ENDOR Studies of a Nitrile Hydratase Model Complex Containing a Novel Sulfenate-ligated Iron Center

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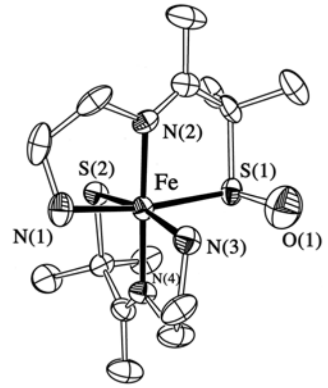
The active site of iron-type nitrile hydratase metalloenzymes is made up of a conserved amino acid sequence that provides two deprotonated amides and three cysteinates as ligands to an Fe^{3+} center. Two of the three cysteinate sulfur atoms are post-translationally modified, one to a sulfenate/sulfenic acid (S=O/S–OH) and the other to a sulfinate/sulfinic acid ($S=(O)_2$/SOOH). The first sulfenate-ligated iron complex $[Fe(ADIT)(ADIT{-}O)]^+$ has recently been synthesized as a model for this important interaction (see figure below).[1] The electronic structures of this complex, the parent complex $[Fe(ADIT)_2]^+$, and their protonated forms are probed using ENDOR spectroscopy. These results are compared to ENDOR studies of the high pH and low pH forms of the nitrile hydratase enzyme that have previously been studied in our laboratory.[2] In addition, the results of DFT calculations on the enzyme active site, including the effects of hydrogen-bonding interactions from nearby conserved arginine residues, are presented.



References

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