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$[Mn(en)_3]CdSnTe_4$ and $[Mn(en)_3]Ag_6Sn_2Te_8$: New Intermetallic Tellurides Synthesized in Superheated Organic Medium

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Two intermetallic tellurides, $Mn(en)_3]CdSnTe_4$ (**I**) and $[Mn(en)_3]Ag_6Sn_2Te_8$ (**II**), have been synthesized in superheated ethylenediamine solutions at 180 °C. Single-crystal X-ray diffraction analyses show that **I** crystallizes in triclinic crystal system, space group $P1$ (No. 1) with lattice parameters $a = 9.134(2)$ Å, $b = 10.085(3)$ Å, $c = 12.691(3)$ Å, $\alpha = 73.52(2)°$, $\beta = 86.05(2)°$, $\gamma = 76.43(2)°$, $V = 1089.7(5)$ Å^3, and $Z = 2$ and **II** belongs to trigonal (rhombohedral) crystal system, space group $R\bar{3}m$ (No. 166) with $a = 8.9590(9)$ Å, $c = 34.795(2)$ Å, $V = 2418.6(4)$ Å^3, and $Z = 3$. Both compounds possess new structure types. The structure of **I** is composed of one-dimensional Zintl chains of alternating edge-sharing MTe_4 ($M = Cd$, Sn) tetrahedra and $[Mn(en)_3]^{2+}$ complex cations that are between the chains. The structure of **II** contains two-dimensional double layers of $Ag_6Sn_2Te_8{}^{2-}$ formed by connecting two single honeycomb-like layers through M−Te bonds (M = Ag, Sn). The double layers are separated by the $[Mn(en)_3]^{2+}$ templates. Optical diffuse reflectance measurements have been performed on the powder samples of **I** and **II** and have suggested that both compounds are semiconductors with band gaps of 1.75 and 0.77 eV, respectively.

Introduction

Our efforts in synthesizing new metal chalcogenides in superheated organic media have shown that solvothermal reactions in ethylenediamine are effective and suitable for crystal growth of many low-temperature phases, particularly those containing Group 10−12 transition and post-transition metals[1] and Group 14−15 main-group metals.[2] Most of these compounds are Zintl phases crystallizing in a wide variety of structure types. Often the solvent molecules incorporate in the final products by forming complex cations with a transition-metal species which acts as a structure-directing agent.[3] While a large number of single metal $M_xQ_y{}^{n-}$ Zintl anions have been prepared via this route, we have recently begun to investigate intermetallic compounds that contain more than one type of metals.[4] The motivation for our investigation is based on the fact that different groups of metal chalcogenides exhibit important yet different properties and show potentials in various types of applications, for example, small band-gap semiconductors, photovoltaics and thermoelectrics for main-group metal chalcogenides[5] and solid-state lasers, heterogeneous catalysts, and reversible battery electrodes for transition-metal chalcogenides.[6] The intermetallic compounds containing metals from two different groups are likely to possess structures and properties that reflect those of the two metals. Herein, we report solvothermal synthesis of two new intermetallic compounds, $[Mn(en)_3]CdSnTe_4$ (**I**) and $[Mn(en)_3]Ag_6Sn_2Te_8$ (**II**), prepared in superheated ethylenediamine solution, and discuss their novel structures and optical properties.

Experimental Section

Materials. $MnCl_2$ (97%, Alfa Aesar), AgCl (99%, Aldrich), $CdCl_2$ (99.9%, Strem), and Te (99.5%, Strem) were used as purchased without further treatment. Tin telluride, SnTe, was prepared by direct reaction of a stoichiometric amount of tin and tellurium (1:1) at 450 °C for 3 days. Ethylenediamine (99%, anhydrous, Fisher Scientific) was used as solvent in all reactions.

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Table 1. Crystallographic Data and Details of Structure Refinement for I

formula	$[Mn(en)_3]CdSnTe_4$
formula weight	976.74
color and habit	dark red prism
crystal size, mm^3	0.2 × 0.3 × 0.3
crystal system	triclinic
space group	*P*1 (No. 1)
a, Å	9.134(2)
b, Å	10.085(3)
c, Å	12.691(3)
α, deg	73.52(2)
β, deg	86.05(2)
γ, deg	76.43(2)
V, Å^3	1089.7(5)
d_{calc}, g/cm^3	2.977
Z	2
λ, Å	0.71073
μ (Mo Kα), mm^{-1}	7.920
T, °C	21
unique reflections, *n*	4003
observed reflections [I ≥ 2σ(I)]	3796
data collection range	$-10 < h < 10$, $-11 < k < 11$, $0 < l < 15$; $\theta_{max} = 25$ °
number of variables, *p*	344
GOF[a]	1.304
R indices [I ≥ 2σ(I)]	R_1[b] 0.0293; wR_2[c] 0.0601
R indices (all data)	R_1 0.0337; wR_2 0.0611

