Electronic Structure, IR and UV-Vis Spectra of Some Suggested Ziegler-Natta Catalysts

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Abstract

Three aluminum metal complexes were suggested as Ziegler-Natta catalysts and studied theoretically at the ground and excited states. Becke's three parameter exchange with Lee, Yang, and Parr correlation functional) density functional theory and SDD (Stuttgart Dresden triple zeta ECPs (Effective-Core Potential))basis sets calculations were employed to study the electronic structure and IR-spectra of the complexes. Time dependent of DFT method is used to calculate the excitation energies and electronic transitions for each complex. The results of density of state(DOS) and the distribution of HOMO and LUMO showed these complexes are good suggestion to play role for polymerization processes as catalysts. Theresults showed that the excitation energies lie in the UV-Vis region.

التركيب الإلكتروني وأطياف الاشعة التحت الحمراء والفوق البنفسجة-المرئية لبعض محفزات زكلر-ناتا المقترحة

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الخلاصة:

ثلاث من معقدات معدن الالمنيوم تم اقتراحها كعوامل مساعدة زكلر-ناتاوتم دراستها نظريا" عند الحالة الارضية والحالة المثارة. تم تطبيق حسابات دالة الكثافة ذات المعاملات الثلاثة لي- يانغ- بارمع دالة القاعدة SDD لدراسة التركيب الالكتروني وأطياف الاشعة تحت الحمراء للمعقدات. تم استعمال نظرية دالة الكثافة المعتمدة على الزمن لحسابات طاقات الاثارة والانتقالات الالكترونية لكل معقد. تبين نتائج كثافة الحالات وتوزيع المدار الجزيئي العلوي المشغول والمدار الجزيئي السفلي غير المشغول بأن تلك المعقدات مقترح جيد لتلعب دور لعمليات البلمرة كعوامل مساعدة. كما تبين النتائج أيضا" أن طاقات الاثارة تقع في منطقة الضوء المرئي.

الكلمات المفتاحية: كثافة الحالات, حالات الانتقال, طيف الاشعة تحت الحمراء و معامل التآلف.

1. Introduction

The Ziegler-Natta catalyst (Z-N catalysts), entitled after the chemists Ziegler and Natta (1955), is a catalyst used in the synthesis of polymers of 1-alkenes (α-olefins). It is considered as one of the most significant discoveries in chemistry and industries in the last century. The Nobel Prize in chemistry (1963) was given to chemists Ziegler and Natta for the landmark discovery of first titanium-based catalysts, and for using them to prepare stereoregular polymers from propylene [1,2].

The Z-N catalysts are generic terms that are utilized to describe a variety of catalysts based on transition metal moieties, which are active in α-olefins polymerization and copolymerization. The Z-N catalysts are produced from a reaction between compounds of transition metal of groups IV to VIII and compounds such as the hydrides or alkyls of groups I-III, for example Ziegler-Natta catalysts: $TiCl_4$, VCl_4, and $ZrCl_4$. In compounds Ziegler-Natta catalysts, the transition metal component is called "the catalyst" while the hydride or alkyl is referred as to "cocatalyst" [1,3,4]. A 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 [3,5] .

The finding of Ziegler-Natta catalysts presented a new dimension to the domain of polymers. It has been used in the commercial manufacture of various polyolefins since 1956. In addition, it is important in many applications such as production of ultra-high molecular weight polyethylene and the Z-N catalysts stay main in industrial production and technology for polyolefin due to important cost benefits and low cost of polymers. These polymers are valuable in the construction of films, plastics and fibers. In recent years a lot of studies on this subject, such as Wang *et al*. (2015) investigated the structural candidates for the active species in ethylene polymerization catalyzed (Z-N catalyzes) by the salicylaldiminato vanadium complex combined with AlEt2Cl using the DFT ,also Likhasit *et al.* (2009) studied the electronic structure, geometric, spectroscopy and some properties of MgCl2 with TiCl4 as Ziegler-Natta catalysts. Application of Z-N catalysts trend clearly reflect the care specified to this area both in researches, academic and industrial laboratories in the world [1-4]. There has been an importance in developing well-defined aluminum catalysts for ethene polymerization. Thealuminum alkyl catalysts would be a very interesting substitute to transition metal based catalysts as a result to the low cost and simplicity of the ligands. In addition, these catalysts would not need methyl aluminoxane as co-catalyst. Therefore, a catalyst based on aluminum could be attractive and minor activity of aluminum catalyst compared to transition metal catalysts can be approved [5-8]. Present study deals with the electronic structure spectroscopy and important properties of three suggested Ziegler-Natta catalysts by using quantum chemical; DFT and T-DFT for using as catalysts ininteractionsespecially polymerization reactions.

