

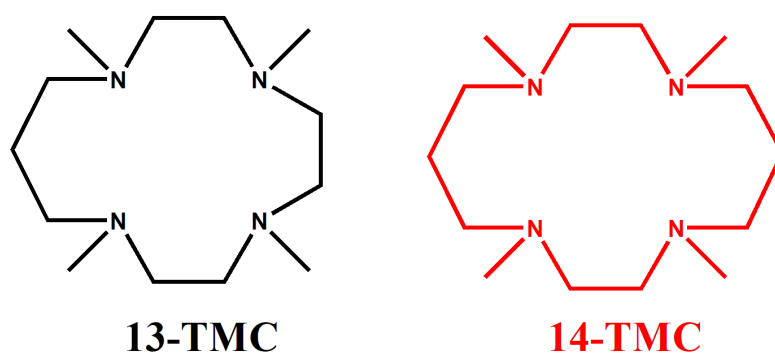
Chapter 5

Effect of TMC Ring Size in Mononuclear Metal Complexes: A DFT Exploration

5.1 Introduction

Dioxygen activation in metalloenzyme results in the formation of metal-dioxygen ($M-O_2$) as the reactive intermediate.¹⁻³ In $M-O_2$ species, the binding nature of dioxygen with metal defines the formation of metal-superoxo (η^1) and metal-peroxo (η^2). Metal-peroxo species are involved in catalase, superoxide dismutase, and the oxygen-evolving complex in photosystem-II are the enzymes that have manganese as a central metal.⁴⁻⁷ In cytochrome P450 and Rieske-dioxygenase, iron-peroxo species are involved.⁸⁻¹⁴ Several metal-peroxo/superoxo complexes have been synthesized and characterized spectroscopically.¹⁵⁻¹⁹ Metal-superoxo species are reported as the reactive intermediate in many catalytic transformation reactions such as hydroxylation, amination, dehydrogenation, and epoxidation which involves C-H bond activation and oxygen atom transfer reactions.²⁰⁻²⁹ The powerful oxidative properties of high valent superoxo species mimic their catalytic activity and are inspired to prepare complexes having such units. Considerable efforts have been devoted to synthesize and characterize models of these transient species with various spectroscopic techniques and X-ray crystallography.³⁰⁻⁴⁴ Structure and chemical reactivity of short-lived metal-superoxo intermediate are found in biomimetic studies.⁴⁵⁻⁵¹ The binding modes of the oxygen unit and metal were elucidated by the X-ray crystallographic analysis and the resonance measurements.⁵² From last few decades, several high valent vanadium, chromium, manganese, iron, and cobalt, -oxo, peroxo, superoxo and hydroperoxo species are reported in the literature.^{31-35,53-58} Recently, metal-superoxo species have attracted much more attention because of their wide application in C-H bond activation and oxygen atom transfer reaction by non-heme iron, manganese, and chromium species.⁵⁹⁻⁷⁷ The biomimetic approach is interesting because cheap and non-toxic reactants, O_2 and H_2O_2 as oxidants are used in such reactions and also provide the capability of C-H bond activation of organic substrates. By bioinorganic chemistry studies, we can understand the structure of active sites of reactive

intermediates and the mechanism of reaction occurring at the active sites, and the factors which determine the ability of catalytic transformation reactions. Electronic structures and geometries of molecules are determined by several factors as the nature of metal ion and ring size of ligand.^{15,17,78-79} Single crystal of Cr(III)-superoxo bearing the chloride ion *trans* to the superoxo species has been reported in which orientation of methyl groups of TMC ligand is *trans* to the superoxo unit.²² Reactivity of the metal-superoxo complexes explained experimentally by Wonwoo Nam group.^{22,58,80} Interaction of organic substrates with the superoxo species is easier than the oxo group and bond strength between chromium and oxygen in the case of superoxo is relatively weaker than the corresponding oxo species. A few theoretical studies have been accounted on the chromium-superoxo towards reactivity.^{22,58} Peroxo-complexes with Mn(III), Fe(III), Co(III), and Ni(III) have been reported in which methyl groups of TMC-ring lies syn to peroxo unit. It is also found that in a higher oxidation state it forms the peroxo species due to greater electron-donating power of peroxo unit than superoxo unit as Cr(III)-superoxo is formed with 14-TMC(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) and the Cr(IV)-peroxo with the 12-TMC (1,4,7,10-tetramethyl-1,4,7,10-tetraazacyclododecane) ligand.^{19,21,80} Mn(III)/Fe(III)/Co(III) metal forms peroxo complex while Ni(II) forms superoxo complex, ring size also affects the geometry of complex.



Scheme 5.1. TMC Ligands Used in the Synthesis of M-O₂[•] Complexes.

Several TMC ligated metal oxo/peroxo/superoxo have been found in earlier studies.¹⁶ Ring size of TMC ligands can affect the electronic structure of metal-superoxo species and also control the reactivity. To clarify the origin of the difference in reactivity due to different ring sizes of ligands and explore the ring size effect of TMC ligand on the stability and C-H activation by the superoxo species. Here, we have undertaken the theoretical studies on the first transition series focused mainly on V, Cr, Mn, Fe, and Co to answer the following questions; (i) to study the structure of metal-superoxo species of the metals with 13/14-TMC ligand followed by (ii) Effect of ring size on C-H activation and (iii) comparative study among them.

5.2 Computational Details

All calculations are performed by using the Gaussian16 program.⁸¹ There is a fragment approach available in Gaussian16, which is used for all calculations. In previous studies, method assessment has been done by using the functionals such as B3LYP,⁸²⁻⁸³ B3LYPD-2,⁸⁴ wB97XD,⁸⁵ B97D,⁸⁴ M06-2X,⁸⁶ TPPSh,⁸⁷ and MP2⁸⁸ and it was found that B3LYP, B3LYPD2, and wB97XD functional predicts the correct spin state of transition metal complexes.^{71,89-91} Among these three functionals, B3LYP-D2 was also found as the superior. So, we have restricted our calculations to B3LYP-D2 functional. LanL2DZ basis set compromising the double- ζ with Los Alamos effective core potential used for transition metals (V, Cr, Mn, Fe, and Co),⁹²⁻⁹⁴ and 6-31G⁹⁵ basis set for other atoms such as H, C, N, O, and Cl are used for geometry optimization. The frequency calculations are performed on the optimized structures to verify the minima on the potential energy surface (PES) and also to calculate free energy corrections. Transition states are confirmed by a single imaginary frequency and are verified by animating the imaginary frequency using visualization software such as GaussView6. The optimized geometries are used for the single point energy calculations using TZVP⁹⁶⁻⁹⁸ basis

set for all the atoms. Acetonitrile is employed as a solvent for computing solvation energies using the polarizable continuum solvent (PCM) model. The quoted DFT energies are B3LYP-D2 solvation energies incorporating the free energies computed at 298.15 K. Intrinsic reaction coordinates (IRC) calculations are performed on the selected transition states to verify that the minimum stationary point that is associated with the reactant and product are connected by the transition state. In metal-superoxo species, the magnetic exchange between the metal center and the distal oxygen is computed by using a spin Hamiltonian.

$$\hat{H} = -J\mathbf{S}_1 \cdot \mathbf{S}_2$$

Where, J denotes the magnetic exchange coupling constant. Noodleman's broken symmetry is used to calculate the magnetic exchange coupling constant. Positive J values indicate the ferromagnetic coupling whereas negative J values indicate antiferromagnetic coupling.⁹⁹⁻¹⁰⁰ Here, $^x\text{M}_{a/b-y}$ notation (where x is overall multiplicity, M is the transition metal (I=V, II=Cr, III=Mn, IV= Fe, V=Co), subscripts a , and b are corresponding for 13-TMC and 14-TMC, respectively, and y is spin-state of metal).

5.3 Results and Discussion

Here, we have modeled vanadium, chromium, manganese, iron, and cobalt-superoxo species with 13/14-TMC started with the available X-ray structure of chromium(III)-superoxo.²²

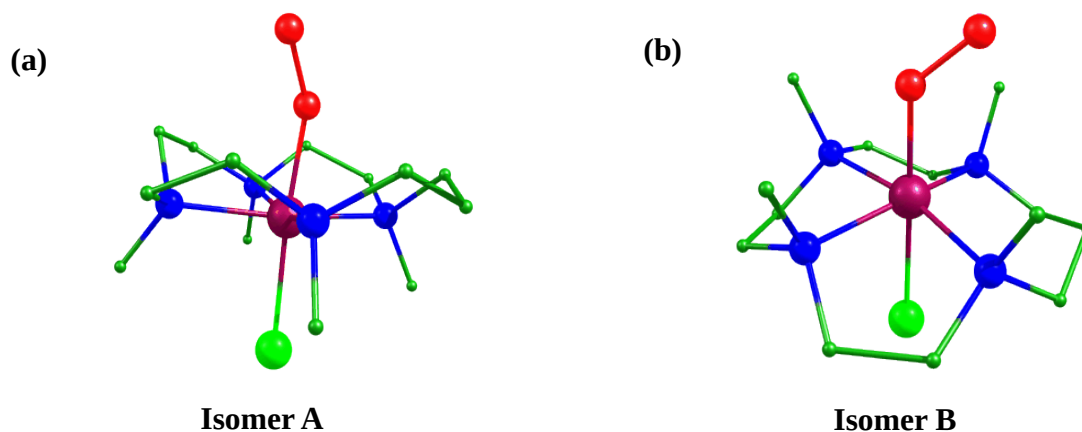


Figure 5.1. B3LYP-D2 optimized structures a) Isomer A and b) Isomer B.**Table 5.1.** B3LYP-D2 computed relative energy (ΔG in kJ mol⁻¹) for species I to IV with both the isomer A and B.

Spin state	13-TMC	14-TMC	
([V(13/14-TMC)O₂Cl]⁺, I)			
⁴ IA _a -hs	43.6	⁴ IA _b -hs	51.5
² IA _a -hs	0	² IA _b -hs	0
⁴ IB _a -hs	62.1	⁴ IB _b -hs	67.1
² IB _a -hs	10.6	² IB _b -hs	14.7
([Cr(13/14-TMC)O₂Cl]⁺, II)			
⁵ IIA _a -hs	13.1	⁵ IIA _b -hs	16.5
³ IIA _a -hs	0	³ IIA _b -hs	0
³ IIA _a -ls	3.9	³ IIA _b -ls	4.1
¹ IIA _a -ls	274.1	¹ IIA _b -ls	264.4
⁵ IIB _a -hs	28.9	⁵ IIB _b -hs	24.9
³ IIB _a -hs	6.6	³ IIB _b -hs	5.5
³ IIB _a -ls	13.7	³ IIB _b -ls	7.8
¹ IIB _a -ls	273.4	¹ IIB _b -ls	265.5
([Mn(13/14-TMC)O₂Cl]⁺, III)			
⁶ IIIA _a -hs	0	⁶ IIIA _b -hs	26.4
⁴ IIIA _a -hs	17.2	⁴ IIIA _b -hs	0
⁴ IIIA _a -is	26.5	⁴ IIIA _b -is	86.0
² IIIA _a -is	35.3	² IIIA _b -is	60.9
² IIIA _a -ls	35.2	² IIIA _b -ls	63.1
⁶ IIIB _a -hs	15.6	⁶ IIIB _b -hs	28.6
⁴ IIIB _a -hs	30.9	⁴ IIIB _b -hs	3.5
⁴ IIIB _a -is	61.8	⁴ IIIB _b -is	93.9
² IIIB _a -is	40.4	² IIIB _b -is	65.1
² IIIB _a -ls	142.5	² IIIB _b -ls	65.0
([Fe(13/14-TMC)O₂Cl]⁺, IV)			
⁷ IVA _a -hs	0	⁷ IVA _b -hs	0
⁵ IVA _a -hs	20.2	⁵ IVA _b -hs	6.8
⁵ IVA _a -is	37.5	⁵ IVA _b -is	38.8
³ IVA _a -is	96.4	³ IVA _b -is	71.7
³ IVA _a -ls	54.4	³ IVA _b -ls	43.9
¹ IVA _a -ls	145.6	¹ IVA _b -ls	135.1
⁷ IVB _a -hs	27.6	⁷ IVB _b -hs	8.2
⁵ IVB _a -hs	27.6	⁵ IVB _b -hs	18.8
⁵ IVB _a -is	40.7	⁵ IVB _b -is	75.4
³ IVB _a -is	62.7	³ IVB _b -is	56.7
³ IVB _a -ls	48.9	³ IVB _b -ls	131.9
¹ IVB _a -ls	136.2	¹ IVB _b -ls	132.0

There are two possible isomers (A and B) based on methyl groups of TMC ring lie anti (A) or syn (B) to the superoxo unit (see Figure 5.1). From our calculations, it was found that the methyl group lies syn to superoxo species (B) has higher energy by 10.6/14.7 kJ/mol of $[\text{V}(13/14\text{-TMC})\text{O}_2\text{Cl}]^+$, 6.5/5.5 kJ/mol with $[\text{Cr}(13/14\text{-TMC})\text{O}_2\text{Cl}]^+$, 15.6/3.6 kJ/mol with $[\text{Mn}(13/14\text{-TMC})\text{O}_2\text{Cl}]^+$ and 27.1/1.6 kJ/mol with $[\text{Fe}(13/14\text{-TMC})\text{O}_2\text{Cl}]^+$ than the corresponding anti isomer (A) respectively, (see Table 5.1) and are in agreement with the available experimental studies.¹⁵ These energy differences may be due to steric repulsion between methyl groups and superoxo units. The space-filling model of optimized geometry of the isomer B is more sterically hindered than the corresponding isomer A (see Figure 5.2). Therefore, we have restricted our calculations to the anti-isomer (A) species. We have also computed the formation energy for superoxo species with metals (V, Cr, Mn, Fe, and Co) along with 13/14-TMC rings and our results show that all these energies are exothermic (see Table 5.2) which indicates a favorable formation of these species.

