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Synthesis, Crystal and Band Structures, and Properties of a New Mixed Three-Dimensional Framework Metal Pnictidehalide Semiconductor, $(Hg_6Sb_4)(CdI_6)$

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A new, quaternary mercury and cadmium pnictidehalide semiconductor $(Hg_6Sb_4)(CdI_6)$ (**1**) has been prepared by the solid-state reaction and structurally characterized by single-crystal X-ray diffraction analysis. Compound **1** crystallizes in the space group *R*-3*c* of the rhombohedral system with four formula units in a cell: $a = 13.3818(9)$ Å, $\alpha = 90.93°$, and $V = 2395.3(3)$ Å^3. The crystal structural novelty of **1** derives from the fact that a 3-D mercury antimonide cationic network interpenetrates with an unusual 3-D cadmium iodide octahedral anionic network through the weak covalent interactions between mercury and iodine atoms to form a mixed 3-D framework. Among them, the cationic moiety features a perovskite-like 3-D network while the anionic moiety is characterized by a 3-D I_6 octahedral anionic network with two-thirds I_6 octahedra being occupied by Cd atoms. The optical properties were investigated in terms of the diffuse reflectance and Fourier transform infrared spectra. The electronic band structure along with density of states calculated by the density functional theory method indicates that compound **1** is a semiconductor with a direct band gap and that the optical absorption of **1** is mainly ascribed to the charge transitions from I-5p and Sb-5p states to Cd-5s and Hg-6s states.

Introduction

Recently, design and syntheses of mixed-framework compounds have attracted much attention because they offer scientifically and technologically significant opportunities for combining attractive features of different framework moieties within a single compound. For instance, inorganic−organic hybrid materials are likely to exhibit diverse structures, improved properties, and unique functions that are not obtained from their purely inorganic or organic moieties.[1] The hybrid materials of mixed covalent and ionic lattices made of transition metal oxides and alkali and alkaline-earth metal halides, which exhibit salt-templated porous structures, noncentrosymmetric lattices, and frameworks containing magnetic nanostructures,[2] are another new class of mixed-framework materials. According to the concept of mixed-framework compounds, metal pnictidehalides are investigated to explore new mixed-framework materials due to the distinct size and electronegativity of pnicogen and halogen anions. Furthermore, metal pnictidehalides have been of much interest in advanced material research because of their diverse structure, unique electronic properties, and good physical properties, such as magnetic, electric, and optical properties.[3] Till now, there are more than twenty mercury pnictidehalides containing 3-D cationic network with two different cavities

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being occupied by discrete anions reported in the literature.[3] To the best of our knowledge, only three compounds, $(Hg_6As_4)(AgCl_3)_2$,[4] $(Hg_6As_4)(CuCl_3)_2$,[5] and $(Hg_6As_4)(CuBr_3)_2$,[5] composed of a 3-D cationic network mixed with a 1-D anionic moiety are found in the literature, but there are no other compounds reported with the structural feature of a 3-D cationic network mixed with a 2-D or 3-D anionic network except for $(Hg_3As_2)(TlCl_3)$ and $(Hg_3Sb_2)(TlBr_3)$.[6]

In the present work, in order to obtain new mercury pnictidehalides with new mixed-framework structural feature, we have chosen to incorporate the Hg^{2+} cation in combination with Cd^{2+} cation because the pnictides of these cations exhibit good semiconducting properties and potential for technological applications.[3,7] During the course of our research, we have tried to use a series of the pnicogen elements from P to Sb and the halogen elements from Cl to I as anions; we succeeded only in obtaining a new quaternary mercury and cadmium pnictidehalide semiconductor, $(Hg_6Sb_4)(CdI_6)$ (**1**), with mixed 3-D framework structural feature. Herein, we report the synthesis, crystal structure, optical properties, and electronic band structure calculation of the title compound.