2. Computation method

Present work deals with the electronic structure of suggested Ziegler-Natta catalysts by employing the three parameters B3LYP(Becke's three parameter exchange with Lee, Yang, and Parr correlation functional) (DFT) and SDD (Stuttgart Dresden triple zeta ECPs (Effective-Core Potential))basis sets[9,10]. The electronic properties were calculated according to Koopmans theorem[11,12]. Excitation energies and electronic transitions are carried out by using the

Time Dependent TD density functional theory[12-14].

3. Results and discussion

The relax structures of the suggested aluminum metal complexes(A-C) as Ziegler-Natta catalysts in Fig. 1 are relax by employing the SDD-B3LYP/DFT method.
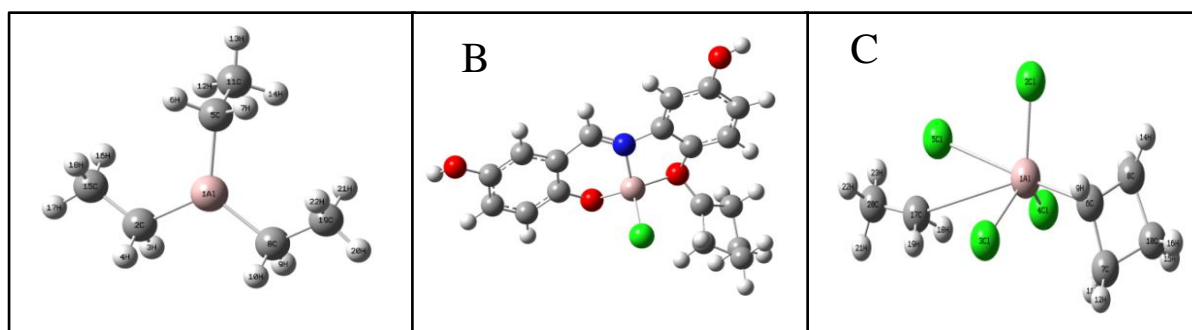

Fig. 1: The relax structures of the suggested Ziegler-Natta catalysts

Energy of highest occupied molecular orbitals (E_{HOMO}), energy of lowest unoccupied molecular orbitals(E_{LUMO})and energy gap(E_{gap}) in eV for the suggested aluminum metal complexes are calculated from the SDD-B3LYP/DFT at the energy minima and listed in table 1.

Table 1: The E_{HOMO}, E_{LUMO} and E_g for aluminum metal complexes.

Ziegler-Natta catalysts	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
A	-6.7472	-0.8653	5.8819
B	-3.4778	-0.6762	2.8016
C	-7.7953	-2.8080	4.9872

Table 1 shows that for all complexes the LUMO energy is greater than HOMO energy. Complex B has the highest values of E_{LUMO} and E_{HOMO}. High values of LUMO energy means low ability of complex to accepting an electron. The order of complexes to acceptance an electron and become anions is as:

C>A>B.

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:

B>A>C.

The LUMO-HOMO energy gap values in Table 1 showed the suggested aluminum metal complexes have E_{gap} between 2.8 eV for complex B to 5.88 eV for complex A,

means these aluminum metal complexes have varying electronic applications. Fig. 2 declare the LUMO-HOMO energy gap of the studied complexes.
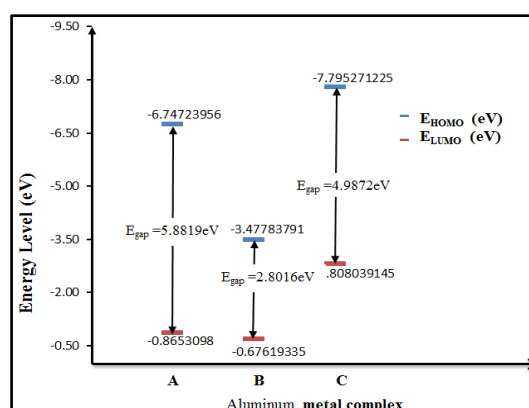

Fig. 2: LUMO-HOMO energy gap of aluminum metal complexes.

