

The Crystal Structure of Bis(diethylammonium) Hexachloridoplumbate(IV) Derived From Powder Diffraction Data and its Relation to Structurally Related Hexachloridometallate Salts

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Received: 23 December 2015 / Accepted: 30 June 2017 / Published online: 11 July 2017
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Abstract Bis(diethylammonium) hexachloridoplumbate(IV) was obtained by the reaction of PbO_2 and $(\text{C}_2\text{H}_5)_2\text{NH}_2\text{Cl}$ in hydrochloric acid solution. From the obtained crystalline powder a Rietveld refinement verified the structure of bis(diethylammonium) hexachloridoplumbate(IV) to be isotopic to the corresponding tin(IV) and platinum(IV) salts. The hexachloridoplumbate(IV) anions act as fourfold hydrogen bond acceptors and the diethylammonium cations as twofold

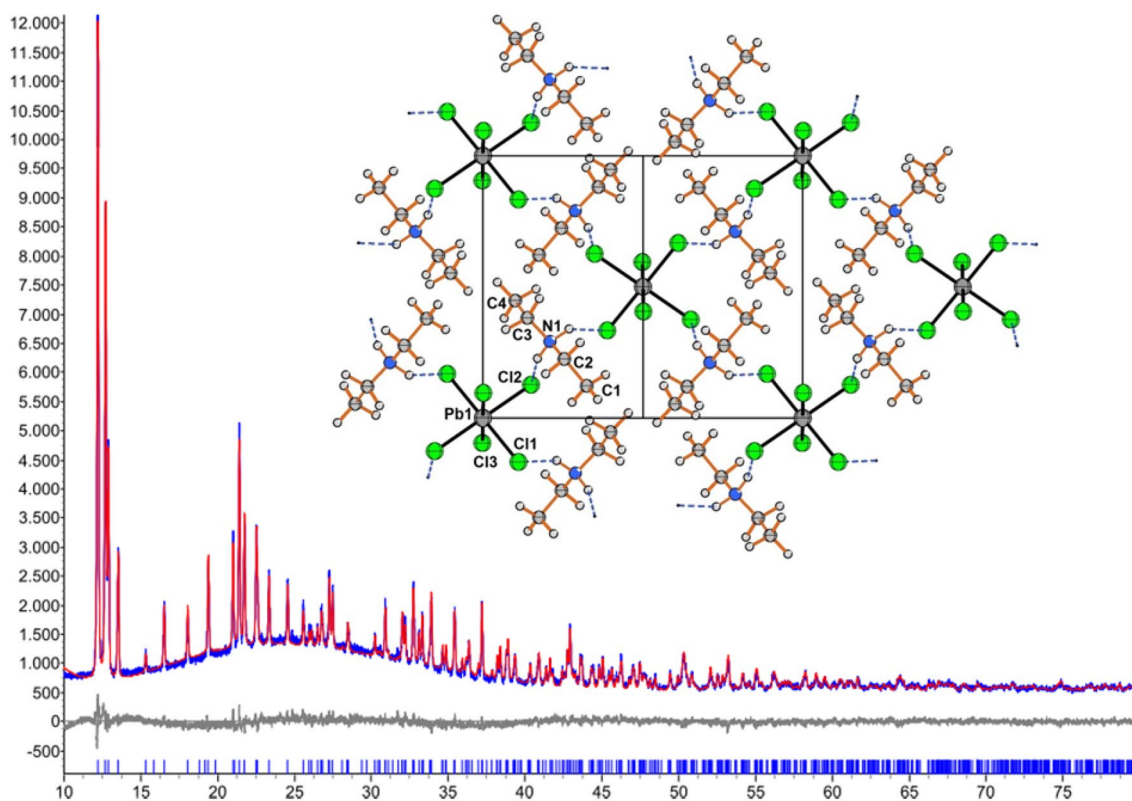
hydrogen bond donors to form a two-dimensional framework perpendicular to the $[-101]$ direction. Similar two-dimensional framework structures are well known for several hexahalogenidometallate salts, which are discussed. The infrared spectrum recorded at room temperature is provided and discussed on the basis of the structural data of the $(\text{C}_2\text{H}_5)_2\text{NH}_2^+$ cation and its connection to $[\text{PbCl}_6]^{2-}$ anions in the title compound.

Electronic supplementary material The online version of this article (doi:10.1007/s10870-017-0695-x) contains supplementary material, which is available to authorized users.

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Graphical Abstract



Keywords X-ray diffraction · Rietveld refinement · Graph Set · Infrared spectroscopy · Diethylammonium

Introduction

Alkylammonium hexahalogenidometallates $(R_nNH_{4-n})_2[MX_6]$ ($1 \leq n \leq 4$; R = alkyl; M = Si and X = F, Cl) show phase transitions that involves changes in hydrogen bonding as well as re-orientational motions of the alkylammonium cations [1–4]. Hexafluorosilicates such as $((C_2H_5)NH_3)_2SiF_6$, $((CH_3)_3NH)_2SiF_6$, $(C_6H_5NH_3)_2SiF_6$, $(CH_3(CH_2)_2NH_3)_2SiF_6$, $(CH_3(CH_2)_3NH_3)_2SiF_6$ and $((C_2H_5)_2NH_2)_2SiF_6$ were studied by X-ray, DSC, Infrared and Raman spectroscopy and computational analyses [5–10]. Furthermore, there is broad scope of hydrogen bonded hexahalogenidometallates with tetravalent metal centers: tin(IV) [11–15], iridium(IV) [16], osmium(IV) [17], ruthenium(IV) [18], platinum(IV) [19]. It has also been shown that some hexahalogenidometallate anions (Sn, Ir) predominantly act as fourfold hydrogen bond acceptor, whereas the dialkylammonium counter cations doubly act as hydrogen bond donors. The combination of these ions yields layered structures [16]. The structure refinement in this class of compounds is hindered by the presence of pseudosymmetry problems. In detail such problems may

arise in this class of compounds because the heavy halogenidometallate anions show a highly symmetrical arrangement, whereas the lighter organic counter cations may break this symmetry [16]. In these and comparable cases a careful refinement, which may be supported by the use of restraints is needed [20–22].

