



Syntheses, structures and magnetic properties of dinuclear oxo-bridged iron(III) complexes

Jong Won Shin, Sankara Rao Rowthu, Ju Eun Lee, Hong In Lee, Kil Sik Min *

Department of Chemistry Graduate School and Green-Nano Materials Research Center, Kyungpook National University, Daegu 702-701, Republic of Korea

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ABSTRACT

The reaction of tris(2-pyridylmethyl)amine (TPyA)/*N,N*-bis(2-pyridylmethyl)-2-aminoethanol (bpaOH), H₂DHBN/Na₂C₂O₄/NaN₃ and Fe(II/III) ions in MeOH leads to the isolation of three iron(III) dimeric complexes, namely [(TPyA)(DHBN)Fe^{III}OFe^{III}(TPyA)(DHBN)]·2H₂O (**1**), [(bpaOH)(C₂O₄)Fe^{III}OFe^{III}(bpaOH)]·2H₂O (**2**) and [(TPyA)(N₃)Fe^{III}OFe^{III}(N₃)(TPyA)](ClO₄)₂ (**3**) (H₂DHBN = 3,4-dihydroxybenzotriole). These complexes have been investigated by single crystal X-ray diffractometry and magnetochemistry. Complexes **1–3** show dimeric structures with a bridging oxo (O²⁻) ion, and all the iron(III) ions have a distorted octahedral geometry. Complexes **1** and **3** have offset face-to-face π - π interactions between the dimers and possess a supramolecular structure, while **2** has O–H...O hydrogen bonding interactions between the dimers, which gives rise to a 1-D chain structure. These (μ -oxo)diiron(III) complexes exhibit antiferromagnetic interactions [**1**: $g = 2.0$, $J/k_B = -112$ K (-78 cm⁻¹), $\theta = -0.29$ K, $\rho = 0.035$; **2**: $g = 2.0$, $J/k_B = -141$ K (-98 cm⁻¹), $\theta = -0.3$ K, $\rho = 0.01$; **3**: $g = 2.0$, $J/k_B = -130$ K (-90 cm⁻¹), $\theta = -0.5$ K, $\rho = 0.009$]. These indicate that very strong antiferromagnetic interactions occur via the oxo bridge within the iron(III) dimer and weak antiferromagnetic interactions exist between the dimers.

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1. Introduction

The design and preparation of polynuclear iron(III) complexes has enabled the understanding and development of molecule-based magnetic materials and the structural elucidation of metalloenzymes in metalloproteins [1]. Of these complexes, oxo-bridged diiron(III) complexes have attracted the attention of bioinorganic chemists as these linkages have been found in many metalloenzymes, such as methane monooxygenase, ribonucleotide reductase and purple acid phosphatases [2]. Furthermore, these systems also show antiferromagnetic coupling attributable to super-exchange coupling of the $S = 5/2$ ferric ions via the linking ligands, similar to the enzymes. In this research we have used tetradentate tripodal ligands, such as tris(2-pyridylmethyl)amine (TPyA) and *N,N*-bis(2-pyridylmethyl)-2-aminoethanol (bpaOH), as capping ligands to obtain oxo-bridged dinuclear complexes [3]. In particular, the bpaOH ligand is a multifunctional ligand, due to the potential N₃ donor from the bis(picoly1)amine moiety and the oxygen atom acting as a proton donor/acceptor. The apical nitrogen atoms of the TPyA and bpaOH ligands can be coordinated via three different binding modes in monooxo-bridged iron(III) complexes, for example, symmetrical [both *trans* to L or the μ -O²⁻ group] and unsymmetrical [one apical nitrogen atom *trans* to L, the other *trans* to μ -O²⁻] [4].

Symmetrical structures have been found for [(TPyA)(Cl)Fe^{III}OFe^{III}(Cl)(TPyA)]²⁺, [(TPyA)(OH)Fe^{III}OFe^{III}(OH)(TPyA)]²⁺ and [(TPyA)(H₂O)Fe^{III}OFe^{III}(H₂O)(TPyA)]⁴⁺ [5], while unsymmetrical structures have been elucidated for [(TPyA)(F)Fe^{III}OFe^{III}(F)(TPyA)]²⁺, [(TPyA)(OH)Fe^{III}OFe^{III}(H₂O)(TPyA)]³⁺ and [(5-Et-TPyA)(OH)Fe^{III}OFe^{III}(H₂O)(5-Et-TPyA)]³⁺ [4,5a,6]. Herein, we report the syntheses, structures and magnetic properties of the oxo-bridged iron(III) dinuclear complexes [(TPyA)(DHBN)Fe^{III}OFe^{III}(TPyA)(DHBN)]·2H₂O (**1**), [(bpaOH)(C₂O₄)Fe^{III}OFe^{III}(C₂O₄)(bpaOH)]·2H₂O (**2**) and [(TPyA)(N₃)Fe^{III}OFe^{III}(N₃)(TPyA)](ClO₄)₂ (**3**) (DHBN²⁻ = 3,4-dihydroxybenzotriolato, C₂O₄²⁻ = oxalato, TPyA = tris(2-pyridylmethyl)amine and bpa e-OH = *N,N*-bis(2-pyridylmethyl)-2-aminoethanol). The complexes **1** and **2** display symmetrical structures, while **3** shows an unsymmetrical one. Moreover, as DHBN²⁻ and C₂O₄²⁻ are coordinated in **1** and **2**, respectively, the TPyA and bpaOH ligands are bound as tridentate ligands, not tetradentate ones.

