

Infinite Anionic Chains Formed by Alternating Bidentately Acting $[\text{SbS}_4]^{3-}$ Anions and $[\text{Mn}(\text{dien})]^{2+}$ Complexes in the Compound $[\text{Mn}(\text{dien})_2][\text{Mn}(\text{dien})\text{SbS}_4]_2$

Nicola Herzberg, Christian Näther and Wolfgang Bensch

Institute of Inorganic Chemistry, Christian-Albrechts-University of Kiel, Max-Eyth-Straße 2, 24118 Kiel, Germany

Reprint requests to Prof. W. Bensch. Phone: +49 431 880-2419. Fax: +49 431 880-1520.

E-mail: wbench@ac.uni-kiel.de

Z. Naturforsch. **2013**, 68b, 605–610 / DOI: 10.5560/ZNB.2013-3039

Received February 9, 2013

Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The new compound $[\text{Mn}(\text{dien})_2][\text{Mn}(\text{dien})\text{SbS}_4]_2$ (dien = diethylenetriamine) was synthesized under solvothermal conditions. It crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ with $a = 7.5736(5)$, $b = 19.1081(16)$, $c = 13.1174(11)$ Å, $\beta = 90.022(9)^\circ$, $V = 1898.3(3)$ Å³, and $Z = 2$. The crystal structure is composed of one $[\text{Mn}(\text{dien})_2]^{2+}$ cation and an anionic chain composed of $[\text{SbS}_4]^{3-}$ anions and $[\text{Mn}(\text{dien})_2]^{2+}$ cations. The $[\text{SbS}_4]^{3-}$ anions connect $[\text{Mn}(\text{dien})_2]^{2+}$ ions in a μ_2 -fashion to form an undulated $\{[\text{Mn}(\text{dien})\text{SbS}_4]\}_2^-$ chain running along [001]. The Mn^{2+} ions in the chain are in a rare distorted rectangular pyramidal coordination environment with 3 N and 1 S atom forming the base and one S atom being located at the apex of the pyramid. The anionic chains and the cations alternate along [010]. Several relatively strong intra- and inter-chain N–H...S bonding interactions are observed. From the Raman spectrum the reduction of the ideal T_d symmetry of the $[\text{SbS}_4]^{3-}$ anions is obvious because more resonances occur than expected for the undistorted geometry.

Key words: Thioantimonates, Solvothermal Syntheses, Crystal Structure

Introduction

During the past decades a large number of fascinating thiometallate compounds were prepared either under solvothermal or ambient conditions as recently reviewed [1–5]. A subgroup of these compounds mainly prepared under solvothermal conditions are thioantimonates(III) which are characterized by a large variety of chemical compositions, Sb:S ratios and structural dimensionalities. It can be assumed that $\text{Sb}(\text{III})\text{S}_x$ units ($x = 3–5$) generated at the early stages of a hydrothermal reaction have a pronounced tendency for further condensation thus leading to the formation of higher hierarchical building blocks with different structural complexity. Compounds with isolated thioantimonate(III) anions like $[\text{Sb}_3\text{S}_6]^{3-}$, $[\text{Sb}_4\text{S}_8]^{4-}$, $[\text{Sb}_6\text{S}_{12}]^{6-}$ [6–8] have been isolated, but also very complex three-dimensional net-

works have been observed. Some selected examples are given in refs. [9–19]. There are only three examples for the coexistence of Sb(III) and Sb(V) in thioantimonate compounds obtained under solvothermal conditions [20–22], and another mixed valent thioantimonate, $\text{Cs}_3\text{Ag}_2\text{Sb}_3\text{S}_8$, was prepared in supercritical ammonia [23].