Experimental Section

Materials and Methods. All of the chemicals were analytically pure (99.999%) purchased from Alfa Aesar and used without further purification. The powder X-ray diffraction pattern was collected with a Rigaku DMAX2500 diffractometer at 40 kV and 100 mA for Cu Kα ($\lambda = 1.5406$ Å) with a scan speed of 5°/min at room temperature. The simulated pattern was produced using the Mercury program and single-crystal diffraction data. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Netzsch Sta449C thermoanalyzer under N_2 atmosphere in the range of 30−1000 °C at a heating rate of 10 °C/min. IR spectrum was recorded on a Magna 750 FT-IR spectrometer as KBr pellet in the range of 4000−400 cm^{-1}. The optical diffuse reflectance spectrum was measured on a PE Lambda 35 UV−vis spectrophotometer equipped with an integrating sphere at 293 K, and the $BaSO_4$ plate was used as the reference. The absorption spectrum was calculated from reflection spectrum by the Kubelka−Munk function:[8] $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance. The energy gap was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge in the α/S versus E (eV) plot. Microprobe elemental analysis on Hg, Cd, Sb, and I for the title compound was performed on a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA).

Synthesis. Crystals of **1** were initially prepared by the solid-state reaction of a mixture of HgI_2 (1 mmol, 454 mg), Cd (0.5 mmol, 56 mg), CdI_2 (0.5 mmol, 183 mg), and Sb (0.5 mmol, 61 mg) in our attempt to obtain a new phase, $(Hg_2Sb)_2(CdI_4)$. The starting materials were ground into fine powders in an agate mortar and pressed into a pellet, followed by being loaded into a Pyrex tube evacuated to 1×10^{-4} Torr and flame-sealed. The tube was placed into a computer-controlled furnace, heated from the room temperature to 250 °C at a rate of 40 °C/h, and kept at 250 °C for 4 h. The tube was then heated to 400 °C at 25 °C/h, kept at 400 °C for 120 h, and slowly cooled to 100 °C at a rate of 2 °C/h; it was finally cooled to the room temperature over 4 h. A crop of black crystals of **1** that is stable in air was obtained. (***Caution!*** *the title compound may be toxic because of the toxicity of Hg.*) Microscopic elemental analysis on several single crystals of **1** confirmed the presence of Hg, Cd, Sb, and I in an approximate molar ratio of 5.7:0.9:3.8:6.1. No other elements were detected. The exact composition was established from the X-ray structure determination. The purity of the crystals of **1** was confirmed by PXRD study (Figure S1). Thermogravimetry-differential thermal analysis (TG-DTA) study shows that compound **1** is thermally stable up to 220 °C and underwent decomposition above that temperature (Figure S2).

Single-Crystal Structure Determination. A black single crystal of **1** was mounted on a glass fiber for the X-ray diffraction analysis. Data set was collected on a Rigaku AFC7R equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) from a rotating anode generator at 293 K. Intensities were corrected for LP factors and empirical absorption using the ψ scan technique. The structure was solved by direct methods and refined on F^2 with full-matrix least-squares techniques using Siemens SHELXTL version 5 package of crystallographic software.[9] The site occupancy factor (SOF) of the Cd site was set to $^1/_3$ for the balance of valence, and the other atoms were refined with SOF of 1. The final refinements included anisotropic displacement parameters for all atoms and a secondary extinction correction. The crystallographic data of **1** are listed in Table 1. The selected interatomic distances and bond angles are given in Table 2.

Computational Descriptions. The crystallographic data of **1** determined by X-ray was used to calculate its electronic band structure. The calculation of electronic band structure along with density of states (DOS) was performed with the CASTEP code[10] based on the density functional theory using a plane-wave expansion

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Table 1. Crystal Data and Structure Refinement Parameters for **1**

chemical formula	$Hg_6CdSb_4I_6$
Fw	2564.34
crystal size (mm^3)	0.03 × 0.03 × 0.14
T (K)	293(2)
λ (Mo Kα, Å)	0.71073
crystal system	rhombohedral
space group	R-3c
a (Å)	13.3818(9)
α (deg)	90.93
V (Å^3)	2395.3(3)
Z	4
D_{calcd} (g cm^{-3})	7.111
μ (mm^{-1})	51.306
F(000)	4200
R^a	0.0655
$R_w{}^b$	0.1247
GOF on F^2	0.997
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e Å^{-3})	5.285 and −3.512

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[(wF_o{}^2)^2]\}^{1/2}$.

