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C=N Bond Activation and Hydration by an Iron(III) Complex with Asymmetric Sulfur-oxygenation

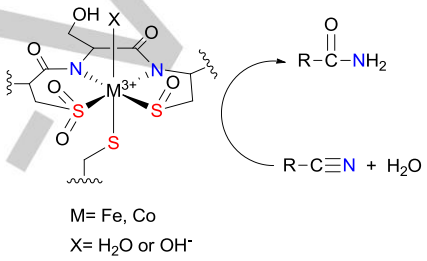
Yun-Ru Wu, Chia-Ming Chang, Chia-Chi Wang, Chang-Chih Hsieh, and Yih-Chern Horng*

Dedicated to Professor Wen-Feng Liaw on the occasion of his 60th birthday

Abstract: The presence of asymmetric cysteine sulfur-oxygenation donors, consisting of sulfenate (SO), sulfinate (SO_2) and thiolate (S), around a trivalent iron is essential for the catalytic function of Fe- or Co-type nitrile hydratase (NHase). In order to gain insight into the role of this asymmetric ligation, an octahedral bisthiolate low-spin Fe(III) complex and two its S-oxygenation derivatives, unprecedented mixed sulfinate/thiolate and O-bound bissufinate complexes, were generated. The placement of anionic nitrogens *trans* to thiolates in bisthiolate complex causes the axial imino C=N bonds more polarized, resembling the activation of bound nitrile in nitrile hydratase. The polarization is even more severe in monosulfinate species, and the hydration of Fe-bound C=N bond by OH^- was observed. The generation of O-bound bissulfinate octahedral complex implies the equatorial carboxamido and axial thiolate ligation in Fe-NHase provides greater electron buffering capacity in keeping constant electron density of Fe(III) ion even in the presence of equatorial S-oxygenations.

Introduction

Nitrile hydratase (NHase) found in bacteria converts nitriles to the corresponding less toxic amide products efficiently under mild conditions.[1] The unique active site of NHase possesses a monouclear low-spin non-heme iron(III) or non-corrin cobalt(III) ion bound with two deprotonated carboxamido nitrogens from the backbone and three cysteine sulfurs in the first coordination sphere.[2] Two of the cysteine residues post-translationally S-oxygenated to cysteinesulfenate (Cys-SO) and cysteinesulfinate (Cys-SO_2) in the deprotonated states,[3] are essential for its catalytic activity.[4] The sixth ligand *trans* to the unmodified cysteinate in the active form was proposed to be hydroxide (OH^-) or water molecule (Scheme 1).[5] Due to this unusual ligation combination around metal center, along with the important industrial application of nitrile hydrolysis,[6] the syntheses of modeling compounds resembling both the structure and function of NHase have been attempted.[7] So far, only Co(III) and bio-inspired Ru(II) complexes have successfully implemented S-oxygenated thiolate(s) as catalytically synthetic analogues of NHase.[8] However, none of them clearly reveal the binding and activation of nitrile on metal ion. No functional Fe(III) synthetic mimics with or without S-oxygenation relevent to Fe-type NHase are known. Only few examples of synthetic well-defined Fe(III) molecules with sulfur oxidation exist,[9] and almost all S-oxygenated low-spin Fe(III) complexes are derived from low-spin Fe(III) precursor.[10] In the light of these structural mimics, multiple anionic ligand system provides a greater chance for the preparation of multiple S-oxygenated species. In addition, the coordinatively saturated Fe(III) complex was suggested for ensuring the isolation of S-bound sulfinato complex and avoiding the unwanted O-bound sulfinato ligation.[9c]



Scheme 1. The active site of NHase along with its catalytic reaction.

