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A Five-Coordinate Bis(p-bromophenyl-salicylaldimino)chloroiron(III) Complex

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Abstract

In the title complex, bis[2-(4-bromophenyliminomethyl)-phenolato-N,O]chloroiron(III), [FeCl($C_{13}H_9BrNO$)$_2$], the Fe^{3+} ion shows a distorted square-pyramidal geometry, with the N and O ligand atoms forming the base [Fe—O 1.857 (3) and 1.864 (3) Å, and Fe—N 2.144 (3) and 2.164 (3) Å] and the Cl atom at the apex [Fe—Cl 2.238 (1) Å].

Comment

The complexes of transition metal ions with Schiff bases are a large and growing 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 ion, the stereochemistry of ligand isomers or the degree of molecular complexity. The nature of the products appears to depend on many factors which include the solvent system, steric constraints imposed by ligand side groups, crystal-packing considerations and hybridization which, if any, is the predominant effect (Elmalı, Elerman, Svoboda & Fuess, 1993; Elmalı, Atakol, Svoboda & Fuess, 1993; Gerloch & Mabbs, 1967).

The reaction of iron(III) chloride with the Schiff base p-bromophenylsalicylaldimine is one from which several complexes with similar steric and magnetic properties may be derived. The present five-coordinate monomeric iron(III) complex, (I), is a distorted square pyramid with the Cl atom at the apex. The Fe atom is 0.495 (2) Å above the least-squares plane defined by the Schiff base N- and O-donor atoms, which show a small tetrahedral distortion with an r.m.s. displacement of 0.199 (3) Å.

(I)
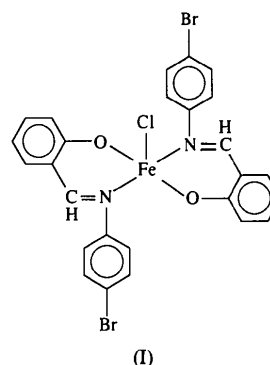
The bond lengths of Fe^{3+} (Table 2) are close to those in the related five-coordinate salen [salen is N,N-ethylenebis(salicylideneaminato)] complexes [FeCl(salen)] (Garnovskii *et al.*, 1973) and [Fe_2(salen)$_2$O] (Maggio et al., 1974), and also in chloro(1,1'-diphenyl-3,3'-ethylenediiminodi-1-butanonato)iron(III) (Morassi *et al.*, 1973). The Fe1 atom is located 0.268 (3) and 0.499 (3) Å above the least-squares planes through O1, C7, C13, N1 (chelate 1) and O2, C14, C20, N2 (chelate 2), respectively. The chelate planes are inclined at angles of
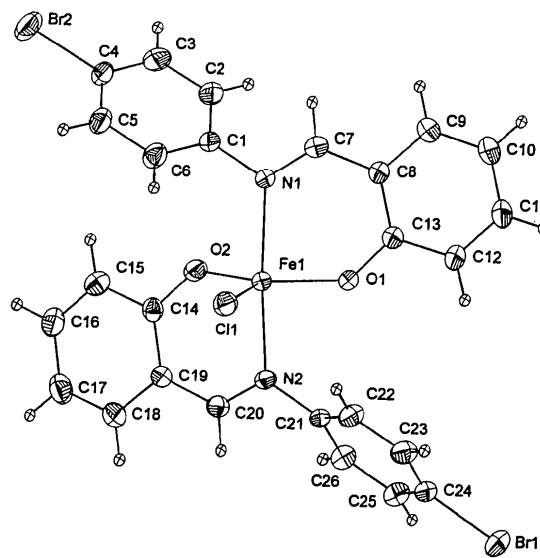

Fig. 1. The molecular structure and atomic numbering of the title compound (*ORTEP*II; Johnson, 1976). The displacement ellipsoids are drawn at the 50% probability level.

13.7 (3) (chelate 1) and 7.7 (3)° (chelate 2) to the O1, N1, O2, N2 coordination plane.