We here present the synthesis, crystal structure and infrared spectra of diethylammonium hexachloridoplumbate(IV), $((C_2H_5)_2NH_2)_2[PbCl_6]$. An assignment of the observed infrared bands to the corresponding vibrational modes, based essentially on the previous works [5, 6, 10] is carried out.

Results and Discussion

Crystal Structure

The asymmetric unit of the title structure contains one diethylammonium (*deaH*) cation located at a general position and one-half of a hexachloridoplumbate(IV) anion located on an inversion center. Each anion acts as fourfold hydrogen bond donor, whereas each *deaH* cation donates two hydrogen bonds. Consequently, a two-dimensional framework is constructed roughly perpendicular to the $[-1\ 0\ 1]$ direction (Fig. 1). The hydrogen bonded rings that

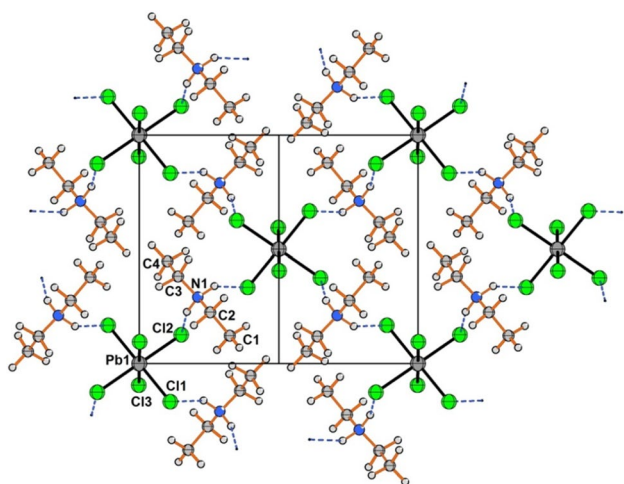


Fig. 1 View along $[-101]$ of the hydrogen bonded polymeric layer of the title structure

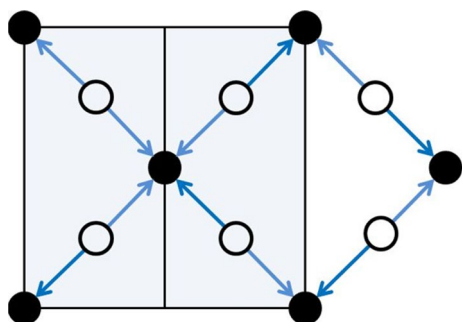


Fig. 2 Constructor graph [25] for the hydrogen bonded topology of the title structure

are formed can be classified with the graph set descriptor $R_8^8(24)$ [23–25] as shown in Fig. 2. The pseudosymmetry element of a face-centering is clearly visible.

The title structure is at least homeotypic to $(deaH)_2[SnCl_6]$ [12] and $(deaH)_2[PtCl_6]$ [19] (Table 1), as in an isotypic relation the atomic coordinates should be the same. The two-dimensional hydrogen bonded framework, which is present in these three structures is also frequently encountered in other compounds of this class. The exchange of the *deaH* cation by another cation leads to structurally closely related compounds. With $(dipH)_2[SnCl_6]$ (*dipH*=diisopropylammonium) a homotypic structure is literature known (Table 1). Other compounds feature the same hydrogen bonding pattern but crystallize in a different way (Table 2).

An inquiry to the Cambridge structural database showed, that there are at least two more structurally related compounds. These two isotypic tetrakis(dimethylammonium) hexachloridometallate chloride double salts $(dmaH)_4[MCl_6]Cl$ ($M=W$ [27], Ru [28]; dimethylammonium (*dmaH*)) contain the aforementioned two dimensional hydrogen bonded framework built from hexachloridometallate(III) anions and dimethylammonium cations which are due to the oxidation state of the metal - are formally negatively charged. Two more dimethylammonium cations and the chloride anion form the neighbouring anionic layers.

In all these structures discussed before the hexahalogenidometallate anions show roughly the same sub structure, which is an arrangement of the four anions with an identical orientation and a fifth, symmetry related one between them with a different orientation (Fig. 3). In the title structure and its isotypic ones (Table 1) the hydrogen bonded layers are located in the diagonal of the unit cell. Consequently, the shortest distances of $[PbCl_6]^{2-}$ anions in the title structure are 8.4697(3), 10.7284(3) and 13.109(4) Å (Figs. 1, 3). These values are similar for all isotypic structures given in Table 1 and can also be found in some of the lattice metrics of the structures of $(dipH)_2[IrCl_6]$, $(dmaH)_4[WCl_6]Cl$ and $(dmaH)_4[RuCl_6]Cl$ (Tables 2, 3). It

