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Theoretical investigation of homoleptic lanthanid complexes $Ln(AlMe_4)_3$

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ABSTRACT

Density functional theory has been used to investigate the electronic structure, coordination number of homoleptic complexes $Ln(AlMe_4)_3$ where Ln = Y, La, Lu. The study reveals that the $AlMe_4$ group is bonded to Ln (Lu,Y) as a bidentate ligand. The results reveal that the central atom La is eight-fold coordinated and L1, L2 are tridentate ligands. The loss of two electrons for the compound 1b(La) generates a gap energetic HOMO/LUMO 0.55eV and translated acceptable stability. The AIM analysis and energy decomposition indicate a strong ionic bond.

KEYWORDS: Lanthanides, Homoleptic complexes, DFT, AIM, Energy decomposition.

1. INTRODUCTION

In 1995, William J. Evans and al published the synthesis and crystal structure of homoleptic $[Ln(AlMe_4)_3]$ complexes, first reported for the metals yttrium, neodymium and samarium (William,1995; Wim,1998; Andreas,2004).The knowledge of the electronic and geometric structure of molecules is essential for understanding their physicochemical properties and the development of their applications in various fields (Liu, 2013; Michel,2006).Thus, control of the coordination sphere of metal is necessary to guide applications.

In the context of an analysis of the mode of coordination of lanthanides, we are interested in the theoretical study of homoleptic lanthanide complexes $Ln(AlMe_4)_3$ recently synthesized and characterized by the group of Melanie Zimmermann and al (William,1995; Melanie, 2007). In this article we carry out a quantum calculation based on the density functional theory (DFT) of the homoleptic complexes, the research focus is to analyze the structural properties. Our aim is to study the coordination number between the $AlMe_4$ ligand and the metal. Among the most significant theoretical work in our view, are those conducted on a series of molecules M $(AlMe_4)_3$ in 2011 by Giovanni Occhipinti and al (Giovanni, 2011).

2. METHODS

Computational methods: The geometry optimizations were performed with the Amsterdam Density Functional (ADF) program developed by Baerends and co-workers (Baerends, 1973). Electron correlation was treated within general gradient approximation with the PW91functional (Perdew, 1992) which is a widely used functional for lanthanides (Hannachi, 2010; Lakehal, 2010; Lakehal, 2012). The atom electronic configurations were described by a triple ζ Slater type orbital (STO) basis set for H 1s, and 2s and 2p for C, 3s and 3p for Al, augmented with 2p single-ζ polarization functions for H atoms, with 3d single-ζ polarization functions for C and 4p single-ζ polarization functions for Al. The atomic basis set of the lanthanide atoms is the following: a triple ζ -STO for the outer 4f, 5d, and 6s orbitals, frozen core approximation for the shells of lower energy. Relativistic corrections were taken into account with the use of the relativistic (ZORA) method (van Lenthe, 1999). The integration parameter and the energy convergence criterion were set to be 6 and 10–3 au, respectively. The topological analyses were calculated with Dgrid (Kohout, 2008), using tape 21 file exported from ADF.

3. RESULTS AND DISCUSSION

Geometry optimization: The most important optimized geometry parameters for the complexes 1a(Y), 1b(La) and 1h(Lu) (Figure 1 and Figure 2) are presented in Table 1. The results were compared to those of the experimental data (The experimental values are given in gras and italic). Figure 3 shows that there is a linear relation (R about 0,994) between these quantities: the distance Ln-C with increasing ionic radii of lanthanide ions. Furthermore, we find the complex which has the shortest distance Ln-C is that which corresponds to the richest metal center in electrons 1h(Lu), the opposite is true in 1b (La). This Ln-C bond of variation in the order: La > Y> La is in agreement with the lanthanide contraction theory (Karl,1994). In addition, the angles AlLnAl (Ln = Y and Lu) are 120°. The complex 1b (La) has the highest value of the Al1-Ln-Al2 angle 133.5 °. The variation in the angles Al-Ln-Al in these complexes 1a (Y), 1b (La) and 1h (Lu) can be explained by the difference in the structures see (Figure 1, Figure 2 and Table 1).

Charge analysis and dipole moments: The result of Hirshfeld population analysis (Hirshfeld, 1977) of 1a(Y), 1b(La) and **1h**(Lu) is given in Table 2. The calculated net metallic charges are generally weak in relation to the oxidation state, this is explained by the strong electronic donation of ligand to the metal, in particular by $AlMe_4$ whose formal negative charge -3 is weakened by the transfer of charge $(AlMe4)^{-3} \rightarrow Ln^{+3}$.

