Synthesis, Crystal Structures and Properties of New Barium Thiocyanato Coordination Polymers with *trans*-1,2-Bis(4-pyridyl)ethylene as Ligand

Susanne Wöhlert, Inke Jess, and Christian Näther

Institut für Anorganische Chemie der Christian-Albrechts-Universität zu Kiel, Max-Eyth-Straße 2,
24118 Kiel, Germany

Reprint requests to PD Dr. Christian Näther. E-mail: cnaether@ac.uni-kiel.de

Z. Naturforsch. **2011**, *66b,* 133 – 141; received November 3, 2010

Reactions of barium thiocyanate with *trans*-1,2-bis(4-pyridyl)ethylene (bpe) in acetonitrile/water using different molar ratios always lead to the formation of a new barium coordination polymer of composition $\{[[Ba(NCS)(H_2O)_5]_2](bpe)\}(NCS)_2(bpe)_3(H_2O)_2$ (**1**). During the preparation of single crystals of compound **1**, three additional new compounds were obtained (**2** – **4**), of which one crystallizes in two different polymorphic modifications (**4I** and **4II**). In compound **1** the Ba cations are coordinated by six water molecules, two *N*-bonding thiocyanato anions and one N atom of a bpe ligand within an irregular polyhedron. Two Ba cations are linked by two water molecules and two μ-1,1-*N*-bridging thiocyanato anions into centrosymmetric dimers that are further connected by the bpe ligands into chains. The coordination topology in the crystal structure of compound **2** is very similar to that in **1** in that two coordinating water molecules are exchanged by two terminal bpe ligands. As in **1**, Ba dimers are observed that are connected by the bpe ligands into chains. In $[[Ba(NCS)_2]_2]$-$(bpe)_3$ (**3**) the barium cations are linked by two μ-1,3-bridging anions and one side-on-bridging thiocyanato anion into chains that are further linked by the bpe ligands into layers. In the first polymorphic modification of composition $[Ba(NCS)_2(bpe)(H_2O)(CH_3CN)]CH_3CN$ (**4I**) each Ba cation is coordinated by one terminal *N*-bonding and two μ-1,1,3(N,N',S)-bridging thiocyanato anions, two bridging water molecules, one acetonitrile molecule and one bpe ligand within an irregular polyhedron. The Ba cations are connected into chains that are further linked *via* O-H$\cdots$N hydrogen bonding. The crystal structure of the second form **4II** is very similar to that of form **4I**, and significant differences are found predominantly in the packing of the complexes. Investigations using simultaneous differential thermoanalysis and thermogravimetry on compound **1** have shown that this compound decomposes in three steps with the formation of compound **3** in the second TG step.

Key words: Coordination Chemistry, Barium(II) Thiocyanates, Crystal Structures, Thermal Properties

Introduction

Recently, investigations on the synthesis, structures and properties of coordination compounds have become of increasing interest [1–7]. In this context, compounds with condensed networks, in which paramagnetic metal atoms are linked by small-sized anionic ligands are of special interest because of their diverse magnetic properties. Therefore, a large number of different compounds based on *e. g.* azides, oxalates or thiocyanates were investigated [8–19]. However, for these anions different coordination modes are known in which they are either only terminally bonded or act as bridging ligands. Whereas these coordination modes are frequently found in *e. g.* azides, terminal bonding is preferred in thiocyanates.

However, we have demonstrated that thiocyanates with bridging ligands can be easily prepared by thermal decomposition reactions as shown in previous work. In these reactions, suitable precursor compounds based on transition metals, terminal bonded thiocyanato anions and additional coligands are heated, which compulsorily leads to the formation of ligand-deficient intermediates, in which the metal atoms are then connected by the anionic ligands [14–19]. This reaction is accompanied with a dramatic change in the magnetic properties such that frequently cooperative magnetic exchange interactions are found in the ligand-deficient compounds. In further work we also have shown that a large number of coligands like amines or even water can be used regardless if the precursor compounds consist of discrete complexes or of coordination polymers in which the metal atoms are linked by the coligands. In all of these reactions we so far used the transition metals Mn, Fe, Co and Ni. To investigate if this method is generally applicable for the preparation of new thiocyanates we have started systematic studies on this topic. First results have shown that zinc(II) thiocyanates can also be prepared by this route, but in some products terminal thiocyanato anions are still found because the precursor compounds with octahedral coordination of the metal atoms were transformed into tetrahedral complexes [20].

In this context precursor compounds with different metal coordination patterns like *e. g.* alkaline earth metal thiocyanates are also of interest in order to investigate the influence of different coordination modes onto their thermal properties. In the beginning we used barium thiocyanate for the preparation of a potential precursor because with the high coordination numbers in barium complexes completely different structures can be expected. Moreover, only a few of such compounds with *N*-donor ligands are known and therefore, their preparation and structural characterization seems to be worthwhile [21–25]. In these investigations we prepared five compounds including two different polymorphic modifications by the reaction of barium thiocyanate with *trans*-1,2-bis(4-pyridyl)ethylene in acetonitrile/water mixtures.

