



Research Article

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Theoretical approach of complexes containing lanthanide linked by bridges

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ABSTRACT

The geometric and theoretical structure of various lanthanide complexes with formula $(M-L)_2(\mu-RX_2)$ ($M = Lu, La$ and Y , $X=N$ and S) are analyzed and compared using calculations based on density functional theory (DFT), performed with the ADF program^[1] using GGA PW91^[2]. Topological approach are analyzed by the AIM (atoms in molecules); method of Richard Bader with Chemcraft 1.4 program^[3].

Keywords: lanthanides, Dinitrogen complexes, DFT, AIM.

INTRODUCTION

Dinitrogen complexes or related bridge of the lanthanide and actinide elements has an important class of compounds in inorganic coordination due to their various properties and applications^[4-5]. Metal complexes of N_2 have been occur since 1960^[6-12], these complexes have attracted the attention of William J.Evans group. We report in this work of newly synthesized compounds for which; type of coordination requires theoretical confirmations $[(C_5Me_4H)_2Lu]_2(\mu-\eta^3-\eta^3-C_{12}H_8N_2)$ **1**, $[(C_5Me_4H)_2La](\mu-\eta^4-\eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]$ **2**.^[13], $[(C_5Me_5)_2La(\mu-SPh)]$ **3** and $[(C_5Me_5)_2Y(\mu-SPh)]$ **4**.

EXPERIMENTAL SECTION

All calculations DFT are performed with the ADF program, using the GGA functional PW91 and the base TZP (Triple Zeta Polarized); we appealed the Density Functional Theory for the study of organometallic complexe of lanthanides, because its successes in this area^[14-18] with the integral of order AIM (Atoms in Molecules); it is a quantum chemistry model characterizing the chemical binding of a system based on a topological approach of the charge density.

RESULTS AND DISCUSSION

3.1.Structural study of 1 and 2

Computational method based on the density functional theory were performed on both complex **1** and **2**, the experimental geometry was modified by replacing the methyl ligand by hydrogen atoms. Main structural data of the optimized complexes are provides in **Tab1**, while, the obtained results are agree with the experimental values; calculated interatomic distances and those measured by X-ray diffraction, is showing much closer (slight deviations can also be attributed in part to the substitution of methyl ligand by hydrogen). Complex **1** and **2** contain a bridging phenazine ($C_{12}H_8N_2$) **Fig 1**, in each of these compounds, the shortest interaction between the metal and ($C_{12}H_8N_2$) is through the nitrogen atoms; the 2.511 Å La(1)-N(1) and 2.475 Å La(2)-N(2) distances in **1** and 2.301 Å Lu(1)-N(1) and 2.300 Å Lu(2)-N(2) distances in **2**.

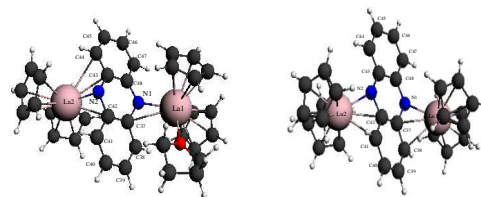


Fig 1: $[(C_5Me_4H)_2Lu]_2(\mu-\eta^3:\eta^3-C_{12}H_8N_2)$ and $[(C_5Me_4H)_2La](\mu-\eta^4:\eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]$

Tab1: Geometrical parameters of $[(C_5Me_4H)_2Lu]_2(\mu-\eta^3:\eta^3-C_{12}H_8N_2)$ and $[(C_5Me_4H)_2La](\mu-\eta^4:\eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]$

