Preparation of a Carboxylate-binding Mononuclear Iron(II) (−)-Sparteine Complex with Structural Distortion and Its Reaction with Oxidants

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A novel iron complex with a distorted coordination geometry, $[Fe^{II}((-)\text{-sp})(OBz)_2]$ (**1**) ((−)-sp = (−)-sparteine, OBz = benzoate anion), was prepared and structurally characterized by X-ray analysis. The stoichiometric reaction of **1** and *m*CPBA (*m*-chloroperbenzoic acid) degraded EtCN to CN^- and CH_3CHO. In CH_2Cl_2, a very short-lived intermediate species was generated, exhibiting an intense absorption band at 420 nm ($\varepsilon \approx 2000\,M^{-1}\cdot cm^{-1}$) and a weak absorption band at 870 nm ($\varepsilon \approx 100\,M^{-1}\cdot cm^{-1}$).

Recently, it has been reported that high-valent iron(IV) oxo species ($Fe^{IV}{=}O$) is formed in a catalytic cycle of non-heme α-keto acid-dependent enzymes.[1] As the active intermediate models of these enzymes, $Fe^{IV}{=}O$ complexes with tetradentate or pentadentate nitrogen ligands have been characterized by spectroscopic methods and X-ray structure analyses.[2] $[Fe^{IV}{=}O(TMC)(MeCN)]^{2+}$ was the first example of structurally characterized non-heme $Fe^{IV}{=}O$ complexes by X-ray diffraction method.[2b,3] The analogous $Fe^{IV}{=}O$ species, $[Fe^{IV}{=}O(TPA)(CH_3CN)]^+$, $[Fe^{IV}{=}O(N4Py)]^{2+}$, and $[Fe^{IV}{=}O(Bn\text{-}tpen)]^{2+}$ were also characterized;[2a,2d,3] however, their reactivities have not gone up to those of non-heme iron enzymes, implying that these reported low-spin $Fe^{IV}{=}O$ complexes ($S = 1$) would be less active than the natural high-spin $Fe^{IV}{=}O$ species ($S = 2$) such as "compound J" discovered in taurine/α-ketoglutarate dioxygenase (TauD).[1b] These features of the synthetic $Fe^{IV}{=}O$ species are considered to depend on their six-coordination environment occupied with nitrogen donors, while the active site of non-heme iron enzymes has distorted and low coordination geometries with mixing imidazole nitrogen and carboxylate oxygen donors.

Therefore, we utilized (−)-sparteine ((−)-sp) ligand supporting the distorted and low coordination geometry.[4,8] In this paper, we described about a crystal structure of novel mononuclear ferrous (−)-sp complex, $[Fe^{II}((-)\text{-sp})(OBz)_2]$ (**1**), with a N_2O_4 distorted coordination geometry and ligating benzoate (OBz) molecules. Subsequently, we carried out oxygenation reactions of **1** with oxidizing reagents as often used in the shunt pathway.

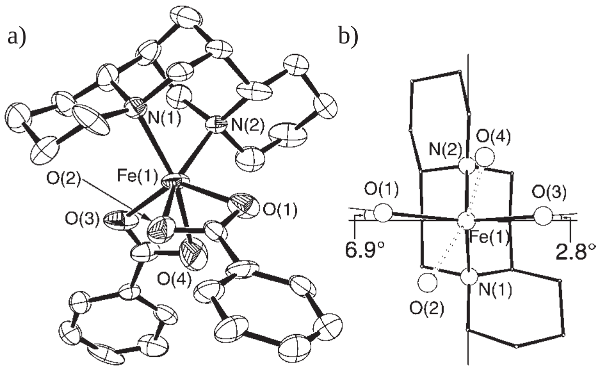

Figure 1. a) Ellipsoid diagram of **1**. H atoms are omitted for the clarity. Bond lengths: Fe(1)–N(1); 2.222(11), Fe(1)–N(2); 2.199(11), Fe(1)–O(1); 2.142(11), Fe(1)–O(2); 2.262(10), Fe(1)–O(3); 2.090(9), Fe(1)–O(4); 2.360(11) Å, respectively. b) Projection view of **1** on the plane perpendicular to pseudo-C_2 axis.

Single crystals of **1** were prepared by a reaction of $Fe^{II}(OBz)_2$ and (−)-sp in EtOH solution under Ar atmosphere.[5] The X-ray structure of **1**[6] (Figure 1a) revealed a remarkably distorted six-coordinate geometry with two nitrogen and four oxygen atoms of one (−)-sp and two benzoate moieties. The average interatomic distances of Fe–N and Fe–O (2.21 Å) are comparable to those of high-spin Fe^{II} complexes reported previously.[7] The Mössbauer parameters of **1** ($\delta = 1.11$ mm/s, $\Delta E_Q = 2.71$ mm/s) are very similar to those of reduced TauD with high-spin Fe^{II} center ($\delta = 1.16$ mm/s, $\Delta E_Q = 2.76$ mm/s) (Figure S1).[1a,15] The binding modes of bidentate oxygen atoms are not equivalent in each benzoate, and Fe–O(1) and Fe–O(3) bond lengths (2.142(11) and 2.090(9) Å) are significantly shorter (by ca. 0.2 Å) than those of Fe–O(2) and Fe–O(4) (2.262(10) and 2.360(11) Å). In the projection view of the Fe^{II} coordination geometry on a plane perpendicular to the pseudo-C_2 rotation axis (Figure 1b), the dominant Fe(1)–O(1)–O(3) coordination plane crossed orthogonally against the nitrogen coordination plane of (−)-sp, their different tortional distortion angles from orthogonality being 6.9 and 2.8° for Fe–O(1) and Fe–O(3), respectively. Indeed, the crystal structure of an analogous Fe^{II}–(−)-sp complex, $[Fe^{II}((-)\text{-sp})Cl_2]$, showed a twisted four-coordination geometry.[8] We could facilely accomplish such the distorted and twisted coordination geometry by using (−)-sp, although an analogous coordination structure of $[Fe^{II}(1\text{-}MeBzIm)_2(O_2C\text{–}Ar^{tol})_2]$ was constructed by further more bulky carboxylate binding to the central Fe^{II} ion.[3,9] These structural findings suggest that the coordination of (−)-sp supports the pseudotetrahedral or distorted geometry around the central Fe^{II} ion of **1**, with non-equivalent bidentate modes of the carboxylate ligands.

