A New Type of 1-D Thioindates, $[M(\text{en})_3]_{0.5}[\text{InS}_2]$ (M = Co, Ni), Synthesized by Solvothermal Reaction

Jian Zhou[a,b], Yong Zhang[a], Ming-Hui Zhang[a], Zhi-Xin Lei[a], and Jie Dai[a]

[a] Department of Chemistry and Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215123, P. R. China
[b] Department of Chemistry and Biology, Yulin Normal University, Yulin 537000, P. R. China

Reprint requests to Prof. J. Dai. E-mail: daijie@suda.edu.cn

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Two thioindates $[M(\text{en})_3]_{0.5}\text{InS}_2$ [en = ethylenediamine; M = Ni (**1**), Co (**2**)] were prepared by the reaction of In_2S_3, Ni (or Co) and S under solvothermal conditions, and their crystal structures have been determined. Both compounds are isostructural and crystallize in the orthorhombic space group *Cmcm*. The crystal structures consist of a new type of 1-D sinusoidal chain, which complements the reported I – III types of 1-D $[\text{In}Q_2^{\,-}]_n$ (Q = S, Te) anions built from $\text{In}Q_4$ tetrahedra. The band gaps of 3.47 eV for **1** and 3.31 eV for **2** have been derived from optical absorption spectra.

Key words: Solvothermal Synthesis, Crystal Structure, Thioindate, One-dimensional

Introduction

The mild solvothermal reaction in organic amines as templates or structure-directing agents has been applied increasingly to the synthesis of main group chalcogenometalates [1 – 5]. With this method, a number of chalcogenidoindates have been obtained in the presence of suitable counter cations that are either protonated amines or transition metal complex cations [6 – 9]. The structures of these materials are usually based on supertetrahedral clusters (T_n) or simple tetrahedra $\text{In}Q_4$ (Q = S, Se, Te) as building blocks. The supertetrahedral units, which are constructed from a number of simple tetrahedra $\text{In}Q_4$, are connected *via* their vertices to form 2 – 3-D structures, as exemplified by $[(\text{CH}_2\text{CH}_3)_2\text{NH}_2]_7\text{In}_{11}\text{S}_{21}\text{H}_2$ (T_3) [10], $[\text{In}_{10}\text{Se}_{18}](\text{tetaH}_2)_3$ (T_3, teta = triethylenetetramine) [11], $\text{Cd}_4\text{In}_{16}\text{S}_{33}\cdot(\text{H}_2\text{O})_{20}(\text{bappH}_4)_{2.5}$ (T_4, bapp = 1,4-bis(3-aminopropyl)piperazine) [12], and $(\text{In}_{34}\text{S}_{54})(\text{In}_{10}\text{S}_{18})(\text{C}_{11}\text{H}_{24}\text{N}_2)_6$ (T_5 and T_3, $\text{C}_{11}\text{H}_{22}\text{N}_2$ = dipiperidinomethane) [13]. On the other hand, condensation of tetrahedral $\text{In}Q_4$ species through corner- or edge-sharing also results in 2 – 3-D open frameworks, such as $[\text{dpaH}]_3\text{In}_6\text{S}_{11}\text{H}$ (dpa = dipropylamine) [14], $[\text{C}_7\text{H}_{10}\text{N}][\text{In}_9\text{Se}_{14}]$ ($\text{C}_7\text{H}_9\text{N}$ = 3,5-dimethylpyridine) [15], $[\text{tmdpH}_2]_{6.5}[\text{In}_{33}\text{S}_{56}]$ (tmdp = 4,4′-trimethylenedipiperidine) [16], and $[\text{tetaH}_4]_{3.25}[\text{In}_{33}\text{Te}_{56}]$ (teta = triethylenetetramine) [16]. These anions are charge-compensated by protonated organic amine cations, which are accommodated in the cavities or the channels of the open frameworks.