Figure 3 illustrates the 3-D distribution of HOMO and LUMO energies of the aluminum metal complexes. HOMOs and LUMOs are molecular orbitals building according to linear combination atomic orbitals-molecular orbitals LCAOs-MOs 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.
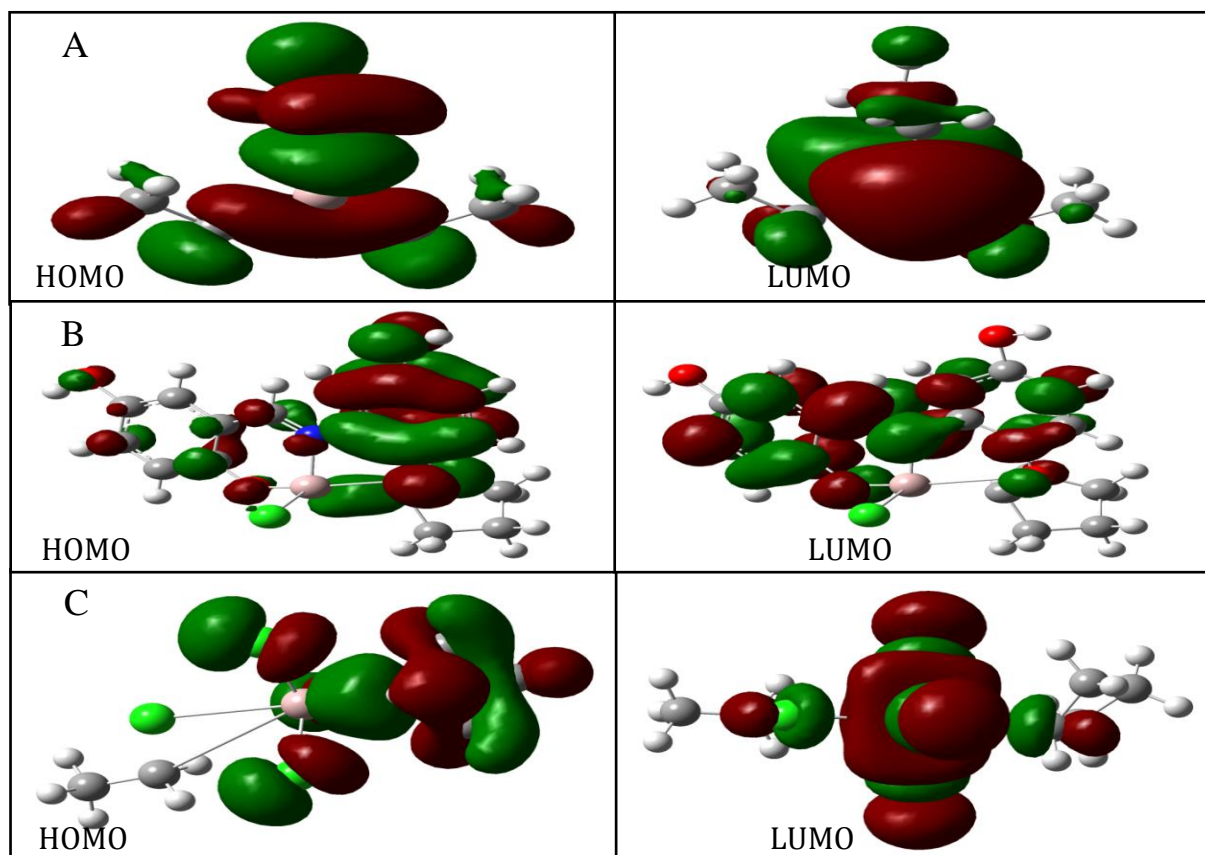

Fig. 3: The HOMO and LUMO distribution of aluminum metal complexes.

