Solid-state transformation of [Co(NCS)₂(pyridine)₄] into [Co(NCS)₂(pyridine)₂]_n: from Curie–Weiss paramagnetism to single chain magnetic behaviour[†]

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Reaction of $Co(NCS)_2$ with pyridine (pyr) in aqueous solution at room temperature leads to the formation of the pyridine-rich 1 : 4 compound of composition $[Co(NCS)_2(pyridine)_4]$ (1) reported recently. On heating, the pyridine-rich 1 : 4 compound transforms into its corresponding pyridine-deficient 1 : 2 compound of composition $[Co(NCS)_2(pyridine)_2]_n$ (2), which decomposes on further heating. In the crystal structure of compound 2 the metal cations are coordinated by four N-atoms of two pyridine ligands and two N-bonded thiocyanato anions, each in mutually *trans* orientation, and by two S-atoms of two adjacent thiocyanato anions in a slightly distorted octahedral geometry. The thiocyanato anions bridge the metal cations forming one-dimensional polymeric chains. IR spectroscopic investigations on the pyridine-deficient 1 : 2 compound reveal different behaviour with Curie–Weiss paramagnetism for compound 1 and single chain magnetic behaviour for compound 2, with a Mydosh-parameter $\varphi = 0.12$ and an effective energy barrier ($-U_{eff}/k_B$) of 62.5 K for the spin relaxation.

Introduction

Recently, the design, synthesis and enlightenment of new coordination polymers, inorganic-organic hybrid compounds or metal-organic frameworks have gained increasing interest.¹ The combination of pure inorganic coordination compounds and organic spacer ligands resulted in new functional materials like energy storage, gasholder, catalyst and photochemical or magnetic switchable materials.² In this context, an interesting class of magnetic systems represents the single molecule magnets (SMMs). They show superparamagnetic behaviour below a blocking temperature $T_{\rm B}$ and slow relaxation of the magnetization.³ Single molecule magnets represent zero-dimensional (0D) compounds, where the magnetic coupling is mediated through superexchange interactions. A related class of compounds represents magnetic one-dimensional (1D) polymeric coordination compounds with slow relaxation of the magnetization and magnetic hysteretic behaviour at low temperatures, called single chain magnets (SCMs). This behaviour was observed for the first time by Caneschi et al.,4 in a compound that contained 1D cobalt(II)-nitronyl nitroxide chains, and a theoretical model for the occurrence of SCMs was first introduced by Glauber, based on Ising spin chains.⁵ Due to the promising opportunities for exploration of magneto-structural

correlations, the enlightenment of the fundamental physical origin of the SCMs and their possible auspicious future application as high-density storage materials or molecular electronics,⁶ the systematic investigations, rational design and synthesis of such magnetic chain compounds received increasing importance.^{7,8} These compounds are in general built up of inorganic MX_n substructures (M = paramagnetic metal; X = *e.g.* SCN⁻, CN⁻, N₃⁻) which are further coordinated by monodentate ligands which separate the chains.⁸

Recently we have investigated the potential of thermal decomposition reactions of ligand-rich (ligand-rich = rich in neutral coligands) precursor compounds for the directed synthesis of multidimensional coordination polymers. In further investigations we have successfully expanded this approach for the rational design of coordination polymers with cooperative magnetic exchange interactions.^{9,10} In these precursors the metal centres are octahedrally coordinated by neutral coligands and smallsized anions that are only terminal bonded and therefore cannot be involved in magnetic exchange interactions. On heating, the neutral coligands are stepwise removed and the anions become bridging and therefore can mediate magnetic exchange interactions. Within this project we have prepared a large amount of compounds based on e.g. thiocyanates, selenocyanates or formates that show ferro- or antiferromagnetism.9,10 Most of these precursor compounds contain bridging coligands like e.g. pyrazine, 4,4'-bipyridine or pyrimidine that directly lead to the formation of 2D coordination networks. Based on these results it can be assumed that substitution of such spacers by monodentate coligands can lead to the formation of chains as ligand-deficient (ligand-deficient = lacking neutral coligands) intermediates that can show single chain magnetic behaviour. Suitable candidates are represented by discrete complexes of composition [MX₂L₄]

