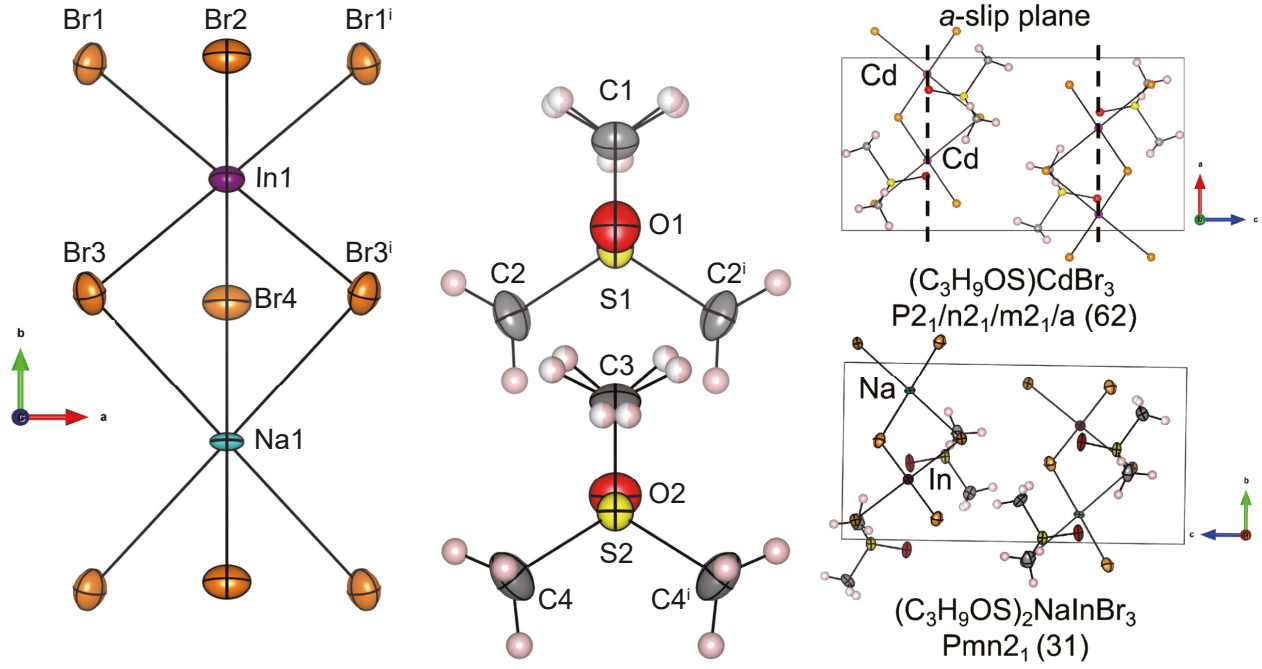
Shifeng Jin* and Jiali Lu

The crystal structure of bis(trimethylsulfoxonium) *catena*-poly[μ_2-hexabromido-indium(III) sodium(I)] $C_6H_{18}O_2S_2NaInBr_6$



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Abstract

$C_6H_{18}O_2S_2NaInBr_6$, orthorhombic, $Pmn2_1$ (no. 31), a = 10.5451(3) Å, b = 7.1169(2) Å, c = 13.7034(4) Å, V = 1028.42(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0354, $wR_{ref}(F^2)$ = 0.0923, T = 293 K.

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***Corresponding author: Shifeng Jin**, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China; and School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 101408, China,
E-mail: shifengjin@iphy.ac.cn. https://orcid.org/0000-0002-3522-1060
Jiali Lu, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China; and College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 101408, China. https://orcid.org/0009-0001-2489-1755

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.1 × 0.1 × 0.1 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	13.0 mm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX-II, φ and ω
θ_{max}, completeness:	28.3°, 97 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11,509, 2123, 0.060
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2060
$N(param)_{refined}$:	101
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

1 Source of material

All chemicals used were purchased commercially. An amount of 0.2 mol of trimethylsulfoxonium bromide, 0.1 mol of sodium bromide, and 0.1 mol of indium bromide were