The total energy E_T of the studied aluminum metal complexes and some of their electronic properties were calculated by using B3LYP-SDD/DFT and listed in Table 2. The electronic properties are computed according to Koopmans theorem. As shown in mentioned Table, the E_T depends on the number of electrons

in the complex, E_T was decreased with increasing the number of electrons in the complex. The values of virial ratio (-V/T) for the studied complexes are in the range (2.0027-2.0038), these results gave an idea for the suitable method used with SDD basis sets for the relaxation of the metal complexes.

Table 2: E_T and some electronic properties of aluminum metal complexes.

Ziegler-Natta catalysts	E_T(a.u)	$-V/T$	I_E(eV)	E_A(eV)	E_N(eV)	ω(eV)
A	-480.2157	2.0038	6.7472	0.8653	3.8063	2.4631
B	-1055.4877	2.0027	3.4778	0.6762	2.0770	1.5398

| C | -2319.1021 | 2.0033 | 7.7953 | 2.8080 | 5.3017 | 5.6359 |

From table 2, all studied complexes have ionization energies I_E are greater than the electron affinities E_A. High value of I_E means difficult tendency of complex to donating an electron. Complex C has the largest value of I_E refers to that it needs high energy to donating an electron in comparison with the other complexes. On the other hand, complex B needs small energy to donating an electron compared with the other complexes. The results in Table 2 showed the first aluminum metal complex A has low value of E_A in which it has low ability to accept an electron with large $E_{gap.}$

The calculated values of electronegativity E_N showed the presence of chlorine and oxygen atoms in active sites in the complex play role of increasing the E_N of the complex. The order of E_N of the studied aluminum metal complexes is as:C>A>B.

The results in table 2 showed the complex C has the higher electrophilic index ω compared with the others. If ω determines the interactions of the complex with the surrounding species, then the ranking is as: C>A>B.

In general, studied complexes have low electrophilicity in comparison with the structures of metal complexes. This indicates to that aluminum metal complexes take place as catalysts in chemical reactions. Fig.4 shows the EN
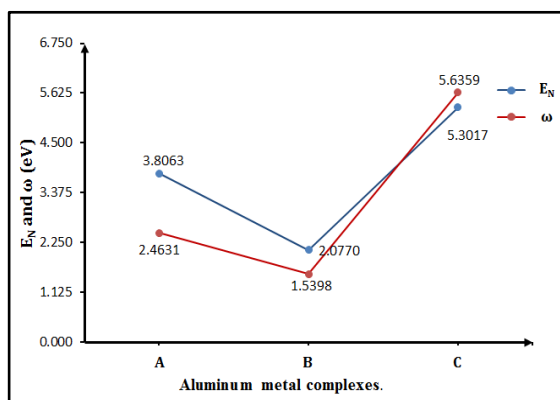
and ω for the aluminum complexes.

Fig. 4:The behavior of E_N and ω of aluminum metal complexes.

Table 3displays the results of global hardness and softness as quantum chemical parameters. As seen, the trend of quantum chemical parameters depend on the coordination and the molecular geometry of the complexes. 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 all weak in electron transfer, therefore, they are catalysts for chemical reactions.

Ziegler-Natta catalysts	A	B	C
Hardness (eV)	2.941	1.4008	2.4936
Softness (eV)$^{-1}$	0.170	0.3569	0.2005

Table 3: Quantum chemical parameters for aluminum metal complexes.

Fig. 5 illustrates the infrared IR spectra of aluminum metal complexes from the B3LYP-SDD/DFT calculations. From the spectrum of complex A, the stretching C-H bonds was observed in the range (2975.33-3068) cm^{-1} with maximum intensity (100.9 km/mol) observed for C-H bonds at (3005.71) cm^{-1}, the bending C-H bonds was observed at (1227.54-1513.67) cm^{-1}. The stretching Al-C bonds was observed at (485.32 cm^{-1}), The stretching C-C bonds was observed at (963.61-1019.8) cm^{-1}.

