

Ligand template synthesis of an undecametallic iron(III) complex: X-ray structure, magnetism and catecholase activity



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ABSTRACT

An undecairon(III) oxo-hydroxo-carboxylato bridged aggregate $[\text{Fe}_{11}(\mu_3\text{-O})_6(\mu_3\text{-OH})_6(\mu\text{-O}_2\text{C-f})_{15}]$ (**1**) has been synthesized and characterized by single crystal X-ray diffraction study. The anionic ligand *N*-(2-hydroxyethyl)-3-methoxysalicylaldehyde (L) has been used as template to synthesize such high nuclearity complex. Interestingly, the ligand neither enters into the coordination sphere nor crystallizes with the iron cluster. Bond distance data indicate that all the iron atoms in **1** are high-spin Fe(III) in O-donor environment. **1** behaves as an effective catalyst towards oxidation of 3,5-di-*tert*-butylcatechol in different solvents, viz. methanol, dichloromethane and acetonitrile, to its corresponding quinone derivative in aerial oxygen. The reaction follows Michaelis–Menten enzymatic reaction kinetics with turnover numbers (K_{cat}) 3.21×10^3 , 1.23×10^3 and $1.11 \times 10^3 \text{ h}^{-1}$ in methanol, dichloromethane and acetonitrile, respectively.

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1. Introduction

Supramolecular chemistry [1] provides a number of ways to design and construct molecular receptors as templates which form different non-covalent complementary interactions with the guest molecules via self assembly [2] and finally new molecules come out leaving the template. Molecular capsules [3] are an example of this kind. Several interesting organic transformations like Dienes–Alder reaction, aza–Cope rearrangement, condensations, photochemically induced reactions, etc [3] have been carried out using this template strategy.

Catechol oxidase known as 1,2-benzenediol or oxygen oxidoreductase, is a less well-known member of type III copper protein [4]. It is also familiar as *o*-diphenol oxidase as it catalyzes exclusively the oxidation of catechols (i.e., *o*-diphenols) to the corresponding quinones, a process known as catecholase activity, and for this peculiar ability catechol oxidase may take key role as disease resistant in higher plants. Quinones are highly reactive compounds, which undergo autopolymerization to produce melanin, a brown

pigment, and this process is most likely responsible to protect the damaged tissues against pathogens and insects.

Long back Lippard and co-workers reported [5] two similar undecametallic $\text{Fe}_{11}^{\text{III}}$ clusters, one, the rhombohedral $[\text{Fe}_{11}\text{O}_6(\text{OH})_6(\text{O}_2\text{CPh})_{15}]\cdot 6\text{THF}$ and another, the triclinic $[\text{Fe}_{11}\text{O}_6(\text{OH})_6(\text{O}_2\text{CPh})_{15}]\cdot \text{H}_2\text{O}\cdot 8\text{MeCN}$. In continuation to our interest in synthesizing model compounds for catechol oxidase [6], we have synthesized and crystallographically characterized a similar iron cluster (**1**) to Lippard and co-workers. The catecholase activity of **1** has also been reported.

2. Experimental

2.1. Preparation of the complex

2.1.1. Chemicals, solvents and starting materials

High purity furoic acid (Fluka, Germany), ferric nitrate nonahydrate (E. Merck, India), 3,5-di-*tert*-butylcatechol (Aldrich, UK) and all reagents were purchased from respective concerns and used as received.

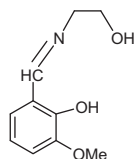
2.1.2. General syntheses

N-(2-hydroxyethyl)-3-methoxysalicylaldehyde (L) (Scheme 1) was synthesized using literature method [7].

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Scheme 1. Line drawing of *N*-(2-hydroxyethyl)-3-methoxysalicylaldehyde.

To the stirred solution of $[\text{Fe}_3\text{O}(\text{RCOO})_6(\text{H}_2\text{O})_3](\text{NO}_3)$ [R = furan ring; RCOOH = furan-2-carboxylic acid] [8] (0.1217 g, 0.1007 mmol) in water-acetonitrile (20 mL), a solution of L (0.0253 g, 0.1031 mmol) in the same solvent mixture (20 mL) was added drop wise. When mixing the solution of L, the orange colored solution was turned deep brown immediately. Finally, the resulting mixture was stirred for 1 h at room temperature to complete the reaction. The deep brown solution was then filtered and allowed to stand undisturbed in the air. After two weeks or so deep brown square shaped crystals appeared.

Yield = 0.0502 g, 41.39% based on $[\text{Fe}_3\text{O}(\text{RCOO})_6(\text{H}_2\text{O})_3]\text{NO}_3$. Anal. Cal. for $\text{C}_{75}\text{H}_{59}\text{O}_{64}\text{Fe}_{11}$ (1): C, 34.65; H, 2.27. Found: C, 34.01; H, 2.66%. Selected IR bands (KBr pellet, cm^{-1}): 3586 (s), 1591 (m), 1553 (m), 1418 (m), 851 (s). UV-Vis (λ , nm): 266, 352, 440.

