Comparison and study on the asymmetric uranyl−salophen to the single carbonyl molecules

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Abstract. Theoretical study of the asymmetric uranyl−salophen (AUS) on the unsaturated aldehyde or ketone is a focus of present research. This study underlines the complexes of asymmetric uranyl−salophen (as modified by unilateral benzene) to single carbonyl molecules, including formaldehyde, acetone, cyclopentanone, and cyclohexanone, using the density functional theory of quantum chemistry. Our results suggest that the C=O double bond of the single carbonyl molecules is weakened by the asymmetric uranyl−salophen. Both the negative charge of oxygen atoms and the positive charge of carbon atoms from the C=O bond of the single carbonyl have increased, and the binding energies and stability between asymmetric uranyl−salophen and acetone, cyclopentanone, or cyclohexanone were higher than that of formaldehyde. These new findings could be used as an important reference for the study of other complexes that the asymmetric uranyl−salophen to the complex carbonyl molecules.

1. Introduction

Compared with many other atoms, the outer layer of the uranium atom has very special electron structure [1, 2], and its 5f orbital can participate in the formation of chemical bonds [3]. Thus, uranium atom can be easily coordinated with many coordination atoms or groups to form multi-coordination complexes [3, 4], just like any other chiral molecule [5, 6]. When uranyl ions and Schiff bases form a four-coordination complex, for example uranyl-salophen, the uranyl ions can also coordinate with other coordination atoms or groups, and uranyl can activate ligands to a certain extent [7, 8]. In addition, the asymmetric affects the uranyl−salophen (U-S), as modified by unilateral benzene, it coordinated with the α-β-unsaturated aldehydes and α-β-unsaturated ketones, makes the catalytic activation effect better to the C=O double bond of the single carbonyl molecules and can help to obtain the production of chiral products [9, 10]. With the advancement of computer chemistry science, the theoretical simulation is well consistent with the experimental results, which can be directly referenced by the experiment [11-13], such as in some complexation through DFT calculation [14-18]. Moreover, theoretical calculation can save considerable resources and reduce unnecessary waste. The theoretical study of uranyl−salophen has often been a hot topic and the focus of researchers’ attention. Recent studies have suggested that some interesting conclusions are yielded for the coordination strength of the asymmetric uranyl-salophen complex with the unsaturated aldehydes and unsaturated ketones [7] However, the asymmetric uranyl−salophen (modified by unilateral benzene) to the monocarbonyl molecules have not been reported for the moment. Since the asymmetric uranyl−salophen can be employed to activate the single carbonyl group, especially in the single carbonyl molecule, and
it is expected to be referenced by the study on the catalysis of mono-carbonylation. Furthermore, it may guide the activation of multiple carbonyl groups and multiple unsaturated crowns meaningfully.

Figure 1. The chemical draw skeletons of the AUS and ligands

2. Methods and contents
The Gaussian 09 software was employed to calculate B3LYP [19] by using the density functional theory (DFT) method for the ligands and complexes. In this paper, the RECP basis [20] was applied to the uranium atom, while the 6-311G**[21] basis group was used for other atoms. All the data was obtained by comparing the structure parameters and Wiberg Bond Indices of the single carbonyl complexes, calculating and analyzing the frontier molecular orbitals, and calculating the binding energy for the complexes.

3. Results and discussion
3.1 Configuration
The optimized configurations of the asymmetric uranyl-salophen (AUS) and the single carbonyl molecules: formaldehyde, acetone, cyclopentanone, and cyclohexanone are shown in Fig. 1. The AUS coordinated with formaldehyde, acetone, cyclopentanone and cyclohexanone are shown in Fig. 2 a, b, c and d, respectively. The uranium atom form the AUS coordinated with the coordination oxygen atoms. As shown in Fig. 2 a, b, c and d, the ligands (acetone, cyclopentanone, and cyclohexanone) and the unilateral benzene from AUS are near parallel planes. It greatly reduced the molecular resistance between the ligands and the AUS, and improved the stability of the complexes. In Fig. 1 the ligands a, b, c and d represent the single carbonyl molecules: formaldehyde, acetone, cyclohexanone and cyclohexanone, respectively. In Fig. 2, a, b, c, and d represent the complexes formed by AUS coordinated with formaldehyde, acetone, cyclopentanone, and cyclohexanone, respectively. Some major parts of the structural parameters of the ligands and complexes are summarized in Table 1, and the numbers of atoms are shown in Fig. 1. As shown in Table 1 that, when the formaldehyde, acetone, cyclopentanone, and cyclohexanone are coordinated with AUS, their O1=C2 bonds length become longer. This suggests that all the O1=C2 are weakened in the complexes to the ligands. Obviously, the electrons of the O1=C2 are shifted, and the electron density of the O1=C2 decrease when the ligands are formed in complexes. This means that the AUS activates the O1=C2 bonds of the formaldehyde, acetone, cyclopentanone, and cyclohexanone [22-23].
Table 1. The comparison of part bond length (Å) of the ligands and complexes