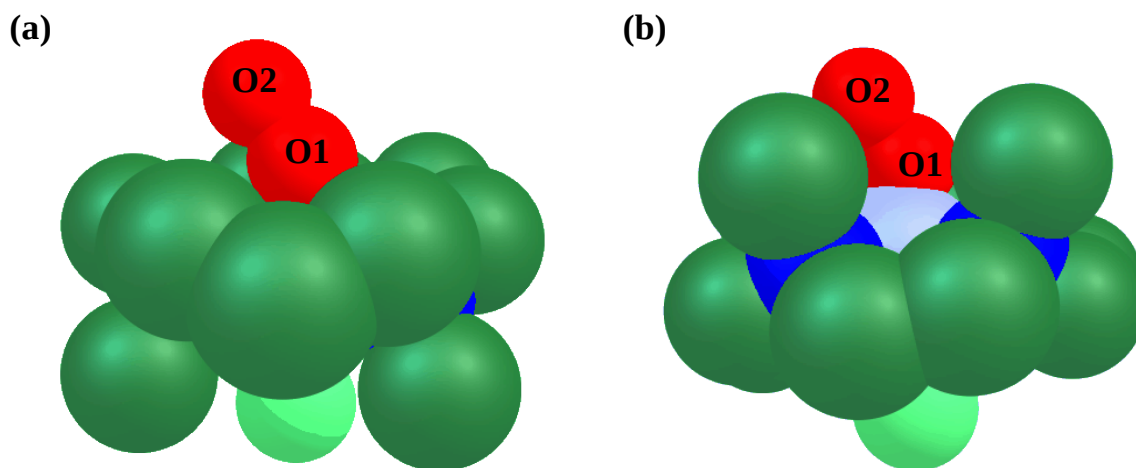


Figure 5.2. Space-filling model of vanadium -superoxo species with a) 13-TMC syn; b) 13-TMC anti, metal silver, C (olive), N (blue), O (red).

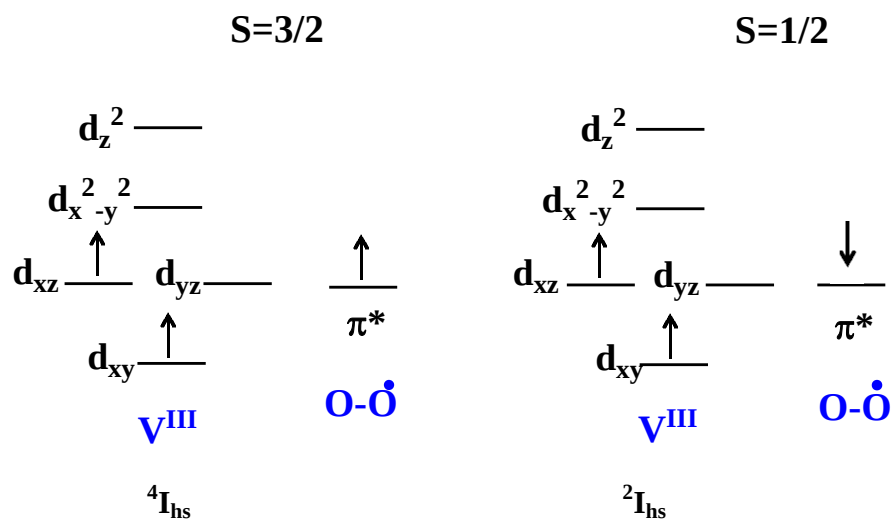
Here, we have started our DFT calculations on the vanadium-superoxo species (I) along with a detailed mechanistic study of C-H bond activation of cyclohexa-1,4-diene and then followed with the other metal-superoxo species.

Table 5.2. B3LYP-D2 computed formation energies of I to V species with the ground state.

Formation energy(kJ/mol)		
Spin State	13-TMC	14-TMC
$^2\text{I}_{\text{hs}}$	-727.4	-725.5
$^3\text{II}_{\text{hs}}$	-688.2	-670.7
$^{6/4}\text{III}_{\text{hs}}$	-586.9	-646.0
$^7\text{IV}_{\text{hs}}$	-652.9	-642.7
$^2\text{V}_{\text{ls}}$	-686.1	-1515.1

5.3.1 Vanadium-superoxo species ($[\text{V}(\text{13/14-TMC})\text{O}_2\text{Cl}]^+$, $\text{I}_{\text{a/b}}$)

There are two possible spin interactions between vanadium center and superoxo unit (such as $^4\text{I}_{\text{a/b-hs}}$, and $^2\text{I}_{\text{a/b-hs}}$) are shown in Scheme 5.1 of ESI and our DFT calculations predicted that $^2\text{I}_{\text{a-hs}}$ and $^2\text{I}_{\text{b-hs}}$ are found to be the ground state with $^4\text{I}_{\text{a-hs}}$, and $^4\text{I}_{\text{b-hs}}$ lie at 43.6, and 51.5 kJ/mol higher in energy, respectively (see Figure 5.3). The optimized structure and spin density plot of the ground state of both the vanadium species ($^2\text{I}_{\text{a/b-hs}}$) are shown in Figure 5.4. The computed angle $\angle\text{V-O1-O2}$ of the ground state ($^2\text{I}_{\text{a/b-hs}}$) are 176.4° , and 173.7° , respectively, and these show that the angle decreases upon the ring size increases, and also indicates towards linearity of V-O-O $^\bullet$ (see Table AX 5.1 and Table AX 5.2 of appendix). The $d_{\text{yz/xz}}$ orbital of vanadium and p -orbital of oxygen unit are orthogonal to each other. The computed V-O1 bond length of $^2\text{I}_{\text{a-hs}}$ and $^2\text{I}_{\text{b-hs}}$ is 1.740 Å, and 1.741 Å and it is found that, as the ring size increases, V-N_{avg}/V-Cl bond lengths also increase 2.159/2.369 Å ($^2\text{I}_{\text{a-hs}}$), and 2.203/2.371 Å ($^2\text{I}_{\text{b-hs}}$), whereas the O1-O2 bond lengths decrease as 1.347 Å ($^2\text{I}_{\text{a-hs}}$) and 1.343 Å ($^2\text{I}_{\text{b-hs}}$). The computed spin density at the vanadium center and the distal oxygen of $^2\text{I}_{\text{a/b-hs}}$ is found as 1.960/2.014, and -0.451/-0.478 (see Table AX 5.3. and Table AX 5.4. of appendix).



Scheme 5.1. A model structure of vanadium-superoxo species with the existence of quartet, and doublet spin states.

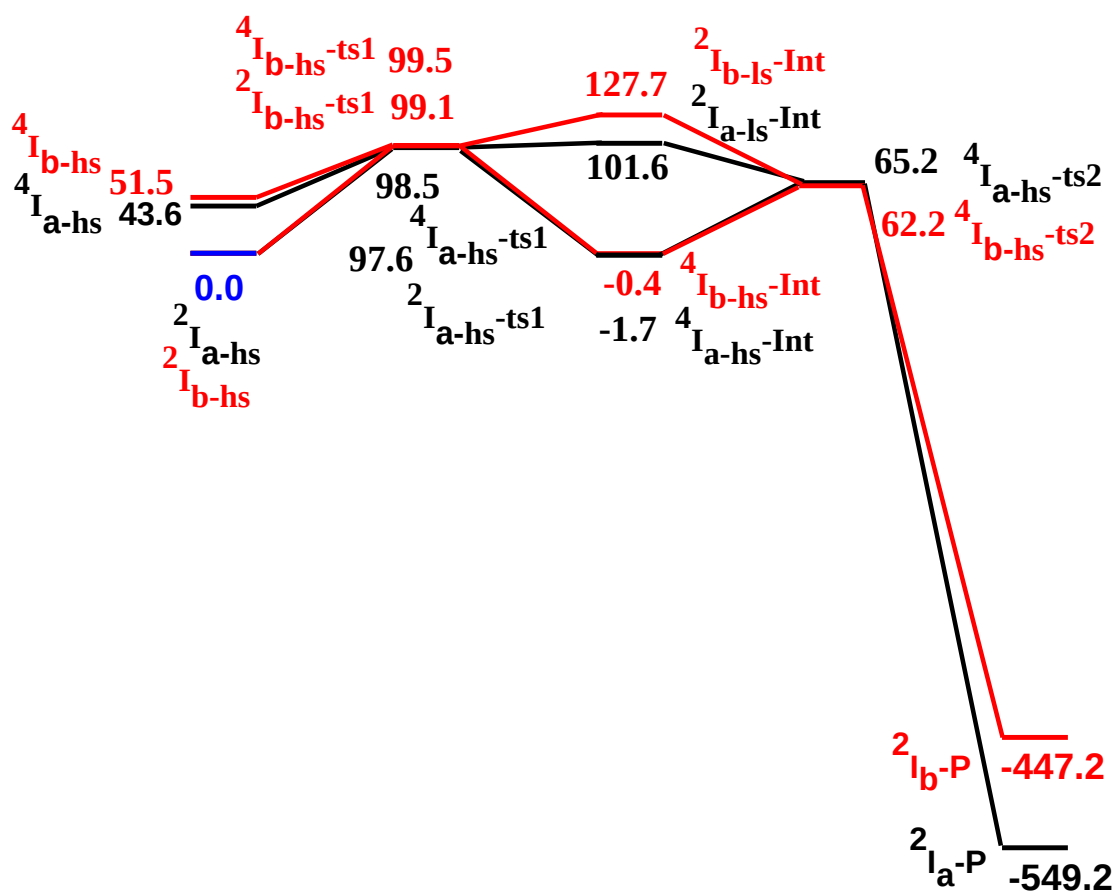


Figure 5.3. B3LYP-D2-computed potential energy surface (ΔG in kJmol^{-1}) for C-H activation by vanadium-superoxo species $2I_{a-hs}$ and $2I_{b-hs}$ (13-TMC (black), 14-TMC (red)).

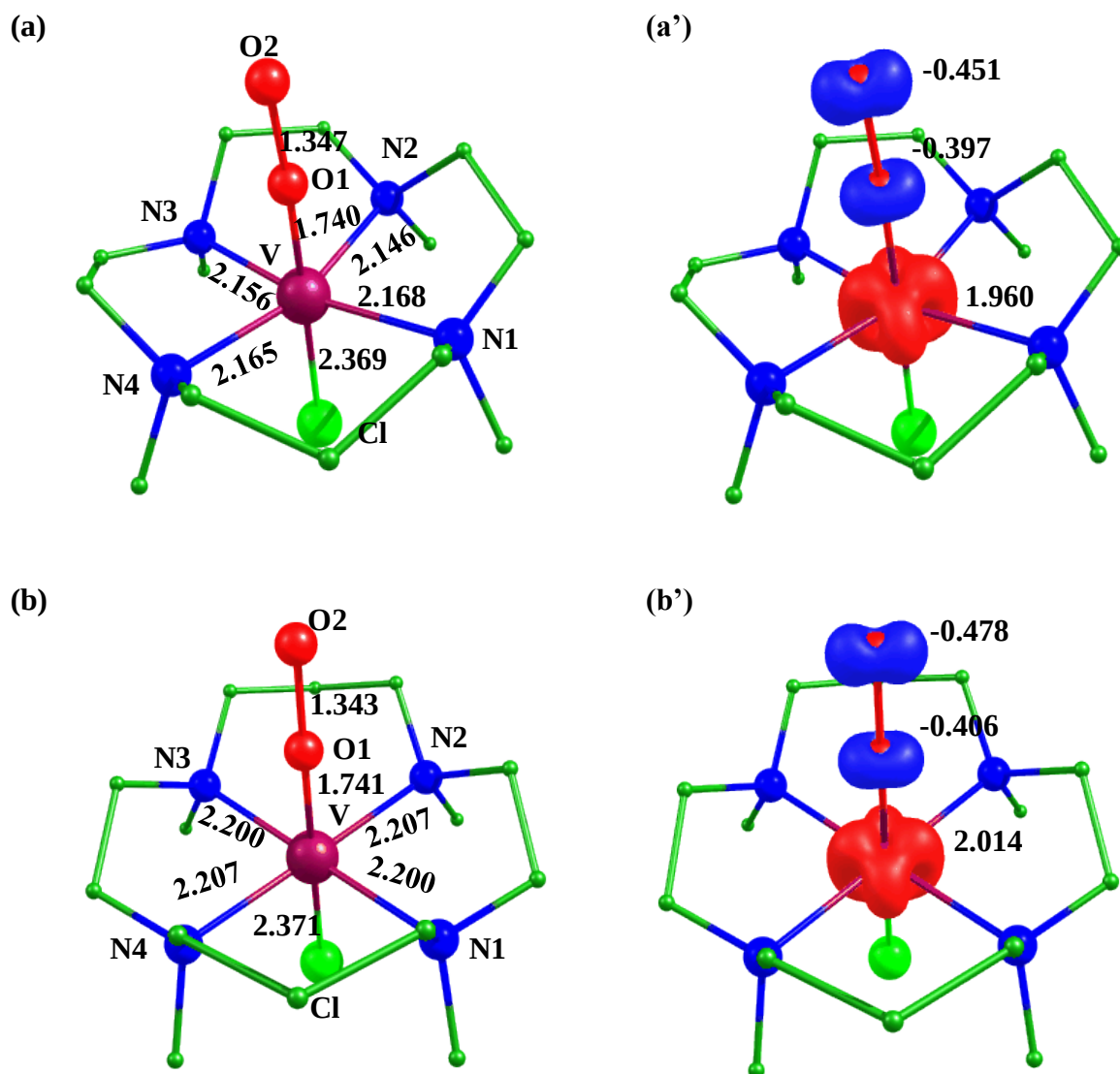


Figure 5.4. B3LYP-D2 a) Optimized structure (bond lengths in Å), a') corresponding spin density plot of $^2I_{a-hs}$, b) optimized structure (bond lengths in Å), and b') corresponding spin density plot of $^2I_{b-hs}$.

The electronic configuration at the vanadium center of the $^2I_{a-hs}$ and $^2I_{b-hs}$ is found the same as $(d_{xy})^1, (d_{xz})^1, (d_{yz})^0, (d_{x^2-y^2})^0, (d_z)^0$ (see Figure 5.5). The magnetic exchange coupling constant (J) of the species I_a and I_b have computed to -1945.1 cm^{-1} and -1965.7 cm^{-1} show the strong antiferromagnetic interaction between metal and superoxo unit. A significant electron density at distal oxygen indicates the reactive nature of superoxo species and may be responsible for C-H activation.

