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Monomeric Iron(II) Hydroxo and Iron(III) Dihydroxo Complexes Stabilized by Intermolecular Hydrogen Bonding

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Using the multidentate ligand bis(*N*-methylimidazol-2-yl)-3-methylthiopropanol (**L**), the mononuclear iron(II) hydroxo and iron(III) dihydroxo complexes $[Fe^{II}(\mathbf{L})_2(OH)](BF_4)$ (**1**) and $[Fe^{III}(\mathbf{L})_2(OH)_2](BF_4)$ (**2**) have been synthesized and characterized by X-ray diffraction and spectroscopic methods. The X-ray data suggest that the remarkable stability of the Fe–OH bond(s) in both compounds results from intermolecular hydrogen-bonding interactions between the hydroxo ligand(s) and the tertiary hydroxyl of the **L** ligands, which prevent further intermolecular reactions.

Mononuclear non-heme iron proteins are involved in various biological processes.[1] On the basis of X-ray diffraction and spectroscopic studies, iron centers with terminal hydroxo ligands (Fe−OH) are proposed to be the active species in many catalytic cycles of enzymes including protocatechuate 3,4-dioxygenase,[2] lipoxygenases,[3] acid phosphatases,[4] and iron-containing nitrile hydratases.[5] It is often suggested that hydrogen bonds between the hydroxo ligand and neighboring amino acid residues play a key role in stabilizing the Fe−OH unit. For instance, X-ray diffraction data (1.7 Å) on iron-containing nitrile hydratases show that the α-Ser[113], β-Arg,[56] and β-Arg[141] residues form a hydrogen-bond network interacting with the $[Fe^{III}N_2S_3(OH)]$ ($[Fe^{III}N_2S_3(NO)]$) metal site of the active (inactive) form of the enzyme.[5b]

Synthesizing the mononuclear Fe−OH moiety (especially Fe^{III}−OH) is a challenge because of its strong propensity to form multinuclear hydroxo- and oxo-bridged complexes. Presumably for this reason, non-heme monomeric Fe−OH complexes are rather scarce. To the best of our knowledge, only five X-ray structures of such complexes have been reported (two with a Fe^{II} ion[6,7a] and three with a Fe^{III} ion[7b,8]). Moro-oka et al. have isolated the first Fe^{II}−OH complex ($[(Tpz^{tBu,iPr})Fe^{II}-OH]$) by using a bulky tris(pyrazolyl)borate derivative ligand ($Tpz^{tBu,iPr}$).[6] Watanabe et al. have reported the mononuclear six-coordinate Fe^{III}−OH complexes ($[Fe^{III}(tnpa)(OH)(RCO_2)]^+$; R = C_6H_5, CH_3), with a hindering tris(2-pyridylmethyl)amine derivative ligand (tnpa), which provides an intramolecular hydrogen-bonding cavity to protect the Fe^{III}−OH bond.[8] Borovik et al. have recently developed a bulky deprotonated urea-derived ligand (H_3buea), which, as in the case of tnpa, stabilizes the Fe−OH units by steric hindrance and intramolecular hydrogen bonds forming a protective cavity.[7]

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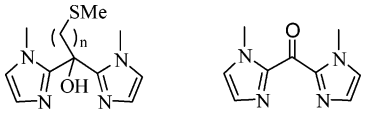
Chart 1



n = 1: $\mathbf{L^a}$
n = 2: **L**

Me_2-BIK

During the past few years, we have synthesized iron complexes with polyimidazole ligands as mimics of the active sites of non-heme metalloproteins including histidine residues.[9] Recently, we have investigated the coordination behavior of the new multidentate ligand $\mathbf{L^a}$ (Chart 1) with $Fe^{2+/3+}$. $\mathbf{L^a}$ was shown to be unstable because, in the presence of $Fe^{2+/3+}$, in aerated MeOH it undergoes an iron-assisted radical C−C bond cleavage to form bis(*N*-methylimidazol-2-yl) ketone (**Me_2-BIK**; Chart 1).[9c]

Herein we report, using **L** (Chart 1), the first mononuclear iron(II) hydroxo and iron(III) dihydroxo complexes, $[Fe^{II}(\mathbf{L})_2(OH)](BF_4)$ (**1**) and $[Fe^{III}(\mathbf{L})_2(OH)_2](BF_4)$ (**2**), stabilized by an *intermolecular* hydrogen-bonding assembly.

