

α -[NH₃(CH₂)₅NH₃]SnI₄: a new layered perovskite structure

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The synthesis and crystal structure of new organic–inorganic layered material, α -[NH₃(CH₂)₅NH₃]SnI₄, is reported, which features an unprecedented $\langle 330 \rangle$ -terminated layered perovskite structure.

Much attention has been devoted to the synthesis and characterization of organic–inorganic multilayered perovskites owing to the tunability of their structural features.^{1–5} The physical and structural properties of these compounds can be fine tuned by substituting or tailoring the organic layers or by modulating the thickness of the perovskite inorganic slabs. Applications of layered perovskite materials involve the development of functional electronic, magnetic and optoelectronic materials.^{2,6,7} Several examples of conducting layered perovskites generally exhibit a trend from semiconducting to metallic behavior with increasing ‘thickness’ of perovskite layers (n).⁸ This was demonstrated with the synthesis of a family of organic-based layered halide perovskites, (C₄H₉NH₃)₂(CH₃NH₃) _{n –1}Sn _{n} I_{3 n +1}.

Layered perovskite structures can be derived by terminating the three dimensional cubic perovskite structure along different crystal faces.⁹ Among the variety of metal oxides with layered perovskite structures, the common terminating planes are $\langle 001 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. In layered organic–inorganic perovskites the ability to control the termination of perovskite sheets through the proper choice of organic cations was demonstrated by the synthesis of [NH₂C(I)=NH₂]₂–(CH₃NH₃) _{m –1}Sn _{n} I_{3 m +2}.⁵ In contrast to the (C₄H₉NH₃)₂–(CH₃NH₃) _{n –1}Sn _{n} I_{3 n +1} family, which consists of $\langle 001 \rangle$ -terminated perovskite layers, this structural class of Sn(II) iodides contains perovskite layers terminated along the $\langle 110 \rangle$ planes. Furthermore, the family of $\langle 110 \rangle$ -terminated Sn(II) iodide layered perovskites were found to be more conducting than their $\langle 001 \rangle$ -terminated analogs. This strongly suggests that termination of the perovskite layers provides an added flexibility in tuning the electronic properties of these layered materials.

Another structural element that modulates the properties of these mica-like materials is the dimensionality of the organic layers. Reducing the organic bilayers in the above mentioned perovskites into single layers may be achieved by using α,ω -substituted diamines, thereby increasing the interlayer coupling within the material.^{1c,3b} Eliminating hydrophobic interactions in the organic bilayers leads to improved crystallization and mechanical strength while maintaining the two-dimensionality of the electronic structure. Herein, we report the synthesis and crystal structure of α -[NH₃(CH₂)₅NH₃]SnI₄ which consists of single layers of 1,5-pentanediammonium ions and an unprecedented inorganic layered perovskite.

α -[NH₃(CH₂)₅NH₃]SnI₄ **1** Was prepared by reacting SnI₂ (2 mmol), CH₃NH₃I (1 mmol) and [NH₃(CH₂)₅NH₃]₂ (1 mmol) in concentrated HI (3 ml) solution. The HI solution of the organic and tin iodides was prepared at room temperature and heated to 120 °C. The resulting red solution was slowly cooled to 20 °C resulting in the formation of dark-red prismatic-column crystals. The dark-red air stable crystals were preserved in the mother liquor and were found to be of compound **1**. As a general precaution, all reactions were carried out under a nitrogen atmosphere and all solvents were degassed before use. The

addition of CH₃NH₃I in the synthesis of **1** is crucial. Analogous reactions without CH₃NH₃I result in the formation of an orange-red polymorph, β -[NH₃(CH₂)₅NH₃]SnI₄, which features the commonly observed $\langle 001 \rangle$ -terminated [SnI₄^{2–}] single perovskite sheets, as in K₂NiF₄.¹⁰ The ‘templating’ role of CH₃NH₃⁺ is presumably related to the stabilization and formation of the perovskite structure, as in CH₃NH₃SnI₃, and allows for its termination into layers along different crystallographic planes. Chemical analysis on several crystals of **1** confirmed the stoichiometry obtained from the structural refinement. Incorporation of CH₃NH₃I results in the formation of higher order layered perovskites [NH₃(CH₂)₅NH₃](CH₃–NH₃) _{x} Sn_{1+ x} I_{3 x +1} ($x = 1–3$).¹⁰ IR spectra recorded from thin disks of α -[NH₃(CH₂)₅NH₃]SnI₄, in the range 500–4000 cm^{–1}, feature characteristic IR bands (C–H at 3000–3180 and 1455 cm^{–1}, and N–H at 3430–3500 cm^{–1}) associated with 1,5-pentanediammonium ions. Measurement of the UV absorption spectra of a thin pressed disk of **1**, in the range 200–800 nm at 30 °C, shows a sharp absorption peak centered at 571 nm, in contrast to that observed at 560 nm in $\langle 001 \rangle$ -terminated β -[NH₃(CH₂)₅NH₃]SnI₄. Thermal measurements indicate that compound **1** and β -[NH₃(CH₂)₅NH₃]SnI₄, melt incongruently at 167 and 190 °C, respectively.

