Exchange Interaction in a Dinuclear Iron(III) Complex of a Heptadentate Schiff Base: Synthesis, Crystal Structure and Magnetic Properties

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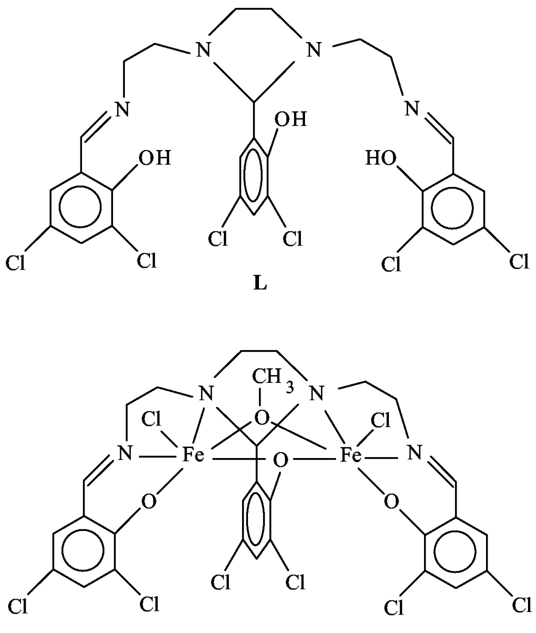
Z. Naturforsch. **60b,** 727 – 731 (2006); received February 4, 2005

Synthesis, crystallographic characterization and magnetic properties of the new dinuclear iron(III) complex $Fe_2L(OCH_3)Cl_2$ (L=1,3-bis[N-(3,5-dichloro-2-hydroxybenzylidene)-2-aminoethyl]-2-(3,5-dichlo ro-2-hydroxyphenyl)imidazolidine) are reported. The structure consists of dinuclear units. The two iron(III) atoms are asymmetrically bridged by a phenoxo and a methoxo group. The iron(III) centers are separated by 3.133(2) Å. The Magnetic susceptibility of the complex was measured over the range 5 – 298 K and the observed data were successfully simulated by the equation based on the spin-Hamiltonian operator $H = -J\vec{S}_1.\vec{S}_2$. Magnetic susceptibility measurements indicate very weak antiferromagnetic coupling between the iron ions with $J = -10.8$ cm^{-1} and g = 2.0.

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

Introduction

In the last decades, the electronic and magnetic properties of dinuclear iron complexes have been extensively studied [1 – 4]. They provide structural models for dinuclear sites in several proteins involved in oxygen storage of hemerytherin and oxygen activation of methanemonooxygenase [5 – 8]. In addition, these systems were treated as model systems for the understanding of the size and magnitude of exchange coupling interactions in theoretical considerations. Studies of some iron complexes have shown that the oxo bridge is responsible for the strong antiferromagnetic coupling (usually $-50 > J > -200$ cm^{-1}) [9 – 12] and that complexes with alkoxo, phenoxo, or hydroxo bridges are weakly coupled (usually $0 > J > -30$ cm^{-1}) [11, 13 – 16]. In an attempt to accumulate more data for further discussions of magneto-structural correlations for this type of complexes, we present here the synthesis, X-ray structural and magnetic characterization of a derivative of a closely related ligand, $Fe_2L(OCH_3)Cl_2$.



L

$Fe_2L(OCH_3)Cl_2$

Fig. 1. Formulae of the ligand and its complex.

Experimental Section

Preparation of $Fe_2L(OCH_3)Cl_2$

The dinuclear Fe(III) complex was prepared in two steps. In the first step, the Schiff base ligand L was synthesized. A solution of triethylenetetramine (2.2 g, 15 mmol) in methanol (20 ml) was added dropwise to a methanolic solution (40 ml)

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Table 1. Crystallographic data for the investigated complex.

