Journal of Molecular Structure 1218 (2020) 128489

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Metal – organic hybrids of tin(IV) with tuneable band gap: Synthesis, spectral, single crystal X-ray structural, BVS and CSM analysis of morpholinium hexahalostannate(IV)



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ARTICLE INFO

Article history: Received 24 March 2020 Received in revised form 3 May 2020 Accepted 19 May 2020 Available online 22 May 2020

Keywords: Tin(IV)-Organic hybrid Morpholinium Crystal structure BVS CSM Band gap

ABSTRACT

Self assembled organic - inorganic hybrid materials such as morpholinium hexachlorostannate(IV) (3) and morpholinium hexabromostannate(IV) (4) have been synthesised from morpholinium chloride (1) and morpholinium bromide (2) at room temperature. The hybrids were characterized by elemental analysis, IR, NMR, TG-DTA, DRS and PL spectroscopy and single crystal X-ray diffraction. IR and NMR spectral data of (3) and (4) show very little changes compared to their parent compounds (1) and (2). However, the = NH^{\ddagger} proton signal of the bromide hybrid (**4**), shows a relatively lower δ value due to extensive hydrogen bonding compared to its chloride analogue (3). Thermal analysis confirmed the proposed formulae of the compounds. Optical absorption measurements showed 3.80 and 2.60 eV as band gaps for (3) and (4) respectively at room temperature implying that the band gaps can be easily tuned by altering the halide ion. Single crystal X-ray structures of compounds (3) and (4) revealed extensive hydrogen bonded interactions between the morpholinium cation and the SnCl²⁻₆ and SnBr²₆ anions in (3) and (4). In (4), two molecules of morpholinium bromide co-crystallized with the hybrid. BVS calculations performed on $SnCl_6^2$ and $SnBr_6^2$ anions (3) and (4) resulted in 4.10 and 4.13 respectively, which clearly established the formal oxidation state of tin in the compounds as 4+. CSM calculation on $SnBr_6^2$ yielded a value of 0.006 signifying a near perfect octahedral geometry of the anion. © 2020 Published by Elsevier B.V.

1. Introduction

Organic-inorganic hybrid materials have received considerable attention in the recent past [1–5]. Hybrid materials demonstrate interesting structural, electrical, optical and thermal properties [6–10]. There has been a surge in the number of publications and patents in this field of research due to the potential use of hybrid perovskites as charge carriers in solar cells [11–16]. The hybrid perovskites with the empirical formula ABX₃, comprise a network of corner-sharing BX₆ octahedra, where $B = Pb^{2+}$ or Sn^{2+} , X = Cl, Br, I and A = organic ammonium cation [17–19]. A hybrid ABX₃ analogue of B = Pb²⁺ ion, and A = morpholinium cation with an Eg = 3.23 eV has been reported from our laboratory [20]. In certain hybrid compounds, BX₆ octahedron exists as well-separated entity

in the unit cell and is held together by weak van der Waals forces. Essentially, hybrid perovskites are complex materials, and the presence of various types of interactions and structural disorder may play an important role in their properties [21]. Therefore, modifications in the alkyl groups, metal atoms and halides, alter the optical and electronic properties of the hybrids [22,23]. The most workable replacements for Pb^{+2} in the perovskite material are Sn and Ge which are also group 14 metals. However, the stability of the 2+ oxidation state decreases when moving up the group 14 elements, thus the major problem with the use of these metals is their chemical instability in the required oxidation state. Under ambient conditions, the Sn²⁺ ion is oxidized to Sn⁴⁺ and therefore Sn⁴⁺ acts as a p-type dopant within the materials in a self doping process [24,25]. Sn⁴⁺ is an attractive dopant due to the resulting high mobility, lower conduction band, increased electron density, and comparable crystal structure [26]. One concern with lead containing hybrid perovskite is its toxicity, and as such attempts are on to replace the lead in the perovskite crystal with a less toxic metal [27,28]. In an effort to identify relatively less toxic tin based hybrid organic-inorganic materials, the present work on synthesis,

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spectral, single crystal X-ray structural, BVS and CSM analysis of morpholinium hexachlorostannate(IV) and morpholinium hexabromostannate(IV) is reported. The iodide analogue could not be stabilized at room temperature.

