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CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF DINUCLEAR IRON(III) COMPLEX WITH ONNO-DONOR LIGAND**B. Safak¹, Y. Yahsi¹, E. Gungor¹, H. Kara^{1,2}**¹*Department of Physics, Faculty of Science and Art, Balikesir University, Balikesir, Turkey*

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A new dinuclear Fe(III) complex, $[\text{Fe}(5\text{-MeOL1})(\text{OH})_{0.86}(\text{CH}_3\text{O})_{0.14}]_2 \cdot 2(\text{CH}_3\text{OH})$, [$\text{H}_2\text{-5-MeOL1} = \text{N,N}'\text{-bis}(5\text{-methoxy-2-hydroxybenzylidene})\text{-2,2-dimethylpropane-1,3-diamine}$], **1** has been synthesized and characterized by single crystal structure analysis. The structure of **1** consists of two Fe(III) centers with one tetradentate schiff base ligand (N_2O_2) which are bridged by dihydroxo/dimethoxo groups to yield a Fe_2O_2 core. Complex **1** exhibits weak antiferromagnetic exchange interaction between Fe(III) ions with $J = -0.21 \text{ cm}^{-1}$.

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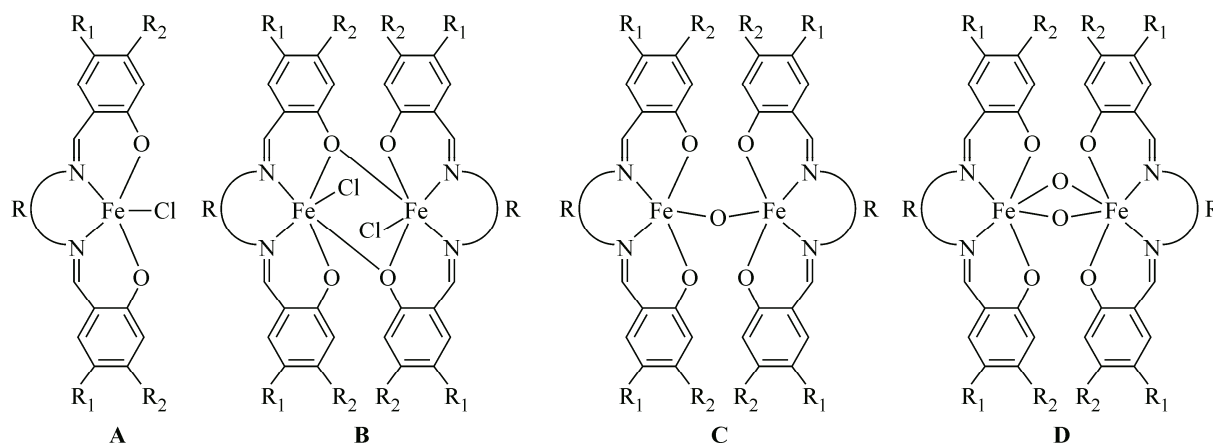
Keywords: Schiff-base ligand, iron(III) complex, X-ray crystal structure analysis, magnetic properties.

INTRODUCTION

A great deal of attention has been paid to studies on synthesis and characterization of diiron (III) complexes because of their importance as synthetic models for the oxidation catalysts [1], bistable molecular materials based on temperature-, pressure- or light-induced spin-crossover behavior [2] and iron-containing enzymes such as methane monooxygenase, ribonucleotide reductase and purple acid phosphatases [3].

There has been also continuous interest in Schiff base metal complexes in the field of coordination chemistry, as the steric and electronic factors of the Schiff base can be tuned systematically by introducing suitable substituents to bring about subtle structural variations that are extremely useful for deducing a relationship between magnetic coupling and structural features [4].

