

# Crystal Structure and Magnetic Properties of a Dinuclear Iron(III) Doubly Oxygen Bridged Schiff Base Complex

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[Fe(L)Cl]<sub>2</sub> (L = N-(4-methylphenyl)-3-methoxy-salicylaldimimine) was synthesized and its crystal structure determined. [C<sub>30</sub>H<sub>26</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub>], triclinic, space group *P*  $\bar{1}$ , *a* = 9.278(2), *b* = 9.4050(10), *c* = 10.489(2) Å,  $\alpha$  = 64.43(2),  $\beta$  = 74.540(10),  $\gamma$  = 62.40(2)°, *V* = 729.1(2) Å<sup>3</sup>, *Z* = 1. Two identical [Fe(L)Cl] fragments, related by an inversion center, are connected by two bridging O atoms to form a binuclear unit. The iron(III) centers are separated by 3.196(2) Å and weakly antiferromagnetically coupled (*J* = −10.1(1) cm<sup>−1</sup>), as derived from temperature-dependent magnetic susceptibility measurements in the range 5.1–283.5 K.

**Key words:** Dinuclear Iron(III) Complex, Super-Exchange Interactions, Antiferromagnetic Coupling

## Introduction

The electronic and magnetic properties of dinuclear iron(III) complexes have been extensively studied [1–3]. Dinuclear iron(III) complexes provide structural models for dinuclear sites in several proteins involved in oxygen storage of hemerythrin and oxygen activation of methanemonooxygenase [4–7]. In addition, these systems were treated as model systems for the understanding of the size and magnitude of super-exchange coupling interactions in theoretical considerations. Two classes of compounds can be distinguished, namely the ( $\mu$ -oxo)-diiron(III) and ( $\mu$  – hydroxo)-diiron(III) types [2]. Several synthetic Fe–O–Fe ( $\mu$ -hydroxo)-diiron(III) complexes showed catalase-like activity and are catalysts for alkane oxidation [8–11]. The present work provides the results of the X-ray structure analysis and of temperature-dependent susceptibility measurements of [Fe(L)Cl]<sub>2</sub> (L = N-(4-methylphenyl)-3-methoxy-salicylaldimimine). We reported previously the structures and magnetic properties of several dimeric iron(III) complexes [12–15]. Our aim is to understand the effect of geometric parameters, including mainly Fe–O bond distances and Fe–O–Fe bond angles, on the super-exchange interactions.

## Experimental Section

### Preparation

For the preparation of the complex, solutions of 0.5 mmol of FeCl<sub>2</sub>·4H<sub>2</sub>O in 30 ml of methanol were added to a solution of 0.5 mmol of 2-hydroxy-4-methoxy-benzaldehyde in 30 ml acetonitrile. The mixture was refluxed for 3 h. Dark black crystals formed during the reflux operation and were washed with cold ethanol. Yield: 71%, m.p. 290° C. – C<sub>30</sub>H<sub>26</sub>Cl<sub>2</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub> (693.1): calcd. C 52.98, H 3.78, N 4.04; found C 52.20, H 3.70, N 4.14.

### Susceptibility measurements

Variable-temperature magnetic susceptibility measurements of a powdered sample were performed with a QUANTUM Design SQUID susceptometer in the temperature range 5.1–283.5 K. The applied field was 1 T. Diamagnetic corrections of the molar magnetic susceptibility of the compound were applied using Pascal's constant [16]. The effective magnetic moments were calculated by the equation  $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$ .

### X-ray structure determination

X-ray data collection was carried out on an Enraf-Nonius CAD-4 diffractometer [17] using a single crystal with dimension 0.48 × 0.22 × 0.18 mm

with a graphite monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Experimental conditions are summarized in Table 1. Precise unit cell dimensions were determined by least-squares refinement on the setting angles of 25 reflections ( $2.50^\circ \leq \theta \leq 9.10^\circ$ ) carefully centered on the diffractometer. Three standard reflections (220, 212, 434) were measured every 7200 s and the orientation of the crystal was checked after every 600 reflections. Data reduction and corrections for absorption and decomposition were achieved using the Nonius Diffractometer Control Software [17]. The structure was solved by SHELXS-97 [18] and refined with SHELXL-97 [19]. The positions of the H atoms bonded to C atoms were calculated (C–H distance 0.96 Å) and refined using a riding model, and H atom displacement parameters were restricted to be 1.2  $U_{eq}$  of the parent atom. The final positional parameters are presented in Table 2. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-198751 [20].

