

Coordination and inclusion compounds formed by addition of quinoline (Q) or isoquinoline (Iq) to a metal(II) dibenzoylmethanate (Co, Ni, Zn, Cd)

Composition, structure and thermal dissociation properties

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Abstract Three isomorphous series of new compounds are reported: complexes $[M(\text{DBM})_2\text{Q}_2]$ and $[M(\text{DBM})_2\text{Iq}_2]$ ($M = \text{M(II)} = \text{Co, Ni, Zn, Cd}$; DBM is $\text{C}_6\text{H}_5\text{COCHCO}_6\text{H}_5^-$) and inclusion compounds $[M(\text{DBM})_2\text{Q}_2] \cdot \text{Q}$ ($M = \text{Co, Zn, Cd}$). All the compounds comprise a *trans* configured octahedral complex molecule. Inclusion compounds of modified Zn and Cd DBM complexes are reported for the first time and their inclusion ability is attributed to the *trans* isomeric state induced by the bulky Q or Iq ligand. The TG measurements indicate the following order of thermal stability of the complexes defined by the strength of the metal–ligand bonds: $\text{Ni} > \text{Co} > \text{Cd} > \text{Zn}$. The inclusion compounds do not follow this trend.

Keywords Metal complexes · Molecular crystals · Clathrates · DBM · *Cis–trans* isomerism · Thermal analysis · Stability

Introduction

The design and studies of new inclusion compounds (clathrates) is a major direction in supramolecular chemistry and crystal engineering [1–3]. Current and potential applications of inclusion compounds are numerous: encapsulation, storage, and controlled release of gases [4, 5] and flavors [6]; separation, purification, and specific nanoconfined reactions of chemicals [7–11]; design of highly selective chemical sensors [12, 13]; creation of new

formulations of pharmaceuticals [14] and design of bio-mimetic systems [15]. One of the most significant future applications of inclusion compounds is their use as materials that can reversibly change their structure and properties in the process of guest inclusion, the change being reproducible and individual for each particular guest [16–18].

Crystalline inclusion compounds have a crystal lattice built by the molecules of host, while the molecules of guest reside in the cavities of this lattice. No chemical bonds exist between host and guest; the solid is stabilized by favorable non-covalent interactions. The utilization of metal complexes as hosts is very convenient as whole series of new host molecules may be created by varying metal center and ligands in the complex formula [19]. Molecular host complexes as well as their inclusion compounds readily form and dissociate. Therefore, their synthesis can be well controlled thermodynamically, while thermal dissociation can be used to examine their stability and other fundamental parameters [20–23].

Our recent studies concentrated on a new type of host complexes, modified metal dibenzoylmethanates, $[M(\text{DBM})_2\text{A}_2]$, where DBM = $\text{C}_6\text{H}_5\text{COCHCO}_6\text{H}_5^-$, dibenzoylmethanate-anion, and $M = \text{M(II)}$ [24–32]. Several axial ligands A, such as pyridine, were utilized to yield a family of host molecules with so-called humming-top overall geometry [19]. In order to maintain such geometry, the complex must have *trans* configuration as shown in Fig. 1. After structural elucidation of the complexes and their inclusion compounds we became interested in better understanding what factors define the stability of these solid materials. In particular, we are interested in the role of the metal center.

In our previous studies on another type of hosts, Werner complexes, we succeeded in preparing several series of isostructural inclusions dissociating in a similar way and differing only by the metal center in the host complex in

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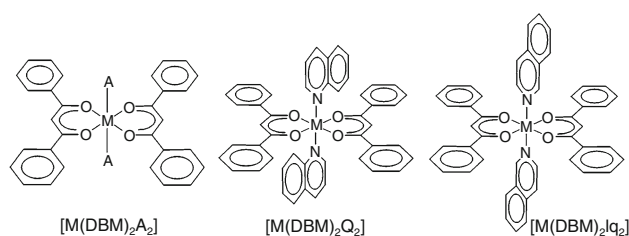


Fig. 1 Molecular structure of a modified metal DBM (*left*) and complexes specifically studied in this work

each of the series. Thermal analysis and equilibrium vapor pressure studies were very helpful in explaining the thermodynamic parameters of the inclusion/dissociation process and factors defining the limits of existence for those solid materials [21, 31–36].

