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La(III) Complex of Assymetrical Heptadentate (N_4O_3) Schiff Base

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A systematic study on the performance of Pople-style basis functions such as 6-31G*, 3-21G* and LanL2MB on the molecular structure and highest occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) of a neutral complex of La(III) with ligand H_3L, [La(L)], where L is of the complex of asymmetrical potentially heptadentate (N_4O_3) Schiff base ligand {N [$(CH_2)_3N=CH(2\text{-}OH\text{-}5\text{-}BrC_6H_3)$]-[$(CH_2)_2N=CH(2\text{-}OH\text{-}5\text{-}BrC_6H_3)$]$_2$} have been carried out. The calculations were performed at both *ab initio* restricted Hartree-Fock (RHF) and DFT (B3LYP) methods. The calculations confirmed that this ligand can effectively encapsulates a lanthanide ion and enforce a seven-coordinate geometry. The results show that the calculated bond lengths and bond angles and also energy levels of this complex are considerably depend on both the method and basis set.

Key Words: *ab initio*, Lanthanum(III), Heptadentate ligand, Schiff base complex.

INTRODUCTION

Lanthanide complexes typically exhibit high coordination numbers and structural diversity. Unlike their transition metal counterparts, the solid-state coordination geometries of lanthanides are difficult to predict, particularly for complexes of simple mono- and bidentate ligands. The tripodal, heptadentate ligand 2,2′,2″-*tris*(salicylideneimino)triethylamine (H3trensal) has been known for some time[1,2]. A number of close analogues of H3trensal are also known that bear substitution of each aromatic ring[1-8]. Regardless of the degree of substitution of the aromatic rings, these ligands typically bind to trivalent lanthanide ions in their trianionic (triphenolate), heptadentate (N_4O_3) form. For first-row transition metals where seven-coordinate complexes are uncommon, the ligands adopt hexadentate binding modes, with the apical tertiary amine free from the metal[9-11].

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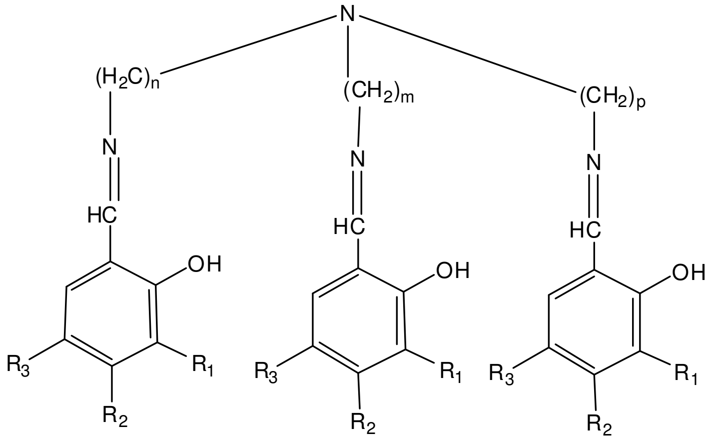
There has been much interest in the coordination chemistry of lanthanide ions with heptadentate ligands in general and in the potential application of lanthanide complexes as magnetic resonance contrasting agents in particular[12]. Recently we reported the synthesis and characterization of some complexes of fully condensed potentially heptadentate (N_4O_3) tripodal Schiff base ligands, derived from template and/or direct condensation reaction[13-16] (Fig. 1). Herein, the effect of the basis sets on molecular structure of a La(III) complex of a heptadentate (N_4O_3) tripodal Schiff base ligand (Fig. 1f) is reported.



