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Synthesis, Properties, and Theoretical Studies of New Stepwise Layered Iodoplumbate: $[\mathrm{Ni(opd)_2(acn)_2}]_n[\mathrm{Pb_4I_{10}}]_n$[†]

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A novel 2D layered iodoplumbate, $[\mathrm{Ni(opd)_2(acn)_2}]_n[\mathrm{Pb_4I_{10}}]_n$ (**1**), yellow-green in color, has been synthesized. The anionic $[\mathrm{Pb_4I_{10}}^{2-}]_n$ layer is comparable to the hexagonal $\mathrm{PbI_2}$ sheet but in a lower symmetry. Although the intercalated cations contribute negligibly to the electron transition, they induce the reconstruction of the inorganic moiety, which leads to a band-gap blue shift with respect to that of $\mathrm{PbI_2}$.

Layered binary $\mathrm{PbI_2}$ ($\mathrm{CdI_2}$ type), a direct wide-band-gap semiconductor, has attracted continuous interest for several decades because of its application as a photocell, X-ray and γ-ray detectors, etc.[1] The closely related iodoplumbate can be understood as a Pb/I hybrid generated by the introduction of suitable organic molecules/ions into $\mathrm{PbI_2}$, which exhibits great structural diversity and a combination of the beneficial properties of both moieties.[2] The majority of the iodoplumbates are isolated clusters,[3] 1D chains,[4] while the derivatives of the 2D layer[4c,5] and 3D framework[6] are relatively rare. Few heterometallic layered hybrids are also reported, such as $[\mathrm{Bi_4Ag_2I_{16}}^{2-}]_n$.[7]

Most of the layered iodoplumbates belong to the perovskite type, in which the packing motif of the vertex-sharing $[\mathrm{PbI_6}]$ octahedra is looser than that of $\mathrm{PbI_2}$.[4a,8] Such a density decrease is because the involvement of cations requires negative charges on the inorganic moiety. On the other hand, the packing density of the Pb/I moiety usually reflects the band gap of the compound. The Pb:r ratio is an empirical parameter to indicate the packing density of the Pb/I moiety, where r is defined as $r = \sum(N\mu_n\text{-I})/n$, $n = 1-6$; $N\mu_n$-I means the number of n-fold-coordinated I atoms per building unit.[9] The lower and upper Pb:r limits are 0.167 and 1.5, respectively. The lower limit is calculated from the loosest example, a discrete $[\mathrm{PbI_6}]^{4-}$ cluster,[10] and the upper limit, from $\mathrm{PbI_2}$, the most condensed example. The perovskite iodoplumbate has a Pb:r ratio between 0.333 and 0.667.[4a,8] A big challenge in the synthetic chemistry is how to increase such a ratio to generate more condensed structures. Here we report a novel layered iodoplumbate $[\mathrm{Ni(opd)_2(acn)_2}]_n$-$[\mathrm{Pb_4I_{10}}]_n$ (**1**), with the highest Pb:r ratio (0.8) among the anionic layered iodoplumates, in which the $[\mathrm{PbI_6}]$ connection is comparable to that in hexagonal $\mathrm{PbI_2}$ sheet but of lower symmetry. The single-crystal structure, optical band gap, thermal stability, and electronic structure are reported.

Compound **1** (Figure 1) crystallizes in the monoclinic space group $P2_1/c$ and features a novel infinite 2D stepwise $[\mathrm{Pb_4I_{10}}^{2-}]_n$ anionic layer with $[\mathrm{Ni(opd)_2(acn)_2}]^{2+}$ as intercalated cations (opd = *o*-phenylenediamine; acn = acetonitrile).

[†] Dedicated to Prof. Xin-Tao Wu on the occasion of his 70th birthday.

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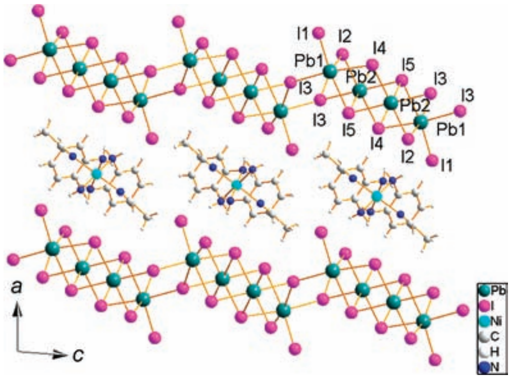

Figure 1. (010) view of **1**.

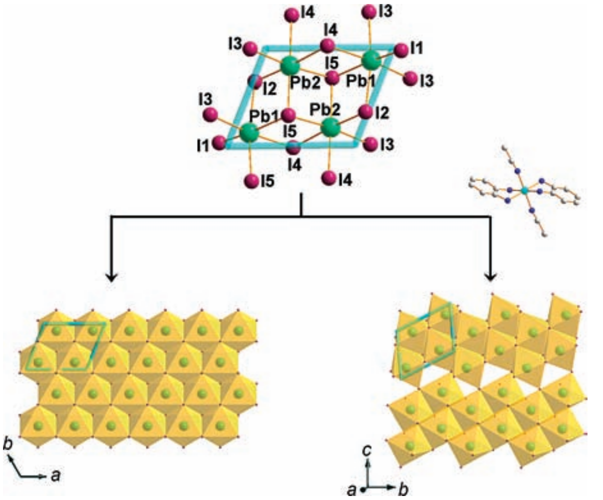

Figure 2. Cation effect leading to symmetry breaking. Left: single hcp layer in PbI_2. Right: single $[Pb_4I_{10}{}^{2-}]_n$ anionic layer in **1**. The blue rhombus confines the 2 × 2 subunit.

