

C1	-0.1204 (6)	-0.3712 (4)	-0.0935 (4)	4.8 (1)
C2	0.0270 (6)	-0.3746 (4)	-0.0760 (4)	5.0 (1)
C3	0.0552 (5)	-0.3494 (4)	-0.1678 (4)	4.8 (1)
C4	-0.0714 (6)	-0.3284 (4)	-0.2434 (4)	4.6 (1)
C5	-0.1803 (5)	-0.3424 (4)	-0.1977 (4)	4.8 (1)
C6	-0.0556 (5)	-0.0427 (3)	-0.1617 (3)	3.3 (1)
C7	-0.1598 (4)	-0.0570 (3)	-0.1111 (3)	3.3 (1)
C8	-0.3705 (5)	-0.1437 (3)	-0.1017 (4)	3.8 (1)
C9	-0.3570 (5)	-0.1029 (4)	0.0088 (4)	5.3 (1)
C10	-0.4675 (5)	-0.0813 (5)	-0.1856 (5)	6.1 (2)
C11	-0.4287 (5)	-0.2460 (4)	-0.1103 (4)	4.8 (1)
C12	0.0401 (5)	-0.0928 (4)	-0.3034 (3)	3.8 (1)
C13	0.1427 (6)	-0.1723 (5)	-0.3125 (4)	5.8 (1)
C14	-0.0846 (6)	-0.0866 (5)	-0.4034 (4)	5.7 (1)
C15	0.1198 (6)	0.0025 (4)	-0.2825 (5)	5.4 (1)

Table 2. Selected bond lengths (Å) and angles (°)

Nb—C11	2.505 (1)	Nb—C2	2.385 (6)
Nb—C12	2.527 (1)	Nb—C3	2.416 (6)
Nb—N1	2.015 (4)	Nb—C4	2.432 (6)
Nb—N2	2.021 (4)	Nb—C5	2.424 (5)
Nb—C1	2.405 (6)		
C11—Nb2—C12	78.78 (5)	C12—Nb2—N1	83.5 (1)
C11—Nb2—N1	140.4 (1)	C12—Nb2—N2	138.2 (1)
C11—Nb2—N2	85.5 (1)	N1—Nb2—N2	84.7 (2)

Di-*tert*-butyl-1,2-ethanediimine (0.47 g, 2.8 mmol) in 10 ml toluene was added to a solution of (η^5 -Cp)NbCl₂(PMe₃)₃ (0.9 g, 1.9 mmol) in 50 ml toluene under argon. The reaction medium was irradiated (125 W) for 10 d during which time the red-brown colour changed to red, with formation of crystals and a precipitate. The crystals, isolated by filtration and shown by analysis to be (η^5 -Cp)NbCl₂(^{*t*}BuNC₂H₂N^{*t*}Bu) (0.5 g, 45%), were slightly soluble in dichloromethane or acetonitrile, but more soluble in nitromethane. The monocystal was introduced, under argon, into a sealed Lindeman capillary.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71135 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1029]

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Structure of the Dimeric Complex of Iron(III) Chloride with Pyridoxine

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Abstract

The structure of di- μ -pyridoxinato-bis[aquadichloro-iron(III)], [FeCl₂(μ -C₈H₁₀NO₃)(H₂O)]₂, consists of centrosymmetrical dimers in which Fe atoms with a slightly distorted octahedral coordination are bridged by the O atoms of two deprotonated 4-hydroxymethyl groups of the chelating pyridoxinato anions. The other four positions of each Fe coordination octahedron are occupied by two Cl atoms, the phenolate O atom of the pyridoxinato ligand and the water molecule. The main interatomic distances are Fe—O(4-hydroxymethyl) 1.998 (2) and 1.990 (2) Å, Fe—O(phenolate) 1.949 (2) Å, Fe—Cl 2.361 (1) and 2.327 (1) Å and Fe—OH₂ 2.185 (2) Å.

