

## A complex containing both five- and six-coordinate [bis(5-bromosalicylidene)benzene-1,2-diimine]chloro-iron(III)

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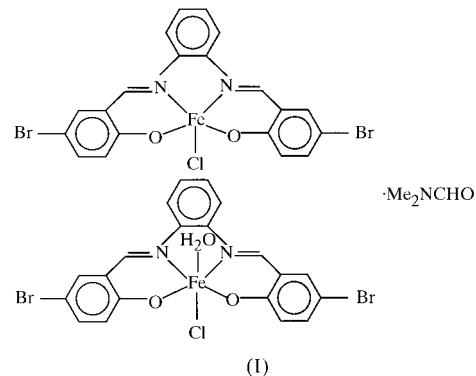
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The title compound, aquachloro{4,4'-dibromo-2,2'-[*o*-phenylenebis(nitrilomethylidene)]diphenolato-*O,N,N',O'*}iron(III)-chloro{4,4'-dibromo-2,2'-[*o*-phenylenebis(nitrilomethylidene)]diphenolato-*O,N,N',O'*}iron(III)-dimethylformamide (1/1/1), [FeCl(C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)] [FeCl(C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)(H<sub>2</sub>O)]·C<sub>3</sub>H<sub>7</sub>NO, contains one independent five-coordinate [FeCl(C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)] monomer, one six-coordinate [FeCl(C<sub>20</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>2</sub>)(H<sub>2</sub>O)] monomer and a non-coordinating dimethylformamide solvent molecule in the asymmetric unit. In the five-coordinate monomer, the Fe atom shows distorted square-pyramidal geometry, with the N and O atoms of the ligand at the base and the Cl atom at the apex of the pyramid. In the six-coordinate monomer, the Fe atom is in a distorted octahedral geometry and coordinated by the donor atoms of the tetrafunctional ligand in the horizontal plane, and the coordination sphere is completed by the O atom of the water molecule and the Cl atom at the axial positions. The title compound contains intermolecular O—H···O hydrogen bonds. Apart from these hydrogen bonds, there are also intermolecular C—H···Cl and C—H···O contacts.

### Comment

The complexes of transition metal ions with Schiff bases provide a large class of compounds of both stereochemical and magnetochemical interest due to their preparative accessibility, diversity and structural variability (Garnovskii *et al.*,

1993). We have previously determined the structures of several dimeric and monomeric Schiff base complexes of iron(III) (Elmali *et al.*, 1992; Elmali *et al.*, 1993, 1993*a*, 1993*b*). We report here the results of the reaction of Fe<sup>III</sup> with the tetradentate ligand *N,N'*-bis(5-bromosalicylidene)-1,2-phenylenediamine, forming the title complex, (I).