(a) H_3L^1:	$R_1=R_3=t\text{-Bu}$, $R_2=H$	n=m=p=3	13
(b) H_3L^2:	$R_1=R_2=R_3=H$,	n=m=p=3	14
(c) H_3L^3:	$R_1=R_2= R_3=H$,	n=m=p=2	13
(d) H_3L^4:	$R_1= R_3=t\text{-Bu}$, $R_2=H$	n=m=p=2	13
(e) H_3L^5:	$R_2=R_3=H$, $R_1=t\text{-Bu}$,	n=m=p=2	8
(f) H_3L:	$R_1=R_2=H$, $R_3=Br$,	n=m=2 p=3	16

Fig. 1

COMPUTATIONAL DETAIL

A systematic study on the performance of Pople-style basis functions such as 6-31G*, 3-21G* and LanL2MB on the molecular structure and highest occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy gap, of [La(L)] complex is carried out. The geometry of this complex at gas phase was fully optimized at both the Hartree-Fock and DFT (B3LYP)[17] levels of theory using the Gaussian 98 set of programs[18]. At first, the complex was optimized at both the Hartree-Fock and DFT (B3LYP) levels of theory using standard LanL2MB basis set (Methods 1 and 2, respectively)[16] and the resulting structures were then used for further calculations using standard 3-21G* basis set for C, H, N and O atoms and LanL2DZ for the bromine and lanthanum ion at same levels (Methods 3 and 4, respectively). The structures resulting from latter calculation were also used for similar calculations at both the HF and B3LYP levels of theory using the 6-31G* basis set for nitrogen and oxygen donor atoms, the 3-21G* basis set for carbon and hydrogen atoms and LanL2DZ for the bromine and metal ion (Methods 5 and 6, respectively). Thus in all methods the effective core potential (ECP) is included for the lanthanum ion. Vibrational frequency analyses, calculated at the same level of theory, indicate that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. Calculations were performed on a Pentium-PC computer with 3000 MHz processor. A starting molecular mechanics structure for the *ab initio* calculations was obtained using the HyperChem 5.02 program[19].

RESULTS AND DISCUSSION

The geometry of [La(L)] complex was fully optimized at both the Hartree-Fock (HF) and density functional B3LYP levels of theory. Selected calculated bond lengths and bond angles of [La(L)] are given in Table-1. The calculations show that the imine and tertiary nitrogen donor atoms as well as the three phenolate oxygen donor atoms are arranged at apices of a distorted capped octahedral (Fig. 2). The considerable difference between the parameters obtained from RHF calculations relative to those from B3LYP is in La-N and La-O bond lengths, where La-N bond lengths are slightly longer and La-O bond lengths are slightly shorter in the former calculation. On the other hand, the significant difference between the parameters obtained from LanL2MB calculation (Table-1) with those derived from calculations at a higher level of theory is only in La-O bond lengths and therefore in calculated values for T_O. Similar results have been obtained for lanthanide complexes of H_3L^1 to H_3L^4 Schiff base ligands[13]. As can be seen the La-tertiary nitrogen distance, La-N(1), is slightly longer than that for other bonds but it can still be considered as a strong bonding interaction. A similar observation was reported for all seven-coordinate complexes of corresponding tren Schiff bases[20-23]. It is clear that upon coordination of the tertiary nitrogen atom to the metal ion the triangle face defined by the other coordinated nitrogen atoms is expanded. The expansion of this triangle can be readily understood by the comparison of the sum of the calculated bond lengths of the sides of the triangle defined by the imine nitrogen atoms, T_N and that of the oxygen atoms, T_O. Comparison of O-La-O bond angles with N_{imine}-La-N_{imine} bond angles also indicates the expansion of the latter triangle due to coordination of the tertiary nitrogen atom.

TABLE-1
COMPARISON BETWEEN SELECTED THEORETICAL BOND LENGTHS (Å) AND BOND ANGLES (°) FOR [La(L)] COMPLEX[a]

