Magnetic Materials

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Coexistence of Metamagnetism and Slow Relaxation of the Magnetization in a Cobalt Thiocyanate 2D Coordination Network**

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Recently, strategies for the design of coordination polymers, hybrid compounds, or metal–organic frameworks (MOFs) that show cooperative magnetic phenomena have become of increasing interest.[1] Because of their great potential for possible applications as storage materials or in molecular electronics, 1D materials with a large magnetic anisotropy, slow relaxation of the magnetization M, and a hysteresis of molecular origin, for example, "single-chain magnets" (SCMs) are of special interest.[2] Moreover, for future applications multifunctional materials are needed, in which different physical properties can be tuned or switched as a function of external parameters.[3] These criteria also apply to metamagnetic compounds, which show different magnetic properties below and above a critical field H_C.[1c,4] Unfortunately, because of strong interchain interactions most of these compounds show only 3D ordering above H_C.[5] Therefore, only a very few metamagnetic coordination compounds have been reported in which slow relaxation of the magnetization is observed.[5,6]

In our research we have developed an alternative method for the synthesis of compounds that show cooperative magnetic interactions.[7] In this approach transition-metal coordination compounds with terminally bound anions and neutral co-ligands are heated leading to a stepwise removal of the co-ligands and the formation of intermediates with bridging anions and modified magnetic interactions. We have found that a large number of different compounds can be prepared by this route and that the dimensionality of the networks can easily be adjusted.[7a,b,d,8] In this context we have reported on the directed synthesis of a compound that shows SCM behavior.[9] Such a behavior usually occurs only in 1D coordination networks, but should, in principle, also be observed in 2D networks if the magnetic chains are separated by magnetically inactive ligands. To investigate this possibility, precursor compounds based on cobalt(II) thiocyanate and the bidentate co-ligand 1,2-bis(4-pyridyl)ethylene (bpe) were prepared, and the intermediates formed by thermal decomposition were characterized for their magnetic properties.

The reaction of $Co(NCS)_2$ with an excess of bpe leads to the formation of $[Co(NCS)_2(bpe)(bpe)]_n$ (**1**).[10] In its crystal structure the cobalt cations are octahedrally coordinated by four bpe ligands and two terminal N-bonded thiocyanato anions (Figure 1, top). The metal cations are linked by the bpe ligands into chains that are further connected by the co-ligands into layers. This arrangement leads to the formation of cavities in which additional bpe ligands are trapped. In further experiments using slightly different reaction conditions the hydrate $[Co(NCS)_2(bpe)_2(H_2O)_2]$[10] (**2**) could be obtained, in which the cobalt(II) cations are surrounded by two bpe ligands, two water molecules, and two terminal N-bonded thiocyanato anions in an octahedral coordination environment (Figure 1, bottom). These complexes are linked into layers by O−H···N hydrogen bonds. Compounds **1** and **2** represent potential precursors for the preparation of ligand-deficient compounds and thus, were investigated by thermoanalytical methods.

On heating compound **1**, a single mass step is observed, which leads to the formation of $[Co(NCS)_2(bpe)]_n$ (**4**).[10] If the hydrate **2** is heated, two mass steps are observed corresponding to the formation of the anhydrate **3** in the first step, which transforms into compound **4** in the second step (see Supporting Information). Based on this information, single crystals of **4** were prepared using hydrothermal conditions. In the crystal structure of **4** the cobalt cations are octahedrally coordinated by two S- and two N-bonded thiocyanato anions as well as two N-bonded bpe ligands. The cations are linked into chains by μ-1,3 bridging thiocyanato anions, which are further connected into layers by the bpe ligands (Figure 1, middle).

Magnetic measurements on all the compounds show significant differences between the ligand-rich precursors **1**–**3** and the ligand-deficient compound **4**. In compounds **1**–**3** the thiocyanato anions are only terminal N-bonded, so that paramagnetic behavior is observed (see Supporting Information). On cooling, decreasing $\chi_m T$ values are observed until at about 25 K from which point increasing $\chi_m T$ values are observed which decrease again at approximately 4 K. A small magnetic exchange through the bpe ligands cannot be completely excluded.

In contrast, for **4** a ferromagnetic coupling is observed between neighbored Co centers at $H_{DC} = 1$ kOe (DC = direct current). Moreover, in the hysteresis curve a step is observed indicating metamagnetic behavior (Figure 2).[4]

Magnetic measurements at $H_{DC} = 0.1$ kOe show antiferromagnetic behavior (Figure 3). Additional field dependent alternating current (AC) measurements using an external static field ($H_{DC} = \pm 2$ kOe, $H_{AC} = 10$ Oe) show a transition from antiferromagnetic to ferromagnetic behavior at $H > H_C$

