Density Functional Theory Calculations of Electronic Structure for Aluminum Metal Complexes

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الخلاصة

التركيب الالكتروني لثلاثة معقدات معدنية مقترحة للألمنيوم تم اجراء الاسترخاء لها باستخدام الدالة الهجينة ذات المعاملات الثلاث (B3LYP) مع دالة أساس. حيث تم حساب الخواص الالكترونية والطاقات لكل معقد. اما طاقات التهيج للمعقد المعدني تمت باستخدام طريقة TD-DFT/B3LYP مع دالة الاساس SDD. ان طاقة اعلى مدار جزيئي مشغول وطاقة أدنى مدار جزيئي غير مشغول، وفجوة الطاقة، الصلابة والمرونة حسبت ليتم التنبؤ بالفعالية الكيميائية لكل معقد. النتائج التي تم الحصول عليها تبين ان معقدات الالمنيوم المعدنية تلعب دور مهم ومؤثر كمحفزات في التفاعلات الكيميائية مثل تفاعلات البلمرة.

الكلمات المفتاحية

معقد الالمنيوم المعدني، B3LYP، دالة الاساس SDD، طيف الاشعة الفوق البنفسجية المرئي.

Abstract

Electronic structures of three suggested aluminum metal complexes are relax using SDD-B3LYP/DFT method. The structural parameters and energies were calculated for each complex. The excitation energy of the complex was obtained by using the TD-DFT/B3LYP method with SDD basis sets. EHOMO, ELUMO and LUMO-HOMO energy gap, global hardness and softness were calculated to predict the chemical activity of the complexes. That results showed the aluminum metal complexes play a significant rule such as catalysts in many chemical reactions as in polymerization processes.

Keywords

Aluminum metal complex, B3LYP, SDD basis set, UV-Vis spectrum.

1. Introduction.

The metal complex compound is a structure consisting of a central metal atom or ion, in which metal is usually attached to a surrounding array by several atoms, ions or molecules, each of which is called a ligand [1]. The atom within a ligand that is bonded to the central metal atom or ion is called the donor atom and bound to the central atom by a coordinate covalent bond into an empty metal orbital. In a metal complex, a metal ion is bonded to a number of donor atoms, which can be a different or a same [2].

The electron density on the the center of molecular (metal) and the physical surroundings around the metal is affected by each ligand present in complex compound. The electronic structure can be described by a relatively ionic model that comes from electrons of the metals and ligands in metal complexes. The properties of metal complex compounds are determined by the electronic structure of molecular compounds [3, 4]. Metal complexes exhibit changed characteristic properties which depend on the nature of metal and the method arrangement of the ligand to which they are bound [5, 6].

The Ziegler-Natta catalysts, entitled after the chemists Ziegler and Natta (1955), is a catalyst used in the synthesis of polymers[7]. The Ziegler-Natta catalysts is a generic term to describe a variety of catalysts based on transition metal moieties, which are active in α-olefins polymerization and copolymerization. The Ziegler-Natta catalysts is produced from reaction between compounds of transition metal and compounds such as the hydrides or alkyls groups [7-9].

A catalyst such as Z-N catalyst is used to decrease the activation energy for the polymerization process thus speeding up the chemical reaction and allowing it to proceed even under mild conditions. The catalysts fundamentally increase a chemical reaction, it increases the chemical reaction rate without being consumed itself [6, 8].

The finding of Ziegler-Natta catalysts presented a new dimension to the domain of polymers. The Ziegler-Natta catalysts added to the development of the long chain polymers of hydrocarbons and produce various commercial polymers such as polypropylene and polyethylene. These polymers are advantageous in the construction of films, plastics and fibers. Application of Ziegler-Natta catalysts trend clearly reflects the care specified to this area both in researches, academic and industrial laboratories in the world [6, 7, 9]. In this study design new aluminum metal complex compounds (1, 2 and 3 molecular in Fig. 1) represented catalysts moleculars such as catalysts Ziegler-Natta and have various applications in many chemical reactions as in polymerization processes.

2. Theory.

The initial structures of the complexes were designed and drawn at Gauss View (5.0.8) program [10]. The calculations were carried out by using Gaussian (09) package of

programs [11]. The studied aluminum metal complexes were fully relax by employing B3LYP-SDD/DFT (52). B3LYP combination of exchange and correlation functional [12,13] in DFT is applied to all calculations of the electronic structure. The electronic excitation energy was calculated for the relaxed aluminum metal complexes by employing TD-DFT/B3LYP method with SDD basis sets. TD-DFT with SDD basis sets has been proved to be depend for calculating the electronic structure of heavy transition metals [14-16].

