Method and basis set investigation for trans-platinum(II) oxime complex

Koray SAYIN*, Duran KARAKAŞ

1Cumhuriyet University, Institute of Science, Department of Chemistry, 58140 Sivas, Turkey
2Cumhuriyet University, Faculty of Science, Department of Chemistry, 58140 Sivas, Turkey

Received: 16.10.2014; Accepted: 15.12.2014

Abstract. The optimized molecular structure and stretching frequencies of platinum(II) oxime complex were investigated with HF, MP2, pure and hybrid DFT methods. CEP-4G, CEP-31G, CEP-121G, LANL2DZ, LANL2MB and SDD basis sets were used in calculations. Correlation coefficients of bond lengths and angles, computational job cpu time and stretching frequencies were used to determine the best method and basis set. The results show that HF/CEP-31G is the best level for bond lengths, angles and computational job cpu time. BPW91/CEP-31G is the best levels for stretching frequencies of oximato-bridged Pt(II) complex.

Keywords: Pt(II) oxime complex, Theoretical Study, Ab Initio and DFT methods, Basis Sets

1. INTRODUCTION

Platinum complexes play an important role in cancer treatments [1-5]. There is a big economic losses and great efforts for development anticancer platinum-based drugs [6-12]. Recent studies have reported that Pt(II) complexes with ketoxime cause cell death via an apoptotic mechanism, posses a higher cytotoxicity, enhanced cellular accumulation and elevated DNA platination [13-16]. Dinuclear platinum(II) complexes with bridging aliphatic and aromatic diamine ligands have been investigated [17-27].

Oximato-bridged trans-[PtCl{μ-(CH3)2C=NO}((CH3)2C=NOH)]2 complex has been synthesized and anticancer properties of this complex have been investigated experimentally by Scaffidi-Domianello et al. in 2012 [28]. They have used B3LYP/LANL2DZ level to support the experimental structural parameters in their calculations. B3LYP/LANL2DZ is an ordinary level and it has been used in many theoretical calculations. Different density functional theory methods (mPW1PW, BPV86, HCTH, PBEPBE, LSDA, PBE1PBE) and basis sets (CEP-4G, CEP-31G, CEP-121G, LANL2DZ, LANL2MB, SDD) have been used in calculations for Pt(II) complexes [25-34]. But ab initio methods have not been tested for these type complexes. The aim of this work is to investigate the best method and basis set for this type complex. In this paper, correlation coefficient of bond lengths, bond angels, job cpu time and average linear scale factors of stretching frequencies were used to determine the best method and basis set for optimized complex structure.
2. COMPUTATION METHODS

The input files of the complex were prepared with GaussView 5.0.8 [35]. Calculations were made using Gaussian 09 AML64L-Revision-C.01 [36]. The structural properties and stretching frequencies of trans-Pt(II) complex were determined through the application of Hartree-Fock (HF), Moller-Plessett (MP2) and density functional theory (DFT) methods (B3LYP [37], B3PW91 [38], MPW1PW91 [39], BHHandLYP [40], BP86 [41], BPW91 [42, 43], PW91PW91 [44] and SVWN5 [45]) with LANL2DZ [46], LANL2MB [47], SDD [47], CEP-4G [34], CEP-31G [34] and CEP-121G [34] basis sets.

The LANL2DZ with effective core potential (ECP) basis set was used for all calculations [48]. This basis set replaces the 1s through 2p electron of the heavy atoms with a potential field for considerable computational savings. LANL2DZ specifies D95V on first row [49], Los Alamos ECP plus DZ on Na-La, Hf-Bi. SDD specifies D95V up to Ar [50] and Stuttgart/Dresden ECPs on the remainder of the periodic table [50, 51]. LANL2MB specifies the STO-3G on first row [52, 53], Los Alamos ECP plus MBS on Na-Bi [54]. CEP-4G, CEP-31G, CEP-121G specify Stevens/Basch/Krauss ECP minimal basis, split valence, triple-split valence, respectively [55-57].

