Beyond templating: Electronic structure impacts of aromatic cations in organic–inorganic antimony chloride

Jakob Blahusch,[a, b] Douglas H. Fabini,*[a] Alberto Jiménez-Solano,[a] and Bettina V. Lotsch*[a, b]

Dedicated to Professor Dr. Peter Klüfers on the Occasion of his 70th Birthday

Organic cations influence the crystal packing and, less commonly, the electronic structure of hybrid organic–inorganic materials. Two new hybrid compounds prepared from solution, (PEA)SbCl₄ and (PEA)₂Sb₂Cl₁₂ (PEA = phenylethylammonium), demonstrate how the aromatic PEA cation modifies the crystal and electronic structures relative to inorganic antimony chlorides. In (PEA)SbCl₄ the ethylammonium conformation results in a polar and chiral crystal structure, and the bandgap is characterized by organic-inorganic charge transfer. In the mixed-valence (PEA)₂Sb⁶⁺Sb⁴⁻Cl₁₂ the structure is a uniaxial elongation of that of inorganic analogs and the optoelectronic properties combine features of intervalence charge transfer and organic–inorganic charge transfer.

Introduction

Hybrid organic–inorganic materials have gained a lot of interest in recent years due to their properties regarding applications in optics and electronics. A large focus has lately been on lead-containing hybrid materials due to their intriguing optical and electronic properties.[11] Due to stability problems and the toxicity of lead salts lead-free alternatives are currently in the research focus. Lee et al. demonstrated the use of Cs₂SnI₄ in solar cells, which renewed the interest in vacancy ordered perovskites as possible alternatives to lead halide perovskites.[2]

Especially antimony halides gained more attention due to a large structural diversity. The ability of antimony to accommodate different polyhedral building units (in the case of oxidation state +3: [SbX₄]³⁻, [Sb₂X₈]⁴⁻, [Sb₃X₁₂]⁵⁻, in the case of the oxidation state +5: [SbX₅]⁵⁻) in combination with two possible oxidation states allows for a large number of compounds with interesting physical properties.[3]

Antimony in oxidation state +5 has recently been considered for optoelectronic applications because the relative energies of bands derived from halides, Sb, and Sb p confer properties favorable for intermediate bandgap solar cells.[4] In (N-EtPy)SbBr₃ (N-EtPy = N-ethylpyridinium) isolated [SbBr₃]⁻ octahedra are present.[5] Mixed-valence antimony halides have been of interest since the synthesis of Cs₂SbCl₄ in the early 1900s.[6] Spectroscopic measurements pointed to the existence of SbCl₄⁻ and SbCl₃⁻, but only in 1983 was superlattice ordering of Sb(III) and Sb(V) revealed by neutron diffraction.[7] Mixed-valence antimony halides can be described by the formula A₅SbX₆ where A is a monovalent cation, Sb is a nominal tetravalent antimony cation and X is a halide.[8] The compounds with small cations on the A position crystallise in a distorted K₂PtCl₆ structure.[10] Several antimony based compounds with the formula A₅Sb⁶⁺Sb⁴⁻X₁₂ (A = Cs, Rb, K, NH₄⁺ and X = Cl, Br) have been reported in the literature.[9, 11, 12] The structure of these compounds is built up by ordered [Sb⁶⁺X₁₂]⁻ and [Sb⁴⁻X₁₂]⁻ units. These mixed-valence compounds gained a lot of interest due to their deep purple color in A₅Sb⁶⁺Sb⁴⁻Cl₁₂ and deep black in A₅Sb⁶⁺Sb⁴⁻Br₁₂.[9, 13] Investigations into the optical absorption showed that this is due to electron transfer from Sb(III) to Sb(V).[14]

The structure and the resulting dimensionality of the inorganic sublattice of organic-inorganic perovskite related materials is controlled by the organic cations.[15] A large family of compounds based on the phenylethylammonium (PEA) cation has been reported so far with varying metal cations and anions.[16, 17, 18] Most of the compounds feature a layered structure based on corner-sharing metal halide octahedra derived from the 3-D perovskite parent structure by taking (100) oriented layers.[15] In-between the layers PEA can exhibit three distinct conformations which can be divided in trans and gauche conformations depending on the rotation of the amine group. (PEA)₂PbCl₄[17] and (PEA)₂CuCl₄[18] exhibit two different trans conformations. In (PEA)₂CuCl₄ the PEA cation possesses a mirror plane perpendicular to the phenyl ring and the ethylammonium group lies in the mirror. In contrast, in (PEA)₂PbCl₄ the phenyl ring and the first ethylammonium carbon lie in a plane but the terminal ethylammonium carbon and the amine are located out of the plane.
Here we report the synthesis and characterisation of two novel hybrid antimony halides with PEA as organic cation, (PEA)\(_2\)SbCl\(_6\) and (PEA)\(_4\)Sb\(_2\)Cl\(_{12}\). (PEA)\(_2\)SbCl\(_6\) crystallises as yellow plate-like crystals with a polar and chiral crystal structure. The aromatic cation decreases the bandgap compared to CsSb\(^\text{III}\)Cl\(_6\), and the bandgap is of charge transfer type with the unusual inorganic-derived conduction band. Mixed-valence combination of an organic-derived valence band and an aromatic cation decreases the bandgap compared to CsSb\(^\text{III}\)Cl\(_6\). The Crystal structure of (PEA)\(_2\)SbCl\(_6\) crystallises as dark red needle-like crystals in a layered structure of alternating planes of ordered [Sb\(^\text{III}\)Cl\(_6\)]\(^\text{−}\) and [Sb\(^\text{V}\)Cl\(_6\)]\(^\text{+}\) octahedra and molecular cation bilayers. This compound exhibits properties that combine features of intervalence charge transfer and organic–inorganic charge transfer.

