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Synthesis, Crystal Structure, and Spectral Properties of a Novel μ-1,1-Diazido-Bridged Dinuclear Fe(III) Complex with an N,N,O-Donor Tridentate Schiff Base Ligand

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Abstract: *A Fe(III) complex, $[Fe_2L_2(\mu\text{-}N_3)_2(N_3)_2]$ (**1**), was synthesized using a tridentate N,N,O-donor Schiff base ligand, HL, formed by the condensation of salicylaldehyde and N,N-dimethyl-1,2-diaminoethane. The complex was characterized through X-ray structural analysis and spectral studies. The crystal structure reveals a centrosymmetric Fe(III) dimer, with two Fe atoms bridged by two μ-1,1-azide ligands. Each iron center adopts a distorted octahedral geometry, coordinated by the chelating tridentate Schiff base ligand and a terminal azido group, completing the hexacoordination environment*

Keywords: Ligand, Crystal structure, Schiff base, Chelating, tridentate

I. INTRODUCTION

The chemistry of iron(III) complexes is predominantly characterized by oxygen-bridged species due to the strong oxygen affinity of the iron(III) ion [1-3]. These oxygen-bridged dinuclear iron(III) units are significant in synthetic chemistry because of their relevance to biological systems [4]. Such units are found at the active sites of various non-heme metalloenzymes, such as hemerythrin, a dioxygen carrier protein [5]. Efforts to synthesize model complexes of iron proteins have led to the discovery of several novel oxygen-bridged polyiron compounds, which exhibit intriguing magnetic properties that have spurred studies into their unique electronic structures [6].

The tridentate Schiff base ligands, formed through the monocondensation of a diamine with a salicylaldehyde derivative, have been widely employed alongside pseudohalides to construct polynuclear complexes of Cu(II) and Ni(II) with notable structural and magnetic properties [7-8]. However, these ligands are rarely used to synthesize Fe(III) complexes, typically yielding mononuclear bis(Schiff base) species, with only a few instances of oxido-, alkoxido-, or hydroxido-bridged dinuclear complexes [9-10]. The mononegative tridentate Schiff bases, combined with two pseudohalide ions, balance the charge of Fe(III), with one pseudohalide ion potentially acting as a bridging ligand to achieve the typical hexa-coordination of Fe(III). These tridentate Schiff bases thus hold potential for forming pseudohalide-bridged Fe(III) complexes, although no such examples are documented in the literature. In this study, a tridentate N,N,O-donor Schiff base (HL), derived from the monocondensation of salicylaldehyde and 1,2-bis(dimethylamino)ethane, was used to synthesize a novel Fe(III) compound, $[Fe_2L_2(\mu\text{-}N_3)_2(N_3)_2]$. The synthesis, crystal structure, and spectral properties of this complex are discussed herein.

II. EXPERIMENTAL SECTION

Materials: The reagents and solvents used were of commercially available reagent quality.

Caution: Azide salts of metal complexes with organic ligand are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

2.1. Synthesis of the Tridantate ligand (HL)

The tridentate Schiff base ligand, HL {2-[(2-dimethylaminoethylimino)methyl]phenol}, was synthesized by the monocondensation of N,N-dimethylethane-1,2-diamine (10 mmol) with salicylaldehyde (10 mmol) in acetonitrile (40 mL). The reaction mixture was refluxed for 1 hour. The synthesis procedure for this ligand has been already reported [11] (**Scheme 1**).

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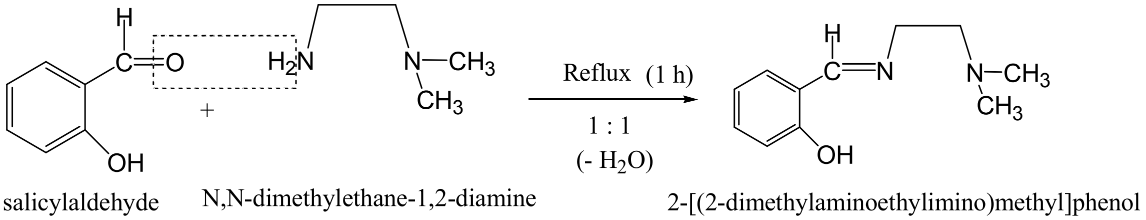
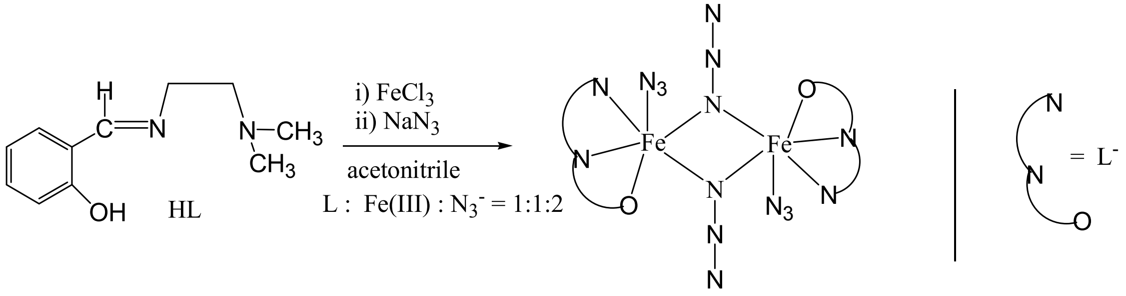


