$[H_3N(CH_2)_7NH_3]_8(CH_3NH_3)_2Sn(IV)Sn(II)_{12}I_{46}$ – a mixed-valent hybrid compound with a uniquely templated defect-perovskite structure†‡

Jun Guan, Zhongjia Tang and Arnold M. Guloy*

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The incorporation of $H_3N(CH_2)_7NH_3$ with $CH_3NH_3SnI_3$ resulted in the formation of a mixed-valent and semiconducting (Eg = 0.84 eV) organic-based perovskite, $[H_3N(CH_2)_7NH_3]_8(CH_3NH_3)_2Sn(IV)Sn(II)_{12}I_{46}$, with a unique 3D defect-perovskite structure with ordered vacancies at the Sn and I sites.

The electronic delocalization properties of mixed-valent perovskites continue to be of great interest, in part because of their relevance to studies on high-Tc superconductivity[1] as well as catalytic, dielectric, optical, transport and magnetic properties of transition metal perovskites.[2,3] Introduction of mixed-valency in perovskite compounds is usually accompanied by significant structural distortions, substitutions and/or formation of vacancies and defects within the perovskite framework. The important structural flexibility of perovskites (ABX_3) is partly due to the ability of the B cations to adopt a variety of coordination numbers, and robustness of the B–X network in accommodating vacancies in the cation (A, B) and anion (X) sites.[3–5] Most defect perovskites (metal oxides and halides) exhibit vacancies at the cation A- (CN = 12) and anion X- (*e.g.* O, F, Cl, Br, I) sites. However, occurrences of vacancies at the B-sites are rare and have been ascribed to thermodynamic instability of vacancies due to the higher charge and smaller size of the B-cations.[5]

Organic-based metal halide perovskites make up an important class of tunable materials.[6] In particular, the tunable electronic properties of the hybrid Sn and Pb halides arise from the systematic modular combinations of the organic and inorganic components.[7] They also exhibit a unique structural flexibility accompanied by a modulation of their electronic properties. This is exemplified by the transition from semiconducting to metallic behavior, with increasing dimensionality, in the different families of layered tin(II) iodide perovskites.[6,7] Their structures are significantly influenced by the nature and molecular conformations of the organic components, as effectively shown in the families of layered perovskites, and in the polymorphism of α- and β-$(NH_3(CH_2)_5NH_3)SnI_4$.[8] The formation of metal defects in organic-based layered perovskites has been templated by organic molecules, albeit in a hybrid Bi(III) iodide.[9]

Efforts to introduce mixed-valency in organic-based Sn halide perovskites have so far been unsuccessful. This important question relates to the metallic cubic perovskites, $CsSnI_3$ and $CH_3NH_3SnI_3$, which exhibit high mobilities and low carrier (hole) densities.[10] Yet to date, efforts to increase the carrier (hole) densities by doping (oxidation) have been unsuccessful. Herein we report the synthesis of a mixed-valent organic-based tin halide defect-perovskite, $[H_3N(CH_2)_7NH_3]_8(CH_3NH_3)_2Sn(IV)Sn(II)_{12}I_{46}$ (**1**).

The title compound was prepared by reacting stoichiometric amounts of SnI_2 (0.2 mmol) and the corresponding organic ammonium iodide salts in concentrated HI solution (3 ml). The resulting HI solution was heated to 130 °C and then slowly cooled to room temperature. Formation of very dark-red brick crystals was observed during slow cooling. The crystals were moderately air stable at room temperature, in that the crystals were unchanged over 2 days. As a general precaution, all reactions and experimental manipulations were carried out under nitrogen atmosphere, and solvents were degassed before use. The typical reaction yield was 95%.