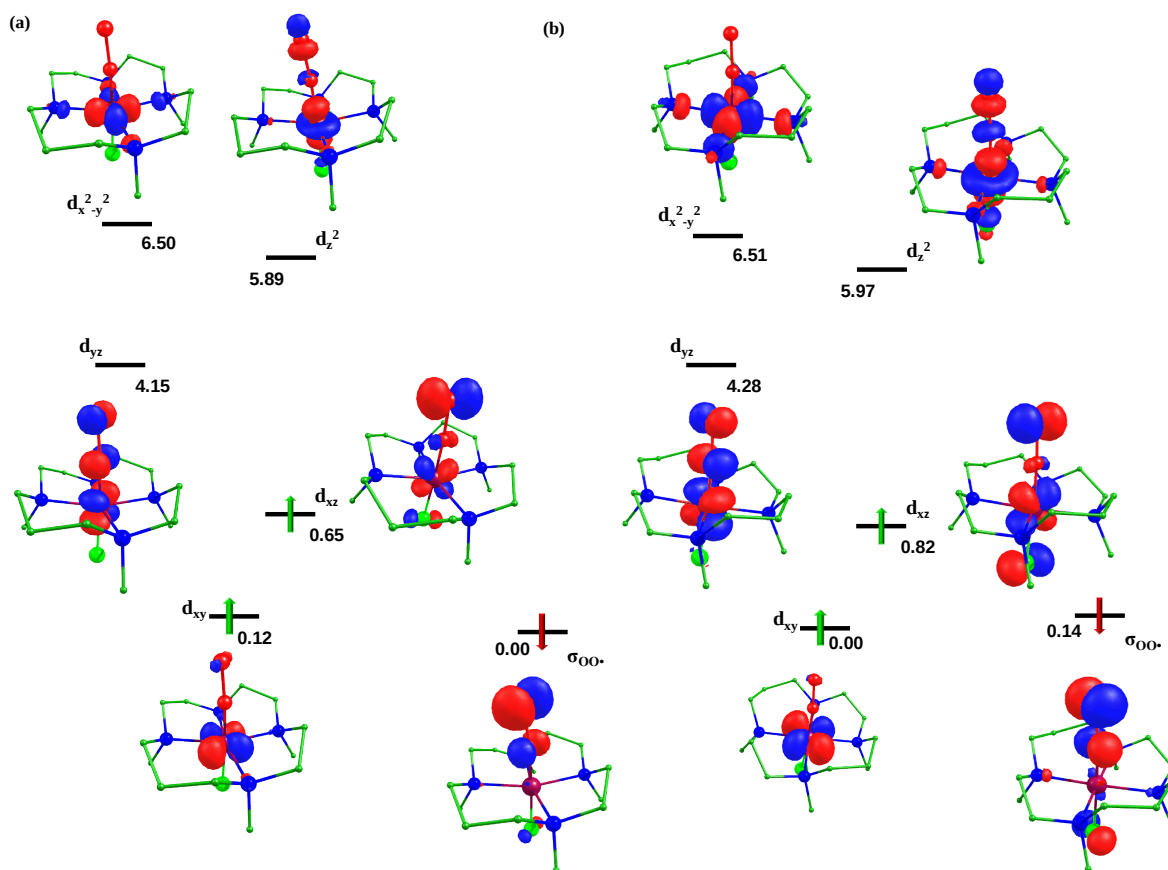
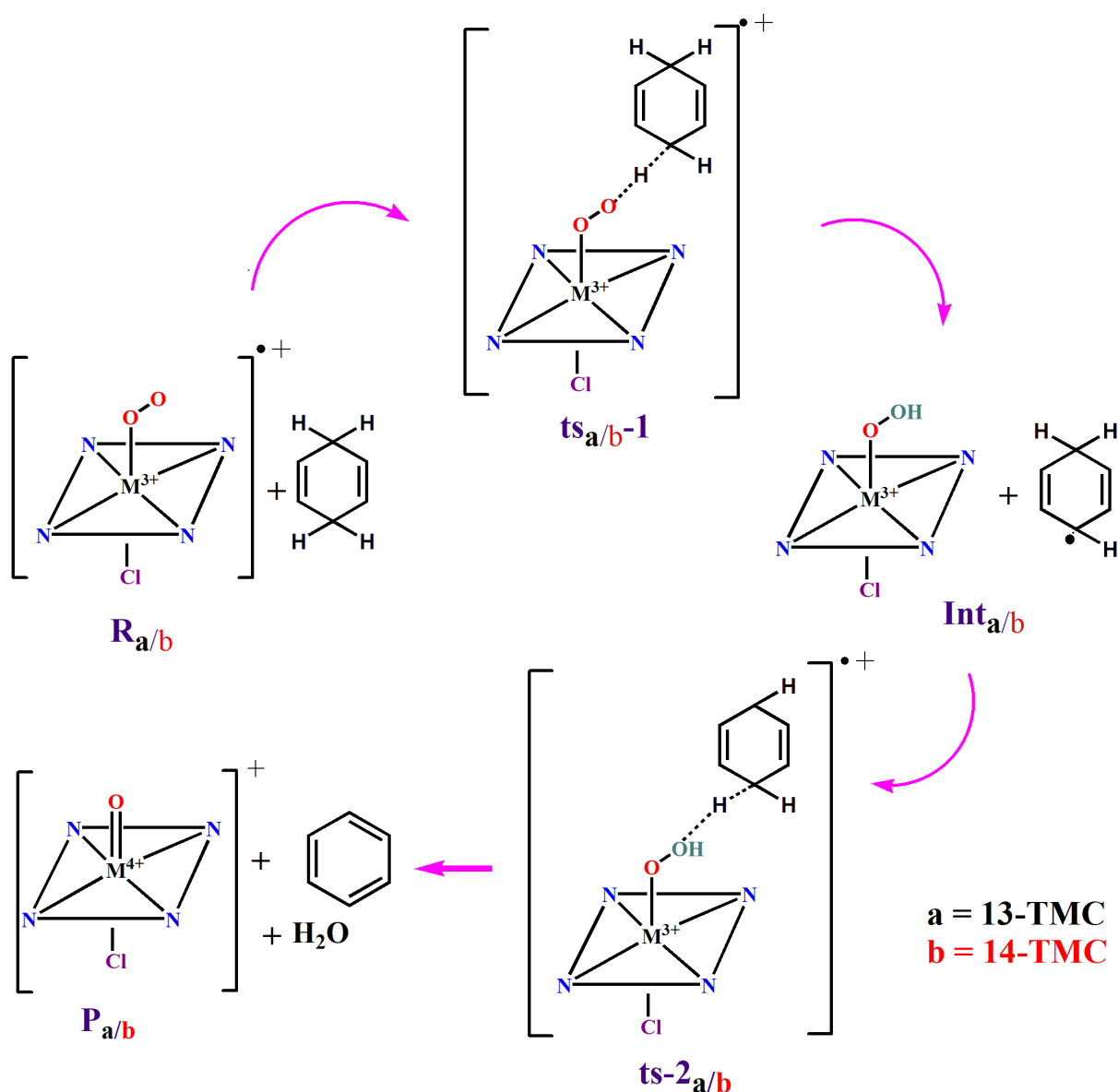


Figure 5.5. Computed eigenvalue plot incorporating energies computed for d based orbitals for alpha and beta spin corresponding to the ground state a) ($^2I_{a-hs}$) of vanadium-superoxo species (energies are given in eV), and b) ($^2I_{b-hs}$).

Here, we have also tested the reactivity of vanadium-superoxo species towards C-H bond activation with cyclohexa-1,4-diene. There are two possible pathways for C-H bond activation, either attacking by proximal oxygen or distal oxygen. In our previous report, it is found that C-H bond activation by the distal oxygen is more favorable.⁵⁶ It can also be seen from space-filling model where the proximal oxygen is showing more sterically hindered than the distal oxygen due to which substrate can easily access by the distal oxygen (see Figure 5.2). So, here we have opted for the distal oxygen for our further calculations. The proposed mechanism of C-H bond activation by superoxo species is shown in Scheme 5.2. From our calculations, it is found that the barrier heights for the C-H bond activation are found as 97.6 and 99.1 kJ/mol at the spin surfaces $^2I_{a-hs-ts1}$, and $^2I_{b-hs-ts1}$, respectively.



Scheme 5.2. Mechanism of C-H bond activation of cyclohexa-1,4-diene by superoxo species.

The optimized structures along with spin density plots of the transition state ($^2\text{I}_{a\text{-hs}}\text{-ts1}$ and $^2\text{I}_{b\text{-hs}}\text{-ts1}$) are shown in Figure 5.6(a/a'b/b'). Spin density on vanadium centers during transition states ($^2\text{I}_{a/b\text{-hs}}\text{-ts1}$) increases by ($\Delta\rho=0.202/0.167$), indicates that extra electron is coming to the metal center. A significant spin density is also located at the C1 center -0.283 ($^2\text{I}_{a\text{-hs}}\text{-ts1}$), -0.272 ($^2\text{I}_{b\text{-hs}}\text{-ts1}$) indicates the formation of radical character rather than cation or anion. The computed spin densities show that C-H bond activation occurs via proton-coupled electron transfer (PCET) mechanism,

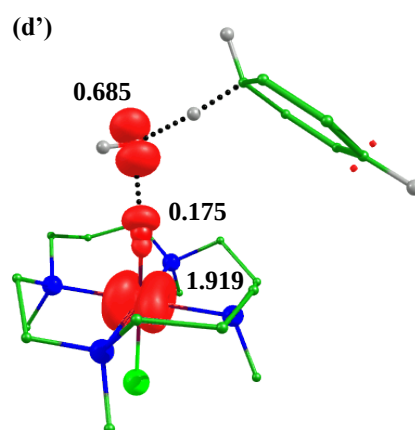
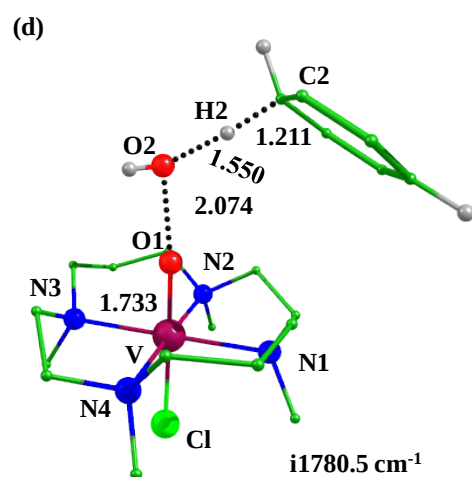
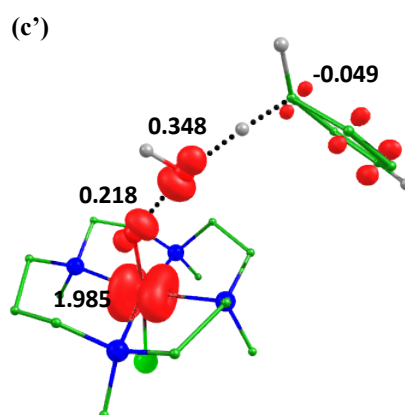
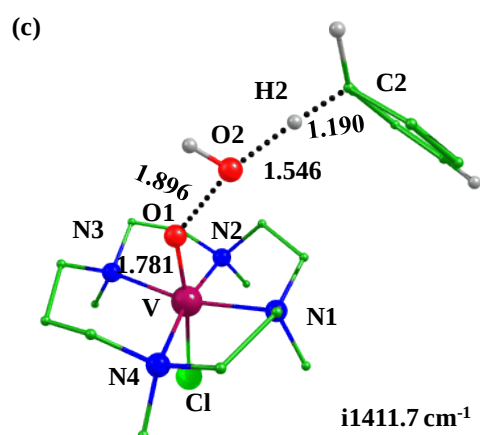
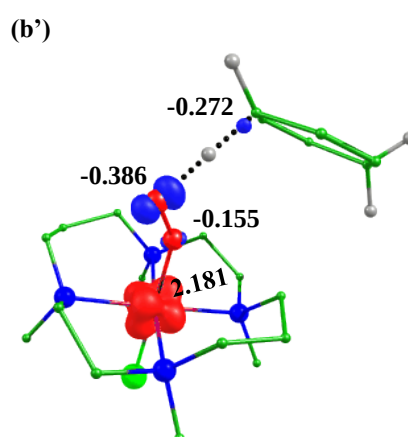
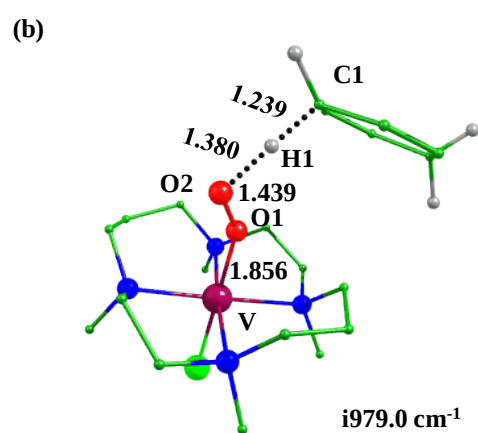
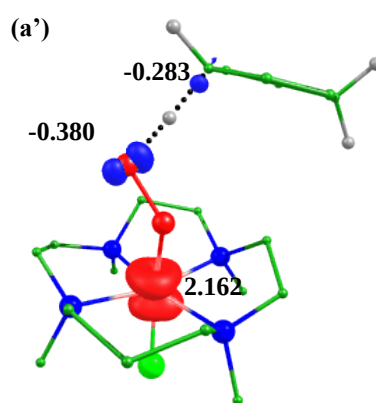
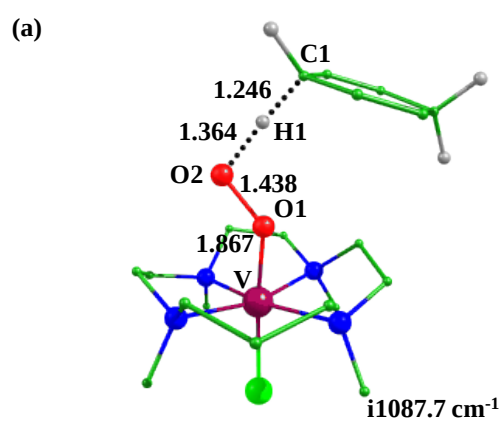


Figure 5.6. B3LYP-D2 a) optimized structures and a') spin density plots of $^2I_{a\text{-hs}}\text{-ts1}$, b) optimized structures and b') spin density plots of $^2I_{b\text{-hs}}\text{-ts1}$, c) optimized structures and c') spin density plots of $^2I_{a\text{-hs}}\text{-ts2}$, d) optimized structures and d') spin density plots of $^2I_{b\text{-hs}}\text{-ts2}$.

