

## SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE TETRANUCLEAR IRON(III) CLUSTER WITH SALICYLIC ACID

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Dedicated to the memory of Professor Constantin Turta on the occasion of his 80<sup>th</sup> birthday anniversary.

**Abstract.** A new tetra-homonuclear iron(III) cluster,  $[\text{Fe}_4\text{O}_2(\text{Sal})_4(\text{H}_2\text{O})_6]\cdot 4\text{DMA}\cdot 0.75\text{H}_2\text{O}$  (where, Sal= salicylic acid and DMA= *N,N*-dimethylacetamide), consolidated via two  $\mu_3$ -oxo- and four salicylate-bridges was synthesized and characterized by IR spectroscopic method as well as by single-crystal X-ray diffraction analysis. The structure of the obtained tetranuclear compound consists of four  $\text{Fe}^{\text{III}}$  atoms in a “butterfly” arrangement. The compound crystallizes in the  $P2_1/c$  space group of the monoclinic system with the following unit cell parameters:  $a= 10.5350(3)$ ,  $b= 11.8840(3)$ ,  $c= 21.7830(5)$  (Å),  $\beta= 101.536(1)^\circ$ . Each  $\text{Fe}^{\text{III}}$  atom is six-coordinated in slightly distorted  $\text{O}_6$  octahedral geometry. The coordination sphere of each of the two central  $\text{Fe}^{\text{III}}$  atoms is generated by two  $\mu_3$ -oxo-bridging atoms and four oxygen atoms provided by the tridentate-bridging  $\text{Sal}^{2-}$  ligands, while the coordination polyhedron of another two iron atoms involve six oxygen atoms from three water molecules, two salicylic and one  $\mu_3$ -oxigen atom. The Fe-O distances within Fe-O-Fe bridge are of 2.102(3) Å (for wing-body) and 2.038(3) Å (for body-body).

**Keywords:** homotetranuclear salicylate, iron(III), cluster, IR spectroscopy, X-ray crystal structure.

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### Introduction

Iron(III) is a very interesting *transition-metal* to investigate due to a large number of unpaired electrons ( $S= 5/2$ ), which offers the possibility to form high-spin clusters [1]. The iron clusters have aroused much interest as they can be used for the design of molecular magnets [2-4]. The interactions between iron(III) centres in polynuclear compounds are usually antiferromagnetic.

Compounds containing iron atoms assembled by one or more oxo-bridges are synthesized and investigated quite extensively not only due to their interesting properties as molecular magnets [5] or mixed-valence formulation  $[\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}]^{6+}$  [6], but also due to their design since oxo-Fe bridges are found in the active sites of different proteins [7]. The growing interest dedicated to the synthesis of polynuclear iron complexes is owing to the discovery of the catalytic sites of several non-haem iron proteins contain oxo- or hydroxo-bridged diiron units and the relevance of large polyiron(II,III)-oxo aggregates to the ferritin core [8]. Polynuclear carboxylates containing iron(III) centres have been found to perform important biological

functions in several proteins, such as oxygen storage and transport.

Nowadays, clusters with a planar or bent tetranuclear  $[\text{Fe}_4\text{O}_2]$  core are an emerging class of oxo-bridged poly-iron aggregates. The class of tetranuclear butterfly compounds has been well studied and has yielded a wealth of interesting structural, spectroscopic, and physical data. The first example for  $\text{Fe}^{\text{III}}$  tetranuclear complex  $[\text{Fe}_4\text{O}_2(\text{O}_2\text{CCF}_3)_8(\text{H}_2\text{O})_6]$  was reported in 1984 [9] followed soon by a number of other compounds [10-18]. The numerous tetranuclear iron complexes reported in the literature include most frequently  $\mu$ -oxo bridging (hydroxo, carboxylato, carbonato, alkoxo, phenoxo groups), yielding a variety of geometries for the  $\text{Fe}_4$  array: butterfly, [9-11,13] square or rectangular planar [19-22], puckered  $(-\text{Fe}-\text{O})_4$  ring [23] and cubane-like tetranuclear cluster [24]. In turn, the “butterfly” arrangement of the cores can be assigned into “bent”, “planar”, or “chairlike” types [15,25-27]. Another example of  $[\text{Fe}_4(\mu_3\text{-O})_2]^{8+}$  core was determined for amino-functionalized ligands bipy- $\text{NH}_2$  and  $\text{O}_2\text{CPh-NH}_2$  [28] and exhibits protonation tuned colour change, which could open new pathways for the development of metal-organic materials.

