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# $(C_4H_3SCH_2NH_3)_2(CH_3NH_3)Pb_2I_7$ : non-centrosymmetrical crystal structure of a bilayer hybrid perovskite

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**The analysis of the crystal stucture of $(C_4H_3SCH_2NH_3)_2(CH_3NH_3)Pb_2I_7$, displaying a well-ordered acentric inorganic $Pb_2I_7{}^{3-}$ bilayer, is reported, and compared to the related monolayer hybrid perovskite.**

Organic–inorganic perovskite materials have received considerable interest since the beginning of the 1990s.[1–5] These hybrid compounds offer the opportunity to combine useful properties of both organic and inorganic components within a single composite. The physical and structural properties can also be tuned either by substituting organic layers or by modulating the thickness of the inorganic slabs. In this way, it was demonstrated in the $(n\text{-}BuNH_3)_2(CH_3NH_3)_{n-1}Sn^{II}{}_nI_{3n+1}$ family, that a metallic to semi-conducting behavior is correlated to the decrease of the numbers of inorganic layers ($n$).[5] At the same time, the carrier mobility decreases from the 3D ($n = \infty$) perovskite (50 $cm^2\ V^{-1}\ s^{-1}$ in $CH_3NH_3SnI_3$) to the monolayer perovskite (0.6 $cm^2\ V^{-1}\ s^{-1}$ in $(RNH_3)_2SnI_4$ (R = phenylethyl).[6] Of high interest is the rather high mobility of the latter compound, and the possibility to use these semi-conducting hybrid perovskites ($n$ = 1–3) as channel materials for thin-film field-effect transistor (FETs).[6] Crystal structures of many monolayer ($n$ = 1) hybrid perovskites or 3D perovskites ($n = \infty$), belonging to the $(RNH_3)_2(CH_3NH_3)_{n-1}M^{II}{}_nI_{3n+1}$ family are known.[1,7] For multilayer perovskite compounds, one structure of the $n$ = 3 (R = butyl)[5] member has been previously reported for a tin compound, while for $n$ = 2, only an average disordered structure for $(RNH_3)_2(CH_3NH_3)Pb_2I_7$ (R = phenylethyl) is discribed in the $P1$ space group, certainly revealing an unresolved superlattice structure.[3]

We now report the synthesis, characterization and crystal structure of $(C_4H_3SCH_2NH_3)_2(CH_3NH_3)Pb_2I_7$, which displays a well-ordered acentric $Pb_2I_7{}^{3-}$ perovskite bilayers ($C_4H_3SCH_2NH_3{}^+$ is the 2-thienylmethylammonium cation, for the first time incorporated in organic–inorganic perovskites). The related monolayer compound $(C_4H_3SCH_2NH_3)_2PbI_4$ is also reported, allowing the comparison between the two corresponding crystal structures.

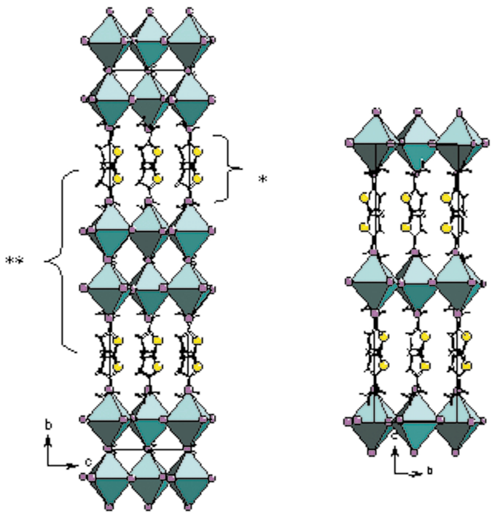

**Fig. 1** Views of the layered crystal structures of **1** (left) and **2** (right). The orientation of thiophene rings of two consecutive organic bilayers is the same in **1**, is different in **2**. The brackets indicate the parts of the structure of **1** projected along $b$ in Fig. 2 (*) and Fig. 3 (**).

$(C_4H_3SCH_2NH_3)_2(CH_3NH_3)Pb_2I_7$ **1** and $(C_4H_3SCH_2NH_3)_2PbI_4$ **2** were prepared from stoichiometric quantities of $PbI_2$ (typically 0.4 mmol), $C_4H_3SCH_2NH_2$ and $CH_3NH_2$ (for **1**) in concentrated HI solution (8 mL). Under argon atmosphere, after heating and evaporation at 60 °C, a slow cooling of yellow and orange solutions allowed the formation of red crystals of **1** and orange plate crystals of **2**, respectively. Crystals were then filtered off and washed with acetonitrile. For both compounds, X-ray powder diffraction indicated single-phase samples. Room-temperature absorption spectra of spin-coated films evidenced strong exciton peaks at 562 and 515 nm for **1** and **2**, respectively. These values are similar to those observed for lead(II)-iodide hybrid perovskites[1,8] and are related to the large exciton binding energy and oscillator strength in the inorganic sheets due to both structural two-dimensionality and dielectric confinement effect.[9] The photoluminescence spectra, excited by 457.9 nm light from an argon ion laser, consist of strong peak at 530 nm and a weaker peak at higher wavelength (553 nm) for **2**, and a quite strong peak at 580 nm for **1**. These values are close to those encountered in compounds based on iodoplumbate(II) perovskite monolayer[1,8] or bilayer.[3]