For complex B, the stretching O-H bonds was observed 728.56 and 3729 cm^{-1} and

the stretching C-H bonds lies in the range (3335.64-3475.19) cm^{-1}. The bending O-H bonds lie at low frequency 441.62 cm^{-1}. The stretching Al-O was observed at 699.15 cm^{-1}. Low intensities were observed for the stretching in plane C-C bonds in phenyl rings at (731.51-895.86)cm^{-1}. C-N bond was appeared stretching at 1388.08 cm^{-1} and C=N bond was appeared stretching at 1420.37 cm^{-1}. The bending and stretching Al-Cl bond was observed at very low frequencies(40-70)cm^{-1} corresponding to very low intensities (1-1.5) km/mol due to presence Al metal in the central of the group of atoms. The other modes were shown in Fig. 9. For complex C, the IR-spectra showed the stretching C-H bonds observed at (3046.5-3226.57)cm^{-1} and the bending C-H was observed at (1105.23-1523.82) cm^{-1}, The stretching Al-Cl bonds was observed at (510.53-526)cm^{-1}. The bending Al-C bond was observed at low frequency (165.72)cm^{-1} corresponds to low intensity (1.64 km/mol). Due to coordination of complex C due to high connection between the central Al metal with Cl atoms.
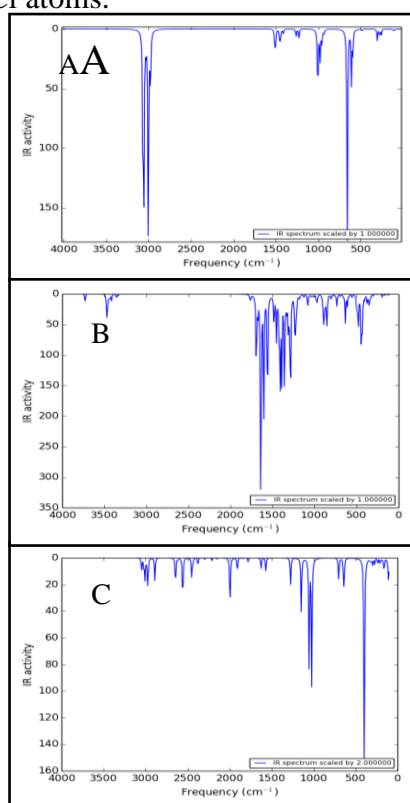

Fig. 5: IR-Spectra of aluminum metal complexes.

The spectra in Fig. 6 illustrate the density of states DOS for aluminum metal complexes analyzed from the calculations of B3LYP-SDD/DFT. DOS is significant to be able to expect the behave for different molecular structures geometries. In present group of aluminum metal complexes, the complexes A and B have a singlet state and the complex Chas a doublet state. As shown, complex A has lower distribution of energy in each energy interval due to the low degeneracy of the eigen states, but the degeneracy of occupied eigen states is more than the degeneracy of unoccupied eigen states. Also, in the other complexes the degeneracies of occupied eigen states are more than those of unoccupied eigen states. The small separation between the occupied and unoccupied molecular eigen states for complex B gave this complex to has a suitable application in electron transform.
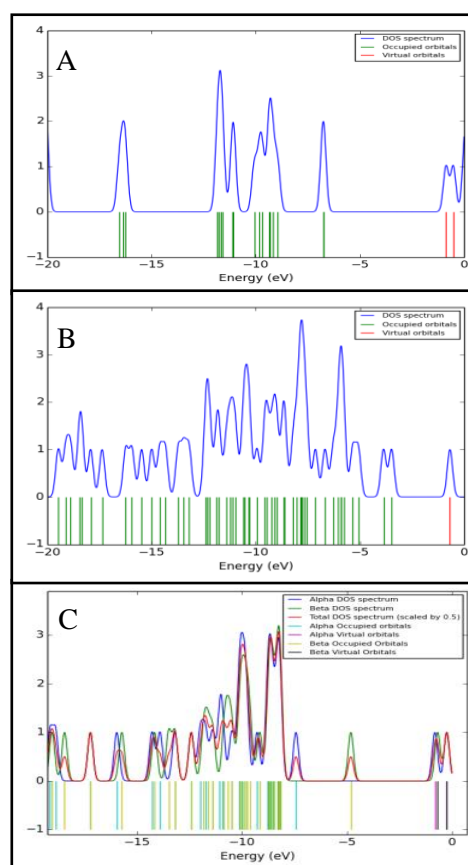

Fig. 6: DOS spectra of aluminum metal complexes.