The chemistry of tetranuclear iron carboxylates has significant importance due to interesting magnetic properties [29-31]. There are several studies [18,32] where the magnetochemical properties of these classes of compounds have been analysed and the inversion of the superexchange pathways from the  $\mu_3$ -oxo-bridge to the  $\mu_2$ -oxo-bridge ongoing from the  $[\text{Fe}_4\text{O}_2]^{8+}$  core to the  $[\text{Fe}_4\text{O}_6]^{6+}$  core was demonstrated.

Previously, it was reported the synthesis and characterization of  $\{\text{FeM}_2\}$  [33] (M= Sr, Ba),  $\{\text{Fe}_2\text{MO}\}$  [34-36] (M= Mg, Co, Mn, Co, Ni, Cu, Zn) and  $\{\text{Fe}_3\text{O}\}$  [37] trinuclear clusters based on the salicylate ligand. As a continuation of this research, here it is presented the synthesis and structural investigation of a new "butterfly-like" iron(III) polynuclear carboxylate  $[\text{Fe}_4\text{O}_2(\text{Sal})_4(\text{H}_2\text{O})_6] \cdot 4\text{DMA} \cdot 0.75\text{H}_2\text{O}$  (**1**), where salicylic acid (Sal) is bi-deprotonated.

*Dedicated to the memory of Professor Constantin Turta on the occasion of his 80<sup>th</sup> birthday anniversary. Professor Constantin Turta was an illustrious, correct, and persevering teacher, a remarkable personality who showed a deep responsibility for the veracity of scientific data and whom many people will long remember with gratitude and respect.*

## Experimental

### General procedures

All chemicals were purchased from commercial sources and used as received without further purification.

Starting materials were:  $\text{C}_6\text{H}_4(\text{OH})\text{COOH}$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  (methanol), DMA (*N,N*-dimethylacetamide).

The  $\text{Ni}(\text{SalH})_2 \cdot 2\text{H}_2\text{O}$  salt was synthesized by the interaction of nickel hydroxide with hot aqueous solution of salicylic acid.

### Synthesis of

#### $[\text{Fe}_4\text{O}_2(\text{Sal})_4(\text{H}_2\text{O})_6](\text{DMA})_4(\text{H}_2\text{O})_{0.75}$ (**1**)

The tetranuclear salicylate cluster was synthesised by the reaction of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1.00 g, 2.47 mmol) and  $\text{Ni}(\text{SalH})_2 \cdot 2\text{H}_2\text{O}$  (3.65 g, 9.9 mmol) in the mixture of  $\text{CH}_3\text{OH}$  (20 mL) and DMA (10 mL) according to the previously reported method [34].

After three weeks, dark red crystals of complex **1** formed as rectangular prisms have been separated. Yield: 1.72 g (54% based on iron salt). Calc. for  $\text{C}_{44}\text{H}_{65.48}\text{Fe}_4\text{N}_4\text{O}_{24.74}$  (%): C, 41.62; H, 5.20; N, 4.41; Fe, 17.59. Found: C, 41.32; H, 5.47; N, 4.08; Fe, 17.70.

IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 3098 sh, 3066 sh, 2938 vs, 1619 sh, 1587 vs, 1516 w, 1482 w, 1454 m,

1388 vs, 1336 sh, 1313 sh, 1244 s, 1221 sh, 1192 w, 1159 w, 1145 m, 1060 w, 1032 m, 1020 sh, 962 w, 865 m, 813 m, 758 vs, 704 s, 664 s, 537 m, 491 m, 429 s.