Besides the aforementioned organoammonium cations, transition metal complex ions can also act as counter ions. But in these cases, the indium-chalcogen anions usually form 1-D chain structures under mild solvothermal conditions. Noteworthy examples include $[\text{In}_2\text{Te}_6^{\,2-}]_n$ chains constructed of fused five-membered rings $[(\text{In}^{3+})_2(\text{Te}_2^{\,2-})(\text{Te}^{2-})]$ joined at the In atoms, such as $[M(\text{en})_3][\text{In}_2\text{Te}_6]$ (M = Fe, Zn) [17], α- and β-$[\text{Mo}_3(\text{en})_3(\mu_2\text{-Te}_2)_3(\mu_3\text{-Te})(\mu_3\text{-O})][\text{In}_2\text{Te}_6]$ [17]. Other 1-D $[\text{InQ}_2^{\,-}]_\infty$ chains built up from InQ_4 tetrahedra sharing opposite edges were observed in $[\text{La}(\text{en})_4\text{Cl}][\text{In}_2\text{Te}_4]$ [18], $[\text{Zn}(\text{taa})(\mu\text{-tren})_{0.5}][\text{InTe}_2]\text{Cl}$ [9] and $[\text{Ni}(\text{dap})_3]_{0.5}[\text{InS}_2]$ [8], but these chains have C_{2v} symmetry with the C_2 axis along the chain axis, which ensures that all the central metal atoms are arranged in a straight line (Fig. 1a, type I). More recently, we reported some new types of 1-D chains with the formula $[\text{In}Q_2^{\,-}]_\infty$. The compounds $[M(\text{en})_3][\text{In}_2\text{Te}_4]\cdot(\text{en})$ (M = Ni, Co) [9] and $[\text{Ni}(\text{dien})_2]_{0.5}[\text{InS}_2]$ [8] contain 1-D sinusoidal chains with $[\text{In}_4Q_8]^{4-}$ (Q = S, Te) periodic units (Fig. 1b, type II), and the compounds $[M(\text{en})_3]_2[\text{In}_4\text{Te}_8]\cdot(\text{en})_{0.5}$ (M = Mn, Fe, Zn) [9] consist of another 1-D sinusoidal chain type with $[\text{In}_8\text{Te}_{16}]^{8-}$ periodic units (Fig. 1c, type III). As an extension of these studies, we have successfully isolated two thioindates $[M(\text{en})_3]_{0.5}[\text{InS}_2]$ [en = ethylenediamine; M = Ni (**1**),

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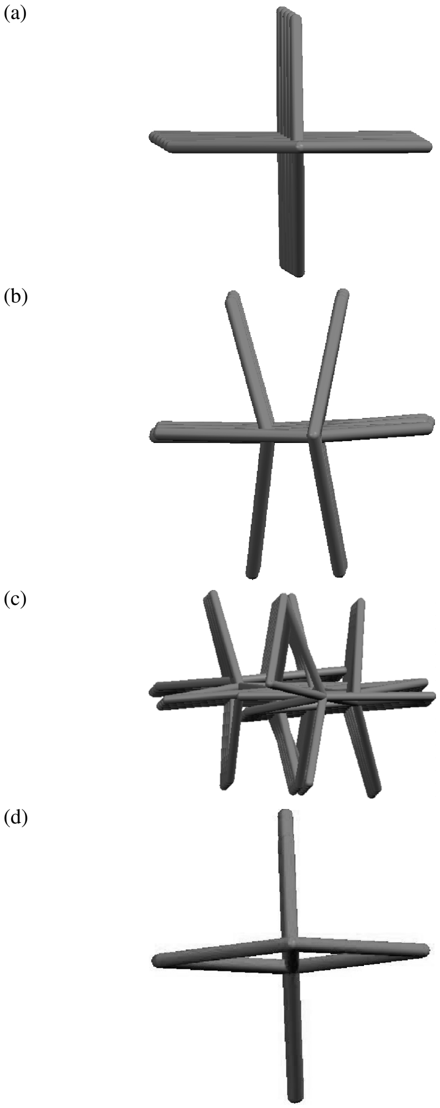

Fig. 1. View of the 1-D chains along the axial direction, showing the type-I (a), type-II (b), type-III (c), and type-IV (d) structures.

