

Crystal structure of $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ ($R = 5,5'$ -bis(ethylsulfanyl)-2,2'-bithiophene): $\text{NH}_3^+ \cdots \text{NH}_2$ interaction as a tool to reach densely packed organic layers in organic-inorganic perovskites

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Abstract

In the layered $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ ($R = 5,5'$ -bis(ethylsulfanyl)-2,2'-bithiophene) organic-inorganic hybrid compound, a PbI_5^{2-} 1D network of corner sharing octahedra defines ordered deficient perovskite layers separated by the organic sheets. The $\text{NH}_3^+ \cdots \text{NH}_2$ interactions together with $\text{NH}_3^+ \cdots \text{I}$ contacts, which take place at the inorganic-organic interface, favor rather strong S...S intermolecular interactions between bithiophene units, compared to those found in purely organic compounds or in $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$. Crystal data: $(\text{C}_{24}\text{H}_{35}\text{S}_8\text{N}_4)\text{PbI}_5$, $M_r = 1477.73$, monoclinic, $P2_1/c$, $a = 17.553(2)$ Å, $b = 8.710(1)$ Å, $c = 27.122(5)$ Å, $\beta = 97.57(2)^\circ$, $V = 4110(1)$ Å³, $Z = 4$, $R = 0.053$, $R_w = 0.119$.
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1. Introduction

Organic-inorganic perovskites have received considerable interest in the past decade. The opportunity to combine the properties of the two components within a single composite material associated with their possible solution processing by room temperature techniques such as spin-coating opens interesting perspectives for technological applications [1]. In most cases, hybrid perovskites consist of MX_4^{2-} two-dimensional (2D) networks of corner sharing divalent metal halide octahedra, separated by an organic part of alkyl- or simple aromatic mono- or diammonium cations, leading respectively to the $(\text{RNH}_3)_2\text{MX}_4$ and $(\text{NH}_3\text{-R-NH}_3)\text{MX}_4$ compounds [1–3]. In these hybrids, the organic entities behave as weakly interacting individual molecules, while properties, including magnetism, con-

ductivity or luminescence, arise from the 2D inorganic network [1].

A recent trend in this field of hybrid materials consists on the incorporation of molecules with reduced HOMO-LUMO gap such as extended π -linear conjugated systems [4], which can combine semi-conducting properties [5], luminescent [6] or nonlinear optical properties [7]. The formation of such organized organic-inorganic hybrids appears to be a convenient method to control the inter-molecular interactions in order to either avoid the quenching of luminescence [4] associated with strongly interacting π -systems, or in contrast to strengthen these interactions in order to enhance hole mobility in the organic layers. In this regard, we have recently demonstrated that new types of packing of bithiophene units were built in such hybrids starting from 2,2'-bithiophene derivatized monoammonium cations [8].

We report here the crystal structure of $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$, where $R = 5,5'$ -bis(ethylsulfanyl)-2,

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2'-bithiophene. We show that strong $\text{NH}_3^+ \cdots \text{NH}_2$ interactions between molecules associated with the $\text{NH}_3^+ \cdots \text{I}$ contacts occurring at the organic–inorganic interface, seem to favor rather strong $\text{S} \cdots \text{S}$ intermolecular interactions between the bithiophene units. A comparison with the structure of the all ammonium salt $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$ will also be provided.

2. Experimental

Halide salt $(\text{NH}_3\text{-R-NH}_3)\text{Cl}_2$ ($R = 5,5'$ bis(ethylsulfanyl)2,2'-bithiophene) was synthesized according to the procedure already mentioned [8]. A mixture of $(\text{NH}_3\text{-R-NH}_3)\text{Cl}_2$ (20 mg, 0.051 mmol), PbI_2 (11.9 mg, 0.026 mmol), with excess KI (5 g), which improve the solubility of PbI_2 , and H_2O (5 mL) was sealed in a pyrex tube and kept at 100°C for 4 h. Subsequent cooling to room temperature at 2°C/h resulted in a mixture of well-formed yellow plate crystals of $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ and well-formed orange plate single crystals of $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$, approximately in 1/1 ratio. It must be noted that $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$ is achieved as a unique phase when a few drops of concentrated HI are added to the starting materials (synthesis and crystal structure already reported [8]). Other attempts with a stoichiometric amount of KOH 0.01 M, or in a different solvent (acetonitrile), could not lead to a unique phase or to better yield of the title compound.