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[†] Electronic supplementary information (ESI) available: Experimental and calculated X-ray powder pattern for compound $[Co(NCS)_2(pyridine)_4]$ (1), IR-spectra of compounds $[Co(NCS)_2(pyridine)_4]$ (1) and $[Co(NCS)_2(pyridine)_2]_n$ (2) and plots of in-phase χ_{M} and out-of-phase χ_{M} AC magnetic susceptibility as a function of frequency for 2. CCDC reference number 793741. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00904k

in which the metal centres are octahedrally coordinated by two terminal anions and four terminal coligands. Examples for such discrete complexes are represented by e.g. the literature known compounds of composition $[M(NCS)_2(pyridine)_4]$ (M = Co (1), Fe, Mn, Ni),¹¹⁻¹³ which are easily accessible and therefore are promising precursor compounds to check our approach. In this context it is mentioned that the structures of the corresponding compounds of composition $[M(NCS)_2(pyridine)_2]_n$ (M = Cu, Co, Ni)¹³⁻¹⁵ are already described in the literature, so that the thermal decomposition products can be easily identified. Because several compounds based on cobalt show single chain magnetic behaviour,^{7,8,16,17} we have investigated [Co(NCS)₂(pyridine)₄] in the beginning. However, these investigations should also show if the pyridine-deficient intermediates can be isolated during the solidstate process or if all pyridine ligands are removed in one step. Here we report on the results of these investigations.

Results and discussion

Thermoanalytical investigations

On heating the pyridine-rich 1:4 compound $[Co(NCS)_2-(pyridine)_4]$ (1) in a thermobalance to 350 °C, two mass steps are observed in the TG curve, which are accompanied with endothermic events in the DTA curve (Fig. 1). The MS trend scan curve shows that only the pyridine ligand (m/z = 79) is lost during these steps (Fig. 1). The experimental mass losses in the first step of Δm_{exp} (1st step) = 31.66% and in the second step of Δm_{exp} (2nd step) = 31.77% are in good agreement with that calculated for the loss of two pyridine molecules in each step [Δm_{exded} .(–2 pyridine) =



Fig. 1 DTG, TG, DTA and MS trend scan curves of compound $[Co(NCS)_2(pyridine)_4]$ (1). Heating rate = 4 °C min⁻¹; m/z = 79 (pyridine); given are the mass changes [%] and the peak temperatures T_P [°C].

32.20%]. The DTG curve shows that both events are well separated (Fig. 1).

Based on the experimental mass losses, it can be assumed that the pyridine-deficient 1:2 compound of composition $[Co(NCS)_2(pyridine)_2]_n$ (2) is formed in the first step. On further heating, the remaining pyridine ligands are removed to give $Co(NCS)_2$, which decomposes on further heating. A similar thermal behaviour is found for several pyridine-type complexes of transition metal halides.¹⁸

In order to verify the nature of the intermediate formed, additional TG measurements were performed and stopped after the first TG step. Elemental analysis of the residue obtained yielded a composition of $[Co(NCS)_2(pyridine)_2]_n$ (see Experimental section). Single crystals of compound **2** were obtained from solution and the crystal structure was determined (see below). Additional XRPD investigations on the residue obtained in thermal decomposition of compound **1** clearly show that its powder pattern is in perfect agreement with that calculated for **2** from single crystal data (Fig. 2).



Fig. 2 Experimental XRPD pattern of the residue **2** obtained in the first TG step in the thermal decomposition reaction of compound **1** and XRPD pattern calculated from single crystal data for compound **2**.

Structural investigations

The crystal structure of $[Co(NCS)_2(pyridine)_2]_n$ has already been described in the literature and refined in the centrosymmetric monoclinic space group *C2/m* with two formula units in the unit cell.¹³ Surprisingly the calculated powder pattern based on this structure shows significant differences to that of the residue obtained by thermal decomposition, indicating a different modification. Interestingly $[Cu(NCS)_2(pyridine)_2]_n$ and $[Ni(NCS)_2(pyridine)_2]_n$ crystallizes in the centrosymmetric triclinic space group $P\overline{1}$ with three formula units in the unit cell.^{14,15} However, a detailed structure investigation on compound **2** shows the occurrence of super structure reflections, leading to a transformation of the monoclinic unit cell with Z = 2 into the triclinic unit cell with Z = 3. Thus, compound **2** is isotypic to $[Cu(NCS)_2(pyridine)_2]_n$ and $[Ni(NCS)_2(pyridine)_2]_n$. The asymmetric unit consists of two crystallographically independent metal cations, of which one is

located on a centre of inversion, as well as of three thiocyanato anions and of three pyridine ligands in general positions.