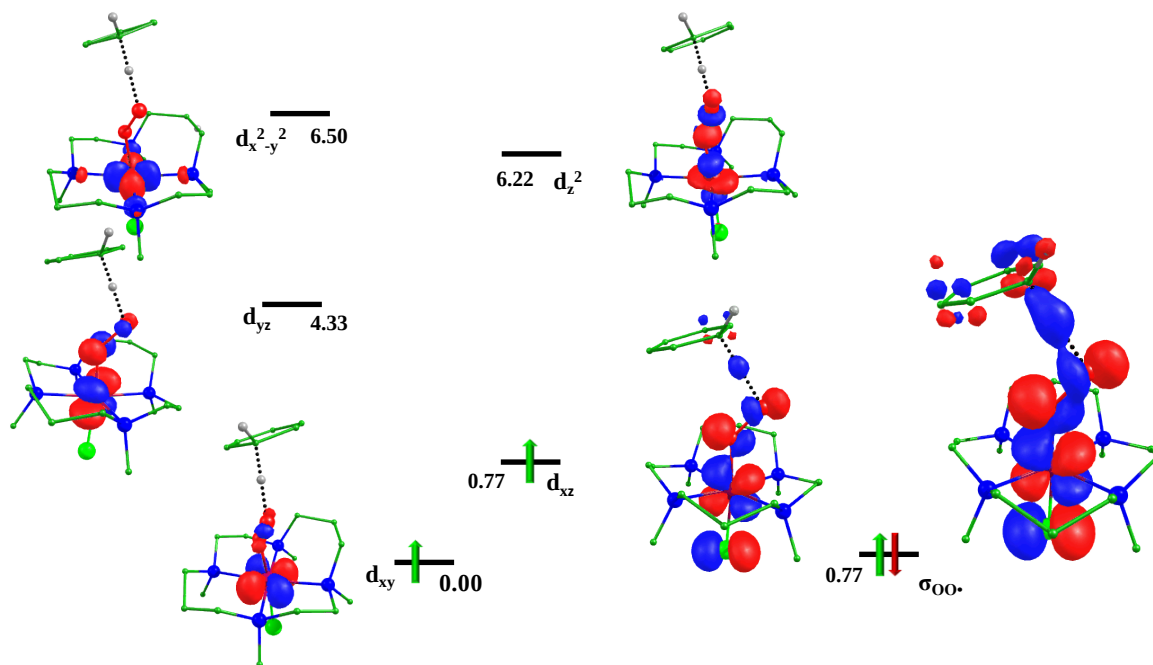
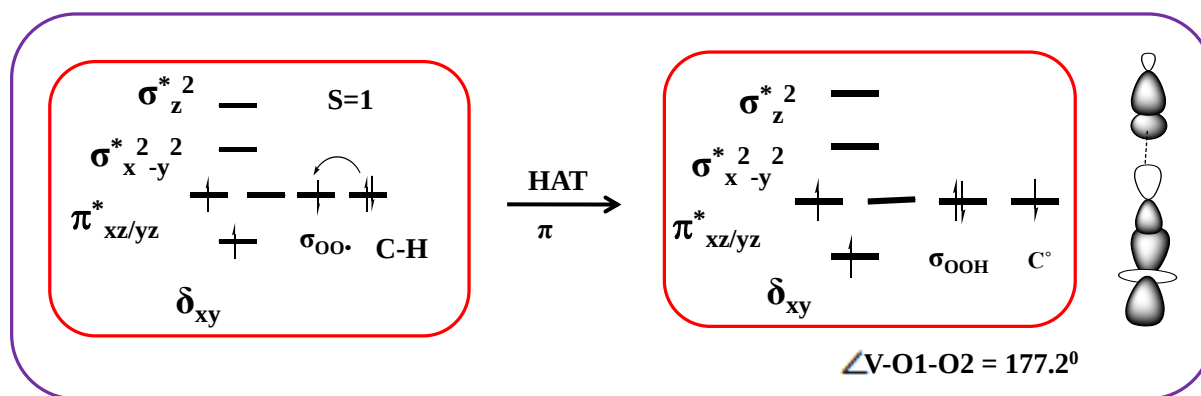


Figure 5.7. Computed eigenvalue plot incorporating energies computed for d based orbitals for alpha and beta spin corresponding to the ground state ($^2I_{a\text{-hs}}\text{-ts1}$) of vanadium-superoxo species (energies are given in eV).

which is confirmed by the eigenvalue plot (see Figure 5.5a and Figure 5.7). The $\angle\text{O2-H1-C1}$ during the C-H bond activation with 13/14-TMC are found to be $177.2^\circ/178.1^\circ$ (see Table AX 5.1 and Table AX 5.2 of appendix), respectively, reveals that C-H activation occurs via the σ pathway (see Scheme 5.3). The V-O1 bond increases by $0.127 \text{ \AA}$ ($^2I_{a\text{-hs}}\text{-ts1}$), and $0.115 \text{ \AA}$ ($^2I_{b\text{-hs}}\text{-ts1}$) whereas the O1-O2 bond increases by $0.091 \text{ \AA}$, and $0.096 \text{ \AA}$ during the transition state. After abstraction of hydrogen vanadium-superoxo species form hydroperoxo ($^4\text{Int}_{a/b\text{-hs}}$) and ($^2\text{Int}_{a/b\text{-ls}}$) and cyclohexa-1,4-dienyl radical, and $^4\text{Int}_{a\text{-hs}}$ and $^4\text{Int}_{b\text{-hs}}$ lie at -1.7 and -0.4 kJ/mol (see Scheme 5.2 and Figure 5.3). After the formation of the vanadium hydrogen peroxide intermediate the reaction may proceed in two possible pathways;



Scheme 5.3. Orbital diagram for sigma (σ) pathway.

(i) the hydrogen peroxide vanadium species obtained from the earlier reaction can attack the cyclohexa-1,4-dienyl radical (pathway 1) and (ii) generation of homolytic/heterolytic cleavage of the O---O bond of the $\text{V}^{\text{III}}\text{O-OH}$ to generate $\text{V}^{\text{IV}}=\text{O}/\text{V}^{\text{V}}=\text{O}$ oxidants which could abstract the second hydrogen atom from cyclohexa-1,4-dienyl radical to form the final product (pathway 2). But it was found that pathway 1 is more favorable over the pathway 2 in the previous report.⁷¹ In the next step, vanadium hydroperoxo further abstracts the hydrogen of cyclohexa-1,4-dienyl radical leads to the formation of vanadium(IV)-oxo species, water, and benzene (see Scheme 5.2) via homolytic O---O bond cleavage. The barrier for the second hydrogen atom abstraction is found to be 65.2 kJ/mol ($^4\text{I}_{\text{a-hs-ts2}}$) and 62.2 kJ/mol ($^4\text{I}_{\text{b-hs-ts2}}$). The optimized structures and spin density plots of $^4\text{I}_{\text{a-hs-ts2}}$ and $^4\text{I}_{\text{b-hs-ts2}}$ are shown in Figure 5.7c,d. The formation of vanadium-oxo species is found to be exothermic by a large margin (see Figure 5.3). As doublet spin state is predicted as the ground state of the vanadium(IV) species which is in agreement with earlier reports.¹⁰¹⁻¹⁰⁹ A significant spin density is also observed at the oxygen of vanadium-oxo may further involve in C-H bond activation of organic compounds (Table AX 5.3, Table AX 5.4 and see Figure 5.4 of appendix). Our computed barrier heights show that 13-TMC ligated vanadium species are more reactive than the corresponding 14-TMC species (see Figure 5.3).

5.3.2 Chromium-superoxo species ($[\text{Cr}(\text{13/14-TMC})\text{O}_2\text{Cl}]^+$, $\text{II}_{\text{a/b}}$)

As we go from vanadium to chromium, one extra electron is added to the d -orbital. Crystal structure of $[\text{Cr}^{\text{III}}(\text{O}_2)(\text{TMC})(\text{Cl})]^+$ along with spectroscopic, structural characterization, and reactivity studies are reported.²² We have also computed all possible spin states ($^5\text{II}_{\text{a/b-hs}}$, $^3\text{II}_{\text{a/b-hs}}$, $^3\text{II}_{\text{a/b-ls}}$, and $^1\text{II}_{\text{a/b-ls}}$) of chromium-superoxo species (see Figure 5.8). From the calculations, it is found that $^3\text{II}_{\text{a-hs}}$ and $^3\text{II}_{\text{b-hs}}$ are the ground state of the species II_{a} and II_{b} . The optimized structure and spin density plot of $^3\text{II}_{\text{a-hs}}$ and $^3\text{II}_{\text{b-hs}}$ are shown in Figure 5.9.

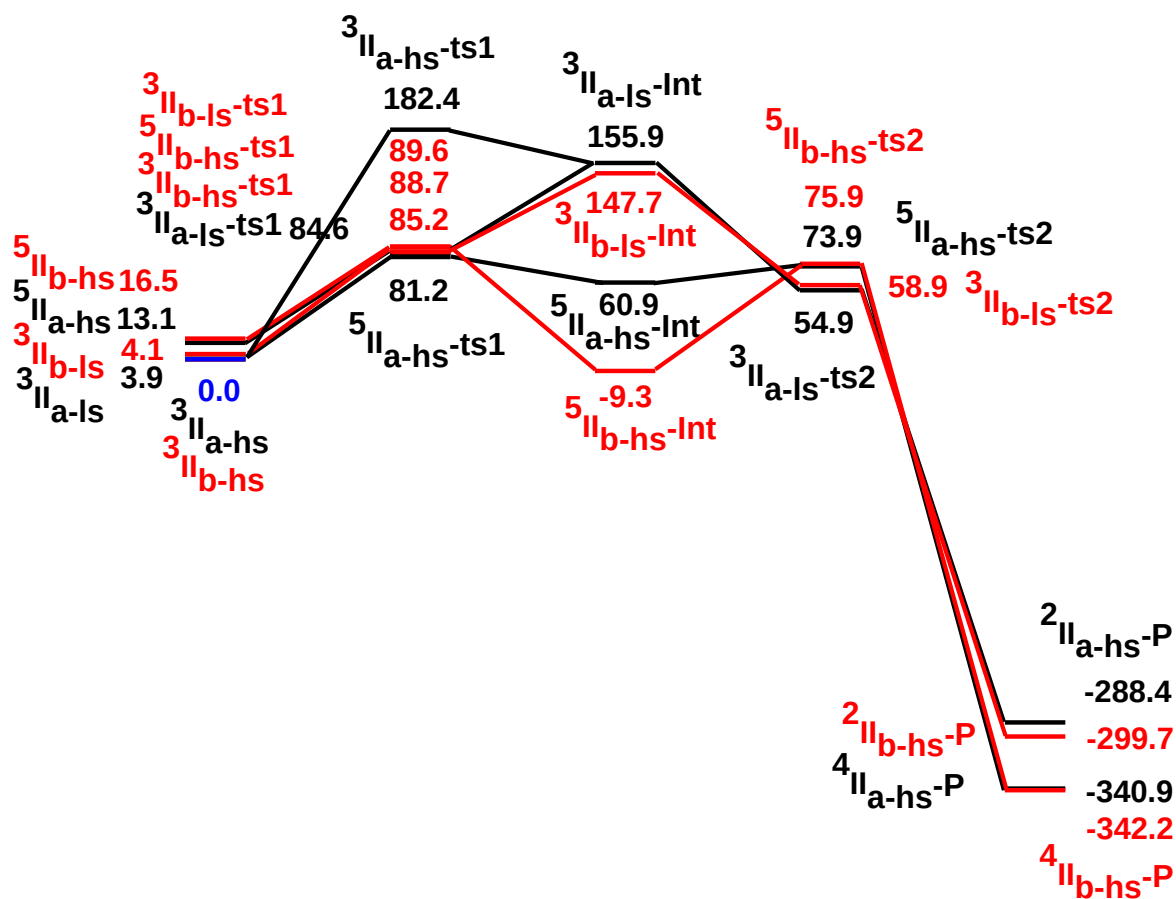


Figure 5.8. B3LYP-D2-computed potential energy surface (ΔG in kJmol^{-1}) for C-H activation by chromium-superoxo species $^2\text{I}_{\text{a-hs}}$ and $^2\text{I}_{\text{b-hs}}$ (13-TMC (black), 14-TMC (red)).

Computed structural parameters are good in agreement with the experimental observation (see Table AX 5.1 of appendix).²² Computed Cr-O1, O1-O2, Cr-Cl, Cr- N_{avg} bond lengths

decrease as ring size increase (see Figure 5.9). Computed $\angle\text{Cr-O1-O2}$ of $^3\text{II}_{a\text{-hs}}$ and $^3\text{II}_{b\text{-hs}}$ are 135.6° and 134.7° respectively, show that O2 is not orthogonal to Cr and O1. Unpaired electron at distal oxygen may couple with the unpaired electron at chromium center. Computed magnetic exchange coupling constant of the species II_a is found to -546.3 cm^{-1} suggests strong antiferromagnetic coupling occurs in between the metal center and the distal oxygen and such interaction is also found for the species II_b in previous reports.^{22,56,71}

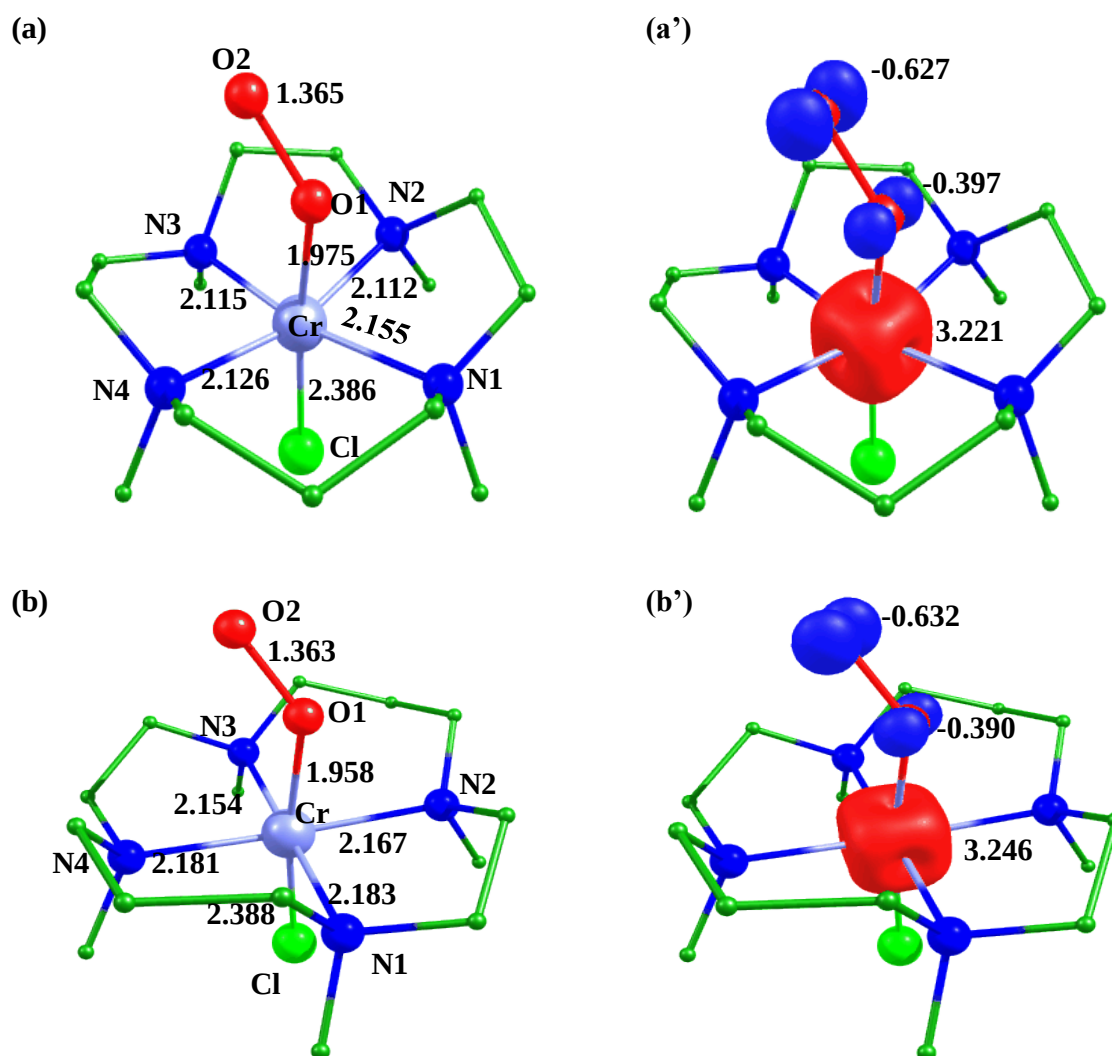


Figure 5.9. B3LYP-D2 a) optimized structures (bond lengths in Å), a') corresponding spin density plots of the ground state $^2\text{II}_{a\text{-hs}}$, b) optimized structures (bond lengths in Å) and b') corresponding spin density plots of the ground state $^2\text{II}_{b\text{-hs}}$.