So far we were not able to prepare such a series for metal DBMs. It turned out that the complexes of Zn(II) and Cd(II) usually adopt *cis* configuration and differ in their properties from complexes formed by metal cations with partially filled *d* subshell. In the series of three $[M(\text{DBM})_2\text{Py}_2]$ complexes (Py = pyridine) only Ni complex has *trans* configuration and forms various inclusion compounds, while the corresponding Zn and Cd complexes have *cis* configuration and exist as guest-free solids [24]. With 2-methylpyridine as A, Ni complex again is *trans* and versatile as host, while the corresponding Zn complex does not form at all and Cd complex forms both *trans* and *cis* isomers, the *cis* isomer being thermodynamically stable and guest-free [27]. Among similar complexes studied by other authors $[\text{Ni}(\text{benzoylacetone})_2(\text{DMSO})_2]$, (DMSO = dimethylsulfoxide) [37] and $[\text{Ni}(\text{benzoylacetone})_2(\text{adamantylamine})_2]$ [38] both reported as *trans* isomers may be compared with $[\text{Cd}(\text{DBM})_2(\text{DMSO})_2]$ which is *cis* [39].

However, the energy difference between *cis* and *trans* configurations does not seem to be very large for this type of complexes. There are many examples when the same complex was isolated in both *trans* and *cis* configurations in different solids. For example $[\text{Zn}(\text{hfa})_2(\text{H}_2\text{O})_2]$ (hfa is perfluorinated acetylacetonate) may be isolated both as *trans* and as *cis* isomers [40]. Analogous Ni complex was observed in both *trans* [41] and *cis* [42] forms; analogous Co complex was also isolated in *trans* [43, 44] and in *cis* [45] forms; finally, only *cis* isomer was reported for $[\text{Cd}(\text{hfa})_2(\text{H}_2\text{O})_2]$ [46]. There are two examples when bis-chelate complexes of Cd were isolated both as *trans* and *cis* isomers related to each other as true polymorphs [47, 48].

In this study, we attempted to prepare and study a series of host complexes of four metal DBMs (Co, Ni, Zn, Cd) using bulky axial ligands, quinoline (Q), and isoquinoline (Iq). These ligands would make *cis* configuration less preferred due to sterical reasons and could favor the formation of desired *trans* isomers for the whole series.

Experimental

Preparations

Metal dibenzoylmethanates $M(\text{DBM})_2$ were synthesized as described elsewhere [24, 49]. Complexes were prepared by adding 125–140 mg (0.25 mmol) of the corresponding $M(\text{DBM})_2$, 78 mg (0.6 mmol) of quinoline or isoquinoline and an excess of solvent (3 ml or more if necessary). The mixtures were transformed into transparent solutions by heating (red, green, or colorless), filtered if needed, and then allowed to slowly cool down to room temperature. Typically the products were recovered the next day. If no solid formed, the solutions were allowed to evaporate.

All products were crystalline. Typical yields were from 50 to 80%. Co compounds were orange, Ni compounds were green, Zn and Cd compounds were colorless. For TG and other experiments, the crystals were pressed to dryness on filter paper and then dried for ~1 h. All products were stable in air for days. For single crystal XRD measurements crystals were taken directly from mother solutions.

For each of four metal DBMs and quinoline, eight solvents were applied: acetone, benzene, DMSO, ethanol, nitromethane, THF, toluene, and neat quinoline. Complexes $[M(\text{DBM})_2\text{Q}_2]$ obtained from non-quinoline solvents grew as plates. Identity of the products formed from different solvents was confirmed by powder XRD analysis. The inclusions $[M(\text{DBM})_2\text{Q}_2]^*\text{Q}$ obtained from quinoline grew up as prisms for Co, Zn, and Cd. Numerous crystallizations of $\text{Ni}(\text{DBM})_2$ from neat quinoline always yielded only $[\text{Ni}(\text{DBM})_2\text{Q}_2]$ complex.

For each of four metal DBMs and isoquinoline five solvents were applied: acetone, benzene, DMSO, nitromethane, and neat isoquinoline. Complexes $[M(\text{DBM})_2\text{Iq}_2]$ obtained from the solvents grew either as plates or slanted truncated blocks. Identity of the products formed from different solvents was confirmed by powder XRD analysis and/or single crystal XRD examination of randomly selected crystals.

XRD studies

Powder XRD patterns were recorded on a STOE or Bruker D8 instruments with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) in $5\text{--}30^\circ$ 2θ range. No special precautions were taken to protect the samples.