X-ray diffraction data of a selected yellow single crystal were collected at room temperature on an Enraf–Nonius MACH3 four-circle diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). From 6630 reflections collected in the $2.5\text{--}48^\circ 2\theta$ range, 6398 were independent ($R_{\text{int}} = 0.042$), and 3641 reflections with $I/\sigma(I) > 2$ were used for refinements. First, Gauss absorption correction was applied (min. 0.448, max. 0.785). The structure was then solved by direct methods, and refined by full-matrix least-squares routines against F^2 using the Shelxl97 package [9]. At a stage of refinements, anisotropic thermal motion parameters of several atoms, belonging to one sulfanyl-ethyl-ammonium part of both independent molecules, appeared high, especially for one U_{ii} component. A disordered model was then applied for three atoms, leading to define two ethyl-ammonium components, the major one (C23A–C24A–N4A) comprising 70% (see Section 3). Mainly due to heavy atoms in the structure (all residual electronic peaks close to Pb and I atoms), a disorder treatment was unsuccessful for the other ethyl-ammonium part, equivalent displacement parameters (in \AA^2) remaining quite high for N2 (0.113) and higher for C11 (0.168) and C12 (0.212). All hydrogen atoms were treated with a riding model. Finally refinements of positions and anisotropic thermal motion parameters of the non-H atoms, except for four C atoms belonging to

the ethyl-ammonium part mentioned above, converge to $R = 0.052$. Crystal data are summarized in Table 1. Supplementary data (atomic positions and thermal parameters, structure factors) are available as supporting informations. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 213751. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

In the structure of the title compound, the asymmetric unit contains one lead and five iodine atoms, and two independent molecules. The pair of thiophene rings in the two molecules is nearly coplanar, with dihedral angles of 5° and 9.5° between least-squares best planes containing adjacent thiophene rings. They adopt a syn conformation for the less distorted molecule, and an anti conformation for the other one (Fig. 1). The sulfur atoms linked to the thiophene units are nominally in the plane of bithiophene molecules, the ethyl ammonium tail pointing out of this plane, as evidenced in Fig. 1. A treatment of disorder which affects an ethylammonium part, allows to define two components, the major one, involving C23A, C24A and N4A, comprising 70% (see Experimental part and Fig. 1).

As shown in Fig. 2a, the crystal structure of $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ consists of organic layers separated by inorganic sheets, and therefore can be compared to the structure of the all ammonium compound $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$ [8] (Fig. 2b). In $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$, PbI_5^{3-} zigzag chains of corner sharing lead iodide octahedra are found along b . Such chains have been already encountered in $[\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{SC}(\text{NH}_2)_2]_3\text{PbI}_5$ [10]. Here, the chains

Table 1
Crystallographic data for $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$

| | |
|---|--|
| Empirical formula | $\text{C}_{24}\text{H}_{35}\text{I}_5\text{N}_4\text{PbS}_8$ |
| F_w (g/mol) | 1477.73 |
| Crystal size (mm^3) | $1 \times 0.1 \times 0.03$ |
| Space group | $P2_1/c$ |
| a (\AA) | 17.553(2) |
| b (\AA) | 8.710(1) |
| c (\AA) | 27.122(5) |
| β , $^\circ$ | 97.57(2) |
| V (\AA^3) | 4110(1) |
| Z | 4 |
| ρ_{calc} (g/cm^3) | 2.39 |
| Abs. coeff (mm^{-1}) | 8.289 |
| Obs. reflns ($I > 2\sigma(I)$)/parameters | 3641/378 |
| R_1/wR_2 ($I > 2\sigma(I)$) | 0.0524/0.1169 |

