

SYNTHESIS, STRUCTURAL, AND INFRARED STUDIES OF TRIS(2-AMMONIOETHYL)AMINIUM CHLORIDE HEXACHLOROBISMUTHATE (III): $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$

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ABSTRACT: A new organic-inorganic hybrid material, tris(2-ammonioethyl)aminium chloride hexachlorobismuthate(III); $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$, has been synthesized and characterized by X-Ray diffraction, SEM (Scanning Electron Microscopy) and IR spectroscopy. The molecule adopts a trigonal (P -31c) cell with the lattice parameters $a=10.400(3)$ Å, $c=24.927(6)$ Å and $Z=4$. The structure exhibits isolated $[BiCl_6]^{3-}$ octahedra leading to a 0D SBU (Secondary Building Unit) anionic network (quantum dots). The crystal cohesion is achieved by hydrogen bonds N-H...Cl between the trigonal organic molecules $\{(C_2H_4NH_3)_3NH\}^{4+}$, $[BiCl_6]^{3-}$ octahedra and the isolated Cl^- anions. Theoretical calculation using the PM3 approach for studying the IR vibrational spectra, shows a good agreement between observed spectrum and calculated one.

Key words: Bismuth (III) complex, Zero-dimensional structure, IR spectroscopy.

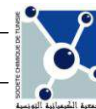
RESUME: Une nouvelle phase hybride à base de bismuth, Chlorure de tris(2-ammonioéthyl)aminiumhexachlorobismuthate(III); $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$, a été synthétisée et caractérisée par diffraction des rayons X sur monocristal, microscopie électronique à balayage et spectroscopie vibrationnelle infrarouge. L'étude structurale révèle que le matériau étudié cristallise dans le système trigonal, groupe d'espace P-31c avec les paramètres de la maille: $a=10,400(3)$ Å, $c=24,927(6)$ Å et $Z=4$. Elle a permis de décrire son architecture cristalline. Il s'agit d'une structure hybride du type « boîtes quantiques » (quantum dots). La cohésion de ce réseau tridimensionnel est renforcée par la présence des liaisons hydrogène de type N-H...Cl entre les cations organiques $\{(C_2H_4NH_3)_3NH\}^{4+}$, les octaèdres $[BiCl_6]^{3-}$ et les anions Cl^- libres. Une étude vibrationnelle a été entreprise par spectroscopie IR. Un traitement de type MNDO-PM3 semi-empirique nous a permis de calculer les fréquences de vibration du sous réseau cationique $\{(CH_2CH_2NH_3)_3NH\}^{4+}$ et facilite l'attribution des bandes d'absorption observées sur le spectre IR.

Mots-clés: Complexe de bismuth, Structure zéro-dimensionnelle, spectroscopie infrarouge.

INTRODUCTION

The organic-inorganic hybrid materials based on bismuth (III) halides and nitrogen-donor ligands have received increased interest recently due to their multiple applications in diverse areas including medicine [1] materials [2], organic synthesis [3], catalysis [4], and optical properties [5,6]. Several of them consist of one-, two-, or three dimensional networks, separated by organic cations. For relatively simple, unconjugated organic molecules, the organic component can be used as a physical and electronic barrier, which insulates the lower dimensional inorganic framework. For more complex conjugated molecules, the organic component contribute more actively to the electrical or semiconducting properties [7,8]. In addition, the important contribution to the lattice stabilization is due to the hydrogen bonding interactions.

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In this work we present the results of structural, vibrational studies on the $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$ compound.

EXPERIMENTAL

• Synthesis

Orange single crystals of the title compound were obtained by slow evaporation at room temperature in about few months from saturated aqueous solution of TREN [tris(2-aminethyl)amine] and $BiCl_3$ (molar ratio 2:1) in 40% HCl.

• Characterization

Fourier Transform Infrared (FT-IR) spectra recorded with 400-4000 cm^{-1} spectral based on a Perkin Elmer Paragon 1000 PC spectrometer by dispersing the material in KBr discs. The calculation was carried out using the computer program CAChe version 7.5.0. [9]. The EDX analysis was made on JEOL-JSM-5400 instrument.