Single crystals, or pieces cut therefrom, were studied on a Bruker diffractometer with Kappa goniometer, CCD detector and MoK_α source ($\lambda = 0.7107 \text{ \AA}$). Unit cell parameters were determined using 300–800 reflections taken from several dozens of frames collected starting at three different φ positions. Some experimental parameters and refined unit cell dimensions are listed in Table 1. Full

diffraction data were collected at $-100\text{ }^{\circ}\text{C}$ and only preliminary data are presented here; complete results of the single crystal structural study will be reported elsewhere.

Thermal analyses

Thermogravimetric measurements were conducted on a Q5000 IR analyzer (TA Instruments). The samples varying in mass (see Table 2) were heated in linear regime ($5^{\circ}/\text{min}$) and in the flow of nitrogen ($25\text{ mL}/\text{min}$) from room temperature to $\sim 400\text{ }^{\circ}\text{C}$. Samples were gently grounded to achieve uniform distribution of heat.

In order to reduce the dependence of the quantitative measurements on texture and size of a sample, a variety of independently prepared samples was analyzed. In particular, the samples of complexes obtained from the different solvents utilized were studied. The results are given with standard deviations enclosed in round brackets and expressed in the units of the last significant figure (Table 2).

As the purpose of this study was to compare thermal properties of compounds with different metals and

different molecular mass, the mass loss on the TG curves was expressed as x , the ratio of moles of volatile component (Q or Iq) per mole of $\text{M}(\text{DBM})_2$ in a compound studied: $x = (m_{\text{exp}} - m_{\text{ref}}) \times M_{\text{ref}}/M_{\text{Q}} \times m_{\text{ref}}$, where m_{exp} is the sample mass measured in a TG experiment, m_{ref} is the mass of $\text{M}(\text{DBM})_2$ in the compound, M_{ref} and M_{Q} are molecular masses of $\text{M}(\text{DBM})_2$ and Q, respectively. The m_{ref} value is readily defined from the TG curve when the plateau of $\text{M}(\text{DBM})_2$ is well pronounced. If the plateau is not satisfactory, m_{ref} is calculated from initial mass assuming certain stoichiometry. For another instance when the described method was applied see our earlier paper [28].

Results and discussion

Structure of the compounds isolated

The 11 compounds isolated and studied in this work fall into three isomorphous series (Table 1):

Table 1 Single crystal XRD measurements of unit cell dimensions of the isolated compounds at room temperature

Compound	Solvent used	Crystal description	Crystal sizes/mm	No of reflections used	$a/\text{\AA}$ $\alpha/^{\circ}$	$b/\text{\AA}$ $\beta/^{\circ}$	$c/\text{\AA}$ $\gamma/^{\circ}$	$V/\text{\AA}^3$ Z^a	$D_{\text{calc}}/\text{g cm}^{-3}$
[Co(DBM) ₂ Q ₂]	Acetone	Red plate	$0.1 \times 0.5 \times 0.5$	796	10.390(5) 90	16.673(7) 90	22.32(1) 90	3867(3) 4	1.312
[Ni(DBM) ₂ Q ₂]	Nitromethane	Green plate	$0.02 \times 0.3 \times 0.3$	550	10.321(6) 90	16.804(8) 90	22.25(1) 90	3859(3) 4	1.314
[Zn(DBM) ₂ Q ₂]	Nitromethane	Colorless plate	$0.3 \times 0.4 \times 0.4$	729	10.394(5) 90	16.765(7) 90	22.26(1) 90	3879(3) 4	1.319
[Cd(DBM) ₂ Q ₂]	Toluene	Colorless plate	$0.3 \times 0.4 \times 0.5$	750	11.048(5) 100.26(1)	17.869(7) 93.18(1)	20.356(9) 91.19(1)	3946(3) 4	1.375
[Co(DBM) ₂ Q ₂]*Q	Quinoline	Orange prism	$0.05 \times 0.05 \times 0.2$	137	9.280(4) 83.86(2)	9.428(4) 88.53(2)	13.380(5) 76.90(2)	1134(1) 1	1.308
[Zn(DBM) ₂ Q ₂]*Q	Quinoline	Colorless prism	$0.35 \times 0.4 \times 0.5$	467	9.302(6) 83.86(1)	9.349(6) 88.51(1)	13.328(9) 76.85(1)	1122(1) 1	1.331
[Cd(DBM) ₂ Q ₂]*Q	Quinoline	Colorless prism	$0.2 \times 0.3 \times 0.4$	575	9.397(7) 84.03(1)	9.164(6) 88.62(1)	13.85(1) 77.36(1)	1158(1) 1	1.358
[Co(DBM) ₂ Iq ₂] ^b	Nitromethane	Orange plate	$0.02 \times 0.5 \times 0.5$	349	17.66(1) 90	11.192(7) 111.00(2)	20.96(1) 90	3868(4) 4	1.312
[Ni(DBM) ₂ Iq ₂] ^b	Isoquinoline	Green plate	$0.1 \times 0.2 \times 0.4$	462	17.81(1) 90	11.012(6) 111.38(1)	20.99(1) 90	3833(4) 4	1.323
[Zn(DBM) ₂ Iq ₂] ^b	Ethylacetate	Colorless block	$0.5 \times 0.5 \times 0.5$	476	17.60(1) 90	11.244(6) 111.02(1)	20.76(1) 90	3835(4) 4	1.334
[Cd(DBM) ₂ Iq ₂] ^b	Isoquinoline	Colorless block	$0.4 \times 0.5 \times 0.5$	689	17.078(7) 90	11.866(5) 109.44(2)	20.01(1) 90	3824(3) 4	1.420