Table 1 Space groups and lattice parameters of the isotypic $(deaH)_2[M(IV)Cl_6]$ structures and a homeotypic $(dipH)_2[SnCl_6]$ (*dipH* diisopropylammonium) structure ($Z'=1$ for all entries)

	Space group	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Ref.
$(deaH)_2[SnCl_6]$	$P2_1/n$	9.078(1)	10.644(2)	9.801(2)	90	93.02(1)	90	[12]
$(deaH)_2[PtCl_6]$	$P2_1/n$	8.8745(2)	10.4444(3)	9.7268(2)	90	93.79	90	[19]
$(deaH)_2[PbCl_6]$	$P2_1/n$	9.1564(3)	10.7284(3)	9.8372(3)	90	92.789(2)	90	
$(dipH)_2[SnCl_6]$	$P2_1/n$	9.54362(13)	11.9818(2)	9.90669(14)	90	92.941(2)	90	[11]

Table 2 Space groups and lattice parameters of two structures, which are structurally related to the title compound (*dipH* diisopropylammonium; $Z' = 2$)

	Space group	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Ref.
$(dipH)_2[IrCl_6]$	$P2_1/c$	16.0939(14)	10.3961(12)	13.6382(13)	90	100.20(1)	90	[16]
$(S_3N_2NH_2)_2[SnCl_6]$	$P2_1/c$	9.084(2)	23.758(4)	6.587(1)	90	101.86(3)	90	[26]

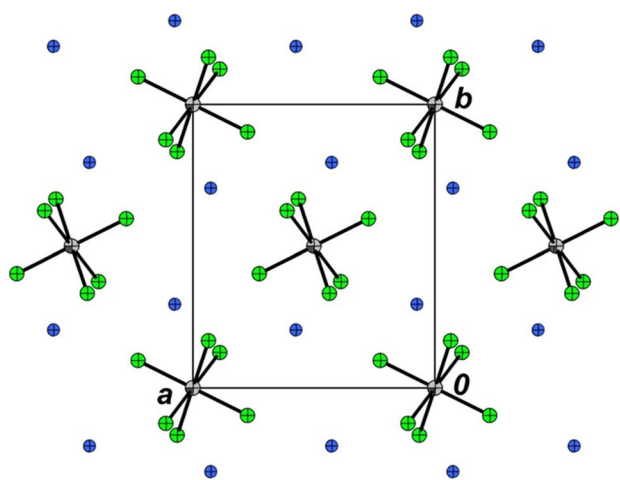


Fig. 3 The packing of the title structure is shown with a view along [001]. For the cations only the nitrogen atoms are shown. (Color figure online)

is worth mentioning that the formal antitype [29] of these hexahalogenidometallates salts has been reported. In the structure of (dimethylphosphoryl)methan ammonium nitrate [30] dimeric units of cations act as fourfold hydrogen bond donor, whereas the nitrate anion acts as a twofold hydrogen bond acceptor.

Symmetry Considerations of Internal Vibrations of $(C_2H_5)_2NH_2^+$ Cation

The free $(C_2H_5)_2NH_2^+$ cation may be taken to belong to the C_{2v} symmetry point group. It has 45 internal vibrational modes which are described by the following representation: $14 A_1$ (IR, Ra) + $9 A_2$ (Ra) + $12 B_1$ (IR, Ra) + $10 B_2$

(IR, Ra). These cationic modes correspond mainly to the vibrations of the NH_2 , CH_2 and CH_3 groups and to those of the cationic skeletal $C-C-N^+$ and $C-N^+-C$. For an isolated cation, the vibrational modes of A_1 , B_1 and B_2 symmetries are infrared active.

Within the $(deaH)_2[PbCl_6]$ crystal which may be belonging to $P2_1/n$ (C_{2h}^5) space group, the $(C_2H_5)_2NH_2^+$ cations have the C_1 sites symmetry that is lower than C_{2v} . Then as a result of two formula units per primitive unit cell, i.e. four cations per cell, each of the A_1 , A_2 , B_1 and B_2 vibrational modes should split into four components by Davydov splitting effect (Table 4). In the crystal (C_{2h} group factor), which is centrosymmetric, the *ungerade* modes of symmetry A_u and B_u are Infrared active. This implies that all the characteristic $(C_2H_5)_2NH_2^+$ infrared bands should be observable for this salt. Details are discussed in the [Experimental](#) section of this contribution.

Experimental

Synthesis

Crystals of $(deaH)_2[PbCl_6]$ were prepared in ice-cold hydrochloric acid solution containing stoichiometric amounts of PbO_2 and $(C_2H_5)_2NH_2Cl$. To a HCl solution still in the ice bath, PbO_2 was slowly added with constant stirring and a yellow solution obtained. The solution was left in the ice bath for a few minutes to allow it to settle. After the yellow solution was decanted into the ice-cold $(C_2H_5)_2NH_2Cl$ solution (still in the ice bath) with stirring; the mixture was allowed to sit in the ice bath for many minutes to complete precipitation of $(deaH)_2[PbCl_6]$.