3. RESULTS and DISCUSSION

3.1. Geometry optimization

The optimized structure of mentioned complex at HF/CEP-31G level was given in Figure 1. Correlation coefficients were calculated for determination of the best structure. According to correlation coefficients of bond lengths and angles, there is a good agreement between theoretical and experimental complex structures. Correlation coefficients at bond lengths and angles were given in Table 1 and 2, respectively.

Figure 1. The optimized molecular structure of Pt (II) oxime complex with atomic number scheme in HF/CEP-31G level. Hydrogen atoms were omitted for clarity.
Method and basis set investigation for trans-platinum(II) oxime complex

Table 1. Correlation coefficients at bond lengths of different levels

<table>
<thead>
<tr>
<th>Methods</th>
<th>Basis Sets</th>
<th>CEP-4G</th>
<th>CEP-31G</th>
<th>CEP-121G</th>
<th>LANL2DZ</th>
<th>LANL2MB</th>
<th>SDD</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td></td>
<td>0.9863</td>
<td>0.9985</td>
<td>0.9963</td>
<td>0.9963</td>
<td>0.9788</td>
<td>0.9973</td>
</tr>
<tr>
<td>MP2</td>
<td></td>
<td>0.9699</td>
<td>0.9963</td>
<td>0.9951</td>
<td>0.9953</td>
<td>0.9804</td>
<td>0.9953</td>
</tr>
<tr>
<td>B3LYP</td>
<td></td>
<td>0.9713</td>
<td>0.9964</td>
<td>0.9968</td>
<td>0.9947</td>
<td>0.9857</td>
<td>0.9962</td>
</tr>
<tr>
<td>B3P86</td>
<td></td>
<td>0.9708</td>
<td>0.9958</td>
<td>0.9963</td>
<td>0.9940</td>
<td>0.9855</td>
<td>0.9959</td>
</tr>
<tr>
<td>B3PW91</td>
<td></td>
<td>0.9712</td>
<td>0.9959</td>
<td>0.9963</td>
<td>0.9941</td>
<td>0.9860</td>
<td>0.9959</td>
</tr>
<tr>
<td>MPW1PW91</td>
<td></td>
<td>0.9789</td>
<td>0.9980</td>
<td>0.9983</td>
<td>0.9962</td>
<td>0.9847</td>
<td>0.9975</td>
</tr>
<tr>
<td>BHandLYP</td>
<td></td>
<td>0.9726</td>
<td>0.9962</td>
<td>0.9966</td>
<td>0.9945</td>
<td>0.9860</td>
<td>0.9962</td>
</tr>
<tr>
<td>BP86</td>
<td></td>
<td>0.9656</td>
<td>0.9932</td>
<td>0.9940</td>
<td>0.9911</td>
<td>0.9846</td>
<td>0.9934</td>
</tr>
<tr>
<td>BPW91</td>
<td></td>
<td>0.9655</td>
<td>0.9937</td>
<td>0.9938</td>
<td>0.9908</td>
<td>0.9853</td>
<td>0.9933</td>
</tr>
<tr>
<td>PW91PW91</td>
<td></td>
<td>0.9648</td>
<td>0.9930</td>
<td>0.9938</td>
<td>0.9910</td>
<td>0.9848</td>
<td>0.9933</td>
</tr>
<tr>
<td>SVWN5</td>
<td></td>
<td>0.9653</td>
<td>0.9912</td>
<td>0.9921</td>
<td>0.9898</td>
<td>0.9806</td>
<td>0.9850</td>
</tr>
</tbody>
</table>

