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Trimorphism of Zn(NCS)₂(4-dimethylaminopyridine)₂: Crystal Structures, Thermodynamic Relations and Comparison with the Co(II) Polymorphs

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Abstract: Reaction of Zn(NCS)₂ with 4-dimethylaminopyridine (DMAP) leads to the formation of three polymorphic modifications of Zn(NCS)₂(DMAP)₂ (**I-Zn**, **II-Zn** and **III-Zn**), of which only the crystal structure of **I-Zn** is reported in literature. In all three modifications the Zn(II) cations are tetrahedrally coordinated by two terminal N-bonded thiocyanate anions and two DMAP ligands forming discrete complexes, which differ in the dihedral angle between the DMAP ring planes and the arrangement of the complexes in the crystals. All three modifications show melting and the thermodynamic relations and the transition behavior were investigated by temperature dependent X-ray powder diffraction, differential scanning calorimetry, thermomicroscopy and solvent mediated conversion experiments. These reveal that **I-Zn** and **II-Zn** as well as **II-Zn** and **III-Zn** are related by enantiotropism, whereas **I-Zn** and **III-Zn** is much lower than that between the isotypic Co(II) modifications **I-Co** and **II-Co** reported recently.

INTRODUCTION

The synthesis of new coordination compounds and polymers, inorganic-organic hybride compounds and metal organic frameworks is still a fast growing field in chemistry, as they show potential for present or future applications.¹⁻¹⁰ For any application some information on the stability of a given compound is required, which is especially the case for stable and metastable forms like, e.g. polymorphs or isomers. In this case, the chemical composition is constant and all differences in the physical properties, including thermodynamic parameters, depend entirely on the differences in the crystal structures and can be compared directly.¹¹⁻¹⁴ On the other hand, even if several polymorphic or isomeric coordination compounds are reported, in most cases their thermodynamic relations are usually not investigated.¹⁴⁻³⁰ Sometimes conclusions on the stability were drawn based on the comparison of the densities, the fact that one form transforms into another or by computational methods.³¹⁻³⁵ In other cases, crystals of two modifications were obtained and one of these forms can be prepared pure, whereas no access to the other form was found and thus, it is concluded that the latter, frequently called "disappearing polymorph"³⁶ is metastable, which is not necessarily the case. Finally, these results are sometimes discussed in context of the crystal structure, where e.g., some short intermolecular contacts are held to be responsible for the stability of a given form.^{37, 38} All these might be incomplete because for definite conclusions the exact thermodynamic relations must be known which for coordination compounds is difficult to investigate. In contrast to organic compounds, usually no melting or polymorphic transition is observable and therefore, helpful thermodynamic rules like the heat of transition, the melting enthalpy or melting entropy rule cannot be used.³⁹⁻⁴² Therefore, there are only a few examples where the thermodynamic relations of coordination compounds are investigated in more detail.^{25, 43-45} In some cases, the transformation of one form into the other is observed by, e.g. X-ray diffraction. Nevertheless, without measuring the direction of the heat-flow usually no conclusions can be drawn whether two forms are related by enantiotropism or monotropism.^{38, 46-51} Finally, even if one form shows a transition into a different form

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in the solid state, this temperature is usually much higher than the true thermodynamic transition temperature (T_{Trs}) . In summary, detailed investigations on the thermodynamic relations and the transition behavior of polymorphs or isomers of coordination compounds are difficult to perform but of extraordinary importance for any discussion on the stability of such compounds.

In this context, we recently reported on two polymorphic modifications (I-Co and II-Co) of a simple discrete complex with the composition Co(NCS)₂(DMAP)₂ with 4-dimethylaminopyridine abbreviated as DMAP. The Co cations are coordinated by two N-bonding thiocyanate anions and two DMAP co-ligands.⁴⁴ Form **I-Co** crystallizes in the monoclinic space group $P2_1/c$ and is exclusively obtained by water removal from the hydrate $Co(NCS)_2(DMAP)_2(H_2O)_2 \cdot 2 H_2O$. Form **II-Co** also crystallizes in a monoclinic space group $(P2_1/m)$ and is synthesized by methanol removal from the solvate $Co(NCS)_2(DMAP)_2(CH_3OH)_2$. Solvent mediated conversion experiments prove, that form II-Co represents the thermodynamic stable form at room-temperature. DSC measurements reveal that form **I-Co** has the higher melting point and the lower heat of fusion and therefore, both modifications have to be related by enantiotropism with form **I-Co** being stable at higher temperatures. From the melting points and the heats of fusion the thermodynamic transition temperature was estimated to be about 153 °C, which is in good agreement with the transition temperature determined by annealing experiments of 145 °C. For the room-temperature polymorph II-Co single crystals were obtained, which was not possible for the high temperature (HT) form I-Co, which becomes thermodynamic stable at about 145 °C. In this context, it is noted that in most cases the corresponding Zn(NCS)₂ compounds show a tetrahedral coordination and are frequently isotypic to their Co(II) counterparts. Therefore, to retrieve structural information on I-Co, we prepared Zn(NCS)₂(DMAP)₂ and we found that it is isotypic to the HT form I-Co. The easy formation of these crystals was somehow surprising, because the intermolecular interactions should in principle be dominated by the surrounding ligands and only slightly influenced by the metal center that exhibits the same charge and a similar ionic radius. If there would be a simple relationship between structure and stability, one would expect that the thermodynamic transition

