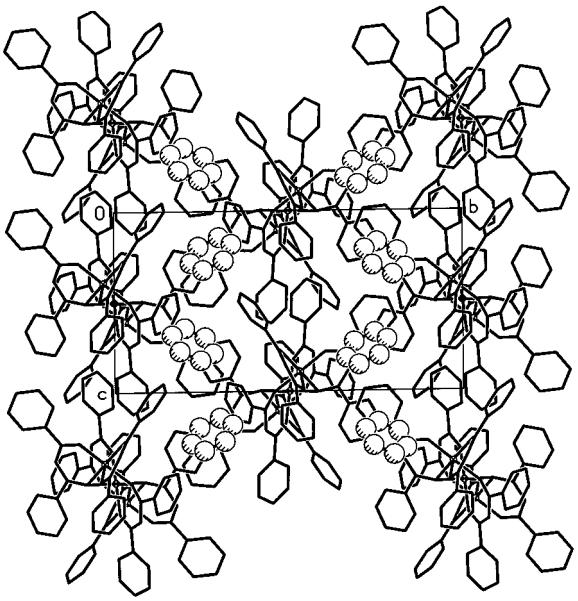


**Figure 6.** Cut-away view of the $[Ni_3(DBM)_6]\cdot 2$(benzene) structure displaying guest benzene molecules (enlarged atoms) in wavy channels going along the *c* axis. H atoms are omitted.

packing of trimeric nickel DBM molecules (host) and benzene molecules (guest) located in channel-like cavities. There are two host and four guest molecules per unit cell, resulting in a molecular formula of "$Ni(DBM)_2\cdot{}^2/_3$(benzene)".

The molecular structure of the host trimer is very similar to that found in the green form (Figure 4). It is also centrosymmetric, and the Ni−Ni distance in the linear $Ni_3$ cluster equals 2.831 Å, with the same mode of ligand coordination. The octahedral environment of the Ni centers is more distorted, with Ni−O distances from 1.95 to 2.32 Å and coordination angles from 80° to 100°. Two DBM ligands (O1, O3, etc. and O4, O6, etc.) chelate to terminal nickels with Ni−O distances of 1.95−2.03 Å, and the second also bridges (by O6) to the central nickel (Ni2) at 2.14 Å. The third ligand (O7, O9, etc.) coordinates to all three nickel atoms, chelating the central one at 1.97−1.99 Å and bridging the terminal atoms at 2.15 (Ni1A−O7) and 2.32 (Ni1−O9) Å.

The packing problem in the inclusion compound is solved partially by rotating the phenyls with respect to the corresponding chelate rings by dihedral angles of 29.1° (C11···), 31.3° (C31···), 20.0° (C41···), 16.9° (C61···), 31.5° (C71···), and 17.3° (C91···). This 17−32° range is significantly shifted compared to 22−38° for the green form, indicating improved planarity of the DBM moieties and thus better predisposition of their aromatic systems to interact.

Another factor facilitating crystal packing is the guest benzene filling up the residual cavity space. Figure 5 compares the packing mode in the green form (a) and in the inclusion compound (b). A dislocation of the bulky trimeric molecules leaves cavities which form individual channels stretching along the *c* crystallographic axis. The channel walls are composed of phenyl moieties. The benzene molecules are disordered. Figure 6 shows a wavy section of the channels and the accommodation of benzene molecules (main orientation) therein. No contacts implying specific interaction between host and guest molecules have been found in the structure. The $Ni_3$ cluster is separated from the benzene molecules by at least 4.4 Å.

