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Synthesis, spectroscopic studies, and single crystal X-ray diffraction analysis of a lead(II) based hybrid perovskite: morpholinium trichloroplumbate(II)

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Abstract: Morpholinium trichloroplumbate(II), [cyclo-O(CH₂CH₂)₂NH]PbCl₂ (1), has been synthesized and characterized by elemental analysis, FTIR and ¹H and ¹³C NMR spectroscopy, thermogravimetric analysis (TGA), diffuse reflectance spectra, and single-crystal X-ray diffraction analysis. An FTIR spectrum showed a shift of 100 cm⁻¹ in the NH₃ stretching due to the protonated nitrogen of the morpholinium ion. ¹H NMR spectrum of the compound showed significant high-frequency shift of the resonance for the CH₂ protons due to the presence of cationic charge on the adjacent nitrogen and hydrogen bonded interactions. Contrary to ¹H NMR, the ¹³C NMR signals showed a lowering of 'δ' in the hybrid material. A diffuse reflectance spectrum (DRS) illustrated intense charge transfer in the compound. The observed band gap value for the compound is 3.23 eV based on the DRS data. TG-DT analysis showed the compound to be stable up to 241°C. Single crystal X-ray diffraction analysis of the hybrid material showed the Pb²⁺ ion being surrounded by six chloride anions in a distorted octahedral geometry. In addition to the six chloride anions, the oxygen atom of the morpholinium cation is also in short contact with the lead cation. Bond valence sum (BVS) calculation confirmed the formal oxidation state of lead to be +2. Continuous symmetry measure (CSM) calculations indicated the PbCl_c to be a distorted octahedron with a magnitude of 5.246 clearly far away from the trigonal prismatic geometry.

Keywords: band gap; BVS; CSM; DRS; hybrid perovskite; lead(II); morpholinium.

Introduction

Naturally occurring perovskites have been extensively studied for their functional, structural, optical, electrical, and other properties (Mitzi et al., 2001; Mitzi et al., 2002; Stoumpos et al., 2013; Aharon et al., 2014; Dirin et al., 2014; Lindblad et al., 2014). Variation in optical and structural features of perovskites strongly depends on the extended network of the MX₆ octahedron (Owczarek et al., 2013; Frost et al., 2014). Organic compounds offer a variety of expedient properties such as mechanical plasticity, ease of processing, diverse structures, and efficient luminescence. As a contrast, inorganic materials show excellent electrical conductivity, tunable band gap, mechanical firmness, and thermal stability. Inorganic-organic hybrids favorably combine the often dissimilar properties of organic and inorganic components in one material. Inorganic-organic hybrid materials of perovskite structure are of the general formula, AMX, where A=organic ammonium moiety; M=Pb^{2+,} Sn²⁺; and X=Cl⁻, Br⁻, and I⁻ (Baikie et al., 2013; Ahmad et al., 2014; Dimesso et al., 2014; Lindblad et al., 2014; Egger and Kronik, 2014; Carrero et al., 2015; Shi et al., 2015; Yin et al., 2015). Organic-inorganic hybrids have generated substantial interest because of their ability to combine the desirable characteristics for solar applications in a single molecular scale (Kieslich et al., 2015). In the last decade, organic-inorganic hybrid perovskites are the most extensively investigated crystalline solids (Kagan et al., 1999; Mitzi, 1999). Generally, the inorganic part of the hybrid materials consists of perovskite-like layers of corner-shared octahedral units (Subbiah et al., 2014). The research spurt in hybrids has reached its zenith in the last 5 years with a phenomenal number of publications (>1600) and patents (~400) worldwide due to their use in harvesting solar energy. The hybrids have pliable electrical mobility, band gap, and thermal stability (Snaith, 2013; Yang et al., 2014; Muller, 2015). In the present work, we report the synthesis of morpholinium trichloroplumbate(II), [cyclo-O(CH₂CH₂)₂NH]PbCl₂, and characterize it by elemental analysis, IR and NMR

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spectroscopy, optical spectrum, thermal behavior, and single crystal X-ray diffraction analysis.

