

Strong hydrogen bonds in the ionic pair (1,3-diisopropyl-4,5-dimethyl-4-imidazolin-2-ylidene)ammonium trichloro(1,3-diisopropyl-4,5-dimethyl-4-imidazolin-2-ylidene-amine)iron(II)

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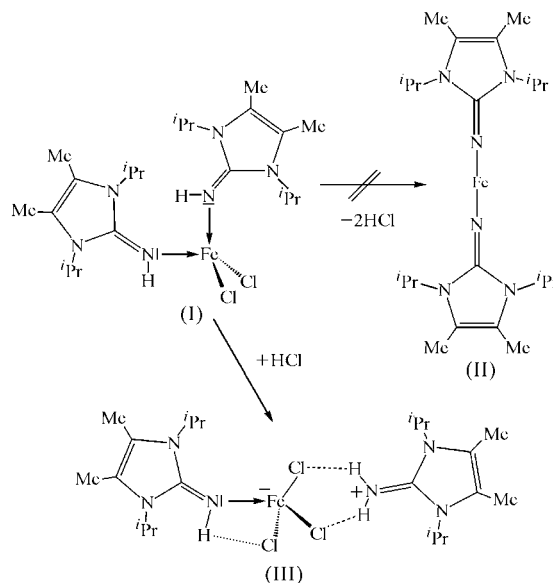
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The title compound, $(C_{11}H_{22}N_3)[FeCl_3(C_{11}H_{21}N_3)]$, is one of the rare examples where an isolated ionic pair of the type $[A]^{n+}[EMX_3]^{n-}$ (E is any non-metal, M is any transition metal and X is any halogen) could be structurally characterized. Two short $N-H\cdots Cl$ contacts between the two ammonium H atoms and two of the three Cl atoms of the counter-anion generate a six-membered ring. The third Cl atom is involved in a weaker intramolecular hydrogen bond to the neutral 1,3-diisopropyl-4,5-dimethyl-4-imidazolin-2-ylideneamine ligand.

Comment

Over the past decade, the coordination chemistry of phosphoraneiminate ligands, R_3PN^- , has developed into a broad area of research which has produced a large number of structurally diverse main group element and transition metal complexes (Dehnicke & Strähle, 1989; Dehnicke & Weller, 1997; Dehnicke *et al.*, 1999; Dehnicke & Greiner, 2003). Based on the striking similarity between electron-rich organophosphanes and nucleophilic carbenes of the imidazolin-2-ylidene type, formal replacement of phosphane by an imidazolin-2-ylidene moiety in phosphoraneimides gives imidazolin-2-imides. The ability of an imidazolium ring to stabilize a positive charge in a more effective manner than a phosphonium group should increase the negative charge on the N atom, and thus lead to the formation of ligands with enhanced basicity and electron-donating capacity. Recently, we have published (Tamm *et al.*, 2004, 2006) examples of titanium complexes bearing imidazolin-2-iminate ligands which proved to be very active and long-lived catalysts for

ethylene polymerization. Due to the capability of phosphoraneimides and imidazolin-2-imides to act as $2\sigma,4\pi$ -electron donors, these anionic ligands can be regarded as monodentate analogues of cyclopentadienyls, $C_5R_5^-$, and this relationship has been described as a pseudo-isolobal phenomenon (Diefenbach & Bickelhaupt, 1999). In that respect, monomeric bis(imidazolin-2-iminate) transition metal complexes can be regarded as metallocene analogues, and therefore, we intended to synthesize the complex bis(imidazolin-2-imine)iron(II) chloride, (I), which could be converted into the corresponding bis(imidazolin-2-iminato)iron(II), (II), by the loss of two equivalents of HCl. Surprisingly, the reaction of two equivalents of 1,3-diisopropyl-4,5-dimethylimidazolin-2-imine with $FeCl_2$ did not result in the formation of the expected bis(imidazolin-2-imine)iron(II) chloride, but instead furnished the title HCl adduct, $[ImNH_2]^+[(ImNH)Fe^{II}Cl_3]^-$ (where ImNH is 1,3-diisopropyl-4,5-dimethyl-4-imidazolin-2-ylideneamine, (III)).



