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# Synthesis, Crystal structure of hepta (pyridinium) bis (hexachlorobismuthate (III)) nitrate $[C_5H_6N]_7(BiCl_6)_2(NO_3)$

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## Abstract

An hepta (pyridinium) bis (hexachlorobismuthate (III)) nitrate, $(C_5H_6N)_7(BiCl_6)_2(NO_3)$ crystallizes at room temperature in the monoclinic system, space group $P2_1/n$, with the following unit-cell parameters: a = 9.555(1) Å, b = 16.847(1) Å, c = 32.522(1) Å, β = 94.37° , V = 5219.8 $Å^3$ and four molecules per unit cell. Its crystal structure was determined and refined down to $R_1$ = 0.0504, $wR_2$ = 0.0667. The structure of the title compound, $(C_5H_6N)_7(BiCl_6)_2(NO_3)$ consists of seven monoprotonated pyridinium $(C_5H_6N)^+$ cations, two independent octahedron $[BiCl_6]^{3-}$ and an isolated $NO_3^-$ anion. These entities are linked together through N-H·····Cl and N-H·····O hydrogen bonds, originating from the $(C_5H_6N)^+$ groups and the isolated anion of nitrate to forming a three dimensional network.

## Indexing terms/Keywords

Organic–inorganic hybrid material; Crystal structure; Halogenobismuthates(III)

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## I. Introduction

Halogenoantimonates(III) and halogenobismuthates(III) containing various organic cations form a large class of the organic– inorganic hybrid materials [**1**–**5**]. These molecular-ionic crystals are built up of the inorganic anions and organic cations. The compounds form various anionic structures in the solid state. The anionic sublattice is built up of either the simple discrete octahedra or one-dimensional chains or two- or three-dimensional anionic framework. In the majority of these hybrid materials the anionic moieties are rigid, whereas the organic cations, placed in large cavities of the anionic substructure, exhibit usually reorientational disorder.

The halogenoantimonates (III) and halogenobismuthates (III) evoke much interest because their single crystals exhibit the polar, non-linear or ferroic properties. The change in the dynamical state of cations is responsible for the mechanisms of the numerous structural phase transitions found in these materials. Such a mechanism of structural phase transitions was classified as 'order–disorder'. A long range ferroelectric order of the dipoles has been found in the compounds containing generally the small in size ammonium cations (like monomethyl-, dimethyl- or trimethyl-ammonium) [**6**–**10**].

A novel group of crystals, containing heteroaromatic cations like: pyridinium, substituted pyridinium and imidazolium ones, have been recently synthesized and characterized [**11**–**13**]. Since aromatic heterocyclic cations are bestowed a significant electric dipole moment thus some halogenoantimonates (III) and halogenobismuthates (III) containing these cations form strongly polar structures. We have studied three pyridinium halogenobismuthates (III), i.e. $(C_5H_5NH)_6Bi_4Cl_{18}$ [**14**], $(C_5H_5NH)BiCl_4$ [**15**] and $(C_5H_5NH)_5Bi_2Br_{11}$ [**16**]. The ferroelectricity was found, however, only in the compound of the $R_5Bi_2X_{11}$ composition, $(C_5H_5NH)_5Bi_2Br_{11}$. This latter compound is a ferroelectric below the Curie temperature of 118 K. Among a dozen of the substituted pyridinium compounds, studied so far, a ferroelectricity is confirmed merely in a case of 4-aminopyridinium tetrachloroantimonate (III),$(4\text{-}NH_2C_5H_4NH)SbCl_4$[**17**], below $T_c$ = 270.5 K. The presence of polar properties in the materials described above is usually a result of the organic cations dynamics, which play a key role in the induction of ferroelectricity. The results, obtained by us for the group of ionic compounds containing aromatic cations, trace a direction of search for the novel polar materials.

Herein we report the synthesis and the crystal structural characterization by X-ray diffraction of the hepta (pyridinium) bis (hexachlorobismuthate (III)) nitrate.

## II. Experimental section

### II.1.Synthesis

Transparents and colorless crystals of $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$ were synthesized by the addition of pyridinium to a solution of bismuth (III) nitrate (molar ratio 7/2) in concentrated hydrochloric acid (36%). Single crystals were grown by the slow evaporation of an aqueous solution at room temperature.

The chemical reaction of the title compound was the following :

$$7\ C_5H_5N + 2Bi(NO_3)_3 + 12\ HCl \xrightarrow{H_2O/H} [C_5H_6N]_7Cl(BiCl_6)_2(NO_3) + 5HNO_3$$

### II.2.Single crystal Structure determination

X-ray data collection was carried out on a Bruker Kappa Apex II CCD diffractometer with graphite monochromated Mo $K_\alpha$ radiation. Bismuth and chlorine atoms positions were located using the direct method with program SHELXS-97 [**18**] program, while the carbon, oxygen, and nitrogen atoms were found from successive difference Fourier calculations using SHELXL97 [**19**] computer program. The structure is refined by full matrix least-squares using anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms and treated as riding atoms. Crystal data, collected reflections, and parameters of the final refinement are reported in Table 1.

