Polyhedron 151 (2018) 446–451

Contents lists available at ScienceDirect

Polyhedron

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

Directed synthesis and magnetic properties of a hexanuclear ferric cluster

Jeff Lengyel [a], Sebastian A. Stoian [b,*], Naresh Dalal [a], Michael Shatruk [a,*]

[a] Department of Chemistry and Biochemistry, Florida State University, 95 Chieftan Way, Tallahassee, FL 32306, USA
[b] Department of Chemistry, University of Idaho, 875 Perimeter Dr, Moscow, ID 83844, USA

ARTICLE INFO

Article history:
Received 14 April 2018
Accepted 1 June 2018
Available online 15 June 2018

Keywords:
Ferric complexes
Clusters
Spin frustration
Antiferromagnetic exchange
Coordination chemistry

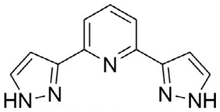
ABSTRACT

The hexanuclear iron(III) complex, $[Fe_6(\mu_3\text{-3-bpp})_4(\mu_3\text{-O})_2(\mu_2\text{-OMe})_{3.67}(\mu_2\text{-OH})_{0.33}Cl_2]\cdot0.33MeOH\cdot H_2O$ (**1**) was synthesized by a redox reaction between $FeCl_2$, $AgNO_2$, and 3-H_2bpp in methanol (3-H_2bpp = 2,6-bis(3-pyrazolyl)pyridine). The crystal structure of the complex is composed of two trinuclear subunits related by an inversion operation. This symmetry results in an overall octahedral arrangement of Fe(III) sites within the cluster. The four equatorial Fe sites are linked together by μ_2-OMe^- and μ_2-OH^- bridges, while each of the four 3-bpp^{2-} bridges spans two axial and one equatorial Fe sites. The two Cl^- ligands cap the axial Fe sites. The difference in the coordination environment for the equatorial and axial Fe sites is validated by the observation of two quadrupole doublets in the Mössbauer spectrum of **1**, which also confirms that all metal sites correspond to the high-spin Fe(III) ions. Temperature-dependent magnetic susceptibility data reveal strong antiferromagnetic exchange coupling between the Fe(III) centers, which is also justified by quantum-chemical calculations at the density-functional level of theory.

1. Introduction

Oxo-bridged ferric complexes have been studied extensively vis-à-vis their magnetic properties. In particular, a detailed analysis was performed by Gorun and Lippard to understand the correlation between interatomic distances in the core of the cluster and the strength of antiferromagnetic exchange coupling [1]. Somewhat later, complexes with ferro- or ferrimagnetic ground states have received renewed attention as potential single-molecule magnets (SMMs) [2–4]. In addition, multinuclear ferric complexes also play an important role as active sites in many metalloproteins [5]. The search for new SMMs has somewhat sidelined attention to ferric complexes with low total spin values, i.e. with antiferromagnetic ground states. Nevertheless, the frequent occurrence of trinuclear μ_3-oxo centered subunits in such complexes is fundamentally interesting, as it offers a fertile playground for testing simple models aimed at understanding how the balance between mutually conflicting antiferromagnetic coupling pathways (briefly, spin frustration) defines the ground spin state in such systems [6–8].

The synthesis of ferrous complexes with N-donating ligands represents an active area of research, due to the proclivity of such compounds to exhibit switching between the low-spin and high-spin electronic configurations (spin crossover) [9–11]. In the course of such studies, one sometimes encounters byproduct ferric complexes – the result of increased air sensitivity of the high-spin Fe(II) ion due to the population of the higher-energy antibonding e_g orbitals, which remain vacant in the low-spin Fe(II) ion. Typically, the yield of such byproducts is low or negligible, as one tries to avoid their formation by careful handling of reaction mixtures under air-free conditions. Occasionally, however, a ferric byproduct might be an unavoidable outcome caused by circumstances accompanying the reaction.



3-H₂bpp

Our interest in certain N-donating ligands that consistently lead to the formation of Fe(II) complexes with abrupt spin transitions, which may be accompanied by crystallographic symmetry breaking [12], led us to investigate the preparation of salts of the

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* Corresponding authors.
E-mail addresses: sstoian@uidaho.edu (S.A. Stoian), shatruk@chem.fsu.edu (M. Shatruk).

https://doi.org/10.1016/j.poly.2018.06.004
0277-5387/

well-known spin-crossover cation, $[Fe(3\text{-}H_2bpp)_2]^{2+}$, where 3-$H_2$bpp = 2,6-bis(3-pyrazolyl)pyridine [13–15]. In the course of these studies, we discovered the formation of an interesting hexanuclear Fe(III) cluster due to the oxidation of the Fe(II) centers by NO_2^- ions. Attempts to synthesize such cluster in a direct manner, i.e. in the absence of NO_2^- as an oxidizing agent, failed, while the use of $AgNO_2$ in the reaction consistently led to the isolation of this product. Herein, we report the synthesis and crystal structure of this hexanuclear complex, $[Fe_6(\mu_3\text{-}3\text{-}bpp)_4(\mu_3\text{-}O)_2(\mu_2\text{-}OMe)_{3.67}(\mu_2\text{-}OH)_{0.33}Cl_2]\cdot 0.33MeOH\cdot H_2O$ (**1**), and provide a detailed analysis of its magnetic properties by a combination of magnetic measurements, Mössbauer spectroscopy, and density-functional theory (DFT) calculations.

2. Materials and methods

2.1. Synthesis

All reactions were performed under an inert N_2 atmosphere using standard Schlenk techniques. All reagents were purchased from Aldrich or Alfa Aesar, except for 3-H_2bpp, which was prepared according to the previously published procedure [16]. ACS grade methanol was purged with dry N_2 gas for 30 min prior to use. Elemental analysis was performed by Atlantic Microlab, Inc. (Norcross, GA, USA).