2. Experimental

2.1. General procedures

All chemicals used in the synthesis were of reagent grade and used without further purification. Tris(2-pyridylmethyl)amine (TPyA) and *N,N*-bis(2-pyridylmethyl)-2-aminoethanol (bpaOH) were prepared according to literature procedures [7]. UV–Vis absorption spectra were recorded with a SCINCO S-2100 spectro-

* Corresponding author. Tel.: +82 53 9505906; fax: +82 53 9505899.

E-mail address: minks@knu.ac.kr (K.S. Min).

photometer. Infrared spectra were recorded with a Thermo Fisher Scientific IR200 spectrophotometer ($\pm 1 \text{ cm}^{-1}$) using KBr disks. Elemental analyses were carried out using a Fissons/Carlo Erba EA1108 instrument. Magnetic susceptibilities were measured in an applied field of 5000 Oe between 5 or 10 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made [545.5 (**1**), 426.5 (**2**) and 534.8×10^{-6} (**3**) emu/mol] by using Pascal's constants.

2.2. Preparation of [(TPyA)(DHBN)Fe^{III}OFe^{III}(TPyA)(DHBN)]·2H₂O (**1**)

To a methanol solution (30 mL) of Fe(NO₃)₃·9H₂O (139 mg, 0.344 mmol) was added a methanol solution (10 mL) of TPyA (100 mg, 0.344 mmol) and a methanol solution of 3,4-dihydroxybenzoinitrile (H₂DHBN, 47 mg, 0.344 mmol). The color of the solution turned dark red. Triethylamine (0.10 mL, 0.688 mmol) was added to the mixture for neutralization, which gave rise to a clear purple solution that was heated to reflux for 30 min. After hot-filtration, the solution was allowed to stand at room temperature for 2 or 3 days, whereupon a dark purple crystalline solid formed which was collected by filtration and washed with methanol and dried in air. Yield: 130 mg (75%). Single crystals suitable for X-ray crystallography were obtained from a mixture solution (MeOH/H₂O) by slow evaporation at room temperature. *Anal. Calc.* for C₅₀H₄₆Fe₂N₁₀O₇: C, 59.42; H, 4.59; N, 13.86. Found: C, 59.10; H, 4.51; N, 14.16%. FT-IR (KBr, cm⁻¹): 3406, 3063, 2919, 2848, 2201, 1605, 1438, 1153, 810, 769.

2.3. Preparation of [(bpaOH)(C₂O₄)Fe^{III}OFe^{III}(C₂O₄)(bpaOH)]·2H₂O (**2**)

To a methanol solution (10 mL) of Fe(BF₄)₂·6H₂O (70 mg, 0.21 mmol) was added a methanol solution (10 mL) of bpaOH (50 mg, 0.21 mmol) and a MeOH/H₂O solution (10 mL, 3:2, v/v) of Na₂C₂O₄ (24 mg, 0.10 mmol). The mixture was heated to reflux for 1 h and the color turned yellow-brownish. After hot-filtration, the solution was allowed to stand at room temperature for several days, whereupon yellow-brownish crystals formed which were collected by filtration, washed with water and methanol, and dried in air. Yield: 24 mg (28%). *Anal. Calc.* for C₃₂H₃₈Fe₂N₆O₁₃: C, 46.48; H, 4.64; N, 10.17. Found: C, 46.08; H, 4.61; N, 10.04%. FT-IR (KBr, cm⁻¹): 3515, 3468, 3084, 2966, 1681, 1664, 1607, 1382, 1258, 815, 780.