are in such a way that the inorganic layer can be considered as a PbI_2 deficient perovskite layer in which one out of every three metal sites is vacant along c (Fig. 3a). In fact, distances between iodine atoms of adjacent chains ($\text{I4}\cdots\text{I1}$: 4.596(2) Å) are comparable to the $\text{I4}\cdots\text{I3}$ intra-octahedra distance (4.533(2) Å). This feature is also underlined by the ratio between c and b parameters (27.12/8.71 = 3.1). For comparison, the perovskite layer ($a = 8.47$ Å, $b = 8.92$ Å) encountered in the structure of $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$ is also given in Fig. 3b. Finally, it is noteworthy that the yellow color

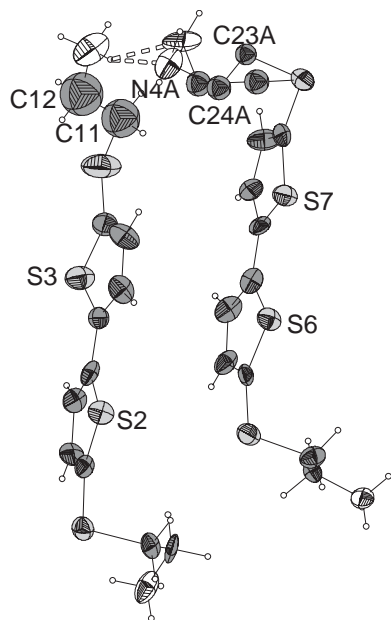
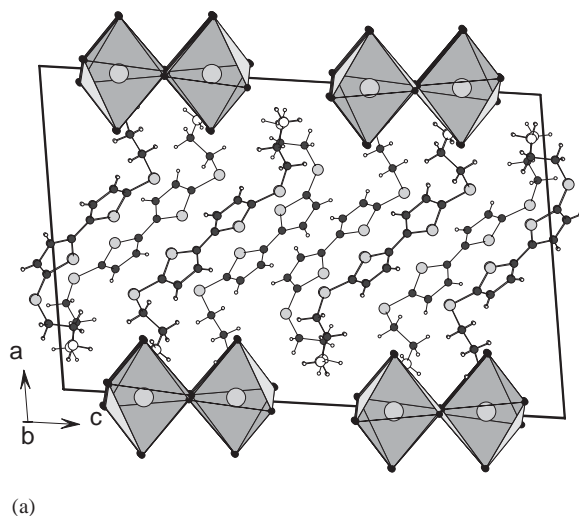
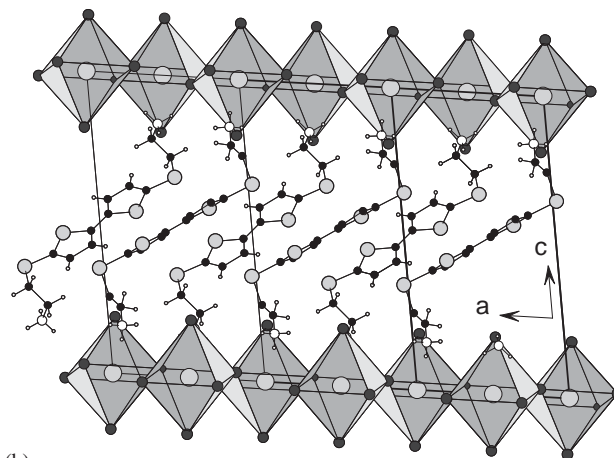


Fig. 1. ORTEP plot of both independent molecules evidenced in the structure of $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ ($R = 5,5'$ -bis(ethylsulfanyl)-2,2'-bithiophene), showing disorder of an ethyl ammonium part. $\text{NH}_3^+\cdots\text{NH}_2$ contacts are drawn as dashed lines.



(a)



(b)

Fig. 2. (a) View down along b axis of the organic-inorganic hybrid structure of $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ and (b) view of the layered structure of the all ammonium related compound $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$.

observed for $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ is in good accordance with a 1D network of lead octahedra [10–12], while PbI_4^{2-} 2D network very often gives orange color [1,13] as in $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$.