Co (**2**)] from the system $M/\mathrm{In}_2\mathrm{S}_3/\mathrm{S}/\mathrm{en}/\mathrm{H}_2\mathrm{O}$ under solvothermal conditions. The crystal structures of the present compounds contain a new type of 1-D $[\mathrm{In}Q_2{}^-]_n$ anionic chain with transition metal complex cations as counterions (Fig. 1d).

Experimental Section

Materials and physical measurements

All analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. Raman spectra were recorded on a Nicolet FT-Raman 960 spectrometer (200 mW, 128 scans). Elemental analyses were carried out on an EA 1110 elemental analyzer. Room-temperature optical diffuse reflectance spectra of the powdered samples were obtained with a Shimadzu UV-3150 spectrometer.

Synthesis of $[\mathrm{Ni(en)}_3]_{0.5}[\mathrm{InS}_2]$ *(**1**)*

$[\mathrm{Ni(en)}_3]_{0.5}[\mathrm{InS}_2]$ was obtained in nearly 35 % yield by the reaction of metallic nickel (0.0181 g, 0.2 mmol), $\mathrm{In}_2\mathrm{S}_3$ (0.0244 g, 0.2 mmol) and sulfur (0.016 g, 0.5 mmol) in 1.5 mL of an aqueous solution of en (70 %). The reagents were placed in a thick Pyrex tube (*ca.* 20 cm long). The sealed tube was heated at about 160 °C for 5 d to yield purple block-shaped crystals. The crystals were washed with ethanol and diethyl ether, dried and stored under vacuum. The compound is stable in air, in water and in acetone. C, H, N analysis (%): calcd. C 10.88, H 3.02, N 8.36; found C 10.76, H 3.09, N 8.44. – IR: ν = 3289(vs), 3241(vs), 2925(m), 2878(m), 1574(m), 1458(w), 1389(w), 1335(w), 1281(w), 1196(w), 1111(m), 1019(vs), 664(m), 609(m), 517(m) cm^{-1}.

Synthesis of $[\mathrm{Co(en)}_3]_{0.5}[\mathrm{InS}_2]$ *(**2**)*

The red crystals of $[\mathrm{Co(en)}_3]_{0.5}[\mathrm{InS}_2]$ were prepared by a similar method as used in the synthesis of the crystals of **1** except that Ni was replaced by Co powder (yield 52 %, based on In). C, H, N analysis (%): calcd. C 10.88, H 3.02, N 8.46; found C 10.75, H 3.07, N 8.38. – IR: ν = 3280(vs), 3241(vs), 2925(w), 2827(w), 1636(m), 1574(m), 1459(w), 1389(vw), 1335(w), 1250(vs), 1196(vs), 1142(w), 1111(vw), 1057(m), 1011(m), 795(m), 648(m), 587(m), 501(m) cm^{-1}.

X-Ray structure determination

A summary of the crystal data and refinement parameters is given in Table 1. Data were collected with a Rigaku Mercury CCD diffractometer at 223(2) K using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) by an ω-scan method with a maximum 2θ value of 50.70°. A light-purple block-shaped crystal of **1** and a light-red crystal of **2** were used for data collection. An absorption correction was applied for both compounds using a multi-scan correction method. The structures were solved by Direct Methods using the program SHELXS-97 [19]. The refinement was performed against F^2 using SHELXL-97 [20]. All non-hydrogen atoms were refined anisotropically, while the H atoms at the C and N atoms were not dealt with because of the disorder of all C atoms, the N3 atom in **1** and the N1 atom in **2**.