[a] GOF = $(\sum[w(F_o^2 - F_c^2)^2]/n - p)^{1/2}$, where *n* is the number of reflections, *p* is the number of refined parameters, and *w* is the weighting: $w = 1/[\sigma^2(F_o^2) + 5.00P]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $R_1 = [\sum||F_o| - |F_c||]/[\sum|F_o|]$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] (Å^2) for I

atoms	*x*	*y*	*z*	U_{equiv}
Sn(1)	0.37927(1)	0.10344(1)	0.81051(1)	0.03185(4)
Sn(2)	0.84022(1)	0.44530(1)	0.36262(1)	0.03777(4)
Cd(1)	0.59628(2)	0.31267(1)	0.59223(1)	0.04021(5)
Cd(2)	1.09571(2)	0.29758(1)	0.59777(1)	0.04001(5)
Mn(1)	0.43277(3)	0.12155(3)	1.23104(3)	0.0406(1)
Mn(2)	−0.01120(3)	−0.26426(3)	0.79182(3)	0.03707(9)
Te(1)	0.45438(2)	−0.16120(1)	0.94264(1)	0.04565(5)
Te(2)	0.07934(1)	0.22634(1)	0.82876(1)	0.04155(4)
Te(3)	0.56902(2)	0.27312(1)	0.81919(1)	0.04808(4)
Te(4)	0.39850(1)	0.13104(1)	0.58450(1)	0.03302(4)
Te(5)	0.55416(2)	0.56341(1)	0.42005(1)	0.04985(5)
Te(6)	0.88504(1)	0.17814(1)	0.51871(1)	0.03722(4)
Te(7)	1.05178(2)	0.55623(1)	0.43342(1)	0.04708(5)
Te(8)	0.87783(2)	0.40660(2)	0.16106(1)	0.06967(7)
N(1)	0.5236(2)	0.2877(2)	1.1014(2)	0.102(1)
N(2)	0.3209(3)	0.3265(2)	1.2650(2)	0.163(2)
N(3)	0.5963(1)	−0.0612(3)	1.1888(2)	0.123(1)
N(4)	0.6388(2)	0.0881(2)	1.3392(2)	0.091(1)
N(5)	0.3087(2)	−0.0101(2)	1.3599(2)	0.146(1)
N(6)	0.2508(2)	0.0974(2)	1.1367(2)	0.121(1)
N(7)	0.1726(1)	−0.4273(2)	0.7391(2)	0.0588(7)
N(8)	0.1637(2)	−0.1372(1)	0.7133(1)	0.0534(7)
N(9)	0.0780(2)	−0.3160(1)	0.9657(1)	0.0608(7)
N(10)	−0.1471(2)	−0.0814(2)	0.84889(9)	0.0517(6)
N(11)	−0.1825(2)	−0.4021(2)	0.8425(1)	0.0481(6)
N(12)	−0.1466(1)	−0.2093(2)	0.6332(2)	0.0474(6)
C(1)	0.4065(2)	0.4206(2)	1.0758(1)	0.096(1)
C(2)	0.3605(3)	0.4520(1)	1.1850(1)	0.102(1)
C(3)	0.7491(1)	−0.0703(2)	1.2270(1)	0.078(1)
C(4)	0.7353(2)	−0.0530(1)	1.3420(1)	0.0638(9)
C(5)	0.1686(2)	−0.0232(3)	1.3172(1)	0.142(2)
C(6)	0.1991(2)	−0.0317(2)	1.2005(1)	0.148(2)
C(7)	0.3046(2)	−0.3725(1)	0.6898(3)	0.138(2)
C(8)	0.2675(2)	−0.2144(1)	0.6461(1)	0.102(1)
C(9)	0.0265(2)	−0.1894(1)	1.0070(1)	0.100(1)
C(10)	−0.1310(2)	−0.1091(3)	0.9679(1)	0.079(1)
C(11)	−0.2554(2)	−0.4039(1)	0.7427(1)	0.0566(8)
C(12)	−0.2889(1)	−0.2575(1)	0.6616(2)	0.0583(8)

[a] U_{equiv} defined as one-third of the trace of the orthogonalized **U** tensor.

