

Dichloro(methanol- κ O)[(methoxy)-tris(1-methyl-1*H*-imidazol-2-yl)-methane- κ^2 N³]iron(II) (ca 153 K)

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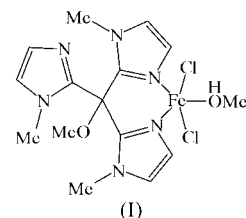
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In the quasi-trigonal-bipyramidal environment of the five-coordinate Fe^{II} atom in the title compound, [FeCl₂(C₁₄H₁₈N₆O)(CH₄O)], the methanol and one of the N-atom donors of the potentially tridentate ligand are disposed axially: Fe–N(axial) is 2.149 (2) Å, Fe–N(equatorial) is 2.108 (2) Å and N–Fe–O is 174.14 (7)°.

Comment

Tris(1-methyl-1*H*-imidazol-2-yl)methanol, (mim)₃COH, is a well known ligand displaying tridentate capability, as described in our accompanying paper [Batten *et al.*, 2004a; see references therein for examples in association with iron(II)]. Less well known is the counterpart ligand described here, in which the hydroxyl H atom is replaced by a methyl group, thus changing the bridgehead functionality to an ether rather than an alcohol. In association with iron(II), examples have been described in which (mim)₃COH behaves in a bidentate or tridentate fashion; in contrast, with the present ligand, all examples hitherto structurally characterized appear to have been solely bidentate. Some examples of complexes containing metals other than Fe are copper(I) (Sorrell & Borovik, 1987), copper(II) (Stibrany *et al.*, 1996) and palladium(II) (R  ther *et al.*, 2001), wherein the particular metal ions concerned commonly exhibit predilections for relatively low coordination numbers. In the copper(I) and palladium(II) complexes, the ligand, although three-coordinate, achieves that status by virtue of the third donor bridging in a binuclear array. In extending its coordination chemistry, we had it in mind to prepare a mononuclear species in which it was tridentate, and, given the facility with which this is achieved about iron(II) by reaction of (mim)₃COH with the metal(II) chloride, the latter was reacted with the present ligand in

methanol solution in a similar manner, and the resulting yellow crystals of the title compound, (I), were subjected to a single-crystal diffraction study, the results of which are reported here.



The results of the X-ray study are consistent with formulation of the material as (I) (Fig. 1), with one formula unit (a neutral molecule), devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. Remarkably, the iron(II) environment is quasi-trigonal-bipyramidal five-coordinate, the ligand being two- rather than three-coordinate, with one of the N-atom donors (N11) axial and *trans* to the methanol O atom. Interestingly, Fe–N11 is longer than Fe–N21 (Table 1), despite the latter lying on an equatorial site, normally considered as less ‘crowded’ and accommodating ‘bulky’ ligands or lone pairs. The five-coordinate geometry, although unusual, is similar to that reported for iron(II) complexes of planar tridentate N-donor ligands, *e.g.* FeCl₂[2,6-(ArNHCH₂)₂C₅H₃N] (Ar is 2,6-Pr^t-C₆H₃; Britovsek *et al.*, 2001).

The overall result is curious in a number of other aspects. The multidentate ligand occupies only two coordination sites, despite the obvious facility of the metal ion to accommodate similar tridentate ligands in a six-coordinate environment. Further, as the following paper shows, the presence of a pair of Cl[−] ligands about the same metal ion does not preclude the attainment of six-coordination in the presence of two rather similar *N,N'*-bidentate ligands (Batten *et al.*, 2004b). While the sample size thus far is limited, we conjecture that the presence of the methyl group (rather than hydroxyl) at the ligand bridgehead may confer some degree of control on the relative disposition of the three heterocycles, precluding a tridentate conformation. We note the disposition of the uncoordinated

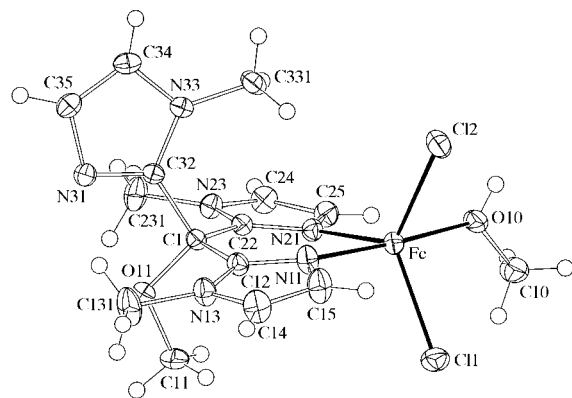


Figure 1
A view of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have arbitrary radii of 0.1 Å.

