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1-D Selenidoindates $\{[In_2Se_5]\}_\infty$ Directed by Chiral Metal Complex Cations of 1,10-Phenanthroline

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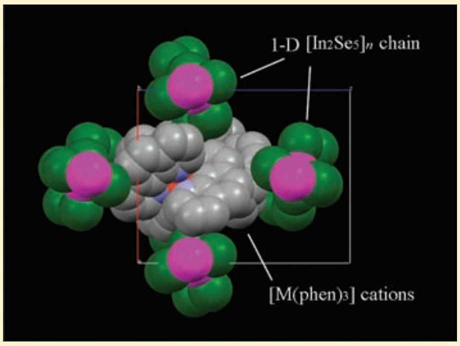
S Supporting Information

ABSTRACT: Two 1-D selenidoindates $\{[M(phen)_3]In_2Se_5 \cdot H_2O\}_n$ (M = Ni, Fe) were synthesized by a solvothermal method. The 1-D $\{[In_2Se_5]^{2-}\}_n$ anion is a new type of single 1-D structure constituted by an alternately fused four-membered In_2Se_2 ring and five-membered In_2Se_3 ring. The chalcogenoindates were separated as mechanical racemic mixtures of single enantiomer crystals, in which the R-helix of 1-D InSe anion is directed by the related clockwise (Δ) cations of $[M(phen)_3]^{2+}$ or the L-helix of 1-D anion is directed by the related anticlockwise (Λ) cation. The $\pi \cdots \pi$, C···Se, and C−H···Se oriented interactions of metal complex cations with selenidoindate anions play an important role in the formation of the chiral crystals. The embedded $[M(phen)_3]^{2+}$ cations improve the optical absorption of the 1-D semiconductor materials.



INTRODUCTION

Low-dimensional materials have been attracting great attention of chemists and physicists for several decades because of their inherent anisotropic physical−chemical properties.[1] Among these materials, one-dimensional main-group metal chalcogenometalates with the formula of $\{[MQ_2]^{n-}\}_\infty$ (M = metal, Q = S, Se, Te) represent a typical family of 1-D structure (Zweier single chain).[2−4] The anions of these compounds have a common structural character that the chains are built by MQ_4 tetrahedron sharing opposite edges. In addition, some 1-D structures of $\{[In_2Te_6]^{2-}\}_\infty$ anions are constructed by fused five-membered rings of $[In_2Te_3]$ joined at the In atoms.[5]

Lately, the solvothermal syntheses of inorganic−organic hybrid low-dimensional chalcogenometalates are of great interest not only for the diversity of their structural chemistry but also for the possible chirality introduced in by the metal complex cations.[6] Chirality and helicity are fundamental phenomena found in various biological systems. Recently, a few chiral chalcogenometalates of main-group metals directed by chiral $M(amine)_m{}^{n+}$ complex cations have been prepared.[7] As the $M(amine)_m{}^{n+}$ cations, the $[M(phen)_3]^{n+}$ (phen = 1,10-phenanthroline) cation is also a well-known chiral complex with clockwise (Δ) and anticlockwise (Λ) configurations and is used in preparation of chiral compounds and supramolecules.[8] However, in most cases, the chalcogenometalate with $[M(phen)_3]^{n+}$ cation as template or directing species is a chemically racemic mixture of achiral crystals; namely, both the Δ and Λ configurations coexist in a crystal.[9] Only limited such mechanical racemic mixtures of single enantiomer crystals have been reported until now based on our knowledge.[10]

Recently, we are engaged in the syntheses of single-phase materials with embedded $[M(phen)_3]^{n+}$ cations.[9] In this paper, we report 1-D selenidoindates $\{[M(phen)_3] \cdot In_2Se_5 \cdot H_2O\}_n$ (M = Ni (**1**) and Fe(**2**)). They are racemic mixtures of single enantiomer crystals in which homochiral 1-D InSe structure is directed by related homochiral $[M(phen)_3]^{2+}$ forming a chiral crystal. The oriented interactions of chiral complex cations with chiral selenidoindate anion in crystal structure are discussed. They are also rare examples of 1-D InSe materials with repeated unit of $[In_2Se_5]$.

