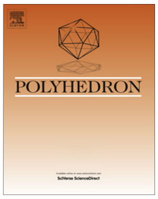
Polyhedron 67 (2014) 19–26

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Catecholase activity of a structurally characterized dinuclear iron(III) complex $[Fe^{III}_2(L)_2]$ [H_3L = *N*,*N*′-bis(3-methoxysalicylaldimine)-1, 3-diaminopropan-2-ol]

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ARTICLE INFO

Article history:
Received 23 June 2013
Accepted 14 August 2013
Available online 7 September 2013

Keywords:
Iron(III)
Schiff base
Crystal structure
Magnetism
Biocatalytic activity

ABSTRACT

A dinuclear Fe(III) complex, $[Fe^{III}_2(L)_2]$ (**1**) [H_3L = *N*,*N*′-bis(3-methoxysalicylaldimine)-1,3-diaminopropan-2-ol], has been synthesized and characterized using microanalysis, spectroscopy and X-ray crystallography. Structural analysis reveals a pentadentate chelation behaviour of the trianionic ligand H_3L, having a distorted octahedral coordination environment around each iron(III) center with an FeN_2O_4 chromophore. Variable-temperature magnetic susceptibility measurements of **1** indicate an antiferromagnetic interaction between the two iron(III) centers, coupled with $J = -28.5$. **1** behaves as an effective catalyst towards the 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}) 7.51×10^2, 1.69×10^3 and $1.23 \times 10^3\ h^{-1}$ in methanol, dichloromethane and acetonitrile, respectively.

1. Introduction

Catechol oxidase, found in bacteria, fungi and plants, belongs to the class of type 3 copper proteins that catalyze the oxidation of a wide range of *o*-diphenols (catechols) to the corresponding *o*-quinones, coupled with $2e/2H^+$ reduction of O_2 to H_2O, in a process known as catecholase activity [1–10]. The crystal structure of the *met* form of the enzyme was determined in 1998, revealing that the active center consists of a hydroxo-bridged dicopper(II) center in which each copper(II) center is coordinated to three histidine nitrogens and adopts a trigonal pyramidal environment with one nitrogen in the apical site [11]. Such a structural finding has prompted extensive investigation on model compounds to understand the structure-property relationship at the molecular level [1–10]. Indeed, several dicopper(II) complexes derived from nitrogen-containing dinucleating ligands have been mainly employed for this purpose [1–4]. Several monocopper(II) complexes are also known to exhibit catecholase activity [5]. Recently, the catecholase activity of complexes of other metal ions, like Mn(III) [5e,6], Fe(III) [7], Co(II/III) [8], Ni(II) [9] and Zn(II) [10] has been explored. In a continuation to our recent report [5e] on catecholase activity, here we present the synthesis and structural characterization of a dinuclear Fe(III) complex, $[Fe^{III}_2(L)_2]$ (**1**) [12], with an (N,O) donor trianionic Schiff base ligand which catalyzes a catechol derivative to its corresponding quinone in methanol (MeOH), dichloromethane (DCM) and acetonitrile (MeCN) in the open air. An investigation of the Michaelis–Menten kinetics and calculation of the turnover numbers are calculated in each case.

2. Experimental

2.1. Materials

High purity *o*-vanillin (Aldrich, UK), 1,3-diaminopropan-2-ol (Aldrich, UK), iron(III) nitrate nonahydrate (Aldrich, UK), benzoic acid (E. Merck, India), sodium bicarbonate (E. Merck, India), 3, 5-di-*tert*-butylcatechol (Aldrich, UK) and all other solvents were purchased from the respective concerns and used as received. Solvents were dried according to standard procedures and distilled prior to use.

The ligand H_3L was prepared using a reported procedure [13]. *O*-vanillin (0.3043 g, 2 mmol) was heated under reflux with 1,3-diaminopropan-2-ol (0.0955 g, 1 mmol) in 30 ml dehydrated ethanol. After 2 h, the reaction solution was evaporated under

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http://dx.doi.org/10.1016/j.poly.2013.08.064

reduced pressure to yield a yellow coloured solid, which was dried under vacuum and stored over $CaCl_2$ for subsequent use.

For the catecholase activity study, a 1×10^{-4} mol dm^{-3} solution of **1** (0.0009 g) was treated with 1×10^{-2} mol dm^{-3} (100 equivalents) of 3,5-DTBC (0.0222 g) under aerobic conditions.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. UV–Vis and IR spectra (KBr discs, 4000–300 cm^{-1}) were recorded using a Shimadzu UV–Vis 2450 spectrophotometer and Perkin-Elmer FT-IR model RX1 spectrometer, respectively. The ^{1}H NMR spectral data were collected in $CDCl_3$ on a Bruker 400 MHz spectrometer. Magnetic measurements were carried out in the "Servei de Magnetoquímica (Universitat de Barcelona)" on polycrystalline samples (30 mg) with a Quantum Design SQUID MPMS-XL magnetometer working in the 2–300 K range. The magnetic field was 0.1 T. The diamagnetic corrections were evaluated from Pascal's constants.

2.3. Preparation of **1**

Compound **1** was prepared by the dropwise addition of a solution of H_3L (0.0224 g, 0.125 mmol) in acetonitrile (15 ml) into a stirring solution of the precursor $[Fe_3O(RCOO)_6(H_2O)_3](NO_3)$ [R = Ph] [14] (0.0641 g, 0.125 mmol) in a methanol-acetonitrile mixture (15 ml). The resulting red-brown coloured solution was kept in the open air for slow evaporation. After 2–3 days, deep brown crystals of **1** were collected, washed with hexane and dried in vacuo over silica gel indicator.