^a Assumed value

^b C-cell

Table 2 The parameters of thermal dissociation of studied compounds as derived from TG experiments: average values with standard deviations

Compound	No of samples studied ^a	Sample mass range/mg	$T_{\text{onset}}/^{\circ}\text{C}$	Mass loss/%	Calc. mass loss/%	Model
Co(DBM) ₂	1	5.7	~280 ^e	–	–	(dec.)
Ni(DBM) ₂	1	4.1	~293 ^e	–	–	(dec.)
Zn(DBM) ₂	1	4.6	~266 ^e	–	–	(dec.)
Cd(DBM) ₂	1	5.8	~252 ^e	–	–	(dec.)
[Co(DBM) ₂ Q ₂]	7 ^b	0.4–6.3	150(2)	34.6(3)	33.8	–2Q
[Ni(DBM) ₂ Q ₂]	7 ^b	2.8–6.0	154(2)	34.8(2)	33.8	–2Q
[Zn(DBM) ₂ Q ₂]	7 ^b	3.8–10.0	96(1)	33.9(1)	33.5	–2Q
[Cd(DBM) ₂ Q ₂]	7 ^b	1.6–7.5	124(1)	31.7(1)	31.6	–2Q
[Co(DBM) ₂ Q ₂]*Q	1	5.1	89	43.6	43.4	–3Q
[Zn(DBM) ₂ Q ₂]*Q	1	4.6	66	43.1	43.1	–3Q
[Cd(DBM) ₂ Q ₂]*Q	1	7.8	103	40.7	40.9	–3Q
[Co(DBM) ₂ Iq ₂]	4 ^c	1.2–6.2	142(3)	34.2(2)	33.8	–2 Iq
[Ni(DBM) ₂ Iq ₂]	3 ^d	2.5–4.3	155(1)	28–31.5 ^f	33.8	–2 Iq
[Zn(DBM) ₂ Iq ₂]	4 ^c	5.3–7.3	107(1)	33.8(1)	33.5	–2 Iq
[Cd(DBM) ₂ Iq ₂]	4 ^c	4.3–7.1	125(2)	32.1(1)	31.6	–2 Iq

^a Independently prepared samples

^b Crystals obtained from acetone, benzene, DMSO, ethanol, nitromethane, THF, and toluene

^c Crystals obtained from acetone, benzene, DMSO, and nitromethane

^d Crystals obtained from acetone, DMSO, and nitromethane

^e Broad onset

^f The plateau of Ni(DBM)₂ is not well defined on the thermograms

[M(DBM)₂Q₂], where M = Co, Ni, Zn, Cd;

[M(DBM)₂Q₂]*Q, where M = Co, Zn, Cd;

[M(DBM)₂Iq₂], where M = Co, Ni, Zn, Cd.

Compounds [M(DBM)₂Q₂] are orthorhombic and isostructural except for Cd-complex which, evidently, has a similar structure distorted to triclinic. Preliminary single crystal XRD studies indicate that the first three compounds crystallize in space group *Pcab* with *trans* [M(DBM)₂Q₂] complex molecules (centrosymmetric) (Fig. 2a). The Cd-compound is similar but crystallizes in *P-1* with three crystallographically different molecules in the unit cell (two are centrosymmetric and one is asymmetric).