EXPERIMENTAL SECTION

General Remarks. 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. Elemental analysis was 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. The absorption (α/S) data were calculated from the reflectance using the Kubelka−Munk function, $\alpha/S = (1 - R)^2/2R$,[11] where R is the reflectance at a given energy, α is the absorption, and S is the scattering coefficient. Thermoanalytical measurements were performed using a DCS-TGA microanalyzer of SDT 2960, and all the samples were heated under a nitrogen stream of 100 mL min^{-1} with a heating rate of 10 °C min^{-1}. PXRD of the products was carried out on a D/MAX-3C X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å). Circular dichroism (CD) spectra were recorded at ambient temperature on an AVIV-410 spectropolarimeter.

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Table 1. Crystal Data and Structural Refinement Parameters for 1, 1′, and 2

	1	**1′**	**2**
formula	$C_{36}H_{26}NiIn_2Se_5N_6O$	$C_{36}H_{26}NiIn_2Se_5N_6O$	$C_{36}H_{26}FeIn_2Se_5N_6O$
Fw	1241.78	1241.78	1238.90
cryst size (mm^3)	0.40 × 0.12 × 0.10	0.30 × 0.10 × 0.05	0.10 × 0.08 × 0.05
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	14.4859(19)	14.501(3)	14.498(4)
b (Å)	14.583(2)	14.584(3)	14.654(4)
c (Å)	18.137(3)	18.146(4)	17.852(5)
V (Å^3)	3831.4(10)	3837.6(13)	3792.8(17)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	2.153	2.146	2.116
F(000)	2352	2344	2336
μ (mm^{-1})	6.469	6.458	6.420
T (K)	223(2)	223(2)	223(2)
flack	0.00(3)	0.05(2)	0.07(2)
reflns collected	22273	15518	12125
unique reflns	6742	8273	6653
observed reflns	5849	5635	4564
no. params	460	460	416
GOF on F^2	1.076	1.044	1.031
$R_1/R_1[I > 2\sigma(I)]$	0.0909/0.0768	0.1137/0.0719	0.1240/0.0801
$_wR_2/_wR_2[I > 2\sigma(I)]$	0.1473/0.1407	0.1429/0.1205	0.1165/0.0999
$P_{max,\ min}$/e Å^{-3}	1.635, −0.852	0.817, −1.091	0.806, −0.748

Synthesis. *{[Ni(phen)$_3$]·In$_2$Se$_5$·H$_2$O}$_n$ (**1**).* Analytically pure indium powder (0.0114 g, 0.1 mmol), selenium powder (0.0079 g, 0.1 mmol), nickel powder (0.0059 g, 0.1 mmol), and 1,10-phenanthroline (0.0595 g, 0.3 mmol) were mixed in a 2 mL solvent of di-*n*-butylamine/H_2O (4:1 in V/V). The mixture was placed in a thick Pyrex tube (ca. 15 cm long). The sealed tube was heated under autogenous pressure at about 140 °C for 4 days to yield orange crystals **1** and **1′** (enantiomer) (yield 31% based on Ni). The crystals were washed with ethanol, dried, and stored under vacuum. The compound is stable in ambient condition. Elemental analysis calcd. for $C_{36}H_{26}NiIn_2Se_5N_6O$ (FW 1241.77): C, 34.82; H, 2.11; N, 6.77. Found: C, 34.69; H, 2.16; N, 6.55. IR (cm^{-1}): 3436(b), 3042(w), 1629(s), 1580(m), 1509(m), 1426(vs), 1337(w), 1222(w), 1143(m), 1103(w), 992(w), 852(vs), 768(m), 724(vs), 639(w).

*{[Fe(phen)$_3$]·In$_2$Se$_5$·H$_2$O}$_n$ (**2**).* Compound **2** was prepared by a similar method used in the synthesis of **1** except that Ni powder was replaced by Fe powder (0.0056 g, 0.1 mmol). The sealed tube was heated under autogenous pressure at about 140 °C for 4 days to yield red block-shaped crystals **2** (yield 35% based on Fe), which were washed with ethanol, dried, and stored under vacuum. The compound is stable in ambient condition. Elemental analysis calcd. for $C_{36}H_{26}FeIn_2Se_5N_6O$ (FW 1238.93): C, 34.90; H, 2.12; N, 6.78. Found: C, 34.76; H, 2.17; N, 6.57. IR (cm^{-1}): 3542(b), 3042(vw), 1629(m), 1572(w), 1492(m), 1417(vs), 1337(w), 1205(w), 1138(m), 935(m), 838(vs), 763(s), 719(vs), 524(s).