## Results and Discussion

### X-ray crystal structure

An ORTEP representation of the structure including the atomic numbering scheme is given Fig. 1 [21]. Selected bond lengths and angles are summarized in Table 3. The two [Fe–L] units are doubly linked by two oxygen atoms. In the structure, from the point of symmetry, the two monomeric units are related by a center of inversion,

Table 1. Crystallographic data for the title compound.

Sum formula	C <sub>30</sub> H <sub>26</sub> Cl <sub>2</sub> Fe <sub>2</sub> N <sub>2</sub> O <sub>6</sub>
$f_w$ (g·mol <sup>−1</sup> )	693.13
Space group	$P\bar{1}$
$a = 9.278(2)$ Å	$\alpha = 64.43(2)^\circ$
$b = 9.4050(10)$ Å	$\beta = 74.540(10)^\circ$
$c = 10.489(2)$ Å	$\gamma = 62.40(2)^\circ$
Vol [Å <sup>3</sup> ]	729.1(2)
$Z$	1
$D_{calc}$ (g·cm <sup>−3</sup> )	1.579
$\mu$ [cm <sup>−1</sup> ]	1.225
$F(000)$	354
Index ranges	$-8 \leq h \leq 12, -12 \leq k \leq 13,$ $-14 \leq l \leq 14$
Reflections collected	6103
Independent reflections	3793 [ $R(int) = 0.0584$ ]
Data/restraints/parameters	3793/0/190
Goodness-of-fit on $F^2$	0.878
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R = 0.0480, wR = 0.1061$
Largest diff. peak and hole	0.614 and $-0.414$ e·Å <sup>−3</sup>

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). Equivalent isotropic  $U(eq)$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

Atom	$x$	$y$	$z$	$U(eq)$
C(1)	807(3)	5612(4)	11778(3)	37(1)
C(2)	−144(4)	6522(4)	12662(3)	43(1)
C(3)	575(4)	6639(4)	13595(4)	45(1)
C(4)	2269(4)	5762(4)	13652(4)	50(1)
C(5)	3223(4)	4865(4)	12778(4)	46(1)
C(6)	2507(3)	4778(4)	11819(3)	36(1)
C(7)	4815(4)	2851(4)	10865(3)	41(1)
C(8)	5688(3)	935(4)	9929(4)	40(1)
C(9)	7348(4)	872(4)	10110(4)	51(1)
C(10)	8243(4)	−36(5)	9233(4)	61(1)
C(11)	7542(4)	70(4)	8171(4)	55(1)
C(12)	5907(4)	1068(4)	7982(4)	48(1)
C(13)	4948(3)	2040(4)	8851(4)	40(1)
C(14)	5999(6)	674(7)	5890(5)	106(2)
C(15)	−444(5)	7676(5)	14518(4)	61(1)
N(1)	3291(3)	3959(3)	10817(3)	37(1)
O(1)	183(2)	5494(3)	10812(2)	44(1)
O(2)	3391(2)	2987(3)	8644(2)	49(1)
O(3)	5104(3)	1269(4)	6970(3)	73(1)
Fe(1)	1808(1)	4716(1)	9263(1)	40(1)
Cl(1)	1891(1)	7149(1)	7574(1)	57(1)

