

Poly[1-ethyl-3-methylimidazolium [tri- μ -chlorido-chromate(II)]]

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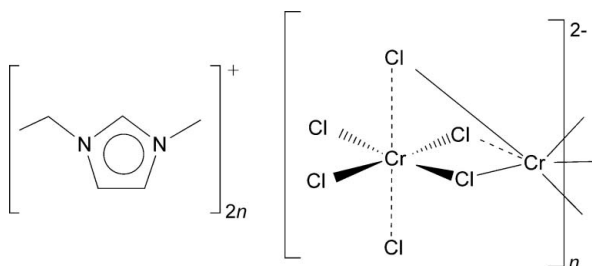
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 Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.026; wR factor = 0.064; data-to-parameter ratio = 15.5.

The title compound, $\{(\text{C}_6\text{H}_{11}\text{N}_2)[\text{CrCl}_3]\}_n$, was generated *via* mixing of the ionic liquid 1-ethyl-3-methylimidazolium chloride with CrCl_2 in ethanol. Crystals were obtained by a diffusion method. In the crystal structure, the anion forms one-dimensional chains of chloride-bridged Jahn–Teller distorted chromium(II) centers extending along the [100] direction. The imidazolium cations are positioned between these chains.

Related literature

For reference to this compound as a possible catalyst for the conversion of glucose to 5-hydroxymethylfurfural (HMF), see: Zhao *et al.* (2007). For the synthesis of the ammonium and tetramethylammonium analogs $[\text{NR}_4][\text{CrCl}_3]$ ($R = \text{H}, \text{CH}_3$), see Hardt & Streit (1970). For the crystal structures of $[\text{M}][\text{CrCl}_3]$, see: Bellitto *et al.* (1984) [$M = \text{N}(\text{CH}_3)_4$]; McPherson *et al.* (1972) ($M = \text{Cs}$); Crama *et al.* (1978) ($M = \text{Rb}, \text{Cs}$); Crama *et al.* (1979) ($M = \text{Rb}$); Crama & Zandbergen (1981) ($M = \text{Cs}$).



Experimental

Crystal data

 $(\text{C}_6\text{H}_{11}\text{N}_2)[\text{CrCl}_3]$
 $M_r = 269.52$

 Monoclinic, $P2_1/a$
 $a = 6.66150$ (10) Å

 $b = 16.4317$ (4) Å

 $c = 9.5258$ (2) Å

 $\beta = 95.6881$ (14)°

 $V = 1037.56$ (4) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 1.82$ mm⁻¹
 $T = 150$ (1) K

 $0.25 \times 0.20 \times 0.15$ mm

Data collection

Nonius KappaCCD diffractometer

Absorption correction: multi-scan

[DENZO-SMN (Otwinowski & Minor, 1997) with scaling algorithm from Fox & Holmes (1966)]

 $T_{\text{min}} = 0.659$, $T_{\text{max}} = 0.772$

4056 measured reflections

2384 independent reflections

 2082 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.064$
 $S = 1.08$

2384 reflections

154 parameters

All H-atom parameters refined

 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³
Table 1

Selected geometric parameters (Å, °).

Cr1—Cl2	2.3876 (5)	Cr1—Cl3	2.4431 (5)
Cr1—Cl1	2.3898 (5)	Cr1—Cl3 ⁱ	2.4476 (5)
Cl2—Cr1—Cl1	177.976 (19)	Cl1—Cr1—Cl3 ⁱ	89.027 (15)
Cl2—Cr1—Cl3	87.073 (15)	Cl3—Cr1—Cl3 ⁱ	176.95 (2)
Cl1—Cr1—Cl3	91.904 (16)	Cr1—Cl3—Cr1 ⁱⁱ	85.856 (13)
Cl2—Cr1—Cl3 ⁱ	91.906 (16)		

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

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: WinGX (Farrugia, 1999); software used to prepare material for publication: CrystalMaker (Palmer, 2005).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2146).