Continued with our interests in nitrile activation[11] and synthetic modeling of Fe-NHase,[12] we now utilized an aromatic conjugated NNS tridentate ligand 2-[(2-mercaptophenyl)iminomethyl]pyrrole (HPyImSH) with thiolato, imino, and pyrrolyl moieties for preparing the Fe(III) modeling complex as well as its S-modification derivatives shown in Figure 1. The pyrrole motif with an acidic N-H bond similar to carboxamido group was installed. The placement of each anionic nitrogen atom *trans* to thiolate in $PyImS^{2-}$ similar to the active site of Fe-NHase have not been found in small molecule active site mimics with NNS tridentate ligands as far. In addition, the imino moiety is situated *cis* to coordinated nitrogen and sulfur to examine the influence of the S-oxygenation on the properties of C=N bond, resembling substrate nitrile bonding on the active site.

Results and Discussion

The synthesizing strategy for [PPN][Fe(PyImS)$_2$] **1** was consulted with the early reports.[13] Treatment of two equiv of (HPyImS)$_2$[14] with [PPN][HFe(CO)$_4$] in THF at room temperature led to the generation of **1** in 61% yield via oxidative-addition reaction with liberation of HPyImSH, $HPyImS^-$, and all carbon monoxide moieties. The wine-red complex **1** is stable in solid state, but gradually transformed to oxygenated species (about 20%) in DMF within two weeks when exposing to air. The slow conversion in air prompted us to employ other oxygenating agents for the preparation of sulfur oxidation species. The S-oxygenation derivatives [PPN][Fe(PyImS)(PyImSO$_2$)] **2** (60%

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yield) and [PPN][Fe(PyImSO$_2$)$_2$] **3** (55% yield) were prepared by using two and four equiv of an O-atom transfer reagent, *tert*-butyl *N*-sulfonyloxaziridine (SOA), capable of oxygenating free thiols[15] and Fe-bound thiolate.[9e] The reactions in DMF were monitored and terminated (about 2 hrs) judged by silica gel thin layer chromatography (TLC) (MeOH/Ethyl acetate 1:30): **1**, R_f = 0.78; **2**, R_f = 0.58; **3**, R_f = 0.88. The purifications were straightforward without the need of any column chromatography. The isolation of yellowish green **3** also can be achieved through the reaction of dark green **2** with 2 equiv SOA in DMF. Although mono- and bissufinate derivatives of **1** were obtained without ambiguity, efforts to obtain pure monosulfenate [PPN][Fe(PyImS)(PyImSO)] and mixed sulfenate/sulfinate [PPN][Fe(PyImSO)(PyImSO$_2$)] for further characterization have been unsuccessful.

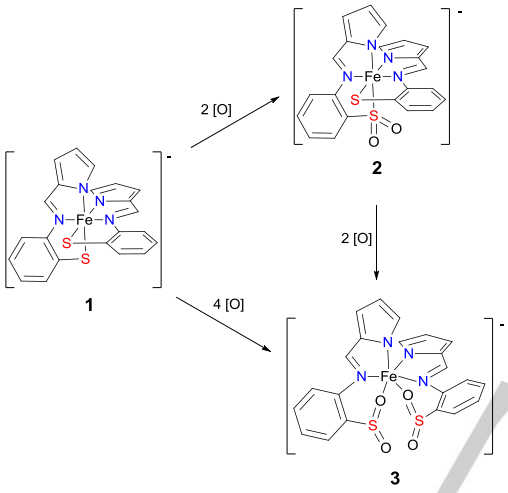

Figure 1. S-oxygenation pathway of **1**. The cations in complexes were omitted for clarity.

The structures and key bond lengths of complexes **1**, **2** and **3** were successfully determined by X-ray crystallography[16] and are shown in Figure 2 and Table 1. The crystal structure of complex **1** revealed that Fe(III) center, sitting in a N4S2 coordination environment, is ligated by two PyImS^{2-} ligands. The frameworks of two PyImS^{2-} ligands, binding to Fe center in a *mer* mode, are nearly planar due to extensive aromatic conjugation. The pyrrolic NH is deprotonated and covalently bound to the Fe(III) center at *trans* position of thiolate. Two thiolates, *cis* to each other, and two pyrrolic nitrogen atoms occupy the equatorial positions with two imino nitrogens in axial positions, resembling the active-site structure of Fe-NHase. The averaged Fe-S bond distance (2.26 Å) in **1** is slightly longer than those observed in low-spin thiolato Fe(III) complexes in the range of 2.14~2.25 Å.[9b, 9c, 9e, 17]