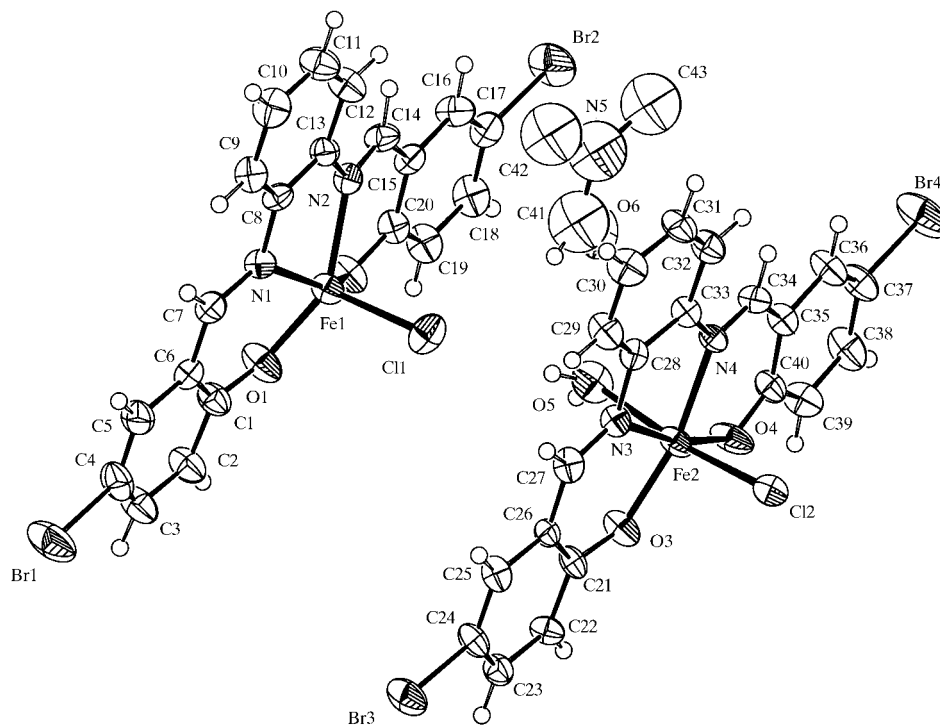


There are two independent monomers and a non-coordinating dimethylformamide solvent molecule in the asymmetric unit of (I). In the five-coordinate monomer, atom Fe1 is coordinated by the N and O atoms of the Schiff base and by a Cl atom in a distorted square-pyramidal geometry. Atom Fe1 is 0.423 (1) Å below the best plane defined by it and the Schiff base N and O donor atoms. The angles between the coordination plane and each of the chelate groups in the five-coordinate monomer (O1/C1/C6/C7/N1 and O2/C20/C15/C14/N2) are 5.3 (1) and 2.9 (1)°, respectively. The angle between the two chelate groups is 8.0 (1)°.

In the six-coordinate monomer, on the other hand, atom Fe2 is in a distorted octahedral geometry. The coordination sphere of atom Fe2 is completed by a water molecule at a distance Fe2—O5 of 2.142 (2) Å. Atom Fe2 is 0.081 (1) Å above the best plane defined by it and the Schiff base N and O donor atoms. The O3—Fe2—N4 and O4—Fe2—N3 angles are bent from linearity with values of 165.6 (1) and 167.6 (1)°, respectively. The Fe2—O3 and Fe2—O4 bond lengths [1.896 (2) and 1.890 (2) Å, respectively] are clearly shorter than the distance between Fe2 and the O5 atom of the water molecule [2.142 (2) Å]. The O5—Fe2—Cl2 angle [169.4 (1)°] indicates that the Fe2 atom is coordinated by O and Cl atoms at the distorted axial positions. The distance between Fe2 and the O5 atom of the water molecule is within the range of other similar six-coordinate monomeric iron(III) complexes reported to date (Cheng & Scheidt, 1995; Okabe & Makino, 1998). The Fe—N, Fe—O and Fe—Cl bond distances in both of the monomers are almost consistent with those found in other similar iron(III) complexes (Elmali *et al.*, 1993*b*; Elerman *et al.*, 1997; Gerloch & Mabbs, 1967).

Neighbouring molecules in the asymmetric unit of (I) are linked *via* intermolecular hydrogen bonds, with O5—H···O1<sup>iv</sup> 3.303 (3) Å and O5—H···O2<sup>iv</sup> 2.732 (3) Å [symmetry code: (iv) 1 - x, 1 - y, -z]. There are also a number of short C—H···Cl and C—H···O interactions (Table 2).

† Alexander von Humboldt fellow.


**Figure 1**

The molecular structure of (I) showing the atom-labelling scheme and with 50% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

## Experimental

The Schiff base ligand *N,N'*-bis(5-bromo-2-hydroxybenzylidene)-1,3-propanediamine was synthesized by reaction of 1,2-phenylenediamine and 5-bromosalicylaldehyde in a 1:2 molar ratio in methanol solution at room temperature. The Schiff base was obtained as an orange crystal. For the preparation of the title complex, this ligand (1 mmol) was dissolved in hot dimethylformamide, and a solution of iron(II) chloride tetrahydrate (1 mmol) in methanol (20 ml) was added. The solution was allowed to evaporate at room temperature and single crystals of (I) were obtained on cooling.