2. Experimental

2.1. Materials and instrumentation

All solvents (Merck), reagents such as morpholine (Sigma Aldrich, assay: 99%), tin metal shots (Merck, assay: 99.5%), hydrobromic acid (Merck 47%) were commercially available analytical grade materials and were used without further purification. Elemental analysis was carried out with Perkin Elmer 2100 Series II instrument. FTIR spectra (as KBr pellets) were recorded with an Avatar Nicolet 360 spectrophotometer over the range of 4000-400 cm⁻¹. NMR spectra were recorded at room temperature using a 400 MHz Bruker AMX-400 spectrometer in DMSO-d₆. ¹³C NMR spectra were obtained at 100.6 MHz at room temperature. Thermal stability studies were carried out using NETZSCH STA 449 F3 JUPITER instrument under nitrogen atmosphere in the range of room temperature to 1200 °C at a heating rate of 20 K/min. DSC was carried out with TA-Q20 Differential Scanning Calorimeter. Diffuse reflectance spectra were recorded on a Varian 5000 UV-Vis spectrophotometer from 200 to 2500 nm using barium sulphate as standard with 100% reflectance. Photoluminescence spectra were recorded at room temperature on a FLUOROLOG-FL - 11 spectrometer.

2.2. Preparation of morpholinium chloride; $C_4H_{10}ONCl(1)$

Morpholinium chloride was prepared by passing hydrogen chloride gas through morpholine (0.34 mL, 4 mM) in diethyl ether (6 mL) and the resultant colourless solid was filtered through a filter paper and dried over anhydrous calcium chloride. Yield: 82%, m. p.: 174 °C. C₄H₁₀ONCl (123.58): cald.: C 38.90; H 8.16; N 11.34%; found: C 38.87; H 8.14; N 11.30%. **IR (KBr):** ν = 3420, 3282, 2947, 2812, 2776, 2595, 1633, 1565, 1451, 1306, 1225, 1186, 1099, 1035, 869, 595, 435 cm⁻¹. ¹H NMR ([D₆] DMSO, 400MH_Z, ppm): δ = 3.779 (2.860) (d, 4H, 2,6 -CH₂), 3.061(3.669) (s, 4H, 3,5 -CH2), 9.367 (2H, br NH₂). ¹³C NMR ([D₆] DMSO, 100MH_Z, ppm): δ = 63.14 (68.16) (2,6-CH₂); 42.59 (46.61) (3,5-CH₂).

2.3. Preparation of morpholinium bromide; $C_4H_{10}ONBr$ (2)

Morpholinium bromide was prepared by adding hydrobromic acid (2 mL) to morpholine (0.34 mL, 4 mM) in diethyl ether (6 mL) and then heated at 60 °C for 10 min. On cooling, morpholinium bromide precipitated out of the solution which was washed with diethyl ether for three times. Yield: 86%, m. p.: 205-206 °C. C₄H₁₀ONBr (168.03): cald.: C 28.59; H 6.00; N 8.34%; found: C 28.56; H 5.96; N 8.30%. **IR (KBr):** ν = 3418, 3112, 2985, 2816, 2716, 2515, 1634, 1562, 1451, 1305, 1186, 1099, 869, 594, 426 cm⁻¹. ¹**H NMR ([D₆] DMSO**, 400MH_Z, ppm): δ = 3.765–3.790 (2.860) (t, 4H, 2,6 -CH₂), 3.081–3.104(3.669) (t, 4H, 3,5 -CH₂), 9.017 (2H, br NH₂). ¹³C **NMR** ([D₆] DMSO, 100MH_Z, ppm): δ = 63.09 (68.16) (2,6- CH₂), 42.67 (46.61) (3,5-CH₂).