Results and discussion

Morpholinium trichloroplumbate(II), $[cyclo-O(CH_2CH_2)_2 NH]PbCl_3$ (1) was synthesized by the reaction of lead dichloride, PbCl₂, with an equimolar amount of morpholinium chloride, $[cyclo-O(CH_2CH_2)_2NH]Cl$ in dimethyl formamide, DMF, at 60°C. Analytical data, FTIR, and NMR spectroscopic analysis confirmed the identity of the compound.

Infrared spectroscopy

An FTIR spectrum of **1** is given in the supplementary material (Figure S1). The NH₂ stretching vibration of **1** was observed at 3432 cm⁻¹, and its deformation vibration was observed at 1570 cm⁻¹. In morpholine, the corresponding vibrations were observed at 3334 and 1463 cm⁻¹, respectively (Jelev et al., 1999). As a result of protonation, the stretching vibration shifted by approximately 100 cm⁻¹ to a higher wave number. The deformation vibration also shifted to a lower wave number to the same extent. Compound 1 showed symmetric stretching vCH₂ vibrations at 3147 and 3072 cm⁻¹, whereas morpholine showed the vibrations at 2949 and 2939 cm⁻¹ (Lan et al., 1990; Furic et al., 1992). In addition, vibrations due to the C-O-C moiety are observed at 1084 and 584 cm⁻¹ in the compound, whereas the two are observed at 1097 and 597 cm⁻¹, respectively, in morpholine. The observation clearly signifies the strong bonding of oxygen to lead in compound 1, and hence, a significant shift to lower wave number is observed.

¹H and ¹³C NMR spectroscopy

¹H and ¹³C NMR spectra of morpholinium trichloridoplumbate(II) are given in the supplementary material (Figures S2, S3). The signals are listed in Table 1. It shows four α , α' - CH_2 protons adjacent to nitrogen observed as a triplet at δ 3.769–3.793 ppm and four β , β' - CH_2 protons at δ 3.074–3.099 ppm. The ¹H NMR signals of the α , α' - and β , β' - CH_2 protons of morpholine are observed at δ 3.669 and 2.860 ppm, respectively (SDBS). The shift of both the signals to higher δ is due to two factors, viz., the presence of a cationic charge on the adjacent nitrogen atom and hydrogen bond interactions. The NH_2^+ proton signals are observed as a broad singlet at 9.188 ppm, whereas the free amine signal is observed at 2.590 ppm. The signals for the α - and β - CH_2 carbon atoms are observed at δ 63.18 and 42.9 ppm, respectively, whereas the corresponding signals for morpholine are observed at 68.16 and 46.61 ppm.

Diffuse reflectance spectrum

DRS spectrum and a plot of hv versus $(F(R) hv)^2$ for the determination of band gap of the hybrid are included in the supplementary material (Figures S4, S5). The strength of the Pb-Cl bond determines the band gaps of this class of materials. The morpholinium cation is involved in strong interaction with the lead(II) ion. It donates one electron to the hybrid perovskite material (Bernal and Yang, 2014). The Eg value of morpholinium trichloroplumbate(II) is 3.23 eV.

Thermal analysis

Thermogravimetric and differential thermal analysis was carried out in an atmosphere of nitrogen at a heating rate of 20 K/min in the temperature range of 0–1200°C and is shown in Figure 1. The TG-DT shows that the compound is thermally stable up to 241°C. Above 241°C, the TG curve shows a weight loss in two stages. In the first stage, a molecule of morpholinium chloride was lost between 296°C and 361°C. The observed weight loss of 30.5% is in excellent agreement with the expected weight loss of 30.8%

Tab	le 1:	IR,	¹ H,	and	¹³ C NMR	spectral	C	lata	for	compound	1.
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	V _{NH}	ν _{ch2}	$\mathbf{v}_{_{CN}}$	δ _{NH}	ν _{c-o-c}	
IR (cm ⁻¹)	3432	3147, 3072	1038	1570	1084, 584	
¹ H NMR (ppm)	α-C(H ₂) (4H, t)		β-C(H ₂) (4H, t)		NH ₂ +(2H, b s)	
	3.767-3.793	(3.669)	3.074-3.099	(2.860)	9.188 (2.590) ^a	
¹³ C NMR (ppm)	α-C(H ₂)		β-C(H ₂)			
	63.18 (68.16	5)	42.69 (46.61)			

^aMorpholine: NH.



