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Full Length Article

Impact of zeolite-Y framework on the geometry and reactivity of Ru (III) benzimidazole complexes – A DFT study

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ABSTRACT

A detailed comparative Density Functional Theory (DFT) study is made to understand the structural changes of the guest complex due to steric and electronic interactions with the host framework. In this study, Ru(III) benzimidazole and 2- ethyl Ru(III) benzimidazole complexes encapsulated in a supercage of zeolite Y. The zeolitic framework integrity is not disturbed by the intrusion of the large guest complex. A blue shift in the d–d transition observed in the UV-Visible spectroscopic studies of the zeolite encapsulated complexes and they shows a higher catalytic efficiency. Encapsulation of zeolite matrix makes the metal center more viable to nucleophilic attack and favors the phenol oxidation reaction. Based on the theoretical calculations, transition states and structures of reaction intermediates involved in the catalytic cycles are derived.

1. Introduction

The transition metal complexes of benzimidazole derivatives have been a matter of constant discussion over the past few decades because of the important catalytic properties of those materials. The material also behaves as a natural mimic and therefore has a relevance in the area of pharmacology as an antioxidant, antimicrobial, anthelmintic, anticancer, anti-inflammatory, antihypertensive, and analgesic activities [1–9]. The biological role of complexes containing an imidazole ring system has a direct connection with the characteristics of the two N atoms in the system. The deprotonated N atom could coordinate with a transition metal ion, and the protonated N atom involves in hydrogen bonding [10–18]. Benzimidazole and imidazoles moieties have extensively studied in the literature as models of biologically relevant molecules present in vitamin B12 and several metalloproteins. In most of the cases, the transition metal complexes of biologically relevant ligands are more efficient than the free ligands [19,20]. Even though intensive studies are available on the zeolite encapsulated transition metals; very few reports are on ruthenium complexes. Ruthenium complexes with imidazole ligands are of substantial interest because of their antitumor activities [21,22]. The encapsulation of these complexes on a host molecule makes it as heterogeneous catalysts for oxidation and epoxidation reactions. Zeolite Y encapsulated imidazole complexes have a functional similarity with cytochrome P-450. This enables the use of Zeolite Y as biomimetic systems [23,24]. The walls of zeolite framework influence the geometry, and physicochemical properties (magnetic, electronic, and redox) of the guest encapsulated complex. Thus, the topology (voids and steric/electrostatic constraints of walls) of the host Zeolite Y matrix controls the reactivity and selectivity of the guest species. Several works have focused on the geometrical and reactivity aspects of various complexes encapsulated into Zeolite Y matrix [25–33].

Zeolite encapsulated transition metal imidazole, and benzimidazole complexes normally use as an oxidant for organic substrates such as phenol, benzyl alcohol, ethylbenzene, benzoin, and cyclohexanol. The role of transition metal centers and its preferred location in the complexes and therefore reaction mechanism became a challenge for theoretical studies. The current work deals with density functional theory studies on zeolite-Y encapsulated Ru(III) with benzimidazole and 2-ethylbenzimidazole.

2. Computational method

All the density functional calculations were done using Gaussian 09 program. For calculations, Becke's three-parameter hybrid functional with the LYP correlation functional (B3LYP) and an effective core potential basis set LanL2DZ were employed [34,35]. Zeo-

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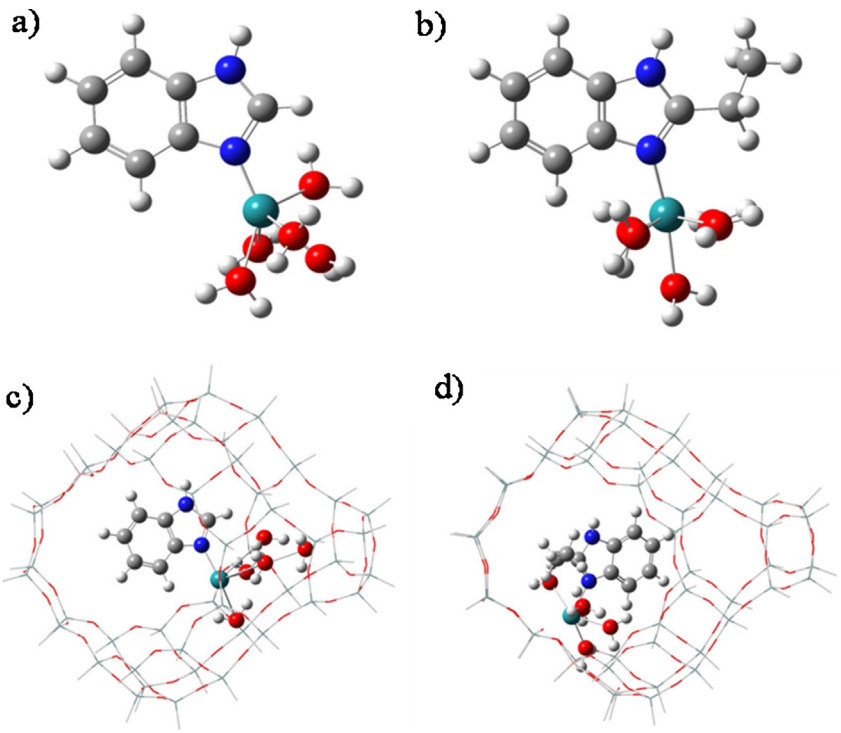