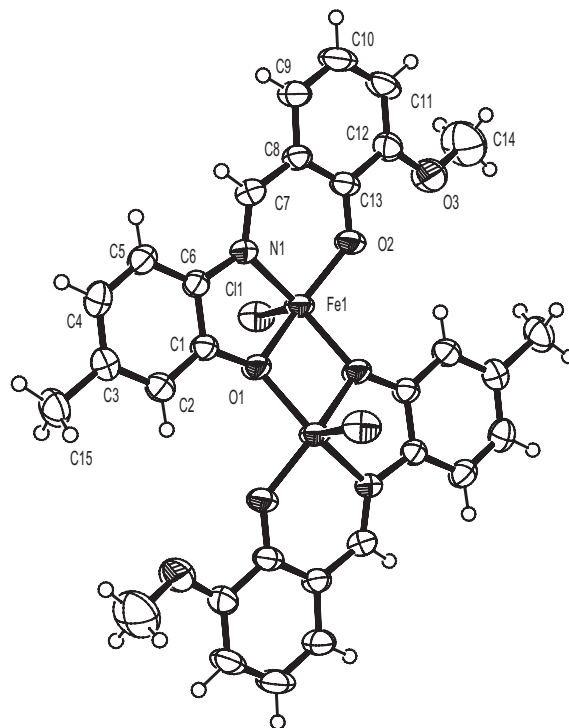


Fig. 1. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level.

Table 3. Selected bond lengths [Å] and angles [°] characterizing the inner coordination sphere of the iron(III) center (see Fig. 1 for labeling scheme adopted.)

Fe1–N1	2.084(2)
Fe1–O1 <sup>a</sup>	1.970(2)
Fe1–O1	2.036(2)
Fe1–O2	1.847(2)
Fe1–Cl1	2.230(1)
Fe1 <sup>a</sup> –O1–Fe1	105.81(9)
O2–Fe1–O1 <sup>a</sup>	100.85(9)
O2–Fe1–O1	150.5(1)
O1 <sup>a</sup> –Fe1–O1	74.19(9)
O2–Fe1–N1	89.19(9)
O1 <sup>a</sup> –Fe1–N1	136.8(1)
O1–Fe1–N1	76.75(8)
O2–Fe1–Cl1	104.95(8)
O1 <sup>a</sup> –Fe1–Cl1	109.61(8)
O1–Fe1–Cl1	104.04(7)
N1–Fe1–Cl1	108.04(8)

Symmetry transformations used to generate equivalent atoms: <sup>a</sup>(1 – x, –y + 1, –z + 2).

which means that the four-membered ring formed by atoms Fe1, O1, Fe1<sup>a</sup> and O1<sup>a</sup> [symmetry transformations used to generate equivalent atoms: <sup>a</sup>(1 – x, –y + 1, –z + 2)] is planar.

Two iron(III) centers are 3.196(2) Å apart and coordinated by two imine N atoms and two phenol O atoms from the imine-phenol ligand. The coordination is completed by one Cl atom. In this way the Fe atom is five-coordinate with a Cl atom at the apex of a square pyramid. The Fe–Cl bond length is 2.230(1) Å. The two Fe–O distances [Fe–O1 and Fe–O1<sup>a</sup>] are different [2.036(2) Å and 1.970(2) Å]. The Fe–N distance is 2.084(2) Å. The Fe1–O1–Fe1<sup>a</sup> angle in the central four membered ring is 105.81(9)° and O1–Fe1–N1 and O1–Fe1–Cl are found to be 76.75(8)° and 104.04(7)°.

### Magnetic properties

The magnetic susceptibilities of the complex are shown as a function of temperature in Fig. 2, and the magnetic moments are shown as a function of temperature in Fig. 3. The magnetic data was fitted using the expression for molar susceptibility vs. *T* derived from the spin exchange Hamiltonian,  $H = -2J(S_1 \cdot S_2)$ , where *J* is super-exchange coupling constant between two spin carriers and with  $S_1 = S_2 = 5/2$  as given in eq. (1) the molar magnetic

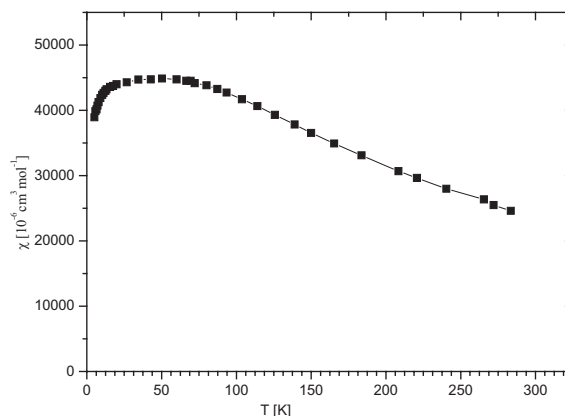


Fig. 2. The molar magnetic susceptibilities  $\chi$  per iron(III) vs. temperature *T* curve.