CCDC 685791 (**1**) and 6CCDC 85792 (**2**) contain the supplementary crystallographic data for this paper. These

Table 1. Crystal data and summary of X-ray data collection and refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{12}H_{48}In_4N_{12}Ni_2S_8$	$C_{12}H_{48}Co_2In_4N_{12}S_8$
Fw	1193.46	1193.94
Color of crystal	light-purple	light-red
Crystal dimens., mm^3	0.30 × 0.24 × 0.12	0.13 × 0.10 × 0.06
Crystal system	orthorhombic	orthorhombic
Space group	*Cmcm*	*Cmcm*
a, Å	9.6465(15)	9.658(3)
b, Å	15.050(2)	15.074(4)
c, Å	13.085(2)	13.087(3)
V, Å^3	1899.7(5)	1905.3(9)
Z	2	2
T, K	223(2)	223(2)
Calcd density, g cm^{-3}	2.09	2.08
Abs coef., mm^{-1}	3.8	3.7
$F(000)$, e	1072	1068
2θ (max), deg	50.68	50.70
Total reflns. collected	8955	9114
Unique reflns.	966	968
No. of ref. param.	73	73
$R1^a$ (F) $[I \geq 2\sigma(I)]$	0.0295	0.0521
$wR2^b$ (F^2) (all data)	0.0785	0.1140
A/B^b (weighting scheme)	0.0348/12.1528	0.0361/41.6870
GOF^c (F^2)	1.193	1.151
$\Delta\rho_{\text{fin}}$ (max/min), e Å^{-3}	0.89/−0.74	0.99/−0.85

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o{}^2,0) + 2F_c{}^2)/3$; [c] $\text{GOF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

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

1	In1–S1	2.4716(16)	In1–S2	2.4706(13)
	In1–S3	2.4374(17)	In1–In1$^{\#1}$	3.2487(9)
	In1–In1$^{\#2}$	3.3107(9)	Ni1–N1	2.133(5)
	Ni1–N2	2.154(5)	Ni1–N3	2.141(7)
	S2–In1–S1	119.18(3)	S3–In1–S1	95.18(5)
	S3–In1–S2	113.28(3)	S2$^{\#1}$–In1–S2	97.78(5)
	N1–Ni1–N1$^{\#3}$	80.7(3)	N1–Ni1–N3	170.31(19)
	N1$^{\#3}$–Ni1–N3	93.7(2)	N3–Ni1–N3$^{\#5}$	92.9(4)
	N3–Ni1–N3$^{\#3}$	90.7(4)	N3$^{\#4}$–Ni1–N2$^{\#5}$	79.45(19)
	N1–Ni1–N2	92.87(12)	N3$^{\#4}$–Ni1–N2	95.31(19)
	N3–Ni1–N2	79.45(19)	N2$^{\#5}$–Ni1–N2	172.5(3)
2	In1–S1	2.474(3)	In1–S2	2.442(3)
	In1–S3	2.470(2)	In1–In1$^{\#6}$	3.2517(17)
	In1–In1$^{\#7}$	3.3093(17)	Co1–N1	2.178(12)
	Co1–N3	2.185(10)	Co1–N2	2.205(10)
	S2–In1–S3	113.16(5)	S3–In1–S3$^{\#6}$	97.68(10)
	S2–In1–S1	95.37(9)	S3–In1–S1	119.24(5)
	N1$^{\#9}$–Co1–N1	90.2(7)	N1$^{\#10}$–Co1–N1	92.8(7)
	N1–Co1–N3$^{\#9}$	94.8(4)	N1–Co1–N3	169.3(4)
	N3$^{\#9}$–Co1–N3	78.8(5)	N1$^{\#8}$–Co1–N2	95.7(4)
	N1–Co1–N2	78.5(4)	N3–Co1–N2	93.24(19)
	N2–Co1–N2$^{\#10}$	171.6(5)		

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y+1, -z+1$; $^{\#2}$ $-x, y, -z+3/2$; $^{\#3}$ $-x+1, y, z$; $^{\#4}$ $x, y, -z+3/2$; $^{\#5}$ $-x+1, y, -z+3/2$; $^{\#6}$ $-x+2, -y, -z$; $^{\#7}$ $-x+2, y, -z+1/2$; $^{\#8}$ $x, y, -z+1/2$; $^{\#9}$ $-x+1, y, z$; $^{\#10}$ $-x+1, y, -z+1/2$.