While thioantimonates(III) exhibit a variable and diverse structural chemistry, compounds containing Sb(V) are rare and mainly structurally characterized by isolated $[\text{SbS}_4]^{3-}$ anions and counterions. There are few examples where bonding interactions between the $[\text{SbS}_4]^{3-}$ anions and transition metal or lanthanoid cations occur. The $[\text{SbS}_4]^{3-}$ anion can act as a monodentate ligand like in *e. g.* $[\text{Mn}(\text{tren})(\text{trenH})]\text{SbS}_4$ (tren = tris(2-aminoethyl)amine) and $[\text{Mn}(\text{trans-1,2-dach})_3]_2[\text{Mn}(\text{trans-1,2-dach})_2(\text{SbS}_4)_2] \cdot 6\text{H}_2\text{O}$ (trans-1,2-dach = trans-1,2-diaminocyclohexane) [24], as

a bidentate bridging ligand as observed in *e. g.* [Nd(en)₃(H₂O)(μ₂-SbS₄)] [25], or as a tridentate ligand like in *e. g.* [La(en)₃(μ₃-SbS₄)] [25], [Ce(dien)₂(μ₃-SbS₄)_n] [26], [La(teta)(en)SbS₄] (teta = triethylenetetramine) [27], [Ln(dien)₂(μ-η¹-η²-SbS₄)_n] (Ln = Pr, Nd, Sm) and [Ln(dien)₂(η²-SbS₄)] (Ln = Eu, Dy) [28], and [Pr(en)₃(H₂O)(μ₂-SbS₄)] [29].

In the past we often observed that Mn²⁺ can easily be integrated into thiometallate networks [30–35], and during further explorative work we obtained and characterized the new compound [Mn(dien)₂][Mn(dien)SbS₄]₂ featuring anionic chains composed of tetrahedral bidentately acting [SbS₄]³⁻ moieties interconnecting [Mn(dien)]²⁺ complexes and additional [Mn(dien)₂]²⁺ ions which are located between the chains.

Experimental Section

Synthesis

All chemicals were purchased and used without further purifications. The title compound was obtained as yellow-orange thin needles upon heating 64.4 mg S (2 mmol), 61.1 mg Sb (0.5 mmol) and 54.8 mg Mn (1 mmol) in 2 mL diethylenetriamine (dien) for 2 d at 140 °C in a Teflon-liner placed in a steel autoclave. Despite a large variation of the synthesis conditions, the yield based on Mn was always only between 5 and 15%. Changing the educt ratio and/or the reaction time led to crystallization of the mixed-valent compound [Mn(dien)₂]₂MnSb₂S₇ [22]. The most sensitive synthesis parameter is the reaction time. An increase beyond 2 d afforded the formation of dense phases like MnS and Sb₂S₃ together with unknown compounds. – Elemental analysis CHN (%): calcd. C 17.8, N 15.6, H 4.9; found C 18.1, N 15.3, H 5.1.

Crystal structure determination

The intensity data were collected using a Stoe IPDS-1 (Imaging Plate Diffraction System) with MoK_α radiation at room temperature. The structure was solved with Direct Methods using the program SHELXS-97 [36], and the refinement was carried out against F² with SHELXL-97 [37]. All non-hydrogen atoms were refined anisotropically. All H atoms were positioned with idealized geometry and refined isotropically using a riding model. An empirical absorption correction was performed. The crystal metric as well as the internal R value indicated orthorhombic symmetry, and an analysis of the systematically absent reflections led to space group P222₁. However, structure refinement in this space group always led to strong disorder and very poor reliability factors which clearly demonstrated that the crystal symmetry

is too high. Further analysis has shown that the compound crystallizes monoclinically in space group P2₁, and that the crystal is non-merohedrally twinned with a 2-fold axis as the twin element (BASF parameter: 0.5249(1)). In this space group no disorder is present, and the absolute structure can easily be determined and is in agreement with the selected setting; *x* (Flack) parameter: 0.06(2).

CCDC 929165 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Raman spectroscopy

The Raman spectrum was recorded with a Bruker IFS 66 Fourier transform Raman spectrometer (wavelength: 541.5 nm) in the region from 100 to 3500 cm⁻¹.

UV/Vis spectroscopy

The UV/Vis spectroscopic investigation was carried out at room temperature using an UV/Vis/NIR two-channel spectrometer Cary 5 from Varian Techtron Pty., Darmstadt. The optical band gap was determined by analyzing the UV/Vis reflectance spectrum of the powdered sample (with BaSO₄ powder used as reference material). The absorption data were calculated applying the Kubelka-Munk relation for diffuse reflectance data.

