# Two Organic Hybrid Thiogermanates $[Ni(dien)_2]_2(H_2dien)Ge_2S_6$ and $[Ni(teta)_2]_2Ge_4S_{10}$

Xing Liu, Jian Zhou, Jun He, and Zhi-wei Huang

Department of Chemistry and Biology, Yulin Normal University, Yulin 537000, P. R. China

Reprint requests to Prof. Dr. Jian Zhou. E-mail: Jianzhou888888@163.com

*Z. Naturforsch.* **2011**, *66b,* 659 – 663; received April 26, 2011

Two new organic hybrid thiogermanates $[Ni(dien)_2](H_2dien)Ge_2S_6$ (**1**, dien = diethylenetriamine) and $[Ni(teta)_2]_2Ge_4S_{10}$ (**2**, teta = triethylenetetramine) were synthesized under solvothermal conditions. **1** contains a $[Ni(dien)_2]^{2+}$ complex cation, a protonated dien molecule and a $[Ge_2S_6]^{4-}$ dimeric anion, while **2** consists of discrete $[Ge_4S_{10}]^{4-}$ adamantane-like cluster anions with $[Ni(teta)_2]^{2+}$ complex cations as counter ions. The $[Ge_4S_{10}]^{4-}$ anion is composed of four nearly tetrahedral $Ge^{4+}$ centers to which are bonded four terminal atoms and six bridging S atoms. Luminescence studies have shown that **2** exhibits an emission at 468 nm.

*Key words:* Thiogermanates, Solvothermal Syntheses, Crystal Structures, Complex Cation, Nickel

## Introduction

In 1989 Bedard *et al.* first forecast the synthesis of microporous thiogermanates with framework topologies resembling those of zeolites, thus inspiring a host of new potential applications [1]. By analogy with the silicates built up from $[SiO_4]^{4-}$ tetrahedral building units, these thiogermanates usually contain the adamantane-like thioanion $[Ge_4S_{10}]^{4-}$ built up by four corner-linked $[GeS_4]^{4-}$ tetrahedra. The $[Ge_4S_{10}]^{4-}$ anions in the presence of quaternary alkylammonium surfactants or non-chelating amines as structure-directing agents further self-organize with other metal cations like $Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Cu^{+}$, and $Ag^{+}$ to create mesostructural thiogermanates [2]. When chelating amines were used as structure-directing agents instead of quaternary alkylammonium surfactants, only $[Ge_2S_6]^{4-}$ anions were charge-balanced by a cationic transition metal complex, as exemplified by $[M(en)_3]_2Ge_2S_6$ (M = Mn, Ni) [3], $[Ni(dien)_2]_2(Ge_2S_6)$ [4], $[Ni(dien)_2](H_2pipe)Ge_2S_6$ [4], $\{[Mn(tren)]_2(\mu_2\text{-}Ge_2S_6)\}$ [4], and $[\{Co(tepa)\}_2(\mu\text{-}Ge_2S_6)]$ (M = Mn, Co, Ni) [4,5]. However, the $[Ge_4S_{10}]^{4-}$ anion has been less characterized in the presence of such complexes. To learn more about the influences of complex cations onto the structure of thiogermanate anions, we started to explore the system $GeO_2$/Ni/S/amine with the goal to synthesize other thiogermanates. Herein, we report on the solvothermal syntheses of two new thiogermanates $[Ni(dien)_2](H_2dien)Ge_2S_6$ (**1**, dien = diethylenetriamine) and $[Ni(teta)_2]_2Ge_4S_{10}$ (**2**, teta = triethylenetetramine).

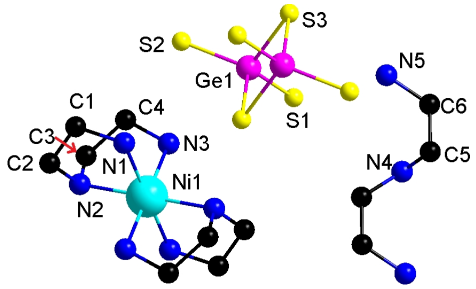

Fig. 1 (color online). Crystal structure of **1** with labeling scheme (H atoms and disordered N4 atom have been omitted for clarity).