Compound **1** crystallizes in the orthorhombic space group *Pbcn*.¹¹ The asymmetric unit consists of three SnI₄^{2–} units (part of a layer of corner-sharing octahedra), and three [NH₃(CH₂)₅NH₃]²⁺ ions. The orthorhombic crystal structure contains organic diammonium cations sandwiched between parallel corrugated sheets, [SnI₂I₄]^{2–}, of corner-shared tin(II) iodide octahedra. The tin layers can be built-up from Sn^{II}I₆ octahedra linked *via* corners into nominal zigzag chains, in the manner *–cis–trans–trans–cis–trans–trans–*, along the crystallographic *a*-axis. Adjacent parallel chains are further linked through their *trans*-vertices along the *b*-axis forming single corrugated [SnI₄^{2–}] sheets along the *ab*-plane. The corrugated sheets are stacked along the crystallographic *c*-axis resulting in interlayer sites defined by eight terminal iodine atoms. The 1,5-pentanediammonium ions are located within the nearly orthorhombic interlayer sites forming single organic layers in contrast to the bilayers found in the monoamine compounds, (RNH₃)₂SnI₄. The [SnI₄^{2–}] layer in compound **1** may be described as a combination of the $\langle 001 \rangle$ and $\langle 110 \rangle$ terminations and hence considered as the first member of the family of $\langle 330 \rangle$ -terminated layered perovskites.^{9a} To our knowledge, the remarkable mixed *cis–trans* $\langle 330 \rangle$ -terminated perovskite layers is unprecedented in metal oxide and halide perovskite structures.

The unprecedented inorganic sheets feature two types of SnI₆ octahedra, namely, *trans*- and *cis*-shared, as shown in Fig. 1. The relatively long Sn–I bonds, 3.464(1) Å, in the *cis*-iodine bridges reflect the significant steric effects present in the *cis* conformation of the SnI₆ octahedra. The bond angles in both types of SnI₆ octahedra are slightly distorted from the ideal geometry as expected in low-order layered perovskite structures.^{4,5,12} These bond angle distortions and the Sn–I bond distance inequalities are reflected in the ‘twists’ and ‘buckles’ of the inter-octahedral linkages and may be attributed to hydrogen-bonding and the stereochemical activity of the Sn(II) 5s² lone pairs.¹²

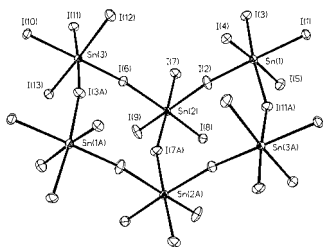


Fig. 1 ORTEP representation of the asymmetric unit of $\langle 330 \rangle$ -terminated $[\text{SnI}_4^{2-}]$ layer. Bond distances (Å): (a) around Sn(1): I(1) 3.307(1), I(2) 3.072(1), I(3) 3.116(2), I(4) 3.010(1), I(5) 3.217, I(11A) 3.217(2); (b) around Sn(2): I(2) 3.429(1), I(6) 3.464(1), I(7) 3.110(2), I(8) 2.961(1), I(9) 2.961(1), I(7A) 3.159(2); (c) around Sn(3): I(6) 3.113(1), I(10) 3.257(1), I(11) 3.154(2), I(12) 3.332(1), I(13) 2.994(1), I(3A) 3.155(2). Ellipsoids are drawn at 50% probability.