	(Ln =La)			(Ln=Lu)		
	Exp	Cal		Exp	Cal	
Bond lengths (Å°)						
Ln(1)-N(1)	2.472	2.511	0.039	2.248	2.301	0.053
Ln(2)-N(2)	2.439	2.475	0.036	2.231	2.300	0.069
Ln(1)-C(37)	3.045	3.061	0.016	2.755	2.755	0.000
Ln(1)-C(38)	3.141	3.211	0.070	2.719	2.757	0.038
Ln(2)-C(41)	.	.	.	2.740	2.754	0.014
Ln(2)-C(42)	3.089	3.024	0.065	2.762	2.759	0.003
Ln(2)-C(43)	2.867	2.990	0.123	3.350	3.314	0.036
Ln(2)-C(44)	3.039	3.233	0.194	3.786	3.930	0.114
N-N	2.881	2.871	0.010	2.866	2.849	0.017
Ln(1)- Ln(2)	6.872	6.865	0.007	6.742	6.671	0.071
N(1)-C(48)	1.400	1.395	0.005	1.408	1.339	0.069
N(1)-C(37)	1.399	1.387	0.012	1.376	1.369	0.007
C(37)-C(38)	1.377	1.405	0.028	1.407	1.413	0.006
C(38)-C(39)	1.415	1.413	0.002	1.426	1.429	0.003
C(39)-C(40)	1.365	1.385	0.020	1.354	1.376	0.022
C(40)-C(41)	1.388	1.413	0.025	1.419	1.429	0.010
C(41)-C(42)	1.407	1.407	0.000	1.410	1.414	0.004
C(37)-C(42)	1.430	1.440	0.010	1.434	1.439	0.005
N(2)-C(43)	1.377	1.391	0.014	1.402	1.393	0.009
N(2)-C(42)	1.392	1.381	0.011	1.371	1.369	0.002
C(43)-C(44)	1.406	1.407	0.001	1.392	1.400	0.008
C(44)-C(45)	1.396	1.405	0.009	1.395	1.403	0.004
C(45)-C(46)	1.372	1.388	0.016	1.375	1.398	0.008
C(46)-C(47)	1.390	1.405	0.015	1.399	1.403	0.004
C(47)-C(48)	1.382	1.397	0.015	1.388	1.400	0.012
C(48)-C(43)	1.434	1.431	0.003	1.416	1.425	0.009
Bond angle (deg)						
C(37)-N(1)-C(48)	115.9	116.1	0.2	116.8	117.9	1.1
C(42)-N(2)-C(43)	115.6	116.6	1.0	117.4	117.9	0.5
N(1)-Ln(1)-C(37)	026.9	026.5	0.4	029.8	029.7	0.1
N(2)-Ln(2)-C(42)	025.9	026.8	0.9	029.5	029.7	0.2
Dihedral angle (deg)						
Ln(1)-N(1)-N(2)-Ln(2)	195.5	200.1	4.6	253.4	246.9	6.5
C(45)-C(47)-C(43)-N(1)	180.7	179.6	1.1	177	178.4	1.4
C(43)-N(1)-C(42)-C(38)	170.9	169.4	1.5	169.7	169.4	0.3
C(45)-C(48)-N(2)-C(37)	171.2	171.0	0.2	173.3	176.2	2.9
C(39)-C(41)-C(42)-N(2)	178.8	178.7	0.1	173.3	178.7	5.4

3.2. Topological analysis of AIM

To clarify the coordination mode of the ligand to metal, we appealed to the AIM approach Bader and all [19,20], this method tells us that there is one bond critical point (BCP) between each pair of atoms that are bonded to one another and describes chemical bonding in terms of bond critical points (BCPs). The value of the electronic charge density $\rho(r)$, Laplacian $\nabla^2\rho(r)$ and the energy density $H(r)$ are represented in **Tab2** and **Tab3**. In general $\rho(r)$ is greater than 0.20 a.u., $\nabla^2\rho(r) < 0$ in covalent bonding and $\rho(r)$ less than 0.10 a.u., $\nabla^2\rho(r) > 0$ in a closed-shell interaction (e.g., ionic, van der Waals, or hydrogen) [21]. Lu1-N1, Lu2-N2, Lu1-C38 and Lu2-C41 for $[(C_5H_5)_2Lu]_2(\mu-\eta^2:\eta^2-C_{12}H_8N_2)$ at variance the experimental results which proved the existence of more interactions. Lu1-N1, Lu2-N2, Lu1-C38, Lu2-C41, Lu1-C39 and Lu2-C42 ($[(C_5Me_4H)_2Lu]_2(\mu-\eta^3:\eta^3-C_{12}H_8N_2)$), the same result for $[(C_5Me_4H)_2La](\mu-\eta^4:\eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]$, **1** and $[(C_5Me_4H)_2Lu]_2(\mu-\eta^3:\eta^3-C_{12}H_8N_2)$, **2** we obtain just the interactions La1-N1 and La2-N2; $[(C_5H_5)_2La](\mu-\eta^1:\eta^1-C_{12}H_8N_2)-[La(THF)(C_5H_5)_2]$, counter to the experimental result which proved more interactions La1-N1, La2-N2, La1-C37, La2-C42, La2-C43 and La2-C44.

