Two Supramolecular Architectures Containing Dinuclear Thiostannate $[Sn_2S_6]$ Units

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Two thiostannates $[Co(dien)_2](H_2dien)Sn_2S_6$ (**1**) (dien = diethylenetriamine) and $[Zn(tren)]_2Sn_2S_6$ (**2**) (tren = tris(2-aminoethyl)amine) were prepared under solvothermal conditions and structurally characterized. Both **1** and **2** contain dinuclear $[Sn_2S_6]^{4-}$ anions built from two SnS_4 tetrahedra sharing a common edge. **1** consists of discrete $[Sn_2S_6]^{4-}$ anions with rare *u-fac*-$[Co(dien)_2]^{2+}$ and H_2dien^{2+} as counterions, while **2** consists of neutral centrosymmetric $[Zn(tren)]_2Sn_2S_6$, in which the $[Sn_2S_6]^{4-}$ anion connects two coordinatively unsaturated complex $[Zn(tren)]^{2+}$ cations as a bidentate ligand *via trans* terminal S atoms. The different cations act as structure-directing agents that have a significant influence on the arrangement of the $[Sn_2S_6]^{4-}$ anions in their crystal structures. **2** exhibits fluorescence properties at room temperature.

Key words: Solvothermal Synthesis, Crystal Structures, Thiostannates, Transition Metal Complex

Introduction

Chalcogenidostannates ($[Sn_xQ_y]^{n-}$, Q = S, Se, and Te) have been a research field with rapid expansion in the past decades, mainly because of their rich structural chemistry and potential applications in non-oxygen molecular sieves, semiconductors, and photoluminescent or magnetic materials [1]. Following the demonstration by Bedard and coworkers in 1989 that template-directed synthesis can be applied to effect the crystallization of thio- and selenidometalates [2], a number of chalcogenidostannates have been synthesized by using organic amines as templates or structure-directing agents under hydro(solvo)thermal conditions [3]. Different organic amines can induce the same structure, but can also lead to different structures, which are related to the framework and the templating molecules. For instance, 2D-layered anions with compositions $[Sn_3S_7]^{2-}$ (denoted as SnS-1) and $[Sn_4S_9]^{2-}$ (denoted as SnS-2) were obtained in the presence of tetraalkylammonium hydroxides. The charge-balancing cations for SnS-1 are tetramethylammonium [4], tetraethylammonium [5], and protonated 1,8-diazabicyclooctane [5], while the cations for SnS-1 are tetrapropylammonium [5] and tetrabutylammonium [5]. When organic amines or transition metal complex cations were used instead of tetraalkylammonium hydroxides, the dinuclear $[Sn_2S_6]^{4-}$ anion was obtained, as exemplified by $(chaH)_4Sn_2S_6$ (cha = cyclohexylamine) [6], $(ddaH)_4[Sn_2S_6]\cdot 2H_2O$ (dda = dodecylamine) [7], $[enH]_4[Sn_2S_6]$ (en = ethylenediamine) [8], $[M(en)_3]_2Sn_2S_6$ (M = Ni, Mn, Co and Zn) [9], $[Ni(dap)_3]_2Sn_2S_6\cdot 2H_2O$ [9a], $[M(dien)_2]_2Sn_2S_6$ (dien = diethylenetriamine, M = Ni and Mn) [10], and $[M(tren)]_2Sn_2S_6$ (tren = tris(2-aminoethyl)amine, M = Ni and Co) [9a]. Among these thiostannates with $[Sn_2S_6]^{4-}$ anions, the arrangement of the $[Sn_2S_6]^{4-}$ anions [9, 10] can be related to the different charge-balancing cations. Most interestingly, these thiostannates with $[Sn_2S_6]^{4-}$ anions made by using hydro(solvo)thermal techniques usually contain only one type of cations, whereas different cations as counterion have not been documented to date. In this paper, we report the solvothermal syntheses and crystal structures of the two thiostannates $[Co(dien)_2](H_2dien)Sn_2S_6$ (**1**) and $[Zn(tren)]_2Sn_2S_6$ (**2**). Compound **1** is the only example of a thiostannate combined with two different cations.