**Table 1:** Experimental data for X-ray diffraction study of $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$

| | |
|---|---|
| *Crystal data* | |
| Empirical formula | $C_{35}H_{42}Bi_2Cl_{12}N_8O_3$ |
| Formula weight (g/mol) | 1466,13 |
| Crystal system, Space group | monoclinic, $P2_1/n$ |
| *a* (Å) | 9.555(1) |
| *b* (Å) | 16.847(1) |
| *c* (Å) | 32.522(1) |
| *β* | 94.37(1)° |
| *V*(Å$^3$) | 5219.8(0) |
| *Z* | 4 |

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| | |
|---|---|
| $D_{calc}$ (g cm$^{-3}$) | 1.866 |
| $\mu$ (mm$^{-1}$) | 7.389 |
| $F$(000) | 2808 |
| Crystal size (mm) | 0.25× 0. 20× 0.15 |
| Crystal habit | Colorless |
| | |
| *Data collection* | |
| Diffractometer | BrukerKappaApex II CCD diffractometer Graphite |
| Monochromator | Mo-*K*/ a, 0.71073 |
| Radiation type, λ (Å) | 293(2) |
| $T$ (K) | 1.26 - 34.99 |
| $\Theta$ Range (°) | $-11 \le h \le 15$ |
| Indexes range | $-26 \le k \le 27$ |
| | $-52 \le l \le 51$ |
| | numerical |
| Absorption correction | 0.2595/0.4036 |
| $T_{min}/T_{max}$ | 84321 |
| Measured reflections | 21099 |
| Independent reflections | 12702 |
| Observed refl. ($I > 2\sigma(I)$) | 0.0354 |
| $R_{int}$ | |
| | |
| *Refinement* | $F^2$ |
| Refinement on | 21099/5/541 |
| Data/restraints/parameters | $R1$ = 0.0504 |
| $R(F_0^2) > 2\sigma(F_0^2)$] | $wR2$ = 0.0667 |
| | 1.021 |
| GooF = $S$ | 926364 |
| CCDC deposition number | |

## III. Results and discussion

The final atomic coordinates obtained from the single crystal refinement with $U_{eq}$ are given in Table 2. The anisotropic displacement parameters are shown in Table 3. Interatomic distances and bond angles schemes are listed in Table 4.

The asymmetric unit of our component, $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$, consists of two distinct octahedra $[BiCl_6]^{3-}$, isolated $NO_3^-$ anion and seven monoprotonated pyridinium cations as shown in Fig. 1.

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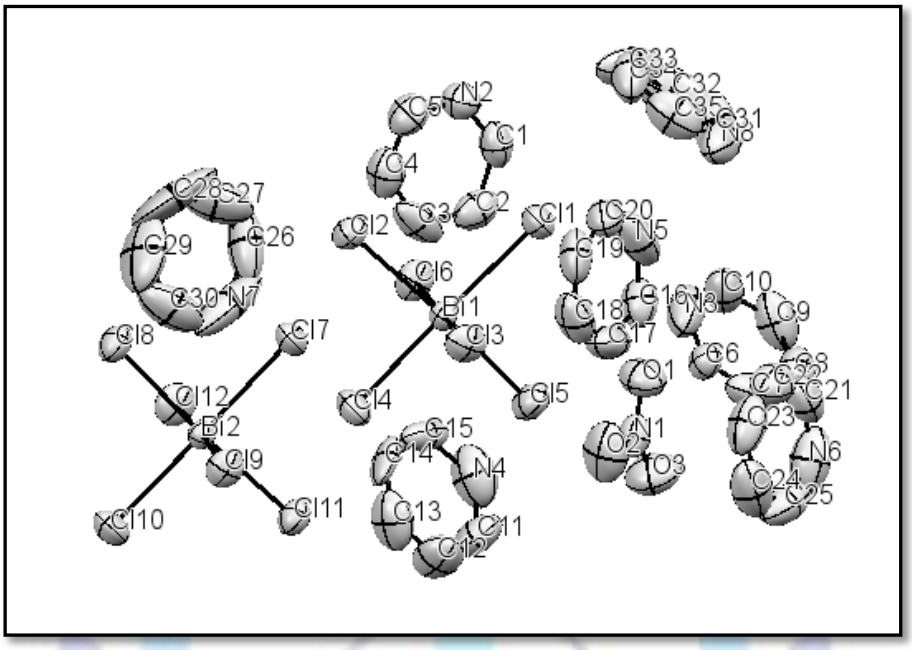


**Figure 1** : The asymmetric unit of $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$, showing the atom-numbering scheme