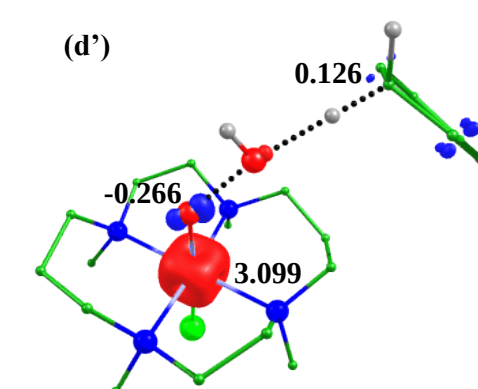
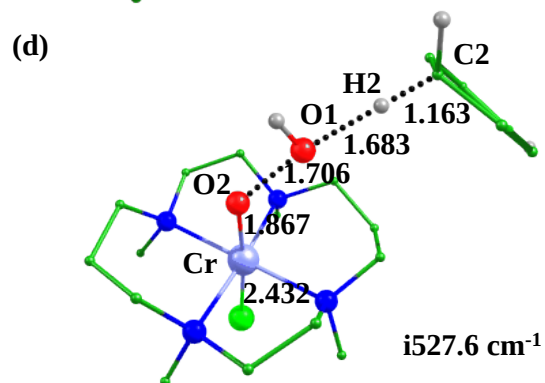
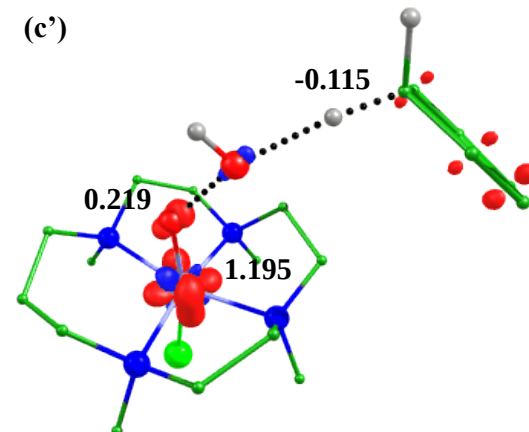
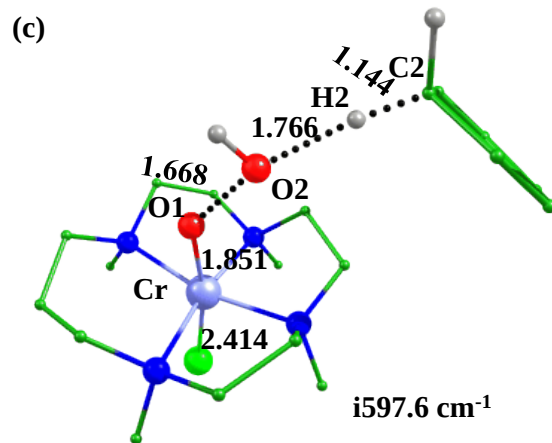
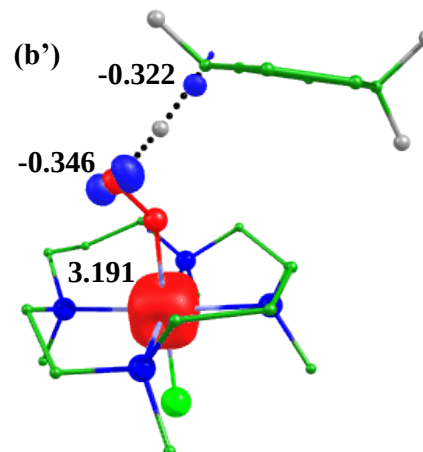
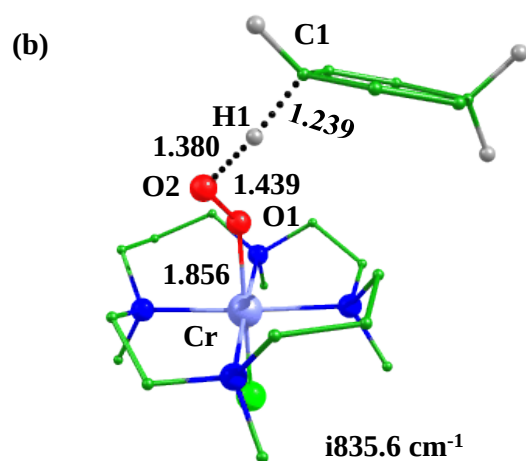
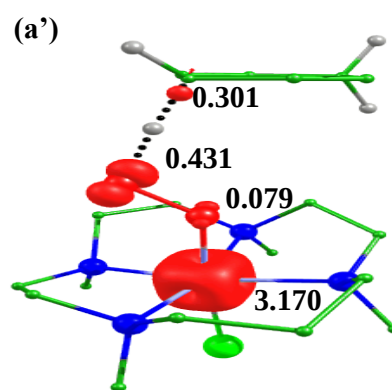
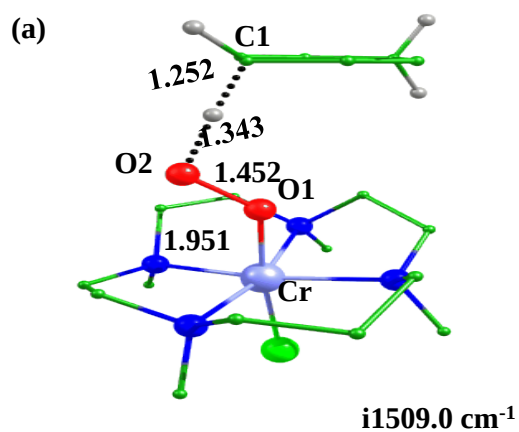


Figure 5.10. B3LYP-D2 a) optimized structures and a') spin density plots of $^3\text{II}_{\text{a-hs}}\text{-ts1}$, b) optimized structures and b') spin density plots of $^3\text{II}_{\text{b-hs}}\text{-ts1}$ and c) optimized structures and c') spin density plots of $^2\text{II}_{\text{a-hs}}\text{-ts2}$, d) optimized structures and d') spin density plots of $^2\text{II}_{\text{b-hs}}\text{-ts2}$.

Its reactivity is also tested with a cyclohexa-1,4-diene²²⁻²³ and computed barrier height of C-H bond activation of the first hydrogen abstraction is found to be 81.2 kJ/mol ($^5\text{II}_{\text{a-hs}}\text{-ts1}$) and 85.2 kJ/mol ($^3\text{II}_{\text{b-hs}}\text{-ts1}$) (see Figure 5.8). The optimized structure and spin density plots of $^5\text{II}_{\text{a-hs}}\text{-ts1}$ and $^3\text{II}_{\text{b-hs}}\text{-ts1}$ are shown in Figure 5.10. It is found that the Cr-O bond length decreases by 0.056 Å ($^5\text{II}_{\text{a-hs}}\text{-ts1}$) and 0.028 Å ($^3\text{II}_{\text{a-hs}}\text{-ts1}$) and the Cr-Cl bond length increases by 0.011 Å ($^5\text{II}_{\text{a-hs}}\text{-ts1}$) and 0.041 Å ($^3\text{II}_{\text{b-hs}}\text{-ts1}$). This abstraction leads to the formation of chromium hydroperoxo species and cyclohexa-1,4-dienyl radical which lie at 60.9 ($^4\text{II}_{\text{a-hs}}\text{-Int}$) and -9.3 kJ/mol ($^4\text{II}_{\text{b-hs}}\text{-Int}$). The ground state is also inconsistent with the earlier report.⁷¹ The second hydrogen abstraction requires 54.9 ($^3\text{II}_{\text{a-hs}}\text{-ts2}$) and 58.9 kJ/mol ($^3\text{II}_{\text{b-hs}}\text{-ts2}$) (see Figure 5.8 and 5.10) leads to the formation of the Cr(IV)=O species. The triplet state is also found as the ground state of the Cr(IV)=O. A significant spin density observed at oxygen can also further activate the C-H bond of organic substrates. The computed energy of the transition states suggests that the first step is the rate-determining step (see Figure 5.8). Formed Cr(IV)=O is highly exothermic with both the ligands (see Figure 5.8) and agrees with the available experimental report.²³ Similar, to vanadium-superoxo species, our computed energy barriers show that the chromium-superoxo ligated with 13-TMC is more reactive than with 14-TMC.

5.3.3 Manganese-superoxo species ($[\text{Mn}(13/14\text{-TMC})\text{O}_2\text{Cl}]^+$, $\text{III}_{\text{a/b}}$)

As we move to manganese, one more extra electron is added to the *d*-orbital. Here, we have also optimized all the possible electronic configurations i.e. $^6\text{III}_{\text{a/b-hs}}$, $^4\text{III}_{\text{a/b-hs}}$, $^4\text{III}_{\text{a/b-is}}$, $^2\text{III}_{\text{a/b-is}}$, and $^2\text{III}_{\text{a/b-ls}}$. From the calculations, it is found that $^6\text{III}_{\text{a-hs}}$ and $^4\text{III}_{\text{b-hs}}$ spin states are the ground

state of the respective species (see Figure 5.11). The optimized structure and spin density plot of the ground states (${}^6\text{III}_{\text{a-hs}}$ and ${}^4\text{III}_{\text{b-hs}}$) are shown in Figure 5.12.

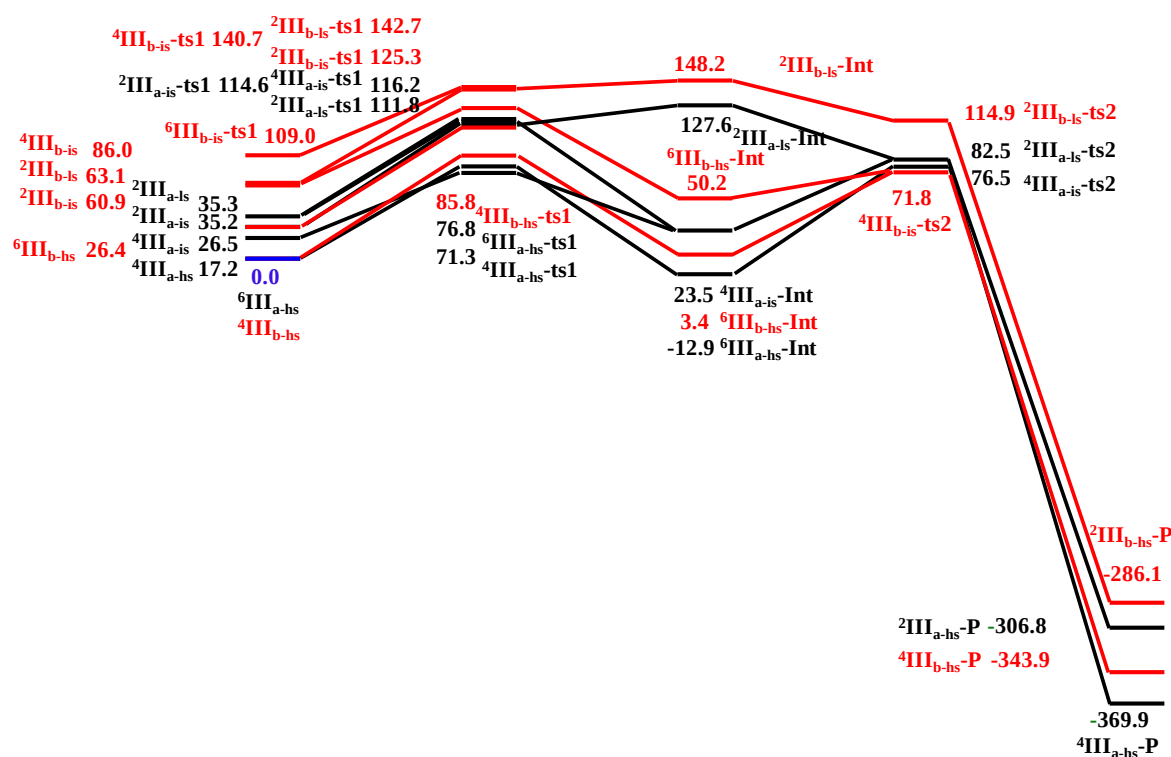


Figure 5.11. B3LYP-D2 computed potential energy surface (ΔG in kJmol⁻¹) for C-H activation by manganese-superoxo species (13-TMC (black), 14-TMC (red)).