Figure 1: TG-DT analysis of morpholinium trichloroplumbate(II).

during the decomposition. The remaining $PbCl_2$ vaporized completely at 800°C.

Single crystal X-ray diffraction analysis

Crystal data collection and structure refinement parameters are given in the online supplementary material. Selected bond parameters are given in Table 2. Molecular plot of the compound is shown in Figure 2. Morpholinium trichloroplumbate(II) contains the lead ion in a distorted octahedral environment of six chloride ions. The Pb-Cl interatomic distances vary from 2.738(2) Å to 2.997(3) Å. However, one of the Pb-Cl bond is quite long, 3.102(2) Å. The Cl-Pb-Cl bond angles vary to a large extent from 81.31(8) to 90.02(8)°, and the associated bond parameters indicate a very large distortion in the PbCl₆ octahedron. PbCl₆ octahedra are linked as an infinite linear chain along the 'a' axis of the unit cell, as shown Figure 3. The six-coordinate Pb atoms are triply bridged by three chloride anions resulting in the effective charge balance. The triple bridging observed in this compound is feasible only when the central atom is bulky enough $(r_{Pb}^{2+}=133 \text{ pm})$ as reported for the bromide analogue (Kawasaki et al., 2012). Moreover, large variations are forced on X-Pb-X bond angles due to triple bridging in these types of hybrids, which are responsible for the distortions of the PbX₆ octahedron (Baikie et al., 2013). Pb-Cl non-bonding distances along the 'a' axis of the unit cell are 2.738, 2.840, 2.923, 2.937, 2.997, and 3.102 Å, and the Cl-Pb-Cl angles along the linear chain are 160.02(5) and 168.28(5)°. The interatomic Pb-Pb nonbonding distance along the chain is 3.918 Å. The morpholinium cation is arranged parallel to the PbCl, chain in the unit cell, and a short contact exists between Pb and O at a distance of 3.122(3) Å, which is less than the sum of the van der Waals radii=3.42 Å. A neutron diffraction study on



Figure 2: Molecular plot of morpholinium trichloroplumbate(II) showing short contact between Pb-O.



Figure 3: Linear PbCl₂ chain extending along the 'a' axis.

the tribromo-substituted analogue showed a similar structural environment in the crystal structure (Kawasaki et al., 2012). Interestingly, the bromide analogue crystallized in the space group: $P_{2,2,2_1}$ with very small increment in the unit cell lengths in keeping with the relatively larger size of the bromide ions in the place of chloride ions. The Pb-O distance in the bromide analogue is 3.235(2) Å, which is significantly longer than the distance observed in the present chloride compound.

The molecule shows extensive hydrogen bonding, as shown in Table 3. Hydrogen atoms at the nitrogen atom of morpholine and the hydrogen atom on the carbon atoms of morpholine are in hydrogen bonding interactions with three chlorine atoms. All the hydrogen bonds observed in the compound are significantly shorter than the sum of the van der Waals radii of H and Cl of 2.85 Å, and therefore, a set of strong hydrogen bonded interaction is observed. The Pb-O and N-H-Cl/Br interactions are responsible for the contribution of the organic part to the conducting property of the material.

Table 2: Selected bond lengths (Å) and bond angles (°) for 1.

Bond lengths			
Pb1-Cl1	2.738 (2)	Pb1-Cl3 ⁱ	2.937 (2)
Pb1-Cl2	2.840 (3)	01-C4	1.418 (13)
Pb1-Cl3	2.926 (2)	01-C1	1.425 (14)
Pb1-Cl1 ⁱⁱ	3.102 (2)	N1-C3	1.468 (15)
Pb1-Cl2 ⁱ	2.997 (3)	N1-C2	1.472 (14)
Bond angles			
Cl1-Pb1-Cl2	83.21 (8)	Cl2 ⁱ -Pb1-Cl3 ⁱ	85.89 (7)
Cl1-Pb1-Cl3	81.31 (8)	Pb1-Cl2-Pb1"	84.30 (7)
Cl2-Pb1-Cl3	89.04 (8)	Pb1-Cl3-Pb1"	83.88 (6)
Cl1-Pb1-Cl3 ⁱ	79.01 (7)	C1-01-C4	108.7 (8)
Cl2-Pb1-Cl3 ⁱ	90.02 (8)	C2-N1-C3	111.7 (8)
Cl3-Pb1-Cl3 ⁱ	160.28 (5)	01-C1-C2	110.4 (9)
Cl1-Pb1-Cl2 ⁱ	76.81 (7)	N1-C2-C1	109.6 (8)
Cl2-Pb1-Cl2 ⁱ	160.02 (5)	N1-C3-C4	109.9 (9)
Cl2 ⁱ -Pb1-Cl3	88.30 (7)	01-C4-C3	111.2 (9)

Symmetry codes: i=1/2+x, 1/2-y, 1-z; ii=x+1/2, -y+1/2, -z+1.

