SYNTHESIS AND CHARACTERIZATION OF A HEPTADENTATE (N_4O_3) SCHIFF BASE LIGAND AND ASSOCIATED La(III), Sm(III) AND Gd(III) COMPLEXES, AND A THEORETICAL STUDY

Sadegh Salehzadeh[1*], Mehdi Bayat[1], Leila Davoodi[1], Reza Golbedaghi[1] and Vida Izadkhah[2]

[1]Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran
[2]Islamic Azad University, Hamedan Branch, Iran

ABSTRACT. A new symmetrical potentially heptadentate (N_4O_3) Schiff base ligand {N[CH$_2$CH$_2$CH$_2$N=CH(2-OH-5-BrC$_6$H$_3$)]$_3$} (H_3L^6) and associated neutral Gd(III), La(III) and Sm(III) complexes, were synthesized. The new compounds were characterized by IR spectroscopy, elemental analysis and mass spectrometry in all cases and in the case of ligand also with NMR spectroscopy. The relative capability of H_3L^6 to encapsulate a lanthanide ion, herein La(III), has been theoretically studied by ab initio restricted Hartree-Fock (RHF) and DFT (B3LYP) methods. The calculation confirmed that the H_3L^6 ligand can effectively encapsulate a lanthanide ion and enforce a seven-coordinate geometry.

KEY WORDS: Ab initio, Heptadentate ligands, Lanthanide ions, Schiff base complexes

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 bi-dentate ligands. The tripodal, heptadentate ligand 2,2′,2′′-tris(salicylideneimino)triethylamine (H$_3$trensal) has been known for some time. A number of close analogues of trensal are also known that bear substitution of each aromatic ring [1-9]. 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 [10-12].

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 [13]. 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 (Figure 1) [14-16]. However, herein we report the synthesis and characterization of a new heptadentate (N_4O_3) tripodal Schiff base ligand (Figure 1(f), H_3L^6) as well as its Gd(III), La(III) and Sm(III) complexes. An *ab initio* RHF and DFT (B3LYP) calculation on La(III) complexes of this ligand is also reported.

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*Corresponding author. E-mail: ssalehzadeh@gmail.com
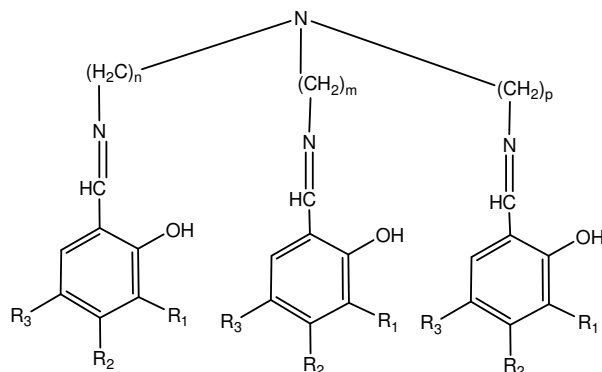
(a) H_3L^1: $R_1 = R_3 =$ t-Bu, $R_2 =$ H   n = m = p = 3   [14]
(b) H_3L^2: $R_1 = R_2 = R_3 =$ H, n = m = p = 3   [15]
(c) H_3L^3: $R_1 = R_2 = R_3 =$ H, n = m = p = 2   [14]
(d) H_3L^4: $R_1 = R_3 =$ t-Bu, $R_2 =$ H   n = m = p = 2   [14]
(e) H_3L^5: $R_2 = R_3 =$ H, $R_1 =$ t-Bu, n = m = p = 2   [9]
(f) H_3L^6: $R_1 = R_2 =$ H, $R_3 =$ Br, n= m= p = 3   [this work]

Figure 1. Structures of the symmetrical tripodal heptadentate (N_4O_3) Schiff base ligands.
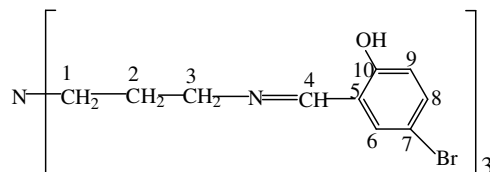

Figure 2. NMR numbering for H_3L^6.