The sums of bond angles at the N atoms, 359.8 (4) (at N1) and 360.0 (4)° (at N2), indicate sp^2 hybridization of these atoms. The phenyl group is nearly planar and the average interatomic C—C distances in the two phenyl rings are found to be 1.386 (3) and 1.390 (3) Å.

The monomeric molecules are held together in the crystal mostly by van der Waals interactions. The minimum intermolecular distances between two non-H atoms such as Cl1⋯C23 and Cl1⋯C5 are 3.746 and 3.805 Å, respectively.

Experimental

Solutions of p-bromophenylsalicylaldimine (2 mmol) in aceto-nitrile (50 ml) and $FeCl_3.6H_2O$ (2 mmol) in methanol (30 ml) were mixed and heated to boiling. The mixture was left to reflux for 1 d whereupon suitable crystals were formed.

Crystal data

$[FeCl(C_{13}H_9BrNO)_2]$	Mo $K\alpha$ radiation
$M_r = 641.54$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 54
$P2_1/n$	reflections
$a = 10.068 (1)$ Å	$\theta = 30\text{–}36°$
$b = 21.731 (2)$ Å	$\mu = 4.02$ mm^{-1}
$c = 11.293 (1)$ Å	$T = 293 (2)$ K
$\beta = 98.26 (1)°$	Plate
$V = 2445.1 (4)$ Å^3	$0.45 \times 0.35 \times 0.12$ mm
$Z = 4$	Black
$D_x = 1.74$ Mg m^{-3}	
D_m not measured	

Data collection

Stoe–Siemens AED	2913 independent reflections
diffractometer	2422 observed reflections
$\omega/2\theta$ scans	$[I > 2\sigma(I)]$
Absorption correction:	$\theta_{max} = 22.52°$
empirical ψ scan	$h = -10 \rightarrow 10$
(Kopfman & Huber,	$k = 0 \rightarrow 23$
1968; North, Phillips &	$l = 0 \rightarrow 12$
Mathews, 1968)	3 standard reflections
$T_{min} = 0.225$, $T_{max} =$	frequency: 180 min
0.481	intensity decay: 2%
2913 measured reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R(F) = 0.035$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
$wR(F^2) = 0.080$	$\Delta\rho_{min} = -0.25$ e Å^{-3}
$S = 1.049$	Extinction correction: none
2913 reflections	Atomic scattering factors
307 parameters	from International Tables
H-atom coordinates fixed	for Crystallography (1992,
$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2]$	Vol. C, Tables 4.2.6.8 and
where $P = (F_o^2 + 2F_c^2)/3$	6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Fe1	0.1269 (1)	0.6401 (1)	0.5802 (1)	0.0352 (2)
Br1	0.5056 (1)	0.5877 (1)	1.1865 (1)	0.0617 (2)
Br2	−0.2402 (1)	0.6506 (1)	−0.0315 (1)	0.0739 (2)
Cl1	0.0280 (1)	0.7250 (1)	0.6379 (1)	0.0490 (3)
O1	0.3098 (3)	0.6367 (2)	0.6346 (2)	0.0496 (8)
O2	0.0009 (3)	0.5894 (1)	0.4908 (2)	0.0444 (7)
N1	0.1783 (4)	0.6705 (2)	0.4119 (3)	0.0353 (8)
N2	0.0958 (3)	0.5857 (2)	0.7343 (3)	0.0359 (8)
C1	0.0799 (4)	0.6682 (2)	0.3066 (3)	0.0382 (11)
C2	0.1102 (5)	0.6375 (2)	0.2064 (4)	0.0528 (13)
C3	0.0138 (6)	0.6326 (3)	0.1065 (4)	0.0599 (14)
C4	−0.1101 (5)	0.6578 (2)	0.1076 (4)	0.0472 (12)
C5	−0.1409 (5)	0.6887 (2)	0.2057 (4)	0.0517 (13)
C6	−0.0446 (5)	0.6936 (2)	0.3069 (4)	0.0493 (12)
C7	0.2981 (5)	0.6868 (2)	0.3967 (4)	0.0438 (11)
C8	0.4181 (4)	0.6843 (2)	0.4839 (4)	0.0402 (11)
C9	0.5393 (5)	0.7052 (2)	0.4505 (4)	0.0574 (14)
C10	0.6575 (5)	0.7010 (3)	0.5263 (5)	0.0639 (15)
C11	0.6582 (5)	0.6745 (2)	0.6363 (4)	0.0577 (13)
C12	0.5422 (5)	0.6528 (2)	0.6733 (4)	0.0533 (13)
C13	0.4201 (5)	0.6578 (2)	0.5976 (4)	0.0405 (11)
C14	−0.1029 (4)	0.5583 (2)	0.5183 (4)	0.0367 (10)
C15	−0.2039 (5)	0.5406 (2)	0.4252 (4)	0.0470 (12)
C16	−0.3091 (5)	0.5059 (2)	0.4491 (4)	0.0547 (13)
C17	−0.3218 (5)	0.4883 (2)	0.5657 (5)	0.0586 (14)
C18	−0.2251 (5)	0.5061 (2)	0.6574 (4)	0.0507 (12)
C19	−0.1137 (4)	0.5406 (2)	0.6366 (3)	0.0386 (11)
C20	−0.0114 (5)	0.5529 (2)	0.7350 (4)	0.0417 (11)
C21	0.1918 (4)	0.5852 (2)	0.8400 (3)	0.0351 (10)
C22	0.2509 (5)	0.6398 (2)	0.8834 (4)	0.0468 (12)
C23	0.3447 (5)	0.6402 (2)	0.9856 (4)	0.0495 (12)
C24	0.3800 (4)	0.5861 (2)	1.0436 (3)	0.0438 (11)
C25	0.3248 (5)	0.5310 (2)	1.0017 (4)	0.0475 (12)
C26	0.2303 (5)	0.5310 (2)	0.9001 (4)	0.0452 (11)