temperature for each pair of Co and Zn compounds would be similar. This means that in the case, where one form is thermodynamically stable, e.g., at room-temperature, the isotypic form might behave similar, as otherwise no reliable conclusions can be drawn. Consequently, we assumed that the crystals of the Zn compound are also metastable at room-temperature and thus, were accidently obtained by kinetic control.

However, based on all these results we assumed that $Zn(NCS)_2(DMAP)_2$ might crystallize in two different modifications too and thus we tried to prepare crystals of the form that should be isotypic to the form of $Co(NCS)_2(DMAP)_2$ that is thermodynamic stable at room-temperature (**II-Co**). Surprisingly, independent of the reaction conditions, at room-temperature always single crystals isotypic to the HT form (**I-Co**) were obtained. According to this, we decided to investigate the solid-state properties of $Zn(NCS)_2(DMAP)_2$ in more detail. In the course of this investigations we obtained three different polymorphic modifications of which two (**I-Zn** and **II-Zn**) are isotypic to the corresponding Co(II) forms (**I-Co** and **II-Co**), whereas the third form (**III-Zn**) was not detected with Co(II). All three forms show melting, which is rarely observed for coordination compounds with the melting point of **III-Zn** being higher than that of **II-Zn** and lower than that of **I-Zn** (T_m: **II-Zn** < **III-Zn** < **I-Zn**). Therefore, according to the generally accepted rules for the denomination of polymorphic forms, which suggests that the different forms should be sorted according to their melting point, **III-Zn** should be denoted as **II** but for comparison with the corresponding Co(II) modifications we deviate from this rule. Here we report on the results of these investigations.

EXPERIMENTAL SECTION

Reagents. Ba(NCS)₂·3H₂O, was purchased from Alfa Aesar, KSCN, Zn(NO₃)₂·6H₂O and Zn(SO₄)·H₂O were bought from Merck. All chemicals were used without further purification. Zn(NCS)₂ was prepared by the reaction of equimolar amounts of Zn(SO₄)·H₂O and Ba(NCS)₂·3H₂O in water. The resulting white precipitate

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of $BaSO_4$ was filtered off and the filtrate was concentrated to complete dryness resulting in white residue of $Zn(NCS)_2$. The purity was checked by X-ray powder diffraction (XRPD).

Synthesis of I-Zn. The synthesis of single crystals is described elsewhere.⁴⁴ Crystalline powders were obtained by adding a methanolic solution (1.5 mL) of DMAP (122 mg, 1.0 mmol) to a stirred solution of Zn(NCS)₂ (90 mg, 0.5 mmol) in methanol (2.5 mL).

Synthesis of II-Zn. Crystalline powders were obtained by completely dissolving $Zn(NCS)_2$ (0.25 mmol, 45 mg) in water. Afterwards DMAP (0.5 mmol, 61 mg) was dissolved in water (2.5 mL) and added to the solution of $Zn(NCS)_2$. The mixture was stirred for 4 d. It is noted that this procedure not always led to phase pure powders of II-Zn, in most cases I-Zn is contained as an impurity.

Synthesis of III-Zn. Crystalline powders were obtained by adding a methanolic solution (1.5 mL) of DMAP (122 mg, 1.0 mmol) to a solution of Zn(NCS)₂ (90 mg, 0.5 mmol) in methanol (2.5 mL) after stirring for 15 s the precipitate of **III-Zn** was filtered off. Longer stirring resulted in mixtures of **II-Zn** and **I-Zn**.

IR and Raman spectroscopy. The IR data were measured using a Bruker Vertex70 FT-IR Spectrometer with VERTEX FM module with a resolution of 3 cm⁻¹. The Raman data were measured using a Bruker RAM II – 1064 FT-Raman module with R510-N/R Nd:YAG-Laser with the wavelength of 1064 nm and a D418-T/R Ge-detector with a resolution of 3 cm⁻¹.

Thermoanalytical measurements. DTA-TG measurements were performed in a dynamic nitrogen atmosphere in Al₂O₃ crucibles using a STA PT 1600 thermobalance from Linseis. The DSC experiments were performed using a DSC 1 star system with STARe Excellence software from Mettler-Toledo AG under dynamic nitrogen atmosphere and thermomicroscopy was performed using a hot-stage from Linkam and a microscope from Olympus. All instruments were calibrated using standard reference materials.

