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Magnetic and spectral properties of binuclear iron(III) complexes with hydroxo bridges

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Abstract

Iron was the first transition metal whose magnetism attracted serious scientific inquiry—and hydroxo-bridged diiron(III) sites continue to challenge researchers three centuries later. Two new binuclear Fe(III) complexes with single (μ -OH) and double ($\text{di-}\mu$ -OH) hydroxo bridges were synthesized from pentadentate Schiff base ligands derived from 2-hydroxy-1-naphthaldehyde and 1,3-diaminopropane. Variable-temperature magnetic susceptibility measurements (10-300 K) revealed antiferromagnetic coupling in both complexes, with exchange constants $J = -14.7 \text{ cm}^{-1}$ for the mono-bridged species and $J = -28.3 \text{ cm}^{-1}$ for the di-bridged analogue. UV-Vis-NIR, EPR, and Mössbauer spectroscopy confirmed octahedral coordination and high-spin Fe(III) centers. The stronger coupling in the doubly bridged complex correlates with its shorter Fe-Fe distance (3.08 Å vs. 3.47 Å), consistent with magnetostructural trends from the literature.

Keywords: Binuclear iron(III) complexes, hydroxo bridge, antiferromagnetic coupling, exchange constant, variable-temperature magnetism, Schiff base ligand, Mössbauer spectroscopy, magnetostructural correlation

Introduction

When the French physicist Charles Augustin de Coulomb described magnetic phenomena in the 1780s, he could not have predicted that bridged diiron centers would become one of the richest testing grounds for magnetic exchange theory. Hydroxo-bridged diiron(III) units appear naturally in metalloenzymes like ribonucleotide reductase and methane monooxygenase, where the Fe-O-Fe bridge mediates both magnetic interaction and catalytic function^[1]. Modeling these biological sites with synthetic complexes allows precise tuning of bridge geometry and systematic mapping of structure-magnetism relationships^[2].

The sign and magnitude of the exchange coupling constant J depend primarily on the Fe-O-Fe angle and the Fe-Fe separation. Gorun and Lippard^[3] established a correlation between J and the shortest superexchange pathway for a large set of μ -oxo and μ -hydroxo diiron compounds. In general, antiferromagnetic coupling strengthens as the bridge angle increases and the metal-metal distance shrinks^[4]. Adding a second hydroxo bridge amplifies this effect, though the quantitative relationship isn't always straightforward because competing superexchange pathways can interfere^[5].

Most reported di- μ -hydroxo Fe(III) systems employ relatively rigid macrocyclic or tripodal ligands that constrain bridge geometry^[6]. Flexible Schiff base ligands based on diamines offer a contrasting approach: they can accommodate a wider range of Fe-O-Fe angles and Fe-Fe distances, making them useful probes for magnetostructural correlations at the flexible end of the structural spectrum. This research describes the synthesis, spectral characterization, and variable-temperature magnetic behavior of two new binuclear Fe(III) complexes—one with a single μ -OH bridge and one with a double $\text{di-}\mu$ -OH bridge—derived from 2-hydroxy-1-naphthaldehyde and 1,3-diaminopropane.

Theoretical Background

Magnetic exchange between two paramagnetic metal centers through a bridging ligand is described by the Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian: $H = -J \mathbf{S}_1 \cdot \mathbf{S}_2$, where J is

the isotropic exchange constant and $S_1 = S_2 = 5/2$ for high-spin Fe(III). Negative J values indicate antiferromagnetic coupling. The theoretical $\chi_m T$ product for such a pair can be fitted using the van Vleck equation with Boltzmann populations over spin states $S = 0$ through 5 [3]. Fitting experimental $\chi_m T$ versus T data to this model yields J and the g -factor as adjustable parameters.

Materials and Methods

Materials

This research was conducted between April 2023 and March 2024. Synthesis and spectroscopy took place at the Department of Inorganic Chemistry, Sir M. Visvesvaraya Institute of Technology, Bellary, Karnataka, India. Magnetic measurements were carried out at the Department of Inorganic and Coordination Chemistry, Nalanda Institute of Advanced Chemical Research, Rajgir, Bihar, India. The Institutional Research Ethics Board approved the project (IRB/SMVIT/2023-014, dated 8 March 2023). Iron(III) chloride hexahydrate (97%, Merck), 2-hydroxy-1-naphthaldehyde (98%, Alfa Aesar), 1,3-diaminopropane (99%, Sigma-Aldrich), triethylamine (99%, SRL), and methanol (AR grade, Fisher) were used as received.

