

Vibrational properties of the mixed-valence iron oxo-complex



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ABSTRACT

The room temperature Raman and infrared studies of the tribridged oxo-iron complex $(\text{NH}_4)_2\{[\text{Fe}^{\text{III}}(\mu_3\text{-O})(\text{HCOO})_6]_2[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2(\text{HCOO})_6]\}$ (**oxoFeFe**) were performed and the proposed assignment of the observed vibrational modes has been presented. The studied mixed-valence compound crystallizes in P-1 space group and is constructed from triangular units $\text{Fe}_3^{\text{III}}\text{O}$ and divalent iron ions linked by formate anions. We prove that using the hydrothermal synthesis with a mixture of acetonitrile and propylamine as a solvent can be an alternative method to obtain the oxoFeFe material. The phase purity of the studied crystal is confirmed by its powder XRD pattern.

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1. Introduction

Oxo-bridged diiron complexes have attracted a lot of attention due to the presence of Fe—O—Fe moiety, which is known as an active site of many biological systems, particularly in non-heme metalloproteins such as methane monooxygenase, hemerythrin and ribonucleotide reductase [1–3]. However, the mechanism of enzyme action is unclear and scientists have synthesized a number of novel oxo-bridged compounds in a variety of iron oxidation states to better understand the properties of these biological materials. The most extensively studied materials are diiron(III) complexes of general formula $(\mu\text{-oxo})\text{L}_2\text{Fe}_2$ (where L = ligand) and homometallic mixed-valence analogues [4,5]. These complexes have been used as a catalyst for alkane hydroxylation and oxidation of various organic reagents. It was shown that $\mu\text{-oxo}$ dinuclear iron compounds affect the increase of selectivity and rate of these reactions [6–9], though, the cleavage of Fe—O—Fe bridge reduces their catalytic activity [10,11]. One of the possibilities to stabilize the oxo-bridge is an encapsulation in porous media [11].

In the past twenty years there has also been an increase in the number of publications about the oxo-carboxylate-bridged iron trinuclear complexes of the composition $[\text{Fe}_3\text{O}(\text{RCOO})_6(\text{L})_6]\text{S}$, where R = alkyl, L = ligand and S = solvate molecule [12–17]. These materials are appropriate models for investigating the electron

transfer in mixed-valence $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}$ compounds [18–22]. It is well known that the size and shape of the used solvent molecule can increase the rate of intramolecular electron transfer [23].

The examination of iron complexes with carboxylate bridging ligands also allows scientists to enhance their knowledge about magnetic metal-metal interactions. Very recently, Wu et al. has synthesized three novel oxo-complexes of general formula $(\text{NH}_4)_2\{[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\text{HCOO})_6]_2[\text{M}^{\text{II}}(\text{H}_2\text{O})_2(\text{HCOO})_6]\}$ (where $\text{M}^{\text{II}} = \text{Mn, Mg, Fe}$) [24]. These compounds are built of triangular Fe^{III} -carboxylate trimeric units $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\text{HCOO})_6]^+$ and divalent metal ions linked by formate anions. The use of magnetically frustrated triangles $\text{Fe}_3^{\text{III}}\text{O}$ and another spin carrier such as Mn^{II} and Fe^{II} yields chain complexes in which antiferromagnetic interactions as well as remarkable frustration is found. Moreover, at low temperatures a ferromagnetic-like transition and metamagnetism has been observed in oxoFeFe [24].

In this paper, we will report an alternative way to obtain oxoFeFe crystals. We will show that the use of acetonitrile with propylamine instead of urea solution also leads to the synthesis of the oxo-complex. Since $\mu\text{-oxo}$ compounds are not very common in the literature we have decided to study phonon properties of the obtained representative of this class of materials. Detailed infrared and Raman studies of this compound as well as proposed assignment are presented. Previous vibrational studies of iron-oxo complexes have mostly been based on the resonance Raman spectroscopy [25] and oxoFeFe has not been the subject of vibrational studies.

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2. Experimental

2.1. Materials and instruments

Commercially available FeCl_2 (98%, Aldrich), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98%, Aldrich), acetonitrile (anhydrous, 99.8%, Aldrich), formic acid (98%, POCH) and propylamine (99%, Aldrich) were of analytical grade and used without further purification.

X-ray diffraction powder pattern was recorded at room temperature by using X'Pert PRO powder diffractometer (PANalytical) working in the transmission or reflection geometry, equipped with a linear PIXcel detector and using $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range from 5 to 75° .

2.2. Raman and infrared measurements

Raman spectrum in the range of $3500\text{--}50 \text{ cm}^{-1}$ was measured using a Renishaw InVia Raman spectrometer equipped with confocal DM 2500 Leica optical microscope, a thermoelectrically cooled CCD as a detector, and an argon laser operating at 488 nm. IR spectra were measured for the sample in KBr pellet in the range $3800\text{--}400 \text{ cm}^{-1}$ and in Apiezon N suspension in the range $500\text{--}50 \text{ cm}^{-1}$ with a Biorad 575C FT-IR. The spectral resolution was 2 cm^{-1} in both Raman and IR measurements.

