Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Structure 743 (2005) 73–77

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

Preparation, crystal structure and characterization of a novel iron(III) oxide cluster containing two different discrete [Fe_3O] units

Kou-Lin Zhang[a,*], Yu-Jun Shi[b], Xiao-Zeng You[c], Kai-Bei Yu[d]

[a]Chemistry and Chemical Engineering College, Yangzhou University, Yangzhou 225002, People's Republic of China
[b]Department of Chemistry, Nantong Teachers University, Nantong 226007, People's Republic of China
[c]State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093, People's Republic of China
[d]Chengdu Branch of Chinese Academy of Science, Analysis Center, Chengdu 610041, People's Republic of China

Received 7 January 2005; revised 22 February 2005; accepted 24 February 2005
Available online 5 April 2005

Abstract

The preparation, X-ray crystal structure, Mössbauer spectra and magnetic properties of a novel iron(III) oxide cluster have been reported. The reaction of excess *trans*-2-butenoic acid with $FeSO_4 \cdot 7H_2O$ in the presence of NaOH gives the novel hexanuclear complex $[Fe_3O(O_2CCH{=}CH{-}CH_3)_6(H_2O)_3][Fe_3O(O_2CCH{=}CH{-}CH_3)_7(H_2O)_2](HO_2CCH{=}CH{-}CH_3)_4(OH)(H_2O)$. The X-ray analysis reveals that it is the first case that contains two different discrete trinuclear oxo-centered [Fe_3O] units. The Mössbauer spectra of the complex are typical of high spin iron(III) complexes. The complex has been found to exhibit antiferromagnetic exchange interactions between the Fe(III) ions.

Keywords: Preparation; Crystal structure; Novel iron(III) oxide cluster; Mössbauer spectra; Magnetic properties

1. Introduction

People have made many efforts to design and synthesize the new molecule-based magnets because they exhibit polyfunctional solid-state properties [1–11]. Among these, the polynuclear iron–oxo complexes are receiving much attention. One of the fascinating aspects of the investigation of large iron clusters is that of providing models for the biomineralization of iron, which leads to such diverse compounds as magnetite and ferritin [12–20]. The recent discovery that iron–oxo clusters offer the potential of acting as precursors to molecule-based magnetic materials and even of functioning as nano-scale magnetic particles that they may display novel properties intermediate between those of simple paramagnets and bulk magnets has added more interest in this area [21–26]. Over the past few years, a great number of such clusters with aesthetically pleasing structures and interesting magnetic properties have been synthesized and studied. Among them, oxo-centered carboxylate-bridged trinuclear iron(III) complexes of general formula $[Fe_3(\mu_3{-}O)(O_2CR)_6L_3]^z$ ($z=0, +1$) have been synthesized and structurally characterized for a long time [27–30]. Attention has focused almost exclusively on various properties of these complexes in the solid state. The highly symmetrical structure and the relatively large metal–metal distances, which exclude the possibility of direct metal–metal bonding make these attractive systems with which to examine magnetic and electronic interactions [28]. The mono cationic complexes which contain three high-spin iron(III) centers were some of the first polynuclear systems to which ideas of magnetic exchange were applied [31]. As an extension to the above areas, we have thus been investigating new synthetic procedures capable of allowing access to new structural types. Over the past years, our interests are mainly focused on the molecular-based magnets, including the azide-bridged, cyanide-bridged, oxamidato-bridged, thiocyanato-bridged, carboxylate-bridged, etc. complexes [32–34]. In this paper, we report the preparation, full X-ray structural analysis, Mössbauer spectra and cryomagnetic behaviors of the title complex. As far as we know, this is the first case that contains two different Fe_3O units in the same complex. The magnetic measurements indicate that the high spin iron(III) sites are antiferromagnetically coupled.

---

* Corresponding author. Tel./fax: +86 514 7695171.
E-mail address: koulinzhang2002@yahoo.com (K.-L. Zhang).

0022-2860/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2005.02.030

2. Experimental section

2.1. Materials and characterization

All reagents were used as purchased. Elemental analyses (C, H, N) were carried out by the Micro analytical Service from the Analysis Center for Materials of Nanjing University. Infrared spectrum (400–4000 cm^{-1}) was recorded from KBr pellet in VECTER22 FT-IR spectrometer. The Mössbauer experiments were carried out in zero applied magnetic fields using a ^{57}Co/Pd source and a constant acceleration spectrometer to collect the transmission spectra at 298 and 77 K (Fig. 4). The spectrometer was calibrated using a standard α-Fe foil. The isomer shifts are determined relative to the center of the α-Fe spectrum. The MOSWIN program was used to determine the Mössbauer parameters. The magnetic susceptibilities were measured in the temperature range 1.88–303.4 K on a Quantum Design MPMS-7 Squid magnetometer in a 10 KG applied field. Pascal's constants were used to estimate the diamagnetic corrections and they were subtracted from the experimental susceptibilities to give the molar paramagnetic susceptibilities.