Fig. 1. Optimized structures of a) RuBzl, b) Ru-2-EtBzl, c) RuBzl –Y and d) Ru-2-EtBzl-Y complexes.

lite frameworks were generated using 40 tetrahedral units (40 T), where hydrogen atoms saturate the supercage structure. Initially, crystallographic positions of Si and O atoms were fixed and the positions of terminal hydrogen atoms are optimized. To generate three negative charges in the six-membered ring, as per Lowenstein's rule, three silicon atoms replaced with three aluminum atoms. Then, neat optimized Ru(III)complex was encapsulated inside the zeolite framework. All geometric optimizations performed without point group constraints. Three positive charges of the complexes compensate the three negative charges generated in the cluster.

Koopmans theorem [36] gives the chemical potential (μ) and global hardness (η) of a system of complexes and it could express as

$$\mu = \frac{E_{LUMO+}E_{HOMO}}{2} \quad (1)$$

$$\eta = \frac{E_{LUMO-}E_{HOMO}}{2} \quad (2)$$

Here, E_{LUMO} and E_{HOMO} represent the lowest unoccupied molecular orbital energy and highest occupied molecular orbital energy respectively.

The global electrophilicity as presented by Parr et al. [37]. can be defined as

$$\omega = \frac{\mu^2}{2\eta} \quad (3)$$

The inverse of the global hardness (η) is the global softness(S)

$$S = 1/2\eta \quad (4)$$

Time-dependent DFT (TD—DFT) calculations were performed at B3LYP/LANL2DZ level from the optimized ground state geometry. 150 excitation energies are computed. Calculation of UV–vis spectra was accomplished using GaussSum 2.0 [38]. The intra molecular interaction in the complexes has been analyzed via the natural bond orbital analysis (NBO). Transition state was confirmed by analysis of first frequency which has a negative value which corresponds to the imaginary frequency. TS1, TS2 and TS3 transition states showed only a single imaginary frequency corresponding to the eigenvector along the reaction path.

Table 1
Geometrical parameters of neat and encapsulated complexes.

Complex	Bond Length (in Å)	Bond Angle (in deg)	
	N – Ru	C1∠N∠Ru	C2∠N∠Ru
RuBzl	2.07	121.7	132.5
Ru-2-EtBzl	2.06	129.5	124.9
RuBzl-Y	2.03	138.2	114.0
Ru-2-EtBzl-Y	2.04	125.6	128.2

3. Results and discussions

3.1. Ground-state geometries

In the present work all the calculations were done using Gaussian 09 program package with the use of the Gauss View visualization program. The geometry of the complexes were optimized using Becke's three-parameter exchange, Lee, Yang, and Parr correlation (B3LYP) hybrid functional with LanL2DZ basis set. The vibrational frequency analysis of the optimized geometry shows all real frequencies and it is confirmed that the optimized geometry corresponded to minimum potential energy surface. The optimized structures of the neat and encapsulated form of the complexes have shown in Fig. 1.

The selected geometric parameters of the optimized neat complex and the zeolite encapsulated complex from LanL2DZ level calculations are provided in Table 1. The geometrical parameters such as bond length and bond angles of the neat complex have been compared with those of encapsulated complexes. The bond length between Ru and metal nitrogen is 2.07 and 2.06 Å. While encapsulating this bond length is decreased by 0.04 and 0.02 Å. Ethyl substituted Ru complexes shows shorter bond length, because ethyl group donates the electron density to the metal centre. Similarly bond angle also varies. The variation in the bond distances and