ABSTRACT

The present thesis deals with investigations in the valence tautomeric coordinations in copper complexes of live molecules like spin carrying hydroxy naphthoquinone oxime viz. lawsone oxime [1] and its C-3 substituted derivatives. Two objectives are set in present research project according to our interest such as “molecular magnetism” and “molecular functional mimicks of metalloenzymes” [2-5]. Very first, in the crystal engineering of coordination polymers via non-covalent H-bonds resulting in supramolecular assembly viz. [Cu(II)(ONQ)₂(H₂O)]ₙ with unique two dimensional ferro- and antiferro magnetic properties [6], lead us to investigate supramolecular coordination polymers of synthetic live molecules viz. LwOx with Cu⁴⁺ as “novel magnetic materials”. The unique molecular magnetism is characteristic of non-innocent ligands like quinones due to their valence tautomeric coordinations [7, 8]. Secondly, a biocatalyst model of “iminosemiquinone” for Galactose oxidase (GOs) active site [9]. indicates interest of research community in development of abiotic functional models as “biomaterials”. With this motivations the research topic is framed in five chapters.

Chapter I provides literature survey on valence tautomers as redox isomers in copper enzyme Galactose oxidase (GOs) and its model compounds [10-13]. The GOs active site exhibiting unusual features such as coordinated tyrosyl radical, past translationally modified amino acids and π-stacked residues, which is a challenge for structural abiotic models. In short, following valence tautomeric model is requirement for GOs different forms such as,

\[
\text{Cu}^{2+} - \text{Tyr}^{++} \xrightleftharpoons{e^-} \text{Cu}^{2+} - \text{Tyr} \xrightleftharpoons{e^-} \text{Cu}^+ - \text{Tyr}
\]

Chapter II deals with detailing of redox isomers and supramolecular assemblies in C-3 substituted lawsone and its oxime derivatives. This report describes first successful attempt of three polymorphs identified as redox isomers in 1 (3-iodolawsone), a 3-substituted spin carrier Lawsone. Like coordinated valence tautomeric ligands, interestingly organic compound 1 shows crystal to crystal magnetic phase transition in diamagnetic polymorphs Form I to paramagnetic Form II as HNSQ radical (g = 2.0052) which is thermodynamically stable. This governs its probable
antioxidant candidature in biological activity of hydroxy naphthoquinones. Crystal engineering based on halogen bondings together with host-guest interactions of water molecules stabilizing supramolecular architectures in chloro(L-4), bromo(L-5) and iodo(L-6) oximes of lawsone are discussed. Non-covalent competitive interactions of asymmetric solvation and halogen bonding can have large influence on the spin distribution in L-4 to L-6 derivatives of spin carrier lawsone revealed by X-ray and EPR studies. The antioxidant activity in terms of oxygen reduction to water molecule is directly proportional to the spin (radical) concentrations in L-4 to L-6 and increases in order L-4 < L-5 < L-6. All L-1 to L-7 ligands perform supramolecular controls of weak non-covalent interactions like H-/ halogen bondings and π-π stacking for spin carrier nature of parent lawsone and perform HNSQox radicals as their ‘redox isomer’ intrinsically.

Chapter III, deals with valence tautomeric coordinations of oximes with Cu(I) and Cu(II) intermediates and its Thermal, Spectroscopic, Magnetostructural and Electrochemical studies. The spectroscopic models of active site in GOS enzyme, are mimicked for oxidized CuII-Tyr+ valence tautomer in Cu-1 to Cu-7 compounds. Detailed EPR and SQUID data reveal that all compounds except Cu-3 are supramolecularly associated π-π stacked dimers, while Cu-3 is trimer. Cu-1A and Cu-6 possess, [CuII. II(ONQox)(ortho-4HNSQox)3], [CuII. II(ONQox)2(o-4HNSQox)2] type valence tautomeric coordinations. While all remaining complexes (except Cu-3) comprise of [CuII(ortho-4HNSQox)2]2 redox isomeric coordination. Ambivalent behaviour of CuII with LwOx and its C-3 substituted ligands in terms of valence tautomers is the result of their self organised molecular assembly as dimer confirmed from their redox chemistry. Thus such spectroscopic magnetostructural models of GOS possess variable “electronic structures” together with typical magnetic behaviour resulting in unique long range interacting magnetic materials.

In Chapter IV, we have compared redox isomeric CuII-oximato Complexes as molecular catalyst for aerobic oxidation of benzyl alcohol as GOS Functional mimicks. All Cu-1 to Cu-7 together with Cu-1A and Cu-1B are efficient and good functional models of GOS catalyzing chemoselective oxidation of primary benzyl alcohol to corresponding benzaldehydes in high turnover numbers under ambient conditions. Monomeric Cu-6 and middle monomer of Cu-3 are structural as well as functional
models of GOs, however others are not analogues to GOs active site in electronic structural aspect, but perform good functional molecular catalyst due to stabilization of radicals in coordination compounds via supramolecular π-π stacking effect. The order of catalytic activity in terms of TON values shown in parenthesis is as follows: Cu-4 (23)< Cu-2 (37)< Cu-1A (41)< Cu-5 (49)< Cu-1B (57)< Cu-1(177)< Cu-6 (184)< Cu-3 (390)< Cu-7 (612). Due to required Cu(II)(Td) symmetry [12, 13] in Cu-3 and Cu-7 which leads to intermediate Cu(II)(Td) state in proposed catalytic cycle. Both become best models for ever ranking between III and IV compared to the functional models in literature till today. The catalytic reactivity is finally tuned with C-3 substituents on spin carrier LwOx ligand.

Chapter V describes the details of experimental procedures and various techniques used in characterization of the valence tautomeric ligands and the model compounds which include Single crystal X-ray diffraction studies, CHN analyses, AAS, TGA, IR, EPR, VTMS measurements and CV studies for the model compounds. The catalytic activity studies were carried out by using HPLC technique.

References:


