Crystal Structure, Spectroscopy and Magnetic Properties of a Novel Fe^{III} Unsymmetric Tetranuclear Complex: A Model for met-Hemerythrin

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N,N,N'-tris(2-pyridylmethyl)-1,3-diamino-2-propanol (HTPPNOL) has been synthesized and a novel tetranuclear antiferromagnetic iron(III) complex, containing bridging acetate, oxo, and alkoxo groups was characterized by X-ray crystallography, infrared, electronic, and Mössbauer spectroscopies and magnetic susceptibility measurements.

There has been considerable interest in the synthesis of dinuclear iron complexes, since these molecules might be useful as model compounds for the active sites of a number of metalloproteins including hemerythrin (Hr), ribonucleotide reductase (RR), purple acid phosphatase (PAP) and methane monooxygenase (MMO).[1]

Coordination number asymmetry has been shown to exist in a number of metalloproteins and may impart unique reactivity, e.g. the interaction of dioxygen with Hr, which necessitates a vacant coordination site.[2,3] However, only a limited number of synthetic model complexes that exhibit asymmetric coordination has been reported.[4,5] Thus the rational design of ligands that can induce unsymmetrical ligation environments and a vacant or a labile site for reactivity is a convenient strategy for developing a more complete understanding of the structure and spectroscopic properties of such metalloenzymes.

In the present approach, the unsymmetrical ligand HTPPNOL (LH) has been synthesized and utilized to investigate the effect of the unsymmetrical ligation on binuclear and polynuclear complexes. Herein we report the synthesis and structural characterization of the tetranuclear iron complex, $[Fe_4^{III}(\mu\text{-}O)_2(\mu\text{-}OAc)_2L_2(H_2O)_2](ClO_4)_4\cdot 7H_2O$, **1**, as a further interesting model for the active site of Hr. The ligand was prepared by condensation reaction between *N,N'*-bis(2-pyridylmethyl)-1,3-diamipropan-2-ol[6] and 2-pyridinecarbaldehyde, in methanol, to give "*in situ*", a Schiff base which was reduced with $NaBH_4$. The product was purified by two extractions at acidic and basic conditions, to give a yellow oil, in a yield of 91%. ^1H NMR ($CDCl_3$) : 2,4–3,0 (4H, m, $(N\text{-}CH_2)_2$); 3,7–4,2 (7H, m, $N\text{-}CH_2\text{-}R$ and $R_2\text{-}CH\text{-}OH$); 7,0–7,8 (9H, m, py); 8,4–8,6 (3H, d, py).

Complex **1** was prepared as follows. To an argon scrubbed solution of $Fe(ClO_4)_2\cdot 6H_2O$ (725 mg, 2 mmol), in methanol (20 mL), was added an methanolic solution of LH (360 mg, 1 mmol) and $Na(OAc).3H_2O$ (184 mg, 1 mmol), resulting in a dark brown-reddish solution. Initially, an olive-green powder was obtained and identified as a mixed-valence complex $Fe^{III}Fe^{II}$. From the filtrate, after some days, was obtained a brown solid, identified as a Fe_2^{III} complex. Recrystallization of this brown complex, in methanol, gives the pure **1**, as brown crystals. Yield: 63%. Its IR spectrum exhibits absorptions in the region 610-690 cm^{-1}, due to $\nu(Fe\text{-}O)$[7], bridging acetate group: $\nu_{as}(COO)$ 1572 cm^{-1},$\nu_s(COO)$1440 cm^{-1}, $\nu(ClO_4)$ 1086 cm^{-1}. The molecular structure of **1** was determined by X-ray crystallography.[8] A perspective view of the complex cation of **1** is shown in Figure 1.

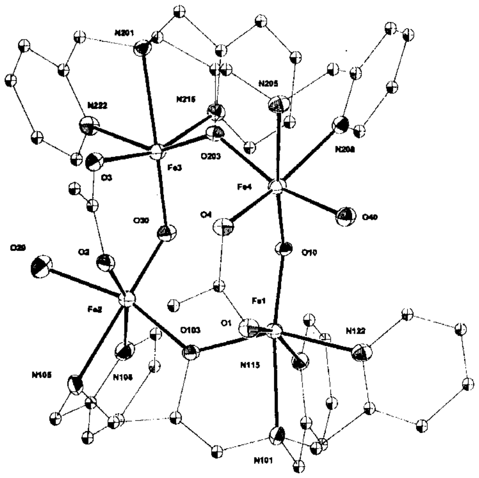


Figure 1. Molecular structure, selected bond lengths (Å) and angles (°) of complex **1**: Fe1-O1 2.024(4), Fe1-O10 1.786(4), Fe1-O103 2.030(4), Fe1-N101 2.240(5), Fe1-N115 2.108(5), Fe1-N122 2.177(6), Fe2-O2 2.020(4), Fe2-O30 1.796(4), Fe2-O103 2.000(4), Fe2-N105 2.248(5), Fe2-N108 2.137(6), Fe2-O20 2.155(5), Fe3-O3 2.020(4), Fe3-O30 1.795(4), Fe3-O203 2.022(4), Fe3-N201 2.243(5), Fe3-N222 2.187(5), Fe3-N215 2.150(5), Fe4-O4 2.031(4), Fe4-O10 1.790(4), Fe4-O203 2.019(4), Fe4-N205 2.227(5), Fe4-N208 2.142(5), Fe4-O40 2.162(4), Fe1···Fe2 3.662, Fe1-O103-Fe2 130.7(2), Fe1···Fe4 3.192, Fe1-O10-Fe4 126.4(2). Fe2···Fe3 3.195, Fe2-O30-Fe3 125.7(2), Fe3···Fe4 3.701, Fe3-O203-Fe4 132.6(2).