2.4. Preparation of morpholinium hexachlorostannate(IV); (C₄H₁₀NO)₂SnCl₆ (3)

Stannic chloride, SnCl₄ was prepared by dissolving tin shots (0.12 g, 1 mM) in concentrated hydrochloric acid (5 mL). To the freshly prepared stannic chloride solution, ethanolic solution of morpholinium chloride (0.25 g, 2 mM) was added with constant

stirring for 2 h at 60 °C. Colourless crystals formed from the solution after one day were filtered, washed with diethylether and dried in air. Yield: 82%, dec.: 225-226°C. $C_8H_{20}O_2N_2SnCl_6$ (507.65): cald.: C 18.93; H 3.97; N 5.51%; found: C 18.89; H 3.93; N 5.47%. **IR** (**KBr**): $\nu = 3415$, 3150, 2939, 2856, 2772, 1635, 1560, 1451, 1376, 1231, 1182, 1102, 1031, 914, 872, 587, 474, 432 cm⁻¹. ¹H NMR ([D₆] DMSO, 400MH_Z, ppm): $\delta = 3.761-3.785$ (3.669) (t, 4H, 2,6 -CH₂, J = 4.4 Hz), 3.070 (2.860) (s, 4H, 3,5 -CH₂), 9.263 (2H, br NH₂). ¹³C NMR ([D₆] DMSO, 100MH_Z, ppm): $\delta = 63.17$ (68.16) (2,6- CH₂), 42.64 (46.61) (3,5-CH₂).

2.5. Preparation of morpholinium hexabromostannate(IV) dimorpholiniumbromide; (C₄H₁₀NO)₂SnBr₆·(C₄H₁₀NO)₂Br₂ (**4**)

Stannic bromide, SnBr₄ was prepared by dissolving tin shots (0.12 g, 1 mM) in hydrobromic acid (5 mL). To the freshly prepared stannic bromide solution, ethanolic solution of morpholinium bromide (0.34 g, 2 mM) was added with constant stirring for 2 h at 60 °C. Yellow crystals formed from the solution after one day were filtered, washed with diethyl ether and dried in air. Yield: 88%, dec.: 207-208 °C. C₁₆H₄₀N₄O₄SnBr₈ (1110.49): cald. :C 17.31; H 3.63; N 5.05%; found: C 17.28; H 3.60; N 5.01%. IR **(KBr):** ν = 3425, 3185, 2939, 2855, 2598, 1654, 1559, 1450, 1397, 1230, 1182, 1104, 910, 871, 587, 434 cm⁻¹. ¹H NMR ([D₆] DMSO, 400MH_Z, ppm): δ = 3.764–3.788 (t, 4H, 2,6 -CH₂, *J* = 4.8Hz), 3.102 (s, 4H, 3,5 -CH₂), 8.937 (2H, br NH₂). ¹³C NMR ([D₆] DMSO, 100MH_Z, ppm): δ = 63.14 (2,6 -CH₂), 42.72, (3,5 - CH₂).

2.6. Single crystal X-ray crystallography studies

Single crystal X-ray intensity data were collected at ambient temperature (295 K) using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) on a Bruker SMART 1000 CCD diffractometer. Data were corrected for absorption using SADABS [29]. The structures were solved by direct methods using SIR97 [30] and were refined by SHELX2014 [31]. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed geometrically. Molecular plots were obtained with ORTEP-3 and Mercury programs [32,33].

3. Results and discussion

3.1. Infrared spectral studies

IR Spectra were recorded in the range of 4000-400 cm⁻¹ and all the FTIR spectra including those of the morpholinium chloride (**1**) and bromide (**2**) are included in the electronic supplementary material. The spectra of morpholinium hexachlorostannate(IV) and its bromide analogue are quite similar with small variations in the band positions. The broad bands observed at 3415 and 3425 cm⁻¹ for compounds (**3**) and (**4**) respectively correspond to the stretching vibrations of NH₂ group. For the morpholinium chloride and its bromide analogue, v_{N-H} bands are observed at 3420 and 3418 cm⁻¹ respectively. The NH₂ bending vibrations are observed at 1560 and 1559 cm⁻¹ in (**3**) and (**4**) respectively. Sharp bands at 1102 and 1104 cm⁻¹ are due to the stretching modes of cyclic C-O-C moiety [**34**,35]. The transmittances at 872 and 871 cm⁻¹ are due to the characteristic C-H rocking vibrations of the morpholine moiety.