Compound **1** crystallizes in the *Aba*2 acentric space group.† The asymmetric unit consists of one $PbI_{3.5}{}^{1.5-}$ unit (part of a bilayer of corner-sharing octahedra), one $C_4H_3SCH_2NH_3{}^+$ and half $CH_3NH_3{}^+$. The crystal structure is built up from 2-thienylmethylammonium cation bilayers separated by double-layer-thick perovskite sheets of lead(II) octahedra (including the methylammonium cations) (Fig. 1). In compound **2**, which crystallizes in the *Pbca* space group,† identical organic bilayers alternate with single-layer-thick perovskite sheets (Fig. 1).

In both structures, a treatment of a statistical disorder of the 2-thienylmethylammonium thiophene ring was applied,† the major component involving S1, C4, C5, C3 atoms being 70% (in the case of **1**, Fig. 2). This disorder does not affect the C2 atom of the ring, and the C1 and N1 atoms belonging to the methyl ammonium part, these three atoms being all charac-

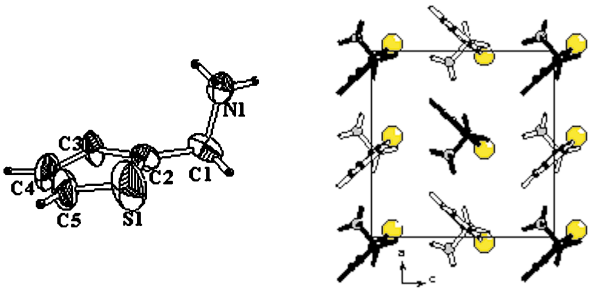

**Fig. 2** ORTEP view (ellipsoids are drawn at 50% probability) with the numbering scheme of 2-thienylmethylammonium cation (left) and projection along $b$ of the organic bilayer (right) in **1** (indicated by a bracket * in Fig. 1). Only the major component of the disordered cation is shown. Cations belonging to a same organic layer are drawn alike.

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terized by usual values of their thermal motion parameters. Finally, the $C_4H_3SCH_2NH_3^+$ cations define bilayers as shown in Figs. 1 and 2. It must be noted, as evidenced in Fig. 2, that the organic part, even if the statistical disorder described above was taken into account, is non centrosymmetrical.

In compound **1**, the inorganic part consists of a well-ordered bilayer of corner-sharing distorted $PbI_{5/2}I$ octahedra (Fig. 3): bond distances range from 3.137(1) Å for the apical Pb–I3 bond to 3.264(5) Å for the Pb–I1 bond (I1, interlayer bridging iodide atom, located on a 2 axis), the equatorial Pb–I distances being in the range 3.137(1)–3.193 (2)Å, while I–Pb–I bond angles range from 86.7(1) to 95.8(1)° and 86.9(1) to 90.5(1)° for $I3_{apical}$–Pb–$I_{equatorial}$ and $I1_{interlayer}$–Pb–$I_{equatorial}$, respectively. All these values are close to those found in $(C_6H_5C_2H_4NH_3)_2(CH_3NH_3)Pb_2I_7$.[3]

There is also a quite strong tilting of these $PbI_6$ octahedra in a layer, with Pb–$I_{equatorial}$–Pb bond angles of 154.6(1)° (I = I2) and 157.8(1)° (I = I4). Finally, a 24° rotation of two neighbouring octahedra along *b* occurs (Fig. 3). These distorsions from the ideal perovkite layers are due to (among other factors) hydrogen bonding between the $NH_3^+$ part of organic cations (both $CH_3NH_3^+$ and $C_4H_3SCH_2NH_3^+$cations in this case) and inorganic layers.[1,10] By comparison, no distorsion is evidenced for instance in the inorganic bilayer perovskites $Sr_3Ti_2O_7$ or $K_3M_2F_7$ ($M^{II}$ = Mg, Mn, Co–Zn).[11]

