Polyoxometalates

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A Stable "End-On" Iron(III)–Hydroperoxo Complex in Water Derived from a Multi-Iron(II)-Substituted Polyoxometalate and Molecular Oxygen**

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The complexation and activation of molecular oxygen by iron(II) complexes is of fundamental importance in the context of both oxidation catalysis and biology. Earlier research into iron(II)–heme–dioxygen complexes was related to the oxygen transport functions of hemoglobin and myoglobin, which was successfully modeled in many synthetic porphyrin compounds.[1] The common motif in these studies was the formation of "end-on" species with Fe-O-O angles of approximately 130° in apolar environments, as found in the proteins. Much current interest is related to iron-based enzymes, many of which, according to the well-known postulate, involve a key step of O_2 complexation to a mono- or diiron(II) species and subsequent reduction to superoxo and peroxo species. The isolation of such intermediates is rather rare, but several recent examples have shown such complexes in oxygenases[2] and a superoxidase.[3] The active sites often contain water molecules, presumably to facilitate subsequent proton transfer to form further reactive high-valent intermediates, which may also be stabilized by hydrogen bonding.[4] In nonheme model systems, the isolation of presumed intermediate dioxygen complexes has also been relatively rare. In some cases diiron(III) μ-peroxo intermediates have been identified,[5] and spectroscopic evidence has also been found for an iron(III) superoxo species.[6] To our knowledge, "end-on" monoiron dioxygen species have to date not been isolated in synthetic nonheme complexes.

Polyoxometalates provide intriguing possibilities for the study of transition-metal reactivity in a purely oxo-ligand environment and also in aqueous media as opposed to the nitrogen-ligand environment typically studied in synthetic heme and nonheme compounds.[7] Catalysts have been developed for reactions using either H_2O_2 or O_2 among others as oxidants.[8] In the context of this research, numerous multi-iron-containing polyoxometalates were prepared,[9] and there are also examples of oxidation using O_2 and H_2O_2.[10] Some "side-on" peroxo compounds of tungsten, niobium, and zirconium, derived from H_2O_2 have also been prepared.[11] Mechanistic understanding of O_2/polyoxometalate reactions has been based mostly on spectroscopy and kinetic studies; for example, a recent report on the outer-sphere reduction of O_2 with reduced polyoxotungstates devoid of low-valent substitution of transition metals.[12] Herein, we report the isolation and characterization of an "end-on" $\{Fe^{III}–O_2\}$ polyoxometalate-based compound in water with unusual properties. The compound is stabilized by hydrogen bonding and is derived from a reaction between a multi-iron(II) polyoxometalate and O_2.

A brown-black sandwich-type polyoxometalate with six iron(II) atoms, $Na_{16}[Fe_4(H_2O)_2(FeW_9O_{34})_2]\cdot46\,H_2O$ (**1**), was prepared by reacting $Na_2WO_4\cdot2\,H_2O$ with $FeCl_2\cdot4\,H_2O$ in water under argon at pH 7 (adjusted with glacial acetic acid, Figure 1). The compound is isostructural with a similar iron(III) compound reported by Krebs and co-workers.[13] The polyanion consists of two $[Fe^{II}W_9O_{34}]^{12-}$ moieties that can be described as α-B-isomers of the defect Keggin anion. These units are linked by a belt of four $\{Fe^{II}O_6\}$ groups. The octahedral coordination spheres of the two terminal Fe^{II} atoms are filled by one additional water ligand. Crystallized **1** was redissolved in water and recrystallized in air at 4 °C to afford a yellow iron(III) polyoxometalate (see below), $Na_{12}[Fe_4(O_2)_2(FeW_9O_{34})_2]\cdot52\,H_2O$, (**2**) with a coordinated dioxy-