EXPERIMENTAL

The solvents, hydrate metal salts and 5-bromosalicylaldehyde were purchased from Aldrich (USA) and were used without further purification. Tris(3-aminopropyl)amine (trpn) was prepared as previously described [17]. IR, ^{1}H and ^{13}C NMR and visible spectra were measured on FT-IR Bomem MB 100 (USA), Bruker 500 FT-NMR (Germany) and Lightwave II spectrophotometers (France), respectively. ES mass spectra were recorded with a Waters LCT instrument (USA).

Computational detail

The geometry of the [La(L^6)] complex in the gas phase was fully optimized at both the Hartree-Fock and DFT (B3LYP)[18] levels of theory using the Gaussian 98 set of programs[19]. At first, all complexes were optimized using the standard LanL2MB basis set and the resulting structures were then used for further calculations using the standard 3-21G* basis set for ligand atoms and LanL2DZ for the bromine and metal ion. The structures resulting from this were also

used for similar calculations 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. The latter basis set includes effective core potential (ECP) for the lanthanide 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 [20].

Preparation of ligand

Preparation of {N[(CH$_2$)$_3$N=CH(2-OH-5-BrC$_6$H$_3$)]$_3$ (H$_3$L^6) (Figure 2)

To a solution of 5-bromosalicylaldehyde (0.603 g, 3 mmol) in absolute ethanol (20 mL) was added trpn (0.188 g, 1 mmol). The resulting yellow solution was stirred for 60 min at room temperature. The bright yellow microcrystals were filtered off, washed with diethyl ether, and dried in air. Yield: 0.7 g (95%), m.p. 78-81 °C, % anal. calcd. (found) for C$_{30}$H$_{33}$N$_4$O$_3$Br$_3$.H$_2$O: C, 47.87 (47.23); H, 4.69 (4.24); N, 7.45 (7.30). ES-MS m/z 735 [MH]$^+$. IR (cm^{-1}, KBr): 3000-2200 (broad weak band, ν(O-H)), 2950-2800 (w or m, ν(C-H)), 1636, 1617, 1570 and 1478 (s, ν(C=N) and ν(C=C)). ^{1}H NMR δ$_H$ (CDCl$_3$) 1.789 (m, 6H, 2-H), 2.506 (t, 6H, 1-H), 3.601 (t, 6H, 3-H), 6.794 (s, 3H, 6-H), 7.306 (m, 6H, 8- and 9-H), 8.229 (s, 3H, 4-H), 13.51 (b, 3H, OH). ^{13}C NMR δ$_C$ 28.723 (C-2), 51.66 (C-1), 57.592 (C-3), 110.210, 119.413, 120.462, 133.648, 135.138 (C-5 to C-9), 160.743 (C-10), 164.134 (C-4). Visible (CHCl3) λ$_{max}$ max (nm) (ε mol^{-1}Lcm^{-1}): 331 (12320).

Preparation of complexes

[Gd(L^6)]. To a hot solution of 5-bromosalicylaldehyde (0.603 g, 3 mmol) was added warm ethanolic solution (10 mL) of trpn (0.188 g, 1 mmol) and stirred for 10 min at 70 °C. Gd(NO$_3$)$_3$.6H$_2$O (0.451 g, 1 mmol) in 5 mL absolute ethanol was then added. To the solution of NaOH (0.12 g, 3 mmol) in ethanol (5 mL) the solution then added and refluxed at room temperature for 12 h. The yellow precipitate of the product was washed with chloroform and diethyl ether and dried under vacuum. Yield: 0.346 (39%), m.p. > 200 °C, % anal. calcd. (found) for C$_{30}$H$_{30}$N$_4$O$_3$Br$_3$Gd.0.5CHCl$_3$.H$_2$O: C, 37.89 (37.61); H, 3.39 (3.10); N, 5.80 (5.98). ES-MS m/z 890 [MH]$^+$. IR (cm^{-1}, KBr): 1625 (ν(C=N)), 1524, 1462 (ν(C=C)).

[Sm(L^6)]. This complex was prepared analogously using Sm(CH$_3$COO)$_3$ (0.082 g, 0.25 mmol), 5-bromosalicylaldehyde (0.151 g, 0.75 mmol), trpn (0.047 g, 0.25 mmol) and NaOH (0.03 g, 0.75 mmol). Yield: 0.095 (43%), m.p. > 200 °C, % anal. calcd. (found) for C$_{30}$H$_{30}$N$_4$O$_3$Br$_3$Sm.: C, 40.77 (40.60); H, 3.42 (3.53); N, 6.34 (6.12). ES-MS m/z 884 [MH]$^+$. IR (cm^{-1}, KBr): 1625 (ν(C=N)), 1525, 1461 (ν(C=C)).