|     | Ligand a | Complex a | Ligand b | Complex b | Ligand c | Complex c | Ligand d | Complex d |
|-----|----------|-----------|----------|-----------|----------|-----------|----------|-----------|
| R   | 2.500    | 2.460     | 2.478    | 2.540     |          |           |          |           |
| R   | 1.227    | 1.246     | 1.233    | 1.255     | 1.227    | 1.249     | 1.234    | 1.225     |

Figure 2. The optimized configurations of the complexes

3.2 Wiberg Bond Indices
In general, the Wiberg Bond Indices (WIBs) order is commonly used to indicate the strength of the force between two atoms in a molecule [24, 25]. The greater the value of the WIBs, the stronger the bond will be, and the more difficult it will be to destroy the bond between two atoms, so it usually indicates the strength of the bond between two atoms. The WIBs value of the ligands in O1-C2 range from 1.825 to 1.948, while under the same calculation levels, the complexes’ WIBs value range from 1.673 to 1.692, as listed in Table 2. Obviously, it is suggested that when the single carbonyl molecules are coordinated with AUS, their O=C bonds are weakened by the value (WIBs) of 0.133 to 0.167. All C=O WIBs value in complexes are smaller than in ligands, which means the AUS weakened the O=C bond as the uranium atom grew closer to the oxygen atom of the O=C bond. From Table 2, it’s clear that the activity of the AUS for O=C bond in formaldehyde and cyclohexanone is stronger than in acetone or cyclopentanone, which means the AUS is better at identifying formaldehyde and cyclopentanone than identifying acetone and cyclohexanone.
| O1=C2 | Complex | O1=C2 | Changed |
|-------|---------|-------|---------|
| 1.948 | a       | 1.781 | 0.167   |
| 1.827 | b       | 1.673 | 0.154   |
| 1.844 | c       | 1.684 | 0.160   |
| 1.825 | d       | 1.692 | 0.133   |

### 3.3 Infrared spectroscopy

| Ligand | νC=O | Complex | νC=O |
|--------|------|---------|------|
| a      | 1760 | a       | 1533, 1670 (major) |
| b      | 1757 | b       | 1674 |
| c      | 1776 | c       | 1681 |
| d      | 1751 | d       | 1657 |

The optimized configurations of formaldehyde, acetone, cyclopentanone, and cyclohexanone and their corresponding complexes are calculated using the B3LYP/6−311G** group in the DFT method under vacuum conditions. There was no imaginary frequency in the simple vibration mode of the calculated results, suggesting that the molecular structure from the single carbonyl molecule and their complexes optimized with a local minimum. These results indicate that all the optimized molecules are stable. As shown in Fig. 3a, the infrared spectrum of the ligands a, b, c, and d are the infrared spectra of formaldehyde, acetone, cyclopentanone and cyclohexanone, respectively. The infrared spectrum of formaldehyde, acetone, cyclopentanone, and cyclohexanone with the AUS are shown in Fig. 3b, while the infrared spectrum of complexes a, b, c and d are the complexes formed by the AUS coordinated with formaldehyde, acetone, cyclopentanone, and cyclohexanone, respectively. The major absorption peaks of the single carbonyl molecules and their complexes are listed in Table 3.