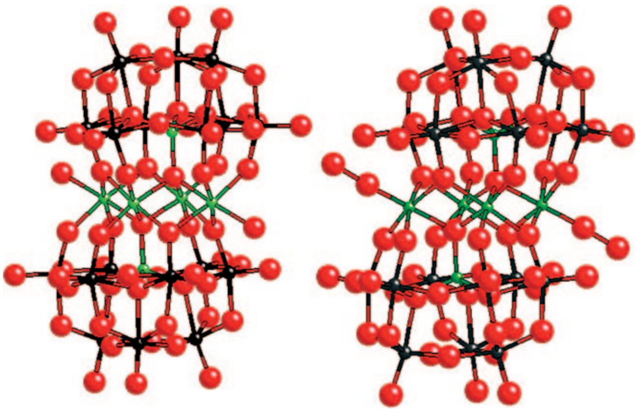

Figure 1. Ball-and-stick models of $Na_{16}[Fe_4(H_2O)_2(FeW_9O_{34})_2]\cdot46\,H_2O$ (**1**) and $Na_{12}[Fe_4(O_2)_2(FeW_9O_{34})_2]\cdot52\,H_2O$ (**2**), both with C_{2h} idealized symmetry (Fe green, O red, W black; only the anion is shown; water molecules and sodium atoms are omitted for clarity).

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gen entity (Figure 1). Similar to the parent compound **1**, the polyanion consists of two defect α-B-isomers, linked by a belt of four {FeO_6} groups. However, in contrast to **1**, dioxygen is coordinated "end-on" to the two terminal iron atoms. The two {Fe–O–O} units, which are the same by symmetry, have Fe–O bond lengths of 1.920(5) Å, long O–O bond lengths of 1.612(9) Å and nearly linear Fe-O-O bond angles of 175.3(4)°.

Figure 2 shows the isolated {Fe–O–O} unit and its nearest neighbor atoms (within 3 Å distance). The Fe atom exhibits an approximately regular octahedral coordination environment; O27, O30, O35, and O36 are the equatorial oxygen atoms and O34 and the coordinated O_2 molecule (O10, O11) are the axial ligands. Importantly, the coordinated O_2 is stabilized through hydrogen bonding by three coordinated water molecules, represented by O38, O41, and O62.[14]

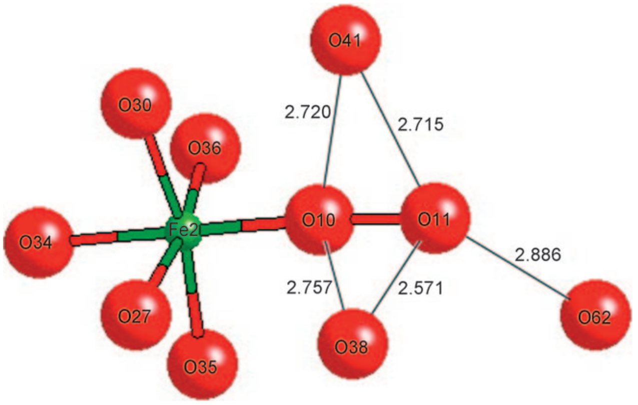

Figure 2. The coordination environment of the {Fe–O–O} unit without the polyoxometalate framework, showing also the water molecules (O38, O41, O62) hydrogen bonded to the coordinated O_2.

The X-ray crystal structure and the elemental analysis both indicated the presence of 16 and 12 sodium atoms per polyanion in **1** and **2**, respectively. However, the oxidation states of iron in **1** and **2** were not revealed by direct measurement. To further characterize the {Fe–O–O} unit, and to differentiate between iron(II)–dioxygen, iron(III)–superoxo, and iron(III)–peroxo formulations, it was important to first determine the oxidation state of iron. Since Mössbauer measurements were not possible, owing to absorption by tungsten, we used a relatively new and little-used method, electron energy-loss spectroscopy (EELS). Energy-loss near-edge structure (ELNES) analysis of the L-ionization edges of iron showed characteristic white lines, corresponding to the transition of the excited 2p core electrons into unoccupied d orbitals. The white-line intensity ratio, L_3/L_2 varied with d-electron occupancy, and thus could be used to determine the oxidation state of iron.[15] We carried out EELS measurements for reference samples ($FeCl_2$ and Fe_2O_3) as well as compounds **1** and **2** (Figure 3, L_3/L_2 ratios are summarized in Table 1). The measurements clearly show that **1** is an all-iron(II) polyoxometalate whereas as **2** is an all-iron(III) polyoxometalate.[16]