Crystal Structure Determination. Data collections of **1**, **1′**, and **2** were performed on a Rigaku Mercury CCD diffractometer using a ω-scan method with graphite monochromated Mo Kα radiation (λ = 0.071073 nm) at temperature of 223(2) K. An absorption correction was applied for all the compounds using a multiscan correction method. The structures were solved with direct methods using the SHELXS-97 program, and the refinement was performed against F^2 using SHELXL-97.[12] All the nonhydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Locating the hydrogen atoms of water is unfeasible, and then, the H atoms of the water molecules were not dealt with. Relevant crystal data, collection parameters, and refinement results can be found in Table 1.

RESULTS AND DISCUSSION

Synthesis and Characterization. Single crystals of **1**, **1′** (enantiomer), and **2** were prepared by the solvothermal method under similar conditions from elements M (M = Ni or Fe), In, and Se powders and phen (see Experimental Section). The optimized molar ratio of M/In/Se/phen is 1:1:1:3, that was different from the molar ratio of the formulas; therefore, the directing species of $[M(phen)_3]^{n+}$ cations were in excess in the reaction system. Part of the selenium was unreacted if its amount was increased. The optimized ratio of the mixed solvent of di-*n*-butylamine/H_2O was 4:1 in volume. No crystals formed if the reactants reacted in pure amine, and the quality of the crystals was not good if more water was added. Dark red square crystals **2** were obtained in a thick Pyrex tube, while there are two obvious different shaped orange crystals in the product of the nickel compound **1**. The one is brick-shaped crystals, and the other is long stick-shaped crystals. The single crystal X-ray diffraction indicated that their crystal cell data are the same one. The different crystal growing speed along the *c* direction contributes to the different shapes of the crystals (also see the structural section). The purity of the samples is checked by PXRD patterns of the experimental and calculated results (Supporting Information, Figure S1). The IR spectra have been presented in Supporting Information, Figure S2. Vibration bands at about 3440 and 1630 cm^{-1} indicate the presence of H_2O molecules, and those at about 3040, 1770, 1510, 840, and 720 cm^{-1} indicate the presence of the aromatic ring. The C═N vibration band appears at about 1580 cm^{-1}. Thermal behavior of compound **1** was measured under nitrogen at the range of 25 to 500 °C (Supporting Information, Figure S3). The platform of loss of the water molecule (calcd. 1.5%, found 2.7%) was not very clear, that might be due to the presence of adsorbed water. The compound began to sharply remove organic components at 350−400 °C, and the onset inflection is at about 360 °C. The first step loss of 23% was observed between 200 and 430 °C, followed by a second weight loss of 5% between 430 and 500 °C. Only about total 28% of organic components was removed (calculated 43%) before 500 °C. The coke formation made the removal of carbon difficult (<500 °C).

Description of Crystal Structures. Since crystals **1** and **1′** are enantiomorphous and compounds **1** and **2** are isomorphous, the discussions of their structures are presented together. Compounds **1** and **2** crystallize in the orthorhombic geometry with space group $P2_12_12_1$, a typical chiral space group with Flack parameter 0.00(3), 0.05(2), and 0.07(2) for **1**, **1′**, and **2**, respectively. Both **1** and **2** have the same space group and similar unit-cell dimensions and containts (Table 1), except for a replacement of the transition metal atoms. The compounds are composed of $[M(phen)_3]^{2+}$ cations, $\{[In_2Se_5]^{2-}\}_n$ anions, and water molecules. The structural data of the cations in **1** and **2** are in accordance with the reported data of $[M(phen)_3]^{2+}$ cations.[9a] The $\{[In_2Se_5]^{2-}\}_n$ anion in **1** or **2** can be described as two $InSe_4$ tetrahedron sharing an edge to form a In_2Se_6 dimer. The dimers are further linked by a coshared corner of Se atom and a Se−Se bond to construct a 1-D chain with alternately connected four-membered In_2Se_2 ring and five-membered In_2Se_3 ring, propagating along the crystallographic *b*-axis (Figure 1). The bond distances of In−Se are 2.556(2)−2.616(2) Å for **1**/**1′** and 2.563(2)−2.622(2) Å for **2**, and the lengths of Se−Se bond are 2.360(3)/2.357(2) and 2.363(2) Å for **1**/**1′** and **2**, respectively. The reported one-dimensional Zweier indium-chalcogenides include edge sharing tetrahedral single chain $[(In_2Q_4)^{2-}]_n^{2-4}$ and 1-D $[(In_2Te_6)^{2-}]_n$ with fused five-membered rings.[5] The chains prepared in this work possess the new structural feature compared with those of the previously reported compounds. Molecular packing of **2** is shown in Figure 2 viewed from the *a* and *b* directions. The 1-D chains and the columns of $[M(phen)_3]^{2+}$ cations are arranged separately and alternately.