3.2. NMR spectra

¹H and ¹³C NMR spectra of morpholinium hexachlorostannate(IV) and morpholinium hexabromostannate(IV) and the corresponding morpholinium salts (¹H and ¹³C NMR spectra of (1) and (2) are included in the supplementary data) were recorded in DMSO- d_6 . The ¹H and ¹³C NMR spectra of (**3**) are shown in Fig. 1 and the signals are listed in Table 1. It shows four protons of 3, 5 -CH₂ protons adjacent to nitrogen observed as a triplet at 3.070 ppm and 2, 6 $-CH_2$ protons adjacent to oxygen observed as a triplet in the range, 3.761-3.785 ppm respectively. The = NH₂⁺ proton signal is observed as a weak signal due to coupling with the quardrupolar ¹⁴N nucleus (I = 1) at 9.263 ppm, the integration corresponding to two protons for (**3**). In the ¹³C NMR spectrum of (**3**), 3, 5– and 2, 6 -C(H₂) signals are observed at 42.64, 63.17 ppm respectively. For compound (4), the spectra are shown in Fig. 2. In the ¹H NMR spectrum, 2, 6 $-CH_2$ proton signals are observed at 3.764–3.788 ppm and 3, 5 –CH₂ proton signals are observed at 3.102 ppm. The = NH_2^+ proton signal is observed at 8.937 ppm. The = NH_2^+ proton signal of (3) is observed significantly at a higher δ compared to the bromide analogue due to intense hydrogen bonded interactions. Synthesis, spectral, crystal structure and band determination studies on diallylammonium gap hexabromostannate(IV) has been reported from our laboratory recently [36]. A similar ¹H chemical shift was observed due to diallylammonium hydrogen bonding in the hexabromostannate(IV) as well. In the 13 C NMR spectrum of (4), 3, 5 – and 2, 6 -C(H₂) signals are observed at 42.72 and 63.14 ppm respectively whereas the free amine signals are observed at 46.61 and 68.16 ppm [35]. Effectively, NMR spectral data of the two morpholinium halides and their hybrids show differences in chemical shifts within the experimental variations. However, the $= NH_2^{\pm}$ proton signal of the bromide hybrid shows a relatively lower δ value due to extensive hydrogen bonding.

3.3. Single crystal X-ray structure analysis

Single crystals of morpholinium hexachlorostannate(IV) and morpholinium hexabromostannate(IV) suitable for X-ray analysis were obtained by slow evaporation of ethanolic solutions of the reaction mixtures at room temperature. Crystal data, data collection and refinement parameters and the results of analyses of two compounds are presented in Table 2. Selected bond parameters are listed in Table 3. Morpholinium hexachlorostannate(IV) (3)

crystallizes in the monoclinic system, with centrosymmetric space group, P2₁/c. ORTEP of the molecule is shown in Fig. 3. Sn-Cl bond distances vary from 2.383(5) - 2.443(11) Å. Cl-Sn-Cl bond angles vary from 87.52(6)° to 92.48(6)° and the chlorine atoms show disorder. The compound shows extensive hydrogen bonded interactions. However, large thermal parameters associated with the chlorine atoms preclude any meaningful discussion on the aspect of hydrogen bonding for (**3**). Morpholinium hexabromostannate(IV) (4) crystallized in the triclinic system, with $P\bar{I}$ space group. Two molecules of morpholinium bromide co-crystallized with the hybrid material in the unit cell. Each tin atom is surrounded by six bromine atoms in an octahedral geometry. ORTEP of the molecule is shown in Fig. 4. Sn-Br bond distances range from 2.5741(7) Å to 2.5926(7) Å and Br-Sn-Br bond angles vary from 89.12(3)° to 90.88(3)°. The SnBr₆²⁻ is relatively less distorted than the SnCl₆²⁻ anion. Compound (4) shows extensive hydrogen bonded interactions as shown in Fig. 5 and the relevant parameters are given in Table 4. = NH_2^+ protons of the compound show short hydrogen bonded distances. H...O, H...Br interactions are responsible for the stabilization of the compound in the solid state and are less than the sum of van der Waals radii of the elements (2.80 and 3.10 Å), indicating their role in the stabilization of the compound (4). In the bromide analogue, $SnBr_6^{2-}$ anion is capped by two morpholinium cations in the unit cell similar to that observed in (3). Hybrid of morpholinium bromide with lead (II) showed a Pb…O non bonded distance of 3.122(3) Å [20]. As a contrast, such a short contact was not observed in (3) and (4). The diallylammonium hexabromostannate(IV) showed perfect octahedral geometry with Sn-Br distances in the range of 2.5809(9) - 2.6132(10) Å [36]. Packing of the molecules in the unit cell is compared in Fig. 6. In both (3) and (4), $SnX_6^{2-}(X = Cl, Br)$ anions occupy the apices of the unit cell and in (3), two additional units of $SnCl_6^{2-}$ anions are also present inside the cuboid.