Synthesis of $[Mn(en)_3]CdSnTe_4$ (I). Single crystals of **I** were obtained from a solvothermal reaction containing 0.25 mmol (0.094 g) of SnTe, 0.75 mmol (0.096 g) of Te, 0.25 mmol (0.032 g) of $MnCl_2$, and 0.25 mmol (0.045 g) of $CdCl_2$. The reagents were weighed and mixed under inert argon atmosphere in a glovebox. The mixture was then transferred to a thick-walled Pyrex tube, and approximately 0.4 mL of solvent (en) was added to the sample. After the liquid was condensed by liquid nitrogen, the tube was sealed with a torch under vacuum (~10^{-2} Torr). The sample was heated at 180 °C for 7 days. After being cooled to room temperature, the mixture was washed with 30% and 95% ethanol followed by drying with anhydrous diethyl ether. Dark red prismlike crystals of **I** (yield ~50%) were isolated from the final product. Its approximate composition was established by the microprobe analysis on a Hitachi S-2400 scanning electron microscope.

Synthesis of $[Mn(en)_3]Ag_6Sn_2Te_8$ (II). Crystals of **II** were grown from a reaction with 0.25 mmol of SnTe (0.094 g), 0.75 mmol of Te (0.096 g), 0.25 mmol of AgCl (0.036 g), and 0.025 mmol of $MnCl_2$ (0.032 g). The weighing procedure was the same as that described for **I**. The sample was heated at 180 °C for 15 days. After being washed with 30% and 95% ethanol followed by drying with anhydrous diethyl ether, black plate crystals of **II** were collected in good yield (~60%).

Crystal Structure Determination of I. A dark red prismlike crystal (0.2 × 0.3 × 0.3 mm^3) of **I** was mounted on a glass fiber in air on an Enraf-Nonius CAD4 automated diffractometer using the graphite-monochromated Mo Kα radiation at room temperature (294 ± 1 K). A unit cell was obtained and refined by 25 well-centered reflections with 6.2° < θ < 10.5°. Data collection was monitored by three standards every 2 h. No decay was observed except the statistic fluctuation in the range of ±2.3%. Raw intensities were corrected for Lorentz and polarization effects and for absorption by empirical method based on ψ-scan data.[7] Direct phase determination yielded the positions of Sn, Cd, Te, and Mn atoms, and the positions of nitrogen and carbon atoms were located in successive difference Fourier syntheses. Hydrogen atoms were calculated theoretically. They were allowed to ride on their parent nitrogen or carbon atoms and assigned fixed thermal parameters in refinement. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix, least-squares refinement on F^2 converged with $R_1 = 0.030$ and $wR_2 = 0.060$ for observed reflections and $R_1 = 0.034$ and $wR_2 = 0.060$ for all reflections. Final difference electron density map shows no features. Details of crystal parameters, data collection, and structure refinement details are given in Table 1. Data collection was controlled by the CAD4/PC program package. Computations were performed using the *SHELX97* program package[8] on a PC 586 system. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.[9] Crystal drawings were produced with *SCHAKAL 92*.[10] Final atomic coordinates, average temperature factors, and selected bond lengths and angles are listed in Tables 2 and 3, respectively.

Crystal Structure Determination of II. Room temperature (294 ± 1 K) single-crystal X-ray experiments were performed on a single crystal of **II** (0.02 × 0.2 × 0.3 mm^3). Unit cell parameters were obtained and refined by 24 well-centered reflections with 7.5° < θ < 11.5°. Data collection was monitored by three standards every 2 h. No decay was observed except the statistic fluctuation in the range of ±2.9%. Raw intensities were corrected for Lorentz and polarization effects, as well as for absorption by empirical method based

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Table 3. Selected Bond Lengths (Å) and Angles (°) for I[a]

