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Comprehensive analysis of bis(4-methylquinolinium) hexahalostannate (IV): Synthesis, spectral, structural and hirshfeld surface analysis

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ABSTRACT

Metal-organic perovskites, bis(4-methylquinolinium) hexachlorostannate(IV) (1) and bis(4-methylquinolinium) hexabromostannate(IV) dihydrate (2), were synthesized from 4-methylquinolinium chloride and bromide at room temperature. Elemental analysis, IR, NMR, TG-DTA, SEM, EDS, XRF, XPS, DRS, PL spectroscopy, and powder and single-crystal X-ray diffraction characterized the hybrids. This study aims to investigate their structural, spectral, and photophysical properties, with an emphasis on hydrogen bonding interactions and potential electronic applications. Powder XRD confirmed bulk-phase purity, while single-crystal XRD revealed that both compounds crystallize in a centrosymmetric triclinic system (space group Pi). Strong hydrogen-bonding interactions were observed between the 4-methylquinolinium cation and the $SnCl_6^{-2}$ and $SnBr_6^{-2}$ anions. Bond valence sum calculations confirmed that the oxidation state of tin is close to 4+, which was further validated by XPS analysis. Diffuse reflectance spectroscopy indicated band gaps of 3.39 eV (1) and 3.11 eV (2), highlighting their optoelectronic potential. TG-DTA analysis validated molecular compositions, and Hirshfeld surface analysis quantified hydrogen bonding interactions, providing insights into the structural framework and electronic properties of these perovskites.

1. Introduction

In recent years, organic-inorganic hybrid materials have garnered significant attention due to their remarkable ionic, magnetic, electrical, thermal, and optical properties, as well as their potential in biomedical applications, including metallodrugs for targeted therapies [1–5]. Among these hybrid materials, tin(IV) halide-based compounds (e.g., hexahalostannates) have attracted interest for their unique optical and electronic characteristics, which make them suitable for applications in photonic devices and nonlinear optical (NLO) materials. The combination of organic cations with Sn(IV) halide anions can yield materials with tunable band gaps, enhanced photoluminescence, and high NLO efficiencies, offering advantages for optical data storage, frequency

doubling, and other photonic applications. This surge in research is partly due to the potential application of hybrid perovskites as efficient charge carriers in solar cells, leading to rapid developments in both research and patents [6–10]. The effectiveness of perovskite materials in solar cells has further accelerated their study, achieving notable milestones in energy conversion efficiency [11–13]. Within a few years, perovskite solar cells have achieved efficiencies surpassing 22 %, competing with established photovoltaic technologies like CdTe and CIGS, which reach efficiencies of 22.4 % and 23.6 %, respectively [14].

Hybrid materials based on Sn(IV) halides are notable for their flexible structural framework. Their structures are often characterized by MX_6 octahedra (where M is typically Sn(IV) and X a halogen), separated by organic cations. These materials can adopt varied dimensionalities

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Scheme 1. Synthesis of (1) and (2).

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

	C ₁₀ H ₉ N (SDBS:491–35–0)	C ₁₀ H ₁₀ Cl ₆ NSn (1)	C ₁₀ H ₁₀ NBr ₆ Sn (2)
¹ H NMR			
G–CH3 (3H,	2.69	3.05	3.06
s)			
A–CH (1H,	8.77	9.04	8.49
d)			
B-H (1H, d)	8.11	8.49	8.20
C-H (1H, d)	7.98	8.18	8.18
D—H (1H,	7.70	8.17-8.19	8.00-8.03
dd)			
E-H (1H, dd)	7.55	8.01-8.02	7.98
F-H (1H, d)	7.21	7.98	7.97-0.7.99
¹³ C NMR			
1–C(H)	150.04	159.88	159.86
2–C	147.96	137.16	137.25
3–C	144.01	143.45	143.48
4-C(H)	129.95	120.57	120.58
5-C(H)	128.93	134.81	134.80
6–C	128.15	129.89	129.84
7-C(H)	126.13	128.66	128.66
8-C(H)	123.69	125.77	125.76
9–C(H)	121.70	122.46	120.41
10CH3	18.39	18.94	18.84

1D chains, 2D layers, 3D frameworks, or even 0D clusters depending on the choice of organic cation and halide, which significantly influences their electronic and optical properties [15–20]. For instance, one-dimensional tin halide chains exhibit desirable charge transport properties for optoelectronic devices, while three-dimensional frameworks provide enhanced thermal stability, broadening their usability in solid-state applications.