[La(L^6)]. This complex was prepared analogously using La(NO$_3$)$_3$.6H$_2$O (0.433 g, 1 mmol), 5-bromosalicylaldehyde (0.603 g, 3 mmol), trpn (0.188 g, 1 mmol) and NaOH (0.12 g, 3 mmol). Yield: 0.340 (39%), m.p. > 200 °C, % anal. calcd. (found) for C$_{30}$H$_{30}$N$_4$O$_3$Br$_3$La: C, 41.38 (41.11); H, 3.48 (3.50); N, 6.44 (6.47). FAB-Mass (positive FAB in nitrobenzyl alcohol): m/z 871 [MH]$^+$. IR (cm^{-1}, KBr): 1652, 1635 (ν(C=N)), 1519, 1453 (ν(C=C)).

RESULTS AND DISCUSSION

Ligand synthesis

A new potentially heptadentate tripodal Schiff base ligand, H_3L^6 was synthesized from the condensation reaction of tripodal tetraamine ligand trpn with 3 equivalent of 5-bromosalicyl-aldehyde in ethanol solution. This ligand is readily soluble in chloroform and is insoluble in water. The analytical and spectral data are completely consistent with the proposed formulation. Complete condensation of all primary amino groups of the trpn are confirmed by the lack of $v(N–H)$ stretching bands in the IR 3400-3100 cm^{-1} region and presence of a strong $v(C=N)$ band at about 1636 cm^{-1}. The existence of strong intramolecular hydrogen bonding interaction between the imine nitrogen and the phenolic proton in each arm is confirmed by the observation of a weak broad band in the IR 2200-3000 cm^{-1} region [14, 15]. The ^{1}H NMR and ^{13}C NMR spectra of this product also clearly confirm their formation and purity. The ^{1}H NMR spectrum of this ligand not only shows the absence of N–H hydrogen resonances but also the presence of one singlet signal due to CH=N hydrogen resonance at 8.23 ppm. This is supported by the existence of a peak at about 164.1 ppm in the ^{13}C NMR spectrum. The strong absorption bands in electronic absorption observed at 331 nm is most probably due to the transition of n→π* of the imine group [21, 22].

Complex synthesis

All complexes were synthesized by template condensation and were characterized (see Experimental section). The IR spectra of the resulting complexes were interpreted by comparing each spectrum with that of the free ligands. The absence of the broad band at 2200-3000 cm^{-1} due to $v(OH)$ of the intramolecularly bonded N…HO in the IR spectra of the complexes indicates the deprotonation of the salicylaldimine moiety of H_3L^6 upon complexation. The shift of the characteristic imine (C=N) band for all complexes, demonstrates the coordination of the azomethine nitrogens to the metal ion, which was also confirmed by a shift in the transition of n → π* of the imine group in the UV/vis spectrum through complexation [14, 15]. In addition to the above observations the mass spectra of all complexes clearly confirm the proposed formulation. The determined isotopic distribution pattern of these complexes is different to that of the free ligand and corresponds with the simulated isotopic distribution.

Ab initio and DFT studies

The geometry of the [La(L^6)] complex was fully optimized at both the Hartree-Fock (HF) and density functional B3LYP levels of theory. Unfortunately due to SCF convergence problems we were not able to easily optimize the gadolinium(III) and samarium(III) complexes synthesized here. This was due firstly to inherent complications, resulting from partially filled f-orbitals, and secondly, to the size of these bulky molecules. On the other hand, because the aim of the present calculations is comparison of the capability of the ligand H_3L^6 with similar ligands to encapsulate a metal ion, we decided to study only the corresponding La(III) complexes. Obviously optimization of La complexes in which there are not any partially filled d- or f-orbitals is considerably easier than that for corresponding Sm(III) and Gd(III) complexes. Selected calculated bond lengths and bond angles of [La(L^6)] 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 (Figure 3). 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$_3$L^1 to H$_3$L^4 Schiff base ligands [14]. 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 [23-26]. 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 calculate 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. Calculations show that the values of T$_N$, N$_{imine}$—La—N$_{imine}$ and N$_{imine}$—La—N$_T$ bond angles are significantly dependent on the type of the initial tetraamine used for preparation of the Schiff base ligands.