Yield: (based on metal salt) 0.0758 g (89.42%). *Anal.* Calc. for $C_{42}H_{44}N_6O_{10}Fe_2$ (**1**): C, 55.77; H, 4.90; N, 9.29. Found: C, 55.93; H, 4.73; N, 9.16%. Selected IR bands (KBr pellet, cm^{-1}): 3433 (s), 1630 (s), 1600 (s), 1548 (s). UV–Vis (λ, nm, MeOH): 499, 330, 271, 226.

2.4. X-ray diffraction study

A single crystal of **1** suitable for X-ray crystallographic analysis was selected following examination under a microscope. Diffraction data were collected at 293(2) K on a Bruker SMART APEX II CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) and the $P2_1/c$ space group was identified. The crystal data and refinement details are listed in Table 1. The structure was solved by direct methods, and the structure solution and refinement were based on $|F|^2$. The final differences Fourier map showed maximum and minimum peak heights at 0.573 and −0.436 e Å^{-3} with no chemical significance. All calculations were carried out using SHELXL-97 [15] and were refined using SHELSL-97 [15]. All the figures have been generated using ORTEP-32 [16].

3. Results and discussion

3.1. Synthesis and formulation

The self-assembly of $[Fe_3O(PhCOO)_6(H_2O)_3](NO_3)$ and the ligand H_3L in methanol-acetonitrile afforded the hexacoordinated dinuclear complex **1**. The complex was characterized by microanalytical (C, H and N), spectroscopic and other physicochemical results. The microanalytical data are in good conformity with the formulation of **1**. The moisture insensitive complex is stable over long periods of time in powdery and crystalline states, and is soluble in methanol, ethanol, acetonitrile, dimethyl formamide and dimethyl sulfoxide, but is insoluble in water. In the IR spectra, relatively intense peaks around 1590-1600 cm^{-1} due to the C=N stretching frequency appear in the complex.

Table 1
Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{42}H_{44}N_6O_{10}Fe_2$
Formula weight	904.53
T (K)	293(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	11.3773(9)
b (Å)	15.1816(10)
c (Å)	23.6480(17)
α (°)	90.00
β (°)	97.156(7)
γ (°)	90.00
V (Å^3)	4052.8(5)
Z	4
D_{calc} (Mg/m^3)	1.482
Absorption coefficient (mm^{-1})	0.783
F(000)	1880
Crystal size (mm^3)	0.42 × 0.32 × 0.18
θ (°)	2.6945–29.0539
Index ranges	$-13 \leqslant h \leqslant 13$, $-18 \leqslant k \leqslant 16$, $-17 \leqslant l \leqslant 28$
Reflections collected	15376
Independent reflections	7137 [R_{int} = 0.0587]
Completeness to theta	99.9 % (θ = 26.37°)
Absorption correction	multi-scan
T_{max} and T_{min}	0.8719 and 0.7345
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	7137/0/547
Goodness-of-fit (GOF) on F^2	0.970
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0566, wR_2 = 0.0864
R indices (all data)	R_1 = 0.1240, wR_2 = 0.1109
Largest difference in peak and hole(e Å^{-3})	0.573, −0.436

3.2. X-ray structure

In order to define the coordination spheres conclusively, a single crystal X-ray diffraction study of **1** was made. The ORTEP diagram along with atom numbering scheme of **1** is shown in Fig. 1. Selected interatomic bond lengths and bond angles are given in Table 2. Structural analysis reveals that compound **1** is a centro-symmetric binuclear entity where the two iron(III) centers are bridged by two alkoxo O atoms (O1 and O2) of L. The coordination geometry around each iron(III) center is best described as distorted octahedral. The two phenolic O (O7 and O9 for Fe1, and O3 and O5 for Fe2) atoms and two bridging alkoxo O (O1 and O2) atoms from the two ligand moieties define the equatorial plane around each metal(III) center. The two imine N (N2 and N3 for Fe1, and N1 and N4 for Fe2) atoms from each ligand framework bind to the metal(III) center *via* the elongated axial direction, with Fe1–N2 and Fe1–N3, and Fe2–N1 and Fe2–N4 bond distances of 2.119(3) and 2.135(3), and 2.140(3) and 2.127(3) Å, respectively. These bonds are considerably longer than those found in the equatorial plane [Fe1–O1 2.024(3) Å; Fe1–O2 2.011(3) Å; Fe1–O7 1.927(3) Å; Fe1–O9 1.919(3) Å, and Fe2–O1 2.032(3) Å; Fe2–O2 2.054(3) Å; Fe2–O3 1.917(3) Å; Fe2–O5 1.930(3) Å], which presumably is due to the different type of coordination mode of ligands. The geometric distortion of each octahedron at the metal(III) center can be characterized by the asymmetric parameter D [17]. The positive D value [18][1] indicates axial elongation at each metal center.

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[1] $D = d_z - (d_x + d_y)/2$, D = +0.1735 for Fe1, +0.2170 for Fe2.