Results and Discussion

$[Co(dien)_2](H_2dien)Sn_2S_6$ (**1**) crystallizes in the centrosymmetric space group $C2/c$ with four formula units in the unit cell. The structure of **1** is com-

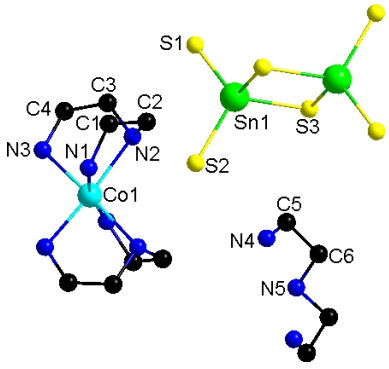

Fig. 1. Crystal structure of **1** with labeling scheme (hydrogen atoms omitted for clarity).

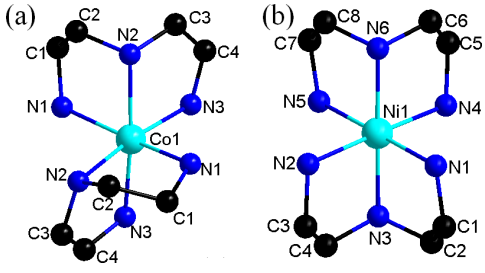

Fig. 2. Structures of the *u-fac*-$[Co(dien)_2]^{2+}$ ion (a) in **1** and the *s-fac*-$[Ni(dien)_2]^{2+}$ ion (b) in $[Ni(dien)_2]Sn_2S_6$ [10a].

posed of discrete $[Sn_2S_6]^{4-}$ anions with $[Co(dien)_2]^{2+}$ and H_2dien^{2+} as counterions (Fig. 1). The dinuclear $[Sn_2S_6]^{4-}$ anion is formed by two edge-sharing $[SnS_4]$ tetrahedra. The Sn–S_b bond lengths (b = bridging bond) are longer than the terminal Sn–S_t distances (t = terminal bond). The S–Sn–S angles in the range from 93.33(3) to 113.65(4)° deviate from the ideal value of 109.5° for a tetrahedron, but all parameters are in the range reported in the literature for related system [6 – 10].

In general, M^{2+} ions (M = transition metal) can be coordinated by six N atoms of two tridentate dien ligands in a distorted octahedral environment. The $[M(dien)_2]^{2+}$ cations can have *s-fac*-, *u-fac*- and *mer*-configuration [11]. The $[Co(dien)_2]^{2+}$ ion in **1** is in a *u-fac* conformation (Fig. 2a). Although the *s-fac*-$[Co(dien)_2]^{2+}$ isomer is observed in $[Co(dien)_2]_2Sb_2Se_6$ [12], the *u-fac*-$[Co(dien)_2]^{2+}$ isomer has not been reported until now. This discretion can be related to the more distorted coordination octahedron of *u-fac*, compared with that of *s-fac*. The Co–N distances are similar to the literature values for $[Co(dien)_2]^{2+}$ cations [12]. The distortion of the octahedral environment of the $[Co(dien)_2]^{2+}$ ion in **1** can

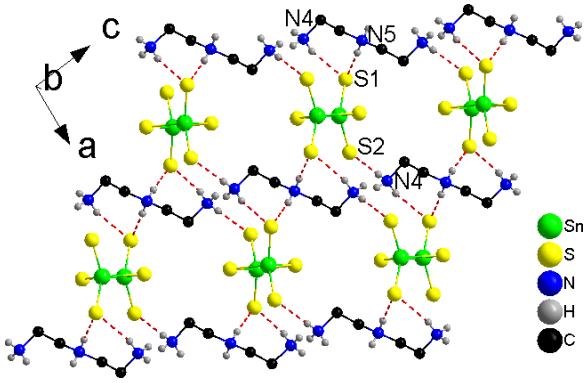

Fig. 3. Part of the crystal structure of **1**, showing the formation of a (010) sheet constructed from N–H···S hydrogen bonds (H atoms bonded to C atoms omitted for clarity).

