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# Crystal structure of room-temperature ionic liquid 1-butyl-isoquinolinium gallium tetrachloride [(BIQL)GaCl<sub>4</sub>]

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## Abstract

The crystal structure of 1-butyl-isoquinolinium gallium tetrachloride [(BIQL)GaCl<sub>4</sub>], which forms room-temperature ionic liquids, has been determined by X-ray diffraction of its single crystal at 113 K. The title crystal belongs to the monoclinic system space group  $P2_1/c$  with  $a = 7.1438(12)$  Å,  $b = 14.3490(14)$  Å,  $c = 16.3531(18)$  Å,  $\beta = 94.885(7)^\circ$ ,  $V = 1670.2(4)$  Å<sup>3</sup> for  $Z = 4$  and  $FW = 397.81$ ,  $\mu = 0.124$  mm<sup>-1</sup>,  $F(000) = 800$ ,  $D_c = 1.582$  mg m<sup>-3</sup>,  $R = 0.0266$  and  $wR = 0.0606$  for 4068 observed reflections ( $I > 2.00\sigma(I)$ ). The ionic liquid of (BIQL)GaCl<sub>4</sub> has lamellar structure as mainly  $\pi$  electron plane of isoquinoline interleave and the layer distance is 3.431 Å connected with GaCl<sub>4</sub><sup>-</sup> structure size. The cation and anion of (BIQL)GaCl<sub>4</sub> arrange orderly in pair and the results indicate that coulombic attraction is dominant, although weak local hydrogen bonds (C–H...Cl) exist simultaneously. **To cite this article:** H. Xue *et al.*, *C. R. Chimie* 11 (2008).

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## 1. Introduction

Room-temperature ionic liquids (RTILs) consist of organic cation and anion which exist in liquid state at room temperature or below 100 °C. They are widely used in various fields of electrochemistry and chemistry because of their unique properties such as nonvolatility and nonflammability. RTILs are promising as solvents for synthetic, catalytic and electrochemical applications in laboratory and in industry [1,2]. The appropriate combination of the anion–cation can obtain many kinds of RTILs possessing characteristic properties,

such as miscibility with water and other solvents, dissolving ability, polarity, viscosity or density. Liquid structures of RTILs have been investigated using X-ray diffraction, neutron diffraction, as well as spectroscopic and computational methods [3–6]. Studies on solid-state structure of a salt are indispensable for understanding its liquid structure, especially for local interactions. Because RTILs are liquids at room temperature, it is technically difficult to grow single crystals and to select suitable sample for single, crystal X-ray diffraction at low temperature. So far a few crystal structures have been determined by X-ray diffraction [7–10]. RTILs are typically formed by a combination of large organic cations, such as imidazolium, pyridinium or quaternary ammonium ions with anions, such as common halides

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or  $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$  or  $[\text{CF}_3\text{SO}_3]^-$ . What kind of role do the organic cations which usually have  $\pi$  electron ring play for structure stability? In this research, large cations of 1-butyl-isoquinolinium cation for short (BIQL)<sup>+</sup> (structure show in Fig. 1) and anion of  $\text{GaCl}_4^-$  were selected to obtain RTILs in the solid state at room temperature and to investigate the action of pi electron rings in the structure. Furthermore, the crystal structure of (BIQL) $\text{GaCl}_4$  was analyzed by X-ray diffraction at low temperature.

## 2. Experiment

### 2.1. Experimental procedure

Moisture unstable samples were handled in a glove box under a dry  $\text{N}_2$  atmosphere. The anhydrous  $\text{GaCl}_3$  purity is 99.9% (made in Dalian Industrial, Co. Ltd. China). 1-Butyl-isoquinolinium chloride was synthesized and purified to 99.5% by adding ethyl acetate and recrystallized in acetonitrile solution. Then it was mixed with anhydrous gallium trichloride and 1-butyl-isoquinoline chloride in a 1:1 ratio, leading to the title room-temperature ionic liquid. The solvent evaporation method was used to grow RTILs crystals in ethyl acetate solvent at room temperature. The product is a colorless single crystal which is air and moisture stable (m.p. 59–60 °C). Infrared spectra was obtained on a Fourier-transform instrument (Nicolet Nexus FT-IR 470) with KBr pellets at room temperature. The elemental analysis (Model 240 PerkinElmer elemental analyzer) results of crystals are as follows (wt%): C at 39.60, H at 3.94 and N at 3.70, closely equal to the calculation based on the chemical formula found (wt%): C at 39.25, H at 4.05 and N at 3.52.

