Solid State Sciences 18 (2013) 10–16

Contents lists available at SciVerse ScienceDirect

Solid State Sciences

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

Mononuclear and dinuclear iron(III) compounds with β-diketonate ligands: Synthesis, magnetic behavior and DFT calculations

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ARTICLE INFO

Article history:
Received 9 July 2012
Received in revised form
6 November 2012
Accepted 16 December 2012
Available online 27 December 2012

Keywords:
Fe(III) compounds
Molecular magnetism
β-Diketonate ligand
DFT calculations

ABSTRACT

The synthesis, crystal structure, magnetic properties and DFT calculations of two low-nuclearity Fe(III) compounds based on β-diketonate ligand, $[Fe(OMe)(BTA)_2]_2$ (**1**) and $Fe(BTA)_3$ (**2**) (BTA = 4,4,4-trifluoro-1-phenyl-2,4-butanedione) are reported. Compound (**1**) is a molecular dimer in which Fe(III) ions are coordinated to two BTA ligands and bridged by two methoxide anions, while compound (**2**) is a tri-schelated Fe(III) monomer. Magnetic measurements revealed antiferromagnetic interactions in both compounds. In (**1**) the magnetic coupling is intramolecular, whereas in (**2**) it occurs via intermolecular interactions as a result of π–π stacking between the phenyl rings. DFT calculations using the broken symmetry approach were carried out to obtain the theoretical coupling constant value for both compounds and to rationalize the pathway for magnetic interactions in (**2**).

1. Introduction

The coordination chemistry involving β-diketonate ligands is widely known [1]. Complexes containing β-diketonate ligands are potential candidates for application as new materials [2] and systematic studies have been performed to understand the influence of the substituents in the 1, 2 or 3 positions of these ligands on the overall properties of compounds [3–6]. In particular, coordination compounds based on lanthanide ions and β-diketonate are extensively studied due to their interesting luminescent properties and are commonly applied to study mechanism of chemiluminescent reactions [7]. Beyond the luminescence, other properties such as catalytic and magnetic can be also obtained by using *3d* metal ions β-diketonate complexes. Recently, Weng and co-workers reported the ability of Fe(III)-β-diketonate complexes to efficiently catalyze transesterification reactions in mild conditions [6]. Besides, low-nuclearity Fe(III) compounds based on β-diketonate ligands have been playing an important role in molecular magnetism [8,9], acting as building blocks for high-nuclearity molecular magnetic compounds [10]. The knowledge of the crystal structure and magnetic properties of these building blocks is fundamental to understand and to control the magnetic properties of more complex systems [11,12]. For example, in a set of dinuclear Fe(III) compounds with general molecular formula $[Fe(OR)(\beta\text{-diketonate})_2]_2$ (R = alkyl chain), magneto-structural relationship revealed the influence of the alkoxide anion and the substituent in the β-diketonate ligand on the magnetic properties, showing a nearly linear dependence between the coupling constant value and the Fe–O–Fe bond angle [11].

In order to investigate the influence of electron withdrawing group in the β-diketonate ligand, we choose the 4,4,4-trifluoro-1-phenyl-2,4-butanedione (BTA) ligand to synthesize Fe(III) based compounds. The presence of the phenyl ring in the 1-position of the ligand also has an interesting appeal because it may provide a path for intermolecular magnetic interactions through π–π stacking. Hence, in this work we report the synthesis, crystal structure, magnetic properties and DFT calculations for two low-nuclearity Fe(III)-β-diketonate complexes, $[Fe(OMe)(BTA)_2]_2$ (**1**) and $Fe(BTA)_3$ (**2**) (Scheme 1). Magnetic measurements reveal antiferromagnetic interactions between the Fe(III) ions in both compounds. We show that intermolecular interactions provided by π–π stacking between the phenyl rings play a key role to explain the magnetic behavior of (**2**).

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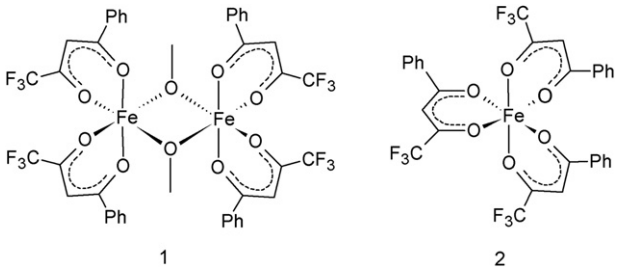
http://dx.doi.org/10.1016/j.solidstatesciences.2012.12.014



Scheme 1. Representation of compounds (**1**) and (**2**).

2. Experimental

2.1. Materials and methods

Analytical grade reagents were purchased from different sources and used without further purification, except for methanol that was treated with Mg°/I_2 shortly before use. Elemental analyses were determined on a Perkin–Elmer 2400 CHN Elemental Analyzer. The infrared spectra were recorded on a Spectrum One Perkin–Elmer spectrometer in the range of 4000–500 cm^{-1}, using KBr pellets. Magnetic measurements were performed on a Cryogenic SX-600 SQUID magnetometer in a range of 2–300 K with an applied field of 0.1 T (**1**) or 0.2 T (**2**). The samples were placed in a gelatin capsule and data were corrected for the diamagnetism and sample holder.