Results and Discussion

Synthesis

(PEA)\(_2\)SbCl\(_6\) and (PEA)\(_4\)Sb\(_2\)Cl\(_{12}\) were prepared from a solution of Sb\(_2\)O\(_3\) and PEA in concentrated hydrochloric acid at 100 °C. Upon cooling the solution yellow plate-like crystals of (PEA)\(_2\)SbCl\(_6\) precipitated at room temperature (see Experimental section). Phase purity and composition were determined by powder X-ray diffraction (PXRD) and energy-dispersive X-ray spectroscopy (EDX, see Figure S1, Table S3, Figure S4, S5).

For (PEA)\(_4\)Sb\(_2\)Cl\(_{12}\) the concentration of the starting materials was increased (see Experimental Section). After heating to 100 °C and obtaining a clear solution the reaction mixture was cooled to room temperature. In the beginning only yellow plate-like crystals of (PEA)\(_2\)SbCl\(_6\) precipitated. After leaving the mixture at room temperature for one week the dissolution of the yellow crystals and the formation of dark needle-like crystals of (PEA)\(_4\)Sb\(_2\)Cl\(_{12}\) can be observed. To obtain a phase pure sample of (PEA)\(_4\)Sb\(_2\)Cl\(_{12}\) the mixture was left to stand in the vial for one week until no yellow crystals were visible. Phase purity and composition were determined by PXRD and EDX (see Figure S2, Table S7, Figure S8, S9).

Crystal structure

The yellow plate-like crystals of (PEA)\(_2\)SbCl\(_6\) crystallise in the monoclinic space group P2\(_1\), (#4) with Z = 2 formula units in the unit cell (see Table 1 and Figure 1a, b). The Flack parameter was refined to 0.012(12) and no additional symmetry elements were found with PLATON.\(^{[19]}\) The asymmetric unit contains one PEA cation, one antimony cation and six chloride ions. The structure contains isolated [Sb\(^\text{III}\)Cl\(_6\)]\(^\text{−}\) octahedra (see Figure 1c). The Sb–Cl bond lengths are in the range of 2.3389(9)–2.3911(10) Å, which indicate the oxidation state +5 (see Table 2),\(^{[20,21]}\) in line with the computed bond valence sum of 5.069.

The conformation of the PEA cation be described by the rotation of the terminal ethylammonium group as described by Ueda et al. In the most stable conformation, according to Ueda et al., the ethylammonium group lies in the mirror plane perpendicular to the phenyl ring. The rotation of the ammonium group around the ethyl bond is described by the

| Table 1. Crystal data and structure refinement for (PEA)\(_2\)SbCl\(_6\) at 102 K and (PEA)\(_2\)SbCl\(_6\) at ambient temperature. |
| Compounds | (PEA)\(_2\)SbCl\(_6\) 102 K | (PEA)\(_2\)SbCl\(_6\) at ambient temperature |
|-------------|-----------------------------|-----------------------------------|
| Empirical formula | C\(_6\)H\(_{12}\)Cl\(_2\)N\(_3\)Sb | C\(_6\)H\(_{12}\)Cl\(_3\)NSb |
| Temperature/K | 101.7 | 297.8 |
| Crystal system | monoclinic | monoclinic |
| Space group | P2\(_1\),/c | P2\(_1\), |
| a/Å | 7.5311(4) | 8.0131(10) |
| b/Å | 24.7449(14) | 101.638(4) |
| c/Å | 12.3074(7) | 14.5663(17) |
| \(β°\) | 90.118(2) | 6.41 to 49.364 |
| \(V\)\(^{\text{Å}}\)^3 | 2293.6(2) | 797.28(16) |
| Z | 4 | 2 |
| 2Θ range for data collection/° | 4.668 to 61.078 | 6.41 to 49.364 |
| Independent reflections | 6832 | 2692 |
| \(R\) | 0.0884 | 0.0228 |
| \(R\) | 0.0729 | 0.0233 |
| Goodness-of-fit on \(F^2\) | 1.028 | 1.061 |
| Final R indexes [I > 2σ (I)] | R\(_I\) | 0.0548, wR\(_I\) = 0.0767 |
| Final R indexes [all data] | R\(_I\) | 0.1240, wR\(_I\) = 0.0936 |
| Largest diff. peak/hole/e Å\(^{-3}\) | 0.72/−0.71 | 0.49/−0.34 |

| Table 2. Torsion angles \(ϕ_\text{α}\) and \(ϕ_\text{β}\) N–H⋯π and Sb–Cl distances for (PEA)\(_2\)SbCl\(_6\) and (PEA)\(_4\)Sb\(_2\)Cl\(_{12}\). |
| Compounds | (PEA)\(_2\)SbCl\(_6\) | (PEA)\(_4\)Sb\(_2\)Cl\(_{12}\), 102 K |
|-------------|-----------------------------|-----------------------------|
| \(ϕ_\text{α}\) | −151.4(8) | −4(5)/−2.2(5) |
| \(ϕ_\text{β}\) | 61.5(7) | −5.2(7)/45.5(9) |
| d(N–H⋯π)/Å | 3.3633(4) | 2.6321(11)/−2.6739(10) |
| Sb\(^\text{III}\)–Cl bond length/Å | 2.3389(9)/−2.3911(10) | 2.3447(19)/−2.3543(16) |
angle $\phi_a$, as depicted in Figure 1d. Rotations around the bond connecting the phenyl and ethyl moieties, which rotate the plane of the phenyl ring with respect to the mirror plane given in Figure 1d, are described by the angle $\phi_b$. $\phi_a = 0^\circ$ and $\phi_b = 0^\circ$ describe the most stable conformation for the free molecule (see Figure 1d). Clockwise rotations from this conformation is denoted with positive angles and counterclockwise rotations with negative angles. For $\phi_a > +90^\circ$ and $< -90^\circ$, the conformation is called gauche, while for $\phi_a > -90^\circ$ and $< 90^\circ$ the conformation is called trans. To accurately describe the overall conformation both angles need to be considered. The angles of the phenylethylammonium cation in (PEA)SbCl$_6$ are $\phi_a = -151.4(8)^\circ$ and $\phi_b = 61.5(7)^\circ$ which corresponds to the gauche conformation of the cation (see Table 2). The cation creates N–H⋯Cl bonds to four chloride ions (see Table S11).