### 2.2. X-ray diffraction analysis

The single crystal of  $0.26 \times 0.24 \times 0.20$  mm was mounted on a Bruker SMART CCD X-ray diffractometer equipped with a graphite-monochromated Mo  $K\alpha$

radiation ( $\lambda = 0.071073$  nm). The data were collected at 113 K by using a scan technique in the range of  $1.89^\circ < \theta < 28.28^\circ$  with index ranges as follows:  $-9 \leq h \leq 9$ ,  $-18 \leq k \leq 19$ ,  $-21 \leq l \leq 21$ . A total of 15,871 reflections were collected, of which 4068 were unique ( $R_{\text{int}} = 0.037$ ) and equivalent reflections were merged. The data obtained were processed using the CRYSTALCLEAR program [11]. The structures were solved and refined using the SHELX-97 suite of programs [12]. All the non-hydrogen atoms were determined via direct method and difference Fourier synthesis by introducing anisotropic displacement parameters, whereas all the hydrogen atoms were refined using appropriate riding models. The final  $R = 0.0266$ ,  $wR = 0.0341$ ,  $\text{calc } w = 1/[\sigma^2(F_o^2 + (0.0321P)^2 + 0.0000P)]$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$ ,  $\sigma = 0.994$ ,  $(\Delta\rho)_{\text{max}} = 0.38 \text{ e}/\text{\AA}^3$ ,  $(\Delta\rho)_{\text{min}} = -0.45 \text{ e}/\text{\AA}^3$  and  $(\Delta\rho/\sigma)_{\text{max}} = 0.001$ . The crystal structure of the ionic liquid (BIQL) $\text{GaCl}_4$  and the molecule arrangement in a unit cell are shown in Figs. 2 and 3. The unit cell parameters and refinement statistics for (BIQL) $\text{GaCl}_4$  are given in Table 1, and the atomic coordinates and displacement parameters are given in Table 2. Their selected bond lengths and angles are listed in Tables 3 and 4, respectively. The distances beyond the asymmetric unit out to 3.60 Å involving hydrogen bond geometries are summarized in Table 5.

## 3. Results and discussion

### 3.1. IR spectrum

The infrared absorption spectrum of (BIQL) $\text{GaCl}_4$  between 4000 and 400  $\text{cm}^{-1}$  was obtained. In the FT-IR, the peak at 3087  $\text{cm}^{-1}$  is the characteristic adsorption stretching vibration of the ArC–H group, shifting to lower frequency at 3090  $\text{cm}^{-1}$  corresponding to the isoquinoline ring. The absorption peaks at 831 and 878  $\text{cm}^{-1}$ , assigned to bending vibrations out of the plane of (C–H) isoquinoline, shift to higher frequency than those of free isoquinoline (827 and 860  $\text{cm}^{-1}$ ). It is indicated that there exists some weak interaction between the C–H and  $\text{GaCl}_4^-$ .

### 3.2. Crystal structure of (BIQL) $\text{GaCl}_4$

The single crystal structure analysis reveals that (BIQL) $\text{GaCl}_4$  contains a pair of ions, one cation (BIQL)<sup>+</sup> and one  $\text{GaCl}_4^-$  anion. It has a monoclinic lattice within its asymmetric unit. The ORTEP diagram of the asymmetric unit is shown in Fig. 2. The expected intra-molecular bond lengths and angles in (BIQL) $\text{GaCl}_4$  show an almost

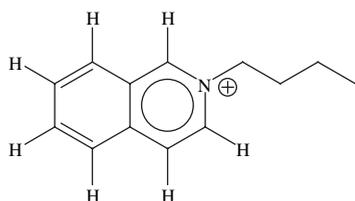


Fig. 1. The cation structure of (BIQL)<sup>+</sup>.

