

A New Organically Templated Noncentrosymmetric Bismuth Chloride: Synthesis, Structure, and Characterization of $[\text{N}(\text{CH}_3)_2\text{H}_2][(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2][\text{BiCl}_6]$

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Since a wide variety of materials either observed in nature or synthesized by chemists exhibit a marked preference to symmetry, it is quite difficult to find asymmetric substances. Nonetheless, discovering noncentrosymmetric (NCS) materials is a continuing challenge in inorganic solid-state materials chemistry field. This is mainly because acentric materials can reveal extremely important physical properties such as dielectric behavior, ferroelectricity, piezoelectricity, pyroelectricity, and nonlinear optical (NLO) properties.¹⁻⁵ On the basis of innumerable theoretical studies and synthetic approaches, it has been known that combining second-order Jahn-Teller (SOJT) cations would be an effective strategy to increase the incidence of asymmetric environments of materials with bond polarization.⁶⁻¹⁵ With oxides, octahedrally coordinated d^0 transition metals and lone pair cations are two representative SOJT cations. Among them, many researchers have been paying special attention to the use of Bi^{3+} cation in order to replace one of the best performing, yet very toxic lead-based NCS materials, e.g., lead zirconate titanate (PZT). In fact, several promising bismuth-based asymmetric oxide materials have been developed.¹⁶⁻¹⁹ Similarly, bismuth chloride materials have been also of great interest due to ferroelectric phase transitions, dielectric, and the related properties.²⁰⁻²² A variety of organic and inorganic template cations such as NH_4^+ , CH_3NH_3^+ , $(\text{CH}_3)_2\text{NH}_2^+$, $\text{C}_3\text{H}_5\text{NH}^+$, K^+ , and Cs^+ have been introduced to prepare those asymmetric bismuth chlorides.²³⁻²⁷ The versatility of the structure-directing agents definitely seems to affect local geometry as well as symmetry of the framework structure of the crystallized materials, which accordingly have influence upon the material properties. We have used a low-temperature (< 120 °C) reflux method to synthesize a new bismuth chloride. In this paper, we report the synthesis, structure, and characterization of a new organically templated zero-dimensional noncentrosymmetric bismuth chloride, $[\text{N}(\text{CH}_3)_2\text{H}_2][(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2][\text{BiCl}_6]$ (**1**).

Experimental Section

Synthesis. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Fluka, 99%), aurintricarboxylic acid ammonium salt ($\text{C}_{22}\text{H}_{14}\text{O}_9 \cdot 3\text{NH}_3$), *N,N*-dimethyl formamide, methanol, $(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$, and HCl were used as received. Single crystals of compound **1** were prepared by using 0.485 g (1.00 mmol) of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 0.158 g (0.33 mmol) of aurintricarboxylic acid ammonium

salt, 0.12 mL of $(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$ (TMEDA), 3 mL of DMF, 0.5 mL of HCl (35 wt%), 4 mL of methanol (99%), and 4 mL of deionized water. The reactants were refluxed for 12 h and then slowly cooled down to room temperature. After cooling down to room temperature, the solvent of the reaction mixture was slowly evaporated in the freezer. Colorless single crystals were grown in about 10 days. A yield of 24% based on bismuth was observed. It is well known that the carbonyl ligand of the Vaska's complex is derived by decomposition of DMF.²⁸ Similarly, the $[\text{N}(\text{CH}_3)_2\text{H}_2]^+$ cation might come from the decomposition of the solvent DMF. The powder X-ray diffraction pattern on the ground crystals was in a good agreement with the calculated pattern from the single crystal structure.