Compounds [M(DBM)₂Q₂]*Q are triclinic (*P-1*) and isostructural with each other. The crystal structure comprises a centrosymmetric *trans* [M(DBM)₂Q₂] host complex (Fig. 2b) and a molecule of guest quinoline. The molecule of the host complex adopts a very similar conformation as in guest-free crystals (cf. Fig. 2a, b). The molecules of guest quinoline are retained inside cavities of the crystal lattice and form only van der Waals contacts to other molecules of the crystal structure (Fig. 3). Therefore, the crystals are inclusion compounds, where two moles of quinoline are incorporated as ligands in the host molecule and one extra mole of quinoline is included as guest.

Inclusion compounds with an organic molecule playing the role of both a ligand and guest are common [21, 34–36, 50–58] and, in the cases where the guest molecule is included only due to van der Waals forces, it may be replaced with another molecule that is chemically different but possesses similar shape and dimensions [59, 60].

Compounds [Ni(DBM)₂Iq₂] are monoclinic (*C2/c*) and isostructural. The crystal consists of *trans* (centrosymmetric) complex molecules (Fig. 2c).

One can immediately see the similarity of the complex molecules observed in the studied structures (Fig. 2). All possess *trans* configuration with two DBMs forming a bis-chelate unit in the equatorial plane and two Q or Iq ligands coordinated axially. The coordination environment is thus a slightly distorted octahedral. For instance, in Zn complexes the Zn–O distance varies within 2.04–2.09 Å, the Zn–N distance varies within 2.19–2.30 Å and coordination angles are in the range 86°–94°. The conformations of the molecules are also quite similar. The phenyl rings of the DBM units rotate from the equatorial planes by 13–30°. The plane of Q or Iq forms 80–86° dihedral angle with the equatorial plane. The Q ligand is almost in the plane dividing the bis-chelate fragment into two DBMs, deviating from the plane by ~12° and ~6° in the guest-free and inclusion crystals, respectively. This positioning is understandable from steric considerations as the only possibility

Fig. 2 Molecules of Zn complexes found in the crystal structure of $[\text{Zn}(\text{DBM})_2\text{Q}_2]$ (a), $[\text{Zn}(\text{DBM})_2\text{Q}_2]\cdot\text{Q}$ (b), and $[\text{Zn}(\text{DBM})_2\text{Iq}_2]$ (c). H-atoms are omitted for clarity

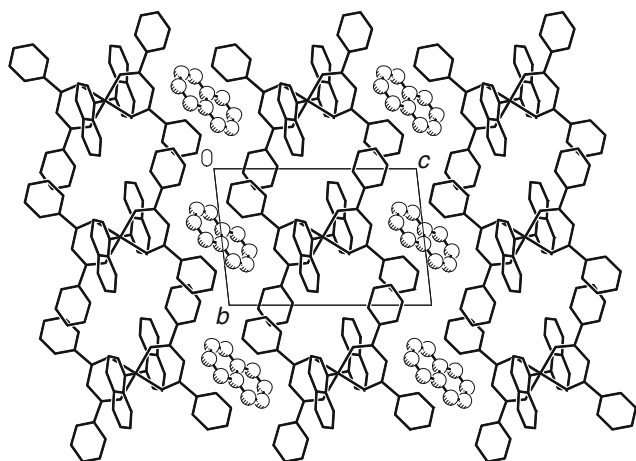
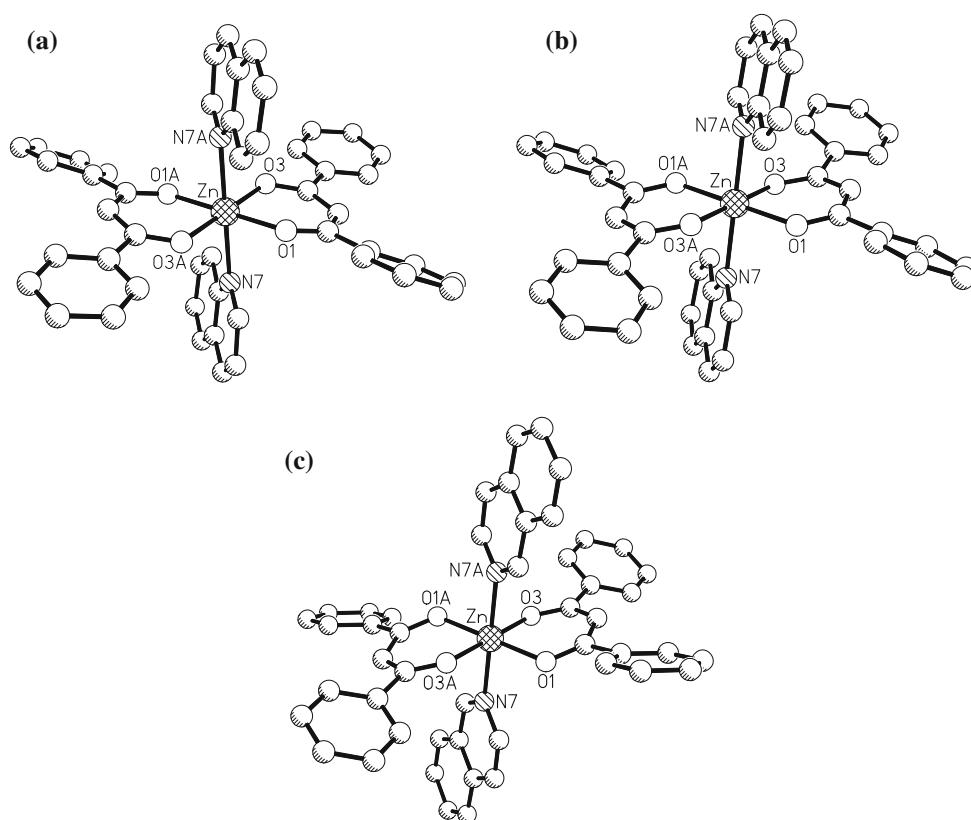


