Metal Stabilised Radical Complexes: Implications For Radicals In Biology

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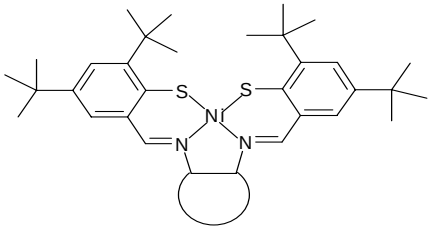
Interest in the biochemical exploitation of protein radicals has been increasing dramatically over the last 10 years as new enzymatic systems are characterized and more examples of radical species as essential co-factors to enzymes are being determined. Enzymes that incorporate amino acid or modified amino acid based radicals include galactose oxidase, in which metal bound phenoxyl radicals are observed in the catalytic cycle.

Thiyl radicals (cysteine radicals) have been shown to be an intermediate in nucleotide reduction. It can be anticipated that in some metalloenzymes, where the metal has a sulfur rich co-ordination sphere and redox processes are occurring, a stabilized metal bound thiyl radical may be involved in catalytic activity.

There are a number of enzymes that exist with nickel in a sulfur rich coordination environment such as Ni SOD and Ni/Fe hydrogenases. There is a possibility that such biological processes may proceed via oxidation/reduction of the 'ligand', possibly via a co-ordinated thiyl radical.

Characterization of this type of species is proposed using the novel molecular building block 3,5-di-*tert*-butyl-thiosalicylaldehyde to stabilize phenylthiyl radicals in an analogous manner to the already well developed metal bound phenoxyl and anilinyl radical compounds. A series of complexes are proposed based around various Schiff base linked amines. The use of bulky diamines will allow variation of the co-ordination geometry around the nickel centre. The effects on the redox chemistry can then be probed, providing insight into bio-relevant enzyme active site mechanisms.



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