Sn(1)−Te(1)	2.6769(9)	Cd(2)−Te(2a)	2.8156(7)
Sn(1)−Te(2)	2.7527(7)	Cd(2)−Te(4a)	2.9008(8)
Sn(1)−Te(3)	2.7330(7)	Mn(1)−N(1)	2.259(2)
Sn(1)−Te(4)	2.7993(7)	Mn(1)−N(2)	2.227(2)
Sn(2)−Te(5)	2.7472(7)	Mn(1)−N(3)	2.253(2)
Sn(2)−Te(6)	2.8137(9)	Mn(1)−N(4)	2.309(2)
Sn(2)−Te(7)	2.7599(6)	Mn(1)−N(5)	2.223(2)
Sn(2)−Te(8)	2.6825(7)	Mn(1)−N(6)	2.211(2)
Cd(1)−Te(3)	2.7953(7)	Mn(2)−N(7)	2.268(2)
Cd(1)−Te(4)	2.8823(7)	Mn(2)−N(8)	2.281(2)
Cd(1)−Te(5)	2.8003(9)	Mn(2)−N(9)	2.281(2)
Cd(1)−Te(6)	2.8927(7)	Mn(2)−N(10)	2.242(2)
Cd(2)−Te(6)	2.8635(6)	Mn(2)−N(11)	2.273(2)
Cd(2)−Te(7)	2.8023(9)	Mn(2)−N(12)	2.297(2)
Te(1)−Sn(1)−Te(2)	112.13(2)	Te(5)−Cd(1)−Te(6)	96.52(2)
Te(1)−Sn(1)−Te(3)	114.79(2)	Te(6)−Cd(2)−Te(7)	97.64(2)
Te(1)−Sn(1)−Te(4)	116.20(2)	Te(6)−Cd(2)−Te(2a)	108.79(2)
Te(2)−Sn(1)−Te(3)	113.83(2)	Te(6)−Cd(2)−Te(4a)	109.60(2)
Te(2)−Sn(1)−Te(4)	100.28(2)	Te(7)−Cd(2)−Te(2a)	133.36(2)
Te(3)−Sn(1)−Te(4)	98.09(2)	Te(7)−Cd(2)−Te(4a)	110.24(2)
Te(5)−Sn(2)−Te(6)	99.63(2)	Te(2a)−Cd(2)−Te(4a)	96.40(2)
Te(5)−Sn(2)−Te(7)	111.16(2)	Sn(1)−Te(2)−Cd(2b)	82.26(2)
Te(5)−Sn(2)−Te(8)	117.12(2)	Sn(1)−Te(3)−Cd(1)	84.98(2)
Te(6)−Sn(2)−Te(7)	99.83(2)	Sn(1)−Te(4)−Cd(1)	82.17(2)
Te(6)−Sn(2)−Te(8)	108.69(2)	Sn(1)−Te(4)−Cd(2b)	79.95(2)
Te(7)−Sn(2)−Te(8)	117.24(2)	Cd(1)−Te(4)−Cd(2b)	105.57(2)
Te(3)−Cd(1)−Te(4)	94.76(2)	Sn(2)−Te(5)−Cd(1)	83.09(2)
Te(3)−Cd(1)−Te(5)	130.12(2)	Sn(2)−Te(6)−Cd(1)	80.28(2)
Te(3)−Cd(1)−Te(6)	115.13(2)	Sn(2)−Te(6)−Cd(2)	80.21(2)
Te(4)−Cd(1)−Te(5)	114.05(2)	Cd(1)−Te(6)−Cd(2)	103.91(2)
Te(4)−Cd(1)−Te(6)	104.77(2)	Sn(2)−Te(7)−Cd(2)	82.22(2)

[a] Symmetry transformations: a ($1 + x, y, z$); b ($-1 + x, y, z$).

Table 4. Crystallographic Data and Details of Structure Refinement for II

formula	$[Mn(en)_3]Ag_6Sn_2Te_4$
formula weight	2140.64
color and habit	black plate
crystal size, mm^3	$0.02 \times 0.2 \times 0.3$
crystal system	trigonal (rhombohedral)
space group	$R\bar{3}m$ (No. 166)
a, Å	8.9590(9)
b, Å	8.9590(9)
c, Å	34.795(2)
V, Å^3	2418.6(4)
d_{calc}, g/cm^3	4.409
Z	3
λ, Å	0.71073
μ(Mo Kα), mm^{-1}	12.563
T, °C	25
unique reflections	580
observed reflections [I ≥ 2σ(I)]	424
data collection range	$0 < h < 9, 0 < k < 9,$ $-41 < l < 41; \theta_{max} = 25°$
number of variables, p	37
GOF[a]	1.704
R indices [$I \geq 2\sigma(I)$]	R_1[b] 0.0455; wR_2[c] 0.0915
R indices (all data)	R_1 0.0701; wR_2 0.0948

[a] $GOF = (\sum[w(F_o^2 - F_c^2)^2]/n - p)^{1/2}$, where n is the number of reflections, p is the number of refined parameters, and w is the weighting: $w = 1/[\sigma^2(F_o^2) + 0.0010P2 + 5.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$. [b] $R_1 = [\sum||F_o| - |F_c||]/[\sum|F_o|]$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$.