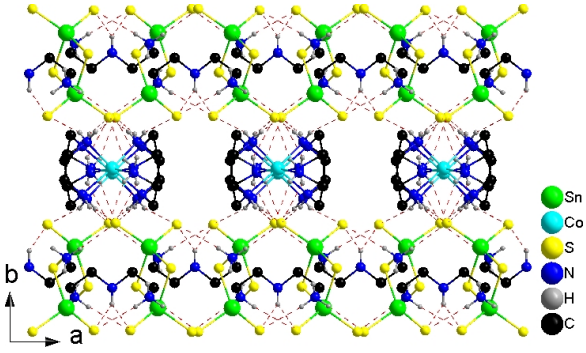

Fig. 4. View of the 3D supramolecular framework of **1** constructed by N–H···S hydrogen bonds (H atoms bonded to C atoms omitted for clarity).

be observed from the axial N–Co–N angles varying from 167.17(14) to 72.07(11)°.

The protonated amine species H_2dien^{2+} in **1** are arranged in chains propagating along the [101] direction and held there *via* weak hydrogen bonds N–H···S. These chains are aligned in an antiparallel fashion. The hydrogen bonds show H···S distances ranging from 2.33(4) to 2.606(16) Å and N–H···S angles ranging from 165(4) to 170(3)°, which results in a 2D layer within the (010) plane (Fig. 3). The $[Co(dien)_2]^{2+}$ cations behave as pillars joining these layers to give an overall 3D supramolecular architecture by intermolecular hydrogen bonds between the terminal S atoms and H–N groups of $[Co(dien)_2]^{2+}$ cations (Fig. 4).

$[Zn(tren)]_2Sn_2S_6$ (**2**) crystallizes in the monoclinic space group $C2/c$ with eight formula units in a unit cell. The coordination geometry of the Zn^{2+} center is a distorted trigonal bipyramid comprised of four N atoms of a tren ligand, and one S atom of a

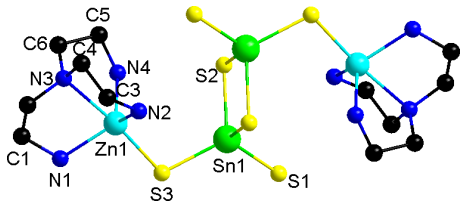

Fig. 5. Crystal structure of **2** with labeling scheme (hydrogen atoms omitted for clarity).

$[Sn_2S_6]^{4-}$ anion (Fig. 5). The $[Sn_2S_6]^{4-}$ anion connects two $[Zn(tren)]^{2+}$ units *via* the *trans* terminal S atoms forming neutral $[Zn(tren)]_2Sn_2S_6$ moieties with a center of inversion. Tris(2-aminoethyl)amine (tren), which is an isomer of triethylenetetramine (teta), was formed by the rearrangement of teta in the solvothermal reaction. This phenomenon has also been observed in the formation of $[B_5O_7(OH)_3Zn(tren)]$ [13] and $[Zn(tren)(\mu\text{-teta})_{0.5}][InTe_2]Cl$ [14]. The Zn–N distances in the range from 2.070(7) to 2.374(7) Å are comparable to those found in other $[Zn(tren)]^{2+}$ cations [13, 14]. The Zn–S distance of 2.369(3) Å is close to that of the Zn–S bond (2.325(1) Å) in $[Ge_3S_6Zn(H_2O)S_3Zn(H_2O)][(Zn(tren)(H_2O)]$ [15]. The moderate distortion of the ZnN_4S polyhedron is manifested by the axial *trans*-N–Zn–S angle of 174.23(19)° and the *cis*-angles in the range 77.6(3)–121.1(3)°. The Sn–S distances are in agreement with corresponding bond lengths of the discrete $[Sn_2S_6]^{4-}$ anions [6 – 10], but the slightly elongated Sn1–S3 distance (2.349(2) Å) shows the influence of the coordination of the S3 atom to the Zn^{2+} ion.

The S atoms of $[Zn(tren)]_2Sn_2S_6$ are involved in N–H···S hydrogen bonding with adjacent ions resulting in a 2D extended layer structure parallel to the (001) plane (Fig. 6). The H···S distances are ranging from 2.55 to 2.97 Å and the N–H···S angles vary from 119.2 to 166.1°, which is in accordance with the values reported in the literature [6 – 10]. These layers are stacked along the *c* axis in an -ABA- sequence (Fig. 7). The layer separation is about 12.15 Å, calculated as the shortest S2 to S2 distance between the layers. It is noteworthy that organic amines as structure-directing agents in previously reported cases are accommodated in voids of the structures where they often interact with the inorganic framework by hydrogen bonds [16], while the tren amines in **2** only decorate both sides of the layers.