## Results and Discussion

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with one formula unit per cell and consists of discrete $[Ge_2S_6]^{4-}$ anions with $[Ni(dien)_2]^{2+}$ and $[H_2dien]^{2+}$ cations as counterions (Fig. 1). The $Ni^{2+}$ ion is in a sixfold coordination of N atoms of two chelating dien ligands, and the coordination polyhedra can be described as distorted octahedra with *s-fac*-conformation. The Ni–N distances vary from 2.110(4) to 2.142(4) Å, which are in agreement with the corresponding values of discrete $[Ni(dien)_2]^{2+}$ cations [4].

0932–0776 / 11 / 0700–0659 \$ 06.00 © 2011 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

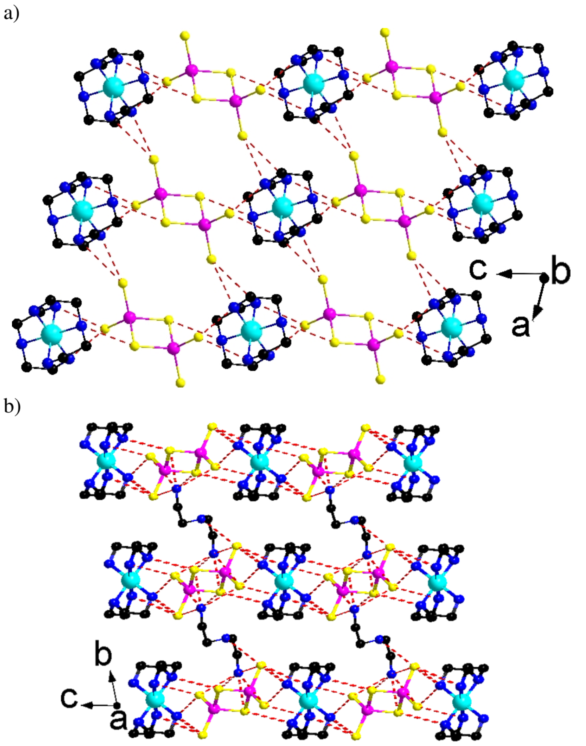

Fig. 2 (color online). a) Part of the crystal structure of **1**, showing the formation of the (010) sheet; b) the 3-D H-bonded network structure. H atoms have been omitted for clarity.

The moderate distortion of the octahedral environment can be manifested from the N–Ni–$N_{cis}$ angles varying from 82.15(15) to 97.85(15)°. The protonated dien molecule displays *trans*-conformation, but the coordinated dien molecules show *cis*-conformation.

The dimeric $[Ge_2S_6]^{4-}$ anion in **1** is formed by two $[GeS_4]$ tetrahedra sharing a common edge. The Ge–$S_b$ ($b$ = bridging) distances varying from 2.2831(15) to 2.2842(14) Å are noticeably longer than the Ge–$S_t$ ($t$ = terminal) bonds scattering from 2.1457(17) to 2.1587(16) Å. The distortion of the $[GeS_4]$ tetrahedra can be seen by the S–Ge–S bond angles varying from 109.92(6) to 116.29(7)°, deviating significantly from the ideal value of 109.5°. The S atoms of the $[Ge_2S_6]^{4-}$ anions form hydrogen bonds to H–N groups of $[Ni(dien)_2]^{2+}$ cations with N···S distances varying from 3.347(4) to 3.641(5) Å and N–H···S angles in the range of 145 – 172°, resulting in a layered arrangement parallel to the (010) plane (Fig. 2a). Then the layers interact also *via* N–H···S hydrogen bonds between $[Ge_2S_6]^{4-}$ anions and protonated dien molecules forming a three-dimensional network (Fig. 2b).

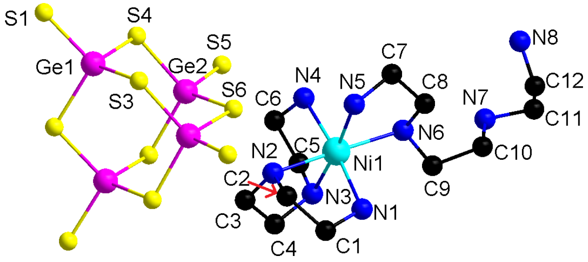

Fig. 3 (color online). Crystal structure of **2** with labeling scheme (H atoms and disordered C/N atoms have been omitted for clarity).