According to the study of AIM is found that the distances La1-N1 and La2-N2 are intermediate interactions, La1-O is closed-shell interaction, also we note appear of new closed-shell interactions (hydrogen bond): C3-H20, H34-

C22, C31-H6, C17-H23 and H2-H2; these complex interactions involved in particular stability between the two metals and di-anion transition phenazine ($C_{12}H_8N_2$) (see **Fig 2** and **Fig 3**).

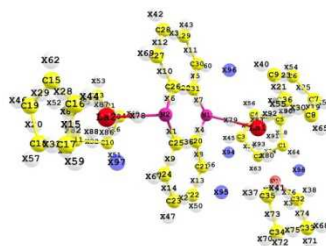


Fig 2: Graphic AIM of $[(C_5Me_4H)_2La](\mu-\eta^4:\eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]_2$

Tab2: electron density $\rho(r)$ and Laplacian of electron density $\nabla^2(r)$ at bond critical point (BCP) of $(C_5Me_4H)_2La(\mu-\eta^4:\eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]$

Interaction	$\rho(r)$	$\nabla^2(r)$	$ V /G$	$H(r)$
bcp 78 La2-N2	0.0613	0.1546	1.1977	-0.0095
bcp 79 La1-N1	0.0553	0.1507	1.1496	-0.0096
bcp 80 La1-O	0.0320	0.1291	0.9385	0.0019
bcp 94 C3-H20	0.0076	0.0206	0.7825	0.0009
bcp 95 C22-H34	0.0073	0.0233	0.7485	0.0012
bcp 96 C31-H6	0.0047	0.0151	0.6893	0.0009
bcp 97 C17-H23	0.0044	0.0120	0.7093	0.0007
bcp 98 H2-H2	0.0037	0.0135	0.6550	0.0009

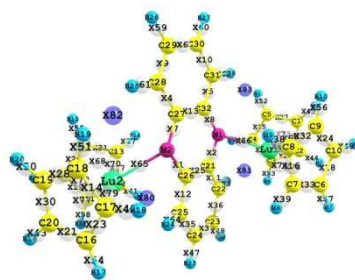


Fig 3: Graphic AIM of $(C_5Me_4H)_2Lu_2(\mu-\eta^3:\eta^3-C_{12}H_8N_2)$

Tab 3: AIM analysis of $[(C_5H_5)_2Lu]_2(\mu-\eta^2:\eta^2-C_{12}H_8N_2)$, $\rho(r)$ and $\nabla^2\rho(r)$ respectively represent the values of the electron density and Laplacian at the critical point

Interaction	$\rho(r)$	$\nabla^2(r)$	$ V /G$	$H(r)$
bcp 65 Lu2-N2	0.0655	0.2211	1.1571	-0.0103
bcp 66 Lu1-N1	0.0653	0.2206	1.1567	-0.0102
bcp 80 Lu2-C41	0.0255	0.0761	1.0494	-0.0010
bcp 81 Lu1-C38	0.0256	0.0763	1.0483	-0.0010
bcp 82 H19-H25	0.0033	0.0104	0.6374	0.0007
bcp 83 H1-H28	0.0032	0.0103	0.6360	0.0007

According to the AIM study, Lu2-N2, N1-Lu1, Lu2-C41 and C38-Lu1 are intermediate interactions, with the appearance of closed-shell interaction between H19-H25 and H1-H28.