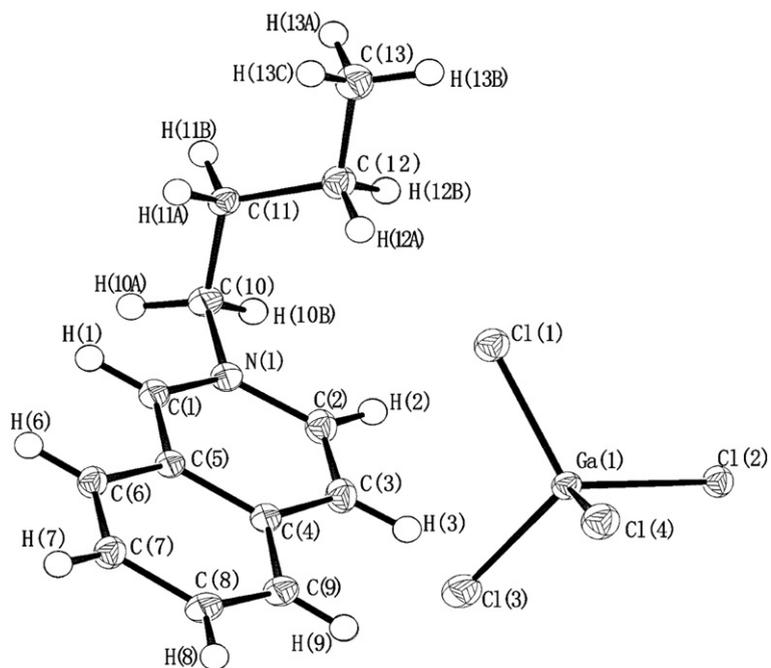


Fig. 2. ORTEP diagram of (BIQL)GaCl<sub>4</sub> structure with an atom numbering scheme.

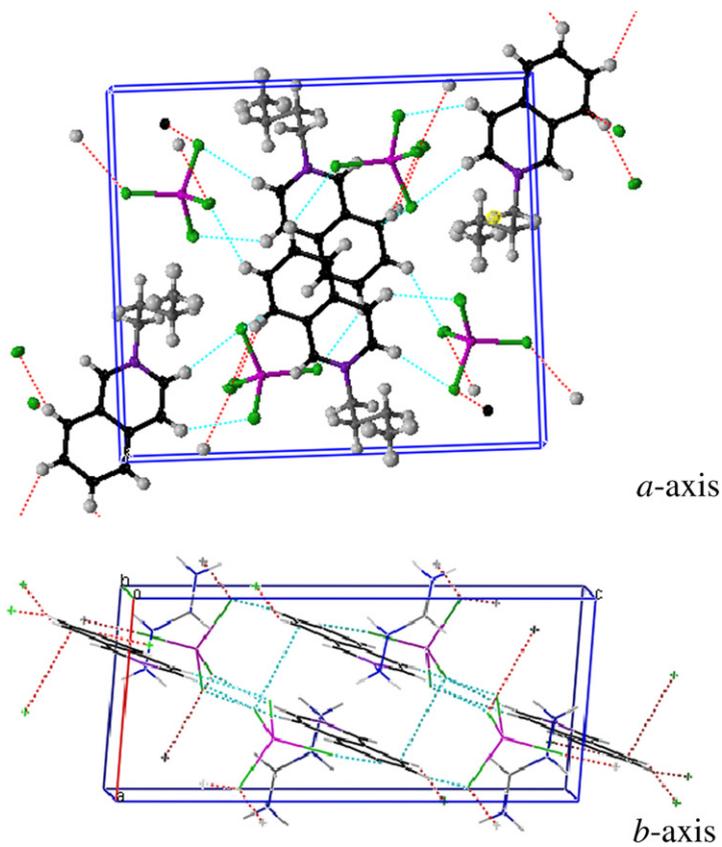


Fig. 3. The packing diagram of a unit cell for (BIQL)GaCl<sub>4</sub> as viewed along *a*-axis and *b*-axis.