The behavior of excitation energies of the studied aluminum metal complexes were studied due to the calculations of the B3LYP-SDD/TD-DFT. Fig. 7 illustrates the UV-Vis spectra of the studied complexes. As seen, complex A appeared one peak of excitation energy at 356.17 nm wavelength with full of one transition between the frontier orbitals HOMO→LUMO and low oscillation strength (0.0047). Two peaks of excitation energy were observed for complex B at 333.33 nm with two main electronic transitions H-5→LUMO and H-4→LUMO due to high oscillation strength (0.294) and 459.82 nm with two main electronic transitions H-1→LUMO and HOMO→LUMO due to the oscillation strength (0.114).Complex C appeared one peak of excitation energy at 362.56 nm due to oscillation strength (0.082) with electronic transitions H-1→LUMO, HOMO→LUMO, H-13(α)→LUMO(α), H-11(α)→LUMO(α), H-10(β)→L+1(β), H-15(α)→LUMO(α), H-4(α)→LUMO(α), H-10(α)→LUMO(α), H-11(β)→L+1(β) and H-9(β)→L+1(β).
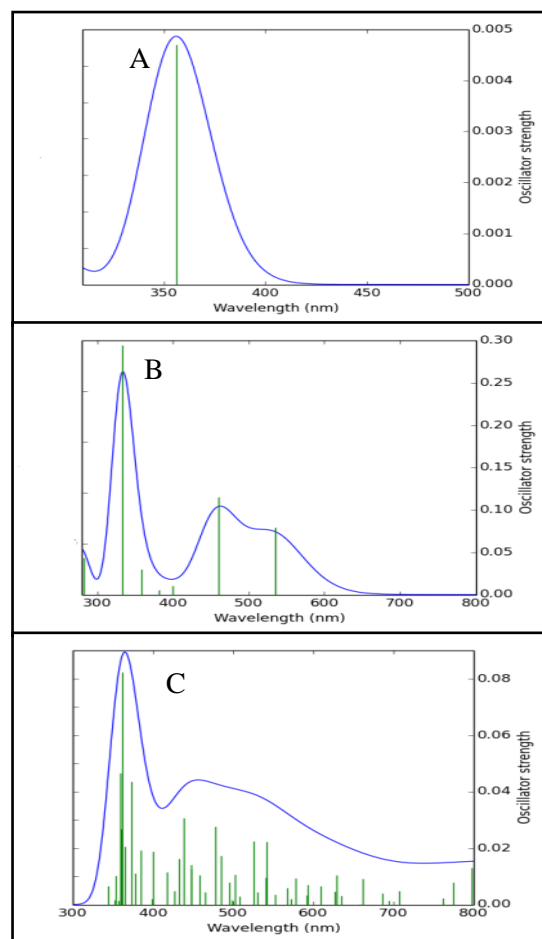

Fig. 7: UV-Vis Spectra of aluminum metal complexes.

4. Conclusions

1. Aluminum metal complexes have varying electronic applications due to different values of energy gap.
2. The difference of the HOMO and LUMO distribution of the aluminum metal complexes refers to more differences in molecular polarizabilities and electronic structures of these complexes, and therefore, differences in chemically reactivity for the complexes as catalysts.
3. Aluminum metal complexes have low electrophilic index in which refers to these complexes used as catalysts in chemical reactions such as polymerization processes.
4. Approximately all studied aluminum metal complexes have low values of hardness and softness, they are all weak in electron transfer. They can be used as catalysts for chemical reactions.
5. The aluminum metal complexes have wide range of energy gap depends on the coordination of the complex and the charge distributions in each complex.
6. The results of UV-Vis spectra showed the aluminum metal complexes have various applications such as Ziegler-Natta catalysts.

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