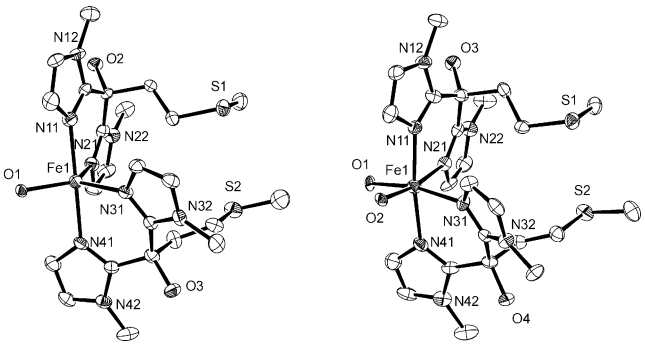


Figure 1. ORTEP views (50% probability) of $[Fe^{II}(\mathbf{L})_2(OH)]^+$ (**1**, left) and $[Fe^{III}(\mathbf{L})_2(OH)_2]^+$ (**2**, right). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): see Table S2 (Supporting Information).

L was synthesized in one step in a manner similar to that of $\mathbf{L^a}$ (see the Supporting Information). Under an argon atmosphere, the reaction of **L** with $Fe(BF_4)_2 \cdot 6H_2O$ in degassed MeOH in a 3:1 molar ratio led to the formation of **1**. Single crystals of **1** were obtained by slow diffusion of EtOAc into a solution of the crude product in MeOH, at 25 °C, for ca. 1 month in a glovebox. An ORTEP view of the cation in **1** is shown in Figure 1 (left). The presence of one BF_4^- counteranion per iron indicates that the iron is in the II+ oxidation state. The methyl thioether moiety is not involved in coordination. The iron center possesses an N_4O coordination sphere with an almost perfect bipyramidal-trigonal geometry ($\tau = 0.95$).[10] Two **L** ligands bind to the iron center in a N_2-bidentate fashion, and the coordination sphere is completed with one hydroxo ligand. The Fe−N distances ranging from 2.105(5) to 2.150(5) Å are comparable to those found in high-spin (HS) ($S = 2$) Fe^{II} complexes of polyimidazole ligands.[9b,c] The Fe1−O1 bond length of **1** is 1.938(3) Å, between 1.830(8) and 2.051(3) Å, the two values reported for the only examples of monomeric Fe^{II}−OH complexes.[6,7a]

The Mössbauer spectrum of **1** (solid state) consists of a single quadrupole doublet with parameters [$\delta = 1.069(2)$; $\Delta E_Q = 3.489(3)$ mm s^{-1} at 80 K; see the Supporting Information] that are typical of a HS Fe^{II} state ($S = 2$),[11] in agreement with the magnetic moment of 4.8−5.2 μ_B (polycrystalline sample) between 10 and 300 K. The ν_{OH} frequency of the coordinated hydroxo is located at 3423 cm^{-1} in the IR spectrum of **1** (KBr pellet), in agreement with the literature data.[7] In dimethylformamide (DMF) at 25 °C, its UV/vis spectrum exhibits an absorption band at 339 nm (ϵ = 2560 L mol^{-1} cm^{-1}) and a shoulder at 296 nm.

In a MeOH solution, **1** is quickly oxidized in air to form the yellow, ferric compound **2**. It slowly crystallized (ca. 1 month) from the MeOH solution. An ORTEP view of the cation in **2** is shown in Figure 1 (right). The presence of one BF_4^- counteranion per iron in the crystal lattice indicates that the iron is in the III+ oxidation state. The iron center possesses a N_4O_2 environment with a distorted octahedral geometry [e.g., 170.14(18)° for the O1−Fe1−N31 angle]. The two **L** ligands maintain their N_2-bidentate coordination as in **1**. Two cis hydroxo anions complete the coordination sphere. As in **1**, the thioether group is not bound to the Fe^{III} center. The Fe−N bond lengths ranging from 2.096(5) to 2.128(5) Å are comparable to the Fe−N imidazole distances found in a HS $[Fe^{III}N_3Cl_3]$ complex [2.111(4)−2.210(4) Å][9a] but much longer than those found for low-spin $[Fe^{III}N_6]$ cores (1.92−2.02 Å).[9a,b] While non-heme Fe^{III}−OH complexes are rather scarce (three crystal structures reported to date[7b,8]), to the best of our knowledge, a mononuclear $Fe^{III}-(OH)_2$ complex has yet to be reported. The Fe1−O1 and Fe1−O2 bond lengths of 1.888(3) and 1.882(4) Å, observed in **2**, are comparable to those found in octahedral HS Fe^{III}−OH complexes.[8] The Fe−O distances are much shorter in **2** than in **1**, indicating an expected stronger coordination of the hydroxo ligand to Fe^{III}.

The X-band electron paramagnetic resonance spectrum of **2** at 10 K in DMF exhibits a signal at $g = 4.23$, typical of a rhombic HS ($S = {}^5/_2$) Fe^{III} complex. The Mössbauer parameters of **2** in the solid state [$\delta = 0.44(2)$; $\Delta E_Q \sim 0$ mm s^{-1} at 80 K; see the Supporting Information] also support a HS Fe^{III} state ($S = {}^5/_2$),[11] in agreement with the magnetic moment of 5.9 μ_B (polycrystalline sample) between 12 and 300 K. The IR spectrum of **2** (KBr pellet) shows an absorption at 3429 cm^{-1} for the ν_{OH} frequency of the coordinated hydroxo anion.[7] In DMF at 25 °C, **2** shows a shoulder at 341 nm in the UV/vis spectrum.