Table 2. Correlation coefficients at bond angle of different levels of theory

<table>
<thead>
<tr>
<th>Methods</th>
<th>Basis Sets</th>
<th>CEP-4G</th>
<th>CEP-31G</th>
<th>CEP-121G</th>
<th>LANL2DZ</th>
<th>LANL2MB</th>
<th>SDD</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td></td>
<td>0.9983</td>
<td>0.9972</td>
<td>0.9968</td>
<td>0.9968</td>
<td>0.9882</td>
<td>0.9970</td>
</tr>
<tr>
<td>MP2</td>
<td></td>
<td>0.9991</td>
<td>0.9968</td>
<td>0.9978</td>
<td>0.9963</td>
<td>0.9800</td>
<td>0.9980</td>
</tr>
<tr>
<td>B3LYP</td>
<td></td>
<td>0.9957</td>
<td>0.9948</td>
<td>0.9945</td>
<td>0.9935</td>
<td>0.9744</td>
<td>0.9941</td>
</tr>
<tr>
<td>B3P86</td>
<td></td>
<td>0.9949</td>
<td>0.9941</td>
<td>0.9936</td>
<td>0.9921</td>
<td>0.9746</td>
<td>0.9927</td>
</tr>
<tr>
<td>B3PW91</td>
<td></td>
<td>0.9958</td>
<td>0.9948</td>
<td>0.9946</td>
<td>0.9927</td>
<td>0.9753</td>
<td>0.9935</td>
</tr>
<tr>
<td>MPW1PW91</td>
<td></td>
<td>0.9963</td>
<td>0.9952</td>
<td>0.9951</td>
<td>0.9938</td>
<td>0.9795</td>
<td>0.9943</td>
</tr>
<tr>
<td>BHandLYP</td>
<td></td>
<td>0.9958</td>
<td>0.9947</td>
<td>0.9944</td>
<td>0.9930</td>
<td>0.9763</td>
<td>0.9938</td>
</tr>
<tr>
<td>BP86</td>
<td></td>
<td>0.9934</td>
<td>0.9940</td>
<td>0.9932</td>
<td>0.9919</td>
<td>0.9714</td>
<td>0.9922</td>
</tr>
<tr>
<td>BPW91</td>
<td></td>
<td>0.9939</td>
<td>0.9963</td>
<td>0.9938</td>
<td>0.9967</td>
<td>0.9721</td>
<td>0.9934</td>
</tr>
<tr>
<td>PW91PW91</td>
<td></td>
<td>0.9933</td>
<td>0.9960</td>
<td>0.9939</td>
<td>0.9915</td>
<td>0.9728</td>
<td>0.9927</td>
</tr>
<tr>
<td>SVWN5</td>
<td></td>
<td>0.9912</td>
<td>0.9898</td>
<td>0.9883</td>
<td>0.9852</td>
<td>0.9722</td>
<td>0.9868</td>
</tr>
</tbody>
</table>

Correlation coefficients of all levels in Table 1 are taken into account in the determination of the best method for each basis set. The best correlation was mainly obtained with HF method for CEP-4G, CEP-31G, LANL2DZ and SDD basis sets. But the best results in SDD basis set were obtained with MPW1PW91 and HF methods. Correlation coefficients of MPW1PW91 and HF methods are 0.9975 and 0.9973, respectively. The difference of correlation coefficient between MPW1PW91/SDD and HF/SDD is 0.0002. This difference is not important for method selection. The results show that HF is the best method for this type complex. As for the basis set selection in HF method, the best result was obtained with CEP-31G basis set. Correlation coefficient of HF/CEP-31G level is 0.9972.

Five bond angles have been presented in Ref. 28. These experimental values and theoretical results were used for determination of correlation coefficients. The best correlations were obtained with HF and MP2 methods for each basis set. As for the determination of the best basis set, the best correlations were obtained at HF/CEP-4G and MP2/CEP-4G levels. But correlation coefficients at CEP-4G, CEP-31G, CEP-121G, LANL2DZ and SDD basis sets are mainly higher than 0.99 (Table 2).
These values mean that the optimized structure of Pt(II) complex is very close to experimental structure. It is hard to determine the best basis set by using correlation coefficients of bond angles.

