

Redox Chemistry of Fe^{II} and Fe^{III} complexes using carboxylate-based ligands

Richa¹, Himanshu Arora^{2,*}

¹Research scholar, DBAS, SoES, G.D. Goenka University

²Assistant Professor, DBAS, SoES, G.D. Goenka University

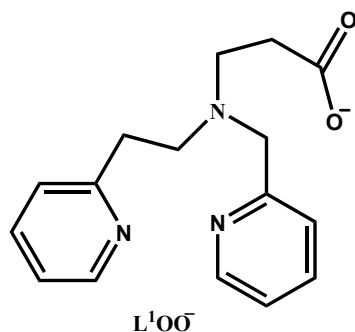
Abstract: Two new complexes [Fe^{II}(L¹OO)(H₂O)₂][ClO₄]₂·2H₂O (**1**), and [Fe^{III}(L¹OO)Cl₃] (**2**), (L¹OO⁻ = 3-[(2-(pyridine-2-yl)-ethyl){2-(pyridine-2-yl)methyl}amino]propionate) have been synthesized and characterized by elemental analysis, IR, and UV/Vis spectroscopy. In **1** distorted octahedral FeN₃O₃ coordination is satisfied by three nitrogen atoms and an appended carboxylate oxygen atom of the ligand, and the oxygen atoms from water molecule. In **2** distorted octahedral FeN₃Cl₃ coordination is satisfied by three nitrogen atoms and three chlorine atoms. When examined by cyclic voltammetry (CV), complex **1** undergoes in DMF one quasi-reversible metal-based (Fe^{II}/Fe^{III}) oxidation [$E_{1/2} = 0.325$ V vs SCE (saturated calomel electrode)]; whereas complex **2** undergoes in CH₃CN one quasi-reversible metal-based (Fe^{III}/Fe^{II}) reduction [$E_{1/2} = -0.055$ V vs SCE (saturated calomel electrode)].

Keywords: Carboxylate-based ligand, mononuclear iron complexes, redox property, Absorption spectra

Introduction

In current area of research of coordination complexes, metal-ligand coordination can be facilitated by interconnecting them with organic ligands. This will generate variety of supramolecular architectures which interest scientist of various domains such as catalysis, material science due to its vast applications. [1] The increasing interest in this field is justified by the intellectual challenge in controlling and manipulating the self-assembly process.[2] Magneto-structural studies on polynuclear complexes, aimed at understanding the underlying structural factors that govern the magnetic-exchange interaction between paramagnetic centers mediated by ligand bridge(s), continue to be of interest.[3–5] Investigating magnetic exchange interaction between metal centers, various bridging groups are explored but carboxylates[6] considered to be ideal candidates as it can bridge metal ions to give rise to different supramolecular architecture ranging from discrete to three dimensional systems.[7–9] Carboxylate group can assume many types of bridging conformations, the most important being triatomic *syn-syn*, *syn-anti*, *anti-anti* and monoatomic.[10,11] The generation of binuclear systems is favored by *syn-syn* conformation whereas *syn-anti* favors the formation of extended structures with varying nuclearity. The former mediates the antiferromagnetic exchange pathway between the metal centers, while the latter favors the ferromagnetic exchange interaction with some exceptions where antiferromagnetic coupling is favored.[8] In our earlier work, we have shown[12,13] that the carboxylate-appended bidentate and tridentate (2-pyridyl)alkylamine ligands afford 1D coordination polymers with Mn^{II}, [13]Co^{II}, [12a]Cu^{II}[12a] and Zn^{II}[13] and discrete Cu^{II}₄, [12a,b] Ni^{II}₄, [12b] Cu^{II}₇[12c] and Ni^{II}₈[12d] coordination clusters. Successful synthesis of these systems provides examples of ligand denticity-controlled self-assembly process. Magnetic measurements revealed varied magnetic systems: (i) weak antiferromagnetic exchange in 1D coordination polymers, [12a,13] (ii) spin-canted antiferromagnetic behavior for 1D coordination polymer of Co^{II}, [12a] (iii) effectively antiferromagnetic exchange interaction in discrete Cu^{II}₇[12c] and Ni^{II}₈[12d] coordination clusters and (iv) ferromagnetic interaction in discrete Cu^{II}₄[12a,b] and Ni^{II}₄[12b] coordination clusters.

