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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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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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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)	$0.42 \times 0.32 \times 0.18$
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.