**2** is composed of $Ge_4S_{10}^{4-}$ cluster anions and $[Ni(teta)_2]^{2+}$ complex cations (Fig. 3). The teta ligands are bi- and tetrachelating the Ni center, forming a distorted octahedral $[Ni(teta)_2]^{2+}$ complex cation. The $[Ni(teta)_2]^{2+}$ cation may be viewed as a tadpole where the $[Ni(teta)_2]^{2+}$ octahedral coordination sphere is the head and the uncoordinated N atoms are the tail. The absolute configuration of the $[Ni(teta)_2]^{2+}$ cation is $\Delta(\lambda\delta\lambda\lambda)$. The Ni–N distances (2.121(6) – 2.160(6) Å) are in the normal range as found in other $Ni^{2+}$ cations in an octahedral coordination environment of amine donor atoms [4]. The $[Ge_4S_{10}]^{4-}$ adamantane-like anion is formed by four edge-sharing $GeS_4$ tetrahedra. The Ge–$S_t$ distances (2.1223(18) – 2.135(2) Å, $t$ = terminal) are shorter than those of the bridging Ge–$S_b$ bonds (2.228(2) – 2.2449(17) Å, $b$ = bridging). The moderate distortion of the $GeS_4$ tetrahedra is demonstrated by the S–Ge–S angles (106.18(8) – 112.50(8)°) deviating from the ideal value of 109.5°. The $[Ge_4S_{10}]^{4-}$ clusters are packed in a *pseudo*-hexagonal fashion, where each cluster is surrounded by six neighbors. This is similar to the arrangement of the $[Ge_4S_{10}]^{4-}$ clusters in other thiogermanates $[C_nH_{2n+1}\text{-}NH_3]_4Ge_4S_{10}$ ($n$ = 12, 14, 16, 18) [6] and $[C_nH_{2n+1}\text{-}N(CH_3)_3]_4Ge_4S_{10}$ ($n$ = 12, 14, 16, 18) [7].

The $[Ge_4S_{10}]^{4-}$ clusters are separated by the $[Ni(teta)_2]^{2+}$ complex cations. There are a lot of short intermolecular N–H···S interactions between the terminal S1/S5 atoms and the H–N groups of teta ligands with N···S distances varying from 3.436 to 3.573 Å and N–H···S angles ranging from 147.44 to 170.05 °, resulting in a three-dimensional H-bonding network structure (Fig. 4). In addition, the N–H···N H-bonded interactions with N···N distances in the range of 2.950 to 3.072 Å also play an important role in stabilizing the structure.

The emission spectrum of **2** in the solid state was investigated at room temperature (Fig. 5). **2** exhibits

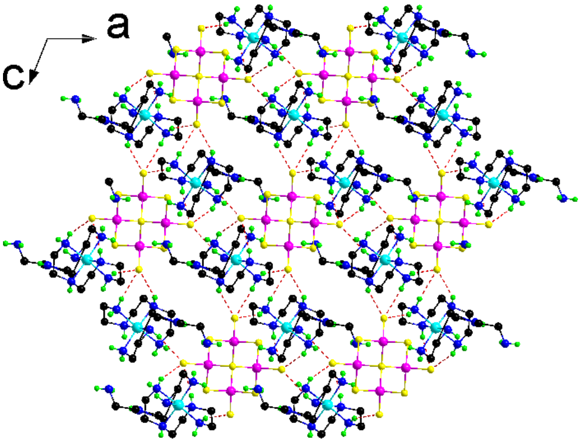

Fig. 4 (color online). The 3-D supramolecular framework of **2** constructed by N–H···S hydrogen bonds (H atoms bonded to C atoms have been omitted for clarity).