The structure of doubly oxygenated product **2** displays that the added two oxygen atoms are attached to the same sulfur atom resulting a sulfinato species, instead of to two thiolates forming a bissulfenato complex, similar to the product of Ru(II) dithiolate complex added with two oxygen atoms.[18] Although rare examples of Fe(III)-sulfinate complexes exist,[9b, 9d] to our knowledge **2** represents the first example of a structurally characterized mixed S-bound thiolate/sulfinate Fe(III) complex.[19] Notably, the two Fe-N$_{imino}$ lengths in **1** are not altered significantly (difference within 0.02 Å), but the unmodified Fe-S bond distance in **1** becomes shorter upon doubly oxygenation. The Fe-N$_{pyrr}$ bond length also shrinks due to S-modification, reflecting the increased Lewis acidity of the trivalent iron. Interestingly, the C=N$_{imino}$ bonds in **1** is slightly polarized as evidenced by the longer distances than typical C=N double bonds (1.29 Å).[20] Although the elongation of C=N$_{imino}$ bond due to the constraints of bound ligand cannot be ruled out, this polarization is even more severe in **2**, especially in the unmodified ligand frame, indicating the oxygenation of equatorial thiolate also play a role on the activation of axial C-N bonds.

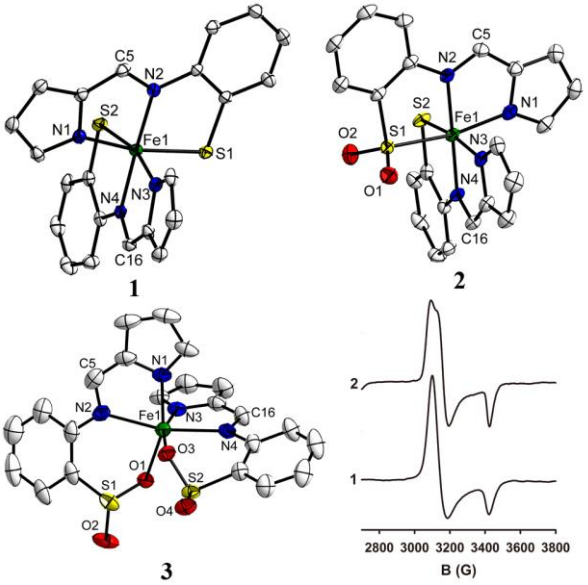

Figure 2. ORTEP drawings of complexes **1**, **2** and **3** and X-band EPR spectra (77K, THF) of **1** and **2**. The thermal ellipsoids were drawn at 35% probability level. The [PPN] cations, solvent molecules and hydrogen atoms were omitted for clarity. The g-values: complex **1**, 2.14, 1.97; complex **2**, 2.19, 2.13, 1.97. Experiment parameters: microwave frequency = 9.46 GHz, microwave power = 0.6 mW, modulation frequency = 30 kHz, modulation amplitude = 1.6 G.

Table 1. Selected bond lengths [Å] for complexes **1**, **2** and **3**.

Complex[a]	Fe-S	Fe-N$_{pyrr}$	Fe-N$_{imino}$	C=N$_{imino}$
1	2.2490(8), 2.2745(9)	1.949(2), 1.968(3)	1.936(3), 1.941(3)	1.315(4), 1.297(4)
2	2.2224(11), *2.2432(11)*	1.928(3), *1.971(3)*	1.932(3), *1.948(3)*	1.321(4), *1.315(5)*
3		*2.063(4), 2.062(4)*	*2.179(4), 2.185(4)*	*1.310(6), 1.321(7)*

[a] The numbers in *italic* style indicate the bond distances derived from S-oxygenated ligand.

