

CRYSTAL STRUCTURE OF A μ -OXO-BRIDGED DIMERIC IRON(III) COMPLEX

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A dimeric $[\{\text{Fe}(5\text{-CIL1})\}_2(\mu\text{-O})]$, $[\text{H}_2\text{-5-CIL1} = N,N'\text{-bis}(5\text{-chloro-2-hydroxybenzylidene})\text{-2-methylpropane-1,2-diamine}]$ tetradentate Schiff-base complex, **1**, has been synthesized and its crystal structure has been determined by single crystal X-ray diffraction analysis. Structural analysis of complex **1** shows that the complex is a centrosymmetric dimer. Each of the Fe(III) ions has a five-coordinate geometry and one oxygen atom bridges two Fe(III) ions to form a μ -oxo structure. The geometry around iron atom can be described as a square based pyramid with the FeN_2O_2 coordination plane and oxo ligand.

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Keywords: synthesis, Schiff-base ligands, iron(III) complexes, X-ray crystal structure analysis, oxo bridged structure.

INTRODUCTION

Oxygen-bridged binuclear iron complexes have been of considerable interest for several decades, due to their various interesting structural, electronic, magnetic and spectroscopic properties [1-14]. In recent times, a great deal of attention has been paid to studies on synthesis and characterization of diiron(III) complexes because of their role in the fields of bioinorganic, organometallic, and catalytic chemistry due to their importance as synthetic models for the oxidation catalysts [15-17], bistable molecular materials based on temperature-, pressure- or light-induced spin-crossover behavior [18, 19] and iron-containing enzymes such as methane monooxygenase, ribonucleotide reductase and purple acid phosphatases [20-24]. In addition, low-nuclearity complexes, such as Fe_2 and Fe_3 , are likely to represent the “molecular nanoscale bricks” for the formation of high-nuclearity molecular clusters and hence studies on their structural characterization and various properties are essential steps for a correct approach to larger systems [25-28]. In general oxygen-bridged diiron(III) complexes fall into four classes, oxo-bridged [29-36], hydroxo-bridged [30, 35-40], alkoxo-bridged [41-44] and phenoxo bridged [8, 14, 45-47] species.

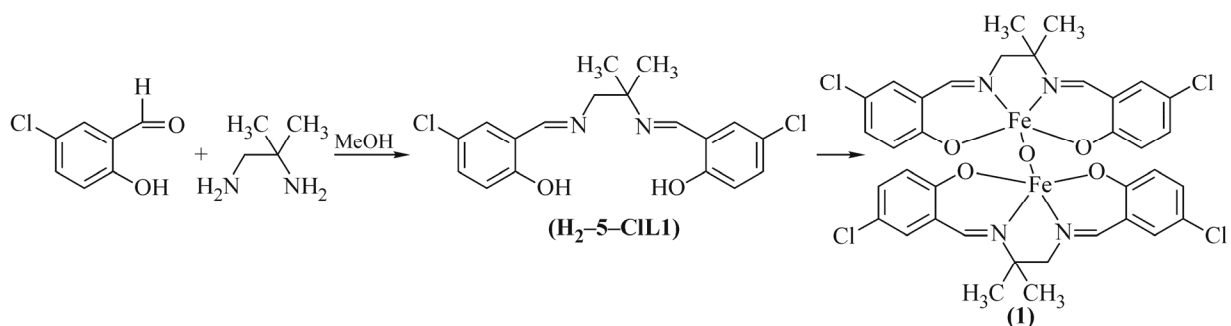
Recently our research group reported the structural and magnetic characterization of mononuclear and phenoxo-bridged binuclear iron(III) complexes containing tetradentate Schiff base ligands with O, N, N, O, donor set [14, 45]. In view of the importance of Fe(III) complexes and our interest in the characterization of transition metal complexes containing Schiff base ligands, we report here the synthesis and single crystal X-ray structure of a μ -oxo-bridged binuclear iron(III) complex, $[\{\text{Fe}(5\text{-CIL1})\}_2(\mu\text{-O})]$, $[\text{H}_2\text{-5-CIL1} = N,N'\text{-bis}(5\text{-Chloro-2-hydroxybenzylidene})\text{-2-methylpropane-1,2-diamine}]$, **1**. The structure is dimeric in which two metal ions are connected by oxo-oxygen atoms.

