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Thermal decomposition reactions as an alternative tool for the preparation of new coordination polymers: synthesis, crystal structure, thermal and magnetic properties of poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] and poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*)-manganese(II)]

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Abstract

Reaction of manganese thiocyanate with pyrazine in acetonitrile leads to the formation of the two new coordination polymers poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) and poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**II**). Whereas **I** can be prepared in large amounts and very pure in solution, **II** is always obtained as mixtures of compound **I** and **II**. In the crystal structure of compound **I** the manganese centers are octahedral surrounded by four pyrazine ligands and two nitrogen atoms of two thiocyanate anions. The manganese centers are connected by the pyrazine ligands via μ -*N,N'* coordination forming layers which are parallel to (001). In the crystal structure of the amine poorer compound **II** the manganese atoms are surrounded by two pyrazine ligands, two nitrogen atoms and two sulfur atoms of four thiocyanate anions. The manganese centers are connected by the thiocyanate anions via μ -*N,S* coordination forming layers which are parallel to (100). On heating compound **I** loses half of the pyrazine ligands forming the amine poorer compound **II**. Magnetic measurements reveal that compound **I** exhibits only weak antiferromagnetic interactions, whereas the latter shows antiferromagnetic ordering at about 26 K which is mediated by the thiocyanate anions.

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Keywords: Coordination polymers; Thermal decomposition; Preparation; Crystal structures; Magnetic properties

1. Introduction

The rational design of multidimensional coordination polymers has attracted much interest in recent years [1–6]. One major goal in this area is the preparation of new compounds with useful physical properties [7–12]. However, for any further characterization and application the phase pure preparation of a new material is required, which is sometimes difficult to achieve. Mostly coordination polymers are prepared in solution, which frequently leads to mixtures or for e.g., in some special cases, thermodynamically metastable compounds cannot be prepared with the solution route. Recently, we have shown that amine rich coordination polymers on

the basis of copper(I) halides or pseudo-halides and aromatic N-donor ligands can be transformed into amine poorer coordination polymers by controlled thermal decomposition [13–21]. These compounds are of interest, e.g., because of its luminescence and thermoluminescence properties [20]. In most cases the amine poorer intermediate compounds can be isolated very pure and in high yield. Therefore, this method is an alternative tool for the preparation of new copper(I) halide or pseudo-halide coordination polymers. In some cases several amine poorer intermediates are observed [16]. The number of compounds observed during the thermal decomposition depends, e.g., on the kinetics of the reactions [18]. Dependent on the reaction conditions also different polymorphic modifications can be prepared [19]. However, to show whether this method is limited to the preparation of only Cu(I) coordination

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polymers or if it can be expanded to other compounds we have prepared several precursor compounds containing magnetic active transition metals and small-sized counter anions. Such compounds are of special interest because the thermal decomposition lead in most cases to compounds with a higher degree of condensation of the coordination networks. Therefore, in the presence of magnetic active transition metal atoms cooperative magnetic phenomena can be expected. In this context one interesting compound is $\text{Mn}(\text{SCN})_2\text{-(pyrazine)}_2$ (**I**) which was prepared previously [22]. It was assumed that the compound is isotypic to the known Co and Fe compounds [22–26]. The magnetic properties of **I** were also investigated. It was shown that this compound shows only weak antiferromagnetic interactions on cooling. However, in order to investigate if amine poorer coordination polymers can be prepared via thermal decomposition of the amine rich compounds we have prepared $\text{Mn}(\text{SCN})_2\text{-(pyrazine)}_2$ (**I**) and have investigated its thermal properties.

2. Experimental section

2.1. Synthesis

General procedures: All educts are commercially available. All reaction products were filtered off, washed with ethanol and diethylether and dried on air. The purity of all compounds were checked by elemental analysis and by comparing the experimental X-ray powder pattern with those calculated from single-crystal data.

Synthesis of **I**: 162.1 mg (1.0 mmol) $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, 196.1 mg (2.0 mmol) KSCN and 160.2 mg (2.0 mmol) pyrazine were stirred in 5 mL water at room temperature. After 2 d a yellow colored microcrystalline powder of compound **I** has formed. Yield: 71.3%. Elemental analysis (%) calculated: C: 36.26, N: 25.37, H: 2.43, S: 19.36; found: C: 35.82, N: 25.53, H: 2.46, S: 19.16. Preparation of single crystals: 81.1 mg (0.5 mmol) $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, 98.1 mg (1 mmol) KSCN and 80.1 mg (1 mmol) pyrazine were reacted in 4 mL water at room temperature without stirring. After 7 d yellow colored crystals of **I** has formed.