The crystal structure of **3** illustrated that the successful process of four-oxygen-atom addition of **1** indeed obtained the quadruple S-oxygenated species. To our surprise, this structure displays an O-bound bissulfinate species. Notably, the pyrrolyl and phenyl rings of chelating ligand in **1** and **2** are essentially coplanar, however, they are non-coplanar in **3** with averaged dihedral angle about 28°. The averaged Fe-OSO bond distance of 1.97 Å compares well with the ones of only three reported Fe(III)-OSO complexes in the range of 1.91~2.03 Å.[9a, 9c, 9f] Although this structure is irrelevant to Fe-NHase, we have not found so far an O-bound sulfinate octahedral Fe(III) complex in the literature. Thus, our results demonstrated the coordinatively saturated Fe(III) complex cannot prevent the production of an O-bound sulfinate species upon sulfur oxidation. The electron deficiency of Fe(III) center and decreased electron donating ability of sulfur atom of Fe-SO_2 resulting in the switch to O-bound bissulfinate and formation of a thermodynamically more stable species even with severe torsion of imino C=N bond. The isolation of S-bound bissufinate complex $[Fe(PyPepSO_2)_2]^-$,[9b] with amido-type NNS ligand reported by Mascharak, implies the anionic carboxamido nitrogens provide more sufficient electron buffering capacity than anionic pyrrolic nitrogens.

The X-band EPR signals of complexes **1** and **2** at RT and 77K revealed low-spin Fe(III) centers (Figure 2). Due to the structural and electronic effects, the axial EPR signals of **1** were altered to rhombic signals when the complex was oxygenated. The g values of **2** are very similar to those from Fe-containing NHase at pH = 9.0 (g= 2.20 2.12 and 1.99).[21] However, complex **3** with Fe-O fragments exhibits an EPR signal with features at g= 8.3 and 4.0 (77 K, THF), typical values for octahedral high-spin Fe(III) systems with nitrogen and oxygen ligation (Figure S1).[22] In CH_3CN, **1** exhibits an absorption band at λ_{max}= 900 nm, generally assigned to a thiolate-to-metal charge-transfer transition (LMCT). The doubly-oxygenation of **1** led to slightly blue shift of band at 900 nm, and appearing of a new band at 616 nm (Figure S2). The generation of new band at 550~750 nm was also observed in reported octahedral Fe(III) complexes upon S-oxygenation.[9b, 9d, 9e] Thus, the blue-shifted band at 855 nm can be tentatively assigned as the LMCT band of unmodified sulfur to metal transition.

The unusual elongation of imino C=N bonds in **1** and **2** prompted us to test the possibility of ligand hydration by hydroxide. Although the extensively conjugated disulphide $(HPyImS)_2$, and **1** was not reacted with 4 equiv $[Et_4N][OH]$ in un-dried CH_3CN within 12 hrs as revealed by ^1H NMR and electrospray ionization mass spectrometry (ESI-MS) (Figure S3), the reaction between **2** and 4 equiv hydroxide in 2 hrs led to the disappearance of **2** (m/z 488.1) and formation of pyrrole-2-carboxaldehyde (^1H NMR, Figure S4), 2-aminobenzenesulfinate (m/z 156.0), $HPyImSO_2^-$ (m/z 233.1), **1** (m/z 456.1) and a few uncharacterized dark brown precipitates (Figure 3). Despite the fact that 2-aminobenzenethiolate cannot be detected by ESI-MS due to the instrument limitation, the detection of $HPyImSO_2^-$ indicates the hydration reaction occurred also at the metal-bound unmodified ligand frame. Thus, the equatorial sulfinate group in **2** can aid the activation of axial C=N bond fragile to be attacked by OH^- through increasing Lewis acidity of Fe(III) center, and exhibited no nucleophilic properties.