Results and Discussion

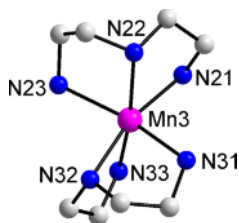
The compound crystallizes in the non-centrosymmetric monoclinic space group P2₁ with all atoms being located on general positions. Selected data of the data collection and refinement results are summarized in Table 1.

In the crystal structure the crystallographically unique δδ-δλ-[Mn₃(dien)₂]²⁺ cation adopts the *u-fac* conformation (Fig. 1). The sterically demanding dien ligands lead to a distortion of the octahedral environment around the Mn²⁺ ion as evidenced by the deviation of the N–Mn–N angles from the ideal values (Table 2) which is not unusual for Mn²⁺-centered complexes with multidentate ligands [38–41]. The Mn–N bond lengths are in a narrow range from 2.283(6) to 2.307(6) Å, and the N–Mn–N *trans*-angles are between 158 and 163° (Table 2).

In the second structural building unit two independent Mn²⁺ cations are surrounded each by three N atoms of a dien ligand and by two S atoms of two unique [SbS₄]³⁻ anions. The final coordination polyhedron may be described as a distorted rectangular

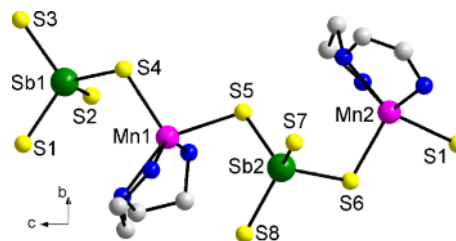
Table 1. Selected details of the data collection and structure refinement result.

Empirical formula	C ₁₆ H ₅₂ Mn ₃ N ₁₂ S ₈ Sb ₂
Formula weight, g cm ⁻³	1077.50
Crystal size, mm ³	0.1 × 0.08 × 0.08
Temperature, K	190(2)
Radiation; wavelength, Å	Mo K _α ; 0.71073
Crystal system	monoclinic
Space group	P2 ₁
<i>a</i> , Å	7.5736(5)
<i>b</i> , Å	19.1081(16)
<i>c</i> , Å	13.1174(11)
β, deg	90.022(9)
Volume, Å ³	1898.3(3)
<i>Z</i>	2
Density (calculated), g cm ⁻³	1.89
Absorption coefficient, mm ⁻¹	2.8
θ range data collection, deg	2.64–27.00
Index ranges <i>hkl</i>	±9, ±24, ±16
Refl. collected / unique / <i>R</i> _{int}	22004 / 7988 / 0.0594
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	7861
Data / restraints / parameters	7988 / 1 / 372
Goodness-of-fit on <i>F</i> ²	1.060
Final <i>R</i> 1 / <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0318 / 0.0769
Final <i>R</i> 1 / <i>wR</i> 2 (all data)	0.0325 / 0.0772
Absolute structure parameter <i>x</i>	0.06(2)
Extinction coefficient	0.0083(4)
Largest diff. peak / hole, e Å ⁻³	0.81 / -0.63

Fig. 1 (color online). The Mn³⁺ cation in the title compound. C atoms are not labeled, and H atoms are not displayed for clarity.

pyramid with one S atom and three N atoms forming the rectangular plane and one S atom at the apical position (Fig. 2). The interconnection of the Mn²⁺ cations and the [SbS₄]³⁻ anions generates a wavy {[Mn(dien)SbS₄]₂}⁻ chain anion running along the crystallographic [001] direction.

The Mn–S bond lengths are between 2.452(2) and 2.509(2) Å, and the Mn–N bonds vary from 2.211(7) to 2.326(6) Å, thus being in the range reported for other Mn containing thiometalates [42]. The MnN₃S₂ coordination environment in the thioantimonate chain is rather unusual, and only few examples are known for such a coordination geometry.