3. Results and Discussion.

The structures of the suggested aluminum metal complexes in Fig. (1) are relax by employing the SDD-B3LYP/DFT method. Table (1) states the results of the optimized parameters (bonds in Angstroms and angles in degrees) for the aluminum metal complexes. The coordination of the molecules after the relaxation showed a suitable method we used with the SDD basis sets where the calculated bonds are in good agreements with the experimental data [4,17]. The theoretical values of Al-O bonds in complex (2) are agree with the results in [17]. Al-O bonds are change depending on the coordination of the complex and the position of the central aluminum metal. The bonds C-C are varied depending on the coordination for each complex and their values are in good agreements with those in open and cyclic carbon compounds. From Table (1) shows that Al-Cl bond in complex (2) is (2.24000) A° and complex (3) is (2.20107-3.09606) A° these value are in good agreement with the results of metal complexes [17,18].

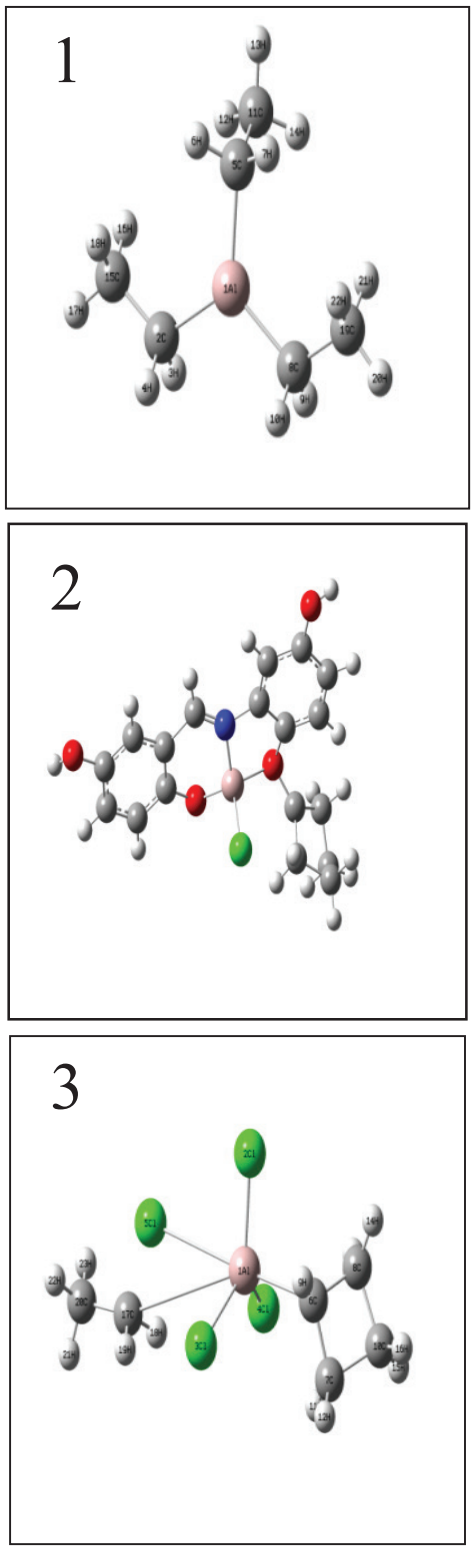

Fig. (1): The relax structures of aluminum metal complexes.

Table (1): The optimized parameters of the aluminum metal complexes.

Aluminum Metal Complex	Bond length (A°)		Bond angle (deg.)	
	Bond	Value	Bond angle	Value
1	Al-C	2.02000	H-C-H	109.47122-109.47125
	C-C	1.54000	C-Al-C	120.000
	C-H	1.07000	C-C-Al	109.47120- 109.4712
2	Al-Cl	2.24000	Cl-Al-O	108.95937-111.87067
	Al-N	1.81545	O-Al-N	96.17055-109.54072
	Al-O	1.86576-1.86592	C-N-Al	103.69243-120.10640
	C-C	1.40272-1.58807	C-O-Al	105.22779
	O-C	1.43000-1.45923	C-C-C	101.51277-118.09572
	H-C	1.07000	H-C-N	120.63898
	H-O	0.96000	H-C-C	114.19864-119.43061
	N-C	1.27681-1.48400	H-C-H	108.31531
			H-O-C	109.47122
			C-C-O	116.70290-126.34110
3	Al-Cl	2.20107-3.09606	Cl-Al-Cl	83.52799-120.23120
	Al-C	2.29878-3.95960	C-Al-Cl	28.35233-71.67279
	C-C	1.52184-1.53632	H-C-Al	75.18740-89.07055
	H-C	1.09066-1.09406	H-C-H	109.10634-111.04073
			H-C-C	113.83217-114.77388
			C-C-Al	113.56426-159.58647
			C-C-C	85.85701-93.60788