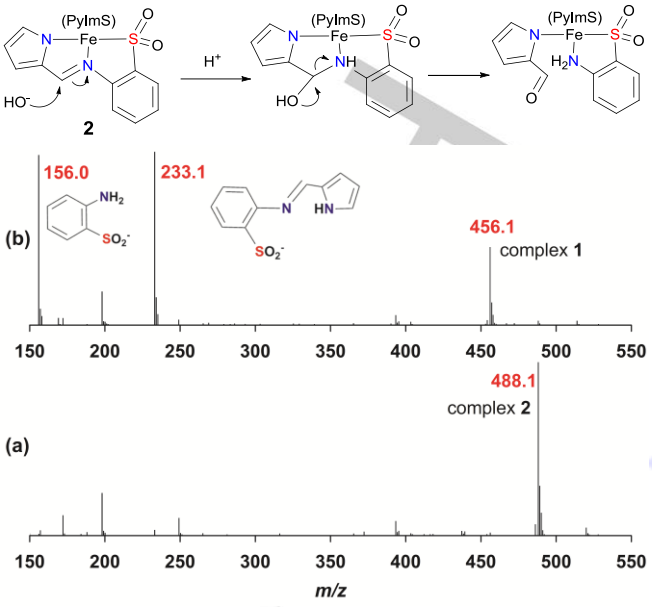

Figure 3. The reaction mechanism proposed for the hydration of metal-bound imino C=N moiety in **2** by hydroxide, and ESI-MS spectra before (a) and after (b) the reaction of **2** with hydroxide in CH_3CN.

Conclusions

In conclusion, a N4S2 six-coordinated low-spin Fe(III) mimic of active form of Fe-NHase along with its S-oxygenation derivatives, the monosulfinate and bissulfinate complexes, were prepared and characterized. The crystal structures show that unmodified thiolate and pyrrolic nitrogen donors can assist maintaining the electron density of Fe(III) ion with single thiolate oxidation. In addition, the presence of coordinatively saturated Fe(III) center cannot avoid the isomerization of Fe-SO_2 into Fe-OSO fragment of bissulfinate complex for the preferential interaction between Fe(III) center and anionic oxygen. Thus, the presence of electron buffering system from equatorial deprotonated amido and axial thiolate donors in Fe-NHase maintains the Lewis acidity of Fe(III) ion and prevent the O-bound bissufinate species upon multiple S-oxygenations. While the effects of S-oxygenation on active nitrile hydration synthetic Co(III) and Ru(II) catalysts have been reported,[8] we demonstrated here for the first time that the activation and further hydration by OH^- of metal-bound C=N bond is influenced by asymmetric S-oxidation (-SO_2) by taking a closer look. The isolation and purification of monosulfenate and mixed sulfenate/sulfinate species, and also the investigations into the nitrile hydration by these Fe(III) complexes are currently underway.

Acknowledgements

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Keywords: Enzyme catalysis • Bioinorganic chemistry • Metalloenzymes• Oxidation • S ligands

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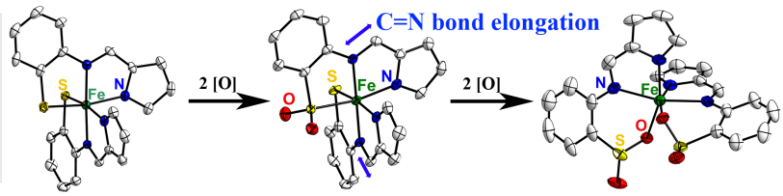

S-oxygenation of a low-spin bisthiolate Fe(III) complex with more Lewis acidic metal center leads to the generation of mixed sulfinate/thiolate and O-bound bissulfinate species. The polarization of Fe-bound C=N bonds is more severe in monosulfinate species, and the hydration of C=N bond by OH^- was observed.

Sulfur Oxygenation*

*Yun-Ru Wu, Chia-Ming Chang, Chia-Chi Wang, Chang-Chih Hsieh, and Yih-Chern Horng**

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C=N Bond Activation and Hydration by an Iron(III) Complex with Asymmetric Sulfur-oxygenation