Fig. 2 (color online). The unique [SbS₄]³⁻ anions and the [Mn(dien)]²⁺ cations in the {[Mn(dien)SbS₄]₂}⁻ chain. Note that not all atoms are labeled, and that H atoms are omitted for clarity.

try, like in [Mn(terpy)](As₂S₄) (terpy = 2,2',6',2''-terpyridine) [42] or in a complex with a pentadentate SNNNS ligand [43]. The Sb–S bond lengths (Table 2) can be grouped into two short terminal bonds (Sb–S: 2.300(2)–2.3070(17) Å) and two bridging bonds (2.3478(16)–2.3674(18) Å). The elongation of the Sb–S bonds to S atoms which are also bound to a transition metal is not unusual. *E. g.*, in [Co(dien)₂][Co(tren)SbS₄] · 0.5H₂O the [SbS₄]³⁻ anion has one bond to the Co²⁺ cation, and the bridging Sb–S bond length of 2.3701(8) Å is significantly longer than the remaining bonds to the terminal S atoms (2.3078(10)–2.3196(11) Å) [44]. In [Ni(tren)SbS₄]⁻ with the bidentately acting [SbS₄]³⁻ ion the difference is less pronounced with two longer (2.3467(8) and 2.3333(12) Å) and two shorter (2.3150(8) and 2.3071(10) Å) distances [45], and in the [Mn(chxn)₂(SbS₄)₂]⁴⁻ anion of [Mn(chxn)₃]₂[Mn(chxn)₂(SbS₄)₂] · 6 H₂O (chxn = 1,2-diaminocyclohexane) all Sb–S bonds are in a narrow range between 2.323(1) and 2.348(1) Å [24]. In the compound [Sm(en)₃(H₂O)(μ-SbS₄)] one of the bridging Sb–S bonds (2.3137(12) Å) is even shorter than the bond to the terminal S atom of 2.3341(8) Å [46], while in [La(teta)(en)SbS₄] the three bridging Sb–S bonds (2.3262(11)–2.3334(10) Å) are longer than the Sb–S_{term} bond (2.3141(12) Å) [27].

The S–Sb–S angles around Sb1 range from 105.56(6) to 113.40(8)°, and for Sb2 they are between 105.56(7) and 113.25(8)°, *i. e.* the distortion from ideal tetrahedral geometry is very similar for both [SbS₄]³⁻ units.

The anionic chains and the [Mn(dien)₂]²⁺ complexes are packed in alternating fashion along [010] (Fig. 3). Several intra- and inter-chain S···H–N bonding interactions are observed with S···H separations between 2.472 and 2.970 Å and N–H···S angles ranging from 142.68 to 167.50°. We note that all S atoms are

Sb(1)–S(1)	2.3573(18)	Sb(2)–S(5)	2.3478(16)
Sb(1)–S(2)	2.300(2)	Sb(2)–S(6)	2.3555(19)
Sb(1)–S(3)	2.3070(17)	Sb(2)–S(7)	2.3031(18)
Sb(1)–S(4)	2.3674(18)	Sb(2)–S(8)	2.3010(18)
S(2)–Sb(1)–S(1)	108.46(9)	S(8)–Sb(2)–S(7)	113.25(8)
S(3)–Sb(1)–S(1)	109.23(6)	S(8)–Sb(2)–S(5)	111.85(7)
S(2)–Sb(1)–S(4)	110.51(7)	S(7)–Sb(2)–S(5)	107.94(7)
S(3)–Sb(1)–S(4)	105.56(6)	S(8)–Sb(2)–S(6)	105.56(7)
S(1)–Sb(1)–S(4)	109.61(8)	S(7)–Sb(2)–S(6)	108.20(7)
S(2)–Sb(1)–S(3)	113.40(8)	S(5)–Sb(2)–S(6)	109.97(7)
Mn(1)–S(4)	2.4423(18)	N(13)–Mn(2)–N(11)	134.3(4)
Mn(1)–S(5)	2.501(2)	N(13)–Mn(2)–N(12)	76.4(3)
Mn(1)–N(1)	2.231(7)	N(11)–Mn(2)–N(12)	76.2(3)
Mn(1)–N(2)	2.326(6)	N(13)–Mn(2)–S(6)	110.9(4)
Mn(1)–N(3)	2.220(6)	N(11)–Mn(2)–S(6)	110.94(19)
Mn(2)–S(1)	2.509(2)	N(12)–Mn(2)–S(6)	104.78(19)
Mn(2)–S(6)	2.452(2)	N(13)–Mn(2)–S(1A)	94.8(3)
Mn(2)–N(13)	2.211(7)	N(11)–Mn(2)–S(1A)	95.61(17)
Mn(2)–N(11)	2.233(7)	N(12)–Mn(2)–S(1A)	155.83(18)
Mn(2)–N(12)	2.281(6)	N(33)–Mn(3)–N(31)	98.8(2)
Mn(3)–N(33)	2.260(6)	N(33)–Mn(3)–N(22)	162.9(2)
Mn(3)–N(21)	2.286(5)	N(31)–Mn(3)–N(22)	96.4(2)
Mn(3)–N(23)	2.298(6)	N(33)–Mn(3)–N(21)	94.2(2)
Mn(3)–N(32)	2.307(6)	N(31)–Mn(3)–N(21)	93.7(2)
Mn(3)–N(31)	2.283(7)	N(22)–Mn(3)–N(21)	76.9(2)
Mn(3)–N(22)	2.283(6)	N(33)–Mn(3)–N(23)	91.4(2)
N(3)–Mn(1)–N(1)	141.5(2)	N(31)–Mn(3)–N(23)	158.0(2)
N(3)–Mn(1)–N(2)	76.3(3)	N(22)–Mn(3)–N(23)	77.1(2)
N(1)–Mn(1)–N(2)	76.1(2)	N(21)–Mn(3)–N(23)	105.0(2)
N(3)–Mn(1)–S(4)	104.18(19)	N(33)–Mn(3)–N(32)	79.2(2)
N(1)–Mn(1)–S(4)	109.91(17)	N(31)–Mn(3)–N(32)	75.2(3)
N(2)–Mn(1)–S(4)	109.12(16)	N(22)–Mn(3)–N(32)	112.5(2)
N(3)–Mn(1)–S(5)	95.66(17)	N(21)–Mn(3)–N(32)	165.9(3)
N(1)–Mn(1)–S(5)	93.23(17)	N(23)–Mn(3)–N(32)	87.7(3)
N(2)–Mn(1)–S(5)	147.18(17)		
S(4)–Mn(1)–S(5)	103.70(7)		

Table 2. Selected bond lengths (Å) and angles (deg) in the title compound. Estimated standard deviations are given in parentheses.

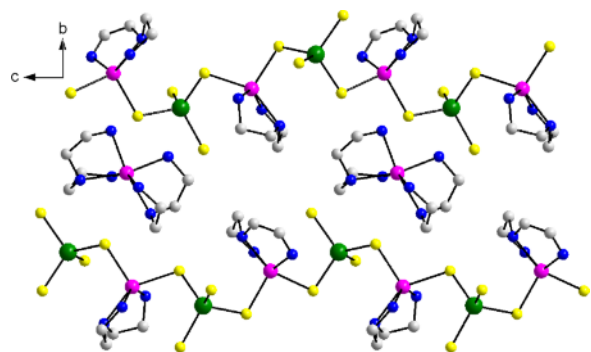


Fig. 3 (color online). Arrangement of the anionic chains and the [Mn(dien)₂]²⁺ cations in the structure of the title compound.

involved in inter-chain interactions generating a three-dimensional network.

Analyzing the transition metal cation containing thiometallate chemistry, the Mn²⁺ ion behaves very

differently from other first row transition metal ions due to its ease of bond formation to both S and N. While cations like Fe²⁺, Co²⁺, Ni²⁺ or Zn²⁺ must be forced to form bonds to S atoms of a thiometallate framework using multidentate N-donor ligands which do not coordinatively saturate the cations, Mn²⁺ is easily integrated in such networks. Examples are *e. g.* the series of compounds Mn₂(L)Sb₂S₅ (L = amine) [31, 33, 34, 47–52]. Mn²⁺ can also easily be integrated into thioantimonate networks as shown by the compounds (1,4-dabH)₂MnSnS₄ [53], {[Mn(trien)]₂SnS₄·4 H₂O} [54] (trien = triethylenetetramine), or {[Mn(tren)]₂Sn₂S₆} [55], and in thiogermanates like in [C₁₄H₂₉N(CH₃)₃]₂MnGe₄S₁₀ (C₁₄H₂₉N(CH₃)₃ = mesityltrimethylammonium) [56], which demonstrates that the special behavior of Mn²⁺ is not restricted to thioantimonates.

The free tetrahedral [SbS₄]³⁻ anion with ideal symmetry is expected to show four normal modes of vi-

brations *viz.* $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$ and $\nu_4(F_2)$. All four vibrations are Raman-active while only ν_3 and ν_4 are infrared-active. For solid Na₃SbS₄ these bands are located at 410, 389 (asymmetric Sb–S stretch, ν_a), 368 (symmetric Sb–S stretch, ν_s), 198, and 162 cm⁻¹ (Sb–S bending vibrations) [57]. The strongest band in the Raman spectrum of the title compound (Fig. 4) at 358 cm⁻¹ is most likely the symmetric Sb–S stretching vibration, while the band at 387 cm⁻¹ is most probably the asymmetric stretching. The two lines at 188 and 158 cm⁻¹ are then due to bending vibrations. Because the two independent [SbS₄]³⁻ ions have bonds to Mn²⁺ cations, the local symmetry is reduced from T_d to C_{3v} for Sb1 and to C_{2v} for Sb2. This reduction of the symmetry leads to the appearance of further bands in the Raman spectrum. The resonances not marked in the Raman spectrum cannot be unambiguously assigned.

The UV/Vis spectrum of the title compound (Fig. 5) shows a not very steep absorption edge, and the optical band gap is estimated to 2.75 eV corresponding to a wavelength of 450.8 nm which is in line with the yellow-orange color of the compound.

In summary, the crystallization of the title compound has provided another illustrative example of the solvothermal approach yielding unexpected thioantimonate compounds with unparalleled structures. It is highly likely that a systematic variation of the synthesis conditions will afford more new thiometalates.

Acknowledgement

Financial support by the State of Schleswig-Holstein is gratefully acknowledged.

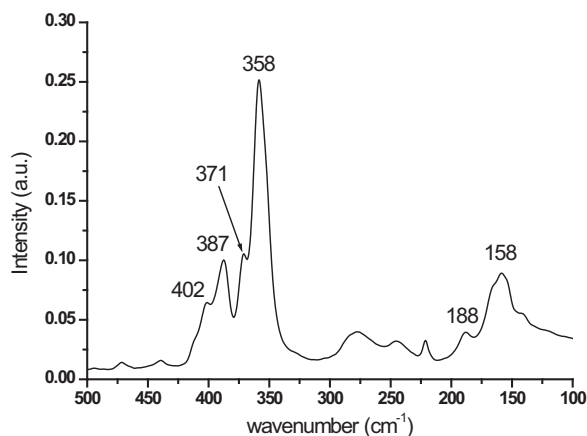


Fig. 4. Raman spectrum of the title compound with wavenumbers indicated for some prominent resonances.

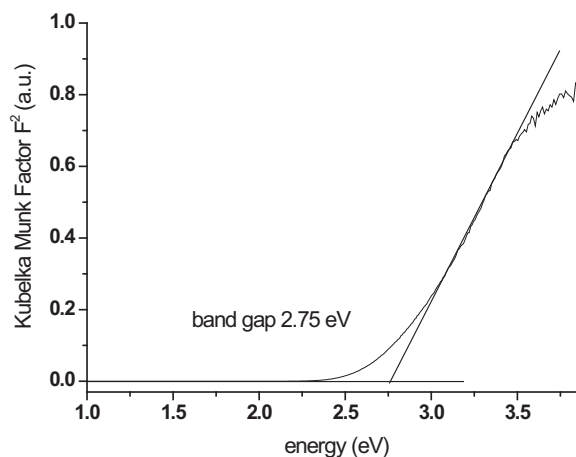


Fig. 5. The UV/Vis spectrum of the title compound drawn as a Kubelka-Munk plot.