Results and Discussion

Synthetic aspects

Our previous investigations have clearly shown that in some cases several compounds can be prepared if the ratio between the metal thiocyanate and the coligand is varied. Therefore, barium thiocyanate was reacted with *trans*-1,2-bis(4-pyridyl)ethylene in different molar ratios (*e. g.* 1 : 4, 1 : 2 and 2 : 1) in an acetonitrile/water mixture at r. t. Investigations using X-ray powder diffraction have shown that independent of the molar ratio the precipitate always exhibits the same powder pattern, which indicates that only one compound **1** might be favored (Fig. 1). Investigations on the stability of this compound using time-dependent X-ray powder diffraction showed that it is unstable and decomposes within a few hours into a further compound that could not be identified. To characterize compound **1** we tried to prepare single crystals at r. t. and under solvothermal conditions. Surprisingly in these experiments three additional compounds (**2**–**4**) with one of them crystallizing in two different polymorphs (**4I** and **4II**) were obtained as single crystals (see Experimental Section). All of these compounds represent solvates and therefore, decompose immediately at r. t. Even under solvent these transformations into unknown compounds are observed which indicate thermodynamic metastablility. Only for the polymorph **4II** we were able to prove that a transformation into compound **1** occurs. However, if the experimental diffraction pattern of compound **1** prepared in solution is compared with that calculated from single crystal data, it appears that **1** was always formed (Fig. 1).

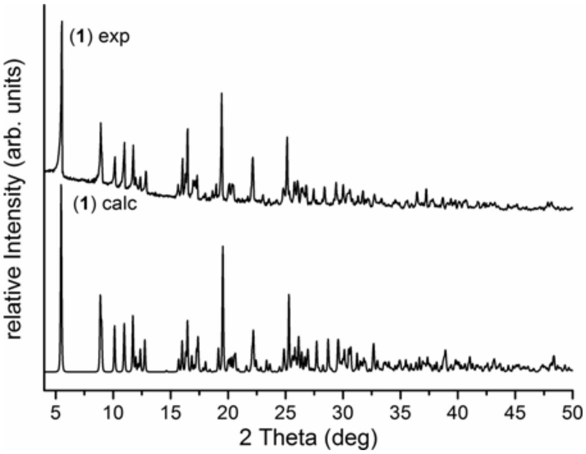

Fig. 1. Experimental X-ray powder pattern of the residue obtained by reacting $Ba(NCS)_2 \cdot 3H_2O$ with *trans*-1,2-bis(4-pyridyl)ethylene in an acetonitrile/water mixture in a ratio of 1 : 2 (top) and X-ray powder pattern for compound **1** calculated from single-crystal data (bottom).

Crystal structures

{[[Ba(NCS)(H₂O)₅]₂](bpe)}(NCS)₂(bpe)₃(H₂O)₂ (**1**)

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$ formula units in the unit cell (see Table 7). The asymmetric unit consists of one Ba cation, two thiocyanato anions, one bpe ligand and six water molecules in general positions, as well as two bpe ligands that are located on centers of inversion. Each Ba cation is ninefold coordinated by two *N*-bonded thiocyanato anions, four O atoms of water molecules and two N atoms of two symmetry-related bpe ligands within irregular polyhedra (Fig. 2, Table 1). Two Ba cations are linked into dinuclear units by two N atoms of two symmetry-related thiocyanato anions *via* μ-1,1 coordination and by symmetry-related water molecules that are located on centers of inversion (Fig. 3, top). These dinuclear units are further linked by the bpe ligands into chains along the direction of the

Table 1. Selected bond lengths (Å) for compound **1**[a].

Ba1–O4	2.729(2)	Ba1–N11	2.909(2)
Ba1–O2	2.741(2)	Ba1–O3	2.919(2)
Ba1–O1	2.834(2)	Ba1–N1	2.933(2)
Ba1–O5	2.866(2)	Ba1–N1A	3.094(2)
Ba1–O3A	2.886(2)	Ba1–Ba1A	4.1452(4)

[a] Symmetry code: A: $-x+1$, $-y+1$, $z+1$.

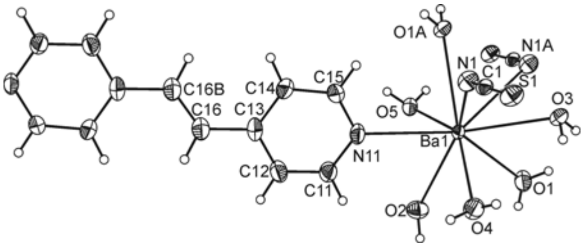

Fig. 2. View of the Ba coordination in compound **1** with atom labelling and displacement ellipsoids drawn at the 50 % probability level. Symmetry codes: A: $-x+1$, $-y+1$, $-z$; B: $-x+1$, $-y+1$, $-z+1$.

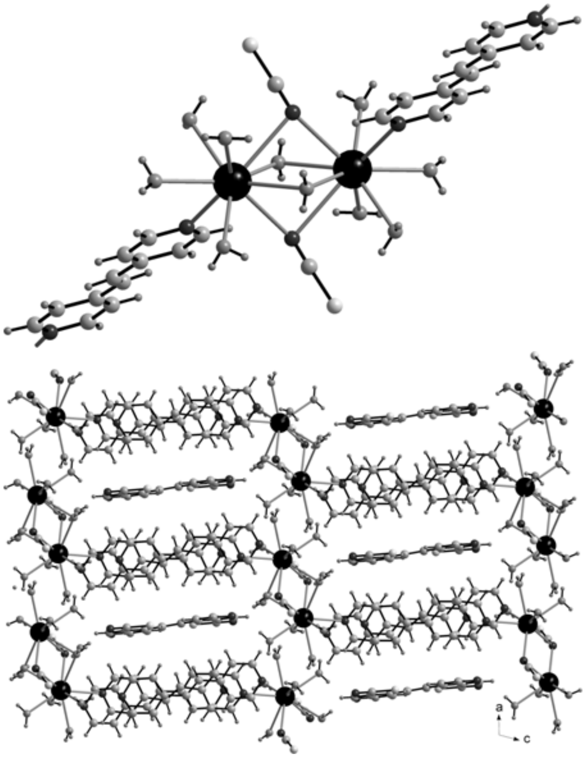

Fig. 3. Crystal structure of compound **1** with a view of the Ba dimers (top) and in the direction of the crystallographic *b* axis (bottom).

crystallographic *c* axis. From this arrangement cavities are formed in which the additional bpe ligands and water molecules are located (Fig. 3, bottom).