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for **1**[a]

Hg(1)−Sb(2) × 2	2.704(2)	Sb(1)−Sb(1)$^{\#9}$	2.804(7)
Hg(2)−Sb(1)	2.682(2)	Sb(2)−Sb(2)$^{\#3}$	2.784(3)
Hg(2)−Sb(2)	2.684(2)	Cd(1)−I(1)	2.766(8)
Hg(3)−Sb(2) × 2	2.669(2)	Cd(1)−I(1)$^{\#6}$	2.797(8)
Hg(1)−I(2) × 2	3.110(3)	Cd(1)−I(2)	2.884(8)
Hg(2)−I(1)	3.142(3)	Cd(1)−I(2)$^{\#5}$	2.929(8)

Sb(2)$^{\#1}$−Hg(1)−Sb(2)	156.7(1)	Cd(1)$^{\#7}$−I(1)−Hg(2)	89.7(2)
Sb(1)−Hg(2)−Sb(2)	161.90(8)	Cd(1)−I(1)−Cd(1)$^{\#5}$	172.3(2)
Sb(2)−Hg(3)−Sb(2)$^{\#4}$	177.9(1)	Cd(1)−I(2)−Cd(1)$^{\#5}$	34.8(3)
Sb(2)$^{\#1}$−Hg(1)−I(2)$^{\#2}$	96.73(6)	Cd(1)−I(2)−Hg(1)$^{\#3}$	110.6(2)
Sb(2)−Hg(1)−I(2)$^{\#2}$	99.09(6)	Cd(1)$^{\#5}$−I(2)−Hg(1)$^{\#3}$	85.9(2)
Sb(1)−Hg(2)−I(1)	100.71(7)	Hg(2)$^{\#8}$−Sb(1)−Hg(2)	111.79(7)
Sb(2)−Hg(2)−I(1)	97.17(7)	Hg(2)$^{\#8}$−Sb(1)−Sb(1)$^{\#9}$	107.04(7)
I(2)$^{\#2}$−Hg(1)−I(2)$^{\#3}$	94.0(1)	Hg(3)−Sb(2)−Hg(2)	109.93(8)
I(1)−Cd(1)−I(1)$^{\#6}$	102.3(3)	Hg(3)−Sb(2)−Hg(1)	110.40(7)
I(1)−Cd(1)−I(2)	95.4(2)	Hg(2)−Sb(2)−Hg(1)	113.54(7)
I(1)$^{\#6}$−Cd(1)−I(2)	107.7(2)	Hg(3)−Sb(2)−Sb(2)$^{\#3}$	106.70(9)
I(1)−Cd(1)−I(2)$^{\#5}$	106.3(2)	Hg(2)−Sb(2)−Sb(2)$^{\#3}$	107.6(1)
I(1)$^{\#6}$−Cd(1)−I(2)$^{\#5}$	94.1(2)	Hg(1)−Sb(2)−Sb(2)$^{\#3}$	108.4(1)
I(2)−Cd(1)−I(2)$^{\#5}$	145.1(3)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + {}^1/_2, -z + {}^1/_2, -y + {}^1/_2$; (#2) $x - {}^1/_2, z + {}^1/_2, y - {}^1/_2$; (#3) $-x, -y + 1, -z$; (#4) $-y + {}^1/_2, -x + {}^1/_2, -z + {}^1/_2$; (#5) $-y + {}^1/_2, -x + {}^1/_2, -z - {}^1/_2$; (#6) $-z, -x, -y$; (#7) $-y, -z, -x$; (#8) z, x, y; (#9) $-x, -y, -z$.

of the wave functions. The total energy is calculated by the generalized gradient approximations in the scheme of Perdew−Burke−Ernzerhof functional.[11] The interactions between the ionic cores and the electrons are described by the norm-conserving pseudopotential,[12] in which the orbital electrons of I-5s^{2}5p^5, Sb-5s^{2}5p^3, Cd-4d^{10}5s^2, and Hg-5d^{10}6s^2 are treated as valence electrons. The number of plane waves included in the basis was determined by a cutoff energy E_c of 450 eV, and the numerical integration of the Brillouin zone was performed using a 4 × 4 × 4 Monkhorst−Pack k-point sampling. The convergent criterion of total energy was set by the default value of the CASTEP code.[10a]