Table 1. A comparison between selected theoretical bond lengths (Å) and bond angles (°) for [La(L^6)] complex[a] and corresponding values for some similar complexes.

	Method 1[b]	Method 2[c]		Method 3[d]		Method 3[d]			
	LaL^6	LaL^6		LaL^6		LaL^1	LaL^2	LaL^3	LaL^4
Bond lengths									
La(5)-N(1)	2.84	2.78	2.73	2.85	2.78	2.81	2.82	2.75	2.82
La(5)-N(9)	2.71	2.71	2.68	2.73	2.70	2.69	2.71	2.75	2.67
La(5)-N(10)	2.77	2.77	2.73	2.80	2.77	2.74	2.75	2.76	2.71
La(5)-N(11)	2.79	2.79	2.75	2.82	2.78	2.76	2.79	2.76	2.72
La(5)-O(12)	2.20	2.32	2.34	2.37	2.36	2.36	2.36	2.36	2.38
La(5)-O(13)	2.19	2.32	2.33	2.37	2.370	2.36	2.36	2.36	2.37
La(5)-O(14)	2.20	2.32	2.34	2.37	2.370	2.37	2.36	2.36	2.36
T$_N$[e]	13.62	13.50	13.38	13.52	13.43	13.30	13.36	12.70	12.38
T$_O$[f]	9.75	10.73	10.69	11.00	10.89	10.80	10.90	10.50	10.73
Bond angles									
N(1)-La-N(9)	73.2	71.4	72.1	70.0	71.0	70.0	70.1	62.5	62.1
N(1)-La-N(10)	73.0	71.0	71.9	69.6	70.7	70.7	70.1	62.5	63.4
N(1)-La-N(11)	72.0	70.4	71.2	69.2	70.2	70.1	69.6	62.5	63.5
N(9)-La-N(10)	98.6	98.1	98.9	97.0	97.7	98.8	95.9	100.1	88.8
N(9)-La-N(11)	120.5	116.7	119.3	116.3	118.0	116.2	117.5	100.5	113.6
N(10)-La-N(11)	114.8	112.8	113.1	111.6	112.4	112.1	112.4	100.4	98.6
N(1)-La-O(12)	122.8	118.1	118.5	117.4	118.6	120.5	118.0	121.4	126.3
N(1)-La-O(13)	114.8	111.1	111.6	110.3	111.1	112.3	110.7	121.5	108.3
N(1)-La-O(14)	126.0	124.0	124.7	121.8	123.2	122.5	123.6	121.3	124.2
O(12)-La(5)-O(13)	99.8	108.1	106.3	107.0	106.2	103.0	106.9	95.3	99.6
O(12)-La(5)-O(14)	92.5	95.9	94.5	98.0	96.1	96.5	96.3	95.6	89.9
O(13)-La(5)-O(14)	94.7	98.8	98.0	100.1	98.8	98.2	98.7	95.5	104.4

[a]The parameters obtained at the HF level are given as plain text, those for the B3LYP level are in bold. [b]Using LanL2MB basis set. [c]Using 3-21G* for ligand atoms and LanL2DZ for the bromine and metal ion. [d]Using 6-31G* basis set for nitrogen and oxygen donor atoms, 3-21G* basis set for carbon and hydrogen atoms and LanL2DZ for the bromine and metal ion. [e]The sum of the calculate lengths of the sides of the triangle defined by the imine nitrogen atoms. The sum of the calculate lengths of the sides of the triangle defined by the oxygen atoms.

As can be seen in Table 1, calculated values of T$_N$ using method 3 for H$_3$L^1, H$_3$L^2 and H$_3$L^6 (which are derived from trpn) (see Figure 1) are about 13.30, 13.36 and 13.43 Å, and for H$_3$L^3