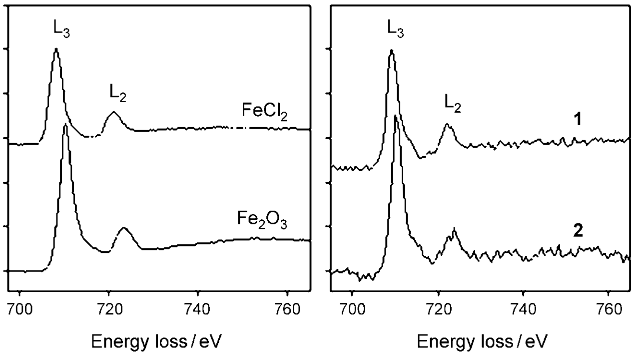

Figure 3. EELS measurements with ELNES analysis of **1**, **2**, and relevant reference samples.

Table 1: L_3/L_2 ratios calculated from the EELS measurements (Figure 3).

Compound	L_3/L_2	Compound	L_3/L_2
$FeCl_2$	4.0 ± 0.1	Fe_2O_3	5.35 ± 0.1
1	4.0 ± 0.25	**2**	5.35 ± 0.35

The UV/Vis spectra of **1** and **2** are very similar and dominated by the strong charge-transfer (CT) bands corresponding to O–W and O–Fe in the polyoxometalate. We were, however, interested in the evolution of the dioxygen-coordinated species, which was elucidated by measurement of difference spectra (Figure 4). The difference spectra show three clear isosbestic points, indicating a clean transformation of **1** to **2** on the measured timescale. The peaks at 206, 235, and 292 nm are associated with the CT bands of the polyoxometalate, and we propose that the peak at 326 nm can be associated with the ligand-to-metal charge-transfer (LMCT) of the {Fe–O–O} group that has an extinction coefficient of absorption ($\varepsilon = 1042\,\text{M}^{-1}\,\text{cm}^{-1}$). It should be noted that neither the Raman nor the IR spectra of **2**, prepared with either $^{16}O_2$ or $^{18}O_2$, showed any clear peaks, expected at around 800 cm^{-1}, associated with a O–O bond of approximately 1.6 Å in length, likely because of the strong absorption associated with the various W–O moieties at 950–550 cm^{-1} (see the Supporting Information).

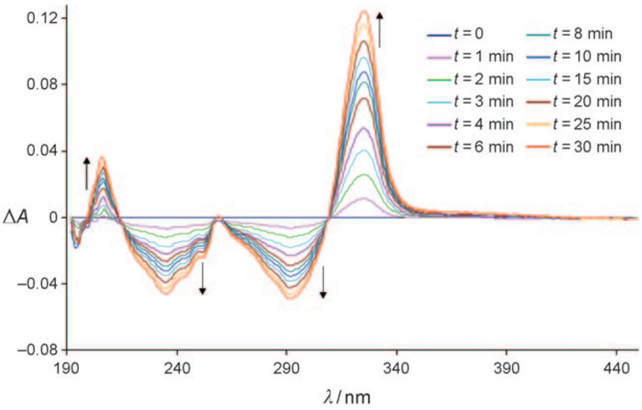

Figure 4. Difference spectra showing the evolution of **2** from 6 μM **1** at 25 °C in double distilled water blanketed by 1 bar O_2.

