

Structural, spectroscopic, and electrochemical properties of two mononuclear iron(III) complexes derived from a tetraaminodiphenolate ligand

Supriya Dutta^{a,*}, Papu Biswas^{b,*}

^a Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India

^b Department of Chemistry, Bengal Engineering and Science University, Shibpur, Howrah 711 103, India

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ABSTRACT

Two iron(III) mononuclear complexes $[\text{Fe}(\text{LH}_2)(\text{H}_2\text{O})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ (**1**) and $[\text{Fe}(\text{LH}_2)(\text{H}_2\text{O})\text{Cl}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**2**) have been prepared using $[\text{Pb}(\text{LH}_2)](\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ for **1** and **2**, respectively. LH_2 refers to the macrocyclic Schiff base ligand derived from the condensation of 1,3-diaminopropane and 4-methyl-2,6-diformyl phenol. Complex **1** crystallizes in the space group Orthorhombic *Pnma*. Complex **1** shows extensive intra- and intermolecular hydrogen bonding involving the iron coordinated water molecules, perchlorate oxygens and the water of crystallization. Seven symmetry-related intermolecular $\text{O}-\text{H} \cdots \text{O}$ bonds in **1** form a remarkable two dimensional network of water channels. Complex **2** crystallized in Monoclinic *P2₁/c* space group, with two $[\text{Fe}(\text{LH}_2)(\text{H}_2\text{O})\text{Cl}](\text{ClO}_4)_2$ units forming a dimeric structure in the unit cell. Iron coordinated chloride, water of crystallization and perchlorate oxygen atoms display a strong network of hydrogen bonds responsible for holding the two mononuclear units together. Electrochemical experiments revealed a facile reduction of **1** in 10:1 acetonitrile–water with $E_{1/2} = 140$ mV while addition of 8-fold excess of tetramethylammonium chloride afforded $[\text{Fe}(\text{LH}_2)\text{Cl}_2]^+$ which got reduced at $E_{1/2} = -80$ mV.

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1. Introduction

Bio-enzymes are a class of compounds that increase the rate of certain reactions in biological systems by many folds [1–3]. Nature has created varieties of such enzymes, containing monometallic, bimetallic, trimetallic and multimetallic proteins that perform versatile catalytic transformations [4]. Apart from copper [5,6], iron is found to be the most abundant metal present at the active sites of a large number of metalloenzymes [7,8] namely Hemerythrin (Hr), Methane monooxygenase (MMO) [9,10], Ribonucleotide reductase (RNR) [11,12], Catechol dioxygenase, Lipoxxygenase, Purple acid phosphatases (PAPs) [13]. Among the above mentioned metalloenzymes, Catechol dioxygenase and Lipoxxygenase contain one iron center at the active site, while Hemerythrin, MMO, RNR are diiron species, where the two iron centers are bridged by hydroxo/oxo, and one or more carboxylates. Purple Acid Phosphatases (PAPs) are phosphate ester hydrolyzing enzymes that contain a iron(III) center linked to a divalent metal ion M(II) (M = Zn, Fe, Mn, etc.) by a hydroxo (OH^-) and one or more carboxylate (RCOO^-) bridges [14]. Protein folding imparts the required configuration and conformation to these protein molecules that are inevitable for their extraordinarily high catalytic behavior. Supramolecular

interactions, like hydrogen bond are fundamental force that guides the folding of these proteins to provide them the necessary tertiary and quaternary structures.

Apart from the bio-molecules, supramolecular architectures formed by conventional covalent or coordinate covalent bonds as well as weak interactions are gaining more and more research attention due to the aesthetic beauty as well as the applicability of the self-assemblies in versatile fields like optoelectronics, conductivity, charge transfer, nanoporous, magnetic and biomimetic materials [15,16]. These weak supramolecular interactions include hydrogen bonds (both strong and weak), $\pi-\pi$, $\text{C}-\text{H} \cdots \pi$, and several other interactions like halogen–halogen, sulfur–sulfur, gold–gold, etc. Halogens coordinated to metal ions are known to act as strong hydrogen bond acceptors forming supramolecular structures resulting in the formation of chains or sheets, while $\text{N}-\text{H} \cdots \text{X}$, $\text{O}-\text{H} \cdots \text{X}$ (X = F, Cl, Br, I) and $\text{C}-\text{H} \cdots \text{X}$ interactions are known to occur within a molecule as well as in between the neighboring molecules.

Macrocyclic homo- and heterodinuclear compounds are highly efficient models [17–20] to study structure–function relations, by tuning the electron density over the two metal sites by varying the carboxylate bridges. In a recent work [21] we have prepared iron(III)–zinc(II) complexes using the tetraaminodiphenol macrocyclic ligand (H_2L) derived from 4-methyl diformyl and 1,3-diaminopropane (as shown in Chart 1) and acetate (OAc^-), pivalate (OPiv^-), and bis(4-nitrophenyl)phosphate (BNPP^-) bridges. It may

* Corresponding authors. Fax: +91 33 2668 4564 (P. Biswas).

E-mail address: biswaspapu@rediffmail.com (P. Biswas).

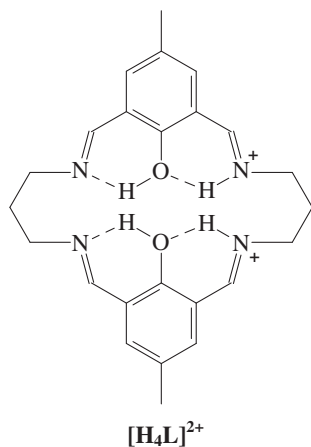


Chart 1.

be mentioned in this context that the macrocyclic ligand [H₄L]²⁺ remains as a zwitter ion where the phenol moieties lose protons to remain as phenolate, while the uncoordinated imino nitrogens take up these protons to form N–H⁺ that forms strong intramolecular hydrogen bonds with the phenolate. Initially the mononuclear iron(III) complexes [Fe^{III}(LH₂)(H₂O)₂](ClO₄)₃·3H₂O and [Fe^{III}(LH₂)(H₂O)Cl](ClO₄)₂·2H₂O were prepared which in turn were used as precursors for the preparation of iron(III)–zinc(II) heterobinuclear complexes.

In the present work we report the crystal structures, supramolecular interactions and topologies, and electrochemical studies of the two mononuclear iron(III) complexes.

2. Experimental section

2.1. Materials

Reagent grade chemicals obtained from commercial sources were used as received. Solvents were purified and dried according to standard methods [22]. [Pb(LH₂)](ClO₄)₂ was prepared according to method described previously [23].

2.2. Physical measurements

Elemental (C, H and N) analyses were performed on a Perkin–Elmer 2400 II elemental analyzer. IR spectra were recorded using KBr disks on a Shimadzu FTIR 8400S spectrophotometer. The electronic absorption spectra were taken at 25 °C on a Perkin–Elmer 950 UV–Vis–NIR spectrophotometer. The cyclic voltammetric (CV) and square wave voltammetric (SWV) measurements were carried out using a BAS 100B electrochemical analyzer in the same way as reported earlier [21]. Room temperature magnetic moments were measured using a Sherwood Scientific (Cambridge, UK) magnetic balance.

2.3. Preparation of metal complexes

Caution: Perchlorate salts used in this study are potentially explosive and therefore should be handled with care.

2.3.1. [Fe(LH₂)(H₂O)₂](ClO₄)₃·3H₂O (**1**) and [Fe(LH₂)(H₂O)Cl](ClO₄)₂·2H₂O (**2**)

Both were obtained in 80% yield from the perchlorate salts of the macrocyclic ligand [H₂(LH₂)](ClO₄)₂ [24] and the lead(II) complex [Pb(LH₂)](ClO₄)₂, with Fe(ClO₄)₃·6H₂O and FeCl₃·6H₂O for **1** and **2**, respectively by adopting the procedures reported earlier by us [21]. X-ray diffraction quality crystals of **1** and **2** were ob-

tained by slow evaporation of their acetonitrile–ethanol (2:3) solutions.