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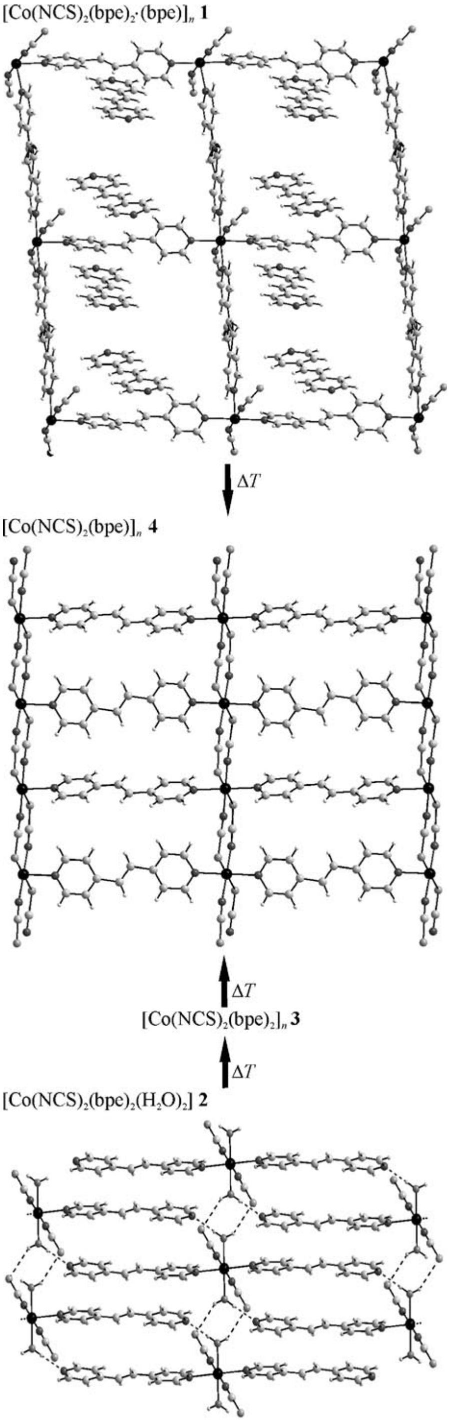

Figure 1. Structural changes in the reaction of **1** and **2** into **4**. The reaction of **2** to **4** proceeds via the anhydrate **3** as an intermediate in which the thiocyanato anions must also be terminally bound through the N atom.

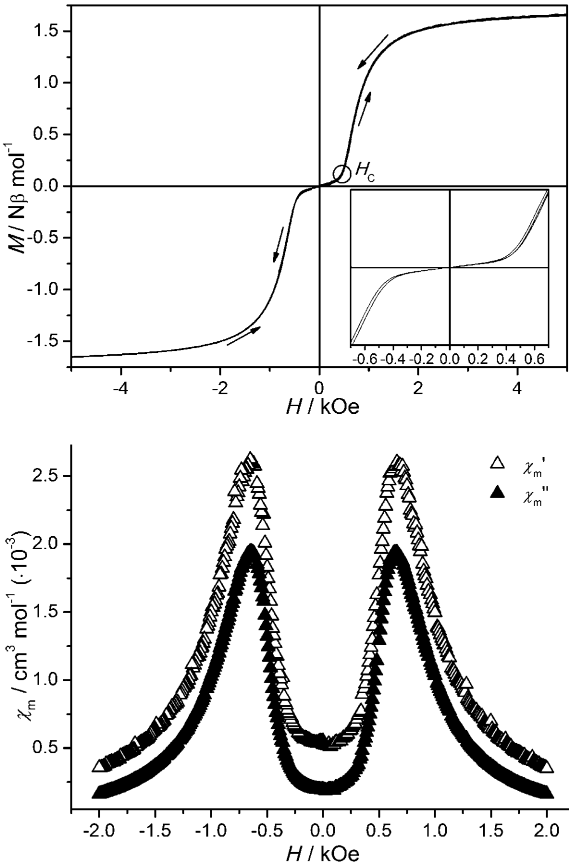

Figure 2. Hysteresis curve for **4** at 2 K (top) and field-dependent χ_m' and χ_m'' curves (bottom) at 5000 Hz and 2.9 K.

(Figure 2). ZFC-FC (zero-field cooling–field cooling), DC, and AC measurements at a static field of $H_{DC} = 1$ kOe were also performed (see Supporting Information). Broad and frequency-dependent maxima were observed in the χ_m' versus T and χ_m'' versus T curves, that indicate a slow relaxation of the magnetization (Figure 4). Analyses of the experimental data yield a Mydosh-parameter $\phi = 0.16$, which is in excellent agreement with superparamagnetic behavior and further confirms slow relaxation of the magnetization (see Supporting Information).[11]

Fitting the χ_m'' versus T data according to the Arrhenius law reveals an effective energy barrier $-U_{eff}/k_B$ of 52.9 K and $\tau_0 = 7.84 \times 10^{-13}$ s. In addition, the isothermal frequency dependence of χ_m' and χ_m'' at 2.5 K was analyzed to investigate the distribution of the relaxation times. The Cole–Cole plot of χ_m'' versus χ_m' can be fitted to a general Debye model in the range of 50–10000 Hz and a Cole exponent from $\alpha = 0.05$ is obtained, which confirms an infinitely narrow distribution of the relaxation time and a single relaxation mechanism (see Supporting Information).[12] Surprisingly additional AC measurements below H_C show maxima in the imaginary part of the AC susceptibility which are shifted dependent on frequency and which are inconsistent with pure antiferromagnetic behavior. This observation clearly shows that below H_C the slow relaxation of the magnetization is not completely suppressed by the antiferromagnetic ordering.

