



Polymorphism

Selective Synthesis and Thermodynamic Relations of Polymorphic Co(NCS)₂-4-Dimethylaminopyridine Coordination Compounds

Tristan Neumann,^[a] Inke Jess,^[a] Florian Pielnhofer,^{[b][‡]} and Christian Näther*^[a]

Abstract: Reaction of $Co(NCS)_2$ with 4-dimethylaminopyridine (DMAP) leads to the formation of four new compounds. The crystal structures of $Co(NCS)_2(DMAP)_2(H_2O)_2 \cdot 2H_2O$ (1), $Co(NCS)_2(DMAP)_2(MeOH)_2$ (2) and $Co(NCS)_2(DMAP)_2(MeCN)_2$ (3) consist of discrete simple solvato complexes in which the Co cations are octahedrally coordinated by two terminally N-bonded thiocyanate anions, two DMAP ligands as well as two solvato ligands. $Co(NCS)_2(DMAP)_2(AIII)$ also forms discrete complexes, but the Co cations are tetrahedral coordinated by two anionic ligands and two DMAP ligands. Upon heating, the hydrate 1 transforms into 4/II, whereas the methanol solvate 2 transforms into a new polymorphic modification of $Co(NCS)_2(DMAP)_2$ (4/I). For structure determination the corresponding $Zn(NCS)_2$ compound was prepared that is isotypic to 4/I. Solvent mediated conversion experiments prove that 4/II represents the thermodynamic stable form at room-temperature and density functional theory (DFT) calculations indicate that this form is also stable at 0 K. Upon heating both modifications show melting with the higher melting polymorph 4/I having the lower melting enthalpy. Temperature dependent X-ray powder diffraction shows that 4/II transforms into 4/I upon heating. All experimental results indicate, that both modifications are related by enantiotropism.

Introduction

Investigations on the synthesis, structures and properties of compounds with defined structures and desired physical properties are still an important goal in solid state chemistry.[1-8] For this purpose coordination compounds can be very useful because based on simple chemical knowledge the connectivity of the cations or networks can be predicted to some extent.^[9] Unfortunately, the energy difference between possible polymorphs or isomers is frequently small, which can lead to the formation of different products under kinetic or thermodynamic control.^[10] In this context, a large number of polymorphic and isomeric coordination compounds were reported in the last vears.^[1,11–29] From a viewpoint of material synthesis this might be of disadvantage but there is also some benefit from these phenomena. For polymorphs or isomers the chemical composition is constant and all changes in the properties of the different forms can be directly correlated with their structural differences, allowing the investigation of structure-property relationships. However, if polymorphs or isomers are detected it should

[a]	Institute of Inorganic Chemistry, Christian-Albrechts-University of Kiel
	Max-Eyth-Strasse 2, 24118 Kiel, Germany
	E-mail: cnaether@ac.uni-kiel.de
	http://www.ac.uni-kiel.de/de/naether
[b]	Max-Planck-Institut for Solid State Research,
	Heisenbergstraße 1, 70569 Stuttgart, Germany
[‡]	Current adress: Institute of Inorganic Chemistry,
	University of Regensburg,
	Universitätsstraße 31, 93040 Regensburg, Germany
	Supporting information and ORCID(s) from the author(s) for this article are
D	available on the WWW under https://doi.org/10.1002/ejic.201800741.

be investigated how a specific form can be prepared phase pure, which of these forms is thermodynamic stable and how these forms can be transformed into each other.

One class of compounds for which polymorphs or isomers frequently occur is represented by coordination compounds based on 3d transition metal thiocyanates with additional coordinating N-donor co-ligands. This anionic ligand can coordinate to metal cations in many different ways, which leads to a large structural diversity of such compounds and this might be one of the reasons why many different polymorphs or isomers were reported for this class of compounds.[30-38] The reason why we became interested in this class of compounds originates from the idea for the preparation of compounds that might show different magnetic properties including cooperative magnetic phenomena, because this ligand can mediate reasonable magnetic exchange.^[39-54] In this context 1D compounds based on Co^{II} are of special interest, because several of them show a slow relaxation of the magnetization, which can partly be traced back to single chain magnetism.[55-60] However, for the synthesis of such compounds paramagnetic metal cations must be linked by these anionic ligands into, e.g., 1D or 2D networks and even if several of such compounds are reported this is sometimes a difficult task. For the less chalcophilic metal cations like, e.g. Mn^{II}, Fe^{II}, Co^{II} or Ni^{II}, the compounds with only terminally N-bonded anionic ligands are usually more stable and easy to synthesize, whereas the desired compounds with a bridging coordination are frequently difficult to synthesize in pure form if they are prepared by crystallization from solution. This is one of the main reasons why we have developed an alternative procedure for the synthesis of the bridging com-





pounds, which is based on thermal decomposition of precursors. The precursors mostly consist of discrete complexes with terminal anionic ligands that upon heating loose the organic co-ligands or solvate molecules in separate steps forming the desired bridging compounds as intermediates in pure form and quantitative yield.^[61] One additional advantage of this approach is the fact that metastable compounds can be obtained that are difficult to prepare or that are not accessible from solution and this might be also one reason why so many polymorphs or isomers were detected by us following this route.^[29,62]

In the course of our investigations we became interested in 4-dimethylaminopyridine (DMAP) as co-ligand, because of its strong donor substituent. Therefore, we investigated if 1D compounds with Co(NCS)₂ chains might be available, which would be of extraordinary importance for the entire project. It is noted, that no crystal structures with Co(NCS)₂ and DMAP are reported in the CCDC database but some discrete complexes with other transition metal cations are known.^[63-68] However, for compounds with other anions in which Co is coordinated by DMAP, more octahedral than tetrahedral compounds are known.^[69-72] It is also noted that a 1 D compound is reported, in which Co cations are linked by pairs of azido ligands into chains, an arrangement that exactly corresponds to that what we expected for thiocyanate coordination polymers and which indicates that also with Co(NCS)₂ the desired chain compound might be available.^[73] Here we report on the results of our investigations.

