



Cite this: *Dalton Trans.*, 2015, **44**, 11542

Utilization of mixtures of aromatic N-donor ligands of different coordination ability for the solvothermal synthesis of thiostannate containing molecules†

J. Hilbert, C. Näther and W. Bensch*

Utilization of mixtures of differently coordinating aromatic N-donor ligands leads to the formation of the two new compounds $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\} \cdot 4,4'\text{-bipy} \cdot \frac{1}{2}\text{H}_2\text{O}$ I and $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\} \cdot 2,2'\text{-bipy}$ II that could be prepared under solvothermal conditions (4,4'-bipy = 4,4'-bipyridine, $\text{C}_{10}\text{H}_8\text{N}_2$; phen = 1,10-phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$; 2,2'-bipy = 2,2'-bipyridine, $\text{C}_{10}\text{H}_8\text{N}_2$). In the structures of both compounds Ni-S bond formation is observed which is highly unusual when only bidentate N-donor ligands are applied in the reaction mixture. The detailed analysis of the crystal structure indicates that the presence of 4,4'-bipy and 2,2'-bipy molecules are essential for the stabilization of the arrangement of the constituents. The main structural motif $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ is arranged generating off center parallel stacking of the phen ligands. The empty spaces between the $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ moieties are occupied by either 2,2'-bipy (I) or 4,4'-bipy (II) molecules which are oriented towards the phen ligands to form intermolecular π - π interactions.

Received 23rd March 2015,
Accepted 22nd May 2015

DOI: 10.1039/c5dt01145k
www.rsc.org/dalton

1 Introduction

Compounds containing thiostannate building blocks may be classified according to different criteria. One group of thiostannates are pure inorganic compounds containing *e.g.* metal cations and thiostannate anions like in $\text{Na}_4\text{Sn}_2\text{S}_6 \cdot 14\text{H}_2\text{O}$,¹ $\text{Rb}_6\text{Sn}_2\text{S}_7$,² $\text{Cs}_2\text{Sn}_4\text{S}_6$,³ $\text{Cs}_2\text{Sn}_2\text{S}_6$ or $\text{K}_2\text{Sn}_2\text{S}_5$,⁴ $(\text{Rb}_4(\text{H}_2\text{O})_4)[\text{Sn}_2\text{S}_6]$,⁵ $\text{K}_{10}\text{M}_4\text{Sn}_4\text{S}_{17}$ ($\text{M} = \text{Mn, Fe, Co, Zn}$)⁶ and $(\text{NH}_4)_4[\text{Sn}_2\text{S}_6] \cdot 3\text{H}_2\text{O}$ ⁷ to mention just a few. In these compounds the cations and anions are held together by mainly electrostatic interactions. The examples demonstrate the structural variability with thiostannate ions displaying different Sn:S ratios and therefore different structural motifs. Another group of compounds is composed of organic cations and thiostannate anions, like *e.g.* $(\text{TMA})[\text{Sn}_3\text{S}_7] \cdot 2\text{H}_2\text{O}$ ($\text{TMA} = \text{tetramethylammonium}$),⁸ $(\text{DABCO})_2[\text{Sn}_3\text{S}_7] \cdot \text{H}_2\text{O}$ ($\text{DABCO} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$),⁹ $(\text{enH})_4[\text{Sn}_2\text{S}_6]$ ($\text{en} = \text{ethylenediamine}$),¹⁰ or $(\text{tmdpH}_2)[\text{Sn}_3\text{S}_7]$ ($\text{tmdp} = 4,4'\text{-trimethylenedipiperidine}$).¹¹ Charge compensation may be also achieved by transition metal or lanthanide

cation centered complexes like in $(\text{M}(\text{en})_3)_2[\text{Sn}_2\text{S}_6]$ ($\text{M} = \text{Mn, Co, Ni, Zn}$),¹²⁻¹⁴ $(\text{M}(\text{dien})_2)_2[\text{Sn}_2\text{S}_6]$ ($\text{M} = \text{Mn, Co, Ni}$; dien = diethylentriamine),¹⁴⁻¹⁶ $(\text{Nd}(\text{dien})_3)_2[\text{Sn}_2\text{S}_6]\text{Cl}_2$, $(\text{Nd}(\text{dien})_3)_2[\text{Sn}_2\text{S}_6]\text{-(SH)}_2$,¹⁷ $(\text{Y}_2(\text{dien})_2(\text{OH})_2)[\text{Sn}_2\text{S}_6]$,¹⁸ $(\text{Ni}(1,2\text{-dap})_3)_2[\text{Sn}_2\text{S}_6] \cdot 2\text{H}_2\text{O}$ ($1,2\text{-dap} = 1,2\text{-diaminopropane}$),¹² $(\text{Ni}(1,2\text{-dach})_3)_2[\text{Sn}_2\text{S}_6] \cdot 4\text{H}_2\text{O}$ ($1,2\text{-dach} = 1,2\text{-diaminocyclohexane}$), $(\text{Ni}(\text{peha}))_2[\text{Sn}_2\text{S}_6] \cdot \text{H}_2\text{O}$ ($\text{peha} = \text{pentaethylenehexamine}$) or $(\text{Ni}(\text{aepa}))_2[\text{Sn}_2\text{S}_6]$ ($\text{aepa} = \text{N-2-aminoethyl-1,3-propandiamine}$).¹⁶

Another class of compounds is characterized by M-S bonds between the thiostannate ion and transition metal cations which are further surrounded by N donor atoms from amine ligands. In such compounds the $[\text{Sn}_2\text{S}_6]^{4-}$ and $[\text{SnS}_4]^{4-}$ anion, respectively, acts as bidentate ligand like in $\{[\text{Mn}(1,2\text{-dach})_2 \cdot (\text{H}_2\text{O})_2][\text{Sn}_2\text{S}_6]\}$,¹⁹ $\{[\text{Mn}(\text{en})_2][\text{Sn}_2\text{S}_6]\}_n$,²⁰ $\{[\text{Mn}(1,2\text{-dap})_2][\text{Sn}_2\text{S}_6]\}_n$,²¹ $\{[\text{M}(\text{tepa})_2][\text{Sn}_2\text{S}_6]\}$ ($\text{M} = \text{Mn, Fe, Co, Ni}$; tepa = tetraethyl-enepentamine),^{22,23} $\{[\text{Mn}(\text{trien})_2][\text{Sn}_2\text{S}_6]\}_n \cdot 4\text{H}_2\text{O}$ ($\text{trien} = \text{triethylenetetramine}$),²⁴ $\{[\text{M}(\text{tren})_2][\text{Sn}_2\text{S}_6]\}_n$,^{22,25} ($\text{M} = \text{Mn, Co}$; tren = tris(2-aminoethyl)-amine), $\{[\text{Co}(\text{cyclam})_2][\text{Sn}_2\text{S}_6]\}_n \cdot 2\text{H}_2\text{O}$,²⁶ ($\text{cyclam} = 1,4,8,11\text{-tetraaza-cyclotetradecane}$), $\text{o-}[\{\text{Ni}(\text{tepa})_2[\text{Sn}_2\text{S}_6]\}_n, \{\text{Mn}(\text{trien})_2[\text{Sn}_2\text{S}_6]\}_n]$,¹⁶ or in a tetradentate fashion as observed for *e.g.* $\{[\text{Mn}(\text{phen})_2][\text{Sn}_2\text{S}_6]\}$,²⁷ $\{[\text{TM}(\text{phen})_2][\text{Sn}_2\text{S}_6]\}_n$,²⁸ ($\text{M} = \text{Fe, Co}$) or $\{[\text{Mn}(\text{phen})_2][\text{SnS}_4]\}_n \cdot \text{H}_2\text{O}$.²⁹