The job cpu time is an additional parameter to be taken into account in the selection of the method and basis set adequate for prediction of the oximato-bridged Pt(II) complex. The job cpu times were given in Table 3.

Table 3. The job cpu times of Pt(II) oxime complex in different levels.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Basis Sets</th>
<th>CEP-4G</th>
<th>CEP-31G</th>
<th>CEP-121G</th>
<th>LANL2DZ</th>
<th>LANL2MB</th>
<th>SDD</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td></td>
<td>1 d 11'</td>
<td>1 d 6 h 35'</td>
<td>4 d 8 h 4'</td>
<td>5 d 4 h 49'</td>
<td>2 h 47'</td>
<td>2 d 11 h 19'</td>
</tr>
<tr>
<td>MP2</td>
<td></td>
<td>6 d 6 h 26'</td>
<td>18 d 43'</td>
<td>-</td>
<td>49 d 3 h 51'</td>
<td>22 h 22'</td>
<td>30 d 22 h 41'</td>
</tr>
<tr>
<td>B3LYP</td>
<td></td>
<td>16 h 15'</td>
<td>3 d 13 h 7'</td>
<td>14 d 15'</td>
<td>4 d 11 h 57'</td>
<td>7 h 27'</td>
<td>8 d 13 h 3'</td>
</tr>
<tr>
<td>B3P86</td>
<td></td>
<td>1 d 11 h 11'</td>
<td>3 d 10 h 43'</td>
<td>16 d 9 h 41'</td>
<td>3 d 17 h 10'</td>
<td>7 h 29'</td>
<td>8 d 22 h</td>
</tr>
<tr>
<td>B3PW91</td>
<td></td>
<td>23 h 28'</td>
<td>3 d 9 h 24'</td>
<td>28 d 1 h 45'</td>
<td>6 d 32'</td>
<td>6 h 15'</td>
<td>11 d 23 h 13'</td>
</tr>
<tr>
<td>MPW1PW91</td>
<td></td>
<td>17 h 33'</td>
<td>3 d 11 h</td>
<td>14 d 22 h 24'</td>
<td>3 d 9 h 21'</td>
<td>7 h 46'</td>
<td>10 d 3 h 24'</td>
</tr>
<tr>
<td>BHandLYP</td>
<td></td>
<td>23 h 27'</td>
<td>2 d 12 h 3'</td>
<td>8 d 21 h 49'</td>
<td>2 d 16 h 32'</td>
<td>7 h 22'</td>
<td>5 d 33 h 9'</td>
</tr>
<tr>
<td>BP86</td>
<td></td>
<td>1 d 23 h 29'</td>
<td>7 d 8 h 43'</td>
<td>4 d 20 h 50'</td>
<td>6 d 15 h 24'</td>
<td>20 h 25'</td>
<td>16 d 16 h 52'</td>
</tr>
<tr>
<td>BPW91</td>
<td></td>
<td>6 d 6 h 2'</td>
<td>10 d 1 h 6'</td>
<td>25 d 3 h 13'</td>
<td>16 d 9 h 10'</td>
<td>11 h 45'</td>
<td>13 d 12 h 41'</td>
</tr>
<tr>
<td>PW91PW91</td>
<td></td>
<td>3 d 19 h 10'</td>
<td>20 d 19 h 26'</td>
<td>15 d 3 h 40'</td>
<td>8 d 6 h 29'</td>
<td>16 h 50'</td>
<td>41 d 10 h 31'</td>
</tr>
<tr>
<td>SVWN5</td>
<td></td>
<td>1 d 18 h 9'</td>
<td>5 d 6 h 30'</td>
<td>13 d 15 h 47'</td>
<td>4 d 2 h 35'</td>
<td>6 h 30'</td>
<td>12 d 23 h 34'</td>
</tr>
</tbody>
</table>

d: day, h: hour and’: minute

According to the job cpu times, two-step analysis was used for the determination of the best method and basis set. The first step is to determine the best method. The performance rankings of methods were done for each basis set. According to job cpu times, HF method has mainly minimum job cpu time and maximum performance. These analyses show that HF is the best method for our complex. MP2 method has mainly maximum job cpu time.