2.2. Synthesis

To a solution of *trans*-2-butenoic acid (2.724 g, 31.6 mmol) in water (50 ml) was added a solution of NaOH (0.210 g, 5.2 mmol) in water (5 ml). Then $FeSO_4\cdot 7H_2O$ (0.733 g, 2.6 mmol) was added to the above solution and refluxed for 24 h and filtered. The filtrate was kept at ambient temperature for several days and brown crystals were formed. They were filtered and washed thoroughly with water and dried in vacuum (yield: 64.8% based on Fe). Anal. Calc. for $C_{68}H_{102}Fe_6O_3$: C, 42.04; H, 5.29. Found: C, 42.42; H, 5.11.

2.3. X-ray crystallography study

A brown crystal having approximate dimensions $0.46\times 0.24\times 0.12$ mm^3 was used for data collection. Diffraction data were collected at 298(2) K with a Siemens P4 diffractormeter using graphite-monochromated (Mo Kα) radiation ($\lambda = 0.71073$ Å), 2θ–θ scan mode. Altogether there were 16,683 reflections collected. The cell constants were determined from the Full-matrix least-squares fit of 20 reflections with θ in the range 3.00 and 13.74°. The structure was solved by direct methods and refined by a Full-Matrix least-squares on F^2 method to $R_1 = 0.0516$ ($wR_2 = 0.1049$) for 15,457 reflections ($I(2\sigma(I))$) collected in the range $1.55° \leq \theta \leq 25.01°$. Intensity data were corrected for Lorenz and polarization effects and an empirical absorption correction was performed. The intensities of three reference reflections, monitored every 100 reflections throughout the data collection, showed no sign of crystal deterioration. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added geometrically and were allowed to ride on their respective parent atoms. The contribution of these hydrogen atoms was included in the structure factor calculations. In the final difference map, the residual maxima and minima were 0.623 and −0.416 $eÅ^{-3}$, respectively. The goodness of fit on F^2 is 0.781. All calculations were carried out on a PC 586 computer using SHELXL-97 program [35]. Details of crystal data, collection and refinement are listed in Table 1.

Table 1
Crystallographic data for the complex

Empirical formula	$C_{68}H_{102}Fe_6O_{43}$
Crystal color, habit	Brown
Formula weight	1942.60
Temperature	298(2) K
Wave length (Å)	0.71073
Crystal system	Triclinic
Space group	$P-1$
a (Å)	14.724(3)
b (Å)	17.818(3)
c (Å)	18.764(5)
α (°)	103.200(10)
β (°)	107.95(2)
γ (°)	92.010(10)
V (Å^3)	4529.8(17)
Z	2
D_{calc} (g cm^{-3})	1.424
μ (Mo Kα) (mm^{-1})	1.024
F(000)	2020
Crystal size (mm)	$0.46\times 0.24\times 0.12$
θ Range for data collection (°)	1.55–25.01
Index ranges	$0\leq h\leq 16$; $-20\leq k\leq 20$; $-22\leq l\leq 21$
Reflections collected	16683
Independent reflections	15457($R_{int} = 0.0393$)
Completeness to $\theta = 25.00°$	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15457/28/1114
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0516$, $wR2 = 0.0877$
R indices (all data)	$R1 = 0.1296$, $wR2 = 0.1049$
Largest diff. Peak and hole (eÅ^3)	0.623 and −0.416

3. Results and discussion

3.1. Preparation

We tried to synthesize the title compound in the excess of *trans*-2-butenoic acid so that the yield of the product could be improved.

3.2. Structural description

The structure of the title complex contains two different Fe_3O units that crystallize in the same unit cell along with one OH^- anion, one water molecule and four free *trans*-2-butenoic acid molecules. The formulae of the two trinuclear oxo-centered units are $[Fe_3O(O_2CC{=}CH–CH_3)_6(H_2O)_3]^+$ (unit 1, Fig. 1) and $[Fe_3O(O_2CC{=}CH–CH_3)_7(H_2O)_2]$