The crystal structure of $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$ was determined by standard crystallographic methods. An orange crystal (approximate dimensions of (0.35 0.35 0.42) mm^3) was used for single X-Ray diffraction. The data were collected using an Enraf-Nonious CAD-4 X-Ray diffractometer at 293 K equipped with graphite-monochromated and $MoK\alpha$ radiation ($\lambda=0.71073$) using the $\omega/2\theta$ scan mode. A total of 3142 reflections was collected in the range of $11^\circ < \theta < 15^\circ$, of which 1069 was unique. The structure was solved and refined by Full-matrix least squares on F^2 using SHELHX-97 [10]. All non hydrogen atoms were directly located from difference Fourier maps and refined with anisotropic displacement parameters and converged for $I > 2\sigma(I)$. Hydrogen atoms attached to carbon were located at their idealized positions using appropriate HFIX instructions in SHELXL-97 [10], and included in subsequent least-squares refinement cycles in riding-motion approximation. Information concerning crystallographic data collection and structure refinement details are summarized in table I. The final atomic coordinates and U_{eq} are given in table III.

Crystallographic data for the complex reported in this paper have been deposited in the Cambridge Crystallographic Data Center (CCDC 768794). These data can be obtained free for charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table I. Crystallographic and experimental data of $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$.

Formula	$C_6H_{22} N_3BiCl_7$
Color	Orange
Crystal size(mm)	0.35 x 0.35 x 0.42
Formula weight(g. mol⁻¹)	607.4
T(K)	293(2)
Crystal system	Trigonal
Space group	P -3 1 c
a(Å)	10.400(3)
c(Å)	24.927(6)
Cell volume(Å³)	2335 (1)
$\mu(mm^{-1})$	8.344
$\rho(g. cm^{-3})$	1.728
Reflections/parameters	3142/69

Independent reflections	1069
R_{int}	0.0404
Goodness of fit on F²	1.021
R1, wR2 [I ≥ 2σ(I)]*	0.072, 0.089
R1, wR2 (all data)*	0.040, 0.080

$$*R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} ; wR2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}]^{1/2}$$

RESULTS AND DISCUSSION

The semi-quantitative energy-dispersive spectroscopy (EDS) analysis of one of the orange crystals obtained with a JEOL-JSM-5400 scanning electron microscope, revealed the presence of only C, N, Cl and Bi elements (Figure 1).

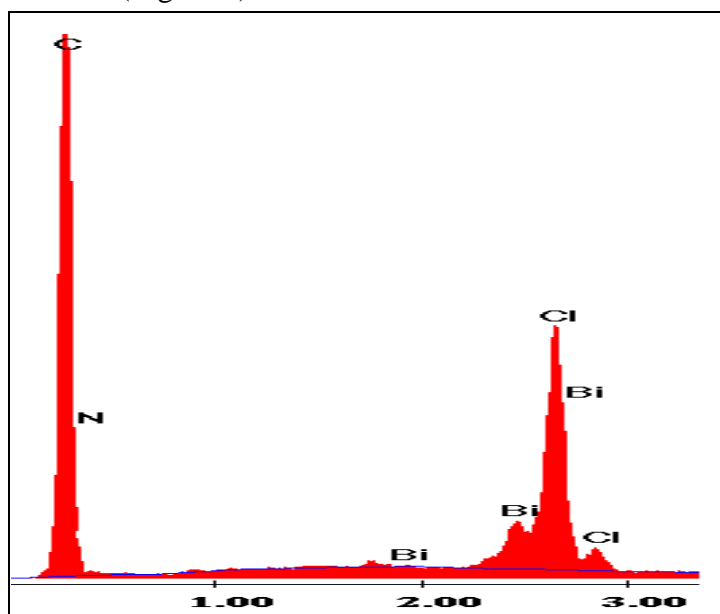


Figure 1: Spectrum of quantitative analysis by S.E.M of $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$.

Morphology prediction with BFDH (Bravais-Fridel and Donnay-Harker model) [11-13] is closer to the experimental observation in crystal (Figure 2).