Crystallographic determination. The structure of compound **1** was determined by standard crystallographic methods. A colorless rod crystal ($0.02 \times 0.03 \times 0.08 \text{ mm}^3$) was used for single crystal X-ray diffraction. The data were collected using a Bruker SMART APEX CCD X-ray diffractometer at 173 K using graphite-monochromated $\text{Mo K}\alpha$ radiation. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in omega, and an exposure time of 5 s per frame. The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability. The maximum correction applied to the intensities was < 1%. The data were integrated using the Bruker SAINT program,²⁹ with the intensities corrected for Lorentz, polarization, air absorption, and absorption attributable to the variation in the path length through the detector faceplate. A semiempirical absorption correction was made on the hemisphere of data with the SADABS program.³⁰ The data were solved and refined using SHELXS-97 and SHELXL-97, respectively.^{31,32} All of the atoms were refined with anisotropic displacement parameters and converged for $I > 2\sigma(I)$. All calculations were performed using the WinGX-98 crystallographic software package.³³ The final Fourier difference map revealed minimum and maximum peaks of -2.057 and $2.380 \text{ e}\text{\AA}^{-3}$. Crystallographic data and selected bond distances and angles for compound **1** are given in Tables 1-2. The X-ray powder diffraction data were collected on a SCINTAG XDS2000 diffractometer using $\text{Cu K}\alpha$ radiation at room temperature with 35 kV and 30 mA in the 2θ range $5\text{-}70^\circ$ with a step size of 0.02° , and a step time of 1 s.

Measurements. Thermogravimetric analysis was per-

Table 1. Crystal data for $[\text{N}(\text{CH}_3)_2\text{H}_2][(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2][\text{BiCl}_6]$

formula	$\text{BiCl}_6\text{C}_8\text{H}_{26}\text{N}_3$
fw	586.00
space group	$P2_12_12_1$ (No. 19)
Z	4
a (Å)	9.4224(19)
b (Å)	12.287(3)
c (Å)	17.232(3)
V (Å ³)	1995.0(7)
T (K)	173.0(2)
ρ_{calc} (g cm ⁻³)	1.951
μ (mm ⁻¹)	9.631
λ (Å)	0.71073
R(F) ^a	0.0267
$R_w(F_o^2)^b$	0.0487

$$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$$

Table 2. Selected bond distances (Å) and bond angles (°) for $[\text{N}(\text{CH}_3)_2\text{H}_2][(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2][\text{BiCl}_6]$

Bond Distances		Bond Angles	
Bi(1)–Cl(1)	2.665(2)	Cl(4)–Bi(1)–Cl(3)	95.80(8)
Bi(1)–Cl(2)	2.717(2)	Cl(4)–Bi(1)–Cl(1)	91.39(9)
Bi(1)–Cl(3)	2.664(2)	Cl(3)–Bi(1)–Cl(1)	88.88(8)
Bi(1)–Cl(4)	2.600(2)	Cl(4)–Bi(1)–Cl(2)	87.07(9)
Bi(1)–Cl(5)	2.766(2)	Cl(3)–Bi(1)–Cl(2)	91.31(8)
Bi(1)–Cl(6)	2.909(2)	Cl(1)–Bi(1)–Cl(2)	178.46(9)
		Cl(4)–Bi(1)–Cl(5)	87.01(8)
		Cl(3)–Bi(1)–Cl(5)	177.13(8)
		Cl(1)–Bi(1)–Cl(5)	91.64(8)
		Cl(2)–Bi(1)–Cl(5)	88.25(8)
		Cl(4)–Bi(1)–Cl(6)	173.47(7)
		Cl(3)–Bi(1)–Cl(6)	90.16(7)
		Cl(1)–Bi(1)–Cl(6)	91.38(8)
		Cl(2)–Bi(1)–Cl(6)	90.15(8)
		Cl(5)–Bi(1)–Cl(6)	87.00(7)

formed on a Setaram LABSYS TG-DTA/DSC Thermogravimetric Analyzer. The polycrystalline compound **1** sample was contained within a platinum crucible and heated at a rate of 10 °C min⁻¹ from room temperature to 600 °C under flowing argon. Infrared spectrum was recorded on a Varian 1000 FT-IR spectrometer in the 400–4000 cm⁻¹ range, with the sample intimately pressed between two KBr pellets. Elemental analysis was carried out by a Carlo Erba EA1108 analyzer. Elemental microanalysis for compound **1** obsd (calcd): C, 16.51% (16.47%); H, 4.56% (4.49%); N, 7.50% (7.21%). SEM/EDX analyses have been performed using a Hitachi S-3400N/Horiba Energy EX-250 instruments. EDX analysis for compound **1** provided a Bi:Cl ratio of 1:6.