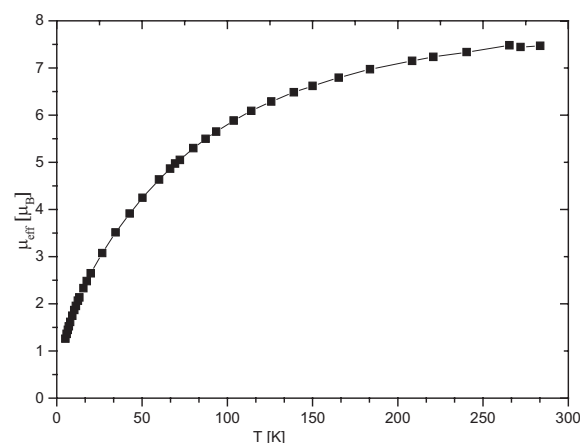


Fig. 3. Magnetic moment per iron(III) vs. temperature curve.

susceptibility for dinuclear iron(III) complexes is expressed.

$$\chi = (1 - x_p)\chi'' + 2x_p\chi' + TIP \quad (1)$$

$$\chi'' = \left(\frac{C}{T}\right) \frac{2\exp(2x) + 10\exp(6x) + 28\exp(12x) + 60\exp(29x) + 110\exp(30x)}{1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x) + 9\exp(20x) + 11\exp(30x)}$$

$$\chi' = \frac{C}{3(T - \Theta)}, \quad x = \frac{J}{kT}, \quad C = \frac{N_L g^2 \mu_B^2}{k}$$

For a satisfactory fit it was necessary to include a Curie-Weiss term in order to correct for a paramagnetic impurity;  $x_p$  is the molar amount of this mononuclear impurity. The temperature-independent paramagnetism ( $TIP = 400 \cdot 10^{-6} \text{ cm}^3/\text{mol}$  for each

iron atom) was also taken into account. The best fit parameters which were obtained with eq. (1) by using a standard least-squares program were  $g = 2.00$ ,  $J = -10.1 \text{ cm}^{-1}$ ,  $x_p = 1.60(2)\%$  and the Weiss constant  $\Theta = -1.2 \text{ K}$ . The effective magnetic moment per iron(III) is 7.47 B.M. at 283.5 K. The magnetic susceptibility is at a maximum near 50 K and decreases rapidly as the temperature is lowered to liquid helium temperature.

The selected structural and magnetic data of the title compound and similar complexes are listed in Table 4. In these compounds, the large average bond lengths between the iron and the bridging O atoms are responsible for the relatively weak antiferromagnetic coupling. The increase in the average Fe–O bond lengths from 1.999 in **c** to 2.044 Å in **b** is connected with a decrease in the antiferromagnetic exchange-coupling constant ( $J$ ) from  $-10.9$  to  $-6.5 \text{ cm}^{-1}$ . **b** has the longest average Fe–O bond length, the largest average Fe–O–Fe bridging angle and the smallest  $J$  constant (see Table 4). However, the Fe–O–Fe angles of **a**, **c**, **e** and of the title compound are almost identical and the difference of the average Fe–O bond lengths between **a** and **c** is 0.026 Å, but the difference of the  $J$  constants is  $3.2 \text{ cm}^{-1}$ . It is clear that the influence of the average Fe–O bond length is more important than the Fe–O–Fe angle in the antiferromagnetic super-exchange coupling. Of course the structural details of the molecular structures are not sufficient to exclude definitely an influence of the Fe–O–Fe angle on the value of the coupling constant.

Gorun and Lippard suggested a quantitative magnetostructural relationship for dinuclear iron(III) centers, doubly bridged by oxygen atoms [22]. This

exponential relationship,  $-J = A \cdot \exp(BP)$ , correlates the antiferromagnetic super-exchange coupling constant  $J$  with a parameter  $P$ , describing the shortest super-exchange pathway between the two metal centers. Using the reported values for  $A$  ( $8.763 \times 10^{11}$ ) and  $B$  ( $-12.663$ ) and the value  $P = 2.003 \text{ Å}$  as found in the present study, a value of  $J_{calc} = -8.5 \text{ cm}^{-1}$  is obtained in fair agreement with  $J_{obs} = -10.1 \text{ cm}^{-1}$ .