### Physical measurements

*Elemental analysis* of the complexes for C, H, and N, was performed on a Vario EL (III) Elemental Analyzer and for metals on an AAS-1N atomic absorption spectrometer (Carl Zeiss).

The *IR spectrum* was recorded as vaseline mulls on a Perkin-Elmer 100 FT-IR spectrometer at room temperature in the range of 4000-400  $\text{cm}^{-1}$ . Intensities are given as: vs= very strong, s= strong, m= medium, w= weak, vw= very weak, and sh= shoulder.

*X-ray diffraction analysis* of compound **1** was carried out at 293 K on a Nonius Kappa CCD diffractometer using  $\text{MoK}_\alpha$  radiation (graphite monochromator) by  $\omega$ - $2\theta$ -scanning. Unit cell parameters were refined using all experimental data. The intensity integration and scaling were carried out with DENZO and SKALEPACK programs [38]. The structure of **1** was solved by the direct method and refined by full-matrix least squares in anisotropic approximation for non-hydrogen atoms using SHELX-97 package [39]. The essential experimental details of structure solution and refinement are listed in Table 1.

The deposition number CCDC 2021457 contains the supplementary crystallographic data for this contribution. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](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 [deposit@ccdc.ca.ac.uk](mailto:deposit@ccdc.ca.ac.uk)).

## Results and discussion

The IR spectrum of **1** comprises various bands in the region 3098-3066  $\text{cm}^{-1}$  which are conditioned by valence oscillations  $\nu(\text{OH})$  of co-crystallized water molecules and salicylate anions, ones being involved in hydrogen bond; 2938  $\text{cm}^{-1}$  to  $\nu(\text{CH})$ , benzene ring of salicylic ion,  $\text{Sal}^{2-}$  and methyl groups of DMA).

The characteristic band for the carbonyl group at 1655  $\text{cm}^{-1}$  presented in the spectrum of free salicylic acid is no longer present in the complex spectrum and two new absorption bands appear, which are characteristic for the asymmetric and symmetric carboxylate stretching vibrations of the salicylate anions  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  at 1587 and 1388  $\text{cm}^{-1}$ , respectively [40].

Table 1

**Crystallographic parameters and the data collection statistics for complex [Fe<sub>4</sub>O<sub>2</sub>(Sal)<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]·4DMA·0.75H<sub>2</sub>O.**

Parameters	Value
Empirical formula	C <sub>44</sub> H <sub>65.5</sub> Fe <sub>4</sub> N <sub>4</sub> O <sub>24.75</sub>
Formula weight, <i>M</i>	1269.903
Temperature (K)	293(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>Z</i>	2
<i>a</i> (Å)	10.5350(3)
<i>b</i> (Å)	11.8840(3)
<i>c</i> (Å)	21.7830(5)
$\beta$ (°)	101.536(1)
<i>V</i> (Å <sup>3</sup> )	2672.10(12)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.578
$\mu$ (mm <sup>-1</sup> )	1.152
<i>F</i> (000)	1319.0
Crystal size (mm <sup>3</sup> )	0.15×0.15×0.1
2 $\theta$ range (°)	4.92–50.04
Limiting indices	-12≤ <i>h</i> ≤12 -14≤ <i>k</i> ≤14 -25≤ <i>l</i> ≤25
Reflections collected	8449
Reflections with [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	4648
Data/restraints/ parameters	4648 / 20 / 330
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.044
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0553, <i>wR</i> <sub>2</sub> = 0.1472
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	<i>R</i> <sub>1</sub> = 0.0607, <i>wR</i> <sub>2</sub> = 0.1520
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.85 and -0.81

The  $\Delta = [\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)]$  is about 200 cm<sup>-1</sup>, which indicates the ligands bidentate-bridging mode. The strong band at 1457 cm<sup>-1</sup> is attributed to a  $\nu(\text{C}=\text{C})$  stretching vibrations of the aromatic rings [40,41]. The carbonyl stretching vibration frequency  $\nu(\text{C}=\text{O})$  in the spectra of compound **1** was lowered by ~32 cm<sup>-1</sup> compared to  $\nu(\text{C}=\text{O})$  of free salicylic acid. The band at 1623 cm<sup>-1</sup> is attributed to  $\nu(\text{C}=\text{O})$  DMA.

