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A *cis*-Octahedral Dichloro Complex of Fe^{III} with a Tetradentate Dipyridyl–Diamino Ligand

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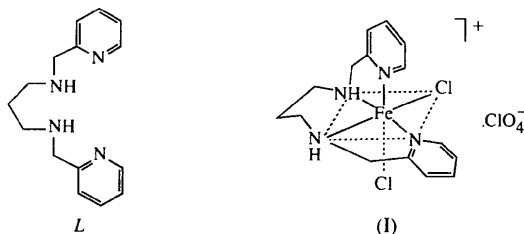
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Abstract

In [*N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine-*N,N',N'',N'''*]dichloroiron(III) perchlorate, [FeCl₂(C₁₅H₂₀N₄)]ClO₄, the linear tetradentate ligand adopts the *cis-β* configuration which provides a favourable geometry for the six-membered chelate ring. The Fe—N distances show lengthening from the *trans* influence of the chloride ligands, with Fe—N_{py} values of 2.152 (3) and 2.179 (3) Å, and Fe—N_{amine} distances of 2.141 (4) and 2.178 (4) Å.

Comment

Transition metal complexes with polydentate amino-pyridyl ligands have been found to catalyse a variety of redox processes (Melnik, Kildahl, Rendina & Busch, 1979; Cairns, Heckman, Melnik, Davis & Busch, 1987; Leising, Kim, Perez & Que, 1993; Rabion *et al.*, 1995). They are also of significance in the formation of magnetically coupled polynuclear transition metal arrays (Hodgson, Michelsen, Pedersen & Towle, 1991). However, in most cases, the assignment of the coordination geometry has been made on the basis of spectroscopic data (Gibson & McKenzie, 1971). Additionally, for iron complexes used as catalysts in redox reactions, the formation of oxo dimers deactivates the catalyst and is considered to be a 'dead end' in the catalytic process (Melnik *et al.*, 1979; Cairns *et al.*, 1987). In this context, the synthesis and structure determination of a monomeric Fe^{III} complex with a tetradentate aminopyridine ligand, *i.e.* (I), was considered to be of value.



In complex (I) (Fig. 1), the Fe^{III} atom has a distorted octahedral geometry, with *cis*-pyridine groups and *cis*-chloride ligands; the tetradentate ligand is in a *cis-β* orientation. This gives the six-membered chelate ring a favourable chair conformation. Similar tetradentate ligands bonded to other metal ions adopt either the *cis-α* conformation, in which the two pyridyl groups are *trans* (Arulsami & Hodgson, 1993), or the *cis-β* conformation (Goodson, Oki, Glerup & Hodgson, 1990; Hodgson *et al.*, 1991; Arulsami, Goodson, Hodgson, Glerup & Michelsen, 1994). Published data show that diaminopropane derivatives, as in the present complex, generally favour the *cis-β* conformation (Hodgson *et al.*, 1991; Arulsami *et al.*, 1994).

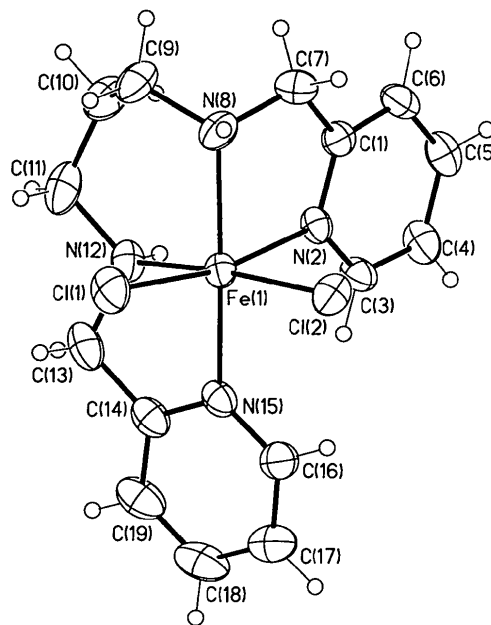


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

The Fe—N_{py} and Fe—N_{amine} bond lengths lie within the usual range for similar complexes (Norman *et al.*, 1990; Holz *et al.*, 1993, and references therein). Usually Fe—N_{py} distances are shorter than Fe—N_{amine} distances, but here the *trans* effect of the chloride ligands causes the *trans* Fe—N_{py} distance to be slightly longer than the shorter amine distance. However, the dimeric Fe^{III} complex with the same tetradentate ligand combined with oxo and carbonato bridging groups has significantly greater differences in its Fe—N distances (Arulsami *et al.*, 1994).