Table 1  
Crystal data and refinement results for (BIQL)GaCl<sub>4</sub>

Empirical formula	C <sub>13</sub> H <sub>16</sub> NCl <sub>4</sub> Ga
Formula weight	397.81
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)
<i>Unit cell dimensions</i>	
<i>a</i> (Å)	7.1438(12)
<i>b</i> (Å)	14.3490(14)
<i>c</i> (Å)	16.3531(18)
$\beta$ (°)	94.885(7)
Volume (Å <sup>3</sup> )	1670.2(4)
Z value	4
Calculated density (g cm <sup>-3</sup> )	1.582
Absorption coefficient (mm <sup>-1</sup> )	0.124
<i>F</i> (000)	800
Crystal size (mm <sup>3</sup> )	0.26 × 0.24 × 0.20
$\mu$ (Mo K $\alpha$ ) (cm <sup>-1</sup> )	22.717
$\theta$ range for data collection (°)	1.89–28.28
Index ranges	–9 ≤ <i>h</i> ≤ 9, –18 ≤ <i>k</i> ≤ 19, –21 ≤ <i>l</i> ≤ 21
Reflections collected	15,871
Independent reflections	4068
Completeness to $\theta_{\max}$ (%)	28.28 (98%)
Max. and min. transmission	0.6350 and 0.559
Data/restraints/parameters	4068/0/175
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.994
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0266, <i>wR</i> <sub>2</sub> = 0.0606
<i>R</i> indices (all data)	<i>R</i> = 0.0341, <i>wR</i> = 0.0586
Largest difference peak and hole (e/Å <sup>3</sup> )	2.745 and –1.097
Max shift/error in final cycle	0.001
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>

tetrahedral geometry with Ga–Cl bond lengths in the range of 2.1760–2.1793 Å and angular [Cl(2)–Ga(1)–Cl(4) 107.710(18)°, Cl(3)–Ga(1)–Cl(4) 111.187(18)°] distortions of less than 1.7567°. The crystal lattice consists of one-dimensional pillars along the *a*-axis

Table 2  
Atomic coordinates (×10<sup>4</sup>) and displacement parameters (Å<sup>2</sup> × 10<sup>3</sup>) of (BIQL)GaCl<sub>4</sub>

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ga(1)	7044(3)	2130(10)	3340(10)	1496(5)	C(5)	2335(2)	1380(12)	–463(10)	1370(2)
Cl(1)	5701(6)	3428(3)	2918(3)	2091(8)	C(6)	1597(2)	1034(12)	–1240(10)	1760(3)
Cl(2)	7862(6)	2230(3)	4653(2)	1782(8)	C(7)	1338(2)	99(12)	–1345(11)	1940(3)
Cl(3)	9513(6)	1895(3)	2675(3)	2298(9)	C(8)	1807(2)	–528(12)	–691(11)	1950(3)
Cl(4)	5049(6)	985(3)	3153(3)	2494(9)	C(9)	2504(2)	–212(12)	66(11)	1840(3)
N(1)	3364(19)	2661(10)	388(8)	1560(2)	C(10)	3691(2)	3686(12)	492(11)	1800(3)
C(1)	2678(2)	2337(12)	–335(10)	1550(2)	C(11)	1871(2)	4206(11)	592(10)	1590(2)
C(2)	3751(2)	2073(12)	1043(11)	1990(3)	C(12)	924(2)	3936(12)	1360(10)	2010(3)
C(3)	3477(2)	1141(12)	961(10)	2010(3)	C(13)	–894(2)	4467(12)	1438(11)	2310(3)
C(4)	2773(2)	755(12)	198(10)	1510(2)					

$$U_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\alpha + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\gamma).$$

(Fig. 3). The BIQL cation forms a pillar with the butyl group sticking out of the isoquinoline ring plane torsion angle [C(1)–N(1)–C(10) 119.30(13)°, and C(2)–N(1)–C(10) 119.78(13)°]. The lengths of Cl(4)⋯H(3) and Cl(1)⋯H(2) are 2.926 and 2.862 Å, respectively, beyond hydrogen bond distance, the chlorine atoms Cl(4) and Cl(1) of (BIQL)GaCl<sub>4</sub> are almost in the plane of isoquinoline, and distances of Cl(2)⋯H(8)<sup>(1)</sup> of the border upon layer molecular and Cl(3)⋯H(7)<sup>(6)</sup> of the molecular border upon the same layer are 2.935 and 2.857 Å, respectively [(1) –*X* + 1, *Y* + 1/2, –*Z* + 1/2; (6) –*X* + 1, –*Y*, –*Z*]. It is indicated that  $\pi$  electron rings of isoquinoline interleave stack in layer and the layer distance is 3.431 Å (Fig. 3, *b*-axis). The cation and anion of (BIQL)GaCl<sub>4</sub> arrange orderly in pair and the results indicate that coulombic attraction is more dominant than that in hydrogen bonding, although some local weak hydrogen bonds exist in the molecules in the same layer and/or border layer.