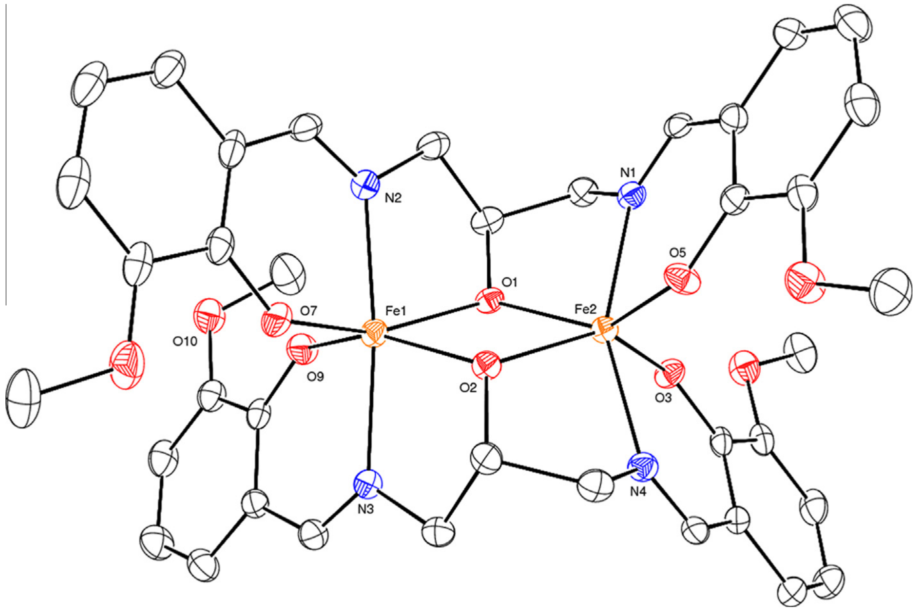

Fig. 1. ORTEP of $[Fe_2(L)_2]$ (**1**) with the atom numbering scheme and 20% probability ellipsoids for all non-hydrogen atoms.

Table 2
Bond lengths [Å] and angles [°] for 1.

Bond distances			
Fe(1)–O(1)	2.024(3)	Fe(2)–O(1)	2.032(3)
Fe(1)–O(2)	2.011(3)	Fe(2)–O(2)	2.054(3)
Fe(1)–O(7)	1.927(3)	Fe(2)–O(3)	1.917(3)
Fe(1)–O(9)	1.919(3)	Fe(2)–O(5)	1.930(3)
Fe(1)–N(2)	2.119(3)	Fe(2)–N(1)	2.140(3)
Fe(1)–N(3)	2.135(3)	Fe(2)–N(4)	2.127(3)
Bond angles			
O(2)–Fe(1)–O(1)	73.76(10)	O(1)–Fe(2)–O(2)	72.67(10)
O(7)–Fe(1)–O(1)	155.50(12)	O(3)–Fe(2)–O(1)	93.81(11)
O(7)–Fe(1)–O(2)	96.10(12)	O(3)–Fe(2)–O(2)	140.17(12)
O(9)–Fe(1)–O(1)	94.33(12)	O(3)–Fe(2)–O(5)	116.89(13)
O(9)–Fe(1)–O(2)	153.59(12)	O(5)–Fe(2)–O(1)	140.66(11)
O(9)–Fe(1)–O(7)	103.18(13)	O(5)–Fe(2)–O(2)	94.50(12)
O(1)–Fe(1)–N(2)	77.21(12)	O(1)–Fe(2)–N(1)	76.21(13)
O(1)–Fe(1)–N(3)	107.09(11)	O(1)–Fe(2)–N(4)	126.25(12)
O(2)–Fe(1)–N(2)	107.99(12)	O(2)–Fe(2)–N(1)	125.27(11)
O(2)–Fe(1)–N(3)	77.50(13)	O(2)–Fe(2)–N(4)	76.43(12)
O(7)–Fe(1)–N(2)	85.21(13)	O(3)–Fe(2)–N(1)	84.96(12)
O(7)–Fe(1)–N(3)	91.86(12)	O(3)–Fe(2)–N(4)	82.93(12)
O(9)–Fe(1)–N(2)	91.62(13)	O(5)–Fe(2)–N(1)	82.33(13)
O(9)–Fe(1)–N(3)	83.94(14)	O(5)–Fe(2)–N(4)	83.84(12)
N(2)–Fe(1)–N(3)	174.00(14)	N(4)–Fe(2)–N(1)	155.05(14)
Fe(1)–O(1)–Fe(2)	106.94(11)	Fe(1)–O(2)–Fe(2)	106.62(11)

3.3. Magnetic properties

Taking into consideration the dinuclear nature of **1**, the magnetic data were analysed for two iron(III) ions. A plot of $\chi_M T$ versus T is shown in Fig. 2. $\chi_M T$ at 300 K is 5.0 cm^3 mol^{-1} K, which is much lower than the typical value for two isolated Fe(III) ions (d^5, $g = 2.00$; $\chi_M T = 8.8$ cm^3 mol^{-1} K), then a rapid decrease in the value is seen and it limits to ~0 cm^3 mol^{-1} K at 2 K. This feature is indicative of antiferromagnetic coupling between the iron(III) ions.

For this dinuclear iron(III) system ($S = 5/2$), the experimental susceptibility data can be fitted using the formula given by Fisher for a model with classical spin [19]. The best fit parameters are: $J = -28.52$ cm^{-1}, $g = 2.00$ (fixed), ρ(mononuclear impurities) = 0.035 and $R = 0.56 \times 10^{-5}$. The R factor is the agreement factor defined as $\Sigma_i[(\chi_m T)_{obs} - (\chi_M T)_{calc}]^2/\Sigma_i[(\chi_M T)_{obs}]^2$.

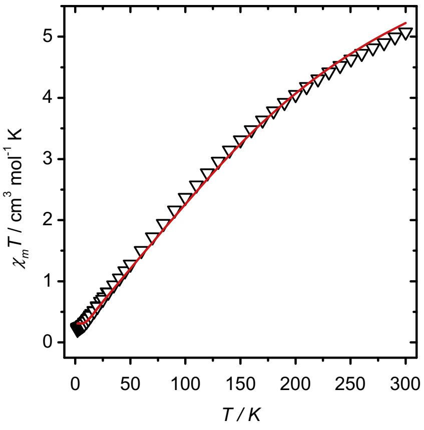

Fig. 2. Plots of $\chi_M T$ vs. T for **1**. The solid line represents the best fit calculation (see text).

