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Computational Evaluation on Molecular Stability and Reactivity of Some Dimethylglyoximato-Nickel Complexes from DFT

Noura Kichou
Mouloud Mammeri University of Tizi-Ouzou (UMMTO)

Nabila Guechtouli
Mouloud Mammeri University of Tizi-Ouzou (UMMTO)

Manel Taferguennit
University of Sciences and Technology Houari Boumediene

Zakia Hank
University of Sciences and Technology Houari Boumediene

Abstract: Complexes Nickel constitute a very widespread axis in coordination chemistry and in medicine, because of their application as well as their activity**.** The Ni(III) species which aroused the interest of many biochemists, the three last decades, was identified to be the active entity of many enzymes, in particular, in hydrogenases. It is also mentioned for its powerful catalytic properties in biological and chemical processes. The Ni(IV) species, for its part, is known for its marked oxidizing capacities**.** In this work, we were interested in the theoretical study of Two complexes of dimethylglyoximato-nickel , using the DFT method, with the functional B3LYP function and LANL2DZ basis set, using Gaussian 03 program package. The experimental results, IR, ^{1}H NMR and electronic spectra (UV) were compared to those obtained theoretically using. The energetic, structural and electronic parameters were determined for ligand and each studied complexes. Bending energies were also theoretically evaluated for each complexes.

Keywords: NICKEL, Dimethylglyoxime, DFT, Reactivity

Introduction

Transition-metal ions show diversity in forming various stable complexes with different organic ligands. These complexes have potential applications in fields such as ion exchange, heterogeneous catalysis, photocatalysis, fluorescence, bioimaging, optical devices, magnetism, gas-storage, and also serve as carbon precursor and catalyst for production of multiwalled carbon nantotubes (MWCNTs) (Krishna, 2012 ; Bar, 2016 ; Chen,2019). Dimethylglyoxime (DMG) is an analytical reagent and usually forms thermodynamically stable chelating complexes with selective divalent transition-metal ions (Rath, 2018). Electronic and spectral properties of metal-DMG complexes are highly dependent on the nature of metal ions. Among Ni^{2+} ion show high affinity for the DMG, and form stable complexes in solution and in the solid-state (Sued, 2019). In this work, Two complexes of dimethylglyoximato-nickel were theoretically evaluated from DFT method.

Theoretical Methods

In the absence of crystal structures and preliminary theoretical studies, we carried out a theoretical study in the DFT method with the functional B3LYP(Becke,1993) and the base LANL2DZ (Hay, 1985) in the gaseous

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phase, using Gaussian 03 program package (Fresch, 2003). No symmetry constraints were imposed. We used the GaussView software (Fresch, 2003) to draw the optimized geometries and visualize the vibrational modes.For this purpose, a complete geometry optimization was performed for each compound followed by a frequency calculation of the normal modes of vibration to confirm the stability. Thus, the structural parameters and electronic parameters, the energies, the HOMO/LUMO gaps, and the NBO atomic charges were evaluated of the ligand and complexes obtained. To compare the stability of the two studied complexes, we computed the bending energies. The population analysis was carried out using the natural orbital bond program (NBO) implemented in the Gaussian program 03. The ^{1}H NMR calculations were carried out in the $CHCl_3$ solvent, at the same level of theory. The absolute isotropic chemical shielding was calculated by the Gauge–Independent Atomic Orbital (GIAO) model (Wolinski, 1990). The characterization of excited states and electronic transitions were performed using the time-dependent DFT method (TD-DFT) on their correspondingly optimized ground state geometry. Vertical excitation energies were computed for the first 20 singlet excited states, in order to reproduce the experimental electronic spectra. Results of theoretical calculations were compared with corresponding experimental data. Currently, the DFT method proves its efficiency in the calculation of molecular structures, the electronic and spectroscopic properties of the compounds.

Results and Discussion

Geometry

In figure 1 is given the optimized structure for a ligand (DMG). The optimized geometries of the synthesized complexes are given in figure 2 and figure 3. The optimization of these complexes led to a slightly deformed square pyramid for the **A** complex. However, the complex **B** has an octahedral structure. The bonds between the atoms forming the fragments bound to the metal are almost the same this is due to the symmetry of the molecule. Indeed, the metal ion is bound to two similar groups on both sides in the two complexes **A** and **B**.