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supplementary materials

Acta Cryst. (2009). E65, m227 [doi:10.1107/S1600536809002281]

Poly[1-ethyl-3-methylimidazolium [tri- μ -chlorido-chromate(II)]]

J. J. Danford, A. M. Arif and L. M. Berreau

Comment

Recently it was shown that a solution of CrCl_2 in the ionic liquid 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) at 100°C will catalyze the conversion of glucose to 5-hydroxymethylfurfural (HMF) in 70% yield (Zhao *et al.*, 2007). The proposed active catalyst in this system is a compound formulated as [EMIM]CrCl₃. While alkali metal, ammonium, and tetramethyl ammonium chromium(II) trihalides have been previously reported in the literature (Hardt & Streit, 1970), the title compound is the first structurally characterized imidazolium analog.

The structure consists of infinite linear chains of Jahn–Teller-distorted chromium centers (Fig. 1) bridged by a facial array of chloride ligands (Fig. 2). Each Cr^{II} has four Cr—Cl bonds of σ 2.39–2.45 Å and two longer Cr—Cl interactions (2.87–2.91 Å). The Cr···Cr distance is 3.33 Å. The Cl—Cr—Cl bond angles are in the range of 87–90°. The shortest Cr···Cr distance between chains is 9.19 Å. A number of differences are evident in the structures of [EMIM]CrCl₃ (collected at 150 (1) K) and the previously reported [N(CH₃)₄]CrCl₃ (collected at room temperature; Bellitto *et al.*, 1984). Specifically, the chromium center in [EMIM]CrCl₃ has pseudo D_{4h} site symmetry whereas [N(CH₃)₄]CrCl₃ contains trigonally distorted chromium centers (C_{3v} site symmetry) positioned in alternating compressed and elongated face-sharing octahedra. Similar site symmetry to that found in [N(CH₃)₄]CrCl₃ was identified in the room temperature structure of α -CsCrCl₃, see: McPherson *et al.* (1972) and Crama & Zandbergen (1981). This C_{3v} site symmetry is described as resulting from randomly distributed elongation of Cr—Cl bonds along three principal axes of the octahedron.

Experimental

Under a N₂ atmosphere, a solution of CrCl₂ (23 mg, 0.19 mmol) in ethanol (2 ml) was added to solid 1-ethyl-3-methylimidazolium chloride (23 mg, 0.16 mmol). The resulting teal colored solution was stirred at ambient temperature until all of the solid had dissolved. Addition of ethyl acetate (2 ml), followed by diffusion of Et₂O, produced pale yellow crystals suitable for X-ray analysis.

Refinement

All H atoms were located and refined isotropically using *SHELXL97* (Sheldrick, 2008).

Figures

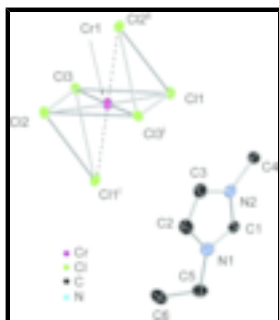


Fig. 1. A view of the coordination environment of the chromium center in the trichloridochromate(II) anion and the imidazolium cation with atom labelling for non-hydrogen atoms. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x - 1/2, -y + 1/2, z$; (ii) $x + 1/2, -y + 1/2, z$.]

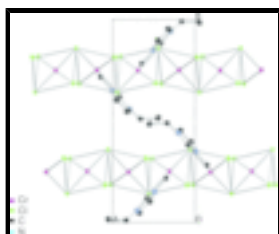


Fig. 2. A view of the one-dimensional chain structure of the trichloridochromate(II) anion extending along [100]. Included in the drawing are the four imidazolium cations within the cell. Displacement ellipsoids are drawn at the 50% probability level.

catena-Poly[1-ethyl-3-methylimidazolium [tri- μ -chlorido-chromate(II)]]

Crystal data

(C₆H₁₁N₂)[CrCl₃]

$M_r = 269.52$

Monoclinic, $P2_1/a$

$a = 6.66150(10) \text{ \AA}$

$b = 16.4317(4) \text{ \AA}$

$c = 9.5258(2) \text{ \AA}$

$\beta = 95.6881(14)^\circ$

$V = 1037.56(4) \text{ \AA}^3$

$Z = 4$

$F_{000} = 544$

$D_x = 1.725 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 8584 reflections

$\theta = 1.0\text{--}27.5^\circ$

$\mu = 1.82 \text{ mm}^{-1}$

$T = 150(1) \text{ K}$

Prism, yellow

$0.25 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Nonius KappaCCD
diffractometer