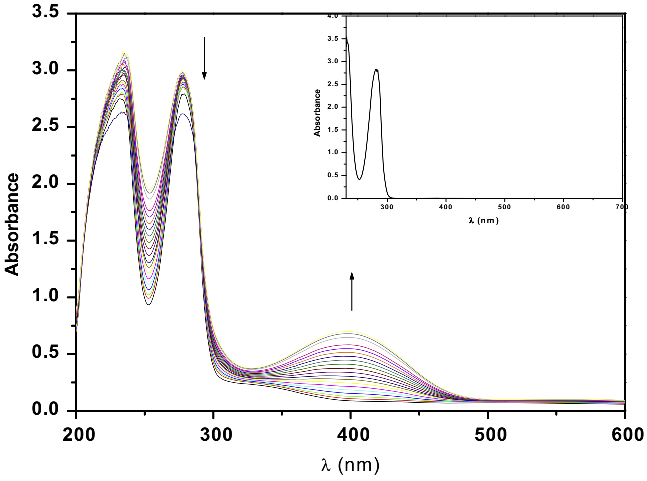

Fig. 3. Change in spectral pattern of complex **1** after reaction with 3,5-DTBC, observing the reaction for 6 h in methanol; inset: spectrum of pure 3,5-DTBC in methanol.

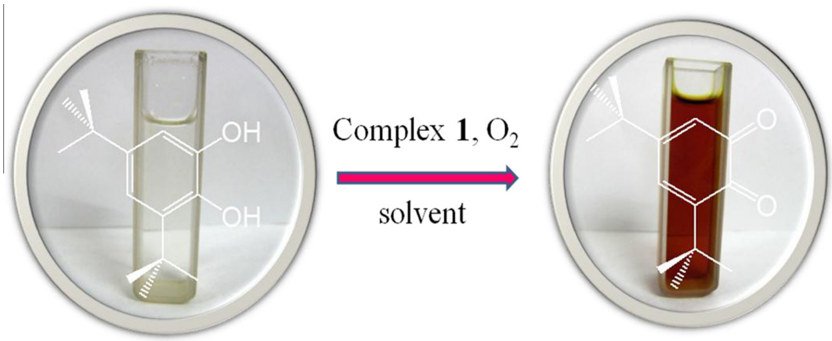

Fig. 4. Colour change during conversion of 3,5-DTBC to 3,5-DTBQ on addition of complex **1**.

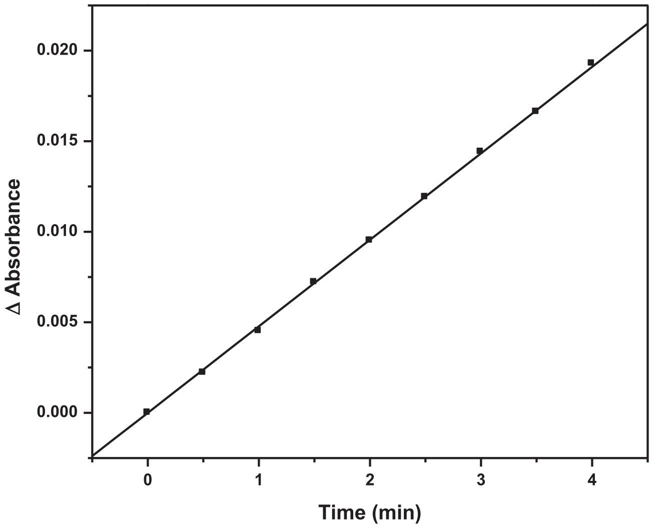

Fig. 5. A plot of the difference in absorbance (ΔA) vs. time to evaluate the initial rate of the catalysis by **1** in methanol.

For alkoxido iron(III) dimers, Gatteschi and co-workers established the dependence of the magnetic properties on geometrical and electronic parameters [20], and from the linear correlation between J and the Fe–O–Fe (θ) angle it was found that with an increase in θ larger J values are obtained. The best-fit straight line through the experimental points is $J = 1.48\ \theta - 135$. In complex **1**, the θ values are 106.9 and 106.6°, so the expected J value will be close to $-23\ \text{cm}^{-1}$. The experimental J value of $-28.5\ \text{cm}^{-1}$ is in good conformity with the formula used. The deviation of the experimental J value from the theoretical one in **1** may be attributed primarily to the strong distortions of the octahedron around each Fe(III) centre. Secondly, the linear fit derived by Gatteschi and co-workers [20] was only for a series of β-diketonate-alkoxido diiron(III) compounds.

3.4. Catecholase activity of 1: spectrophotometric study

In order to study the catecholase activity of complex **1**, 3,5-DTBC with two bulky *t*-butyl substituents on the ring and a low quinone-catechol reduction potential has been chosen as the test substrate. This makes it easily oxidized to the corresponding *o*-quinone, 3,5-DTBQ, which is highly stable and shows a maximum absorption at 401 nm in methanol [6c]. A solution of **1** was treated with 100 equivalents of 3,5-DTBC under aerobic conditions.