Table 3 Space groups and lattice parameters of two isotopic, layered structures which contain hydrogen bonded $\{(dmaH)_2[MCl_6]\}^+$ layers (*dmaH* dimethylammonium, *M* Ru(III), W(III))

	Space group	<i>a</i>	<i>b</i>	<i>c</i>	α	β	γ	Refs.
$(dmaH)_4[WCl_6]Cl$	$P2_12_12$	10.297(2)	13.107(3)	8.7121(17)	90	90	90	[27]
$(dmaH)_4[RuCl_6]Cl$	$P2_12_12$	10.087(5)	12.744(6)	8.698(14)	90	90	90	[28] ^a

^aThe lattice constants given in the literature has to be permuted to fit the needs of a stand setting for the space group $P2_12_12$

Table 4 Correlations diagramme ($C_{2v} \rightarrow C_1 \rightarrow C_{2h}$): vibrational modes of $(C_2H_5)_2NH_2^+$

Point group : C_{2v}	Site group : C_1 (4)	Factor group : C_{2h}
14 A_1 (IR, Ra)	45 A (Ra, IR)	45 A_g (Ra)
9 A_2 (Ra)		45 B_g (Ra)
12 B_1 (IR, Ra)		45 A_u (IR)
10 B_2 (IR, Ra)		45 B_u (IR)

Powder Diffraction

The crystalline powder was characterized by X-ray diffraction. XRD data were collected with a STOE STADI-P diffractometer working with $\text{CuK}\alpha_1$ radiation. Independent from using the parameters of the probably isostructural $(\text{deaH})_2[\text{SnCl}_6]$ [12] indexing was carried out using the program TOPAS [31]. The solution was adopted from the literature known $(\text{deaH})_2[\text{SnCl}_6]$ [12] in the monoclinic space group $P2_1/n$. The pattern was refined with the program TOPAS [31] (classical Rietveld method) using a TCHZ pseudo-Voigt function [32] for peak modelling. Chebyshev polynomials were used for shaping the background. Preferred orientation has been minimized by using spherical harmonics [33] (Fig. 4).

Table 5 Selected bond length [Å] and bond angles [°]

Pb1–Cl1	2.460(8)	Pb1–Cl2	2.496(8)
Pb1–Cl3	2.469(8)	C1–C2	1.55(2)
C3–C4	1.55(2)	C2–N1	1.40(2)
C3–N1	1.40(2)	Cl1–Pb1–Cl2	91.6(2)
Cl1–Pb1–Cl3	91.0(2)	Cl2–Pb1–Cl3	88.0(2)
C2–N1–C3	115(1)		

The structure was refined by the Rietveld method using the $[(\text{C}_2\text{H}_5)_2\text{NH}_2]^+$ ion and $[\text{PbCl}_6]^{2-}$ ion with restrained bond length and angles (Pb–Cl 2.4–2.7 Å and 86–94°; C–C 1.45–1.55 Å and 110–115°; C–N 1.4–1.5 Å and 110–115°). Final refined bond length and angles are shown in Table 5. These soft rigid bodies stabilize the refinement [34]. The necessity for these restrained refinements is based on the fact that the diffraction pattern is dominated by the $[\text{PbCl}_6]^{2-}$ ions. Consequently, the orientation of the cation is badly defined. The orientation of the diethylammonium cation was checked via pattern fitting. The best fitting was found building the shortest H···Cl hydrogen bonds between N–H···Cl as shown in Fig. 1 (N···Cl distances: 4.41–3.45 Å). Rotating the cation to get shorter C–H···Cl hydrogen bonds carried out only a local minimum-energy configuration with the best result. Therefore we decided on a chemical reasonable orientation, which is almost the same as those, which was reported for $(\text{deaH})_2[\text{SnCl}_6]$ [12]. Observed, calculated and difference pattern of the final refinement of the title structure are represented in Fig. 4.

Crystal data and structure refinement parameters are given in Table 6.