3.4. Bond valence sum analysis (BVS)

Bond valence sum analysis is used to estimate the valence of the central atom from the experimentally determined bond distances. BVS calculations are carried out based on the bond distances



Fig. 1. ¹H and ¹³C NMR spectra of morpholinium hexachlorostannate(IV).

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¹ H and ¹³ C NMR	chemical	shifts	(ppm).

	C ₄ H ₁₀ ONCl (1)	$C_4H_{10}ONBr(2)$	$C_{8}H_{20}O_{2}N_{2}SnCl_{6}(3)$	$C_{16}H_{40}O_4N_4SnBr_8$ (4)
¹ H NMR				
2, 6 -CH ₂ (4H, t)	3.779	3.778	3.761-3.785	3.764-3.788
3, 5 -CH ₂ (4H, t)	3.061	3.091	3.070	3.102
$= NH_2^+ (2H, b)$	9.367	9.017	9.263	8.937
¹³ C NMR				
2, 6 -C(H ₂)	63.14	63.09	63.17	63.14
3, 5 - C(H ₂)	42.59	42.67	42.64	42.72



Fig. 2. $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of morpholinium hexabromostannate(IV).

Table 2

Crystal data, data collection and refinement parameters of (3) and (4).

Parameters	(3)	(4)
Empirical formula	$C_8H_{20}Cl_6N_2O_2Sn$	$C_{16}H_{40}Br_8N_4O_4Sn$
Formula weight	507.65	1110.49
Colour	Colourless	Yellow
Crystal dimension(mm)	$0.15 \times 0.10 \times 0.10$	$0.20\times0.15\times0.10$
Crystal system	Monoclinic	Triclinic
Habit	Block	Block
Space group	P2 ₁ /c	ΡĪ
a(Å)	8.0967(7)	8.3041(5)
b(Å)	9.0589(6)	10.0745(6)
c(Å)	12.7149(9)	11.2721(7)
α(deg)	90	70.671(4)
β(deg)	96.346(2)	71.103(3)
γ(deg)	90	73.314(3)
V(Å ³)	926.89(12)	824.63(9)
Z	2	1
T(K)	293(2)	293(2)
D _{calc} (g cm ⁻³)	1.819	2.236
$\mu(mm^{-1})$	2.241	10.493
F(000)	500	526
θ range (deg)	2.531-28.000	1.979-24.999
Diffractometer	Bruker axs Kappa apex2 CCD	Bruker axs kappa apex2 CCD
Scan type	ω and ϕ scan	ω and ϕ scan
Index range	$-10 \leq h \leq$ 10,-11 $\leq k \leq$ 11,-16 $\leq l \leq$ 16	$-9 \leq h \leq 9, -11 \leq k \leq 11, -13 \leq l \leq 13$
Reflection collected	11192	23822
Unique reflection	2236	2895
Observed reflections $[I > 2\sigma(I)]$	1761	2220
Weighting scheme	$w = 1/[\sigma^2 (F_o^2) + (0.0162 P)^2 + 1.5838P]$ where $P = (F_o^2 + 2F_c^2)/3$	W = $1/[\sigma^2 (F_o^2) + (0.0308p)^2 + 4.1805p]$ where $p = (F_o^2 + 2F_c^2)/3$
Number of Parameters refined	117	152
Final R, R _W (observed data)	0.029, 0.059	0.0393, 0.0855