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heterocycle, with the substituent directed 'inwards' toward the metal, possibly precluding six-coordination, and the inherent crowding about the ether grouping if the opposite disposition (in coordinating mode) is adopted. The present disposition is presumably assisted by the intermolecular hydrogen-bond from a neighbouring methanol hydroxyl group (Table 2). A further point of possible relevance is the quasi-planarity of the chelate ring [χ^2 for the C_3N_2Fe ring is 3475, with deviations for atoms C1, C12, C22, N11, N21 and Fe of -0.032 (3), 0.104 (2), -0.044 (4), -0.072 (8), 0.043 (2) and -0.104 (3) Å, respectively. The interplanar dihedral angles to the coordinated imidazole C_3N_2 planes are 12.24 (9) and 3.71 (9) $^\circ$, and the dihedral between the pair of coordinated imidazole C_3N_2 planes is 15.1 (1) $^\circ$.

Experimental

A solution of (mim)₃COMe (0.057 g, 0.20 mmol) in methanol (5 ml) was added to a stirred solution of iron(II) chloride (0.029 g, 0.23 mmol) in methanol (5 ml). Diethyl ether (65 ml) was allowed to diffuse into the pale-yellow solution. After 1 d, a small amount of a colourless precipitate formed; the yellow supernatant was cannula filtered and light petroleum (313–333 K, 70 ml) was added. After 2 d, a yellow crystalline material was obtained. This was cannula filtered and the yellow crystals of (I) were washed with diethyl ether (3 × 2 ml).

Crystal data

[FeCl₂(C₁₄H₁₈N₆O)(CH₄O)]
 $M_r = 445.13$
 Monoclinic, $P2_1/n$
 $a = 9.8803$ (8) Å
 $b = 16.329$ (1) Å
 $c = 12.246$ (1) Å
 $\beta = 101.953$ (2) $^\circ$
 $V = 1932.9$ (3) Å³
 $Z = 4$

$D_x = 1.53$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 8192 reflections
 $\theta = 2.5$ – 37.3 $^\circ$
 $\mu = 1.08$ mm⁻¹
 $T = 150$ (2) K
 Prism, yellow
 $0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.572$, $T_{\max} = 0.806$
 39 725 measured reflections

10 108 independent reflections
 6646 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.063$
 $\theta_{\text{max}} = 37.6$ $^\circ$
 $h = -16 \rightarrow 16$
 $k = -27 \rightarrow 27$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
 $R(F) = 0.054$
 $wR(F^2) = 0.157$
 $S = 1.11$
 6646 reflections
 239 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F^2) + 2.6F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.01$
 $\Delta\rho_{\text{max}} = 1.77$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.78$ e Å⁻³

Table 1

Selected geometric parameters (Å, $^\circ$).

Fe—Cl1	2.3246 (7)	Fe—N21	2.1080 (18)
Fe—Cl2	2.3290 (6)	Fe—O10	2.242 (2)
Fe—N11	2.149 (2)		
Cl1—Fe—Cl2	126.09 (3)	Cl2—Fe—N21	119.66 (5)
Cl1—Fe—N11	93.80 (6)	Cl2—Fe—O10	86.77 (5)
Cl1—Fe—N21	114.14 (5)	N11—Fe—N21	84.22 (8)
Cl1—Fe—O10	90.05 (5)	N11—Fe—O10	174.14 (7)
Cl2—Fe—N11	94.50 (6)	N21—Fe—O10	90.17 (7)

Table 2

Hydrogen-bonding geometry (Å, $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O10—H10 \cdots N31 ⁱ	0.85 (5)	1.90 (5)	2.745 (3)	169 (4)

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

The hydroxyl H atom was refined freely. The remaining H atoms were located in difference Fourier maps and placed in idealized positions, with C—H = 0.95 Å and with $U_{\text{iso}}(\text{H}) = 1.25U_{\text{eq}}(\text{C})$ for CH or $1.5U_{\text{eq}}(\text{C})$ for CH₃. The largest peak in the final difference map was located 0.71 Å from the Fe atom.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: Xtal3.5 (Hall *et al.*, 1995); program(s) used to refine structure: CRYLSQ in Xtal3.5; molecular graphics: Xtal3.5; software used to prepare material for publication: BONDLA and CIFIO in Xtal3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1446). Services for accessing these data are described at the back of the journal.

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