Finally, in the low-frequency regions, the strong bands at 758 and 704 cm<sup>-1</sup> could be attributed to the  $\pi(\text{CH})$  vibrations of the aromatic hydrogen atoms. According to the description by Nakamoto, K. [40], Telijenskaya, P.N. [41], Johnson, M.K. *et al.* [42], the two medium bands at 537, 490 cm<sup>-1</sup> could be assigned to the  $\nu_{\text{as}}$  and  $\nu_{\text{s}}$  vibrations of Fe<sup>III</sup>- $\mu_3\text{O}$  bonds.

According to X-ray crystallography data, compound **1** has a molecular crystal structure, built up from tetranuclear [Fe<sub>4</sub>O<sub>2</sub>(Sal)<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>] neutral units, DMA, and water co-crystallized solvent molecules in 1:4:0.75 molar ration. As illustrated in Figure 1, four iron centres arranged in a “chairlike butterfly” conformation are connected by two oxygen bridges. Selected bond lengths and angles are summarized in Table 2.

The molecular structure of compound **1** is characterized as a “butterfly” tetranuclear entity, where four iron(III) atoms are bound *via* two  $\mu_3$ -oxygen bridging atoms, and four salicylate bridging ligands. The coordination polyhedron of two iron atoms is completed by six water molecules. Two symmetrical iron atoms, Fe1 and Fe1(symmetry code: *I*-*x*, 2-*y*, *I*-*z*) separated at 5.395(6) Å, are located along the “body” of the “butterfly”, while the other two atoms Fe2 and Fe2(symmetry code: *I*-*x*, 2-*y*, *I*-*z*) at 3.224(6) Å are positioned at the tip of the “wings” bridging with  $\mu_3\text{-O}$  (O<sub>4</sub>, O<sub>4</sub>(symmetry code: *I*-*x*, 2-*y*, *I*-*z*)) atom. All the salicylic acid ligands are bi-deprotonated and behave as bridging ligands coordinated in  $\mu_2\text{-}\eta^2\text{:}\eta^1$  mode.

The O<sub>6</sub> slightly distorted octahedral geometry for the two iron atoms (Fe2, Fe2<sup>1</sup>) is provided by two  $\mu_3$ -oxygen atoms, two monodentate bridging carboxylate groups, and two deprotonated oxygen atoms from hydroxyl groups, while for the other two atoms (Fe1, Fe1<sup>1</sup>) by one  $\mu_3$ -oxygen atom, two monodentate bridging carboxylate groups, and three water molecules.

The central part of the tetranuclear unit comprises a  $\{\text{Fe}_4\text{O}_2\}^{8+}$  core, the topology of which can be described as two edge-sharing  $\{\text{Fe}_3(\mu_3\text{-O})\}^{7+}$  triangular subunits, where four  $\eta^1:\eta^2:\mu_2$  Sal<sup>2-</sup> ligands bridge the iron atoms.

The bridges involving O1 and O5 atoms have very similar geometries; Fe2-O5 and Fe2-O1, of 2.023(3) and 2.019(3) Å, do not differ significantly, Fe1-O5<sup>i</sup> and Fe1-O1, 2.104(3) and 2.102(3) respectively, are also very similar (Table 2, Figure 2). The angles between Fe1-O4-

Fe2 and Fe1-O4-Fe2<sup>i</sup> are 100.02(12) and 100.76(12)° respectively, and the angles between Fe2-O1-Fe1 of 99.13(12)° and Fe2-O5-Fe1<sup>i</sup> of 99.60(12)°, are also effectively identical.