Method	1	2	3	4	5	6
Bond lengths						
La(16)-N(20)	2.888	**2.856**	2.940	**2.898**	3.006	**2.961**
La(16)-N(19)	2.710	**2.691**	2.693	**2.670**	2.737	**2.712**
La(16)-N(18)	2.808	**2.783**	2.766	**2.718**	2.796	**2.755**
La(16)- N(12)	2.684	**2.664**	2.663	**2.639**	2.713	**2.684**
La(16)-O(21)	2.201	**2.236**	2.328	**2.346**	2.369	**2.370**
La(16)-O(22)	2.204	**2.241**	2.325	**2.334**	2.369	**2.364**
La(16)-O(13)	2.197	**2.234**	2.318	**2.327**	2.362	**2.356**
T_N	13.213	**13.167**	12.909	**12.797**	12.918	**12.870**
T_O	9.711	**9.753**	10.721	**10.615**	10.992	**10.797**
Bond angles						
O(13)-La-O(21)	89.150	**87.639**	92.117	**89.357**	93.117	**90.506**
O(13)-La-O(22)	94.916	**93.789**	100.549	**98.990**	104.609	**102.168**
O(21)-La-O(22)	100.296	**98.539**	109.714	**107.978**	107.121	**105.527**
N(12)-La-N(20)	64.048	**64.973**	62.803	**63.784**	61.460	**62.647**
N(18)-La-N(20)	77.997	**78.416**	74.754	**74.739**	72.788	**73.710**
N(19)-La-N(20)	63.934	**64.877**	62.630	**63.468**	61.086	**62.212**
O(13)-La-N(20)	115.449	**116.169**	114.586	**115.589**	111.679	**113.301**
O(21)-La- N(20)	128.926	**130.432**	120.693	**122.832**	124.094	**125.500**
O(22)-La- N(20)	119.638	**120.590**	115.187	**116.591**	113.092	**115.153**
N(12)-La-N(18)	103.549	**102.982**	102.830	**100.814**	96.936	**97.166**
N(12)-La-N(19)	101.043	**102.223**	98.792	**100.105**	99.210	**100.673**
N(18)-La-N(19)	118.195	**119.853**	114.830	**117.219**	114.081	**116.039**

[a] The parameters obtained at the HF level are given as plain text, those for the B3LYP level are in bold.

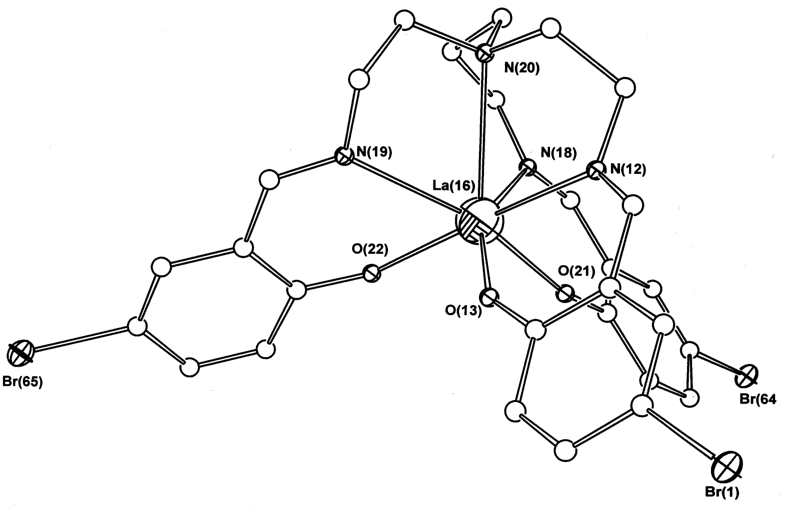
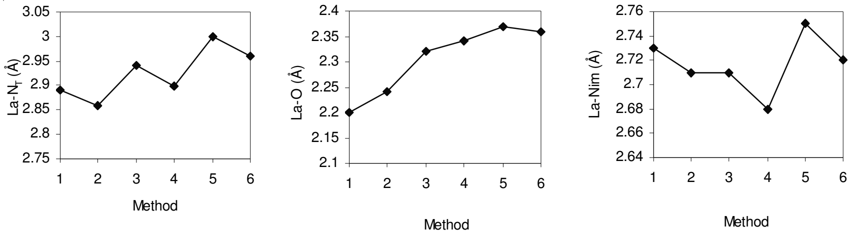


Fig. 2. Calculated molecular structure of [La(L)] complex using the method 6 (see section 2). Hydrogen atoms are omitted for clarity