Results and Discussion

Synthesis and Thermoanalytical Investigations

Reaction of Co(NCS)₂ with DMAP in different molar ratios in water, methanol or acetonitrile lead to the formation of four new compounds with the compositions Co(NCS)₂(DMAP)₂- $(H_2O)_2 \cdot 2H_2O$ (1), $Co(NCS)_2(DMAP)_2(MeOH)_2$ (2), $Co(NCS)_2$ -(DMAP)₂(MeCN)₂ (3) and Co(NCS)₂(DMAP)₂ (4/II). It is noted that the composition of 4/II corresponds exactly to that of the desired chain compound. The asymmetric CN stretching vibration of the thiocyanate anions is observed at 2090 cm⁻¹ for 1, 2 and 3, which is in the range expected for terminally N-bonded thiocyanate anions with an octahedral coordination indicating that simple discrete solvato complexes have formed with additional water solvate molecules in 1 (Figure S1-S3 in the SI). For compound 4/II, the CN stretch is found at 2054 cm⁻¹, which is much lower than expected for bridging anionic ligands and therefore, it can be assumed that a tetrahedral complex with terminal anionic ligands instead of a chain has formed (Figure S4).

For all compounds single crystals were prepared and characterized by single-crystal X-ray diffraction, which proves that compounds **1–3** consist of octahedral and **4/II** of tetrahedral discrete complexes (see below). Comparison of the experimental X-ray powder diffraction pattern (XRPD) with those, calculated from the single crystal structures shows that compounds **1** and **3** were obtained as pure phases, whereas the methanol compound **2** is contaminated with a further crystalline phase (Figure S5–7). The amount of this new form increases with increasing storage time, which indicates that **2** is unstable and loses methanol already at room-temperature (Figure S6). Thus, it must be assumed that solvent removal from the methanol solvate will lead to a different crystalline form (**4**/**I**) with the same composition as that of **4**/**II**. All batches of **4**/**II** prepared from water contain predominantly the hydrate **1**, which is more stable and thus, this compound cannot be obtained pure under these conditions (Figure S8).

Thermoanalytical Investigations

To investigate which crystalline form is obtained on solvent removal, the thermal properties of 1-3 were investigated by simultaneous thermogravimetry and differential thermoanalysis (TG-DTA). Upon heating compound 1-3 in a thermobalance, two mass losses are observed in the TG curves that are accompanied with endothermic events in the DTA curve (Figure 1 and Figures S9–S11). For the methanol solvate 2 there is an indication that the first mass step consists of two not well resolved steps. For all three compounds the experimental mass loss in the first step is in reasonable agreement with that expected for the removal of the water, methanol or acetonitrile molecules, indicating that intermediates with the composition Co(NCS)₂(DMAP)₂ are formed. The experimental mass loss in the second TG step is larger than that expected for the removal of each two DMAP ligands and thus, ligand removal and decomposition of Co(NCS)₂, that must form as intermediate, occur simultaneously. It is noted that for all three compounds after



Figure 1. TG curves of compounds $1{-}3$ measured at 8 °C/min. DTG, TG and DTA curves curves can be found Figures S9–S11.





solvent removal an additional endothermic peak is observed at about 177 °C, where the sample mass does not change, which indicates that the intermediates show an additional transition (Figure S9-S11).

If the residues obtained after the first mass loss are investigated by XRPD it is proven that compound 1 has been transformed into the discrete complex 4/II, whereas compound 2 decomposes into a new crystalline form with the composition Co(NCS)₂(DMAP)₂ (4/I) that is different from 4/II (Figure S12-S13). The intermediates obtained by acetonitrile removal from 3 at 8 °C/min and 1 °C/min are different and correspond to crystalline phases that are unknown (Figure S14). The CN stretching vibration of the thiocyanate anion in 4/I measured by IR spectroscopy occurs at 2060 cm⁻¹, indicating that the anionic ligands are still terminally N-bonded (Figure S15). Therefore, it can be assumed that a further polymorphic modification of a tetrahedral discrete complex has formed. In this context it is noted that tetrahedral discrete complexes with the composition $M(NCS)_2(L)_2$ (M = divalent metal cation; L = pyridine derivative) are also formed with Zn(NCS)₂. In previous investigations we have shown, e.g. that the corresponding compounds with Co(NCS)₂ and Zn(NCS)₂ and 2-methylpyridine form isotypic pairs with each pair crystallizing in two different polymorphic modifications.^[12] Therefore, we reacted Zn(NCS)₂ with DMAP in ethanol which was overlayed with heptane, which easily lead to crystals of a discrete tetrahedral complex with the composition $Zn(NCS)_2(DMAP)_2$ (5), for which the CN stretching vibration is observed at 2073 cm⁻¹ and 2097 cm⁻¹ (Figure S16) If the calculated XRPD pattern of 5 is compared with the experimental pattern of the residue obtained after methanol removal (4/I), it is obvious that both compounds are isotypic (Figure S17). This is proven by a Pawley-Fit of 4/I, which also shows that this compound is obtained as a pure phase (Figure S18 and S19). Finally, we checked if compounds 4 can be retransformed into the solvates 1-3. Therefore, a sample of 4/II was stored for 12 h in a water, a methanol and an acetonitrile atmosphere. XRPD investigations of the residue formed in acetonitrile reveal that 4/II has been transformed into 3, whereas the residues stored in a water and methanol atmosphere still correspond to 4/II (Figure S20).

Crystal Structures

Crystal Structure of Co(NCS)₂(DMAP)₂(H₂O)₂·2 H₂O (1)

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. The asymmetric unit consists of one Co^{II} cation located on a center of inversion, one thiocyanate anion and one DMAP ligand as well as two water molecules in general positions (Figure 2: top and Figure S21). The Co^{II} cations are coordinated by two N-bonded thiocyanato anions, two DMAP ligands and two water molecules in a slightly distorted octahedral geometry to form discrete complexes (Figure 2: top). The Co–N bond lengths to the thiocyanate N atom of 2.1140 (14) Å and to the DMAP ligands of 2.1134 (14) Å are surprisingly very similar (Table S1). This points to a stronger interaction between the Co^{II} cation and the pyridine N atom, because usually a shorter bond length to the anionic ligands is observed in similar compounds reported in literature. Presumably, the Co–N bond to the DMAP ligands is stronger because of the strong donor-substituent in para position.



Figure 2. View of a discrete complex of **1** (top) and crystal structure with view along the crystallographic *c* axis (bottom). Intermolecular O–H···O and O–H···S hydrogen bonding is shown as dashed lines and an ORTEP plot can be found in Figure S21 in the Supplemental.