Table 2. Selected bond lengths (Å) for compound **2**[a].

Ba1–O2	2.709(2)	Ba1–N41	2.928(3)
Ba1–O3	2.749(3)	Ba1–N1	2.967(3)
Ba1–O1A	2.832(2)	Ba1–N1A	2.994(3)
Ba1–O1	2.845(2)	Ba1–N11	3.119(3)
Ba1–N21	2.900(3)	Ba1–Ba1A	4.0828(5)

[a] Symmetry code: A: $-x+1$, $-y+1$.

*$\{[[Ba(NCS)(bpe)_2(H_2O)_3]_2](bpe)\}(NCS)_2(bpe)_4$ (**2**)*

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$ formula unit in the unit cell (see Table 7). The asymmetric unit contains one Ba cation, two thiocyanato anions, three bpe ligands, and three water molecules in general positions and one bpe ligand located on a center of inversion. Each Ba cation is coordinated by two terminally *N*-bonded thiocyanato anions, two terminal ligands and one bridging bpe ligand as well as two non-bridging and two bridging water molecules (Fig. 4, Table 2). The coordination pattern around the Ba cations can be described as an irregular polyhedron. Two Ba cations are linked by bridging O atoms of water molecules and two bridging bpe ligands into dinuclear units that are located on centers of inversion (Fig. 5). These units are additionally linked by the bridging bpe ligand into chains. The non-coordinating water molecules and bpe ligands are located between these chains (Fig. 6). The overall topology of this structure is very similar to that of com-

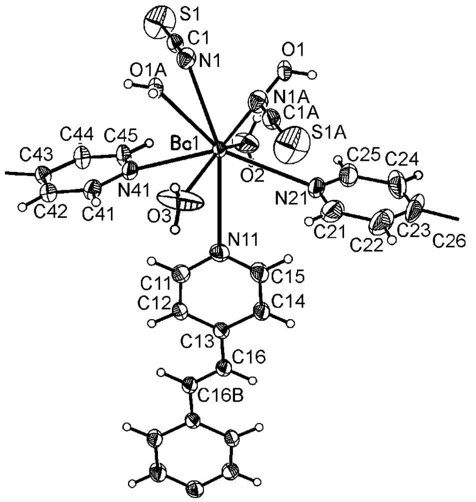

Fig. 4. View of the Ba coordination in compound **2** with atom labelling and displacement ellipsoids drawn at the 50 % probability level. Symmetry codes A: $-x+1$, $-y+1$, $-z$; B: $-x+1$, $-y+1$, $-z+1$. For clarity one half of each of the two bpe ligands is omitted.

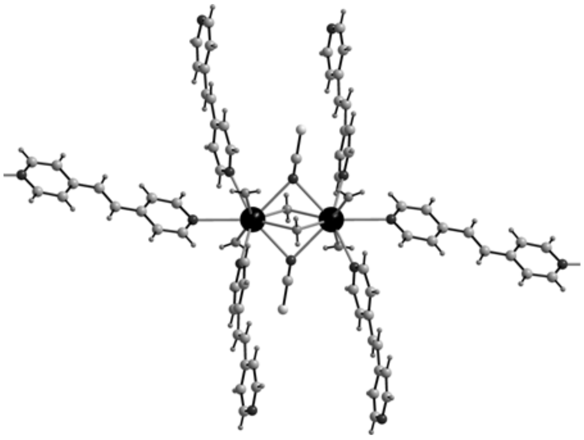

Fig. 5. Crystal structure of compound **2** with view of the Ba dimers.

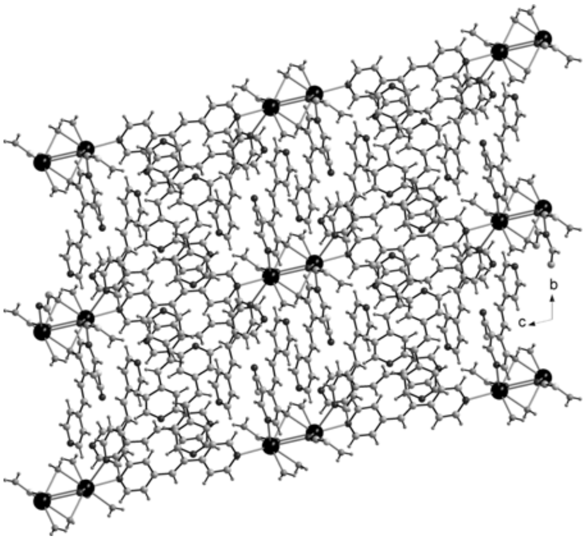

Fig. 6. Crystal structure of compound **2** with view along the crystallographic *c* axis.

pound **1**. To transform compound **1** into **2**, only two of the four non-bridging water molecules must be exchanged by terminal bpe ligands.