Table (2) declare the results of High Occupied Molecular Orbital Energy E_{HOMO}, Low Unoccupied Molecular Orbital Energy E_{LUMO} and LUMO-HOMO Energy gap E_g for the studied aluminum metal complexes from the SDD-B3LYP/DFT calculations at the minima energy. As shown, for each complex the LUMO energy is greater than HOMO energy. Complex (2) has the highest values of E_{LUMO} and E_{HOMO}. High values of LUMO energy means low ability of complex to accepting an electron. Therefore, the order of complexes to acceptance an electron and become anions is as: 3 > 1 > 2. Also, we noted from Table (2) the highest bond (Al-C) found in compound 3 and the highest bond (Al-Cl) in compound 3. In addition, the highest angle in this compounds were found in compound 1 according to the position of atoms in metal complexes.

Low value of HOMO for complex means high energy that complex required to donating an electron. Therefore, the order of complexes to donating an electron and become cation is as: 2 > 1 > 3.

The LUMO-HOMO energy gap (Eg) values in Table (2) showed the suggested aluminum metal complexes have Eg between (2.8) eV for complex (2) and (5.88) eV for complex1, means these aluminum metal complexes have varying electronic applications such as catalyst in polymers process. The lowest Eg is (2.8) eV for complex (2) refers to that this complex has a suitable semiconducting electronic applications. Fig. (2) declare the LUMO-HOMO energy gap of the studied complexes. Also we noted from Table (2) that the complexes (1) and (3) needed higher energy to exaction the electrons from level to other comparing with complex (2) according to energy gab (Eg).

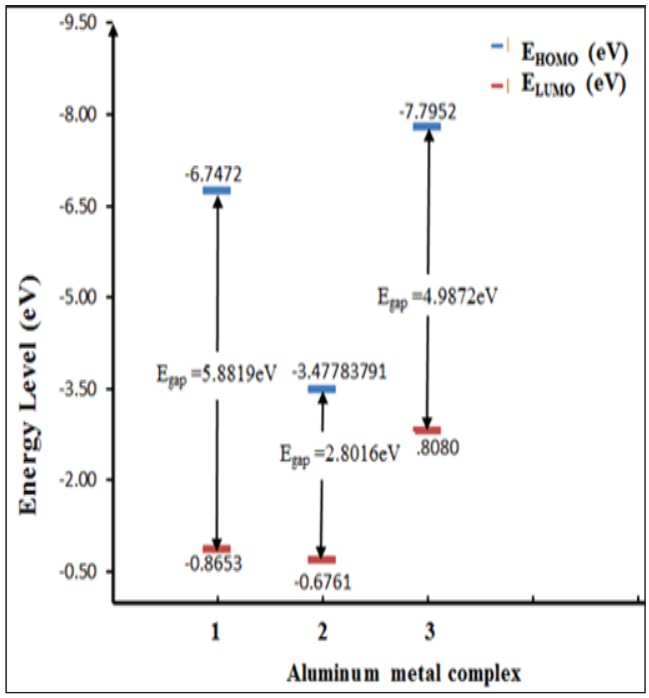

Fig. (2): LUMO-HOMO energy gap of metal complexes.

We noted from Fig. (2) and Table (2) the compound 1 has large energy gab this mean this compound can be using in chemical reactions applicatins as in polymerization isolated processes. Also, we noted that metal complexes (1) gives the highest Eg as shown from Table (2). This may relate to the highest angle obtained for complexes (1) in Table (1).

Table (2): The E_{HOMO}, E_{LUMO} and E_g for aluminum metal complex.