Bond distances and bond angles around the lead atom are given in Table 2. As often encountered in low dimensional (0D, 1D) iodoplumbate salts, lead octahedra are not regular: first, two Pb–I bonds (mean value of 3.319 Å), involving the shared iodine atoms, are slightly

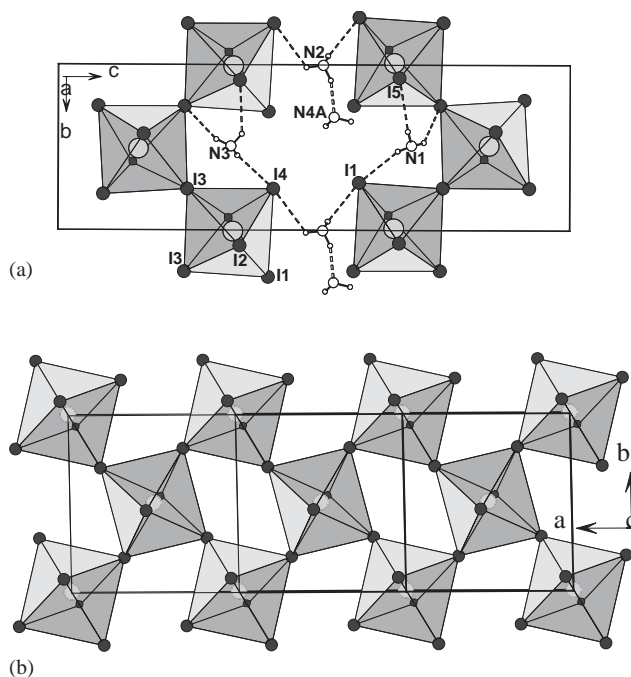


Fig. 3. (a) View of the PbI_3^{3-} chains of lead octahedra building a PbI_2 deficient perovskite layer in $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$, together with the hydrogen bonding at the organic-inorganic interface, and (b) PbI_4^{2-} perovskite layer encountered in $(\text{NH}_3\text{-R-NH}_3)\text{PbI}_4$.

longer than the four other Pb–I bonds (mean value of 3.163 Å); second, the I–Pb–I bond angles are in the range 88–101° (adjacent iodide) and 169–178° (opposite iodide). These features certainly reveal the stereoactivity of the electronic lone pair of lead atoms [13]. Fig. 3a also evidences the hydrogen bonding at the organic–inorganic interface between iodine atoms and ammonium parts, together with the strong $\text{NH}_3^+ \cdots \text{NH}_2$ interaction, while related values are given in Table 3. As mentioned in the experimental part, hydrogen atoms were located with a riding model, and four ammonium groups were first defined. A close examination of the structure, especially the $\text{H} \cdots \text{I}$ contacts, reveals that N2 is the nitrogen atom bearing the positive charge, while N4A belongs to the amino group. In fact, as illustrated in Fig. 3a, the $(\text{N}2)\text{H}_3^+$ ammonium parts point between two octahedra, and make $\text{H} \cdots \text{I}$ contacts, bringing the octahedra closer, while no $(\text{N}4\text{A})\text{H} \cdots \text{I}$ contact is observed. It must be noted that $\text{N}2 \cdots \text{N}4\text{A}$ and $\text{N}2 \cdots \text{N}4\text{B}$ distances (2.79(4) Å and 2.45(6) Å respectively, Table 3, are close to those found in *N,N*-bis(2-

aminoethyl)-2-aminoethylammonium tetracarbonyl-cobalt ($d(\text{N} \cdots \text{N})$: 2.804(4) Å) [14].