**Table 2:** Atomic coordinates and $U_{eq}$ or $U_{iso}$ for $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$

| Atomes | x | y | z | $U_{éq}$ |
|---|---|---|---|---|
| Bi1 | 0.044479(13) | 0.648857(9) | 0.285559(4) | 0.03835(4) |
| Bi2 | 0.758222(13) | 0.740706(8) | 0.491828(4) | 0.03762(4) |
| Cl1 | 0.21692(11) | 0.72253(8) | 0.23300(4) | 0.0634(3) |
| Cl2 | 0.26306(10) | 0.57334(7) | 0.32870(4) | 0.0562(3) |
| Cl3 | 0.03392(12) | 0.51559(8) | 0.23403(4) | 0.0674(3) |
| Cl4 | -0.12433(11) | 0.57297(8) | 0.33372(4) | 0.0654(3) |
| Cl5 | -0.18081(11) | 0.71957(8) | 0.24617(4) | 0.0687(3) |
| Cl6 | 0.07738(12) | 0.76756(7) | 0.33769(4) | 0.0638(3) |
| Cl7 | 0.93579(11) | 0,81443(8) | 0,44270(4) | 0,0613(3) |
| Cl8 | -0.99095(11) | 0.67426(8) | 0.53184(4) | 0.0628(3) |
| Cl9 | 0.73347(11) | 0.61258(7) | 0.44107(4) | 0.0600(3) |
| Cl10 | 0.58374(12) | 0.67365(8) | 0.54308(4) | 0.0713(3) |
| Cl11 | 0.54242(10) | 0.80979(7) | 0.44775(3) | 0.0576(3) |
| Cl12 | 0.77755(13) | 0.86515(8) | 0.54412(4) | 0.0687(3) |
| O1 | 0.9038(4) | 0.6237(2) | 0.13693(14) | 0.0905(12) |
| O2 | 0.7792(5) | 0.5196(3) | 0.13845(15) | 0.1150(16) |
| O3 | 0.6832(4) | 0.6313(3) | 0.13652(16) | 0.1136(16) |
| N1 | 0.7854(5) | 0.5915(3) | 0.13727(12) | 0.0613(10) |
| N2 | 0.1329(4) | 0.5251(3) | 0.13220(14) | 0.0719(12) |
| N3 | 0.9661(6) | 0.8279(5) | 0.15846(17) | 0.124(2) |
| N4 | -0.1099(8) | 0.3541(3) | 0.1720(2) | 0.120(2) |
| N5 | 0.4614(9) | 0.5583(4) | 0.24511(18) | 0.127(2) |
| N6 | 0.6850(9) | 0.6524(5) | 0.02821(18) | 0.120(2) |

| | | | | |
|---|---|---|---|---|
| N7 | 0.0986(12) | 0.6144(10) | 0.4288(3) | 0.172(6) |
| N8 | 0.3469(6) | 0.8201(7) | 0.12434(18) | 0.138(3) |
| C1 | 0.2495(6) | 0.5616(3) | 0.14554(16) | 0.0712(14) |
| C2 | 0.3759(5) | 0.5293(4) | 0.13689(17) | 0.0733(15) |
| C3 | 0.3771(6) | 0.4615(4) | 0.11502(19) | 0.0830(18) |
| C4 | 0.2538(8) | 0.4267(4) | 0.10216(19) | 0.0875(18) |
| C5 | 0.1343(6) | 0.4592(4) | 0.11105(19) | 0.0799(16) |
| C6 | 0.8686(5) | 0.7878(3) | 0.13562(15) | 0.0535(11) |
| C7 | 0.7845(6) | 0.8221(4) | 0.10967(19) | 0.0846(18) |
| C8 | 0.7904(7) | 0.9002(5) | 0.1028(2) | 0.093(2) |
| C9 | 0.8847(8) | 0.9434(4) | 0.1248(2) | 0.0944(19) |
| C10 | 0.9742(7) | 0.9101(4) | 0.1522(2) | 0.0860(18) |
| C11 | 0.0079(6) | 0.3152(5) | 0.1838(2) | 0.0905(19) |
| C12 | 0.0230(7) | 0.2424(4) | 0.1745(2) | 0.100(2) |
| C13 | -0.0809(11) | 0.2038(4) | 0.1528(2) | 0.109(2) |
| C14 | -0.1941(7) | 0.2402(5) | 0.14071(17) | 0.0782(18) |
| C15 | -0.2143(5) | 0.3122(6) | 0.14944(19) | 0.093(2) |
| C16 | 0.6059(7) | 0.5551(4) | 0.24427(18) | 0.0833(17) |
| C17 | 0.6649(6) | 0.4874(6) | 0.2394(2) | 0.099(2) |
| C18 | 0.5848(9) | 0.4206(4) | 0.2348(2) | 0.101(2) |
| C19 | 0.4452(8) | 0.4273(5) | 0.23570(18) | 0.095(2) |
| C20 | 0.3864(5) | 0.4934(5) | 0.24094(17) | 0.0741(16) |
| C21 | 0.8287(10) | 0.6546(5) | 0.0283(2) | 0.099(2) |
| C22 | 0.8972(6) | 0.5873(7) | 0.0326(2) | 0.105(3) |
| C23 | 0.8251(10) | 0.5196(5) | 0.0359(2) | 0.104(2) |
| C24 | 0.6870(11) | 0.5219(5) | 0.0358(2) | 0.107(2) |
| C25 | 0.6207(7) | 0.5877(7) | 0.0319(2) | 0.101(2) |
| C26 | 0.213(2) | 0.6586(5) | 0.4292(3) | 0.149(5) |
| C27 | 0.3274(12) | 0.6302(9) | 0.4465(4) | 0.148(4) |
| C28 | 0.3240(13) | 0.5630(10) | 0.4632(4) | 0.175(6) |
| C29 | 0.214(2) | 0.5197(5) | 0.4640(4) | 0.147(4) |
| C30 | 0.1049(12) | 0.5468(10) | 0.4470(5) | 0.151(5) |
| C31 | 0.3605(13) | 0.8918(7) | 0.1470(4) | 0.141(5) |
| C32 | 0.4364(14) | 0.8937(5) | 0.1794(4) | 0.134(4) |
| C33 | 0.5117(8) | 0.8355(9) | 0.1913(3) | 0.132(4) |
| C34 | 0.5117(8) | 0.7712(6) | 0.1724(3) | 0.109(3) |
| C35 | 0.4306(9) | 0.7609(4) | 0.1390(3) | 0.100(2) |
| H1 | 0.2464 | 0.6085 | 0.1606 | 0.085 |
| H2 | 0.0535 | 0.5452 | 0.1376 | 0.086 |
| H2A | 0.4596 | 0.5539 | 0.1460 | 0.088 |
| H3 | 1.0221 | 0.8043 | 0.1764 | 0.149 |