**Structure of Monomeric $[Zn(DBM)_2]$.** The structure is triclinic, $P\bar{1}$, with two molecules per unit cell. There are only van der Waals contacts between molecules. The molecule is

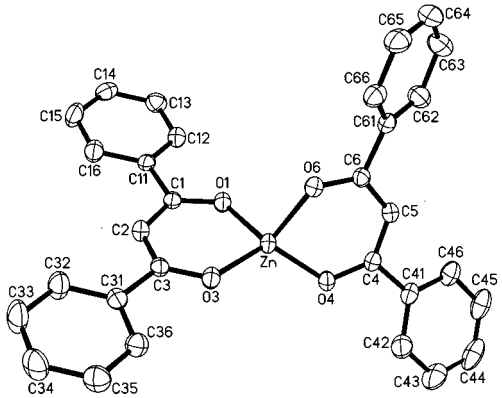


**Figure 7.** ORTEP drawing of the $[Zn(DBM)_2]$ molecule in the monomeric form of zinc DBM. H atoms are omitted.

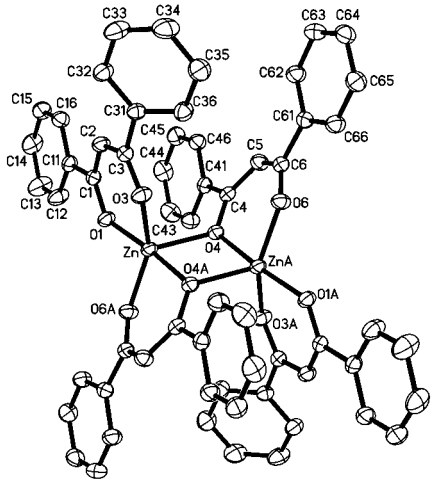


**Figure 8.** ORTEP drawing of the $[Zn_2(DBM)_4]$ molecule in the dimeric form of zinc DBM. H atoms are omitted.

asymmetric (Figure 7). The zinc atom is chelated with two DBM ligands, one at 1.947 (Zn−O1) and 1.915 (Zn−O3) Å and the second at 1.933 (Zn−O4) and 1.971 (Zn−O6) Å. The coordination polyhedron is a very distorted tetrahedron; the coordination angles vary from 95° to 124°, and the dihedral angle between the planes of the chelate rings is 100.6°. The phenyl rings are rotated from the corresponding chelate rings by +11.0° (C11···C16), −11.6° (C31···C36), +30.0° (C41···C46), and −39.4° (C61···C66). The significant inequivalence of the two DBM units is also apparent in the MAS $^{13}C$ NMR spectra, as described below. In general, the observed tetrahedral coordination to Zn(II) is common and was found, for instance, for the analogous $\beta$-diketonate zinc bis(dipivaloylmethanate).[41] The observed distortions may be attributed to the stress of creating dense molecular packing.

**Structure of Dimeric $[Zn_2(DBM)_4]$.** The structure is monoclinic, *C*2/*c*. There are four dimeric molecules per unit cell, and there are only van der Waals contacts between the dimers. The dimer is centrosymmetric. Two ligands chelate to zinc by four oxygen donors while one oxygen also bridges to a neighboring zinc center (Figure 8). The coordination environment of the zinc atom is intermediate between trigonal bipyramidal (with central Zn and apical O1 and O4A) and square pyramidal (with central Zn and apical O4), with average angular deviations from the ideal polyhedra of 9.5° and 10.1°, respectively. One ligand (O1, O3, etc.) chelates to a zinc center at 1.986 (O1) and 1.981 Å (O3). Another one (O4A, O6A, etc.) chelates to zinc at 2.087 (O4A) and 1.983 (O6A) Å but also bridges to the neighboring zinc (ZnA−O4A) at 2.071 Å. The Zn−Zn distance is 3.14 Å. The dihedral angle between two chelate rings of 37.3° excludes significant interaction between the chelate systems. The phenyl rings rotate from their adjacent chelate rings by +14.7° (C11···), +35.0° (C31···), −18.9° (C41···), and +16.5° (C61···). As described below, the inequivalence of the DBM units in the dimer is also observed in the MAS $^{13}C$ NMR spectra.