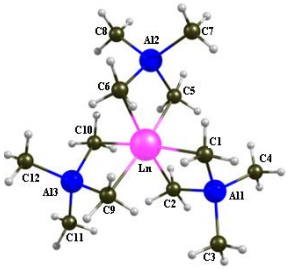


Figure.1. Optimized geometry of complexes 1a and 1h

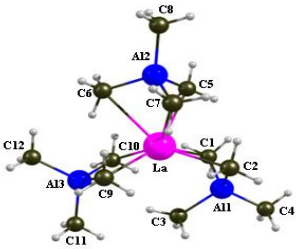


Figure.2. Optimized geometry of complexe 1b

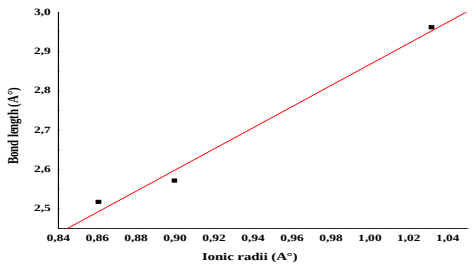


Figure.3. The optimized bond length Ln-C as a function of the ionic radius of the lanthanide

Table.1. Main Geometry Parameters of $Ln(AlMe_4)_3$/Ln= (Lu, Y et La)

$Ln(AlMe_4)_3$	1a(Y)	1b(La)	1h(Lu)
Bond lengths (Å)			
Ln-C1	2.570; 2.510(6)	2.960; 2.902(3)	2.516; 2.466(2)
Ln-C2	2.569; 2.507(7)	2.805; 2.735(3)	2.513; 2.471(2)
Ln-C3	4.459	3.165; 3.154	4.402; 4.362
Ln-C5	2.572; 2.505(6)	2.807; 2.772(3)	2.513;2.455(2)
Ln-C6	2.572; 2.505(6)	3.109; 2.892(3)	2.513; 2.455(2)
Ln-C9	2.569; 2.505(7)	2.730; 2.701(3)	2.513; 2.471(2)
Ln-C10	2.570; 2.514(8)	2.729; 2.697(3)	2.516; 2.466(2)
Ln-Al1	3.111	3.058; 3.032(1)	3.056; 3.017(5)
Ln-Al2	3.114	3.045; 2.996(1)	3.052; 3.006(8)
Ln-Al3	3.111	3.311; 3.264(1)	3.055; 3.017
Al1-C1	2.114	2.060; 2.048(4)	2.112; 2.018
Al1-C2	2.115	2.086; 2.072(4)	2.113; 2.078
Al2-C5	2.112	2.085; 2.056(4)	2.112; 2.088
Al2-C6	2.112	2.028; 2.036(4)	2.112; 2.089
Al2-C7	1.983	2.054; 2.040(4)	1.982; 1.961
Al3-C9	2.115	2.109; 2.080(3)	2.113;2.078
Al3-C10	2.114	2.110; 2.080(3)	2.112; 2.084
Angles (°)			
Al1-Ln-Al2	119.9	133.5; 133.3	119.9;119.5
Al2-Ln-Al3	119.8	113.6; 116.5	119.8; 119.5
Al3-Ln-Al1	120.2	112.8; 110.2	120.2;121.1
C1-Ln-C2	84.8	71.7; 72.5	86.5; 86.3(7)
C5-Ln-C6	84.6	66.5; 69.1	86.4; 86.3
C9-Ln-C10	84.8	78.8; 78.8(1)	86.6; 87.1

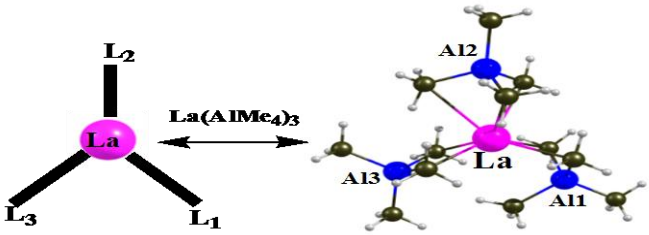
All carbon atoms are negatively charged. The negative charge on the tow carbons linked to the lanthanide and the positive charge of the latter, shows the existence of electrostatic attraction The charge on the aluminum atoms is positive, so the electrostatic interaction with the metal is repulsive, the Ln-Al bond nonexistent. We notice that the dipole moment of 1b (La) is most high in the series.

