



Phenol oxidation through its adduct formation with chromium complex of 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane: A theoretical study



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ARTICLE INFO

Article history:

Received 3 September 2016

Received in revised form

25 November 2016

Accepted 28 November 2016

Available online 30 November 2016

Keywords:

Chromium (III) complexes

Phenol oxidation

DFT

TD-DFT

Molecular orbital

ABSTRACT

Structural and electronic properties of $[cis-[Cr(tmpcH)X_2]^{n+}]$ ($n = 2$ or 4 ; $X = OH^-$, Cl^- , Br^- and H_2O ; $tmpcH = 1,4,8,11$ -tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane) were analyzed by DFT and TD-DFT methods. The local reactivity active site of the ligand was determined by the condensed-to atom Fukui indexes (CAFI) $f(r)$. In the study, the axial bond distance with metal ion undergoes a considerable change from shorter to longer as $OH^- < Cl^- < Br^- < H_2O$, agreeing with the molecular orbital analysis where the d_{z^2} energy is lowered for OH^- compared to H_2O at the axial position. After analyzing the geometrical data collected from literature for the complexes of Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with $tmpcH$, it was found that the bond distance decreases with increasing number of d-electrons in the 3d orbital, suggesting that the over-lapping of orbital (π) from N_{py} with the metal d-orbital is more effective than those from N_{cyclam} with metal d-orbital. Therefore, the change of different oxidation states for $[cis-[Cr(tmpcH)X_2]^{n+}]$ influences significantly the geometrical and electronic parameters. For $cis-[Cr(tmpcH)Cl_2]^{2+}$ the calculated bands are red shifted except for the lower energy band (595 nm) which agrees qualitatively with the experimental one; in addition, the effect of solvent on the electronic transition was analyzed. Furthermore, we collected the electronic data for several chromium complexes from the literature, and compared with our results by plotting the data against number of chromium compounds. Finally, the phenol oxidation properties of the chromium complexes were studied, and phenol forms an adduct with $[Cr(tmpcH)Cl]^{3+}$ to yield $[Cr(tmpcH)Cl-OPh]^{2+}$ which could produce the phenol radical, which is enhanced by the presence of $-OCH_3$ group at *para*- position in the phenolic ring.

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1. Introduction

There has been growing interest in chromium complexes for use as a therapeutic agent for the treatment of insulin insensitivity [1,2]. The molecular mechanism of chromium (III) in the biological functions [3] is mainly dependent on the nature of the ligand coordination to the metal ion [4,5], that dictates the structurally dependent functions. Macrocyclic ligands containing *N*-pyridyl are of interest because of the sterical hindered pyridyl groups which push the metal ion in the various geometrical configurations

[6–10]; for example, tetra-azamacrocyclic has four pentant pyridyl groups that form binuclear metal complexes [11–18], and the cavity of these types of ligands stabilizes a particular oxidation state to generate kinetically and thermodynamically stable compounds [19], in particular, the $tmpcH$ ligand forms exclusively binuclear complexes [20] where each metal ion is bonded with four nitrogen atoms (two from *cyclam* ring and other two from pendant pyridyl group). Crystal structure and the electronic properties of chromium (III) with $tmpcH$ [21,22] were reported, establishing the presence of an unusual hydrogen bond ($N-H \cdots N$) between pyridine nitrogen and one of the nitrogen atoms from the macrocyclic ring. Molecular orbital studies are used to predict geometry and cavity size of these types of tetraazamacrocyclic ligands to generate the biological

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functions at specific oxidation states [23].

Interestingly, the chromium complexes are also oxidants for the degradation of organic compounds; for example, the complexes $[\text{Cr}(\text{phen})_3]^{3+}$ phen = 1,10-phenanthroline [24], or $[\text{Cr}(\text{H}_2\text{Saldien})]^{3+}$ H₂Saldien = *N,N'*-bis(salicyliden) diethylenetriamine [25], and $[\text{CrH}_2\text{Salpn}]^{3+}$ H₂Salpn = *N,N*-bis(salicylidene) propane-1,3-diamine encapsulated in zeolite-Y matrix have been employed to oxidize organic compounds in the presence of H₂O₂ [26,27]. We have analyzed theoretically the adduct formation of chromium complex with phenol because this step is a crucial in the phenol oxidation. Yet, there is no study in the literature on the adduct formation to illustrate the bonding of phenol with the chromium complex. Thus the ligand tmpcH and its *cis*-[Cr(tmpcH)Cl₂]²⁺ were first optimized by DFT and then analyzed for their electronic properties by TD-DFT. The change of different metal oxidation states and their influence in the geometrical and electronic parameters were analyzed as those parameters are also important in determining reactivity. In order to show which atom in the molecule has the highest Fukui function $f(r)$ using the frontier orbital (FO) theory, the chemical reactivity of the ligand (tmpcH) = 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane is analyzed [28] (Scheme 1). Finally, the adduct formation of phenol with *cis*-[Cr(tmpcH)Cl₂] was studied in order to analyze the phenol oxidation; in the step, an electron can be removed from OH of phenol by the chromium complex to produce phenoxy radical, and this was analyzed for different phenols to show the effect of substituent on the bond formation.