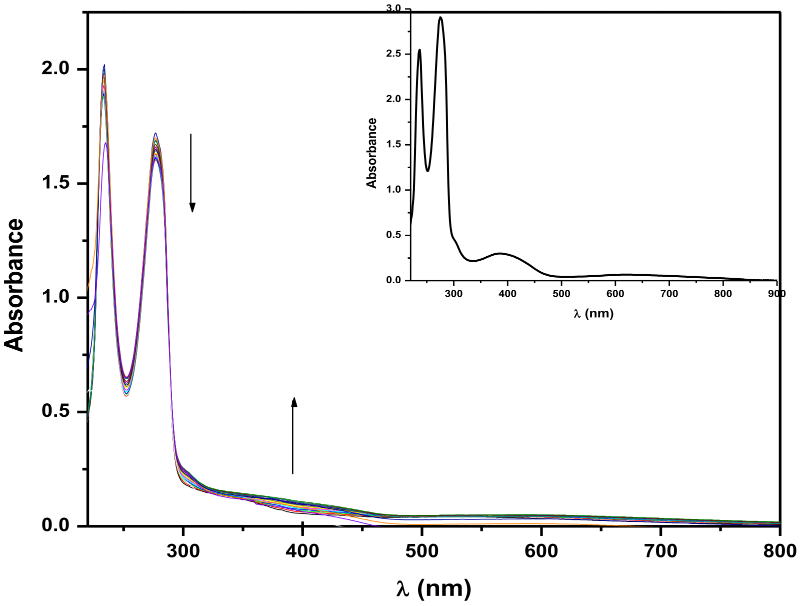

Fig. 6. Change in the spectral pattern of complex **1** in dicholoromethane after reaction with 3,5-DTBC, observing the reaction for 4 h; inset: spectrum of the resulting solution after 24 h.

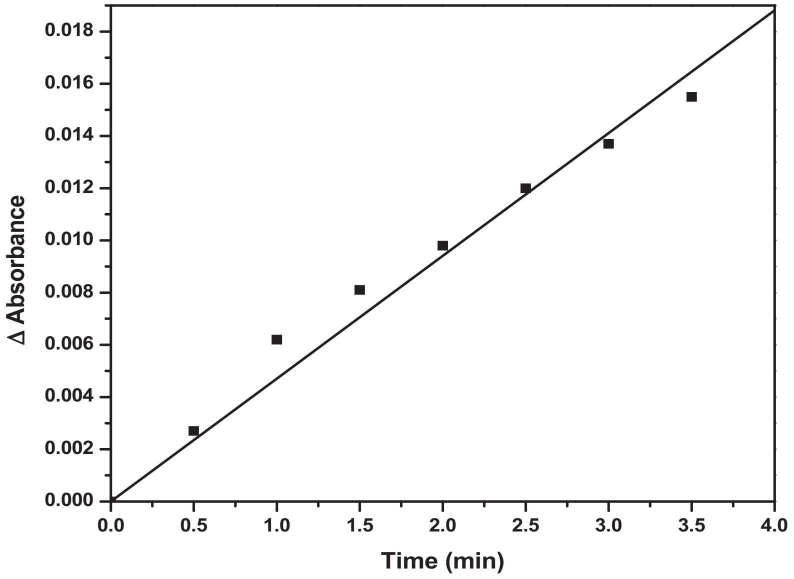

Fig. 7. A plot of the difference in absorbance (ΔA) vs. time to evaluate the initial rate of the catalysis by **1** in dichloromethane.

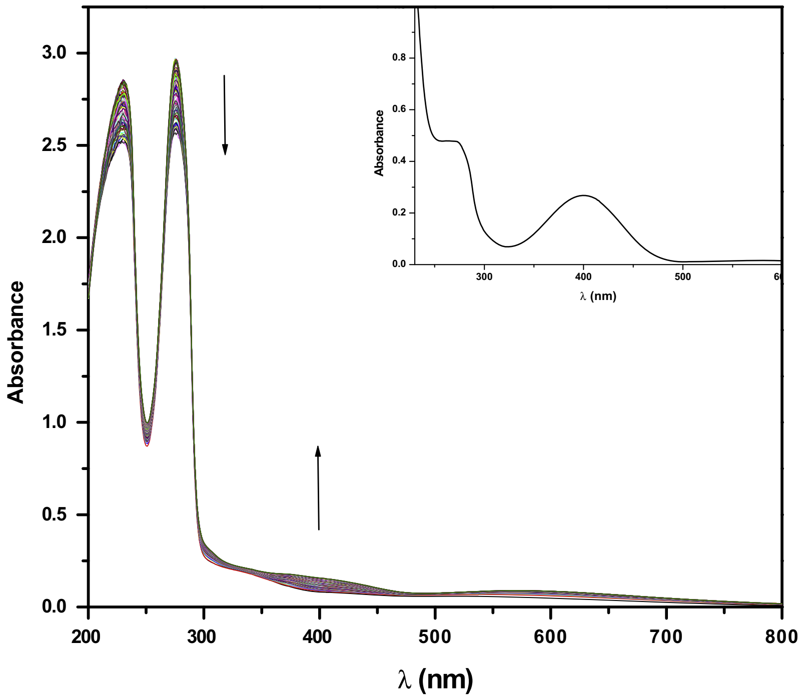

Fig. 8. Change in the spectral pattern of complex **1** in acetonitrile after reaction with 3,5-DTBC, observing the reaction for 6 h; inset: spectrum of the resulting solution after 24 h.

The repetitive UV-Vis spectral scan was recorded in pure methanol (Fig. 3). Spectral bands at 499, 330, 271 and 226 nm appear in the electronic spectrum of complex **1**, whereas 3,5-DTBC shows a single band at 282 nm. After addition of 3,5-DTBC, the time dependent spectral scan shows a very smooth increase of a quinone band at ~401 nm, as reported by Krebs *et al* [21], concomitant with a decrease in the characteristic ~282 nm band for 3,5-DTBC, which indicates the formation of the respective quinone derivative, 3,5-DTBQ, which was purified by column chromatography. The product was isolated in high yield (96.4%) by slow evaporation of the eluant and was identified by ^{1}H NMR spectroscopy (Fig. S1; Supplementary file). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H: 1.16 (s, 9H), 1.20 (s, 9H), 6.15 (d, J = 2.4 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H).

