

Notes

Synthesis and crystal structure of an iron(II) dimeric complex

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Received 27 July 2007; accepted 30 October 2007

An iron(II) complex, [Fe₂(salen)₂] has been prepared by the reaction of [Fe^{III}(salen)Cl] with copper(II) malonate dihydrate [salen = N,N'-ethylenebis(salicylideneiminato) dianion] in N,N-dimethylformamide-water mixture. The complex has been characterized by FT-IR spectroscopy, UV-vis spectra, thermogravimetric analysis, cyclic voltammetry and X-ray crystallography. The iron(II) complex **1** crystallizes in the monoclinic, space group *C2/c*, *a* = 26.664(5) Å, *b* = 6.9943(11) Å, *c* = 14.727(2) Å, β = 97.498(3)°, and *Z* = 8. The structural study reveals that it is a penta-coordinate Fe(II) dimeric complex.

IPC Code: Int Cl.⁸ C07F15/02

Schiff bases are able to stabilize various metal ions in different oxidation states, thereby controlling the performance of metals in a large variety of useful catalytic transformations. A variety of enzymes are able to catalyze different reactions such as oxidation, reduction and isomerization, containing iron bound to porphyrin (Heme)^{1,2}. The salen ligands, with four coordinating sites and two axial sites open to ancillary ligands, are very much like porphyrins. Given the similarity between salen and porphyrins, recent works have been directed towards exploiting iron-Schiff base complexes for promoting different catalytic reactions³. The chemistry of Fe(III) complexes with salen ligand has been extensively investigated. A large variety of anionic ligands including halide, pseudohalide, carboxylate, phenolate, and thiphenolate has been shown to form stable, mononuclear, high-spin complexes that have distorted square-pyramidal stereochemistry.

Apart from the mononuclear complexes, diiron(II) centers participate in the binding or activation of dioxygen at a number of metalloprotein sites. Among the group of compounds exhibiting magnetic phenomena, the spin transition of six-coordinate

iron(II) compounds has been receiving broad attention because of its diverse change in physical properties (magnetism, color, structure etc.). This change can be triggered by applying external parameters such as temperature, pressure, and light intensity to the macroscopic sample^{4,5}. Supramolecular approaches (coordination polymers, hydrogen bonding, π - π stacking, etc.) have recently been applied to molecular spin-transition modules, partially with the objective of increasing the spin-transition temperature and magnitude of cooperativity⁶⁻¹⁶.

An interesting approach to the synthesis of the sensitive Fe(II)(salen) considers the use of an organometallic reagent. Fe₂Mes₄ has been prepared from FeCl₂(THF)_{1.5} using standard mesityl Grignard¹⁷. Fe₂Mes₄ is a rather sensitive compound, but can react with the acidic phenolic oxygens of the salen leading to the formation of the desired Fe(II)(salen) in pure form. Fe(II)(salen) is sensitive to oxygen and moisture, and difficult to handle. The easy oxidation of Fe(II)(salen) hampered its use in catalysis. Different approaches to the synthesis of Schiff base complexes using stable precursors have also been considered. Bolm reported the preparation of a tridentate Schiff base-iron catalyst, prepared *in situ* from Fe(acac)₃ which is also able to promote the enantioselective oxidation of sulfide to sulfoxides¹⁸. The dimeric μ -oxo Fe(salen)s prepared by Nguyen have found an interesting use as stable precursors for the generation of iron carbene complexes, and are able to catalyze the enantioselective cyclopropanation of olefins with ethyl diazoacetate¹⁹.

Herein we report the synthesis and crystal structure of the complex, [Fe^{II}₂(salen)₂]. The structural characterization reveals that this is the first penta-coordinate complex of iron(II) with salen ligand.

Experimental

All chemicals and solvents used for the synthesis were of reagent grade, purchased from commercial sources and used without further purification. Solvents were purified and dried according to standard methods²⁰. The quadridentate Schiff base ligand, H₂salen, was synthesized by mixing salicylaldehyde and ethylenediamine in 2:1 mole ratio in ethanol, according to the literature procedure²¹. Iron(III) complex, [Fe(salen)(Cl)], was prepared by

mixing anhydrous iron(III) chloride and H₂salen in absolute methanol in the molar ratio of 1:1 according to a previously reported method^{22,23}. Copper(II) malonate dihydrate was also prepared following a known procedure²⁴.