2384 independent reflections

Radiation source: fine-focus sealed tube

2082 reflections with $I > 2\sigma(I)$

Monochromator: graphite

$R_{\text{int}} = 0.018$

$T = 150(1) \text{ K}$

$\theta_{\text{max}} = 27.5^\circ$

φ and ω scans

$\theta_{\text{min}} = 2.5^\circ$

Absorption correction: multi-scan

[DENZO-SMN (Otwinowski & Minor, 1997) with
scaling algorithm from Fox & Holmes (1966)]

$h = -8 \rightarrow 8$

$T_{\text{min}} = 0.659, T_{\text{max}} = 0.772$

$k = -20 \rightarrow 21$

4056 measured reflections

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.6211P]$
$wR(F^2) = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{\max} < 0.001$
2384 reflections	$\Delta\rho_{\max} = 0.42 \text{ e } \text{\AA}^{-3}$
154 parameters	$\Delta\rho_{\min} = -0.48 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0064 (9)

Special details

Experimental. The program *DENZO-SMN* (Otwinowski & Minor, 1997) uses a scaling algorithm (Fox & Holmes, 1966) which effectively corrects for absorption effects. High redundancy data were used in the scaling program hence the 'multi-scan' code word was used. No transmission coefficients are available from the program (only scale factors for each frame). The scale factors in the experimental table are calculated from the 'size' command in the *SHELXL97* input file.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cr1	0.30848 (4)	0.251150 (16)	0.79201 (3)	0.01432 (10)
Cl1	0.09238 (6)	0.18418 (3)	0.61278 (4)	0.01959 (12)
Cl2	0.52336 (6)	0.31399 (3)	0.97636 (4)	0.01856 (12)
Cl3	0.55581 (5)	0.14110 (3)	0.79810 (4)	0.01695 (12)
N1	0.7020 (2)	0.05812 (10)	0.24223 (15)	0.0209 (3)
N2	0.4931 (2)	0.14965 (9)	0.30051 (15)	0.0191 (3)
C1	0.5869 (3)	0.11968 (12)	0.19414 (18)	0.0198 (4)
C2	0.6805 (3)	0.04791 (13)	0.3837 (2)	0.0301 (4)
C3	0.5517 (3)	0.10515 (13)	0.4202 (2)	0.0281 (4)
C4	0.3515 (3)	0.21791 (13)	0.2924 (2)	0.0243 (4)
C5	0.8379 (3)	0.01037 (13)	0.1611 (2)	0.0269 (4)
C6	1.0520 (3)	0.01492 (15)	0.2275 (3)	0.0339 (5)

supplementary materials

H1	0.574 (3)	0.1415 (13)	0.104 (2)	0.022 (5)*
H2	0.748 (4)	0.0075 (16)	0.435 (3)	0.043 (7)*
H3	0.508 (4)	0.1180 (16)	0.506 (3)	0.044 (7)*
H4A	0.350 (5)	0.2419 (19)	0.206 (4)	0.071 (10)*
H4B	0.236 (5)	0.1996 (19)	0.309 (3)	0.068 (9)*
H4C	0.384 (4)	0.2545 (18)	0.356 (3)	0.059 (9)*
H5A	0.829 (4)	0.0344 (15)	0.067 (3)	0.042 (7)*
H5B	0.787 (4)	-0.0452 (16)	0.156 (2)	0.040 (6)*
H6A	1.142 (4)	-0.0168 (17)	0.176 (3)	0.047 (7)*
H6B	1.061 (3)	-0.0057 (16)	0.319 (3)	0.040 (7)*
H6C	1.099 (4)	0.0705 (19)	0.240 (3)	0.059 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.01154 (15)	0.01684 (18)	0.01412 (15)	0.00097 (10)	-0.00098 (10)	-0.00138 (10)
Cl1	0.0171 (2)	0.0254 (3)	0.0157 (2)	-0.00134 (16)	-0.00144 (15)	-0.00269 (16)
Cl2	0.0179 (2)	0.0211 (2)	0.0160 (2)	-0.00030 (15)	-0.00131 (15)	-0.00306 (16)
Cl3	0.0136 (2)	0.0164 (2)	0.0207 (2)	-0.00014 (14)	0.00140 (15)	-0.00127 (15)
N1	0.0225 (7)	0.0204 (8)	0.0203 (7)	-0.0013 (6)	0.0042 (6)	0.0004 (6)
N2	0.0186 (7)	0.0226 (8)	0.0161 (7)	-0.0017 (6)	0.0011 (5)	-0.0013 (6)
C1	0.0210 (8)	0.0225 (9)	0.0161 (8)	-0.0027 (7)	0.0021 (7)	-0.0006 (7)
C2	0.0343 (10)	0.0329 (12)	0.0234 (9)	0.0053 (9)	0.0043 (8)	0.0090 (9)
C3	0.0303 (10)	0.0373 (12)	0.0172 (9)	0.0022 (9)	0.0043 (7)	0.0039 (8)
C4	0.0195 (9)	0.0278 (11)	0.0256 (10)	0.0013 (8)	0.0027 (7)	-0.0044 (9)
C5	0.0284 (10)	0.0215 (10)	0.0321 (10)	-0.0001 (8)	0.0087 (8)	-0.0030 (8)
C6	0.0277 (11)	0.0314 (13)	0.0434 (13)	0.0049 (9)	0.0072 (9)	0.0024 (10)