Due to the screw coordination arrangement in D_3 mode, phen transition metal complexes are a type of important chiral complexes and have been an increasingly active area of research.[8] However, when the chiral complex ions aggregate and crystallize, in most cases, they form a chemically racemic mixture of achiral crystals in which the clockwise and anticlockwise enantiomers coexist. Sometimes, directed by interion's interactions, such as

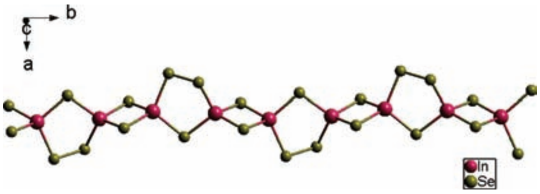


Figure 1. The 1-D anion structure of **1** with alternately connected four-membered In_2Se_2 ring and five-membered In_2Se_3 ring.

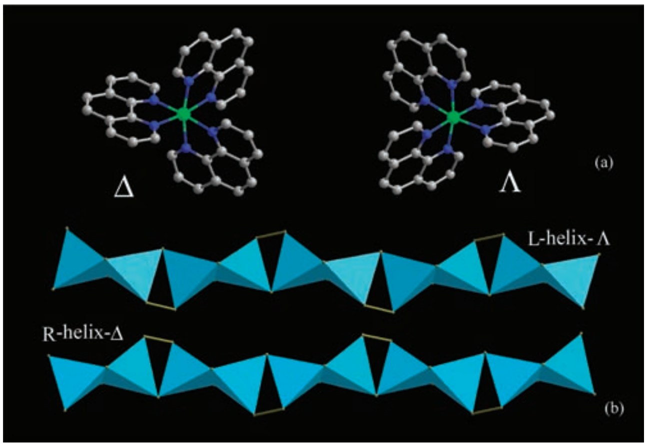


Figure 3. Homochiral $[Ni(phen)_3]^{2+}$ (Δ) with the related R-helical 1-D anion of **1** and homochiral $[Ni(phen)_3]^{2+}$ (Λ) with the related L-helical 1-D anion of **1′**.

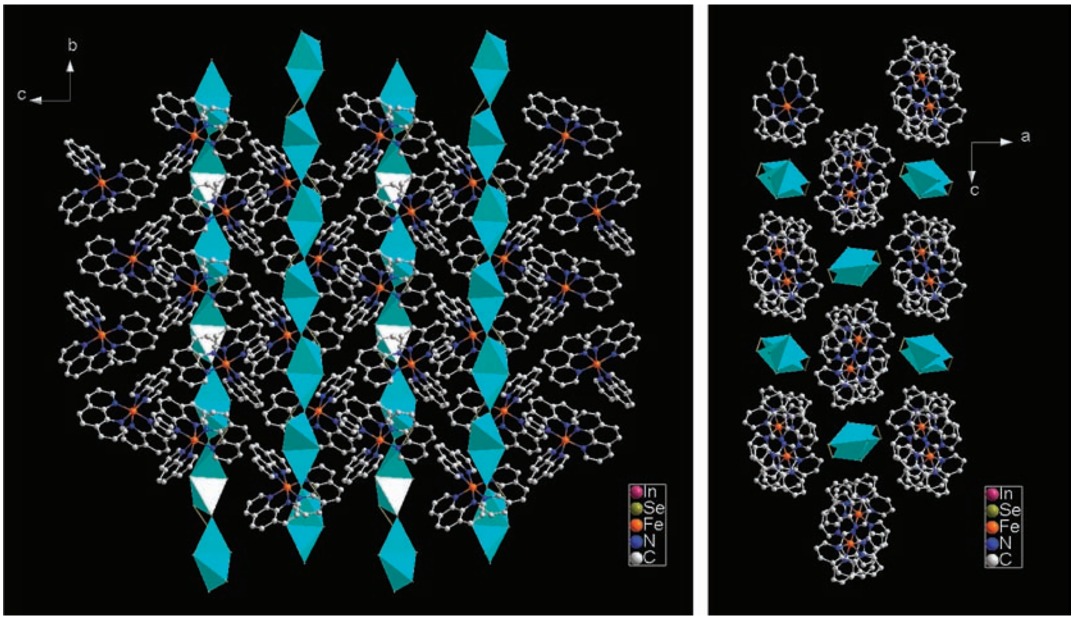


Figure 2. Molecular packing of **2** showing the 1-D anion chains and the columns of $[M(phen)_3]^{2+}$ cations viewed from *a* direction and *b* direction.

