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Structural Characterization of Iron (III)-Salen Complexes Containing Axial Ligands – A Computational Study

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ABSTRACT

The proximal axial ligands in non-heme enzymes play an important role in tuning the reactivities of iron (III)-salen complexes in various oxidation reactions. The present study reports the influence of axial ligands: Br^-, Cl^-, F^-, I^-, H, CH_3, OCH_3, CH_3CN, CN, NO_2, ClO_4, $OOCCF_3$, SO_3H, SO_3CF_3, N_3 and pyridine in the structural aspects of iron(III)-salen complexes. Computational study of iron (III)-salen complexes containing these axial ligands gives the bond lengths and bond angles in the optimized structures. These values are in accordance with the reported X-ray values. The calculated energy of spin multiplicity sextet (S = 6) obtained from DFT(Density Functional Theory) lies below doublet (S = 2) and quartet (S = 4) surfaces by 13.7 and 5.8 kcal mol^{-1} respectively, indicating that sextet is more stable compared to the other two multiplicities for all the iron(III)–salen complexes. Indeed the structural elucidation of the iron (III)-salen complexes and the corresponding oxo-iron derivatives is of paramount importance to understand the mechanism of important biological oxygenation reactions. These electron donating axial ligands in the complexes stabilize the iron centre and are responsible for the weakening of the Fe-O bond in the transition state of the oxygenation reactions.

1. Introduction

Salen (salen=N,N -bis(salicylidene)ethylenediaminato) complexes of iron received much importance in recent times [1,2]. Rajagopal and coworkers have successfully used Mn, Fe, Cr, Co and V salen complexes to probe the active intermediates and the mechanism of enzyme-catalyzed oxidation reactions of biologically important organic substrates [3–11]. Iron salen complexes have other biological applications, and their inherent ability to bind with DNA through the electrostatic interaction [12, 13] is of great importance. In previous occasions, a number of iron derivatives have been reported to have good interaction with the anticancer antibiotic adriamycin and nucleic acids [14, 15]; especially, anthracycline has the wonderful affinity to chelate with metal cations, particularly with ferric ions to form ferric anthracycline complexes [16]. It is interesting to note that iron (III)–salen complexes have influence over the viability of cultured human cells and they have ability to cause DNA damage [3]. So a continuous interest to study the iron (III)–salen complexes from the stand point of the electronic and structural aspects is quite obvious. The monomer of iron (III)–salen complexes in the solid state is five-coordinated with a pyramidal geometry, with the tetradentate salen ligand in a square planar coordination, by two nitrogen and two oxygen atoms, with the chloride ligand in an apical position and an open sixth coordination site [17–20]. Recent studies throw much interest to elucidate the structural aspects of these iron (III) complexes by DFT calculations [21–23]. In this work, we have taken the above method of computational analysis for its excellent utility and reliability to investigate the open shell systems. Although the DFT method inclines more to overestimate the stability of high-spin states of the transition metal complexes, the share of the exchange functional applied in the B3LYP parameterization deserves more for its accountability toward optimal parameters [24].

2. Experimental Methods

2.1 Computational Details

The models for iron (III)–salen complexes were built using Gauss View 5.0 package [25]. The model complexes were optimized using density functional theory (DFT) with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) [26,27]. The LanL2DZ basis set for iron represents the Los Alamos nonrelativistic effective core potential (ECP) [28] and 6-31G (d, p) basis set [29] for other elements. The valence shell, including the 3d orbitals, is described by a basis set of essentially double-ζ quality including a diffuse 3d function. All geometries reported in this work are optimized without any geometrical constraints. To ensure that the optimized geometries correspond to true minima on the potential energy surface, vibrational frequencies were computed using DFT (B3LYP/6-31G (d,p)∪ LanL2DZ) level. All calculations were made using Gaussian 09 (Revision A.02) package [30].

3. Result and Discussion

3.1 Computational Studies

The optimized structures of the iron (III)–salen complex (b) (Cl^- as an axial ligand) with different spin multiplicities are shown in Fig. 1. Geometry optimization is carried out for complex b with spin multiplicities of S = 2, 4 and 6. The sextet spin is found to be more stable compared to the other two multiplicities. The energy of the complex b with sextet spin lies below doublet and quartet surfaces by 13.7 and 5.8 $kcalmol^{-1}$, respectively (Table 1).