Synthesis of **II**: Independent on the reaction conditions compound **II** cannot be prepared as a pure phase and is always contaminated with large amounts of compound **I**. Single crystals of **II** can be prepared by the reaction of 81.1 mg (0.5 mmol) $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$, 98.1 mg (1 mmol) KSCN and 80.1 mg (0.5 mmol) pyrazine in 4 mL of water at room temperature. After 10 d only a few yellow colored crystals of **II** has formed which are embedded in a large amount of a microcrystalline powder of compound **I**.

2.2. Crystal structure investigation

Crystal structure determination: All structure solutions were performed with direct methods using SHELXS-97 [26]. The structure refinements were performed against F^2 using SHELXL-97 [27]. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters using the riding model. Selected crystal data and results of the structure refinement as well as atomic coordinates and equivalent isotropic displacement parameters are given in Tables 1 and 2.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 195185 (**I**), (CCDC 195186 (**II**)). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: int. Code + (44)01223/3 36-033, e-mail: deposit@chemcrys.cam.ac.uk).

Table 1

Crystal data and results of the structure refinement for poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) and poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**II**)

Compound	I	II
Formula	$\text{C}_{10}\text{H}_8\text{N}_6\text{S}_2\text{Mn}$	$\text{C}_6\text{H}_4\text{N}_4\text{S}_2\text{Mn}$
MW/g mol ⁻¹	331.28	251.19
Crystal color	Light yellow	Light yellow
Crystal system	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	10.421(2)	10.616(2)
<i>b</i> (Å)	10.556(2)	7.445(2)
<i>c</i> (Å)	7.165(1)	5.765(1)
α (deg)	—	—
β (deg)	118.85(2)°	94.37(2)°
γ (deg)	—	—
<i>V</i> (Å ³)	690.4(1)	454.9(2)
Temperature (K)	293	293
<i>Z</i>	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.594	1.834
<i>F</i> (000)	334	250
Diffractometer	Nonius CAD4	STOE AED-II
2 θ -range	3–56°	3–58°
<i>h/k/l</i> ranges	0/13, –13/13, –9/8	0/14, –10/10, –7/7
Absorption corr.	None	None
μ (MoK α) (mm ⁻¹)	1.25	1.86
Max./min. transm.	—	—
Measured refl.	1748	1271
<i>R</i> _{int}	0.0453	0.0525
Independent refl.	876	651
Refl. with $I > 2\sigma(I)$	664	501
Refined parameters	50	37
<i>R</i> ₁ [$I > 2\sigma(I)$]	0.0297	0.0333
w <i>R</i> ₂ [all data]	0.0745	0.0665
Goodness-of-fit	1.053	1.043
Min./max. res. (<i>e</i> Å ⁻³)	0.27/–0.29	0.60/–1.00

Table 2

Atomic coordinates [10^4] and isotropic displacement parameters [$\text{\AA}^2 10^3$] for poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) and poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**II**)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Poly[bis(thiocyanato- <i>N</i>)-bis(μ_2 -pyrazine- <i>N,N'</i>)-manganese(II)] (I)				
Mn(1)	0	0	5000	25(1)
S(1)	3611(1)	0	12374(2)	69(1)
N(1)	1580(2)	1565(1)	5066(3)	32(1)
C(1)	2903(2)	1776(2)	6681(4)	50(1)
C(2)	1183(2)	2303(2)	3391(4)	49(1)
N(3)	1121(3)	8409(4)	0	37(1)
C(3)	2148(3)	0	10078(5)	34(1)
Poly[bis(μ_2 -thiocyanato- <i>N,S</i>)-(μ_2 -pyrazine- <i>N,N'</i>)-manganese(II)] (II)				
Mn(1)	0	5000	0	23(1)
S(1)	2169(1)	5000	2793(1)	31(1)
C(3)	1565(3)	5000	5327(4)	25(1)
N(3)	1136(2)	5000	7117(4)	33(1)
N(1)	0	1879(3)	0	26(1)
C(1)	485(2)	925(3)	1818(3)	33(1)

U_{eq} calculated as a third of the trace of the orthogonalized U_{ij} tensors.