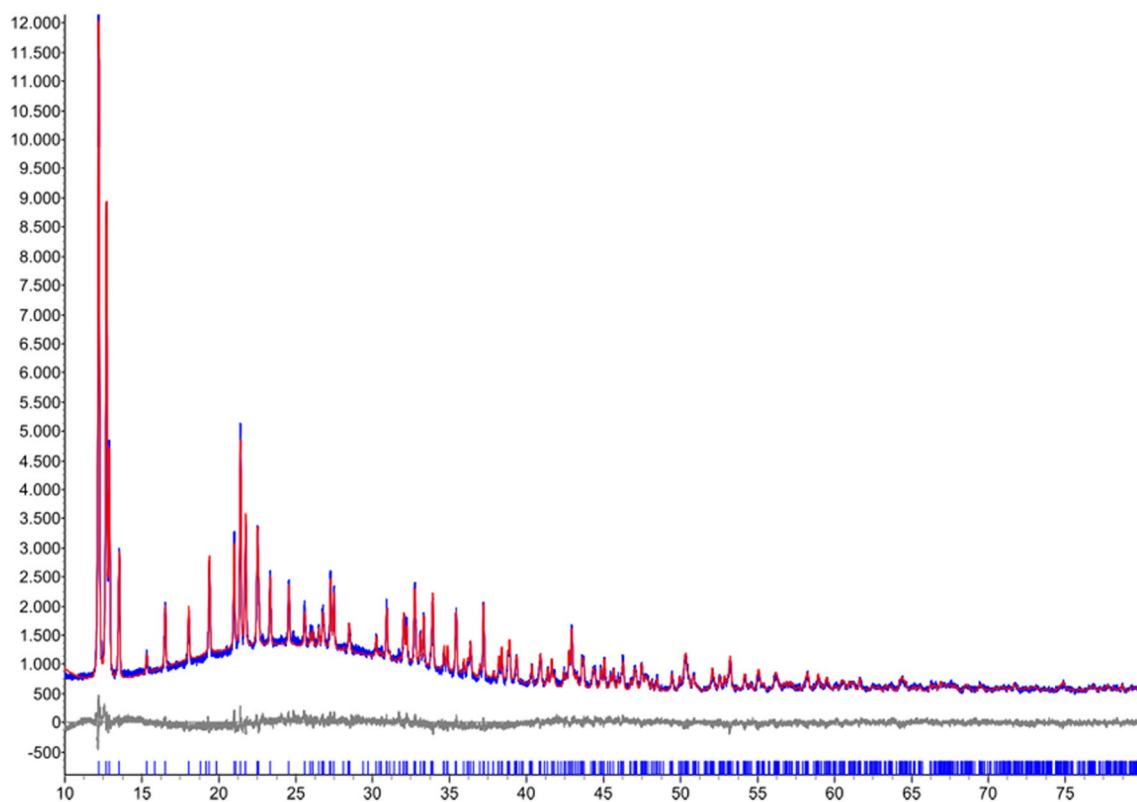


Fig. 4 Blue line measured pattern; Red line: simulated pattern; Grey line difference pattern; vertical bars Bragg-Positions $(\text{deaH})_2[\text{PbCl}_6]$

The Infrared Spectrum of $(deaH)_2[PbCl_6]$

The infrared spectrum of $(deaH)_2[PbCl_6]$ was recorded at room temperature, in the 600–4000 cm^{-1} spectral range, on a VERTEX 70 FTIR spectrometer (BRUKER Optics) by using the ATR MIRACLE DIAMANT technique. The spectral resolution was 4 cm^{-1} (20 scans).

The infrared spectrum of this compound is presented in Fig. 5. Several characteristic bands corresponding to cationic $(C_2H_5)_2NH_2^+$ vibrational modes were observed in the infrared spectrum of this compound. The assignment of the majority of infrared bands (Tables 7, 8), especially in the $(C_2H_5)_2NH_2^+$ cationic spectral ranges (600–4000 cm^{-1}) is made on the basis of literature data of some alkylammonium compounds [3–7, 10] and the factor group analysis.

In the 3500–2700 cm^{-1} spectral region, appeared generally the N–H and C–H stretching modes. So, the strong band located at 3142 cm^{-1} is assigned to the asymmetric modes of NH_2 group $\nu_{as}(NH_2)$; while the two medium bands observed at 3089 and 3004 cm^{-1} may be due to the symmetric $\nu_s(NH_2)$ modes. The C–H stretching modes give rise in the infrared spectrum of this compound to five bands. The band of medium intensity observed at 2806 cm^{-1} and the two weak features occurred at 2838 and 2885 cm^{-1} are assigned to the symmetric stretching modes $\nu_s(CH_2)$ and $\nu_s(CH_3)$; while the two weak bands observed at 2969 and 2990 cm^{-1} correspond to the asymmetric $\nu_{as}(CH_2)$ and $\nu_{as}(CH_3)$ stretching modes.

The bands observed at lower frequencies of NH and CH stretching spectral region (2700–2000 cm^{-1}) have been

Table 6 Crystal data and structure refinement parameters of $(deaH)_2[PbCl_6]$

Empirical formula	$\{(C_2H_5)_2NH_2\}_2[PbCl_6]$
Formula weight [g/mol]	568,21
Crystal system	Monoclinic
Space group	$P2_1/n$
a [Å]	9.1636(2)
b [Å]	10.7319(3)
c [Å]	9.8386(3)
β [°]	92.750(1)
V [Å ³]	966.45(5)
Z	2
D_{calc} [g/cm ³]	1.955
Start and finish angle [°]	$8 < 2\theta < 80$
Wavelength [Å]	Cu $K\alpha_1$ (1.54056)
R_p^a	0.0397
R_{wp}^a	0.0483
R_{Bragg}^a	0.0205
CCDC-no	1534988

^a R_p, R_{wp}, R_{Bragg} as defined in the program system TOPAS [31]

considered as being due to overtones and combinations modes. These bands with appreciable intensities may be intensified by Fermi resonance as has been stated for several hybrid compounds in the literature [3–5, 7]. The observation of these non-fundamental modes in this IR spectral region may be an indication of the formation of appreciable N–H...Cl hydrogen bonds in the $(deaH)_2[PbCl_6]$ crystal. This is in agreement with the X-ray results that showed that the stabilisation of the structure of this compound by shorter hydrogen bonds [2.37(3) Å]. An attempt of assigning bands observed at 2650 and 2100 cm^{-1} to corresponding combination and overtone modes is given in Table 8.

The bands appeared in the 1650–600 cm^{-1} range correspond generally to asymmetric and symmetric bending

Table 7 Assignment at room temperature of $(deaH)_2[PbCl_6]$ infrared bands (cm^{-1})