Finally metal cations may be integrated into the thiostannate unit as observed for $(1,4\text{-dabH})_2\text{MnSnS}_4$,³⁰ ($1,4\text{-dab} = 1,4\text{-diaminobutane}$), $(\text{DBUH})\text{CuSnS}_3$ ($\text{DBU} = 1,8\text{-dialaza-bicyclo}[5.4.0]\text{undec-7-ene}$) and $(1,4\text{-dabH}_2)\text{Cu}_2\text{SnS}_4$,³¹ ($1,4\text{-dabH}_2 = \text{Ag}_2\text{SnS}_4$,³² $(\text{enH})_3\text{Cu}_7\text{Sn}_4\text{S}_{12}$,³³ $(\text{DBNH})_2\text{Cu}_6\text{Sn}_2\text{S}_8$,³⁴ ($\text{DBN} = 1,5\text{-diazabicyclo}[4.3.0]\text{non-5-ene}$), $(\text{dienH}_2)\text{Cu}_2\text{Sn}_2\text{S}_6$,³⁵ (NH_4)₂

Institute of Inorganic Chemistry, Christian-Albrechts-University of Kiel, Max-Eyth-Str. 2, 24118 Kiel, Germany. E-mail: wbensch@ac.uni-kiel.de; Fax: +49 431 880-1520; Tel: +49 431 880-2419

†Electronic supplementary information (ESI) available: PXRD pattern, selected angles of the octahedral Ni^{2+} environment, IR- and Raman spectra. CCDC 1054460 and 1054461. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01145k



$\text{Ag}_6\text{Sn}_3\text{S}_{10}$,³⁶ $(\text{enH}_2)\text{Ag}_2\text{SnS}_4$,³⁷ $(\text{enH}_2)\text{HgSnS}_4$,³⁸ $(\text{enH}_2)_2\text{Cu}_8\text{Sn}_3\text{S}_{12}$,³⁹ and $[\text{Mn}(\text{dien})_2]\text{MnSnS}_4$.²¹

Many of the above-mentioned compounds were obtained under solvothermal conditions and state-of-art of the chemistry of thiostannates and other thiometallates was reviewed in several articles highlighting the synthetic approaches, the structural variability and flexibility of the anions.⁴⁰ Analyzing the structures of thiometallate compounds with transition metal cations having bonds to S atoms of the anions, the Mn^{2+} ion can be easily integrated in the anions independent from the amine applied, whereas Fe^{2+} , Co^{2+} , Ni^{2+} , or Zn^{2+} prefer bond formation to the N atoms of the amine molecules and M–S bond formation must be forced by applying multidentate amine molecules (tetra- or pentadentate) in the synthesis mixture which do not satisfy the coordination requirements of the cations. Mn^{2+} seems to have a comparable affinity to both S and N atoms as can be seen from the thiostannate examples presented above but a similar observation was also made for *e.g.* thioantimonates.⁴¹

During a systematic study of the Mn/phen/Sn/S system we prepared $\{[\text{Mn}(\text{phen})_2]_2(\mu_2\text{-Sn}_2\text{S}_6)\}\text{-phen}$ and $\{[\text{Mn}(\text{phen})_2]_2(\mu_2\text{-Sn}_2\text{S}_6)\}\text{-phen}\cdot\text{H}_2\text{O}$ containing co-crystallized phen molecules which are arranged with respect to phen ligands of the Mn^{2+} centered complexes to achieve attractive so-called π – π interactions.²⁷ The energy involved in these interactions is between *ca.* 10 and 13 kcal mol⁻¹.^{42–45} While the interaction energy between stacked phen molecules is low compared to that of covalent or ionic bonds, it seems to be large enough to stabilize frequently observed arrangements of aromatic molecules with respect to each other, like *e.g.* face-to-face, off-center, slipped or edge-to-face. Modifying the synthesis conditions originally applied for the preparation of $\{[\text{Mn}(\text{phen})_2]_2(\mu_2\text{-Sn}_2\text{S}_6)\}\text{-phen}$ and $\{[\text{Mn}(\text{phen})_2]_2(\mu_2\text{-Sn}_2\text{S}_6)\}\text{-phen}\cdot\text{H}_2\text{O}$ and using Co, Fe instead of Mn we were able to crystallize $\{[\text{TM}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}\text{-phen}\cdot\text{H}_2\text{O}$ ($\text{TM} = \text{Co, Fe}$) with similar arrangements of the phen molecules found for the analogous Mn compound.²⁸ This was a surprising result because Co^{2+} / Fe^{2+} have a strong preference for N donor atoms yielding normally isolated $[\text{TM}(\text{L})_n]^{2+}$ (L = bidentate or tridentate ligands) complexes and thiometallate anions.^{13,16,46–49} All thiometallate compounds displaying a Co–S/Fe–S bond were obtained in the presence of a tetradentate or pentadentate ligand like tren,^{12,48–50} tpea²³ and cyclam,²⁶ with one exception where 1,2-dach (1,2-dach = 1,2 diaminocyclohexane) was used as amine.⁵¹

In our ongoing synthetic work all attempts to synthesize the analogous Ni^{2+} containing compounds failed despite varying the reaction conditions reported in.^{27–29} One possible reason is the high stability of the $[\text{Ni}(\text{phen})_3]^{2+}$ complex, which is *in situ* formed under the solvothermal reaction conditions. Hence, we developed a new synthetic strategy applying mixtures of aromatic N-donor ligands which are either strong (phen), medium (2,2'-bipyridine), weak/monodentate co-ordinating (4,4'-bipyridine) which should lead to the solely coordination of Ni^{2+} by phen and the other molecule-donor ligands might act as structural stabilizers *via* intermolecular π – π -interactions.

During the experiments we were able to prepare and characterize the two new compounds $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}\cdot 4\cdot 4'\text{-bipy}\cdot \frac{1}{2}\text{H}_2\text{O}$ (**I**) and $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}\cdot 2\cdot 2'\text{-bipy}$ (**II**). Here we report the syntheses, crystal structures and spectroscopic data of these compounds.

2 Results and discussion

Synthetic aspects

For the synthesis of thiometallates applying elemental Sn and S a very weak coordinating amine like methylamine is necessary which generates the basic conditions for production of polysulfide anions which attack Sn to form the thiostannate ion.

In our previous investigations of the TM/Sn/S/phen systems ($\text{TM} = \text{Mn, Fe, Co, Ni}$) we demonstrated that Mn^{2+} easily forms bonds to thiostannate anions and five compounds with compositions $\{[\text{Mn}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$, $\{[\text{Mn}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}\text{-phen}$, $\{[\text{Mn}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}\text{-phen}\cdot\text{H}_2\text{O}$ and $\{[\text{Mn}(\text{phen})_2]_2[\text{SnS}_4]_2\cdot[\text{Mn}(\text{phen})_2]\cdot\text{H}_2\text{O}$ could be prepared of which four were accessible even under stirring conditions.²⁷ The syntheses with Fe and Co yielded only two compounds ($\{[\text{M}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ and $\{[\text{M}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}\text{-phen}\cdot\text{H}_2\text{O}$, $\text{M} = \text{Fe, Co}$) and only under static conditions.²⁸ Applying the synthesis conditions used for $\text{TM} = \text{Mn, Fe, and Co}$ no compounds were accessible with Ni and the reaction products only contained the crystallized $[\text{Ni}(\text{phen})_3]^{2+}$ complex (counter ion: Cl^-) and X-ray amorphous sulfides. One reason may be the differing stabilities of the $[\text{TM}(\text{phen})_3]^{2+}$ complexes with $\log \beta$ (TM): Mn: 10.5, Fe: 21.2, Co: 19.9, Ni: 24.3.⁵² To force bond formation between Ni^{2+} and the thiostannate anion syntheses were performed with mixtures of aromatic bidentate N-donor ligands which have different coordination abilities. The bidentate amine phen is a strong coordinating ligand,⁵² while 2,2'-bipy has a weak/medium coordination tendency⁵² and 4,4'-bipy can only act as a monodentate ligand to one Ni^{2+} center. Both 4,4'-bipy and 2,2'-bipy may act as stabilizing molecules *via* π – π interactions and both are not strong competitors for phen. During the explorative synthetic work we observed that the ratio phen:bipy is an important parameter. Compound **I** containing co-crystallized 4,4'-bipy was only obtained when the amount of 4,4'-bipy was between 20–65% of the total amount of amine. The highest yield was observed for a Ni:phen:4,4'-bipy molar ratio of 1:1:1. Applying mixtures of phen and 2,2'-bipy compound **II** crystallized only applying 20–50% 2,2'-bipy of the total amount of amine. For compound **II** the highest yield was obtained at a molar ratio of 1:2:1 for Ni:phen:2,2'-bipy. When the syntheses were carried out using the analogue cobalt and iron salts ($\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ or $\text{FeCl}_2\cdot 4\text{H}_2\text{O}$) under the conditions mentioned above, the known compounds $\{[\text{Co}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ ²⁸ and $\{[\text{Fe}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$,²⁸ were obtained.