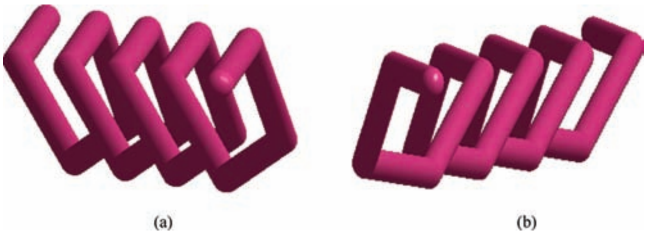
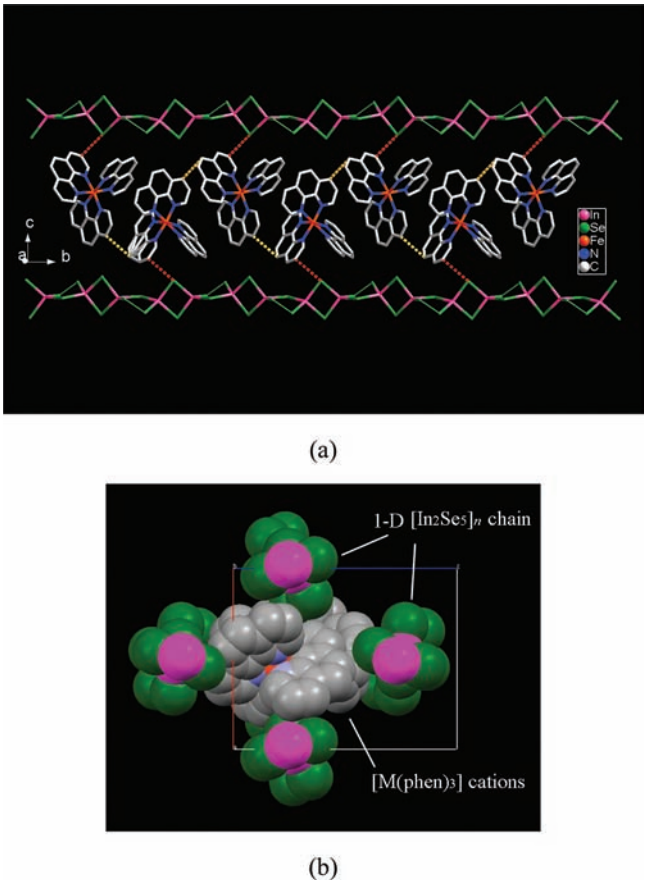


Figure 4. (a) The right-handed helical structure of $\{[In_2Se_5]^{2-}\}_n$ in **1** and (b) the left-handed helical structure of $\{[In_2Se_5]^{2-}\}_n$ in **1′**.



(a)

(b)

Figure 5. (a) The $\pi\cdots\pi$ (yellow dash lines) and C···Se contacts (red dash lines) within the *bc* plane of **2**. (b) The chiral space fitting for the cation and anions.

Table 2. Important C···S and C···C Contacts in 1, 1′, and 2 (Å)[a]

	1		
Se(1)···C(14)[a]	3.576	Se(1)···C(32)[b]	3.567
Se(2)···C(1)[a]	3.579	Se(3)···C(19)[c]	3.527
Se(5)···C(30)	3.593		
	1′		
Se(1)···C(13)[d]	3.567	Se(2)···C(6)[e]	3.598
Se(4)···C(31)[d]	3.527	Se(5)···C(8)[e]	3.589
Se(5)···C(26)[f]	3.590		
	2		
Se(2)···C(25)[g]	3.571	Se(4)···C(7)[h]	3.549
Se(4)···C(27)[i]	3.596	Se(5)···C(2)[j]	3.488
C(11)···C(20)	3.392		