#### 4. Conclusion

The room-temperature ionic liquid of (BIQL)GaCl<sub>4</sub> is of lamellar structure as mainly  $\pi$  electron plane of isoquinoline interleave and its layer distance is 3.431 Å, connected with GaCl<sub>4</sub><sup>–</sup> structure size. The  $\pi$  electron ring is stacked interleaving between two layers. The results of cation and anion of (BIQL)GaCl<sub>4</sub> arranged orderly in pair indicate that coulombic attraction is more dominant. Simultaneously, the weak local hydrogen bonds C–H⋯Cl exist in the molecules in same layer and/or border layer.

*Supplementary material:* The supplementary material has been sent to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, as supplementary materials No. CCDC: (for (BIQL)GaCl<sub>4</sub>).

Table 3  
Selected bond lengths (Å) for (BIQL)GaCl<sub>4</sub> (at 113 K)

Bond	Dist	Bond	Dist	Bond	Dist
Ga(1)–Cl(1)	2.1791(4)	C(1)–C(5)	1.407(2)	C(7)–C(8)	1.416(2)
Ga(1)–Cl(3)	2.1760(5)	C(2)–C(3)	1.355(2)	C(8)–C(9)	1.371(2)
Ga(1)–Cl(2)	2.1833(3)	C(3)–C(4)	1.418(2)	C(10)–C(11)	1.520(2)
Ga(1)–Cl(4)	2.1793(4)	C(4)–C(5)	1.419(2)	C(11)–C(12)	1.527(2)
N(1)–C(1)	1.325(2)	C(4)–C(9)	1.414(2)	C(12)–C(13)	1.521(2)
N(1)–C(2)	1.374(2)	C(5)–C(6)	1.422(2)		
N(1)–C(10)	1.497(2)	C(6)–C(7)	1.364(2)		

Table 4  
Selected bond angles (deg) for (BIQL)GaCl<sub>4</sub> (at 113 K)

Angle	(°)	Angle	(°)	Angle	(°)
Cl(1)–Ga(1)–Cl(2)	109.201(18)	N(1)–C(1)–C(5)	121.48(15)	C(5)–C(6)–C(7)	119.45(15)
Cl(1)–Ga(1)–Cl(3)	109.156(18)	N(1)–C(2)–C(3)	120.76(15)	C(6)–C(7)–C(8)	120.63(15)
Cl(1)–Ga(1)–Cl(4)	109.588(18)	C(2)–C(3)–C(4)	120.69(15)	C(7)–C(8)–C(9)	121.06(15)
Cl(2)–Ga(1)–Cl(4)	107.710(18)	C(3)–C(4)–C(5)	117.46(15)	C(4)–C(9)–C(8)	119.72(15)
Cl(2)–Ga(1)–Cl(3)	109.968(18)	C(3)–C(4)–C(9)	123.44(15)	N(1)–C(10)–C(11)	111.55(13)
Cl(3)–Ga(1)–Cl(4)	111.187(18)	C(5)–C(4)–C(9)	119.09(14)	C(10)–C(11)–C(12)	114.02(13)
C(1)–N(1)–C(2)	120.91(14)	C(1)–C(5)–C(4)	118.66(14)	C(11)–C(12)–C(13)	112.55(14)
C(1)–N(1)–C(10)	119.30(13)	C(1)–C(5)–C(6)	121.30(15)		
C(2)–N(1)–C(10)	119.78(13)	C(4)–C(5)–C(6)	120.03(15)		

Table 5  
Distances beyond the asymmetric unit out to 3.60 Å involving hydrogens for (BIQL)GaCl<sub>4</sub>