Crystal structures

The compound $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}\cdot 4\cdot 4'\text{-bipy}\cdot \frac{1}{2}\text{H}_2\text{O}$ (**I**) crystallizes in the monoclinic space group $C2/c$ with four formula



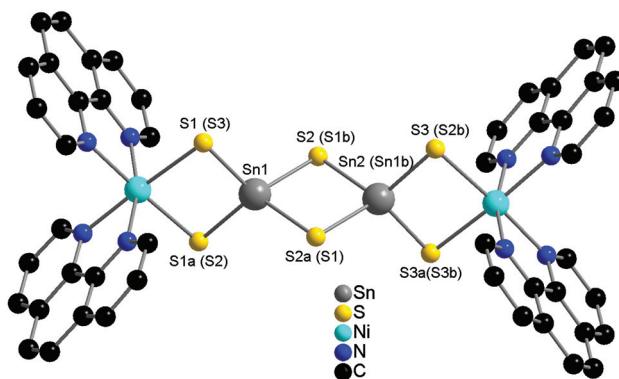


Fig. 1 Structure of the $\{[Ni(phen)]_2\}_2Sn_2S_6$ moieties in I as a representative. Labelling of the atoms for II are given in parentheses. The hydrogen atoms are omitted for clarity.

units in the unit cell with all atoms on general positions except the two unique Ni and Sn atoms. $\{[Ni(phen)]_2\}_2Sn_2S_6$ ·2,2'-bipy (II) crystallizes in the monoclinic space group $P2_1/n$ with two formula units in the unit cell and all atoms are located on general sites.

Both structures feature the $[Sn_2S_6]^{4-}$ anion and charge compensating Ni^{2+} centered complexes. The Ni^{2+} cations of the $[Ni(phen)]_2^{2+}$ complexes have two Ni-S bonds leading to the formation of discrete molecules (Fig. 1).

The Ni-S bond lengths (2.4960 Å–2.5047 Å) as well as the Ni-N bonds (2.083 Å–2.124 Å) are within the range reported in literature.^{12–14,16,23} (Table 1).

The angles around Ni^{2+} scatter between $78.64(13)^\circ$ and $175.86(9)^\circ$ (I) and between $77.38(11)^\circ$ and $172.28(9)^\circ$ (II), respectively, indicative for a severe distortion of the octahedra, but still in the range of literature data.¹⁶ The distortion is caused by the fixed position of the N-atoms in the phen-

molecule leading to acute angles around the Ni^{2+} cations (I: N1–Ni1–N2: $78.64(13)$, N21–Ni1–N22: $79.03(13)$; II: N1–Ni1–N2: $77.38(11)$, N21–Ni1–N22: $78.25(12)$) (Table S1†). The values of the dihedral angles between the phen ligands are around $90^\circ \pm 10^\circ$ (Table S2†) and they are comparable with literature data.^{27,28} The $[Sn_2S_6]^{4-}$ ion which is generated by edge-sharing of two SnS_4 tetrahedra exhibits the typical Sn-S bonding pattern of short Sn-S_t (t = terminal) and longer Sn-S_b (b = bridging) bonds. Comparing the geometric parameters of the thiostannate ion of the title compounds with those of the discrete anion $[Sn_2S_6]^{4-}$ (ref. 1,12–16,46) the Sn-S bond lengths do not differ significantly (Table 1). Different, however, are the bond angles which cover a wide range from 87.46 to 117.27° in I and they are between 87.54° and 120.84° in II evidencing a strong deviation from ideal tetrahedral geometry, a phenomenon also observed previously.^{12,23,26–28,53}

Besides the $\{[Ni(phen)]_2\}_2Sn_2S_6$ moiety, the structure of I contains an additional 4,4'-bipy and a water molecule, which is disordered over two half occupied positions. The $\{[Ni(phen)]_2\}_2Sn_2S_6$ units are arranged as rods in all three crystallographic directions (Fig. 2). The 4,4'-bipy molecules are assembled in a chain-like fashion along [100] and [001] (Fig. 2). The water molecule is located between adjacent

Table 1 Selected bond lengths (Å) and angles (°) of compounds I and II^a

I		II	
Sn1–S1	2.3366(10)	Sn–S3	2.3296(9)
Sn1–S1 ^a	2.3382(10)	Sn–S2	2.3475(9)
Sn1–S2	2.4532(9)	Sn–S1 ^b	2.4488(9)
Sn1–S2 ^a	2.4630(9)	Sn–S1	2.4524(9)
S1–Sn–S1 ^a	100.59(5)	S2–Sn–S3	100.43(3)
S2–Sn–S2 ^a	92.78(4)	S1–Sn–S1 ^b	92.46(3)
S1–Sn–S2 ^a	117.27(4)	S1–Sn–S3	120.84(3)
S1 ^a –Sn–S2 ^a	115.02(3)	S1–Sn–S2	113.00(3)
S2–Sn–S3	117.28(4)	S2–Sn–S1 ^b	118.10(3)
S2 ^a –Sn–S3	114.57(3)	S3–Sn–S1 ^b	113.30(3)
Sn1–S1–Sn2	87.46(3)	Sn–S1–Sn ^b	87.54(3)
Ni1–N1	2.103(3)	Ni1–N1	2.120(3)
Ni1–N2	2.122(3)	Ni1–N2	2.161(3)
Ni1–N21	2.083(3)	Ni1–N21	2.106(3)
Ni1–N22	2.124(3)	Ni1–N22	2.112(3)
Ni1–S1	2.4960(11)	Ni1–S2	2.4946(10)
Ni1–S3	2.5047(11)	Ni1–S3	2.4984(10)

^a Symmetry transformations used to generate equivalent atoms: a: $-x + 1, y, -z + 1/2$; b: $-x + 1, -y + 1, -z$.

