Crystal structure of bis(2,2′-biimidazol-1-ium) tetrachloroferrate(III) chloride, $(C_6H_7N_4)_2[FeCl_4]Cl$

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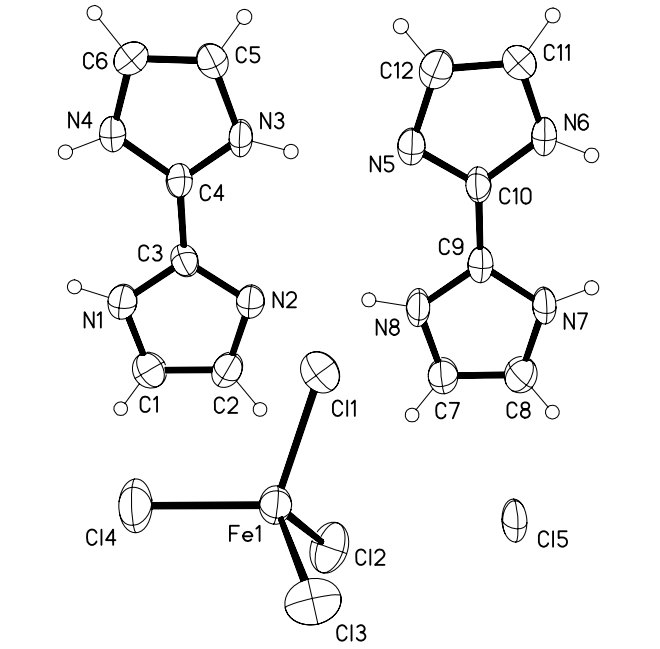

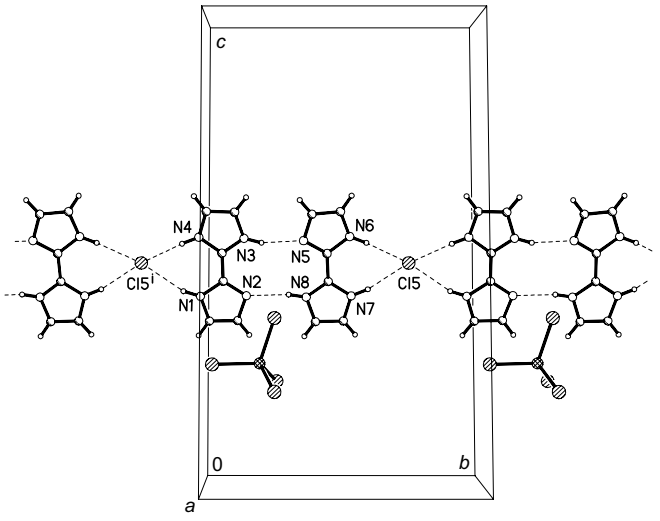

Abstract

$C_{12}H_{14}Cl_5FeN_8$, monoclinic, $P12_1/c1$ (no. 14), a = 7.1902(5) Å, b = 12.7155(9) Å, c = 21.753(2) Å, β = 96.405(1)°, V = 1976.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.085, $wR_{ref}(F^2)$ = 0.166, T = 298 K.

Source of material

2,2′-Biimidazole (2 mmol, 0.28 g) was suspended in 30 mL water. To the resulting suspension was added trichloroferrate(III) (1 mmol, 0.16 g), an then concentrated aqueous trichloroacetic acid was added until the suspension became clear. The resulting solution was filtered and allowed to evaporate slowly at room temperature. After four weeks, yellow crystals were obtained.

Experimental details

All H atoms bonded to N atoms were located from Fourier difference density maps and refined with N—H distances restrained to 0.85(2) Å, and with $U_{iso} = 1.2U_{eq}$(parent atom). The other H atoms were positioned geometrically and allowed to ride on their parent atoms at C—H distances of 0.93 Å with $U_{iso} = 1.2U_{eq}$(parent atom). The anisotropic crystal dimensions and the poor crystal quality resulted in high R values.