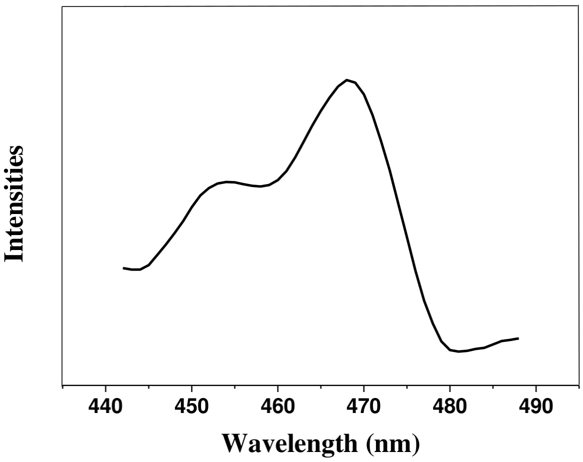

Fig. 5. Solid-state photoluminescence of **2** at r. t.

a strong and broad emission band at 468 nm upon photo-excition at 310 nm, which is consistent with the solid-state luminescence of other thiogermanates (440 – 489 nm) [4]. This emission probably originates from the amine ligands because a similar weak emission is also found for the amine hydrochlorides [8].

## Experimental Section

All chemicals were used as purchased without purification. Elemental analyses (C, H, and N) were performed on a PE2400 II elemental analyzer. The IR spectra were obtained on an ABB Bomen MB 102 spectrometer in the range of 4000 – 400 cm$^{-1}$ with pressed KBr pellets. Fluorescence spectral analyses were performed using a Cary Eclips fluorescence spectrometer.

Table 1. Crystal structure data for **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Formula | $C_{12}H_{41}Ge_2N_9NiS_6$ | $C_{12}H_{36}Ge_2N_8NiS_5$ |
| $Fw$ | 707.83 | 656.75 |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $C2/c$ |
| $a$, Å | 7.2195(14) | 21.939(6) |
| $b$, Å | 9.2561(19) | 11.035(3) |
| $c$, Å | 11.502(2) | 22.905(9) |
| $\alpha$, deg | 73.68(3) | 90 |
| $\beta$, deg | 72.98(3) | 111.793(3) |
| $\gamma$, deg | 71.15(3) | 90 |
| $V$, Å$^3$ | 680.6(3) | 5149(3) |
| $Z$ | 1 | 8 |
| $T$, K | 296(2) | 296(2) |
| Calcd. density, g cm$^{-3}$ | 1.72 | 1.69 |
| Abs. coeff., mm$^{-1}$ | 3.4 | 3.5 |
| $F(000)$, e | 359 | 2688 |
| $2\theta_{max}$, deg | 50.20 | 52.00 |
| Total reflns. collected | 3742 | 14656 |
| Unique reflns. | 2387 | 5059 |
| No. of ref. param. | 142 | 300 |
| $R1$ [$I \geq 2\sigma(I)$] | 0.0337 | 0.0549 |
| $wR2$ (all data) | 0.0753 | 0.1466 |
| $\Delta\rho_{fin}$ (max / min), eÅ$^{-3}$ | 0.78 / –0.56 | 0.86 / –0.66 |

### *Synthesis of [Ni(dien)$_2$]$_2$(H$_2$dien)Ge$_2$S$_6$ (**1**)*

[Ni(dien)$_2$]$_2$(H$_2$dien)Ge$_2$S$_6$ (**1**) was synthesized hydrothermally in a 23-mL Teflon-lined autoclave by heating a mixture of Ni (0.0075 g, 0.13 mmol), GeO$_2$ (0.0062 g, 0.06 mmol), S (0.0129 g, 0.40 mmol), and dien (3 mL) at 160 °C for 10 d. After the mixture was slowly cooled to room temperature, purple crystals were obtained (yield: 42 % based on GeO$_2$). – Anal. for **1**: calcd. C 20.36, H 5.84, N 17.81; found C 20.31, H 5.79, N 17.76. – IR (cm$^{-1}$): $v$ = 3228(m), 3153(m), 2955(m), 2862(m), 1617(m), 1565(w), 1503(m), 1455(s), 1389(m), 1358(s), 1311(m), 1253(w), 1121(s), 1066(s), 967(m), 743(w), 678(m), 589(m), 529(s), 495(w), 423(s).

### *Synthesis of [Ni(teta)$_2$]$_2$Ge$_4$S$_{10}$ (**2**)*

[Ni(teta)$_2$]$_2$Ge$_4$S$_{10}$ (**2**) was synthesized hydrothermally in a 23 mL Teflon-lined autoclave by heating a mixture of Ni (0.0072 g, 0.12 mmol), GeO$_2$ (0.0071 g, 0.07 mmol), S (0.0121 g, 0.38 mmol), and teta (3 mL) at 160 °C for 10 d. After the mixture was slowly cooled to r. t., purple crystals were obtained (yield: 53 % based on GeO$_2$). – Anal. for **2**: calcd. C 21.95, H 5.53, N 17.06; found C 21.97, H 5.46, N 17.13. – IR (cm$^{-1}$): $v$ = 3413(m), 3313(m), 2939(s), 2834(m), 1599(s), 1552(m), 1476(s), 1383(w), 1318(w), 1294(m), 1183(w), 1102(s), 1019(s), 961(s), 773(m), 657(w), 534(w), 422(s).