on ψ-scan data. The possible space groups were reduced to $R\bar{3}m$, $R3m$, $R32$, $R\bar{3}$, and $R3$ by checking the systematic absences of reflections. The results of refinement indicated that **II** belongs to $R\bar{3}m$. The positions of Mn, Sn, Ag, and Te atoms were yielded by direct phase determination, whereas the positions of nitrogen and carbon atoms were located in successive difference Fourier syntheses. Hydrogen atoms were not included in refinement and calculations of structure factors. It should be noted that Mn(1) is at the Wychoff position 3a which requires a $\bar{3}m$ symmetry. Since the $Mn(en)_3$ group does not possess this symmetry, it suggests that the two enantiotropic isomers of $Mn(en)_3$ with a ratio of 1:1 occupying the positions randomly with MnN_6 coincided to give a statistical $\bar{3}m$ symmetry. Therefore, the C atoms of ethylenediamine (en) were assigned to half sof (site occupation factor), and the refinement yielded reasonable thermal parameters. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix, least-squares refinement on F^2 converged with $R_1 = 0.0480$ and $wR_2 = 0.0978$ for observed reflections and $R_1 = 0.0701$ and $wR_2 = 0.0948$ for all reflections. No features were observed in the final difference electron density map. Details of data collection and structure refinement, as well as unit cell constants, are tabulated in Table 4. Tables 5 and 6 give fractional coordinates of all non-hydrogen atoms,

Table 5. Atomic Coordinates and Equivalent Isotropic Temperature Factors[a] (Å^2) for II

atoms	x	y	z	U_{equiv}
Sn(1)	0.0000	0.0000	0.20448(6)	0.0235(6)
Ag(1)	0.17869(11)	0.3574(2)	0.14181(5)	0.0500(6)
Te(1)	0.0000	0.0000	0.12669(7)	0.0273(6)
Te(2)	−0.33975(16)	−0.16987(8)	0.22921(4)	0.0287(4)
Mn(1)	0.0000	0.0000	0.0000	0.030(2)
N(1)	0.260(2)	0.130(1)	0.0323(4)	0.057(5)
C(1)[b]	0.375(2)	0.089(2)	0.0083(7)	0.06(1)

[a] U_{equiv} defined as one-third of the trace of the orthogonalized **U** tensor. [b] The sof of C(1) was assigned to be 0.5 in the refinement.

Table 6. Selected Bond Lengths (Å) and Angles (°) for II[a]

Sn(1)−Te(1)	2.707(3)	Ag(1)−Ag(1c)	2.958(3)
Sn(1)−Te(2)	2.773(2)	Ag(1)−Te(2b)	2.797(1)
Ag(1)−Te(1)	2.822(2)	Mn(1)−N(1)	2.31(2)
Ag(1)−Te(2a)	3.044(2)		
Te(1)−Sn(1)−Te(2)	108.07(5)	Sn(1)−Te(1)−Ag(1)	79.26(6)
Te(1)−Sn(1)−Te(2a)	108.07(5)	Sn(1)−Te(1)−Ag(1a)	79.26(6)
Te(1)−Sn(1)−Te(2e)	108.07(5)	Sn(1)−Te(1)−Ag(1e)	79.26(6)
Te(2)−Sn(1)−Te(2a)	110.83(5)	Ag(1)−Te(1)−Ag(1a)	116.61(4)
Te(2)−Sn(1)−Te(2e)	110.83(5)	Ag(1)−Te(1)−Ag(1e)	116.61(4)
Te(2a)−Sn(1)−Te(2e)	110.83(5)	Ag(1a)−Te(1)−Ag(1e)	116.61(4)
Te(1)−Ag(1)−Te(2a)	98.17(7)	Sn(1)−Te(2)−Ag(1b)	107.99(5)
Te(1)−Ag(1)−Te(2b)	108.06(6)	Sn(1)−Te(2)−Ag(1e)	74.50(7)
Te(1)−Ag(1)−Te(2f)	108.06(6)	Sn(1)−Te(2)−Ag(1 g)	107.99(5)
Te(2a)−Ag(1)−Te(2b)	119.10(5)	Ag(1b)−Te(2)−Ag(1e)	60.68(5)
Te(2a)−Ag(1)−Te(2f)	119.11(5)	Ag(1b)−Te(2)−Ag(1 g)	95.97(9)
Te(2b)−Ag(1)−Te(2f)	103.49(8)	Ag(1e)−Te(2)−Ag(1 g)	60.68(5)

[a] Symmetry transformations: a ($-x + y, -x, z$); b ($-0.333 - x, 0.333 - y, 0.333 - z$); c ($0.667 + x - y, 0.333 + x, 0.333 - z$); d ($x - y, -y, -z$); e ($-y, x - y, z$); f ($0.667 + y, 0.333 - x + y, 0.333 - z$); g ($-0.333 + x - y, -0.667 + x, 0.333 - z$); h ($-x, -y, -z$); i ($y, -x + y, -z$); j ($x - y, x, -z$).