4. The molecular orbital diagram

The molecular orbital diagram obtained by DFT method for two optimized compounds **1** and **2** are presented in **Fig 4**. We notice a significant energy gap HOMO - LUMO equal to 1.788 eV for the complex **1** and 1.473 eV for complex **2**.

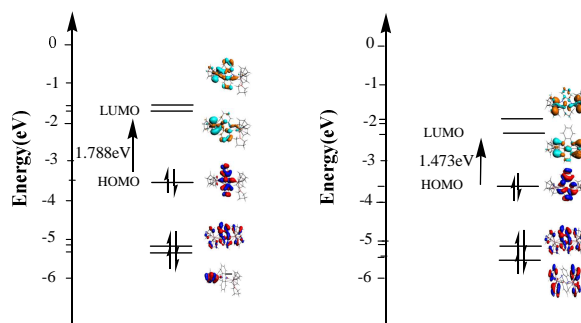


Fig 4. Molecular orbital diagram of $(C_5Me_4H)_2La[(\mu-\eta^4: \eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]]$ and $[(C_5Me_4H)_2Lu]_2[(\mu-\eta^3: \eta^3-C_{12}H_8N_2)]$

5. Chemical descriptors analysis

The electronic chemical potential μ and η overall hardness can be calculated from the frontier orbital energies E_{HOMO} and E_{LUMO} [22-23].

$$\mu = \frac{E_H + E_L}{2}, \quad \eta = E_L - E_H$$

The electrophilicity index ω is related to the chemical potential μ by the following relationship [24]:

$$\omega = \frac{\mu^2}{2\eta}$$

The electric chemistry potential μ , chemical hardness η and the electrophilicity index ω calculated for the complexes $[(C_5Me_4H)_2Lu]_2[(\mu-\eta^3: \eta^3-C_{12}H_8N_2)]$ 1 and $(C_5Me_4H)_2La[(\mu-\eta^4: \eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]]$ 2 are presented in **Tab4**.

Tab 4. Overall reactivity descriptors (eV) of $(C_5Me_4H)_2La[(\mu-\eta^4: \eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]]$ and $[(C_5Me_4H)_2Lu]_2[(\mu-\eta^3: \eta^3-C_{12}H_8N_2)]$

	μ	η	ω	E_{LUMO}	E_{HOMO}
1 La	-2.633	1.887	1.837	-1.690	-3.577
2 Lu	-2.949	1.473	2.952	-2.213	-3.686

The electronic chemical potential μ is 2.633 eV for the complex $(C_5Me_4H)_2La[(\mu-\eta^4: \eta^2-C_{12}H_8N_2)-[La(THF)(C_5Me_4H)_2]]$ 2 and 2.949 eV for the complex $[(C_5Me_4H)_2Lu]_2[(\mu-\eta^3: \eta^3-C_{12}H_8N_2)]$ 1. The largest electronic chemical potential is awarded to the most reactive complex and we note the substitution reduces the reactivity. The chemical hardness η is associated with stability and reactivity of a chemical system, correspond to the energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied (LUMO)[25-28].

2- Structural study of complex $[(C_5Me_5)_2La(\mu-SPh)]_2$ (3) and $[(C_5Me_5)_2Y(\mu-SPh)]_2$ (4)