Considering the strong tendency of mononuclear Fe−OH (especially Fe^{III}−OH) species to dimerize, it is noteworthy

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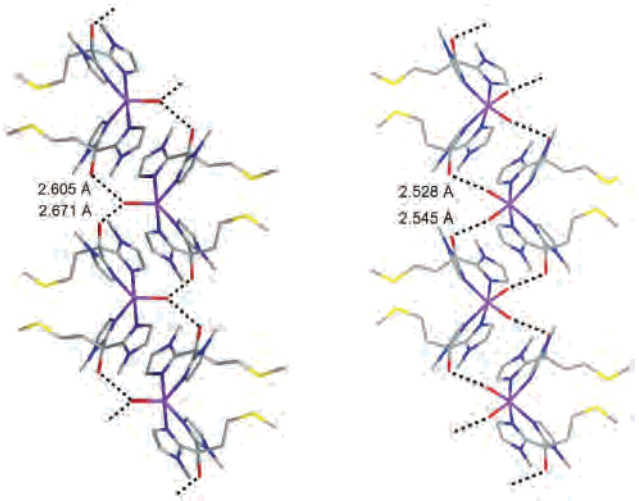

Figure 2. Representation of the intermolecular packing in crystal structures of **1** (left) and **2** (right): hydrogen-bonding networks result in infinite helical chains. The BF_4^- counteranions are omitted for clarity.

that the ligand **L** gives stable monomeric complexes, while it does not present steric bulkiness and is not able to provide an intramolecular hydrogen-bonding cavity to protect the Fe−OH unit. We suggest that the noncoordinated tertiary hydroxyl in **L** plays a key role. The crystal packings (Figure 2) show that in both **1** and **2** the hydroxo ligand(s) is (are) involved in an *intermolecular* hydrogen-bond network. The neighboring complexes are connected to each other through hydrogen bonds, yielding an infinite helical-chain assembly. In **1**, the hydroxo ligand is hydrogen-bonded to the tertiary hydroxyl groups of two **L** ligands of two adjacent complexes, with $O_{hydroxo}-O_{alcohol}$ distances of 2.671 and 2.605 Å. In **2**, the two hydroxo ligands are involved in hydrogen bonds with the tertiary hydroxyl group of one **L** ligand of each adjacent complex, resulting in $O_{hydroxo}-O_{alcohol}$ distances of 2.528 and 2.545 Å, shorter than those formed with **1**. The additional hydroxo ligand in **2** does not appear to disturb the overall crystal packing and even seems to strengthen it, as indicated by the stronger hydrogen bonding in **2** than in **1**. These *intermolecular* hydrogen-bond networks stabilize the $Fe^{II}-OH$ and $Fe^{III}-(OH)_2$ units.

It is well-known that the equilibrium between the mononuclear Fe−OH and the corresponding dinuclear $Fe_2O(H)$ complexes favors largely the latter because of their stability and insolubility. The transformation of a mononuclear species **L**Fe(OH) to a dinuclear species is irreversible unless acidic conditions are employed.[12]

Thus, the fact that **1** and **2** crystallized as *monomeric* species from MeOH for ca. 1 month strongly suggests that these monomers were the species present in solution. Even if one cannot expect a structural intermolecular hydrogen-bond network between the hydroxo ligand(s) and the tertiary hydroxyl of the **L** ligand(s) in solution, the solvent MeOH could bind sufficiently to the terminal hydroxide(s) to prevent the formation of the hydroxo-bridged dimers.

In conclusion, we have isolated two mononuclear $Fe^{II}-OH$ and $Fe^{III}-(OH)_2$ complexes using a one-substituted bis(*N*-methylimidazol-2-yl)methanol-type ligand and $Fe(BF_4)_2\cdot 6H_2O$. Two molecules of this ligand give an N_4 coordination and allow the stable coordination of one hydroxo ligand in **1** and two hydroxo ligands in **2**. Our X-ray data suggest that the remarkable stability of **1**, and particularly **2**, results from hydrogen-bonding interactions between the hydroxo ligand(s) and the tertiary hydroxyl of the **L** ligands. In methanol, hydrogen-bonding interactions with the solvent seem to prevent further intermolecular reactions. The study of biomimetic catalytic reactions of **1** and **2** is under current investigation.

Supporting Information Available: X-ray crystallographic files of **1** and **2** in CIF format and an experimental section (synthesis, fitted Mössbauer spectra, and crystal data collection and refinement parameters). This material is available free of charge via the Internet at http://pubs.acs.org.

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