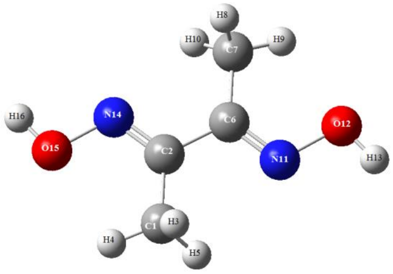

Figure 1. Molecular structure of the H_2L(DMG) ligand optimized at DFT/B3LYP/ LANL2DZ level of theory

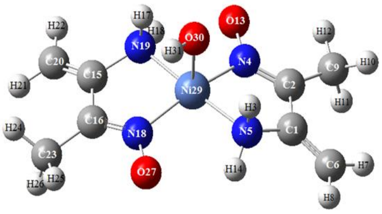

Figure 2. Molecular structure of the A complex optimized at DFT/B3LYP/LANL2DZ level of theory

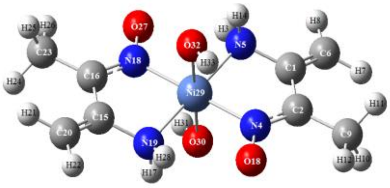

Figure 3. Molecular structure of the **B** complex optimized at DFT/B3LYP/LANL2DZ level of theory.

This result clearly confirms that the studied complexes are symmetric.We report the formation of hydrogen bonds (NH....O) in all the compounds considered. Indeed, In the **A**complex, two hydrogen bonds are formed, one between H_{17} bound to N_{19} and O_{30}, which is 2.202 Å and the other between $N_{19}H_{28}$ and O_{13}, which is 2.177

Å. Thus, in the **B** complex, two hydrogen bonds were determined: N5H3 ... O30, 1.586 Å and O30H31 ... O27, which is 2.043 Å. These established intramolecular hydrogen bonds reinforce the stability of these complexes.

Caracterization

The experimental results, IR, ^{1}H NMR and electronic spectra (UV) were compared to those obtained theoretically. They are in good agreement with those found experimentally.

Table 2. Experimental and theoretical characteristic Infrared spectral (IR) bands for the dimethylglyoxime ligand and its Complexes as KBr Pellets (cm^{-1})

Compound	ν(O-H)	ν(N-H)	ν(CH$_3$)	νCH$_2$=	δ(N-H)	νC=C	νC=N	νCH$_2$*	δCH$_3$ Sym	δCH$_2$**	ν(N-O)	νNi-O	νNi-N
H$_2$L	3000- 3500		2900- 3000				1447		1364		980		
H$_2$L^a	3696 3697	3349- 3511	3033- 3169				1642 1651		1341 1343		995		
A	3100- 3500	3100- 3500	3000- 3050	2800- 2940	1560 sh	1572	1571	1453 sh	1368	871	957	541	497 443
A^a	3624	3349- 3511	3033- 3169	2882- 2942	1485	1668- 1691	1675- 1695	1400 1402	1402 1410	891	-	437	496 429
B	3100- 3500	3100- 3500	2950- 3050	2850- 2930	1560 sh	1572 sh	1572	1453 sh	1369	889	992	520	496 426
B^a	3574 3652	3485- 36661	2924- 3031	2856 2924	1422	1605 1614	1575 1578	1454 1450	1401 1403	898	-	561 480	-

*in the plan, **out of the plan, sh : shoulder. a: calculated by DFT

Table 2. ^{1}H NMR data of the ligand and the complex in deuterated chloroform.