Table 1 Calculated energy values (kcal mol^{-1}), relative to the most stable spin state of mononuclear five-coordinated iron(III)–salen complex (b)

Spin multiplicity	Calculated energy values (kcal mol^{-1})
S = 6	0
S = 4	5.8
S = 2	13.7

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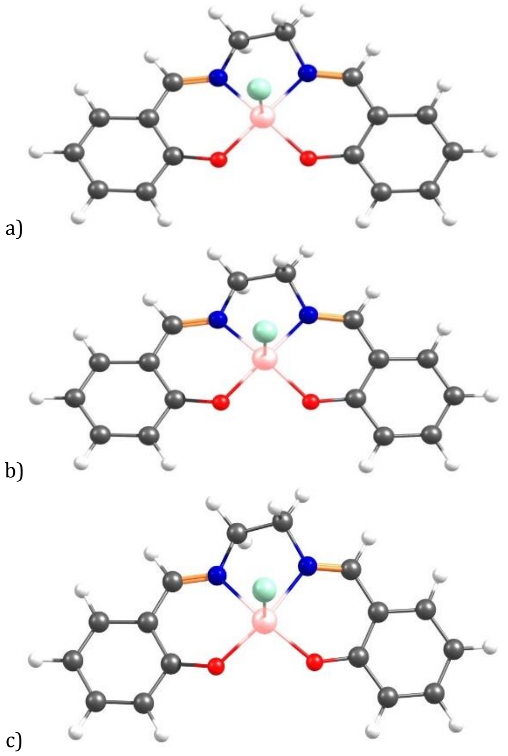


Fig. 1 Optimized structures of iron (III)-salen complex (b) at B3LYP/6-31G* level for different spin multiplicity a).S=2 b). S=4 c).S=6. Atom colors O-● N-● Br-● Cl-● Fe-● C-●

Hence, all the axial ligand substituted iron(III)–salen complexes are found to be most stable in the sextet spin state and optimized with sextet spin multiplicity for all complexes. The calculated geometrical parameters of complex (b) are listed in Table 2 along with the experimental values obtained from X-ray data.

Table 2 Comparison of the optimized calculated geometrical parameters (bond distance (Å) and angles (degrees)) for mononuclear five coordinated iron (III)-salen complex (b) in different spin multiplicity states with available X-ray structural data of [Fe^{III}-(salen)]Cl.

	Calculated			X-ray structure[d]
Bond Distance (Å)[a]	doublet	quartet	sextet	
M–Ns (average)	1.94	1.96	2.15	2.08
M–Os (average)	1.85	1.87	1.89	1.88
M–Cl	2.27	2.33	2.27	2.23
M–Salen N/O plane	0.29	0.38	0.58	---
Cl–Salen N/O plane	2.55	2.70	2.79	---
Bond Angle (deg)				
Ns–M–Ns	83.4	82.5	76.0	77.9
Os–M–Os	87.8	87.0	98.6	93.9
Ns–M–Os[b]	92.2	91.3	84.85	87.35
Ns–M–Cl[c]	93.55	97.15	99.4	100.95
Os–M–Cl[c]	103.75	105.25	110.2	107.35

[a] The salen nitrogen and oxygen atoms are designated as Ns and Os. The plane formed by the two N and O atoms is defined as the salen N/O plane. The distance between the Cl atom and the center of the N/O plane is denoted as Cl-salen N/O plane. M is metal ion (Fe(III)). [b] The average Ns–M–Os (near and opposite) bond angles of the equatorial ligand. [c] Average Ns–M–Cl and Os–M–Cl bond angles of the axial ligands. [d] Taken from ref [21].

In this table, the salen nitrogen and oxygen atoms are designated as Ns and Os. The plane formed by the two N and O atoms is defined as the salen N/O plane. The distance between the Cl atom and the center of the N/O plane is denoted as Cl-salen N/O plane. It can be found from the Table 2 that M–Ns, M–Os, M–Cl, M–Salen N/O plane and Cl–Salen N/O plane distances are in good agreement with the X-ray structure. It is evident from Table 2 that the Fe-Os, Fe-Ns and Fe-Cl bond distances generally increase with increasing spin multiplicity. The Ns–M–Os (near and opposite) and Ns–M–Cl/Os–M–Cl are the equatorial and axial bond angles, respectively. A systematic comparison of bond angles obtained from DFT (B3LYP) calculation with X-ray diffraction structure was made, and the theoretical values are in better agreement with the X-ray studies Table 2. It can be noted from the results that the deviations in M (III)–L distances and L–M (III)–L angles are within the experimental error. The calculated geometrical parameters of all the other axial ligand substituted iron (III)–salen complexes (a,c–p) with the spin multiplicity (S = 6) are listed in Tables 3 and 4. The data show that for complexes c, b, a and d the bond distance of M-F is 1.81Å, M-Cl is 2.27 Å, M-Br is 2.42 Å and M-I is 2.62 Å. It is observed here that as the size of the halogen atom increases in the order F< Cl< Br< I the bond length also increases. This trend also in accordance with the electronegativity values of the halogen atoms. Generally the electron donating nature of anionic axial ligands stabilizes the iron center and in the above case as the electronegativity values decrease there is corresponding increase in the bond lengths. However for the other bond distances M–Ns, M–Os, C-Os, C-Ns (average) in the complexes a very small change in the values have been observed.