Formula	$C_{28}H_{24}Cl_8Fe_2N_4O_4$
Formula weight (g.mol^{-1})	875.81
Crystal system	monoclinic
Space group	$P2_1$
a [Å]	9.187(1)
b [Å]	12.849(1)
c [Å]	14.569(2)
β [°]	97.68(1)
Vol [Å^3]	1704.4(3)
Z	2
D_{calc} [g.cm^{-3}]	1.707
μ [cm^{-1}]	1.520
F(000)	880
θ Range for data collection	$2.60° < \theta < 30.15°$
Index ranges	$-12 \le h \le 12$ $0 \le k \le 17$ $0 \le l \le 20$
Reflections collected	5123
Independent reflections	4880
Data / parameters	4880 / 185
Goodness-of-fit on F^2	1.154
Final R indices $[I > 2\sigma(I)]$	$R = 0.0483$, $wR = 0.9875$
Final R indices (all data)	$R = 0.0591$, $wR = 0.1138$
Flack parameter [x] (Flack, 1983) [31]	0.06(1)
Largest diff. peak and hole	0.367 and -0.584 e Å^{-3}

of 3,5-dichlorosalicylaldehyde (8.6 g, 45 mmol) with stirring at room temperature. The Schiff base ligand was obtained in the form of yellow crystals. In the second step, for the preparation of the Fe(III) complex, a 15 ml quantity of a 0.1 M solution of CH_3ONa in methanol was added to a solution of $FeCl_3{\cdot}6H_2O$ in the same solvent (0.54 g, 2 mmol, in 20 ml). To the resulting solution, was added with stirring the ligand L dissolved in methanol (0.61 g, 1 mmol). The dark blue solution was allowed to evaporate at room temperature for one day to give prismatic dark blue crystals, which were collected, washed with cold absolute ethanol and dried in air. The chemical formula of $Fe_2L(OCH_3)Cl_2$ and L are shown in Fig. 1. Yield 0.83 g (72.2%) $C_{28}H_{24}Cl_8Fe_2N_4O_4$ (875.81): calcd. C 38.40, H 2.76, N 6.40, Fe 12.75; found C 38.91, H 2.86, N 6.49, Fe 12.81. Infrared spectrum (cm^{-1}, KBr disk): $\tilde{\nu}$ (phenolic OH) 3445(w); $\tilde{\nu}$ (C=N) 1642(s); $\tilde{\nu}$ (phenolic C–O) 1376(s).

X-ray structure determination

A crystal of dimensions $0.40 \times 0.18 \times 0.02$ mm^3 was mounted on a Rigaku AFC7S diffractometer with graphite monochromatized Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Experimental conditions are summarized in Table 1. The final positional parameters are presented in Table 2. Data collection, reduction and corrections for absorption and decomposition were achieved using TEXAN Single Crystal Structure Analysis 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. H atom displacement parameters were restricted to be 1.2 U_{eq} of the parent atom. Selected bond distances and bond angles are listed in Table 3. An ORTEP view of the molecular structure is given in Fig. 2 [20, 21]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 262604 for $Fe_2L(OCH_3)Cl_2$ [22].

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) of the non-hydrogen atoms.