*[[Ba(NCS)$_2$]$_2$](bpe)$_3$ (**3**)*

Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with Z = 1 formula unit in the unit cell (see Table 7). The asymmetric unit consists of one Ba cation, two crystallographically independent thiocyanato anions and one bpe ligand in general positions as well as of one bpe ligand that is located on a center of inversion. Each Ba cation is coordinated by one side-on coordinating and two μ-1,3-thiocyan-

Table 3. Selected bond lengths (Å) for compound **3**[a].

Ba1–N2	2.734(6)	Ba1–C1	3.111(5)
Ba1–N1A	2.825(7)	Ba1–N1	3.184(6)
Ba1–N21	2.902(5)	Ba1–S2C	3.195(3)
Ba1–N22B	2.936(5)	Ba1–S1	3.535(2)
Ba1–N11	2.947(5)	Ba1–Ba1A	4.762(5)

[a] Symmetry codes A: $-x$, $-y+1$, $-z+1$; B: $x-1$, $y+1$, z; C: $-x$, $-y+1$, $-z+2$.

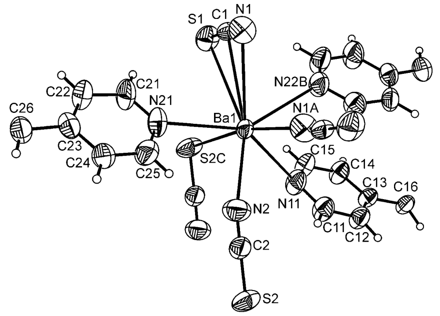

Fig. 7. View of the Ba coordination in compound **3** with labelling and displacement ellipsoids drawn at the 50 % probability level. Symmetry codes A: $-x$, $-y+1$, $-z+1$; B: $x-1$, $y+1$, z; C: $-x$, $-y+1$, $-z+2$. For clarity half of each of the bpe ligands is omitted.

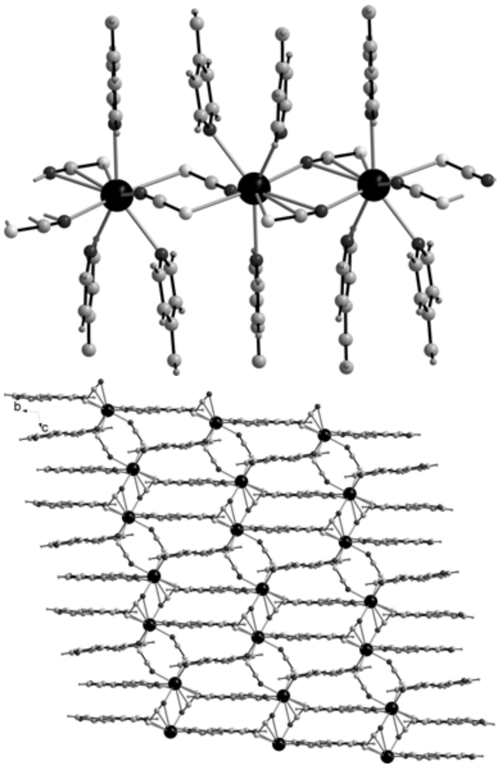

Fig. 8. Crystal structure of compound **3** with a view of the chains (top; for clarity only half of some bpe ligands are shown) and in the direction of the crystallographic *a* axis (bottom).

Table 4. Selected bond lengths (Å) for form **4I** and **4II**[a].

4I		**4II**	
Ba1–O1	2.837(2)	Ba1–O1	2.839(2)
Ba1–O1B	2.920(2)	Ba1–O1B	2.870(2)
Ba1–N11	2.883(3)	Ba1–N11	2.886(3)
Ba1–N1	2.890(3)	Ba1–N1	2.889(3)
Ba1–N2	2.905(2)	Ba1–N2	2.944(3)
Ba1–N2B	2.896(2)	Ba1–N2B	2.917(3)
Ba1–N3	2.903(3)	Ba1–N3	2.901(4)
Ba1–N1A	2.918(3)	Ba1–N1A	2.938(3)
Ba1–S2A	3.3834(1)	Ba1–S2A	3.3801(9)
Ba1–Ba1A	4.0471(4)	Ba1–Ba1A	4.0686(5)
Ba1–Ba1B	4.6224(4)	Ba1–Ba1B	4.6715(6)

[a] Symmetry codes: A: $-x, -y+1, -z+1$; B: $-x+1, -y+1, -z+1$ (**4I**); A: $-x-1, -y+2, -z+1$; B: $-x, -y+2, -z+1$ (**4II**).

ato anions and three bpe ligands within an irregular polyhedron (Fig. 7). The Ba–N and Ba–S bond lengths to the side-on coordinating thiocyanato anion are significantly longer than those to the μ-1,3 thiocyanato anions (Table 3). Unfortunately these values cannot be compared with those from other structures because according to a search in the CCDC database (version 1.12, 2009 [26, 27]) side-on thiocyanato coordination to barium cations was never observed before.

The metal cations are further connected into chains *via* alternating μ-1,3-bridging and side-on coordinating thiocyanato anions into chains along the crystallographic *c* axis (Fig. 8). These chains are further linked by bridging bpe ligands into layers that are located in the *ac* plane (Fig. 8, bottom). The bpe ligands are stacked onto each other suggesting significant π-π interactions.