2. Computational procedure

The geometry of 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tmpcH) is fully optimized by DFT with using Gaussian-09 [29]. The data were then used as input for the optimization of *cis*-[Cr(tmpcH)Cl₂]²⁺, *cis*-[Cr(tmpcH)Cl₂]²⁺, *cis*-[Cr(tmpcH)(OH)₂]²⁺, *cis*-[Cr(tmpcH)Br₂]²⁺, *cis*-[Cr(tmpcH)(H₂O)₂]⁴⁺. The calculation was performed with spin unrestricted orbitals for the complexes by considering low-spin (LS) and high spin (HS) states.

The exchange correlation was treated at the B3LYP Fukui [28,30] and this choice method was based on the results obtained from 6-31G** used for C, N, Cl, P, and H atoms, and for Cr³⁺, only DGDZVP full electron basis set was used [31]. The molecular orbital contribution to the electronic absorption of the complexes was analyzed

by using DFT-TDDFT with the B3LYP exchange-correlation functional; the DGDZVP basis set was employed to calculate the electronic transitions in the gaseous state, in solvent medium (in MeCN) and in solid state to see the solvent effect [32]. We also performed frequency calculations on the complexes and ligands.

To rationalize chemical reactions in analyzing the reactive sites in a ligand molecule, several local and global descriptors are being considered [33–37]; in the present work, the condensed-to atom Fukui indexes (CAFI) $f(r)$ was used to identify the local reactivity of the ligand as suggested in published reports [29,34,38]. The most suitable descriptor, Hirshfeld charge, was employed to calculate CAFI as proposed in previous reports [39,40]. The calculation yielded reliable NPA charges at different basis sets (DGDZVP and 6-31G**) in the B3LYP framework. The Fukui function $f(r)$ defines the derivative of the electronic density $\rho(r)$ with respect to the number of electrons *N* at a constant external potential $\alpha(r)$ and allows the identification of the most active sites in the ligand:

$$f(r) = \left[\frac{\partial \rho(r)}{\partial N} \right]$$

If the relaxation effect associated with the addition or removal of electronic charges is not considered, then

$$f^+(r) \approx \rho_{LUMO}(r)$$

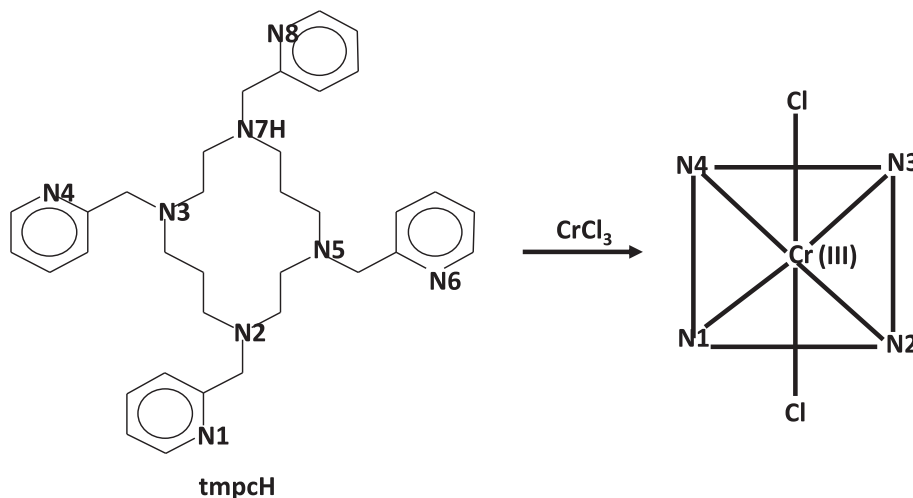
$$f^-(r) \approx \rho_{HOMO}(r)$$

$$f^0(r) \approx \frac{1}{2} [\rho_{HOMO}(r) + \rho_{LUMO}(r)]$$

$\rho_{LUMO}(r)$ = density of the first unoccupied molecular orbital; $\rho_{HOMO}(r)$ = density of the highest occupied molecular orbital [41]. The condensed Fukui functions [29] are found by taking the finite difference approximations from the population analysis of atoms in molecules, depending on the direction of the electron transfer.

For electrophilic attack, $f_x^- = [q_x(N) - q_x(N-1)]$; for nucleophilic attack, $f_x^+ = [q_x(N+1) - q_x(N)]$ (q_x = charge on atom *x* in the molecule); for radical attack, $f_x^0 = \left[\frac{f_x^+ + f_x^-}{2} \right]$.

The interaction of phenol with the chromium complex was studied theoretically in order to determine the dissociation of phenol as radical form from adduct. Thus the structure of [Cr(tmpcH)Cl-OHPh]³⁺ (multiplicity = 4) and [Cr(tmpcH)Cl-OPh]²⁺



Scheme 1. Ligand tmpcH and the complex formation with chromium ion.

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