### *X-Ray structure determination*

Data collections were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromatized Mo$K_\alpha$

radiation ($\lambda$ = 0.071073 nm) at 296(2) K. The intensities were corrected for Lorentz and polarization effects. The structures were solved with Direct Methods using the program SHELXS-97 [9], and the refinement was performed against $F^2$ using SHELXL-97 [10]. All the non-hydrogen atoms were refined anisotropically. The H atoms of the organic amines were positioned with idealized geometry and refined with fixed isotropic displacement parameters. For **1**, the N4 atom was disordered over two positions with an occupation ratio of 0.50 : 0.50. For **2**, the atoms C9, C10, C11, C12, N7, and N8 were disordered over two positions with an occupation ratio of 0.71 : 0.29. Relevant crystal and data collection parameters and refinement results can be found in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2.

CCDC 822833 (**1**) and 822834 (**2**) contain 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.

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2**[a].

| | | | |
|---|---|---|---|
| **1** | | | |
| Ge1–S1 | 2.1587(16) | Ni1–N1 | 2.115(4) |
| Ge1–S2 | 2.1457(17) | Ni1–N2 | 2.110(4) |
| Ge1–S3 | 2.2842(14) | Ni1–N3 | 2.142(4) |
| Ge1–S3$^{\#1}$ | 2.2831(15) | | |
| S2–Ge1–S1 | 116.29(7) | S1–Ge1–S3 | 110.33(6) |
| S2–Ge1–S3$^{\#1}$ | 112.30(6) | S3$^{\#1}$–Ge1–S3 | 93.68(5) |
| S1–Ge1–S3$^{\#1}$ | 109.92(6) | Ge1$^{\#1}$–S3–Ge1 | 86.32(5) |
| S2–Ge1–S3 | 112.08(6) | N1–Ni1–N3$^{\#2}$ | 89.75(15) |
| N2$^{\#2}$–Ni1–N2 | 180 | N3–Ni1–N3$^{\#2}$ | 180 |
| N2–Ni1–N1$^{\#2}$ | 97.85(15) | N2$^{\#2}$–Ni1–N3 | 97.06(15) |
| N2–Ni1–N1 | 82.15(15) | N1–Ni1–N3 | 90.25(15) |
| N1$^{\#2}$–Ni1–N1 | 180 | N2–Ni1–N3 | 82.94(15) |
| **2** | | | |
| Ge1–S1 | 2.1223(18) | Ge2–S5 | 2.135(2) |
| Ge1–S2 | 2.2417(17) | Ge2–S4 | 2.2254(19) |
| Ge1–S3 | 2.230(2) | Ge2–S3$^{\#3}$ | 2.2332(19) |
| Ge1–S4 | 2.228(2) | Ge2–S6 | 2.2449(17) |
| Ni1–N1 | 2.128(6) | Ni1–N4 | 2.151(6) |
| Ni1–N2 | 2.121(7) | Ni1–N5 | 2.121(6) |
| Ni1–N3 | 2.126(6) | Ni1–N6 | 2.160(6) |
| S1–Ge1–S4 | 108.37(8) | S5–Ge2–S4 | 106.26(8) |
| S1–Ge1–S3 | 110.64(8) | S5–Ge2–S3$^{\#3}$ | 106.18(8) |
| S4–Ge1–S3 | 108.53(8) | S4–Ge2–S3$^{\#3}$ | 112.50(8) |
| S1–Ge1–S2 | 108.01(9) | S5–Ge2–S6 | 112.04(8) |
| S4–Ge1–S2 | 110.78(6) | S4–Ge2–S6 | 109.53(7) |
| S3–Ge1–S2 | 110.50(6) | S3$^{\#3}$–Ge2–S6 | 110.26(6) |
| N5–Ni1–N2 | 95.7(3) | N2–Ni1–N4 | 93.7(2) |
| N5–Ni1–N3 | 174.1(3) | N3–Ni1–N4 | 81.9(3) |
| N2–Ni1–N3 | 82.0(3) | N1–Ni1–N4 | 173.4(3) |
| N5–Ni1–N1 | 92.3(3) | N5–Ni1–N6 | 82.1(3) |
| N2–Ni1–N1 | 81.7(2) | N2–Ni1–N6 | 176.2(3) |
| N3–Ni1–N1 | 92.7(2) | N3–Ni1–N6 | 100.5(2) |
| N5–Ni1–N4 | 92.9(3) | N1–Ni1–N6 | 95.2(2) |
| N4–Ni1–N6 | 89.5(2) | | |

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x-1$, $-y+3$, $-z+2$; $^{\#2}$ $-x-1$, $-y+3$, $-z+1$; $^{\#3}$ $-x+1$, $y$, $-z+1/2$.

*Acknowledgement*

This work was supported by the National Natural Science Foundation (No. 20961011), the Natural Science Foundation of Guangxi Province (No. 2010GXNSFB013017), and the Natural Science Foundation of the Education Committee of Guangxi Province (No. 201012MS182). The authors are also grateful to the Yulin Normal University for financial support.

---

[1] a) R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett, E. M. Flanigen in *Zeolites: Facts, Figures, Future. Proceedings of the 8th International Zeolite Conference* (Eds.: P. A. Jacobs, R. A. van Santen), Elsevier, Amsterdam, **1989**, pp. 375 – 387; b) N. Zheng, X. Bu, B. Wang, P. Feng, *Science* **2002**, *298*, 2366 – 2369; c) M. J. MacLachlan, N. Coombs, G. A. Ozin, *Nature* **1999**, *397*, 681 – 684; d) A. Kromm, T. Almsick, W. S. Sheldrick, *Z. Naturforsch.* **2010**, *65b*, 918 – 936; e) B. Seidlhofer, N. Pienack, W. Bensch, *Z. Naturforsch.* **2010**, *65b*, 937 – 975.

[2] a) O. Achak, J. Y. Pivan, M. Maunaye, M. Loüer, D. Loüer, *J. Solid State Chem.* **1996**, *121*, 473 – 478; b) K. Tan, Y. Ko, J. B. Parise, A. Darovsky, *Chem. Mater.* **1996**, *8*, 448 – 453; c) C. L. Bowes, W. U. Huynh, S. J. Kirkby, A. Malek, G. A. Ozin, S. Petrov, M. Twardowski, D. Young, *Chem. Mater.* **1996**, *8*, 2147 – 2152; d) C. L. Cahill, J. B. Parise, *Chem. Mater.* **1997**, *9*, 807 – 811; e) C. L. Cahill, Y. Ko, J. C. Hanson, K. Tan, J. B. Parise, *Chem. Mater.* **1998**, *10*, 1453 – 1458; f) O. M. Yaghi, Z. Sun, D. A. Richardson, T. L. Groy, *J. Am. Chem. Soc.* **1994**, *116*, 807 – 808.

[3] D.-X. Jia, J. Dai, Q.-Y. Zhu, L.-H. Cao, H.-H. Lin, *J. Solid State Chem.* **2005**, *178*, 874 – 881.

[4] G.-N. Liu, G.-C. Guo, M.-S. Wang, L.-Z. Cai, J.-S. Huang, *J. Mol. Struct.* **2010**, *983*, 104 – 111.

[5] J.-F. Chen, Q.-Y. Jin, Y.-L. Pan, Y. Zhang, D.-X. Jia, *Z. Anorg. Allg. Chem.* **2010**, *636*, 230 – 235.

[6] K. K. Rangan, M. G. Kanatzidis, *Inorg. Chim. Acta* **2004**, *357*, 4036 – 4044.

[7] F. Bonhomme, M. G. Kanatzidis, *Chem. Mater*. **1998**, *10*, 1153 – 1159.

[8] M.-L. Fu, G.-C. Guo, X. Liu, B. Liu, L.-Z. Cai, J.-S. Huang, *Inorg. Chem. Commun*. **2005**, *8*, 18 – 21.

[9] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467 – 473.

[10] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112 – 122.