### Crystal data

|                                                                                                                                                                                                                                      |                                           |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------|
| [FeCl(C <sub>20</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> )]·<br>[FeCl(C <sub>20</sub> H <sub>12</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> )(H <sub>2</sub> O)]·C <sub>3</sub> H <sub>7</sub> NO | $V = 2135.4 (7) \text{ \AA}^3$            |
| $M_r = 1218.01$                                                                                                                                                                                                                      | $Z = 2$                                   |
| Triclinic, $P\bar{1}$                                                                                                                                                                                                                | $D_x = 1.885 \text{ Mg m}^{-3}$           |
| $a = 11.623 (2) \text{ \AA}$                                                                                                                                                                                                         | Mo $K\alpha$ radiation                    |
| $b = 13.426 (3) \text{ \AA}$                                                                                                                                                                                                         | Cell parameters from 25 reflections       |
| $c = 15.156 (2) \text{ \AA}$                                                                                                                                                                                                         | $\theta = 2.96\text{--}13.33^\circ$       |
| $\alpha = 76.44 (1)^\circ$                                                                                                                                                                                                           | $\mu = 4.603 \text{ mm}^{-1}$             |
| $\beta = 71.30 (1)^\circ$                                                                                                                                                                                                            | $T = 303 (2) \text{ K}$                   |
| $\gamma = 75.16 (2)^\circ$                                                                                                                                                                                                           | Needle, black                             |
|                                                                                                                                                                                                                                      | $0.40 \times 0.10 \times 0.05 \text{ mm}$ |

### Data collection

|                                                                                |                                     |
|--------------------------------------------------------------------------------|-------------------------------------|
| Enraf–Nonius CAD-4 diffractometer                                              | $R_{\text{int}} = 0.025$            |
| $\theta/2\theta$ scans                                                         | $\theta_{\text{max}} = 25.48^\circ$ |
| Absorption correction: empirical via $\psi$ scans (North <i>et al.</i> , 1968) | $h = -13 \rightarrow 14$            |
| $T_{\text{min}} = 0.156$ , $T_{\text{max}} = 0.794$                            | $k = -15 \rightarrow 16$            |
| 9150 measured reflections                                                      | $l = 0 \rightarrow 18$              |
| 7926 independent reflections                                                   | 3 standard reflections              |
| 7911 reflections with $I > 2\sigma(I)$                                         | frequency: 90 min                   |
|                                                                                | intensity decay: 3.6%               |

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.121$   
 $S = 1.014$   
 7926 reflections  
 540 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0126P)^2 + 1.3469P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.002$   
 $\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -1.34 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