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EXPERIMENTAL SECTION

Preparation of complex 1. The ligand H₂-5-CIL1 (N,N'-bis(5-Chloro-2-hydroxybenzylidene)-2-methylpropane-1,2-diamine) was prepared by reaction of 1,2-diamino-2-methylpropane (1 mmol, 0.088 g) with 5-chlorosalicylaldehyde (2 mmol, 0.312 g) in hot ethanol (100 mL). The yellow product of the ligand was precipitated from solution on cooling. The complex **1** was prepared by the addition of FeCl₃ (1 mmol, 0.162 g) in 30 mL of hot methanol to the ligand (1 mmol, 0.369 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.



Scheme 1. Schematic diagram of complex **1**.

X-ray structure determination. Diffraction measurement was made on a Stoe-IPDS-2 diffractometer (at 296 K for **1**) using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection and cell refinement: Stoe X-AREA [48] and data reduction: Stoe X-RED [48] for **1**. The structure was solved by direct methods and refined using full-matrix least-squares against F^2 using SHELXL [49]. 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 all others. 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. Molecular structure of complex **1** is shown in Fig. 1, while packing diagram is given in Fig. 2.

TABLE 1. Crystal Data and Structure Refinement of Complex **1**

CCDC No.	834942
Chemical formula	C ₃₆ H ₃₂ Cl ₄ Fe ₂ N ₄ O ₅
M_w	854.16
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions $a, b, c, \text{ \AA}$	7.4543(10), 10.8357(15), 12.0391(17)
$\alpha, \beta, \gamma, \text{ deg}$	70.115(10), 84.819(11), 87.802(11)
$V, \text{ \AA}^3$	910.7(2)
$T, \text{ K}$	293(2)
Z	1
$\rho_{\text{calc}}, \text{ g/cm}^3$	1.557
$\mu, \text{ mm}^{-1}$	1.138
Reflections collected / independent	15569 / 4318
$R_1 [I > 2\sigma(I)]$	0.0559
wR_2 (all data)	0.1492

TABLE 2. Some Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

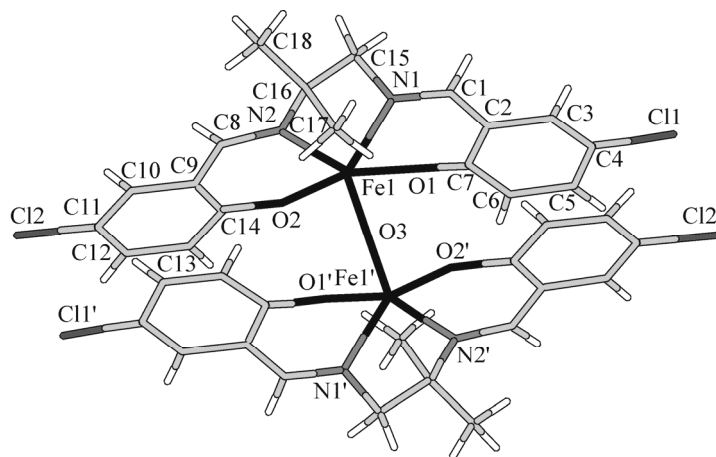
Bond lengths		Bond angles			
Fe1—O1	1.933(4)	O1—Fe1—N1	85.46(16)	O3—Fe1—O1	103.84(13)
Fe1—O2	1.906(4)	O1—Fe1—N2	152.08(17)	O3—Fe1—O2	106.24(12)
Fe1—O3	1.7604(9)	O2—Fe1—N1	148.10(17)	O3—Fe1—N1	103.61(13)
Fe1—N1	2.095(4)	O2—Fe1—N2	87.83(16)	O3—Fe1—N2	100.61(12)
Fe1—N2	2.114(4)	O2—Fe1—O1	97.99(16)	N1—Fe1—N2	75.81(17)
O3—Fe1*	1.7604(9)			Fe1*—O3—Fe1	180.00(5)