| | | | | |
|---|---|---|---|---|
| H311 | 0.4617 | 0.4388 | 0.1088 | 0.100 |
| H4 | 0.2533 | 0.3799 | 0.0870 | 0.105 |
| H4A | -0.1206 | 0.4033 | 0.1780 | 0.143 |
| H5 | 0.0499 | 0.4349 | 0.1022 | 0.096 |
| H5A | 0.4207 | 0.6032 | 0.2484 | 0.152 |
| H6 | 0.8624 | 0.7331 | 0.1389 | 0.064 |
| H6A | 0.6381 | 0.6959 | 0.0256 | 0.144 |
| H7 | 0.7162 | 0.7921 | 0.0948 | 0.102 |
| H7A | 0.0210 | 0.6308 | 0.4165 | 0.206 |
| H8 | 0.7290 | 0.9239 | 0.0829 | 0.112 |
| H8A | 0.2894 | 0.8149 | 0.1028 | 0.165 |
| H9 | 0.8877 | 0.9980 | 0.1207 | 0.113 |
| H10 | 1.0415 | 0.9405 | 0.1672 | 0.103 |
| H11 | 0,0800 | 0.3415 | 0.1991 | 0.109 |
| H12 | 0.1059 | 0.2160 | 0.1828 | 0.121 |
| H13 | -0.0705 | 0.1504 | 0.1464 | 0.131 |
| H14 | -0.2638 | 0.2129 | 0.1250 | 0.094 |
| H15 | -0.2986 | 0.3369 | 0.1408 | 0.112 |
| H16 | 0.6596 | 0.6011 | 0.2472 | 0.100 |
| H17 | 0.7619 | 0.4841 | 0.2390 | 0.119 |
| H18 | 0.6261 | 0.3714 | 0.2311 | 0.122 |
| H19 | 0.3900 | 0.3820 | 0.2324 | 0.113 |
| H20 | 0.2894 | 0.4959 | 0.2418 | 0.089 |
| H21 | 0.8760 | 0.7022 | 0.0253 | 0.119 |
| H22 | 0.9947 | 0.5866 | 0.0335 | 0.126 |
| H23 | 0.8721 | 0.4713 | 0.0382 | 0.124 |
| H24 | 0.6372 | 0.4750 | 0.0387 | 0.128 |
| H25 | 0.5234 | 0.5879 | 0.0317 | 0.122 |
| H26 | 0.2106 | 0.7087 | 0.4173 | 0.179 |
| H27 | 0.4107 | 0.6588 | 0.4468 | 0.178 |
| H28 | 0.4074 | 0.5433 | 0.4758 | 0.210 |
| H29 | 0.2163 | 0.4703 | 0.4768 | 0.177 |
| H30 | 0.0232 | 0.5169 | 0.4473 | 0.182 |
| H31 | 0.3127 | 0.9371 | 0.1376 | 0.169 |
| H32 | 0.4381 | 0.9394 | 0.1955 | 0.161 |
| H33 | 0.5699 | 0.8407 | 0.2154 | 0.158 |
| H34 | 0.5703 | 0.7303 | 0.1822 | 0.131 |
| H35 | 0.4305 | 0.7126 | 0.1251 | 0.120 |

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**Table 3:** Anisotropic displacement parameters (Å$^2$) for $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$