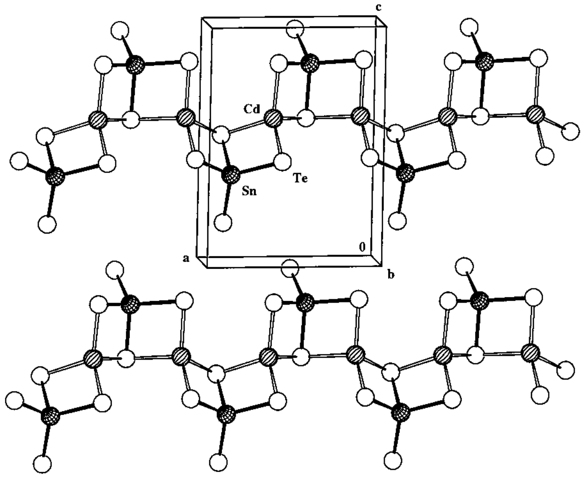

Figure 1. View along the b axis showing the $^1_\infty[(CdSnTe_4)^{2-}]$ one-dimensional chains in **I**. Single-shaded circles are Cd atoms, and cross-shaded circles are Sn atoms. Open circles are Te atoms. Both metal atoms have tetrahedral geometry. Unit cell is outlined in the figure.

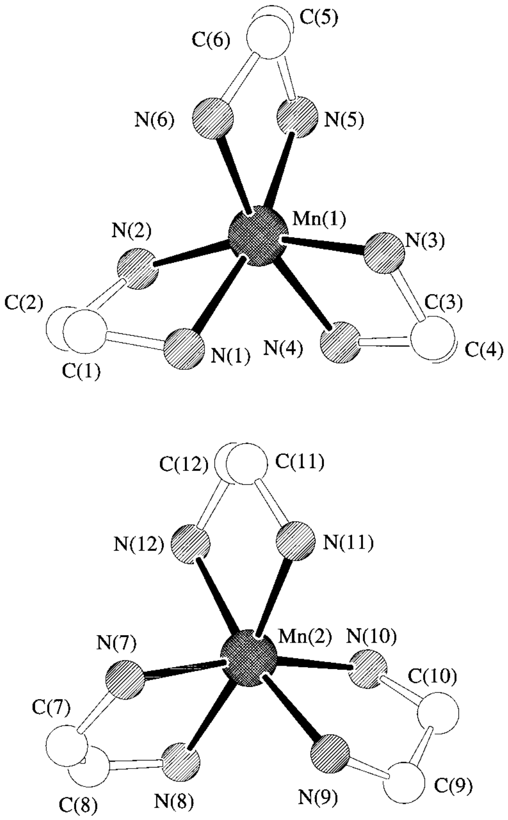

Figure 2. Two independent $[Mn(en)_3]^{2+}$ ions. Top: the *lel*$_3$ isomer with configuration $\Delta(\lambda\lambda\lambda)$. Bottom: the *lel*$_2$*ob* isomer with configuration $\Lambda(\delta\delta\lambda)$. Large solid circles are Mn atoms. Shaded and open circles are N and C atoms, respectively.

equivalent isotropic displacement parameters, and selected bond distances and angles.

Diffuse Reflectance Measurements. To assess the band gaps for the title compounds, a Shimadzu UV-3101PC double beam, double-monochromator spectrophotometer was used to measure the diffuse reflectance of polycrystalline samples of **I** and **II**. $BaSO_4$ powder was used as reference (100% reflectance). The absorption data was calculated from reflectance data using the Kubelka−Munk function.[11] The scattering coefficient has been shown to be practically wavelength-independent for particles larger than 5 μm, which is smaller than the particle size of the samples used in our experiment.