In recent studies, Sn(IV)-based hybrid materials have demonstrated promising third-order nonlinear optical (NLO) properties, making them valuable candidates for photonic applications. Our group has extensively investigated the structures and NLO behaviors of hexahalostannate(IV) complexes with various organic cations, including azepane, tetrahydroquinoline, and tetrahydroisoquinoline [21-24]. These compounds exhibit significant NLO responses and structural flexibility, which can be leveraged to enhance material performance and tailor their properties for specific applications. The synthesis of bis (4-methylquinolinium) hexachlorostannate(IV) (1)and bis (4-methylquinolinium) hexabromostannate(IV) dihydrate (2) builds on this body of work, incorporating 4-methylquinolinium cations that provide distinct structural and electronic environments compared to previously reported systems. These compounds expand the library of Sn (IV)-based hybrids and enable a comparative investigation of halide substitution (Cl vs. Br) on their structural and potential photonic properties. Structural analysis using single-crystal X-ray diffraction and bond valence sum (BVS) calculations offers insights into their stability and bonding characteristics. Additionally, our inability to stabilize the iodide analogue at room temperature highlights critical structural challenges within this family of hybrids, underscoring the importance of halide selection in influencing the overall stability and adaptability of these materials.

2. Experimental

2.1. Synthesis of 4-methylquinolinium hexachlorostannate(IV) (1)

4-Methylquinoline (1.4 mL, 10 mM) and hydrochloric acid (2 mL) in diethyl ether (10 mL) were mixed at room temperature to obtain a 4-methylquinolinium chloride precursor solution and then heated at 60 °C for 10 min. On cooling, 4-methylquinolinium chloride precipitated out of the solution which was washed with diethyl ether and it was dissolved in ethanol. Tin shots (0.118 g, 5 mM) were dissolved in 5 mL hydrochloric acid (37 %) at room temperature for seven hours to prepare tin chloride. Tin chloride was added to the freshly prepared ethanolic solution of 4-methylquinolinium chloride precursor solution while being continuously stirred (Scheme 1). Crystals were formed from the solution after 12–14 d Yield: 84 %. Elemental analysis: %, Anal. Calcd., for C₂₀H₂₀N₂SnCl₆ (620 g/mole): C, 38.7; H, 3.22; N, 4.5. Found (%) C, 38.12; H, 3.25; N, 4.43. FTIR (KBr): v = 3259, 3112, 3013, 2850, 1626, 1593, 1540, 1285, 813, 706 cm⁻¹ (Fig. S1(a)). ¹H NMR ([D₆] DMSO,



Fig. 1. UV spectra (Tauc plot is given as an inset) of (1) and (2).

400MHZ, ppm): δ = 3.05 (s, 3H), 9.04 (d, 1H, A-CH), 8.49 (d, 1H, B-H), 8.18 (d, 1H, C—H), 8.17–8.19 (dd, 1H, d-H), 8.01–8.02 (dd, 1H, E-H), 7.98 (d, 1H, F-H). ¹³C NMR ([D₆] DMSO, 100 MHZ, ppm): δ = 159.88 (1-C(H)), 137.16 (2-C), 143.45 (3-C), 120.57 (4-C(H)), 134.81 (5-C(H)), 129.89 (6-C), 128.66 (7-C(H)), 125.77 (8-C(H)) 122.46 (9-C(H)), 18.94 (10-CH₃) (Fig. S2, Table 1).

2.2. Synthesis of 4-methylquinolinium hexabromostannate(IV) dihydrate (2)

4-Methylquinoline (1.4 mL, 10 mM) and hydrobromic acid (2 mL) in diethyl ether (10 mL) were mixed at room temperature to obtain a 4methylquinolinium bromide precursor solution and then heated at 60 °C for 10 min. On cooling, 4-methylquinolinium bromide precipitated out of the solution which was washed with diethyl ether and it was



Fig. 2. Photoluminescence spectra of compounds (a) (1) and (b) (2) in the solid state at room temperature.

dissolved in ethanol. Tin shots (0.118 g, 5 mM) were dissolved in 5 mL hydrobromic acid (48 %) at room temperature for seven hours to prepare tin bromide. Tin bromide was added to the freshly prepared ethanolic solution of 4-methylquinolinium bromide precursor solution while being continuously stirred (Scheme 1). Crystals were formed from the solution after 16–18d Yield: 76 %. Elemental analysis: % Anal. Calcd., for C₂₀H₂₄N₂O₂SnBr₆ (923 g/mole): C, 26; H, 2.6; N, 3.03; O, 6.93. Found (%): C, 26.8; H, 2.23; N, 3.11; O, 6.83. FTIR (KBr): v = 3547, 3267, 3106, 3014, 2882, 1631, 1598, 1541, 1288, 833, 709 cm⁻¹

(Fig. S1(b)). ¹H NMR ([D₆] DMSO, 400MHZ, ppm): δ = 3.06 (s, 3H), 8.49 (d, 1H, A-CH), 8.20 (d, 1H, B-H), 8.18 (d, 1H, C—H), 8.00–8.03 (dd, 1H, d-H), 7.98 (dd, 1H, E-H), 7.97–7.99 (d, 1H, F-H). ¹³C NMR ([D₆] DMSO, 100 MHZ, ppm): δ = 159.86 (1–C(H)), 137.25 (2-C), 143.48 (3-C), 120.58 (4-C(H)), 134.80 (5-C(H)), 129.84 (6-C), 128.66 (7-C(H)), 125.76 (8-C(H)) 120.41 (9–C(H)), 18.84 (10-CH₃) (Fig. S3, Table 1).