Atom	x	y	z	$^*U$(eq)
C1	0.7303(3)	0.9766(2)	0.0743(2)	0.0239(4)
C2	0.8495(4)	1.0429(3)	0.0659(2)	0.0367(7)
C3	0.9365(4)	1.0354(4)	−0.0018(2)	0.0434(8)
C4	0.9085(4)	0.9539(4)	−0.0690(2)	0.0412(8)
C5	0.7962(3)	0.8846(3)	−0.0619(2)	0.0352(7)
C6	0.7033(3)	0.8957(3)	0.0081(2)	0.0269(5)
C7	0.5877(3)	0.8205(3)	0.0070(2)	0.0265(5)
C8	0.3671(3)	0.7446(3)	0.0466(2)	0.0294(5)
C9	0.2280(3)	0.7886(2)	0.0768(2)	0.0254(5)
C10	0.1288(3)	0.9085(3)	0.1858(2)	0.0299(6)
C11	0.1327(3)	0.9132(3)	0.2903(2)	0.0301(6)
C12	0.2306(3)	0.7886(2)	0.4135(2)	0.0267(5)
C13	0.3697(3)	0.7403(2)	0.4664(2)	0.0293(5)
C14	0.6093(3)	0.7978(2)	0.5249(2)	0.0286(5)
C15	0.7448(3)	0.8568(2)	0.5310(2)	0.0293(5)
C16	0.8611(3)	0.8221(3)	0.5940(2)	0.0356(6)
C17	0.9927(3)	0.8739(4)	0.6033(2)	0.0397(8)
C18	1.0113(5)	0.9630(4)	0.5528(2)	0.0472(9)
C19	0.8961(4)	0.9997(4)	0.4908(2)	0.0405(7)
C20	0.7595(3)	0.9467(2)	0.4774(2)	0.0247(4)
C21	0.2591(2)	0.7689(2)	0.2467(1)	0.0189(4)
C22	0.3953(3)	0.6976(2)	0.2579(2)	0.0200(4)
C23	0.3765(3)	0.5895(2)	0.2564(2)	0.0218(4)
C24	0.5003(3)	0.5283(3)	0.2602(2)	0.0270(5)
C25	0.6403(3)	0.5714(3)	0.2655(2)	0.0291(5)
C26	0.6554(3)	0.6766(2)	0.2698(2)	0.0253(5)
C27	0.5328(3)	0.7441(2)	0.2659(2)	0.0186(4)
C28	0.4511(3)	1.1366(3)	0.2624(3)	0.0452(9)
N1	0.4868(2)	0.8222(2)	0.0611(1)	0.0214(4)
N2	0.2549(2)	0.8419(2)	0.1686(1)	0.0195(4)
N3	0.2568(2)	0.8433(2)	0.3274(1)	0.0175(3)
N4	0.4937(2)	0.8142(2)	0.4655(2)	0.0230(4)
O1	0.6523(2)	0.9906(2)	0.1410(2)	0.0273(4)
O2	0.5449(2)	0.8478(2)	0.2686(1)	0.0175(3)
O3	0.6558(2)	0.9859(2)	0.4174(1)	0.0195(3)
O4	0.4268(2)	1.0261(2)	0.2622(2)	0.0309(4)
Cl1	0.33426(8)	1.04532(6)	0.04421(6)	0.0367(2)
Cl2	0.34235(9)	1.03690(7)	0.46808(6)	0.0383(2)
Cl3	0.88924(8)	1.14067(6)	0.14876(6)	0.0367(2)
Cl4	1.01530(7)	0.94008(8)	−0.15553(4)	0.0356(2)
Cl5	0.91845(8)	1.10816(6)	0.42572(6)	0.0362(2)
Cl6	1.14556(8)	0.82728(6)	0.67739(6)	0.0361(2)
Cl7	0.82780(8)	0.73157(6)	0.27890(6)	0.0364(2)
Cl8	0.47898(9)	0.39221(7)	0.25843(6)	0.0369(2)
Fe1	0.46535(4)	0.93577(4)	0.37205(3)	0.0307(2)
Fe2	0.46203(5)	0.93949(4)	0.15674(3)	0.0316(1)

* $U(\mathrm{eq}) = (1/3)\Sigma_i\Sigma_j \mathrm{U}_{ij} a_i^* a_j^* a_i a_j$.

Table 3. Selected bond lenghts (Å) and bond angles (°) characterizing the inner coordination sphere of the iron(III) centers (see Fig. 2 for labeling scheme adopted).

Fe1···Fe2	3.133(2)	O3–Fe1–O4	98.04(9)
Fe1–N3	2.274(2)	O3–Fe1–N4	89.88(9)
Fe1–N4	2.065(2)	O3–Fe1–O2	92.27(7)
Fe2–N1	2.085(2)	O4–Fe1–O2	77.01(9)
Fe2–N2	2.305(2)	N4–Fe1–O2	92.35(8)
Fe1–O2	2.092(2)	O3–Fe1–N3	168.17(8)
Fe1–O3	1.899(2)	O4–Fe1–N3	91.29(9)
Fe2–O1	1.910(2)	N4–Fe1–N3	79.67(8)
Fe2–O2	2.071(2)	O2–Fe1–N3	82.74(7)
Fe1–Cl2	2.312(1)	O3–Fe1–Cl2	95.81(6)
Fe2–Cl1	2.324(1)	O4–Fe1–Cl2	96.38(8)
		N4–Fe1–Cl2	93.15(7)
Fe1–O2–Fe2	97.63(8)	O2–Fe1–Cl2	170.24(5)
Fe1–O4–Fe2	107.78(9)	N3–Fe1–Cl2	90.32(6)
O1–Fe2–O4	98.53(9)	O1–Fe2–O2	92.50(8)
O4–Fe2–O2	77.73(8)	O1–Fe2–N1	89.15(9)
O4–Fe2–N1	168.19(9)	O2–Fe2–N1	93.07(8)
O4–Fe2–N2	91.48(8)	O2–Fe2–N2	81.47(7)
N1–Fe2–N2	79.72(8)	O1–Fe2–Cl1	95.66(8)
O4–Fe2–Cl1	95.76(7)	O2–Fe2–Cl1	170.25(5)
N1–Fe2–Cl1	92.37(6)	N2–Fe2–Cl1	91.56(5)