*[Ba(NCS)$_2$(bpe)(H$_2$O)(CH$_3$CN)]CH$_3$CN (**4I** and **4II**)*

The polymorph **4I** crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ formula units in the unit cell, whereas the polymorph **4II** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ (Table 7). In both modifications the asymmetric unit consists of one Ba cation, two thiocyanato anions, one water molecule, one bpe ligand and two crystallographically independent acetonitrile molecules, all of them located in general positions. In contrast to **4I**, in **4II** both acetonitrile molecules are disordered in two orientations with a s. o. f. of 0.75 : 0.25. The barium coordination is very similar in both forms with only slight changes in the geometric parameters (Table 4). Each Ba cation is coordinated by four μ-1,1 *N*- and two μ-1,3 *N*,*S*-coordinating thiocyanato anions, one bpe and two bridging water molecules within an irregular polyhedron (Fig. 9). The Ba–S bond lengths are longer than those in related compounds like *e. g.* **3**. The Ba cations are connected into chains by either two μ-1,3 *N*,*S*- and two μ-1,1 *N*-coordinating thiocyanato anions, or by two μ-1,1 *N*-coordinating thiocyanato anions and two bridging water molecules (Fig. 10). These chains are further linked into layers by O–H···N hydrogen bonding between the oxygen atoms of the water molecules and the N atoms of the bpe ligands (Fig. 11, Table 5). In addition, weak hydrogen bonding interactions are found between the water H atoms and the S atoms of the thiocyanato anions (Table 5). Significant differences between both forms are found in the packing of the building blocks, in that the orientation of the chains and the non-coordinating acetonitrile ligands are completely different in **4I** and **4II**.

Table 5. Hydrogen bonding geometry (Å, deg) for form **4I** and **4II**.

D-H	*d*(D-H)	*d*(H··A)	∠(DHA)	*d*(D··A)	A
4I					
O1-H1O1	0.823	2.711	145.85	3.424	S1 $(x+1, y, z)$
O1-H2O1	0.823	1.948	163.52	2.747	N12 $(x, y, z+1)$
4II					
O1-H1O1	0.854	2.603	155.12	3.397	S1 $(x+1, y, z)$
O1-H2O1	0.960	1.778	176.54	2.738	N12 $(x-1, y-1, z-1)$

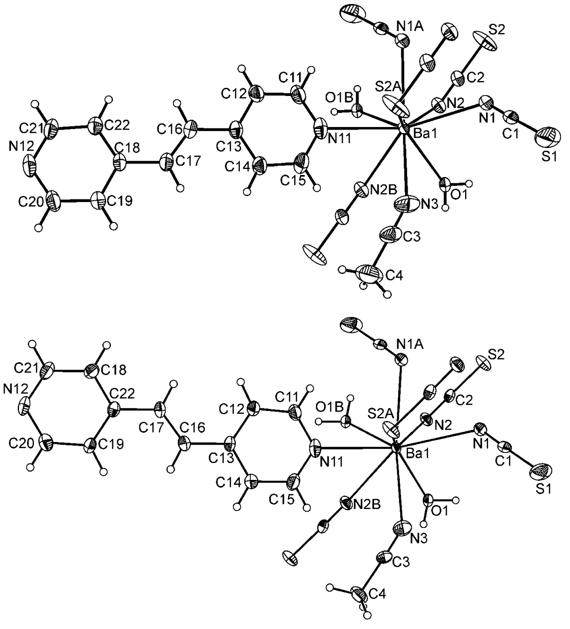

Fig. 9. View of the Ba coordination in forms **4I** (top) and **4II** (bottom) with atom labelling and displacement ellipsoids drawn at the 50 % probability level. Symmetry codes: A: $-x, -y+1, -z+1$; B: $-x+1, -y+1, -z+1$ (**4I**); A: $-x-1, -y+2, -z+1$; B: $-x, -y+2, -z+1$ (**4II**). The disorder in **4II** is not shown for clarity.

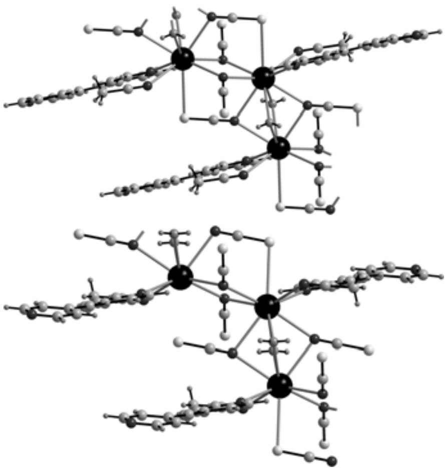

Fig. 10. Part of the chains in the crystal structures of the polymorphs **4I** (top) and **4II** (bottom). The disorder in **4II** is not shown for clarity.

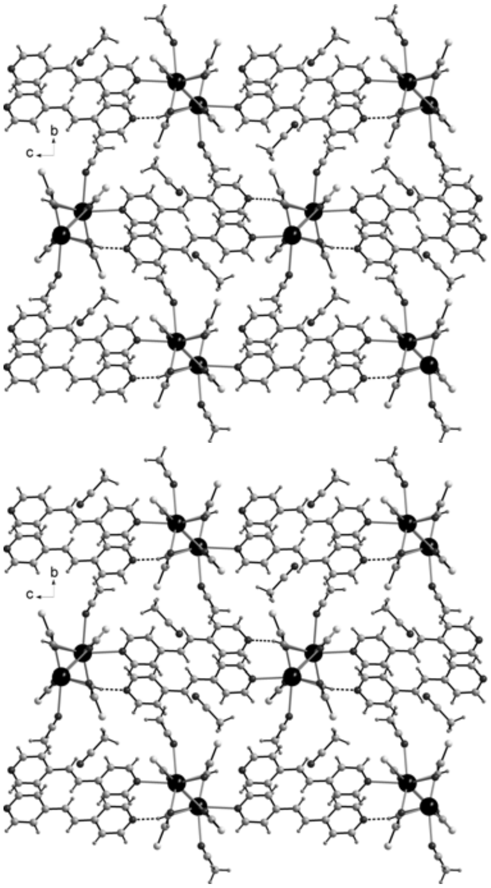

Fig. 11. Crystal structure of the polymorphs **4I** (top) and **4II** (bottom). O–H···N hydrogen bonds are shown as dashed lines, and the disorder in **4II** is not shown for clarity.