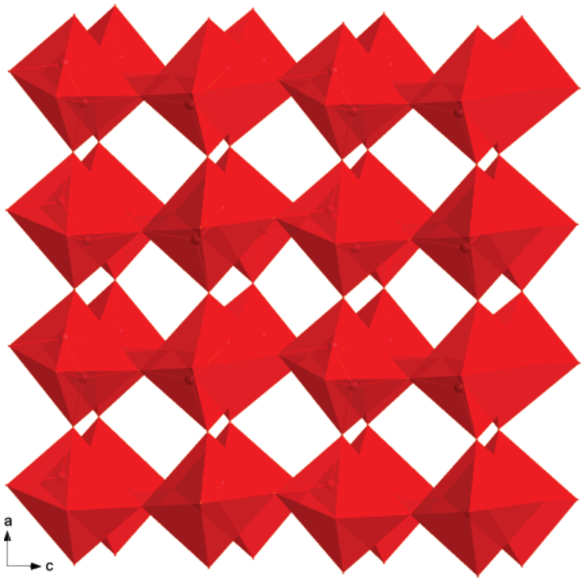

Figure 1. The perovskite-like 3-D mercury antimonide cationic network in **1** viewed along the b-axis.

Results and Discussion

Crystal Structure. The crystal structural novelty of **1** is that a 3-D mercury antimonide cationic network interpenetrates with an unusual 3-D cadmium iodide octahedral anionic network through the weak covalent interactions between mercury and iodine atoms to form a mixed 3-D framework (Figure S3). Among the cationic moiety, the distorted (Sb_2Hg_6) octahedra, built up of the bonded pair of Sb atoms octahedrally coordinated by six Hg atoms to form distorted octahedron with normal Sb−Sb bond distance being 2.78−2.80 Å,[3g,13] corner-share each other to form a perovskite-like 3-D cationic network (Figure 1), which is also found in other compounds.[3a,3g] The anionic moiety can be regarded as a 3-D corner-sharing I_6 octahedral anionic network with two-thirds I_6 octahedra being occupied by Cd atoms. Eight I_6 octahedra, each consisting of four I1 atoms and two I2 atoms, corner-share each other along the octahedral equatorial plane to form an approximate square arrangement with four octahedra lying at the corner and the other four at midpoint of edge, which extend along the a and b directions to form an octahedral layer (Figure S4). The octahedral layers stack with -*ABAB*- mode along the c direction via corner-sharing the axial I atoms of the octahedra at midpoint of square edge to form a 3-D I_6 octahedral anionic network (Figure 2). It is notable that the 3-D I_6 octahedral anionic network in **1** is the first example among the cadmium halides and absolutely different from the most known cadmium halides with the 2-D layer structures, among which (CdX_6) (X = F, Cl, I) octahedra edge-share to form steplike layers.[14]

Unlike most of inorganic supramolecular complexes based on mercury−pnicogen or mercury−pnicogen−halogen, where

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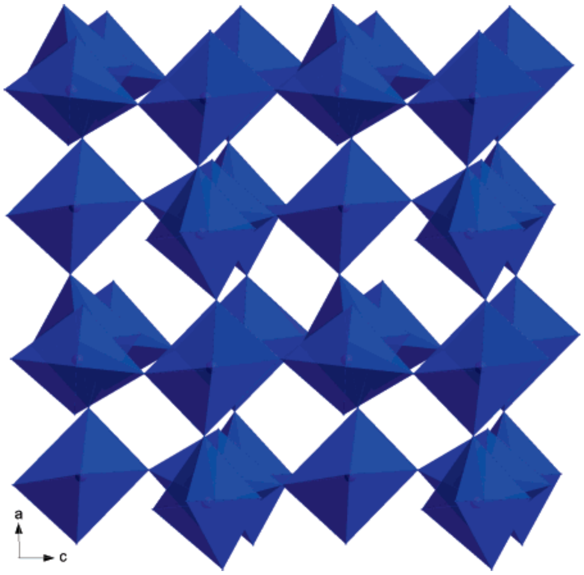

Figure 2. View of the 3-D I_6 octahedral anionic network in **1** along the *b*-axis.

the guest anions embedded in the cavities of the host framework are discrete or 1-D infinite structural units,[3a,f−h,15] the present compound contains a new type of "guest anions" with a 3-D I_6 octahedral anionic network mixed with 3-D cationic network.[3,6,15] In comparison with $(Hg_6Sb_4)(CdI_6)$-$Hg_{0.6}$[3g] that contains discrete (CdI_6) octahedral anions and Hg atoms located in the different cavities of the host framework, compound **1** contains a 3-D I_6 octahedral anionic network interpenetrated with the 3-D cationic network although they have the nearly same formula except for the discrete mercury atoms.