Microanalysis (CHN) was performed on a Perkin–Elmer 240C elemental analyzer. IR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Spectral measurements were performed in an UV–vis spectrophotometer (UV-2100, Shimadzu, Japan) equipped with thermostated cell compartments. Cyclic voltammetry was performed at a platinum electrode using an EG&G PARC electrochemical analysis system (Model 250/5/0) with a conventional three electrode configuration in acetonitrile medium under dry nitrogen atmosphere with a scan rate of 0.05 Vs⁻¹. Thermal stability (TG-DTA) studies were carried out on a Mettler Toledo TGA/SDTA 851° instrument with a heating rate of 5°C min⁻¹ in nitrogen atmosphere.

Synthesis of [Fe₂(salen)₂] (1)

To a 10 cm³ aqueous solution of copper(II) malonate dihydrate (0.257 g, 1.28 mmol) was added 20 cm³ N,N dimethylformamide solution of [Fe(salen)Cl] (0.460g, 1.28 mmol) and stirred at 60°C for 30 min. The mixture was cooled to room temperature and filtered to remove any suspended materials. The solution was kept in air and after 2 days rectangular shaped blue colored single crystals suitable for X-ray diffraction study were formed. (Yield 65% based on Fe). Anal.: Calc. for C₃₂H₂₈Fe₂N₄O₄ (%): C, 59.60; H, 4.35; N, 17.38. Found: C, 59.23; H, 4.16; N, 17.30. FT-IR (KBr phase) (cm⁻¹): 2924 br, 1647 vs, 1634 s, 1540 vs, 1511 m, 1449 m, 1193 w, 1142 w, 743 w.

X-ray crystallography

Single crystals of **1** were grown on slow evaporation of a 2:1 DMF-water solution of the complex. A crystal of 0.34 × 0.44 × 0.56 mm size was mounted on a glass fiber using epoxy cement. X-ray diffraction data were measured in frames with increasing ω (width of 0.3° per frame) at a scan speed of 20 s per frame using a Bruker SMART APEX CCD diffractometer, equipped with a fine focus sealed tube Mo-K α X-ray source. SMART software was used for data acquisition and SAINT for data extraction. Empirical absorption corrections were made on the intensity data²⁵. The structure was solved

and refined using the SHELX system of programs²⁶. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms belonging to the complex were in a fixed position and refined using a riding model. The structure was refined with a goodness-of-fit (GoF) value of 1.069. The maximum shift/esd value and the highest peak in the final difference Fourier maps were 0.0 and 0.94 e Å⁻³, respectively. Selected crystallographic data are given in Table 1.

Results and discussion

The title complex was synthesized by the reaction of [Fe(salen)Cl] and copper(II) malonate dihydrate in a 2:1 DMF-water mixture. Here, actually Fe³⁺ is reduced to Fe²⁺ by copper malonate. This is evident from the absorption spectra. As the single crystal of the complex was obtained from the reaction between [Fe(salen)Cl] and copper(II) malonate dihydrate in 2 : 1 DMF-water mixture at 60°C, we examined the change of spectral behavior of the reaction keeping all the parameters unaltered (Fig. 1). The successive spectral scans were done at a time interval of 2 min for a total period of 1 h. The final spectrum of the reaction product was taken after 24 h of mixing of the reactants. [Fe(salen)Cl] showed a peak at 480 nm. When an aqueous solution of copper(II) malonate (2.0 × 10⁻⁴ M) was added to a DMF solution of

Table 1 — Crystallographic data of [Fe₂(salen)₂]

Empirical formula	C ₁₆ H ₁₄ Fe N ₂ O ₂
Formula weight	322.14
Crystal system	Monoclinic
Space group	C2/c (No. 15)
<i>a</i> (Å)	26.664(5)
<i>b</i> (Å)	6.9943(11)
<i>c</i> (Å)	14.727(2)
α (°)	90
β (°)	97.498(3)
γ (°)	90
<i>V</i> (Å ³)	2723.0(8)
<i>Z</i>	8
<i>D</i> _{calc} (g cm ⁻³)	1.572
μ (Mo K α) (mm ⁻¹)	1.113
<i>F</i> (000)	1328
<i>T</i> (K)	293
λ (Mo K α)	0.71073
Maximum and minimum θ range (°)	27.0, 2.8
Total data, unique data	7575, 3121
<i>R</i> _{int}	0.095
Final <i>R</i> indices (<i>R</i> ₁ , <i>wR</i> ₂)	0.0972, 0.2168
Goodness-of-fit	1.069