Hoping that synthetic generality of the formation of 1D coordination polymers supported by carboxylate-appended anionic (2-pyridyl)alkylamine ligands could be established, and from the aforesaid perspective in this work we have included another ($\text{L}^1\text{OO}^- = 3\text{-}[(2\text{-}(6\text{-methyl-pyridine-2-yl)ethyl)}\{(\text{dimethylamino})\text{ethyl}\} \text{amino}] \text{propionate}$) (Scheme 1) with flexible carboxylate linker. Specifically, we have synthesized and characterized two mononuclear complexes Fe^{II} and Fe^{III} of L^1OO^- , comprising of one carboxylate group and two pyridyl nitrogen and one amine nitrogen. Herewith, we present a preliminary report on the redox chemistry of $[\text{Fe}^{\text{II}}(\text{L}^1\text{OO})(\text{H}_2\text{O})_2][\text{ClO}_4] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Fe}^{\text{III}}(\text{L}^1\text{OO})\text{Cl}_3]$ (**2**).



Scheme 1

Methodology

General Procedure. All reagents and solvents were obtained from commercial sources and used as received. Solvents were dried/purified as reported previously.[12] The ligand L^1OO^- was synthesized as before.[12a]

Synthesis of Complexes

Synthesis of $[\text{Fe}^{\text{II}}(\text{L}^1\text{OO}^-)(\text{H}_2\text{O})_2][\text{ClO}_4]$ (**1**): To a degassed solution of L^1OO^- (0.075 g, 0.25 mmol) in MeCN (5 ml) was added solid $[\text{Fe}^{\text{II}}(\text{MeCN})_4][\text{ClO}_4]_2$ (0.105 g, 0.25 mmol). The resulting intense yellow solution was stirred for 30 min at room temperature. The pale yellow solid that precipitated was filtered, washed with MeCN, and dried in vacuo. Pure compound was obtained by diffusion of Et_2O into a MeOH solution of the complex under dinitrogen atmosphere. Yield: 0.050 g (ca. 41%). Anal. Calc. for $\text{C}_{16}\text{H}_{22}\text{N}_3\text{ClFeO}_8$ (1): C, 40.40; H, 4.66; N, 8.83. Found: C, 40.76; H, 4.34; N, 8.59%. Conductivity (1 mM solution in MeOH at 25 °C): $\Lambda_{\text{M}} = 81 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (expected range for 1:1 electrolytes: 80–115 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).[14] IR (KBr, cm^{-1} , selected peaks): 3437 $\nu(\text{OH})$ of coordinated water, 1094, 624 $\nu(\text{ClO}_4^-)$. Absorption spectrum [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$)] (in MeOH): 880 (14), 550 (sh, 28), 360 (sh, 3180), 260 (16, 600).

Synthesis of $[\text{Fe}^{\text{III}}(\text{L}^1\text{OO}^-)\text{Cl}_3]$ (**2**): The complex was obtained by the addition of a solution of the ligand L^1OO^- (0.075 g, 0.25 mmol) to a solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.25 mmol). The reaction has been carried out in EtOH. A yellow solid was immediately formed, which was filtered off and washed with ethanol. The solid was recrystallized in acetonitrile, resulting in yellow-reddish crystals suitable for X-ray analysis.

(yield:). Anal. Calc. for $C_{16}H_{18}N_3Cl_3FeO_2(1)$: C, 43.04; H, 4.06; N, 9.41. Found: C, 42.76; H, 4.24; N, 9.35%. Conductivity (1 mM solution in MeCN at 25 °C): $\Lambda_M = 5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (expected range for 1:1 electrolytes: 80–115 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$).[14] IR (KBr, cm^{-1} , selected peaks): 3415 $\nu(\text{OH})$ of uncoordinated ethanol, 1731 $\nu(\text{CO})$. Absorption spectrum [λ_{max} , nm (ϵ , $\text{M}^{-1} \text{ cm}^{-1}$)] (in MeCN): 570 (sh, 30), 360 (6880), 308 (8250), 248 (15, 900).