IR bands	Assignment
760 s	$\nu_s(C-N)/\nu_s(C-C)$
792 w	$\nu_s(C-N)/\nu_s(C-C)$ $\rho(CH_2)$
870 w	$\rho(CH_2)/\rho(CH_3)$
922 w	$\rho(CH_2)/\rho(CH_3)$
1033 s	$\nu_{as}(C-N)/\nu_{as}(C-C)$
1063 s	$\nu_{as}(C-N)/\nu_{as}(C-C)$
1160 m	$\rho(CH_3)/\omega(CH_2)$
1201 w	$\rho(CH_3)/\omega(CH_2)$ $\rho(CH_3)/\omega(CH_2)$
1320 w	$\omega(CH_2)$
1333 sh	$\omega(CH_2)$
1373 m	$\omega(CH_2)$
1387 s	$\delta_s(CH_3)/\omega(CH_2)$
1424 s	$\delta_s(CH_3)/\omega(CH_2)$
1456 s	$\delta_{as}(CH_3)/\delta_{as}(CH_2)$
1465 s	$\delta_{as}(CH_3)/\delta_{as}(CH_2)$
1571 s	$\delta(^+NH_2)$
1635 m	$\delta(H_2O)$ of moisture
2100–2650	Combination and overtone modes
2806 w	$\nu_s(CH_2)/\nu_s(CH_3)$
2838 w	$\nu_s(CH_2)/\nu_s(CH_3)$
2885 w	$\nu_s(CH_2)/\nu_s(CH_3)$ $\nu_s(CH_2)/\nu_s(CH_3)$
2969 vw	$\nu_{as}(CH_2)/\nu_{as}(CH_3)$
2990 w	$\nu_{as}(CH_2)/\nu_{as}(CH_3)$
3004 m	$\nu_s(^+NH_2)$
3089 m	$\nu_s(^+NH_2)$
3142 s	$\nu_{as}(^+NH_2)$
3387 m, b	$\nu(H_2O)$ of moisture

s Strong, vs very strong, m medium, w weak, vw very weak, b broad, sh shoulder

Table 8 Assignment of the combination and overtone bands observed on the IR spectrum of $(deaH)_2[PbCl_6]$ at room temperature

Combination and overtone bands (cm^{-1})	Assignment
2121 w, b	$\approx 1201 + 921 = 2122$ $\approx \rho(CH_3)/\omega(CH_2) + \rho(CH_2)/\rho(CH_3)$
2326 w	$\approx 1387 + 921 = 2308$ $\approx \delta_s(CH_3)/\omega(CH_2) + \rho(CH_2)/\rho(CH_3)$
2432 w	$\approx 1387 + 1033 = 2420$ $\approx \delta_s(CH_3)/\omega(CH_2) + \rho(CH_2)\rho(CH_3)$
2485 w	$\approx 1424 + 1063 = 2487$ $\approx \delta_s(CH_3)/\omega(CH_2) + \delta_{as}(C-N)/\delta_{as}(C-C)$

w weak, vw very weak

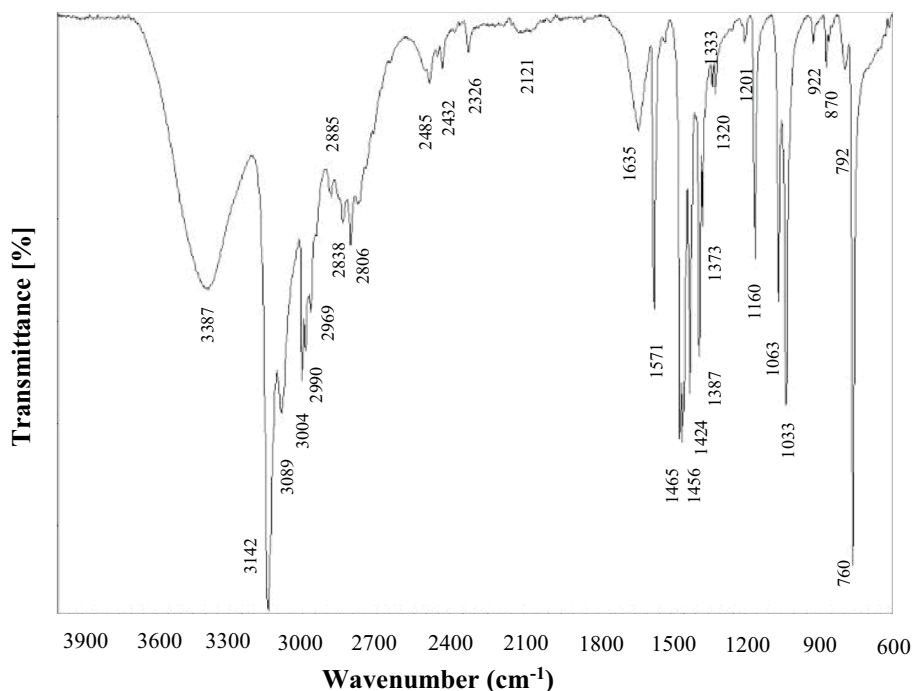
modes of CH_3 , CH_2 and NH_2 groups, to CH_3 and CH_2 rocking modes, to CH_2 wagging, to scissoring ($\delta_{as} CH_2$) vibrations and to the skeletal stretching and bending modes of the diethylammonium cations. So, the band of strong intensity observed at 1571 cm^{-1} is assigned to $\delta(^+NH_2)$. The band of medium intensity appeared at 1635 cm^{-1} may be due to $\delta(H_2O)$ deformation of moisture that is present in the compound itself. The TGA curve (cooling) confirms that $(deaH)_2[PbCl_6]$ is hygroscopic and the elimination of moisture water was made in the $30\text{--}80^\circ\text{C}$ temperature domain. The two strong bands observed at 1465 and 1456 cm^{-1} were assigned to $\delta_{as}(CH_2)$ or $\delta_{as}(CH_3)$ modes, whereas the two features of strong intensity at 1424 and 1387 cm^{-1} were attributed to $\delta_s(CH_3)$ modes or CH_2 wagging ones. The bands corresponding to CH_2 wagging, CH_3 and CH_2 rocking

modes, the skeletal stretching and bending modes were all observed between 1400 and 600 cm^{-1} (Tables 7, 8).