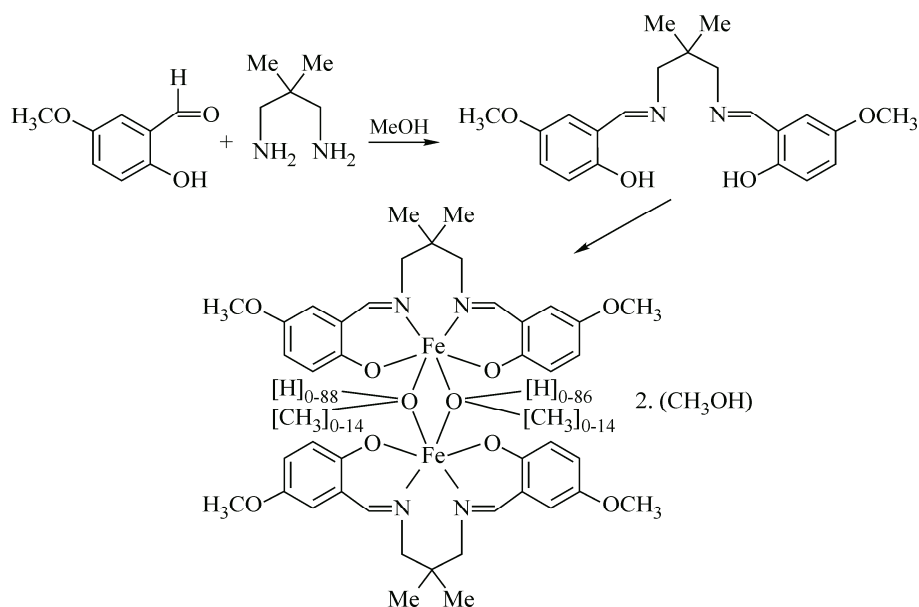
Recently our research group and others have reported the structural and magnetic characterization of **A** type, mononuclear iron(III) Schiff base complexes [5], **B** type, dinuclear iron(III) Schiff base complexes [6] and **C** type, μ -oxo-bridged dinuclear iron (III) Schiff base complexes [7]. It is interesting to note that although some structural analyses of **D** type, μ -dimethoxo bridged dinuclear iron(III) Schiff base complexes [8] and μ -dihydroxo bridged dinuclear iron(III) Schiff base complexes [9] have been reported, to the best of our knowledge, which is based on a recent CCDC database search, both structural and magnetic studies of μ -dihydroxo or μ -dimethoxo bridged dinuclear iron(III) Schiff base complexes remains rare [8d, 9c]. In view of the importance of iron(III) Schiff base complexes and in an effort to enlarge the library of such complexes, we report herein the preparation, crystal structure and magnetic characterization of complex **1**, **D** type $[\text{Fe}(5\text{-MeOL1})(\text{OH})_{0.86}(\text{CH}_3\text{O})_{0.14}]_2 \cdot 2(\text{CH}_3\text{OH})$, [$\text{H}_2\text{-5-MeOL1} = \text{N,N}'\text{-bis}(5\text{-methoxy-2-hydroxybenzylidene})\text{-2,2-dimethylpropane-1,3-diamine}$].



Scheme

EXPERIMENTAL SECTION

Materials and physical measurements: 2,2-Dimethyl-1,3-diaminopropane, 2-hydroxy-5-methoxybenzaldehyde, FeCl_3 have been purchased from Aldrich Chemical Co. Ethanol and methanol have been purchased from Riedel. DC Magnetic measurements were performed with a Cryogenics Squid S600 magnetometer with applied field of 0.1 T. To avoid possible orientation effects, microcrystalline powders were pressed in pellets. The data were corrected for sample holder contribution and diamagnetism of the sample using Pascal constants. The effective magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi_m T)^{1/2}$ [11], where χ_m , the molar magnetic susceptibility, was set equal to M_m/H . The synthetic route to the Schiff base ligand and metal complex is outlined in Scheme 1.