obtained from the single crystal X-ray structural analysis. Therefore, BVS studies indirectly prove the correctness of the crystal structures determined [37]. The method depends on the Rij value for an i-j bond which is primarily ionic [38–40]. In a compound, the oxidation state of a central atom 'i' bonded to 'j' match up to the bond valence, V and the total valence of the central atom is its oxidation state, $V = \Sigma v_{ij} = \exp[(Ro - Rij)/b]$ where *Ro* is used as reported for a large number of ionic compounds [41] and *Rij* is the experimentally determined bond distance. The constant *b* can be assumed to be 0.37 [42]. Bond valence sums of (**3**) and (**4**) are 4.10

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Table 3	3
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Selected bond distances (Å) and bond angles (°) of (**3**) and (**4**).

(3)		(4)	
bond distances			
Sn-Cl1	2.425 (3)	Sn1-Br1	2.5780(9)
Sn-Cl2	2.413(1)	Sn1-Br2	2.5926(7)
Sn-Cl3	2.413(1)	Sn1-Br2	2.5741(7)
C1-N1	1.487 (5)	C1-N2	1.465(11)
C1-C2	1.499 (6)	C1-C2	1.485(11)
C2-01	1.404 (5)	C2-02	1.398(10)
C3-01	1.411 (5)	C3-O2	1.391(11)
Angles			
Cl1-Sn1-Cl2	90.42 (7)	Br1-Sn1-Br2	89.12(3)
Cl2-Sn1-Cl3	91.60 (7)	Br2-Sn1-Br3	90.88(3)
Cl1-Sn1-Cl3	92.48 (6)	Br1-Sn1-Br3	90.44(3)
N1-C1-C2	108.7 (3)	N2-C1-C2	109.0(7)
N2-C4-C3	109.7 (3)	N2-C4-C3	108.5(7)
01–C2–C1	112.4 (3)	01-C5-C6	110.6(7)
01–C3–C4	111.8 (3)	01-C2-C1	111.6(7)

Symmetry transformations used to generate equivalent atoms: (3) -x+2, -y, -z+2; (4) 1 -x+2,-y,-z.



Fig. 3. ORTEP of the capped unit of $2[C_8H_{20}N_2 O_2] + SnCl_6^{2-}$ (3) (Thermal ellipsoids are with 50% probability).



Fig. 4. ORTEP of 2[C₄H₁₀N O] + SnBr₆²⁻ (4) (Thermal ellipsoids are with 50% probability) Two molecules of co crystallized [C₄H₁₀N O] Br are not included.

and 4.13 respectively which established the formal oxidation state of tin as 4+ unequivocally as shown in Table 5.

3.5. Continuous symmetry measure (CSM)

Continuous symmetry measure (CSM) computes the distance of a given structure from the desired ideal symmetry or from a reference shape [43–46]. Various geometries associated with molecules have been described as 'slightly distorted' or 'severely distorted' with reference to a polyhedron. Extent of distortion of a particular molecular structure from an ideal polyhedron can be assessed by symmetry measures. CSM methodology has been successful in such quantification in dealing with transition metal complexes and metal oxides. In the case of hexacoordinated atom, the idyllic geometries are ideal octahedron (iOh) or ideal trigonal prism (itp). In a scale of 0 (iOh) to 100 (itp), the geometrical deviation of an octahedral molecule can be calculated. In this investigation, SnCl₆^{2–} anion showed disorder with respect to three chloride ions and therefore CSM of the ion could not be computed. CSM calculation on SnBr₆^{2–} anion depicted in Fig. 7 showed a CSM value of 0.006, clearly indicating the near perfect octahedral geometry associated with it.



Fig. 5. Hydrogen bonded interactions of the bromine atoms in (4) and the H atoms identified in the adjacent morpholium cations.

 Table 4

 Hydrogen bonded distances (Å), bond angles (°) in (4).