Incorporation of the cation reduces the symmetry of (PEA)SbCl$_6$ compared to CsSbCl$_6$ (reported space group $Cc$; though we note in the ab initio calculations section below that the correct space group appears to be $C2/c$ to space group $P2_1$ and introduces chirality to the structure. To address the origins of the chiral crystal structure, we consider whether the molecular building blocks are chiral or achiral, and how they assemble in the solid. If any building block is chiral and enantiomerically pure, achiral crystal structures are forbidden. On the other hand, if the building blocks are achiral or chiral and racemic, both achiral and chiral crystal structures are permitted, as achiral building blocks can still assemble to a chiral crystal structure by a suitable rotation of bonds or helical arrangement.

For antimony halides Denhardt et al. reported the synthesis of several compounds based on the chiral cation $(R)$-1-(4-fluoro)phenylethylammonium and probed their nonlinear optical properties. The crystal structures are chiral due to the chiral cation but the compounds crystallise in the acentric, achiral Sohncke group, $P2_1$. In the case of (PEA)SbCl$_6$ the free PEA cation in itself is achiral in the most stable conformation ($\phi_a = 0^\circ$, $\phi_b = 0^\circ$), but the conformationally flexible bonds of the ethylammonium group in the free cation all rotate in the same sense in the solid state, so this building block is chiral and enantiomerically pure, guaranteeing a chiral crystal structure. However, we note that in this case, the enantiomerically pure, chiral nature of the cation is intimately intertwined with the crystal packing: The free molecule is conformationally flexible, and could thus easily adopt both conformations equally (a racemate) or be disordered at finite temperature in such a way that an intramolecular mirror plane is restored. This is in contrast with molecules where chirality derives from the arrangement of the substituents and the barrier to exchanging handedness involves bond breaking and re-formation. In (PEA)SbCl$_6$, the conformation of the cation, perhaps related to a favorable hydrogen bonding interaction arrangement, causes this chiral configuration to be favorable. There are no mirror planes and no inversion center in the crystal structure, which is therefore acentric and chiral, and the space group is the acentric, achiral Sohncke group, $P2_1$. Strictly speaking, while the crystal structure is chiral, the space group itself is not as it does not belong to one of the 11 enantiomorphous pairs (e.g. $P4_1$ and $P4_4$).

The dark-red needle-shaped crystals of (PEA)$_2$Sb$_2$Cl$_8$ crystallise in the monoclinic spacegroup $P2_1/c$ ($\#14$) with Z = 4 formula units in the unit cell (see Table 1). The asymmetric unit contains four PEA cations, two antimony cations, and twelve chloride ions. The structure contains isolated [Sb$^+$Cl$_6$]$^-$ and [Sb$^+$Cl$_4$]$^-$ octahedra (see Figure 2a, b). The antimony cations occupy two special crystallographic positions. The Sb–Cl bond lengths for Sb02 is in the range of 2.3447(19)–2.3543(16) Å which are comparable to the bond lengths in (PEA)SbCl$_6$ and indicate the oxidation state +5, while for Sb01 the Sb–Cl bond lengths are in the range of 2.6321(11)–2.6739(10) Å which indicate the oxidation state +3 (see Table 2). Bond valence sum calculations led to the calculated valences of 2.637 for Sb01 and 5.231 for Sb02.

The four PEA cations in the asymmetric unit exhibit two conformations of the cation with different angles $\phi_a = -45(5)^\circ$, $\phi_b = -5.2(7)^\circ$ and $\phi_a = -2.2(5)^\circ$, $\phi_b = 45.5(9)^\circ$, respectively (see Table 2, Figure S2d, e). In this case the cations exhibit trans...
two-step synthesis of (PEA) compounds. The composition is not fixed). In a manner analogous to Ostwald's step rule (strictly, the analog CsSb(V) ordering. The uniaxial elongation is along one (PEA)SbCl$_4$ and (PEA)$_4$Sb$_4$Cl$_{12}$. The major bands were assigned based on the literature.$^{[30,31]}$ In general the bands can be assigned to PEA cation in (PEA)$_4$SbCl$_4$ and (PEA)$_4$Sb$_4$Cl$_{12}$. However, the bands of NH and CH$_2$ are broadened for (PEA)$_4$Sb$_4$Cl$_{12}$ due to the presence of two conformations of PEA cation in the structure. The bands in the fingerprint region are very similar in both compounds. In general, all vibrations with NH contribution are red shifted in (PEA)$_4$SbCl$_4$ compared to (PEA)$_4$Sb$_4$Cl$_{12}$. The conformation of the cation in (PEA)$_4$SbCl$_4$ is stabilized by weak NH–π interactions which lower the energy of vibrations with NH contributions compared to (PEA)$_4$Sb$_4$Cl$_{12}$. In (PEA)$_4$Sb$_4$Cl$_{12}$, the free NH stretching modes are at 3254 cm$^{-1}$ and 3185 cm$^{-1}$, respectively while the free NH stretching mode in (PEA)SbCl$_4$ is at 3185 cm$^{-1}$. The band at 3227 cm$^{-1}$ in (PEA)$_4$SbCl$_4$ corresponds to the NH stretching mode with NH–π interactions and is redshifted compared to the band at 3254 cm$^{-1}$ in (PEA)$_4$Sb$_4$Cl$_{12}$, which is in accordance with the conformation of the cation and the resulting presence of NH–π interactions in (PEA)$_4$SbCl$_4$. Instead of distinct bands in (PEA)$_4$SbCl$_4$ broad signals in the range of 3000–3300 cm$^{-1}$ are present, which can be attributed to the NH stretch vibrations and aromatic CH stretch vibrations of the two conformations (see Figure 3b).