Aluminum Metal Complex	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
1	-6.7472	-0.8653	5.8819
2	-3.4778	-0.6762	2.8016
3	-7.7953	-2.8080	4.9872

Fig. (3) illustrates the 3-D distribution of HOMO and LUMO energies of the aluminum metal complexes. $HOMO_s$ and $LUMO_s$ are molecular orbitals building according to linear combination atomic orbitals-molecular orbitals $LCAO^s$-MO^s theory. Each MO constructs due to charge distribution in the complex, and therefore, the atomic charge density population in the metal and the ligands in the complex. The difference of the HOMO and LUMO distribution of the aluminum metal complexes in Fig. (3) refers to more differences in molecular polarizabilities and electronic structures of these complexes, and therefore, differences in chemically reactivity for the complexes as catalysts.

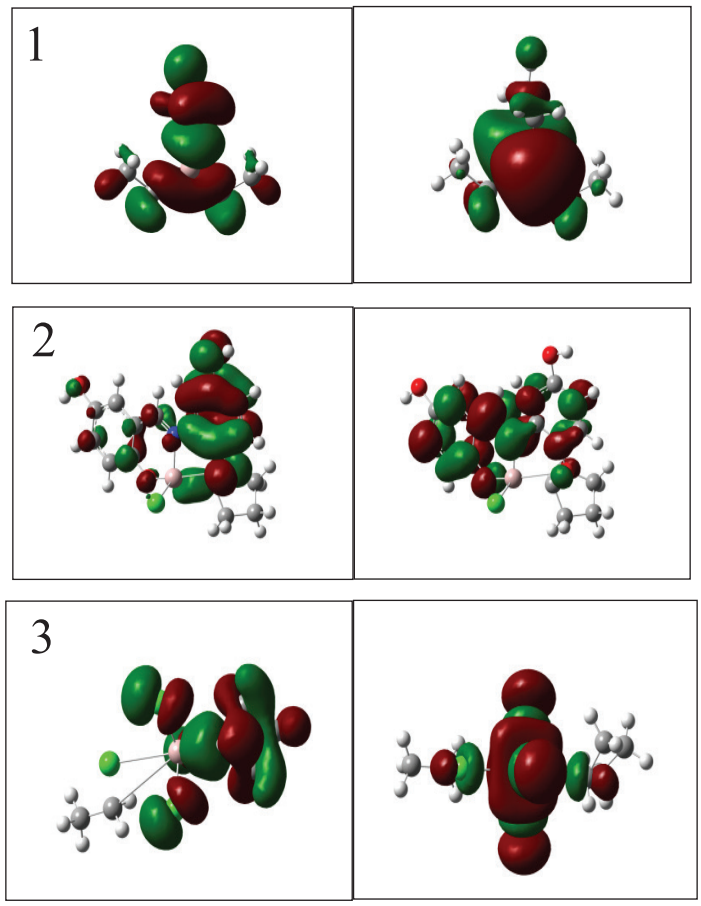

Fig. (3): 3-D HOMO (Left) and LUMO(Right) distribution of the complexes.

The electrostatic potential (ESP) surfaces distribution of aluminum metal complexes calculated from the total self-consistent field SCF and shown in Fig. (4). In complex 1, the ESP surface was approximately drag uniformly in space of the complex towards the three ligand groups connected to the central aluminum metal. In complex (2), the ESP surface were dragged towards the chlorine and oxygen atoms due to their high electronegativity in comparison with hydrogen and carbon atoms. In complexes 3, the ESP surface were approximately dragged towards the chlorine atoms only. These results means that the determination of the active areas of the ESP for these complexes to play an important factor as catalysts in many chemical reactions as in polymerization processes.