Second step is to determine the best basis set. Basis set rankings were done for each method by using cpu time. In HF method, the ranking of basis sets should be:

LANL2MB < CEP-4G < CEP-31G < SDD < CEP-121G < LANL2DZ

According to this ranking, job cpu time of LANL2MB basis set is minimum and job cpu time of CEP-121G is maximum. But correlation coefficients at bond lengths of LANL2MB and CEP-4G are lower than CEP-31G.

Taken into account the correlation coefficients of bond lengths and job cpu times, HF/CEP-31G is the best level for our Pt(II) oxime complex. According to the correlation coefficients of bond angles, HF and MP2 methods were selected the best method. But MP2 has longer job cpu time than HF method. Therefore HF method is more appropriate than MP2 method. The theoretical structural parameters in HF/CEP-31G level were given in Table 4 with experimental data.
Table 4. Calculated and experimental structural parameters of Pt(II) complex in HF/CEP-31G level.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt1 - N1</td>
<td>2.063</td>
<td>2.009</td>
<td>N1 - Pt1 - N2</td>
<td>173.6</td>
<td>177.0</td>
<td></td>
</tr>
<tr>
<td>Pt1 - N2</td>
<td>2.096</td>
<td>2.019</td>
<td>N1 - Pt1 - Cl1</td>
<td>89.8</td>
<td>90.9</td>
<td></td>
</tr>
<tr>
<td>Pt1 - Cl1</td>
<td>2.410</td>
<td>2.296</td>
<td>N2 - Pt1 - Cl1</td>
<td>95.5</td>
<td>91.1</td>
<td></td>
</tr>
<tr>
<td>Pt1 - O3</td>
<td>2.071</td>
<td>2.030</td>
<td>N3 - Pt2 - N4</td>
<td>173.1</td>
<td>176.0</td>
<td></td>
</tr>
<tr>
<td>Pt2 - N3</td>
<td>2.055</td>
<td>2.012</td>
<td>N3 - Pt2 - Cl2</td>
<td>90.5</td>
<td>90.3</td>
<td></td>
</tr>
<tr>
<td>Pt2 - N4</td>
<td>2.093</td>
<td>2.026</td>
<td>N4 - Pt2 - Cl2</td>
<td>96.2</td>
<td>92.0</td>
<td></td>
</tr>
<tr>
<td>Pt2 - Cl2</td>
<td>2.410</td>
<td>2.298</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt2 - O1</td>
<td>2.063</td>
<td>2.016</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N1 - C1</td>
<td>1.284</td>
<td>1.294</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N2 - C4</td>
<td>1.285</td>
<td>1.273</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N3 - C7</td>
<td>1.284</td>
<td>1.289</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N4 - C10</td>
<td>1.286</td>
<td>1.272</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Experimental values were taken from Ref. 28.

3.2. IR Spectra

Calculated and experimental stretching frequencies and average linear scale factors (λ_average) were listed in Table 5 by using HF, MP2 and DFT methods with CEP-31G basis set. Average linear scale factors were calculated by using Eq. (2).

\[
\lambda = \frac{\nu_{\text{exp.}}}{\nu_{\text{theo.}}}
\]

\[
\lambda_{\text{average}} = \frac{\sum \lambda}{n}
\]

where n, \(\nu_{\text{exp.}}\), \(\nu_{\text{theo.}}\) are the number of linear scale factor in each method, experimental frequency and theoretical frequency, respectively.