The main structural feature of this hybrid concerns the density of the molecular packing, which appears higher than in purely organic compounds or in $(\text{NH}_3\text{--R--NH}_3)\text{PbI}_4$. Thus, considering three consecutive cells of the all ammonium salt (Fig. 3b, projection along *c*), six molecules are linked to the inorganic sheet, as each NH_3^+ part points in cavities defined by four adjacent lead octahedra. By comparison, and considering an identical area of the inorganic sheet, two NH_2 parts are added, pointing roughly in cavities of the lacking octahedra of the deficient perovskite layer (cell origin and (b, c) plane center (Fig. 3a)), in $(\text{NH}_3\text{--R--NH}_3)(\text{NH}_3\text{--R--NH}_2)\text{PbI}_5$. This comparison is also conclusive by looking at Fig. 2, where eight molecules are enumerated per cell for the title compound (Fig. 2a), while three consecutive cells of $(\text{NH}_3\text{--R--NH}_3)\text{PbI}_4$ ($a = 8.4741(1)$ Å, $b = 8.9255(6)$ Å, $c = 16.876(1)$ Å, $\alpha = 88.33(1)^\circ$, $\beta = 81.80(1)^\circ$, $\gamma = 88.67(1)^\circ$, $V = 1262.7(1)$) contain only six molecules (Fig. 2b). As a consequence, stronger contacts between molecules are found in the structure of $(\text{NH}_3\text{--R--NH}_3)(\text{NH}_3\text{--R--NH}_2)\text{PbI}_5$: the corresponding packing is given in Fig. 4a, viewed along the long molecular axis, while $\text{S} \cdots \text{S}$ contacts are drawn for six molecules in Fig. 4b. The molecular arrangement is built up alternately from both types of infinite ribbons, along *b*, of molecules parallel from each other. $\text{S} \cdots \text{S}$ intermolecular contacts often give good indications of potentially charge transport properties in the corresponding organic layers, even if the orbital overlap mode, and $\text{C} \cdots \text{C}$ or $\text{C} \cdots \text{S}$ contacts must also be considered. Thus, a 1D network of molecules linked via $\text{S} \cdots \text{S}$ contacts smaller than 3.9 Å is evidenced along *b* in the title compound. This chosen limit value (3.9 Å) is higher than twice the van der Waals radius of the sulfur atom, but shorter contacts are however not so common in neutral molecules based oligothiophene compounds [15–17]. For example, the shorter $\text{S} \cdots \text{S}$ intermolecular contact is 4.2 Å in the α -sexithiophene structure [17], a well-known compound for displaying high field effect mobility in thin film transistor [18]. In addition, it is worth noting that such $\text{S} \cdots \text{S}$ contact is not found in $(\text{NH}_3\text{--R--NH}_3)\text{PbI}_4$ [8]. Also, considering $\text{C} \cdots \text{C}$ and $\text{C} \cdots \text{S}$ interactions, quite short contacts are found in the title compound (3.59(2) and 3.74(2) Å respectively), compared to those evidenced in the α -sexithiophene for instance (3.67 and 3.91 Å, respectively [17]).

The $(\text{NH}_3\text{--R--NH}_3)(\text{NH}_3\text{--R--NH}_2)\text{PbI}_5$ $R = 5, 5'$ -bis(ethylsulfanyl)-2, 2'-bithiophene) structure constitutes a model structure demonstrating that $\text{NH}_3^+ \cdots \text{NH}_2$ interactions between molecules, together with $\text{NH}_3^+ \cdots \text{I}$ contacts which occur at the organic–inorganic interface, seem to favor rather strong intermolecular interactions, especially of $\text{S} \cdots \text{S}$ type between bithiophene units, in the