Furthermore, we tried to investigate the oxygenation reaction of the biomimetic Fe^{II} complex **1** in several organic solvents by using the shunt pathway. The reaction of **1** and *m*-chloroperbenzoic acid (*m*CPBA) in EtCN solution at −40 °C immediately

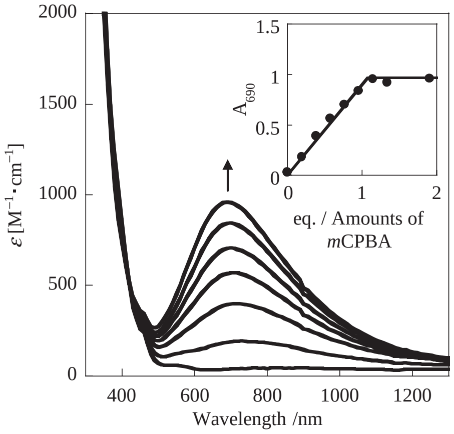

Figure 2. Generation of **3** by the reaction of **1** (1 mM) and *m*CPBA in EtCN at −40 °C. (Inset): Plot of absorption intensity at 690 nm vs stoichiometric amounts of *m*CPBA added.

gave a stable blue species. The absorption intensity at 691 nm was increased with an adding amount of *m*CPBA, and the spectral change was saturated by addition of almost 1 equiv of *m*CPBA (Figure 2). A FT-IR spectrum of the resulting blue species in the reaction, a new peak assignable to characteristic stretching vibration of C≡N group appeared at 2069 cm^{-1}. Differed from the ν(C≡N) peak of solvent EtCN (2247 cm^{-1}), the new ν(C≡N) peak at 2069 cm^{-1} is similar to that of Prussian blue-type compound (2080 cm^{-1}).[10] In a GC-MS analysis of the reaction solution, CH_3CHO was observed in 7.0(8)% yield based on **1**,[11] suggesting that the reaction of **1** and *m*CPBA significantly degraded EtCN molecule to generate CN^- ion and CH_3CHO molecule. This type of nitrile degradation was also reported in Cu^{II}_2-μ-1,1-OOH system.[12] The absorption band at 691 nm of **3** is also possibly assigned to intervalence charge-transfer band of Fe^{II}–CN–Fe^{III} moieties as observed in Prussian blue-type compounds.[10] Additionally, in a positive mode ESI-MS measurement of the same reaction mixture, an organic component peak cluster was detected as an oxygenated (−)-sp ligand ($m/z = 250.4$, [(−)-sp + O + H]$^+$). The peak intensity at $m/z = 250.4$ was about 40% relative to that of the free (−)-sp ligand ($m/z = 234.4$, [(−)-sp + H]$^+$) as a base peak. These data evidenced that the generated active intermediate species oxidized both (−)-sp ligand and EtCN molecule. These intra- and intermolecular reaction are competitive, and the degradation of EtCN was proportional to the amount of an active intermediate species. In the case of using H_2O_2, ^{t}BuOOH, and PhIO as an oxidant, similar reactions also proceeded, although those were very slow without the saturation behavior. On the contrary, [Fe^{II}(TPA)(MeCN)$_2$](ClO$_4$)$_2$[3,13] and $Fe^{II}(ClO_4)_2 \cdot nH_2O$ did not degrade EtCN molecule in the same reaction condition, indicating that distorted coordination geometry with (−)-sp is essential for degradation of EtCN molecule.

Finally, the same reaction was performed in CH_2Cl_2. In a stopped-flow measurement, very short-lived intermediate species **1a** was formed immediately, which showed an intense and broad absorption band at 420 nm ($\varepsilon \approx 2000$ M^{-1}·cm^{-1}) and a weak one at 870 nm ($\varepsilon \approx 100$ M^{-1}·cm^{-1}) (Figure S2).[15] This spectral feature is similar to the reported $Na_4Fe^{IV}O_4$ with high-spin configuration ($S = 2$), which showed two intense and weak absorption bands at 400–600 and 750–850 nm, respectively.[14] The decomposition of **1a** was first-order kinetic process, and the half-life period of **1a** at −40 °C was $t_{1/2} = 1.7$ s. The detail characterization of **1a** is now under investigation.

References and Notes

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3 Ligand abbreviations: TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; TPA = tris(2-pyridylmethyl)-amine; N4Py = *N*,*N*-bis(2-pyridylmethyl)-bis(2-pyridyl)-methylamine; Bn-tpen = *N*-benzyl-*N*,*N'*,*N'*-tris(2-pyridylmethyl)-1,2-diaminoethane; 1-MeBzIm = 1-methylbenzimidazole; O_2C-Ar^{tol} = 2,6-di(p-tolyl)benzoate.
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