Molecular orbital analysis: The molecular orbital diagram obtained by DFT method to the different compounds optimized 1a(Y), 1b(La),1h(Lu) are compared in Figure 4. The composition of the frontier orbitals is given in Table 3. At the first view, we notice a wide gap between the energetic occupied orbitals of the vacant orbitals (respectively 3.86, 3.25, and 4.43 eV). The loss of two electrons for the compound 1b(La) generates a gap energetic HOMO/LUMO 0.55eV and translated acceptable stability.

Table.2. Hirshfeld atomic charges of the main atoms of (1a(Y), 1b(La) et 1h(Lu))

	1a(Y)	1b(La)	1h(Lu)
Ln	0.751	0.719	0.744
Al1	0.370	0.362	0.369
Al2	0.369	0.363	0.368
Al3	0.370	0.365	0.369
C1	-0.239	-0.236	-0.238
C2	-0.239	-0.241	-0.237
C3	-0.267	-0.238	-0.268
C4	-0.267	-0.265	-0.268

C5	-0.239	-0.241	-0.237
C6	-0.239	-0.237	-0.237
C7	-0.267	-0.236	-0.268
C8	-0.267	-0.265	-0.267
C9	-0.239	-0.234	-0.237
C10	-0.239	-0.234	-0.238
C11	-0.267	-0.267	-0.268
C12	-0.267	-0.267	-0.268
μ (debye)	0.047	2.485	0.013



Scheme 1

In compounds 1a(Y),1b(La),1h(Lu) the highest occupied molecular orbitals HOMO, HOMO-1, HOMO-2 are located on the ligand $AlMe_4$, with a carbon participation 76 % and 24% aluminum. For the three complexes, the lowest unoccepied molecular orbital (LUMO) are metallic nature, involving the carbon atom is only 7 %(see Table 3). The interaction between the metal and the two ligands (L1,L2) Scheme I.1 in 1b(La) complex appears in Figure 5, this result indicates the existence of a link between the La-C3 therefore the ligand (L1,L2) is tridendate and the metal center (La) has a coordination equal to eight. The existence of a covalent bond between the ligands L1,L2 and lanthanum is displayed in Figure 5.

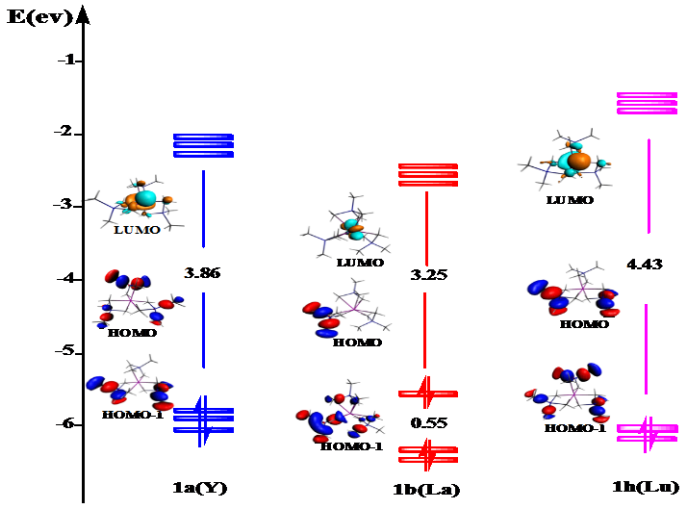


Figure.4.DFT molecular orbital diagrams of 1a(Y), 1b(La) and 1h(Lu)

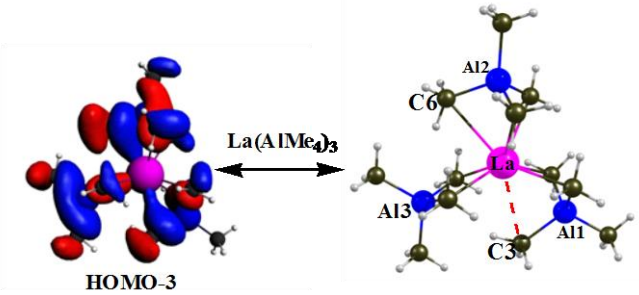


Figure.5.Molecular orbital HOMO-3 of complex 1b(La)