Compound **1** crystallizes in the tetragonal space group $P4_2/mnm$ and its crystal structure is shown in Fig. 1.[11] The complex 3D perovskite structure can be described using three structural components: a) perovskite columns of corner-shared octahedra, $CH_3NH_3SnI_{(4\ =\ 4/2+2/1)}$; b) chains of *trans* corner-shared square pyramids, $SnI_{(4\ =\ 2/2+3/1)}$; c) isolated SnI_6 octahedra. The columns are normal perovskite units with CH_3NH_3, Sn and I at the A-, B- and X-sites, respectively. The Sn–I bonding distances (d_{ave} = 3.144 Å) within the columns are similar to those observed in $CH_3NH_3SnI_3$ and their Sn(II) layered derivatives.[6–10] The

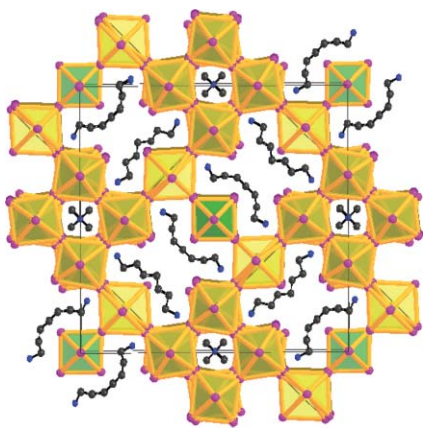

Fig. 1 A [001] view of the crystal structure of **1**. The $[Sn(II)I_6]$ and $[Sn(IV)I_6]$ octahedra are represented as dark-yellow and green polyhedra, respectively; $[Sn(II)I_5]$ square pyramids are shown as light yellow pyramids; C and N are represented as black and blue spheres, respectively. The unit cell is outlined.

† Electronic supplementary information (ESI) available: crystallographic tables and diffuse reflectance spectrum for **1**. See http://www.rsc.org/suppdata/cc/b4/b411322e/

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*aguloy@uh.edu

columns are further linked through their iodine-vertices, along the *a–b* plane, with the unshared basal vertices of the square pyramidal SnI_4 chains. The Sn–I distances (d_{ave} = 3.11 Å) in the SnI_5 square pyramids are also comparable to those in low-dimensional Sn(II)–I networks. The remaining A-sites are occupied by the terminal $-NH_3$ of the diamine cations, $H_3N(CH_2)_7NH_3$. The cations template cross-like cavities within the 3D perovskite network with vacancies occuring at the B- (Sn) and X- (I) sites. One type of empty B-sites, collinear with the Sn and the apical I of the square pyramids, are occupied by Sn which is further coordinated by six I atoms that do not coordinate to any other tin atom. However, two iodine atoms of the isolated octahedral SnI_6 units can be derived from a nominal octahedral coordination around the neighboring square pyramidal Sn. The square pyramidal SnI_5 and isolated SnI_6 units can be derived from a breathing mode distortion (contraction and elongation) of the Sn–I distances around adjacent SnI_6 octahedra with a concomitant formation of stereochemical lone pairs and isolation of the other SnI_6 octahedra. Inspection of the Sn–I distances within the different Sn–I polyhedra indicate the isolated SnI_6 octahedra exhibit significantly shorter Sn–I distances (d_{ave} = 2.862(1) Å) than those observed in other Sn(II) iodide perovskites. The observed Sn–I distances are comparable to Sn^{4+}–I distances in $Cs_2Sn^{4+}I_6$ (Sn–I (CN = 6): 2.864(1) Å) and in tin(IV) iodide organometallic complexes (Sn–I (CN = 6): 2.78–82 Å).[12] Assignment of the tetravalent oxidation state to the corresponding Sn atom yields the proper ionic charge balance: $[H_3N(CH_2)_7NH_3]^{2+}{}_8(CH_3NH_3)^{+}{}_2[Sn(IV)Sn(II)_{12}I_{46}]^{18-}$.