Computed Mn-O1, O1-O2, Mn-Cl bond lengths decrease while Mn-N_{avg} bond length increases upon an increment of the ring size. The computed magnetic exchange coupling constant of the species III_a and III_b are -523.7 cm⁻¹ (${}^6\text{III}_{\text{a-hs}}$) and -735.0 cm⁻¹ (${}^4\text{III}_{\text{b-hs}}$) suggests antiferromagnetic coupling.⁷¹ Here, we have also computed transition state of the C-H bond activation of cyclohexa-1,4-diene and barrier height is found to be 71.3 kJ/mol (${}^4\text{III}_{\text{a-hs}}-\text{ts1}$), 85.8 kJ/mol (${}^4\text{III}_{\text{b-hs}}-\text{ts1}$) (see Figure 5.11 and 5.13). During the transition state, Mn-O and Mn-Cl bond lengths decreased by 0.346 Å/0.115 Å and 0.138 Å/0.001 Å (${}^4\text{III}_{\text{a-hs}}-\text{ts1}/{}^4\text{III}_{\text{b-hs}}-\text{ts1}$) shown in Figure 5.13. After this, the manganese hydroperoxo and cyclohexa-1,4-dienyl radical are formed which lie at -12.9 kJ/mol (${}^5\text{III}_{\text{a-hs}}\text{Int}$) and 3.4 kJ/mol (${}^5\text{III}_{\text{b-hs}}\text{Int}$). The barrier height for the abstraction of the second hydrogen is found to be at 76.5 kJ/mol (${}^4\text{III}_{\text{a-hs}}-$

ts2) and 71.8 kJ/mol (${}^4\text{III}_{\text{b-hs}}$ -ts2) (see Figure 5.11 and 5.13). After the second hydrogen abstraction leads to the formation of manganese-oxo species and this is also exothermic. Here also, our computed energy barriers show that the manganese superoxo ligated with 13-TMC is more reactive than with 14-TMC.

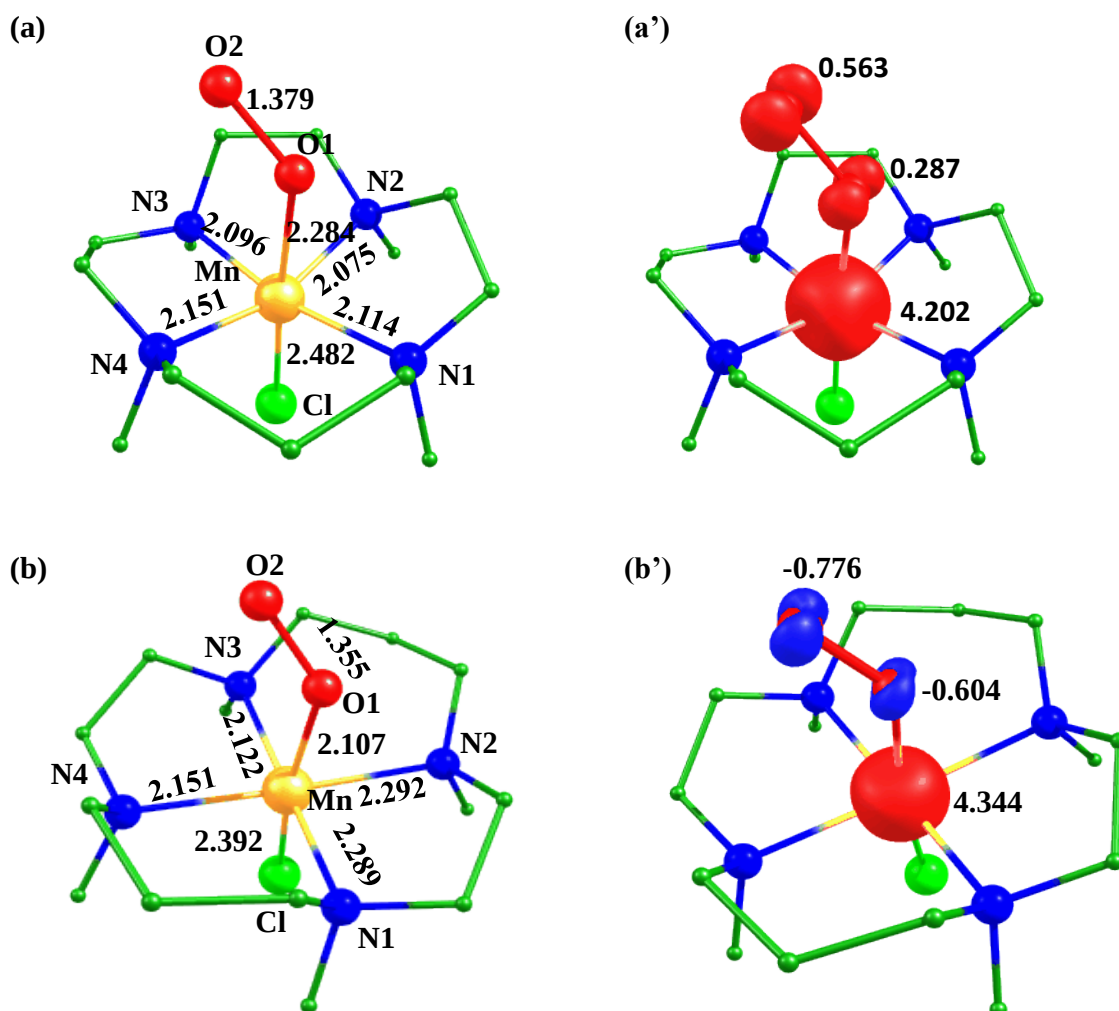


Figure 5.12. B3LYP-D2 a) optimized structures (bond lengths in Å), a') corresponding spin density plots of ${}^6\text{III}_{\text{a-hs}}$, b) optimized structures (bond lengths in Å), and b') corresponding spin density plots of ${}^4\text{III}_{\text{b-hs}}$.

5.3.4 Iron-superoxo species ($[\text{Fe}(\text{13/14-TMC})\text{O}_2\text{Cl}]^+$, $\text{IV}_{\text{a/b}}$)

Similar to V, Cr, and Mn, we have also computed DFT calculations on possible electronic configurations (${}^7\text{IV}_{\text{a/b-hs}}$, ${}^5\text{IV}_{\text{a/b-hs}}$, ${}^5\text{IV}_{\text{a/b-is}}$, ${}^3\text{IV}_{\text{a/b-is}}$, ${}^3\text{IV}_{\text{a/b-ls}}$, and ${}^1\text{IV}_{\text{a/b-ls}}$) of the iron-superoxo species and spin states ${}^7\text{IV}_{\text{a-hs}}$, and ${}^7\text{IV}_{\text{b-hs}}$ are found to be the ground state (see Figure 5.14).

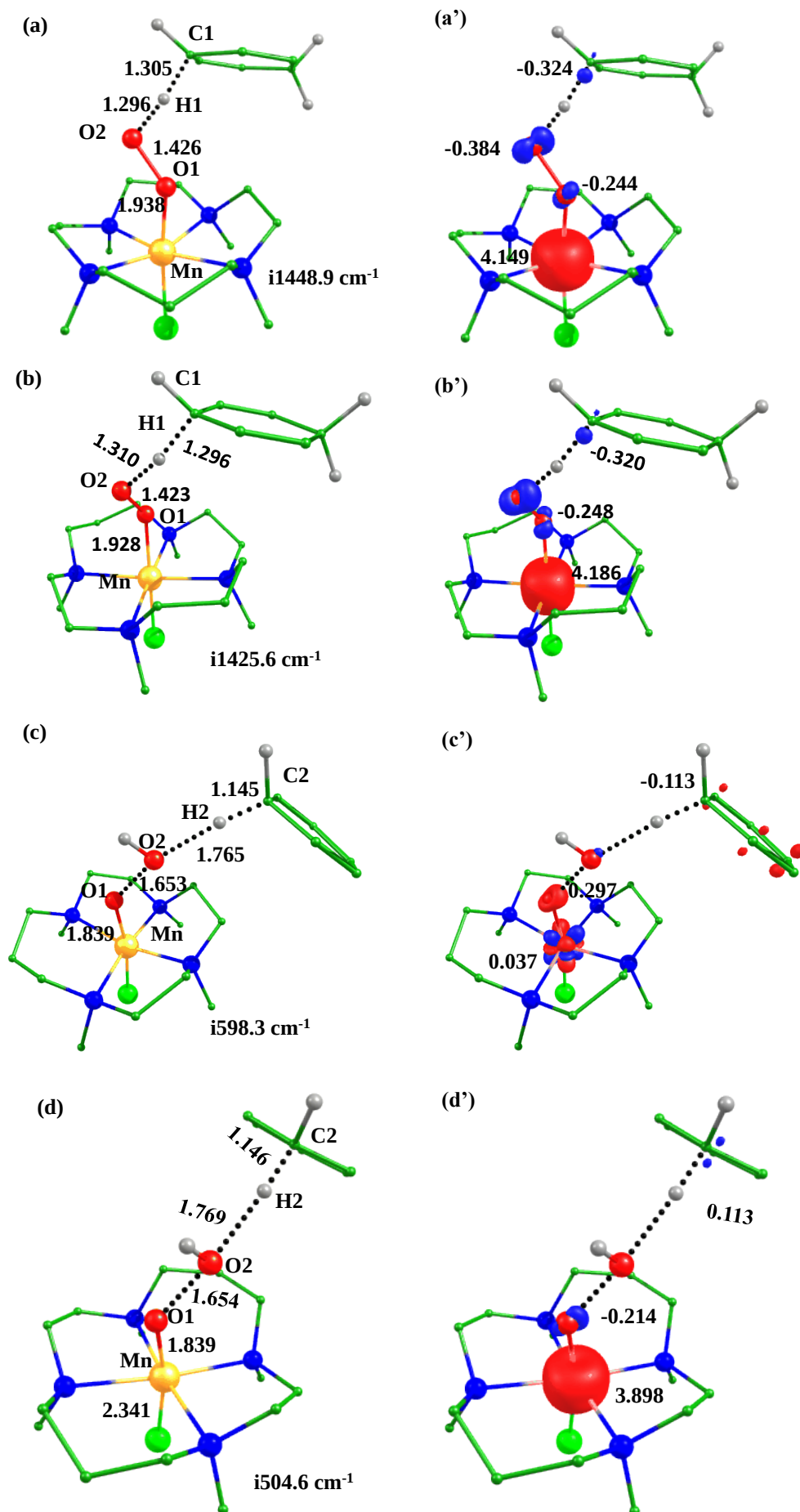


Figure 5.13. B3LYP-D2 a) optimized structures and a') spin density plots of $^4\text{III}_{\text{a-hs}}\text{-ts1}$, b) optimized structures and b') spin density plots of $^4\text{III}_{\text{b-hs}}\text{-ts1}$ c) optimized structures (bond lengths in Å), c') corresponding spin density plots of $^4\text{III}_{\text{a-hs}}\text{-ts2}$, d) optimized structures and d') corresponding spin density plots of $^4\text{III}_{\text{b-hs}}\text{-ts2}$.

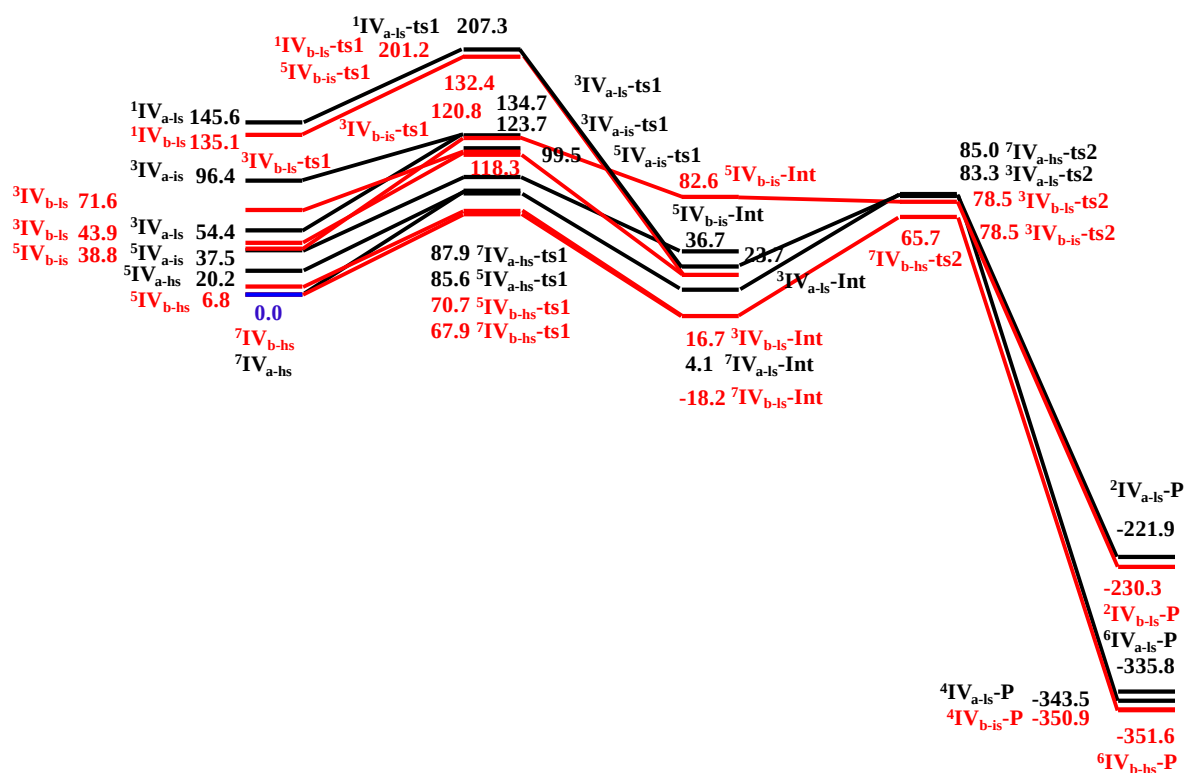


Figure 5.14. B3LYP-D2-computed potential energy surface (ΔG in kJmol⁻¹) for C-H activation by iron-superoxo species (13-TMC (black), 14-TMC (red)).

Here, Fe-O1, O1-O2, Fe-Cl, Fe-N_{avg} bond lengths increase as the ring size increase. The computed magnetic exchange coupling constant of the species IV_a and IV_b are 563.2 cm⁻¹ ($^7\text{IV}_{\text{a-hs}}$) and 188.6 cm⁻¹ ($^7\text{IV}_{\text{b-hs}}$), showing ferromagnetic coupling in between the iron center and the distal oxygen.^{56,71} It is also an active oxidant and involved in the H-abstraction atom of organic substrates. Reactivity towards the C-H bond activation by the iron-superoxo species is also tested and found that the $^5\text{IV}_{\text{a-hs}}\text{-ts1}$ and $^5\text{IV}_{\text{b-hs}}\text{-ts1}$ have 85.6 and 67.9 kJ/mol (see Figure 5.14). The optimized structure and spin density plot of the ground state of transition state are shown in Figure 5.15.