Thermoanalytical investigations

On heating compound **1** in a thermobalance three mass steps are observed that are associated with endothermic events in the DTA curve (Fig. 12). In the DTG curve the first step is well resolved, but the second and third mass losses are poorly resolved. The experimental mass loss of the first step (10.0 %) is only in rough agreement with that calculated for the removal of the water molecules ($\Delta m_{\mathrm{calcd}}$ = 14.9). How-

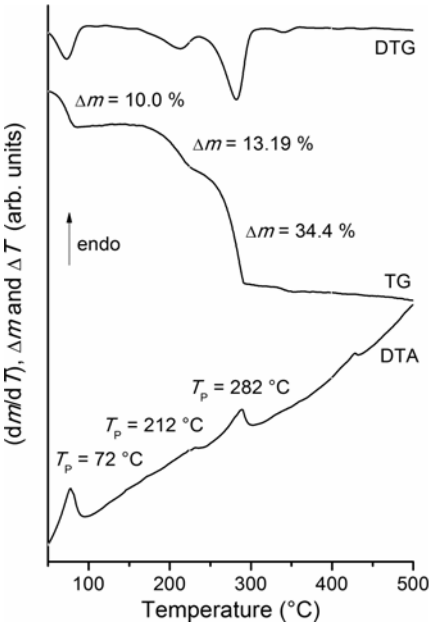

Fig. 12. DTA-TG and DTG curves for compound **1** (given are the mass loss in % and the peak temperatures T_P in °C).

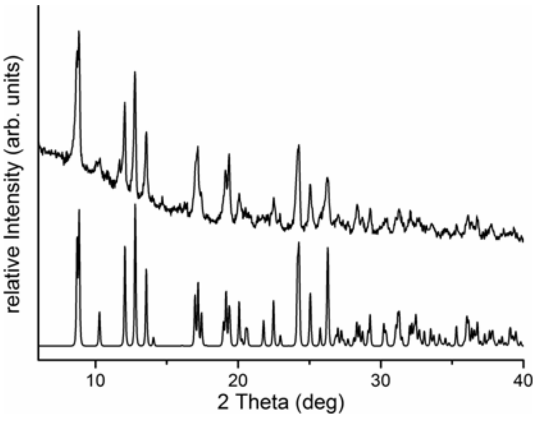

Fig. 13. Experimental X-ray powder pattern of the residue isolated after the second mass loss in the TG measurements of compound **1** (top) and calculated pattern for compound **3** (bottom).

ever, since this compound starts to decompose at r. t. it can be assumed that water is already lost during sample preparation. The second mass loss (13.2 %) is in reasonable agreement with that calculated for the removal of one of the bpe ligands ($\Delta m_{\text{calcd}} = 12.5$). Based on the experimental mass loss it can be assumed that in the first step a compound of composition $Ba(NCS)_2(bpe)_2$ is formed, that transforms into a compound of composition $[Ba(NCS)_2]_2(bpe)_3$ in the second TG step, which presumably corresponds to compound **3**. To prove the formation of compound **3** as an intermediate in the thermal decomposition of **1**, a second TG measurement was performed which was stopped after the second TG step. Afterwards this residue was investigated by X-ray powder diffraction (Fig. 13). These investigations have clearly proven the formation of compound **3** in the second step. Surprisingly, despite the low resolution of the TG steps, this compound was obtained in a very pure state. Similar experiments were also performed in order to characterize the intermediate formed in the first step. However, the residue is poorly crystalline, and from the X-ray powder pattern no further information can be extracted. In addition, further investigation have indicated that this compound is very hygroscopic.

Conclusions

Based on previous studies on the synthesis and thermal decomposition of precursor compounds with transition metal thiocyanates and *N*-donor ligands we investigated if similar systems can also be prepared with barium cations. Only very few of such compounds had been structurally characterized which was an additional incentive for this work. We have prepared five new barium thiocyanato compounds with *trans*-1,2-bis(4-pyridyl)ethylene as ligand. In contrast to previous investigations using *e. g.* Mn, Fe, Co and Ni as cations, in which, based on simple considerations, the topology of the coordination networks can be predicted or influenced to some extent, the situation is much more complex with barium. This is due to the large ionic radius of this cation that leads to a completely different coordination behavior and to structures that are difficult to predict. In order to saturate the coordination sphere of this cation, additional solvent molecules are accumulated leading to the formation of hydrates and solvates that are unstable and therefore, difficult to investigate. The occurrence of so many different compounds that are obviously metastable also hinders the preparation of phase-pure samples and therefore, such compounds are less applicable for the rational preparation of ligand-deficient coordination polymers with bridging anions and thus, to the formation of more condensed networks than those we have shown in previous work.