The discrete complexes are linked via intermolecular O–H···O hydrogen bonding between the coordinated and the solvate water molecules into chains, that elongate along the crystallographic *a* axis (Figure 2: bottom and Table S2). Each of the two H atoms of the coordinated water molecules are connected to a water hydrate molecule forming four-membered (H₂O)₄ rings. The H atoms of the two hydrate water molecules that do not participate in this interaction are hydrogen bonded to two thiocyanate S atoms by intermolecular O–H···S hydrogen bonding forming four-membered (H₂O)₂S₂ rings (Figure 2: bottom and Table S2). There are additional short S···H contacts indicating for weak C–H···S interactions (Table S2).

Crystal Structure of Co(NCS)₂(DMAP)₂(MeOH)₂ (2)

Compound **2** also crystallizes triclinic in space group $P\overline{1}$. The Co cations are located on centres of inversion and are coordinated by two N-bonded anionic ligands, two DMAP ligands as well as two methanol molecules (Figure 3: top and Figure S22). As in compound **1**, the Co–N bond lengths to the anionic and the neutral ligands are very similar (Table S3). The angles around the Co cations show that the octahedra is slightly distorted (Table S3).







Figure 3. View of a discrete complex of 2 (top) and crystal structure with view along the crystallographic *c* axis (bottom). Intermolecular O–H···S hydrogen bonding is shown as dashed lines and an ORTEP plot can be found in Figure S22 in the Supplemental.

In the crystal structure the discrete complexes are linked into chains along the *a* axis by pairs of intermolecular O–H···S hydrogen bonding between the thiocyanate S atom and the hydroxyl H atom (Figure 3: bottom and Table S4). There are also weak C–H···S interactions between the anionic and the neutral N-donor ligands (Table S4).

Crystal Structure of Co(NCS)₂(DMAP)₂(MeCN)₂ (3)

Compound **3** also forms discrete complexes with octahedral coordinated Co cations (Figure 4 and Figure S23). As compounds **1** and **2** it also crystallizes in space group $P\overline{1}$ with the Co cations located on centres of inversion. In contrast to the former complexes, the differences in the bond lengths between the anionic and the neutral ligands are more pronounced (Table S5). The discrete complexes are linked via weak C–H···S interactions into a hydrogen-bonded network (Table S6).



Figure 4. Crystal structure of **3** with view of one discrete complex. An ORTEP plot can be found in Figure S23.

Crystal Structures of $M(NCS)_2(DMAP)_2$ with M = Co (4/l) and M = Zn (5)

As mentioned above, compound 4/I is isotypic to the corresponding Zn compound 5. Compound 4/II crystallizes monoclinic in space group $P2_1/c$ with all atoms located in general position, whereas compound 5 crystallizes in space group $P2_1/m$ with the cations and the thiocyanate anions located on a twofold rotation axis (Figures S24 and S25). In contrast to most other Co(NCS)₂ coordination compounds with same metal thiocyanate to co-ligand ratio, the metal cations are tetrahedral coordinated by two terminally N-bonded thiocyanate ligands and two DMAP co-ligands into discrete complexes (Figure 5 and Table S7 and S9). The formation of a tetrahedral instead of an octahedral coordination is surprising. It is noted that a tetrahedral coordination of the Co cation is frequently found if the pyridine substituent is directly neighboured to the coordinating N atom in 2-position^[12] and this might be traced back to steric reasons, but this cannot be valid for compound 4. Therefore, electronic reasons might be responsible that the tetrahedral coordination is preferred over the octahedral environment. In this context it is mentioned that the Co-N bond lengths to the DMAP ligands in compound 1–4 are much shorter than that to other pyridine co-ligands, which points to a stronger interaction. Therefore, it is assumed that the strong electron donor DMAP transfers more electron density to the Co cation as other pyridine derivatives and that the metal cation in an octahedral coordination can accept only a limited amount and as a consequence the tetrahedral coordination might become energetically favoured.



Figure 5. Crystal structure of **4/II** (top) and the corresponding Zn compound **5** that is isotypic to **4/I** (bottom) with view of one discrete complex. An ORTEP plot can be found in Figure S24 and S25.



However, concerning the structural differences between **4/I** and **4/II** or **5** it is noted that the arrangement of the DMAP ligands is already different as it is obvious when both discrete complexes are superimposed (Figure S26). In form **4/I**, the planes of the six-membered rings are nearly perpendicular to each other, which is not the case in **5** or **4/II**.

Differences in both forms are also found in the arrangement of the complexes in the crystal. In form **4/II** the complexes are interwoven leading to a relatively dense packing (Figure 6: top). Moreover, each two DMAP ligands forms pair, that are located around centres of inversion (Figure S27).



Figure 6. Crystal structure of 4/II (top) and 5 (bottom) with view along the crystallographic *a* axis.

In **5** or **4/I** the complexes are arranged in columns, that elongate in the direction of the crystallographic *a* axis (Figure 6: bottom). These columns are packed in a less dense arrangement. Moreover, the DMAP ligand as well as the $Co(NCS)_2$ building blocks are arranged in layers, that are parallel to the *a/c* plane. In each second $Co(NCS)_2$ layers the anionic ligands point into different directions, from which the centrosymmetric arrangement becomes obvious (**Figure** S28).



The question why the solvent removal from compound 1 leads to the formation of 4/II, whereas 4/I is exclusively obtained from the methanol solvate 2 is difficult to answer. First of all, the formation of 4/II is not surprising, because it can be assumed that this form represents the thermodynamic stable modification starting from room-temperature (see below). Therefore, form 4/I should be formed by kinetic control and this might be easier if there would be some structural relation between the solvate 2 and the form obtained by solvent removal (4/I), even if this is no necessary condition. This does not mean that the reaction is topotactic, because it is obvious that large structural changes are needed to transform 2 into 4/I. However, as mentioned above, in 4/I the building blocks are arranged in layers and the DMAP ligands of neighbouring complexes are shifted by half of the *a* axis (Figure 6: bottom). A similar arrangement is also found in the methanol solvate 2, which indicates that the arrangement of the complexes in 4/I is somehow predefined in compound 2 (Figure S29).