**Vibrational spectroscopy**

Figure 2 shows the infrared (IR) spectra of (PEA)SbCl$_4$ and (PEA)$_4$Sb$_4$Cl$_{12}$. The bands in the fingerprint region are very similar in both compounds. In general, all vibrations with NH contribution are red shifted in (PEA)SbCl$_4$ compared to (PEA)$_4$Sb$_4$Cl$_{12}$. The conformation of the cation in (PEA)SbCl$_4$ is stabilized by weak NH–π interactions which lower the energy of vibrations with NH contributions compared to (PEA)$_4$Sb$_4$Cl$_{12}$. In (PEA)$_4$Sb$_4$Cl$_{12}$, the free NH stretching modes are at 3254 cm$^{-1}$ and 3185 cm$^{-1}$, respectively while the free NH stretching mode in (PEA)SbCl$_4$ is at 3185 cm$^{-1}$. The band at 3227 cm$^{-1}$ in (PEA)$_4$SbCl$_4$ corresponds to the NH stretching mode with NH–π interactions and is redshifted compared to the band at 3254 cm$^{-1}$ in (PEA)$_4$Sb$_4$Cl$_{12}$, which is in accordance with the conformation of the cation and the resulting presence of NH–π interactions in (PEA)$_4$SbCl$_4$. Instead of distinct bands in (PEA)$_4$Sb$_4$Cl$_{12}$ broad signals in the range of 3000–3300 cm$^{-1}$ are present, which can be attributed to the NH stretch vibrations and aromatic CH stretch vibrations of the two conformations (see Figure 3b).

Furthermore, the bands in the range 850–900 cm$^{-1}$ and 1050–1080 cm$^{-1}$ are influenced by NH–π interactions (see Figure 3c). For (PEA)SbCl$_4$ a band at 870 cm$^{-1}$ is present which according to Chiavarino et al. can be attributed to bending vibration of NH with NH–π interactions.$^{[30]}$ The band at 1070 cm$^{-1}$ can be attributed to the NH bending in combination with CH$_2$ twisting and rocking. The bands described above are shifted to higher wavenumbers in (PEA)$_4$Sb$_4$Cl$_{12}$, which is in agreement with the different conformations present in the two compounds.
Thermal stability

The thermal stability of (PEA)SbCl₆ and (PEA)₂Sb₂Cl₁₂ was characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in Argon atmosphere (see Figure 4).

Both compounds decompose at around 180°C. (PEA)SbCl₆ exhibits several peaks in the DSC, which are convoluted with the mass loss. This makes it impossible to unambiguously assign the thermal events in the heating process, but the mass loss can be safely attributed to the removal of volatile SbCl₅ and (PEA)Cl. (PEA)₂Sb₂Cl₁₂ exhibits two endothermic peaks in the DSC curve corresponding to the melting of the material at 163°C and subsequent decomposition. The peak at 250°C is in the range of the boiling point of SbCl₃ and phenylethylamine hydrochloride. The weight loss between the endothermic peaks can be attributed to the loss of SbCl₅.

Optical properties

The Kubelka-Munk-transformed diffuse reflectance spectra for (PEA)SbCl₆ and (PEA)₂Sb₂Cl₁₂ are given in Figure 5, with the reported spectrum of inorganic Cs₂SbCl₆ for comparison[14].

The absorption of mixed-valence (PEA)Sb⁺Sb⁵⁺Cl₁₂ is very similar to that of (PEA)SbCl₆ when a Gaussian distribution capturing the intervalence charge transfer is subtracted. (*) The scaled, reported spectrum for mixed-valence Cs₂SbCl₆ from Atkinson and Day is shown for comparison.[14]

Tauc plot assuming a direct, dipole-allowed gap.

Figure 3. (a) IR vibrational spectra of (PEA)SbCl₆ and (PEA)₂Sb₂Cl₁₂. (b) Detail view showing NH stretch vibrations and aromatic CH stretch vibrations. (c) Detail view showing bending vibration of NH with NH-π interactions.

Figure 4. TGA and DSC of (a) (PEA)SbCl₆ and (b) (PEA)₂Sb₂Cl₁₂.

Figure 5. Optical properties in the UV-visible region. (a) Kubelka-Munk-transformed diffuse reflectance, \( F(R) \), which is proportional to the absorption coefficient. The absorption of mixed-valence (PEA)Sb⁺Sb⁵⁺Cl₁₂ is very similar to that of (PEA)SbCl₆ when a Gaussian distribution capturing the intervalence charge transfer is subtracted. (*) The scaled, reported spectrum for mixed-valence Cs₂SbCl₆ from Atkinson and Day is shown for comparison.[14] (b) Tauc plot assuming a direct, dipole-allowed gap.
(similar measurements for CsSbCl₆ are not available). Yellow (PEA)SbCl₆ absorbs somewhat in the blue, with the absorption rising significantly in the near-UV. The spectrum for dark red, mixed-valence (PEA)₄Sb⁵⁺Sb³⁻Cl₁₂ looks rather similar in the UV. But there is also weaker, flat absorption in the blue, green, and yellow, which then diminishes gradually approaching the near-infrared. The low energy absorption is likely due to intervalence Sb(III) to Sb(V) charge transfer, as corroborated by the similarity with the low energy feature for Cs₂SbCl₆, which has been studied in detail.[14]

Three key features of the optical absorption are evident. First, compared to inorganic Cs₂SbCl₆, whose absorption drops significantly in the blue, violet, and near-UV before rising again above 3.5 eV, absorption of (PEA)₄SbCl₁₂ plateaus above the intervalence charge transfer, which peaks around 2.4 eV. This explains the dark red color, compared to blue Cs₂SbCl₆. Second, after subtracting a Gaussian distribution which captures the broad, intervalence charge transfer feature (E₀ = 2.36 eV, FWHM = 0.91 eV), the spectrum of (PEA)₄SbCl₁₂ is remarkably similar to that of (PEA)SbCl₆, suggesting strong similarity of some aspects of the electronic structures. In fact, these first two features are essentially one and the same: The “plateau” in (PEA)₄SbCl₁₂ absorption is fully explained by the additional absorption that is identical to that seen in (PEA)SbCl₆. Third, excluding the intervalence charge transfer, the absorption onsets for the hybrid compounds (fit by Tauc analysis assuming a direct, dipole-allowed bandgap, as shown in Figure 5b) are bathochromically shifted by several hundred meV with respect to the UV absorption onset in Cs₂SbCl₆.