2.3. Characterization techniques

The FT-IR spectra were recorded by Bruker FT-IR spectrophotometer. Using the Dumas technique, the elemental analyzer ELEMENTARY UNICUBE® IZI (CHNS/O) determined the elemental proportion of the compounds. NMR spectra were obtained at room temperature using a 400 MHz Bruker AMX-400 spectrometer. For ¹H NMR spectra, compounds (1) and (2), each weighing 10 mg, were dissolved in 1 mL of DMSO-d₆ containing 1 % TMS. Additionally, ¹³C NMR spectra were acquired at 100.6 MHz, with 50 mg of the compounds dissolved in 1 mL of DMSO-d₆. All chemical shifts reported are referenced to TMS. The Shimadzu UV3600 UV–Vis spectrophotometer and the Jobin Yvon Fluorolog-FL3–11 spectrofluorometer were used to record the UV-DRS and photoluminescence spectra, respectively. A NETZSCH STA 449 F3 thermal analyzer was employed to carry out thermogravimetric (TG) and differential thermal analysis (DTA) under a nitrogen atmosphere. Using a JSM IT-200 LV SEM with EDS, the surface morphologies and elemental composition of the samples were examined. The X-ray fluorescence (XRF) spectra were recorded by Epsilon4 hardware (in Epsilon3 software package) with Omnian automatic standard (He 0.61L/min). An Ultima-IV, Rigaku X-ray diffractometer (CuK α radiation, $\lambda = 1.5406$ Å) was used to record powder X-ray diffraction patterns. An Oxford Diffraction Xcalibur-R CCD diffractometer was used for collecting data for the crystal structure determinations. The computer

Mass losses in compounds (1) and (2).

Compound	Mass loss (%)	Decomposition Range (°C)	Fragment lost
C ₂₀ H ₂₀ Cl ₆ N ₂ Sn (1)	57.8 (calcd.: 57.9)	224 - 349	2(C ₁₀ H ₁₀ NCl)
	22.8 (calcd.: 22.9)	350 - 442	$2Cl_2$
	19.2 (calcd.: 19.2)	> 443	Residual Sn evaporation
$C_{20}H_{24}Br_6N_2O_2Sn$ (2)	3.9 (calcd.: 3.9)	83 - 131	2H ₂ O
	48.5 (calcd.: 48.6)	132 – 355	$2(C_{10}H_{10}NCl)$
	34.5 (calcd.: 34.6)	356 - 461	2Br ₂
	12.9 (calcd.: 12.9)	> 462	Residual Sn evaporation

programs SHELXS-97 and SHELXL-97 were used to solve and refine the structure. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Fisher Nexsa XPS system equipped with a monochromatic Al K α X-ray source (400 μ m spot size). Pass energies were set to 200 eV for survey scans and 50 eV for high-resolution scans, with electron and argon flood guns employed to mitigate static charge. Crystal Explorer 3.1 produced fingerprint plots and Hirshfeld surface maps [25].

3. Results and discussion

3.1. Infrared spectral studies

infrared bis(4-methylquinolinium) The spectra of hexachlorostannate(IV) (1) and bis(4-methylquinolinium) hexabromostannate(IV) dihydrate (2) have been shown in Fig. S1. (1): The bands observed at 3112 and 3259 cm⁻¹ correspond to the symmetric and asymmetric stretching frequencies of the N-H group. The aromatic C-H stretching vibration appears at 3013 cm⁻¹. The alkyl C-H symmetric and asymmetric stretching vibrations appear at 2755 and 2850 cm^{-1} respectively. The peaks at 1626, 1593, and 1540 cm^{-1} are associated with the aromatic ring C = C stretching vibrations. The band observed at 1285 cm⁻¹ is attributed to the stretching mode of C-N vibration. (2): The water molecule's symmetric stretching vibration of the O—H group is represented by the band seen at 3547 cm^{-1} . The bands observed at 3106 and 3267 cm⁻¹ correspond to the symmetric and asymmetric stretching frequencies of the N-H group. The aromatic C—H stretching vibration appears at 3014 cm⁻¹. The alkyl C—H symmetric and asymmetric stretching vibrations appear at 2779 and 2882 cm⁻¹ respectively. The peaks at 1631, 1598, and 1541 cm⁻¹ are associated with the aromatic ring C = C stretching vibrations. The band observed at 1288 cm⁻¹ is attributed to the stretching mode of C-N vibration.