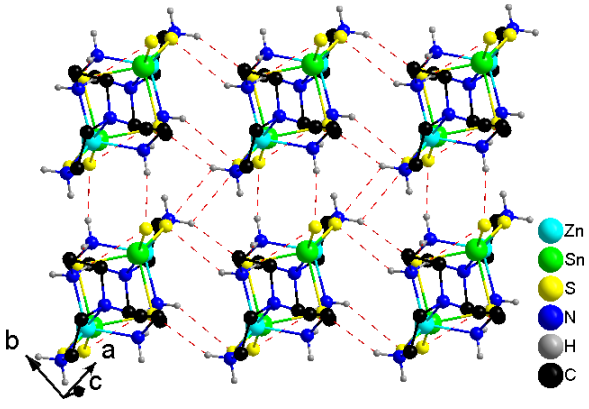

Fig. 6. Part of the crystal structure of **2**, showing the formation of a (001) sheet constructed from N–H···S hydrogen bonds (H atoms bonded to C atoms omitted for clarity).

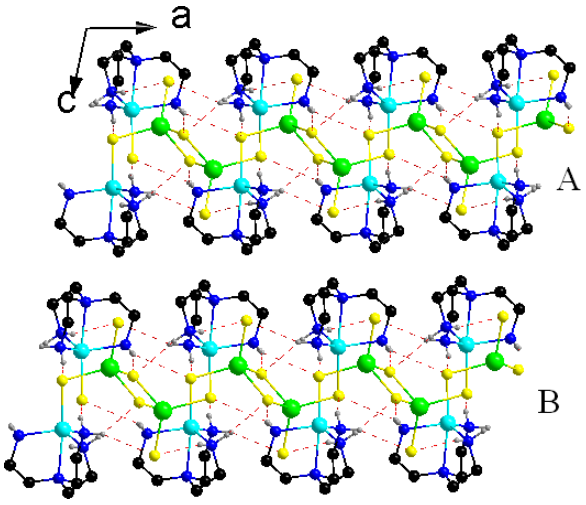

Fig. 7. The stacking sequence of the layers of **2** described as type ABA (H atoms bonded to C atoms omitted for clarity).

The arrangement of the $[Sn_2S_6]^{4-}$ anions in **1** is significantly different from that of $[Mn(dien)_2]_2Sn_2S_6$ [10b] and $[Ni(dien)_2]_2Sn_2S_6$ [10a]. In the former, there are two crystallographically independent *u-fac*-$[Mn(dien)_2]^{2+}$ ions in the fundamental unit, and the anions display two different orientations and are arranged alternately along the *c* axis (Fig. 8a). Although the conformation of the $[Co(dien)_2]^{2+}$ ion in **1** is the same as that of the $[Mn(dien)_2]^{2+}$ ion, the anions with identical orientation in **1** are arranged in a rod-like manner along the *b* and *c* axis (Fig. 8b), which could be due to one protonated H_2dien ion instead of one $[Mn(dien)_2]^{2+}$ ion. The $[Ni(dien)_2]^{2+}$ ion in the latter displays a different configuration (*s-fac*) (Fig. 2b), resulting in a different arrangement of the $[Sn_2S_6]^{4-}$ anions. Two directionally different $[Sn_2S_6]^{4-}$ anions are arranged alternately in a rod-like manner along

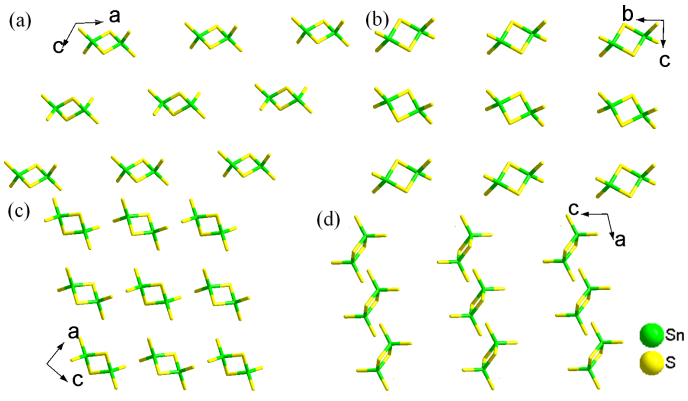

Fig. 8. The packing of the $[Sn_2S_6]^{4-}$ anions in $[Mn(dien)_2]_2Sn_2S_6$ (a) [10b], **1** (b), $[Ni(dien)_2]_2Sn_2S_6$ (c) [10a], and **2** (d).