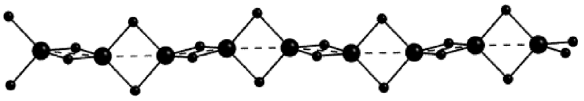

Fig. 2. View of a fragment of the $[\text{InS}_2{}^-]_n$ chain in **1**.

data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/-data_request/cif.

Results and Discussion

Syntheses of the compounds

The telluroindates with transition metal complex cations are generally obtained from $InCl_3/MCl_x/A_yTe/Te$/amine (x = 2,3; y = 1,2; A = alkali or alkaline earth metal) or $InCl_3/MCl_2$/Te/amine mixtures under solvothermal conditions, to produce $[M(\text{en})_3][\text{In}_2\text{Te}_6]$ (M = Fe, Zn) [17], $[\text{La}(\text{en})_4\text{Cl}][\text{In}_2\text{Te}_4]$ [18] or $[M(\text{en})_3][\text{In}_2\text{Te}_4] \cdot \text{en}$ (M = Ni, Co) [9]. Metal chlorides have been employed in these reactions as a source of metal ions. Cl^- ion is an effective mineralizer [21]. A_yTe or Te are used as sources of $\text{Te}_z{}^{2-}$ ($z \geq 1$) anions. Attempts to synthesize the related thioindates by a similar method had failed, and compounds $M(\text{en})_3\text{Cl}_2$ were the usual products. The crystal structure of $\text{Ni}(\text{en})_3\text{Cl}_2$ has been determined by single crystal X-ray analysis. To insure that Cl^- ions are not incorporated into the final structures, metal powder and In_2S_3 were now used as the source material instead of metal chlorides for the solvothermal synthesis of the thioindates. However, in pure amine solvents, no high-quality single crystals could be obtained. In this work, better quality and larger crystals of $[M(\text{en})_3]_{0.5}[\text{InS}_2]$ were successfully obtained by adding small amounts of water (lower boiling point and viscosity) to the reaction system.

Structure description

Compounds **1** and **2** are isostructural and crystallize in the orthorhombic space group *Cmcm* with four formula units in the unit cell. The 1-D polymeric structures of **1** and **2** show a new type of sinusoidal anionic chains $[\text{In}_4\text{S}_8^{4-}]_n$ (type IV, Fig. 1d) constructed of InS_4 tetrahedra sharing opposite edges and propagating along the crystallographic c axis (Fig. 2). There are two kinds of In–In distances, 3.2487(9) Å for In1–In1B and 3.3107(9) Å for In1–In1A (symmetry operations: (A) $-x$, y, $1.5-z$; (B) $-x$, $1-y$, $1-z$),