Table 2

Selected bond distances (Å) and angles (deg) for $(\text{NH}_3\text{--R--NH}_3)(\text{NH}_3\text{--R--NH}_2)\text{PbI}_5$

| | | | |
|--------------|------------|----------------|------------|
| Pb–I(1) | 3.1536(13) | I(5)–Pb–I(2) | 178.67(4) |
| Pb–I(2) | 3.2131(15) | I(4)–Pb–I(3) | 89.81(4) |
| Pb–I(5) | 3.1804(14) | I(1)–Pb–I(3) | 165.86(4) |
| Pb–I(4) | 3.1066(14) | I(5)–Pb–I(3) | 82.36(3) |
| Pb–I(3) | 3.3109(13) | I(2)–Pb–I(3) | 98.08(4) |
| Pb–I(3)#1 | 3.3275(13) | I(4)–Pb–I(3)#1 | 169.07(4) |
| I(4)–Pb–I(1) | 100.71(4) | I(1)–Pb–I(3)#1 | 88.46(4) |
| I(4)–Pb–I(5) | 89.75(4) | I(5)–Pb–I(3)#1 | 96.53(4) |
| I(1)–Pb–I(5) | 88.21(4) | I(2)–Pb–I(3)#1 | 84.78(4) |
| I(4)–Pb–I(2) | 89.00(4) | I(3)–Pb–I(3)#1 | 82.207(18) |
| Pb–I(3)–Pb#2 | 174.70(4) | I(1)–Pb–I(2) | 91.58(4) |

Symmetry transformations used to generate equivalent atoms: #1: $-x + 2, y - 1/2, -z + 3/2$; #2: $-x + 2, y + 1/2, -z + 3/2$.

Table 3

Hydrogen bonds (Å) and angles (deg) for $(\text{NH}_3\text{--R--NH}_3)(\text{NH}_3\text{--R--NH}_2)\text{PbI}_5$

| $D\text{--H} \cdots A$ | $d(D \cdots \text{H})$ | $d(\text{H} \cdots A)$ | $d(D \cdots A)$ | $\angle(D\text{H}A)$ |
|---|------------------------|------------------------|-----------------|----------------------|
| $\text{N}(3)\text{--H}(3\text{A}) \cdots \text{I}(4)\#3$ | 0.89 | 2.83 | 3.655(14) | 154.3 |
| $\text{N}(3)\text{--H}(3\text{B}) \cdots \text{I}(3)\#4$ | 0.89 | 3.03 | 3.843(14) | 152.9 |
| $\text{N}(3)\text{--H}(3\text{C}) \cdots \text{I}(2)\#5$ | 0.89 | 2.91 | 3.614(14) | 137.5 |
| $\text{N}(1)\text{--H}(1\text{A}) \cdots \text{I}(3)\#6$ | 0.89 | 3.06 | 3.809(15) | 142.8 |
| $\text{N}(1)\text{--H}(1\text{B}) \cdots \text{I}(5)\#6$ | 0.89 | 2.86 | 3.680(15) | 153.5 |
| $\text{N}(1)\text{--H}(1\text{C}) \cdots \text{I}(1)\#4$ | 0.89 | 2.87 | 3.738(17) | 163.7 |
| $\text{N}(2)\text{--H}(2\text{C}) \cdots \text{N}(4\text{B})$ | 0.89 | 1.90 | 2.45(6) | 118.2 |
| $\text{N}(2)\text{--H}(2\text{C}) \cdots \text{N}(4\text{A})$ | 0.89 | 1.94 | 2.79(4) | 159.0 |
| $\text{N}(2)\text{--H}(2\text{D}) \cdots \text{I}(1)$ | 0.89 | 2.95 | 3.77(2) | 153.7 |
| $\text{N}(2)\text{--H}(2\text{E}) \cdots \text{I}(4)\#7$ | 0.89 | 3.10 | 3.61(2) | 118.1 |
| $\text{N}(4\text{B})\text{--H}(4\text{B}1) \cdots \text{I}(1)\#7$ | 0.89 | 2.87 | 3.54(4) | 135(3) |

Symmetry transformations used to generate equivalent atoms: #1: $-x + 2, y - 1/2, -z + 3/2$; #2: $-x + 2, y + 1/2, -z + 3/2$; #3: $x - 1, y, z$; #4: $-x + 1, y + 1/2, -z + 3/2$; #5: $x - 1, y + 1, z$; #6: $-x + 1, y - 1/2, -z + 3/2$; #7: $-x + 2, -y + 1, -z + 2$.