Investigations on the Transition Behaviour and the Thermodynamic Relation between 4/I and 4/II

To prove which of the two polymorphic modifications **4/I** and **4/II** is thermodynamically stable at room-temperature, a mixture of both forms was stirred in ethanol with an excess of solid. If the solid residues obtained after 7 d are investigated by XRPD, it is obvious that all crystals of form **4/I** disappeared and that only crystals of **4/II** are present (Figure 7). This indicates, that **4/II** represents the thermodynamically stable form at roomtemperature, where **4/I** is metastable.



Figure 7. Experimental XRPD pattern of a mixture of **4/I** and **4/II** (B) and after stirring this mixture for 7 d in ethanol (A) together with the pattern calculated for **4/II** (C) and **4/I** (D).

To compare the densities of both forms, their unit cell parameters were determined by Pawley fits, using XRPD data measured at room temperature, which proved that the density of form **4/II** is significantly higher than that of form **4/I** (Table S11). According to the density rule this indicates that **4/II** should also be thermodynamically stable at low temperatures.^[74]

The stability of both polymorphs was further compared by their total electronic energies (at 0 K) as obtained by quantum





chemical calculations. **4/II** is energetically favored to **4/I** by 11 kJ mol⁻¹, and therefore predicted to be the thermodynamically stable modification which is in good agreement with experimental observations.

Measurements on **4/I** using differential scanning calorimetry (DSC) show one endothermic event upon heating, that is absent in the cooling curve (Figure 8: top). On reheating a very broad exothermic event is observed, that is followed by an endothermic peak at the same temperature as observed in the first heating run. The DSC curve for **4/II** is very similar but the endothermic transition in the first heating run is at significantly lower temperature than in the second heating (Figure 8).



Figure 8. DSC curves for 4/I (top) and 4/II (bottom) at 10 °C/min.

If the residues obtained after the heating and cooling cycle are investigated by XRPD, it is proven that amorphous samples have formed (Figure S30). This indicates that the first endothermic event corresponds to the melting of both forms with the melting point of **4/I** significantly higher than that of **4/II**. XRPD investigations of the residue obtained after the first exothermic event in the second heating run shows that **4/I** has formed (Figure S31). This is in agreement with the DSC results on **4/II** because melting of this residue occurs at the same temperature as observed for **4/I** (Figure 8: top). It is also noted that XRPD investigations of samples of both forms heated just before their first endothermic event show no changes and thus, gave no hint for any further transformation (Figure S32 and S33). Thermomicroscopic measurements on both forms are in full agreement with the interpretation of the DSC measurements, because clearly melting is observed with a melting point for **4/I** that is higher than that of **4/II** (Figure 9). All this strongly indicates that form **4/I** becomes thermodynamically stable at higher temperatures and that therefore, both modifications should behave enantiotropically with the free energy temperature curves crossing somewhere between room temperature and the melting point of **4/II**.



Figure 9. Microscopic images of **4/II** (left) and **4/I** (right) at different temperatures.

Additional DSC measurements on form 4/II at 1 °C/min show an endo-exo-endo sequence, which might be traced back to the fact that 4/II melts in the beginning and that on further heating 4/I crystallizes from the melt because its melting point is higher (Figure S34). This is in agreement with XRPD measurements of residues obtained after the first endothermic and exothermic event (Figure S35). After the first endothermic peak an amorphous samples is obtained, because this event correspond to the melting of 4/II (Figure S35). If the measurement is stopped after the exothermic event 4/I is obtained, which can be traced back to the crystallization of this form from the melt (Figure S35). Interestingly, the same endo-exo-endo sequence is observed for a different batch already at a heating rate of 10 °C/min and in this case it can be assumed that a small amount of 4/I is present with a content too low to detect it by XRPD. In this case these crystals act as nuclei for the crystallization of this form as previously observed (Figure S34).^[75] For this batch (batch 2) the heat of fusion 4/II is much lower than that for batch 1, because the intensity ratio between both endothermic peaks, will depend on how much of 4/I crystallizes from the melt upon heating.

Finally, form **4/II** was investigated by temperature dependent XRPD, which shows that at a temperature of about 158 °C new reflections occur, which definitely belong to that of **4/I** (Figure 10). Upon further heating all reflections of **4/II** disappear slowly and the transformation into **4/I** is completed at about 178 °C (Figure 10).

Interestingly, from these measurements it is obvious that both forms coexist over a large temperature range and this is typical for a solid-to-solid polymorphic transition, that proceed





Figure 10. Temperature dependent XRPD pattern of **4/II**. For the full temperature range see Figure S36.

via nucleation and growth of a new phase and for which each nucleus has his own predetermined transition temperature. Therefore, in contrast to the DSC measurements presented above, where the transition proceeds via melting and crystallization of a new form (4/I), in this case it must proceed via the solid state, because otherwise the powder pattern should change in a much smaller temperature range.

All these findings indicate that both forms are related by enantiotropism, with 4/I thermodynamically stable at high and 4/II at low temperatures. To additional prove this, the heat of fusion and heat of entropy rule might be useful, which state that in those cases where the higher melting polymorph has the higher melting enthalpy or entropy, both forms are related by monotropism. In the case where its melting enthalpy or entropy is lower they are enantiotropically related.^[76] Surprisingly, the melting enthalpy and entropy of the high temperature polymorph 4/I is always higher than that of 4/II and this indicates a monotropic relation, which is in complete contradiction with our previous results. There might be some exceptions from this rule but only if the melting temperatures and heat-capacity are very different, which seems to be not the case here. In this case it is possible that the outcome of the solvent mediated conversion experiment performed in ethanol might be wrong, because, e.g. an unstable solvate will form that decomposes on isolation into a metastable form. Therefore, the solvent mediated conversion experiment was repeated at room-temperature in butanol, which again leads clearly to the formation of 4/II which proves that it must be the thermodynamically stable form at this temperature (Figure S37).

We additionally determined the solubility of both forms in ethanol by atomic absorbtion spectroscopy (AAS). Therefore, a saturated solution with excess of **4/I** was stirred in ethanol at room-temperature before transformation into **4/II** was observed and the Co content in the solution was determined by AAS. The same procedure was used for **4/II** using longer reaction times. This proves that the solubility of **4/II** (160 mg/L) is lower than that of **4/I** (170 mg/L), which is in agreement with previous investigations, because the latter is metastable at room-temperature.