Polyoxometalate **2** is a quite stable compound and can be stored for several months at room temperature with no noticeable decomposition. Its reactivity was tested both as an oxidant and as a reductant. Addition of a series of substrates, such as $P(PhSO_3Na)_3$, dimethylsulfoxide, diethylsulfide, and cyclohexen-2-one to a solution of **2** in water under Ar showed no formation of oxidized species. Furthermore, when I^- was added to **2** in water under Ar, no oxidation to I_2 was detected in the temperature range 25–80 °C. Apparently **2** is neither an oxidant nor a nucleophilic or electrophilic oxygen transfer reagent. Conversely, addition of a tenfold excess of 1,4-benzoquinone to a solution of **2** in water resulted in the formation within 5 min of two equivalents of the $2e^-$-reduced product, 1,4-hydroquinone, indicating that **2** acts as a four-electron reducing agent (two electrons for each $\{FeO_2\}$ unit). Using **2** prepared in the presence of labeled $^{18}O_2$, quantification of the amount of $^{18}O_2$ formed by mass spectrometry showed that indeed one equivalent of $^{18}O_2$ (accuracy to within 10 %) was released per equivalent benzoquinone reduced.

In summary, the structural, analytical, spectroscopic and reactivity data for **2** indicate that it is an all-iron(III) compound with "end-on" coordination of two hydroperoxo moieties at the two terminal positions of the polyoxometalate "belt", $Na_{12}[Fe^{III}_2(Fe^{III}O_2^{2-}H)_2(Fe^{III}W_9O_{34})_2]\cdot 52\,H_2O$. It should be noted that the sum of charges dictates a hydroperoxo rather than a peroxo species. This compound is accessible, because polyoxometalate **1** is a potential six-electron reducing agent, four of which are required for the reduction of the coordinated dioxygen molecules at the two terminal iron positions. Notably, the unusually long O–O bond length is not consistent with that for a superoxo species, which is typically in the range 1.2–1.3 Å for iron compounds.[17] The bond length is more consistent with a (hydro)peroxo species, which typically incorporate O–O bonds in the 1.45–1.55 Å range,[17] although stabilization by multiple hydrogen-bonding interactions with water can lead to additional lengthening of the bond, as shown by computation.[18] This is, to our knowledge, the first example of an "end-on" iron hydroperoxo species crystallized in a synthetic compound from O_2,[19] although such a species has been identified in superoxide reductase with H_2O_2.[3] The almost linear Fe-O-O bond angle is also apparently unprecedented and is likely to be a result of the hydrogen bonding mode and also repulsive interactions arising from the high negative charge of the polyoxometalate. A space-filling model based on van der Waals radii of **2** shows a crowded structure that perhaps enforces the linear bond angle (see the Supporting Information). $Na_{12}[Fe^{III}_2(Fe^{III}O_2^{2-}H)_2(Fe^{III}W_9O_{34})_2]\cdot 52\,H_2O$ was stable in water and did not react as an oxidant. It did, however, efficiently reduce benzoquinone. A possible explanation of this reactivity suggests that the $\{FeO_2H\}$ moiety could act as a nucleophile, which has precedent in aromatase enzymes and related model iron porphyrin peroxo compounds.[20] However, a $\{FeO_2H\}$ moiety substituted in a polyoxometalate species would be expected to be very weakly nucleophilic, because of the high negative charge polarization of the structure, which leads to the propensity of electron-transfer reactions in polyoxometalate compounds. Therefore, in this case a reduction reaction occurs rather than a substitution reaction that would have yielded the epoxide of 1,4-benzoquinone.

Experimental Section

1: $Na_2WO_4\cdot 2\,H_2O$ (5 g, 0.015 mol) was dissolved in double-distilled water (DDW, 10 mL) and the pH was altered to 7 by with glacial acetic acid. The solution was heated to 85 °C and $FeCl_2\cdot 4\,H_2O$ (0.298 g, 0.0015 mol), dissolved in a minimum amount of DDW, was added dropwise. The resulting brown suspension was stirred for 30 mins, until it became black. After removal of solids by filtration, the filtrate was left at pH 6.7 under Ar at ambient temperature for two days, resulting in the crystallization of **1** as brown-black needles(95 mg, 6.4 %). Elemental analysis (Na, Fe by atomic absorption, W as WO_3, and H_2O by thermogravimetry) calcd (%) for $Na_{16}[Fe_4(H_2O)_2(FeW_9O_{34})_2]\cdot 46\,H_2O$: Na 6.17, W 55.48, Fe 5.62, H_2O 13.89; found: Na 6.21, W 55.35, Fe 5.71, H_2O 13.70.