As the most prominent feature in the solid-state structure of (III), one strong $N4-H2\cdots Cl1$ hydrogen bond [3.173 (2) Å] and one weaker $N4-H3\cdots Cl2$ hydrogen bond [3.379 (2) Å] connect the cation and the anion to form an ion pair (Fig. 1 and Table 2). No other short intramolecular contacts are observed. This hydrogen-bonding type is unique within complexes of the formula $[A]^{n+}[EMX_3]^{n-}$ (E is any non-metal, M is any transition metal and X is any halogen) or zwitterionic salts such as [(1-methylpiperazin-1-ium- κN^4) $Co^{II}Cl_3$] or [(1,4-dimethylpiperazin-1-ium- κN^4) $Zn^{II}Cl_3$]. The latter salt exhibits a linear assembly in the crystal structure (Clemente *et al.*, 2002), whereas the cobalt complex forms a layer structure *via* hydrogen bonds (Clemente *et al.*, 1999). All other such compounds build up a three-dimensional network of hydrogen bonds, for example, in bis[*N,N*-dimethyl-*N'*-(3-chlorophenyl)guanidinium] tetrachlorocopper(II) (Davydov *et al.*, 1992) or bis(1,1-dimethylguanidinium) tetrachlorocopper(II) (Fernandez *et al.*, 1997).

The Fe^{II} ion of (III) is tetrahedrally coordinated by three Cl atoms and the imine N atom (Fig. 1). The tetrahedral coord-

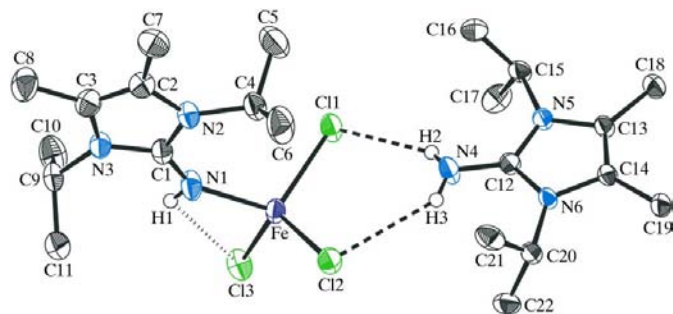


Figure 1
A perspective view of (III) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

dination is rather distorted (Table 1), as can be seen by the Cl3–Fe–N1 angle of 95.58 (6)°, with a deviation of about 14° from the ideal tetrahedral value of 109.5°. The mean Fe–Cl distance [2.3084 (6) Å] fits exactly to the mean value of 2.314 (2) Å found for 21 mononuclear [FeCl₄]²⁻ tetrahedral complexes found in the Cambridge Structural Database (CSD, Version 5.26; Allen, 2002). Comparable complexes having a 3Cl+1N ligand set are not currently known (0 hits in the CSD). Effects responsible for such a conspicuous deviation are packing effects and a possible Jahn–Teller effect, as well as strong hydrogen bonds (Weller & Petz, 1994). In addition, the third contact, a non-classical (N1–H1)···Cl3 agostic contact [3.229 (2) Å], has to be considered.

Experimental

The title compound was prepared by the reaction of 1,3-diisopropyl-4,5-dimethyl-4-imidazolin-2-imine (0.185 g, 0.947 mmol) with FeCl₂ (0.060 g, 0.473 mmol) in tetrahydrofuran (20 ml). After stirring the reaction mixture for 10 h at ambient temperature, the product was precipitated with an excess of *n*-hexane, filtered off and washed several times with *n*-hexane. Prolonged drying *in vacuo* afforded 0.165 g of the title compound as a yellow solid (yield 63%). Elemental analysis calculated for [ImNH₂]⁺[(ImNH)Fe^{II}Cl₃]⁻: C 47.71, H 7.83, N 15.17%; found: C 47.85, H 7.90, N 15.01%. Crystals of (III) could be obtained selectively as clear yellow prisms by diffusion of *n*-hexane into a tetrahydrofuran solution.

