Dichloro(4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane)-iron(III) hexafluorophosphate

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The title compound, [FeCl₂(C₁₂H₂₆N₄)]PF₆, is the first mononuclear Fe³⁺ complex of an ethylene cross-bridged tetraaza-macrocycle to be structurally characterized. Comparison with the mononuclear Fe²⁺ complex of the same ligand shows that the smaller Fe³⁺ ion is more fully encapsulated by the cavity of the bicyclic ligand. Comparison with the oxo dinuclear complex of an unsubstituted ligand of the same size demonstrates that the methyl groups of 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane prevent dimerization upon oxidation of the metal centre. The Nₐx–Fe³⁺–Nₐx bond angles (ax is axial) in the reduced complex (Hubin et al., 2000) are quite different between the mononuclear and dinuclear oxo species, which is probably the consequence of steric considerations.

Comment

The tendency for iron complexes to form rust limits the utility, especially in aqueous media, of functional catalysts based on common ligands (Ortiz de Montellano, 1986). Even so, iron is one of the predominant metal ions found in biological catalytic systems (Jang et al., 1991; Wallar & Lipscomb, 1996; Boyington et al., 1993). A major feature of numerous synthetic catalysts having familiar nitrogen donors and vacant coordination sites is their propensity to form dimers in which higher-valent metal ions are present. One of us has produced iron(II) (Hubin et al., 2000) and iron(III) (Hubin et al., 2001) complexes of ethylene cross-bridged tetraaza-macrocyclic ligands that are remarkably resistant to oxidative hydrolysis while still having available sites for binding of the metal ion to either a terminal oxidant or a substrate. The ability of the complex to remain mononuclear, and thus catalytically useful, appears to hinge on the substitution pattern of the non-bridgehead N atoms of the bicyclic ligands (Hubin et al., 2001). Methyl or benzyl substitution results only in mononuclear complexes, even in the M³⁺ (Hubin et al., 2001, 2003) or M⁴⁺ (Yin et al., 2006) oxidation state, while oxidation of the unsubstituted ligand complexes results in μ-oxo iron(III) dimers (Hubin et al., 2003).

Structural characterization of an Fe³⁺ mononuclear complex has not been achieved prior to the present study, which (i) demonstrates that even upon oxidation the methyl-substituted ligand does not allow dimerization to occur and (ii) provides a structure for comparison to the lower valent analogue and to the unsubstituted analogue’s iron(III) μ-oxo dimer. Comparison of the Fe³⁺ 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane dichloride complex, (I) (Fig. 1 and Table 1), with the Fe²⁺ 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane dichloride complex primarily demonstrates the reduction in ionic radius of the iron ion upon oxidation. The Nₐx–Fe³⁺–Nₐx angle (ax is axial) is 153.20 (9)° in (I), while the Nₐx–Fe²⁺–Nₐx angle is 146.91 (7)° in the reduced complex (Hubin et al., 2000). The smaller Fe³⁺ ion is pulled further into the ligand cavity as the favored octahedral geometry is approached. Interestingly, the two methyl substituents are almost exactly eclipsed when viewed down the Nₐx–Fe²⁺–Nₐx axis, as might be expected from the symmetry of the complex (Fig. 2). However, they are more skewed in the...
Fe$^{3+}$ structure. Perhaps the ligand must twist to accommodate the Fe$^{3+}$ ion further into the ligand cavity. The Fe–N bond lengths are also affected, having an average of 2.26 Å in the Fe$^{2+}$ complex and 2.17 Å in the Fe$^{3+}$ complex.

Comparison of the Fe$^{3+}$ monomer with the µ-oxo dimer complex is also informative. The secondary amine–Fe$^{3+}$ bond lengths in the dimer are similar to the tertiary amine–Fe$^{3+}$ bond lengths; the Fe–N(secondary) distances average 2.17 Å, with one longer Fe–N(tertiary) bond of 2.258 (5) Å (see Table 2). This may be associated with the asymmetric accommodation of a longer Fe–Cl bond and a shorter Fe–O bond. In the monomer, with all tertiary amines, the average Fe–N bond distance is 2.17 Å, matching the shorter Fe–N bonds in the dimer. The N$_{ax}$–Fe–N$_{ax}$ bond angle averages 147.6 (2)° in the dimer, while this value is 153.20 (9)° in the monomer. Clearly, dimerization and its associated steric consequences push the Fe$^{3+}$ ion further out of the ligand cavity than it is in the Fe$^{3+}$ monomer. In fact, the dimer N$_{ax}$–Fe–N$_{ax}$ bond angle is much closer to that of the Fe$^{2+}$ monomer [146.91 (7)°] than that of the Fe$^{3+}$ monomer [153.20 (9)°]; Table 2]. This steric consequence is consistent with the observation that the more sterically demanding methyl-substituted ligand prevents dimerization altogether. This is supported by a comparison of all three structures viewed along the N$_{ax}$–Fe–N$_{ax}$ axis, where a skewing of the methyl groups and a twist in the macrocyclic backbone are observed for the Fe$^{3+}$ monomer relative to the other two structures (Fig. 2).

