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A biologically relevant iron(III) phenoxyl radical complex: A thermodynamic investigation on the structure-radical stability relationship

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HIGHLIGHTS

- A binuclear Fe(III) complex of aminophenol ligand synthesized.
- Thermodynamic parameters of electrochemically produced radicals were investigated.
- Radical complex/Fe(III) center interaction make it stabilized such as RNR enzyme.

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ABSTRACT

A kind of new amine-chloro substituted phenol and its iron(III) complex has been prepared and characterized by spectroscopic, X-ray techniques and magnetic susceptibility studies. X-ray analysis revealed a binuclear complex, $Fe_2(L^{THF})_3$ in which two Fe(III) centers were surrounded by three ligands. The magnetic susceptibility indicates antiferromagnetic coupling between two iron centers through phenolate bridges. Voltammetric study of ligand (H_2L^{THF}) and complex $Fe_2(L^{THF})_3$ revealed that the coordinated phenolate ligands undergo reversible two-electron oxidations with formation of coordinated phenoxyl radicals. It has seen that the oxidation of $Fe_2(L^{THF})_3$ comparing to its analog, $Fe_2(L^{tBu})_2$ occurs at significantly higher potentials. It was attributed to the relationship between the radical stability with electronic and steric properties of ligands. Stability constants and thermodynamic parameters for the formation of $Fe_2(L^{THF})_3$ complex and the role of ligand coordination to iron center in phenoxyl radical stabilization has been investigated using anodic peaks potentials.

1. Introduction

Radicals are highly reactive species due to their unpaired electrons. They have a key role in living organism's physiology, biochemistry and some chemical processes, such as polymerization.

Interest in the field of protein and amino acid radicals has been dramatically increasing because these active species serve as enzyme co-factors to lots of enzymatic reactions in living organisms. [1]. One of the most important amino acid radicals is tyrosyl radical which plays vital roles in the chemistry of living systems [1,2]. Enzymes that incorporate this kind of radical include active form of galactose oxidase (GO) [1,3,4], glyoxal oxidase (GLO) [2] and ribonucleotide reductase, RNR (Scheme 1) [5–9].

This last one is the only known enzyme that carries a stable free radical in its resting state and catalyzes DNA synthesis by reducing ribonucleotides to their corresponding deoxyribonucleotides (Scheme 2). It has shown that the catalytic action of this enzyme involve formation of a tyrosyl radical close (tyrosyl 122 radical, $Y122^{\cdot}$), to the redox active iron center which is responsible for the radical stability in RNR [8,9].

Stabilization of the mentioned radicals is very important due to their role in biological processes [1,10]. Scientists have found two mechanisms for tyrosyl radical stabilization:

1. Stabilization by hydrogen bonding to its neighbor amino acid residues (e.g. in GO).
2. Stabilization by interaction with a transition metal center (e.g. in RNR).

The key role of the second mechanism in biological and catalytic radical processes is due to two major reasons [1,11]: (a) Redox reaction assisted radical generation. (b) Interaction of transition metals with their adjacent radicals.

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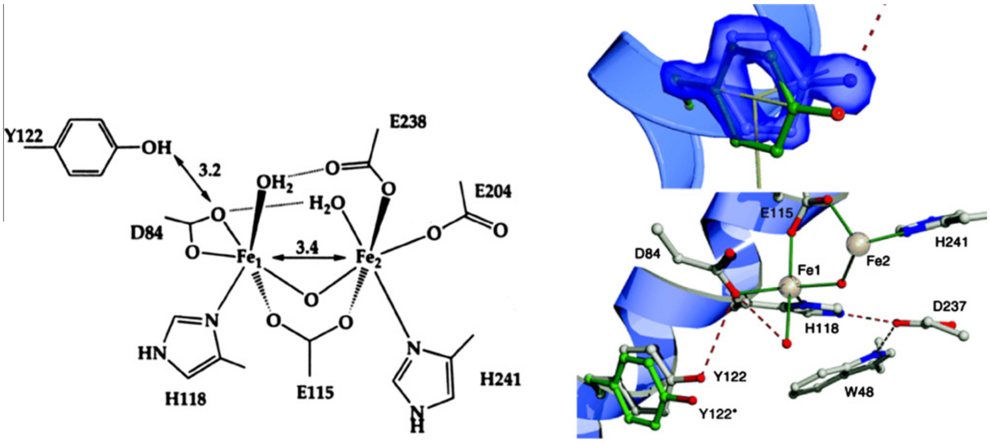
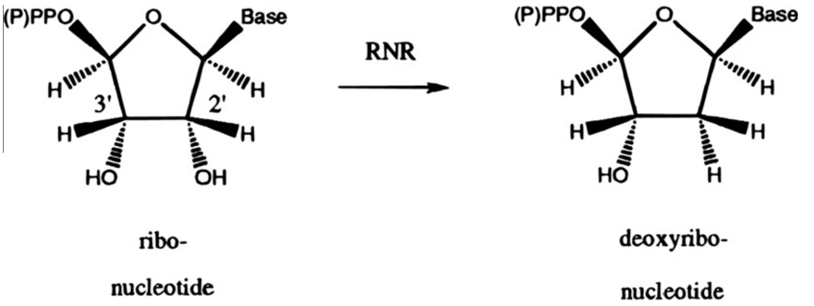