Scheme 1. The synthetic route of the Schiff base ligand and complex 1

Synthesis of complex 1. The ligand has been prepared by reaction of 2,2-dimethyl-1,3-diaminopropane (1 mmol, 0.102 g) with 2-hydroxy-5-methoxybenzaldehyde (2 mmol, 0.304 g) in hot ethanol (100 mL). The yellow product of the ligand was precipitated from solution on cooling. The complex 1 has been prepared by the addition of FeCl_3 (1 mmol, 0.162 g) in 30 mL of hot methanol to the ligand

(1 mmol, 0.374 g) in 30 mL of hot methanol. This solution has been warmed to 60 °C and stirred for 2 h. The resulting solution has been filtered rapidly and then allowed to stand at room temperature. Several weeks of standing have led to the growth of red crystals of **1** suitable for X-ray analysis.

X-ray structure determination. Diffraction measurements were made on a Bruker ApexII kappa CCD diffractometer at 100 K for **1** using graphite monochromated MoK α radiation ($\lambda = 0.71073$ Å). The intensity data were integrated using the APEXII program [12] and absorption corrections were applied based on equivalent reflections with SADABS [13]. The structures were solved by direct methods and refined by full-matrix least-squares treatment against F^2 using SHELXL [14]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were included in idealized positions with isotropic displacement parameters constrained to 1.5 times the U_{eq} of their attached carbon atoms for methyl hydrogens, and 1.2 times the U_{eq} of their attached carbon atoms for the others.

Coordinated bridging methoxide is not fully occupied. The methyl group is disordered [0.14(1):0.86(1)] and associated with a position partially occupied by H atom of the OH group [0.86(1)]. The apparent shortening the O5—C23 bond distance (1.251(10) Å) is mainly due to this disorder. Level B error (D—H without Acceptor O5→H5A) in check CIF also comes from this disorder.

RESULTS AND DISCUSSION

X-ray structural analysis of complex 1. The crystal data and structure refinement details for complex **1** are listed in Table 1. Selected bond lengths and angles are summarized in Table 2. A representative structural diagram of complex **1** is shown in Fig. 1.

The structure consists of two Fe(III) centers bridged by two hydroxo/methoxo groups to yield a Fe₂O₂ core with Fe...Fe separation of 3.186 Å. The center of symmetry lies in the center of this core. Each iron is coordinated by two phenolic oxygen atoms and two imine nitrogen atoms of the tetradentate ligand, and the octahedral environment is completed by a pair of hydroxo/methoxo groups which asymmetrically bridge the two Fe(III) ions. Both the angles at oxygen (105.28(5)°) and those at iron

Table 1

Crystal structure data for **1**

| | |
|---|--|
| Formula | [Fe(5-MeOL1)(OH) _{0.86} (CH ₃ O) _{0.14}] ₂ ·2(CH ₃ OH) |
| M_r | 950.63 |
| Crystal size, mm | 0.28×0.28×0.45 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a, b, c, \text{Å}; \beta, \text{deg.}$ | 10.3091(2), 18.5618(3), 11.3260(2); 99.938(1) |
| $V, \text{Å}^3; Z$ | 2134.77(7); 2 |
| $D_{\text{calcd}}, \text{g/cm}^3$ | 1.483 |
| $\mu(\text{MoK}\alpha), \text{cm}^{-1}$ | 0.749 |
| $F(000), e$ | 1000.5 |
| hkl range | $-13 \leq h \leq +7, -24 \leq k \leq +24, -14 \leq l \leq +14$ |
| Refl. meas. / unique / R_{int} | 16864 / 4911 / 0.0175 |
| Param. refined | 300 |
| $R(F) / wR(F^2)^a$ (all reflexions) | 0.0310 / 0.0730 |
| GOOF (F^2) ^a | 1.026 |
| $\Delta\rho_{\text{fin}}$ (max/min), e/Å ³ | 0.377 / -0.429 |

^a Definition of R values and GOOF, as well as information on weighting scheme applied.

