Structural and DFT/TD-DFT Investigation of New Rhenium Metal Complexes

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Abstract. Density functional calculations have been performed to study new rhenium metal complexes. Several molecular properties, such as conformational equilibrium, optimal geometry, and vibrational frequencies, have been computed for these molecules. Ionization energy, electronic affinity and energy gap were also computed. The results showed a suitable SDD basis sets were used to investigate the relaxation of such complexes. We showed the types and positions of ligands in the complex play a significant role in electronic applications.

Keywords: DFT, rhenium metal Complex, Electrophilic index.

1. Introduction

Inorganic chemistry has generated significant interest in the design of metal complexes as potential diagnostic and therapeutic agents. Several metal complexes are already in use for these purposes. These applications have encouraged further research on new metallodrugs such as metal-mediated antibiotics and anticancer and antiviral compounds [1]. The coordination chemistry of transition metal complexes with more than one type of ligands is of current interest because they serve as models for biochemical reactions [2]. In addition, they provide new materials with useful properties such as magnetic exchange [3, 4], electrical conductivity [5], photoluminescence [6], and nonlinear optical property [7]. Mixed ligand complexes play important roles in biological processes like activation of enzymes by metals [8, 9], storage and transport of active substances through membranes [10]. The element rhenium (Re) is a refractory metal that has gained significant recognition as a high-performance engineering material because it exhibits an exclusive combination of properties. Rhenium coatings are used in thermophotovoltaic (TPV) power generation systems, in which the radiator emits infrared photons from its surface to the TPV cells for conversion to electrical power. In this regard, CVD of Re whiskers was found to increase the emissivity of Mo, Nb and the Haynes 230 alloy [11]. Electrodeposited Re-selenium (Se) thin films are used as photosensitive elements in the visible range [12]. Electro-deposition of Re on silicon (Si) has been suggested for application in micro-systems [13]. Electroplated Co-Ni-Re-W-P micro-arrays have been suggested for future application in magnetic micro-electro-mechanical-system (MEMS) devices [14].

2. Computation method

Present work deals with the electronic structure of rhenium metal complexes 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 [15,16]. The electronic properties were calculated according to Koopmans theorem [17, 18]. Excitation energies and vibration transitions are carried out by using the Time Dependent TD density functional theory [19-21].
3. Results and discussion
The relax structures of the suggested rhenium metal complexes (A-D) in Figure 1 are relax by employing the SDD-B3LYP/DFT method.

![Relax structures of rhenium metal complexes](image)

**Figure 1.** The relax structures of the rhenium metal complexes (gray≡ carbon, white≡ hydrogen, blue≡ nitrogen, red≡ oxygen, green≡ chlorine violet≡ rhenium)

The total energy ET of the studied rhenium metal complexes and some of their electronic properties were calculated by using B3LYP-SDD/DFT and listed in Table 1. The electronic properties are computed according to Koopmans theorem. As shown in mentioned Table, the ET depends on the number of electrons in the complex, ET was decreased with increasing the number of electrons in the complex. The values of the ratio of the potential energy to kinetic energy at the ground state energy virial ratio (-V/T) for the studied complexes are in the range (2.0235-2.0245), these results gave an idea for the suitable method used with SDD basis sets for the relaxation of the metal complexes.

| Rhenium metal complexes | ET(a.u) | -V/E | IE(eV) | EA(eV) | EN(eV) | w(eV) | μ(eV) | Eg(eV) |
|-------------------------|--------|------|-------|-------|-------|------|-------|-------|
| A                       | -2570.53 | 2.0253 | 5.9198 | 3.7192 | 4.8195 | 10.5552 | -4.8195 | 2.2006 |
| B                       | -2740.38 | 2.0241 | 5.6104 | 3.5151 | 5.5627 | 9.9361 | -4.5627 | 2.0953 |
| C                       | -2681.23 | 2.0245 | 5.5230 | 3.4158 | 4.4694 | 9.4796 | -4.4694 | 2.1072 |
| D                       | -2799.54 | 2.0236 | 5.6104 | 3.6433 | 5.7298 | 10.2947 | -4.7298 | 2.1731 |

Table 1. ET and some electronic properties of rhenium metal complexes.

From table 1, all studied complexes have ionization energies IE are greater than the electron affinities EA. High value of IE means difficult tendency of complex to donating an electron. Complex A has the largest value of IE refers to that it needs high energy to donating an electron in comparison with the other complexes. On the other hand, complex C needs small energy to donating an electron compared
with the other complexes. The results in Table 1 showed complex C has low value of EA in which it has low ability to accept an electron with large Egap.

The calculated values of electronegativity EN showed the presence of methoxy, group in active sites in the complex play role of increasing the EN of the complex. The order of EN of the studied rhenium metal complexes is as: D>B>A>C due to presence of oxygen atoms of high electronegativity (3.44 eV), while the electronegativity of carbon atoms is (2.55 eV).

The results in Table 1 showed the complex A has the higher electrophilic index compared with the others. If determines the interactions of the complex with the surrounding species, then the ranking is as: A>D>B>C depending on the types and positions of the ligands in each complex [21].