2.3. X-ray powder diffraction experiments

X-ray powder diffraction experiments were performed using a STOE STADI P transmission powder diffractometer with a 4° PSD (position sensitive detector) using $\text{CuK}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$). For temperature or time resolved X-ray powder diffraction the diffractometer is equipped with a graphite oven and a position sensitive detector (scan range: $5\text{--}50^\circ$) from STOE & CIE. All temperature resolved X-ray powder experiments were performed in glass capillaries under a static air atmosphere.

2.4. Differential thermal analysis, thermogravimetry and mass spectroscopy

DTA-TG measurements were performed in Al_2O_3 crucibles simultaneously using an STA-429 and STA-409CD balance from Netzsch. Several measurements under argon, nitrogen and air atmosphere with heating rates of 1 and $4^\circ\text{C}/\text{min}$ with and without capes were performed. DTA-TG-MS measurements were performed simultaneously using the STA-409CD with Skimmer coupling from Netzsch, which is equipped with a quadrupole mass spectrometer QMA 400 (max. 512 amu) from Balzers. The MS measurements were performed in analog and trend scan mode, in Al_2O_3 crucibles under a dynamic helium atmosphere (purity: 4.6) using heating rates of 1, 4 and $8^\circ\text{C}/\text{min}$. For the kinetic heating rate-dependent measurements the instrument is equipped with a Pt–Rh furnace. All measurements were performed with a flow rate of 75 mL/min

and were corrected according to buoyancy and current effects.

2.5. Elemental analysis

C, H, N analysis was performed using a CHN-O-RAPID combustion analyzer from Heraeus. Elemental analysis (%) of the residues obtained from the thermal decomposition of **I**: calculated for (**II**): C: 28.69, N: 22.30, H: 1.61, S: 25.53; found: C: 28.39, N: 22.60, H: 1.59, S: 25.83 (obtained with $4^\circ\text{C}/\text{min}$).

2.6. Magnetic measurements

The 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. The fitting of the susceptibility curves was performed in the range between 60 and 300 K.

3. Results and discussion

3.1. Crystal structures

The amine-rich compound poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) crystallizes in the centrosymmetric monoclinic space group $C2/m$ with two formula units in the unit cell. The asymmetric unit consists of one manganese atom which occupy the position $2/m$, one thiocyanate anion located on a

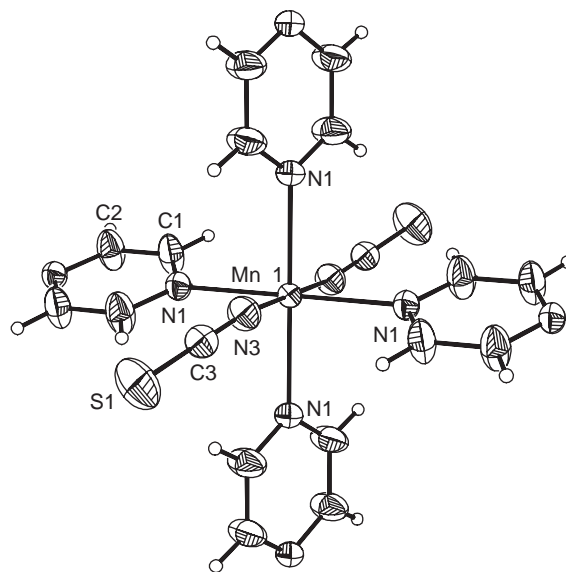


Fig. 1. Crystal structure of poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) with view of the manganese coordination with labeling and displacement ellipsoids drawn at the 50% probability level.