Table 2

Selected bond lengths (Å), angles (deg.) for **1** with estimated standard deviations in parentheses

| Bond lengths | | Bond angles | | | |
|--------------|------------|-------------|-----------|------------|-----------|
| Fe1—O1 | 1.9329(10) | O1—Fe1—O2 | 95.90(4) | O5—Fe1—N1 | 95.21(4) |
| Fe1—O2 | 1.9576(9) | O1—Fe1—O5 | 93.53(4) | O5—Fe1—N1* | 89.58(4) |
| Fe1—O5 | 1.9837(10) | O2—Fe1—O5 | 98.71(4) | O1—Fe1—N2 | 99.78(4) |
| Fe1—O5* | 2.0243(10) | O1—Fe1—O5* | 166.33(4) | O2—Fe1—N2 | 85.22(4) |
| Fe1—N1 | 2.1489(11) | O2—Fe1—O5* | 92.83(4) | O5—Fe1—N2 | 165.68(4) |
| Fe1—N2 | 2.1508(11) | O5—Fe1—O5* | 74.72(5) | O5—Fe1—N2* | 91.39(4) |
| | | O1—Fe1—N1 | 84.48(4) | N1—Fe1—N2 | 80.95(4) |
| | | O2—Fe1—N1 | 166.02(4) | Fe1—O5—Fe* | 105.28(5) |

(74.72(5)°) are typical for an Fe—O—Fe—O ring. The preference of a Fe—O—Fe—O ring for the acute O—Fe—O angle close to 75° leads to distortions in the remaining angles in the coordination sphere from ideal octahedral ones. Deviation from the ideal value of 90° occurs for coordination angles N2—Fe1—O5* (91.39(4)°), N1—Fe1—O5* (89.58(4)°), and O5—Fe1—N1 (95.21(4)°) and a decrease from 180° is observed for O5—Fe1—N2 (165.68(4)°) and O1—Fe1—O5* (166.33(4)°) angles (* = 1-x, -y, -z), making the coordination geometry a distorted octahedral. The four coordination atoms from 5-MeOL1 ligand are not in the plane due to a distortion of the carbon linkage and the requirement of coordination of hydroxo/methoxo-bridging groups being at the same side to take *cis*-disposition. The basal Fe—O_{phenolic} and Fe—N_{imine} bond distances are in the range 1.9329(10)—1.9576(9) Å, 2.1489(11)—2.1508(11) Å, respectively. The Fe—O bond distances in the bridging unit are 1.9837(10) Å and 2.0243(10) Å, respectively. The long Fe—O bond is relatively weak; this is because it is *trans* to the stronger and hence shorter Fe—O_{phenolic} bond, which mitigates the Lewis acidity of the iron center and hence decreases its affinity for the bridge. Thus, the asymmetry of the Fe—O—Fe—O bridge is not an intrinsic feature but originates from the *cis*-phenolate coordination of the tetradentate 5-MeOL1 ligand [10]. These geometrical features of the iron centers in **1** are quite comparable to those of the similar dinuclear complexes reported in the literature [5–9].

Magnetic properties of complex 1. The variable temperature magnetic susceptibilities for complex **1** were measured in the 3–300 K temperature range and are shown as χT and $1/\chi$ versus T plots in Fig. 2. The χT value at room temperature is 8.74 emu·K·mol⁻¹ (8.36 μ_B). At room temperature, the observed magnetic moments per dinuclear complexes are slightly lower than the spin only value (8.37 μ_B) expected for a system with two uncoupled high-spin ($S = 5/2$) iron(III) centers. On lowering the temperature, the $\chi_m T$ value remains almost constant until 50 K, then decreases to attain a value of

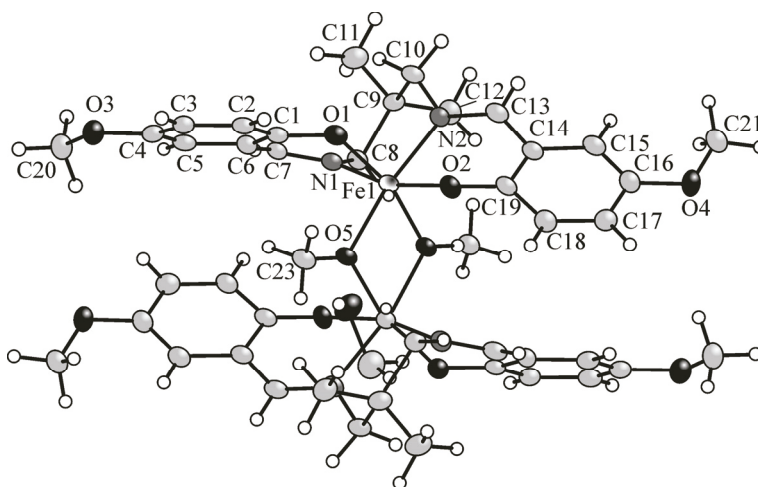


Fig. 1. The molecular structure of **1**. The thermal ellipsoid plot of **1** is at a 50 % probability level