Table 3 Relevant geometrical parameter (bond distance (Å)) of the mononuclear five coordinated anionic axial ligand subsituted iron (III)-salen complexes (a-l).

Bond Distance (Å)[a]	Calculated, spin multiplicity (S=6)											
	a	b	c	d	e	f	g	h	i	j	k	l
M–Ns	2.15	2.15	2.16	2.14	2.15	2.13	2.16	2.16	2.13	2.15	2.16	2.14
M–Os	1.90	1.89	1.91	1.90	1.90	1.89	1.91	1.92	1.88	1.90	1.91	1.89
M–X	2.42	2.27	1.81	2.62	2.0	1.99	2.11	1.92	2.55	2.17	1.90	2.15
C-Os	1.38	1.30	1.31	1.31	1.31	1.31	1.31	1.31	1.31	1.30	1.31	1.32
C-Ns	1.29	1.31	1.29	1.30	1.30	1.30	1.29	1.30	1.29	1.29	1.29	1.30

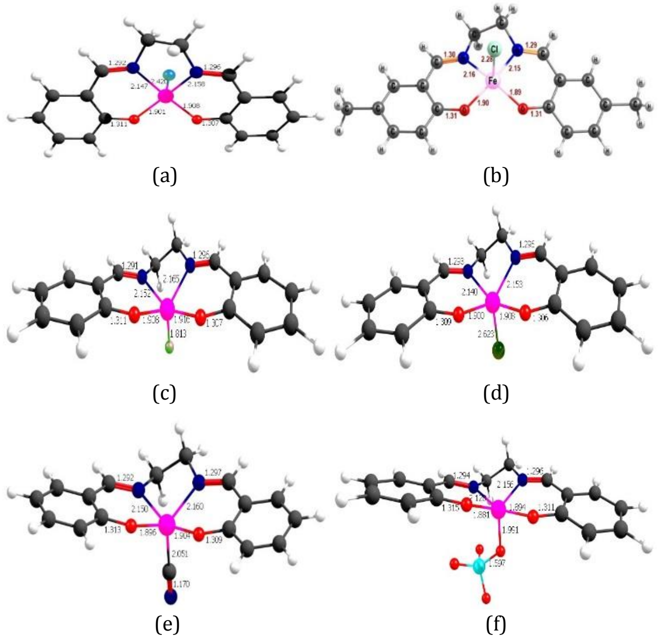
X= -Br, -Cl, -F, -I, -CN, -ClO_4, -NO_2, -SO_3H, -SO_3CF_3, -$OOCCF_3$, -Pyridine

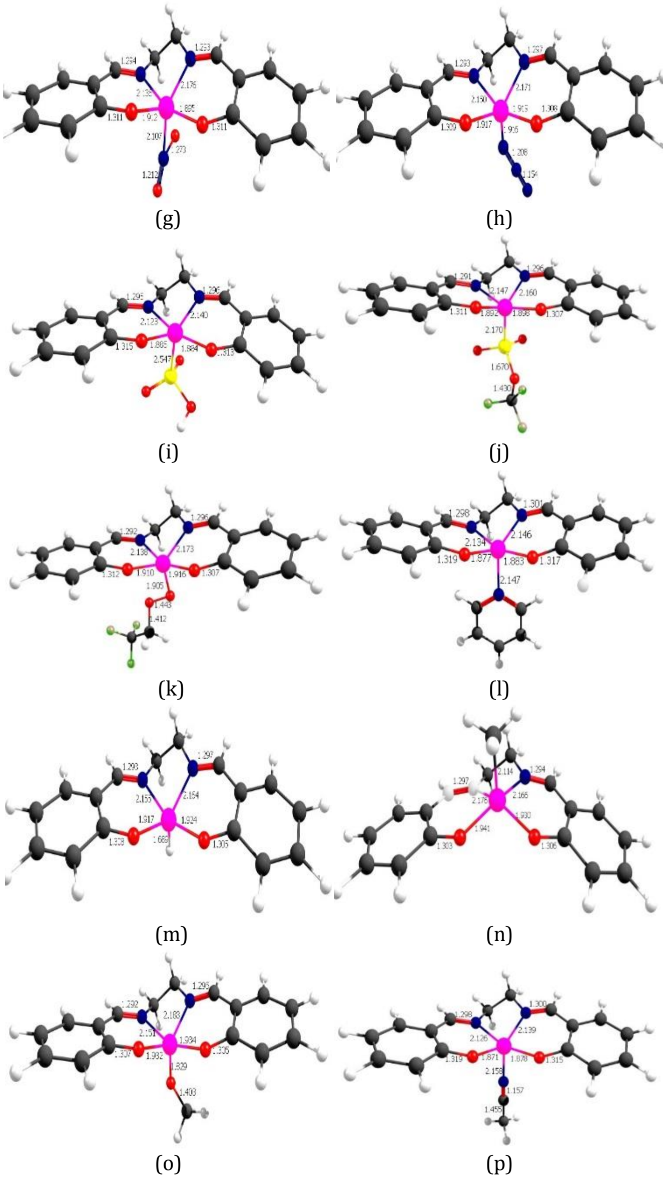
Table 4 Relevant geometrical parameters (bond distance (Å)) of the mononuclear five coordinated anionic axial ligand subsituted iron (III)-salen complexes (m-p).