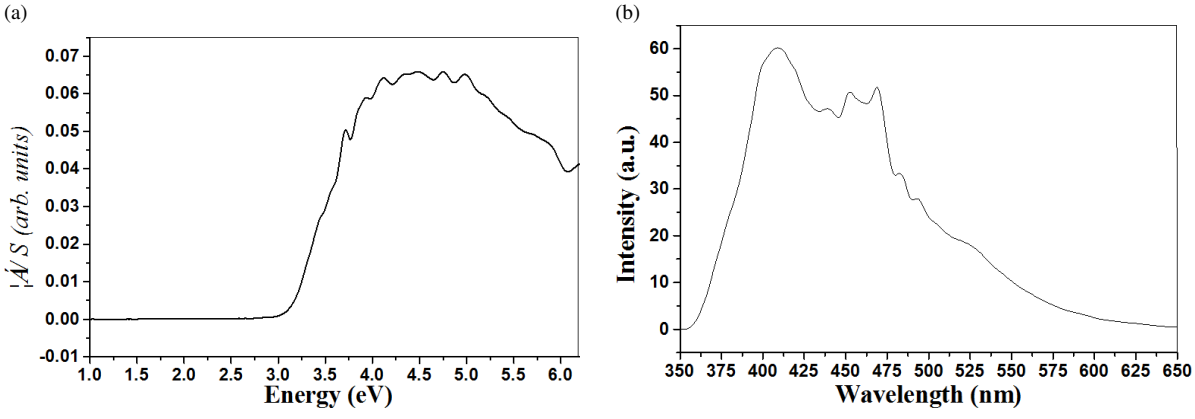

Fig. 9. (a) Solid-state optical absorption spectrum of **2**. (b) Solid-state emission spectrum of **2** at r. t.

the *a* and *c* axis, respectively (Fig. 8c). One directional kind of $[Sn_2S_6]^{4-}$ anion is surrounded by four of directionally different $[Sn_2S_6]^{4-}$ anions. The $[Sn_2S_6]^{4-}$ anions in **2** are isolated from the $[Zn(tren)]^{2+}$ cations. The $[Sn_2S_6]^{4-}$ anions form rods parallel to the *a* axis. These rods are arranged in a pseudo-layer fashion within the (001) plane. The pseudo-layers with different orientations are further stacked in ABA fashion along the *c* axis (Fig. 8d). Clearly, the different cations have a significant effect on the packing of the $[Sn_2S_6]^{4-}$ anions.

The UV/Vis absorption spectrum of **2** (Fig. 9a) was calculated from the diffuse reflectance data by using the Kubelka-Munk function [17]. The colorless crystals of **2** do not show any UV/Vis absorption below 3.00 eV, suggesting that **2** could be used for optical window applications. The optical band gaps (E_{onset}) obtained by extrapolation of the linear portion of the absorption edges are estimated to be 3.12 eV, which can be assigned to the lowest possible electronic excitation of the anion. This value is to be compared with that of the thiostannate $[Na_{10}(H_2O)_{32}][Zn_5Sn(\mu_3\text{-}S)_4(SnS_4)_4]\cdot 2H_2O$ (3.3 eV) [18], which exhibits the properties of a wide-band-gap semiconductor. The luminescence spectrum of **2** excited with light above the band gap of 3.76 eV (330 nm) shows emission bands at 409, 452, and 469 nm (Fig. 9b).

Experimental Section

General: All analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer from dry KBr pellets. Elemental analysis was carried out on an EA-1110 elemental analyzer. Fluorescence spectral analyses were performed using a Cary Eclips fluorescence spectrometer. The UV/Vis spectra were recorded at room temperature using a computer-controlled PE Lambda 900 UV/Vis spectrometer equipped with an integrating sphere in the wavelength range of 190 – 2000 nm.