Comment

Pyridoxine (PN) is a vitamin of the B₆ group and plays an important role in the transformations of amino acids in biological systems (Robinson, 1966). The biological activity of pyridoxine is affected by its transition into the biologically active form of vitamin B₆ which is commonly known as pyridoxal. Metal ions have been shown to accelerate the transformation of pyridoxine to pyridoxal and their complexes with pyridoxine are used in the treatment of several diseases (Clements & Anderson, 1980; Hakimov, 1976), for example the iron(III) complex is used in

the treatment of iron-deficiency anaemia. A crystal structure determination of the title complex (I), was carried out to establish the mode of pyridoxine coordination with the iron ions and also to elucidate the effect of metal-ion coordination on tautomeric forms of pyridoxine.

As can be seen in Fig. 1, the title complex consists of the dimeric $[\text{FeCl}_2(\mu\text{-PN-H})(\text{H}_2\text{O})]_2$ unit (where PN-H is monodeprotonated pyridoxine) located across the inversion centre. The Fe atoms are bridged by the O(4') atoms of the deprotonated 4-CH₂OH groups of two pyridoxinato anions. The octahedral coordination of each Fe atom is completed by the phenolate O(3) atom of the PN-H ligand, two Cl atoms and the water O atom. The Fe—O(4') distances [1.990 (2) and 1.998 (2) Å] are comparable with the average value (1.998 Å) for the corresponding distance in iron complexes with μ -O-coordinated alkoxy ligands (Orpen *et al.*, 1989) but are somewhat longer than in complexes with μ -OH-coordinated terminal alkoxy ligands (1.967 Å). The Fe—O(3) distance to the phenolic O atom [1.949 (2) Å] is significantly longer than the Fe—O(C_{aryl}) distance (1.913 Å; Orpen *et al.*, 1989). The Fe—O(W) distance [2.185 (2) Å] is longer than the sum of the ionic radii of octahedral Fe³⁺ and tricoordinated O²⁻ (1.36 Å). The Fe—Cl bond lengths [2.327 (1) and 2.361 (1) Å] are shorter than the sum of the ionic radii of Fe³⁺ and Cl⁻ (0.645 and 1.81 Å, respectively).

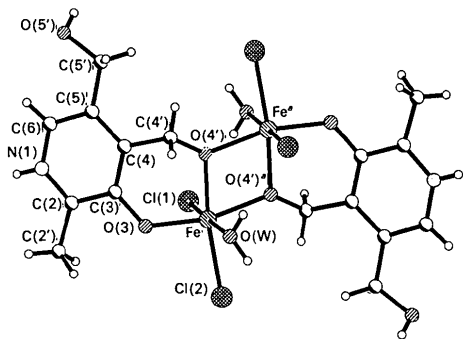


Fig. 1. Molecular structure of $[\text{FeCl}_2(\mu\text{-PN-H})_2(\text{H}_2\text{O})]_2$.

The O(4') bond configuration is strictly planar, in accordance with the 4-HOCH₂-group deprotonation. The C(4')—O(4') distance does not change on deprotonation of the HO(4') hydroxy group; this fact may be explained by the absence of any conjugation of the O(4') electrons with the aromatic system of the pyridine ring. Indeed, the C(4')—O(4') distance [1.417 (3) Å] is comparable with those observed previously in non-coordinated PN [1.391 (5); Longo, Franklin & Richardson, 1982] and $[\text{O}_2\text{Mo}(\text{PN-}$

$\text{H})_2] \cdot 3\text{H}_2\text{O}$ [1.417 (7) and 1.403 (7) Å; Sabirov, Litvinov & Junuskhodjaev, 1991] but somewhat different from that found in the dimeric $[\text{VO}_2(\mu\text{-PN-H})_2]$ [1.446 (7) Å; Sabirov *et al.*, 1984].