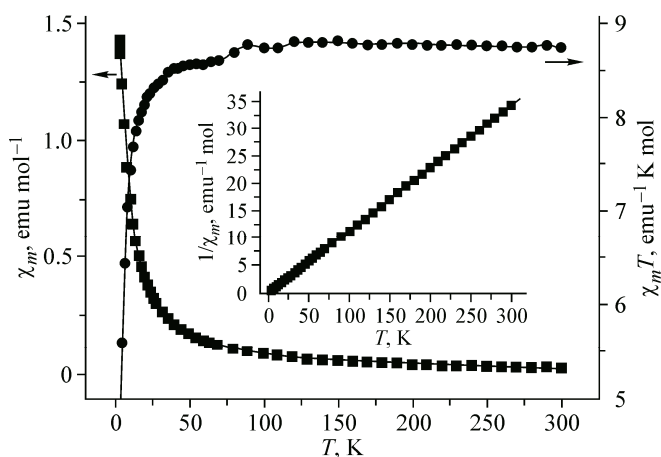


Fig. 2. Temperature dependence of χ_m , $\chi_m T$ and $1/\chi$ for **1**. The solid line represents the best fit for using Eq.(1)

4.47 emu·K·mol⁻¹ for **1** K at 3 K. The magnetic susceptibilities conform well to the Curie–Weiss law, with a negative Weiss constant ($\theta = -1.8$ K and $C = 8.80$ cm³·K·mol⁻¹). These results indicate the presence of a dominant antiferromagnetic coupling in **1**.

For diiron(III) complexes, the theoretical expression of the magnetic susceptibility based on the Heisenberg Hamiltonian ($H = -2JS_1S_2$) is:

$$\chi = \frac{Ng^2\mu_B^2}{kT} \times \frac{[2e^{2J/kT} + 10e^{6J/kT} + 28e^{12J/kT} + 60e^{20J/kT} + 110e^{30J/kT}]}{[1 + 3e^{2J/kT} + 5e^{6J/kT} + 7e^{12J/kT} + 9e^{20J/kT} + 11e^{30J/kT}]}, \quad (1)$$

where N is Avogadro's number, g is the g factor of the Fe³⁺ ion; μ_B is the Bohr magneton; J is the magnetic exchange parameter; k is the Boltzmann's constant and T is the temperature. The best agreement with the experimental data was obtained for $J = -0.219 \pm 0.001$ cm⁻¹ and $g = 2.033 \pm 0.002$, $R^2 = 0.999$ for complex **1** (Fig. 2). As a whole, these results indicate a weak antiferromagnetic exchange interaction in dinuclear units.

CONCLUSIONS

We report here the preparation, crystal structure and magnetic characterization of [Fe(5-MeOL1)·(OH)_{0.86}(CH₃O)_{0.14}]₂·2(CH₃OH), [H₂-5-MeOL1 = N,N'-bis(5-methoxy-2-hydroxybenzylidene)-2,2-dimethylpropane-1,3-diamine] (**1**). The structure of the complex **1** consists of two Fe(III) centers with one tetradentate schiff base ligand (N₂O₂) which are bridged by two hydroxo/methoxo groups to yield a Fe₂O₂ core. Complex **1** exhibits a weak antiferromagnetic exchange interaction with $J = -0.21$ cm⁻¹ between Fe(III) ions.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>; fax: +44 1223 336033) and are available free of charge on request, quoting the Deposition No. CCDC 834940.

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