Clearly, the inclusion of the aromatic PEA cation has a significant impact on the optical properties. In the subsequent section, electronic structure calculations will be used to rationalize these optical features. In contrast to the behavior of some Sb(III) chlorides with alkali metal or crown ether counterions,[32] no photoluminescence was observed from either compound at room temperature.

**Electronic structure**

The electronic structure of both compounds was studied within the framework of density functional theory (DFT), under the generalized gradient approximation (GGA). The monoclinic symmetry and complex structures (196 atoms in the mixed-valence compound) rendered hybrid functionals prohibitively expensive. At the GGA level of theory, bandgaps are severely underestimated, and we focus here on qualitative features like the relative energetic ordering of various bands.

The computed band structures and partial charge densities associated with key bands are shown in Figure 6. In agreement with the experimental colors and optical absorption, the bandgap of (PEA)SbCl₆ is significantly wider than that of mixed-valence (PEA)₄Sb⁵⁺Sb³⁻Cl₁₂. As expected for the nominally isolated [Sb⁵⁺Cl₆]⁻ and [Sb³⁻Cl₆]³⁻ octahedra in both compounds, band widths are relatively narrow (~200 meV in the conduction band). Both bandgaps are computed to be direct, but the crystal momenta at the band edges could conceivably change with a costlier functional.

**Figure 6.** Computed electronic band structures of (PEA)SbCl₆ and (PEA)₄Sb⁵⁺Sb³⁻Cl₁₂, at the GGA level. Bandgaps are indicated by gray shading, and Eₓₓₓ is the energy of the valence band maximum. Red isosurfaces of the partial charge densities associated with key bands are shown alongside, with the bands labeled (“CB1” = lowest conduction band, “VB3” = third highest valence band, etc.).
Atkinson and Day have previously observed that the breadth of the intervalence charge transfer optical absorption in similar mixed-valence antimony chlorides is both wide and T-dependent (e.g. FWHM = 710 meV at 4 K and 970 meV at 300 K in \([\text{CH}_3\text{NH}_2]\)_2SbSnCl_6, and have fit the T-dependent widths to a model involving substantial distortion of the excited state.\(^{[14]}\) They further note that no vibronic structure was observed at low temperature. While the band widths computed here are narrow with respect to conventional semiconductors, they are far from the zero width that would occur for a completely localized system. Indeed, these band widths (~300 meV in the valence band, ~200 meV in the conduction band) could account already for a substantial fraction of the breadth of the optical absorption feature, simultaneously explaining the residual breadth and the lack of vibronic structure at low temperature. This is not to say that there are not additionally substantial distortions of the excited state, but rather that both factors play a role, with the band widths setting a lower bound on the breadth of the absorption feature. These calculated band widths underscore the fact that though these systems have isolated polyanions at first glance, halogen-halogen interactions between neighboring octahedral anions cannot be ignored, much as they give rise to substantial band widths in structurally-related Sn(IV) and Te(IV) iodides.\(^{[9]}\)

Interestingly given the very small aromatic π system of the molecular cation, the valence band of (PEA)SbCl_6 ("VB1" in Figure 6) is derived from the phenyl ring, rather than from the filled chloride p bands (vide infra). The conduction band ("CB1") derives from the antibonding interaction of Sb p and Cl p. Thus excitations across the bandgap result in charge transfer from organic to inorganic sublattices. This is contrary to most of the studied hybrid organic–inorganic main-group halides, where the organic molecular cations do not contribute states near the band edges. The π* orbitals of the phenyl ring ("CB3") and the Sb p states ("CB7") lie significantly higher in energy.

On the other hand, the bandgap of (PEA)SnSbCl_6 is as expected for such a mixed-valence system: the valence band derives from the antibonding Sb(III) s–Cl p interaction, and the conduction band from the corresponding Sb(V) s–Cl p antibonding interaction. This results in the similar low energy optical absorption to that of CsSbCl_6. The next lowest excited states ("CB3" in Figure 6) derive from the antibonding Sb(III) p–Cl p interaction and lie several eV higher. As in (PEA)SnCl_6, the π orbitals of the phenyl ring fall slightly above the manifold of Cl p bands in energy, but they no longer make up the valence band due to the higher filled states from Sb(III). However, transitions from the phenyl π orbitals to the empty Sb(III) s orbitals would explain the blue/near-UV absorption in both compounds (and thus, the “plateau” in (PEA)SnSbCl_6 absorption, which is really the sum of the interband charge transfer and this blue/near-UV organic-to-inorganic charge transfer).

To further examine the electronic structures, we compute the densities of states (DOS) for the title compounds and for the inorganic analogs CsSbCl_6 and CsSbCl_6, which have similar structures with isolated, Sb–Cl octahedra. The results are given in Figure 7. Information on CsSbCl_6 is quite limited, but it is reported to be colorless and to crystallize in space group Cc (9).\(^{[10]}\) Relaxing the reported structure resulted in a higher symmetry, centro-symmetric space group (C2/c, #15), which matches the entry for CsSbCl_6 in the Materials Project database.\(^{[33]}\) Given that the reported structure appears to be separated from this centrosymmetric, relaxed structure only by a small distortion with no activation barrier, we have studied the centrosymmetric structure as it is likely the correct one (no experimental confirmation of non-centrosymmetry was provided, e.g. by anomalous scattering or second harmonic generation measurements). CsSbCl_6 and related mixed-valence compounds have been studied somewhat extensively. The crystal structure is derived from the K₃PtCl_6 structure, with Sb(III) and Sb(V) ordering resulting in a structure of I₄₁/amd (#141) space group symmetry. The Sb(III)/Sb(V) ordering persists at least up to 423 K.\(^{[11]}\)