We suppose that the deprotonation of the reactive 4-CH₂OH group is related to the transformation of pyridoxine to pyridoxal, the biologically active form of vitamin B₆. The deprotonation of the 4-hydroxymethyl group was found previously in dimeric $[\text{VO}_2(\mu\text{-PN-H})_2]$ in which O(4') is also the bridging atom. It was subsequently found in mononuclear $[\text{Co}(\text{bipy})_2(\text{PN-H})]$ (Sudhakara Rao, Varughese & Manohar, 1986) and $[\text{MoO}_2(\text{PN-H})_2]$ where the 4-hydroxymethyl group was also deprotonated, but O(4') was not the bridging atom. The chelating O(3), O(4')-coordination of pyridoxine has been found in pyridoxine complexes with cadmium(II) (Mosset, Nepvey-Juras, Haran & Bonnet, 1978) and copper(II) (Sabirov, Struchkov, Batsanov & Azizov, 1982, 1983), but no corresponding deprotonation was observed. Thus, the deprotonation of the coordinated 4-HOCH₂ group has so far only been observed in the high-valency metal complexes of pyridoxine. This can be explained by the increase of the hydroxymethyl-group acidity as a result of the inductive effects of metal ions.

As a result of the deprotonation of the phenol group, the C(3)—O(3) distance [1.329 (3) Å] is shorter than those found in non-coordinated PN [1.374 (4) Å] or PN.HCl [1.343 (6) Å; Bacon & Plant, 1980]. There is no difference between the value of the angle C(2)—C(3)—C(4) in (I) [119.5 (2)°] and in non-coordinated PN with an undepronated phenol group [120.3 (3)°]. This shows that the inductive effect of the aromatic ring is negligible and that the shortening of the C(3)—O(3) bond occurs as a result of the increasing ionic character of this bond. The C(2)—N(1)—C(6) angle is 125.2 (2)°, as expected for a protonated pyridine ring and very close to the value of 124.7 (2)° observed in PN.HCl where protonation of the pyridine ring also takes place, but significantly larger than in non-coordinated PN [119.3 (3)°] which has an unprotonated pyridine ring. In contrast, the value of C(2)—N(1)—C(6) depends upon the protonation of N(1); in (I) it is protonated and the angle is 125.2 (2)° but in non-coordinated PN where the N(1) atom is unprotonated it is 119.7 (4)°.

The dimeric molecules (I) are linked by intermolecular hydrogen bonds O(5')—H(O5')...O(3) and O(W)—H(W1)...Cl(1) in infinite chains along the *b* direction (Fig. 2). These chains are interlinked by the hydrogen bonds O(W)—H(W2)...Cl(2), N(1)—H(N1)...O(5') and N(1)—H(N1)...Cl(2) to form a three-dimensional network. Thus, in this structure, the atom H(N1) is involved in two hydrogen bonds (or one bifurcated hydrogen bond). Besides these

hydrogen bonds, a short intermolecular contact Cl(1)⋯H(6) is observed [Cl(1)⋯C(6) ($-x+1, y-0.5, z-0.5$) 3.489 (3), H(6)⋯Cl(1) 2.797 (2) Å, C(6)—H(6)—Cl(1) 132.3 (1)°]; the distance is shorter than the sum of the van der Waals radii of H and Cl (3.00 Å).