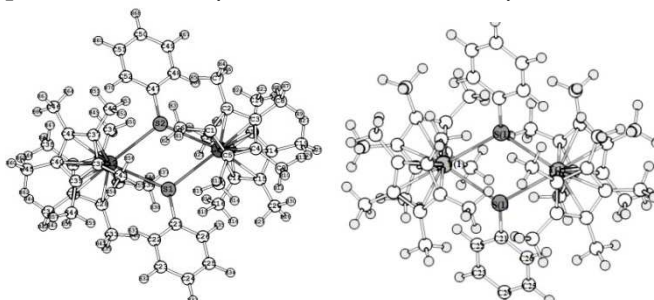
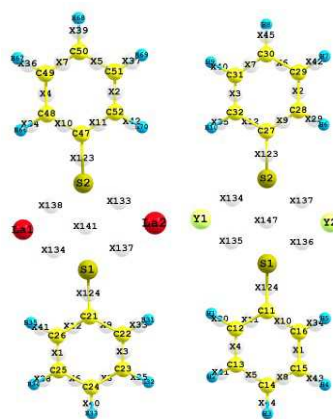


Fig 5 : Experimental compound structure of $[(C_5Me_5)_2La(\mu-SPh)]_2$ (3) and $[(C_5Me_5)_2Y(\mu-SPh)]_2$ (4) obtained by X-ray diffraction

Tab 5 : Structural data experimental geometries and optimized geometries of compounds [(C5Me5)2La(μ -SPh)] 2 and [(C5Me5) 2Y (μ -SPh)] 2

	(Ln=La) Exp	(Ln=La) Exp		(Ln=Y) Exp	(Ln=Y) Cal	
Bond lengths (Å°)						
Ln(1)-S(1)'	3.008	3.024	0.016	2.893	2.921	0.028
Ln(1)-S(1)	3.010	3.026	0.016	2.903	2.926	0.023
Ln(1)'-S(1)'	3.010	3.026	0.016	2.903	2.945	0.042
Ln(1)'-S(1)	3.008	3.024	0.016	2.893	2.933	0.040
Ln(1)-Ln(1)'	5.135	5.168	0.033	4.979	4.903	0.076
S(1)-S(1)'	3.137	3.147	0.010	2.968	3.212	0.244
S(1)-C(21)	1.766	1.772	0.006	1.766	1.786	0.020
C(21)-C(22)	1.393	1.404	0.011	1.386	1.403	0.017
C(22)-C(23)	1.390	1.391	0.001	1.397	1.394	0.003
C(23)-C(24)	1.367	1.397	0.010	1.374	1.396	0.022
C(24)-C(25)	1.369	1.398	0.029	1.373	1.397	0.024
C(25)-C(26)	1.393	1.392	0.001	1.386	1.392	0.006
C(26)-C(21)	1.386	1.403	0.017	1.390	1.404	0.014
angles (deg)						
C(21)-S(1)- Ln(1)	117.0	116.6	0.4	35.1	35.3	0.2
S(1)'-Ln(1)- S(1)	062.8	062.7	0.1	61.6	66.7	5.1
Ln(1)'-S(1)- Ln(1)	117.2	117.3	0.1	118.4	113.6	4.8


Fig 6: Graphic description of calculation AIM for the complex [(C5Me5) 2La (μ -SPh)] 3 and [(C5Me5) 2Y (μ -SPh)] 4

We note the emergence of an interaction between the atom S1 and S2.

CONCLUSION

The study of structural parameters showed that the calculated length of bonds are always overestimated compared to experimental values, the loss of two electrons for two compound 1 and 2 generates an energy gap HOMO / LUMO equal to 1.788 eV for the complex 1 and 1.473 eV for complex 2, which translated acceptable stability.

The most important point is that obtained by AIM analysis ;where the number of coordination between the metal and phenazine (C₁₂H₈N₂) in the complexes [(C₅Me₄H)₂Lu]₂(μ - η^3 : η^3 -C₁₂H₈N₂)**1** and [(C₅Me₄H)₂La](μ - η^4 : η^2 -C₁₂H₈N₂)-[La(THF)(C₅Me₄H)₂]**2**. The theoretical results have shown that the phenazine bridge is bound μ - η^1 : η^1 in the compound **1** and μ - η^2 : η^2 in the compound **2**. The calculations also revealed the existence of a sulfur-sulfur bond in compounds **3** and **4**.

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