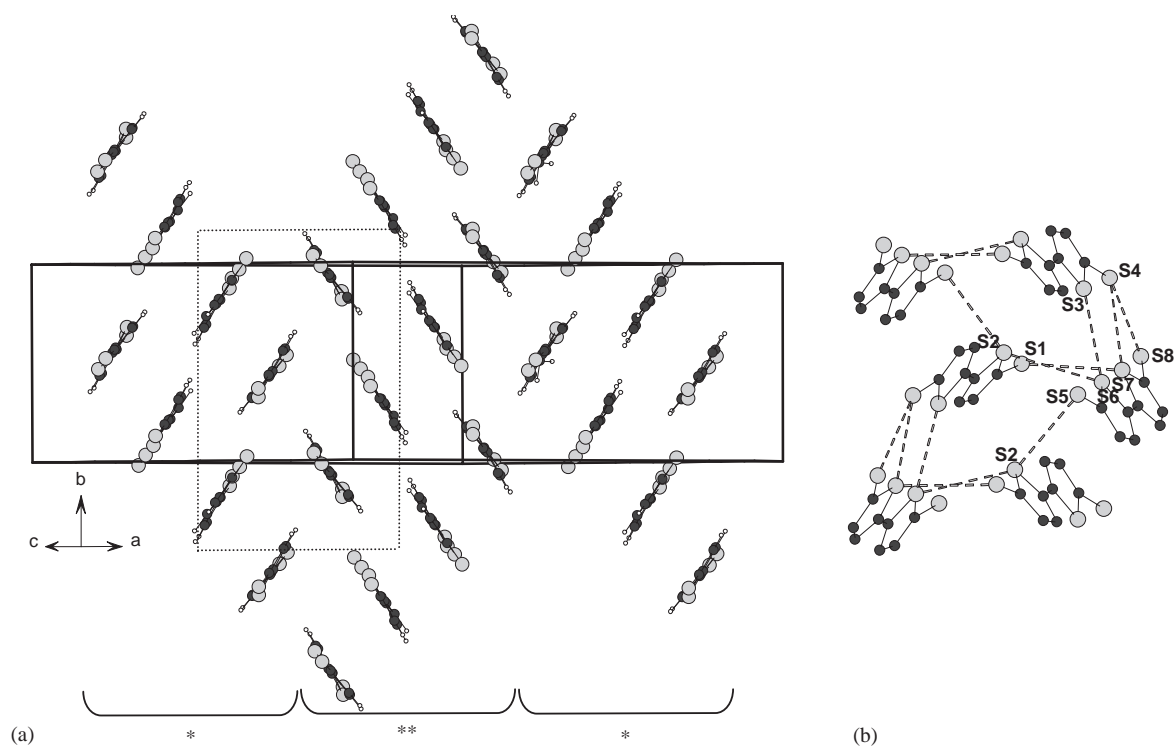


Fig. 4. (a) View down the long molecular axis of one molecular layer in $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$, ethyl ammonium or ethyl amino parts of molecules being not drawn for clarity. * and ** brackets indicate infinite ribbons along b in which molecules are parallel to each other. (b) Perspective view of six molecules (found in the defined box by dashed lines in (a)) and $\text{S}\cdots\text{S}$ contacts shorter than 3.9 Å: $\text{S2}\cdots\text{S5}$ 3.866(7) Å; $\text{S6}\cdots\text{S2}$ 3.861(7) Å; $\text{S7}\cdots\text{S1}$ 3.796(7) Å; $\text{S6}\cdots\text{S3}$ 3.764(7) Å; $\text{S7}\cdots\text{S4}$ 3.597(10) Å; $\text{S8}\cdots\text{S4}$ 3.822(10) Å.

related organic-inorganic hybrid. The synthesis should be optimized to get $(\text{NH}_3\text{-R-NH}_3)(\text{NH}_3\text{-R-NH}_2)\text{PbI}_5$ as a unique phase. We also plan in the future to incorporate new functionalized oligomer derivatives in such hybrids, notably by taking advantage of the amino-ammonium interaction.

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