Fig. 3 Crystal packing in the inclusion compound $[\text{Zn}(\text{DBM})_2\text{Q}_2]\cdot\text{Q}$: projection down the a axis. For clarity the host molecules are outlined by sticks, while the guest molecules are shown in stick-and-balls. H-atoms are omitted

for the bulky Q moiety to approach the coordination center. The Iq ligand is less restricted and rotates from the plane by $\sim 20^\circ$.

The main results of the structural studies are the following. First, the complex molecules in the isolated crystals are all *trans*. Therefore, the utilization of bulky ligands helped to produce *trans* complexes that are more likely to form inclusion compounds. It should be noted that big

ligands were used in the past to modulate properties of known host complexes [61, 62] but in this study we use the bulky ligands to endow complexes that do not have host properties with inclusion capability. Second, the complexes with quinoline do form inclusion compounds. The guest quinoline can be replaced with other molecules. Our ongoing studies yielded a series of such inclusions with naphthalene, substituted benzenes, and cyclohexanes; this work is currently underway. Third, the compounds isolated in this study form three series with the same stoichiometry and similar molecular and crystal structure in each of the series and thus they are convenient objects for comparative thermoanalytical studies.

Thermal stability and dissociation of the compounds

TG results confirm stoichiometry of all the compounds studied (as shown in Table 2). All the compounds contain one volatile component (Q or Iq), while $\text{M}(\text{DBM})_2$ complex salts have relatively high thermal stability and start to decompose only after the volatile component has been completely released (Table 2). Therefore, the TG curves display a well-defined plateau of $\text{M}(\text{DBM})_2$ almost in all experiments (Figs. 4, 5, 6). The presence of only one volatile component makes TG results unambiguous and useful for the determination of stoichiometry of inclusion/coordination compounds and identification of the products

of their thermal dissociation [21, 34, 36, 63–68]. Although closer look reveals that the stoichiometry of intermediate states in some cases is irregular, the total amounts of released Q or Iq correspond well to the values calculated from the formulas (Table 2; Figs. 4, 5, 6). It should be noted that irregular stoichiometries have been observed in thermal dissociation of complexes with quinoline and other bulky ligands [64–68] and may indicate either solid-state chemical transformations or the formation of a liquid phase in the sample.

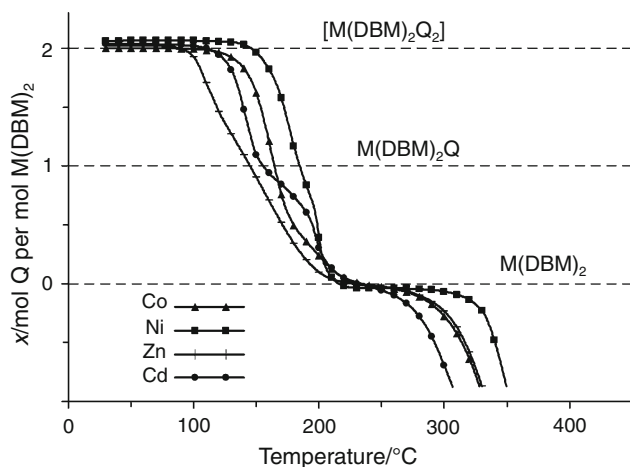


Fig. 4 Thermal dissociation of $[M(\text{DBM})_2\text{Q}_2]$ complexes. For easier comparison, the graphs show the ratio $x = \text{Q} : \text{M}(\text{DBM})_2$ in the compound (for further explanation see “Experimental”). Calculated compositions are shown by *dashes*. Symbols on the curves are added to distinguish curves belonging to different compounds