Experimental

N,N'-Bis(2-pyridylmethyl)-1,3-propanediamine (*L*) was prepared according to a published procedure (Goodwin & Lions,

1960) and purified by vacuum distillation (b.p. 470–473 K Torr⁻¹; 1 Torr = 133.322 Pa). (Caution: perchlorates are potentially explosive and must be handled with care!) The title compound was prepared when a solution of 0.93 g of FeCl₃·6H₂O in 10 ml of ethanol was added with stirring to a solution of 0.9 g of *L* in 15 ml of ethanol. The resulting brown–green solution was stirred at room temperature for 0.5 h and 1 g of NaClO₄ dissolved in a minimum amount of ethanol was added. The dark-green precipitate was filtered off, washed with ethanol and ether, and air dried. The crude product was redissolved in a minimum amount of acetonitrile, separated from undissolved admixtures of inorganic salts, and precipitated by addition of ethanol (yield 45%). Slow evaporation of solvent from a dilute acetonitrile–ethanol (1:5 v/v) solution gave a crystalline product. Analysis found: C 38.10, N 12.10, H 4.58%; calculated for FeC₁₅H₂₀N₄Cl₃O₄: C 37.34, N 11.61, H 4.18%. Mass spectrum (FAB, NBA/CH₃CN): 312 (FeL), 347 (FeLCl), 411 (FeLClO₄). IR (KBr discs): 3443, 3119, 2923, 1606, 1571, 1486, 1442, 1292, 1144, 1120, 1090, 1020, 768, 636, 628 cm⁻¹.

Crystal data

[FeCl₂(C₁₅H₂₀N₄)]ClO₄

M_r = 482.55

Monoclinic

*P*2₁/*c*

a = 12.2981 (10) Å

b = 12.873 (3) Å

c = 12.508 (3) Å

β = 97.358 (10)°

V = 1963.8 (7) Å³

Z = 4

D_x = 1.632 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 4605 reflections

θ = 3–20°

μ = 1.205 mm⁻¹

T = 180 (2) K

Prisms

0.40 × 0.12 × 0.08 mm

Yellow

Data collection

Siemens SMART area detector diffractometer with Oxford Cryosystems Cryostream cooler (Cosier & Glazer, 1986)

ω rotation scans with narrow frames

Absorption correction: empirical from equivalent reflections (SADABS; Sheldrick, 1996a)

T_{min} = 0.728, *T_{max}* = 0.908

9492 measured reflections

3445 independent reflections

2582 reflections with

I > 2σ(*I*)

R_{int} = 0.041

θ_{max} = 25°

h = -14 → 14

k = -15 → 11

l = -14 → 14

Refinement

Refinement on *F*²

R(*F*) = 0.048

wR(*F*²) = 0.114

S = 1.032

3445 reflections

250 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.038*P*)² + 3.75*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 0.739 e Å⁻³

Δρ_{min} = -0.571 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Fe(1)—N(8)	2.141 (4)	Fe(1)—N(2)	2.179 (3)
Fe(1)—N(15)	2.152 (3)	Fe(1)—Cl(1)	2.2722 (12)
Fe(1)—N(12)	2.178 (4)	Fe(1)—Cl(2)	2.2928 (12)
N(8)—Fe(1)—N(15)	164.73 (13)	N(12)—Fe(1)—Cl(1)	91.01 (10)
N(8)—Fe(1)—N(12)	91.63 (14)	N(2)—Fe(1)—Cl(1)	168.88 (9)
N(15)—Fe(1)—N(12)	76.14 (13)	N(8)—Fe(1)—Cl(2)	94.89 (10)
N(8)—Fe(1)—N(2)	77.79 (13)	N(15)—Fe(1)—Cl(2)	96.07 (10)
N(15)—Fe(1)—N(2)	92.05 (12)	N(12)—Fe(1)—Cl(2)	169.73 (10)
N(12)—Fe(1)—N(2)	85.93 (13)	N(2)—Fe(1)—Cl(2)	87.69 (9)
N(8)—Fe(1)—Cl(1)	91.63 (11)	Cl(1)—Fe(1)—Cl(2)	96.72 (5)
N(15)—Fe(1)—Cl(1)	97.60 (9)		

The data collection nominally covered over a hemisphere of reciprocal space, by a combination of three sets of exposures with different φ angles for the crystal; each exposure covered 0.3° in ω. The crystal-to-detector distance was 4.99 cm. Coverage of the unique set is over 99% complete. Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections; this was found to be negligible. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the carrier atom. The anisotropic displacement parameters of the perchlorate anion are very high, indicative of partial disorder, but it was not considered that an attempt to model this using split atoms would be of value.