Close inspection of the organic–inorganic heterostructure in **1** reveals important characteristics. The $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]^{2+}$ ions lie between the corrugated sheets of $[\text{SnI}_4^{2-}]$ within two types of interlayer sites formed by terminal iodides of the single perovskite sheets, as shown in Fig. 2. These are sites formed between *trans*- SnI_6 octahedral units of adjacent layers, and sites formed by adjacent *cis*- SnI_6 units. In the *trans* interlayer sites, both $-\text{NH}_3$ ends of the cation are directed near the center of the ‘bay’ formed by four terminal iodines on each inorganic layer. The diammonium ions within the smaller *cis* interlayer sites are crowded into the ‘open bay’ area of these sites by close contacts with terminal iodines. The spatial environment of the different interlayer sites can be correlated with the N–N distances between the terminal nitrogen of the dications. The N–N distances are 6.10(2) and 6.65(2) Å for the dications in the *trans* sites, and 5.18(2) Å in the *cis*-sites. The N–N distances of the same diammonium ions in the interlayer sites of $\langle 001 \rangle$ -terminated β - $[\text{NH}_3(\text{CH}_2)_5\text{NH}_3]\text{SnI}_4$ range from 5.98(2) to 6.12(2) Å.¹⁰ The variation in the observed N–N distances indicates significant differences in the conformation of the organic dications within the different interlayer sites in **1**. Moreover, steric effects present in the *cis* interlayer sites of **1** are reflected in the short N–N distances and the observed molecular shape of the diammonium ions which may be attributed to the torsional rotations around the chain backbone. Hence, formation of the unusual *cis*- SnI_6 linkage is related to a ‘recognition’ of the different conformations of the organic diammonium ions. The conformational differences of the cations are manifested by the differences in the C–H bands of the IR spectra of both polymorphs. The IR spectrum of the β -form features broader C–H bands (2860–3180 cm^{-1}) than those of the α -form, reflecting larger changes in the dipole moments and decreased steric restrictions on the C–H vibrations of the conformers in the β -form.¹³ The thermodynamic stability and lower steric effects present in the

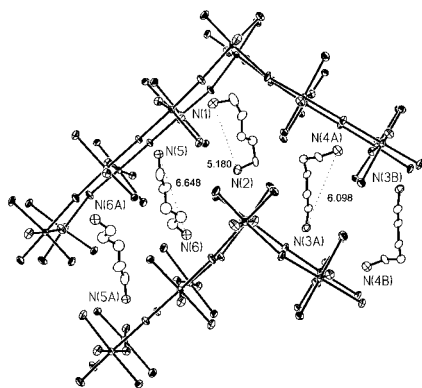


Fig. 2 ORTEP representation of the packing of 1,5-pentanediammonium ions between two $\langle 330 \rangle$ -terminated $[\text{SnI}_4^{2-}]$ layers in compound **1**. Dashed lines represent distances between α - and ω -N atoms. Ellipsoids are drawn at 50% probability.

$\langle 001 \rangle$ -terminated β -form may be correlated to its higher melting point and density ($\rho_\beta = 3.055 \text{ g cm}^{-3}$) compared to the $\langle 330 \rangle$ -terminated α -form ($\rho_\alpha = 3.035 \text{ g cm}^{-3}$). Band structure calculations on the two layered structures indicate that the $\langle 330 \rangle$ -terminated sheets have a smaller band gap than the $\langle 100 \rangle$ -terminated layer in accord with the UV absorption spectra.^{4,14} The optical absorption attributed to transitions from Sn 5s and I 5p derived valence states to mainly Sn 5p conduction bands.

The control of the layer termination of the inorganic component is significantly dictated by cooperative non-covalent organic–inorganic interactions, as well as by the stereochemistry of the organic moieties. These provide additional fine variables in tuning the structure and electronic properties of layered organic–inorganic perovskites. The synthesis of **1** demonstrates the unusual structural chemistry exhibited by layered organic-based Sn(II) iodide perovskites.

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- Single crystal X-ray analysis, using a Siemens SMART diffractometer equipped with a CCD detector was carried out at -50°C . Monochromatized Mo-K α radiation was used to collect a hemisphere of data. Empirical absorption correction was applied and redundant reflections were averaged. Laue photos and systematic absences unambiguously indicated the space group to be *Pbcn*. The final cell constants are: $a = 30.255(2)$, $b = 12.352(7)$, $c = 25.6706(14)$ Å, $V = 9593.0(5)$ Å³. Other relevant crystallographic data are: $M = 730.49$, $Z = 24$, $\mu = 9.291 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 48.40^\circ$; total data collected, 44333; independent reflections, 8381; observed reflections ($> 3\sigma$), 7618; total variables, 309. The final *R* indices, $[I > 4\sigma(I)]$: $R1 = 0.0506$, $wR2 = 0.1282$; (all data): $R1 = 0.0691$, $wR2 = 0.1432$. The structure was solved by direct methods and refined by full-matrix least-squares calculations. Thermal parameters of all non-hydrogen atoms were treated anisotropically. Five carbon sites (C3, C4, C13, C14, C15) exhibited conformational disorder and were refined based on a rotational disorder model. All hydrogen atoms were treated with a riding model ($d\text{C}-\text{H} = d\text{N}-\text{H} = 0.89$ Å, $U_{\text{iso}} = 0.050$). CCDC 182/1361.
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