	D—H	$H{\cdots}A$	D···A	D—H···A
C(1)-H(1A)Br(3)	0.97	2.92	3.653(8)	132.7
$C(1)-H(1B)\cdots Br(1)$	0.97	2.95	3.884(9)	161.9
C(2)-H(2A)Br2)	0.97	2.86	3.672(8)	141.8
$C(3)-H(3B)\cdots Br(4)$	0.97	3.12	3.868(9)	135.2
$C(4)-H(4B)\cdots Br(1)$	0.97	3.09	3.966(9)	151.6
C(6)-H(6A)Br(4)	0.97	3.12	3.742(8)	123.3
C(6)-H(6B)…O(2)	0.97	2.43	3.363(10)	161.1
C(7)-H(7A)Br(2)	0.97	3.13	3.794(8)	127.4
C(8)-H(8A)O(1)	0.97	2.50	3.293(10)	138.8
N(1)-H(1C)Br(2)	0.97	2.53	3.404(6)	149.5
N(1)-H(1D)Br(3)	0.97	2.99	3.466(6)	111.4
N(1)-H(1D)Br(4)	0.97	2.35	3.249(6)	153.5
$N(2)-H(2C)\cdots Br(4)$	0.97	2.31	3.254(6)	165.2
N(2)-H(2D)Br(4)	0.97	2.42	3.299(7)	150.8

Symmetry transformations used to generate equivalent atoms: (4) i –x+2, –y, –z+2; ii x, –y+1/2, z+1/2; iii x, –y–1/2, z+1/2; iv –x+3, y+1/2, –z+5/2; v –x+2, y+1/2, –z+5/2.

3.6. Thermal analysis

Thermal stability is an important quality of the application of organic-inorganic hybrid perovskites. Fig. 8(a) shows thermogravimetric and differential thermal analysis of morpholinium hexachlorostannate(IV) and 8(b) shows morpholinium hexabromostannate(IV). Thermogravimetric analysis was carried out in an atmosphere of nitrogen at a heating rate of 20 K/min. Morpholinium hexchlorostannate(IV) shows a mass loss of 10.4% corresponding to the loss of NH₄Cl (calcd.: 10.5%) before 100 °C associated with an endothermic signal in the DTA. In the second step of thermal decomposition between 300 and 380 °C, a total mass of 66.0% comprising of all the organic components along with the five chlorine atoms (cald.: 66.1%) are lost in an exothermic process. Above 380 °C, free tin metal corresponding to 23.3% (calcd.: 23.4%) evaporated continuously leaving no significant residue in an exothermic process.

Morpholinium hexabromostannate(IV) shows its first thermal decomposition above 280 °C, as an exothermic process corresponding to the loss of 2 mol of co-crystallized morpholinium



Fig. 6. Unit cell packing of (3) and (4) along 'a' axis.

Table	5				
Bond	valence	sums	of (3)	and	(4).

Compound	C N	Ro (Sn ⁺⁴ -X)	Bond distan	Bond distances (R _{ij})					$V = \Sigma \; v_{ij}$
(3)	6	2.276	Sn₁-Cl₁ 2.425	Sn₁-Clⁱ 2.425	Sn₁-Cl₂ 2.4133	Sn₁-Clⁱ 2.4133	Sn₁-Cl₃ 2.4123	Sn₁-Clⁱ 2.4127	4.10
(4)	6	2.444	Sn₁-Br₁ 2.5780	Sn₁-Brⁱ 2.5780	Sn₁-Br₂ 2.5926	Sn₁-Brⁱ 2.5926	Sn₁-Br₃ 2.5741	Sn₁-Brⁱ 2.5741	4.13



Fig. 7. Near perfect octahedral geometry of SnBr_6^{2-} anion with a CSM value of 0.006.

bromide accounting for a mass loss of 30.1% (cald.: 30.3%) and in the following step another set of morpholinium bromide molecules were lost accounting for 60.4% (calcd.: 60.6%) of total loss of mass within 340 °C. The above two stages show a gradation in the slope of the mass loss indicating the stage wise loss. In the next stage, with in the temperature range of 340–600 °C, the following reaction takes place corresponding to the loss of four bromine atoms

28.6% (calcd.: 28.8%):

Such a loss of bromine atoms from $SnBr_4$ at elevated temperatures has been documented [47,48]. In the last stage of decomposition above 600 °C, tin metal evaporates continuously in an exothermic process. Thermal analysis of the two hybrids clearly supports their proposed formulae and establishes the fact that the thermal stability of the chloride compound (**3**) is less than its bromide analogue (**4**).