Physical Measurements.Elemental analyses were obtained using a Thermo Quest EA 1110 CHNS-O, Italy.Spectroscopic measurements were made using the following instruments: Bruker Vector 22; electronic, Perkin Elmer Lambda 2 and Agilent 8453 diode-array spectrophotometer. Cyclic voltammetric experiments were performed at 298 K by using a PAR model 370 electrochemistry system consisting of M-174A polarographic analyzer, M-175 universal programmer, and RE 0074 X-Y recorder. The cell contained a Beckman (M 39273) platinum-inlay working electrode, a Pt wire auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode. Details of the cell configuration are as described before.[15]

Result and Discussions

Spectroscopic Properties

The absorption spectral feature of **1** was studied in CH_3OH (Fig. 1). The yellow solution shows a broad band at 880 nm ($\epsilon = 14 \text{ M}^{-1} \text{ cm}^{-1}$) which is tentatively assigned to ${}^5\text{T}_{2g}(\text{D}) \rightarrow {}^5\text{E}_g(\text{D})$. The shoulder at 550 nm (sh, $\epsilon = 28 \text{ M}^{-1} \text{ cm}^{-1}$) is due to spin-forbidden transition. The high-energy bands at 360 nm (sh, $\epsilon = 3180 \text{ M}^{-1} \text{ cm}^{-1}$) and 260 nm ($\epsilon = 16600 \text{ M}^{-1} \text{ cm}^{-1}$) are due to metal-perturbed intraligand charge-transfer. On the other hand, the absorption spectral feature of **2** was studied in CH_3CN (Fig. 2). The yellow solution shows a shoulder at 570 nm (sh, $\epsilon = 30 \text{ M}^{-1} \text{ cm}^{-1}$) is due to spin-forbidden transition. The high-energy bands at 360 nm ($\epsilon = 6880 \text{ M}^{-1} \text{ cm}^{-1}$), 308 nm ($\epsilon = 8250 \text{ M}^{-1} \text{ cm}^{-1}$) and 248 nm ($\epsilon = 15900 \text{ M}^{-1} \text{ cm}^{-1}$) are due to metal-perturbed intraligand charge-transfer.

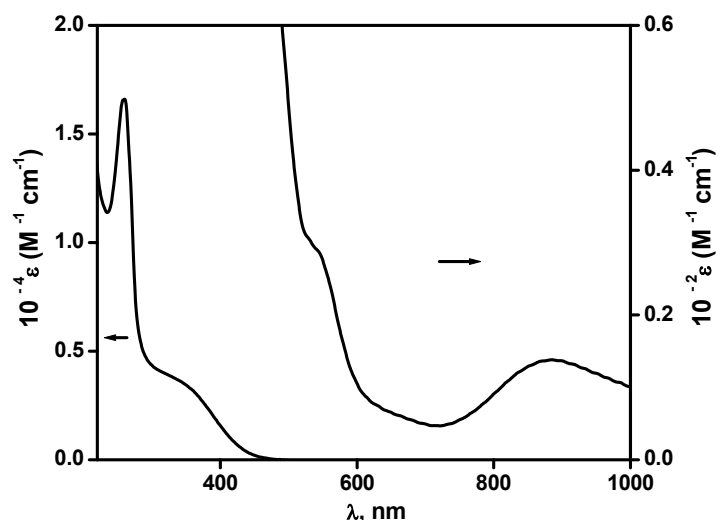


Fig 1: Absorption spectrum of $[\text{Fe}^{\text{II}}(\text{L}^1\text{OO})(\text{H}_2\text{O})_2][\text{ClO}_4] \cdot 2\text{H}_2\text{O}$ (**1**) in MeOH

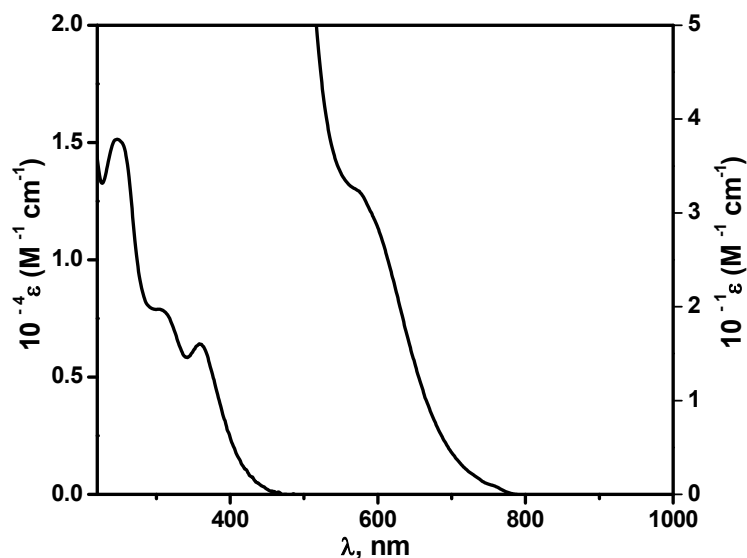


Fig 2: Absorption spectrum of $[\text{Fe}^{\text{III}}(\text{L}^1\text{OO})\text{Cl}_3]$ (**2**) in MeCN