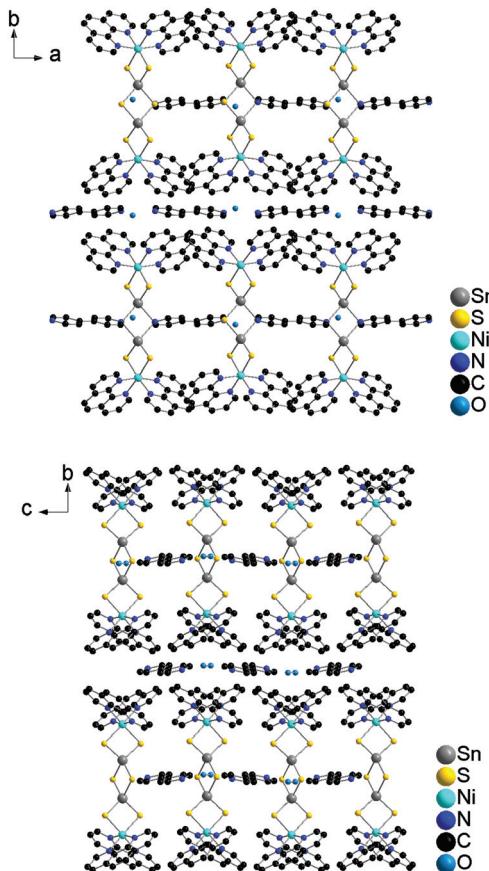


Fig. 2 Parallel arrangement of the molecules in I within the ab-plane (top) and bc-plane (bottom), respectively. Hydrogen atoms are omitted for clarity.



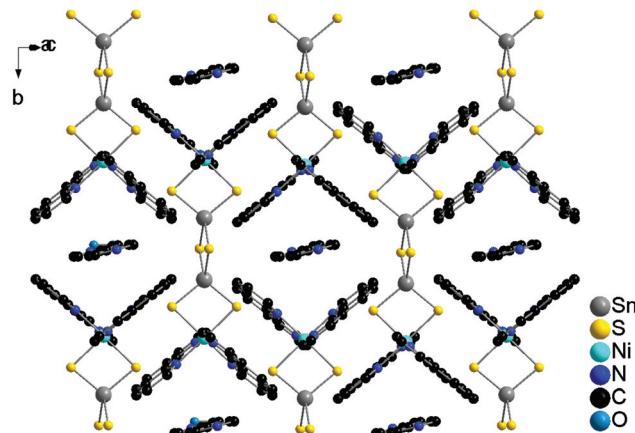


Fig. 3 Arrangement of the molecules in **I** viewed along [10-1]. The 4,4'-bipy molecules are located in the free spaces between the $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ moieties. Hydrogen atoms are omitted for clarity.

4,4'-bipy molecules and the N...O separation of 2.922 Å indicates hydrogen bonding interaction.

The arrangement of the constituents for optimal intermolecular interactions in **I** becomes clear viewing along [10-1]: The $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ moieties are interlaced along [101] and the 4,4'-bipy molecules are located in the thus generated voids (Fig. 3).

The phen ligands of neighbored complexes exhibit a short intermolecular distance of 3.489 Å and two even shorter separations are observed between phen and co-crystallized 4,4'-bipy molecules at 3.343–3.455 Å. Such short distances between off-centered parallel stacked aromatic molecules indicate π - π interactions (Fig. 4 and 5).^{42–45,54,55}

In the structure of **II** the $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ moieties are lined-up along a and c , respectively (Fig. 6). The 2,2'-bipy molecules are located between two adjacent $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ units yielding a sequence AAB along [100] where A stands for the phen Ligand and B for the 2,2'-bipy molecule.

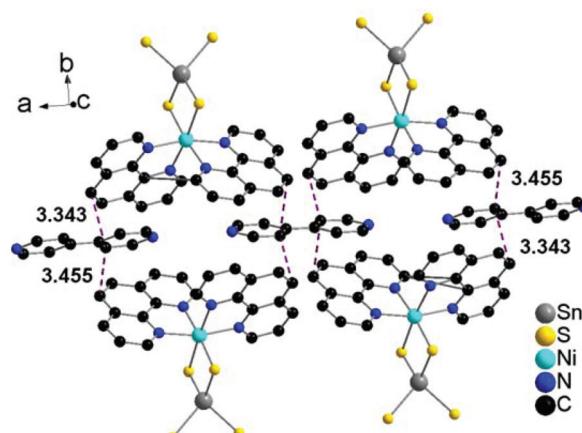


Fig. 5 Off-center parallel orientation of the phen ligands as well as 4,4'-bipy molecules in **I** along [101]. The purple dashed lines indicate the shortest intermolecular distances. Hydrogen atoms are omitted for clarity.

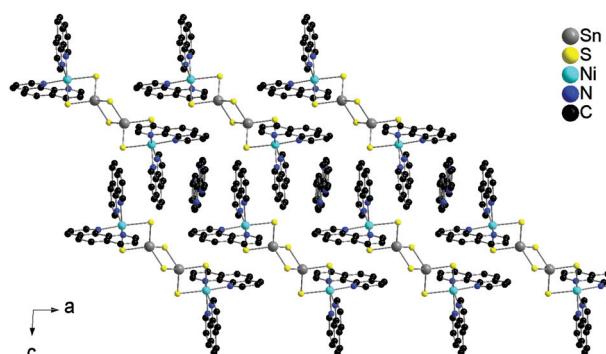


Fig. 6 Arrangement of the molecules in **II** within the ac -plane. The 2,2'-bipy molecules are disordered over two positions between two pairs of phen ligands of the $\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ moieties. Hydrogen atoms are omitted for clarity.

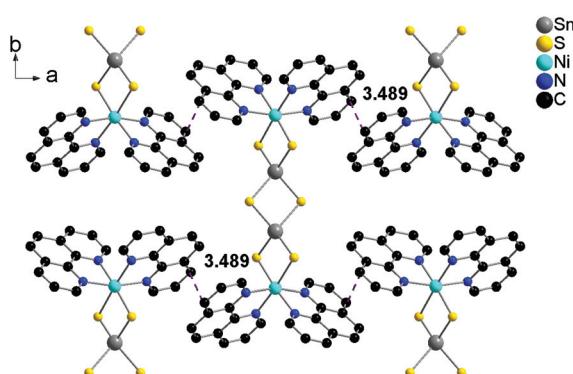


Fig. 4 Off-center parallel orientation of the phen ligands in **I** within the ab -plane. The purple dashed lines indicate the shortest intermolecular distances. Hydrogen atoms are omitted for clarity.

Like in compound **I** the aromatic components adopt orientations which allow attractive intermolecular interactions. Along [010] all molecules are arranged in rows, while along [101] the phen ligands are staggered. The 2,2'-bipy molecules can now be aligned parallel to the upper and the lower phen ligand of adjacent rows (Fig. 7, top) leading either to a parallel arrangement or a staggered arrangement (Fig. 7, bottom). The intermolecular distances for these orientations between the 2,2'-bipy molecule and the phen ligands are almost identical with 3.279–3.826 Å for the parallel and 3.335–3.921 Å and 3.396–4.059 Å for the staggered orientations. As discussed above and in agreement with literature data such distances can be regarded as π - π interactions.^{54,55}

Physical properties

The Sn-S modes in the Raman spectra of thiostannates are located in the region of 400 to 100 cm⁻¹. The assignment of