However, the sample used for the DSC measurements was prepared from ethanol and even if the identity of **4/II** was proven by XRPD we decided to prepare this form by a different route. Therefore, the water was removed by heating from the hydrate **1** and the sample was stored at 110 °C until the measurement. DSC measurements on this batch show two endothermic peaks, that correspond to the melting of both forms, where the latter is formed by consecutive melting and crystallization of **4/II** (Figure 11). To suppress the transformation of **4/II** into **4/I** via the melt measurements with faster heating rates were performed (Figure 11).



Figure 11. DSC curves of 4/I and 4/II at different heating rates.

These experiments reveal that the heat of fusion (ΔH_f) for **4/II** is about 34.8 kJ mol⁻¹, whereas that for **4/I** is about 25.8 kJ mol⁻¹, which indicates that the higher melting polymorph has a lower heat of fusion and therefore that both polymorphs are related by enantiotropism (Table S12). Neglecting the differences in the heat capacity, the energy difference between both forms is about 9 kJ/mol, which is much for polymorphic modifications. From these values the entropy of fusion (S_f) was calculated according to

$$\Delta S_f = \frac{\Delta H_f}{T_m}$$

which also proves the enantiotropic relation (Table S12). Based on the melting temperatures (T_m in K) and melting enthalpies (ΔH_f) the thermodynamic transition temperature (T_t) can be estimated using the following equation:^[77]

$$T_{t} = \frac{T_{m(I)}T_{m(II)}(\Delta H_{f(II)} - \Delta H_{f(I)})}{T_{m(I)}\Delta H_{f(II)} - T_{m(II)}\Delta H_{f(I)}}$$

Using the values given above as well as the onset temperatures (Table S12), the transition temperature is calculated to be about 153 °C, even if there surely is an error of several degrees. This value is lower than that observed in the temperature dependent XRPD measurements, which is expected because of the kinetics of this reaction. Therefore, a sample of **4/II** was annealed at different temperatures. At 135 °C no changes are observed, but at 145 °C the transformation into **4/I** is completed within 92 hours (Figure S38). This transition temperature is in reasonable agreement with that calculated. From all these results the free





energy temperature diagram can be drawn, from which the thermodynamic relation becomes obvious (Figure 12).



Figure 12. Qualitative energy-temperature diagram showing the thermodynamic relation between **4/I** and **4/II** (*G* = free energy; *H* = enthalpy; *T*_t = transition temperature; *T*_m = melting point; $\Delta H_{\rm f}$ = enthalpy of fusion).

Conclusions

In the present contribution two polymorphic modifications of the compound Co(NCS)₂(DMAP)₂ were obtained selectively by solvent removal from two different precursors. The form obtained from the hydrate (4/II) is thermodynamically stable at room-temperature, whereas that obtained from the methanol complex is metastable at this temperature. For the latter there is some rough relation between the structure of the reactant and that of the product, but it is difficult to prove if this is responsible for the formation of this form. Interestingly, both modifications show melting, which is rarely observed for coordination compounds, but which is of advantage to investigate the thermodynamic relations. Moreover, at fast heating rates melting of each form is observed exclusively, whereas at lower heating rates 4/II transforms into 4/I via melting and crystallization, which shows that the kinetics play an important role for this transition. At very low heating rates, like in the temperature dependent XRPD measurements, there is a strong indication that the reaction proceeds in the solid state as frequently observed for polymorphic transitions. Most experiments strongly indicate that both forms are related by enantiotropism with 4/II thermodynamic stable at low and 4/I at high temperatures, but this was in contradiction to our quantitative DSC measurements on samples of 4/II prepared from ethanol. The reason for this observation is not clear and there were no indications for the formation of a solvate or that 4/II is hygroscopic. However, if 4/II is prepared by water removal from the hydrate and carefully dried, the melting enthalpy of the higher melting polymorph is definitely lower than that of 4/II, which indicates that the enantiotropic relation is correct, in agreement with all previous results. Based on the melting temperatures and melting

enthalpies the thermodynamic transition temperature was estimated, which is in good agreement with that determined experimentally by annealing samples of **4/II** at different temperatures. Finally, we have demonstrated that crystallization of the corresponding $Zn(NCS)_2$ compounds can be an useful alternative to structurally characterize $Co(NCS)_2$ intermediates with a tetrahedral coordination.

Experimental Section

Synthesis: Ba(NCS)₂•3H₂O, Co(NCS)₂ and 4-dimethylaminopyridine (DMAP) were purchased from Alfa Aesar, Zn(SO₄)•H₂O was 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 with Ba(NCS)₂•3H₂O in water. The resulting white precipitate of BaSO₄ was filtered off and the filtrate was concentrated to complete dryness resulting in a white residue of Zn(NCS)₂. All compounds were obtained in almost quantitative yields.

Synthesis of 1: Single crystals suitable for single-crystal X-ray structure determination were obtained by the reaction of $Co(NCS)_2$ (56.0 mg, 0.32 mmol) with DMAP (18.7 mg, 0.15 mmol) in 1.0 mL of demin. water at room temperature after several days. A crystalline powder was obtained by the reaction of $Co(NCS)_2$ (87.5 mg, 0.5 mmol) with DMAP (122 mg, 1.0 mmol) in 5.0 mL of demin. water.

Synthesis of 2: Single crystals suitable for single-crystal X-ray structure determination were obtained by the reaction of $Co(NCS)_2$ (109.5 mg, 0.63 mmol) with DMAP (20.2 mg, 0.17 mmol) in 1.0 mL of methanol at room temperature after several days. A microcrystalline powder was obtained by the reaction of $Co(NCS)_2$ (87.5 mg, 0.5 mmol) with DMAP (122.0 mg, 1.0 mmol) in 5.0 mL of MeOH.

Synthesis of 3: Single crystals suitable for single-crystal X-ray structure determination were obtained after a few hours by solving of $Co(NCS)_2$ (4.4 mg, 0.03 mmol) and DMAP (25.1 mg, 0.10 mmol) in 1.5 mL of boiling acetonitrile. The heat source was removed, and the still warm solution was overlayed with 1.5 mL *n*-heptane. A crystalline powder was obtained by the reaction of $Co(NCS)_2$ (175.1 mg, 1:0 mmol) with DMAP (61.0 mg, 0.5 mmol) in 3.5 mL of MeCN.