RESULTS AND DISCUSSION

Structural Analysis of $\{[Fe(5-CIL2)]_2(\mu-O)\}$, **1.** Complex **1** is the μ -oxo-bridged dinuclear Fe(III) complex. The asymmetric unit of **1** contains one $[Fe(5-CIL2)]_2(\mu-O)$ molecule. It crystallizes in the triclinic space group $P-1$. The bridging oxo group O3 lies on the crystallographic center of symmetry. The four coordinating atoms N1, N2, O1 and O2 are nearly coplanar (Fig. 1). The metal center Fe1 deviates from the mean plane towards the apical oxo-bridge by 0.474 Å. The structural distortion index of **1** were found $\tau_{Fe1} = 0.169$, indicate that Fe1 and Fe1* polyhedron are all close to distorted square-pyramidal. The basal plane of the square pyramid (Fe1) is formed by N_2O_2 donors from the 5-CIL2 ligand and the axial position is occupied by a bridging oxygen atom. Also, the FeN_2O_2 coordination plane in each iron(III) is oriented trans to the other relative to the oxo bridge in order to avoid interligand steric repulsions. The $Fe^{III}\cdots Fe^{III}$ separation (3.521 Å) compares favorably with the corresponding distances observed in related μ -oxo-monobridged dinuclear complexes of iron(III) (3.39-3.62 Å) [26, 30, 50, 51]. The bond lengths between the metal and donor atoms in the base of the pyramid are as follows: Fe— N_{imine} , 2.095(4)-2.114(4) Å; Fe— $O_{phenolic}$, 1.933(4)-1.906(4) Å. The Fe—(μ -O) bond distance is 1.7604 Å, which is shorter than those reported for other μ -oxo complexes [52, 53]. These observed geometrical features of iron(III) centers in **1** are quite comparable to those of the similar dinuclear complexes reported in the literature [52-73].

CONCLUSIONS

New dinuclear Fe(III) complex has been obtained with the tetradentate Schiff base ligand. We report here the synthesis and structural determination of μ -oxo-bridged Fe(III) dimer complex, **1**. The molecular structure of **1** has been successfully determined by single crystal X-ray diffraction. In complex **1**, each of the two Fe(III) ions has a five-coordinate structure and one oxygen atom bridges two Fe(III) ions to form a μ -oxo structure.

**Fig. 1.** The molecular structure of **1**.

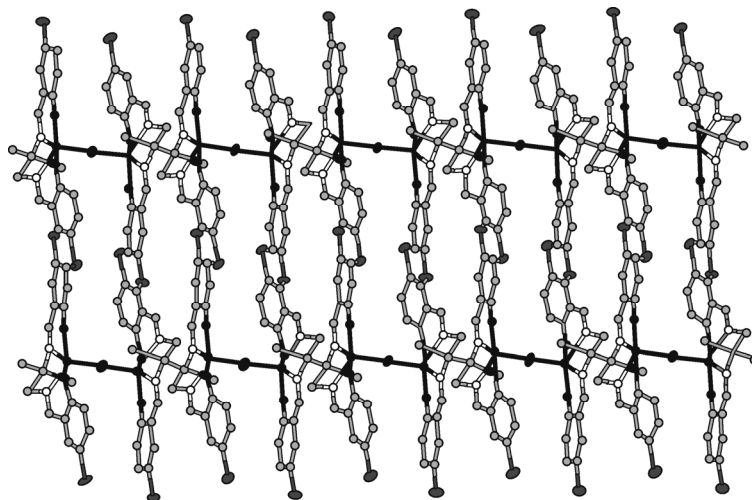


Fig. 2. Molecular packing diagram in the *ac*-plane of complex 1.

CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 834942, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

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