In the crystal structure the metal cations are coordinated by four N-atoms of two pyridine ligands and two N-bonded thiocyanato anions, each in mutually trans orientation, and by two S-atoms of two adjacent thiocyanato anions in a slightly distorted octahedral geometry (Fig. 3). The thiocyanato anions bridge the metal cations forming one-dimensional polymeric chains (Fig. 4).



Fig. 3 Crystal structure of $[Co(NCS)_2(pyridine)_2]_n$ (2) with view of the coordination sphere of the metal cations with labelling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes: I = -x + x1,-y+1,-z+1; II = -x+2,-y+2,-z+2. The disordered pyridine rings are omitted for clarity.



Fig. 4 Packing diagram of $[Co(NCS)_2(pyridine)_2]_n$ (2) with view onto the polymeric chains (aqua = Co, blue = N, yellow = S, grey = C, light-grey = H).

The Co-N distances ranges from 2.06 Å to 2.18 Å and the M-S distances are between 2.60 Å and 2.62 Å (Table 1). The intra-chain metal to metal separation through the thiocyanato anions range between 5.62 Å and 5.64 Å. The latter vary in the literature from 4.98 Å¹⁹ to 6.17 Å.²⁰

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Table 1	Selected bond lengths [Å] and angles [°] for the ligand-deficie	nt
1:2 com	ound	

$\begin{array}{c cccc} Co(1)-Co(2) & 5.6399(14) \\ Co(1)-S(1) & 2.6199(12) \\ Co(1)-N(2) & 2.062(4) \\ Co(1)-N(31) & 2.177(4) \\ S(1)-Co(1)-S(1I) & 180.0 \\ N(2)-Co(1)-S(1I) & 93.42(10) \\ N(2)-Co(1)-S(1I) & 86.58(10) \\ N(2)-Co(1)-N(2I) & 180.0 \\ N(2)-Co(1)-N(3I) & 88.30(16) \\ N(2)-Co(1)-N(3II) & 91.70(16) \\ N(31)-Co(1)-S(1) & 90.81(12) \\ \end{array}$	2]n
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N(2)-Co(1)-S(1I)86.58(10) $N(2)$ -Co(1)-N(2I)180.0 $N(2)$ -Co(1)-N(31)88.30(16) $N(2)$ -Co(1)-N(31I)91.70(16) $N(31)$ -Co(1)-S(1)90.81(12)	
N(2)-Co(1)-N(2I) 180.0 $N(2)-Co(1)-N(3I)$ 88.30(16) $N(2)-Co(1)-N(3II)$ 91.70(16) $N(31)-Co(1)-S(1)$ 90.81(12)	
$\begin{array}{llllllllllllllllllllllllllllllllllll$	
N(2)-Co(1)-N(311) 91.70(16) N(31)-Co(1)-S(1) 90.81(12)	
$N(31) = C_0(1) = S(1)$ 90 81(12)	
1((51) CO(1) D(1)	
N(31)–Co(1)–S(1I) 89.19(12)	
N(31)–Co(1)–N(31I) 180.0	
Co(2)–S(2) 2.6043(13)	
Co(2)–N(1) 2.063(4)	
Co(2)–N(3II) 2.062(4)	
Co(2)–N(11) 2.169(4)	
Co(2)–N(21) 2.169(4)	
S(2)-Co(2)-S(3) 178.17(4)	
N(3II)–Co(2)–N(1) 179.17(13)	
N(3II)–Co(2)–N(11) 88.02(15)	
N(3II)–Co(2)–N(21) 89.67(16)	
N(3II)-Co(2)-S(3) 94.68(11)	
N(3II)–Co(2)–S(2) 87.15(11)	
N(11)–Co(2)–S(2) 89.57(11)	
N(11)–Co(2)–S(3) 90.43(11)	
N(11)–Co(2)–N(21) 177.67(14)	
N(21)–Co(2)–S(2) 89.98(10)	
N(21)–Co(2)–S(3) 90.10(10)	