Synthesis of 4/II: Single crystals suitable for single-crystal X-ray structure determination were obtained by the reaction of $Co(NCS)_2$ (26.3 mg, 0.15 mmol) with DMAP (36.7 mg, 0.30 mmol) in 1.0 mL of demin. water at room temperature after several days.

Synthesis of 5: Single crystals suitable for single-crystal X-ray structure determination were obtained by overlaying a solution of $Zn(NCS)_2$ (18.2 mg, 0.1 mmol in 1.5 mL of EtOH) with 2.0 mL *n*-heptane to which a solution of DMAP (6.1 mg, 0.05 mmol in 0.5 mL of EtOH) was carefully added.

XRPD Investigations: The XRPD measurements for phase analysis and temperature dependent XRPD measurements were performed using a Stoe Transmission Powder Diffraction System (STADI P) with Cu- $K_{\alpha 1}$ radiation ($\lambda = 1.540598$ Å) equipped with a MYTHEN 1K detector (Dectris Ltd.) and a Ge(111) Johann monochromator. For the temperature dependent XRPD measurements a STOE capillary furnace was used.

Quantum Chemical Calculations: Quantum chemical calculations in the framework of density functional theory (DFT) with CRYS-TAL17^[78,79] were performed to compare total energies of both investigated polymorphs. For that purpose full structural optimiza-



tions using the hybrid-functional HSE06^[80] were carried out. Optimized all-electron basis sets for all atoms were taken from [basis3, basis4, basis5, basis6].^[81–84] The Kohn–Sham matrix was diagonalized on a *k*-mesh of $2 \times 2 \times 2$ for **4/II** and $4 \times 4 \times 4$ for **4/I**. The convergence criterion was set to 10^{-7} a.u. The optimized lattice parameters are given in Table S13.

Single-Crystal Structure Analysis: Data collections were performed with an imaging plate diffraction system (IPDS-1) for 1-3 and **4/II** and an IPDS-2 for **5** from STOE & CIE using Mo- K_{α} -radiation. Structure solution was performed with SHELXT and structure refinement was performed against F^2 using SHELXL-2014.^[85,86] A numerical absorption correction was applied using programs X-RED and X-SHAPE as part of the program package X-Area.^[87] All non-hydrogen atoms were refined with anisotropic displacement parameters. The C-H hydrogen atoms were positioned with idealized geometry (methyl H atoms allowed to rotate but not to tip) and were refined isotropic with $U_{iso}(H) = -1.2 U_{eq}(C)$ (1.5 for methyl H atoms) using a riding model. The O-H hydrogen atoms were in the difference fourier map, their bond lengths were set to ideal values and afterwards they were refined isotropic with $U_{iso}(H) = -1.5 U_{eq}(O)$ using a riding model. Selected crystal data and details of the structure refinements can be found in Table S14.

CCDC 1847711 (for 1), 1847712 (for 2), 1847713 (for 3), 1847714 (for 4/II), and 1847715 (for 5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Thermoanalytical Measurements: DTA-TG measurements were performed in a dynamic nitrogen atmosphere in Al_2O_3 crucibles using a STA PT 1600 thermobalance from Linseis. The DSC measurements were performed using a DSC 1 Star System with STARE Excellence Software from Mettler-Toledo AG. Thermomicroscopy was performed using a hot-stage from Linkam and a microscope from Olympus. All thermoanalytical instruments were calibrated using standard references materials.

Other Physical Methods: The IR data were obtained using an ATI Mattson Genesis Series FTIR Spectrometer, control software: WIN-FIRST, from ATI Mattson. Atomic absorptions spectroscopy (AAS). The AAS experiments were performed with a Perkin–Elmer Aanalyst 300.

Acknowledgments

This project was supported by the Deutsche Forschungsgemeinschaft (Project No. NA 720/5-2) and the State of Schleswig-Holstein. We thank Prof. Dr. Wolfgang Bensch for access to his experimental facilities, Christoph Krebs for the AAS measurements and Dr. Rolf Hilfiker for helpful discussions on the thermodynamic relations. F. P. thanks the Computer Service Group at MPI-FKF (Stuttgart, Germany) for providing computational resources.

Keywords: Coordination compounds · Crystal structures · Thermal properties · Enantiotropism · Polymorphism

- [1] B. Moulton, M. J. Zaworotko, Chem. Rev. 2001, 101, 1629-1658.
- [2] C. Näther, S. Wöhlert, J. Boeckmann, M. Wriedt, I. Jeß, Z. Anorg. Allg. Chem. 2013, 639, 2696–2714.
- [3] D. Braga, F. Grepioni, G. R. Desiraju, Chem. Rev. 1998, 98, 1375–1406.
- [4] C. Janiak, Dalton Trans. 2003, 2781-2804.