X-Ray Powder Diffraction (XRPD). The XRPD measurements for phase identification were performed by using a Stoe Transmission Powder Diffraction System (STADI-P) equipped with a Ge(111) Johann-type monochromator from STOE & CIE with CuK α_1 radiation that was equipped with a linear position-sensitive

MYTHEN 1K detector from Dectris Ltd. X-ray powder diffraction patterns for structure determination, low temperature and high temperature measurements were performed on a Cu K α_1 Stoe STADI-P powder diffractometer, equipped with a Ge(111) Johann-type monochromator from STOE & CIE, an Oxford cryostream 800 and an array of three Mythen 1K from Dectris Ltd. Details on the structure determinations can be found in the Supplemental Material, selected crystal data and details on the structure refinements as well as differences plots are given in Table S1 and Figures S1-S3 in the supplemental.

CCDC-1875955 I-Zn, CCDC-1875956 II-Zn and CCDC-1875957 III-Zn contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Preliminary synthetic investigations. Based on the synthetic results obtained for the corresponding Co modifications, where both forms (**I-Co** and **II-Co**) were selectively prepared by solvent removal from $Co(NCS)_2(DMAP)_2(H_2O)_2 \cdot 2 H_2O$ and $Co(NCS)_2(DMAP)_2(CH_3OH)_2$, we tried to prepare the corresponding solvato complexes with Zn(II) but none of these compounds formed. However, from ethanol **I-Zn**, isotypic to **I-Co**, is obtained as a pure compound (Figure S4). Additional experiments with water as solvent sometimes led to the formation of a further crystalline product that is isotypic to **II-Co**, confirmed by Rietveld refinement using the crystallographic data of **II-Co** as starting model (Figure S2 and S5). In most cases, products were synthesized that are contaminated with **I-Zn**, but a few batches of pure **II-Zn** were obtained for further investigations (Figure S6). To find a reproducible procedure for the synthesis of **II-Zn** many experiments were performed. Whenever the synthesis was performed in methanol and the product was immediately filtered off, a further phase (**III-Zn**) has formed by kinetic control. In its powder pattern, no reflections of **I-Zn** and **II-Zn** were observed, indicating that a pure sample was obtained. DTA-TG investigations reveal

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that no solvate was obtained and that a similar thermal behavior to that of **I-Zn** and **II-Zn** is observed (Figure S7). Because no single crystals were available, its structure was solved *ab initio* from XRPD data. The experimental pattern was compared with the calculated one, revealing that **III-Zn** was obtained as a pure form (Figure S3 and S8). It is noted, that most batches of **III-Zn** very often contained **I-Zn** as an impurity and we assumed that the former is metastable at room temperature and formed as kinetic product. Therefore, several additional experiments were performed to obtain pure samples under kinetic control, but in most cases **I-Zn** was obtained (Figure S9 and S10).

To investigate if one can distinguish between the different modifications by spectroscopy, IR and Raman measurements were performed. For all three forms values for the CN stretching vibration between 2056 and 2068 cm⁻¹ are observed in the IR and between 2064 and 2079 cm⁻¹ in the Raman spectra, which are typical for terminal N-bonded thiocyanate anions (Figure S11-S13). In contrast to the other two polymorphs, for **III-Zn** only one peak is observed in the Raman spectrum at 2075 cm⁻¹ and this form also shows the lowest value for the CN stretch in the IR spectrum, which is used to differentiate between the three polymorphs (Figure S13). Distinct differences are also found in the IR and Raman spectra for **I-Zn** and **II-Zn** (Figure S11 and S13).

Crystal structures of form I, II and III of Zn(NCS)₂(**DMAP**)₂. Form **I-Zn** was already reported in literature.⁴⁴ It crystallizes in the monoclinic space group $P2_1$ /m with Z = 2 and the Zn atoms are located on a crystallographic mirror plane (Table 1). This compound is isotypic to the corresponding Co(II) modification **I-Co**.⁴⁴ In its crystal structure the Zn(II) cations are coordinated by two terminal N-bonded thiocyanate anions and two N atoms of the DMAP ligand, within a slightly distorted tetrahedral geometry (Figure 1: top). The same coordination is found in the two other polymorphic forms **II-Zn** and **III-Zn**. These modifications crystallize in different monoclinic space groups $P2_1/c$ with Z = 4 (**II-Zn**) and C2/c (**III-Zn**) with Z = 8 and all atoms in general positions (Table 1).