Crystal data

(C ₁₁ H ₂₂ N ₃)[FeCl ₃ (C ₁₁ H ₂₁ N ₃)]	Mo K α radiation
<i>M_r</i> = 553.82	Cell parameters from 2997 reflections
Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	θ = 2.2–25.3°
<i>a</i> = 9.6108 (1) Å	μ = 0.84 mm ⁻¹
<i>b</i> = 9.6349 (1) Å	<i>T</i> = 173 (1) K
<i>c</i> = 30.6453 (3) Å	Prism, yellow
<i>V</i> = 2837.73 (5) Å ³	0.60 × 0.51 × 0.46 mm
<i>Z</i> = 4	
<i>D_x</i> = 1.296 Mg m ⁻³	

Data collection

Nonius KappaCCD area-detector diffractometer	5193 independent reflections
φ and ω scans	4875 reflections with <i>I</i> > 2 σ (<i>I</i>)
Absorption correction: multi-scan (DENZO-SMN; Otwinowski & Minor, 1997)	<i>R</i> _{int} = 0.040
<i>T</i> _{min} = 0.582, <i>T</i> _{max} = 0.677	θ _{max} = 25.3°
56451 measured reflections	<i>h</i> = -11 → 11
	<i>k</i> = -11 → 11
	<i>l</i> = -36 → 36

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (F_o^2)^2 + (0.0251P)^2 + 0.7647P]$
$R[F^2 > 2\sigma(F^2)] = 0.025$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.055$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.07	$\Delta\rho$ _{max} = 0.37 e Å ⁻³
5193 reflections	$\Delta\rho$ _{min} = -0.24 e Å ⁻³
461 parameters	Absolute structure: Flack (1983),
All H-atom parameters refined	with 2223 Friedel pairs
Weighting scheme based on measured s.u.'s	Flack parameter: 0.001 (11)

Table 1

Selected geometric parameters (Å, °).

Fe–Cl1	2.3109 (6)	N3–C3	1.407 (3)
Fe–Cl2	2.3053 (6)	N3–C9	1.477 (3)
Fe–Cl3	2.3091 (7)	N4–C12	1.338 (3)
Fe–N1	2.0445 (19)	N5–C13	1.410 (2)
N1–C1	1.305 (3)	N5–C12	1.346 (2)
N2–C1	1.372 (3)	N5–C15	1.483 (2)
N2–C2	1.415 (3)	N6–C14	1.410 (2)
N2–C4	1.472 (3)	N6–C20	1.485 (2)
N3–C1	1.371 (3)	N6–C12	1.350 (2)
Cl1–Fe–Cl2	108.86 (2)	Cl2–Fe–N1	110.88 (6)
Cl1–Fe–Cl3	110.00 (2)	Cl3–Fe–N1	95.58 (6)
Cl1–Fe–N1	111.21 (6)	Fe–N1–C1	145.14 (16)
Cl2–Fe–Cl3	119.69 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N4–H2···Cl1	0.80 (3)	2.47 (3)	3.173 (2)	147 (3)
N4–H3···Cl2	0.753 (19)	2.739 (19)	3.379 (2)	144.2 (19)
N1–H1···Cl3	0.75 (3)	2.89 (2)	3.229 (2)	111 (2)

The final difference Fourier map shows no striking features. All H atoms could be located in the difference Fourier maps and were allowed to refine freely.

Data collection: *KappaCCD Control Software* (Nonius, 2001); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1998); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3010). Services for accessing these data are described at the back of the journal.

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