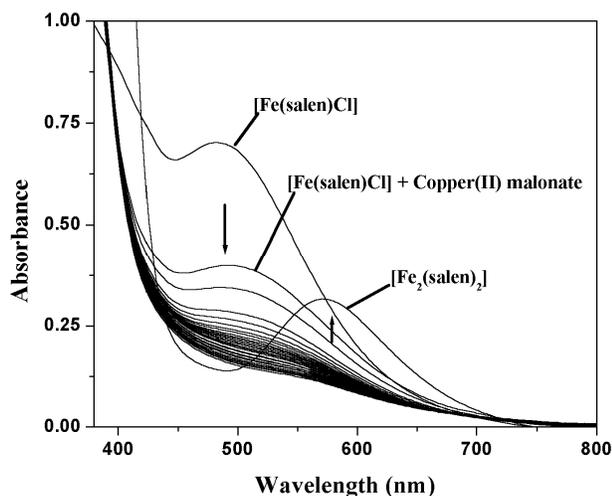


Fig. 1— Progress of the reaction of [Fe(salen)Cl] with copper(II) malonate dihydrate in a 2:1 DMF-water mixture at 60 °C.

[Fe(salen)Cl] (2.0×10^{-4} M), a new peak generated at 495 nm. The intensity of the peak at 495 nm decreased with time. Consequently the position of the absorption peak at 495 nm was shifted to a new position at 570 nm. Complex **1** showed its *d-d* transition at 570 nm.

Structure of [Fe₂(salen)₂] (**1**)

Complex **1** crystallizes in the monoclinic system, space group C2/c (No. 15) from a 1 : 2 water and N,N-dimethylformamide mixture solvent. A perspective view of [Fe₂(salen)₂] (**1**) with the atom numbering scheme is shown in Fig. 2. Selected bond lengths and bond angles are given in Table 2. The asymmetric unit of compound **1** consists of two Fe²⁺ ions and two salen moieties. Each iron atom of the dimeric unit is in the same coordination environment. Both the iron atoms are located in an almost perfectly square pyramidal environment as revealed by the trigonal index, $\tau = 0.0102$. The value of τ is defined as the difference between the two largest donor-metal-donor angles divided by 60, a value which is 0 for the ideal square pyramid and 1 for the trigonal bipyramid²⁷. The square pyramidal geometry consists of three oxygen and two nitrogen atoms. The four coordination sites of the quasi-square girdle are occupied by the O and N atoms of a single tetradentate salen ligand. O1, O2, N1 and N2 atoms form the square for Fe1 atom. The axial position is occupied by O1_a ($a = 1/2-x, 1/2-y, 1-z$) atom. The chelating atoms are coplanar to within 0.003 Å, with the Fe atom being slightly displaced out of the plane from the ligand by a distance of 0.144 Å. The in-plane Fe–O and Fe–N bond distances vary from 1.909(5) to

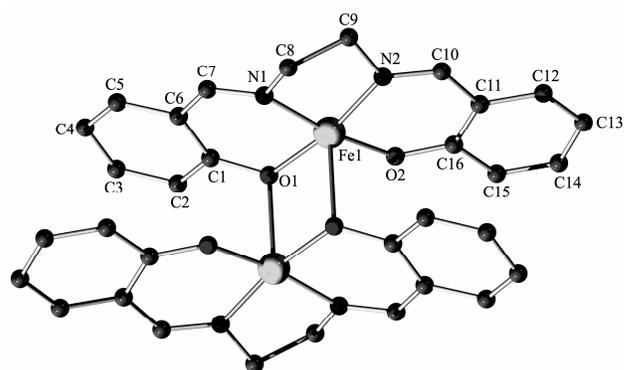


Fig. 2— A perspective view and atom numbering scheme for Fe₂(salen)₂ (**1**). H atoms are omitted for clarity.