and H_3L^4 (which are derived from tren) are about 12.70 and 12.38 Å, respectively. The mean bond angles of N_{imine}—La—N_T (see Table 2) for H_3L^1, H_3L^2 and H_3L^6 are about 70.3, 69.9 and 71.7, respectively and are considerably greater than the corresponding angles, 62.5 and 63.0, in H_3L^3 and H_3L^4. The mean N_{imine}—La—N_{imine} bond angles for H_3L^1, H_3L^2 and H_3L^6 are about 109.3, 108.6 and 110.4, respectively and are also considerably greater than the corresponding angles, in $H3L^3$ and $H3L^4$, both of which are 100.3. It is interesting that the unique X-ray crystal structure reported for La complexes of such ligands confirms the above theoretical results. As can be see in Table 2, all experimental bond angle values for LaL^5 are close to the corresponding theoretical values for LaL^3 and LaL^4 and far from the corresponding values for LaL^1, LaL^2 and LaL^6 complexes. Note that L^3 and L^4, similar to L^5 are derived from the tren but the L^1, L^2 and L^6 derived from the trpn.
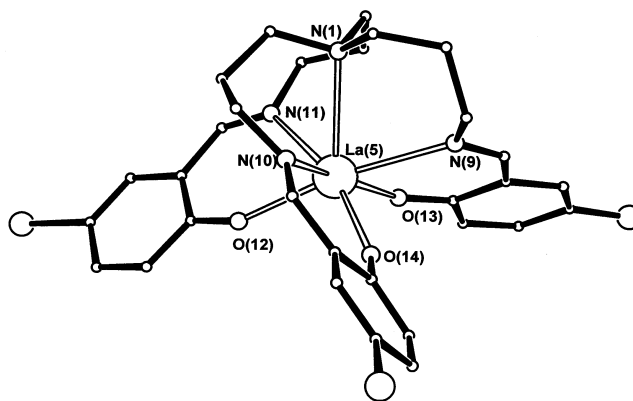

Figure 3. Calculated molecular structure of [La(L^6)] complex at the B3LYP level of theory, using the standard 6-31G* basis set for ligand atoms and LanL2DZ for the metal ion. Hydrogen atoms are omitted for clarity.

Table 2. A comparison between the mean bond lengths (Å) and bond angles (deg) for the calculated structures[a] of [La(L^6)], [La(L^1)], [La(L^2)], [La(L^3)], [La(L^4)] and corresponding experimental values for the LaL^5 complex.

	Method 1[b]	Method 2[c]		Method 3[d]		Method 3[d,e]				Exp.[f]
Bond lengths	LaL^6	LaL^6		LaL^6		LaL^1	LaL^2	LaL^3	LaL^4	LaL^5
La-N$_T$	2.84	2.78	2.73	2.85	2.80	2.81	2.82	2.75	2.82	2.98
La-N$_{im}$	2.76	2.76	2.72	2.78	2.75	2.73	2.75	2.76	2.70	2.66
La-O	2.20	2.32	2.33	2.37	2.36	2.36	2.36	2.36	2.37	2.33
Bond angles										
N$_{im}$-La-N$_T$	72.7	71.0	71.7	69.6	70.3	70.3	69.9	62.5	63.0	62.0
O-Cd-N$_T$	121.27	117.7	118.2	116.5	118.4	118.4	116.0	121.4	119.6	123.1
N$_{im}$-La-N$_{im}$	111.3	109.2	110.4	108.3	109.4	109.3	108.6	100.3	100.3	99.8
O-La-O	95.7	100.9	99.6	101.7	100.4	99.2	100.6	95.5	98.0	93.1

[a]The parameters obtained at the HF level are given as plain text, those for the B3LYP level are in bold. [b]Using LanL2MB basis set. [c]Using 3-21G* for ligand atoms and LanL2DZ for the bromine and metal ion. [d]Using 6-31G* basis set for nitrogen and oxygen donor atoms, 3-21G* basis set for carbon and hydrogen atoms and LanL2DZ for the bromine and metal ion. [e]Ref 14. [f]Ref. 9.

The mean bond lengths about the metal centre for this complex, LaL[6], are quite close to those for similar complexes [14, 16], and thus the introduction of bromo substituents seems to have essentially no significant effect upon the bond lengths in the LaN$_4$O$_3$ core.

CONCLUSIONS

A new potentially heptadentate (N$_4$O$_3$) tripodal Schiff base ligand was synthesized, purified and characterized. The neutral Gd(III), La(III) and Sm(III) complexes of this ligand were also synthesized. Theoretical studies show that the ligand is capable of completely encapsulating the lanthanide ions, producing neutral seven-coordinated complexes. The results also show that the geometry of the LaN$_4$O$_3$ core is significantly influenced by the type of tetraamine used in preparation of such Schiff base ligands.

AKNOWLEDGEMENTS

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