Results and Discussion

Compound **1** crystallizes in a noncentrosymmetric orthorhombic space group $P2_12_12_1$ (No. 19). The crystal structure

is composed of distorted BiCl_6 octahedra and two organic cationic templates, $(\text{CH}_3)_2\text{H}_2\text{N}^+$ and $(\text{CH}_3)_2\text{N}^+\text{H}(\text{CH}_2)_2\text{N}^+\text{H}(\text{CH}_3)_2$, which result in a new zero-dimensional molecular compound (see Figure 1). The unique bismuth atom possesses a six-coordinate octahedral environment with six chlorine atoms, and the BiCl_6 octahedra are separated by two organic cations. The bond distances for $\text{Bi}^{3+}\text{--Cl}$ in the BiCl_6 octahedron range from 2.600(2) to 2.909(2) Å. Three of the Bi–Cl bond lengths are relatively shorter; from 2.600(2) to 2.665(2) Å. However, the other three Bi–Cl distances are quite longer; 2.717(2) to 2.909(2) Å. Especially, the Bi–Cl(6) bond is very long, which might be due to the stereochemically active bismuth(III) lone pair.^{22,34} Overall, the three short and three long Bi–Cl bonds result in a C_3 -

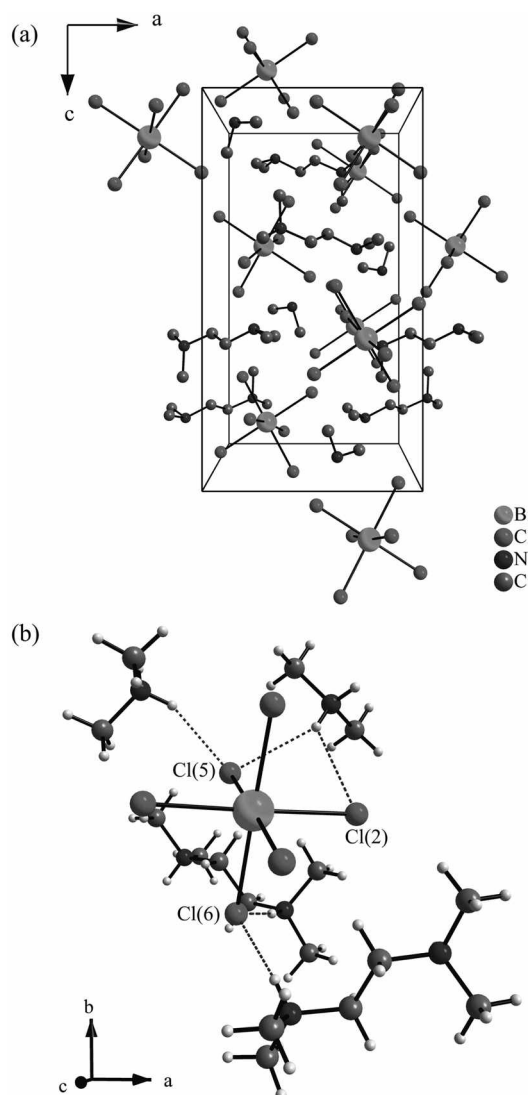


Figure 1. (a) Ball-and-stick representation of $[\text{N}(\text{CH}_3)_2\text{H}_2][(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2][\text{BiCl}_6]$ in the *ac* plane. Note the distorted BiCl_6 octahedra are separated by organic cations. (b) Hydrogen-bonding interactions between the Cl and H–N group in $[\text{N}(\text{CH}_3)_2\text{H}_2][(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2][\text{BiCl}_6]$. Note the three hydrogen bonded chlorine atoms, Cl(2), Cl(5), and Cl(6) are affecting the coordination environment of BiCl_6 , which result in three long Bi–Cl bonds and C_3 distortion of the octahedron.