In order to find out the comparative reaction rate between 3,5-DTBC and **1**, the reaction kinetics between **1** and 3,5-DTBC were studied by observing the time dependent change in absorbance at a wavelength of 401 nm, which is characteristic of 3,5-DTBQ in methanol. The colour of the solution gradually turned deep brown (Fig. 4), indicative of a gradual conversion of 3,5-DTBC to 3,5-DTBQ. The difference in absorbance ΔA at 401 nm was plotted against time to obtain the initial rate for that particular catalyst to substrate concentration ratio (Fig. 5). A

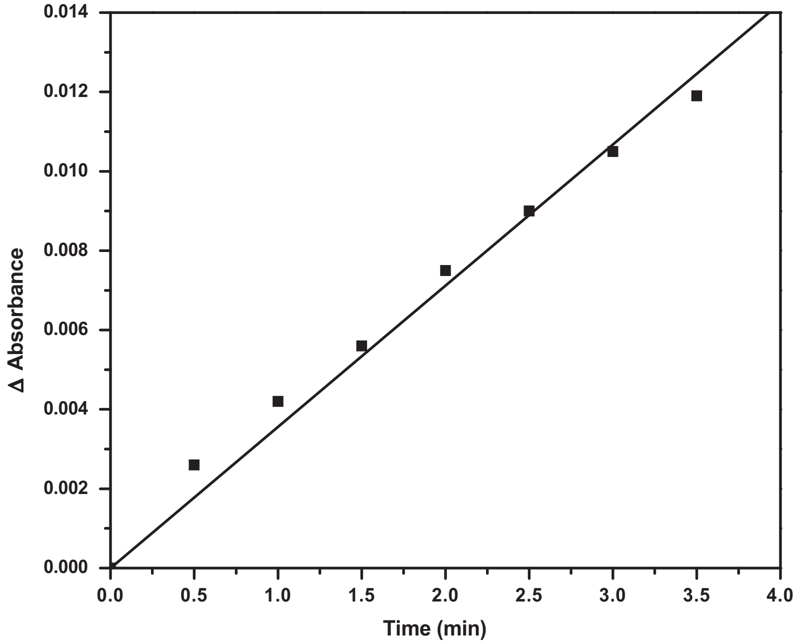

Fig. 9. A plot of the difference in absorbance (ΔA) vs. time to evaluate the initial rate of the catalysis by **1** in acetonitrile.

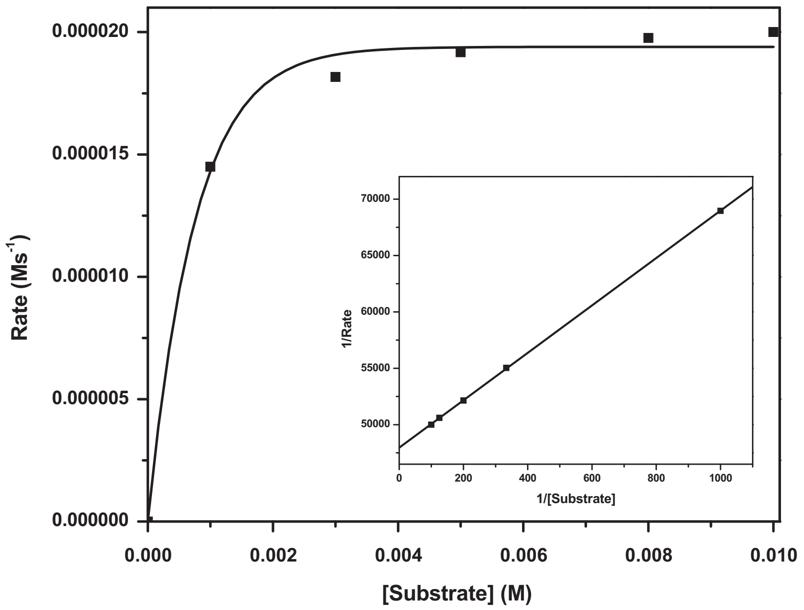

Fig. 10. Plot of rate vs. [substrate] in the presence of **1** in MeOH; inset: Lineweaver–Burk plot.

Table 3
Kinetic parameters for the oxidation of 3,5-DTBC catalyzed by **1**.

Solvent	V_{max} ($M\,s^{-1}$)	Std. error	K_M (M)	Std. error	K_{cat} (h^{-1})
MeOH	2.08×10^{-5}	1.45×10^{-6}	4.38×10^{-4}	7.01×10^{-5}	7.51×10^{2}
DCM	4.71×10^{-5}	5.59×10^{-6}	9.04×10^{-4}	5.65×10^{-5}	1.69×10^{3}
MeCN	3.42×10^{-5}	3.68×10^{-6}	8.70×10^{-4}	2.25×10^{-5}	1.23×10^{3}

first-order catalytic reaction is observed, with an initial rate of 4.78×10^{-3} min^{-1}.

The catecholase activity of complex **1** was similarly studied in DCM and MeCN media. In DCM 3,5-DTBQ shows a maximum absorption at 386 nm (Fig. 6), while in MeCN it shows a maximum absorption at 401 nm (Fig. 8), similar to that in methanol. The 3,5-DTBQ obtained in each medium was purified by column chromatography with yields of 64.30% in dichloromethane and 60.56% in acetonitrile. This was characterized by determining its melting point (~110 °C), which agreed well with that reported in the literature [22]. The reaction kinetics were studied by observing the time dependent change in absorbance at wavelengths of 386 and 401 nm respectively for catalysis in dichloromethane and in acetonitrile. The differences in absorbance, ΔA, at these particular wavelengths were plotted against time to obtain the intial rate of the reaction. A first-order catalytic reaction is observed in both the solvents, where the initial rates are found to be 4.70×10^{-3} min^{-1} (Fig. 7) and 3.56×10^{-3} min^{-1} (Fig. 9), respectively in DCM and MeCN.