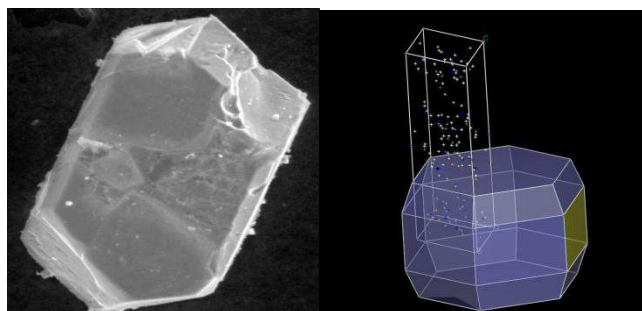


Figure 2: Photograph of idiomorphically grown specimen of $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$ and estimated morphology with the Bravais-Fridel, Donnay-Harker models.

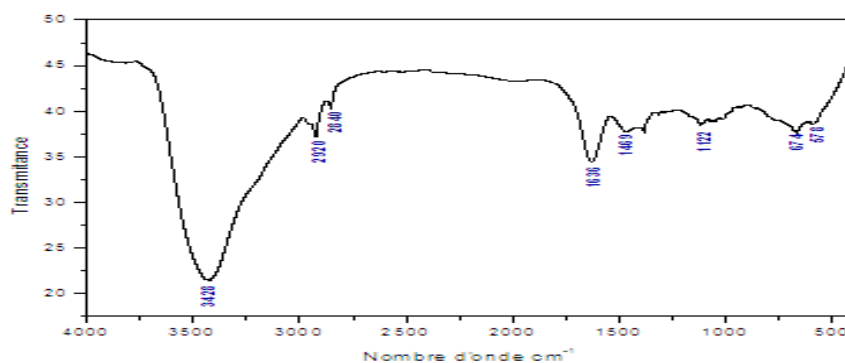
• SPECTROSCOPIC CHARACTERIZATION

The IR spectrum of the complex shown in figure (3.a) exhibits a characteristic absorption at 3433-1633 cm^{-1} that may be assigned to the N-H vibrations $\nu_s(\text{N-H})$ and $\delta_s(\text{N-H})$. The C-H stretching is superimposed in 2920 cm^{-1} and 2829 cm^{-1} , but the bending is observed around 1460 cm^{-1} . Vibrations attributable to the C-N are also observed about 1100-1222 cm^{-1} . The assignments are consistent with those previously reported [14, 15]. Theoretical infrared spectrum of the complex using semi-empirical PM3 Hamiltonian is shown in figure (3.b) and assignment was made through the structural animation at every peak. Observed spectral data of the title compound shows a great agreement with the calculated one. Calculated, observed frequencies and attributions are summarized in table II.

Table II: IR data of $\{(\text{C}_2\text{H}_4\text{NH}_3)_3\text{NH}\}^{4+} \cdot \text{Cl}^- \cdot [\text{BiCl}_6]^{3-}$.

Calculated frequencies	Observed frequencies	Attributions
3520	3433	$\nu_s(\text{NH}_3)$
2950	2920	$\nu_a(\text{CH}_2)$
2800	2829	$\nu_s(\text{CH}_2)$
1750	1636	$\delta_s(\text{NH}_3)$
1450	1469	$\delta_a(\text{CH}_2)$
1200	1122	$\nu_s(\text{C-N})+\nu_s(\text{C-C})$
800	674	$\delta_{as}(\text{C-C})$

(a)



(b)

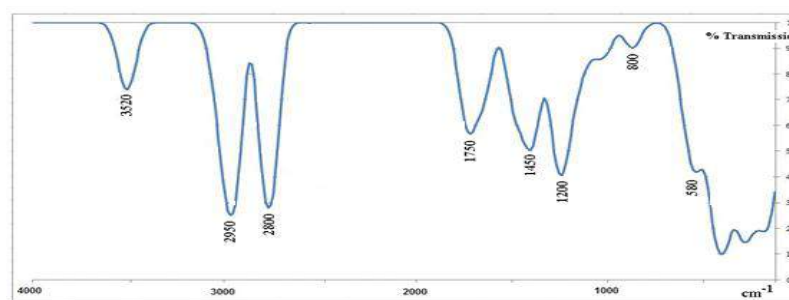


Figure 3: Infrared spectrum of $\{(\text{C}_2\text{H}_4\text{NH}_3)_3\text{NH}\}^{4+} \cdot \text{Cl}^- \cdot [\text{BiCl}_6]^{3-}$; (a) experimental (KBr pellet) and (b) Calculated (applying semi-empirical PM3 method).

