Tetragonal
$P4_12_12$
$a = 8.9054\,(13)$ Å
$c = 37.978\,(8)$ Å
$V = 3011.9\,(9)$ Å^3
$Z = 4$
$D_x = 1.531$ Mg m^{-3}
D_m not measured

Cell parameters from 34 reflections
$\theta = 15.1–19.8°$
$\mu = 1.388$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.6 × 0.4 × 0.2 mm
Orange–yellow

Data collection

Stoe–Siemens Stadi-4 diffractometer
ω scans
Absorption correction: ψ scans (Sheldrick, 1994)
$T_{\min} = 0.389$, $T_{\max} = 0.758$
8888 measured reflections
4393 independent reflections
2707 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0069$
$\theta_{\max} = 30.01°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 53$
3 standard reflections
frequency: 120 min
intensity decay: 26.5%

Refinement

Refinement on F^2
$R(F) = 0.0738$
$wR(F^2) = 0.1530$
$S = 1.130$
4392 reflections
168 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 8P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.025$ e Å^{-3}
$\Delta\rho_{\min} = -0.416$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.15 (11)

Table 1. *Selected geometric parameters (Å, °)*

Pd—C14	2.112 (12)	Pd—Cl^i	2.423 (3)
Pd—C3	2.138 (10)	Pd—Pd^i	3.100 (2)
Pd—C2	2.141 (9)	C2—C3	1.425 (13)
Pd—Cl	2.412 (3)	C3—C14	1.381 (15)
C14—Pd—C3	37.9 (4)	C2—Pd—Cl^i	101.1 (3)
C14—Pd—C2	68.6 (4)	Cl—Pd—Cl^i	88.01 (11)
C3—Pd—C2	38.9 (3)	Pd—Cl—Pd^i	79.73 (8)
C14—Pd—Cl	102.4 (3)	C3—C2—C1	125.0 (8)
C3—Pd—Cl	132.7 (3)	C14—C3—C2	117.3 (9)
C2—Pd—Cl	170.9 (3)	C14—C3—C4	123.3 (9)
C14—Pd—Cl^i	167.3 (3)	C2—C3—C4	117.8 (8)
C3—Pd—Cl^i	135.9 (3)		

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

H atoms were idealized, except for those of the allyl group (H2, H141 and H142), which were refined with the C2—H2, C14—H141 and C14—H142 distances restrained to be the same, and the C3—C14—H141 and C3—C14—H142 angles also restrained to be the same. Isotropic displacement parameters for H atoms were fixed at 1.2 times the equivalent isotropic displacement parameters of their parent C atom. The high *R* value is associated with data collection at high angle (to 60° in 2θ); there is still significant intensity at such high angles.

Data collection: *STADI4* (Stoe & Cie, 1995*a*). Cell refinement: *STADI4*. Data reduction: *X-RED* (Stoe & Cie, 1995*b*). Program(s) used to solve structure: *XS* in *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *XL* in *SHELXTL*. Molecular graphics: *XP* in *SHELXTL*. Software used to prepare material for publication: *XL* in *SHELXTL*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1169). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 712-714

A Five-Coordinated Monomer of Chloro-[*N*,*N*′-(di-2-hydroxy-1-naphthylidene)-1,2-diaminobenzene]iron(III)

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(*Received 2 January 1996; accepted 15 January 1997*)

Abstract

In the dioxane solvate of the title complex, chloro-{2,2′-[*o*-phenylenebis(nitrilomethylidyne)]dinaphtholato-*N*,*N*′,*O*,*O*′}iron(III), [$FeCl(C_{28}H_{18}N_2O_2)$].$C_4H_8O_2$, the

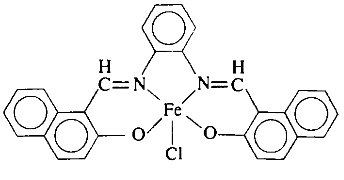
Acta Crystallographica Section C
ISSN 0108-2701 © 1997

Fe^{III} ion shows a distorted square-pyramidal geometry with the N_2O_2 atoms of the ligand at the base and the Cl atom at the apex of the pyramid.