The observation of some non-fundamental bands with appreciable intensities are interesting since they are indicative of the formation of moderate to strong $N\text{--}H\text{--}Cl$ hydrogen bonding between $(C_2H_5)_2NH_2^+$ cations and $[PbCl_6]^{2-}$ anions. But, this makes the assignment of some characteristic cationic bands, in the NH and CH stretching spectral region, more difficult since the hydrogen bonding may be the origin of such deviations of some frequencies values in this region.

Conclusion

The X-ray powder diffraction pattern of the title compound $deaH_2PbCl_6$ shows monoclinic symmetry. A detailed analysis of the powder diffraction pattern verified that the title compound is isotypic to $deaH_2MCl_6$ ($M = Sn, Pt$). Even though, alkylammonium hexahalogenidometallates of lead(IV) are well known for decades [35], a search in the Cambridge Structural database proved that there is no structure containing a $[Pb(IV)Cl_6]^{2-}$ anion reported until now and even the $[Pb(II)Cl_6]^{4-}$ containing structures are rare [36–38]. This is surprising as hexahalogenidometallates are well known to be useful tectons for the construction of hybrid solids [39]. The main structural feature of the title structure is a hydrogen bonded two-dimensional framework, which is discussed on the basis of a constructor graph. In all the discussed layered structures each cation

Fig. 5 Infrared spectrum of $(deaH)_2[PbCl_6]$ 

donates two hydrogen bonds, whereas each halogenidometallate accepts four hydrogen bonds. The isotopic structures $deaH_2MCl_6$ ($M = Sn, Pt, Pb$) and other structurally related ones seem to be dominated by this hydrogen bonding motif.

Funding Funding was provided by Deutsche Forschungsgemeinschaft (Grant No. INST 208/533-1).