There are three crystallographic independent mercury atoms in **1**. Analogues to the compound $(Hg_6Sb_4)(CdI_6)$-$Hg_{0.6}$,[3g] the mercury atoms are almost linearly coordinated by two antimony atoms in the present compound. The Hg−Sb bond distances range from 2.682(2) to 2.704(2) Å, which lie in the normal range of the Hg−Sb separations in mercury pnictidehalides.[3g,15a,16] The Cd−I bond distances range from 2.766(8) to 2.929(8) Å, which are shorter than those found in cadmium iodides and cadmium pnictidehalides[14,17] but-comparable to those found in $(Hg_2As)_2(CdI_4)$.[3h]

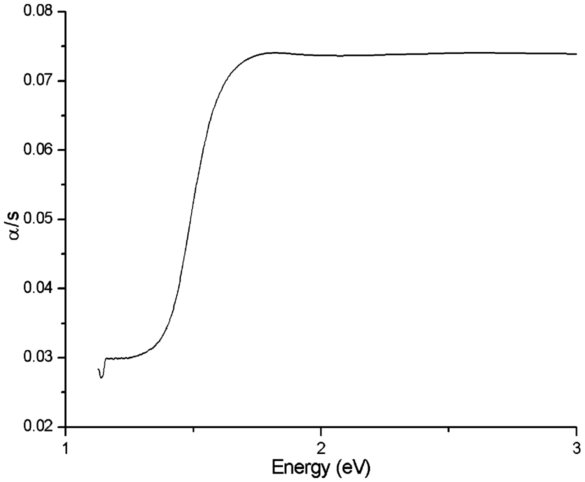

Figure 3. Diffuse reflectance spectrum of **1**.

The shortest distance between the cationic and anionic frameworks in **1** is much longer than the value for covalent bonding suggesting the typical supramolecular interactions between them. The interatomic distances between the mercury atoms in the cationic moiety and the iodine atoms in the anionic moiety range from 3.110(3) to 3.142(3) Å, which are rather longer than the Hg−I covalent bond distance but shorter than the sum of van der Waals radii of Hg and I. This indicates that there are weak covalent interactions between the cationic and anionic moieties in the crystal structure of **1**, as the case found in the literature.[3a,g,h,15]

Optical Properties. The diffuse reflectance spectrum of **1** reveals the presence of an optical gap of 1.25 eV (Figure 3), which suggests that the present compound is semiconductor and is consistent with its color. The energy gap of **1** is approximate to those of CdTe (1.44 eV), GaAs (1.43 eV), and $CuInSe_2$ (1.04 eV), all of which are highly efficient photovoltaic materials.[18] Thus, it can be supposed that the present compound may become potential material for the efficient absorption of solar radiation in solar cell applications. The IR spectrum of **1** (Figure S5) shows no obvious absorption in the range of 4000−400 cm^{-1}. This in combination with its good thermal stability (Figure S2) supports the idea that the compound may be potentially used as window materials for laser delivery media and infrared transmitting for optical fiber applications in telecommunication.[19]

Electronic Band Structure. The calculated band structure of **1** along high symmetry points of the first Brillouin zone is plotted in Figure 4, where the labeled *k*-points are present as *F* (0.5, 0.0, −0.5), *G* (0.0, 0.0, 0.0) and *Z* (0.5, 0.5, −0.5). It is found that the top of valence bands (VBs) and the bottom of conduction bands (CBs) have small dispersions. The lowest energy (1.04 eV) of CBs and the highest energy (0.00 eV) of VBs are both localized at G. Accordingly, the present compound shows a semiconducting character with a direct

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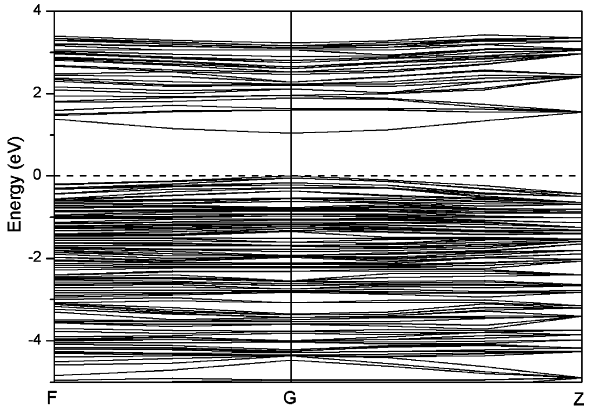

Figure 4. The band structure of **1**. (The Femi level is set at 0 eV, and the bands below −5 eV have been cut for clarity.)