- [5] C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski, T. G. Scharmann, J. Chem. Soc., Dalton Trans. 1999, 3121–3131.
- [6] J. S. Miller, CrystEngComm 2005, 7, 458-461.
- [7] C. Rovira, J. Veciana, CrystEngComm 2009, 11, 2031-2031.
- [8] M. J. Zaworotko, Nat. Chem. 2011, 3, 653-653.
- [9] M. U. Schmidt, U. Englert, J. Chem. Soc., Dalton Trans. 1996, 2077-2082.
- [10] H. Ohtsu, M. Kawano, Chem. Commun. 2017, 53, 8818-8829.
- [11] C. Näther, G. Bhosekar, I. Jeß, Inorg. Chem. 2007, 46, 8079-8087.
- [12] S. Wöhlert, I. Jess, U. Englert, C. Näther, CrystEngComm 2013, 15, 5326– 5336.
- [13] A. Karmakar, A. Paul, A. J. L. Pombeiro, CrystEngComm 2017, 19, 4666– 4695.
- [14] C. Bartual-Murgui, L. Piñeiro-López, F. J. Valverde-Muñoz, M. C. Muñoz, M. Seredyuk, J. A. Real, *Inorg. Chem.* 2017, 56, 13535–13546.
- [15] I. Kalf, P. Mathieu, U. Englert, New J. Chem. 2010, 34, 2491–2495.
- [16] V. Ischenko, U. Englert, M. Jansen, Chem. Eur. J. 2005, 11, 1375–1383.
- [17] J. Werner, T. Runčevski, R. Dinnebier, S. G. Ebbinghaus, S. Suckert, C. Näther, Eur. J. Inorg. Chem. 2015, 3236–3245.
- [18] B. Nowicka, M. Reczynski, M. Rams, W. Nitek, M. Koziel, B. Sieklucka, *CrystEngComm* **2015**, *17*, 3526–3532.
- [19] J. Tao, R.-J. Wei, R.-B. Huang, L.-S. Zheng, Chem. Soc. Rev. 2012, 41, 703– 737.
- [20] A. A. Khandar, A. Klein, A. Bakhtiari, A. R. Mahjoub, R. W. H. Pohl, *Inorg. Chim. Acta* 2011, 366, 184–190.
- [21] W. J. Zhang, X. B. Tang, H. W. Ma, W. H. Sun, C. Janiak, *Eur. J. Inorg. Chem.* 2008, 2830–2836.
- [22] S. A. Bourne, Supramolecular Isomerism, John Wiley & Sons, Ltd, 2012,.
- [23] D. M. Shin, I. S. Lee, D. Cho, Y. K. Chung, Inorg. Chem. 2003, 42, 7722– 7724.
- [24] I. S. Lee, D. M. Shin, Y. K. Chung, Chem. Eur. J. 2004, 10, 3158-3165.
- [25] D. Braga, M. Curzi, F. Grepioni, M. Polito, Chem. Commun. 2005, 2915– 2917.
- [26] T. Morita, Y. Asada, T. Okuda, S. Nakashima, Bull. Chem. Soc. Jpn. 2006, 79, 738–744.
- [27] C.-F. Wang, Z.-Y. Zhu, X.-G. Zhou, L.-H. Weng, Q.-S. Shen, Y.-G. Yan, *Inorg. Chem. Commun.* 2006, *9*, 1326–1330.
- [28] J.-P. Zhang, X.-C. Huang, X.-M. Chen, Chem. Soc. Rev. 2009, 38, 2385– 2396.
- [29] T. Neumann, M. Ceglarska, M. Rams, L. S. Germann, R. E. Dinnebier, S. Suckert, I. Jess, C. Näther, *Inorg. Chem.* 2018, 57, 3305–3314.
- [30] Y. P. Prananto, A. Urbatsch, B. Moubaraki, K. S. Murray, D. R. Turner, G. B. Deacon, R. Batten Stuart, Aust. J. Chem. 2017, 70, 516–528.
- [31] M. H. Sadhu, A. Solanki, T. Kundu, V. Hingu, B. Ganguly, S. B. Kumar, *Polyhedron* 2017, 133, 8–15.
- [32] S. Suckert, M. Rams, M. M. Rams, C. Näther, Inorg. Chem. 2017, 56, 8007– 8017.
- [33] I. Nawrot, B. Machura, R. Kruszynski, CrystEngComm 2016, 18, 2650-2663.
- [34] F. A. Mautner, C. Berger, R. C. Fischer, S. S. Massoud, Inorg. Chim. Acta 2016, 439, 69–76.
- [35] F. A. Mautner, C. Berger, R. C. Fischer, S. S. Massoud, Inorg. Chim. Acta 2016, 448, 34–41.
- [36] D. A. Buckingham, Coord. Chem. Rev. 1994, 135, 587–621.
- [37] M. Kabesová, R. Boca, M. Melník, D. Valigura, M. Dunaj-Jurco, Coord. Chem. Rev. 1995, 140, 115–135.
- [38] S. S. Massoud, A. E. Guilbeau, H. T. Luong, R. Vicente, J. H. Albering, R. C. Fischer, F. A. Mautner, *Polyhedron* 2013, 54, 26–33.
- [39] C. D. Mekuimemba, F. Conan, A. J. Mota, M. A. Palacios, E. Colacio, S. Triki, *Inorg. Chem.* **2018**, *57*, 2184–2192.
- [40] J. Palion-Gazda, B. Machura, F. Lloret, M. Julve, Cryst. Growth Des. 2015, 15, 2380–2388.
- [41] J. L. Guillet, I. Bhowmick, M. P. Shores, C. J. A. Daley, M. Gembicky, J. A. Golen, A. L. Rheingold, L. H. Doerrer, *Inorg. Chem.* **2016**, *55*, 8099–8109.
- [42] B. Machura, A. Świtlicka, P. Zwoliński, J. Mroziński, B. Kalińska, R. Kruszynski, J. Solid State Chem. 2013, 197, 218–227.
- [43] S. Wöhlert, M. Wriedt, T. Fic, Z. Tomkowicz, W. Haase, C. Näther, *Inorg. Chem.* 2013, *52*, 1061–1068.
- [44] R. González, A. Acosta, R. Chiozzone, C. Kremer, D. Armentano, G. De Munno, M. Julve, F. Lloret, J. Faus, *Inorg. Chem.* 2012, *51*, 5737–5747.
- [45] B. Machura, A. Świtlicka, I. Nawrot, J. Mroziński, R. Kruszynski, Polyhedron 2011, 30, 832–840.