In ligand a, the C=O stretching vibration absorption peak appears at 1760 cm⁻¹, while such peak appears between 1533 cm⁻¹ (weak) and 1670 cm⁻¹ (strong) in complex a. In ligand b, the C=O stretching vibration absorption peak appears at 1757 cm⁻¹, while it appears at 1674 cm⁻¹ in complex b. In ligands c and d, the C=O almost completely appears at 1776 cm⁻¹ and 1751 cm⁻¹, while it appears at 1681 cm⁻¹ and 1657 cm⁻¹ in complex c and d, respectively. The C=O skeleton stretching absorption of the complexes are shifted to the lower wavelengths by comparing with the corresponding C=O in the single carbonyl molecules. This suggests that the AUS interacting with the single carbonyl molecules greatly weakens the C=O bonds.
3.4 Natural Bond Orbital atomic charges

Natural Bond Orbital (NBO)[26] atomic charges obtained by the same level of simulations for the ligands and the complexes are also analyzed. As shown in Table 4, the NBO atomic charges of each atom in complexes differs from the corresponding atom in ligands. The atoms’ net charges of the O1 and C2 in ligand are $-0.357$ and $+0.061$, while they are $-0.369$ and $+0.075$, respectively, in complex a. The atoms net charges of the O1 and C2 in ligand b are $-0.430$ and $+0.404$, while they are $-0.434$, and $+0.492$ in complex b, respectively. The atoms net charges of the O1 and C2 in ligand c are $-0.450$ and $+0.450$, and are $-0.455$ and $+0.538$ in complex c, respectively. The atoms net charges of the O1 and C2 in ligand d are $-0.444$ and $+0.445$, and are $-0.452$ and $+0.554$ in complex d, respectively. These results show that after the complexes are formed, the negative charge of the O atom in C=O bonds becomes more negative but also the positive charge of C atom in C=O is improved, and the C=O bond is weakened by the synergism from the C atom and O atom. The conclusion sequence value is consistent with the bond length of Table 1 and the WIBs of Table 2. This may be due to the formation of this complex. The coordination of the U atom with the O atom in C=O causes the negative charge of the O atom in C=O to increase, and then leads to an increase in the positive charge of the C atom in C=O. Furthermore, after the complexes are formed, not only the negative charge of O atom in C=O bonds but also the positive charge of C atom in C=O is increased, and the C=O bond is weakened more strongly by the synergism from the C atom and O atom. This may provide some new ideas for the electrophilic and nucleophilic reactions of unsaturated molecules such as C=O bonds.

Table 4. The partial NBO charge distributions of charge in ligands and complexes

| Ligand | O1   | C2   | Complex  | O1   | C2   |
|--------|------|------|----------|------|------|
| a      | $-0.357$ | $+0.061$ | a        | $-0.369$ | $+0.075$ |
| b      | $-0.430$ | $+0.404$ | b        | $-0.434$ | $+0.492$ |
| c      | $-0.450$ | $+0.450$ | c        | $-0.455$ | $+0.538$ |
| d      | $-0.444$ | $+0.445$ | d        | $-0.452$ | $+0.554$ |

3.5 Thermodynamic properties

Table 5 showed the calculated thermal properties of the complexes at 298.15 K and 1 atm. It showed that under constant volume (Cv) the inabsolute data, Complex d $>$ Complex c $>$ Complex b $>$ Complex a for the total molecular energies (E) and the heat capacity.
3.6 Molecular orbitals and energies

Molecular bonding orbitals and anti-bonding orbitals of the complexes are given by molecular simulation. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) plots of the complexes are shown in Fig. 4 and Table 6. The ΔE (gap between $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$) helps characterize the chemical reactivity and kinetic stability of the molecule[27]. In the structures of the three complexes, all electron delocalizations increase, and the energies of the occupied orbitals decrease. This suggests that stability is certainly improved in the system. The noted results suggest that the three configurations may be stable.