Table 2. *Selected geometric parameters (Å, °)*

Fe1—O1	1.857 (3)	N2—C20	1.295 (5)
Fe1—O2	1.864 (3)	N2—C21	1.423 (5)
Fe1—N1	2.144 (3)	C1—C6	1.369 (6)
Fe1—N2	2.164 (3)	C1—C2	1.385 (6)
Fe1—Cl1	2.238 (1)	C2—C3	1.383 (6)
Br1—C24	1.902 (4)	C3—C4	1.364 (7)
Br2—C4	1.902 (4)	C8—C9	1.403 (6)
O1—C13	1.323 (5)	C9—C10	1.365 (6)
O2—C14	1.318 (5)	C10—C11	1.368 (7)
N1—C7	1.291 (5)	C11—C12	1.379 (7)
N1—C1	1.435 (5)		
O1—Fe1—O2	136.12 (14)	C14—O2—Fe1	132.5 (3)
O1—Fe1—N1	87.21 (13)	C7—N1—C1	116.5 (3)
O2—Fe1—N1	86.24 (13)	C7—N1—Fe1	123.4 (3)
O1—Fe1—N2	87.87 (13)	C1—N1—Fe1	119.9 (3)
O2—Fe1—N2	86.96 (12)	C20—N2—C21	117.2 (3)
N1—Fe1—N2	164.24 (13)	C20—N2—Fe1	121.5 (3)
O1—Fe1—Cl1	113.47 (11)	C21—N2—Fe1	121.3 (3)
O2—Fe1—Cl1	110.39 (10)	C6—C1—N1	120.5 (4)
N1—Fe1—Cl1	100.29 (10)	C2—C1—N1	119.1 (4)
N2—Fe1—Cl1	95.41 (9)	C3—C4—Br2	118.8 (4)
C13—O1—Fe1	136.0 (3)	C5—C4—Br2	120.0 (4)

Values of R_{int} have not been calculated since symmetry-related reflections were deleted before calculation. H atoms were located geometrically and not refined.