Table 2 — Selected bond lengths (Å) and bond angles (°) of [Fe₂(salen)₂]

Bond lengths (Å)

Fe1–O1	1.945(5)
Fe1–O2	1.909(5)
Fe1–O1_a	2.418(5)
Fe1–N1	1.942(6)
Fe1–N2	1.960(6)

Bond angles (°)

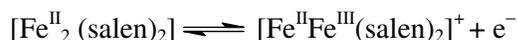
O1–Fe1–O2	91.3(2)	O2–Fe1–N2	92.8(2)
O1–Fe1–N1	91.3(2)	O1_a–Fe1–O2	94.0(2)
O1–Fe1–N2	170.2(2)	N1–Fe1–N2	83.3(2)
O1–Fe1–O1_a	86.40(17)	O1_a–Fe1–N1	94.8(2)
O2–Fe1–N1	170.9(3)	O1_a–Fe1–N2	102.2(2)

Symmetry codes: $a = 1/2-x, 1/2-y, 1-z$

1.945(5) Å and 1.942(6) to 1.960(6) Å respectively. These are in agreement with the average Fe–O and Fe–N bond distances seen in previous reports^{28, 29}. The axial Fe–O bond distance (Fe1–O1_a 2.418(5) Å ($a = 1-x, y, 2-z$)) is longer than basal Fe–O bond distances. The iron atoms are positioned in an almost perfect geometry where the angles subtended at the iron atom vary from *ca* 91.3 to 170.9° (Table 2).

Electrochemical studies

The cyclic voltammogram of complex **1** has been studied in acetonitrile with TBAP as a supporting electrolyte in the potential range + 0.2 to + 1.4 V versus SCE and the results are illustrated in Fig. 3. In the available range of potential, the complex exhibits an electrochemically quasi-reversible one-electron oxidation at +1.1 V ($E_{1/2} = 1.05$ V). These are in good agreement with those reported previously³⁰. The corresponding redox couple may be shown as follows:



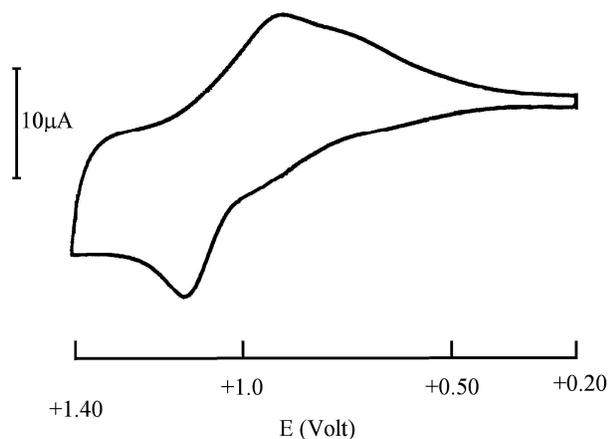


Fig. 3 — Cyclic voltammograms (scan rate 50 mV s^{-1}) of complex **1** in acetonitrile with TBAP as a supporting electrolyte in the potential range +0.2 to +1.4 V versus SCE.

The irreversible oxidation at +1.4 V is attributed to the oxidation of salen ligand.

Thermogravimetric analysis

Complex **1** is very stable in air at ambient temperature. Thermogravimetric analysis was carried out to examine the thermal stability of the complex. Sample **1** was heated from room temperature to 500°C in nitrogen atmosphere with heating rate of 5°C min^{-1} . The TGA curve shows that **1** is stable up to 270°C . A total weight loss of 5.11% occurred in the temperature range of $270 - 301^\circ\text{C}$, presumably due to the removal of oxygen molecule (Calc. 4.97%). A weight loss of 41.94% occurs in the temperature range $301 - 345^\circ\text{C}$, corresponding to the removal of salen ($\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$) ligand per formula unit.

Supplementary material

Crystallographic data for the structure are deposited with the Cambridge Crystallography Data Centre with CCDC reference number for the complex as CCDC 650384.

Acknowledgement

KD acknowledges the Council of Scientific and Industrial Research, New Delhi, India, for financial support.

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