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
In1	1.000000	0.34184 (11)	0.80861 (7)	0.01694 (17)
Br1	0.82409 (8)	0.12288 (13)	0.72308 (7)	0.0263 (2)
Br2	1.000000	0.10833 (18)	0.96279 (9)	0.0255 (3)
Br3	0.82369 (8)	0.55848 (13)	0.89490 (7)	0.0263 (2)
Br4	1.000000	0.57592 (17)	0.65460 (8)	0.0260 (3)
S1	0.500000	0.4728 (4)	0.7017 (2)	0.0214 (5)
S2	1.000000	0.0245 (4)	0.41421 (19)	0.0208 (5)
Na1	1.000000	0.8419 (6)	0.8077 (4)	0.0138 (7)
O1	0.500000	0.4330 (14)	0.8045 (8)	0.034 (2)
O2	1.000000	0.0554 (14)	0.3096 (8)	0.033 (2)
C1	0.500000	0.2694 (19)	0.6284 (10)	0.030 (3)
H1A[a]	0.577438	0.201220	0.638438	0.045*
H1B[a]	0.493338	0.304824	0.560952	0.045*
H1C[a]	0.429223	0.191468	0.645730	0.045*
C2	0.6330 (10)	0.6017 (15)	0.6660 (8)	0.033 (2)
H2A	0.708395	0.538805	0.687799	0.050*
H2B	0.629269	0.724859	0.694363	0.050*
H2C	0.634459	0.612156	0.596152	0.050*
C3	1.000000	0.2354 (19)	0.4800 (11)	0.033 (3)
H3A[a]	0.935173	0.316903	0.454936	0.050*
H3B[a]	1.081130	0.295355	0.473561	0.050*
H3C[a]	0.983697	0.209671	0.547626	0.050*
C4	0.8673 (11)	−0.0982 (16)	0.4541 (8)	0.039 (3)
H4A	0.877036	−0.229105	0.438947	0.058*
H4B	0.793097	−0.050243	0.422028	0.058*
H4C	0.858381	−0.083075	0.523384	0.058*

[a]Occupancy: 0.5.

dissolved in deionized water. To prevent the hydrolysis of the indium cation, 2 mL of hydrobromic acid was added. Bulk, colorless crystals were obtained by slow evaporation of the saturated solution.

2 Experimental details

The Flack parameter (*x*) larger than 0 indicates that the structure may be centrosymmetric. Based on the available isomorphous structures, a potential space group could be *Pnma* (no. 62). However, subsequent nonlinear optical experiments shows that this material is second harmonic generation active, proving it is non-centrosymmetric. Detailed structure analysis reveals the ordering of In and Na atoms in two distinct sites, making the slip plane perpendicular to the *c*-axis in *Pnma* (no. 62) impossible (*cf.* right part of the figure). Finally, the correct space group is determined to be $Pmn2_1$ (no. 31), which is a subgroup of *Pnma* (no. 62). For all hydrogen atoms, their positions were assigned geometrically based on their corresponding parent carbon atoms. The hydrogen atoms bonded to C2 and C3 exhibit orientational disorder, with an occupancy of 0.5 each.

3 Comment

Organic–inorganic metal halide hybrids are an emerging generation of functional materials with potential applications in ferroelectrics, piezoelectrics, pyroelectrics, barocalorics, and magnetics [5–8]. The title compound is a new one-dimensional organic–inorganic composite double perovskite compound. According to the single-crystal structure analysis, the compound consists of two parts: organic C_3H_9OS cations and one-dimensional chains formed by the coplanar and alternating $NaBr_6$ and $InBr_6$ octahedra, the chain is almost along the *b*-axis (*cf.* left part of the figure). Similar one-dimensional organic–inorganic metal halide hybrids were widely reported such as $C_3H_9OSCdCl_3$, $C_3H_9OSCdBr_3$, $C_3H_9OSPbBr_3$ and $C_3H_9OSPbI_3$ [9, 10] with the space group *Pnma* (no. 62). However, it is important to note that while the organic motifs remain the same, the inorganic framework in the title double perovskite compound differs from those previously reported. In the title structure, the central metal atoms within the octahedra are arranged alternately as In and Na, distinguishing it from the aforementioned centrosymmetric structures (*cf.* the figure). This arrangement disrupts the slip plane perpendicular to the *c*-axis along the one-dimensional chain, resulting in a reduction of the space group from *Pnma* (no. 62) to $Pmn2_1$ (no. 31).

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Data availability: The raw data can be obtained on request from the corresponding author.

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