The different coordination modes of the thiocyanato anions can also be distinguished by their vibrational spectra.^{10,12–14,21} For terminal N-bonded thiocyanato anions the very strong stretching vibration v(CN) is observed < 2100 cm⁻¹, whereas for bridging thiocyanato anions v(CN) is found $\geq 2100 \text{ cm}^{-1}$. These results are in full agreement with IR-spectroscopic investigations, in which for compound 1 v(CN) is found at 2073 cm⁻¹, whereas for compound 2 v(CN) is observed at 2099 cm⁻¹.

Magnetic investigations

In $[Co(NCS)_2(pyridine)_4]$ (1) the metal centres are not bridged by the anions, whereas in $[Co(NCS)_2(pyridine)_2]_n$ (2) the Co atoms are linked by only 3 atoms of the thiocyanato anions, which might enable cooperative magnetic phenomena. To investigate the differences in the magnetic properties of 1 and 2 the temperature dependence of the magnetic susceptibility was investigated applying a magnetic field of H = 0.1 T in the temperature range of 300– 2 K. It has to be mentioned that for compound 1 μ_{eff} has already been measured at selected temperatures by Hunter et al.²⁴ and Figgis et al.25 but it was reinvestigated by us for better comparison of the magnetic behavior of compound 1 and 2.

For the pyridine-rich 1:4 compound $[Co(NCS)_2(pyridine)_4]$ (1) only Curie-Weiss paramagnetism is found with a Weiss constant $\theta = -18.4$ K (Table 2) (Fig. 5). However, the Weiss constant is unavoidably overestimated on the negative side for a mononuclear octahedral Co(II) complex, due to zero-field splitting and similar magnetic behaviour is found in different mononuclear octahedral Co(II) complexes.²² The effective magnetic moment μ_{eff} for compound 1 of 5.30 $\mu_{\rm B}$ is larger than the spin-only value for a high spin Co²⁺ ion (3.87 $\mu_{\rm B}$, S = 3/2, g = 2.00) (Table 2). However, it is



Fig. 5 Results of the magnetic measurements by plots of paramagnetic susceptibility and reciprocal paramagnetic susceptibility (left; red solid line = fit to the Curie–Weiss law) and $\chi_M T$ (right) as a function of temperature for the pyridine-rich 1:4 compound [Co(NCS)₂(pyridine)₄] (1).



Fig. 6 Results of the magnetic measurements for compound $[Co(NCS)_2(pyridine)_2]_n$ (2) by plots of paramagnetic susceptibility as a function of temperature (A), zero-field-cooled (ZFC, at H = 0.1 T) and field-cooled (FC, at H = 0.1 T) paramagnetic susceptibility as a function of temperature (B), $\chi_M T$ as function of temperature (C), and hysteresis loop at 2 K in the range of ± 0.3 T.

well documented that for cobalt *g*-values strongly deviating from 2.00 yield greater effective magnetic moments.²³

For the pyridine-deficient 1:2 compound $[Co(NCS)_2-(pyridine)_2]_n$ (2) the χ_M vs. T curve clearly shows weak ferromagnetic behaviour (Fig. 6A). Fitting the magnetic data according to the Curie–Weiss law $\chi_M = C/(T - \theta)$ yielding a negative Weiss constant of $\theta = -2.73$ K and an effective magnetic moment $\mu_{eff} = 5.65 \ \mu_B$ for compound 2 (Table 2). However, it must be kept in mind that besides the ferromagnetic interactions also zero-field splitting is involved and therefore, without the latter effects a

positive Weiss constant can be expected. In the temperature range of 300–50 K the $\chi_{\rm M}T$ values decrease upon cooling indicating antiferromagnetic interactions, and below 50 K the curve passes a sharp maximum at T = 3.8 K suggesting a transition to the ferromagnetic state (Fig. 6C). Further hints of the presence of ferromagnetic behaviour are provided by the magnetization saturation experiments performed at T = 2 K up to ± 0.3 T, (Fig. 6D).