3.2. ¹H and ¹³C nmr spectra

The ¹H and ¹³C NMR spectra for compounds (1) and (2) are presented in Figs. S2 and S3, respectively, and the detailed peak assignments are summarized in Table 1. Compound (1) 4-methylquinolinium exhibited distinct features in its ¹H NMR spectrum (Fig. S2(a)). The methyl group protons (3H) resonated as a sharp singlet at δ 3.05 ppm, positioned in the upfield region due to the electron-donating effect of the methyl group. Aromatic protons displayed a range of chemical shifts between δ 7.96 and 9.04 ppm. Notably, an isolated doublet signal at δ 9.04 ppm was assigned to the C—H(A) proton, indicating its deshielded position adjacent to the positively charged nitrogen. Additionally, three doublet signals were observed in the range of δ 7.90–8.49 ppm, corresponding to the C—H(B), C—H(C), and C—H(D) protons (C—H(B): δ 8.49, d; C—H(C): δ 8.18, d; C—H(D): δ 7.90, d, J = 8.4 Hz;). Two doublet signals observed at 8.17–8.19 ppm and 8.01–8.02 ppm indicated the presence of C—H(E) and C—H(F) protons, which transitioned into the aromatic region. The ¹³C NMR spectrum (Figure S3) confirmed the proposed structure. Carbon C1 resonated at δ 159.88 ppm, consistent with its deshielded environment adjacent to the positively charged nitrogen. Signals for the fused ring carbons C2 and C6 were observed at δ 137.16 and δ 129.89 ppm, respectively. The methyl group attached to carbon C3 appeared at δ 143.45 ppm downfield, while the methyl carbon itself resonated at the upfield δ 18.94 ppm. Chemical shifts for the remaining aromatic carbons ranged from δ 120.57 to 134.81 ppm. Similarly, ¹H and ¹³C NMR chemical shift values for compound (2) were also observed within the expected ranges, comparable to those of compound (1).

3.3. Diffuse reflectance spectroscopy

Diffuse reflectance spectra for compounds (1) and (2) (Fig. 1) revealed significant differences in their optical properties. For compound (1), reflectance increased notably above 280 nm, while for compound (2), the increase occurred above 390 nm. By employing the Kubelka-Munk function and plotting $(F(R)hv)^2$ versus hv (inset of Fig. 1), the band gaps were determined to be 3.39 eV for (1) and 3.11 eV for (2). This bandgap variation can be attributed to the substitution of halides, where the transition from Br to Cl induces an upshift in the conduction band and a downshift in the valence band. Consequently, the bromo-hybrid exhibits a lower band gap compared to the chloro-hybrid [26]. These distinct band gap values position the compounds as potential candidates for various optoelectronic applications [27]. Compound (1), with its higher band gap, could be suitable for ultraviolet light-sensitive devices, whereas compound (2), with its lower band gap, shows promise for visible-light applications, including light-emitting diodes, photovoltaic cells, and photocatalytic systems [28]. The halide-dependent tunability of electronic properties further enhances their utility in designing materials for tailored optoelectronic and energy applications [29].

3.4. Photoluminescence spectral studies

Upon excitation, bis(4-methylquinolinium) hexachlorostannate(IV) (1) and bis(4-methylquinolinium) hexabromostannate(IV) dihydrate (2) exhibit photoluminescence (PL) bands with distinct emission maxima. Excitation of compound (1) at 340 nm results in an emission maximum at 391 nm, while excitation of compound (2) at 400 nm leads to a more dominant emission peak at 465 nm, along with secondary peaks at 430 and 449 nm (Fig. 2). The emission bands of compound (2), ranging from 360 to 560 nm, indicate multiple luminescent processes that could stem from structural and electronic differences influenced by halide variations. The observed PL characteristics in both compounds suggest that the electronic transitions responsible for these emissions are likely dominated by charge-transfer mechanisms. The emissions at 391 nm for (1) and at 465 nm dominant for (2) imply transitions that are primarily governed by ligand-to-metal charge transfer (LMCT) [30]. In LMCT, the excitation involves the transfer of an electron from the organic ligand (4-methylquinolinium) to the Sn(IV) metal center, generating an excited state that relaxes by emitting photons at specific wavelengths. The presence of different halides (chloride in compound 1 and bromide in compound 2) can influence the electronic environment around the Sn (IV) center, leading to shifts in emission maxima, as observed here. The slight proximity in the emission maxima of compounds (1) and (2) suggests similar photophysical processes [31]. However, the redshift observed in compound (2) is likely due to the heavier bromide ions, which alter the ligand field around the Sn(IV) center, enhancing spin-orbit coupling and resulting in lower-energy emission compared to compound (1). This effect aligns with the typical behavior of halide substitutions, where heavier halides induce a shift toward longer



Fig. 4. Simulated and experimental XRD patterns of (a) (1) and (b) (2).

wavelengths in emission spectra [32,33].