| Atomes | U11 | U22 | U33 | U23 | U13 | U12 |
|---|---|---|---|---|---|---|
| Bi1 | 0.03903(6) | 0.03560(8) | 0.04035(8) | -0.00004(6) | 0.00259(5) | 0.00134(5) |
| Bi2 | 0.03866(6) | 0.03664(8) | 0.03720(8) | -0.00024(6) | 0.00053(5) | -0.00083(5) |
| Cl1 | 0.0552(5) | 0.0708(8) | 0.0650(8) | 0.0167(6) | 0.0102(5) | -0.0056(5) |
| Cl2 | 0.0532(5) | 0.0518(7) | 0.0620(7) | -0.0001(5) | -0.0065(4) | 0.0048(4) |
| Cl3 | 0.0723(7) | 0.0695(9) | 0.0600(8) | -0.0228(6) | 0.0038(5) | -0.0137(6) |
| Cl4 | 0.0614(6) | 0.0656(8) | 0.0722(8) | 0.0154(6) | 0.0241(5) | 0.0009(5) |
| Cl5 | 0.0591(6) | 0.0618(8) | 0.0824(9) | 0.0115(7) | -0.0123(5) | 0.0068(5) |
| Cl6 | 0.0799(7) | 0.0497(7) | 0.0601(8) | -0.0154(6) | -0.0061(5) | 0.0071(5) |
| Cl7 | 0.0565(5) | 0.0751(8) | 0.0535(7) | 0.0127(6) | 0.0114(5) | -0.0121(5) |
| Cl8 | 0.0557(5) | 0.0717(8) | 0.0594(7) | 0.0065(6) | -0.0069(5) | 0.0126(5) |
| Cl9 | 0.0707(6) | 0.0483(7) | 0.0596(7) | -0.0137(6) | -0.0043(5) | 0.0006(5) |
| Cl10 | 0.0670(6) | 0.0819(9) | 0.0672(8) | 0.0136(7) | 0.0194(5) | -0.0176(6) |
| Cl11 | 0.0535(5) | 0.0605(7) | 0.0574(7) | 0.0041(6) | -0.0039(4) | 0.0120(5) |
| Cl12 | 0.0847(7) | 0.0591(8) | 0.0614(8) | -0.0239(6) | 0.0001(6) | 0.0011(6) |
| O1 | 0.070(2) | 0.076(3) | 0.128(4) | 0.011(2) | 0.020(2) | 0.0118(19) |
| O2 | 0.175(4) | 0.053(3) | 0.113(4) | 0.005(3) | -0.013(3) | -0.004(3) |
| O3 | 0.070(2) | 0.108(4) | 0.162(5) | -0.012(3) | 0.004(3) | 0.015(2) |
| N1 | 0.080(3) | 0.041(3) | 0.062(3) | -0.001(2) | 0.001(2) | 0.008(2) |
| N2 | 0.063(2) | 0.079(3) | 0.074(3) | 0.005(3) | 0.012(2) | 0.006(2) |
| N3 | 0.107(4) | 0.186(7) | 0.080(4) | 0.045(4) | 0.012(3) | 0.061(4) |
| N4 | 0.165(6) | 0.072(4) | 0.125(5) | -0.005(4) | 0.036(5) | 0.010(4) |
| N5 | 0.193(7) | 0.105(6) | 0.084(4) | 0.004(4) | 0.024(4) | 0.076(5) |
| N6 | 0.151(6) | 0.121(6) | 0.085(4) | -0.007(4) | -0.011(4) | 0.065(5) |
| N7 | 0.142(7) | 0.247(13) | 0.117(7) | -0.058(8) | -0.056(6) | 0.130(8) |
| N8 | 0.080(4) | 0.270(11) | 0.064(4) | 0.019(6) | 0.005(3) | 0.000(5) |
| C1 | 0.097(4) | 0.054(3) | 0.063(3) | -0.009(3) | 0.002(3) | 0.001(3) |
| C2 | 0.065(3) | 0.080(4) | 0.073(4) | 0.015(3) | -0.004(2) | -0.010(3) |
| C3 | 0.092(4) | 0.081(5) | 0.079(4) | 0.023(4) | 0.022(3) | 0.041(3) |
| C4 | 0.130(5) | 0.052(4) | 0.079(4) | -0.008(3) | 0.001(4) | 0.013(3) |
| C5 | 0.088(4) | 0.067(4) | 0.083(4) | -0.003(3) | -0.008(3) | -0.020(3) |
| C6 | 0.066(3) | 0.035(3) | 0.059(3) | 0.005(2) | 0.001(2) | -0.0001(2) |
| C7 | 0.068(3) | 0.101(5) | 0.085(4) | -0.018(4) | 0.008(3) | -0.020(3) |
| C8 | 0.090(4) | 0.108(6) | 0.080(5) | 0.008(4) | -0.004(3) | 0.031(4) |
| C9 | 0.142(6) | 0.057(4) | 0.088(5) | 0.010(4) | 0.028(4) | 0.015(4) |
| C10 | 0.108(4) | 0.071(4) | 0.078(4) | -0.006(4) | -0.004(3) | -0.028(3) |
| C11 | 0.069(3) | 0.090(5) | 0.108(5) | -0.003(4) | -0.025(3) | -0.014(3) |
| C12 | 0.091(4) | 0.081(5) | 0.125(6) | 0.001(4) | -0.021(4) | 0.033(4) |
| C13 | 0.185(8) | 0.042(4) | 0.103(6) | -0.016(4) | 0.031(5) | -0.004(4) |
| C14 | 0.085(4) | 0.093(5) | 0.054(3) | -0.015(3) | -0.010(3) | -0.052(4) |

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| | | | | | | |
|---|---|---|---|---|---|---|
| C15 | 0.048(3) | 0.166(7) | 0.065(4) | 0.026(5) | -0.001(2) | 0.020(4) |
| C16 | 0.098(4) | 0.070(4) | 0.082(4) | -0.008(3) | 0.008(3) | -0.027(3) |
| C17 | 0.056(3) | 0.146(7) | 0.096(5) | -0.001(5) | 0.006(3) | 0.015(4) |
| C18 | 0.141(6) | 0.074(5) | 0.092(5) | -0.002(4) | 0.026(4) | 0.039(4) |
| C19 | 0.134(6) | 0.095(6) | 0.056(4) | -0.021(4) | 0.019(4) | -0.048(4) |
| C20 | 0.060(3) | 0.097(5) | 0.066(4) | -0.015(4) | 0.009(2) | -0.006(3) |
| C21 | 0.140(7) | 0.086(5) | 0.074(5) | 0.006(4) | 0.025(4) | -0.027(5) |
| C22 | 0.064(3) | 0.172(9) | 0.080(5) | -0.015(5) | 0.012(3) | 0.016(5) |
| C23 | 0.142(7) | 0.088(6) | 0.079(5) | -0.003(4) | -0.008(4) | 0.046(5) |
| C24 | 0.143(7) | 0.101(6) | 0.074(5) | -0.008(4) | 0.001(4) | -0.039(5) |
| C25 | 0.071(4) | 0.133(8) | 0.098(5) | -0.022(6) | -0.002(3) | -0.004(5) |
| C26 | 0.301(17) | 0.061(6) | 0.091(7) | 0.033(5) | 0.053(10) | 0.037(8) |
| C27 | 0.118(7) | 0.138(10) | 0.191(13) | -0.049(9) | 0.029(7) | -0.075(7) |
| C28 | 0.143(9) | 0.186(13) | 0.179(11) | -0.016(11) | -0.095(9) | 0.076(8) |
| C29 | 0.232(13) | 0.068(6) | 0.146(10) | 0.030(6) | 0.040(10) | 0.001(8) |
| C30 | 0.087(6) | 0.180(12) | 0.192(14) | -0.076(10) | 0.046(7) | -0.064(7) |
| C31 | 0.172(10) | 0.102(8) | 0.162(10) | 0.069(7) | 0.093(8) | 0.089(7) |
| C32 | 0.176(11) | 0.051(5) | 0.184(12) | -0.044(7) | 0.082(8) | -0.013(5) |
| C33 | 0.090(5) | 0.214(12) | 0.092(6) | -0.067(8) | 0.008(4) | -0.036(6) |
| C34 | 0.109(5) | 0.134(8) | 0.087(6) | 0.045(5) | 0.029(4) | 0.048(5) |
| C35 | 0.116(6) | 0.056(4) | 0.132(7) | -0.023(4) | 0.042(5) | -0.010(4) |