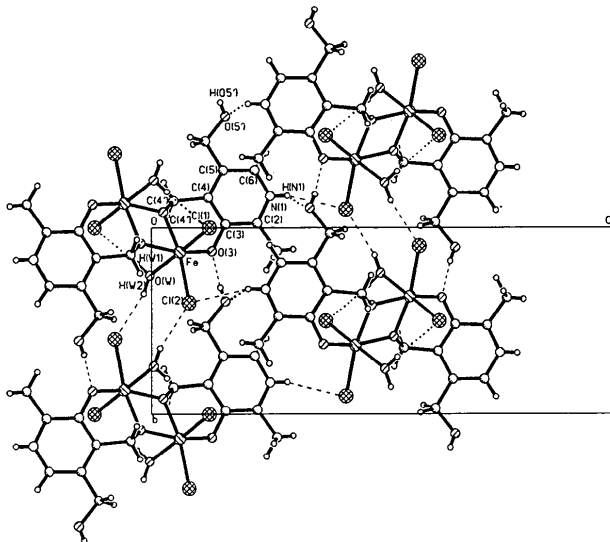


Fig. 2. Part of the crystal structure viewed along the a axis. In-plane hydrogen bonds are shown by dashed lines while dotted lines represent the out-of-plane bonds.

Experimental

Crystal data

[Fe₂(C₈H₁₀NO₃)₂Cl₄(H₂O)₂]

$M_r = 625.87$

Monoclinic

$P2_1/c$

$a = 7.139$ (1) Å

$b = 7.907$ (1) Å

$c = 20.199$ (2) Å

$\beta = 93.09$ (1)°

$V = 1138.5$ (4) Å³

$Z = 2$

$D_x = 1.826$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 34 reflections

$\theta = 12.5$ – 14°

$\mu = 1.79$ mm⁻¹

$T = 173$ K

Wedge

$0.3 \times 0.2 \times 0.2$ mm

Red

Data collection

Siemens P3/PC diffractometer

$\theta/2\theta$ scans

Absorption correction: none

2653 measured reflections

2467 independent reflections

1855 observed reflections

[$I > 2\sigma(I)$]

$R_{int} = 0.012$

$\theta_{max} = 28^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 10$

$l = -26 \rightarrow 26$

2 standard reflections

monitored every 98

reflections

intensity variation: 5%

Refinement

Refinement on F

Final $R = 0.0235$

Unit weights applied

$(\Delta/\sigma)_{max} = 0.06$

$wR = 0.0257$

$S = 0.93$

1855 reflections

145 parameters

All H-atom parameters refined

$\Delta\rho_{max} = 0.43$ e Å⁻³

$\Delta\rho_{min} = -0.31$ e Å⁻³

Atomic scattering factors

from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Fe	0.4954 (1)	0.1311 (1)	0.0592 (1)	0.017 (1)
Cl(1)	0.7399 (1)	0.0001 (1)	0.1238 (1)	0.029 (1)
Cl(2)	0.6096 (1)	0.4027 (1)	0.0797 (1)	0.028 (1)
O(W)	0.2810 (3)	0.2566 (3)	-0.0045 (1)	0.024 (1)
O(3)	0.3170 (3)	0.1256 (2)	0.1289 (1)	0.021 (1)
O(4')	0.3801 (2)	-0.0838 (2)	0.0246 (1)	0.017 (1)
O(5')	0.0818 (3)	-0.6053 (3)	0.1579 (1)	0.031 (1)
N(1)	0.2210 (3)	-0.1701 (3)	0.2549 (1)	0.024 (1)
C(2)	0.2703 (4)	-0.0236 (3)	0.2273 (1)	0.021 (1)
C(2')	0.3212 (5)	0.1245 (4)	0.2699 (1)	0.030 (1)
C(3)	0.2696 (3)	-0.0182 (3)	0.1576 (1)	0.018 (1)
C(4)	0.2151 (3)	-0.1617 (3)	0.1208 (1)	0.018 (1)
C(4')	0.2066 (4)	-0.1443 (4)	0.0461 (1)	0.020 (1)
C(5)	0.1679 (3)	-0.3112 (3)	0.1528 (1)	0.018 (1)
C(5')	0.1120 (4)	-0.4689 (3)	0.1148 (1)	0.024 (1)
C(6)	0.1726 (4)	-0.3115 (3)	0.2214 (1)	0.023 (1)

Table 2. Bond lengths (Å) and angles (°)