2.1.1. $[Fe_6(\mu_3\text{-}3\text{-}bpp)_4(\mu_3\text{-}O)_2(\mu_2\text{-}OMe)_{3.67}(\mu_2\text{-}OH)_{0.33}Cl_2]\cdot 0.33MeOH\cdot H_2O$ (1)

A 50-mL Schlenk flask was charged with 50 mg (0.25 mmol) of $FeCl_2\cdot 4H_2O$ and 210 mg (1.00 mmol) of 3-H_2bpp, and 20 mL of methanol was added with stirring to result in a clear gold-yellow solution. To this solution was added 230 mg (1.50 mmol) of $AgNO_2$, and the reaction mixture was stirred for 1 h. After this time, a black precipitate that formed was filtered off via cannula. The dark-orange solution obtained was allowed to slowly evaporate under a flow of N_2 gas or layered with anhydrous diethyl ether. In both cases, X-ray quality single crystals were obtained within a few days. The crystals were isolated by filtration, washed with cold MeOH, and dried under suction. Yield = 24 mg (41%). *Anal.* Calc. (Found) for $Fe_6Cl_2O_{7.66}N_{20}C_{48}H_{43.3}$ (**1**),%: C 41.3 (40.35), H 3.22 (3.06), N 18.8 (19.61).

2.1.2. X-Ray crystallography

Single-crystal X-ray diffraction was performed on a Bruker APEX-II diffractometer equipped with a CCD detector and a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). A single crystal of **1** was suspended in Paratone-N oil (Hampton Research) and mounted on a cryoloop which was cooled to 100 K in an N_2 cold stream. The data set was recorded as ω-scans at 0.3° step width and integrated with the Bruker SAINT software package [17]. A multi-scan adsorption correction was applied based on multiple equivalent measurements (SADABS) [18]. The space group was determined with XPREP [19], and the crystal structure solution and refinement were carried out using the SHELX software [20]. The final refinement was performed with anisotropic atomic displacement parameters for all non-hydrogen atoms, except for the atoms that belonged to a disordered part of the structure. The latter included one of the bridging units (see the Crystal Structure section below), which was occupied either by methoxide or hydroxide group. The total occupancy of these groups was set to 1. Based on interatomic distances observed, a nearby methanol molecule was modeled as present when the bridge was occupied by $\mu_2\text{-}OH^-$ and absent when the bridge was occupied by $\mu_2\text{-}OMe^-$. Such disorder model also led to more meaningful atomic displacement parameters for the non-hydrogen atoms. All H atoms were placed in calculated positions and refined in the riding model. Full details of the crystal structure refinement have been deposited with the Cambridge Crystallographic Data Centre (CCDC). A brief summary of data collection and refinement are provided in Table 1.

Table 1
Data collection and crystal structure refinement parameters for **1**.

Formula	$Fe_6Cl_2O_{7.66}N_{20}C_{48}H_{43.3}$ (**1**)
CCDC number	1832672
T (K)	100(2)
Molar mass (g/mol)	1428.81
Space group	$C2/c$
a (Å)	23.265(9)
b (Å)	11.918(4)
c (Å)	22.438(8)
β (°)	107.754(4)
V (Å^3)	5925.14
Z	4
Crystal color	Red
D_{calc} (g cm^{-3})	1.602
μ (mm^{-1})	1.588
λ (Å)	0.71073
$2\theta_{max}$ (°)	28.62
Total reflections	30239
R_{int}	0.074
Unique reflections	7116
Parameters refined	415
Restraints used	8
R_1, wR_2 [$I > 2\sigma(I)$][a]	0.086, 0.225
R_1, wR_2 (all data)	0.147, 0.258
Goodness-of-fit (GOF) on F^2[b]	1.042
Difference in peak/hole (e Å^{-3})	1.25, −1.10

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{½}$.

[b] Goodness-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{½}$, based on all data.

2.1.3. Magnetic measurements

Magnetic properties of **1** were measured on a polycrystalline sample, using a superconducting quantum interference device (SQUID) magnetometer MPMS-XL (Quantum Design). Magnetic susceptibility was measured in a direct-current (DC) applied magnetic field of 0.1 T in the 1.8–300 K temperature range. The data were corrected for the diamagnetic contribution from the sample holder and for the intrinsic diamagnetism using tabulated constants [21].

2.1.4. Mössbauer spectroscopy

The zero-field, 80-K ^{57}Fe Mössbauer spectrum of **1** was recorded using a spectrometer operated in a constant acceleration mode. The instrument was equipped with a liquid nitrogen cooled cryostat. The sample consisted of ~50 mg of polycrystalline powder of **1** dispersed in eicosane and placed directly in a custom-made polyethylene cup closed with a lid. Isomer shifts were referenced against the centroid of a spectrum recorded at room temperature for a Fe metal foil.

2.1.5. Electrochemistry

Cyclic voltammetry (CV) was recorded on complex **1** dissolved in a 0.100 M solution of $(Bu_4N)PF_6$ in MeCN at room temperature. The measurements were performed using a 600D electrochemical analyzer (CH Instruments), at the sweep rate of 0.100 V·s^{-1}, with a Pt-disk working electrode, a Pt-wire counter electrode, and an Ag/AgCl reference electrode. All the potentials were referenced to the Fc^+/Fc couple (Fc = ferrocene), which was added as an internal standard upon completion of the CV experiment.

2.1.6. Theoretical calculations

Electronic structure calculations were performed at the density-functional theory (DFT) level using the GAUSSIAN 09