Surprisingly, alternating current (AC) susceptibility measurements (Fig. 7A and B) showed that both the χ_{M}' and χ_{M}'' (in-phase

[Co(NCS)₂(pyridine)₄] $[Co(NCS)_2(pyridine)_2]_n$ C/cm3 K mol-1 3.98 3.51 θ/K -18.4-2.7 $\mu_{\rm eff} \,({\rm exp})/\mu_{\rm B}$ 5.30 5.65 $\mu_{\rm eff}$ (calc)²³/ $\mu_{\rm B}$ 3.87 3.87 $T_{\rm B} = 3.8$ Ordering state/K 48-300 35-300 Fit/K

 Table 2
 Results of the fit of the magnetic susceptibility data with the Curie–Weiss law

 Table 3
 Frequency dependence of the maximum AC susceptibility temperature

f [Hz]	$T\left(\chi_{\mathrm{M}}'\right)[\mathrm{K}]$	$T\left(\chi_{\mathrm{M}}''\right)[\mathrm{K}]$
10	3.60	2.74
50	3.75	2.96
250	4.00	3.19
500	4.10	3.31
1000	4.20	3.44
2500	4.25	3.62

and out-of-phase) curves exhibit broad and frequency-dependent peak maxima in the range between 2 K and 6 K. This is a typical behaviour for single chain magnets and a similar AC behaviour has been found in other magnetic Co chain compounds.^{7,8,16,17} The shift of the frequency dependent maxima (Table 3) is measured by the Mydosh-parameter $\varphi = (\Delta T_P/T_P)/\Delta(\log f) = 0.12$, which is close to the value for a superparamagnet ($0.1 < \varphi < 0.3$) and two orders larger than that for a canonical spin glass.^{8,16,26} Thus, a frustrated spin glass system can be excluded.

In the case of a single chain magnet, a thermally activated Orbach process can be assumed and the magnetization relaxation times (τ) are obtained from the relationship $\omega \tau = 1$ at the maxima of the $\chi_{\rm M}'' vs. T$ curves. Fitting the experimental data according to the Arrhenius law $\tau = \tau_0 \times \exp[-U_{\rm eff}/k_{\rm B}T]$; where τ is the relaxation time, $U_{\rm eff}$ is the effective anisotropy energy barrier,

 $k_{\rm B}$ is the Boltzmann constant, and *T* is the temperature, yields an effective energy barrier for $-U_{\rm eff}/k_{\rm B}$ of 62.5 K and $\tau_0 = 2.02 \times 10^{-12}$ s (Fig. 7C).

These values are in very good agreement with previously reported values for single chain magnet (SCM) and single molecule magnet (SMM) systems.^{8,27} To further support the SCM behaviour the isothermal frequency dependence of χ_{M}' and χ_{M}'' at 3.5 K was analysed in order to investigate the distribution of the relaxation times. For a single chain magnet a narrow distribution is expected. The χ_{M}'' vs. v and the χ_{M}''' vs. v plot (see Fig. S4 in the ESI†) show that the χ_{M}'' values are decreasing with increasing frequency and the χ_{M}''' vs. χ_{M}' can be fitted to a general Debye model (eqn (1))²⁸ in the 50–10000 Hz range (Fig. 7D), leading



Fig. 7 Temperature dependence of in-phase $\chi_{M}'(A)$ and out-of-phase $\chi_{M}''(B)$ AC magnetic susceptibility ($H_{ac} = 10$ Oe; 10/50/250/500/1000/2500 Hz), Arrhenius-plot of relaxation rate as a function of reciprocal temperature for compound **2** (C), and χ_{M}'' as a function of χ_{M}' at 3.5 K, known as a Cole–Cole plot (D).

to a maximum in the Cole-Cole plot at an resonance frequency of 650 Hz and an α value of 0.09 indicating a relative narrow distribution of the relaxation time. Please note: $0 < \alpha < 1$; $\alpha = 0$ indicates an infinitely narrow distribution of τ ; $\alpha = 1$ indicates a wide distribution of τ .