Discussion

Directional intermolecular interactions are the primary tool in assembling supramolecular intriguing structures and hydrogen bonding is currently the best among them [1-2]. 2,2′-biimidazole (H_2biim) is an excellent candidate for the development of supramolecular networks by the aforementioned interactions in crystals and not only a proton donor, but also a proton acceptor, so that it can assume five possible forms: mono-deprotonated (monoanion, Hbiim$^-$), di-deprotonated (dianion, biim^{2-}), non-deprotonated (neutral, H_2biim), mono-protonated (monocation, H_3biim$^+$) or di-protonated (dication, H_4biim^{2+}). Several supramolecular motifs assembled by H_2biim, such as monomeric hydrogen-bonded motifs $R_2^2(10)$ [3], heteromeric hydrogen-bonded motifs $R_2^2(9)$ [4] and $R_2^1(7)$ [5] as well as mixed hydrogen-bonded motifs $R_2^2(10)$ and $R_2^1(7)$ [6] have been structurally described. To extend this research, the title compound was prepared and its crystal structure determined.

The title crystal structure consists of two H_3biim$^+$ monocations, a tetrachloroferrate(III) and a chloride anion (figure, top). The bond distances and angles of the mono-protonated H_3biim$^+$ are unexceptional and compare well with the neutral H_2biim [3]. The two rings are almost coplanar to each other in both molecules. The dihedral angle between the two five-membered rings in the neutral H_2biim is 4.6°, but those in the two independent H_3biim$^+$ cations are 3.89(3)° and 5.59(3)°. Two N–H···N hydrogen bonds connect two H_3biim$^+$ cations to produce a dimer, and two adjacent dimers are linked into a linear chain by N1–H1N···Cl5^i and N4–H4N···Cl5^i (i: x,y–1,z) hydrogen bonds (figure, bottom). The hydrogen bonding pattern can be described in graph-set motif notation [7-9] as $R_2^2(10)$ and $R_2^1(7)$.

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Table 1. Data collection and handling.

Crystal:	yellow block, size 0.08 × 0.09 × 0.27 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	14.54 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD, φ/ω
$2\theta_{max}$:	50.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	19027, 3584
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3134
$N(param)_{refined}$:	253
Programs:	SHELXS-97 [10], SHELXL-97 [11], SHELXTL [12]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1N)	4*e*	0.113(9)	–0.091(2)	0.405(3)	0.046
H(3N)	4*e*	0.289(9)	0.203(2)	0.512(3)	0.043
H(4N)	4*e*	0.270(9)	–0.092(2)	0.510(3)	0.041
H(6N)	4*e*	0.267(9)	0.592(2)	0.512(3)	0.042
H(7N)	4*e*	0.106(9)	0.600(2)	0.409(3)	0.045
H(8N)	4*e*	0.106(9)	0.303(2)	0.398(3)	0.044
H(1)	4*e*	–0.0402	–0.0386	0.3058	0.055
H(2)	4*e*	–0.0306	0.1537	0.3071	0.050
H(5)	4*e*	0.4456	0.1478	0.6094	0.050
H(6)	4*e*	0.4179	–0.0436	0.6123	0.047
H(7)	4*e*	–0.0427	0.3622	0.3038	0.052
H(8)	4*e*	–0.0464	0.5545	0.3074	0.054
H(11)	4*e*	0.4226	0.5345	0.6133	0.047
H(12)	4*e*	0.4447	0.3442	0.6036	0.053