Data collection: *DIF4* (Stoe & Cie, 1991a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1355). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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anti,mer-[Bis(2-diphenylphosphinoethyl)-(n-propyl)amine-N,P,P'](phenylethynyl)-[(Z)-1-p-tolyl-4-phenyl-η³-but-1-en-3-ynyl]-ruthenium(II) Chloroform Solvate

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Abstract

The title structure, $[Ru(C_8H_5)(C_{17}H_{13})(C_{31}H_{35}NP_2)]$.CHCl$_3$, consists of discrete anti,mer-[Ru(C≡CPh){η³-PhC≡C—C≡CH(p-tolyl)}(PNP)] neutral molecules, where PNP is $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$, and CHCl$_3$ solvate molecules. The Ru^{II} metal centre is pseudo-octahedrally coordinated by a meridional tridentate PNP ligand, a phenylethynyl ligand and a η³-bonded (Z)-1-p-tolyl-4-phenyl-η³-but-1-en-3-ynyl ligand. The butenynyl moiety is *anti* with respect to

the *n*-propyl tail on the N-atom donor of the amino-diphosphine ligand and lies in a plane almost perpendicular to that containing the Ru(PNP) moiety.

Comment

In recent years, there has been considerable interest in the synthesis, structure and reactivity of Ru^{II}–enynyl complexes (Hill, 1995). In particular, we have reported recently that the Ru^{II}–vinylidene complexes *fac,cis*- and *mer,trans*-[RuCl$_2${C=C(H)R}(PNP)], where R is Ph or p-tolyl and PNP is $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$, react with LiC≡CPh in tetrahydrofuran to afford enynyl and dienynyl complexes, respectively (Bianchini, Innocenti, Peruzzini, Romerosa & Zanobini, 1996).

As a complement to our studies of C—C coupling reactions involving 1-alkynes, we report here the X-ray diffraction analysis of the Ru^{II}–enynyl complex anti,mer-[Ru(C≡CPh){η³-PhC≡C—C≡CH(p-tolyl)}-(PNP)].CHCl$_3$, (I), prepared by treatment of *fac,cis*-[RuCl$_2${C=C(H)(p-tolyl)}(PNP)] in tetrahydrofuran with two equivalents of LiC≡CPh (Bianchini, Innocenti, Peruzzini, Romerosa & Zanobini, 1996). The structure of this complex is of great relevance in confirming that the C—C bond-forming reaction leading to the enynyl fragment involves vinylidene and σ-alkynyl ligands.

(I)
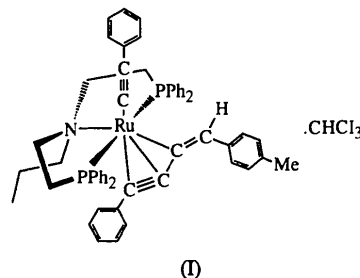
An *ORTEPII* (Johnson, 1976) drawing of the title compound with the atomic numbering scheme is shown in Fig. 1. For clarity, the phenyl substituents of the PNP ligand have been omitted. The crystal structure consists of discrete anti,mer-[Ru(C≡CPh)-{η³-PhC≡C—C≡CH(p-tolyl)}(PNP)] molecules and clathrated chloroform molecules. The metal atom is pseudo-octahedrally coordinated by the three donor atoms of a meridional PNP ligand, by a phenylethynyl ligand and by a η³-PhC≡C—C≡CH(p-tolyl) group.

The two diphenylphosphine ends of the PNP ligand are bent towards the N atom [P(1)—Ru(1)—N(1) 82.0(2) and P(2)—Ru(1)—N(1) 84.2(2)°] as a consequence of the chelate-ring bite. The Ru(1)—N(1) [2.267(6) Å], Ru(1)—P(1) and Ru(1)—P(2) distances [2.319(2) and 2.307(2) Å, respectively], although somewhat shorter than those found in anti,mer-[Ru(C≡CPh)-(η³-PhC≡C—C≡CHPh)(PNP)] (Bianchini, Innocenti, Peruzzini, Romerosa & Zanobini, 1996), are in the range of those found for related Ru(PNP) complexes