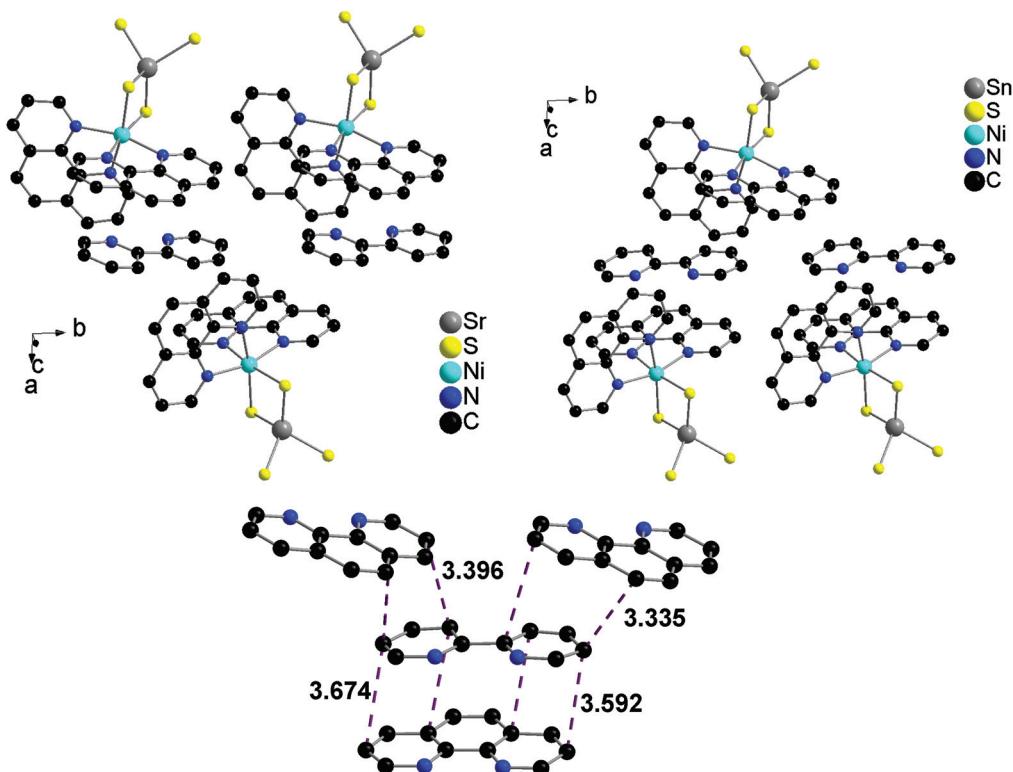


Fig. 7 Arrangement of the 2,2'-bipy molecules between the $\{[Ni(phen)2]2Sn2S6\}$ moieties (top) in the structure of **II**. The shortest intermolecular distances are shown (purple dashed lines, distances in Å, bottom). For reasons of clarity only one arrangement of the 2,2'-bipy molecule is shown. Hydrogen atoms and part of the $\{[Ni(phen)2]2Sn2S6\}$ moieties as well as hydrogen atoms are omitted.

the modes for compounds **I** and **II** was done on the basis of the data documented for the $[Sn2S6]^{4-}$ anion^{1,56,57} and $NiS2$ ⁵⁸ (Table 2).

The resonance of the symmetric Sn-S_t stretching mode is found around 390 cm^{-1} in the discrete anion. In the title compounds the $[Sn2S6]^{4-}$ unit has bonds to Ni^{2+} resulting in slightly shorter Sn-S bonds leading to a shift of the signal to higher wave numbers. The Sn-S-Sn vibrations are located at lower wave numbers at about 340 cm^{-1} . The mode at 280 cm^{-1} could be caused by a $Sn2S2$ ring vibration, the energetic differences between the resonances of **I** and **II** and those reported for $Na4Sn2S6 \cdot 14H2O$ could be generated by slightly differing bond lengths and angles. But since the Ni-S vibrations are located in this region as well, a detailed assignment is not possible.

Table 2 Data of the signals in the Raman spectra of $Na4Sn2S6 \cdot 14H2O^1$ and compounds **I** and **II** compared to the $[Sn2S6]^{4-}$ anion^{1,56,57} and $NiS2$ ⁵⁸ in cm^{-1}

$[Sn2S6]^{4-}$	$NiS2$	I	II
391		394	399
341		336	340
	301	298	298
281	283	273	276
	222	219	212
190	181		180

In the IR spectra, the absorptions can be assigned to phen⁵⁹⁻⁶¹, the Ni-N stretching vibration at $\approx 420\text{ cm}^{-1}$ (ref. 27 and 28) and to one of the bipy molecules⁶²⁻⁶⁵ (Table 3). The absorptions of the 4,4'-bipy molecule are mostly overlapping with the absorptions of phen, but for example at *ca.* 800 cm^{-1} only 4,4'-bipy causes a signal, which therefore can only be observed in compound **I**. For 2,2'-bipy (**II**) this absorption is shifted to slightly higher wavenumbers ($818/819\text{ cm}^{-1}$) due the different position of the N-atoms in the aromatic ring.

In the UV/vis spectra of both compounds three bands are observed (see Fig. S4 and S5†). The first two absorptions (**I**: $\sim 2.48\text{ eV}$ and $\sim 3.32\text{ eV}$; **II**: $\sim 2.55\text{ eV}$ and $\sim 3.16\text{ eV}$) can be assigned to the Ni^{2+} d-d transition $^3A_{2g} \rightarrow ^3T(^3F)$ and $^3A_{2g} \rightarrow ^3T(^3P)$.⁶⁶ The third band (**I**: 4.63 eV ; **II**: 4.59 eV) might probably be traced back to the $\pi \rightarrow \pi^*$ transition of the aromatic amines.⁵⁹

The thermal properties of both compounds were investigated by simultaneously differential thermoanalysis and thermogravimetry. On heating compound **I** at $4\text{ }^{\circ}\text{C min}^{-1}$ one mass step of 40.8% is observed in the TG curve that is accompanied with an endothermic peak in the DTA curve at about $340\text{ }^{\circ}\text{C}$ (Fig. S6†). On further heating a second much smaller mass step is observed and in the following the samples mass decreases continuously. The experimental mass loss observed in each step are not in agreement with those calculated for a stepwise removal of the organic ligands.

Table 3 Absorptions in the IR-spectra of compounds **I** and **II** compared to 1,10-phen^{59–61}, 4,4'-bipy^{62,63} and 2,2'-bipy^{64,65}

1,10-phen	4,4'-bipy	2,2'-bipy	I	II	Assignment
3035	3023	—	3042	3035w	$\nu(\text{C}-\text{H})$
—	—	2982	—	2979w	$\nu(\text{C}-\text{H})$
—	—	2916	—	2922w	$\nu(\text{C}-\text{H})$
1616	1604	—	1624	1620	$\nu(\text{C}=\text{C})$
—	—	1595	—	1598	$\nu(\text{C}-\text{C}) + \nu(\text{C}-\text{N})$
1586	1585	—	1587	—	$\nu(\text{C}-\text{C})$
—	—	1579	—	1578	$\nu(\text{C}=\text{C})$
1560	—	1555	—	1557	$\nu(\text{C}=\text{C})$
1516	—	1517	1510	1510	$\nu(\text{C}=\text{C})$
1494	1491	—	1494	1491	$\nu(\text{C}=\text{C})$
—	—	1458	—	1456	$\delta(\text{C}=\text{C}-\text{H})$
1421	1416	—	1419	1416	Combination band
1344	—	—	1342	1344	$\nu(\text{C}=\text{C})$
—	—	1253	—	1255	$\nu(\text{C}=\text{C})$
1216	1218	—	1218	1222	$\nu(\text{C}=\text{C})$
—	—	1210	—	1206	$\delta(\text{C}=\text{C}-\text{H})$
1137	1133	1238	1136	1134	$\delta(\text{C}=\text{C}-\text{H})$
1092	—	—	1096	1096	$\nu(\text{C}=\text{C})$
—	1068	—	1065	—	Ring breathing
1035	—	1038	—	1036	$\nu(\text{C}-\text{N})$
996	992	—	991	—	$\delta(\text{C}=\text{C}-\text{H})$
987	—	—	—	985	$\delta(\text{C}=\text{C}-\text{H})$
869	—	—	866	—	$\nu(\text{ring})$
853	—	—	—	858	$\delta(\text{C}=\text{C}=\text{C})$
848	—	—	844	846	$\delta(\text{C}=\text{C}=\text{C})$
—	—	818	—	819	$\delta(\text{C}=\text{C}-\text{H})$
—	800	—	802	—	$\delta(\text{C}=\text{C}-\text{H})$
779	—	—	780	779	$\delta(\text{C}-\text{H})$
—	—	758	—	753	$\delta(\text{C}=\text{C}-\text{H})$
721	724	—	724	722	$\delta(\text{C}-\text{H})$
643	—	—	640	637	$\nu(\text{ring})$
625	—	616	—	620	$\delta(\text{C}-\text{H})$
606	607	—	609	—	$\delta(\text{C}=\text{C}=\text{C})$
478	—	—	476	—	$\nu(\text{ring})$
—	—	—	422	422	$\nu(\text{Ni}-\text{N})$

Therefore, this reaction seems to be more complex. For compound **II** several poorly resolved mass steps are observed, all of them accompanied with endothermic events in the DTA curve, indicating that the organic ligands are stepwise removed.