A projection of the structure on the (100) plane (Fig. 2) shows that each bismuth is surrounded by six Cl atoms, forming a distorsed octahedral configuration, with Bi-Cl distances range from 2.6251(11) to 2.7990(12) Å for the first octahedron and from 2.6852 (10) to 2.7295(10) Á for the second octahedron (see Table 4). These values are comparable with those reported by other reasearches [**20**]. In addition to the bond-lengths differences, the Cl-Bi-Cl angles within each $[BiCl_6]^{3-}$ anion extend from 85.72 (4) to 94.52 (4)° and from 86.87(4) to 93.04(4)° for cis and from 174.20(4) to 177.48(4)° and 175.42(4) to 177.99(4)° for trans arrangements. These values, which they listed in Table 4, do not indicate any stereochemical activity of the Bi lone electron pair [**20**,**21**] but this distorsion is correlated to deformations resulting from strong hydrogen bond interactions [**20**,**21**], which involves all coordinated chlorine atoms [**21**]. The isolated nitrate anions play an important role in cohesion of the structure so they are located in the gaps left between the octahedra of bismuth and monoprotonated organic cations. In fact, the presence of those anions as a part of an anionic sublattice in the family of organic – inorganic hybrids was also found in other structure [**22**,**23**]. The seven organic template cations, $[C_5H_5NH]^+$, reside within the crystal lattice and maintain the charge neutrality (see Fig. 1). Also, the C-N bond lentghs in organic cations are ranging 1.467 (12) - 1.504 (10) Á (see Table 4). The observed C-C distances in pyridinium are extended from 1.481 (16) to 1.533 (13) Á (see Table 4). These values are comparable with those reported by other reaserchers [**24**]. Besides in this compound, the aromatic rings built up by (C1,C2,C3,C4,C5,N2),(C11,C12,C13,C14,C15,N4) and (C16,C17,C18,C19,C20,N5) (rms deviation of fitted atoms equal to 0.0007 ; 0.0033 and 0.0046 respectively) are more planar than those built pu by (C6,C7,C8,C9,C10,N3), (C21,C22,C23,C24,C25,N6), (C26,C27,C28,C29,C30,N7) and (C31,C32,C33,C34,C35,N8) (rms deviation of fitted atoms equal to 0.0052 ; 0.0053 ; 0.0077 and 0.0180 respectively).

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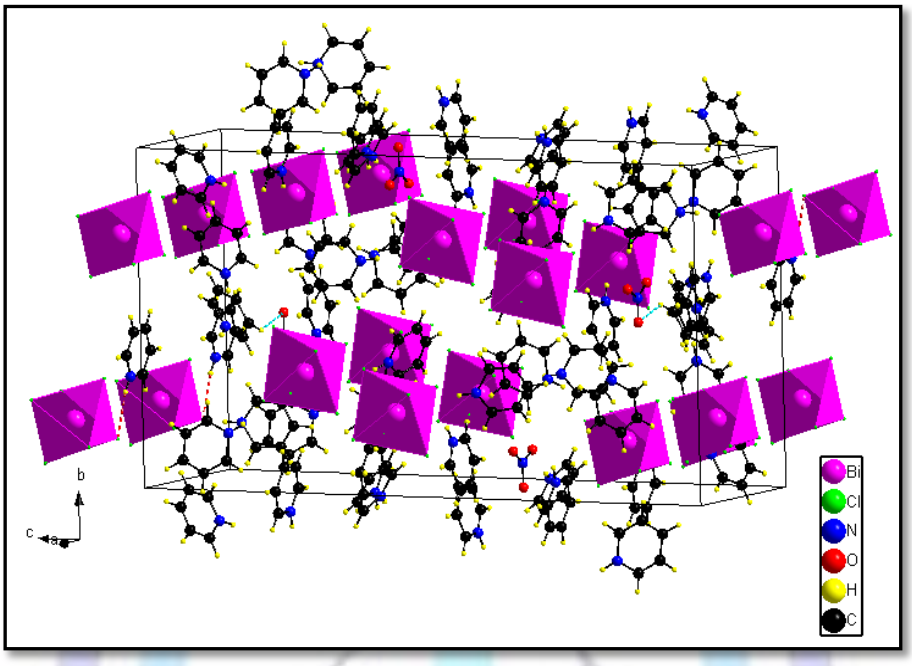