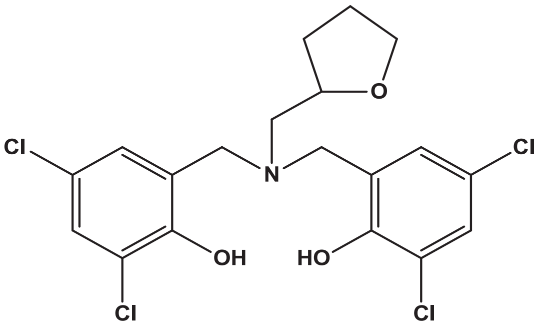
Scheme 1. The enzyme structure ribonucleotide reductase (RNR) [9].



Scheme 2. Enzymatic reaction catalyzed by ribonucleotide reductase [8].

On the other hand, the "metal–radical" approach has been noticed by scientists as one of the more attractive strategies for the design of biocatalysts and molecule-based materials. Therefore, nature and properties of d-transition metal bound to one or more radicals is much interest. Phenoxyl type radicals are one of these groups that their chemistry has been much interest because of key participation in biological redox processes [12–18]. Because of their close relationship with tyrosine-containing metalloenzymes, iron and copper complexes of chelating amine-phenolate ligands have been studied [19–27].

We report here the coordination chemistry, magnetic and redox properties of [6,6′-((((tetrahydrofuran-2-yl)methyl)azanediyl) bis(methylene))bis(2,4-dichlorophenol)] (H_2L^{THF}) (Scheme 3) and its iron(III) complex with this ligand. In this way, the role of phenoxyl radical/iron(III) center interaction in radical stabilization has been investigated.



Scheme 3. Structure of [6,6′-((((tetrahydrofuran-2-yl)methyl) azanediyl)bis(methylene))bis(2,4-dichlorophenol)] (H_2L^{THF}).

2. Experimental

2.1. Materials and physical measurements

Reagents or analytical grade materials were obtained from commercial suppliers and used without further purification, except those for electrochemical measurements. Elemental analyses (C · H · N) were performed by the Research Institute of Petroleum Industry (RIPI). Fourier transform infrared spectroscopy on KBr pellets was performed on a FT-IR Bruker Vector 22 instrument. NMR measurements were performed on a Bruker 400 instrument. UV–Vis absorbance digitized spectra were collected using a CARY 100 spectrophotometer. Magnetic susceptibility were measured from powder samples of solid material in the temperature range 2–300 K by using a SQUID susceptometer (Quantum Design MPMS-XL-5) in a magnetic field of 1000 Oe.

Voltammetric measurements were made with a computer controlled electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PGSTA 30 model and driven by GPES (ECO Chemie). The reference electrode was an Ag wire as the quasi reference electrode. A glassy carbon electrode with a surface area of 0.035 cm^2 was used as a working electrode and a platinum wire served as the counter electrode. Prior to the measurement, the GC electrode was polished with 0.1 mm alumina powder and washed with distilled water. The voltage scan rate was set at 50 mV sec^{-1}. The solutions were deoxygenated by bubbling nitrogen gas through them. Ferrocene was added as an internal standard after completion of a set of experiments, and potentials are referenced vs. the ferrocenium/ferrocene couple (Fc^+/Fc).

Diffraction data for $Fe_2(L^{THF})_3$ was measured on a Bruker–Nonius X8 ApexII diffractometer equipped with a CCD area detector by using graphite-monochromated Mo Ka radiation ($k = 0.71073$)