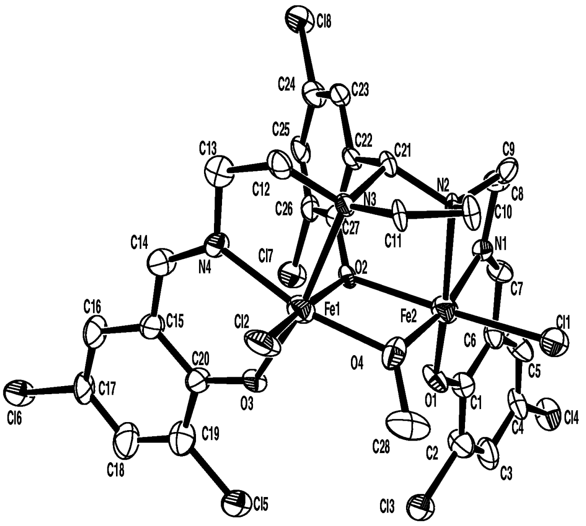

Fig. 2. View of the molecule (numbering of atoms corresponds to Table 2). Displacement ellipsoids are plotted at the 50% probability level. The hydrogen atoms are omitted for clarity.

Susceptibility measurements

Variable-temperature magnetic susceptibility measurements of a powdered sample were performed with a QUANTUM Design SQUID magnetometer in the temperature range 5-298 K. The applied field was about 1 T. Diamagnetic corrections of the molar magnetic susceptibility were applied using Pascal's constant [23]. The effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$, where χ is the magnetic susceptibility per Fe(III) ion.

Table 4. Least-squares pseudomirror plane within the $Fe_2L(OCH_3)Cl_2$ molecule, $-0.686(4)x\ -0.139(5)y + 14.543(3)z = 3.379(4)$.

Atom	Dev (Å)	Atom	Dev (Å)
O2	0.040(2)	C21	−0.050(2)
C22	0.019(2)	C23	0.023(2)
C24	−0.005(2)	C25	−0.040(2)
C26	0.0023(2)	C27	0.025(2)
Cl7	0.010(1)	Cl8	−0.005(2)
O4	0.012(2)	C28	−0.019(3)

Results and Discussion

X-ray crystal structure

The structure of $Fe_2L(OCH_3)Cl_2$ consists of dinuclear units that are well separated from one another. The two iron(III) ions are asymmetrically bridged by phenoxy and methoxy oxygen atoms to form a four-membered ring. The geometry around the metal atoms is distorted octahedral, as shown in Fig. 2. The molecule has a nearly perfect C_s symmetry with the mirror plane perpendicular to the iron-oxygen ring. The bridging oxygen atoms O2 and O4 and the carbon atoms C21-C27 and C28 lie approximately on this mirror plane. Deviations of these atoms from the least-squares pseudomirror plane are given in Table 4. The dihedral angle between the Fe1O2O4 and Fe2O2O4 planes is 13.1(1)°. The iron(III) ions are displaced from the coordination plane by $-0.089(1)$ Å for Fe1 and $-0.090(1)$ Å for Fe2. The Fe···Fe and O2···O4 separations are 3.133(2) and 2.531(2) Å, respectively. The bridging angle at the phenoxy oxygen atoms, 97.6(2) °, is smaller than that at the methoxy oxygen atoms, 107.9(1)°. The Fe–N(imine) bond lengths of 2.065(2) and 2.085(2) Å are significantly shorter than the Fe–N(amine) bond lengths of 2.274(2) and 2.305(2) Å. The overall geometry distortion is as expected for an octahedral low-spin d^5 iron(III) ion with hexadentate chelation. The geometry is similar to that of related binuclear iron complexes [24, 25]. The phenoxy and methoxy carbon atoms attached to the bridging oxygens are displaced on opposite sides of the bridging plane by $-0.037(2)$ Å for C27 and 0.252(2) Å for C28, respectively.