[a] Symmetry: −*x*, −1/2 + *y*, 1/2 − *z*. [b] Symmetry: *x*, −1 + *y*, *z*. [c] Symmetry: 1/2 + *x*, 1.5 − *y*, −*z*. [d] Symmetry: −1/2 + *x*, 1/2 − *y*, −*z*. [e] Symmetry: 1/2 + *x*, 1/2 − *y*, −*z*. [f] Symmetry: 2.5 − *x*, 1 − *y*, 1/2 + *z*. [g] Symmetry: 1/2 + *x*, 1.5 − *y*, 1 − *z*. [h] Symmetry: −1/2 + *x*, 1.5 − *y*, 1 − *z*. [i] Symmetry: 1/2 − *x*, 2 − *y*, 1/2 + *z*. [j] Symmetry: 1 − *x*, 1/2 + *y*, 1/2 − *z*.

short contacts and hydrogen bonds, single-chiral crystals can be isolated as a mechanical racemic mixture of crystals that is also known in nature. Study on the directing forces in such self-separated systems is a significative work. The Ni(II) ion in crystal **1** is octahedrally clockwise coordinated by three phen molecules showing Δ configuration, while the Ni(II) ion in crystal **1′** is anticlockwise coordinated by three phen molecules showing Λ configuration (Figure 3). It is notable that the $\{[In_2Se_5]^{2-}\}_n$ chain in crystal **1** has a right-handed helical structure, R-helix, while the chain in crystal **1′** has a left-handed helical structure, L-helix (Figure 3). To be more clear, Figure 4 shows the simplified helical structures by connecting the In−In centers and deleting all the Se atoms of the anion. The chiralily of crystal **2** is the same as that of crystal **1** with clockwise Δ-$[Fe(phen)_3]^{2+}$ cations and R-helix of anions (Supporting Information, Figure S4).

Study on the selective self-separation of chiral structure in crystallization is fascinating. What are the forces for self-selection of the chirality of the anionic chains and the metal complex cations? In the sense of supramolecular chemistry, the inter- or intra- cations and anions interactions contribute to the selection of clockwise (Δ) cations with R-helix of 1-D anion in **1** and **2** and anticlockwise (Λ) cation with L-helix of 1-D anion in **1′**. Since the compounds are isomorphous, only the structure of **2** is used for discussion. The three phen in $[M(phen)_3]^{2+}$ cations have the same spacial orientation that allows them to pack closely with $\pi\cdots\pi$ interaction and form the chiral spaces for the occupation of anions. Figure 5a illustrates the $\pi\cdots\pi$ (3.392 Å) and C···Se (3.488 Å) contacts within the *bc* plane of structure of **2**. There are similar interactions in the perpendicular *ab* plane. Figure 5b shows the chiral space fitting for the cation and anions. The weak C−H···Se hydrogen bonds should also contribute to the cation−anion chiral recognition. Only one C−H···O hydrogen bond was found in the structure of these compounds, and there is not any water−anion interaction. The cation−anion interactions of **1** are also illustrated in Figure S5 (Supporting Information), and all the contact data for the three structures are listed in Table 2.

Spectral Studies. Some transition metal complexes of phen have an intense metal-to-ligand charge-transfer (MLCT) transition in the visible region, suitable ground and excited state, and good stability in the oxidized and reduced forms.[13] They have attracted significant attention as sensitizers of inorganic semiconductors during the past decade in the conversion of sunlight to electricity because of their low cost and high efficiency.[14] Chalcogenido compounds of **1** and **2** are a new type of compound, in which the M-phen complexes are embedded into the 1-D structure of inorganic semiconductor, forming a single-phase material, which can improve the absorption property for visible light.