Both compounds exhibit paramagnetic behaviour (see Fig. S8 and S9†). The value for the Weiss constant is near zero demonstrating that the Ni^{2+} cations are magnetically isolated. The effective magnetic moment for Ni^{2+} amounts to 2.88 μ_{B} which is near the spin only value.

3 Experimental section

Synthesis

General. All chemicals were used as purchased without further purifications. The compounds were prepared under solvothermal conditions in glass tubes (inner volume 11 mL) using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Sn, sulfur, phen, 4,4'-bipy and 2,2'-bipy, respectively. The reaction products were filtered off after reaction, washed with water and ethanol and dried *in vacuo*. Afterwards crystals in the products were separated manually. The homogeneity of the separated samples was checked by X-ray powder diffraction and elemental analysis.

Synthesis of $[\{\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_2\}_2\text{Sn}_2\text{S}_6\} \cdot \text{C}_{10}\text{H}_8\text{N}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ (I). 59.5 mg (0.25 mmol) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 29.7 mg (0.25 mmol) Sn, 24.1 mg (0.75 mmol) S, 45.1 mg (0.25 mmol) phen ($\text{C}_{12}\text{H}_8\text{N}_2$) and 39.0 mg (0.25 mmol) 4,4'-bipy ($\text{C}_{10}\text{H}_8\text{N}_2$) with 1.5 mL methylamine (40%, aqueous solution, abcr) and 0.5 mL water ($\text{pH} \approx 14$) were reacted at 120 °C for 7 days. The product consisted of dark red-brown crystals of **I** and black to brown powder and crumbs. The yield of the manually separated crystals was app. 15% (based on tin). According to EDX analysis the brownish-black product contains Ni, Sn and S in varying composition. However, the X-ray powder diffraction pattern did not show reflections and one can only assume that these are X-ray amorphous Ni/Sn sulfides. When the synthesis is carried out under stirring conditions, a brownish powder of **I** is obtained after five hours with a yield being about more than twice as high as under static conditions (appr. 45%, based on tin). Elemental analysis, results in %: found: C 48.47, H 2.71, N 9.54, calculated: C 48.61, H 2.88, N 9.77.

Synthesis of $[\{\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)_2\}_2\text{Sn}_2\text{S}_6\} \cdot \text{C}_{10}\text{H}_8\text{N}_2$ (II). 59.5 mg (0.25 mmol) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 29.7 mg (0.25 mmol) Sn, 24.1 mg (0.75 mmol) S, 90.1 mg (0.5 mmol) phen ($\text{C}_{12}\text{H}_8\text{N}_2$) and 39.0 mg (0.25 mmol) 2,2'-bipy ($\text{C}_{10}\text{H}_8\text{N}_2$) with 1.5 mL methylamine (40%, aqueous solution, abcr) and 0.5 mL water were reacted in a glass tube ($\text{pH} \approx 14$). The mixture was heated at 120 °C for 7 days. The product contained deep red crystals of **II** and greyish-black powder and crumbs. The yield of the crystals was app. 20–25% (based on tin). The yield could be increased significantly under stirring conditions (appr. 65%, based on tin). The byproduct is X-ray amorphous and according to EDX data contains Ni, Sn and S. Elemental analysis, results in %: found: C 48.65, H 2.79, N 9.73, calculated: C 48.91, H 2.83, N 9.83.

Structure determination

The intensity data for the compounds were collected using a STOE IPDS-1 (Imaging Plate Diffraction System) with $\text{Mo}-\text{K}_{\alpha}$ radiation. The structures were solved with direct methods using the program SHELXS-97⁶⁷ and the refinements were done against F^2 with SHELXL-97.⁶⁸ For all non-hydrogen atoms anisotropic displacement parameters were used. The hydrogen atoms were positioned with idealized geometry and were refined using a riding model. In compound **I** the O–H hydrogen atoms were located in the difference Fourier map, their bond lengths set to ideal values and refined using a riding model. The water molecule is disordered over two half occupied positions and was refined using a split model. The structure contains additional non-coordinating 4,4'-bipy molecules that are located on centres of inversion. In compound **II**, the non-coordinating 2,2'-bipy molecule is disordered and was refined using a split model with restraints for bond lengths and angles.

Selected refinement results are summarized in Table 4. Structural data have been deposited in the Cambridge Crystallographic Data Centre as publication no. CCDC 1054460 (**I**), CCDC 1054461 (**II**).



Table 4 Selected details of the data collection and structure refinement results

	$\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ 4,4'-bipy- $\frac{1}{2}\text{H}_2\text{O}$	$\{[\text{Ni}(\text{phen})_2]_2\text{Sn}_2\text{S}_6\}$ 2,2'-bipy
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
M (g mol $^{-1}$)	1442.18	1424.16
a (Å)	18.3431(6)	10.5715(2)
b (Å)	19.4475(6)	9.9086(2)
c (Å)	15.0835(5)	24.9960(4)
α (°)	90	90
β (°)	95.556(2)	92.8000(10)
γ (°)	90	90
V (Å 3)	5355.4(3)	2615.17(8)
Temperature (K)	200(2)	200(2)
Z	4	2
$D_{\text{calculated}}$ (g cm $^{-3}$)	1.789	1.809
μ (mm $^{-1}$)	1.9.03	1.946
Scan range (°)	$1.53 \leq \theta \leq 28.00$	$1.63 \leq \theta \leq 27.93$
Reflections collected	31 723	44 107
Independent reflections	6419	6238
Observed reflections	5042	5617
Goodness-of-fit on F^2	1.084	1.059
R values ($I > 2\sigma(I)$)	$R_1 = 0.0466$ $wR_2 = 0.1038$	$R_1 = 0.0480$ $wR_2 = 0.1274$
R values (all data)	$R_1 = 0.0641$ $wR_2 = 0.1113$	$R_1 = 0.0520$ $wR_2 = 0.1307$
Res. elec. dens. (e Å $^{-3}$)	0.706 and -0.801	1.024 and -0.770

X-ray powder diffractometry

The X-ray powder diffraction patterns were recorded on a STOE Stadi-P powder diffractometer (Cu-K α_1 radiation, $\lambda = 1.540598$ Å, Ge monochromator) in transmission geometry.

SEM and EDX

Scanning electron microscopy investigations and energy dispersive X-ray analyses (EDX) were done with a Philips Environmental Scanning Electron Microscope ESEM XL30 equipped with an EDAX detector.

Raman spectroscopy

Raman spectra were recorded with a Bruker IFS 66 Fourier transform Raman spectrometer (wavelength: 541.5 nm) in the region from 100 to 3500 cm $^{-1}$.

Infrared spectroscopy

MIR spectra (400–4000 cm $^{-1}$) were recorded with a Bruker Alpha P spectrometer.

UV/visible spectroscopy

UV/vis spectra were recorded with an UV-vis-NIR two channel spectrometer Cary 5 from Varian Techtron Pty., Darmstadt at room temperature of powdered samples with BaSO $_4$ powder as reference material. The absorption data were calculated applying the Kubelka–Munk relation for diffuse reflectance data.