3.5. Enzyme kinetics study

Kinetic experiments were performed spectrophotometrically with complex **1** and the substrate 3,5-DTBC in methanol, dichloromethane and acetonitrile, thermostated at 20 °C. 0.04 ml of the complex solution, with a constant concentration of 1×10^{-4} M, was added to 2 ml of 3,5-DTBC at a particular concentration (varying its concentration from 1×10^{-3} M to 1×10^{-2} M) to achieve the ultimate concentration of the complex as 1×10^{-4} M. The conversion of 3,-5-DTBC to 3,5-DTBQ was monitored with time at a wavelength of 401 nm for solutions in MeOH and MeCN, and 386 nm for solutions in DCM. The rate for each concentration of the substrate was determined by the initial rate method.

The rate versus concentration of substrate data were analyzed on the basis of the Michaelis–Menten approach of enzymatic kinetics to get the Lineweaver–Burk (double reciprocal) plot as well as the values of the various kinetic parameters, V_{max}, K_M and K_{cat}. The observed rate vs. [substrate] plot in methanol solution, as well as Lineweaver–Burk plot, is given in Fig. 10. Similar plots in dichloromethane and acetonitrile are given in the Supplementary file (Figs. S2 and S3). The kinetic parameters are listed in Table 3. The turnover numbers (K_{cat}) are 7.51×10^2, 1.69×10^3 and 1.23×10^3 h^{-1} in MeOH, DCM and MeCN, respectively.

4. Conclusion

We have synthesized and structurally characterized a dinuclear iron(III) complex (**1**) with a (N,O) donor Schiff base ligand. The ligand congregates the two Fe(III) metal centres. Variable temperature magnetic measurements of **1** show antiferromagnetic interactions between the two metal centres. The catalytic property of **1** has been kinetically investigated for the aerobic oxidation of 3,5-DTBC to 3,5-DTBQ in MeOH, DCM and MeCN, which reveals that the catalytic reaction follows a first order reaction pathway with rates about 10 times higher in MeOH and DCM than MeCN. The turnover numbers of **1** in different solvents are much greater than some other results reported recently [3b,3d,3e,4b,6a,8,9,23]. This indicates that **1** is a good and effective catalyst towards the aerial oxidation of 3,5-DTBC to 3,5-DTBQ.

Acknowledgements

RG acknowledges financial support from the Department of Science & Technology, New Delhi, India (F. No. SR/FT/CS-83/2010 dt. 11-02-2011). We sincerely thank Dr. K.C. Bhowmick, Department of Chemistry, Visva Bharati, Shantiniketan 731 235, India for NMR spectroscopic studies. Valuable discussion regarding Michaelis–Menten kinetics with Dr. D. Das, Department of Chemistry, University of Calcutta, Kolkata 700 009, India is gratefully acknowledged. MM acknowledges The University of Burdwan, Burdwan for her research fellowship. JR acknowledges the financial support from the Spanish Government (Grant CTQ2009/07264/BQU).

Appendix A. Supplementary data

CCDC 945632 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.08.064.

References

[1] (a) M. Merkel, N. Möller, M. Piacenza, S. Grimme, A. Rompel, B. Krebs, Chemistry–A European Journal 11 (2005) 1201;
(b) J. Reim, B. Krebs, Journal of the Chemical Society, Dalton Transactions (1997) 3793;
(c) B. Sreenivasulu, F. Zhao, S. Gao, J.J. Vittal, European Journal of Inorganic Chemistry (2006) 2656;
(d) C.-T. Yang, M. Vetrichelvan, M. Yang, B. Moubaraki, K.S. Murrey, J.J. Vittal, Dalton Transactions (2004) 113.

[2] (a) I.A. Koval, P. Gamez, C. Belle, K. Selmeczi, J. Reedijk, Chemical Society Reviews 35 (2006) 814;
(b) I.A. Koval, K. Selmeczi, C. Belle, C. Philouze, E. Saint-Aman, I. Gautier-Luneau, A.M. Schuitema, M. van Vliet, P. Gamez, O. Roubeau, M. Lüken, B. Krebs, M. Lutz, A.L. Spek, J.-L. Pierre, J. Reedijk, Chemistry–A European Journal 12 (2006) 6138.

[3] (a) K.S. Banu, T. Chattopadhyay, A. Banerjee, S. Bhattacharya, E. Suresh, M. Nethaji, E. Zangrando, D. Das, Inorganic Chemistry 47 (2008) 7083;
(b) S. Majumder, S. Sarkar, S. Sasmal, E. Carolina Sãnudo, S.S. Mohanta, Inorganic Chemistry 50 (2011) 7540;
(c) A. Biswas, L.K. Das, M.G.B. Drew, C. Diaz, A. Ghosh, Inorganic Chemistry 51 (2012) 10111;
(d) S. Mandal, J. Mukherjee, F. Lloret, R. Mukherjee, Inorganic Chemistry 51 (2012) 13148;
(e) A. Banerjee, S. Sarkar, D. Chopra, E. Colacio, K.K. Rajak, Inorganic Chemistry 47 (2008) 4023.

[4] (a) P. Comba, B. Martin, A. Muruganantham, J. Straub, Inorganic Chemistry 51 (2012) 9214;
(b) A. Neves, L.M. Rossi, A.J. Bortoluzzi, B. Szpoganicz, C. Wiezbicki, E. Schwingel, Inorganic Chemistry 41 (2002) 1788;
(c) S. Torelli, C. Belle, I. Gautier-Luneau, J.L. Pierre, E. Saint-Aman, J.M. Latour, L.L. Pape, D. Luneau, Inorganic Chemistry 39 (2000) 3526;
(d) S.-C. Cheng, H.-H. Wei, Inorganica Chimica Acta 340 (2002) 105.

[5] (a) A.L. Abuhijleh, J. Pollitte, C. Woods, Inorganica Chimica Acta 215 (1994) 131;
(b) A.L. Abuhijleh, C. Woods, E. Bogas, G.L. Guenniou, Inorganica Chimica Acta 195 (1992) 67;
(c) M.R. Malachowski, M.G. Davidson, J.N. Hoffman, Inorganica Chimica Acta 157 (1989) 91;
(d) M.R. Malachowski, M.G. Davidson, Inorganica Chimica Acta 162 (1989) 199;
(e) M. Mitra, A.K. Maji, B.K. Ghosh, G. Kaur, A.R. Choudhury, C.-H. Lin, J. Ribas, R. Ghosh, Polyhedron 61 (2013) 15.

[6] (a) P. Kar, R. Haldar, C.J. Gómez-García, A. Ghosh, Inorganic Chemistry 51 (2012) 4265;
(b) S. Mukherjee, T. Weyhermüller, E. Bothe, K. Wieghardt, P. Chaudhuri, Dalton Transactions (2004) 3842;
(c) K.S. Banu, T. Chattopadhyay, A. Banerjee, M. Mukherjee, S. Bhattacharya, G.K. Patra, E. Zangrando, D. Das, Dalton Transactions (2009) 8755.

[7] (a) L.I. Simándi, T.M. Simándi, Z. May, G. Besenyei, Coordination Chemistry Reviews 245 (2003) 85;
(b) T. Megyes, Z. May, G. Schubert, T. Grósz, L.I. Simándi, T. Radnai, Inorganica Chimica Acta 359 (2006) 2329;
(c) Z. May, L.I. Simándi, A.J. Vértes, Mol. Cat. 266 (2007) 239;
(d) S.-I. Lo, J.-W. Lu, W.-J. Chen, S.-R. Wang, H.-H. Wei, M. Katada, Inorganica Chimica Acta 362 (2009) 4699.

[8] S. Majumder, S. Mondal, P. Lemonie, S.S. Mohanta, Dalton Transactions 42 (2013) 4561.

[9] A. Biswas, L.K. Das, M.G.B. Drew, G. Aromí, P. Gamez, A. Ghosh, Inorganic Chemistry 51 (2012) 7993.

[10] A. Guha, T. Chattopadhyay, N.D. Paul, M. Mukherjee, S. Goswami, T.K. Mondal, E. Zangrando, D. Das, Inorganic Chemistry 51 (2012) 8750.

[11] (a) C. Gerdemann, C. Eicken, B. Krebs, Accounts of Chemical Research 35 (2002) 183;
(b) T. Klabunde, C. Eicken, J.C. Sacchettini, B. Krebs, Natural Structural Biology 5 (1998) 1084;
(c) C. Eicken, F. Zippel, K. Büldt-Karentzopoulos, B. Krebs, FEBS Letters 436 (1998) 293.

[12] Y. Lan, G. Novitchi, R. Cĺerac, J.-K. Tang, N.T. Madhu, I.J. Hewitt, C.E. Anson, S. Brooker, A.K. Powell, Dalton Transactions (2009) 1721.

[13] Y. Nishida, S. Kida, Journal of the Chemical Society, Dalton Transactions (1986) 2633.

[14] (a) R. Murugavel, N. Gogoi, R. Howlader, R. Clérac, Inorganica Chimica Acta 363 (2010) 3004;
(b) S. Konar, A. Clearfield, Inorganic Chemistry 47 (2008) 5573;
(c) C. Canada-Vilalta, E. Rumberger, E.K. Brechin, W. Wernsdorfer, K. Folting, E.R. Davidson, D.M. Hendrickson, G. Christou, Journal of the Chemical Society, Dalton Transactions (2002) 4005.

[15] G.M. Sheldrick, Acta Crystallogr., Sect. A 64 (2008) 112.

[16] L.J. Farrugia, ORTEP-32 for Windows, University of Glasgow, Scotland, 1998.

[17] R. Boca, Foundations of Molecular Magnetism, Elsevier, Amsterdam, 1999.

[18] (a) P.N. Turowski, W.H. Armstrong, S. Liu, S.N. Brown, S.J. Lippard, Inorganic Chemistry 33 (1994) 636;
(b) S. Yoon, S.J. Lippard, Journal of the American Chemical Society 127 (2005) 8386;

(c) P.N. Turowski, W.H. Armstrong, M.E. Roth, S.J. Lippard, Journal of the American Chemical Society 112 (1990) 681.

[19] (a) M.E. Fisher, American Journal of Physics 32 (1964) 343;
(b) O. Kahn, Molecular Magnetism, VCH, New York, 1993. 258.

[20] F. Le Gall, F.F. de Biani, A. Caneschi, P. Cinelli, A. Cornia, A.C. Fabretti, D. Gatteschi, Inorganica Chimica Acta 262 (1997) 123.

[21] F. Zippel, F. Ahlers, R. Werner, W. Haase, H.-F. Nolting, B. Krebs, Inorganic Chemistry 35 (1996) 3409.

[22] S. Tsuruya, Inorganic Chemistry 25 (1986) 141.

[23] P. Seth, L.K. Das, M.G.B. Drew, A. Ghosh, European Journal of Inorganic Chemistry (2012) 2232.