Bond Distance (Å)a	Calculated, spin multiplicity (S=6)			
	m	n	o	p
M–Ns (average)	2.16	2.17	2.16	2.14
M–Os (average)	1.91	1.94	1.93	1.87
M–X	1.69	1.83	2.11	2.16
C-OS (average)	1.30	1.30	1.31	1.32
C-Ns (average)	1.29	1.29	1.29	1.30

X= -H, -CH_3, -OCH_3, CH_3CN

Interestingly, all the geometrical data of the complexes are in close agreement with the reported experimental values obtained from X-ray diffraction [21] of monomeric iron (III)–salen complex (b). The optimized structures of axial ligand substituted monomeric iron(III)–salen complexes (a–p) at B3LYP/6-31G(d,p)∪ LanL2DZ level are given in Fig. 2 It is also inferred that all the monomeric square pyramidal iron(III)–salen complexes (a–p) show experimental magnetic moment value around 5.9 ± 0.5 B.M. The distance between the center metal ion and the salen N/O plane is referred to as the core size. The sensitivity of this bond length with respect to the spin or oxidation state changes reflects variations in the core size associated with the M–Ns/Os bond expansion or contraction. The Fe atom lies above the plane formed by Ns and Os with the distances of 0.3, 0.4 and 0.6 Å for spin multiplicities S = 2, 4 and 6, respectively. Evidence reveals that the iron ion is perfectly fitted in the salen core, and there is no core size effect.





(g) (h) (i) (j) (k) (l) (m) (n) (o) (p)

Fig. 2 Optimized structures of substituted iron (III)-salen complexes (a-p) at B3LYP/6-31G (d,p) level for spin multiplicity S=6 (Cs).

3.2 Applications

The Schiff base metal complexes are having an excellent inhibitive action against Gram negative bacterium (*E. coli*) and Gram positive bacterium (*S. aureus*) microbial stains [34]. These results prove that the antibacterial potential of Schiff bases will alter by the change of axial ligands in iron (III)-salen complexes, hence these Schiff base iron (III)-complexes may be an effective alternative for the conventional antibiotics and emerging infection causing pathogens. Indeed the structural elucidation of the iron (III)-salen complexes and the corresponding oxo-iron derivatives is of paramount importance to understand the mechanism of important biological oxygenation reactions. These electron donating axial ligands in the complexes stabilize the iron centre and are responsible for the weakening of the Fe-O bond in the transition state of the oxygenation reactions.

4. Conclusion

The axial ligands have marked influence in the geometrical parameters of the iron (III)-salen complexes (a-p). The DFT calculations of all the complexes (a–p) reveal that the sextet (S=6) spin is found to be more stable compared to the other two multiplicities (S=2 and 4). It lies below doublet and quartet surfaces by 13.7 and 5.8 kcalmol^{-1}, respectively. The anionic axial ligands stabilize the iron (III)-center and weakens the Fe-O bond in the transition state of the reactions. The Fe atom lies above the plane formed by Ns and Os with the distances of 0.3, 0.4 and 0.6 Å for spin multiplicities S = 2, 4 and 6, respectively. Evidence reveals that the iron ion is perfectly fitted in the salen core, and there is no core size effect.

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