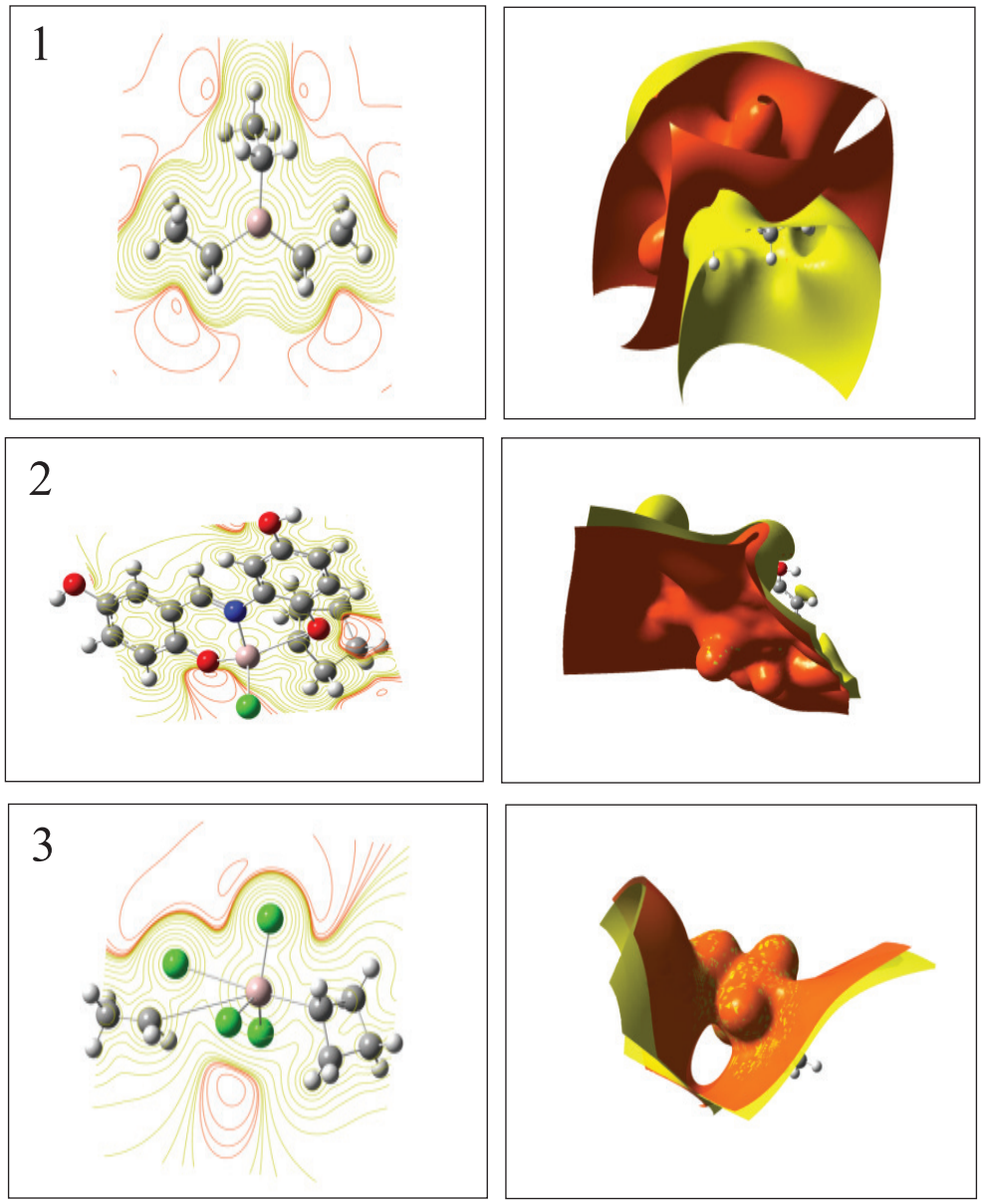

Fig. (4): The 2-D counter (Left) and 3-D (Right)ESP distribution of the complexes.

Table (3) lists the results of global hardness and softness as quantum chemical parameters. The computation of molecules properties (hardness and softness) are carried out by Koopmans theorem (KT) [4] as shown in the following:

Here H indicates the hardness, is the ionization potential, is the electron affinity and S denoted the softness.

As can be seen, the trend of the quantum chemical parameters depend on the coordination and the molecular geometry of each complex. The coordination tendencies of complexes as catalysts can be discussed with the global hardness and softness. Soft complexes have small energy gap and therefore, small excitation energies required for electron transfer. Hard complexes have large energy gap and more complex to interact with other species. Approximately, all studied aluminum metal complexes have low values of H and S, they are weak in electron transfer, therefore, they can work catalysts for chemical reactions.

Table (3): Quantum chemical parameters for aluminum metal complexes.

Aluminum metal complexes	1	2	3
Hardness (eV)	2.9410	1.4008	2.4936
Softness $(eV)^{-1}$	0.1700	0.3569	0.2005

As shown previously, the energy gap of the studied aluminum metal complexes was varied from (2.8) eV for complex (2) to (5.88) eV for complex 1. Know, the behavior of excitation energies of the studied complexes that are analyzed in the B3LYP-SDD/TD-DFT. Table (4) illustrates the wavelength of excitation energies for the main band, oscillator strength, electronic transitions HOMO-LUMO and the state for the aluminum metal complexes.