distorted BiCl_6^{3-} octahedron. The Cl–Bi–Cl bond angles *cis* and *trans* to each other are ranging 87.00(7)–95.80(8) $^\circ$ and 173.47(7)–178.46(9) $^\circ$, respectively. The two organic template cations, $[\text{N}(\text{CH}_3)_2\text{H}_2]^+$ and $[(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{NH}(\text{CH}_3)_2]^{2+}$ reside within the crystal lattice and maintain the charge neutrality. The C–N bond lengths in organic cations are ranging 1.460(12)–1.512(11) Å. The observed C–C distance in $[\text{TMEDA}\text{H}_2]^{2+}$ is 1.528(12) Å. There are significant hydrogen bonding interactions between Cl and H–N, which induce the distorted BiCl_6 environment. The two organic alkylammonium cations are connected to the chlorine atoms by N–H \cdots Cl hydrogen bonds (see Figure 1(b)). The three chlorine atoms, Cl(2), Cl(5), and Cl(6), are weakly connected to the N–H through the hydrogen bonds. Interestingly, all these three chlorines contain longer Bi–Cl bonds in the BiCl_6 octahedron due to the hydrogen bonding interactions. It has been known that the macroscopic noncentrosymmetry could be facilitated by the asymmetric environment of the lone pair on the Bi(III) cation as well as structural alignment from the hydrogen bonding interactions.^{35,36} Compound **1** possesses three unique 2_1 screw axes along *a*, *b*, and *c*-directions, resulting in a noncentrosymmetric space group $P2_12_12_1$. Bond valence calculations^{37,38} resulted in a value of 2.88 for the Bi^{3+} cation.

The thermal behavior of compound **1** was investigated using thermogravimetric analysis. Compound **1** shows a weight loss of 19.3% between 240 to 380 $^\circ\text{C}$ that might be attributed to the loss of the organic, TMEDA ($(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2$) from the material (Calcd 19.8%). Powder XRD pattern of the calcined material to 600 $^\circ\text{C}$ seems to be quite similar to that of cubic $[\text{N}(\text{CH}_3)_4]_2\text{SnCl}_6$.³⁹

The infrared spectrum of compound **1** revealed N–H vibrations at *ca.* 2700–3200 and 1560 cm^{-1} . The C–H stretchings are superimposed to those of N–H, but the bending is observed around 1400 cm^{-1} . The involvement in hydrogen bonding of the NH group is observed around 2730, 1560 and 790 cm^{-1} . Vibrations attributable to the C–N are also observed about 1048–1222 cm^{-1} . The assignments are consistent with those previously reported.^{27,40}

Compound **1** contains a distorted asymmetric coordination environment in Bi^{3+} . Hoffmann *et al.* have plotted the bond angle (θ) versus the bond length asymmetry parameter, *asym* for the antimony-halide systems.³⁴ The plots revealed similarities that are dense groupings of points with small *asym* and θ close to 180 $^\circ$. Thus, we have plotted the bond angle versus bond length asymmetry parameter for bismuth-chloride systems in order to compare the degree of asymmetry for Bi–Cl environment as well as to see if this system follows the similar trend (see Figure 2). As can be seen in Figure 2, BiCl_6 system shows similar features; as *asym* increases, the deviations from $\theta = 180^\circ$ also increase. However, the *asym* values in BiCl_6 system are smaller than those of SbCl_6 . This might be due to the larger size of bismuth, which results in smaller magnitude of the intra-octahedral distortion of Bi^{3+} compared with Sb^{3+} . The magnitude of the distortions in the BiCl_6 octahedra might be also quantified by determining the local dipole moments. The detailed

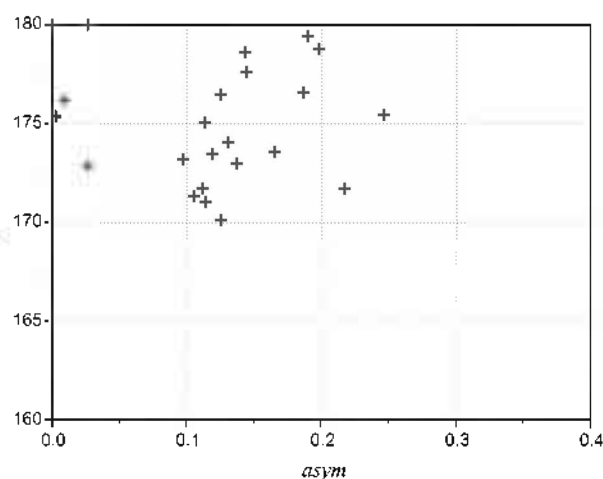


Figure 2. Scatter plot of the bond asymmetry parameter (*asym*) and angle θ for the bismuth-chloride systems.