$$\chi''(\chi') = -\frac{\chi_0 - \chi_s}{2\tan\left[\frac{\pi}{2}(1-\alpha)\right]} \left[\left[\frac{\chi_0 - \chi_s}{2}\right]^2 - \left[\frac{\chi_0 - \chi_s}{2\tan\left[\frac{\pi}{2}(1-\alpha)\right]}\right]^2 - \left[\chi' - \frac{\chi_0 + \chi_s}{2}\right]^2 \right]^{1/2}$$
(1)

Eqn (1) shows a fit to the general Debye model with isothermal (χ_0) and adiabatic (χ_s) susceptibilities. Note that in the relevant part of the diagram eqn (1) represents a circular arc of size (1 - α) π cutting the χ' axis at $\chi' = \chi_s$ and $\chi' = \chi_0$.²⁸

Experimental section

Synthesis

Co(NCS)₂·H₂O was obtained from Alfa Aesar, KNCS was obtained from Sigma-Aldrich, and pyridine was obtained from Riedel-de Haën. Solvents were used without further purification. Crystalline powders of compounds 1 and 2 were prepared by stirring the reactants in appropriate solvents at room temperature. The residues were filtered off and washed with ethanol and diethyl ether and dried in air. The purity of all compounds was checked by X-ray powder diffraction and elemental analysis.

Synthesis of [tetrakis(pyridine- κN)-bis(thiocyanato- κN)cobalt(II)] (1)

Co(NCS)₂·H₂O (193.1 mg, 1.00 mmol) and pyridine (632.8 mg, 8.00 mmol) reacted in water (2.00 mL) to give 1 (228.6 mg, 47%) as a pink crystalline solid (Found: C, 54.0; H, 4.1; N, 17.3; S, 13.4. Calc. for C₂₂H₂₀CoN₆S₂: C, 53.8; H, 4.1; N, 17.1; S, 13.1%). IR $v_{\rm max}$ /cm⁻¹ 2073 s, 1599 s, 1572 w, 1486 m, 1442 s, 1355 w, 1212 m, 1147 w, 1069 m, 1038 m, 1006 m, 801 w, 766 m, 756 m, 712 s, 700 s, 625 m, 482 w, 431 w, 422 w.

Synthesis of catena-poly[bis(pyridine- κN)bis(thiocyanato- $\kappa N, \kappa S$)-cobalt(II)] (2)

This compound was isolated in the first heating step (see the Thermoanalytic investigations section in the Results and discussion) of compound 1. It can also be prepared by the reaction of Co(NCS)₂·H₂O (579.3 mg, 3.00 mmol) and pyridine (79.1 mg, 1.00 mmol) in water (2.00 mL) to give 2 (158.8 mg, 48%) as a purple crystalline solid (Found: C, 43.2; H, 2.9; N, 16.5; S, 19.4. Calc. for C₁₂H₁₀CoN₄S₂: C, 43.2; H, 3.0; N, 16.8; S, 19.3%). Single crystals suitable for X-ray structure determination were prepared by the reaction of Co(NCS)₂·H₂O (0.50 mmol, 96.60 mg) with pyridine (0.25 mmol, 20.20 µL) in 1.00 mL ethanol at RT in a closed 3 mL snap cap vial. After 1 day, purple well-shaped single crystals were obtained in a mixture with unknown phases. IR v_{max}/cm^{-1} 2099 s, 1601 m, 1487 w, 1442 m, 1216 w, 1071 w, 1040 w, 1010 w, 755 w, 696 m, 629 w, 475 w, 426 w.