2.4. Preparation of [(TPyA)(N₃)Fe^{III}OFe^{III}(N₃)(TPyA)](ClO₄)₂ (**3**)

To a methanol solution (6 mL) of Fe(ClO₄)₂·6H₂O (44 mg, 0.17 mmol) was added a methanol solution (6 mL) of TPyA (50 mg, 0.17 mmol) and a methanol solution (6 mL) of NaN₃ (22 mg, 0.344 mmol). The mixture was stirred for 10 min and the color turned dark red. After a filtration, the solution was allowed to stand at room temperature for 2 or 3 days, whereupon dark red-dish-brown crystals formed which were collected by filtration, washed with methanol and dried in air. Yield: 36 mg (43%). *Anal. Calc.* for C₃₆H₃₆Cl₂Fe₂N₁₄O₉: C, 43.62; H, 3.66; N, 19.78. Found: C, 43.78; H, 3.64; N, 19.90%. FT-IR (KBr, cm⁻¹): 3084, 2926, 2054, 1606, 1441, 1094, 1024, 808, 767, 622.

2.5. X-ray crystallographic data collection and refinement

Single crystals of **1** and **3** were mounted on a Bruker SMART APEX CCD-based diffractometer (Korea Basic Science Institute, Chonju Branch). X-ray data for **1** and **3** were collected at 200(2) K, using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$, graphite monochromator). The raw data were processed to give structure factors

using the Bruker SAINT program and corrected for Lorentz and polarization effects [8]. X-ray diffraction data of **2** were collected at 293(2) K on an ADSC Quantum 210 detector at Beamline 6B1MXI of the Pohang Light Source. The basic data file was prepared by using the program HKL2000 [9]. The reflections were successfully indexed by the automated indexing routine of the DENZO program [9]. The intensity data of **1** were corrected for absorption using the SADABS program with multi-scan data ($T_{\text{min}}/T_{\text{max}} = 0.785$) [10]. The crystal structures were solved by direct methods for **1** and **2** and by Patterson methods for **3** [11], and refined by full-matrix least-squares refinement using the SHELXL97 computer program [12]. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL97, except for the water molecules in **1** and **2**. The aqua hydrogen atoms in **2** were located from the difference Fourier maps and refined with isotropic displacement factors, however, the aqua hydrogen atoms in **1** could not be located due to a large thermal disorder. The crystallographic data and the results of the refinements are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The reaction of one equivalent of tris(2-pyridylmethyl)amine (TPyA) and 1 equiv of 3,4-dihydroxybenzoinitrile (H₂DHBN) with Fe(NO₃)₃·9H₂O in MeOH under aerobic conditions affords air stable [(TPyA)(DHBN)Fe^{III}OFe^{III}(TPyA)(DHBN)]·2H₂O (**1**) in good yield (75%). The IR spectrum of **1** in KBr has peaks characteristic of coordinated TPyA and DHBN, as well as ν_{OH} absorptions characteristic of H₂O as a lattice solvent [13]. A strong absorption at 2201 cm⁻¹ was assigned to the cyano group of coordinated DHBN²⁻. Bands for C–H of the TPyA ligand appeared at 3063, 2919 and 2848 cm⁻¹. The reaction of one equivalent of *N,N*-bis(2-pyridylmethyl)-2-aminoethanol (bpaOH) and 1 equiv of Na₂C₂O₄ with Fe(BF₄)₂·6H₂O in MeOH under aerobic conditions affords air stable [(bpaOH)(C₂O₄)Fe^{III}OFe^{III}(C₂O₄)(bpa-

Table 1
Crystallographic data and structure refinement for **1**, **2** and **3**.

Compound	1	2	3
Empirical formula	C ₅₀ H ₄₆ Fe ₂ N ₁₀ O ₇	C ₃₂ H ₃₈ Fe ₂ N ₆ O ₁₃	C ₃₆ H ₃₆ Cl ₂ Fe ₂ N ₁₄ O ₉
Formula weight	1010.67	826.38	991.39
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	P2 ₁ /n	P $\bar{1}$
<i>a</i> (Å)	20.900(2)	10.644(1)	13.6127(6)
<i>b</i> (Å)	19.855(2)	9.066(1)	13.9013(6)
<i>c</i> (Å)	12.9696(14)	18.175(2)	14.0201(6)
α (°)			87.591(1)
β (°)	115.614(2)	94.513(7)	69.106(1)
γ (°)			60.704(1)
<i>V</i> (Å ³)	4853.2(9)	1748.4(3)	2132.85(16)
<i>Z</i>	4	2	2
<i>D</i> _{calc} (g cm ⁻³)	1.383	1.570	1.544
λ (Å)	0.71073	0.90000	0.71073
<i>T</i> (K)	200(2)	293(2)	200(2)
μ (mm ⁻¹)	0.660	0.905	0.876
<i>F</i> (000)	2096	856	1016
Collected	17691	3920	15828
Unique	6013	3920	10408
Observed	1647	2456	5195
Parameters	313	253	544
GOF	0.762	1.020	1.015
<i>R</i> ₁ ^a (4 σ data)	0.0724	0.0819	0.0795
<i>wR</i> ₂ ^b (4 σ data)	0.1745	0.1937	0.2095

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

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