

Solution Thermodynamics, Photophysical and Computational Studies of TACH2OX, a C-3 Symmetric 8-Hydroxyquinoline: Abiotic Siderophore Analogue of Enterobactin

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Abstract : 8-hydroxyquinoline, (8HQ), experiences a renaissance due to its utility as a building block in metallosupramolecular chemistry and its versatile use of its derivatives in various fields of analytical chemistry, materials science, and pharmaceuticals. It forms stable complexes with a variety of metal ions. Assembly of more than one such unit to form a polydentate chelator enhances its coordinating ability and the related properties due to the chelate effect resulting in high stability constant. Keeping in view the above, a nonadentate chelator N-[3,5-bis(8-hydroxyquinoline-2-amido)cyclohexyl]-8-hydroxyquinoline-2-carboxamide, (TACH2OX), containing a central cis,cis-1,3,5-triaminocyclohexane appended to three 8-hydroxyquinoline at 2-position through amide linkage is developed, and its solution thermodynamics, photophysical and Density Functional Theory (DFT) studies were undertaken. The synthesis of TACH2OX was carried out by condensation of cis,cis-1,3,5-triaminocyclohexane, (TACH) with 8-hydroxyquinoline-2-carboxylic acid. The brown colored solid has been fully characterized through melting point, infrared, nuclear magnetic resonance, electrospray ionization mass and electronic spectroscopy. In solution, TACH2OX forms protonated complexes below pH 3.4, which consecutively deprotonates to generate trinegative ion with the rise of pH. Nine protonation constants for the ligand were obtained that ranges between 2.26 to 7.28. The interaction of the chelator with two trivalent metal ion Fe³⁺ and Al³⁺ were studied in aqueous solution at 298 K. The metal-ligand formation constants (ML) obtained by potentiometric and spectrophotometric method agree with each other. The protonated and hydrolyzed species were also detected in the system. The in-silico studies of the ligand, as well as the complexes including their protonated and deprotonated species assessed by density functional theory technique, gave an accurate correlation with each observed properties such as the protonation constants, stability constants, infra-red, nmr, electronic absorption and emission spectral bands. The nature of electronic and emission spectral bands in terms of number and type were ascertained from time-dependent density functional theory study and the natural transition orbitals (NTO). The global reactivity indices parameters were used for comparison of the reactivity of the ligand and the complex molecules. The natural bonding orbital (NBO) analysis could successfully describe the structure and bonding of the metal-ligand complexes specifying the percentage of contribution in atomic orbitals in the creation of molecular orbitals. The obtained high value of metal-ligand formation constants indicates that the newly synthesized chelator is a very powerful synthetic chelator. The minimum energy molecular modeling structure of the ligand suggests that the ligand, TACH2OX, in a tripodal fashion firmly coordinates to the metal ion as hexa-coordinated chelate displaying distorted octahedral geometry by binding through three sets of N, O- donor atoms, present in each pendant arm of the central tris-cyclohexaneamine tripod.

Keywords : complexes, DFT, formation constant, TACH2OX

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