The pair of iron atoms that are connected by the (μ-TPPNOL) ligand are joined through oxo and carboxylate bridges to form the tetranuclear core (dimer of dimers), in which the oxo bridges coordinate *trans* to the N_{amine} and the oxygen atoms of the acetate groups coordinate *trans* to the pyridyl nitrogens. A comparison of **1** with the related tetranuclear iron (III) complex $[Fe_4^{III}(\mu\text{-}O)_2(\mu\text{-}BMDP)_2(\mu\text{-}OAc)_2](NO_3)_3(OH)\cdot 12H_2O$, **2**, reported by Satcher and co-workers[4], where HBMDP is the unsymmetrical binucleating ligand *N,N',N'*- tris(*N*-methyl)-2-benzimidazolylmethyl)-*N'*-methyl-1, 3-diamino-2-propanol, reveals that despite the similarity between the ligands HTPPNOL and HBMDP, there are some significant structural differences in their corresponding Fe_4^{III} complexes. While in the dinuclear unit of **2** one Fe^{III} is five-coordinated with distorted square pyramidal geometry, in the title complex **1** one labile water molecule is coordinated and the corresponding Fe^{III} atom lies in an octahedral environment. In addition, the $Fe\text{-}O_{alkoxo}$-Fe angles (av. 131.7(2)°) and the corresponding Fe···Fe distances (av. 3.681 Å) are somewhat larger than those observed in **2** (124.9(2)° and 3.532(4) Å). However, the $Fe\text{-}O_{oxo}$(1.791(4) Å), $Fe\text{-}O_{oxo}$-Fe (126.0(2)°) in **1** and $Fe\text{-}O_{oxo}$ (1.776(5) Å), $Fe\text{-}O_{oxo}$-Fe (128.4(3)°) in **2** are similar and comparable to the bond angle (127°) and bond distances (av.1.80 Å) in met-Hr.[9]

As shown in Figure 2, the room temperature value of μ_{eff} is significantly below the theoretical spin only value of $11.83\mu_B$ for four uncoupled iron (III) ions indicating the presence of strong antiferromagnetic coupling. From $0.93\mu_B$ per iron(III) at room temperature (290.3 K) μ_{eff} decreases continuously with decreasing temperature, reaching a plateau of $0.29\mu_B$ per iron at 30 K. Further lowering the temperature leads to 0.19 μ_B per iron at 2 K.

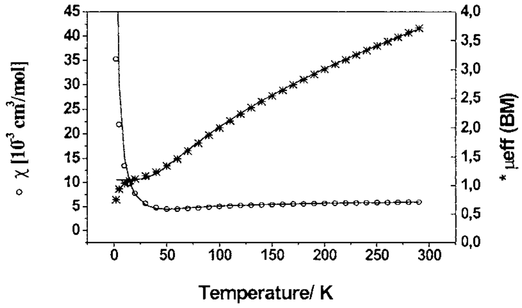
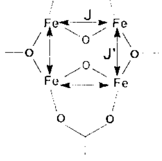


Figure 2. Magnetic Susceptibility (°) and effective magnetic moment (*) as a function of temperature for complex **1**.

Since the exchange coupling in polynuclear Fe(III) species is known to be dominated by the superexchange pathway via oxo bridges one can assume strong antiferromagnetic interactions between the irons bridged by the μ-oxo moiety and fairly weaker antiferromagnetic interactions between the iron ions bridged by the alkoxo group (see Scheme 1).

Therefore we assigned the following Hamiltonian to simulate the experimental data: $H= -2J(S_1.S_2 + S_3.S_4) - 2J'(S_1.S_3 + S_2.S_4)$. The obtained values for the exchange parameters J= -94.65 and J'= -11.81 cm^{-1} are in the expected order for the superexchange via μ-oxo and μ-alkoxo, respectively, and are in good agreement with the values reported for the met form of Hr isolated from *Golfingia gouldii* (J = - 134 cm^{-1})[9], and with the compound reported by Satcher and co-workers (J= -103.3 cm^{-1}),[4] attributed to similarity of the $Fe\text{-}O_{oxo}$ bonds in these complexes. The antiferromagnetic interaction in compound **1** is considered consistent with the values calculated by Gorun and Lippard's equation : -125.5 and -7.02 cm^{-1}, respectively.[10]



Scheme 1. Antiferromagnetic interactions between the iron ions in complex **1**.

The Mössbauer spectrum of **1** at 115 K shows only one quadrupole doublet, with δ= 0.46 and ΔE_Q= 1.62 mm/s. These parameters are typical of high-spin Fe^{III} ions[11] and are comparable to those observed for met-Hr (δ= 0.46 and ΔE_Q= 1.57 mm/s).[1]

In conclusion, the asymmetry in the ligand and the structural, magnetic and Mössbauer parameters, described here for complex **1** are very similar to those found in the met-Hr and therefore we can propose that **1** is a further and very interesting model for the active site of this metalloenzyme. The characterization of further dinuclear Fe^{III} and mixed-valence complexes are underway and will be the subject of future reports.

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8 X-Ray data for Complex **1**: $C_{46}H_{70}Cl_4Fe_4N_{10}O_{33}$, FW = 1656.32 $g.mol^{-1}$. Space group $P2_1/n$ [nr.14], a = 23.416(3), b = 25.015(3), c = 24.536(3) Å, β = 111.01(2)°, V = 13417(3) $Å^3$, Z = 8, d_c = 1.64 Mg m^{-3}, R= 0.0574 for 17527 unique reflections, and 1790 parameters.

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