A so-called terminal halogen configuration[10] is encountered in **1** where H atoms from the ammonium part of the thiophene derivative are linked to two terminal I3 iodide atoms ($d$ = 2.76, 2.78 Å) and two bridging iodide atoms at higher distances ($d$ = 3.05 Å), leading to one-dimensional hydrogen bond network along *c*, if only the former interactions are considered (Fig. 3). A similar situation occurs in compond **2** where this hydrogen bond network is related by one of the symmetry centers located either at the center of the rhomb defined by four corner-sharing octahedra or on the Pb1 atom (as in most cases of the monolayer perovskites). In **1**, the way in which the well-ordered apical I3 iodide atoms are shifted from the *b* direction running through Pb atoms, involves a loss of a symmetry center which could be found between I2 and I4 on the projection of Fig. 3, located in the mean plane containing interlayer bridging iodide atoms. Finally, a glide plane (*n* plane) perpendicular to *b* at $y$ = 1/2 is observed, leading to the acentric nature of the bilayers. The crystal structure of **1** then appears non-centrosymmetrical, taking also into account the acentric organic bilayers, as illustrated in Fig. 1, where the thiophene rings of the organic bilayers are faced in the same way, while opposite orientation of thiophene rings of two consecutive organic bilayers occurs in **2**. It is interesting to note that the known $n$ = 3 hybrid perovskite structure, $(C_4H_9NH_3)_2(CH_3NH_3)_2Sn_3I_{10}$ is described in the *Cmca* space group,[5] a symmetry center being evidenced at the center of the rhomb defined by four corner-sharing octahedra belonging to the inner perovskite layer, and it is foreseable that a tetra-layer-thick perovskite sheet ($n$ = 4) in such compound could be non-centrosymmetrical.

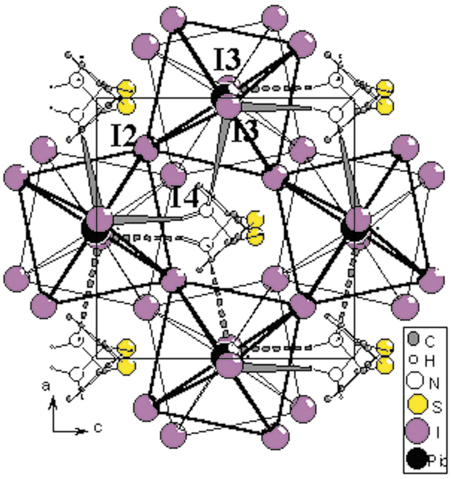

**Fig. 3** Projection along *b* of a part of the crystal structure of **1** (indicated by a bracket ** in Fig. 1). Octahedra bones are drawn alike for octahedra belonging to the same single layer. The I1 bridging interlayer iodide atoms are superposed to lead atoms. The hydrogen bond network is shown by grey full and dashed lines for the two sides of the $Pb_2I_7$ inorganic bilayer respectively. The $CH_3NH_3^+$ cation is omitted.

In summary, the first well-ordered $Pb_2I_7^{3-}$ perovskite bilayer is found in $(C_4H_3SCH_2NH_3)_2(CH_3NH_3)Pb_2I_7$. The acentric character of the inorganic component, and also of the whole structure, is proved to be partially involved by cooperative non-covalent organic–inorganic interactions. This inorganic part, composed of highly polarizable atoms, could be a good tool for the obtention of second-order NLO hybrid compounds[12] by incorporating suitable organic NLO cations. Physical properties of related $(C_4H_3SCH_2NH_3)_2(CH_3NH_3)_{n-1}M^{II}{}_nI_{3n+1}$ compounds (M = Sn, Pb; $n$ = 1,2) involving optical and electroconductivity studies are also being pursued.

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## Notes and references

† *Crystal data* for **1**: $C_{11}H_{22}N_3S_2I_7Pb_2$, $M$ = 1563.1, orthorhombic, space group *Aba*2, $a$ = 8.838(2), $b$ = 41.520(1), $c$ = 8.769(5) Å, $V$ = 3218(2) Å$^3$, $Z$ = 8, $D_c$ = 3.22 ($\lambda_{Mo\text{-}K\alpha}$ = 0.71069). 5330 reflections collected in the range $\theta$ 2.5–31°, 122 parameters from 1854 reflections with $I/\sigma(I) > 2$ converged to $R(F)$ = 0.034, $wR2(F^2)$ = 0.093.

*Crystal data* for **2**: $C_{10}H_{16}N_2S_2I_4Pb$, $M$ = 943.16, orthorhombic, space group *Pbca*, $a$ = 8.842(2), $b$ = 8.693(1), $c$ = 28.995(5) Å, $V$ = 2228.7(7) Å$^3$, $Z$ = 4, $D_c$ = 2.81 ($\lambda_{Mo\text{-}K\alpha}$ = 0.71069). 6243 reflections collected in the range $\theta$ 2.5–30°, 95 parameters from 1844 reflections with $I/\sigma(I) > 2$ converged to $R(F)$ = 0.028, $wR2(F^2)$ = 0.066.

For both structures, all hydrogen atoms were treated with a riding model and a thiophene ring disorder treatment was applied. For instance, in **1**, rather abnormal thermal motion of S1, C3, C4, C5 atoms together with abnormal distances lead to apply a disorder treatment for S1 and C3 atoms by partial interchange in corresponding positions: atom pairs S1/C3a and C3/S1a were then constrained to each occupy a single site while the occupancies were also refined. The major component, involving S1 and C3 atoms, comprises 70% (66% in the case of compound **2**). In **1**, nitrogen atom of methyl ammonium cation is also disordered and refined in general position with a 0.5 occupancy rate, while the carbon atom (C6) is located on a 2 axis. CCDC 187951 and 187952. See http://www.rsc.org/suppdata/cc/b2/b205543k/ for crystallographic data in CIF of other electronic format.

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