Scheme – 1: Preparation of Schiff base ligand

2.2. Synthesis of the Complex (1)

$FeCl_3$ (0.810 g, 5.00 mmol) was dissolved in acetonitrile (10.0 mL) and added to a solution of the ligand (HL, 5.00 mmol) in acetonitrile (10.0 mL) under constant stirring. After 5 minutes, a solution of NaN_3 (0.650 g, 10.0 mmol) in an acetonitrile / water mixture (9:1 v/v, 10.0 mL) was added. The solution turned reddish-black. Upon slow evaporation of the solvent, needle-shaped, black, X-ray quality single crystals were obtained overnight (**Scheme 2**).



compound -1

Scheme – 2: Synthesis of compound **1**

III. PHYSICAL MEASUREMENTS

Elemental analyses (C, H, N) were conducted using a PerkinElmer 2400 Series II CHN Analyzer. Infrared (IR) spectra were recorded in KBr pellets (4500–500 cm⁻¹) using a PerkinElmer RX1 FT-IR Spectrophotometer. Electronic spectra in acetonitrile (1000–200 nm for complex **1**) were obtained with a Hitachi U-3501 Spectrophotometer.

3.1 Crystal Data Collection and Refinement

Crystal data for the compound **1** is presented in Table 1. A total of 4,289 independent reflections were collected for Compound **1** using Mo-Kα radiation at 150 K with the Oxford Diffraction X-Calibur CCD System. The crystal was positioned 50 mm from the CCD, and 321 frames were measured with a counting time of 10 seconds per frame. Data analysis was performed using the CrysAlis program [12]. The structure was solved by direct methods using the Shelxs97 program [13]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon were placed in geometric positions and assigned thermal parameters equivalent to 1.2 times (or 1.5 times for methyl groups) those of the atom to which they were attached. Absorption corrections were applied using the ABSPACK program [14]. The structure was refined on F² using Shelxl97 [13], yielding R_1 values of 0.0333 and 0.0414, and wR_2 values of 0.0835 and 0.0941 for 3,102 and 2,478 reflections, respectively, with $I > 2\sigma(I)$.

Table 1. Crystal data of the complex **1**

	1
Formula	$C_{22}H_{30}Fe_2N_{16}O_2$
Formula wt.	662.32
Space group	$P2_1/n$
Crystal system	Monoclinic
a / Å	11.0863(9)
b / Å	10.9650(14)

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c / Å	12.1782(17)
β / deg	107.868(11)
V / Å^3	1409.0(3)
Z	2
d_{cal} (g.cm^{-3})	1.561
μ (mm^{-1})	1.083
R_{int}	0.0501
unique reflections	4080
Data with I>2σ(I)	2478
R1 on I>2σ(I)	0.0414
wR_2 on I>2σ(I)	0.0941
T(K)	150(2)

IV. STRUCTURAL DESCRIPTION OF THE COMPLEX (1)

The structure of complex **1** is depicted in Figure 1, accompanied by the atomic numbering scheme. Bond lengths and angles are listed in Table 2. In complex **1**, each iron atom adopts an octahedral geometry, coordinated to three atoms of a meridionally arranged tridentate ligand with the following bond distances: Fe(1)–O(11) 1.911(2) Å, Fe(1)–N(19) 2.109(2) Å, and Fe(1)–N(22) 2.240(2) Å. The equatorial plane is completed by a bridging azido group with an Fe–N(4)a bond length of 2.088(2) Å. In the axial positions, a second azido group, N(4), with a bond length of 2.137(2) Å, and a terminal azido group, N(1), with a bond length of 2.002(2) Å, are present. The axial bridging azido bond length is 2.137(2) Å, longer than the equatorial bridging azido bond length of 2.088(2) Å. The intradimer metal-metal distance is 3.413(1) Å, with N(bridging)–Fe–N(bridging) and Fe–N–Fe bond angles of 72.21(9)° and 107.79(9)°, respectively. These values are comparable to those reported for other high-spin dinuclear bis(μ-end-on-azido)iron(III) complexes [15–16]. Both bridging and terminal azido ligands are nearly linear, with N–N–N angles ranging from 178.2(3)° to 179.4(3)°.