Clearly, the variation of the strength of the super-exchange interaction cannot be explained completely by the structural features of dinuclear iron(III) complexes. A different approach must be discussed to clarify the origin of the super-exchange mechanism of this system. To gain a reasonable explanation for these facts one can consider the super-exchange mechanism of this system in terms of Hoffman's theory [23]. In Hoffman's theory, the exchange coupling constant of the Hamiltonian  $\mathbf{H} = -2\mathbf{J}(\mathbf{S}_1 \cdot \mathbf{S}_2)$  is expressed as the sum of an antiferromagnetic term,  $J_{AF} (< 0)$  and a ferromagnetic contribution  $J_F (> 0)$ ;  $J = J_F + J_{AF}$  for a dinuclear Fe(III) complex with local octahedral environment about the metal ions and high-spin ( $S_1 = S_2 = 5/2$ ). A tentative explanation of the apparent inadequacy of Hoffman's formalism to account for the changes in small antiferromagnetic coupling observed for the compounds proposed herein brings into question the general validity of the assumption [24] that the ferromagnetic contribution to  $J$  is small and not affected a great deal by structural distortions or substituent effects in a series of chemically related compounds. Actually, experimental and theoretical results [25–27] on  $d^1$  bimetallic systems suggest that this contribution is geometry-dependent and, in ad-

Table 4. Structural and magnetic data of the related compounds.

Compound	Fe···Fe [Å]	Fe–O–Fe [°]	<Fe–O> [Å] <sup>f</sup>	$J$ [cm <sup>-1</sup> ]	$J_{calc}$ [cm <sup>-1</sup> ] <sup>g</sup>	$x_p$ [%] <sup>h</sup>	$\theta$ [K] <sup>i</sup>
<b>a</b>	3.216(2)	105.1(2)	2.025	-7.7(1)	-6.4	2.00	-0.7
<b>b</b>	3.348(2)	110.0(2)	2.044	-6.5(1)	-5.0	1.40	-3.1
<b>c</b>	3.186(4)	105.6(3)	1.999	-10.9(1)	-8.9	1.80	-2.1
<b>d</b>	3.189(1)	104.3(3)	2.020	8.3(1)	-6.9	1.50	-1.3
<b>e</b>	3.196(2)	105.7(2)	2.006	-10.4(1)	-8.1	1.65	-1.2
<b>This work</b>	3.196(2)	105.8(2)	2.003	-10.1(1)	-8.5	1.60	-1.2

<sup>a</sup> [Fe(L<sup>1</sup>)(MeOH)Cl]<sub>2</sub> (L<sup>1</sup> = N-2-hydroxy-4-chlorophenyl-salicylaldehyde) [12]; <sup>b</sup> [Fe(L<sup>2</sup>)Cl]<sub>2</sub> (L<sup>2</sup> = N-2-hydroxy-3-hydroxy-2-naphthaldehyde) [12]; <sup>c</sup> [Fe(L<sup>3</sup>)Cl]<sub>2</sub> (L<sup>3</sup> = N-2-hydroxy-4-chlorophenyl-3-hydroxy-2-naphthaldehyde) [12]; <sup>d</sup> [Fe(L)(MeOH)Cl]<sub>2</sub> (L = N-(5-methylphenyl)-3-methoxy-salicylaldehyde) [13]; <sup>e</sup> [Fe(L)(MeOH)Cl]<sub>2</sub> (L = N-(5-methylphenyl)-3-methoxy-salicylaldehyde) [14]; <sup>f</sup> <Fe–O> is the average distance between the iron and the bridging O atoms; <sup>g</sup> the calculated spin exchange coupling constant according to Gorun *et al.* [22]; <sup>h</sup>  $x_p$  is the molar amount of mononuclear impurity; <sup>i</sup>  $\Theta$  is the Weiss constant.

dition, may be important. Since the changes in  $J$  for the present compounds appear to be in the opposite direction of what would be expected upon consideration of the antiferromagnetic term only, it is possible that a description of the relative magnetic properties of  $\text{Fe}_2\text{O}_2$  compounds requires an explicit consideration of both  $J_F$  and  $J_{AF}$ . Further work on

additional members of this series of oxygen-bridged iron(III) compounds is in progress.

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