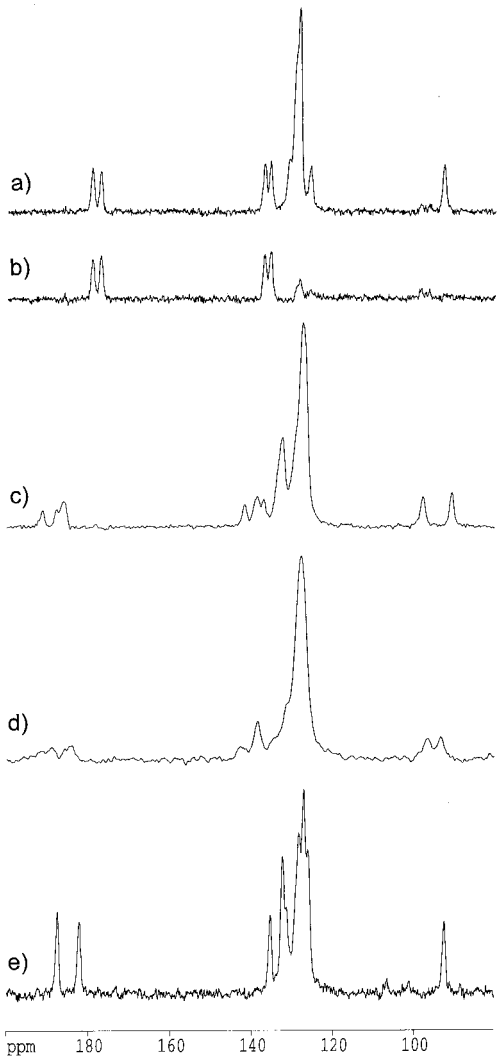


**Figure 9.** Solid-state $^{13}C$ CP/MAS NMR spectra of (a) $[Ni(DBM)_2]$, brown form, (b) $[Ni(DBM)_2]$, brown form, dipolar dephased, (c) $[Zn(DBM)_2]$, (d) $[Zn_2(DBM)_4]$, and (e) H-DBM.

Analogous zinc dimers have been reported for complexes with bridge-chelating ligands of other types,[42] but for zinc acetylacetonate a trimeric structure has been reported.[43]

**MAS $^{13}C$ NMR Spectra.** $^{13}C$ CP/MAS NMR spectra of the diamagnetic metal DBM compounds and the parent H-DBM are shown in Figure 9, and shifts and assignments are given in Table 4. As a whole, the data confirm both the gross composition

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**Table 4.** Assignments of $^{13}C$ NMR Resonances in DBM Metal Complexes[a]

| | C2 (>C−H) | C1 (C−O) | C11 (*ipso*) | C12/C13 (*o*/*m*)[b] | C14 (*p*)[b] | pyridine |
|---|---|---|---|---|---|---|
| H-DBM | 93.4 | 185.6 | 134.3 | 127.5 (*o*) | 133.6 | |
| ($SO_2$ soln at 60 °C)[c] | | | | 129.2 (*m*) | | |
| H-DBM | 92.6 | 187.7 | 135.6 | 128.8 | 131.8 | |
| (solid) | | 182.4 | 132.7 | 127.5 | 129.5 | |
| | | | | 126.4 | | |
| | s[d] | d | d | 2q | d | |
| [Ni(DBM)$_2$] | 92.9 | 179.4 | 137.3 | 129.6 | 131.2 | |
| (brown form) | | 177.4 | 135.8 | 129.0 | 129 | |
| | | | | 125.9 | | |
| | s | d | d | 2q | d | |
| [Zn(DBM)$_2$] | 97.8 | 191.3 (1)[e] | 141.9 (1) | 129 | 132.8 br d | |
| | 90.6 | 187.9 (1) | 138.8 (2) | 127.9 | | |
| | | 185.9 (2) | 137.2 (1) | | | |
| | d | q | q | 2o | q | |
| [Zn$_2$(DBM)$_4$] | 96.5 | 191.5 (1) | 142.9 (1) | 128.4 br d | 134.5 | |
| | 93.3 | 189.0 (1) | 138.7 (3) | | 132 | |
| | | 184.2 (2) | | | | |
| | d | q | q | 2o | q | |
| [ZnPy$_2$(DBM)$_2$][f] | 92.8 br d | 187.7 (1) | 142.8 (1) | 128.3 | 130135 | 149.6 (*o*) q |
| | | 186.3 (2) | 139.4 (3) | | | ? (*m*) q |
| | | 182.6 (1) | | | | 139.0 (*p*) d |
| | d | q | q | 2o | q | |
| [CdPy$_2$(DBM)$_2$][f] | 94.3 | 190.4 | 143.0 (1) | 129.6 | 133.0 | 148.8 (*o*) q |
| | 92.0 | 188.2 | 141.6 (1) | 128.0 | 131.2 | 125.0 (*m*) q |
| | | 187.1 | 140.2 (2) | | | 138.7 (*p*) d |
| | | 183.7 | | | | |
| | d | q | q | 2o | q | |