The body-wingtips Fe...Fe pairs are bridged by four carboxylate groups from salicylic acid in the *syn-syn* binding mode. Each iron atom at the tips complete its coordination sphere with three water molecules. The hydroxyl groups of salicylic acid are deprotonated and form hydrogen bonds with oxygen atom from a water molecule.

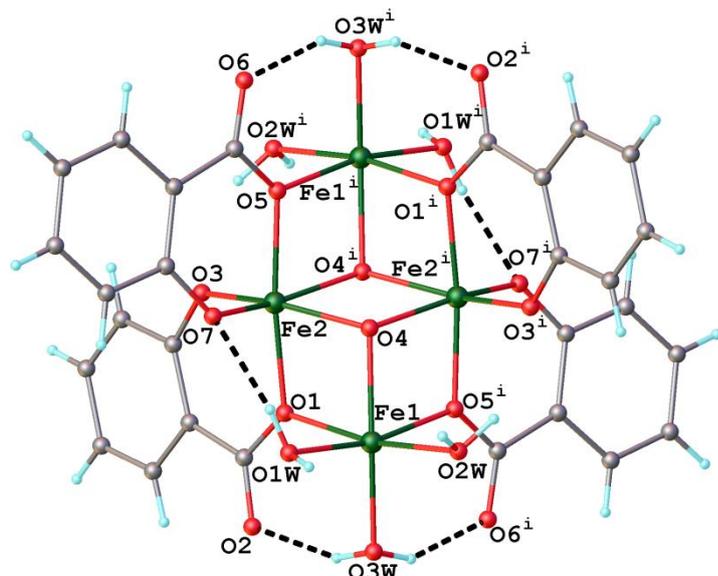


Figure 1. X-ray molecular structure of tetranuclear unit  $[\text{Fe}_4\text{O}_2(\text{Sal})_4(\text{H}_2\text{O})_6]$  (1). Symmetry transformations used to generate equivalent atoms: *I-x*, *2-y*, *I-z*.

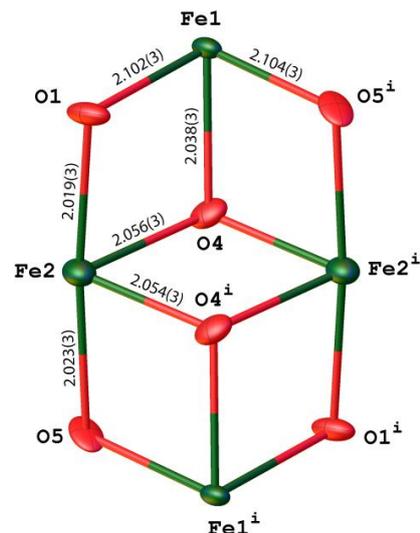


Figure 2. Structure of the  $[\text{Fe}_4\text{O}_6]^{6+}$  core including Fe-O bond distance. Symmetry transformations used to generate equivalent atoms: *I-x*, *2-y*, *I-z*.

Table 2

Selected bond lengths and angles for complex 1.

Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)	Bond	<i>d</i> (Å)
Fe1-O1	2.102(3)	Fe1-O4	2.038(3)	Fe2-O4 <sup>i</sup>	2.054(3)
Fe1-O1 <sub>w</sub>	2.037(3)	Fe1-O5 <sup>i</sup>	2.104(3)	Fe2-O4	2.056(3)
Fe1-O2 <sub>w</sub>	2.060(4)	Fe2-O1	2.019(3)	Fe2-O5	2.023(3)
Fe1-O3 <sub>w</sub>	2.018(3)	Fe2-O3	1.913(3)	Fe2-O7	1.916(3)
Angle	$\omega$ (°)	Angle	$\omega$ (°)	Angle	$\omega$ (°)
O1 <sub>w</sub> -Fe1-O1	86.57(12)	O4-Fe1-O2 <sub>w</sub>	91.04(13)	O5-Fe2-O4	95.45(11)
O1 <sub>w</sub> -Fe1-O2 <sub>w</sub>	93.86(17)	O4-Fe1-O5 <sup>i</sup>	78.84(11)	O5-Fe2-O4 <sup>i</sup>	80.36(11)
O1 <sub>w</sub> -Fe1-O4	90.23(12)	O5 <sup>i</sup> -Fe1-O1	91.12(11)	O7-Fe2-O1	96.38(12)
O1 <sub>w</sub> -Fe1-O5 <sup>i</sup>	169.07(12)	O1-Fe2-O4	80.66(11)	O7-Fe2-O4	90.07(13)
O2 <sub>w</sub> -Fe1-O1	170.18(13)	O1-Fe2-O4 <sup>i</sup>	93.35(11)	O7-Fe2-O4 <sup>i</sup>	161.90(13)
O2 <sub>w</sub> -Fe1-O5 <sup>i</sup>	86.61(16)	O1-Fe2-O5	173.28(11)	O7-Fe2-O5	89.07(13)
O3 <sub>w</sub> -Fe1-O1	94.47(12)	O3-Fe2-O1	88.97(12)	Fe2-O1-Fe1	99.13(12)
O3 <sub>w</sub> -Fe1-O1 <sub>w</sub>	96.41(13)	O3-Fe2-O4 <sup>i</sup>	92.62(13)	Fe1-O4-Fe2	100.02(12)
O3 <sub>w</sub> -Fe1-O2 <sub>w</sub>	95.24(14)	O3-Fe2-O4	164.37(13)	Fe1-O4-Fe2 <sup>i</sup>	100.76(12)
O3 <sub>w</sub> -Fe1-O4	170.52(12)	O3-Fe2-O5	93.67(13)	Fe2 <sup>i</sup> -O4-Fe2	103.53(12)
O3 <sub>w</sub> -Fe1-O5 <sup>i</sup>	94.41(12)	O3-Fe2-O7	102.75(14)	Fe2-O5-Fe1 <sup>i</sup>	99.60(12)
O4-Fe1-O1	79.14(11)	O4 <sup>i</sup> -Fe2-O4	76.47(12)		

Symmetry transformations used to generate equivalent atoms: *I-x*, *2-y*, *I-z*.

In the crystal, all the components are interconnected *via* intermolecular O-H...O hydrogen bonds. Thus, the crystal structure can be described as the packing of discrete associates constituted by hydrogen-bonded tetranuclear molecules and DMA as well as H<sub>2</sub>O solvent molecules.

Depending on the arrangement of the iron atoms within the tetranuclear cluster, {Fe<sub>4</sub>(μ<sub>3</sub>-O)<sub>2</sub>}<sup>8+</sup> can be described as in “bent”, “planar”, or “chairlike” configuration [15,27,29]. However, in some cases, the planar and “chairlike” forms could not be clearly distinguished. The X-ray diffraction study has revealed that compound **1** is stabilized in the “chairlike” form.

### Conclusions

The new tetranuclear complex [Fe<sub>4</sub>O<sub>2</sub>(Sal)<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]·4DMA·0.75H<sub>2</sub>O containing the salicylate ligand was designed and synthesized using the Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ni(SalH)<sub>2</sub>·2H<sub>2</sub>O salts mixture. The obtained compound was characterized by single-crystal X-ray diffraction technique and IR spectroscopy.

The results revealed that the tetranuclear entity contains a {Fe<sub>4</sub>(μ<sub>3</sub>-O)<sub>2</sub>}<sup>8+</sup> core comprising four Fe<sup>III</sup> atoms in a “butterfly” arrangement and two μ<sub>3</sub>-O ions bridging each Fe<sup>III</sup> “wing”. The IR data are in good agreement with the obtained structure.

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