In agreement with the differences in color (yellow (PEA)SbCl_6, colorless CsSbCl_6), the bandgap of (PEA)SbCl_6 is somewhat narrower than that of CsSbCl_6 due to the valence band states from the phenyl ring. On the other hand, the electronic structures of (PEA)SnSbCl_6 and CsSbCl_6 are very similar, with narrow bandgaps due to Sb(III)–Sb(V) charge transfer, and the frontier states from the phenyl ring occurring away from the band edges of the solid. However, as noted above, these additional states from the phenyl π orbitals are shallow in energy, and explain the absorption in the blue and near-UV seen in both compounds.
(PEA)SbCl₆ is seen to absorb visible light because of the staggered alignment of the bands derived from the inorganic and organic sublattices: Both the inorganic (as in colorless CsSbCl₆) and organic (as in colorless benzene) parts would be colorless on their own, but together they make up a yellow charge transfer semiconductor. On the other hand, in (PEA)₂Sb⁵⁺Sb⁺Cl₁₂, the filled Sb(III) s bands fall above the π bands from the phenyl group, and the compound absorbs light like the simple sum of the intervalence Sb(III)–Sb(V) charge transfer and the organic–inorganic charge transfer seen for (PEA)SbCl₆ (recall the difference curves in Figure 5).

The rational design of charge transfer semiconductors by selecting conjugated molecules and inorganic components of appropriate energetic alignment is a desirable goal. In this context, the new compounds reported here suggest that in the influence of the cation on the crystal packing and the electronic structure was elucidated. In (PEA)SbCl₆, the crystal packing results in a chiral conformation. In the case of mixed-valence (PEA)SbCl₆, the structure can be seen as an elongation of the K₃PtCl₆ structure along one (100) direction, with two conformations of the organic cation preserving centrosymmetry. Inclusion of the aromatic cation causes (PEA)SbCl₆ to be a charge transfer semiconductor, with an unusual energetic order. In (PEA)SbCl₆, the π orbitals of PEA lie above Cl p orbitals and only slightly below Sb(III) s orbitals in energy. Less electron–negative anions may lead the phenyl HOMO to be lower than the highest anion p orbitals, while larger bandwidths from either aromatic π–π stacking or condensation of the inorganic sublattice may have more complex impacts. It appears that (PEA)SbCl₆, a charge transfer semiconductor with an organic-derived valence band and inorganic-derived conduction band, is somewhat unusual. Of the relatively few charge transfer organic–inorganic halides that have been prepared, most appear instead to have an inorganic-derived valence band and an organic-derived conduction band, including tropolium halides (Sn(IV) and Pb(II) iodides, Bi(III) and Sb(III) chlorides, bromides, and iodides) and Pb(II) iodides of tetraphiafulvalene.

Conclusions

In summary, two novel hybrid organic–inorganic antimony chloride-chlorides based on phenylethylamine have been prepared and the influence of the cation on the crystal packing and the electronic structure was elucidated. In (PEA)SbCl₆, the cation has a chiral conformation, and the crystal packing results in a chiral crystal structure. In the case of mixed-valence (PEA)Sb⁵⁺Sb⁺Cl₁₂, the structure can be seen as an elongation of the K₃PtCl₆ structure along one (100) direction, with two conformations of the organic cation preserving centrosymmetry. Inclusion of the aromatic cation causes (PEA)SbCl₆ to be a charge transfer semiconductor, with an unusual energetic order of the organic and inorganic frontier bands. (PEA)Sb⁵⁺Sb⁺Cl₁₂ exhibits optical properties that are a combination of typical intervalence Sb(III)–Sb(V) charge transfer and the organic–inorganic charge transfer seen in (PEA)SbCl₆. These two new compounds show how the same relatively simple organic cation can have complex and varying impacts on crystal packing and electronic structure. The computed energetic alignment of bands from organic and inorganic components, corroborated by the observed optical properties, provides guidance for the rational design of new charge transfer semiconductors.

Experimental Section

Starting materials were procured from standard commercial sources and used as received. Sb₂O₅ was prepared from Sb₂O₃ by heating in air to 550 °C for 12 hours.

Synthesis: (PEA)SbCl₆ and (PEA)Sb⁺Cl⁻ were prepared by solution-based synthesis. For the synthesis of (PEA)SbCl₆, phenylethylamine (1 mmol, 0.126 mL) and Sb₂O₅ (0.25 mmol, 76.9 mg) were heated in conc. HCl (10 mL) to 100 °C until a clear solution was obtained. Upon cooling at room temperature yellow plate-like crystals precipitated from the solution. The crystals were filtered off and dried at 60 °C in air. For the preparation of (PEA)Sb⁵⁺Sb⁺Cl₁₂, the concentration of the reagents was increased to 4 mmol (0.503 mL) for phenylethylamine and 0.5 mmol (154 mg) for Sb₂O₅. The solution was heated to 100 °C until everything was dissolved. Upon cooling at room temperature yellow crystals of (PEA)SbCl₆ precipitated. The reaction mixture was left in the vial for one week. After one day the formation of dark needles-like crystals of (PEA)Sb⁵⁺Sb⁺Cl₁₂ can be observed. To obtain a phase pure sample the reaction mixture was left in the vial for a week until no more yellow crystals were visible.

X-ray crystallography: Single-crystal X-ray diffraction data were collected at room temperature and at 100 K on a Bruker D8 Venture diffractometer equipped with a rotating anode generator with Mo Kα radiation (λ = 0.71073 Å). The diffraction intensities were integrated using the SAINT software package and a multiscan absorption correction was applied with SADABS-2016/2 (Bruker,2016/2). The crystal structure was solved using direct methods (SHELXS) for (PEA)SbCl₆ and using intrinsic phasing (SHELXT) for (PEA)Sb⁺Cl⁻ and refined against F² by applying the full-matrix least-squares method (SHELXL) using the software OLEX2. Hydrogen atoms were inserted at idealised positions and refined using a riding model. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares. Crystallographic data and refinement details are summarised in the supporting information in Table S13 ((PEA)SbCl₆, 100 K), Table S14 ((PEA)Sb⁺Cl⁻, 100 K and CCDC-2053099 (PEA)Sb⁺Cl⁻ 100 K and CCDC-2053101 (PEA)Sb⁺Cl⁻, RT).

