metal-organic compounds

Tris(1-ethyl-3-methylimidazolium) hexachlorolanthanate

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In the title complex, $(C_6H_{11}N_2)_3[LaCl_6]$, centrosymmetric octahedral hexachlorolanthanate anions are located at the corners and face-centers of the monoclinic unit cell. The ring H atoms of the cations interact with the Cl atoms of the anions *via* hydrogen bonding, and bifurcation of the hydrogen bonding is observed. Cation–cation interactions *via* hydrogen bonding between the ring H atoms and π-electrons of aromatic rings are also observed as in other imidazolium salts.

Comment

Various imidazolium salts are known as room-temperature ionic liquids and some exhibit interesting characteristics with respect to practical applications in many fields of chemistry and electrochemistry (Welton, 1999; Hagiwara & Ito, 2000). Studies of the interactions between the ions are important for the understanding of the physical and chemical properties of ionic liquids. The structural analyses of solid imidazolium salts provide important information regarding the ionic interactions. The electrochemical behavior of the lanthanum ion in the $LaCl_3$-saturated 1-ethyl-3-methylimidazolium chloride–$AlCl_3$ ionic liquid system has been reported recently (Tsuda *et al.*, 2000, 2001). In the present study, the solid imidazolium salt tris(1-ethyl-3-methylimidazolium) hexachlorolanthanate, $(EMI)_3[LaCl_6]$, (I), has been prepared and its structure determined by X-ray single-crystal diffraction.

(I)
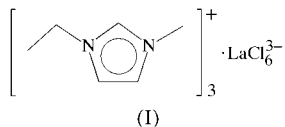
The title structure is built up from EMI cations and slightly distorted $LaCl_6$ octahedra. The structure contains three crystallographically independent EMI cations (Figs. 1 and 2). Typical C—C(N) bond distances are observed for the imidazolium cations (Dymek *et al.*, 1989; Ortwerth *et al.*, 1998). The average bond distances of N1—C2, N11—C12 and N21—C22

(1.306 Å), and C2—N3, C12—N13 and C22—N23 (1.309 Å) are shorter than those of N3—C4, N13—C14 and N23—C24 (1.357 Å), C4—C5, C14—C15 and C24—C25 (1.331 Å), and C5—N1, C15—N11 and C25—N21 (1.365 Å). The β carbon of each ethyl substituent is above or below the plane of the five-membered ring, with torsion angles of $-117.8\,(9)°$ for C2—N1—C6—C7, $-94.8\,(6)°$ for C12—N11—C16—C17 and $92.2\,(9)°$ for C22—N21—C16—C17. $LaCl_6$ shows the expected octahedral geometry, with La—Cl bond distances in the range 2.76–2.81 Å and *cis*-Cl—La—Cl angular distortions of less than 3°. $LaCl_6$ anions are located at the corners and face-centers of the monoclinic unit cell.

One would expect the cation–anion interactions in EMI salts to be dominated by the hydrogen bonding between the ring H atoms and anions, since the ring H atoms have more positive charge than the H atoms of the side-chain alkyl groups. The strength of hydrogen bonding depends on the basicity of the hydrogen-bond acceptor. Strong hydrogen-bond acceptors, like atomic halide ions, can form strong hydrogen bonds, while larger molecular anions do not (Abdul-Sada *et al.*, 1986; Dymek *et al.*, 1989; Fuller *et al.*, 1994; Ortwerth *et al.*, 1998). Table 1 shows the hydrogen-bonding geometry in (I). All Cl atoms except Cl1 are involved in short contacts with ring H atoms. Cl1 does not interact with ring H atoms; however, it is at a short distance from one of the H atoms (H8*b*) of the methyl group of a cation. Thus, hydrogen bonding is observed between some H atoms attached on the
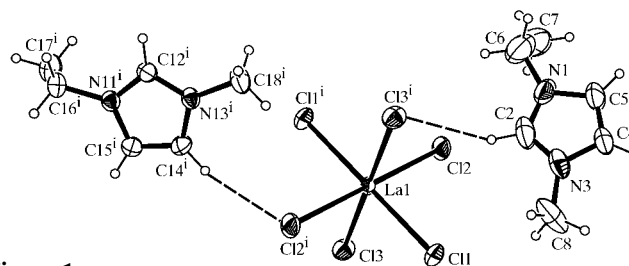
Figure 1
The molecular structure of the $[LaCl_6]^{3-}$ anion and EMI$^+$ cations around La1 in (I). The dashed lines denote the hydrogen bonding. Displacement ellipsoids are shown at the 30% probability level and H atoms are drawn as small circles of arbitrary radii. [Symmetry code: (i) $1-x$, $-y$, $1-z$.]
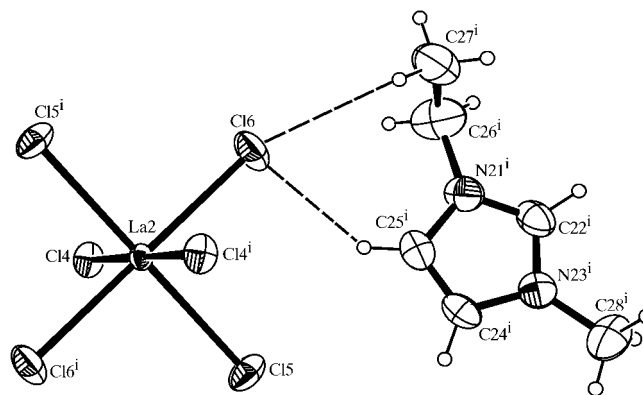
Figure 2
The molecular structure of the $[LaCl_6]^{3-}$ anion and EMI$^+$ cation around La2 in (I). The dashed lines denote the hydrogen bonding. Displacement ellipsoids are shown at the 30% probability level and H atoms are drawn as small circles of arbitrary radii. [Symmetry code: (i) $-x$, $-y$, $-z$.]