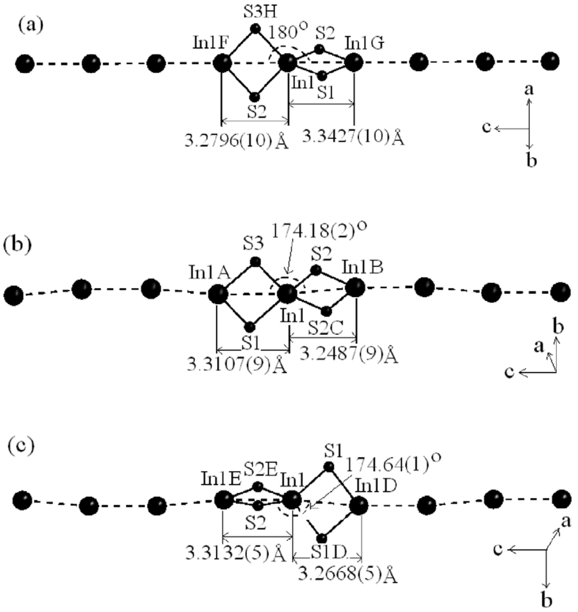

Fig. 3. View of the arrangement of the indium atoms along the 1-D chains in $[\text{Ni(dap)}_3]_{0.5}[\text{InS}_2]$ (a), $[\text{Ni(en)}_3]_{0.5}$-$[\text{InS}_2]$ (b) and $[\text{Ni(dien)}_2]_{0.5}[\text{InS}_2]$ (c) (Symmetry operations: (A) $-x$, y, $1.5-z$; (B) $-x$, $1-y$, $1-z$; (C) $-x$, $1-y$, $1-z$; (D) $1-x$, $1-y$, $1-z$; (E) $1-x$, y, $1.5-z$; (F) x, $-y$, $1-z$; (G) $1-x$, y, $0.5-z$; (H) $1-x$, $-y$, $1-z$).

along the $[\text{InS}_2{}^-]_n$ chain in **1**, comparable to those in other thioindates (Fig. 3b). The repeating units consist of four edge-sharing tetrahedra $[\text{In}_4\text{S}_8]^{4-}$ with periods of 13.085(2) Å for **1** and 13.087(3) Å for **2**, which are less than the sum of the four In–In distances (13.119 Å for **1** and 13.122 Å for **2**). Each InS_4 tetrahedron is slightly distorted with In–S distances in the range of 2.4374(17)–2.474(3) Å (Table 2).

The sinusoidal $[\text{InS}_2{}^-]_n$ chains in both compounds are different from those in type-I $[\text{In}Q_2{}^-]_n$ chains [8, 9, 18], where the anionic chains feature the straight-line structure. Although the dihedral angle (90°) between two adjacent In_2S_2 four-membered rings in **1** and **2** is equal to that in type-I compounds [8], the In–In–In angles are different: 180° for type-I compounds, but 174.18(2)° for **1** and 174.04(3)° for **2** (Figs. 3a and 3b), respectively. Hence, in type-I compounds, the sum of the four In–In distances are equal to the unit cell length.

The In atoms in **1** and **2** are arranged in a sinusoidal line, similar to those of type-II compounds (Fig. 3c). All four-membered rings In_2S_2 in these sinusoidal $[\text{InS}_2{}^-]_n$ chains are planar, but in type-II compounds some In_2Q_2 rings have a butterfly structure, and the dihedral angle between the wing planes is less than 180° [8, 9]. Considering compound $[\text{Ni(dien)}_2]_{0.5}[\text{InS}_2]$ [8] as example, the dihedral angle between the In1/In1E/S2 plane and In1/In1E/S2E plane (Fig. 3c) is 168.3°. When viewed down the axial direction (Figs. 1b and 1d), the conformations of the two types of the $[\text{InS}_2{}^-]_n$ chains are distinctly different. Therefore, the sinusoidal 1-D structures in **1** and **2** represent a new type of $[\text{In}Q_2{}^-]_n$ anionic chains (type IV).

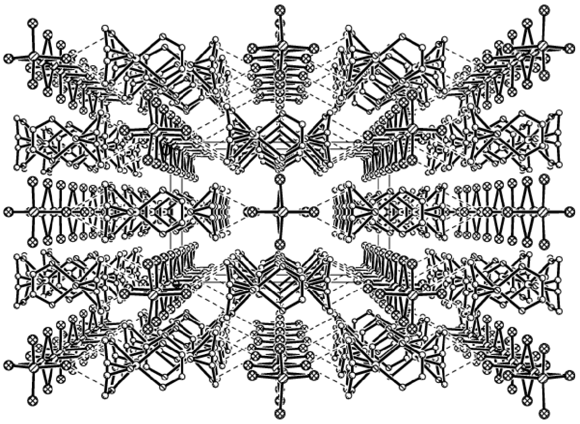

Fig. 4. Packing diagram of **2**, showing the hydrogen bond scheme.