Table 3: Hydrogen bond distances (Å).

D-H	H…A	D…A	D-H···A
0.89	2.49	3.270 (9)	1.46
0.89	2.69	3.339 (9)	1.31
0.89	2.79	3.431 (8)	1.30
0.97	2.78	3.540 (11)	1.36
	D-H 0.89 0.89 0.89 0.97	D-H H···A 0.89 2.49 0.89 2.69 0.89 2.79 0.97 2.78	D-HH···AD···A0.892.493.270 (9)0.892.693.339 (9)0.892.793.431 (8)0.972.783.540 (11)

Symmetry codes: i=1/2+x, 1/2-y, 1-z; ii=x+1/2, -y+1/2, -z+1; iii=-x+1, y-1/2, -z+1/2; iv=-x+1/2, -y+1, z-1/2; v=-x+1, y+1/2, -z+1/2.

Bond valence sum (BVS) calculation

BVS calculations offer a reliable method of determining the formal oxidation state of an atom in a compound from the structural data, particularly the bond lengths. For an ionic compound, the method depends on the Rij, the bond distance for the bond between the atoms *i* and *j* in a compound (Brown and Altermatt, 1985; Bresse and O'Keefe, 1991; Brown, 2002, 2009). In a compound, the oxidation state of a central atom *i* bonded to *i* is equivalent to the bond valence, *Sij*, and the total valence of the central atom, which is its oxidation state, $\Sigma Sij = \exp[(Ro - Rij)/b]$ (Brown and Altermatt, 1985). Ro is the bond distance determined from a large volume of X-ray structural data for predominantly ionic compounds, and Rij is the experimentally determined bond distance in this study. The constant *b* is assumed to be 0.37. For compound 1, the BVS was calculated by summing up the bond valence contributions from six Pb-Cl bonds, and it was found to be 2.166. However, the BVS for PbCl₂O, including the contribution from the Pb-O short contact, was found to be 2.219. In the present case, the BVS value clearly establishes the formal oxidation state of lead as +2.0. Therefore, a considerable ionic character to the predominantly covalent bonding in the compound is clearly established (Summers et al., 1994) besides proving the fact that the X-ray structure determined in this study is perfect.

Continuous symmetry measure (CSM)

CSM assesses the deviation of a given structure from the desired ideal symmetry or from a reference shape (Zabrodsky et al., 1992; Keinan and Avnir, 2000; Alvarez et al., 2002; Ok et al., 2006). The descriptions such as 'slightly distorted' or 'highly distorted' relative to the reference polyhedron is highly qualitative in nature. The extent of deviation of a structure from an ideal polyhedron can be quantified by symmetry measures. The ideal geometries associated with hexa-coordinated atoms are ideal octahedron (iOh) or ideal trigonal prism (itp). The CSM value is to a scale of 0-100 with 0 corresponding to an ideal octahedron and 100 to an ideal trigonal prism for a six coordinated central atom. In the present investigation, the coordination around lead has been found to be in a distorted octahedron (dOh) environment of six chloride ions. In the present case, the CSM of PbCl core is 5.246. The observed CSM value clearly indicates the proximity of the compound to octahedral geometry rather than trigonal prism.