Compound	^{1}H chemical shift (δ) (ppm)	Assignment
H$_2$L	(H3, H8) 1.9 (0.9-2.3)	CH$_3$
	(H5, H10) 1.9 (0.9-2.3)	
	(H4, H9) 1.9 (0.9-2.3)	
	(H13, H16) 10 (7.0)	-C=NOH
B	(H11, H24) 2.00 (1.8)	CH$_3$-C-
	(H10, H25) 2.0 (1.5)	
	(H12, H26) 2.0 (2.2)	
	(H7, H21) 3.40 (4.40)	
	(H8, H22)3.4 (4.33)	CH$_2$=C- and
	(H3, H28) 3.4 (2.8)	-C-NH$_2$
	(H14, H7) 3.4 (5.5)	

Found: experimental; (calc.): calculated by DFT.

Table 3. Electronic absorption data (UV) of the ligand and the complexes in CHCl$_3$.

Compound	λ (nm) (Assignment)	Probable Environment
DMG	$\pi \rightarrow \pi^*$ 250 (242)	
	$\sigma \rightarrow \sigma^*$ (144, 158, 148, 149, 154, 160)	
A	sh $\pi \rightarrow \pi^*$ 290 (283)	Distorted Square Pyramidal
	sh $n \rightarrow \pi^*$ 320 (299)	
	LMCT 430 (422, 429)	
	$d \rightarrow d$ 550 (529, 571)	
	$d \rightarrow d$ 890 (839, 889)	
B	$\pi \rightarrow \pi^*$ 290 (292)	Distorted Octahedral
	sh $n \rightarrow \pi^*$ 340 (341)	
	sh LMCT 376 (380)	
	sh $d \rightarrow d$ ($^1A_1 \rightarrow {}^1T_{2g}$) 425 (480)	
	$d \rightarrow d$ ($^1A_1 \rightarrow {}^1T_{1g}$) 500 (511)	
	$d \rightarrow d$ ($^1A_1 \rightarrow {}^1T_{1g}$) 550 (551)	

sh: shoulder; Found: experimental; (calc.): calculated by DFT.

Bonding Energy

By definition it is the equivalence in absolum value of the energy of dissociation between the metal and the ligandIt is defined by the following relation:

$$E_{bonding} = E_{complex} - (E_{metal} + \sum E_L)$$

The complex A ($E_{bonding}$ = -1656.9 Kcal/mol is the most stable compared to the other ($E_{bonding}$ = -3083.7 Kcal/mol. It corresponds to the lowest bending energy (highest negative value). We note that the bending energy values are very high. We have explained this result by the number of oxidation of the high metal Ni(III) et Ni(IV). We find that when the metal has a strongly ionic character, the complexation by the ligand H_2L leads to very stable complexes.

Frontier Molecular Orbitals

The calculated values of HOMO and LUMO energies and HOMO/LUMO band gap ($\Delta E_{|HOMO-LUMO|}$) of A and B obtained by a full geometry optimization at the DFT level were schematized in figure 11. For A, the HOMO density is distributed over ligands while the LUMO density covers the metal and OH^-. As for Ca complex, the HOMO of the B complex is localized on the ligands, whereas the LUMO is situated over the complex. Also, HOMO and LUMO energy values show that A and B have comparable ability to receiving and accepting electron.