The counterions to balance the charge of the 1-D $[\text{InS}_2{}^-]_n$ anions in **1** and **2** are transition metal complex cations with bidentate en ligands. The en ligands of the $[M(\text{en})_3]^{2+}$ cations are disordered in the crystal so that it is very difficult to determine the exact conformations of the $[\text{Ni(en)}_3]^{2+}$ and $[\text{Co(en)}_3]^{2+}$ cations. The Ni–N and Co–N bond lengths vary from 2.133(5) to 2.154(5) and from 2.178(12) to 2.205(10) Å, respectively, and lie within the range of other compounds containing $[M(\text{en})_3]^{2+}$ cations [9]. There exists weak N–H···S hydrogen bonds with distances varying from 3.288(13) to 3.290(7) Å, generating a 3-D hydrogen bond network structure with channels running parallel to the *c* axis (Fig. 4).

Optical properties

The optical properties of compounds **1** and **2** have been studied by UV/Vis/near-IR reflectance spectroscopy, as shown in Fig. 5. From the well-defined abrupt absorption edges the band gaps can be estimated as 3.45(2) eV for **1** and 3.30(2) eV for **2**, which can be assigned to the electronic excitation of the anions. The values are larger than those of other thioindates, such

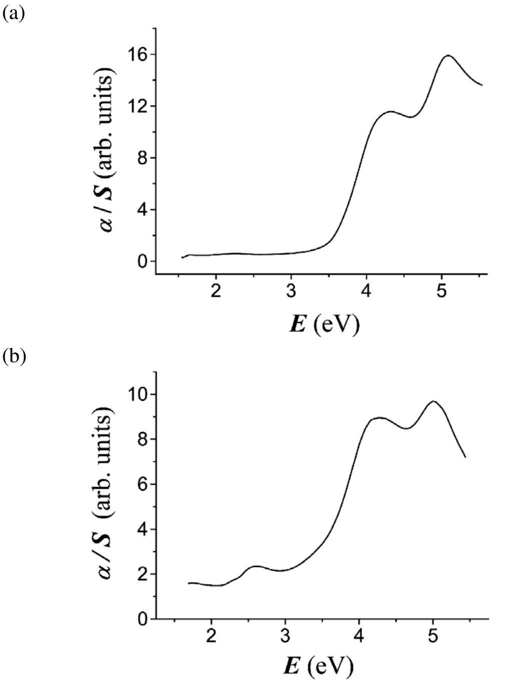

Fig. 5. Diffuse reflectance spectra for **1** (a) and **2** (b).

as $[\mathrm{In_8S_{13}(S_3)_{1/2}(SH)}][\mathrm{In_4S_6(S_3)_{1/2}(SH)}](\mathrm{TMDPH_2})_5$ (3.1 eV) [22] and $[\mathrm{Ni(tepa)}]_2[\mathrm{In_4S_7(SH)_2}]\cdot\mathrm{H_2O}$ (3.28 eV) [8]. The absorption at 2.58 eV in **2** can be attributed to *d-d* transition of Co(II), but no such band could be observed for **1**.

Conclusions

Two new 1-D thioindates with transition metal complex cations have been successfully synthesized by the solvothermal method in a mixed solvent of amine and water. The crystal structures of $[M(\mathrm{en})_3]_{0.5}[\mathrm{InS}_2]$ [M = Ni (**1**), Co (**2**)] consist of a new type of 1-D $[\mathrm{In}Q_2{}^-]_n$ chains built up from $\mathrm{In}Q_4$ tetrahedra sharing opposite edges with two special characteristics. The first is that the sinusoidal $[\mathrm{In}Q_2{}^-]_n$ chains are different from those in type I (Fig. 1a), which are generally straight. The second is that all four-membered rings In_2Q_2 in the sinusoidal $[\mathrm{In}Q_2{}^-]_n$ chains are planar, while those in types II and III (Figs. 1b, c) are not planar. Therefore, the present compounds **1** and **2** are new examples of 1-D $[\mathrm{In}Q_2{}^-]_n$ chains in chalcogenidoindates (type IV).

Acknowledgements

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