3.5. Thermal analysis

The thermal behaviour of compounds is shown in Fig. 3 and the data is reported in Table 2. The compounds (1) and (2), weighing 24.55 mg and 37.33 mg, respectively, were analyzed using a thermal analyzer operating in the temperature range of 30-1100 °C in a nitrogen atmosphere at a heating rate of 20 K min⁻¹. Compound (1), is stable up to 224

°C. The first weight loss of 57.8 % (calcd.: 57.9 %) was observed between 224 and 349 °C, which corresponds to two molecules of 4-methylquinolinium chloride. Upon further heating, a mass loss of 22.8 % (calcd.: 22.9 %) was observed due to the loss of chlorine, and finally above 443 °C the residual tin evaporated continuously. All the processes are exothermic. The compound (2) is stable up to 83 °C. The compound comprises two water molecules and undergoes weight loss of 3.9 % (calcd.: 3.9) in the temperature range of 83–131 °C. The second mass loss of 48.5 % (calcd.: 48.6 %) was noted between 132 and 355 °C, due to the loss of two

Cryst	al da	ita	and	structure	refinement	for	(1)	and	(2)).
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	(1)	(2)
Formula	C ₂₀ H ₂₀ Cl ₆ N ₂ Sn	C ₂₀ H ₂₄ Br ₆ N ₂ O ₂ Sn
Formula Weight (g/	619.79	922.52
mol)		
Temperature (K)	293(2)	293(2)
Wavelength	1.54184 (Cu Kα)	1.54184 (Cu Kα)
Crystal size (mm ³)	$0.21 \times 0.18 \times 0.14$	0.18×0.18×0.14
Colour	Metallic greenish grey	Metallic whitish-yellow
Shape	Plate	Plate
Crystal System	Triclinic	Triclinic
Space Group	Pī	Pī
a, b, c (Å)	7.7816(6), 8.8092(15),	7.7753(6), 8.9760(6),
	9.2926(11)	10.7505(8)
α, β, γ (°)	75.865(13), 70.314(10),	80.409(6), 71.464(7),
	84.121(12)	76.215(7)
Volume (A ³)	581.47(14)	687.51(9)
Z	1	1
Density (calculated)	1.77	2.228
(g/cm^{-3})		
Absorption coefficient	15.168	17.77
(mm^{-1})		
F(000)	306	434
Theta range for data	5.179 to 75.689°	4.359 to 76.092°
collection		
Index ranges	$-9 \leq h \leq 9, -11 \leq k \leq 11,$	$-9 \leq h \leq 9$, $-11 \leq k \leq 11$,
	$-13 \le l \le 13$	$-11 \le l \le 11$
Reflections collected	3777	4716
Reflections with $I > 2$	2329 [R(int) = 0.0736]	2785 [R(int) = 0.0382]
(I)		
Data/restraints/	2329 / 0 / 136	2785 / 0 / 147
parameters		
Goodness-of-fit on F ²	1.0330	1.04
Final R indices $[I >$	R1 = 0.0633, $wR2 =$	R1 = 0.0442, $wR2 =$
2sigma(I)]	0.1600	0.1149
R indices (all data)	R1 = 0.0702, $wR2 =$	R1 = 0.0507, $wR2 =$
	0.1697	0.1210
Largest diff. peak and	0.2550 and -0.5230	1.533 and -0.845
hole (e. \check{A}^{-3})		
CCDC	2,298,491	2,298,492

molecules of 4-methylquinolinium bromide in an exothermic process. Upon additional heating, a mass loss of 34.5 % (calcd.: 34.6 %) was perceived due to the loss of bromine and finally above 462 $^{\circ}$ C, the residual tin evaporated continuously.

3.6. SEM/EDS analysis

Figs. S4 and S5 show the surface morphology of compounds (1) and (2) examined by scanning electron microscopy (SEM). SEM micrographs are utilized to identify defects and provide detailed information on surface morphology. Both hybrids exhibit uneven arrangements of porous particles with rough surfaces. Energy-dispersive X-ray spectroscopy (EDS) was used to analyze the elemental composition of the hybrids. EDS identifies elements based on the characteristic X-ray energies they emit when excited by incident X-rays. For compound (1), carbon, nitrogen, tin, and chlorine were detected, with X-ray energies approximately at 0.27 keV for carbon, 0.39 keV for nitrogen, 3.50 keV for tin, and 2.80 keV for chlorine. For compound (2), carbon, nitrogen, oxygen, tin, and bromine were identified, with X-ray energies approximately at 0.28 keV for carbon, 0.39 keV for nitrogen, 0.53 keV for oxygen, 2.10 keV for tin, and 1.50 keV for bromine. These energies correspond to transitions between energy levels within the atoms, resulting in the emission of specific X-ray wavelengths. EDS analysis thus allows for the identification and quantification of the elements present in the compounds.

3.7. X-ray fluorescence (XRF) analysis

The XRF spectra confirm the presence of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ anions,

displaying characteristic peaks for tin, chlorine, and bromine. In compound (1), peaks for tin and chlorine are observed (Fig. S6). Tin emits Xrays in the 20–25 keV range (K α and K β lines), chlorine between 2.5–3.0 keV (K α line), and bromine in the 11–15 keV range (K α and K β lines) (Fig. S6). The intensity of these peaks correlates with element concentration, with stronger peaks indicating higher concentrations [34,35].