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side-chain alkyl groups and the Cl atoms in LaCl₆; for example, 2.86 for Cl1—H8b, 2.86 for Cl2(x, $-y-\frac{1}{2}$, $z-\frac{1}{2}$)··· H28c, 2.86 for Cl4($-x$, $y+\frac{1}{2}$, $-z+\frac{3}{2}$)···H8a and 2.86 Å for Cl6($-x$, $-y$, $1-z$)···H27b are short enough to allow the formation of a bond stronger than a van der Waals interaction. Bifurcation of C—H···Cl bonds is observed, namely, one ring H atom (H12) interacts with two Cl atoms [Cl4(x, $-y-\frac{1}{2}$, $z-\frac{1}{2}$) and Cl5($-x$, $y-\frac{1}{2}$, $-z+\frac{3}{2}$)] of LaCl₆.

In some EMI salts, a cation interacts with the neighboring cations *via* hydrogen bonds between the ring H atom and π-electron cloud. As a result of the compensation by Coulombic repulsion between the cations, the bonding is attenuated to the van der Waals interaction. A similar cation–cation interaction exists locally in the unit cell of the title compound, although the peculiar cation stacking through the crystal observed in other EMI salts (Wilkes & Zaworotko, 1992; Fuller *et al.*, 1994) is not observed. H24(x, $-y-\frac{1}{2}$, $z+\frac{1}{2}$) interacts with the π electrons on the imidazolium ring; the distance between the H atom and the ring is approximately 3.2 Å. Two imidazolium rings are not parallel to each other and the nearest distance between C and N atoms belonging to different rings [C24(x, $-y-\frac{1}{2}$, $z+\frac{1}{2}$) and N13] takes the sum of the van der Waals distances of C and N [3.371 (7) Å].

Experimental

Compound (I) was synthesized by recrystallization in an LaCl₃-saturated basic EMICl–AlCl₃ ionic liquid (40 mol% AlCl₃). LaCl₃ dissolves well in the basic system (Tsuda *et al.*, 2000). According to the results of thermogravimetric analysis and differential thermal analysis, compound (I) decomposes at around 600 K without melting. Rigid crystals of (I) were obtained from the basic system supersaturated by LaCl₃, and some grew into large blocks with a 10 mm edge length. A suitable crystal was mounted and sealed in a quartz capillary.

Crystal data

(C₆H₁₁N₂)₃[LaCl₆]	$D_x = 1.534$ Mg m⁻³
$M_r = 685.11$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 8989
$a = 15.566$ (10) Å	reflections
$b = 12.664$ (10) Å	$\theta = 1.3$–30.5°
$c = 15.046$ (2) Å	$\mu = 2.00$ mm⁻¹
$\beta = 90.46$ (6)°	$T = 293$ (2) K
$V = 2965.89$ (5) Å³	Block, colorless
$Z = 4$	0.25 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer	5505 reflections with $I > 2\sigma(I)$
CCD scans	$R_{int} = 0.039$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SORTAV*; Blessing (1995)	$h = 0 \rightarrow 20$
$T_{min} = 0.630$, $T_{max} = 0.671$	$k = 0 \rightarrow 16$
71 635 measured reflections	$l = -19 \rightarrow 19$
6823 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0112P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 5.1940P]$
$wR(F^2) = 0.086$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.38$	$(\Delta/\sigma)_{max} < 0.001$
6823 reflections	$\Delta\rho_{max} = 0.64$ e Å⁻³
283 parameters	$\Delta\rho_{min} = -0.60$ e Å⁻³
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Cl3ⁱⁱ	0.93	2.71	3.557 (8)	152
C4—H4···Cl4ⁱⁱⁱ	0.93	2.79	3.614 (6)	148
C8—H8a···Cl4ⁱⁱⁱ	0.96	2.86	3.766 (9)	157
C8—H8b···Cl1	0.96	2.86	3.584 (8)	133
C12—H12···Cl4ⁱ	0.93	2.78	3.612 (4)	150
C12—H12···Cl5ⁱᵛ	0.93	2.83	3.393 (4)	120
C14—H14···Cl2	0.93	2.80	3.636 (5)	150
C15—H15···Cl5	0.93	2.83	3.632 (5)	146
C22—H22···Cl3	0.93	2.79	3.479 (6)	132
C24—H24···Cl4ⁱ	0.93	2.88	3.693 (5)	147
C25—H25···Cl6ᵛ	0.93	2.82	3.565 (6)	138
C27—H27b···Cl6ᵛ	0.96	2.86	3.686 (8)	145
C28—H28c···Cl2ⁱ	0.96	2.86	3.729 (7)	151

Symmetry codes: (i) x, $-\frac{1}{2}-y$, $z-\frac{1}{2}$; (ii) $1-x$, $-y$, $1-z$; (iii) $-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$; (iv) $-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$; (v) $-x$, $-y$, $1-z$.

The space group was determined from the systematic extinctions. All the H atoms were refined using appropriate riding models, with C—H distances of 0.97 Å for CH₂, 0.96 Å for CH₃ and 0.93 Å for aromatic groups. The displacement parameters of H atoms were fixed at $1.2U_{eq}$ of their parent atoms ($1.5U_{eq}$ for methyl groups).

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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