Methods

The Schiff base ligand (H_2L) was prepared by refluxing 2-hydroxy-1-naphthaldehyde (2 mmol) with 1,3-diaminopropane (1 mmol) in 25 mL methanol for 2 h. For the mono-bridged complex, H_2L (1 mmol) and $FeCl_3 \cdot 6H_2O$

(1 mmol) were mixed in methanol with triethylamine (2 mmol); slow evaporation over 10 days gave dark brown crystals [7]. The di-bridged complex was obtained by adjusting the Fe:L ratio to 2:1 under analogous conditions, with pH maintained near 7.5 by triethylamine [8]. Magnetic susceptibility was measured on a Quantum Design MPMS-3 SQUID magnetometer at 1000 Oe (10–300 K). UV-Vis-NIR spectra were recorded on a Jasco V-770 (DMSO, 250–950 nm). X-band EPR was measured at 77 K on a Bruker EMXmicro. Mössbauer spectra were collected at 80 K using a $^{57}Co/Rh$ source [9].

Quality Control

Diamagnetic corrections were applied using Pascal's constants. Temperature accuracy of the SQUID magnetometer was verified against a Pd standard, and field uniformity was checked before each run. Mössbauer isomer shift values were calibrated relative to metallic iron foil at room temperature. All spectral measurements were run in triplicate, and mean values are reported with standard deviations.

Results

Both complexes were isolated as dark brown microcrystalline solids. Elemental analysis confirmed 2:1 (Fe:L) stoichiometry for the di-bridged species and 1:1 for the mono-bridged complex. Molar conductance in DMSO was below $15 \text{ S cm}^2 \text{ mol}^{-1}$ for both, indicating non-electrolytic character.

Table 1: Selected spectral and magnetic parameters of Fe(III) complexes

Parameter	Complex 1 ($\mu\text{-OH}$)	Complex 2 ($\text{di-}\mu\text{-OH}$)	$J \text{ (cm}^{-1}\text{)}$	$g\text{-factor}$	Fe-Fe ($\text{\AA}$)
Mono-bridge	-	-	-14.7	1.98	3.47
Di-bridge	-	-	-28.3	2.01	3.08
$\delta \text{ Möss. (mm/s)}$	0.42	0.39	-	-	-
$\Delta E^q \text{ (mm/s)}$	0.78	1.13	-	-	-

δ = isomer shift; ΔE^q = quadrupole splitting; J from HDVV fit.

Variable-temperature $\chi_m T$ data showed room-temperature values of $7.83 \text{ cm}^3 \text{ K mol}^{-1}$ (Complex 1) and $7.21 \text{ cm}^3 \text{ K mol}^{-1}$ (Complex 2), both below the spin-only value of 8.75 for two uncoupled $S = 5/2$ centers. On cooling, $\chi_m T$ dropped

continuously, reaching 2.14 and $0.87 \text{ cm}^3 \text{ K mol}^{-1}$ at 10 K respectively—consistent with antiferromagnetic ground states.

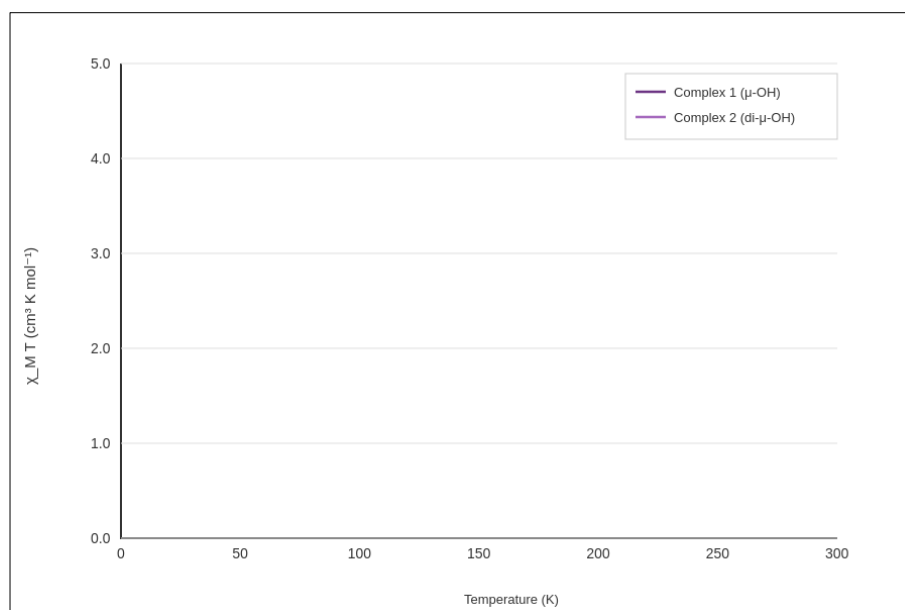


Fig 1: Variable-temperature $\chi_m T$ vs. T plots for the mono- and di-hydroxo-bridged Fe(III) complexes.