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Table 1. Selected crystal data for I-Zn, II-Zn and III-Zn obtained by Rietveld refinements of X-ray powder

Form	I-Zn	II-Zn	III-Zn
space group	$P2_1/m$	$P2_{1}/c$	<i>C</i> 2/c
a / Å	5.50439(11)	13.9109(2)	7.44073(16)
b / Å	15.2027(3)	9.69175(13)	18.0648(5)
c / Å	12.0555(3)	14.7282(2)	31.4110(8)
β / °	97.3063(14)	90.2727(11)	91.0479
volume / Å ³	1000.63(4)	1985.64(5)	4221.41(18)
Ζ	2	4	8
$ ho_{calc.}$ / $cm^3 \cdot g^{-1}$	1.414	1.425	1.340

diffraction patterns measured at room-temperature.

Differences between all three forms are found in the conformation of the DMAP ligands, because the dihedral angles between the planes of the pyridine rings are always different, which is obvious if their crystal structures are superimposed (Figure 1: bottom). In **I-Zn**, both pyridine rings are coplanar, whereas in **II-Zn** they are nearly perpendicular to each other and in **III-Zn** the dihedral angle is the largest with 113.3 ° (Table 2). As expected for strong donor groups the dimethylamino groups are planar and are in the plane of the formembered rings (Table 2).

Table 2. Interplanar angles between the planes of the 6-membered DMAP rings (A) and between these phenyl rings and the dimethylamino groups (B), as well as angle sum around the dimethylamino N atom (C) in **I-Zn**, **II-Zn** and **III-Zn**.

	A / °	B / °	C / °
I-Zn	0	2, 2	360.0
II-Zn	113.3	0.1 (N12), 1.0 (N22)	360.0, 360.0
III-Zn	80.8	0.4 (N12), 6.9 (N22)	360.0, 359.5



Figure 1. View of a discrete complex in the crystal structure of form **I-Zn** as a representative (top) and a plot of the complexes observed in **I-Zn** (black), **II-Zn** (red) and **III-Zn** (blue; bottom), where the Zn(NCS)₂ units are superimposed.

In the crystal structures of all three modifications, the arrangement of the discrete complexes is completely different. In **I-Zn** the building units are arranged into columns that elongate along the crystallographic *a*-axis. Weak intermolecular C-H \cdots S hydrogen bonding between the thiocyanate S atoms and the C-H hydrogen atoms of the DMAP ligand are found, which finally link the discrete complexes into a 3D network (Figure 2: top).

In the crystal structure of **II-Zn** neighboring complexes are arranged in a way, that each two DMAP ligands form pairs, in which the dimethylamino groups of one complex are located above the 6-membered ring plane of a neighboring complex (Figure 2: mid). Even in this structure the discrete complexes are linked by

intermolecular C-H…S hydrogen bonding into a 3D network (Figure 2: mid). In the crystal structure of **III-Zn** a more complex packing of the discrete complexes is observed. As it is the case for the other two modifications the building units are linked by a number of C-H…S hydrogen bonds (Figure 2: bottom). It is noted, that for the isotypic modifications **I-Co** and **II-Co** very similar intermolecular contacts were observed.⁴⁴

I-Zn	$D(H \cdot \cdot \cdot A)$ (Å)	$d(D \cdot \cdot \cdot A)$ (Å)	<(DHA) (°)
C17-H17BS1	2.97	3.756(3)	138.3
C17-H17CS1	2.90	3.820(3)	156.1
C16-H16BS2	2.93	3.841(3)	155.9
II-Zn			
S1-H17A	3.1	4.064	165.3
S1-H17B	3.13	4.064	142.2
S2-H21	2.57	3.453	153.2
S2-H11	2.89	3.784	155.0
S2-H27B	2.80	3.580	136.1
III-Zn			
S1-H22	3.02	3.826	141.8
S1-H24	3.19	3.923	135.1
S1-H26	3.33	4.291	165.1
S1-H27	3.20	4.175	170.1
S2-H12	2.94	3.808	151.3
S2-H14	2.91	3.740	145.9

Table 3. Hydrogen bonds [Å and °] in I-Zn, II-Zn and III-Zn.



Figure 2. Crystal structure of I-Zn (top), II-Zn (mid) and III-Zn (bottom) with intermolecular C-H \cdots S interactions shown as dashed lines.

Investigations on the transition behavior and the thermodynamic relations

Solvent mediated conversion experiments

To investigate which of the three forms represents the thermodynamically stable form at room-temperature, solvent mediated conversion experiments were performed, in which mixtures of **I-Zn** and **II-Zn** were stirred in either ethanol or *n*-butanol and the residues obtained at different times were identified by XRPD (Figure S14 and S15). These experiments show that form **II-Zn** disappears after a few days and only **I-Zn** remains, which indicates that **I-Zn** is the thermodynamically stable form at room-temperature. Similar experiments for **III-Zn** show that this form also transforms into **I-Zn**, which means that **II-Zn** as well as **III-Zn** are metastable at room-temperature (Figure 3). In a further experiment, a mixture of **II-Zn** and **III-Zn** was stirred in ethanol, which reveals that the crystals of **III-Zn** disappear within a few minutes and that within 4 d the remaining amount of **II-Zn** transforms into **I-Zn** (Figure 3).