Table 3

Selected bond lengths (Å) and angles (deg) for poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) and poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**II**)

Poly[bis(thiocyanato- <i>N</i>)-bis(μ_2 -pyrazine- <i>N,N'</i>)-manganese(II)] (I)			
Mn(1)–N(1)	2.317(2)($\times 4$)	Mn(1)–N(3)	2.139(2)($\times 2$)
N(3A)–Mn(1)–N(1A)	89.16(6)($\times 3$)	N(3)–Mn(1)–N(1)	90.84(6)($\times 4$)
N(1A)–Mn(1)–N(1B)	90.96(7)($\times 2$)	N(1)–Mn(1)–N(1B)	89.04(7)($\times 3$)
N(1)–Mn(1)–N(1)	180.00(7)($\times 2$)	N(3A)–Mn(1)–N(3)	180.00(7)
Poly[bis(μ_2 -thiocyanato- <i>N,S</i>)-(μ_2 -pyrazine- <i>N,N'</i>)-manganese(II)] (II)			
Mn(1)–N(1)	2.327(2)($\times 2$)	Mn(1)–N(3)	2.126(2)($\times 2$)
Mn(1)–S(1)	2.707(1)($\times 2$)		
N(3)–Mn(1)–N(1)	90.0($\times 4$)	N(1)–Mn(1)–S(1)	90.0($\times 4$)
N(3)–Mn(1)–S(1)	92.42(7)($\times 2$)	N(3)–Mn(1)–S(1)	87.58(7)($\times 2$)
N(3)–Mn(1)–N(3)	180.00(–10)	N(1)–Mn(1)–N(1)	180.0
S(1)–Mn(1)–S(1)	180.0		

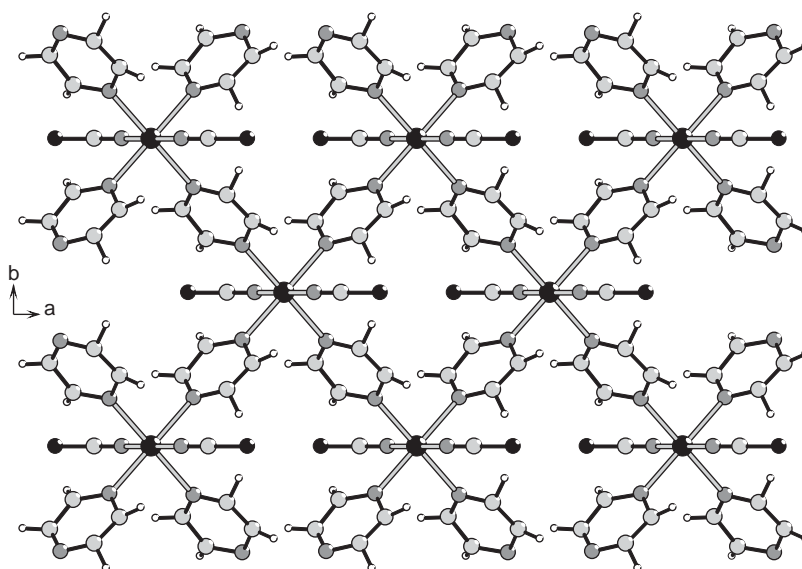


Fig. 2. Crystal structure of poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) with view onto the layers.

crystallographic mirror plane and one pyrazine ligand which is located around a center of inversion. In the crystal structure the Mn^{2+} cations are coordinated by four pyrazine ligands and two thiocyanate anions within slightly distorted octahedra (Fig. 1). The thiocyanate anions does not act as bridging ligands and are only coordinated by the N atom to the metal center. The Mn–N distances to the negatively charged nitrogen atom of the thiocyanate anion is significantly shorter than that to the nitrogen atom of the N-donor ligand (Table 3). The manganese atoms are connected by the pyrazine ligands via μ -*N,N'* coordination forming layers that are parallel to (001) (Fig. 2).

The amine-poorer compound poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**II**) crystallizes in the centrosymmetric monoclinic space group $C2/m$ with two formula units in the unit cell. The asymmetric unit consists of one manganese atom and one pyrazine ligand which occupy the position $2/m$ as

well as one thiocyanate anion that is located on a crystallographic mirror plane. In this compound the Mn^{2+} cations are coordinated by only two pyrazine ligands, two S and two N atoms of four symmetry related thiocyanate anions within a slightly distorted octahedron (Fig. 3). In contrast to compound **I** the Mn atoms are each connected by two thiocyanate ligands forming chains in the direction of the *c*-axis. Distances and angles are comparable to those in **I** (Table 3). The Mn thiocyanate chains are connected by the pyrazine ligands into layers which are parallel to (100) (Fig. 4). It must be noted that the topology of the coordination network is similar to that in $\text{Mn}(\text{N}_3)_2(\text{pyrazine})$ [9]. In contrast to compound **II** here the azide anions bridges the Mn atoms with only one nitrogen atom. On cooling, this compound shows ferromagnetism.