Electrochemical study

To investigate the redox properties of complex (**1**), cyclic voltammetric experiment was performed in dmf by using platinum as working electrode and TBAP as supporting electrolyte. Cyclic voltammogram of complex (**1**) exhibits a single quasireversible oxidative redox process, for the redox couple $[\text{Fe}^{\text{II}}(\text{L}^1\text{OO})(\text{H}_2\text{O})_2]^+ / [\text{Fe}^{\text{III}}(\text{L}^1\text{OO})(\text{H}_2\text{O})_2]^{2+}$ at $E_{1/2} = 0.325\text{V}$ vs SCE (Fig.3).

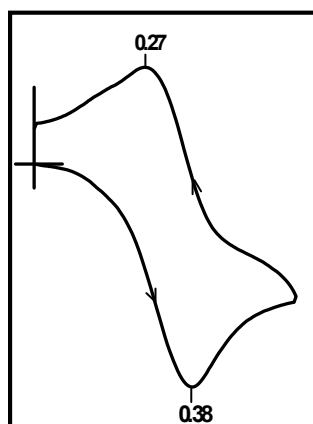


Fig. 3 Cyclic Voltammogram (scan rate 100 mV/s) of (**1**) in DMF at a platinum electrode; supporting electrolyte: TBAP

To investigate the redox properties of complex (**2**), cyclic voltammetric experiment was performed in CH_3CN by using platinum as working electrode and TBAP as supporting electrolyte. Cyclic

voltammogram of complex **(2)** exhibits a single quasireversible reductive redox process, for the redox couple $[\text{Fe}^{\text{III}}(\text{L}^{\text{I}}\text{OO})\text{Cl}_3]/[\text{Fe}^{\text{II}}(\text{L}^{\text{I}}\text{OO})\text{Cl}_3]^-$ at $E_{1/2} = -0.055\text{V}$ vs SCE (Fig.4).

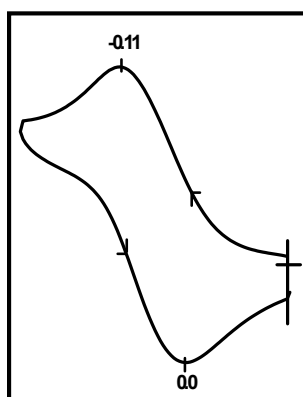


Fig. 4. Cyclic Voltammogram (scan rate 100 mV/s) of **(2)** in MeCN at a platinum electrode; supporting electrolyte: TBAP

Conclusions

In this work, we have synthesized and characterized two mononuclear complexes $\{[\text{Fe}^{\text{II}}(\text{L}^{\text{I}}\text{OO})(\text{H}_2\text{O})_2][\text{ClO}_4] \cdot 2\text{H}_2\text{O}$ (**1**), and $[\text{Fe}^{\text{III}}(\text{L}^{\text{I}}\text{OO})\text{Cl}_3]$ (**2**) $\}$ with 3-[(2-(pyridine-2-yl)-ethyl){2-(pyridine-2-yl)methyl}amino]propionate($\text{L}^{\text{I}}\text{OO}^-$). Octahedral coordination of Fe(II) (FeN_3O_3) in **1** is satisfied by three nitrogen atoms and an appended carboxylate oxygen atom of the ligand, and the oxygen atoms from water molecule. On the other hand, Fe(III) octahedral coordination (FeN_3Cl_3) in **2** is satisfied by three nitrogen atoms and three chlorine atoms. Cyclic voltammogram of complex **1** gives one quasi-reversible metal-based ($\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$) oxidation [$E_{1/2} = 0.325\text{V}$ vs SCE (saturated calomel electrode)] in DMF; whereas complex **2** gives one quasi-reversible metal-based ($\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$) reduction [$E_{1/2} = -0.055\text{V}$ vs SCE (saturated calomel electrode)] in CH_3CN . This has given us an opportunity to investigate the effect of such a coordination sphere on spectroscopic and redox properties on iron complexes.

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