References

- Knop O, Cameron TS, James MA, Falk M (1983) Alkylammonium hexachlorostannates(IV), $(R_nNH_{4-n})_2SnCl_6$: crystal structure, infrared spectrum, and hydrogen bonding. *Can J Chem* 61:1620–1646
- Ben Ghazlen MH, Daoud A, Bates JW (1981) Dimethylammonium hexachlorostannate(IV). *Acta Crystallogr B* 37:1415–1416
- Ouasri A, Rhandour A, Dhamelincourt M-C, Dhamelincourt P, Mazzah A (2002) Vibrational study of $(CH_3)_4NSbCl_6$ and $[(CH_3)_4N]_2SiF_6$. *J Spectrochim Acta Part A* 58:2779–2788
- Ouasri A, Rhandour A, Dhamelincourt M-C, Dhamelincourt P, Mazzah A (2002) Structural and vibrational study of hydrazinium hexafluorosilicate. *J Raman Spectrosc* 33:726–729
- Ouasri A, Rhandour A, Dhamelincourt M-C, Dhamelincourt P, Mazzah A (2003) The infrared and Raman spectra of ethylammonium hexafluorosilicate $[C_2H_5NH_3]_2SiF_6$. *J Spectrochim Acta Part A* 59:357–362
- Ouasri A, Rhandour A, Dhamelincourt M-C, Dhamelincourt P, Mazzah A (2003) Structure and vibrational study of the trimethylammonium hexafluorosilicate $[(CH_3)_3NH]_2SiF_6$ compound. *J Spectrochim Acta Part A* 59:851–857
- Jeghno H, Ouasri A, Rhandour A, Dhamelincourt M-C, Dhamelincourt P, Mazzah A (2003) Structural phase transition in $(n-C_4H_9NH_3)_2SiF_6$: DSC and Raman studies. *J Raman Spectrosc* 34:126–130
- [8] Jeghno H, Ouasri A, Rhandour A, Dhamelincourt M-C, Dhamelincourt P, Mazzah A (2003) Structural phase transitions in $[C_6H_5NH_3]_2SiF_6$: differential scanning calorimetry and Raman studies. *J Raman Spectrosc* 34:399–403
- Jalbout AF, Jiang Z-Y, Ouasri A, Jeghno H, Rhandour A, Dhamelincourt M-C, Dhamelincourt P, Mazzah A (2003) Theoretical and experimental vibrational analysis of $[C_6H_5NH_3]_2SiF_6$. *J Vib Spectros* 33:21–30
- Jalbout AF, Ouasri A, Jeghno A, Rhandour A (2007) Experimental and theoretical studies of monoalkylammonium hexafluorosilicate $[CH_3(CH_2)_nNH_3]_2SiF_6$ ($n = 2, 3$) and ethylammonium hexafluorosilicate $[(C_2H_5)_2NH_2]_2SiF_6$. *J Vib Spectrosc* 44:94–100
- Reiss GJ, Helmbrecht C (2012) Bis(diisopropylammonium) hexachloridostannate (IV). *Acta Crystallogr E* 68:m1402–m1403
- Cameron TS, James MA, Knop O, Falk M (1983) Bis(diethylammonium) hexachlorostannate(IV), $(Et_2NH)_2SnCl_6$, and tris(di-*n*-propylammonium) hexachlorostannate(IV) chloride, $(n-Pr_2NH)_3(SnCl_6)Cl$: crystal structure and hydrogen bonding. *Can J Chem* 61:2192–2198
- Daszkiewicz M (2015) X-ray, vibrational and theoretical studies of weak hydrogen bonds in bis(4-nitroanilinium) hexachloridostannate. *Spectrochim Acta A* 139:102–107
- Daszkiewicz M (2014) Weak hydrogen bonds in bis(3-nitroanilinium) hexachloridostannate monohydrate. X-ray, vibrational and theoretical studies. *Spectrochim Acta A* 131:335–341.
- Hajji R, Oueslati A, Hajlaoui F, Bulou A, Hlel F (2015) Structural characterization, thermal, ac conductivity and dielectric properties of $(C_7H_{12}N_2)_2[SnCl_6]Cl_2 \cdot 1.5H_2O$. *Phase Transit* 89:1–20.
- Reiss GJ (2002) The pseudosymmetric structure of bis(diisopropylammonium) hexachloroiridate(IV) and its relationship to potassium hexachloroiridate(III). *Acta Crystallogr E* 58:m47–m50
- Reiner T, Waibel M, Marziale AN, Jantke D, Kiefer FJ, Fässler TF, Eppinger J (2010) η^6 -Arene complexes of ruthenium and osmium with pendant donor functionalities. *J Organomet Chem* 695:2667–2672
- Spek AL, Veldman N, Velders AH, Reedijk J (2005) Bis(6,8-Dimethyl-(1,2,4)triazolo(4,3-b)pyridazinium) hexachlororuthenium(IV), *YARREP*, private communication to the Cambridge structural database
- Bokach NA, Pakhomova TB, Kukushkin VY, Haukka M, Pombeiro AJL (2003) Hydrolytic metal-mediated coupling of dialkylcyanamides at a Pt(IV) center giving a new family of diimino ligands. *Inorg Chem* 42:7560–7568
- Reiss GJ, Engel JS (2002) Hydrogen bonded 1,10-diammoniododecane - an example of an organo-template for the crystal engineering of polymeric polyiodides. *CrystEngComm* 4:155–161
- Reiss GJ, Konietzny S (2002) How realistic are alternating C–C bond lengths in bis(*s-cis*-butadiene) transition metal-complexes? *J Chem Soc Dalton Trans.* 862–864. doi:10.1039/B109454H
- Reiss GJ (2002) A reinvestigation of Wilm's salt, - synthesis, structure, spectroscopy and thermal analysis. *Z Kristallogr* 217:550–556
- Grell J, Bernstein J, Tinhofer G (2002) Investigation of hydrogen bond patterns: a review of mathematical tools for the graph set approach. *Crystallogr Rev* 8:1–56
- Eitter MC, MacDonald JC, Bernstein J (1990) Graph-set analysis of hydrogen-bond patterns in organic crystals. *Acta Crystallogr B* 46:256–262
- Grell J, Bernstein J, Tinhofer G (1999) Graph-set analysis of hydrogen-bond patterns: some mathematical concepts. *Acta Crystallogr B* 55:1030–1043
- Holl K, Thewalt U (1986) S_4N_4 und seine Derivate: Isolierung und Struktur von $S_4N_4H^+[SnCl_5(H_2O)]^-$ und $(S_3N_2NH_2^+)_2[SnCl_6]^{2-}$. *Z Naturforsch B* 41:581–586
- Kahrovic E, Orioli P, Bruni B, Di Vaira M, Messori L (2003) Crystallographic evidence for decomposition of dimethylformamide in the presence of ruthenium(III) chloride. *Inorg Chim Acta* 355:420–423
- Xu W, Lin JL, Tetrakis(dimethylammonium) hexachlorotungstate(III) chloride. *Acta Crystallogr E* 63:m767–m769
- Lima-de-Faria J, Hellner E, Liebau F, Makovicky E, Parthé E (1990) Nomenclature of inorganic structure types. Report of the International Union of Crystallography Commission on Crystallographic Nomenclature Subcommittee on the Nomenclature of Inorganic Structure Types. *Acta Crystallogr A* 46:1–11
- Bianga CM, Eggeling J, Reiss GJ (2013) Dimethylphosphoryl methanaminium nitrate. *Acta Crystallogr. E* 69:o1639–o1640
- Coelho AA (2012) TOPAS, academic version 5. Brisbane
- Young RA (1995) The rietveld method, IUCr monographs on crystallography. Oxford University Press, Oxford
- Järvinen M (1993) Application of symmetrized harmonics expansion to correction of the preferred orientation effect. *J Appl Crystallogr* 26:525–531
- Dinnebier RE (1999) Rigid bodies in powder diffraction: a practical guide. *Powder Diffract* 14:84–92
- Whealy RD, Lee DR (1967) Hexachloroplumbate(IV) salts. *Inorg Chim Acta* 1:397–398
- Dobrzycki L, Wozniak K (2009) 1D vs 2D crystal architecture of hybrid inorganic–organic structures with benzidine dication. *J Mol Struct* 921:18–33

37. Dobrzycki L, Wozniak K (2008) Inorganic–organic hybrid salts of diaminobenzenes and related cation. *CrystEngComm* 10:577–589
38. Geselle M, Fuess H (1995) Hexakis(2-chloroethylammonium) hexachloroplumbate(II) chloride. *Acta Crystallogr C* 51:242–244
39. Gillon AL, Lewis GR, Orpen AG, Rotter S, Starbuck J, Wang X-M, Rodriguez-Martin Y, Ruiz-Perez C (2000) Organic-inorganic hybrid solids: control of perhalometallate solid state structures. *J Chem Soc Dalton Trans* 21:3897–3905