3.7. DSC analysis

DSC traces of (**3**) and (**4**) are shown in Fig. 9. In morpholinium hexachlorostannate(IV) during the heating process up to 160 °C, no heat change was observed. On cooling, an exothermic process is observed at 145 °C indicating a phase change. In the case of morpholinium hexabromostannate(IV), an endothermic peak was observed at 167 °C on heating while an exothermic peak appeared on cooling at 165 °C. The observed heat changes in (**3**) and (**4**) are characteristic of the chloro- and bromo-analogues of the hybrid.

3.8. Diffuse reflectance spectroscopy

Diffuse reflectance spectra of (**3**) and (**4**) are shown in Fig. 10. The reflectance increased above 300 nm for (**3**). Similarly for (**4**), the reflectance increased above 450 nm. The absorptions below 450 nm are of organic origin in the hybrids. The band gap was determined to be 3.80 eV and 2.60 eV for (**3**) and (**4**) using a plot of $(F(R) hv)^2$ versus (hv) as shown in Fig. 11 (**a**) and (**b**) respectively.



Fig. 8. Thermal analyses of compound (a) morpholinium hexachlorostannate(IV) (3) and (b) morpholinium hexabromostannate(IV) (4).

Fig. 9. Differential scanning calorimetric analysis of (a) morpholinium hexachlorostannate(IV) and (b) morpholinium hexabromostannate(IV).

Fig. 10. Diffuse reflectance spectra of (a) morpholinium hexachlorostannate(IV) and (b) morpholinium hexabromostannate(IV).

Fig. 11. Determination of band gap energies of (a) morpholinium hexachlorostannate(IV) and (b) morpholinium hexabromostannate(IV).

Fig. 12. PL spectra of (a) morpholinium hexachlorostannate(IV) and (b) morpholinium hexabromostannate(IV).

The bromo hybrids show lower band gap compared to chlorohybrids as reported earlier [15,49]. Interestingly, the diallylammonium hexabromostannate(IV) reported earlier from our laboratory showed a band gap of 2.70 eV [36]. Therefore, the band gaps associated with these hybrids can be easily tuned by altering the halide ion. emission bands as shown in Fig. 12. The maxima appeared at 490 and 495 nm for (**3**) and (**4**) respectively. Relatively low FWHM associated with the emission bands show the good quality of epilayers in the semiconductors. In addition, the proximity of emission maxima of the two compounds (**3**) and (**4**) show the identical nature of photoluminescence process responsible for the emission [50].

3.9. P L spectra

On excitation of morpholinium hexachlorostannate(IV) (3) and morpholinium hexabromostannate(IV) (4) with 326 nm and 479 nm radiations respectively, the compounds exhibited narrow

4. Conclusions

Metal – organic hybrids of morpholinium hexachlorostannate(IV) and its bromide analogues have been synthesised and characterized by spectroscopic and single crystal X-ray diffraction techniques. IR spectral analysis of the compounds show that different vibrational bands of the organic moiety show very little change on hybrid formation with tin. ¹H NMR spectrum of morpholinium hexabromostannate(IV) shows significant changes in its NH signal due to extensive hydrogen bonding. DRS spectral analysis showed the band gap of the chloride hybrid to be larger than the bromide. Therefore, by changing the halide ion it is possible to tune the band gap of the hybrid material. Attempts to separate the iodide analogue have been unsuccessful. Single crystal X-ray structural analysis showed the octahedral nature of the hexahalo dianions. Morpholinium cations capped the central hexahalo anion in the unit cell. Extensive hydrogen bonded interactions in both the hybrids stabilize the solids and contribute to the effective band gap. BVS established the formal oxidation state of tin as 4+. CSM analysis of the SnBr_6^{2-} indicated its near perfect octahedral geometry.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Kuppukkannu Ramalingam: Conceptualization, Methodology, Software, Writing - review & editing. **Thangarasu Rajaraman:** Writing - original draft.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.molstruc.2020.128489.

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