As can be seen in the Fig. 3 (Table-2) the all greatest calculated values for La-N$_T$, La-N$_{im}$ and La-O are resulted using HF/6-31G* method. On the other hand, the smallest calculated values for La-N$_T$, La-N$_{im}$ and La-O are resulted using B3lYP/LanL2MB, B3lYP/3-21G* and HF/lanl2mb methods, respectively. About bond angles (Fig. 4), the calculated maximum bond angles for N$_{im}$-La-N$_T$, N$_{im}$-La-N$_{im}$ and O-Cd-N$_T$, were derived at B3LYP method using LanL2MB basis set. The calculated maximum bond angle for O-La-O was resulted using HF/6-31G*. The minimum bond angles for N$_{im}$-La-N$_T$, N$_{im}$-La-N$_{im}$ and O-La-N$_T$ were resulted at HF/6-31G*. The minimum bond angle for O-La-O was derived at B3lyp method using LanL2MB basis set. Thus it is clear that the 6-31G* basis set at Hartree-Fock method gives longer La-O and La-N bond lengths than other basis sets studied here. The calculated energies for HOMO and LUMO of this molecule was given in Table-3. The hardeness of a molecule is defined by Pearson as[24]:



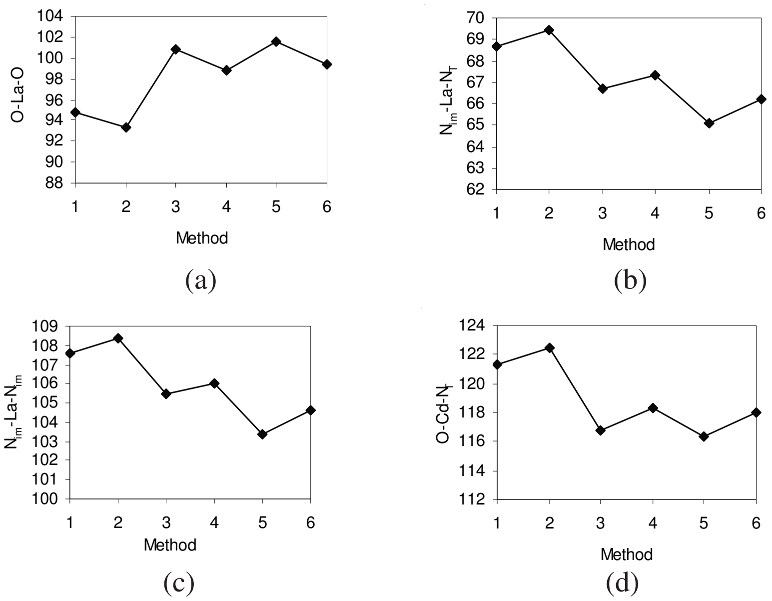
(a) (b) (c)

Fig. 3. Comparison between the mean bond lengths (Å) for the calculated structure of [La(L)] at methods 1-6 described in section 2.

TABLE-2
COMPARISON BETWEEN THE MEAN BOND LENGTHS (Å) AND BOND ANGLES (°) FOR THE CALCULATED STRUCTURES[a] OF [La(L)] USING METHODS 1-6

Method	1	2	3	4	5	6
Bond lengths						
La-N$_T$	2.89	**2.86**	2.94	**2.90**	3.00	**2.96**
La-N$_{im}$	2.73	**2.71**	2.71	**2.68**	2.75	**2.72**
La-O	2.20	**2.24**	2.32	**2.34**	2.37	**2.36**
Bond angles						
N$_{im}$-La-N$_T$	68.66	**69.42**	66.73	**67.33**	65.11	**66.19**
O-Cd-N$_T$	121.30	**122.40**	116.80	**118.30**	116.30	**118.00**
N$_{im}$-La-N$_{im}$	107.60	**108.40**	105.50	**106.00**	103.40	**104.60**
O-La-O	94.80	**93.30**	100.80	**98.80**	101.60	**99.40**

[a]The parameters obtained at the HF level are given as plain text, those for the B3LYP level are in bold.