Experimental

The title complex was prepared by a procedure slightly modified from those described by Hubin _et al._ (2000, 2001). In an inert atmosphere glove-box, 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane (0.226 g, 0.001 mol) [prepared according to the procedure described by Wong _et al._ (2000)] was dissolved in acetonitrile (20 ml) in a 50 ml Erlenmeyer flask. Anhydrous iron(II) chloride (0.127 g, 0.001 mol) was added to the stirring ligand solution. The reaction was stirred at room temperature overnight. Dimethylformamide (12 ml) was added to dissolve a purple solid that had formed, and the reaction was then stirred for an additional 3 h, during which time the solid dissolved to give a light-brown solution. The solution was then filtered through filter paper and the solvent was removed under vacuum to give a brown solid, viz. the iron(II) dichloride complex of 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane. In the glove-box, the divalent iron complex was dissolved in methanol (20 ml) in a round-bottomed flask. Five equivalents of NH$_4$PF$_6$ (0.005 mol, 0.815 g) were dissolved in the solution. The flask was stoppered to protect it from air before being removed from the glove-box. In a fume-hood, a stream of nitrogen gas was directed over the surface of the solution. Br$_2$ (4–6 drops) was added and the reaction was stirred for 15 min. A bright-yellow precipitate formed immediately. The nitrogen gas was allowed to bubble through the solution for 15 min to remove excess Br$_2$. The flask was then stopped and placed in a freezer for 30 min to complete the precipitation. The yellow solid product was collected by vacuum filtration on a glass frit and washed successively with methanol and ether. The product was analytically pure as calculated with one-third molar equivalents of water of crystallization. X-ray quality crystals were grown from ether diffusion into an acetonitrile solution.

Crystal data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fe$^{3+}$Me$_2$L$^2$</th>
<th>Fe$^{2+}$Me$_2$L$^2$</th>
<th>Fe$^{3+}$H$_2$L dimer$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–N1</td>
<td>2.179 (2)</td>
<td>2.179 (2)</td>
<td>2.179 (2)</td>
</tr>
<tr>
<td>Fe–N2</td>
<td>2.158 (2)</td>
<td>2.158 (2)</td>
<td>2.158 (2)</td>
</tr>
<tr>
<td>Fe–N3</td>
<td>2.171 (2)</td>
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<tr>
<td>Fe–N4</td>
<td>2.163 (2)</td>
<td>2.163 (2)</td>
<td>2.163 (2)</td>
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<tr>
<td>N$<em>{ax}$–Fe–N$</em>{ax}$</td>
<td>153.20 (9)</td>
<td>146.91 (7)</td>
<td>147.6 (2)</td>
</tr>
<tr>
<td>N$<em>{eq}$–Fe–N$</em>{eq}$</td>
<td>77.85 (9)</td>
<td>77.15 (7)</td>
<td>77.7 (2)</td>
</tr>
</tbody>
</table>

Notes: (a) where there are two independent molecules in the asymmetric unit, an average value is given; (b) this work; (c) Hubin _et al._ (2003); (d) Hubin _et al._ (2000).
H atoms were placed in idealized positions and refined using a riding model, with C−H distances of 0.96 and 0.97 Å for CH₃ and CH₂ H atoms, respectively, and with $U_{iso}(H)$ values of, respectively, 1.5 and 1.2 times $U_{eq}$ of the carrier atom.

Data collection: X-AREA (Stoe & Cie, 2002); cell refinement: X-AREA; data reduction: X-RED (Stoe & Cie, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP (Johnson, 1965) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3055). Services for accessing these data are described at the back of the journal.

References