Conclusions

Morpholinium trichloroplumbate(II) is an organic-inorganic hybrid perovskite material synthesized at 60°C in DMF. An FTIR spectrum of the compound shows characteristic shift of C-H and N-H stretching vibrations to lower wave numbers on forming the hybrid material. The ¹H NMR signals of α , α' - and β , β' -CH₂ protons of morpholine shifted to higher ' δ ' due to the presence of cationic charge on the adjacent nitrogen atom and extensive hydrogen-bonded interactions. The NH_{a}^{+} proton signals are observed as a broad singlet at 9.188 ppm, compared to the free amine signal observed at 2.590 ppm. ¹³C NMR signals showed a lowering of 'δ' in the hybrid material. DRS spectrum confirmed intense charge transfer being present in the compound. The observed band gap value for the hybrid is 3.23 eV based on the DRS data, which indicated its suitability as a semiconductor for various applications. TG-DT analysis showed the compound to be stable up to 241°C and established the correctness of proposed formula of the compound. Single crystal X-ray diffraction analysis of compound 1 shows the divalent lead ion to be in an environment of six chloride ions resulting in a distorted octahedral geometry. PbCl, octahedra formed a rigid [MX,] chain along the unit cell 'a' axis, and the organic morpholinium cation juxtapositioned itself in the lattice. In addition to the six chloride ions, the oxygen atom of the morpholinium cation is at a short distance of 3.122(3) Å, which is less than the sum of the van der Waals radii=3.42 Å. BVS calculation confirmed the formal oxidation state of lead to be +2. The Pb-O and N-H-Cl/Br interactions are responsible for the contribution of organic part to the conducting property of the material. CSM calculations indicated the PbCl₂ to be a distorted octahedron with a magnitude of 5.246 clearly far away from the trigonal prismatic geometry.

Experimental section

Reagents and equipment

All reagents were acquired commercially and were used without further purification. Morpholine (Merck, India), DMF (Merck, India), and lead nitrate (Merck, India) were used in the synthetic process. Avatar Nicolet 360 spectrophotometer (USA) was employed to record IR spectrum. ¹H and ¹³C NMR spectra were recorded on Bruker AMX-400 spectrometer (USA). The elemental analysis was performed on a Perkin Elmer 2100 series II CHN/S Analyzer (USA). TGA analyses were performed on a NETZSCH-STA 449 F3 JUPITER thermal analyzer (Germany). Optical diffuse reflectivity was measured using Varian 5000 UV-vis spectrophotometer (USA) from 200 to 2500 nm using barium sulfate as standard with 100% reflectance.

X-ray crystallography

Single crystal X-ray intensity data were collected at ambient temperature (295 K) using graphite monochromated Mo-K α radiation (λ =0.71073 Å) on a Bruker SMART 1000 CCD diffractometer (USA). Data were corrected for absorption using SADABS (Bruker, 2001). The structures were solved by direct methods using SIR97 (Altomare et al., 1999) and were refined by SHELX2014 (Sheldrick, 2015). The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were fixed geometrically. Molecular plots were obtained with ORTEP-3 (Farrugia, 1999) program.

Synthesis of morpholinium chloride

Morpholinium chloride, $[cyclo-O(CH_2CH_2)_2NH]Cl$, was prepared by passing HCl gas through morpholine (0.34 mL, 4 mM) in diethyl ether (5 mL), and the resultant colorless solid was filtered through a filter paper and dried over anhydrous calcium chloride (yield: 82%, m.p.: 174°C). Elemental analysis showed as follows: %Calcd. for C₄H₁₀ONCl: C, 38.90; H, 8.16; N, 11.34; Foud C, 38.87; H, 8.14; N, 11.30.

Preparation of lead(II) chloride

Lead(II) nitrate (0.662 g, 2 mmol) was dissolved in water (30 mL). To this solution, concentrated hydrochloric acid (35%, 5 mL) was added. Amorphous colorless precipitate of lead(II) chloride was filtered from the solution and was recrystallized from boiling water.

Preparation of morpholinium trichloridoplumbate(II)

Lead chloride (0.278 g, 1 mM) in DMF (5 mL) was mixed with morpholinium chloride (0.247 g) in DMF (5 mL) (1:2) and was stirred at 60°C for 6 h. The resultant colorless solution was filtered and allowed to stand for crystallization. Colorless crystals were formed on evaporation of the solution after 2 weeks (yield: 76%; m.p.: 254–256°C). Elemental analysis showed as follows: %Calcd. for $C_4H_9ONPbCl_3$: C, 11.99; H, 2.26; N, 3.50. Found C, 12.02; H, 2.22; N, 3.48.

Supplementary crystallographic data

CCDC **1055004** contains the supplementary crystallographic data for compound **(2)**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/con-ts/ retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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