- [1] B. Seidlhofer, N. Pienack, W. Bensch, *Z. Naturforsch.* **2010**, *65b*, 937–975.
- [2] A. Kromm, T. van Almsick, W. S. Sheldrick, *Z. Naturforsch.* **2010**, *65b*, 918–936.
- [3] S. Dehnen, M. Melullis, *Coord. Chem. Rev.* **2007**, *251*, 1259–1280.
- [4] J. Zhou, J. Dai, G.-Q. Bian, C. Y. Li, *Coord. Chem. Rev.* **2009**, *253*, 1221–1247.
- [5] P. Feng, X. Bu, N. Zheng, *Acc. Chem. Res.* **2005**, *38*, 293–303.
- [6] B. Seidlhofer, J. Djamil, C. Näther, W. Bensch, *Cryst. Growth Des.* **2011**, *11*, 5554–5560.
- [7] R. Kiebach, F. Studt, C. Näther, W. Bensch, *Eur. J. Inorg. Chem.* **2004**, 2553–2556.
- [8] W. Bensch, C. Näther, R. Stähler, *Chem. Commun.* **2001**, 477–478.
- [9] R. Stähler, C. Näther, W. Bensch, *J. Solid State Chem.* **2003**, *174*, 264–275.
- [10] V. Spetzler, R. Kiebach, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **2004**, *630*, 2398–2404.
- [11] R. Stähler, W. Bensch, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1657–1662.
- [12] A. Puls, M. Schaefer, C. Näther, W. Bensch, A. V. Powell, S. Boissière, A. M. Chippindale, *J. Solid State Chem.* **2005**, *178*, 1171–1181.