Fig. (5) declare the Ultraviolet-Visible (UV-Vis.) spectra of the studied complexes. As seen, complex 1 have one peak of excitation energy at (356.17) nm wavelength with full transition between the frontier orbitals HOMO→LUMO. Two peaks of excitation energy were observed for complex (2) at (333.33) nm and (459.82) nm with two main electronic transitions H-5→LUMO and H-4→LUMO. Complex C exhibits one peak of excitation energy at (362.56) nm with many electronic states in the doublet.

Table (4): UV-Vis results of aluminum metal complexes.

Complex	Wavelength (nm)	Oscillator Strength	Electronic Transition HOMO→LUMO	State
1	356.17	0.0047	HOMO→LUMO (99%)	Singlet
2	333.33	0.2944	H-5→LUMO (79%) H-4→LUMO (16%)	Singlet
	459.82	0.1147	H-1→LUMO (95%) HOMO→LUMO (3%)	
3	362.56	0.0823	H-13(α) →LUMO(α) (21%) H-11(α) →LUMO(α) (12%) H-10(β) →L+1(β) (33%) H-15(α) →LUMO(α) (4%) H-14(α) →LUMO(α) (6%) H-10(α) →LUMO(α) (2%) H-11(β) →L+1(β) (6%) H-9(β) →L+1(β) (6%)	Doublet

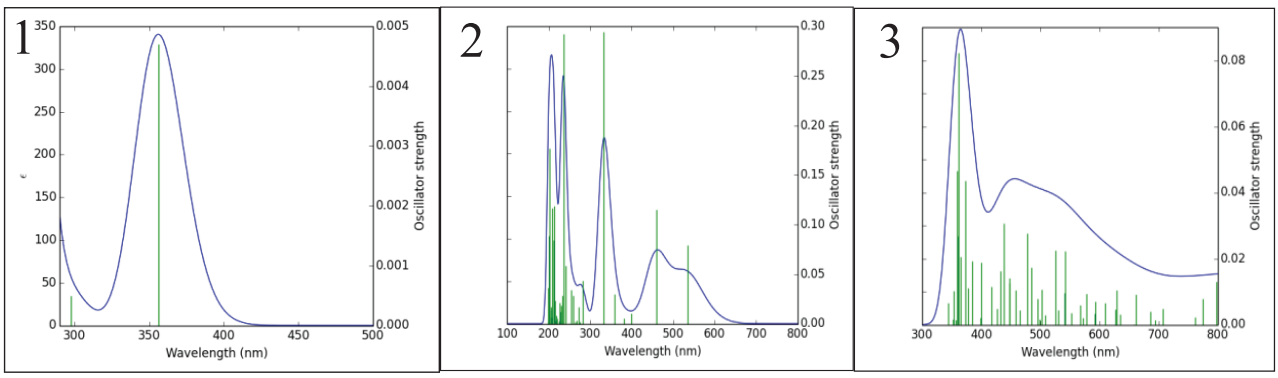

Fig. (5): UV-Vis Spectra of aluminum metal complexes.

86.09, 125.64)

The results of molecular polarizability for complexes (1,2 and 3) showed the catalyst (1) has low dipole momentum (D.M) (0.137) Debye, catalyst (2) has large D.M (8. 119) Debye and catalyst (3) has D.M of (3.979) Debye, means complex (1) has the highest symmetry in comparison with the others while complex (2) has very low symmetry and this due the coordination of each catalyst. From the results, the studied aluminum metal complexes have large values of molecular polarizability (101.72, 86.09, 125.64) a. u, respectively, and therefore, they have high ability to interact with other molecules. Aluminum metal complexes play a significant role in chemical reactions as catalysts and all compounds in this study represented Ziegler-Natta catalysts according to the results and it properties.

4. Conclusions:

1. Aluminum metal complexes have different electronic applications due to different values of LUMO-HOMO energy gap obtained.

2. The differences of HOMO and LUMO distribution and ESP distribution of the complexes refer to more differences in molecular polarizabilities and electronic structures of these complexes and therefore, differences in chemically reactivity as catalysts.

3. Aluminum metal complexes play a significant influence as catalysts in many chemical reactions as in polymerization processes.

4. Approximately all studied aluminum metal complexes have low values of global hardness and softness, they are all weak in electron transfer and can be used as catalysts in chemical reactions.

5. The results of UV-Vis spectra declare the studied aluminum metal complexes have various applications such as Ziegler-Natta catalysts.

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