2.3. Synthesis

The oxoFeFe compound was prepared under solvothermal conditions at 140°C . A mixture of FeCl_2 (2 mmol), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (2 mmol), acetonitrile (35 ml), formic acid (25 ml) and propylamine (1.7 ml) was heated in a Teflon-lined microwave autoclave for 24 h. After slow overnight cooling, dark-brown crystals were collected, washed with methanol and dried at room temperature. The applied acidic conditions allowed the hydrolysis of acetonitrile, which lead to the formation of the acetic acid and ammonia [26]. The mechanism of this reaction is shown in Scheme 1. Likewise, the use of propylamine in our synthesis is worth commenting. Our aim was to obtain a mixed-valence formate-framework containing $\text{C}_3\text{H}_7\text{NH}_3^+$ ions in the cavities, which was compatible with our search for novel metal-organic framework possessing electric and/or magnetic properties. However, this synthetic method allowed us to obtain $(\text{NH}_4)_2[\{\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\text{HCOO})_6\}_2\{\text{Fe}^{\text{II}}(\text{H}_2\text{O})_2(\text{HCOO})_6\}]$ crystals instead of $[(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2)[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{HCOO})]]$ ones. It is worth to mention that the approach to produce oxoFeFe compound without use of propylamine has failed. Our synthesis process differs from the one presented by Wu et al., in which a mixture of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, HCOOH and urea is used [24]. In our case a good match of the powder XRD pattern confirms the phase purity of the grown crystals with the simulation from the single-crystal structure determination (Fig. 1).

3. Results and discussion

We would like to make a comparison between our method of synthesizing and the previously reported one [24]. Both approaches are based on the solvothermal conditions at 140°C . An advantage of our synthesis is shorter time of reaction (24 h instead of 48 h), whereas the benefit from Wu's method is the reaction mixture containing less components, which is only formic acid, urea solution and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salt [24]. The oxidation-



Scheme 1. The hydrolysis of acetonitrile under acid conditions.

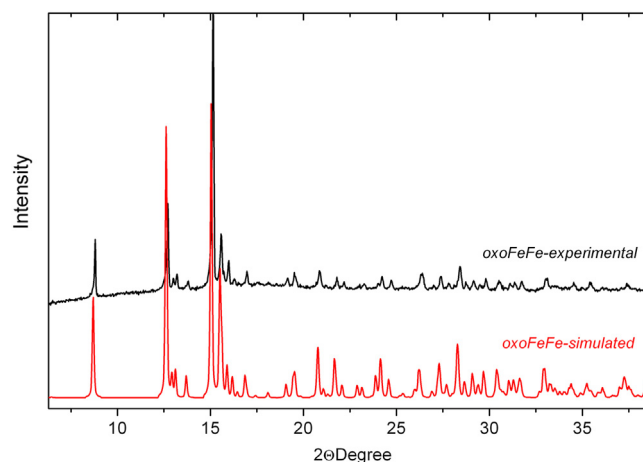


Fig. 1. Powder XRD pattern for the as-prepared bulk sample of oxoFeFe, with the calculated one based on the single crystal structure at 295 K.

reduction properties of the formic acid enable the reduction of Fe^{3+} ions to Fe^{2+} . The yield of our method is about 85% based on the starting FeCl_2 salt. However, there is no information about the yield in Ref. [24].

The correct interpretation of Raman and infrared data requires knowledge of the structure of the measured compounds. Therefore, a brief crystallographic description of the oxo-FeFe is given. This iron complex crystallizes in the triclinic system in the centrosymmetric space group $P\bar{1}$, with $Z=1$ and $a=6.8366$, $b=10.967$ and $c=14.884 \text{ \AA}$ [24]. As it has been mentioned before, the oxo-FeFe compound is built of $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\text{HCOO})_6]^+$ cations and divalent metal ions linked by formate anions. In the case of $[\text{Fe}^{\text{III}}_3(\mu_3\text{-O})(\text{HCOO})_6]^+$ cations unsaturated coordinated Fe^{III} ions are connected by three formate anions, while Fe^{II} ions are connected by four HCOO^- anions and two water molecules. All the atoms except for Fe^{II} are placed in general positions. There is a variety of coordination modes of formate ions in the oxo-FeFe compound. They act as monodentate as well as bidentate ligands in *anti-anti* and *syn-anti* mode of configuration (Fig. 2) [24]. Such

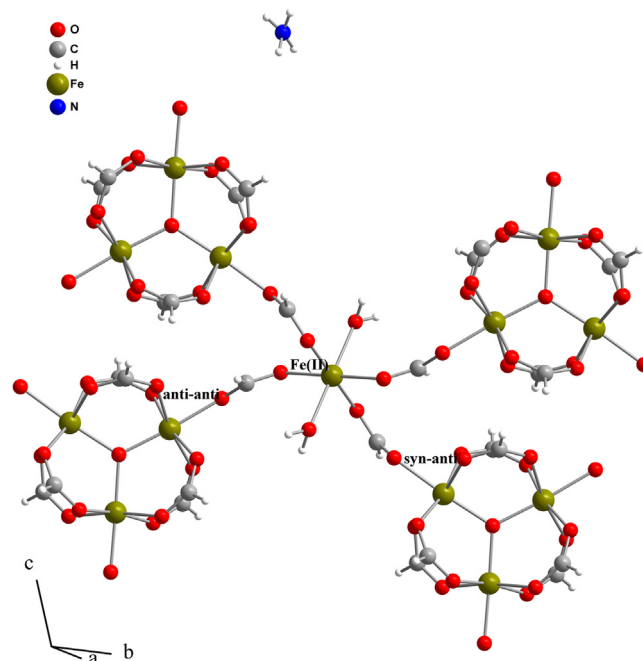


Fig. 2. Structure of oxo-FeFe compound with a linkage of the formate ions.

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