DESCRIPTION

The title compound crystallizes in the trigonal system, space group P-31c (N° 163). A projection along b axis of the atomic arrangement of $\{(C_2H_4NH_3)_3NH\}^{4+}$, Cl^- , $[BiCl_6]^{3-}$ is depicted in figure 4. The crystal structure shows a layer arrangement parallel to the [100] direction: planes of $[BiCl_6]^{3-}$ octahedral leading to a zero-dimensional anionic network (quantum dots), alternate with planes of cationic templates of $\{(C_2H_4NH_3)_3NH\}^{4+}$ and isolated Cl^- anions.

Each Bi atom is surrounded by six Cl^- anions with average Bi-Cl bonds lengths is 2.720(3) Å and 2.671(1) Å for Bi1 and Bi2 respectively. The elongation of these distances is due to the hydrogen bonds between cations and anions, no to the stereo-activity of ion pair of bismuth (III) [16,17]. The Cl-Bi-Cl bond angles cis and trans together are between $80.7(4)^\circ - 99.3(4)^\circ$ and $177.95(1)^\circ - 180.0(1)^\circ$, respectively.

Table III. Atomic coordinates and U_{eq} of $\{(C_2H_4NH_3)_3NH\}^{4+}$, Cl^- , $[BiCl_6]^{3-}$

Atoms	x/a	y/b	z/c	Occupation	$U_{eq}(\text{Å}^2)^a$
Bi1	2/3	1/3	1/4	1	0.042(3)
Bi2	1	1	1/2	1	0.034(3)
Cl1	0.4578(3)	0.339 (3)	0.6859(1)	1	0.062(7)
N1	1/3	2/3	0.5934(7)	1	0.035(3)
H11	1/3	2/3	0.5569	1	0.05(5)
N2	0.6615(8)	0.6016 (8)	0.5997(5)	1	0.053(2)
H21	0.7424	0.6890	0.5935	1	0.064
H31	0.6733	0.5296	0.5856	1	0.064
H41	0.6473	0.5875	0.6349	1	0.064
C1	0.4797(7)	0.6827 (8)	0.6128(5)	1	0.041(2)
H1	0.4673	0.6424	0.6488	1	0.049
H2	0.5550	0.7870	0.6141	1	0.049
C2	0.5303(8)	0.5996 (8)	0.5747(5)	1	0.043(2)
H3	0.4508	0.4981	0.5697	1	0.051
H4	0.5568	0.6482	0.5400	1	0.051
Cl2	0.3333	0.6667	0.468(1)	1	0.042(8)
Cl3	1.225(1)	0.999 (1)	0.449(6)	0.40(8)	0.072(3)
Cl3'	1.201(1)	1.006 (1)	0.428(1)	0.59(9)	0.068(5)

$$^a U_{eq} = 1/3 \sum \sum U_{ij} a_i^* a_j^* a_i a_j$$

It should be noted that during the refinement of anisotropic thermal motion factors of the chlorine atoms, the Fourier synthesis suggested relocation site Cl3 in two positions relatively close. The refinement of occupancy rates converge to the values 40 and 60% respectively assigned to sites corresponding to Cl3 and Cl3'.

In this complex each TREN is found to be triprotonated with a single charge at each primary nitrogen site. Resulting organic cations adopts a plane configuration (figure 5). The central amine is also protonated. The C-N bond lengths are ranging 1.490(1) Å– 1.525(8) Å. One template cation is linked to two inorganic chains by N-H...Cl hydrogen bonds with H...Cl distances in the range

2.214 Å - 2.982 Å (Table IV). The central nitrogen N1 is hydrogen bonded with an interstitial Cl2 ($D_{H11...Cl2} = 2.214$ Å) which insures the connection between two organic layers. Indeed, the Cl2 anion establishes with one layer three hydrogen bonds type N2-H31...Cl2 and with the another layer one hydrogen bond type N1-H11...Cl2, so it's on the center of a tetrahedron of which vertices are the hydrogen atoms of the nitrogen of organic cations (Figure 6).