Different from the vertex sharing in perovskite iodoplumbates, the $[PbI_6]$ octahedra are edge-shared in **1** (Figure 1). The 2 × 2 subunit $[Pb_4I_{10}]^{2-}$, which is made of four edge-shared $[PbI_6]$ octahedra, extends along the *c* axis in a zigzag motif via sharing of the I3−I3 edges and propagates along the *b* axis via the common I3−I4 and I4−I4 edges (Figures 1 and 2 and Supporting Information, Figure S7). Similar 2 × 2 subunits could be abstracted from PbI_2 with a different formula: $[Pb_4I_8]^0$. Two more I^- anions per subunit are involved in **1** because of the occurrence of the less coordinated μ_t-I1 (terminal I, one-fold coordination) and μ_2-I2, while the I^- anions in PbI_2 are all 3-fold-coordinated (μ_3-I). The μ_t- and μ_2-I atoms are responsible for the loose packing of $[PbI_6]$ octahedra (Figure 2). The anionic layer in **1** also distinguishes it from that in β-(EDT-TTF-I_2)$_2$[$Pb_{5/6}\square_{1/6}I_2$]$_3$, in which the charge balance has been achieved differently via the Pb^{2+} defects.[5] The formation of the stepwise anionic layers in **1** may be attributed to the cation effect because the smaller cation in [Me_2HN-$(CH_2)_2$-NMe_2H][Sn_3I_8] induces a stepwise $[Sn_3I_8{}^{2-}]^n$ anionic layer but with a narrower step.[11]

The Pb−I bonds in **1** are quite distorted in the range of 3.001(1)−3.529(9) Å, with 3.22 Å as the average (the Pb−I bond is 3.22 Å in PbI_2), and the I−Pb−I angles range from 81.63° to 104.15° and from 164.56° to 172.25° for Pb1, which is coordinated with one μ_t-I, one μ_2-I, and four μ_3-I atoms, and from 84.45 to 93.67 and from 174.28° to 177.10° for Pb2, which is coordinated by one μ_2-I and five μ_3-I atoms (see details in the Supporting Information, Table S2). The angles in PbI_2 are nearly 90° or 180°, in which all Pb atoms coordinate to six μ_3-I atoms.

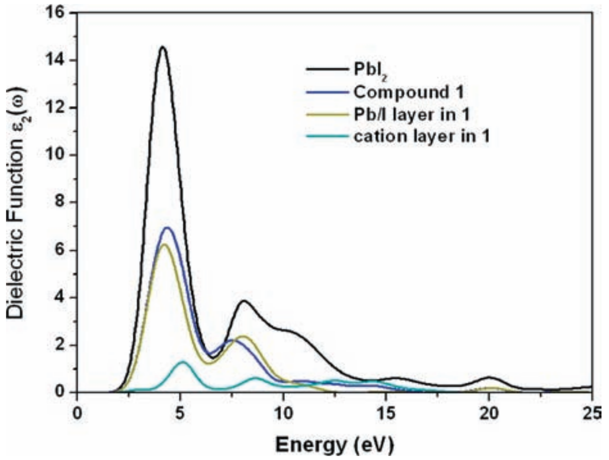

Figure 3. Imaginary parts $\epsilon_2(\omega)$ of the dielectric functions of **1** and PbI_2.

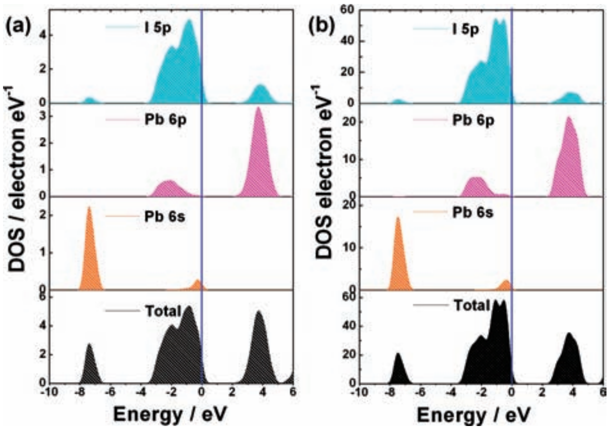

Figure 4. Total and partial density of states of (a) PbI_2 and (b) **1**.

The diffuse-reflectance spectra of **1** and PbI_2 have been measured, and the band gaps have been evaluated by the extrapolation method (Supporting Information, Figure S1). Their optical band gaps are 2.67 and 2.34 eV, respectively (the latter is comparable to the reported 2.27 eV for PbI_2[12]).