However, independent on the stoichiometry and the experimental conditions applied always compound **I** is obtained. We note that under special conditions a small

amount of crystals of compound **II** can be obtained as the minor phase in a mixture with compound **I** but we never succeeded to prepare phase pure **II** in solution (see experimental part). Starting from the results of our investigations on the thermal properties of the copper(I) halide and pseudo-halide coordination polymers we investigated the thermal properties of the amine rich compound **I** in order to prepare the amine poorer compound **II** by thermal decomposition [13–21].

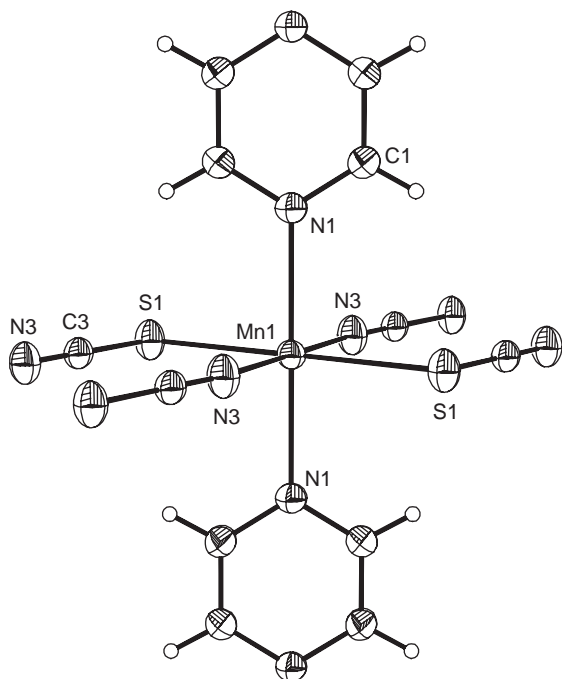


Fig. 3. Crystal structure of poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*-manganese(II)) (**II**) with view of the manganese coordination with labeling and displacement ellipsoids drawn at the 50% probability level.

3.2. Thermoanalytical investigations

When compound **I** is heated in a thermobalance up to 450°C three mass loss steps are observed in the TG curve which are accompanied with endothermic events in the DTA curve (Fig. 5). The experimental mass losses of the first two events are in good agreement with that calculated for a stepwise removal of the pyrazine ligand

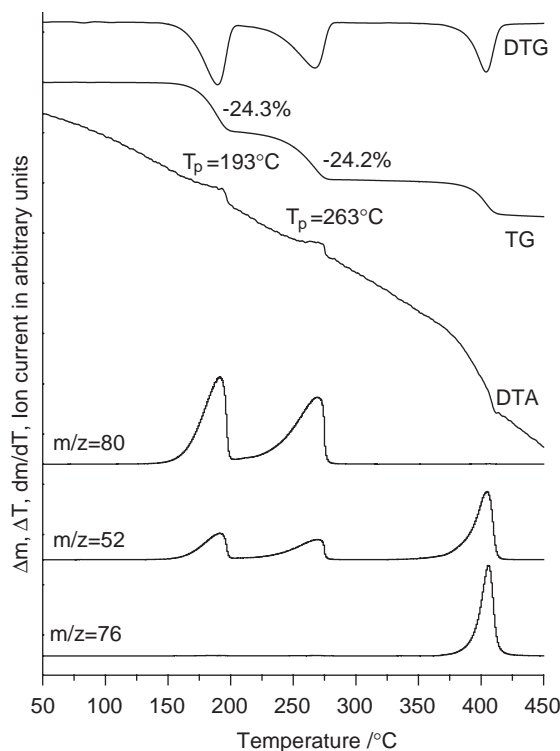


Fig. 5. DTA, TG, DTG and MS trend scan curve for poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*-manganese(II)) (**I**) (weight: 51.02 mg; heating rate: 4°C/min; $m/z = 52$ (dicyane/pyrazine); $m/z = 76$ (carbonyl disulfide); $m/z = 80$ (pyrazine)).