Data collection: SMART and SAINT (Siemens, 1995). Cell refinement: SMART and SAINT. Data reduction: SMART and SAINT. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL96 (Sheldrick, 1996b). Molecular graphics: SHELXTL-Plus (Sheldrick, 1991).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1163). Services for accessing these data are described at the back of the journal.

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catena-Poly[[1,4-dioxane-*O*¹]iodolithium]- μ -(1,4-dioxane-*O*¹:*O*⁴)

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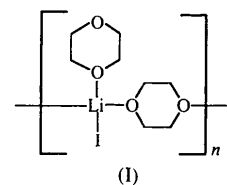
Abstract

In the title compound, $[\text{LiI}(\text{C}_4\text{H}_8\text{O}_2)(\mu\text{-C}_4\text{H}_8\text{O}_2)]_n$, obtained by recrystallization of LiI from 1,4-dioxane, the ligand is present in both monodentate and bridging modes, the latter resulting in a linear polymeric structure.

Comment

A few structures are known in which 1,4-dioxane is coordinated to Li (Bartlett *et al.*, 1986; Evans, Dominguez, Levan & Doedens, 1985; Veith, Ruloff, Huch & Töllner, 1988; Belzner, Dehnert & Stalke, 1994; Müller & Krause, 1972; Taube, Windisch, Görlitz & Schumann, 1993; Andrews *et al.*, 1995; Uhl, Klinkhammer, Layh & Massa, 1991; Cramer, Bruck & Gilje, 1986; Nöth, Thomas & Schmidt, 1996; West, Sohn, Powell, Müller & Apeloig, 1996). In a small number of these, the dioxane bridges through its two O atoms between two Li centres (Evans *et al.*, 1985), in some cases to give polymers (Taube *et al.*, 1993; Andrews *et al.*, 1995; Nöth *et al.*, 1996), and there are two rather complex species in which there is both bridging and monodentate coordination (Cramer *et al.*, 1986; Uhl *et al.*, 1991). The

title compound, (I), provides a rather striking example of such dual functionality in which the bridging mode gives rise to a very simple linear polymeric structure aligned along a twofold screw axis.



We initially isolated crystals of the title compound, (I), unexpectedly as a consequence of using 1,4-dioxane during work-up of a product mixture formed from a reaction of Sm with $(\text{Me}_2\text{NMe}_2\text{Si})_3\text{Cl}$ that had evidently retained a little of the LiI generated during its preparation. Having identified the solvated salt by determination of its crystal structure, we then made it simply by recrystallizing LiI from 1,4-dioxane, as described in the *Experimental* section, confirming by determination of the unit cell that the crystals were identical to those examined previously.

The structure is shown in Fig. 1, and bond lengths and angles are listed in Table 1. As can be seen from Table 1, there is no significant difference between the Li—O bonds to the bridging and terminal 1,4-dioxane ligands or between the geometries of the two types of dioxane rings, which are in chair conformations.

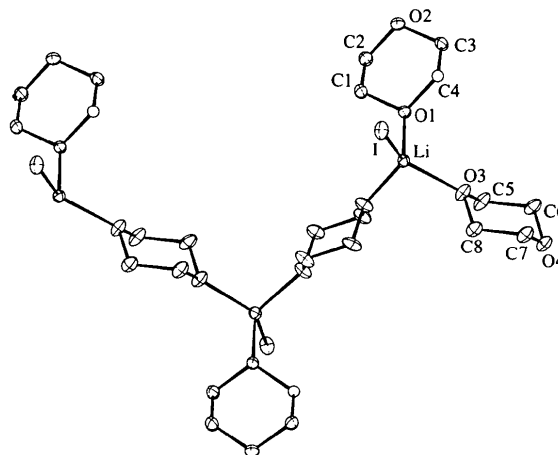


Fig. 1. The structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Experimental

To ensure the absence of traces of water, LiI was generated by adding a solution of BuLi (3.55 mmol) in hexane (1.42 ml) dropwise to a stirred solution of $\text{ICH}_2\text{CH}_2\text{I}$ (3.55 mmol) in heptane (30 ml). A white precipitate separated immediately