The $E_{\text{HOMO}}$ and the $E_{\text{LUMO}}$ of the complex a are $-5.5370$ eV and $-2.2719$ eV, as shown in Fig 4 a and b, respectively. The energy gap between $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$ is equal to 3.2651 eV, i.e., $\Delta E=3.2651$ eV, suggesting that to yield the excited state, 3.2651 eV will be absorbed by the complex a ground state molecule. Yet for the complex b, the $E_{\text{HOMO}}$ and the $E_{\text{LUMO}}$ are calculated to be $-5.4251$ eV and $-2.1040$ eV as shown in Fig. 4 c and d, respectively, and the energy gap ($\Delta E$) is 3.2851 eV. $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ calculated of the complex c are $-5.4670$ eV and $-2.1356$ eV, respectively, and the energy gap ($\Delta E$) is 3.3314 eV. $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ calculated of the complex d are $-5.4246$ eV and $-2.0510$ eV, respectively, and the energy gap ($\Delta E$) is 3.3736 eV. The above noted results suggested that the stability of complexes c and d are obviously above that of complexes a and b, as can be seen from the molecular orbitals and energies of the complexes a, b, c and d. In a way, as the electron donor groups containing C=O is increased, the stability is enhanced. This is probably because the cyclopentanone and cyclohexanone complexes have more stable systems than the formaldehyde and acetone complexes. This can provide a reference for the stability of other complexes containing unsaturated groups (C=O) coordinate with AUS. However, it should be noted that when the ligand space structure is too large, the formation of complexes will produce space resistance, which will reduce the stability[28].

Table 5. Thermodynamic properties of the Complexes (KCal/mol)

| Complex | 298.15 Cv | 298.15 S | H       | E       |
|---------|-----------|----------|---------|---------|
| a       | 34.18     | 57.00    | -1252004.44 | -1252206.21 |
| b       | 37.27     | 61.55    | -1301065.06 | -1301318.59 |
| c       | 39.04     | 64.07    | -1349362.03 | -1349637.53 |
| d       | 40.18     | 65.80    | -1373880.52 | -1374173.58 |
Figure 4. The complexes’ molecular orbitals and energies. The green and red portions represent the negative and positive phase of the molecular orbitals, respectively.

3.7 Binding energy
The binding energies for the complexes are calculated under the same level. All the binding energies are calculated from the equation (1) in which the term $\Delta W_{AB}(R)$ is the binding energy, and $W_{AB}(R)$ is the total energy of the interacting system. The terms $W_A(R)$ and $W_B(R)$ denote the energies of the two separate molecules A and B, respectively.

$$\Delta W_{AB}(R) = W_{AB}(R) - W_A(R) - W_B(R).$$

The binding energy of the complexes a, b, c, and d are -31.54Kcal/mol, -34.62Kcal/mol, -33.87Kcal/mol and -34.92Kcal/mol, respectively, which indicated that the AUS has greater binding
capacity to acetone, cyclopentanone, and cyclohexanone than formaldehyde. This is due to the
increase in negative charge of oxygen atom in C = O, and the enhancement of coordination ability
between the O atom with the U atom in AUS, thus increasing the binding ability of molecules.
Therefore, when we synthesize some complexes, we can refer to the charge of some coordination
atoms. It means, for some similar ligands, the higher the negative charge of the coordination atoms,
the greater the binding energy between molecules and the higher the stability of the molecules.

| Complex | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ | $\Delta E_{\text{L-H}}$ |
|---------|----------------|----------------|---------------------|
| a       | -5.5370        | -2.2719        | 3.2651              |
| b       | -5.4251        | -2.1040        | 3.2851              |
| c       | -5.4670        | -2.1356        | 3.3314              |
| d       | -5.4246        | -2.0510        | 3.3736              |

4. Conclusion
The present paper gains the computational insight into the AUS coordinated with the single carbonyl
molecules by making theoretical studies. The improved geometry, spectral properties, frontier
molecular orbitals, energy levels and the binding energies between the AUS and the single carbonyl
molecules are studied using DFT calculations. The results from this study suggest that the AUS
activated the single carbonyl molecules, which may provide important inferences for the asymmetric
uranyl–salophen to the single carbonyl molecules on activation. This will provide some new ideas for
the electrophilic and nucleophilic reactions of unsaturated molecules such as C=O bonds. From the
molecular orbitals and binding energy, there is an increase of electron donor groups containing C=O,
the stability of other complexes containing unsaturated groups (C=O) coordinate with AUS enhanced,
and the higher the negative charge of the coordination atoms, the greater the binding energy between
molecules and the higher the stability of the molecules. All of these new findings may provide
important guidance for experimental research about the complexes formed by AUS and carboxylation
molecules in future.

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