Figure 2 illustrates the infrared IR spectra of rhenium metal complexes from the B3LYP-SDD/DFT calculations. From the spectrum of complexes the stretching C-H bonds was observed in the range (3165.33-3241) cm\(^{-1}\) with maximum intensity (100.9 km/mol) observed for C-H bending at (1504.71-1231) cm\(^{-1}\), the bending C-N bonds was observed at (1619-1559) cm\(^{-1}\). The stretching Re-Cl bonds was observed at (369-339 cm\(^{-1}\)), the stretching C-C bonds was observed at (1664.8-1619.5) cm\(^{-1}\).

![IR Spectra of rhenium metal complexes](image)

**Figure 2.** IR-Spectra of rhenium metal complexes, where IR activity in Km/mol.

The spectra in Figure 3 illustrate the density of states DOS for rhenium 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 rhenium metal complexes, all the complexes A, B, C and D have doublet state in which each energy level was degenerated into two levels, the first involves the spin up (\(\alpha\)) electrons and the second involves the spin down (\(\beta\)) electrons. 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 as seen in Figure 3. The small separation between the occupied and unoccupied molecular eigen states for complex B gave this complex to have a suitable application in electron transform.

The behavior of excitation energies of the studied rhenium metal complexes were studied due to the calculations of the B3LYP-SDD/TD-DFT. Figure 4 illustrates the UV-Vis spectra of the studied complexes. As seen, complex A appeared three peaks of excitation energy at (5498.1524, 2612.3754 and 1564.8534) nm wavelength with transition between the frontier orbitals HOMO( β )→LUMO( β ), H-1( α )→LUMO( α ), HOMO( β )→L+1( β ), H-1( α )→LUMO( α ), HOMO( α )→LUMO( α ), HOMO( β )→LUMO( α ), HOMO( α )→LUMO( α ), HOMO( β )→L+1( β ) and H-2( α )→LUMO( α ) low oscillation strength (0.0009, 0.0003 and 0.0006 consequently). Three peaks of excitation energy were observed for complex B at 5755.9580 nm with four main electronic transitions H-1( β )→LUMO( β ), HOMO( β )→LUMO( β ), H-1(A)→LUMO(A) and H-1( β )→L+1( β ) due to
oscillation strength (0.0008) and 2743.6011 nm with seven main electronic transitions \( H-2(\alpha) \rightarrow \text{LUMO}(\alpha), H-1(\alpha) \rightarrow \text{LUMO}(\alpha), H-1(\beta) \rightarrow \text{LUMO}(\beta), HOMO(\beta) \rightarrow \text{LUMO}(\beta), H-3(\alpha) \rightarrow \text{LUMO}(\alpha), \) \( \text{HOMO}(\alpha) \rightarrow \text{LUMO}(\alpha), \) and \( H-1(\beta) \rightarrow \text{LUMO}(\beta) \) due to the oscillation strength (0.0002) and 1538.0639 nm with seven main electronic transitions \( H-2(\alpha) \rightarrow \text{LUMO}(\alpha), H-1(\alpha) \rightarrow \text{LUMO}(\alpha), H-1(\beta) \rightarrow \text{LUMO}(\beta), HOMO(\beta) \rightarrow \text{LUMO}(\beta), \) \( \text{HOMO}(\alpha) \rightarrow \text{LUMO}(\alpha), \) and \( H-1(\beta) \rightarrow \text{LUMO}(\beta) \) due to the oscillation strength (0.0002). Complex C appeared one peak of excitation energy at 1858.5419 nm due to oscillation strength (0.025) with electronic transitions \( H-2(\alpha) \rightarrow \text{LUMO}(\alpha), HOMO(\alpha) \rightarrow \text{LUMO}(\alpha) \) and \( \text{HOMO}(\beta) \rightarrow \text{LUMO}(\beta) \). Two peaks of excitation energy were observed for complex D at 7482.3981 nm with two main electronic transitions \( \text{HOMO}(\beta) \rightarrow \text{LUMO}(\beta) \) and \( H-2(\beta) \rightarrow \text{LUMO}(\beta) \) due to oscillation strength (0.0004) and 1659.5279 nm with four main electronic transitions \( H-1(\beta) \rightarrow \text{LUMO}(\beta), HOMO(\alpha) \rightarrow \text{LUMO}(\alpha), \) \( \text{HOMO}(\beta) \rightarrow \text{LUMO}(\beta), \) \( \text{HOMO}(\alpha) \rightarrow \text{LUMO}(\alpha), \) and \( H-2(\alpha) \rightarrow \text{LUMO}(\alpha) \) due to the oscillation strength (0.0017).

**Figure 4.** UV-Vis spectra of rhenium metal complexes.

### 4. Conclusions

From the above results, one can conclude that the rhenium metal complexes have varying electronic applications due to different values of energy gap. On the other hand, the rhenium metal complexes have low electrophilic index in which refers to these complexes used as catalysts in chemical reactions such as polymerization processes. The results showed the rhenium metal complexes have various applications in electronic devices.
5. References

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