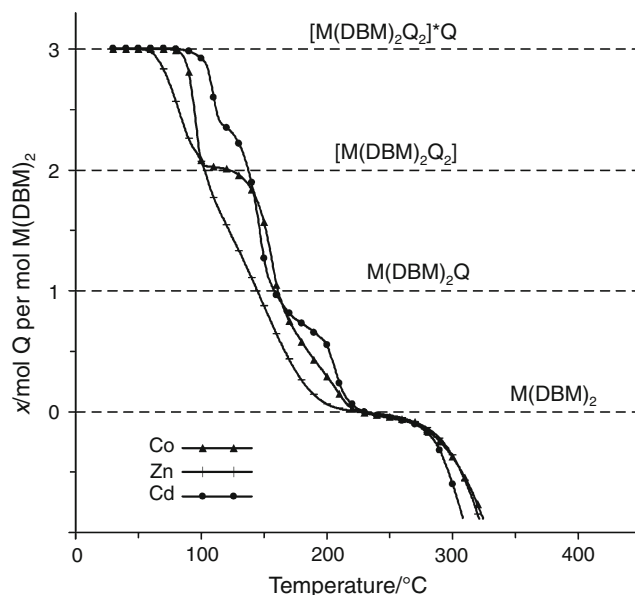


Fig. 5 Thermal dissociation of $[M(\text{DBM})_2\text{Q}_2]^*\text{Q}$ inclusion compounds (see comments to Fig. 4)

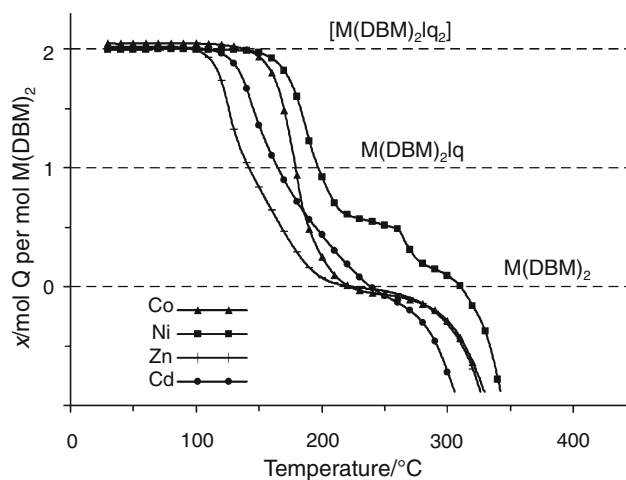
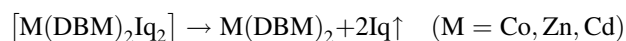
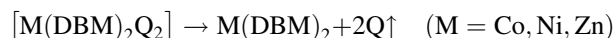
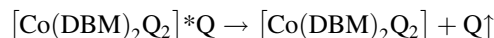


Fig. 6 Thermal dissociation of $[M(\text{DBM})_2\text{Iq}_2]$ complexes (see comments to Fig. 4)

Qualitative consideration reveals a one-step dissociation mode for most complexes:



Among inclusions, only the Co-compound dissociates exhibiting a clear plateau of the corresponding host complex:

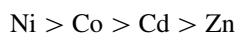


For the Zn-compound, the plateau is barely pronounced. The dissociation curve of Cd-compound is complicated due to melting of $[\text{Cd}(\text{DBM})_2\text{Q}_2]^*\text{Q}$ and $[\text{Cd}(\text{DBM})_2\text{Q}_2]$ at 120 and 157 °C (DSC results), respectively.

