Iron Coordination and Halogen-Bonding Assisted Iodosylbenzene Activation

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The iron(III) complex of the carboxylato-containing hexadentate (NSO) ligand N,N,N′-tris(2-pyridylmethyl)ethylendiamine-N′-acetate (tpena) shows biomimetic reactivities: It catalyzes the selective oxidation of electron-rich olefins and sulfides, and by treating it with a one-electron oxidant, the high-valent oxo species, [FeIV(tpena)]2+, is accessible in water. In these processes one methylpyridine arom is bifunctional: It can coordinate so the ligand is hexadentate, or it can act as a second coordination sphere base. Its reaction with insoluble oxygen atom transfer reagent stands in stark contrast to analogous reactions observed for iron(II) complexes of N4 and N5 ligands which are inaccessible. The metal-based oxidant is electrophilic since the reaction rate is tuned by the EWGs on the substrate.

[FeII(tpena)(OIPh)]2+ can be envisaged to be a “protected” hypervalent [FeO2(tpena)]2+. Potentially this could be exposed via a heterolytic I-O cleavage and the product Fe=O species be the direct catalytically competent oxidant in the catalysis. Knowledge of the iodine oxidation state of the coordinated vs uncoordinated PhIO is useful for gaining insight into mechanism. The three iron(III) tpena species can be co-precipitated. All are present in not strictly dried non-aqueous solutions.

Mössbauer parameters* EPRb

| Species                  | d/ mm s-1 | H/ B | FWHM/ mm s | Assignment | Ref. area/ % | g
|--------------------------|-----------|------|------------|------------|-------------|----
| [Fe(II)(tpena)(OIPh)]2+  | 0.46      | 1.71 | 0.33       | high-spin Fe(II) | 25 | silent |
| fac-[Fe(III)(tpena)]2+   | 0.18      | 2.26 | 0.55       | low-spin Fe(II) | 41 | g' = 4.20 |
| mer-[Fe(III)(tpena)]2+   | 0.25      | n.a. | 4.19       | high-spin Fe(II) | 34 | g = 2.74, 2.29, 1.68 |

* solid state, 12K
* solution state, O6Ch, 100K

[FeII(tpena)]2+ solubilizes and activates PhIO. A unique and highly reactive Fe-OIPh adduct can be isolated thanks to stabilization by strong supramolecular halogen-bonding in the solid state.

Intradimer Halogen Bonds

Halogen bonding

Decomposition of FeII-OIPh complex in solution T = mins in CH3CN (cannot exist in most other solvents)

Iodine L3-edge XANES suggests +1.6 for the average oxidation state for the iodine atoms in iron(III)-coordinated PhIO. This represents a reduction of iodine oxidation state relative to PhIO (+3) and no electron transfer from iron(III). Thus the charge must be distributed over the intra- and intermolecular I-O and I–O bonds.

Catalysis

Note: The mer isomer. This is the most reactive Fe(III) species. The fac isomer and the aquo adduct are spectators.

Electron Transfer from Fe to I?

[FeII(tpena)] + OIPh → ([tpena]FeII'OIPh) → ([tpena]FeII'O) + IPh

Iodine L3-edge

Iron K edge

Decomposition of FeIV-OIPh complex in solution T = mins in CH3CN (cannot exist in most other solvents)


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