*Synthesis of $[Co(dien)_2](H_2dien)Sn_2S_6$ (**1**)*

$[Co(dien)_2](H_2dien)Sn_2S_6$ (**1**) was synthesized hydrothermally in a 23-mL Teflon-lined autoclave by heating

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

	1	**2**
Formula	$C_{12}H_{41}CoN_9S_6Sn_2$	$C_{12}H_{36}N_8S_6Sn_2Zn_2$
M_r	800.31	853.11
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$
a, Å	8.8601(18)	12.211(2)
b, Å	22.798(5)	9.7335(19)
c, Å	14.419(3)	23.386(5)
β, deg	106.4500(10)	102.77(3)
V, Å^3	2897.0(10)	2710.8(9)
Z	4	4
T, K	293(2)	293(2)
Density (calcd.), g cm^{-3}	1.84	2.09
Abs. coeff., mm^{-1}	2.729	4.050
$F(000)$, e	1596	1680
2θ (max), deg	50.16	50.20
Total reflns. collected	7730	6583
Unique reflns.	2562	2349
No. of ref. param.	169	136
$R1$ [$I \geq 2\sigma(I)$]	0.0241	0.0594
$wR2$ (all data)	0.0554	0.1529
GOF on F^2	1.036	1.012
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.43 / −0.50	1.85 / −1.68

a mixture of Co (0.0143 g), Sn (0.0379 g), S (0.0351 g), and dien (2 mL) at 160 °C for 14 d. After the mixture was slowly cooled to room temperature, yellow crystals were obtained (yield: 35 % based on Sn). – Anal. for **1**: calcd. C 18.01, H 5.16, N 15.75; found C 17.97, H 5.23, N 15.68. – IR (KBr disk, cm^{-1}): v = 3231(m), 3155(m), 3086(m), 2965(m), 2872(m), 1626(w), 1569(w), 1505(vw), 1460(m), 1395(m), 1367(m), 1314(m), 1267(m), 1123(s), 1076(s), 1018(s), 978(s), 885(m), 752(m), 677(m), 591(w), 528(m), 493(vw), 417(s).

*Synthesis of [Zn(tren)]$_2$Sn$_2$S$_6$ (**2**)*

[Zn(tren)]$_2$Sn$_2$S$_6$ (**2**) was synthesized hydrothermally in a 23-mL Teflon-lined autoclave by heating a mixture of Zn (0.0142 g), Sn (0.0377 g), S (0.0375 g), and teta (2 mL) at 170 °C for 10 d. After the mixture was slowly cooled to r. t., colorless crystals were obtained (yield: 65 % based on Sn). – Anal. for **2**: calcd. C 16.90, H 4.25, N 13.14; found C 16.97, H 4.36, N 13.23. – IR (KBr disk, cm^{-1}): v = 3215(m), 3150(m), 3067(m), 2952(w), 2862(w), 1562(m), 1459(m), 1396(m), 1357(m), 1306(m), 1261(m), 1133(s), 1075(vs), 1012(s), 986(s), 889(s), 749(vw), 672(m), 589(w), 525(s), 441(w).

X-Ray structure determination

Data collections were performed on a Rigaku Mercury CCD diffractometer with graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71073 Å) at 293(2) K with a maximum 2θ value of 50.20°. The intensities were corrected for Lorentz