In summary, we have shown that thermal decomposition reactions of suitable precursor compounds are an effective method for the exploration or preparation of compounds with more condensed networks and modified magnetic properties. Based on the design of the precursors, the dimensionality of the coordination network can be controlled to a large extent.

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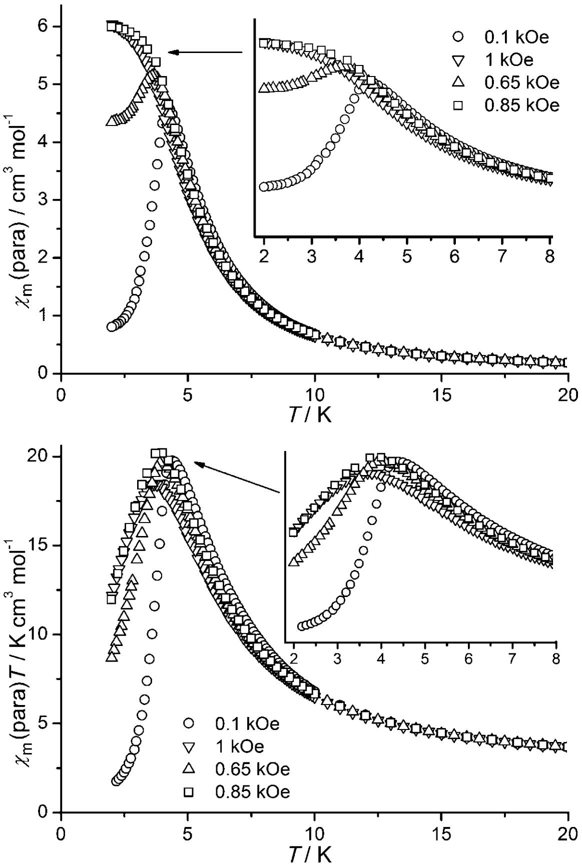

Figure 3. χ_m versus T (top) and $\chi_m T$ versus T (bottom) for **4** at 2–20 K and different magnetic fields; para: paramagnetic.

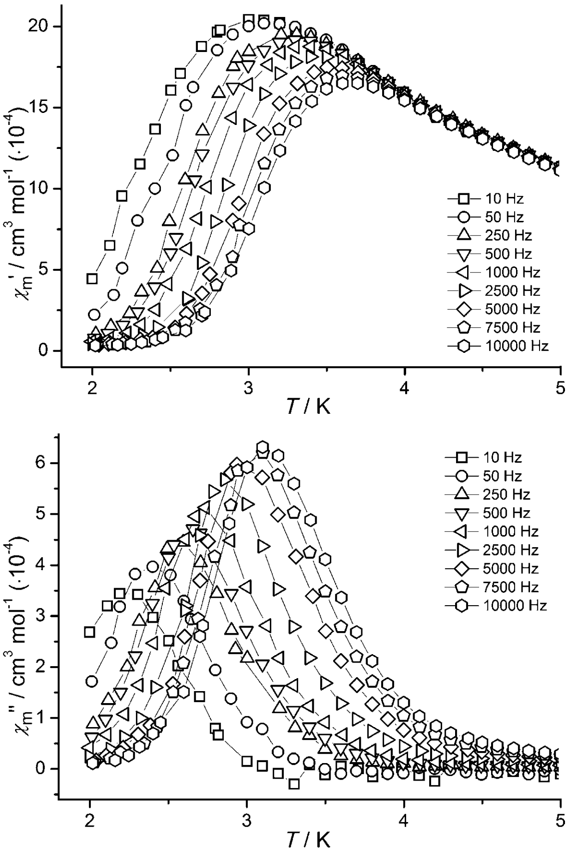

Figure 4. χ_m' versus T (top) and χ_m'' versus T curves (bottom) for **4** at H_{DC} = 1 kOe and H_{AC} = 4 Oe.

If the precursors contain monodentate co-ligands and small-sized anionic ligands, chain compounds are obtained that are promising candidates for SCM behavior, for example. However, a slow relaxation of the magnetization can also be observed in 2D coordination polymers as shown herein. Therefore, our approach offers the opportunity for the rational preparation of a wide range of compounds that are potential candidates for materials in which an interesting magnetic behavior can be observed. In this context, note that the combination of metamagnetism and the slow relaxation of magnetization is still a rare phenomenon and to our knowledge has never be observed for thiocyanates before.

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[10] CCDC 803979 (**1**), 803976 (**2**), and 803978 (**4**) contain the supplementary crystallographic data for this paper. These data

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can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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