3.8. Powder X-Ray diffraction analysis

Fig. 4 illustrates the agreement between the peak positions in the simulated and experimental XRD patterns. It indicates the specimen's uniformity and bulk phase purity [36,37]. The sample's preferred orientation during diffractogram measurement would be the cause of the relative intensity variation. Sharp, high-intensity peaks reveal the complex's good crystalline nature.

3.9. Single crystal X-Ray structure analysis

By slowly evaporating ethanolic solutions of the reaction mixture at room temperature, single crystals of bis(4-methylquinolinium) hexachlorostannate(IV) (1) and bis(4-methylquinolinium) hexabromostannate(IV) dihydrate (2) appropriate for X-ray analysis were produced. The crystal structure was redetermined for the calculation of BVS. Table 3 displays crystal data, data collection and refinement, and the results of the two compounds' analyses. Selected bond parameters are listed in Tables S1 and S2. The compounds have a centrosymmetric space group of $P\bar{1}$ and crystallize in the triclinic system.

The molecular structure of the (1) is shown in Fig. 5(a). The complete $SnCl_6^{2-}$ octahedron is produced by the inversion symmetry operator. Fig. S7 compares the molecular packing within the unit cell. Sn-Cl bond distances vary from 2.4169(17) to 2.4464(19) Å and the Cl-Sn-Cl bond angles vary from 89.13(6) to $90.87(7)^{\circ}$ and the chlorine atoms show mild distortion. Table 4 lists the polyhedral properties of the compound (1). The $SnCl_6^{2-}$ anion is an octahedral coordination (Fig. S8(a)). With a bond angle variance of 0.3293° and a bond length distortion index of 0.00500, the effective coordination number is 5.9942. These values unambiguously show that it has nearly perfect octahedral geometry. The compound displays extensive hydrogen-bonded interactions. With a contact distance of 2.343 Å [H•••A], the atoms H(1) and Cl(1) have the shortest hydrogen bond that has been found (Fig. 6(a), Table 5). The centroid-centroid contact distance ranges from 3.721 to 3.857 Å with an angle is 20.82° This distance is in close agreement with the standard cutoff distance of 3.8 Å for accepted $\pi \bullet \bullet \bullet \pi$ contacts [38]. The stacking arrangement looks like offset or slipped stacking with a ring horizontal displacement ranging from 1.353 to 1.423 Å and the plane-plane distance is 3.451 Å (Fig. 7(a)).

The molecular structure of the (2) is shown in Fig. 5(b). The asymmetric unit consists of half of $SnBr_6^{2-}$ anion, one 4-methylquinolinium cation and a water molecule which are connected via O-H•••Br and N-H•••O hydrogen bonding interactions. The compound displays extensive hydrogen-bonded interactions. Water molecules act as a bridge between the 4-methylquinolinium cation and hexabromostannate anion through hydrogen bonds (Fig. 6(b)). Sn-Br bond distances vary from 2.5942(6) to 2.6075(7) Å and the Br-Sn-Br bond angles vary from 89.86(6) to 90.40(2) $^{\circ}$ and the bromine atoms show mild distortion. Table 4 lists the polyhedral properties of the compound (1). The $SnBr_6^{2-}$ anion is an octahedral coordination (Fig. S8(b)). With a bond angle variance of 0.0720° and a bond length distortion index of 0.00208, the effective coordination number is 5.9990. These values unambiguously show that it has nearly perfect octahedral geometry. With a contact distance of 1.892 Å [H•••A] (Table 5), the atoms H(1) and O(1) have the shortest hydrogen bond that has been found. The centroid-centroid contact distance ranges from 3.584 to 3.718 Å with an angle of 21.75° The stacking arrangement looks like slipped stacking with a ring horizontal displacement ranging from 1.348 to 1.415 Å and the plane–plane distance is 3.556 Å (Fig. 7(b))



Fig. 5. Displacement ellipsoid plot (35 % probability level) of (a) (1) and (b) (2).

Table 4	
Polyhedral parameters for compounds (1) and (2).	