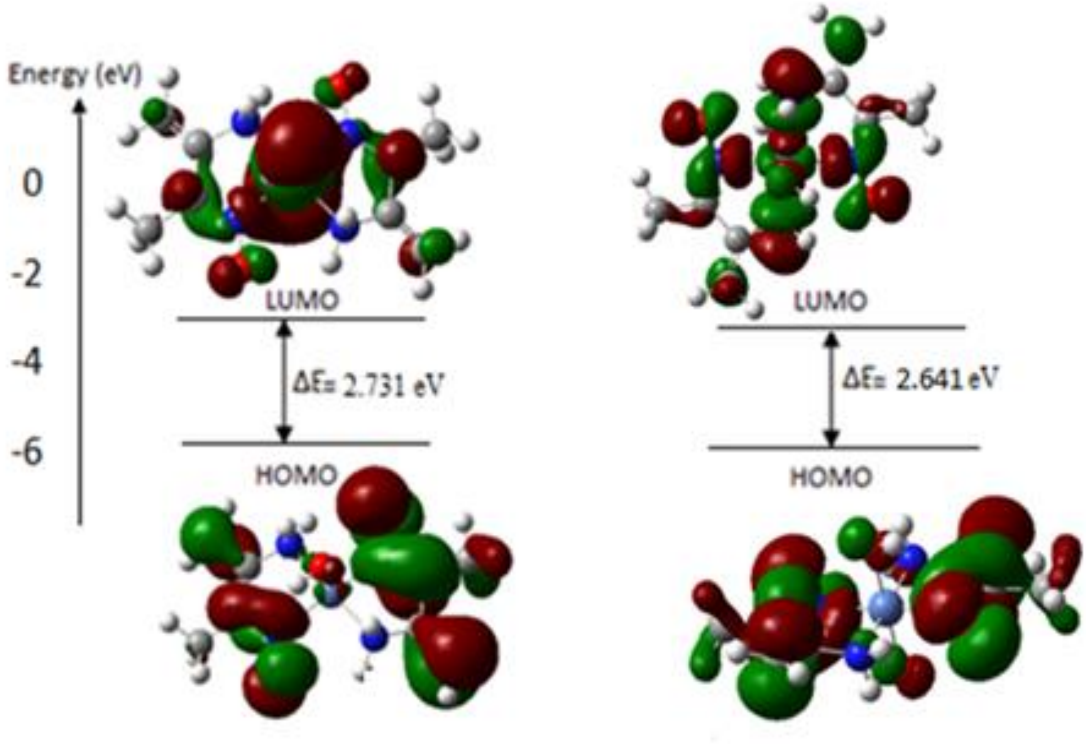

Figure 4. Frontier molecular orbitals HOMO and LUMO of the synthesized complexes

NBO Charges and the Dipole Moment

NBO charge is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reaction. The valence of Nickel in the A and B complexes is +III and +IV, respectively. While the net charges of this metals is +0.740 e, and + 0.578 e, in A and B respectively, showing that the metal center obtained part electron from ligand donor atoms. These results show that the covalent character of metal-ligand bands in B is the most important comparing to A. The net charges of donor atoms (Table. 4) confirm the electron transfer to metallic ion.

Table 4. NBO charge and dipole moment calculated in DFT/B3LYP/LANL2DZ.

Parameters	Complex A	Complex B			
NBO Charge					
Ni(III)	0.740	Ni(IV)	0.578		
N_1	-0.005	N1	- 0.889		
N_2	-0.851	N2	-0.107		
N_3	-0.845	N3	-0.117		
N_4	-0.100	N4	-0.868		
O	-0.920	O30	-0.995	O32	-1.033
H	0.464	H31	0.450	H33	0.480
Dipole moment (Debye)	2.4	1.2			

The dipole moment is an important electronic parameter that results from non-uniform distribution of charges on the various atoms in a given molecules. Herein, low value of the dipole moment of **B** comparing to **A** (Table 4) reflect a superior symmetries of the **B** complex.

Conclusion

From this study, we found that the DFT/B3LYP/LANL2DZ method gives satisfactory results for this type of complex. Indeed, the experimental results obtained for The al FT-IR, UV–Visible spectra and ^{1}H NMR for Ni (III) and Ni (IV) are in reasonable correlation with the theoretical data (DFT). We have also confirmed that the complexes **A** and **B** have the geometries distorted square pyramidal and distorted octahedral, respectively. The dimethylglyoxime ligand stabilise its complexes in the distorted octahedral geometry around the metallic center. The calculation of the bending energy showed us that the complex **B** is more stable with respect to **A**. The values of these energies are too high; this is due to the number of oxidation of the metal which is high and unusual. The values of the HOMO/LUMO differences found confirm the stability of these complexes.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

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Author Information

Noura Kichou
University Mouloud Mammeri of Tizi-Ouzou,
Tizi-Ouzou, Algeria
Contact e-mail: *noura.kichou@ummto.dz*

Nabila Guechtouli
University Mouloud Mammeri of Tizi-Ouzou,
Tizi-Ouzou, Algeria

Manel Taferghennit
University of Sciences and Technology Houari Boumediene
Algiers, Algeria

Zakia Hank
University of Sciences and Technology Houari Boumediene
Algiers, Algeria

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