The defect structure of **1** from the perovskite can be traced to two B-site (Sn) vacancies in the structure. These are shown in Fig. 2. The first type (**A**) is surrounded by three iodines from neighboring SnI_6 octahedral units. Three other missing iodines (2/2 + 1) are associated with this vacancy resulting in a vacant "SnI_2" unit. Similarly, the second vacancy (B) has 4 neighboring I from the neighboring Sn–I polyhedra (2 SnI_6 + 2 SnI_5). Two other missing iodines are part of a missing "SnI_2" unit in vacancy **A**. The occurrence of Sn and I vacancies allows the alkyldiamine cations to occupy the A-sites of the perovskite framework, and the voids created by the vacancies are effectively compensated by the alkyl backbone of the cations. The ratio of **A** to **B** sites is 4 and the vacancies account for "Sn_5I_8" in the idealized perovskite; *i.e.* "$A_{18}Sn_{18}I_{54}$" − "Sn_5I_8" = "$A_{18}Sn_{13}I_{46}$". The unit cell relationships also confirm the assignment, and a superstructure

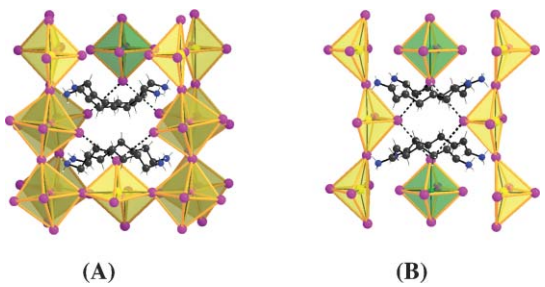

Fig. 2 The B-site vacancies, **A** and **B**, viewed along 001 and 110, respectively. Dashed lines indicate I coordination around each vacancy. The [Sn(II)I_6] and [Sn(IV)I_6] octahedra are shaded dark-yellow and green, respectively. The [Sn(II)I_5] square pyramids are shaded light-yellow. The C and N atoms are represented as black and blue spheres, respectively.

(**1**$_{cell}$ ≈ $3\sqrt{2}a_p \times 3\sqrt{2}a_p \times 2a_p$) of the perovskite cell (p) results from the ordered vacancies.

A crucial factor in the formation of the structure is that the distance between nearest neighbor A-sites (∼6.3 Å) and the *syn*-conformation length of the alkyl chain in the cation (∼6.9 Å) are essentially matched, and the $-CH_2NH_3$ ends of the diamine cations correspond to the CH_3NH_3 of the parent perovskite. Furthermore, incorporation of other diamine cations $NH_3(CH_2)_nNH_3$, $n \neq 7$ results in the expected non-defect layered perovskites.[13] Thus, the critical templating role of the organic cation is convincingly exhibited in the novel structure. The end member of this new family of 3-D defect-perovskite structures, $[NH_3(CH_2)_7NH_3]_2Sn_3I_{10}$, has also been prepared.[13]

UV-Vis-NIR diffuse reflectance measurements indicated an optical band gap of 0.84 eV.[14] The observed crystal structure and narrow-gap semiconducting behavior are consistent with a mixed-valent assignment, in accord with the Robin–Day model.[15] This is surprising considering the cubic Sn(II) iodide perovskites are metallic and conducting due to delocalized Sn $5s^2$ electrons. Introducing 'electronic holes' in the form of Sn(IV) states apparently results in localization of the carriers (holes) at the Sn(IV)I_6 octahedra. In addition, some Sn 5s states in the perovskite network are further localized at the Sn(II)I_5 square pyramids as evidenced by the appearance of stereochemically active lone pairs. However, the remaining perovskite columns may still exhibit electronic character more associated with the conducting parent $CH_3NH_3SnI_3$. Interestingly, high-pressures may be needed in inducing the delocalization of the localized states (holes and lone-pairs), as in the mixed-valent Au(I/III) perovskites.[16] More intriguing is that the hole concentration in **1** is 8% which closely approaches the hole concentrations in the superconducting perovskites.[1]

Jun Guan, Zhongjia Tang and Arnold M. Guloy*
Department of Chemistry and the Center for Materials Chemistry, University of Houston, Houston, TX 77204-5003, USA.
E-mail: aguloy@uh.edu

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*wR*2 = 0.1320 (all data); Crystallographic Software: SHELXTL. Thermal parameters of non-hydrogen atoms were treated anisotropically. Idealized positions of H atoms were calculated (C–H = 0.96 Å, N–H = 0.90 Å). CCDC 246164. See http://www.rsc.org/suppdata/cc/b4/b411322e/ for crystallographic data in .cif or other electronic format.

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