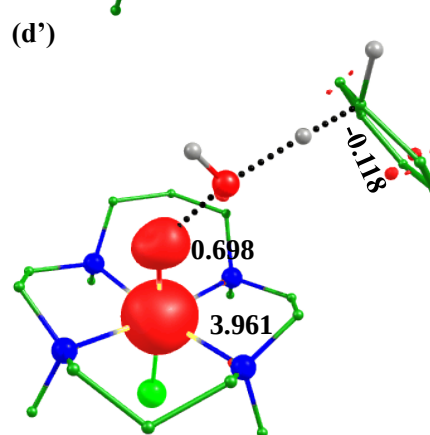
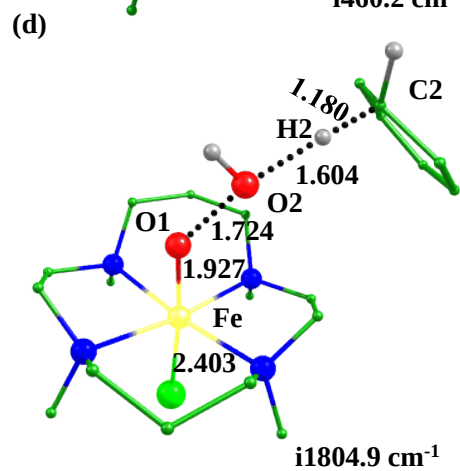
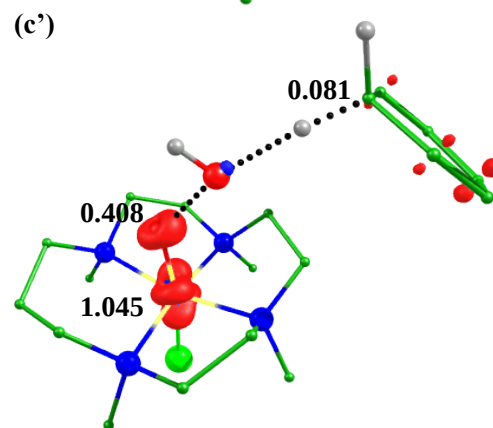
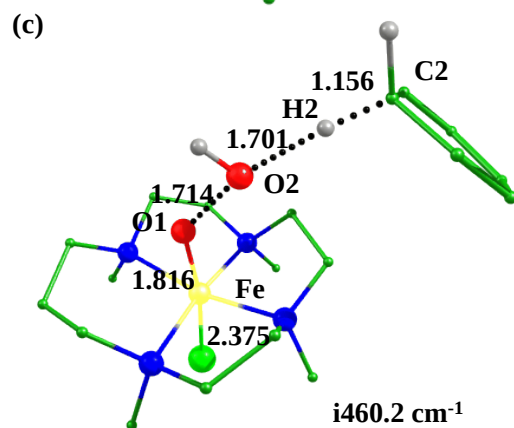
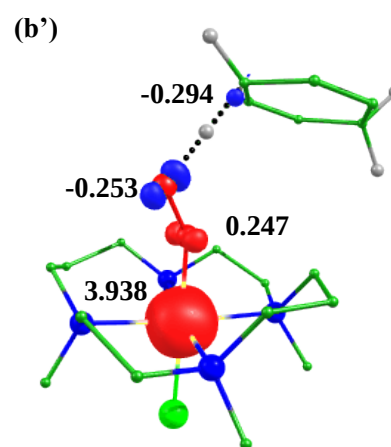
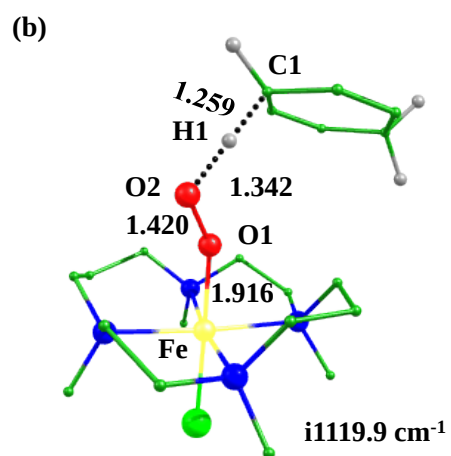
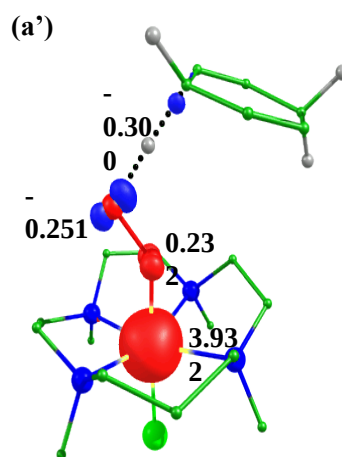
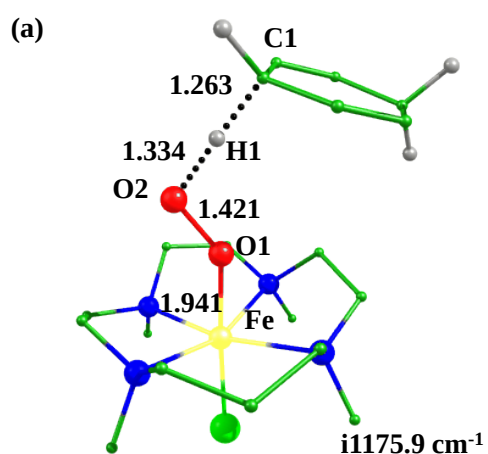


Figure 5.15. B3LYP-D2 a) optimized structures and a') spin density plots of $^5\text{IV}_{\text{a-hs-ts1}}$ and b) optimized structures and b') spin density plots of $^5\text{IV}_{\text{b-hs-ts1}}$ c) optimized structures (bond lengths in Å), c') corresponding spin density plots of $^3\text{IV}_{\text{a-hs-ts2}}$, d) optimized structures (bond lengths in Å) and d') corresponding spin density plots of $^7\text{IV}_{\text{b-hs-ts2}}$.

Structural parameters also show that the Fe-O1 bond length decreases while O1-O2, Fe-Cl, and Fe-N_{avg} bond distances increase on the increment of the ring size. The Fe-O1 bond distance also decreases from the reactant to the corresponding transition state by 1.263 Å ($^5\text{IV}_{\text{a-hs-ts1}}$) and 1.259 Å ($^5\text{IV}_{\text{b-hs-ts1}}$) while the Fe-Cl bond length increase by 0.021 Å ($^5\text{IV}_{\text{a-hs-ts1}}$) and 0.024 Å ($^5\text{IV}_{\text{b-hs-ts1}}$). Iron-hydroperoxo species lie at 23.7 ($^2\text{IV}_{\text{a-ls-Int}}$) and -18.2 kJ ($^2\text{IV}_{\text{b-ls-Int}}$). The transition states for the second hydrogen abstraction of species IV_a and IV_b lie at 83.3 kJ/mol ($^2\text{IV}_{\text{a-hs-ts2}}$), and 65.7 kJ/mol ($^7\text{IV}_{\text{b-hs-ts2}}$), respectively (see Figure 5.14 and 5.15). This transition state leads to the formation of iron(IV)-oxo species which is also found exothermic (see Figure 5.14). Computed structural parameters of iron(IV)=O species are in good agreement with the experimental.⁶⁶ In this case, 14-TMC species is more reactive than the corresponding 13-TMC.

5.3.5 Cobalt-superoxo species ($[\text{Co}(\text{13/14-TMC})\text{O}_2\text{Cl}]^+, \text{V}_{\text{a/b}}$)

Similar to the earlier species, we have also performed calculations on the corresponding cobalt species and $^2\text{V}_{\text{a-ls}}$ and $^2\text{V}_{\text{b-ls}}$ are found to be the ground state (see Figure 5.16). These are also in good agreement with the experimental reports.¹⁰¹ The energy barrier towards the C-H bond activation by species V is found to be 90.4 kJ/mol and 93.5 kJ/mol at spin surfaces $^2\text{V}_{\text{a-ls-ts1}}$ and $^2\text{V}_{\text{b-ls-ts1}}$, respectively (see Figure 5.16). Computed Co-O1 and O1-O2 bond distances decrease on an increment of the ring size while Co-N_{avg} bond length increases in same. It is found that the Co-O bond length decreases from the reactant to the corresponding transition state by 0.041 Å ($^2\text{V}_{\text{a-ls-ts1}}$) and 0.020 Å ($^2\text{V}_{\text{b-ls-ts1}}$) and the Co-Cl bond length increases by 0.016 Å ($^2\text{V}_{\text{a-ls-ts1}}$) and 0.011 Å ($^2\text{V}_{\text{b-ls-ts1}}$).

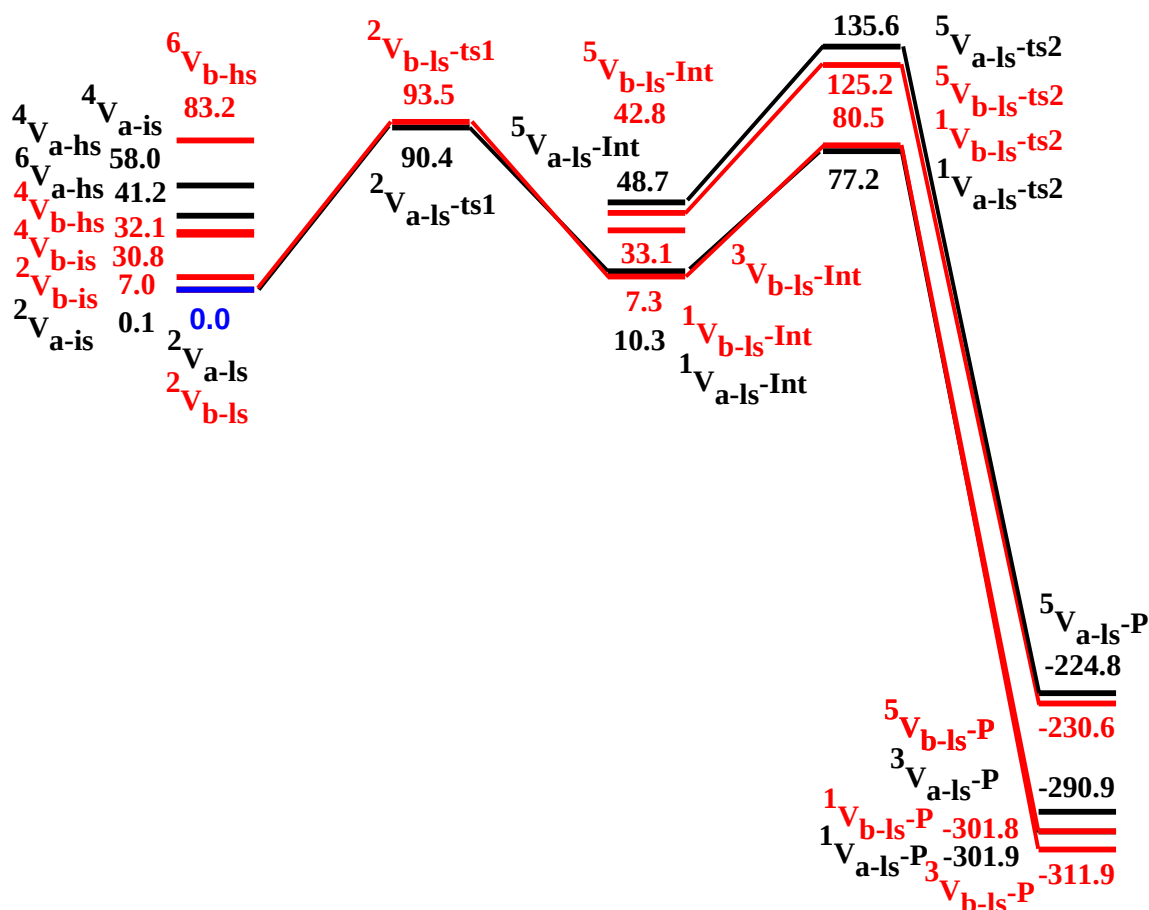


Figure 5.16. B3LYP-D2-computed potential energy surface (ΔG in kJmol^{-1}) for C-H activation by cobalt-superoxo species (13-TMC (black), 14-TMC (red)).

After the hydrogen abstraction, cobalt hydroperoxo species are formed which lie at 10.3 and 7.3 kJ/mol with ${}^2V_{a-ls-Int}$ and ${}^2V_{b-ls-Int}$, respectively. Second transition state by species V_a and V_b lie at 77.2 kJ/mol (${}^2V_{a-ls-ts2}$) and 80.5 kJ/mol (${}^2V_{b-ls-ts2}$), respectively, (see Figure 5.16 and 5.17e,f). Here, also first transition state is the rate determining step. It also supports that smaller ring TMC metal-superoxo species are more reactive. The second transition state leads to the formation of cobalt(IV)-oxo species. Formed cobalt(IV)-oxo species is exothermic and its structural parameters are in agreement with the earlier cobalt(IV)=oxo species reported.