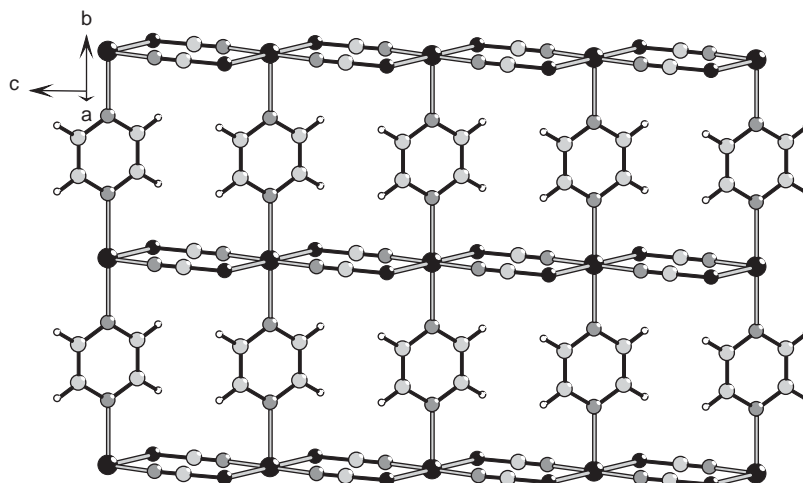


Fig. 4. Crystal structure of poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*-manganese(II)) (**II**) with view onto the layers.

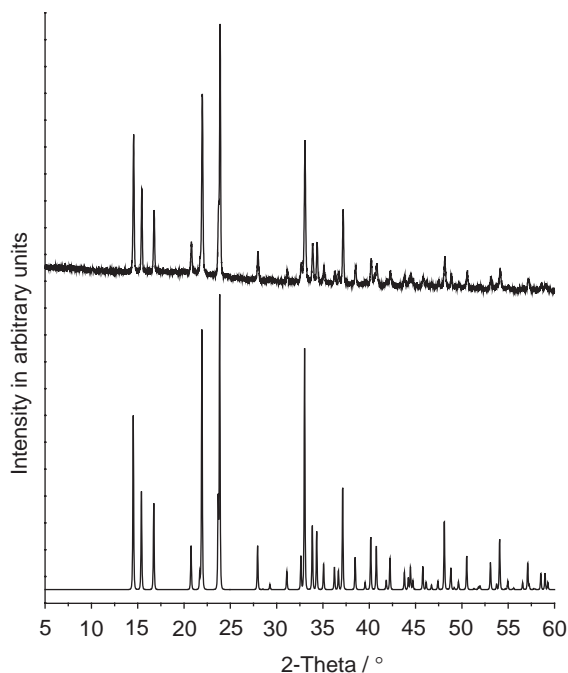


Fig. 6. X-ray powder pattern of the residue obtained after the first mass loss at about 205°C in a TG experiment with 1°C/min from the thermal decomposition of poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) (top) and calculated powder pattern for poly[bis(μ_2 -thiocyanato-*N,S*)-(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**II**) (bottom).

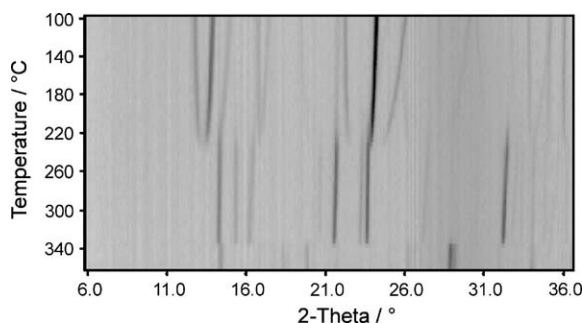


Fig. 7. Temperature-dependent X-ray powder patterns for poly[bis(thiocyanato-*N*)-bis(μ_2 -pyrazine-*N,N'*)-manganese(II)] (**I**) (glass capillaries, static air, powder pattern were measured each 5°C, heating rate: 5°C/min).