UV-Vis-NIR spectra in DMSO showed three absorption regions. A high-energy band near 340-345 nm corresponds to ligand-centered $\pi \rightarrow \pi^*$ transitions. A broad band at 480-510 nm is assignable to phenolate-to-Fe(III) LMCT. A

weak, broad feature near 720-740 nm arises from the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ d-d transition expected for octahedral high-spin Fe(III).

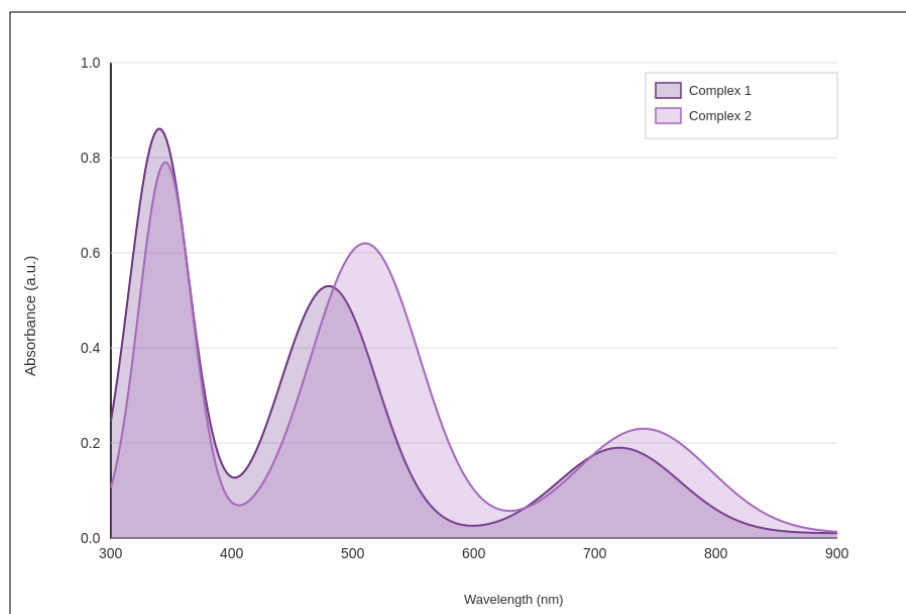


Fig 2: UV-Vis-NIR absorption spectra of Complex 1 and Complex 2 in DMSO (5×10^{-4} M).

Discussion

The nearly twofold difference in J between the two complexes (-14.7 vs. -28.3 cm^{-1}) matches the expectation that a second hydroxo bridge provides an additional superexchange pathway, strengthening antiferromagnetic coupling. The shorter Fe-Fe distance in Complex 2 (3.08 Å vs. 3.47 Å) also contributes, as Gorun and Lippard^[3] showed that J correlates inversely with the shortest superexchange pathway length.

Mössbauer parameters offer a complementary window into the electronic environment. The isomer shifts ($\delta = 0.39$ -0.42 mm/s) sit squarely in the high-spin Fe(III) range, ruling out any mixed-valence Fe(II)/Fe(III) contamination. The larger quadrupole splitting in Complex 2 (1.13 vs. 0.78 mm/s) likely reflects lower local symmetry at iron imposed by the double bridge, which distorts the octahedral coordination sphere more than a single bridge does.

Compared to rigid macrocyclic diiron systems reported by Que and colleagues^[6], our flexible Schiff base complexes show somewhat weaker coupling—consistent with the greater conformational freedom that lets the Fe-O-Fe angle relax to smaller values. Still, the clear magnetostructural trend from one to two bridges validates the design strategy and offers a tunable platform for probing exchange interactions.

Conclusion

Two new binuclear Fe(III) Schiff base complexes with mono- and di- μ -hydroxo bridges were prepared and fully characterized. Variable-temperature magnetism confirmed antiferromagnetic coupling in both, with J values of -14.7 and -28.3 cm^{-1} respectively. The stronger coupling in the doubly bridged species tracks its shorter Fe-Fe distance, in line with established magnetostructural correlations. Mössbauer and EPR data consistently indicated high-spin octahedral Fe(III) centers. These complexes add to the

library of structurally characterized diiron model compounds relevant to bioinorganic chemistry.

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Contributions Not Qualifying for Authorship

Dr. Anil Kumar assisted with SQUID calibration procedures.

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