The comparison of thermal stability is useful in series of stoichiometrically similar compounds undergoing the same kind of dissociation reaction. The order of thermodynamic stability can be estimated in such studies taking into account that major contributors to the difference in thermodynamic stability are the volatility of the released component and how strongly the volatile component is retained in the solid. For coordination compounds (volatile component is a ligand), the second parameter is defined mainly by the enthalpy term, which is the strength of the coordination bond. For inclusion compounds (volatile component is a guest), the enthalpy contribution to the second parameter is defined by the complementarity of the guest molecule to the cavity in the host lattice. More extended discussion on the subject was given elsewhere [28, 69–71]. However, inclusion compounds usually demonstrate the compensation effect [72–78] and inclusion compounds with guest occupying larger cavities gain in stability due to higher entropy. The stability of inclusion compounds based on metal complexes may be also limited

by the strength of coordination bonds in the host complex if it is not sufficiently stable [34–36].

In this study, the comparison can be made using the onset temperatures of the initial dissociation step in series of isomorphous compounds. The comparison is based on the assumption that at the beginning the dissociation processes are similar and not complicated by melting or other events. In both $[M(\text{DBM})_2\text{Q}_2]$ and $[M(\text{DBM})_2\text{Iq}_2]$ series, the order of stability is



The sequence is well defined and beyond experimental errors (Table 2). The stabilities of $M(\text{DBM})_2$ clearly follow the same trend (Table 2). The trend is defined by the relative strength of metal–ligand bonds and often seen in other series of coordination compounds [79–83]; in many such studies the thermal stability of coordination solids correlates with the strength of the metal–ligand bonds determined spectroscopically; although, the structural similarity of the compounds was not always confirmed.

The onset temperatures of thermal dissociation of the host complexes $[M(\text{DBM})_2\text{Q}_2]$ approximately define the limits of thermal stability for the corresponding inclusion compounds these complexes may form. The Co-, Cd-, and Zn-complexes start to dissociate at 150, 124, and 96 °C, respectively (Table 2). The dissociation of $[M(\text{DBM})_2\text{Q}_2]^*\text{Q}$ inclusions occurs at much lower temperature (89, 103, and 66 °C) and so does not have to be affected by the stability of the host. It is clear that the relative stability among the inclusion compounds differs from that for host complexes. In particular, the Cd-inclusion is the most stable. The released guest is the same in the $[M(\text{DBM})_2\text{Q}_2]^*\text{Q}$ series and therefore, as elaborated above, the stability difference should be a result of host–guest interactions.

The crystal structure analysis (at –100 °C) shows that the cavity in Cd-inclusion is larger than in Co- and Zn-compounds and only in the Cd-inclusion the guest in the cavity is disordered over two positions. The unit cell dimensions at room temperature (Table 2) suggest that the tendency remains upon heating. Due to this disordering, the dissociation reaction entropy change is lower in case of Cd-inclusion (the guest in its cavities has already some disorder before entering gas phase) and the dissociation temperature defined by $T = \Delta H/\Delta S$ is higher. This way, the disordering of guest extends the temperature limit of existence of $[\text{Cd}(\text{DBM})_2\text{Q}_2]^*\text{Q}$ inclusion. Similar phenomenon was previously observed for inclusions that experience polymorphous transitions due to order–disorder change in the guest subsystem: the conversion into more disordered phase reduces the temperature-caused growth of guest vapor pressure over the clathrate thus making it possible for the inclusion compound to exist at higher temperatures [34, 84].

Conclusions

This study introduces bulky quinoline and isoquinoline ligands in the modified $M(\text{DBM})_2$ unit to yield two series of complexes ($M = \text{Co}, \text{Ni}, \text{Zn}, \text{and Cd}$). The special choice of ligands made it possible to produce *trans* configured complexes for Zn and Cd, with their overall geometry being similar to the analogous complexes of Co and Ni. For the first time, inclusion compounds of modified Zn and Cd dibenzoylmethanates were prepared proving that the inclusion ability of the host molecules is defined by their overall shape rather than chemical nature of the metal center. Therefore, appropriate choice of ligands may become a useful strategy of generating host complexes for metal cations which tend to exist in *cis* configuration through stabilization of their corresponding *trans* isomers. Moreover, the same strategy may become successful in creating complexes with switchable *cis–trans* capability. The phenomena of molecular and conformational isomerism controlled by weak intermolecular interactions is frequently encountered in molecular crystals [27, 40–45, 47, 48, 85–93] and may be utilized in the design of stimuli-responsive materials [17].

The *trans* complexes of Zn and Cd, as well as inclusion compounds they form, compare to those of Co and Ni not only structurally but also in terms of their bulk properties such as thermal stability and dissociation. The differences observed are rather quantitative than fundamental and reasonable correlations can be observed throughout each of the series. In overall, this study provides better understanding of the factors that on molecular level control the formation and properties of inclusion materials.

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