Table 6. Gram amounts and molar ratios used for the preparation of compounds **1** – **4**.

Compound	$Ba(NCS)_2 \cdot 3H_2O$	*trans*-1,2-bis(4-pyridyl)ethylene
1	93.6 mg (0.3 mmol)	27.3 mg (0.15 mmol)
2	48.3 mg (0.15 mmol)	110.6 mg (0.6 mmol)
3	26.2 mg (0.10 mmol)	57.6 mg (0.3 mmol)
4I	46.1 mg (0.15 mmol)	57.0 mg (0.3 mmol)
4II	46.8 mg (0.15 mmol)	56.7 mg (0.3 mmol)

Nevertheless compound **1** could be prepared phase pure and its thermal properties investigated, showing that a "ligand-deficient" intermediate **3** can indeed be isolated. At first glance, this structure is as expected in that the metal atoms are connected by the thiocyanato anions into chains that are further linked into layers by the additional *N*-donor ligand. However, significant structural differences are found compared to the compounds investigated previously in that in addition to μ-1,3 coordination of the anions also side-on coordination is observed. Moreover, in the more "condensed" compound **3**, each metal atom is coordinated by three additional *trans*-1,2-bis(4-pyridyl)ethylene ligands, which we never observed in other compounds before. This also is certainly due to the large ionic radius of barium. The complexity of composition and structures of such barium compounds is manifested in the occurrence of different polymorphic modifications. Our results indicate that barium thiocyanato coordination compounds with *N*-donor ligands are not suitable as precursor compounds for the preparation of more condensed coordination networks by thermal decomposition reactions.

Experimental Section

Synthesis of compounds 1 – 4

$Ba(NCS)_2 \cdot 3H_2O$ was obtained from Alfa Aesar and *trans*-1,2-bis(4-pyridyl)ethylene from Sigma Aldrich. All chemicals were used without further purification. Single crystals suitable for X-ray structure determination were obtained by the reaction of different molar ratios of $Ba(NCS)_2 \cdot 3H_2O$ and *trans*-1,2-bis(4-pyridyl)ethylene. The reactants were mixed in 1 mL of an acetonitrile/water mixture (99 : 1). Light-yellow block-shaped single crystals were obtained within three days (Table 6).

Larger amounts of compound **1** can be prepared by stirring $Ba(NCS)_2 \cdot 3H_2O$ (50.1 mg, 0.15 mmol) and *trans*-1,2-

Table 7. Selected crystal data and details of the structure determinations for compounds **1**, **2**, **3**, **4I**, and **4II**.

Compound	**1**	**2**	**3**	**4I**	**4II**
Formula	$C_{52}H_{64}Ba_2N_{12}O_{12}S_4$	$C_{112}H_{102}Ba_2N_{22}O_6S_4$	$C_{40}H_{30}Ba_2N_{10}S_4$	$C_{18}H_{18}BaN_6OS_2$	$C_{18}H_{18}BaN_6OS_2$
Crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic
M_r	1452.07	2255.08	1053.66	535.84	535.84
Crystal size, mm^3	$0.14 \times 0.11 \times 0.02$	$0.13 \times 0.10 \times 0.07$	$0.15 \times 0.10 \times 0.06$	$0.69 \times 0.57 \times 0.48$	$0.14 \times 0.11 \times 0.08$
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a, Å	9.4625(8)	12.2241(9)	10.0059(8)	7.3774(4)	7.5090(6)
b, Å	10.8240(9)	12.8536(9)	10.6514(9)	18.5786(12)	11.7807(10)
c, Å	17.1911(13)	18.0931(12)	10.677(10)	16.6842(9)	13.3182(16)
α, deg	102.474(9)	101.633(8)	107.471(10)	90	91.549(10)
β, deg	101.226(9)	102.260(8)	92.628(10)	98.491	100.070(10)
γ, deg	106.368(9)	97.144(8)	92.346(10)	90	105.855(9)
V, Å^3	1587.0(2)	2679.1(3)	1082.5(10)	2261.7(2)	1112.38(16)
T, K	200(2)	200(2)	293(2)	200(2)	170(2)
Z	1	1	1	4	2
$D_{\text{calcd.}}$, g cm^{-3}	1.52	1.40	1.62	1.57	1.60
$F(000)$, e	732	1152	516	1056	528
μ, mm^{-1}	1.4	0.9	2.0	2.0	2.0
Transm. (min / max)	0.6040 / 0.9147	0.8014 / 0.9243	0.6448 / 0.7882	0.1776 / 0.2404	0.6813 / 0.7730
$\theta_{\max}$, deg	27.00	27.02	27.14	28.07	27.00
Reflections collected	15028	24777	4670	21815	8710
Independent reflections / R_{int}	6678 / 0.0450	11276 / 0.0456	4670 / 0.0216	5274 / 0.0284	4688 / 0.0377
Refl. with $F_0 \geq 4\sigma(F_0)$	6191	9372	3180	4213	4154
Restraints / ref. parameters	0 / 371	0 / 695	0 / 254	0 / 243	3 / 282
Final $R1$ / $wR2$ $[I \geq 2\sigma(I)]$	0.0252 / 0.0653	0.0381 / 0.0926	0.0393 / 0.0754	0.0280 / 0.0656	0.0281 / 0.0692
Goodness-of-fit on F^2	1.031	0.997	0.883	1.036	0.974
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.51 / −0.91	0.68 / −1.24	0.66 / −0.64	0.47 / −1.02	0.71 / −1.06

bis(4-pyridyl)ethylene (55.4 mg, 0.3 mmol) in 1 mL acetonitrile for 1 d in a closed test tube at 120 °C. The residue is filtered off, washed with water and diethyl ether and dried in air. The purity was checked by XRPD (see Fig 1). CHNS analysis. $C_{52}H_{64}N_{12}O_{12}S_4Ba_2$ (1452.09): calcd. C 43.01, H 4.44, N 11.58, S 8.83; found C 43.19, H 4.44, N 11.73, S 8.08.