Atom...atom	Dist	Atom...atom	Dist	Atom...atom	Dist
Ga(1)···H(2)	3.411	Cl(2)···H(10A) <sup>(2)</sup>	3.154	Cl(4)···H(1) <sup>(2)</sup>	3.228
Cl(1)···H(2)	2.862	Cl(2)···H(11A) <sup>(4)</sup>	2.966	Cl(4)···H(2)	3.250
Cl(1)···H(3) <sup>(1)</sup>	3.506	Cl(2)···H(11B) <sup>(5)</sup>	3.395	Cl(4)···H(3)	2.926
Cl(1)···H(6) <sup>(2)</sup>	3.279	Cl(2)···H(12A) <sup>(4)</sup>	3.343	Cl(4)···H(10A) <sup>(2)</sup>	3.131
Cl(1)···H(9) <sup>(1)</sup>	3.024	Cl(2)···H(13C) <sup>(4)</sup>	3.089	Cl(4)···H(10B) <sup>(5)</sup>	3.447
Cl(1)···H(10B)	3.245	Cl(3)···H(1) <sup>(4)</sup>	3.170	Cl(4)···H(11B) <sup>(5)</sup>	3.154
Cl(1)···H(12B)	3.288	Cl(3)···H(6) <sup>(4)</sup>	2.848	Cl(4)···H(12B) <sup>(5)</sup>	3.563
Cl(1)···H(13B) <sup>(3)</sup>	2.966	Cl(3)···H(7) <sup>(6)</sup>	2.857	Cl(4)···H(13A) <sup>(7)</sup>	3.491
Cl(2)···H(1) <sup>(4)</sup>	3.385	Cl(3)···H(8) <sup>(6)</sup>	3.305	Cl(4)···H(13B) <sup>(7)</sup>	3.551
Cl(2)···H(8) <sup>(1)</sup>	2.935	Cl(3)···H(12A) <sup>(3)</sup>	3.087	Cl(2)···C(1) <sup>(2)</sup>	3.495
Cl(2)···H(9) <sup>(1)</sup>	3.099	Cl(3)···H(13A) <sup>(5)</sup>	2.977	Cl(1)···C(6) <sup>(1)</sup>	3.431

(1)  $-X + 1, Y + 1/2, -Z + 1/2$ ; (2)  $X, -Y + 1/2, Z + 1/2$ ; (3)  $X + 1, Y, Z$ ; (4)  $X + 1, -Y + 1/2, Z + 1/2$ ; (5)  $-X + 1, Y + 1/2 - 1, -Z + 1/2$ ; (6)  $-X + 1, -Y, -Z$ ; (7)  $-X, Y + 1/2 - 1, -Z + 1/2$ .

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## References

- [1] Yanna NuLi, Jun Yang, Pu Wang, Appl. Surf. Sci. 252 (2006) 8086.
- [2] Shu-I Hsiu, Chia-Cheng Tai, I.-Wen Sun, Electrochim. Acta 51 (2006) 2607.
- [3] C. Hardacre, J.D. Holbrey, S.E.J. McMath, D.T. Bowron, A.K. Soper, J. Chem. Phys. 118 (2003) 273.
- [4] E.A. Turner, C.C. Pye, R.D. Singer, J. Phys. Chem. A 107 (2003) 2277.
- [5] J.K. Shah, J.F. Brennecke, E.J. Maginn, Green Chem. 4 (2002) 112.
- [6] J. de Andrade, E.S. Böes, H. Stassen, J. Phys. Chem. B 106 (2002) 13344.
- [7] J.D. Holbrey, W.M. Reichert, R.D. Rogers, Dalton Trans. (2004) 2267.
- [8] A. Babai, R. Hagiwara, J. Alloys Compd. 418 (2006) 122.
- [9] K. Matsumoto, A.V. Mudring, Z. Mazej, P. Benkič, B. Žemva, Solid State Sci. 8 (2006) 1250.
- [10] H. Katayanagi, S. Hayashi, H. Hamaguchi, K. Nishikawa, Chem. Phys. Lett. 392 (2004) 460.
- [11] CRYSTALCLEAR, Rigaku Corporation, Woodlands, TX, 1999.
- [12] G.M. Sheldrick, SHELX-97, University of Göttingen, Germany, 1997.