Fe—Cl(1)	2.361 (1)	N(1)—C(2)	1.341 (4)
Fe—Cl(2)	2.327 (1)	C(2)—C(3)	1.407 (3)
Fe—O(3)	1.949 (2)	C(3)—C(4)	1.401 (3)
Fe—O(4')	1.998 (2)	C(4)—C(5)	1.397 (4)
Fe—O(4') ^a	1.990 (2)	C(5)—C(6)	1.385 (3)
Fe—O(W)	2.185 (2)	N(1)—C(6)	1.342 (3)
O(3)—C(3)	1.329 (3)	C(2')—C(2)	1.487 (4)
O(4')—C(4')	1.417 (3)	C(4)—C(4')	1.514 (3)
O(5')—C(5')	1.409 (3)	C(5)—C(5')	1.506 (4)
Cl(1)—Fe—O(3)	94.8 (1)	C(4')—O(4')—Fe ^a	129.4 (1)
Cl(1)—Fe—O(4')	95.7 (1)	C(2)—N(1)—C(6)	125.2 (2)
Cl(1)—Fe—Cl(2)	93.7 (1)	N(1)—C(2)—C(3)	117.1 (2)
Cl(1)—Fe—O(4')	92.1 (1)	C(4)—C(3)—C(2)	119.5 (2)
Cl(1)—Fe—O(W)	176.7 (1)	C(5)—C(4)—C(3)	120.5 (2)
Cl(2)—Fe—O(3)	97.4 (1)	C(4)—C(5)—C(6)	118.1 (2)
Cl(2)—Fe—O(4')	168.9 (1)	N(1)—C(6)—C(5)	119.6 (2)
Cl(2)—Fe—O(W)	85.0 (1)	C(2')—C(2)—C(3)	122.9 (2)
O(3)—Fe—O(W)	88.3 (1)	N(1)—C(2)—C(2')	120.0 (2)
O(3)—Fe—O(4')	161.7 (1)	O(3)—C(3)—C(4)	122.1 (2)
O(3)—Fe—O(4')	87.7 (1)	O(3)—C(3)—C(2)	118.4 (2)
O(4')—Fe—O(W)	85.3 (1)	C(4')—C(4)—C(3)	116.8 (2)
O(4')—Fe—O(4')	74.7 (1)	C(5)—C(4)—C(4')	122.7 (2)
Cl(2)—Fe—O(4')	99.0 (1)	C(4)—C(5)—C(5')	122.0 (2)
O(W)—Fe—O(4')	85.1 (1)	C(6)—C(5)—C(5')	119.9 (2)
Fe—O(3)—C(3)	121.8 (2)	O(4')—C(4')—C(4)	110.3 (2)
Fe—O(4')—C(4')	122.0 (1)	O(5')—C(5')—C(5)	111.4 (2)
Fe—O(4')—Fe ^a	105.3 (1)		

Note: (a) related to reference atom by the inversion centre.

Table 3. Geometry of the possible hydrogen bonds (Å, °)

$D-H \cdots A$	$D \cdots A$	$H \cdots A$	$D-H \cdots A$
O(5')—H(O5') ⁱ ⋯O(3 ⁱ)	2.792 (3)	2.008 (2)	174.3 (1)
O(W)—H(W1) ⁱⁱ ⋯Cl(1 ⁱⁱ)	3.147 (2)	2.398 (1)	176.1 (1)
O(W)—H(W2) ⁱⁱⁱ ⋯Cl(2 ⁱⁱⁱ)	3.210 (2)	2.370 (1)	167.7 (1)
N(1)—H(N1) ^{iv} ⋯O(5' ^{iv})	2.907 (3)	2.401 (2)	124.3 (1)
N(1)—H(N1) ^v ⋯Cl(2' ^v)	3.537 (3)	2.890 (2)	143.0 (1)

Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + 1, -y, -z$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, y - \frac{1}{2}, \frac{1}{2} - z$.