2: A black solution of **1** in water was stored under air at 4 °C. Over several weeks, the solution turned yellow, and crystals of **2** formed as yellow-brown needles (80 mg, 84.2 %). Elemental analysis calcd (%) for $Na_{12}[Fe^{III}_2(Fe^{III}O_2^{2-}H)_2(Fe^{III}W_9O_{34})_2]\cdot 52\,H_2O$: Na 4.59, W 55.07, Fe 5.58, H_2O 15.59; found: Na 4.68, W 54.89, Fe 5.50, H_2O 15.50.

Crystal data were collected at 120 K using a Nonius Kappa CCD diffractometer with $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) radiation. The data were processed using Denzo-scalepack.[21] Structures were solved by direct methods with SHELXS.[22] Full-matrix least-squares refinement was based on F^2 with SHELX-97. The crystallographic data are presented in Table 2. For **1**, 94279 (29701 unique) reflections were collected over a range of $\theta = 2.77$–30.52 with $0 \leq h \leq 18$, $-25 \leq k \leq 25$, $-29 \leq l \leq 29$. For **2** 55347 (12900 unique) reflections were collected over a range of $\theta = 3.16$–27.84 with $-16 \leq h \leq 16$, $0 \leq k \leq 34$, $0 \leq l \leq 21$.

Electron Energy Loss Spectroscopy (EELS) Measurements: The samples for EELS measurements were prepared by grinding crystals and suspending the resultant powder in absolute ethanol using an ultrasonic bath. One drop (5 μL) of the suspension was placed on a carbon–copper grid (Quantifoil) and blotted after 30 s. Air-sensitive samples were prepared in glove bags under constant flow of Ar gas and immediately introduced into the microscope. EELS measurements were performed on a Tecnai–F30 transmission electron microscope (TEM) operating at 300 keV and equipped with a post-column Gatan Imaging Filter (GIF). The energy spread of the FEG was 0.7 eV (FVHM of the zero-loss peak). EELS spectra were recorded in diffraction mode at a camera length of 90 mm and at a dispersion of 0.3 eV/channel. The convergence angle and collection angle were $2\alpha = 5$ mrad and $2\beta = 13$ mrad respectively. Spectra were recorded on

Table 2: Crystal data and structure refinement for compounds **1** and **2**.

Compound	1	2
Formula	$Fe_6Na_{16}O_{108}W_{18}$	$Fe_6Na_{12}O_{124}W_{18}$
M_r	5740.24	5904.28
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a [Å]	13.0620(1)	12.641(3)
b [Å]	17.8501(2)	26.281(5)
c [Å]	20.9796(3)	16.142(3)
β [°]	93.1976(4)	92.75(3)
V [Å^3]	4884.01(10)	5356.5(18)
Z	2	4
ρ_{calc} [mg cm^{-3}]	3.903	3.661
μ [mm^{-1}]	22.158	20.206
R [$I > 2\sigma(I)$]	$R_1 = 0.0406$ $wR_2 = 0.0964$	$R_1 = 0.0336$ $wR_2 = 0.0760$
R (all data)	$R_1 = 0.0660$ $wR_2 = 0.1054$	$R_1 = 0.0467$ $wR_2 = 0.0797$

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{1/2}$.

a thin area of the crystalline grains. About 10–15 grains were measured for each sample with an acquisition time of 30 s per measurement. Ratios of white-line intensities were carried out using a script (written by David Mitchell, ANSTO Materials) from Digital Micrograph database. This script calculates the second derivative of an EELS spectrum and from that, the positive component. The positive component is analyzed to determine the presence and location of peaks. The energy of these peaks and their integral is then calculated and displayed (Table 1).

Supporting Information for this article (various presentations of the structure of **2**, Raman, and IR spectra, and magnetic measurements) is available on the WWW under http://www.angewandte.org or from the author. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-419347 and CSD-419348.

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