methodology has been described earlier.^{41–44} The method uses a bond-valence approach to calculate the degree of the local dipole moments. Using this method, the dipole moment for the BiCl_6 octahedron in compound **1** is approximately 1.58 Debyes (D). In fact, an examination of 20 examples shows that the dipole moments for BiCl_6 octahedra range from 0 to 4.37 D with the average value of 1.36 D (see Table 3). Comparing to those of oxides, the average dipole moment values for BiCl_6 octahedra are smaller. This might be due to the longer bond lengths and less distortions of BiCl_6 octahedra than those of oxides. With the BiCl_6 octahedra in $\text{Cs}_2\text{NaBiCl}_6$,⁴⁵ $\text{K}_6(\text{BiCl}_6)\text{Cl}_2(\text{H}_3\text{F}_4)$,⁴⁶ and $(\text{NH}_4)_3(\text{BiCl}_6)$,²⁵ a

Table 3. Calculation of dipole moments for BiCl_6 octahedra

Compound	BiCl_6	Dipole moment (D) ^a
$\text{CsK}_2\text{BiCl}_6$ ²³	Bi(1)Cl ₆	0.0001
	Bi(2)Cl ₆	0.0686
$\text{Cs}_2\text{NaBiCl}_6$ ⁴⁷	Bi(1)Cl ₆	0
	Bi(2)Cl ₆	0.0018
Cs_3BiCl_6 ²⁵	Bi(1)Cl ₆	0.1395
	Bi(2)Cl ₆	0.7900
$\text{Cs}_3\text{Bi}_2\text{Cl}_6$ ⁴⁸	Bi(1)Cl ₆	3.9450
	Bi(2)Cl ₆	1.7692
$[(\text{CH}_3)\text{NH}_2]_3[\text{Bi}_2\text{Cl}_6]$ ²⁶	Bi(1)Cl ₆	1.3729
	Bi(2)Cl ₆	3.9202
$[(\text{CH}_3)\text{NH}_2]_3[\text{Bi}_2\text{Cl}_6]$ ⁵⁰	Bi(1)Cl ₆	4.3713
	Bi(2)Cl ₆	1.6953
$[\text{NH}_2(\text{CH}_3)_2]_2[\text{BiCl}_6]$ ⁵¹	Bi(1)Cl ₆	2.1953
$[(\text{CH}_3)_2\text{NH}]_4\text{Cl}[\text{BiCl}_6]$ ⁵²	Bi(1)Cl ₆	2.4537
$[(\text{CH}_3)_2\text{N}]_3[\text{Bi}_2\text{Cl}_6]$ ²²	Bi(1)Cl ₆	1.4449
$\text{K}_6[\text{BiCl}_6]\text{Cl}_2(\text{H}_3\text{F}_4)$ ⁴⁶	Bi(1)Cl ₆	0
$\text{K}_4[\text{Bi}_2\text{Cl}_{10}](\text{H}_2\text{O})_4$ ⁵³	Bi(1)Cl ₆	1.2706
	Bi(2)Cl ₆	0.1900
$(\text{NH}_4)_3[\text{BiCl}_6]$ ²⁵	Bi(1)Cl ₆	0
	Bi(2)Cl ₆	0
$[\text{N}(\text{CH}_3)_2\text{H}_2][(\text{CH}_3)_2\text{NH}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2][\text{BiCl}_6]$ ¹	Bi(1)Cl ₆	1.5805
Average		1.36

^aD = Debyes. ^bThis work

dipole moment of 0 D is estimated, which is attributable to the same Bi–Cl bond distances *trans* to each other, which cancels the dipole moments out.

We have successfully synthesized a new organically templated noncentrosymmetric zero-dimensional bismuth chloride material under mild aqueous conditions. The structure of the new compound has been determined by a single crystal X-ray diffraction and the material has been further characterized by Infrared spectroscopy, elemental analyses, and thermogravimetric analysis. Additional experiments using different organic templates and mineralizers to make various frameworks are ongoing and will be reported shortly.

Supplementary material. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 693966. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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