IR: FT-IR spectra were recorded on a Spectrum BX by Perkin Elmer equipped with a diamond ATR unit from Smiths Detection. The measurement was performed in the range of 4000–650 cm⁻¹. (PEA)SbCl₆: 3226, 3027, 2925, 1579, 1461, 1383, 1304, 1241, 1069, 996, 917, 871, 741, 697. (PEA)Sb⁺Cl⁻: 3025, 2922, 2509, 2358, 1576, 1477, 1384, 1318, 1259, 1118, 998, 904, 749, 696.

UV-Vis: Diffuse reflectance spectra were obtained on an integrated sphere attached to a double monochromator spectrophotometer (FLS980, Edinburgh Instruments) working in synchronous mode. The double monochromator configuration, both in the excitation and in the collection, allows us to discard any photoluminescence signal coming from the sample. The diffuse reflectance spectra were converted using the Kubelka-Munk function: F(R) = (1-R)²/(2R).

STA: STA measurements were obtained with a STA 449 Jupiter instrument by Netzsch. Corundum crucibles were filled with the sample. They were heated dynamically with heating rates of...
10 K·min⁻¹ under Ar flow. The data was analysed with the Netzsch Proteus 61 software package.

DFT: Electronic structure calculations were performed with the Vienna Ab initio Simulation Package (VASP),[39] which implements the Kohn–Sham formulation of density functional theory (DFT) using a plane wave basis set and the projector augmented wave formalism.[40] The generalized gradient approximation (GGA) exchange and correlation functional of Perdew, Burke, and Ernzerhof (PBE) was employed.[41] The plane wave basis set cutoff energy was 700 eV to accurately model the short bonds in the molecular cations. Structures were relaxed to a force tolerance on the ions of 0.01 meV Å⁻¹ and the resulting symmetries checked against those of the input structures using FINDSYM.[42] Spin-orbit coupling was not included. Reciprocal-space integration was performed on Γ-centered Monkhorst-Pack grids[43] with densities of 50 to 200 k-points per reciprocal atom for convergence of the self-consistent charge density, and 5000 to 8000 k-points per reciprocal atom for calculation of the electronic density of states (DOS). The LOBSTER program[44] was used to compute DOS orbital projections.[45] Manipulation of crystal structures and LOBSTER outputs was performed with the pymatgen package.[46] Crystal structures and charge densities were visualised with VESTA.[46]

PXRD: The X-ray powder patterns were obtained with a Stoe Stadi-P diffractometer in the Debye–Scherrer geometry, employing Cu Kα radiation, a Ge(111) monochromator, and a Mythen 1k detector.[47]

EDX: Scanning electron microscopy of polycrystalline samples was performed on a Carl Zeiss EVO-MA 10 instrument with a SE detector, which was controlled by the SmartSEM software.[47] The microscope was equipped with a Bruker Nano EDX detector (X-Flash detector 410-M) for EDX investigations using the QUANTAX 200 software to collect and evaluate the spectra.[48] Elements contained in the sample holder and adhesive carbon pads were disregarded.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft DFG via the Cluster of Excellence e-conversion (Grant No. EXC2089), the Center for Nanoscience, the Max Planck Society and the University of Munich (LMU) is gratefully acknowledged. The authors thank Dr. Peter Mayer (LMU Munich) for Single Crystal X-Ray Diffraction measurements and Arthur Haffner (LMU Munich) for EDX measurements. D.H.F. gratefully acknowledges financial support from the Alexander von Humboldt Foundation. A.J.S. gratefully acknowledges a postdoctoral scholarship from the Max Planck Society. Open access funding enabled and organized by Projekt DEAL.

Keywords: Mixed-valent compounds Organic–inorganic hybrid composites · Crystal growth · Ab initio calculations