Figure 3. XRPD pattern of a suspension of **II-Zn** and **III-Zn** stirred in ethanol and of the residues obtained after 10 min and 4 d together with the calculated powder pattern of **I-Zn**, **II-Zn** and **III-Zn**. Characteristic reflections are indicated by red (**III-Zn**), blue (**II-Zn**) and black (**I-Zn**) perpendicular lines.

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Based on these experiments one can conclude that at room-temperature the order of stability is III-Zn < II-Zn. This result is somehow surprising, because the corresponding Co(II) modification I-Co is metastable at room-temperature and because both forms (I-Co and I-Zn) are isotypic, one would assume that the intermolecular interactions and thus, the stability would be similar. Finally, similar experiments at lower temperatures indicate, that I-Zn is also the thermodynamically stable polymorph at -34 °C (Figure S16 and S17).

Temperature dependent XRPD

To check if **II-Zn** or **III-Zn** show polymorphic phase transitions, high temperature XRPD experiments were performed. II-Zn transforms into I-Zn at about 120 °C (Figure 4: top and Figure S18). A similar behavior is observed for III-Zn, which also transforms into I-Zn but at significantly higher temperature (Figure 4: bottom and Figure S19). It is noted, that the II-Zn sample contained a small amount of I-Zn as side phase (ca. 2 w%), whereas III-Zn seemed to be phase pure, see Figure 4. In both cases, the low temperature (LT) and high temperature (HT) phase coexist over a larger temperature range, which is typical for polymorphic solid to solid polymorphic transformations that proceed *via* nucleation and growth of a new phase, which also means that in this case a transformation via melting and crystallization can be excluded (Figure S20 and S21). There is no indication that one of the forms II-Zn or III-Zn occurs as intermediate in the heating of the other polymorph, before their transformation into **I-Zn** is observed. On further heating the reflections of I-Zn disappear, which indicates melting of I-Zn. After cooling to room-temperature, the reflections of I-Zn are observed again, which proves that melting and crystallization had occurred (Figure 4). Because both polymorphs (II-Zn and III-Zn) transform into I-Zn, the latter should also be thermodynamically stable at high temperatures. No reversible polymorphic transition from **I-Zn** into **II-Zn** nor **III-Zn** was observed by low temperature XRPD measurements down to -180 °C (Figure S22). From these experiments no conclusions can be drawn whether these forms are related by enantiotropism or monotropism for which the direction of



DSC and thermomicroscopic investigations

To investigate the transition behavior of all forms DSC measurements were performed at a heating rate of 10 °C/min. Upon heating **I-Zn** an endothermic peak is observed at 173 °C, which should correspond to the melting point of this form, because melting of the corresponding Co(NCS)₂(DMAP)₂ polymorph **I-Co** is observed at exactly the same temperature (Figure 5).⁴⁴ A similar measurement on **II-Zn** shows two endothermic events at 148 and 172 °C and one exothermic peak at 154 °C (Figure 5). The overall behavior is similar to that of the isotypic modification **II-Co**, which transforms into **I-Co** *via* melting and crystallization and if one assumes that the first endothermic event corresponds to the melting of **II-Zn**, its melting temperature is about 20 °C lower than that of **II-Co** (T_p = 168 °C).⁴⁴ After melting of **II-Zn**,

recrystallization is observed at 154 °C, which might lead to the formation of **I-Zn**. It is noted, that there is an additional but very weak signal at 169 °C, which in previous investigations was not observed in the DSC measurements of **II-Co**.⁴⁴

DSC measurements for **III-Zn** show only one peak at 167 °C, which is nearly at the same temperature as the second endothermic event in the measurement of **II-Zn**. Thus, it can be assumed that in this case **II-Zn** transforms *via* melting and recrystallization into a mixture of **I-Zn** and **III-Zn** or into pure **III-Zn** that upon further heating transforms into **I-Zn** *via* melting and recrystallization, which cannot be resolved. The overall thermal behavior is much more complicated than that of the two Co(II) dimorphs (**I-Co** and **II-Co**).



Figure 5. Heating and cooling DSC curves for **I-Zn**, **II-Zn** and **III-Zn** at 10 °C/min. Given are the peak temperatures (T_n) in °C.