Energy-decomposition analysis: We come to the analysis of the nature and energy of metal–ligand bonding in the homoleptic complexes Ln $(AlMe_4)_3$.In this study, we based on Ziegler-Rauk energy diagram decomposition. For this complexes, we selected $[Ln]^{+3}$ and $[AlMe_4]^{-3}$ as reference fragments in their appropriate geometry. The energy-

partitioning scheme available in ADF is particularly well suited for this purpose (Bickelhaupt, 2000; Ziegler, 1979). Indeed, the bond decomposition energy (BDE) between [Ln] (Ln=Lu, Y and La) and ($AlMe_4$) fragments is the sum of three terms: BDE=E_{elec}+E_{orb}+E_{pauli} Eq(1)

Table.3.Energies and compositions of selected orbitals of Ln($AlMe_4$)$_3$

OM	Energy(eV)	Occup	Ln%	C %	Al%
1a(Y)					
HOMO-2	-6.02	2	0	78	22
HOMO-1	-5.98	2	0	79	21
HOMO	-5.97	2	0	76	24
LUMO	-2.11	0	93	7	0
LUMO+1	-2.09	0	95	5	0
LUMO+2	-2.08	0	96	4	0
1b(La)					
HOMO-2	-6.28	2	0	80	20
HOMO-1	-6.20	2	0	81	19
HOMO	-5.65	2	0	76	24
LUMO	-2.40	0	100	0	0
LUMO+1	-2.37	0	100	0	0
LUMO+2	-2.35	0	100	0	0
1h(Lu)					
HOMO-2	-6.08	2	0	77	23
HOMO-1	-6.03	2	0	78	22
HOMO	-6.03	2	0	79	21
LUMO	-1.60	0	93	7	0
LUMO+1	-1.56	0	94	6	0
LUMO+2	-1.55	0	95	5	0

Where ΔE_{elec} is the electrostatic stabilization energy between Ln and $AlMe_4$ when placed in the final geometry and ΔE_{pauli} is the Pauli energy due to repulsions between the electron clouds of both fragments in the molecular geometry. ΔE_{orb} mainly accounts for the interaction between occupied and vacant orbitals. This analysis has been performed on 1a(Y), 1b(La) and 1h(Lu). The energy-decomposition results obtained using Eq. (1) are reported in Table 4. The trend for BDE (Table 4) in complexes (1a(Y), 1b(La) and 1h(Lu)) vary little from one system to another and follows almost the same trend as the electrostatic energy. the complex 1a(Y) has the biggest interaction energy and the complex 1h(Lu) has the lowest interaction energy, this comparison of the BDE values computed for the two complexes indicates that the Y-C is slightly stronger in 1a(Y) than the bond Lu-C in 1h(Lu) (–52.00 and –47.59 eV, respectively).

Table.4.Various energy contributions

Structure	E_{Pauli}	E_{elec}	E_{Orb}	BDE
1a(Y)	6.51	-37.62	-20.89	-52.00
1b(La)	5.74	-36.54	-19.86	-50.66
1h(Lu)	5.72	-35.12	-18.19	-47.59

The covalent character and steric repulsion (*E*orb+*E*pauli) for both 1a(Y) and 1b(La) complexes are much more negative than for the complex 1h(Lu). The ratio of electrostatic and orbitalaire energy, as obtained by this method, can give an approximate measurement of the covalency degree in the metal-ligand bonding (Lein, 2003). In Table 5 the Eele/Eorb ratio indicates a majority of ionic bonding can be well confirmed by analyzing Table 4.

Table.5.Percentage of electrostatic and orbital contributions to the Ln–$AlMe_4$ bonding

	1a(Y)	1b(La)	1h(Lu)
%Eorb+Pauli	28	28	26
%Eelec	72	72	74

Topological analysis: Structural analysis of the complexes Ln ($AlMe_4$)$_3$ to the X-ray shows that the coordination number of the lanthanide ion is between 6 and 7 (William,1995; Melanie, 2007).Lanthanides Y and Lu are related to three groups η^2-$AlMe_4$ but the ion La is bound to two groups η^2- $AlMe_4$ and η^3 a ligand - $AlMe_4$.