Comment

The complexes of transition metal ions with Schiff bases provide a large class of compounds of both stereochemical and magnetochemical interest (Garnovskii, Nivorozhkin & Minkin, 1973; Maggio, Pizzino & Romano, 1974; Morassi, Bertini & Sacconi, 1973). Characteristically, several distinct compounds may be isolated from one reaction mixture. The products may differ in the coordination number of the metal ions, the stereochemistry of ligand isomers or the degree of molecular complexity. The nature of the Schiff-base complexes appears to be dependent on several factors which include the solvent system, steric constraints imposed by ligand side groups, crystal packing considerations and hybridization states defined by the metal atom. However, it has been observed that on rare occasions some other factors, which include coordination preferences of the metal ion and specific intermolecular interactions, may also affect the result (Elmalı, Elerman, Svoboda & Fuess, 1993; Elmalı, Atakol, Svoboda & Fuess, 1992, 1993*a*,*b*; Gerloch & Mabbs, 1967).

The monomeric title complex, (I), has a distorted square-based pyramidal geometry with a chloro ligand on the apical site. The metal atom is displaced by 0.545 (3) Å above the best plane defined by the Schiff-base N and O donor atoms. The basic metal coordination, and the Fe—Cl and Fe—O/N bond lengths of the Fe^{III} ion are close to those in the related pentacoordinate salen [*N*,*N*-ethylenebis(salicylideneaminato)] complexes [FeCl(salen)] (Garnovskii *et al.*, 1973) and $[Fe_2(salen)_2O]$ (Maggio *et al.*, 1974), and in chloro[(1,1′-diphenyl-3,3′-ethylenediimino)di-1-butanonato]iron(III) (Morassi *et al.*, 1973), as well as in the structures referred to above.



(I)

The Fe atom lies 0.424 (4) and 0.523 (4) Å, respectively, above the best planes of O1, C1, C11, N1 (chelate 1) and O2, C28, C18, N2 (chelate 2). The two chelate planes are mutually inclined at 7.0 (4)° and are nearly symmetrically inclined to the coordination plane at angles of 5.0 (4) (chelate 1) and 2.2 (3)° (chelate 2). There is no significant difference between the torsion angles Fe1—N2—C17—C12 [12.5 (8)°] and Fe1—N1—C12—C17 [−13.5 (8)°]. The sum of the bond angles at the N1 and N2 atoms, which are 359.9 (5) and 359.8 (5)°, are consistent with hybridization. The structure contains dioxane solvent molecules on inversion centres. They have the expected chair conformation, with O atoms 0.654 (4) and 0.676 (4) Å out of the plane of the C atoms for the two independent molecules. The molecules of complex and solvent are held together in the crystal by normal van der Waals forces; contact distances between non-H atoms are all ≥3.4 Å.

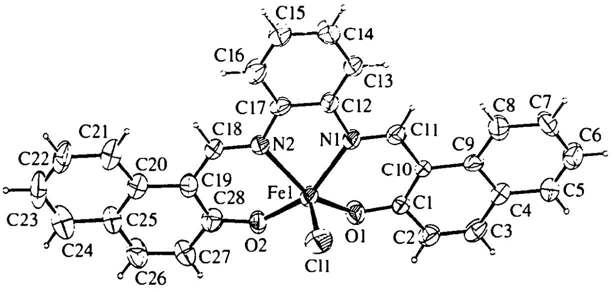


Fig. 1. The molecular structure of the title compound shown with 50% probability ellipsoids. The dioxane solvent molecule is not shown.

Experimental

Crystals were obtained directly from the synthesis of the title compound. Solutions of *N*,*N*′-(di-2-hydroxy-1-naphthylidene)-1,2-diaminobenzene in 50 ml dioxane and $FeCl_3.6H_2O$ in 30 ml methanol were heated to boiling point and mixed. The resulting solution was refluxed for 1 d and suitable crystals were obtained on cooling.