Geometric parameters (\AA , $^\circ$)

Cr1—Cl2	2.3876 (5)	C2—H2	0.91 (3)
Cr1—Cl1	2.3898 (5)	C3—H3	0.91 (3)
Cr1—Cl3	2.4431 (5)	C4—H4A	0.91 (3)
Cr1—Cl3 ⁱ	2.4476 (5)	C4—H4B	0.86 (3)
N1—C1	1.323 (2)	C4—H4C	0.86 (3)
N1—C2	1.380 (2)	C5—C6	1.503 (3)
N1—C5	1.473 (2)	C5—H5A	0.97 (2)
N2—C1	1.336 (2)	C5—H5B	0.97 (3)
N2—C3	1.378 (2)	C6—H6A	0.96 (3)
N2—C4	1.463 (3)	C6—H6B	0.93 (3)
C1—H1	0.93 (2)	C6—H6C	0.97 (3)
C2—C3	1.342 (3)		
Cl2—Cr1—Cl1	177.976 (19)	C2—C3—H3	131.2 (17)
Cl2—Cr1—Cl3	87.073 (15)	N2—C3—H3	121.7 (17)
Cl1—Cr1—Cl3	91.904 (16)	N2—C4—H4A	109 (2)
Cl2—Cr1—Cl3 ⁱ	91.906 (16)	N2—C4—H4B	108 (2)
Cl1—Cr1—Cl3 ⁱ	89.027 (15)	H4A—C4—H4B	113 (3)
Cl3—Cr1—Cl3 ⁱ	176.95 (2)	N2—C4—H4C	112 (2)

Cr1—C13—Cr1 ⁱⁱ	85.856 (13)	H4A—C4—H4C	108 (3)
C1—N1—C2	108.55 (16)	H4B—C4—H4C	106 (3)
C1—N1—C5	126.20 (16)	N1—C5—C6	111.08 (17)
C2—N1—C5	125.20 (17)	N1—C5—H5A	106.3 (14)
C1—N2—C3	108.45 (16)	C6—C5—H5A	109.7 (14)
C1—N2—C4	126.18 (16)	N1—C5—H5B	107.4 (14)
C3—N2—C4	125.37 (15)	C6—C5—H5B	112.2 (14)
N1—C1—N2	108.52 (15)	H5A—C5—H5B	110 (2)
N1—C1—H1	127.8 (13)	C5—C6—H6A	111.9 (15)
N2—C1—H1	123.6 (13)	C5—C6—H6B	110.2 (15)
C3—C2—N1	107.38 (18)	H6A—C6—H6B	107 (2)
C3—C2—H2	131.7 (16)	C5—C6—H6C	112.4 (17)
N1—C2—H2	121.0 (16)	H6A—C6—H6C	111 (2)
C2—C3—N2	107.08 (16)	H6B—C6—H6C	104 (2)
C12—Cr1—C13—Cr1 ⁱⁱ	-48.298 (16)	C5—N1—C2—C3	176.88 (18)
C11—Cr1—C13—Cr1 ⁱⁱ	133.450 (13)	N1—C2—C3—N2	0.6 (2)
C2—N1—C1—N2	0.4 (2)	C1—N2—C3—C2	-0.4 (2)
C5—N1—C1—N2	-177.10 (16)	C4—N2—C3—C2	179.39 (18)
C3—N2—C1—N1	0.0 (2)	C1—N1—C5—C6	121.0 (2)
C4—N2—C1—N1	-179.80 (17)	C2—N1—C5—C6	-56.1 (3)
C1—N1—C2—C3	-0.7 (2)		