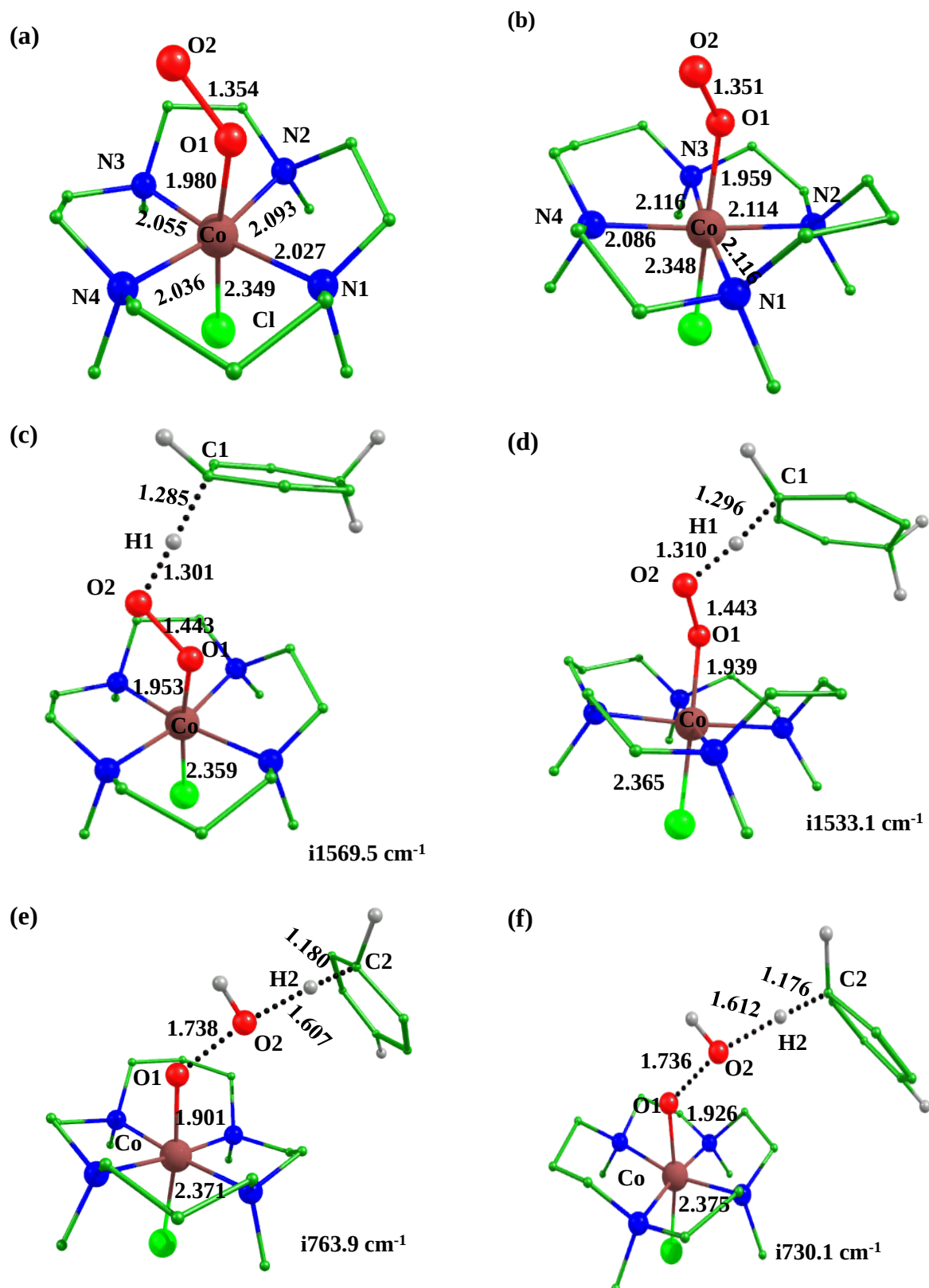


Figure 5.17. B3LYP-D2 a) optimized structure (bond lengths in Å) of ${}^2V_{a-ls}$, b) optimized structure (bond lengths in Å) of ${}^2V_{b-ls}$, c) optimized structures and ${}^2V_{a-hs-ts1}$, d) optimized

structures of ${}^2V_{b\text{-hs}}\text{-ts1}$, e) optimized structure (bond lengths in Å) of ${}^2V_{a\text{-ls}}\text{-ts2}$, f) optimized structure (bond lengths in Å) of ${}^2V_{b\text{-ls}}\text{-ts2}$.

5.3.6 Origin of difference in reactivity during C-H activation

Metal complexes show the difference in reactivity towards catalytic transformation reactions due to several factors such as different architectures of ligands, the effect of axial/equatorial ligands, and the size of ligands. The ring size of ligands is also one of the important factors that regulate reactivity. Here, we have focused on two different ring sizes of TMC ligands such as 13-TMC (smaller ring) and 14-TMC (larger ring) in our studies. We have carried out thorough DFT calculations on both the ring size species.

We have computed the formation energies from the $[M(13/14\text{-TMC})(Cl)]^{n+}$ complex and the computed energies are exothermic and this suggests a favorable formation energy for superoxo species. Our calculated results show antiferromagnetic coupling in the V(III)-O₂^{•-}, Cr(III)-O₂^{•-} and Mn(III)-O₂^{•-} and ferromagnetic coupling in Fe(III)-O₂^{•-} and Co(III)-O₂^{•-} species with both the rings. Our computed electron density at the distal oxygen of the metal-superoxo species are found to be -0.451/-0.478 (${}^2I_{a\text{-hs}}/{}^2I_{b\text{-hs}}$), -0.627/-0.632 (${}^3II_{a\text{-hs}}/{}^3II_{b\text{-hs}}$), -0.765/-0.776 (${}^6III_{a\text{-hs}}/{}^4III_{b\text{-hs}}$), 0.810/0.799 (${}^7IV_{a\text{-hs}}/{}^7IV_{b\text{-hs}}$) and 0.638/0.642 (${}^2V_{a\text{-ls}}/{}^2V_{b\text{-ls}}$) these different electron densities can play an important role towards C-H activation barrier. So we have also tested reactivity with the distal oxygen of the superoxo group towards C-H activation of 1,4-cyclohexadiene. Our DFT calculations show that first hydrogen abstraction is the rate-determining step in all the studied species and the C-H activation barrier by species I_a/I_b , II_a/II_b , III_a/III_b , IV_a/IV_b , and V_a/V_b are found to be 97.6/99.1, 81.2/85.2, 71.3/85.8, 85.6/67.9, 90.4/93.5 kJ/mol, respectively.

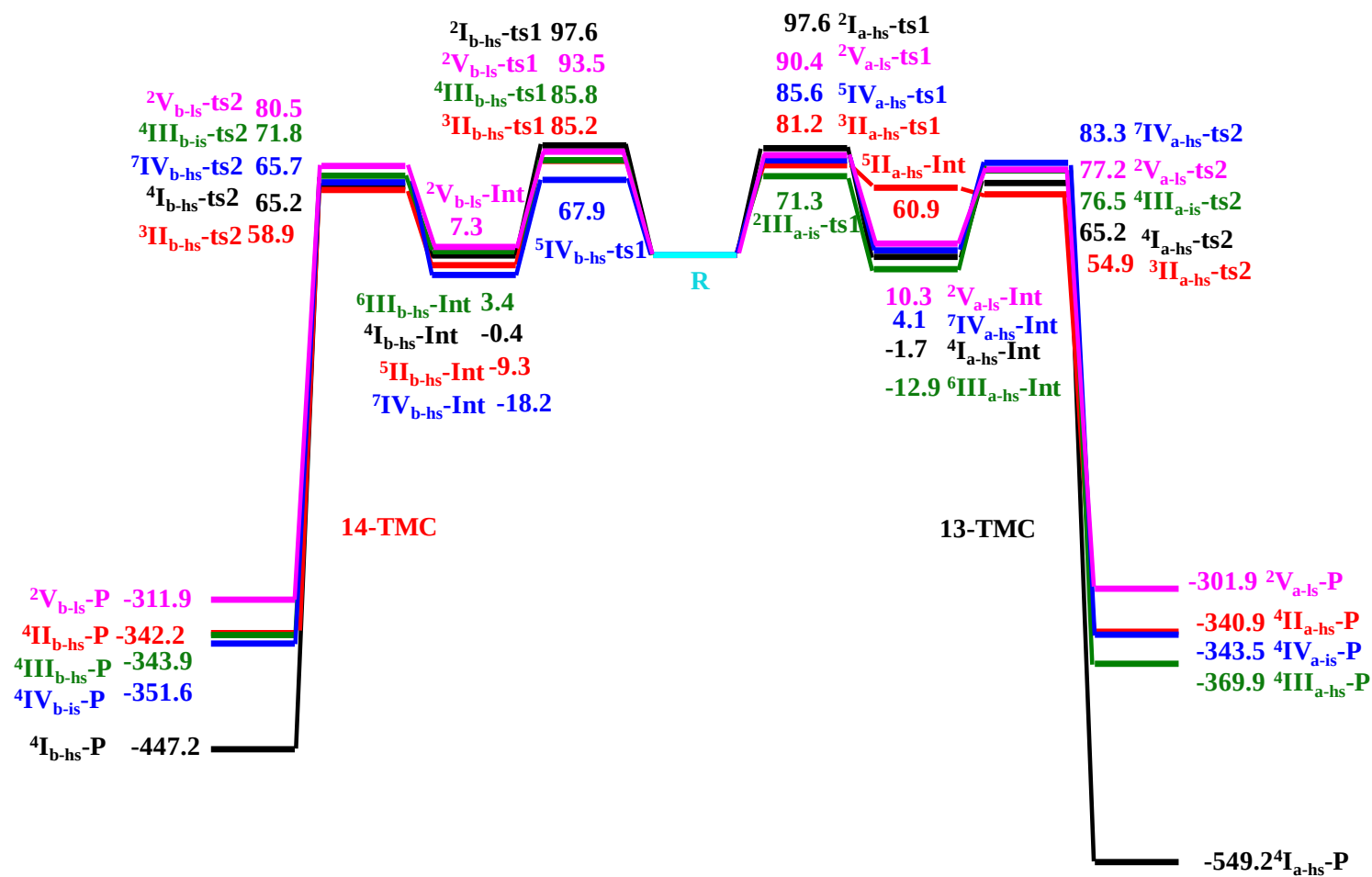


Figure 5.18. B3LYP-D2-computed potential energy surface (ΔG in kJmol^{-1}) for C-H activation by species I (black), II (red), III (olive), IV (blue), V (magenta) species with 13-TMC and 14-TMC.

Our computed data unequivocally reveal that $M-O_2^{\bullet-}$ are extremely reactive and activate the C-H bond in 1,4-cyclohexadiene with lower kinetic barrier heights. The energy barrier trend reflected that 13-TMC ligated metal-superoxo species are more reactive towards C-H activation than the corresponding 14-TMC except by iron-superoxo species (see Figure 5.18). Computed spin density at C1 of the transition state of I_a/I_b , II_a/II_b , III_a/III_b , IV_a/IV_b , and V_a/V_b species is -0.283/-0.272, -0.301/-0.322, -0.324/-0.320, -0.300/-0.294/, 0.322/0.323 indicate that the C-H activation occurs via proton-coupled electron transfer mechanism which is also shown in earlier reports.^{56,91} The computed bond angles $\angle N1-M-N3$ and $\angle N2-M-N4$ of I_a/I_b , II_a/II_b , III_a/III_b , IV_a/IV_b , and V_a/V_b species also show more contraction with 13-TMC species than the 14-TMC (see Table AX 5.1 and 5.2 of appendix) which in turn push the metal out of the plane (see Figure 5.19) and hence increase the reactivity of electrophilic reaction. The computed parameters of O---O bond during the transition state are observed 1.438/1.439, 1.447/1.451, 1.426/1.423, 1.420/1.420, 1.443/1.443 Å, and these parameters lead towards the further step indicates the higher reactivity with species 13-TMC. Space-filling of metal-superoxo also clearly shows slightly more steric hindrance at distal oxygen towards hydrogen atom retard the reactivity (see Figure 5.2). Our computed imaginary frequency of the first transition state of species a/b is found to be 1087.7/979.0, 1509.0/835.6, 1448.9/1425.6, 1175.9/1119.9, and 1569.5/1533.1 cm^{-1} , respectively, also indicate that the higher imaginary frequency can show a large tunneling contribution and hence suggest the higher C-H bond reactivity. Our energy barriers and structural correlations suggest the higher reactivity with 13-TMC ligated complexes towards C-H bond activation than the 14-TMC except for iron species.

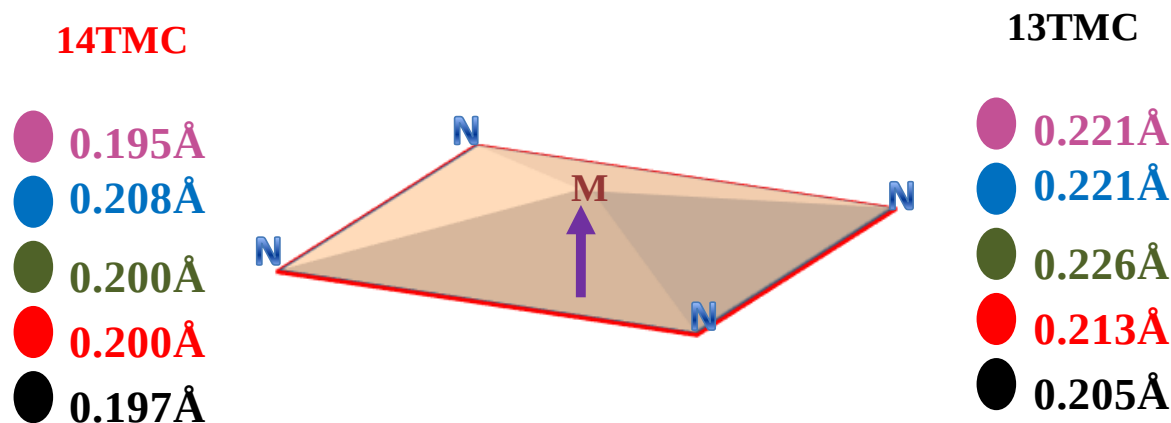


Figure 5.19. Computed displacement in the position of metal along the Z-axis.

5.4 Conclusions

Here, we have studied the electronic structures of metal-superoxo species (vanadium, chromium, manganese, iron, and cobalt) with two different 13/14-TMC ligands in detail. There are two possible isomers (A and B), by our calculations, it is found that isomer A is more stable than isomer B, which is also supported by the space-filling model showing the more steric repulsion in isomer B than the isomer A. Our DFT studies also shed light on C-H activation by metal-superoxo species. The ring size of TMC rules the oxidizing power of metal-superoxo species. This is the first computational study on the effect of ring size and metal ion on the electronic structure and catalytic reactivity of metal-superoxo species towards C-H bond activation. Here, we have explored the effect of ring size on the electronic structures and reactivity of these species towards C-H bond activation. From DFT calculations, it is found that 13-TMC ligated metal-superoxo species are more reactive than 14-TMC rings except for iron-superoxo species. C-H activation barrier is small with 13-TMC, and due to smaller ring size metal displaced out of plane along the z-axis compare to the 14-TMC ligand. It is found that iron-superoxo is most reactive, and the vanadium-superoxo species is least reactive. The reactivity pattern for the superoxo is found Fe (14-

TMC) > Mn (13-TMC) > Cr (13-TMC) > Cr (14-TMC) > Fe (13-TMC) > Mn (14-TMC) > Co (13-TMC) > Co (14-TMC) > V (13-TMC) > V (14-TMC).

To this end, our calculations show that the ring size of the TMC ligand plays an important role to control reactivity. By tuning the ring size one can alter the reactivity of metal-superoxo species towards organic substrates.

5.5 References

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