All calculations were performed on an IBM PC/AT computer using *SHELXTL-Plus* (Sheldrick, 1989) programs.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71137 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: VS1005]

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Structure of an Iridium Complex of 1,1'-Bisdiphenylphosphinoferrocene†

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Abstract

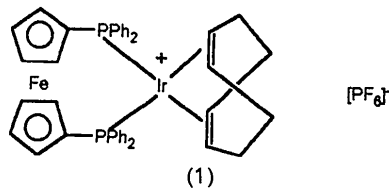
The structure of [1,1'-bis(diphenylphosphino)ferrocene](η^4 -1,5-cyclooctadiene)iridium(I) hexafluorophosphate, $[\text{Ir}(\text{C}_8\text{H}_{12})\{\text{(C}_5\text{H}_4\text{-PPh}_2)_2\text{Fe}\}][\text{PF}_6]$, shows

† [2(η^4 -1,5-Cyclooctadiene)-bis[μ -2 κ P:1(η^5 -cyclopentadienyl)-idenediphenylphosphine]iridiumiron hexafluorophosphate.

approximately square-planar geometry at iridium. The cyclopentadienyl rings of the dppf ligand are close to parallel and staggered.

Comment

We have been interested for some time in the structures and solution conformations of cationic iridium complexes of hindered monophosphines, (Abbassioun, Hitchcock & Chaloner, 1989, 1990*a,b*; Abbassioun, Chaloner, Hitchcock & Kozirowski, 1991; Chaloner, Hitchcock & Reisinger, 1992). Many such complexes have been used as catalysts for homogeneous hydrogenation of hindered alkenes (Crabtree, 1979). There have been fewer structural studies on complexes of chelating biphosphines. The structures of $[\text{IrCl}(\text{cod})(\text{diop})]$ [cod = 1,5-cyclooctadiene; diop = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (Brunie, Mazan, Langlois & Kagan, 1976)], $[\text{IrCl}(\text{cod})(\text{diphol})]$ [diphol = (2*R*,3*R*)-2,3-*O*-isopropylidene-1,4-bis(5*H*-dibenzophosphol-5-yl)-2,3-butanediol (Hayashi, Tanaka, Ogata, Kodama, Takahashi, Uchida & Uchida, 1983)] and $[\text{IrMe}(\text{cod})(\text{dppe})]$ [dppe = 1,2-bis(diphenylphosphino)ethane (Churchill & Bezman, 1973)] have been determined, but all of these are neutral and five-coordinate. Complex (1) was prepared by reaction of $[\text{Ir}(\text{cod})(\text{py})_2][\text{PF}_6]$ (py = pyridine) with 1,1'-bis(diphenylphosphino)ferrocene (dppf) (Crabtree & Moorehouse, 1986). A previous synthesis of $[\text{Ir}(\text{cod})(\text{dppf})][\text{ClO}_4]$ used $\{[\text{IrCl}(\text{cod})]_2\}$, dppf and $\text{Ag}[\text{ClO}_4]$ (Mague & Lloyd, 1988).



The structure of the complex is shown in Fig. 1. The geometry at iridium is approximately square planar, as expected. The Fe...Ir distance is 4.340 (2) Å, too long for any significant intermetallic interaction. It is useful to compare the geometry of the dppf ligand with that in a number of other complexes, most of which have found uses as hydrogenation catalysts. The angle between the cyclopentadienyl rings is 3.25°, as compared with 6.2° in $[\text{PdCl}_2(\text{dppf})]$ or $[\text{NiBr}_2(\text{dppf})]$ (Butler, Cullen, Kim, Rettig & Trotter, 1985). The P(1)...P(2) distance is 3.583 (4) Å which lies within the previously reported range [3.45–3.78 Å (Hayashi, Konishi, Kobori, Kumada, Higuchi & Hirotsu, 1984)]. The distances between the Fe atom and the cyclopentadienyl rings (1.630–1.640 Å) are also within normal ranges