(a) (b)

(c) (d)

Fig. 4. Comparison between the mean bond angles (°) for the calculated structure of [La(L)] at methods 1-6 described in section 2

TABLE-3
CALCULATED ENERGIES FOR HOMO AND LUMO, (HARTREE), HARDNESS (ev) AND ENERGY GAP (ev) BETWEEN HOMO AND LUMO OF [La(L)]

Method	LUMO	HOMO	η	Gap
1	0.16370	-0.21769	5.19	10.38
2	**-0.00126**	**-0.14177**	**1.91**	**3.82**
3	1.26678	1.13472	1.80	3.60
4	**1.19014**	**1.17077**	**0.26**	**0.52**
5	1.27740	1.16453	1.54	3.08
6	**1.19017**	**1.17020**	**0.27**	**0.54**

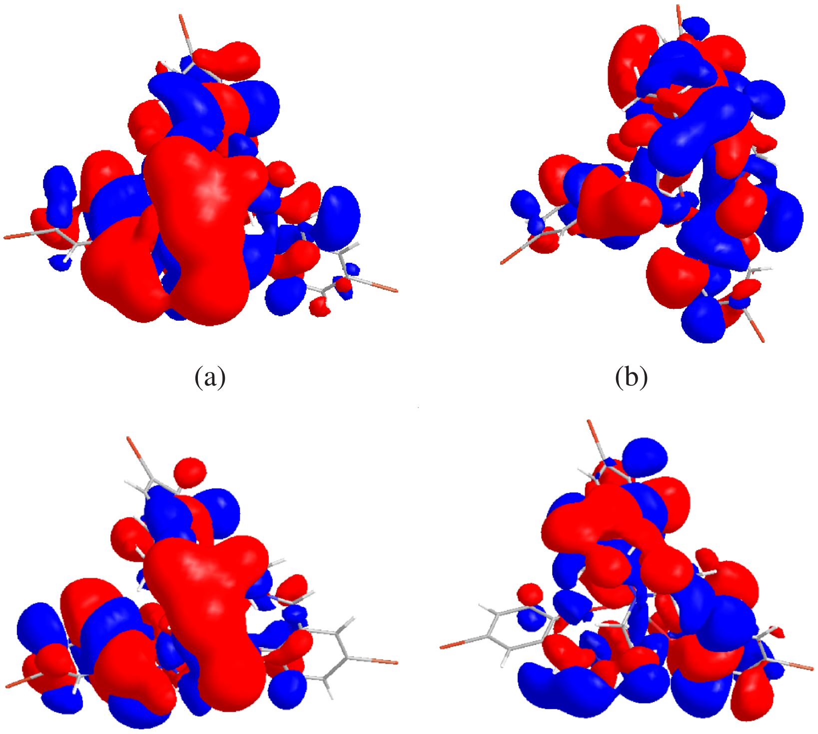
$$\eta = \frac{(I - A)}{2} \tag{1}$$

where I and A are the ionization potential and electron affinity of the system, respectively. It is clear that the energy gap between the HOMO and LUMO is equal to (I-A). Thus we can calculate the hardness of present molecule using eqn. 2 which is approximated as follows, using the Koopmans' theorem[25].

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

Hard molecules thus have a large HOMO-LUMO gap and soft molecules have a small one[23].

The result of calculation show that, using expensive methods both the HOMO and LUMO demonstrated with positive charge, but in the case of cheaper basis set, LanL2MB, this is completely opposite and these orbitals demonstrated with negative charge. Furthermore the calculated energy gap between the latter orbitals in the case of expensive calculation is more reliable than that of LanL2MB calculations. The HOMO and LUMO for [La(L)] are illustrated in Fig. 5. As can be seen, neither HOMO nor LUMO is essentially distributed on central metal ion. The bridgehead tertiary nitrogen atom have considerable contribution in HOMO.



(a) (b)

(c) (d)

Fig. 5. Calculated HOMO (a and c) and LUMO (b and d) for [La(L)]. The Figures a and b are derived form the method 6 and Figures c and d are resulted from the method 5

Conclusion

The results of this work show that the calculated bond lengths and bond angles and also energy levels of Ln complexes are considerably depend on level of calculations including both the method and basis set.

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