Crystal data

$[FeCl(C_{28}H_{18}N_2O_2)].C_4H_8O_2$
$M_r = 593.85$
Triclinic
$P\bar{1}$
$a = 9.3218 (7)$ Å
$b = 9.5837 (5)$ Å
$c = 15.5376 (8)$ Å
$\alpha = 94.431 (10)°$
$\beta = 101.179 (11)°$
$\gamma = 99.730 (10)°$
$V = 1333.44 (2)$ Å^3
$Z = 2$
$D_x = 1.479$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 3–13°$
$\mu = 0.708$ mm^{-1}
$T = 293 (2)$ K
Needle
0.25 × 0.15 × 0.15 mm
Black

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Kopfmann & Huber, 1968; North, Phillips & Mathews, 1968)
$T_{min} = 0.76$, $T_{max} = 0.90$
2161 measured reflections

2161 independent reflections
2023 reflections with $I > 2\sigma(I)$
$\theta_{max} = 23.1°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -17 \rightarrow 16$
4 standard reflections
frequency: 120 min
intensity decay: 6.2%

Refinement

Refinement on F^2
$R(F) = 0.067$
$wR(F^2) = 0.165$
$S = 1.143$
2161 reflections
361 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0951P)^2 + 2.6167P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.798$ e Å^{-3}
$\Delta\rho_{\min} = -0.452$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Fe1—O1	1.897 (5)	Fe1—N2	2.099 (6)
Fe1—O2	1.910 (5)	Fe1—Cl1	2.227 (3)
Fe1—N1	2.065 (6)		
O1—Fe1—O2	93.9 (2)	N1—Fe1—N2	77.4 (2)
O1—Fe1—N1	85.9 (2)	O1—Fe1—Cl1	109.1 (2)
O2—Fe1—N1	148.9 (2)	O2—Fe1—Cl1	107.2 (2)
O1—Fe1—N2	145.1 (2)	N1—Fe1—Cl1	102.2 (2)
O2—Fe1—N2	85.6 (2)	N2—Fe1—Cl1	104.3 (2)

Data collection: *SDP* (Frenz, 1985). Cell refinement: *SDP*. Data reduction: *SDP*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

The authors wish to acknowledge the purchase of CAD-4 diffractometer under Grant DPT/TBAG1 of the Scientific and Technical Council of Turkey.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: CF1079). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 714–716

Tetrakis(μ-2-biphenylcarboxylato-*O*:*O'*)bis[chlororhenium(III)] Bis(dichloromethane) Solvate

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(Received 11 October 1996; accepted 28 January 1997)

Abstract

The title complex, $[Re_2Cl_2(C_{13}H_9O_2)_4].2CH_2Cl_2$, has the well known 'paddle-wheel' structure common in many $M_2(O_2CR)_4$ structures and the Cl ligands occupy the axial positions. The Re atoms are joined by a quadruple bond of length 2.2363 (7) Å and each metal atom is in a pseudo-octahedral environment. The molecule contains an inversion centre and two *ortho*-phenyl groups of the carboxylate ligands extend out over each axial region.

Comment

The chemistry of dirhenium(III) carboxylates has occupied a crucial place in the development of the chemistry of the metal-to-metal quadruple bond. Over 20 such compounds have been structurally characterized and their properties and reactivities are well documented (Cotton & Walton, 1993).

The first dimetal tetrakis(2-biphenylcarboxylate) compound reported was that of chromium (Cotton & Thompson, 1981*a*), in which the strategy was to use the pendant phenyl group to block the axial position of the molecule. This would, in principle, keep the molecule from forming infinite chains in which the coordinated O atoms of one molecule interact with the axial position of the next, a mode of interaction common in dichromium tetrakis(carboxylate) compounds. In this case, however, the pendant phenyl groups of all four of the 2-biphenylcarboxylate ligands were oriented towards one end of the molecule, leaving the other end free to associate with a similar molecule.

Tetracarboxylato compounds of Mo_2^{4+} have a much lower propensity for the type of intermolecular association found in the Cr_2^{4+} compounds and therefore the $[Mo_2\{O_2C(2\text{-biphenyl})\}_4]$ compound crystallized without such interaction (Cotton & Thompson, 1981*b*). While the steric bulk of the 2-biphenylcarboxylate ligand is somewhat useful in preventing intermolecular association, it does not adequately shield the axial position from coordination by a sufficiently small moiety, *e.g.* CH_3CN in the rhenium compound (Cotton &