($\Delta m_{\text{theo}} - \text{C}_6\text{H}_4\text{N}_2$) = 24.1%). The DTG curve shows that both events are well separated. A similar behavior was found for the Co compound but no further investigations were performed [25]. However, this interesting behavior suggests that in the first step an amine-poorer compound $\text{Mn}(\text{SCN})_2$ -pyrazine (**II**) has formed which decomposes upon further heating to $\text{Mn}(\text{SCN})_2$. These assumptions are supported by simultaneous MS measurements which demonstrate that in the first two steps only pyrazine is emitted (Fig. 5). If the reaction is stopped after the first mass loss and the

residue is investigated by elemental analysis a composition is found which corresponds to $\text{Mn}(\text{SCN})_2$ -pyrazine (**II**) (see experimental part). If this residue is investigated using X-ray powder diffraction it can be shown that compound **II** has formed very pure (Fig. 6). To proof the sequence of the reaction and to check if additional compounds occur during the thermal decomposition investigations using temperature dependent X-ray powder diffraction were performed (Fig. 7). On heating, decomposition into the amine poorer phase starts at about 220°C which is finished at about 340°C. From this experiment there are no hints for the occurrence of additional phases.

3.3. Magnetic investigations

Due to the connection of the metal centers via the small-sized ligands cooperative magnetic phenomena can be expected for **II** which are not observed for compound **I**. For **I** the value of the Weiss constant indicates some weak antiferromagnetic interactions [24] (Fig. 8). For compound **II** antiferromagnetic ordering is found at an ordering temperature of about 26 K (Fig. 8). Because the metal–metal distances are too large for direct exchange interactions ($\text{Mn}-\text{Mn}_{\text{intra}}(-(\text{SCN}-)) = 5.765 \text{ \AA}$; $\text{Mn}-\text{Mn}_{\text{intra}}(-(\text{pyrazine}-)) = 7.455 \text{ \AA}$; $\text{Mn}-\text{Mn}_{\text{inter}} = 6.486 \text{ \AA}$) the ordering may be attributed to indirect exchange interactions mediated by the thiocyanate ligand. However, also an exchange via the pyrazine ligands cannot be excluded.

4. Conclusions

In this work we have demonstrated that the thermal decomposition of suitable precursor compounds is an alternative preparative tool for the synthesis of new and interesting coordination polymers and that this method is not limited to the preparation of the Cu(I) halide or pseudo-halide coordination compounds [13–21]. Such decomposition reactions lead in most cases to components with a higher degree of condensation. In this context, the present work impressively demonstrate the power of the method for the preparation of molecular-based magnetic materials. As mentioned above the amine-rich compounds with Fe, Co and Ni were also investigated but to the best of our knowledge the amine-poorer compounds were never observed. These compounds are of high interest because interesting magnetic behavior can be expected. It might be that they were not observed applying the solution route because only the amine-rich compounds occur. Therefore, the investigations of the magnetic properties of these compounds prepared via thermal decomposition will be the subject of further investigations.

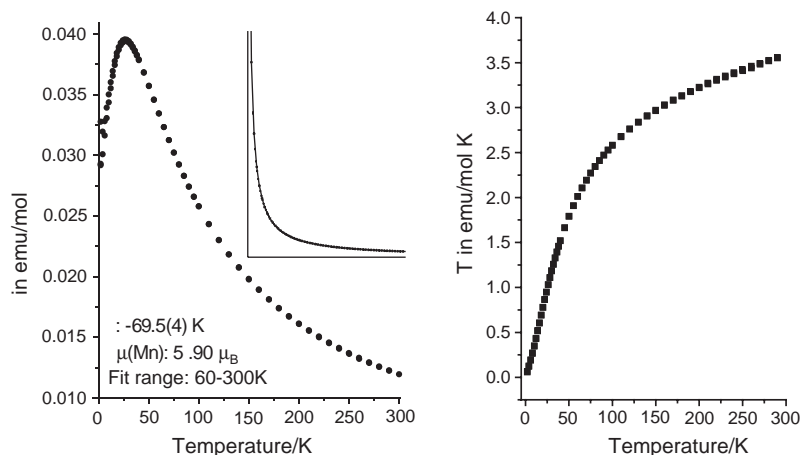


Fig. 8. Left: Susceptibility as function of temperature (left) and χT versus T curve (right) for poly[bis(μ_2 -thiocyanato- N,S)-(μ_2 -pyrazine- N,N' -manganese(II))] (II) (The inset of the left figure shows the same plot for the amine-rich compound poly[bis(thiocyanato- N)-bis(μ_2 -pyrazine- N,N' -manganese(II))] (I) as remeasured in our lab; the line acts as a guide for the eyes).

Acknowledgments

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