(1)		(2)	
	Bond distance (Å)		Bond distance (Å)
Sn(1)-Cl(1)	2.446(3)	Sn(1)-Br (1)	2.6075(7)
Sn(1)-Cl(1) ⁱ	2.446(3)	Sn(1)-Br (1) ⁱ	2.6075(7)
Sn(1)-Cl(2)	2.4171(19)	Sn(1)-Br (2)	2.5942(10)
Sn(1)-Cl(2) ⁱ	2.4171(19)	Sn(1)-Br (2) ⁱ	2.5942(10)
Sn(1)-Cl(3)	2.421(2)	Sn(1)-Br (3)	2.6053(7)
Sn(1)-Cl(3) ⁱ	2.421(2)	Sn(1)-Br (3) ⁱ	2.6053(7)
Average bond length (Å)	2.4280	2.6023	
Polyhedral volume (Å ³)	19.0822	23.4962	
Distortion index (bond length)	0.00500	0.00208	
Quadratic elongation	1.0001	1.0000	
Bond angle variance (deg. ²)	0.3293	0.0720	
Effective coordination number	5.9942	5.9990	

3.10. Bond valence sum (BVS) analysis

BVS calculations were performed on the bond distances obtained from single-crystal X-ray structural investigation [39]. In a compound, the bond valence sum is determined by the oxidation state of a central atom "i" bonded to neighboring atoms "j". The total valence (V) of the central atom represents its oxidation state and is calculated as $V = \Sigma v_{ij} = \exp[(R_0-R_{ij})/b]$, where R_0 is the reference bond distance (as reported for several ionic compounds) [40], and R_{ij} is the experimentally determined bond distance. The constant b is typically assumed to be 0.37 [41]. With bond valence sums of 3.98 and 3.95 for compounds (1) and (2), respectively, the analysis conclusively indicated that the oxidation state of tin is close to the formal 4+ state (Table 6).

3.11. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was employed to analyze the chemical composition of the surface of the compounds $(C_{10}H_{10} N)_2[SnCl_6]$ (1) and $(C_{10}H_{10} N)_2[SnBr_6].2H_2O$ (2), with a focus on confirming the oxidation state of tin. The XPS survey spectra were recorded by scanning the analyzer over a binding energy range of 0–1000 eV, as depicted in Fig. 8 (Table S3). The survey spectra revealed distinct binding energy peaks for the surface elements of each compound. For compound (1), the identified peaks included Cl 2p at 198.91 eV, C 1 s at 285.07 eV, N 1 s at 401.16 eV, and Sn 3d at 487.17 eV (Fig. 8(a)). Similarly, for compound (2), the peaks were Br 3d at 68.82 eV, C 1 s at 285.01 eV, N 1 s at 401.10 eV, Sn 3d at 487.02 eV, and O 1 s at 532.39 eV



Fig. 6. Hydrogen-bonding network for (a) (1) and (b) (2) (most of the hydrogens are omitted for clarity).

(Fig. 8(b)). High-resolution XPS measurements focused on the Sn 3d5/2 and Sn 3d3/2 regions confirmed a single prominent feature in the Sn 3d5/2 region at binding energies of 495.87 eV for (1) (Fig. 8(c)) and 495.62 eV for (2) (Fig. 8(d)). These binding energy values conclusively indicate that the tin in both compounds exists in the Sn(IV) oxidation state [42–44].

3.12. Hirshfeld surface analysis

Hirshfeld surface mapping delineates the spatial arrangement

surrounding molecules, emphasizing non-covalent interactions within a crystal. Additionally, Hirshfeld surfaces correlate with the internal structural variations within individual molecules [45]. Fig. S9 presents the three-dimensional molecular Hirshfeld surfaces of compounds (1) and (2), showcasing surfaces mapped across d_{norm} , d_e , d_i , and shape index parameters. The exploration of distances from the Hirshfeld surface to the closest nucleus inside (d_i) and outside (d_e) the surface constituted the initial functions of distance examined for mapping on these surfaces. Circular spots in deep red signify close contacts, transitioning through green to blue colours indicating longer contacts. This

Hydrogen bonds for (1) and (2) [Å and $^{\circ}$].

D-H●●●A	d(D-H)	d(H•••A)	d(D•●●A)	<(DHA)
(1)				
N(1)-H(1)•••Cl(1)	0.86	2.343	3.177(7)	163.3
C(3)-H(3)•••Cl(1)	0.93	2.831	3.743(9)	167.2
C(7)-H(7)•••Cl(3)	0.93	2.939	3.67(1)	136.5
C(10)-H(10A)•••Cl(1)	0.96	2.800	3.72(1)	159.9
C(10)-H(10B)•••Cl(2)	0.96	2.862	3.79(1)	163.5
C(10)-H(10C)•••Cl(3)	0.96	2.846	3.793(9)	169.0
(2)				
C(3)-H(3)•••O(1)	0.93	2.443	3.25(1)	145.7
N(1)-H(1)•••O(1)	0.86	1.892	2.709(7)	158.3
O(1)-H(1B)•••Br(3)	0.85	2.8177	3.564(6)	147.5
O(1)-H(1A)•••Br(1)	0.85	2.7738	3.616(7)	171.5

Symmetry transformations used to generate equivalent atoms:.

colour gradient corresponds to the normalized contact distance, delineated with d_e , d_i , and the van der Waals radii of the atoms. The Hirshfeld surfaces mapped using d_{norm} employ a consistent colour scale: red represents a fixed negative value of -0.113 for (1) and -0.216 for (2), blue signifies a constant positive value of 1.003 for (1) and 1.278 for (2), and white denotes zero. In Fig. S9(b), the molecular surface of compounds (1) and (2) displays red regions that equally represent hydrogen bond donors and acceptors.