**Figure 2** : Crystal packing of the $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$

**Table 4:** Selected bond (Å) lengths and angles (°) for $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$

| | | | |
|---|---|---|---|
| Bi1-Cl1 | 2.7580(11) | N1-O1 | 1.255(5) |
| Bi1-Cl2 | 2.7390(10) | N1-O2 | 1.213(5) |
| Bi1-Cl3 | 2.7989(12) | N1-O3 | 1.184(5) |
| Bi1-Cl4 | 2.6597(11) | N2-C1 | 1.317(6) |
| Bi1-Cl5 | 2.6969(11) | C1-C2 | 1.373(7) |
| Bi1-Cl6 | 2.6251(11) | C2-C3 | 1.347(8) |
| Bi2-Cl7 | 2.7179(10) | C3-C4 | 1.353(9) |
| Bi2-Cl8 | 2.7295(10) | N2-C5 | 1.307(7) |
| Bi2-Cl9 | 2.7167(11) | C4-C5 | 1.318(8) |
| Bi2-Cl10 | 2.6938(11) | N3-C6 | 1.330(8) |
| Bi2-Cl11 | 2.6853(10) | C6-C7 | 1.261(7) |
| Bi2-Cl12 | 2.6970(12) | C7-C8 | 1.336(9) |
| | | C8-C9 | 1.324(9) |
| | | N3-C10 | 1.403(9) |
| | | C9-C10 | 1.314(9) |
| | | C11 N4 | 1.334(8 |
| | | C11-C12 | 1.274(8) |
| | | C12-C13 | 1.343(10) |
| | | C13-C14 | 1.279(9) |
| | | N4-C15 | 1.385(9) |
| | | C14-C15 | 1.264(9) |
| | | C16-N5 | 1.385(9) |
| | | C16-C17 | 1.287(9) |

| | | | |
|---|---|---|---|
| | | C17 -C18 | 1.362(9) |
| | | C18-C19 | 1.341(9) |
| | | C19-C20 | 1.264(9) |
| | | C20-N5 | 1.308(8) |
| | | N6-C21 | 1.374(10) |
| | | C21-C22 | 1.310(10) |
| | | C22-C23 | 1.342(10) |
| | | C23-C24 | 1.320(10) |
| | | N6-C25 | 1.261(9) |
| | | C24-C25 | 1.278(10) |
| | | N7-C26 | 1.320(14) |
| | | C26-C27 | 1.283(14) |
| | | C27-C28 | 1.256(10) |
| | | C28-C29 | 1.283(12) |
| | | N7-C30 | 1.283(14) |
| | | C29-C30 | 1.230(12) |
| | | N8-C31 | 1.416(13) |
| | | C31-C32 | 1.233(13) |
| | | C32-C33 | 1.260(13) |
| | | C33-C34 | 1.246(11) |
| | | N8-C35 | 1.343(10) |
| | | C34-C35 | 1.297(11) |
| Cl6-Bi1-Cl4 | 91.94(4) | O3-N1-O2 | 121.6(5) |
| Cl6-Bi1-Cl5 | 91.28(4) | O3-N1-O1 | 119.8(5) |
| Cl4-Bi1-Cl5 | 89.66(4) | O2-N1-O1 | 118.6(5) |
| Cl6-Bi1-Cl2 | 88.50(3) | C5-N2-C1 | 121.8(5) |
| Cl4-Bi1-Cl2 | 87.02(3) | C7-C6-N3 | 121.7(5) |
| Cl5-Bi1-Cl2 | 176.67(4) | N2-C1-C2 | 118.8(5) |
| Cl6-Bi1-Cl1 | 90.56(4) | C3-C2-C1 | 119.2(5) |
| Cl4-Bi1-Cl1 | 177.48(4) | C12-C11-N4 | 120.8(6) |
| Cl5-Bi1-Cl1 | 89.98(4) | C15-C14-C13 | 122.1(5) |
| Cl2-Bi1-Cl1 | 93.34(3) | C6-N3-C10 | 117.7(5) |
| Cl6-Bi1-Cl3 | 174.19(4) | C9-C8-C7 | 119.1(6) |
| Cl4-Bi1-Cl3 | 88.35(4) | C2-C3-C4 | 119.2(5) |
| Cl5-Bi1-Cl3 | 94.52(4) | C9-C10-N3 | 118.6(6) |
| Cl2-Bi1-Cl3 | 85.72(4) | C6-C7-C8 | 122.0(6) |
| Cl1-Bi1-Cl3 | 89.19(4) | C10-C9-C8 | 120.9(6) |
| Cl11-Bi2-Cl10 | 91.48(4) | N2-C5-C4 | 120.8(5) |
| Cl11-Bi2Cl12 | 90.72(4) | C5-C4-C3 | 120.1(6) |
| Cl10-Bi2-Cl12 | 87.23(4) | C11-N4-C15 | 117.4(6) |
| Cl11-Bi2-Cl9 | 89.56(4) | C14-C15-N4 | 119.4(5) |