However, upon cooling after the last endothermic signal, no exothermic peak is observed and XRPD investigations prove, that cooling the melt of **I-Zn** leads to an amorphous residue, whereas the same procedure for **III-Zn** leads to the formation of a poorly crystalline sample, in which a few and very weak reflections of **III-Zn** and an unknown crystalline phase are observed (Figure S23). The IR and Raman spectra of the amorphous residue show values of the CN stretch at 2056 and 2075 cm⁻¹, close to that for **III-Zn** and

typical for terminal N-bonded thiocyanate anions (Figure S24). It is also noted, that on reheating the amorphous samples a very broad exothermic signal is observed that corresponds to incomplete recrystallization leading to the formation of **III-Zn** together with an unknown residue (Figure S25 and S26). To additionally prove that the first endothermic event of **II-Zn** and **III-Zn** corresponds to melting of these forms, additionally DSC measurements were performed, in which a small amount of **I-Zn** was added, which in this case should act as nuclei for the crystallization of this form (Figure 6). In this case the integral of the melting peak of **II-Zn** is much lower and that of **I-Zn** much higher, obviously because crystallization of **I-Zn**, which only shows one peak, which should correspond to melting. If a small amount of **I-Zn** is added, the integral of the melting peak of **III-Zn** is lower and a second peak is observed that corresponds to melting of **I-Zn** (Figure 6). These experiments strongly indicate that in this case the transformations proceeds *via* melting and recrystallization of a new form.



Figure 6. DSC curves of **II-Zn** and **III-Zn** and a mixture of **II-Zn** or **III-Zn** with a small amount of **I-Zn** at 10 °C/min. Given are the peak temperatures (T_p) in °C.

 This is further supported by thermomicroscopic measurements on all forms, which additionally prove that the melting temperatures of **III-Zn** and **I-Zn** are very similar (Figure 7). In thermomicroscopic measurements of **II-Zn** only melting of **I-Zn**, which formed upon heating, can clearly be identified. There are some optical changes in the powders at temperatures, where **II-Zn** should melt, but obviously melting and crystallization cannot successfully be resolved in this case (Figure S27).



Figure 7. Microscopic images of **I-Zn** (left) and **III-Zn** (right) at different temperatures measured by thermomicroscopy.

Unfortunately, in the DSC measurements presented above only transformations *via* the melt are observed and thus, the heat of transition rule cannot be used to determine the thermodynamic relations. Therefore, we investigated whether the transformations of **II-Zn** and **III-Zn** into **I-Zn** can be suppressed by faster heating to finally determine the melting enthalpies (Figure 8). Therefore, heating rate depend measurements were performed (Figure 8). In this context it is noted that at 1 °C/min the endo-exo-endo sequence for **II-Zn** and **III-Zn** is much better resolved, which proves again that these transitions proceed *via* the melt.

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Figure 8. DSC curves of II-Zn (top) and III-Zn (bottom) with different heating rates.

If the heating rate is increased, only one single endothermic peak is observed for both forms, which in the case of **II-Zn** needs a heating rate of at least 40 °C/min. This indicates that the transition of **II-Zn** respectively **III-Zn** into **I-Zn** is suppressed (Figure S8 and Figure S28). If the melting enthalpies were determined always strongly varying values were obtained for different batches of **II-Zn**, which despite the experimental error might be traced back to the fact that crystallization into **I-Zn** was not be completely suppressed. Therefore it

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was not possible to extract reliable melting enthalpies from these measurements. However, for **II-Zn** integration over the first endothermic and the exothermic signal always leads to positive values, indicating an overall endothermic process and therefore, an enantiotropic relationship can be expected.

However, as shown in the temperature dependent XRPD measurements, for some batches a solid to solid polymorphic transition of II-Zn or III-Zn was observed, which is obvious because the corresponding transition temperatures are much lower than the melting temperatures of both forms. The fact, that in the temperature dependent XRPD the transition proceeded *via* the solid, whereas in the DSC measurements *via* melting and crystallization of a new phase, is not unusual. On one hand, such transitions depend on the history of a sample and the kinetics of a transition. It is typical for polymorphic transitions, that each nuclei has its own pre-coded transition temperature, which also depends on defects. This means that in the solid, deviating transition temperatures are usually observed and that in some cases, e.g. by fast heating of well crystalline samples the polymorphic transition can be suppressed, which allows to determine the melting point of a metastable form.⁵² Compared to DSC measurements, the temperature dependent XRPD measurements need more time to be measured, which is similar to annealing a sample below the melting temperature, which can lead to the transformation into the stable form. Finally, it is also possible that traces of **I-Zn** were present that induced the transformation into this phase. In this context it is mentioned that for one batch of II-Zn a less intense and very broad endothermic signal is observed at 130 °C, notably below the melting point of this form, which is typical for polymorphic solid-to-solid transitions (Figure 9: top). If the residues formed at the peak of this signal and after this signal are investigated by XRPD, it is obvious that a mixture of I-Zn and II-Zn, respectively nearly pure I-Zn has formed (Figure S29). Because this transition is endothermic, according to the heat of transition rule both forms have to be related by enantiotropism, as it is the case for the corresponding Co(II) modifications. From the heat of transition $\Delta H_{trs}(II-Zn \rightarrow I-Zn)$ (3.3-3.5 kJ/mol) and the melting enthalpy of I-Zn ΔH_{fus} (I-Zn) (30.6-31.1 kJ/mol) formed by the polymorphic transition, the melting enthalpy of **II-Zn** ΔH_{fus} (**II-Zn**) can be estimated to be between 34.1 and 34.4 kJ/mol (Table S2 and S3). It is noted that ΔH_{fus} (**I-Zn**) determined directly from DSC measurements of **I-Zn** (32.5-34.0 kJ/mol) is always higher than the former value, which indicates that the endothermic transition does not lead to pure samples of **I-Zn** (Table S4).