Formula	$C_{12}H_{10}CoN_4S_2$
MW/g mol ⁻¹	333.29
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.5816(13)
b/Å	8.6752(12)
c/Å	15.520(2)
$\alpha /^{\circ}$	92.700(17)
β/°	96.254(17)
γ/°	114.754
$V/Å^3$	1037.5(3)
T/K	170
Ζ	3
$D_{\rm calc}/{\rm g~cm^{-3}}$	1.600
μ/mm^{-1}	1.532
$\theta_{\rm max}/{ m deg}$	25.00
Measured reflns.	7776
Unique reflns.	3632
Refins. $[F_0 > 4\sigma(F_0)]$	2173
Parameter	310
R _{int}	0.0707
$R_1^{a} [F_0 > 4\sigma(F_0)]$	0.0552
wR_2^{b} [all data]	0.1652
GOF	1.027
$\Delta ho_{ m max}, \Delta ho_{ m min}/e { m \AA}^{-3}$	0.722, -0.784
^{<i>a</i>} $R_1 = \sum F_0 - F_c / \sum F_0 $. ^{<i>b</i>} $wR_2 = [\sum w] / [w] / [F_0]$	$[F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]]^{\frac{1}{2}}.$

Single-crystal structure analysis

Data measurement was performed with an imaging plate diffraction system (IPDS-1) with Mo-K_{α}-radiation from STOE & CIE. The structure solution was done with direct methods using SHELXS-97 and structure refinements were performed against F^2 using SHELXL-97.29 All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters $[U_{eq}(H) = -1.2U_{eq}(C)]$ using a riding model with $d_{C-H} = 0.95$ Å for aromatic H atoms. In 2 the pyridine ligands are disordered and were refined using a split model. Details of the structure determinations are given in Table 4.

X-Ray powder diffraction (XRPD)

XRPD experiments were performed using a PANalytical X'Pert Pro MPD Reflection Powder Diffraction System with Cu-K_αradiation ($\lambda = 154.0598$ pm) equipped with a PIXcel semiconductor detector from PANalytical.

Differential thermal analysis, thermogravimetry, and mass spectroscopy (DTA-TG-MS)

The DTA-TG measurements were performed in a nitrogen atmosphere (purity: 5.0) in Al₂O₃ crucibles using a STA-409CD instrument from Netzsch. The DTA-TG-MS measurements were performed with the same instrument, which is connected to a quadrupole mass spectrometer from Balzers via Skimmer coupling from Netzsch. The MS measurements were performed in trend scan mode in Al₂O₃ crucibles in a dynamic nitrogen atmosphere (purity: 5.0) using heating rates of 4 °C min⁻¹. All measurements were performed with a flow rate of 75 mL min⁻¹ and were corrected for buoyancy and current effects. The instrument was calibrated using standard reference materials.

CHNS analyses were performed using an EURO EA elemental analyzer, fabricated by EURO VECTOR Instruments and Software.

Spectroscopy

Fourier transform IR spectra were recorded on a Genesis series FTIR spectrometer, by ATI Mattson, in KBr pellets.

Magnetic measurement

Magnetic measurements were performed using a Physical Property Measuring System (PPMS) from Quantum Design, which is equipped with a 9 T magnet. The data were corrected for core diamagnetism.30

Conclusion

In previous investigations we have reported the thermal decomposition reactions of ligand-rich precursor compounds for the directed synthesis of new coordination polymers with condensed networks. In most cases bridging coligands were used, which in this case leads directly to the formation of 2D and 3D coordination networks with different magnetic properties. In this work we investigated if this approach could also be used for the rational design of 1D structures, which may show interesting magnetic properties, like e.g. single chain magnetic behaviour. In this case the precursors must contain monodentate coligands, which are removed in the course of the reaction. As a model compound we have selected $[Co(NCS)_2(pyridine)_4]$ reported recently. These investigations clearly show that these volatile ligands are not removed in one step and that a pyridine-deficient intermediate can be isolated pure and in quantitative yield. As expected, the structure of this intermediate consists of 1D chains, in which the Co atoms are connected by the thiocyanato ligands. Magnetic measurements reveal that the pyridine-rich precursor compound shows only Curie-Weiss paramagnetism, whereas in the pyridinedeficient intermediate single chain magnetic behavior is observed. Even if the pyridine-deficient compound can also be prepared from solution, these results clearly show the potential of this method, because in several cases ligand-deficient intermediates with bridging anions cannot be prepared pure in solution, as we have shown in previous work. However, these are only first results which do not prove if this approach can be used more generally for the rational design of 1D structures and therefore, other systems will be investigated. In this context it would be of special importance to reveal how the magnetic properties will change, if the coligands are only slightly changed.

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