Results and Discussion

Crystal Structure of I. The structure of **I** represents a new type. It contains linear chains of ${}^{1}_{\infty}[(CdSnTe_4)^{2-}]$ formed by "fused" edge- and corner-sharing $CdTe_4$ and $SnTe_4$ tetrahedra (Figure 1). Within a chain, the metal centers are both coordinated to four Te atoms to form distorted tetrahedra in an alternate fashion. Each $CdTe_4$ tetrahedron shares two opposite edges with two $SnTe_4$, and each $SnTe_4$ tetrahedron shares two adjacent edges with two $CdTe_4$, while each $CdTe_4$ also shares two corners with its two nearest neighboring $CdTe_4$ via edge-sharing Te to result in a fused chain extending along the *a* direction. The Sn−Te interatomic distances range from 2.678(1) to 2.815(1) Å, similar to those found in $K_2HgSnTe_4$ (Sn−Te = 2.821 Å),[12] $(Et_4N)_2HgSnTe_4$ (Sn−Te = 2.804 Å),[12] $K_2Ag_2SnTe_4$ (Sn−Te = 2.745 Å),[13] Ba_2SnTe_5 (Sn−Te = 2.730−2.825 Å),[14] and $[M(en)_3]_2Sn_2Te_6$, M = Mn, Zn (Sn−Te = 2.673−2.808 Å).[2c] Of the eight independent tellurium atoms, Te(4) and Te(6) function as μ_3-bridging ligands to connect to one Sn and two Cd atoms. Te(2), Te(3), Te(5), and Te(7) act as μ_2-bridging ligands bonded to one Cd and one Sn, and Te(1) and Te(8) are terminal ligands coordinated to Sn. The closest interchain distance is 5.117 Å. The discrete $[Mn(en)_3]^{2+}$ complex cations are accommodated between the chains. As shown in Figure 2, there are two independent $[Mn(en)_3]^{2+}$ ions in the structure, both Mn are 6-fold coordinated by three chelating ethylenediamine to form a distorted octahedral geometry. The Mn(1) group is *lel*$_3$ with a configuration of $\Delta(\lambda\lambda\lambda)$, and that of the Mn(2) group is *lel*$_2$*ob* with a configuration of $\Lambda(\delta\delta\lambda)$.[15] A simple electron assignment gives +4, +2, and −2 for the

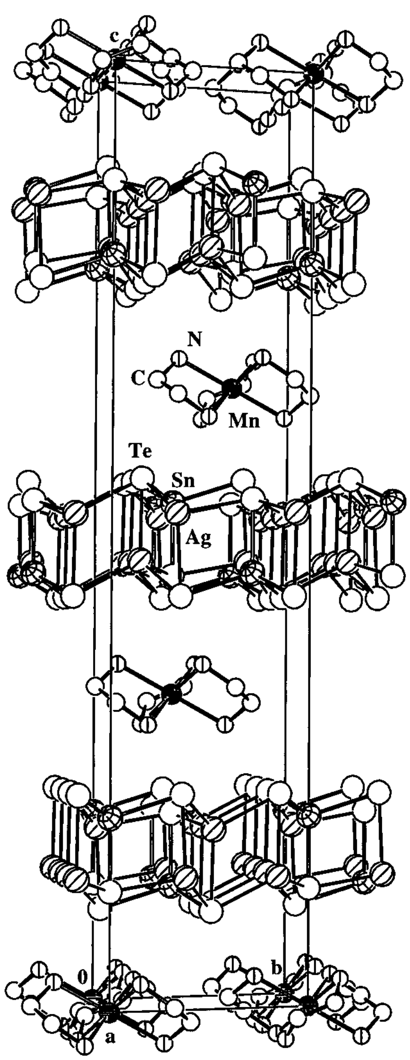

Figure 3. View of **II** along the *a* direction. The two-dimensional ${}^{2}_{\infty}[Ag_6Sn_2Te_8{}^{2-}]$ double-layers stack along the *c* axis with $[Mn(en)_3]^{2+}$ cations accommodated between these layers. The labeling scheme is the same as those in Figures 1 and 2, with cross-shaded circles representing Ag atoms. The unit cell is outlined.

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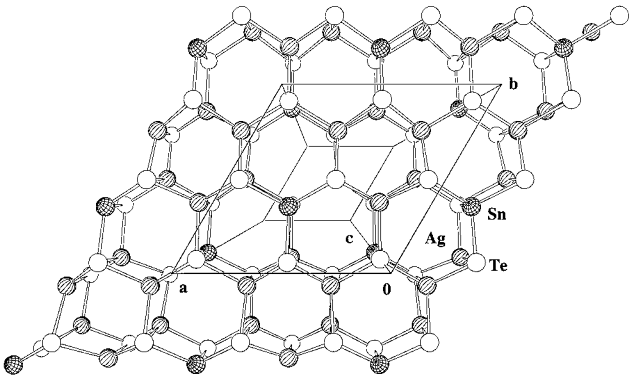

Figure 4. View of a $^{2}_{\infty}[Ag_6Sn_2Te_8{}^{2-}]$ honeycomb-like double layer. Both Ag and Sn are tetrahedrally coordinated to four Te atoms. All Te atoms are μ_4-bridging to three Ag and one Sn.