[a] For the atom numeration scheme see Figure 3. [b] C12, C13, C14 (*o*, *m*, *p*) = *ortho*, *meta*, and *para* carbons of the phenyl rings. [c] Olah, G. A.; Grant, J. L.; Westerman P. W. *J. Org. Chem.* **1975**, *40*, 2102−2108. [d] Multiplicities expected from X-ray structures: s, d, q, and o refer to singlet, doublet, quartet, and octet. [e] Numbers in parentheses refer to the quartet intensity distribution. [f] The structure of these materials has been discussed previously, ref 1.

and chemical individuality of the brown Ni form and the two Zn polymorphs. $^{13}C$ MAS NMR of powdered samples is sensitive to crystallographic inequivalence of chemically equivalent sites. Therefore, independent resonances for crystallographically inequivalent carbons in the asymmetric unit are expected. In brown [Ni(DBM)$_2$] the two DBM units are identical due to an inversion center at the Ni atom, but the two halves of each unit are not equivalent (no mirror plane or $C_2$ axis). Consequently doublets are expected for the C−O bonds (C1, C3) and the *ipso* (C11, C31) and *para* (C14, C34) carbons of the phenyl rings, and quartets for the *ortho* and *meta* carbons (Figure 9a; for the atom numeration scheme see Figure 3). In the dipolar dephased spectra, illustrated for [Ni(DBM)$_2$] in Figure 9b, those carbons which have no attached H atoms show strongly. Carbons with attached H disappear completely if they are static, but if there is any motion which causes a reorientation of the C−H bond, and a consequent reduction of the dipolar coupling, then usually the resonance appears but at significantly reduced intensity. For [Ni(DBM)$_2$] the unique C−H bond (singlet), C−O bonds (doublet), and *ipso* ring carbon (doublet) are therefore readily assigned (Table 4). Many resonances of the C−H bonds of the phenyl rings are not resolved in the 125−135 ppm region (only peaks and shoulders are given values in Table 4), but a partial assignment can be made on the basis of the dipolar dephased spectra. It is quite noticeable in all the dipolar dephased spectra that there is a small amount of intensity in this region. Closer inspection reveals that this is only present for some of the peaks and shoulders. Two-fold reorientation of phenyl groups in solids is well-known,[44] and typically this causes some intensity for the *ortho* and *meta* carbons to appear in the dephased spectrum, since their C−H bonds change orientation, whereas the *para* carbon does not appear since its C−H bond lies along the 2-fold axis and does not change orientation. Sufficiently rapid reorientation could also make the two *ortho* carbons on the same ring equivalent by exchange, and likewise the two *meta* carbons, thus reducing their multiplicity by a factor of 2 from that expected from the X-ray structure.