Single-crystal structure analysis

Crystallographic measurements were performed with an imaging plate diffraction system (Stoe IPDS-1) with MoK_α radiation. All data were corrected for absorption. The structures were solved with Direct Methods using SHELXS-97, and the structure refinements were performed against $|F|^2$ using SHELXL-97 [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{eq}}(\text{C})$] using a riding model. The O-H hydrogen atoms were located in a difference map, their bond lengths set to ideal values and finally refined using a riding model. In form **4II** both acetonitrile molecules are disordered and were refined using a split model. Details of the structure determination are given in Table 7.

CCDC 804582 (**1**), 804583 (**2**), 804584 (**3**), 804585 (**4I**) and 804586 (**4II**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

X-Ray powder diffraction (XRPD)

XRPD experiments were performed on a Stoe Transmission Powder Diffraction System (STADI P) equipped with a linear position-sensitive detector from Stoe and an Image Plate Detector using CuK_α radiation (λ = 154.0598 pm).

Additional XRPD experiments were performed on a PANalytical X'Pert Pro MPD Reflection Powder Diffraction System equipped with a PIXcel semiconductor detector (PANalytical B.V., Almelo (Netherlands)) using CuK_α radiation (λ = 154.0598 pm).

Elemental analysis

CHNS analysis was performed using an EURO EA elemental analyzer (EURO VECTOR Instruments and Software).

Differential thermal analysis and thermogravimetry

The DTA-TG measurements were performed in nitrogen atmosphere in Al_2O_3 crucibles using a Netzsch STA-409CD thermobalance. 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.

Acknowledgements

This project was supported by the Deutsche Forschungsgemeinschaft (Project No. NA 720/3-1) and the State of Schleswig-Holstein. We thank Professor Dr. W. Bensch for access to his experimental facilities.

---

[1] A. Y. Robin, K. M. Fromm, *Coord. Chem. Rev.* **2006**, *250*, 2127.

[2] D. Maspoch, D. Ruiz-Molina, J. Veciana, *Chem. Soc. Rev.* **2007**, *36*, 770.

[3] C. Janiak, *Dalton Trans.* **2003**, 2781.

[4] D. Maspoch, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.* **2004**, *14*, 2713.

[5] S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276.

[6] G. Férey, *Dalton Trans.* **2009**, 4400.

[7] G. Férey, C. Serre, *Chem. Soc. Rev.* **2009**, *38*, 1380.

[8] W. X. Zhang, W. Xue, J. B. Lin, Y. Z. Zheng, X. M. Chen, *CrystEngComm* **2008**, *10*, 1770.

[9] W. Li, H.-P. Jia, Z.-F. Ju, J. Zhang, *Dalton Trans.* **2008**, 5350.

[10] J. L. Manson, A. M. Arif, J. S. Miller, *Chem. Commun.* **1999**, 1479

[11] Y.-F. Zeng, X. Hu, F.-C. Liu, X.-H. Bu, *Chem. Soc. Rev.* **2009**, *38*, 469.

[12] R. Vicente, B. Bitschnau, A. Egger, B. Sodin, F. A. Mautner, *Dalton Trans.* **2009**, 5120.

[13] P. Talukder, A. Datta, S. Mitra, G. Rosair, M. S. E. Fallah, J. Ribas, *Dalton Trans.* **2004**, 4161.

[14] M. Wriedt, I. Jeß, C. Näther, *Eur. J. Inorg. Chem.* **2009**, 1406.

[15] M. Wriedt, C. Näther, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2459.

[16] M. Wriedt, C. Näther, *Dalton Trans.* **2009**, 10192.

[17] M. Wriedt, C. Näther, *Eur. J. Inorg. Chem.* **2010**, 3201.

[18] M. Wriedt, S. Sellmer, C. Näther, *Inorg. Chem.* **2009**, *48*, 6896.

[19] M. Wriedt, S. Sellmer, C. Näther, *Dalton Trans.* **2009**, 7975.

[20] G. Bhosekar, J. Boeckmann, I. Jeß, C. Näther, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2595.

[21] M. Czugler, A. Kálmán, *J. Mol. Struct.* **1981**, *75*, 29.

[22] K. Henke, D. A. Atwood, *Inorg. Chem.* **1998**, *37*, 224.

[23] B. Metz, D. Moras, R. Weiss, *Acta Crystallogr.* **1973**, *29*, 1382.

[24] W. H. Watson, D. A. Grossie, F. Vogtle, W. M. Muller, *Acta Crystallogr.* **1983**, *39*, 720.

[25] G. Weber, *Inorg. Chim. Acta* **1982**, *58*, 27.

[26] F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rodgers, D. G. Watson, *Acta Crystallogr.* **1979**, *B35*, 2331.

[27] F. H. Allen, O. Kennard, R. Taylor, *Acc. Chem. Res.* **1983**, *16*, 146.

[28] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; *ibid.* **2008**, *A64*, 112.