- [46] A. Barasiński, P. Sobczak, A. Drzewiński, G. Kamieniarz, A. Bieńko, J. Mroziński, D. Gatteschi, *Polyhedron* **2010**, *29*, 1485–1491.
- [47] P. Bhowmik, S. Chattopadhyay, M. G. B. Drew, C. Diaz, A. Ghosh, *Polyhe-dron* **2010**, *29*, 2637–2642.
- [48] Q. Ma, M. Zhu, L. Lu, S. Feng, J. Yan, Inorg. Chim. Acta 2011, 370, 102– 107.
- [49] E. Shurdha, S. H. Lapidus, P. W. Stephens, C. E. Moore, A. L. Rheingold, J. S. Miller, *Inorg. Chem.* **2012**, *51*, 9655–9665.
- [50] E. Shurdha, C. E. Moore, A. L. Rheingold, S. H. Lapidus, P. W. Stephens, A. M. Arif, J. S. Miller, *Inorg. Chem.* **2013**, *52*, 10583–10594.
- [51] M. Mousavi, V. Bereau, C. Duhayon, P. Guionneau, J.-P. Sutter, Chem. Commun. 2012, 48, 10028–10030.
- [52] S. Suckert, M. Rams, M. Böhme, L. S. Germann, R. E. Dinnebier, W. Plass, J. Werner, C. Näther, *Dalton Trans.* **2016**, *45*, 18190–18201.
- [53] A. R. Nassief, M. Abdel-Hafiez, A. Hassen, A. S. G. Khalil, M. R. Saber, J. Magn. Magn. Mater. 2018, 452, 488–494.
- [54] C. Wellm, M. Rams, T. Neumann, M. Ceglarska, C. Näther, Cryst. Growth Des. 2018, 18, 3117–3123.
- [55] J. Werner, M. Rams, Z. Tomkowicz, C. Näther, *Dalton Trans.* 2014, 43, 17333–17342.
- [56] J. Werner, Z. Tomkowicz, M. Rams, S. G. Ebbinghaus, T. Neumann, C. Näther, Dalton Trans. 2015, 44, 14149–14158.
- [57] S. Wöhlert, T. Fic, Z. Tomkowicz, S. G. Ebbinghaus, M. Rams, W. Haase, C. Näther, *Inorg. Chem.* **2013**, *52*, 12947–12957.
- [58] S. Wöhlert, Z. Tomkowicz, M. Rams, S. G. Ebbinghaus, L. Fink, M. U. Schmidt, C. Näther, *Inorg. Chem.* 2014, 53, 8298–8310.
- [59] M. Rams, M. Böhme, V. Kataev, Y. Krupskaya, B. Büchner, W. Plass, T. Neumann, Z. Tomkowicz, C. Näther, *Phys. Chem. Chem. Phys.* 2017, 19, 24534–24544.
- [60] M. Rams, Z. Tomkowicz, M. Böhme, W. Plass, S. Suckert, J. Werner, I. Jess, C. Näther, Phys. Chem. Chem. Phys. 2017, 19, 3232–3243.
- [61] S. Suckert, M. Rams, L. Germann, D. M. Cegiełka, R. E. Dinnebier, C. Näther, Cryst. Growth Des. 2017, 17, 3997–4005.
- [62] J. Werner, M. Rams, Z. Tomkowicz, T. Runčevski, R. E. Dinnebier, S. Suckert, C. Näther, *Inorg. Chem.* **2015**, *54*, 2893–2901.
- [63] S. Wöhlert, I. Jess, C. Näther, Acta Crystallogr., Sect. E 2013, 69, m33.
- [64] S. Wöhlert, I. Jess, C. Näther, Acta Crystallogr., Sect. E 2012, 68, m1528.
- [65] P. M. Secondo, J. M. Land, R. G. Baughman, H. L. Collier, *Inorg. Chim. Acta* 2000, 309, 13–22.
- [66] F.-j. Chen, G.-q. Liu, Z.-z. Zeng, Anal. Sci. X-ray Struct. Anal. Online 2007, 23, x253–x254.

- [67] H. T. Wang, L. Zhou, Acta Crystallogr., Sect. C 2015, 71, 549–553.
- [68] C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, Acta Crystallogr., Sect. B 2016, 72, 171–179.
- [69] F. Guenifa, N. Hadjadj, O. Zeghouan, L. Bendjeddou, H. Merazig, Acta Crystallogr., Sect. E 2013, 69, m379–380.
- [70] A. M. Selvi, CCDC 1024662: CSD Communication 2014.
- [71] F. Jian, J. Zheng, P. Zhao, Y. Li, J. Coord. Chem. 2008, 61, 705–714.
- [72] M. Büyükyazi, C. Hegemann, T. Lehnen, W. Tyrra, S. Mathur, *Inorg. Chem.* 2014, 53, 10928–10936.
- [73] F. Guenifa, O. Zeghouan, N. Hadjadj, L. Bendjeddou, H. Merazig, Acta Crystallogr., Sect. E 2013, 69, m175.
- [74] A. I. Kitaigorodski, Organic Chemical Crystallography, Consultants Bureau, New York, 1961.
- [75] C. Näther, I. Jess, P. G. Jones, C. Taouss, N. Teschmit, Cryst. Growth Des. 2013, 13, 1676–1684.
- [76] A. Burger, R. Ramberger, Mikrochim. Acta 1979, 259-271.
- [77] R. Hilfiker, Polymorphism: in the Pharmaceutical Industry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2006.
- [78] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, F. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco, M. LLlunell, M. Causà, Y. Noël, L. Maschio, A. Erba, M. Rerat, S. Casassa, *CRYSTAL17 User's Manual*, University of Torino, Torino, **2017**.
- [79] R. Dovesi, A. Erba, R. Orlando, M. Zicovich-Wilson Claudio, B. Civalleri, L. Maschio, M. Rérat, S. Casassa, J. Baima, S. Salustro, B. Kirtman, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* **2018**, *0*, e1360.
- [80] J. Heyd, G. E. Scuseria, M. Ernzerhof, J. Chem. Phys. 2003, 118, 8207-8215.
- [81] R. Dovesi, F. Freyria Fava, C. Roetti, V. R. Saunders, Faraday Discuss. 1997, 106, 173–187.
- [82] C. Gatti, V. R. Saunders, C. Roetti, J. Chem. Phys. 1994, 101, 10686–10696.
- [83] A. Lichanot, E. Aprà, R. Dovesi, Phys. Status Solidi B 1993, 177, 157-163.
- [84] R. Dovesi, M. Causa', R. Orlando, C. Roetti, V. R. Saunders, J. Chem. Phys. 1990, 92, 7402–7411.
- [85] G. M. Sheldrick, Acta Crystallogr., Sect. A 2015, 71, 3-8.
- [86] G. M. Sheldrick, Acta Crystallogr., Sect. C 2015, 71, 3-8.
- [87] X-Area, Version 1.44, Program Package for Single Crystal Measurements, Darmstadt (Germany), 2008.

Received: June 12, 2018





Polymorphism

T. Neumann, I. Jess, F. Pielnhofer, C. Näther* 1–11

 Selective Synthesis and Thermodynamic Relations of Polymorphic Co(NCS)₂-4-Dimethylaminopyridine Coordination Compounds



Two polymorphic Co(NCS)₂ coordination compounds were synthesized by solvent removal from different precursors, structurally characterized and investigated for their stability, thermodynamic relations and transition behaviour. Both forms are related by enantiotropism and the thermodynamic transition temperature was estimated from their melting enthalpies and confirmed by annealing experiments.

DOI: 10.1002/ejic.201800741