[Zn(DBM)$_2$] shows a doubling of all lines (Figure 9c) since the two independent DBM units are distinctly different, and the whole complex is asymmetric. Quite a large splitting (7.2 ppm) of the methanate carbon (C2 and C5; see Figure 7) is observed. [Zn$_2$(DBM)$_4$] has four DBM units, but only two are crystallographically inequivalent because of an inversion center; consequently this complex also shows a doubling of lines, Figure 9d.

The H-DBM parent material (the extra H maintains charge neutrality) is present in the solid phase in the enol form,[18,19] and consequently the two halves of the molecule on either side of the >C−H bond are inequivalent. Its spectrum (Figure 9e) therefore shows a singlet for the unique >C−H bond, a doublet for the C−O bonds, and so on as for [Ni(DBM)$_2$].

Also included in Table 4 are assignments of spectra obtained for the pyridine complexes [ZnPy$_2$(DBM)$_2$] and [CdPy$_2$(DBM)$_2$] whose structures were discussed previously.[1] The present assignments for the DBM complexes facilitated the assignment of the DBM and pyridine components in these spectra.

All the NMR powder spectra are fully consistent with the X-ray structural data, and furthermore the dipolar dephasing experiments indicate 2-fold reorientational dynamics of the phenyl rings. A remarkable feature is the decrease in the shift of the C−O doublet in the [Ni(DBM)$_2$] complex as compared to all the other materials; the average shift is 6.6−9.4 ppm lower. Its average *ipso* carbon shift is also 2.6−4.7 ppm lower than those of the other complexes (but 2.4 ppm higher than that of

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H-DBM). The replacement of the enol hydrogen in H-DBM with a metal cation should lead, due to electrostatics, to an electron density decrease on all the ligand atoms. This is indeed observed to a greater or lesser extent for the Zn and Cd compounds. The opposite effect observed for the C−O carbons in $[Ni(DBM)_2]$ may be a consequence of electron donation from nickel d orbitals to the pseudoaromatic system of the bischelate fragment (geometrically favorable due to the planarity of the fragment and shortened coordination bonds).

**Main Conclusions.** The structural chemistry of nickel and zinc DBMs, the metal DBM host-type precursors, is complex. The $[MA_2(DBM)_2]$ host compounds have coordinatively saturated metal centers, and the structural stability becomes a matter of appropriate 3D packing. The possibility of the host molecule to form a *trans* or *cis* isomer is the most notable molecular feature. As the metal(II) DBMs possess a deficiency of donors for the metal acceptors, they have a potential to transform into polymeric species by sharing donor sites of DBM ligands. The diversity of metal(II) $\beta$-diketonates, including DBMs, is remarkable as monomeric,[4,5,6,20,21,41] dimeric,[45] trimeric,[36,43,46] tetrameric,[47] and even polymeric[48] entities have been studied in the solid state. Further, equilibria between monomeric and polymeric forms of nickel $\beta$-diketonates in solution have been studied,[39,40] and both monomeric and trimeric forms were recently reported for a nickel complex with 3-phenyl-substituted acetylacetonate.[37] The structural diversity revealed in the current work is unprecedented as one inclusion plus three guest-free polymorphs of one compound of nickel DBM have been isolated and characterized. For zinc DBM two polymorphs, essentially different at the molecular level, have also been prepared. On the basis of examination of all these materials, the following general conclusions may be stated.