Symmetry codes: (i) $x-1/2, -y+1/2, z$; (ii) $x+1/2, -y+1/2, z$.

Fig. 1

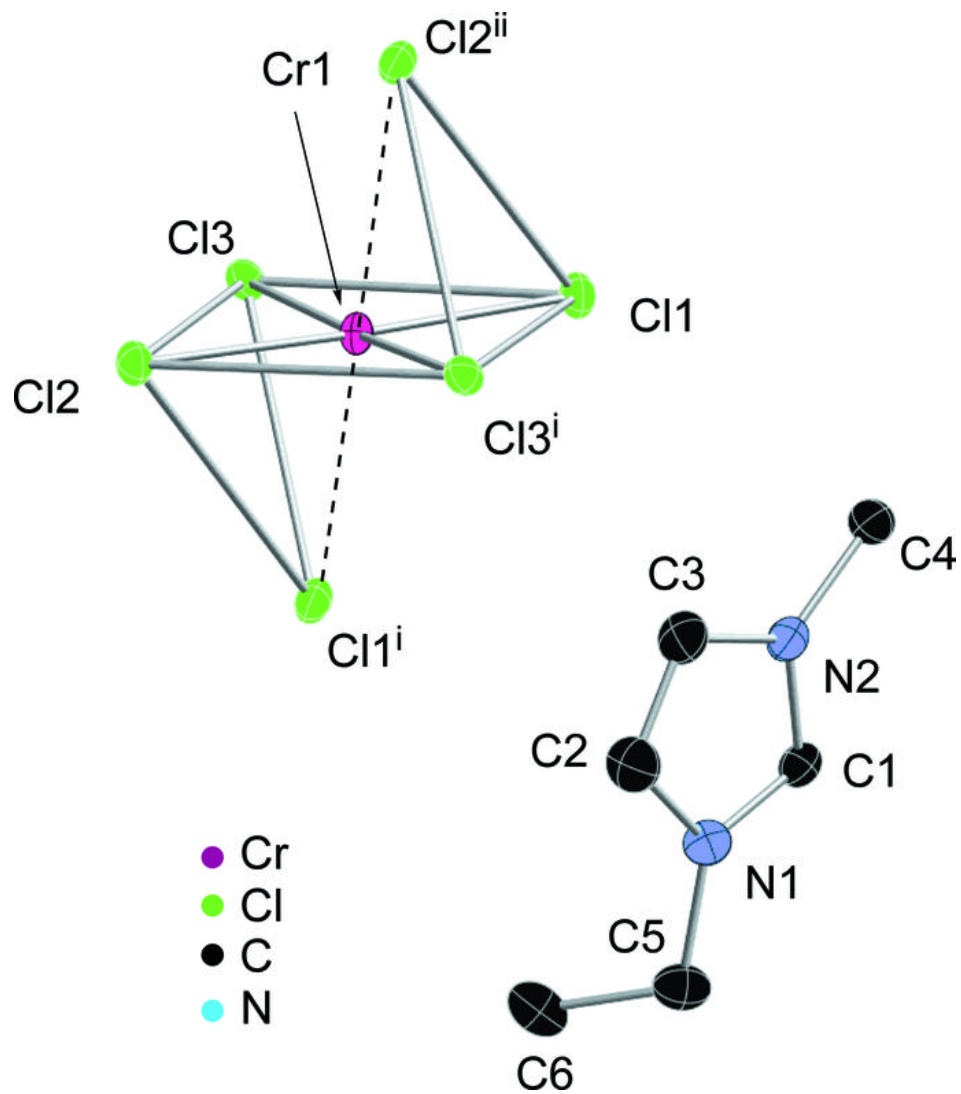


Fig. 2