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	4*e*	0.4925(1)	0.19960(7)	0.25667(4)	0.0407(5)	0.0264(5)	0.0356(5)	0.0021(4)	–0.0015(4)	0.0003(4)
Cl(1)	4*e*	0.5453(3)	0.2531(1)	0.35283(8)	0.092(1)	0.0374(9)	0.041(1)	–0.005(1)	0.0025(9)	–0.0076(8)
Cl(2)	4*e*	0.2248(2)	0.2587(1)	0.21219(9)	0.0391(9)	0.043(1)	0.072(1)	0.0065(8)	–0.0007(8)	0.0123(9)
Cl(3)	4*e*	0.7165(2)	0.2544(2)	0.20347(8)	0.0412(9)	0.071(1)	0.048(1)	–0.0018(9)	0.0025(8)	0.0053(9)
Cl(4)	4*e*	0.4875(3)	0.0284(1)	0.25441(9)	0.102(2)	0.0278(9)	0.064(1)	0.005(1)	–0.020(1)	–0.0050(9)
Cl(5)	4*e*	0.1620(3)	0.7524(1)	0.46767(8)	0.075(1)	0.0174(7)	0.055(1)	0.0000(8)	–0.0022(9)	–0.0019(7)
N(1)	4*e*	0.0919(8)	–0.0282(4)	0.3939(2)	0.052(3)	0.026(3)	0.037(3)	0.000(3)	0.000(3)	0.002(2)
N(2)	4*e*	0.0990(7)	0.1443(4)	0.3954(2)	0.047(3)	0.023(3)	0.033(3)	0.000(2)	–0.002(2)	0.001(2)
N(3)	4*e*	0.3045(8)	0.1385(4)	0.5217(2)	0.051(3)	0.015(3)	0.040(3)	0.001(2)	–0.004(2)	0.000(2)
N(4)	4*e*	0.2827(7)	–0.0293(4)	0.5240(2)	0.046(3)	0.020(3)	0.036(3)	0.002(2)	0.002(2)	–0.001(2)
N(5)	4*e*	0.3042(7)	0.3585(4)	0.5166(2)	0.046(3)	0.021(3)	0.039(3)	0.001(2)	0.000(2)	0.000(2)
N(6)	4*e*	0.2847(7)	0.5294(4)	0.5255(2)	0.046(3)	0.017(3)	0.042(3)	–0.001(2)	0.004(3)	0.000(2)
N(7)	4*e*	0.0947(8)	0.5376(4)	0.3950(2)	0.053(3)	0.017(3)	0.041(3)	0.002(2)	0.000(3)	–0.001(2)
N(8)	4*e*	0.0903(8)	0.3690(4)	0.3922(2)	0.047(3)	0.017(2)	0.044(3)	0.002(2)	–0.001(2)	0.000(2)
C(1)	4*e*	0.010(1)	0.0038(5)	0.3383(3)	0.062(5)	0.034(4)	0.039(4)	–0.010(3)	–0.001(3)	–0.005(3)
C(2)	4*e*	0.0156(9)	0.1102(5)	0.3396(3)	0.056(4)	0.029(4)	0.038(4)	–0.001(3)	–0.002(3)	0.007(3)
C(3)	4*e*	0.1464(8)	0.0582(4)	0.4274(3)	0.031(3)	0.023(3)	0.032(3)	0.000(2)	0.002(3)	–0.005(3)
C(4)	4*e*	0.2418(8)	0.0557(4)	0.4893(3)	0.034(3)	0.022(3)	0.034(3)	0.007(3)	0.005(3)	0.000(3)
C(5)	4*e*	0.3887(9)	0.1052(5)	0.5780(3)	0.059(4)	0.029(4)	0.035(3)	0.007(3)	–0.004(3)	–0.006(3)
C(6)	4*e*	0.3742(9)	0.0004(5)	0.5796(3)	0.051(4)	0.034(4)	0.031(3)	0.005(3)	–0.002(3)	0.005(3)
C(7)	4*e*	0.006(1)	0.4040(5)	0.3368(3)	0.059(4)	0.028(3)	0.039(4)	–0.002(3)	–0.007(3)	–0.001(3)
C(8)	4*e*	0.005(1)	0.5094(5)	0.3385(3)	0.059(5)	0.033(4)	0.040(4)	0.010(3)	–0.008(3)	0.003(3)
C(9)	4*e*	0.1456(8)	0.4512(4)	0.4269(3)	0.030(3)	0.019(3)	0.039(3)	0.001(2)	0.006(3)	0.000(2)
C(10)	4*e*	0.2422(8)	0.4460(4)	0.4886(3)	0.037(3)	0.018(3)	0.037(3)	–0.004(3)	0.005(3)	–0.001(3)
C(11)	4*e*	0.3767(9)	0.4942(5)	0.5792(3)	0.053(4)	0.032(4)	0.032(3)	–0.003(3)	0.001(3)	–0.004(3)
C(12)	4*e*	0.388(1)	0.3893(5)	0.5735(3)	0.056(4)	0.032(4)	0.043(4)	–0.002(3)	–0.002(3)	0.006(3)

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