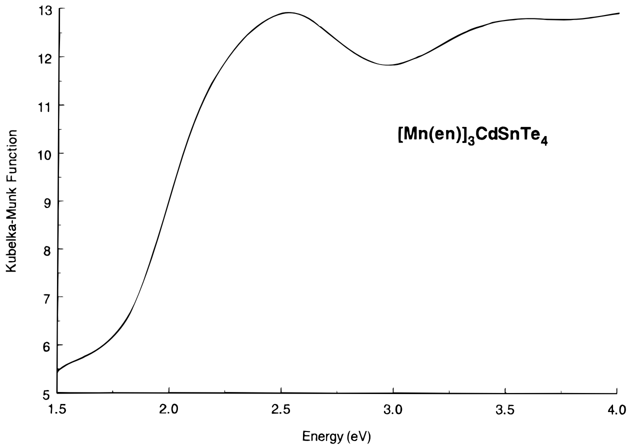

Figure 5. Optical absorption spectrum (Kubelka−Munk Function) for **I**. The estimated band gap is 1.75 eV.

oxidation states of Sn, Cd, and Te, respectively, indicating $^{1}_{\infty}[(CdSnTe_4)^{2-}]$ as a Zintl anion.

Crystal Structure of II. Compound **II** also crystallizes in a new structure type. It consists of $^{2}_{\infty}[Ag_6Sn_2Te_8{}^{2-}]$ double layers and discrete $[Mn(en)_3]^{2+}$ complex cations which act both as a charge-compensating and structure-directing agent separating the inorganic layers.[16] Shown in Figure 3 is a view of the structure along the *a* axis. A $^{2}_{\infty}[Ag_6Sn_2Te_8]^{2-}$ double layer along the *c* direction is shown in Figure 4. Both Ag and Sn are tetrahedrally coordinated to four tellurium atoms. All Te atoms are μ_4-bridging and link to one tin and three silver to result in a honeycomb-like double layer which, to the best of our knowledge, represents a new structure motif for chalcogenides. The Sn−Te bonds, 2.707(3) and 2.773(2) Å, are comparable with those of **I** and other aforementioned tin telluride compounds. The three Ag−Te interatomic distances, 2.797(1), 2.822(2), and 3.044 Å, are similar to those observed in $CsAg_5Te_3$ (2.743−3.060 Å),[17] $CsFe_{0.72}Ag_{1.28}Te_2$ (2.785 Å),[18] $K_{0.33}Ba_{0.67}AgTe_2$ (2.905 Å),[19] and $K_2Ag_2SnTe_4$ (2.686, 2.750, 2.983 Å).[13] The metal−metal distance between the silver atoms is 2.958(3) Å, which compares well with that found in $CsAg_5Te_3$ (2.902 Å) and is somewhat longer than that in $RbAg_3Te_2$ (2.836 Å).[20] The $[Mn(en)_3]^{2+}$ complex cations exist as two enantiotropic isomers in the structure, both being ob_3 with configurations of $\Lambda(\lambda\lambda\lambda)$ and $\Delta(\delta\delta\delta)$, respectively. Compound **II** is also a Zintl phase with +1, +4, and −2 oxidation states for Ag, Sn, and Te, respectively.

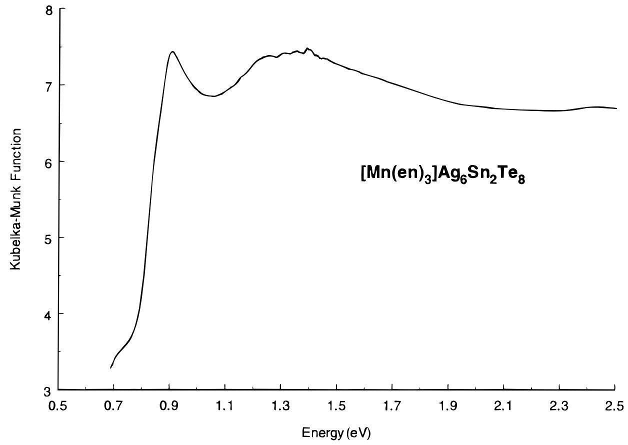

Figure 6. Optical absorption spectrum (Kubelka−Munk Function) for **II**. The estimated band gap is 0.77 eV.

Diffuse Reflectance Measurements. Both compounds are electron-precise and are most likely semiconductors. The optical properties of **I** and **II** were assessed by obtaining their optical diffuse reflectance data. The Kubelka−Munk (or remission, *F*) functions converted from the diffuse reflectance data were plotted in Figures 5 and 6 for **I** and **II**, respectively. From the sharp absorption edges, the band gaps can be estimated. Values of 1.75 eV for compound **I** and 0.77 eV for compound **II** were obtained, suggesting that both compounds are semiconductors with relatively small band gaps.

Acknowledgment. Financial support from the National Science Foundation (DMR-9553066) is greatly appreciated.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for **I** and **II** (22 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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