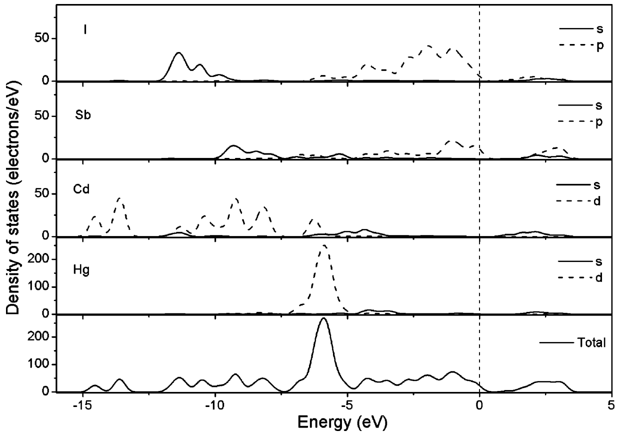

Figure 5. The total and partial density of states for **1**. (The Femi level is set at 0 eV.)

band gap of 1.04 eV, which is comparable with the experimental value (1.25 eV). The bands can be assigned according to the total and partial densities of states (DOS) as plotted in Figure 5. The Hg-5d, Cd-4d, and I-5s states mixing with small Sb-5s and Cd-5s states create the VBs localized between about −15.0 and −5.0 eV. The VBs between energy −5.0 eV and the Fermi level (0.0 eV) are mostly formed by I-5p and Sb-5p states mixing with a small amount of the s orbital of the transition metals, while the CBs between 1.0 and 5.0 eV are almost a contribution from the Cd-5s, Hg-6s, and Sb-5p states hybridized with a small amount of I-5s, I-5p, and Sb-5s states. Accordingly, it can be considered that the optical absorption of **1** is mainly ascribed to the charge transitions from I-5p and Sb-5p states to Cd-5s and Hg-6s states.

In addition, we calculated the atomic site and angular momentum projected DOS of **1** to elucidate the nature of the electronic band structure and chemical bonds. As shown in Figure 5, it can be observed that the density and shape of Sb-5p state are similar to those of the Hg-6s state between −5.0 and −2.5 eV while the density and shape of I-5p are much different from those of the Cd-5s state, which indicates that there are strong covalent interactions in the Hg−Sb bond and weak covalent interactions in the Cd−I bond. In other words, the Hg−Sb bond is mainly covalent in character whereas the Cd−I bond is mainly ionic in character, which supports the idea of mixed-framework compound.

Semiempirical population analysis allows for a more quantitative bond analysis. The calculated bond orders of the Cd−I, Hg−Sb, Sb−Sb, and Hg−I are from 0.09 to 0.32, 0.71 to 1.05, 0.57 to 0.88, and −0.68 to −0.36, respectively, in a unit cell of **1** (pure covalent single bond order is generally 1.0). This indicates that the Hg−Sb and Sb−Sb bonds are mainly covalent in character whereas the Cd−I bond is mainly ionic character and the Hg−I bond is weak covalent interaction, which is in good agreement with the crystal structure of **1**.

Conclusion

In summary, a new quaternary mercury and cadmium pnictidehalide semiconductor, $(Hg_6Sb_4)(CdI_6)$ (**1**), has been synthesized and characterized. Studies on the optical properties of **1** support that the present compound may be a potential candidate for applications as efficient photovoltaic materials and window materials for laser delivery media. The calculations of the electronic band structure along with DOS indicate that the present compound is a semiconductor with a direct band gap and that the optical absorption is mainly originated from the charge transitions from I-5p and Sb-5p states to Cd-5s and Hg-6s states. The DOS and semiempirical population analyses indicate that the Hg−Sb and Cd−I bonds are mainly covalent and ionic in characters, respectively, which support the idea that the present compound possesses the structural feature of mixed 3-D framework composed of the covalent framework of $(Hg_6Sb_4)^{4+}$ and ionic framework of $(CdI_6)^{4-}$.

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Supporting Information Available: X-ray crystallographic file in CIF format, experimental and simulated powder X-ray diffraction pattern, TG and DTA curves, IR spectrum, and molecular structure figures for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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