The linear absorption optical properties were described in terms of the imaginary part $\epsilon_2(\omega)$ of the dielectric function and calculated with the *CASTEP* code (Supporting Information). As shown in Figure 3, the onset of the transition edges of **1** and the Pb/I anionic moiety is nearly identical. Therefore, the organic complex cations have minor contributions to the electron transition, similar to that previously reported.[4b] The electronic structures of **1** and PbI_2 have been calculated (Figures 4 and 5). For the sake of a clear comparison, the cations in **1** have not been considered. As shown in Figure 5a, PbI_2 has a direct band gap, and the highest occupied crystal orbitals (HOCOs) are mainly the

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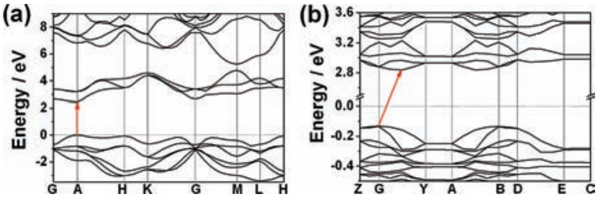

Figure 5. Electronic band structures of (a) PbI_2 and (b) **1**. The arrows indicate the direct and indirect band gaps.

antibonding states of Pb 6s and I 5p (p_x/p_y) at *A* ($k = 0.0, 0.0, 0.5$) and the lowest unoccupied crystal orbitals (LUCOs) are mostly Pb $6p_z$ orbitals (Supporting Information, Figures S2 and S3). The HOCO antibonding interactions are along the *z* axis (parallel to the crystallographic *c* axis), and p_z orbitals of LUCOs show σ interactions between neighboring layers. The maximum destabilization is at A ($k = 0.0, 0.0, 0.5$),[13] while the lowest energy of the conducting band is also observed at A, which therefore indicates the direct band-gap character. Both HOCOs and LUCOs of **1** have similar components but with larger degrees of distortion (Supporting Information, Figures S4 and S5). The interlayer orbital interactions are slightly off the *x* direction (parallel to the crystallographic *a* axis); the flat band structures from Y ($k = 0.0, 0.5, 0.0$) to A ($k = -0.5, 0.5, 0.0$) and E ($k = -0.5, 0.5, 0.5$) to C ($k= 0.0, 0.5, 0.5$) indicate that there is only a very weak interaction along the *a* axis because of intercalation of the cations. So, nearly no electron transition would occur along such an axis, and the electron transition should be confined to the Pb/I layer. This may be in response to the band-gap blue shift observed between **1** and PbI_2. On the other hand, the orbital distortion may affect the transition direction of the electrons and lead to an indirect band gap for **1** (Figure 5b). These simple correlations suggest that, although the intercalated cations between Pb/I layers contribute negligibly to the electronic transition, the template effect of the cations causes the reconstruction of the Pb/I inorganic moiety and thus leads to different properties.

The thermal stability of **1** has been studied by thermogravimetric/differential thermal analysis (TG/DTA) on hand-picked crystals, of which the phase purity has been confirmed by the X-ray diffraction pattern (Supporting Information, Figure S6). As shown in Figure 6, **1** first loses 3.13% weight (calcd 3.37%) above 210 °C, because of the loss of CH_3CN molecules, and then 8.39% weight (calcd 8.90%) above 290 °C, because of the loss of opd molecules. Finally, **1** has been completely decomposed to PbI_2, which melts at 400 °C.

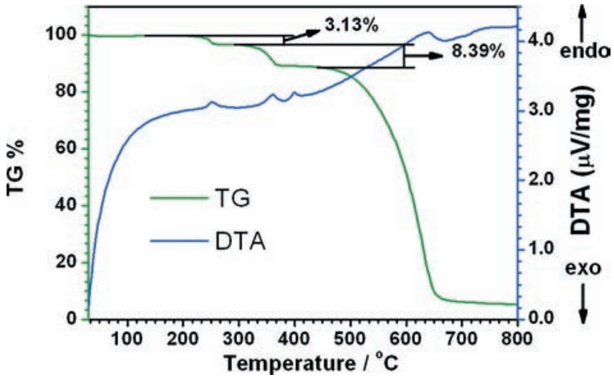

Figure 6. TG/DTA curves of compound **1**.

In summary, a novel type of stepwise Pb/I inorganic layer has been found in compound $[Ni(opd)_2(acn)_2]_n[Pb_4I_{10}]_n$ with the highest Pb:*r* ratio (0.8) among the anionic layered iodoplumbates. The inorganic layer is more condensed than that in the perovskite type but less symmetric than the hexagonal PbI_2 sheet. The linear absorption optical property calculation indicates a minor contribution of the cations to the transition edge. However, the cation template effect leads to such a novel packing motif of the $[PbI_6]$ unit. Compared with PbI_2, **1** has a 0.33 eV wider band gap and less thermal stability. New layered iodometalates are expected via the choice of suitable intercalate species and a new combination of inorganic building units.

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Supporting Information Available: Crystallographic data in the form of a CIF file, details of synthesis methods, experimental measurements of compound **1**, theoretical calculation details, and other supporting tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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