1: Anal. Calcd for C₂₄H₃₈Cl₃FeN₄O₁₉: C, 33.93; H, 4.48; N, 6.60. found: C, 34.26; H, 4.38; N, 6.71. FTIR (KBr, ν/cm⁻¹): 3430(br), 3175(w), 1660(s), 1624(s), 1556(s), 1446(m), 1349(m), 1283(m), 1238(m), 1100(s, br), 865(w), 820(w), 627(m), 518(w). UV–Vis–NIR (λ_{max}/nm) (ε/M⁻¹ cm⁻¹) in acetonitrile: 555 (3080), 375 (13,000). μ_{eff} (298 K): 5.83 B.M.

2: Anal. Calcd for C₂₄H₃₄Cl₃FeN₄O₁₃: C, 38.46; H, 4.54; N, 7.48. found: C, 38.28; H, 4.60; N, 7.42. FTIR (KBr, ν/cm⁻¹): 3420(br), 3165(w), 1655(s), 1626(s), 1558(s), 1448(s), 1350(m), 1280(m), 1236(m), 1090(s, br), 872(w), 820(w), 626(m), 515(w). UV–Vis–NIR (λ_{max}/nm) (ε/M⁻¹ cm⁻¹) in acetonitrile: 530 (3500), 435 (sh), 385 (13,750). μ_{eff} (298 K): 5.80 B.M.

2.4. Crystal structure determinations

Crystals suitable for structure determinations of [Fe(LH₂)(H₂O)₂](ClO₄)₃·3H₂O (**1**) and [Fe(LH₂)(H₂O)Cl](ClO₄)₂·2H₂O (**2**) were mounted on glass fibers and coated with perfluoropolyether oil. Intensity data were collected at a low temperature (100 K and 150 K for **1** and **2** respectively) on a Bruker–AXS SMART APEX II diffractometer equipped with a CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were processed with SAINT [25], and absorption corrections were made with SADABS [25]. The structures were solved by Direct and Fourier methods and refined by full-matrix least-squares based on F² using WINGX software of SHELXTL [26] and SHELX-97 [27]. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were placed at geometrically calculated position with fixed isotropic thermal parameters. Despite our best efforts, the hydrogen atoms of the water of crystallization in **2** were not found. The esd's (10.34 and 17.46) associated with the bond distances of Fe(1)–Cl(1) and Fe(2)–Cl(2), respectively could not be bettered with further refinements and we believe it to be a result of strong hydrogen bonding involving Cl(1) and Cl(2) as well as the mode of packing of the asymmetric units in the unit cell. The crystallographic data of compounds **1** and **2** are given in Table 1.

Table 1

Crystallographic data for [Fe(LH₂)(H₂O)₂](ClO₄)₃·3H₂O (**1**), and [Fe(LH₂)(H₂O)Cl](ClO₄)₂·2H₂O (**2**).

	1	2
Formula	C ₂₄ H ₃₈ Cl ₃ FeN ₄ O ₁₉	C ₂₄ H ₃₄ Cl ₃ FeN ₄ O ₁₃
<i>M</i>	848.78	1497.50
Crystal size (mm ³)	0.30 × 0.22 × 0.18	0.20 × 0.12 × 0.10
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pnma</i>	<i>P2₁/c</i>
<i>a</i> (Å)	14.5668(17)	18.094(2)
<i>b</i> (Å)	17.8730(20)	18.105(2)
<i>c</i> (Å)	12.8038(15)	19.186(2)
α (°)	90	90
β (°)	90	95.247(4)
γ (°)	90	90
<i>U</i> (Å ³)	3333.6(7)	6258.9(14)
<i>Z</i>	4	4
<i>D_x</i> (g cm ⁻³)	1.691	1.589
<i>T</i> (K)	100(2)	150(2)
μ (mm ⁻¹)	0.782	0.808
No. measured/observed reflections	26,636/3953	69,704/10,423
Parameters refined	295	858
Final <i>R</i> 1 ^a	0.0456, 0.1110	0.0703, 0.1674
w <i>R</i> 2 ^b [<i>I</i> > 2σ(<i>I</i>)]		
<i>R</i> 1 ^a , w <i>R</i> 2 ^b (all data)	0.0583, 0.1197	0.1520, 0.2140
<i>S</i> ^c	1.077	1.068

^a $S = [\sum w(F_o^2 - F_c^2)^2 / (N - P)]^{1/2}$ where *N* is the number of data and *P* the total number of parameters refined.

^b $R_1(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^c $wR_2(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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