The fingerprint map, representing the total intermolecular interactions in compounds (1) and (2) in two dimensions, illustrates the relationship between the distances d_i and d_e (Fig. 9). The notable pseudo-symmetry observed around the diagonal ($d_i = d_e$) in the fingerprint plot mainly arises from the dense packing of the Hirshfeld surface, which is a key feature of the plot. In Fig. 9(a), the fingerprint plot displays two sharp symmetric peaks corresponding to H•••Cl interactions. These peaks occupy 42.0 % of the Hirshfeld surface area for compound (1) and 45.4 % for compound (2). The presence of red and blue triangles on the surface of the shape index (Fig. S9(d)) indicates representative C•••C contacts or π ••• π stacking interactions, which are significant for understanding molecular packing. The fingerprint plot in Fig. 9(b) highlights the C•••C contacts shown in the blue colour region along the diagonal for de and di ($d_e \simeq d_i \simeq 1.8$ Å), with these interactions



Fig. 7. Molecular packing with $\pi \bullet \bullet \bullet \pi$ interactions of (a) (1) and (b) (2).

Bond valance sum calculation of compounds (1) and (2).

Compound	Co.No.	Bond distances (Å	Bond distances (Å)						
$C_{20}H_{20}Cl_6N_2Sn$ (1)	6	Sn 1– Cl 1 2.446(3)	Sn 1– Cl ⁱ 2.446(3)	Sn₁–Cl₂ 2.4171(19)	Sn₁–Clⁱ 2.4171(19)	Sn₁–Cl₃ 2.421(2)	Sn1–Cl ⁱ 2.421(2)	3.98*	
$C_{20}H_{24}Br_6N_2O_2Sn$ (2)	6	Sn₁–Br₁ 2.6075(7)	Sn₁–Br ⁱ 2.6075(7)	Sn₁–Br₂ 2.5942(10)	Sn1–Brⁱ 2.5942(10)	Sn ₁ – Br ₃ 2.6053(7)	Sn1–Br ⁱ 2.6053(7)	3.95*	

Values rounded off.



Fig. 8. (a,b) XPS survey spectra and (c, d) high-resolution Sn3d narrow region spectra of compounds (1) and (2).

covering 5.4 % of the Hirshfeld surface area for compound (1) and 6.1 % for compound (2). These prominent molecular interactions are comprehensively displayed in Fig. 9 as fingerprint plots, offering insights into the types and extent of contacts present in the compounds. Additionally, all reciprocal contacts are depicted as a 3D stacked bar chart in Fig. S10, providing a detailed visualization of the intermolecular interactions and their contributions to the overall structure.

4. Conclusions

Metal-organic hybrids comprising bis(4-methylquinolinium) hexachlorostannate(IV) and its bromide analogues were synthesized and characterized using spectroscopic and single-crystal X-ray diffraction techniques. Both compounds crystallize in a triclinic crystal system with the space group $P\bar{I}$. The halide ions participate in hydrogen bonding or weak van der Waals interactions, primarily contributing to the stabilization of the compounds. The compounds' bond valence sums of 3.98 and 3.95, along with the distinct binding energy peaks observed in the Sn 3d5/2 region from the XPS results, confirm that tin exists in its formal 4+ (Sn(IV)) oxidation state in both compounds, highlighting the utility of XPS in understanding their electronic and chemical environments. The band gap of the chloro hybrid was shown to be greater than that of the bromo hybrid by DRS spectral analysis. The FT-IR spectra of compounds (1) and (2) exhibit peaks at 3259 and 3267 cm⁻¹, respectively, indicating the presence of -NH symmetric vibrations. Thermal analysis was employed to validate the proposed formulas of the compounds. The key observation across compounds is the consistent presence of elemental tin as the final residue above 440 °C, indicating its continuous



Fig. 9. Fingerprint plots of (1) and (2).

evaporation at elevated temperatures. Hirshfeld surface analysis was employed to quantitatively assess the 2D fingerprint plots, revealing their significant role in stabilizing crystal packing via non-covalent interactions.

CRediT authorship contribution statement

M. Prabakaran: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. B.T. Ibragimov: Validation, Software, Investigation, Formal analysis, Data curation. A. Raja: Formal analysis, Validation, Writing – review & editing. L. Guganathan: Validation, Software, Formal analysis, Data curation. P.K. Kodamboev: Visualization, Validation, Formal analysis. A.B. Ibragimov: Validation, Software, Formal analysis, Data curation, Conceptualization. T.M. Almutairi: Validation, Formal analysis, Resources, Writing – review & editing, Project administration. P. Suppuraj: Validation, Software, Formal analysis. N. Vijayan: Formal analysis. C. Balakrishnan: Writing – review & editing, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no conflict of interest.

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Supplementary materials

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Data availability

Data will be made available on request.

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