Table.6.Topological properties at Ln- AlMe4 BCP's of Ln(AlMe4)3

Complexes	Critical Points	ρ(r)	∇^2 ρ(r)	|V|/G	H(r)
1a(Y)	BCP1	0.0376	0.1048	1.0900	-0.0026
	BCP2	0.0377	0.1047	1.0918	-0.0026
	BCP3	0.0374	0.1042	1.0897	-0.0026
	BCP4	0.0374	0.1042	1.0892	-0.0025
	BCP5	0.0376	0.1048	1.0897	-0.0026
	BCP6	0.0377	0.1047	1.0917	-0.0026
	BCP1	0.0323	0.0764	1.0928	-0.0020

1b(La)	BCP2	0.0323	0.0767	1.0918	-0.0019
	BCP3	0.0253	0.0576	1.0476	-0.0007
	BCP4	0.0266	0.0600	1.0593	-0.0009
	BCP5	0.0210	0.0492	1.0044	-0.0369
	BCP6	0.0350	0.0909	1.0913	-0.0023
	BCP7	0.0350	0.0913	1.0900	-0.0023
	BCP8	0.0189	0.0452	0.9916	0.0633
1h(Lu)	BCP1	0.0428	0.1145	1.1671	-0.0057
	BCP2	0.0431	0.1151	1.1689	-0.0059
	BCP3	0.0430	0.1151	1.1683	-0.0058
	BCP4	0.0430	0.1151	1.1683	-0.0058
	BCP5	0.0428	0.1145	1.1672	-0.0057
	BCP6	0.0431	0.1152	1.1689	-0.0059

We will analyze the number of coordination in complexes 1a(Y), 1b(a) and 1h(u) by AIM method (Bader,1990; Matta,2007). The results of this analysis clearly indicate the existence of a critical point (BCP) between each pair of bonded atoms. The nature of this bond may be described by the value of the electron density ρ(r), and the Laplacian of the electron density $\nabla^2\rho(r)$. AIM calculation results are summarized in Table 6. From the results of the analysis AIM is observed the existence of six critical points for complexes 1a(Y), 1h(u) see Figure 6. For complex 1b (La), the results for the AIM analysis indicates the existence of eight critical points Figure 7. The value of the Laplace density at bond critical point Ln-ligand ∇^2(BCP) is largely positive in all cases (Table 6) is between 0.04 and 0.11 a.u. which is an indicator of a closed-shell interaction (ionic bond) (Matta,2007).The BCP8 The La- $AlMe_4$ (Figure 7) is characterized by relatively low value of the electron density ρ(r), the positive value of the Laplace $\nabla^2\rho(r)$ and a positive value of H(r). These parameters; as ranked by Espinosa and al correspond to the ionic bond (Espinosa, 2002).

Calculation of geometry optimization with constraint: The analysis of complex 1b(La) by the method AIM and analysis of molecular have shown that the ligand L1 (Sheme 1, Figure 5) is tridentate and the metal center has the coordination equals to eight. After the geometre optimization without constraints, then we made a calculation with constraint on the ditances La-C1, La-C2, the latter are set respectively at the value 2.960 and 2.805Å. The comparison (Table 7) of the two binding energies obtained after geometry optimization with and without constraint, shows that the structure having the coordination number of eight is more stable than the one that has the the number seven coordination.

Table.7. Binding energy for the two calculations

1b(La)	Calculation with constraint	Calculation without constraint	ΔE
E (eV)	-257.7843 eV	-257.7852 eV	0.0009 eV

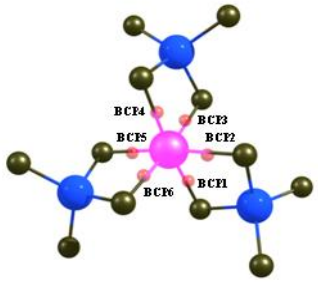


Figure.6.Molecule Graph of 1a(Y) and1h(Lu) BCPs (red)

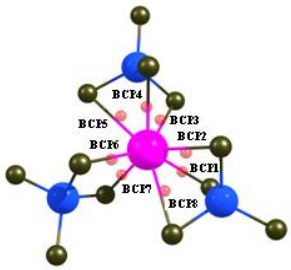


Figure.7. Molecule Graph of 1b(La), BCPs (red)

4. CONCLUSION

In this work, we have probed the electronic and the molecular structure of homoleptic complexes $Ln(AlMe_4)_3$ for the lanthanide metal of the tetramethylaluminate ligand. The most important point is that obtained by orbital analysis and AIM analysis, where the number of coordination between the metal central and $AlMe_4$ ligand in the complexe $La(AlMe_4)_3$ equal to eight contrary to the experimental data which indicate the existence of the coordination number equal to 7. The loss of two electrons for the compound 1b(La) generates a gap energetic HOMO/LUMO 0.55eV and translated acceptable stability. The AIM analysis and energy decomposition indicate a strong ionic bond Ln-($AlMe_4$) with a covalent contribution, the highest is obtained with 1a (Y) and 1b (La).

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