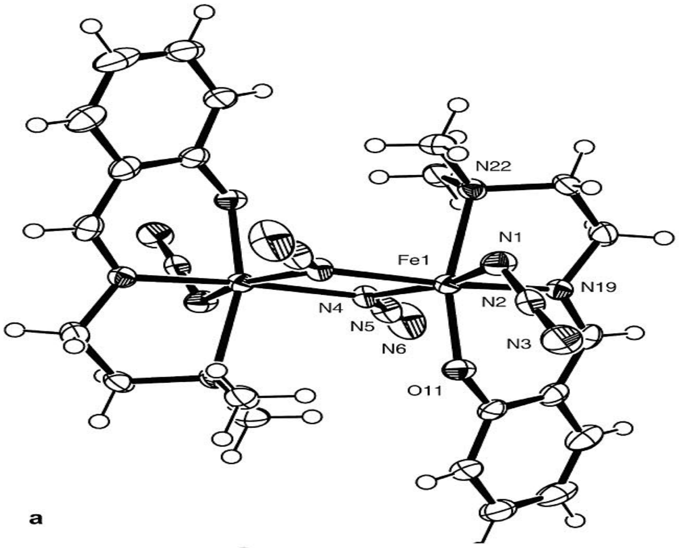

Figure -1: Structure of complex **1**. The centrosymmetric structure with ellipsoids drawn at 50% probability..

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Table 2. Crystal data of the complex **1**

Atoms	**Distance [Å]**	**Atoms**	**Angle [°]**
Fe(1)–N(19)	2.109(2)	O(11)–Fe(1)–X(4)a	101.21(7)
Fe(1)–N(22)	2.240(2)	O(11)–Fe(1)–X(4)	91.40(7)
Fe(1)–O(11)	1.911(2)	X(4)–Fe(1)–X(4)a	72.21(9)
Fe(1)–N(1)	2.002(2)	O(11)–Fe(1)–N(1)	93.82(8)
Fe(1)–N(4)^a	2.088(2)	X(4)a–Fe(1)–N(1)	92.12(8)
Fe(1)–N(4)	2.137(2)	X(4)–Fe(1)–N(1)	164.19(8)
		O(11)–Fe(1)–N(19)	86.47(7)
		X(4)a–Fe(1)–N(19)	164.15(7)
		X(4)–Fe(1)–N(19)	93.94(7)
		N(1)–Fe(1)–N(19)	101.26(8)
		O(11)–Fe(1)–N(22)	163.03(7)
		X(4)a–Fe(1)–N(22)	95.60(7)
		X(4)–Fe(1)–N(22)	91.52(7)
		(1)–Fe(1)–N(22)	87.83(8)
		N(19)–Fe(1)–N(22)	76.65(7)

V. IR AND UV/VIS SPECTRA OF THE COMPLEX 1

The IR spectrum of complex **1** exhibits a strong, sharp peak at 1619 cm^{-1}, corresponding to the ῡ(C=N) stretching frequency, confirming the presence of the Schiff base. Additionally, two overlapping but distinct peaks between 2051 and 2063 cm^{-1} indicate the presence of two types of azido groups (terminal and μ-1,1 bridging, respectively) in the complex [8].

The electronic spectrum of complex **1**, recorded in acetonitrile solution, displays two key absorption bands. A higher-energy band in the near-UV region at λ_{max} = 325 nm is attributed to the π–π* transition of the azomethine linkage. A lower-energy band in the near-visible region at λ_{max} = 425 nm corresponds to an azide-to-Fe(III) charge-transfer transition.

VI. CONCLUSIONS

The tridentate Schiff base ligand, 2-[(2-dimethylaminoethylimino)methyl]phenol, forms a novel dinuclear complex, $[Fe_2L_2(\mu\text{-}N_3)_2(N_3)_2]$ (**1**), with azide as a pseudo-halide co-ligand. In this complex, two Fe(III) centers are linked by a rare double μ-1,1-azido bridge, which is uncommon in Fe(III) complexes. This demonstrates that, under appropriate conditions, azido-bridged Fe(III) complexes can be synthesized with tridentate N,N,O-donor Schiff base ligands, similar to those observed with other metal ions such as Cu(II) and Ni(II).

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