| | | | |
|---|---|---|---|
| Cl10-Bi2-Cl9 | 90.77(4) | C11-C12-C13 | 119.9(6) |
| Cl12-Bi2-Cl9 | 177.99(4) | C14-C13-C12 | 120.2(6) |
| Cl11-Bi2-Cl7 | 88.65(3) | C19-C20-N5 | 120.3(6) |
| Cl10-Bi2-Cl7 | 177.21(4) | C17-C16-N5 | 119.0(6) |
| Cl12-Bi2-Cl7 | 89.98(4) | C19-C18-C17 | 118.6(6) |
| Cl9-Bi2-Cl7 | 92.02(4) | C20-C19-C18 | 122.0(6) |
| Cl11-Bi2-Cl8 | 175.42(4) | C16-C17-C18 | 119.9(6) |
| Cl10-Bi2-Cl8 | 93.05(4) | C20-N5-C16 | 120.3(5) |
| Cl12-Bi2-Cl8 | 90.23(4) | C25-N6-C21 | 121.1(7) |
| Cl9-Bi2-Cl8 | 89.65(4) | C35-N8-C31 | 114.9(7) |
| Cl7-Bi2-Cl8 | 86.87(4) | C21-C22-C23 | 119.3(6) |
| | | N6-C25-C24 | 121.2(7) |
| | | C33-C34-C35 | 120.5(8) |
| | | C34-C35-N8 | 119.9(7) |
| | | C32-C31-N8 | 119.5(8) |
| | | C24-C23-C22 | 119.6(7) |
| | | C25-C24-C23 | 120.9(7) |
| | | C31-C32-C33 | 121.8(10) |
| | | C22-C21-N6 | 117.9(7) |
| | | C34-C33-C32 | 123.1(9) |
| | | C30-N7-C26 | 119.0(8) |
| | | C27-C26-N7 | 118.3(9) |
| | | C28-C27-C26 | 118.3(9) |
| | | C27-C28-C29 | 124.8(9) |
| | | C29-C30-N7 | 123.1(9) |
| | | C30-C29-C28 | 116.5(9) |

In the same time, the hydrogen atoms bonded to nitrogen atoms participate in the formation of N-H…Cl hydrogen bonding with chlorine atoms of $BiCl_6^{3-}$ anions and in the formation of N-H…O hydrogen bonding with to oxygen atoms of isolaten nitrate anions (Fig. 3). All of these hydrogen bonds, N-H¨Cl and N-H…O (see Table 5) give rise to a three – dimensional network in the structure and add stability of this compound.

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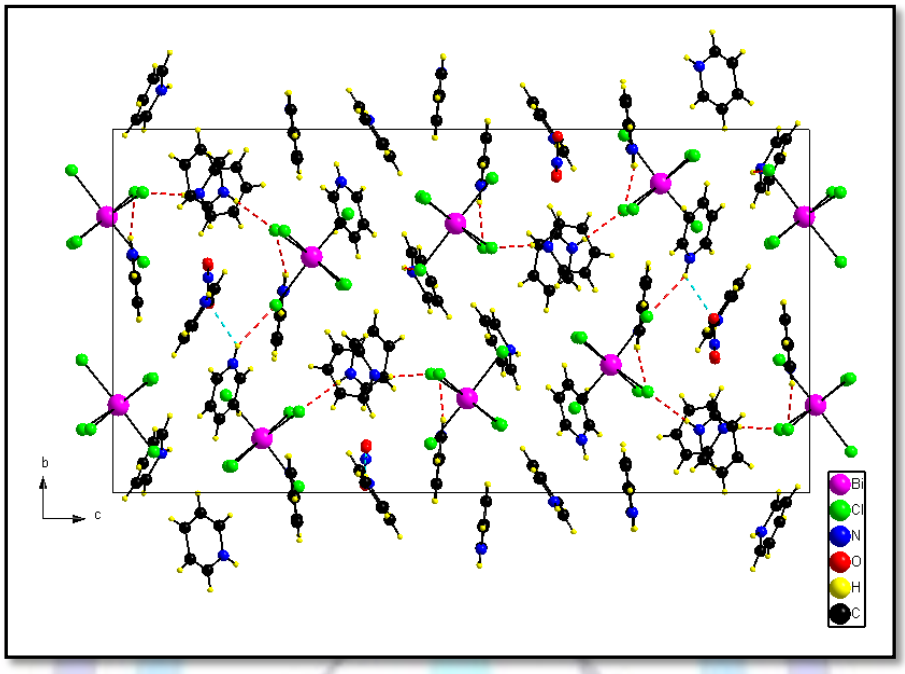


**Figure 3**: Hydrogen bond between the constituents of the structure of $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$ along the axis a

**Table 5:** Hydrogen bonds for $[C_5H_5NH]_7(BiCl_6)_2(NO_3)$

| D–H···A | d(D–H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| N2-H2···O1 | 0,860 | 1,946 | 2,760 | 157,44 |
| N2–H2···O2 | 0,860 | 2,658 | 3,401 | 145,41 |
| N2-H2···N1 | 0,860 | 2,676 | 3,518 | 166,36 |
| N3-H3···Cl1 | 0,860 | 2,867 | 3,726 | 177,13 |
| N4-H4A···O2 | 0,860 | 2,496 | 3,148 | 133,22 |
| N4-H4A···Cl3 | 0,860 | 2,942 | 3,597 | 134,40 |
| N5-H5A···Cl1 | 0,860 | 2,818 | 3,623 | 156,55 |
| N6-H6A···Cl8$^{i}$ | 0,860 | 2,616 | 3,466 | 169,85 |
| N7-H7A···Cl9 | 0,860 | 2,934 | 3,540 | 129,15 |
| N8-H8A···Cl10$^{i}$ | 0,860 | 2,664 | 3,508 | 167,45 |

Codes de symétries: *(i) x-1/2, - y+3/2, z-1/2*

## Conclusion

In this study, a novel organic–inorganic bismuth–chloride based compound with general formula $[C_5H_6NH]_7(BiCl_6)_2(NO_3)$ has been synthesized. Single-crystal X-ray diffraction showed the formation of title compound consisting of two independent octahedra of Bismuth, seven monoprotonated organic cations and isolated nitrate anion. Those components are connected themselves by two types of intermolecular hydrogen bonds.

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