- [13] A. Puls, C. Näther, R. Kiebach, W. Bensch, *Solid State Sci.* **2006**, *8*, 1085–1097.
- [14] E. Quiroga-González, C. Näther, W. Bensch, *Solid State Sci.* **2010**, *12*, 1235–1241.
- [15] H. Lühmann, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1007–1012.
- [16] B. Seidlhofer, V. Spetzler, E. Quiroga-Gonzalez, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1296–1303.
- [17] B. Seidlhofer, C. Näther, W. Bensch, *CrystEngComm* **2012**, *14*, 5441–5445.
- [18] P. Vaqueiro, A. M. Chippindale, A. V. Powell, *Inorg. Chem.* **2004**, *43*, 7963–7965.
- [19] A. V. Powell, R. J. E. Lees, A. M. Chippindale, *Inorg. Chem.* **2006**, *45*, 4261–4267.
- [20] R. Stähler, B.-D. Mosel, H. Eckert, W. Bensch, *Angew. Chem. Int. Ed.* **2002**, *41*, 4487–4489.
- [21] X. Liu, J. Zhou, *Inorg. Chem. Commun.* **2011**, *14*, 1286–1289.
- [22] N. Herzberg, C. Näther, W. Bensch, *Z. Kristallogr.* **2012**, *227*, 552–556.
- [23] P. T. Wood, G. L. Schimek, J. W. Kolis, *Chem. Mater.* **1996**, *8*, 721–726.
- [24] M. Schaefer, L. Engelke, W. Bensch, *Z. Anorg. Allg. Chem.* **2003**, *629*, 1912–1918.
- [25] D. Jia, Q. Zhao, Y. Zhang, J. Dai, J. Zuo, *Inorg. Chem.* **2005**, *44*, 8861–8867.
- [26] J. Lichte, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **2010**, *636*, 108–113.
- [27] D. Ye, M.-L. Feng, K.-Z. Du, Y.-Y. Huang, *Chin. J. Struct. Chem.* **2012**, *31*, 783–790.
- [28] W. Tang, R. Chen, J. Zhao, W. Jiang, Y. Zhang, D. Jia, *CrystEngComm* **2012**, *14*, 5021–5026.
- [29] D. Jia, J. Deng, Q.-X. Zhao, Y. Zhang, *J. Mol. Struct.* **2007**, *833*, 114–120.
- [30] M. Schaefer, C. Näther, N. Lehnert, W. Bensch, *Inorg. Chem.* **2004**, *43*, 2914–2921.
- [31] L. Engelke, R. Stähler, M. Schur, C. Näther, W. Bensch, R. Pöttgen, M. H. Möller, *Z. Naturforsch.* **2004**, *59b*, 869–876.
- [32] H. Lühmann, Z. Rejai, K. Möller, P. Leisner, M.-E. Ordolff, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1687–1695.
- [33] M. Schaefer, D. Kurowski, A. Pfitzner, C. Näther, Z. Rejai, K. Möller, N. Ziegler, W. Bensch, *Inorg. Chem.* **2006**, *45*, 3726–3731.
- [34] W. Bensch, M. Schur, *Eur. J. Inorg. Chem.* **1996**, *33*, 1149–1160.
- [35] Z. Rejai, C. Näther, R. K. Kremer, W. Bensch, *Inorg. Chem.* **2010**, *49*, 1651–1657.
- [36] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.
- [37] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.
- [38] M. L. Fu, G. C. Guo, L. Z. Cai, Z. J. Zhang, J. S. Huang, *Inorg. Chem.* **2005**, *44*, 184–186.
- [39] D. Jia, Y. Zhang, Q. Zhao, J. Deng, *Inorg. Chem.* **2006**, *45*, 9812–9817.
- [40] J. Ellermeier, W. Bensch, *Monatsh. Chem.* **2002**, *133*, 945–957.
- [41] M. Schaefer, D. Kurowski, A. Pfitzner, C. Näther, W. Bensch, *Acta Crystallogr.* **2004**, *E60*, m183–m185.
- [42] A. Kromm, W. S. Sheldrick, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2948–2953.
- [43] K. Dürer, D. A. Yalalov, F. W. Heinemann, S. B. Tso-goeva, I. Ivanović-Burmazović, *Z. Naturforsch.* **2010**, *65b*, 258–262.
- [44] J. Lichte, H. Lühmann, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2021–2026.
- [45] R. Stähler, W. Bensch, *Acta Crystallogr.* **2002**, *C58*, m537–m538.
- [46] D.-X. Jia, Q.-Y. Zhu, J. Dai, W. Lu, W.-J. Guo, *Inorg. Chem.* **2005**, *44*, 819–821.
- [47] M. Schur, C. Näther, W. Bensch, *Z. Naturforsch.* **2001**, *56b*, 79–84.
- [48] M. Schur, W. Bensch, *Z. Naturforsch.* **2002**, *57b*, 1–7.
- [49] M. Schaefer, C. Näther, W. Bensch, *Solid State Sci.* **2003**, *5*, 1135–1139.
- [50] A. Puls, C. Näther, W. Bensch, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1239–1243.
- [51] X. Wang, T.-L. Sheng, S.-M. Hu, R.-B. Fu, X.-T. Wu, *Inorg. Chem. Commun.* **2009**, *12*, 399–401.
- [52] B. Seidlhofer, V. Spetzler, C. Näther, W. Bensch, *J. Solid State Chem.* **2012**, *187*, 269–275.
- [53] N. Pienack, K. Möller, C. Näther, W. Bensch, *Solid State Sci.* **2007**, *9*, 1110–1114.
- [54] N. Pienack, C. Näther, W. Bensch, *Eur. J. Inorg. Chem.* **2009**, 1575–1577.
- [55] N. Pienack, D. Schinkel, A. Puls, M.-E. Ordolff, H. Lühmann, C. Näther, W. Bensch, *Z. Naturforsch.* **2012**, *67b*, 1098–1106.
- [56] K. K. Rangan, S. J. L. Billinge, V. Petkov, J. Heising, M. G. Kanatzidis, *Chem. Mater.* **1999**, *11*, 2629–2632.
- [57] W. Mikenda, A. Preisinger, *Spectrochim. Acta* **1980**, *36A*, 365–370.