[1] M. A. Loi, J. C. Hummelen, Nat. Mater. 2013, 12, 108
[2] B. Lee, C. C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C. Yeh, T. J. Marks, M. G. Kanatzidis, R. P. H. Chang, J. Am. Chem. Soc. 2014, 136, 15379.
[3] N. Shen, Z. Wang, J. Jin, L. Gong, Z. Zhang, X. Huang, CrystEngComm 2020, 22, 3395.
[4] D. A. Egger, J. Phys. Chem. Lett. 2018, 9, 4652.
[5] S. A. Adonin, L. A. Frolova, M. N. Sokolov, G. V. Shilov, D. V. Korchagin, V. P. Fedin, S. M. Aldoshin, K. J. Stevenson, P. A. Troshin, Adv. Energy Mater. 2017, 8, 1701140.
[6] H. L. Wells, F. J. Metzger, Am. J. Sci. 1901, 54-11, 451
[7] a) P. Day, Inorg. Chem. 1963, 2, 452; b) T. Birchall, B. Della Valle, E. Martinez, J. B. Milne, J. Chem. Soc. A 1971, 0, 1855.
[8] K. Prassides, P. Day, A. K. Cheetham, J. Am. Chem. Soc. 1983, 105, 3366.
[9] A. E. Maughan, A. M. Ganose, D. O. Scanlon, J. R. Neilson, Chem. Mater. 2019, 31, 1184.
[10] S. L. Lawton, R. A. Jacobson, J. Am. Chem. Soc. 1966, 88, 616.
[11] K. Prassides, P. Day, A. K. Cheetham, Inorg. Chem. 1985, 24, 545.
[12] S. L. Lawton, R. A. Jacobson, Inorg. Chem. 1971, 10, 709.
[13] S. A. Adonin, A. M. Bondarenko, P. A. Abramov, A. S. Novikov, P. E. Plyusnin, M. N. Sokolov, V. P. Fedin, Chem. Eur. J. 2018, 24, 10165.
[14] L. Atkinson, P. Day, J. Chem. Soc. A 1969, 2423.
[15] D. B. Mitzi, J. Chem. Soc. Dalton Trans. 2001, 1.
[16] a) G. C. Papavassiliou, I. B. Koutselas, A. Terzis, M.-H. Whangbo, Solid State Commun. 1994, 91, 695; b) D. G. Billing, A. Lemermer, M. Rademeyer, Acta Crystallogr. Sect. C 2007, 63, m101–m104; c) Y.-D. Huh, J. H. Kim, S. S. Kweon, W.-K. Kuk, C.-S. Hwang, J.-W. Hum, Y.-J. Kim, Y. Park, Curr. Appl. Phys. 2006, 6, 219; d) M. Braun, W. Frey, Z. Kristallogr. New Cryst. Sect. 1999, 214, 337; e) J. Calabrese, N. L. Jones, R. L. Harlow, N. Herron, D. L. Thorn, Y. Wang, J. Am. Chem. Soc. 1991, 113, 2328; f) A. Ebina, S. Nishikiori, T. Iwamoto, J. Chem. Soc. Chem. Commun. 1994, 233; g) A. O. Polyakov, H. A. Arkenbout, J. Baas, G. R. Blake, A. Meetsma, A. Caretta, P. H. M. van Loosdrecht, T. T. M. Palstra, Chem. Mater. 2011, 24, 133; h) M. Groh, R. Spengler, H. Burzlaff, F. Zouari, A. Ben Salah, Acta Crystallogr. Sect. C 1997, 53, 1199; i) S. Kassou, A. Kaiba, P. Guionneau, A. Belaaraj, J. Struct. Chem. 2016, 57, 73; j) I.-H. Oh, D. Kim, Y.-D. Huh, Y. Park, J. M. S. Park, S.-H. Park, Acta Crystallogr. Sect. E 2011, 67, m522–m523.
[17] D. B. Mitzi, J. Solid State Chem. 1999, 145, 694.
[18] R. D. Willett, Acta Crystallogr. Sect. C 1990, 46, 565.
[19] A. L. Spek, Acta Crystallogr. Sect. D 2009, 65, 148.
[20] E. G. Zaitseva, S. V. Medvedev, L. A. Aslanov, J. Struct. Chem. 1990, 31, 92.
[21] B. Bednarska-Bolek, Z. Cziunik, R. Jakubas, G. Bator, P. Ciapala, J. Phys. Chem. Solids 2002, 63, 507.
[22] T. Ueda, M. Omo, K. Shimizu, H. Ohki, T. Okuda, Z. Naturforsch. A 1997, 52, 502.
[23] A. L. Spek, Acta Crystallogr. Sect. C 2003, 86, 905.
[24] F. A. L. Anet, S. S. Miura, J. Siegel, K. Mislow, J. Am. Chem. Soc. 1983, 105, 1419.
[25] T. Matsuura, H. Koshima, J. Photochem. Photobiol. C 2005, 6, 7.
[26] N. Dehnhardt, M. Axt, J. Zimmermann, M. Yang, G. Mette, J. Heine, Chem. Mater. 2020, 32, 4801.
[27] M. B. Robin, P. Day (Eds.) Mixed Valence Chemistry-A Survey and Classification, Elsevier, 1968.
[28] K. Prassides, P. Day, J. Chem. Soc. Faraday Trans. 2 1984, 80, 85.
[29] B. Chiavarrino, M. E. Crestoni, M. Schütz, A. Bouchet, S. Piccirillo, V. Steinmetz, O. Dopfer, S. Fornarini, J. Phys. Chem. A 2014, 118, 7130.
[30] a) H. G. Brittain, Cryst. Growth Des. 2011, 11, 2500; b) B. Ivanova, M. Spieltier, Spectrochim. Acta Part A 2010, 77, 849; c) E. Sacher, Spectrochim. Acta Part A 1987, 43, 747; d) L. J. Bellamy, R. L. Williams, Spectrochim. Acta Part A 1957, 9, 341.
[31] a) K. M. McCall, V. Morad, B. M. Benin, M. V. Kovalenko, ACS Materials. Lett. 2020, 2, 1218; b) V. Morad, S. Yakunin, M. V.
Kovalenko, ACS Materials. Lett. 2020, 2, 845; c) M. Li, Z. Xia, Chem. Soc. Rev. 2021.

[33] A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder et al., APL Mater. 2013, 1, 11002.

[34] A. E. Maughan, J. A. Kurzman, J. R. Neilson, Inorg. Chem. 2015, 54, 370.

[35] I. W. H. Oswald, E. M. Mozur, I. P. Moseley, H. Ahn, J. R. Neilson, Inorg. Chem. 2019, 58, 5818.

[36] H. A. Evans, A. J. Lehner, J. G. Labram, D. H. Fabini, O. Barreda, S. R. Smock, G. Wu, M. L. Chabinyc, R. Seshadri, F. Wudl, Chem. Mater. 2016, 28, 3607.

[37] G. M. Sheldrick, Acta Crystallogr. Sect. A 2015, 71, 3.

[38] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339.

[39] a) G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15; b) G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169; c) G. Kresse, J. Hafner, Phys. Rev. B 1994, 49, 14251; d) G. Kresse, J. Hafner, Phys. Rev. B 1993, 47, 558.

[40] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953.

[41] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.

[42] H. T. Stokes, D. M. Hatch, J. Appl. Crystallogr. 2005, 38, 237.

[43] H. J. Monkhorst, J. D. Pack, Phys. Rev. B 1976, 13, 5188.

[44] S. Maintz, V. L. Deringer, A. L. Tchougrevéeff, R. Dronskowski, J. Comput. Chem. 2016, 37, 1030.

[45] R. Dronskowski, P. E. Blöchl, J. Phys. Chem. A 1993, 97, 8617.

[46] K. Momma, F. Izumi, J. Appl. Crystallogr. 2011, 44, 1272.

[47] Version 5.07 Beta (SmartSEM), Carl Zeiss Microscopy Ltd.: Cambridge, U. K. 2014.

[48] QUANTAX 200 Version 1.9.4.3448, Bruker Nano GmbH: Berlin, Germany, 2013.

Manuscript received: December 31, 2020
Revised manuscript received: February 4, 2021
Accepted manuscript online: February 22, 2021