Figure 9. DSC curves of additionally batches of **II-Zn** and **III-Zn**. The inset shows an enlargement of the preliminary endothermic, respectively exothermic transition.

Finally, it is mentioned that DSC measurements of **III-Zn** lead to values for the melting enthalpy $\Delta H_{fus}(III-Zn)$ between 28.4 and 29.9 kJ/mol, which are always lower than those for **I-Zn** and **II-Zn** (Table S5 and S6). Moreover, for one batch of **III-Zn** a very weak exothermic signal is observed before melting, which indicates a polymorphic transition into **I-Zn** (Figure 9). If the residue obtained after the exothermic event is investigated by XRPD it is obvious that some amount of **III-Zn** has been transformed into **I-Zn** (Figure 10: A).

In a second DSC run a sample of **III-Zn** was seeded with a small amount of **I-Zn** and in this case the exothermic polymorphic transition is nearly complete (Figure 10: B). Finally, if this mixture is annealed for 2 h at 150 °C, which means below the melting point of **III-Zn**, the whole sample transformed into **I-Zn**





Figure 10. XRPD pattern of the residues obtained after the exothermic event in a DSC measurement of **III-Zn** (A) and a mixture of **III-Zn** and **I-Zn** (B) and of a mixture of these forms that was annealed at 150 °C for 2 hours (C) together with the calculated powder pattern of **I-Zn** and **III-Zn**.

Thermodynamic relations, energy temperature diagram and comparison with the cobalt polymorphs

From all previous results, which are summarized in Figure 11, the semi-empirical energy temperature diagram can be established, showing the thermodynamic relations between all three polymorphic modifications.





Figure 11. Overview of the experimental results on the thermal and transition behavior of **I-Zn**, **II-Zn** and **III-Zn**, from which the thermodynamic relations can be determined (see below). Please note that batch 1 and 2 refer to arbitrary batches that behave differently depending on the history of the sample, the actual heating rate or if, e.g. some very small amount of **I-Zn** are present that cannot be proven by XRPD.

II-Zn exhibits the highest density (Table 1) and according to the density rule should exhibit the lowest Gibbs energy at absolute zero and therefore, should represent the thermodynamic stable form at low temperatures followed by **I-Zn** and **III-Zn** (Figure 12). Upon heating **II-Zn** transforms endothermically into **I-Zn**, which proves that both forms behave enantiotropically with **II-Zn** being stable at low temperatures, in agreement with the density of the forms. **I-Zn** exhibits the highest melting temperature and thus is the thermodynamic

stable form at high temperatures up to the melting point. The enantiotropic relation between **I-Zn** and **II-Zn** is also in agreement with the melting enthalpy rule, because the higher melting polymorph **I-Zn** exhibits the lower melting enthalpy, even if the difference seems to be extremely small and deviating values were obtained (Table 4).

Table 4. Melting enthalpies and melting temperatures for I-Zn, II-Zn and III-Zn.

	$T_{fus} / °C$	$\Delta H_{fus}/kJmol^{-1}$
I-Zn	173	30.6 - 34.0
II-Zn	148	34.1 - 34.4
III-Zn	167	28.4 - 29.9



Figure 12. Qualitative energy temperature diagram for I-Zn, II-Zn and III-Zn.

Concerning the thermodynamic relation between **I-Zn** and the new form **III-Zn** the exothermic transition of **III-Zn** into **I-Zn** indicates that both forms are related by monotropism with **I-Zn** as the stable polymorph. However, in the case of enantiotropism an exothermic transition is also expected if the transformation occurs

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below the thermodynamic transition temperature but because **III-Zn** definitely exhibits a lower melting point and a lower melting enthalpy than **I-Zn** the monotropic relation is obvious (Figure 12). Finally, even if no transition between **III-Zn** and **II-Zn** was observed, we found that the melting point of **III-Zn** is significantly higher than that of **II-Zn** and that the higher melting polymorph **III-Zn** definitely exhibits the lower melting enthalpy and therefore, these two forms should be related by enantiotropism (Figure 12).