Table IV: hydrogen bonding parameters for $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$.

N-H ...Cl	N-H (Å)	H...Cl(Å)	N-H...Cl(°)	N...Cl(Å)
N1-H11... Cl2	0.910	2.214	180.00	3.123
N2-H21... Cl3 ⁱ	0.890	2.586	134.93	3.275
N2-H31... Cl2 ⁱⁱ	0.890	2.412	166.89	3.285
N2-H41... Cl1	0.890	2.663	127.73	3.284
N2-H41... Cl1 ⁱⁱⁱ	0.890	2.982	111.36	3.408

Symmetry code :

i : y, -x+y+1, -z+1

ii : -x+1, -y+1, -z+1

iii : -x+y+1, -x+1, z

Both ionic interactions and the hydrogen bridging including the N- H bonded and all covalent bonded Cl atoms together with an interstitial Cl⁻ anion build up a three dimensional network.

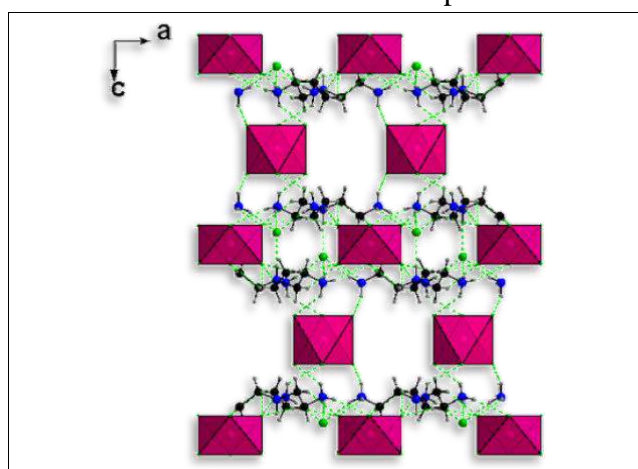


Figure 4. Projection along the b axis of the atomic arrangement of $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$.

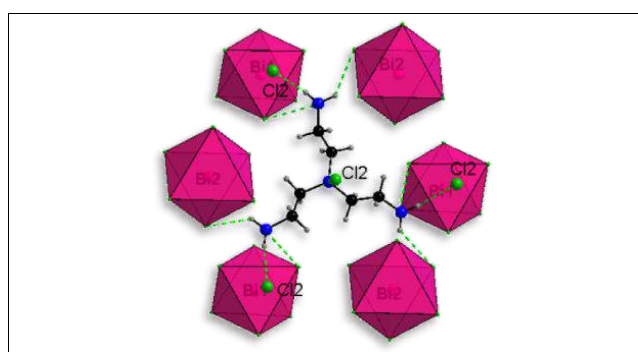


Figure 5. Projection along c axis of the atomic arrangement of $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$.

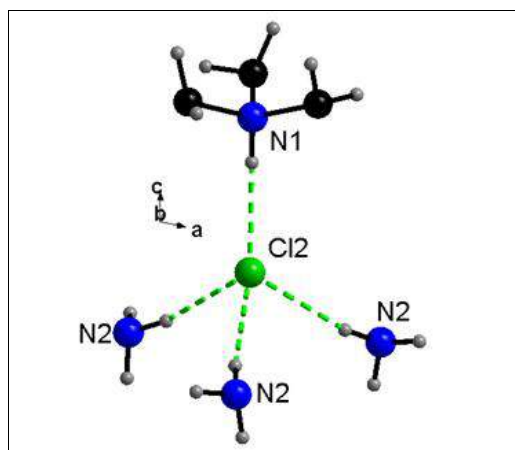


Figure 6: Representation of the cationic environment of the Cl2 anion.

CONCLUSION

In summary, this work describes the synthesis, structure, IR spectroscopy and SEM (Scanning Electron Microscopy) of a new chlorobismuthate(III) organic hybrid; $\{(C_2H_4NH_3)_3NH\}^{4+} \cdot Cl^- \cdot [BiCl_6]^{3-}$, which belongs to the trigonal system with P-31c space group. We have calculated the vibrational frequencies for the complex using PM3 method. The optimized bond lengths obtained by PM3 method shows a good agreement with experimental values.

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