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

1	Sn1–S1	2.3376(10)	Sn1–S3$^{\#1}$	2.4437(11)
	Sn1–S2	2.3436(9)	Sn1–S3	2.4564(10)
	Co1–N3	2.136(3)	Co1–N2	2.209(3)
	Co1–N1	2.164(3)		
	S1–Sn1–S2	113.65(4)	S1–Sn1–S3	111.57(3)
	S1–Sn1–S3$^{\#1}$	112.65(4)	S2–Sn1–S3	112.90(4)
	S2–Sn1–S3$^{\#1}$	111.10(4)	S3$^{\#1}$–Sn1–S3	93.33(3)
	N3–Co1–N3$^{\#2}$	98.02(15)	N1$^{\#2}$–Co1–N2$^{\#2}$	79.43(10)
	N3–Co1–N1$^{\#2}$	93.09(11)	N1–Co1–N2$^{\#2}$	92.51(10)
	N3$^{\#2}$–Co1–N1$^{\#2}$	95.32(11)	N3–Co1–N2	80.23(10)
	N3–Co1–N1	95.32(11)	N3$^{\#2}$–Co1–N2	172.07(11)
	N3$^{\#2}$–Co1–N1	93.09(10)	N1$^{\#2}$–Co1–N2	92.51(10)
	N1$^{\#2}$–Co1–N1	167.17(14)	N1–Co1–N2	79.43(10)
	N3–Co1–N2$^{\#2}$	172.07(11)	N2$^{\#2}$–Co1–N2	102.55(14)
	N3$^{\#2}$–Co1–N2$^{\#2}$	80.23(10)		
2	Zn1–N4	2.070(7)	Zn1–N2	2.080(7)
	Zn1–N1	2.115(8)	Zn1–S3	2.369(3)
	Zn1–N3	2.374(7)	Sn1–S1	2.304(2)
	Sn1–S3	2.349(2)	Sn1–S2	2.453(2)
	Sn1–S2$^{\#3}$	2.457(2)		
	N4–Zn1–N2	114.5(3)	N4–Zn1–N1	111.2(3)
	N2–Zn1–N1	121.1(3)	N4–Zn1–S3	104.6(2)
	N2–Zn1–S3	105.7(2)	N1–Zn1–S3	96.5(2)
	N4–Zn1–N3	77.9(3)	N2–Zn1–N3	77.6(3)
	N1–Zn1–N3	77.7(3)	S3–Zn1–N3	174.23(19)
	S1–Sn1–S3	115.35(9)	S1–Sn1–S2	111.05(9)
	S3–Sn1–S2	114.55(8)	S1–Sn1–S2$^{\#3}$	111.73(8)
	S3–Sn1–S2$^{\#3}$	109.29(7)	S2–Sn1–S2$^{\#3}$	92.64(7)
	Sn1–S2–Sn1$^{\#3}$	87.36(7)		

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

Table 3. Hydrogen bond geometries for **1** (Å and deg)[a].

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N1–H1A···S2$^{\#2}$	0.90	2.89	3.655(3)	143.3
N1–H1B···S2$^{\#1}$	0.90	2.57	3.390(3)	151.3
N2–H2···S2	0.91	2.63	3.455(3)	151.2
N3–H3A···S2$^{\#3}$	0.90	2.61	3.507(3)	175.6
N3–H3B···S1$^{\#2}$	0.90	2.78	3.527(3)	140.8
N4–H4E···S2	0.90(3)	2.40(3)	3.285(4)	168(3)
N4–H4D···S1$^{\#4}$	0.90(3)	2.606(16)	3.482(4)	165(4)
N5–H5···S1$^{\#4}$	0.88(4)	2.33(4)	3.209(3)	170(3)

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, y, -z+3/2$; $^{\#2}$ $x, -y+1, z+1/2$; $^{\#3}$ $-x, -y+1, -z+1$; $^{\#4}$ $x-1, y, z$.

Table 4. Hydrogen bond geometries for **2** (Å and deg)[a].

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N1–H1B···S2$^{\#2}$	0.90	2.70	3.517(9)	151.8
N1–H1B···S3$^{\#3}$	0.90	2.97	3.494(9)	119.2
N2–H2A···S3$^{\#4}$	0.90	2.86	3.603(8)	140.3
N2–H2B···S1$^{\#1}$	0.90	2.71	3.568(9)	160.0
N4–H4A···S2	0.90	2.55	3.428(8)	166.1
N4–H4B···S1$^{\#5}$	0.90	2.62	3.466(8)	156.0

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x+1, -y, -z+1$; $^{\#2}$ $x+1/2, y-1/2, z$; $^{\#3}$ $-x+2, -y, -z+1$; $^{\#4}$ $-x+3/2, -y-1/2, -z+1$; $^{\#5}$ $-x+3/2, -y+1/2, -z+1$.

and polarization effects. The structures were solved with Direct Methods using SHELXS-97 [19], and the refinement was performed against F^2 using SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically. The C4 and H4c atoms were disordered over two positions with occupation factors of 0.5 and 0.5. The H atoms on N4, N5, C5, and C6 atoms were located in a difference map and refined, while other H atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal data collection and refinement results can be found in Table 1. Selected bond lengths and angles for compounds **1** – **2** are listed in Table 2. Hydrogen bonds for **1** and **2** are listed in Table 3 and Table 4, respectively.

CCDC 780652 (**1**) and 780653 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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