2.2. Synthesis

2.2.1. $[Fe(OMe)(BTA)_2]_2$

To a solution of BTA (0.546 g, 2.5 mmol) in 20 mL of dried methanol was added 1.1 mL of 30% sodium methoxide solution (w/v) in methanol under constant stirring. After 20 min, $FeCl_3$ (0.406 g, 2.5 mmol) was added and immediately an orange precipitate was formed. The reaction mixture was stirred for additional 30 min, filtered and the solid washed with methanol. Then, the product was dissolved in a 2:1 diethyl ether:methanol solution and stored at 8 °C. After one week, orange rod-like single crystals were obtained. Yield: 0.670 g. Anal. Calc. for $C_{42}H_{30}O_{10}F_{12}Fe_2{\cdot}4H_2O$: C = 45.59%; H = 3.46%. Found C = 45.44%; H = 3.16%. Selected IR data (KBr, ν/cm^{-1}): 2931(C–H); 2823 (C–H); 1604, 1572, 1458 (C=C); 1296 (C–F); 771 and 772 (C–H).

2.2.2. $Fe(BTA)_3$

To a solution of $FeCl_3$ (0.406 g, 2.5 mmol) in 20 mL of methanol, BTA (0.546 g, 2.5 mmol) and 1.1 mL of a 30% (w/v) sodium methoxide solution were added under constant stirring. After 5 min, a small amount of a yellow precipitate appeared, which was isolated by filtration. The filtrate was evaporated and the obtained red solid was dissolved in 20 mL of acetonitrile and filtered to remove any insoluble solid. The washing liquid was evaporated once. The remaining solid was washed with distilled water and dried under vacuum. Single crystals were obtained through slow solvent evaporation from 15 mL of a methanolic solution containing 5 mg of the product. Sodium methoxide in this synthesis acts only as a Brönsted base removing a BTA α-hydrogen atom, however compound (**2**) can be also obtained without adding it following the procedure previously reported [13]. Yield: 0.432 g. Anal. Calc. for $C_{30}H_{18}F_9FeO_6$: C = 51.38%; H = 2.59%. Found C = 51.59%; H = 2.64%. Selected IR data (KBr, ν/cm^{-1}): 2825 (C–H); 1570, 1486, 1454 (C=C); 1291(C–F); 1200 and 1145 (C–H).

2.3. X-ray crystallographic data

Single crystal X-ray diffraction data for compounds (**1**) and (**2**) were collected on an Enraf Nonius Bruker KAPPA CCD diffractometer at room temperature, using graphite monochromatic MoKα radiation (λ = 0.71069 Å). Final unit cell parameters were based on the fitting of all reflection positions using DIRAX [14]. Collected reflections were integrated using the EVALCCD program [15]. Empirical multiscan absorption corrections using equivalent reflections were performed with the SADABS program [16]. The structure solutions and full-matrix least-squares refinements based on F^2 were performed with the SHELXS-97 and SHELXL-97 program packages [17]. All atoms except hydrogen were refined anisotropically. Hydrogen atoms were treated by constrained refinement. Details of data collection and structure refinement for compounds (**1**) and (**2**) are summarized in Table 1. Selected distances are given in Table 2.

2.4. Computations

DFT calculations were carried out with the B3LYP [18] functional and the 6-31G(d) [19] basis set implemented in the NWCHEM 6.0 software package [20]. Single point calculations were performed with tight convergence using the atomic positions obtained from the crystal structures. Nevertheless, the geometry of (**1**) was fully optimized with B3LYP/6-31(d) level, under C_i point group restrictions to analyze the role of structural parameters to the magnetic coupling constant. The fragment approach was used to calculate ferromagnetic and antiferromagnetic states in both compounds. For (**1**), three fragments were used: one containing two methoxide groups and two consisting in symmetrical $[Fe(BTA)_2]^+$ moieties. In order to verify the intermolecular magnetic interactions in (**2**) we considered two interacting $Fe(BTA)_3$ molecules. This choice was based on the crystal structure. The magnetic coupling constant (J) was calculated using Eq (1), where the E_{BS} and E_{HS} terms are the energies of the antiferromagnetic and ferromagnetic spin states,

Table 1
Summary of the crystal structure, data collection and refinement for compounds (**1**) and (**2**).

Identification	(**1**)	(**2**)
Formula	$C_{42}H_{30}F_{12}Fe_2O_{12}$	$C_{30}H_{18}F_9FeO_6$
Molecular weight (g mol^{-1})	1066.36	701.29
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$
a (Å)	11.018(4)	12.357(5)
b (Å)	14.319(5)	37.751(5)
c (Å)	16.137(8)	14.072(5)
α (°)	84.88(3)	90.000
β (°)	84.69(3)	110.522(5)
γ (°)	70.05(3)	90.000
Volume ($Å^3$)	2378.3(17)	6148(3)
Z	2	8
D_{calc} (g cm^{-3})	1.489	1.515
μ (mm^{-1})	0.71	0.59
F (000)	1076	2824
Crystal size (mm)	0.03 × 0.02 × 0.02	0.24 × 0.15 × 0.09
θ range for data collection (°)	3.1–25.0°	3.5–22.6°
Reflections collected	15,846	19,938
Independent reflections/R_{int}	8391/0.046	2481/0.11
Data/restraints/parameters	4929/72/622	7920/66/784
Goodness-of-fit on $F2$	1.01	0.98
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.061	$R1$ = 0.091
	$wR2$ = 0.179	$wR2$ = 0.249
R indices (all data)	$R1$ = 0.1145	$R1$ = 0.294
	$wR2$ = 0.1555	$wR2$ = 0.175
Max peak/hole (e $Å^{-3}$)	0.85/−0.59	0.48/−0.45

For compound (**1**): $w = 1/[\sigma^2(Fo^2) + (0.0949P)^2]$; (**2**): $w = 1/[\sigma^2(Fo^2) + (0.0956P)^2]$.