To know the role of L in this Fe cluster formation Thin Layer Chromatographic (TLC) experiment was done just after doing the synthesis and then in certain time intervals (1 h, 2 h, etc. and then 1 day, 2 days, etc.) but no spot for the L was obtained. But after a week or so when the crystals were isolated, the TLC with the mother liquor, interestingly, gave a prominent spot for L (Supplementary file, Fig. S1). Dichloromethane was used as solvent for elution. After a minute or so the solvent front reached the upper part of the TLC plate. Then it was put in the iodine chamber where the spot for L was developed. This concludes that during the reaction L helps to congregate the Fe atoms through some physical complexation and after formation of the coordination cluster, L comes out of the coordination zone. The UV-Vis band of the final mother liquor (after isolation of the iron cluster) also overlaps with the free L (Supplementary file, Fig. S2). The NMR and Mass spectra (Supplementary file, Figs. S3 and S4) of column chromatographically (using 1:1 ethylacetate and hexane eluent) separated pure L agree well with the free ligand structure (Scheme 1).

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a PerkinElmer 2400 CHNS/O elemental analyzer. IR spectrum was recorded (KBr discs, 4000–300 cm^{-1}) using a PerkinElmer RX1 FTIR spectrometer. Ground state absorption was measured with a JASCO V-530 UV-Vis spectrophotometer. Thermal analysis was done by PerkinElmer Diamond TG/DTA system. Magnetic measurements were carried out in the “Unitat de Mesures Magnètiques (Universitat de Barcelona)” on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic fields used in the measurements were 0.03 T (from 2 to 30 K) and 0.5 T (from 2 to 300 K). Diamagnetic corrections were evaluated from Pascal’s constants.

2.3. X-ray diffraction study

Crystal diffraction data were measured using a Bruker SMART APEX CCD diffractometer. The data were collected with graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 200 K. The structure was resolved by direct method and refined by full-matrix

least-squares procedures using the SHELXL-97 software package [9,10]. The crystallographic data are summarized in Table 1. Hydrogen atoms associated with carbon atoms were fixed in geometrically constrained positions. Hydrogen atoms associated with oxygen and nitrogen atoms were included in the located positions.

3. Results and discussion

3.1. Synthesis and formulation

The reaction of $[\text{Fe}_3\text{O}(\text{RCOO})_6(\text{H}_2\text{O})_3](\text{NO}_3)$ [R = furan ring; RCOOH = furan-2-carboxylic acid] and L in acetonitrile-water with constant stirring yielded a deep brown colored solution which after slow evaporation yielded square shaped crystals of **1**. The reaction was repeated several times but no compound is formed without the addition of L though L enters neither into the first nor into the second coordination sphere. The air-stable moisture-insensitive salt is soluble in all the common solvents.

To investigate the role of L in this reaction, TLC experiment of the mother liquor (after the isolation of the compound) showed the spot for L though no spot was found before the compound isolation. This proves that L behaves like a template and helps to congregate the Fe cluster on it by some physical complexation and after formation of the compound, L comes out of the coordination zone. L was isolated by column chromatography. The NMR and Mass spectrometric data (Supplementary file, Figs. S3 and S4) match well with the free L structure (Scheme 1).

3.2. Spectroscopic measurements

The well resolved peaks are observed at 3586 and 851 cm^{-1} attributed to the $\nu(-\text{OH})$ and $\nu(-\text{O}-)$ stretching mode, respectively in the molecular cluster [11]. Weak bands in the range 2980–2900 cm^{-1} are assignable to the aliphatic C–H stretching vibration. Strong infrared spectral peaks are observed at 1591, 1553 and 1418 cm^{-1} originates in the bridging furoate groups. UV-Vis absorption spectrum of **1** in CH_3CN solution was recorded in the wavelength range 200–900 nm. The electronic spectrum of **1** is dominated by strong absorptions from the phenyl group and by ligand-to-metal charge-transfer bands. The positions and the approximate intensity of the shoulders below 490 nm suggest a charge transfer transition [12].

3.3. Description of crystal structure

The metal cluster **1** crystallizes in the monoclinic space group $C2/c$. The asymmetric unit contains half molecule of **1** as it sits on a mirror plane. A furoate molecule, which sits on the mirror plane, has disordered atoms of ‘O’ and ‘C’ (ortho position) with equal occupancy. The crystallographic view of ORTEP diagram is shown in Fig. 1. The crystallographic parameters are set in Table 1. The bond distance and bond angle data are given in Tables S1 and S2 (Supplementary file). The structure of the Fe_{11} cluster (Fig. 1) consists of an $[\text{Fe}_{11}\text{O}_{12}]$ core containing six $\mu_3\text{-O}$ and $\mu_3\text{-OH}$ each, and fifteen furoate bridges. The protonation levels were confirmed by bond valence sum (BVS) calculations (Table 2). The Fe atoms in **1** form a distorted pentacapped trigonal antiprism with Fe2, Fe2ⁱ and Fe6 forming one face, and Fe4, Fe4ⁱ and Fe6 the other face. Fe1, Fe1ⁱ, Fe3, Fe3ⁱ and Fe5 cap the Fe2–Fe2ⁱ–Fe6, Fe2–Fe2ⁱ–Fe6ⁱ, Fe2–Fe4–Fe6, Fe2ⁱ–Fe4ⁱ–Fe6ⁱ and Fe4–Fe4ⁱ–Fe6 planes, respectively (‘i’ in the superscript indicates the symmetrically equivalent species of the corresponding Fe atom). All Fe atoms are six-coordinate with distorted octahedral geometry. The Fe–O bond lengths are as expected for high-spin Fe(III) (Tables S1 and S2, Supplementary file) [13]. The bond distances and angles are in parity as

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