|            |             |              |             |
|------------|-------------|--------------|-------------|
| N1–Fe1     | 2.0918 (19) | O4–Fe2       | 1.8904 (18) |
| N2–Fe1     | 2.0715 (19) | Cl1–Fe1      | 2.2356 (8)  |
| N3–Fe2     | 2.1215 (19) | Cl2–Fe2      | 2.3926 (8)  |
| N4–Fe2     | 2.0974 (17) | Fe2–O5       | 2.142 (2)   |
| O1–Fe1     | 1.8775 (18) | O5–HO51      | 0.943 (2)   |
| O2–Fe1     | 1.8834 (17) | O5–HO52      | 0.7897 (17) |
| O3–Fe2     | 1.8956 (17) |              |             |
| C7–N1–Fe1  | 124.31 (16) | N2–Fe1–Cl1   | 98.75 (5)   |
| C8–N1–Fe1  | 113.53 (14) | N1–Fe1–Cl1   | 103.58 (6)  |
| C14–N2–Fe1 | 124.46 (15) | O4–Fe2–O3    | 102.19 (7)  |
| C13–N2–Fe1 | 114.22 (14) | O4–Fe2–N4    | 90.25 (7)   |
| C27–N3–Fe2 | 124.09 (15) | O3–Fe2–N4    | 165.61 (7)  |
| C28–N3–Fe2 | 114.14 (14) | O4–Fe2–N3    | 167.63 (8)  |
| C34–N4–Fe2 | 123.88 (15) | O3–Fe2–N3    | 88.70 (7)   |
| C33–N4–Fe2 | 114.56 (13) | N4–Fe2–N3    | 78.25 (7)   |
| C1–O1–Fe1  | 132.97 (16) | O4–Fe2–O5    | 89.77 (9)   |
| C20–O2–Fe1 | 130.20 (14) | O3–Fe2–O5    | 89.61 (8)   |
| C21–O3–Fe2 | 133.71 (14) | N4–Fe2–O5    | 83.17 (7)   |
| C40–O4–Fe2 | 131.79 (15) | N3–Fe2–O5    | 84.39 (8)   |
| O1–Fe1–O2  | 90.84 (8)   | O4–Fe2–Cl2   | 95.34 (7)   |
| O1–Fe1–N2  | 148.96 (8)  | O3–Fe2–Cl2   | 98.30 (6)   |
| O2–Fe1–N2  | 87.64 (8)   | N4–Fe2–Cl2   | 87.56 (5)   |
| O1–Fe1–N1  | 87.32 (8)   | N3–Fe2–Cl2   | 88.78 (6)   |
| O2–Fe1–N1  | 147.03 (8)  | O5–Fe2–Cl2   | 169.44 (6)  |
| N2–Fe1–N1  | 77.55 (7)   | Fe2–O5–HO51  | 112.99 (14) |
| O1–Fe1–Cl1 | 111.18 (7)  | Fe2–O5–HO52  | 118.32 (19) |
| O2–Fe1–Cl1 | 107.73 (6)  | HO51–O5–HO52 | 105.8 (2)   |

**Table 2**

Hydrogen-bonding geometry (Å, °).

| <i>D</i> —H... <i>A</i>      | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|------------------------------|-------------|---------------|-----------------------|-------------------------|
| C9—H9...C11 <sup>i</sup>     | 0.93        | 2.75          | 3.654 (2)             | 165                     |
| C12—H12...C12 <sup>ii</sup>  | 0.93        | 2.74          | 3.643 (3)             | 163                     |
| C14—H14...C12 <sup>ii</sup>  | 0.93        | 2.63          | 3.537 (3)             | 165                     |
| C16—H16...C12 <sup>ii</sup>  | 0.93        | 2.94          | 3.777 (4)             | 150                     |
| C32—H32...C12 <sup>iii</sup> | 0.93        | 2.74          | 3.648 (2)             | 167                     |
| C34—H34...C12 <sup>iii</sup> | 0.93        | 2.86          | 3.731 (3)             | 156                     |
| C2—H2...O6 <sup>iv</sup>     | 0.93        | 2.44          | 3.332 (4)             | 161                     |
| C14—H14...O3 <sup>ii</sup>   | 0.93        | 2.92          | 3.364 (3)             | 111                     |
| C41—H41...O5                 | 0.93        | 2.75          | 3.062 (10)            | 101                     |

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

H atoms bonded to C atoms were refined using a riding model with C—H = 0.93 Å and H-atom displacement parameters were restricted to be  $1.2U_{eq}$  of the parent atom. Since the dimethylformamide solvent is highly mobile, the C and N atoms of the solvent were refined isotropically and the H atoms of the solvent methyl groups were not determined. In the difference Fourier map, it was found that one of the residual densities larger than  $1 e \text{ \AA}^{-3}$  was close to Br3, at a distance of 0.07 Å.

Data collection: *CAD-4 Diffractometer Control Software* (Enraf-Nonius, 1993); cell refinement: *CAD-4 Diffractometer Control Software*; data reduction: *REDU4* (Stoe & Cie, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics:

*PLUTON92* (Spek, 1992); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1097). Services for accessing these data are described at the back of the journal.

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