Thermal properties

DTA-TG measurements were performed using a Netzsch STA 409 CD under a nitrogen flow of 75 mL min $^{-1}$ and at a heating

rate of 4 K min $^{-1}$. The instrument was calibrated using standard reference materials.

Magnetic properties

The magnetic properties were investigated using a physical properties measurement system (PPMS) Model 600 from Quantum Design at $H = 100$ Oe in the temperature range 1.9–325 K.

4 Conclusions

In the manuscript we presented a new synthesis strategy based on the observation of different coordination abilities of aromatic N-donor ligands towards Ni $^{2+}$. Applying suitable mixtures of the aromatic amine molecules with the proper ratio between Ni $^{2+}$ and the strong coordinating phen ligand, products crystallized where the medium/weak or non-resp. monodentate aromatic amine molecule acts as stabilizer of the structures *via* π - π -interactions. Currently we experimentally investigate whether this is a new general concept, which can be applied to other transition metals opening new opportunities for the generation of hitherto not accessible thiostannates.

Acknowledgements

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

Notes and references

- B. Krebs, S. Pohl and W. Schiwy, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 897–898.
- (a) K. O. Klepp and F. Fabian, *Z. Naturforsch., B: Chem. Sci.*, 1999, **54**, 1505–1509; (b) Klepp, O. Kurt and F. Fabian, *Z. Naturforsch., B: Chem. Sci.*, 1999, **54**, 1505–1509.
- G. A. Marking, M. Evain, V. Petricek and M. G. Kanatzidis, *J. Solid State Chem.*, 1998, **141**, 17–28.
- J.-H. Liao, C. Varotsis and M. G. Kanatzidis, *Inorg. Chem.*, 1993, **32**, 2453–2462.
- E. Ruzin, S. Jakobi and S. Dehnen, *Z. Anorg. Allg. Chem.*, 2008, **634**, 995–1001.
- O. Palchik, R. G. Iyer, J. H. Liao and M. G. Kanatzidis, *Inorg. Chem.*, 2003, **42**, 5052–5054.
- P. Nørby, J. Overgaard, P. S. Christensen, B. Richter, X. Song, M. Dong, A. Han, J. Skibsted, B. B. Iversen and S. Johnsen, *Chem. Mater.*, 2014, **26**, 4494–4504.
- J. B. Parise, Y. Ko, J. Rijssenbeek, D. M. Nellis, K. Tan and S. Koch, *J. Chem. Soc., Chem. Commun.*, 1994, 527.
- T. Jiang, A. Lough and G. A. Ozin, *Adv. Mater.*, 1998, **10**, 42–46.
- H. Pada Nayek, Z. Lin and S. Dehnen, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1737–1740.
- X. Wang, T.-L. Sheng, S.-C. Xiang, S.-M. Hu, R.-B. Fu and X.-T. Wu, *Chin. J. Struct. Chem.*, 2010, **29**, 260–264.



12 M. Behrens, S. Scherb, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1367–1373.

13 D.-X. Jia, Y. Zhang, J. Dai, Q.-Y. Zhu and X.-M. Gu, *Z. Anorg. Allg. Chem.*, 2004, **630**, 313–318.

14 D.-X. Jia, J. Dai, Q.-Y. Zhu, Y. Zhang and X.-M. Gu, *Polyhedron*, 2004, **23**, 937–942.

15 M.-L. Fu, G.-C. Guo, B. Liu, A.-Q. Wu and J.-S. Huang, *Chin. J. Inorg. Chem.*, 2005, **21**, 25–29.

16 N. Pienack, H. Lühmann, B. Seidlhofer, J. Ammermann, C. Zeisler, F. Danker, C. Näther and W. Bensch, *Solid State Sci.*, 2014, **33**, 67–72.

17 X.-H. Lu, J.-J. Liang, J. Zhao, Y. Zhang and D.-X. Jia, *J. Chem. Crystallogr.*, 2011, **41**, 557–562.

18 J. Zhou, X. Liu, L. An, F. Hu, W. Yan and Y. Zhang, *Inorg. Chem.*, 2012, **51**, 2283–2290.

19 N. Pienack, C. Näther and W. Bensch, *Z. Naturforsch., B: Chem. Sci.*, 2008, **63**, 1243–1251.

20 Z. Wang, G. Xu, Y. Bi and C. Wang, *CrystEngComm*, 2010, **12**, 3703.

21 C.-Y. Yue, X.-W. Lei, L. Yin, X.-R. Zhai, Z.-R. Ba, Y.-Q. Niu and Y.-P. Li, *CrystEngComm*, 2015, **17**, 814–823.

22 J. Zhou, G.-Q. Bian, J. Dai, Y. Zhang, A.-B. Tang and Q.-Y. Zhu, *Inorg. Chem.*, 2007, **46**, 1541–1543.

23 N. Pienack, S. Lehmann, H. Lühmann, M. El-Madani, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2323–2329.

24 N. Pienack, C. Näther and W. Bensch, *Eur. J. Inorg. Chem.*, 2009, 1575–1577.

25 N. Pienack, D. Schinkel, A. Puls, M.-E. Ordolff, H. Lühmann, C. Näther and W. Bensch, *Z. Naturforsch., B: Chem. Sci.*, 2012, **67**, 1098–1106.

26 C. Zeisler, C. Näther and W. Bensch, *CrystEngComm*, 2013, **15**, 8874.

27 J. Hilbert, C. Näther and W. Bensch, *Inorg. Chem.*, 2014, **53**, 5619–5630.

28 J. Hilbert, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2014, **640**, 2858–2863.

29 G.-N. Liu, G.-C. Guo, F. Chen, S.-P. Guo, X.-M. Jiang, C. Yang, M.-S. Wang, M.-F. Wu and J.-S. Huang, *CrystEngComm*, 2010, **12**, 4035.

30 N. Pienack, K. Möller, C. Näther and W. Bensch, *Solid State Sci.*, 2007, **9**, 1110–1114.

31 N. Pienack, C. Näther and W. Bensch, *Solid State Sci.*, 2007, **9**, 100–107.

32 N. Pienack and W. Bensch, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1733–1736.

33 M. Behrens, M.-E. Ordolff, C. Näther, W. Bensch, K.-D. Becker, C. Guillot-Deudon, A. Lafond and J. A. Cody, *Inorg. Chem.*, 2010, **49**, 8305–8309.

34 N. Pienack, C. Näther and W. Bensch, *Eur. J. Inorg. Chem.*, 2009, 937–946.

35 N. Pienack, A. Puls, C. Näther and W. Bensch, *Inorg. Chem.*, 2008, **47**, 9606–9611.

36 M. BaiYin, L. Ye, Y. An, X. Liu, C. Jia and G. Ning, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1283–1284.

37 Y. An, B. Menghe, L. Ye, M. Ji, X. Liu and G. Ning, *Inorg. Chem. Commun.*, 2005, **8**, 301–303.

38 Y. Wang, M. BaiYin, S. Ji, X. Liu, Y. An and G. Ning, *Chem. Res. Chin. Univ.*, 2006, **22**, 411–414.

39 R.-C. Zhang, H.-G. Yao, S.-H. Ji, M.-C. Liu, M. Ji and Y.-L. An, *Chem. Commun.*, 2010, **46**, 4550–4552.

40 (a) A. Rabenau, *Angew. Chem., Int. Ed. Engl.*, 1985, **97**, 1017–1032; (b) W. S. Sheldrick and M. Wachhold, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 206–224; (c) W. S. Sheldrick and M. Wachhold, *Coord. Chem. Rev.*, 1998, **176**, 211–322; (d) S. Dehnen and M. Melullis, *Coord. Chem. Rev.*, 2007, **251**, 1259–1280; (e) G. Demazeau, *J. Mater. Sci.*, 2008, **43**, 2104–2114; (f) W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 2000, 3041–3052; (g) X. Bu, N. Zheng and P. Feng, *Chem. – Eur. J.*, 2004, **10**, 3356–3362; (h) B. Seidlhofer, N. Pienack and W. Bensch, *Z. Naturforsch., B: Chem. Sci.*, 2010, **65**, 937–975; (i) W.-W. Xiong, G. Zhang and Q. Zhang, *Inorg. Chem. Front.*, 2014, **1**, 292.