Magnetic properties

The magnetic susceptibilities of the complex are shown as a function of temperature in Fig. 3, and the

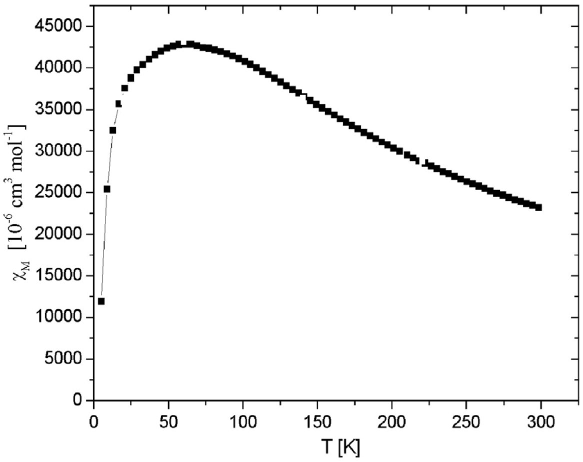

Fig. 3. The molar magnetic susceptibilities χ per iron(III) *vs.* temperature T curve.

magnetic moments are shown as a function of temperature in Fig. 4. The magnetic data was fitted using the expression for molar susceptibility *vs.* T derived from the spin exchange Hamiltonian, $H = -J\vec{S}_1.\vec{S}_2$, where J is the interaction parameter between two spin carriers with $S_1 = S_2 = 5/2$ as given in eq. (1).

$$\begin{aligned}\chi &= (1-x_p)\chi'' + 2x_p\chi' + TIP\\ \chi'' &= \frac{C}{T}[2\exp(2x) + 10\exp(6x) + 28\exp(12x)\\ &\quad + 60\exp(20x) + 110\exp(30x)]\\ &\quad \cdot [1 + 3\exp(2x) + 5\exp(6x) + 7\exp(12x)\\ &\quad + 9\exp(20x) + 11\exp(30x)]^{-1}\\ \chi' &= \frac{C}{3T}, \quad x = \frac{J}{kT}, \quad C = \frac{N_L g^2 \mu_B^2}{k}\end{aligned} \tag{1}$$

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 $= 400.10^{-6}$ cm^3/mol for each iron atom) was also taken into account. The best fit parameters obtained with eq. (1) by using a standard least-squares program were $J = -10.8$ cm^{-1}, $x_p = 0.1$. An isotropic g value of 2.0 was assumed. The effective magnetic moment per iron(III) at 298.4 K is 7.44 B. M., but 0.69 B. M. at 5 K. The magnetic susceptibility is at a maximum near 61 K and decreases rapidly as the temperature is lowered to liquid helium temperature.

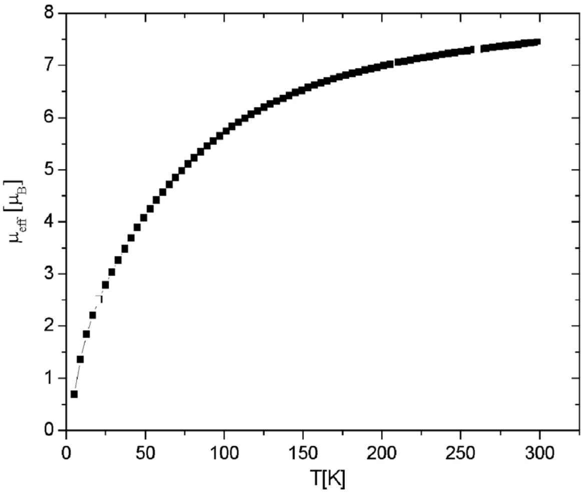

Fig. 4. Magnetic moment per iron(III) *vs.* temperature curve.

The extent of antiferromagnetism exhibited by $Fe_2L(OCH_3)Cl_2$ is in the range so far observed ($7 \le |J| \le 17$ cm^{-1}) for iron(III) complexes involving Fe_2O_2 bridging units [13–16, 25–27]. Recently, Gorun and Lippard suggested a quantitative magnetostructural relationship for dinuclear iron(III) centers, doubly bridged by oxygen atoms [28]. This exponential relationship, $-J = A.\exp(BP)$, 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 $P = 1.965$ Å as found in the present study, a value of $J_{calc} = -13.7$ cm^{-1}, is obtained in fair agreement with $J_{obs} = -10.7$ cm^{-1}.

The magnetic properties of exchange coupled dinuclear complexes of transition metal ions are known to depend on the particular metal ions, the chemical nature of the bridging ligands, and the bridging geometries. Both bridging angles and bridging ligand-metal distances as well as electronic factors are important [13–19, 29, 30].

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