As well as $[MA_2(DBM)_2]$ hosts, the nickel and zinc DBMs experience packing problems manifested as a tendency to structural variability (for both molecular species and polymorphs) instead of one very preferable stable form. In a broad sense the inclusion compounds also can be considered as polymorphic modifications of the host component, which are stable only in the presence of a templating guest.[49] From this viewpoint, conventional polymorphism and affinity to include are closely related to each other, and it is not surprising that they are often found together.[50] The trimeric nickel DBM species form an inclusion compound with benzene, and possibly can include other solvents as there are no specific interactions of the included species with the host matrix. Though monomeric $[Ni(DBM)_2]$ does not include, complexes of a similar structure were recently utilized to entrap such bulky molecules as fullerenes and carboranes.[51]

Magnetic and structural features of nickel DBM polymorphs indicate that polymorphism can be accompanied by isomerization/polymerization on the molecular level. The question as to whether molecular structure is responsible for formation of a given solid phase or vice versa is arguable in this case. Nevertheless, the guest benzene plays a decisive role in the formation of trimers in the $[Ni_3(DBM)_6]\cdot 2$(benzene) inclusion compound at room temperature as the guest-free green phase containing analogous trimers is stable only above 202 °C. Other solvents with chemical and physical properties similar to those of benzene were not able to stabilize this structure by virtue of their different geometry, thus resulting in a solid containing monomeric $[Ni(DBM)_2]$ units.

The monomer−trimer equilibrium for nickel acetylacetonate which occurs in solution is a well-known example in Cotton and Wilkinson's textbook.[52] The equilibrium depends on concentration and temperature and reveals a positive enthalpy of dissociation. In noncoordinating solvents both forms coexist in commensurable quantities; for more dilute solutions about 25% dissociation occurs at 160 °C.[40] Similar observations were made for other related complexes.[39,40] So, on the molecular level these two situations are similar in energy, and which one appears in the solid may be a matter of noncovalent interactions present in a potential solid phase.

Stabilization by noncovalent interactions of the metal complex molecular isomers[3] and unstable molecules[53] has been reported and is an attractive way of isolating unstable or unusual chemical species. The present study suggests an interesting means of stabilizing polymeric species by a suitable templating guest in the solid phase. Perhaps appropriate templates could control the formation of other species, of tetrameric or larger size. Unlike square planar Ni(II) complexes those containing octahedrally coordinated nickel atoms are paramagnetic, and upon formation of the nickel cluster a ferromagnetic interaction arises,[54] suggesting the possibility of controlling the physical properties

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of the material. Two more relevant examples were recently reported on the remarkable redox properties of the $Cr_3$ cluster in a complex with bis(2-pyridyl)amine[55] and a mixed-valence 1D chain of rhodium atoms, a "solvated molecular wire".[56]

Another conclusion is that, as for $[MA_2(DBM)_2]$ hosts, the tendency to planarity of the bischelate fragment is observed for nickel but not for zinc. This is quite evident from a comparison of the monomeric forms of the metal DBMs, the nickel complex showing square planar geometry and the zinc complex showing tetrahedral geometry. The remarkable planarity of $[Ni(DBM)_2]$ demonstrates that the *trans* configuration adopted by the $[MA_2(DBM)_2]$ complexes when M = Ni is controlled by the nickel bischelate unit itself. In the green form and $[Ni_3(DBM)_6]\cdot 2$(benzene) this tendency yields to providing each nickel atom with octahedral coordination and is observed only for the central nickel atom. The zinc complex does not follow this tendency at all. Note a similar distinction between trimeric nickel[36] and zinc[43] acetylacetonates; while the former incorporates a linear $Ni_3$ cluster with a planar bischelate fragment about the central nickel atom, the latter contains a bent $Zn_3$ cluster with no planar bischelate fragment present.

The present study has shown that the main properties responsible for the ability of metal DBM hosts to form supramolecular architectures are already observable in their precursors. These properties, packing problems, and the tendency to certain conformational and isomeric states become more striking upon modification of the basic metal DBM unit to yield this family of versatile host complexes.

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**Supporting Information Available:** Full data for the structure determination of five studied compounds (see Table 1) and $^{13}C$ CP/MAS NMR spectra of $[MPy_2(DBM)_2]$ (M = Zn, Cd). This material is available free of charge via the Internet at http://pubs.acs.org.

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