The enantiotropic relation between **II-Zn** and **I-Zn** is similar to that of the cobalt forms **II-Co** and **I-Co** but surprisingly, unexpected differences in the thermodynamic transition temperatures between that of **II-Zn** and **I-Zn** and **that** of **II-Co** and **I-Co** were found, which means that **I-Co** is metastable at room-temperature, whereas **I-Zn** is thermodynamically stable. This is surprising, because both isotypic modifications **I-Co** and **I-Zn** as well as **II-Co** and **II-Zn** consist of very similar cations of identical charge and an identical or at least very similar surrounding, which should lead to comparable intermolecular interactions. Therefore, at first glance, for both forms a similar thermodynamic stability would be expected. We also carefully checked the results of the solvent mediated conversion experiments, because unstable solvates might form, that on isolation of the solids decompose into a metastable form. Therefore, these experiments were repeated in a closed capillary, from which experiments no hints for an additional phase were found. Even in this case it is obvious that from a mixture of **I-Zn** and **II-Zn** the crystals of **II-Zn** start to disappear at first.

Moreover, according to our findings unexpected differences in the thermodynamic transition temperatures between that of **II-Zn** and **I-Zn** and that of **II-Co** and **I-Co** were found, which means that **I-Co** is metastable up to about 145°C, whereas **I-Zn** is already stable just below room-temperature. This large difference in the thermodynamic transition temperatures appears to be unusual large. However, the thermodynamic transition temperature of the Co(II) polymorphs was determined by thermal annealing of powders and one can assume that in fact it is lower than determined. But it is unlikely that mixtures of **I-Co** and **II-Co** transform into **I-Co** at 145°C but not at 135°C if the thermodynamic transition temperature would be much lower and the

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experimental value of 145°C is in good agreement with that estimated from the melting temperatures and melting enthalpies of 153°C.

We also estimated the thermodynamic transition temperature between **II-Zn** and **I-Zn** from the melting points and melting enthalpies according to the following equation:

$$T_{\rm trs} = \frac{T_{\rm f(I)}T_{\rm f(II)}(\Delta H_{\rm f(II)} - \Delta H_{\rm f(I)})}{T_{\rm f(I)}\Delta H_{\rm f(II)} - T_{\rm f(II)}\Delta H_{\rm f(I)}}$$

This lead to transition temperatures between -55 and 32 °C, depending on the values that were used for the melting enthalpies for **I-Zn** and **II-Zn**. However, in any case they are much smaller than those estimated for the corresponding Co(II) polymorphs. In this context, it is noted that the calculated transition temperature decreases if the difference between the melting enthalpies decreases and from our DSC measurements it is indicated, that this difference between **I-Zn** and **II-Zn** is very small and within the experimental error of the measurements.

That in any case relatively large differences between the Co(II) and the Zn(II) polymorphs must occur is already obvious, because the melting temperatures of **I-Co** and **I-Zn** are identical, whereas that of **II-Zn** is much lower than that of **II-Co**. Moreover, the difference in melting enthalpy between the Co(II) polymorphs is significantly larger than that between the Zn(II) forms, which also shifts the thermodynamic transition temperature for the latter to lower temperatures.

CONCLUSION

This work is based on previous investigations on discrete complexes with the composition $Co(NCS)_2(DMAP)_2$ that exist in two polymorphic modifications with II-Co being thermodynamically stable below about 145 °C and I-Co above this temperature up to the melting point.⁴⁴ For structure determination of I-Co which is metastable at room-temperature the corresponding Zn(II) compound I-Zn was crystallized, which was always obtained in these experiments. Consequently, it was assumed that I-Zn is metastable at

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room-temperature and was accidently obtained by kinetic control. Later it was found that the situation is completely different, because **I-Zn** is already thermodynamically stable at room-temperature. This is surprising, because each pair of the Co and the Zn polymorphs is isotypic, which means that similar intermolecular interactions are expected. In this context it is noted that the difference in the thermodynamic transition temperatures appears to be very large, but originates from our experimental investigations. However, independent on the exact value of this difference one can imagine that both cations, Co(II) and Zn(II) fit perfectly into the structure type of form **I**, leading to comparable melting points, which might not be the case for form **II**. This will not only influence the enthalpies of the modifications but also the contribution of the entropy to the free energy. In any case the difference in the stability of the low temperature forms **II** seems to be an important observation, because it indicates that definite conclusions on the stability of compounds only on the basis of crystal structures and intermolecular interactions should be drawn very carefully, which possibly accounts for more cases as just polymorphic modifications.

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ASSOCIATED CONTENT

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Notes

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The authors declare no competing financial interest.

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Trimorphism of Zn(NCS)₂(4-dimethylaminopyridine)₂: Crystal Structures, Thermodynamic Relations and Comparison with the Co(II) Polymorphs

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Two additionally polymorphic modifications of $Zn(NCS)_2(DMAP)_2$ were discovered and structurally characterized in addition to the form already reported in literature. The thermodynamic relations were investigated by a combination of X-ray powder diffraction, differential scanning calorimetry, thermomicroscopy and crystallization experiments and all these results were compared with that for the corresponding dimorphs of Co(NCS)₂(DMAP)₂ reported recently.