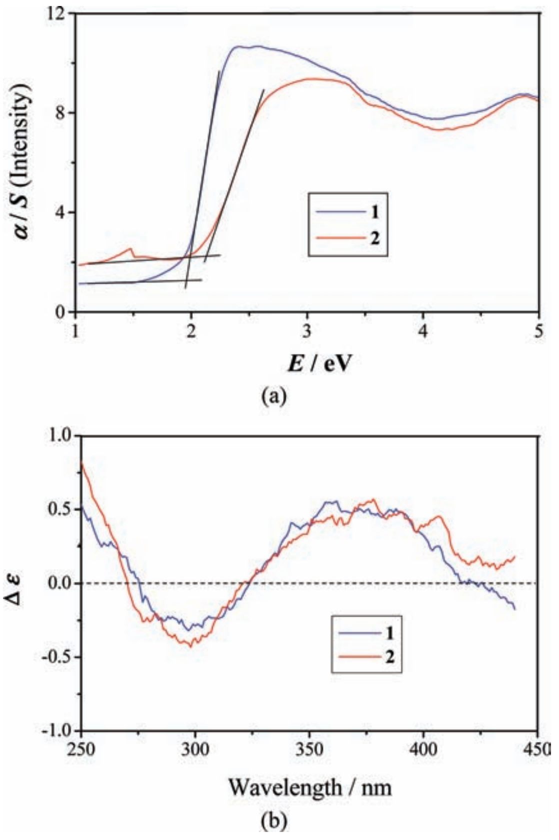


Figure 6. (a) Optical diffuse-reflection spectra of **1** (blue curve) and **2** (red curve) and (b) CD spectra of crystals **1** (blue curve) and **2** (red curve); only very few crystals were used as the measured samples.

Optical diffuse reflection spectra were measured at room temperature. The absorption (α/S) data were calculated from the reflectance.[11] The optical band gaps (E_g) obtained by extrapolation of the linear portion of the absorption edges are estimated to be 2.13 eV for **1** and 1.96 eV for **2**, respectively (Figure 6a). The band gap of **2** is narrow compared to that of **1** due to the optical contribution of $[\mathrm{Fe(phen)_3}]^{2+}$ complex cation, which has a very strong MLCT absorption at about 2.0 eV (solid state, Supporting Information, Figure S6a). The intense absorption at about 2.5 eV for Ni compound is attributed to the charge transfer between cation and anion (CACT), compared with the spectrum of $[\mathrm{Ni(phen)_3}]\mathrm{Cl_2}$ (Supporting Information, Figure S6b), that is within the energy range suitable for photocatalytic applications using light in the visible region. The CACT is overlapped with the MLCT for compound **2**. However, when compared with the condensed phase such as α-$\mathrm{In_2Se_3}$ (1.4 eV), the E_g of the title 1-D compound is somewhat larger.[15] The two compounds belong to a semiconductor with room temperature conductivity of 1.56×10^{-6} and 3.12×10^{-6} $\mathrm{S \cdot m^{-1}}$, respectively, for the pressed powder samples.

A bulk polycrystalline sample is usually a racemic mixture of 1:1 R-helix-Δ and L-helix-Λ crystals. For this reason, the CD results should be silent. Because only very few crystals were used as the measured samples in which the crystals of L-helix-Λ isomer are somewhat more than those of R-helix-Δ isomer, very weak CD spectra were recorded. The circular dichroism (CD) spectra of both **1** and **2** measured in solid state exhibit a weak positive Cotton effect,[16] and a negative and a positive dichroic signal is centered at $I_{\max} = 295$ and 375 nm, respectively (Figure 6b). The results proved the chirality of the crystals. Unfortunately, large single crystals have not been obtained after attempts, so that the high quality single crystal CD spectra could not be measured.

■ CONCLUSIONS

In summary, we have presented the synthesis and the chiral structures of two selenidoindates, $\{[\mathrm{M(phen)_3}]\cdot\mathrm{In_2Se_5}\cdot\mathrm{H_2O}\}_n$ (M = Ni (**1**) and Fe(**2**)). Instead of the complex cations of traditional aliphatic chelating amines, complex cations of chelating π-conjugated imine ligands, having potential optical properties, are used as the structure directing cations of main-group metal chalcogenometalates. The 1-D $\{[\mathrm{In_2Se_5}]^{2-}\}_n$ anion can be described as a chain with an alternately fused four-membered $\mathrm{In_2Se_2}$ ring and five-membered $\mathrm{In_2Se_3}$ ring, which is a new type of 1-D structure of chalcogenoindates. The compounds were separated as mechanical racemic mixtures of single enantiomer crystals, in which R-helix of 1-D InSe anion is directed by related clockwise (Δ) cations of $[\mathrm{M(phen)_3}]^{2+}$ or L-helix of 1-D anion is directed by related anticlockwise (Λ) cation. The oriented contacts of metal complex cation with selenidoindate anion direct the formation of chiral crystals with related clockwise $[\mathrm{M(phen)_3}]^{2+}$ cation and helical structure of $\{[\mathrm{In_2Se_5}]^{2-}\}_n$. Further studies of the relationship between the interion interactions and the chirality are significant.

■ ASSOCIATED CONTENT

S Supporting Information. CIF tables, PXRD, TG, and diffuse-reflection spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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