41 (a) W. Bensch and M. Schur, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 1149–1160; (b) W. Bensch and M. Schur, *Z. Naturforsch., B: Chem. Sci.*, 1997, **52**, 405–409; (c) M. Schur, C. Näther and W. Bensch, *Z. Naturforsch., B: Chem. Sci.*, 2001, **56**, 79–84; (d) A. Puls, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1239–1243.

42 L. Goerigk, H. Kruse and S. Grimme, *ChemPhysChem*, 2011, **12**, 3421–3433.

43 S. Grimme, *Angew. Chem., Int. Ed.*, 2008, **47**, 3430–3434.

44 S. Grimme, *WIREs Comput. Mol. Sci.*, 2011, **1**, 211–228.

45 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

46 J. Zhou, X. Liu, G.-Q. Chen, F. Zhang and L.-R. Li, *Z. Naturforsch., B: Chem. Sci.*, 2010, **65**, 1229–1234.

47 (a) C.-Y. Yue, X.-W. Lei, Y.-X. Ma, N. Sheng, Y.-D. Yang, G.-D. Liu and X.-R. Zhai, *Cryst. Growth Des.*, 2014, **14**, 101–109; (b) R. J. Lees, A. V. Powell and A. M. Chippindale, *Polyhedron*, 2005, **24**, 1941–1948; (c) H.-O. Stephan and M. G. Kanatzidis, *Inorg. Chem.*, 1997, **36**, 6050–6057; (d) H. Lühmann, Z. Rejai, K. Möller, P. Leisner, M.-E. Ordolff, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2008, **634**, 1687–1695; (e) R. Stähler, C. Näther and W. Bensch, *Eur. J. Inorg. Chem.*, 2001, 1835–1840; (f) R. Kiebach, W. Bensch, R.-D. Hoffmann and R. Pöttgen, *Z. Anorg. Allg. Chem.*, 2003, **629**, 532–538; (g) C. Anderer, N. Delwa de Alarcon, C. Näther and W. Bensch, *Chem. – Eur. J.*, 2014, **20**, 16953–16959; (h) J. Zhou and L. An, *CrystEngComm*, 2011, **13**, 5924–5928; (i) J. Zhou, L. An, X. Liu, L. Huang and X. Huang, *Dalton Trans.*, 2011, **40**, 11419–11424; (j) M.-L. Feng, W.-W. Xiong, D. Ye, J.-R. Li and X.-Y. Huang, *Chem. – Asian J.*, 2010, **5**, 1817–1823; (k) J. Zhou, L. An and F. Zhang, *Inorg. Chem.*, 2011, **50**, 415–417; (l) X. Liu, *Inorg. Chem. Commun.*, 2011, **14**, 437–439; (m) W. Tang, C. Tang, F. Wang, R. Chen, Y. Zhang and D. Jia, *J. Solid State Chem.*, 2013, **199**, 287–294; (n) P. Vaqueiro, A. M. Chippindale and A. V. Powell, *Inorg. Chem.*, 2004, **43**, 7963–7965; (o) H.-O. Stephan and

M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1996, **118**, 12226–12227; (p) X. Liu and J. Zhou, *Inorg. Chem. Commun.*, 2011, **14**, 1286–1289; (q) M.-F. Wang, C.-Y. Yue, Z.-D. Yuan and X.-W. Lei, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2013, **69**, 855–858; (r) P. Vaqueiro, D. P. Darlow, A. V. Powell and A. M. Chippindale, *Solid State Ionics*, 2004, **172**, 601–605; (s) R. J. Lees, A. V. Powell and A. M. Chippindale, *J. Phys. Chem. Solids*, 2007, **68**, 1215–1219; (t) L. Engelke, C. Näther, P. Leisner and W. Bensch, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2959–2965.

48 C.-Y. Yue, X.-W. Lei, R.-Q. Liu, H.-P. Zhang, X.-R. Zhai, W.-P. Li, M. Zhou, Z.-F. Zhao, Y.-X. Ma and Y.-D. Yang, *Cryst. Growth Des.*, 2014, **14**, 2411–2421.

49 J. Zhou, G.-Q. Bian, Y. Zhang, J. Dai and N. Cheng, *Z. Anorg. Allg. Chem.*, 2007, **633**, 2701–2705.

50 (a) R. Stähler and W. Bensch, *J. Chem. Soc., Dalton Trans.*, 2001, 2518–2522; (b) M. Schaefer, R. Stähler, W.-R. Kiebach, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2004, **630**, 1816–1822; (c) J. Lichte, H. Lühmann, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2009, **635**, 2021–2026; (d) J. Zhou, X. Liu, L. An, F. Hu, Y. Kan, R. Li and Z. Shen, *Dalton Trans.*, 2013, **42**, 1735–1742.

51 R. Kiebach, R. Warratz, C. Näther and W. Bensch, *Z. Anorg. Allg. Chem.*, 2009, **635**, 988–994.

52 H. Irving and J. Mellor, *J. Chem. Soc.*, 1962, 5222–5237.

53 (a) Y. Zhang, J. Zhou, A.-B. Tang, G.-Q. Bian and J. Dai, *J. Chem. Crystallogr.*, 2010, **40**, 496–500; (b) X.-M. Gu, J. Dai, D.-X. Jia, Y. Zhang and Q.-Y. Zhu, *Cryst. Growth Des.*, 2005, **5**, 1845–1848.

54 E. C. Lee, D. Kim, P. Jurecka, P. Tarakeshwar, P. Hobza and K. S. Kim, *J. Phys. Chem. A*, 2007, **111**, 3446–3457.

55 C. R. Martinez and B. L. Iverson, *Chem. Sci.*, 2012, **3**, 2191.

56 B. Krebs and W. Schiwy, *Z. Anorg. Allg. Chem.*, 1973, **398**, 63–71.

57 W. Schiwy, C. Blutau, D. Gähde and B. Krebs, *Z. Anorg. Allg. Chem.*, 1975, **412**, 1–10.

58 D. W. Bishop, P. S. Thomas and A. S. Ray, *Mater. Res. Bull.*, 1998, **33**, 1303–1306.

59 M. S. Atanassova and G. D. Dimitrov, *Spectrochim. Acta, Part A*, 2003, **59**, 1655–1662.

60 M. Reiher, G. Brehm and S. Schneider, *J. Phys. Chem. A*, 2004, **108**, 734–742.

61 D. A. Thornton and G. M. Watkins, *J. Coord. Chem.*, 1992, **25**, 299–315.

62 R. Podgajny, M. Bałanda, M. Sikora, M. Borowiec, L. Spałek, C. Kapusta and B. Sieklucka, *Dalton Trans.*, 2006, 2801–2809.

63 J. G. Contreras and C. J. Díz, *J. Coord. Chem.*, 2007, **16**, 245–249.

64 E. Castellucci, L. Angeloni, N. Neto and G. Sbrana, *Chem. Phys.*, 1979, **43**, 365–373.

65 M. L. Niven and G. C. Percy, *Transition Met. Chem.*, 1978, **3**, 267–271.

66 S. P. Roe, J. O. Hill and R. J. Magee, *Monatsh. Chem.*, 1991, **122**, 467–478.

67 G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

68 G. M. Sheldrick, *SHELXS-97, Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