According to average linear scale factors in Table 5, BPW91/CEP-31G is the best level for determining the stretching frequencies of mentioned complex. In addition, good correlations were also obtained by using MP2, B3LYP and PW91PW91 methods. Average linear scale factor values of BPW91, MP2, B3LYP and PW91PW91 methods are 1.0112, 0.9843, 1.0120, and 1.0177, respectively. The calculated stretching frequencies (in cm\(^{-1}\)) of oximato-bridged Pt(II) complex were obtained as \(\nu_{\text{O-H}}\) (3340), \(\nu_{\text{C-H}}\) (3151-2978), \(\nu_{\text{C=N}}\) (1614, 1581), \(\nu_{\text{C-C}}\) (1321-1255), \(\nu_{\text{N-O}}\) (926), \(\nu_{\text{Pt-O}}\) (646) and \(\nu_{\text{Pt-Cl}}\) (312, 309) in the best level. IR spectrum of Pt(II) oxime complex was shown in Figure 2.
Table 5. Calculated and experimental stretching frequencies (in cm$^{-1}$) and average linear scale factors ($\lambda_{\text{Average}}$).

<table>
<thead>
<tr>
<th>Methods</th>
<th>$\nu_{\text{O-H}}^a$</th>
<th>$\nu_{\text{C=N}}^a$</th>
<th>$\nu_{\text{C=N}}^a$</th>
<th>$\nu_{\text{N-O}}^a$</th>
<th>$\lambda_{\text{Average}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>3839</td>
<td>1882</td>
<td>1866</td>
<td>1160</td>
<td>0.8519</td>
</tr>
<tr>
<td>MP2</td>
<td>3492</td>
<td>1667</td>
<td>1612</td>
<td>939</td>
<td>0.9843</td>
</tr>
<tr>
<td>B3LYP</td>
<td>3303</td>
<td>1646</td>
<td>1501</td>
<td>965</td>
<td>1.0120</td>
</tr>
<tr>
<td>B3P86</td>
<td>3237</td>
<td>1674</td>
<td>1666</td>
<td>1027</td>
<td>0.9705</td>
</tr>
<tr>
<td>B3PW91</td>
<td>3276</td>
<td>1668</td>
<td>1660</td>
<td>1023</td>
<td>0.9702</td>
</tr>
<tr>
<td>MPW1PW91</td>
<td>3320</td>
<td>1692</td>
<td>1684</td>
<td>1043</td>
<td>0.9557</td>
</tr>
<tr>
<td>BHandLYP</td>
<td>3522</td>
<td>1759</td>
<td>1753</td>
<td>1093</td>
<td>0.9127</td>
</tr>
<tr>
<td>BP86</td>
<td>3122</td>
<td>1605</td>
<td>1580</td>
<td>912</td>
<td>1.0334</td>
</tr>
<tr>
<td>BPW91</td>
<td>3340</td>
<td>1614</td>
<td>1581</td>
<td>926</td>
<td>1.0112</td>
</tr>
<tr>
<td>PW91PW91</td>
<td>3317</td>
<td>1621</td>
<td>1577</td>
<td>907</td>
<td>1.0177</td>
</tr>
<tr>
<td>SVWN5</td>
<td>2821</td>
<td>1633</td>
<td>1614</td>
<td>968</td>
<td>1.0346</td>
</tr>
<tr>
<td>Exp.</td>
<td>3143</td>
<td>1666</td>
<td>1620</td>
<td>969</td>
<td>-</td>
</tr>
</tbody>
</table>

*Frequencies were given in cm$^{-1}$

Figure 2. IR Spectrum of Pt(II) oxime complex in BP86/CEP-31G level.

4. CONCLUSION

HF method, MP2 method, pure and hybrid DFT functions (BP86, BPW91, PW91PW91, SVWN5, B3LYP, B3P86, B3PW91, MPW1PW91, BHandLYP) with CEP-4G, CEP-31G, CEP-121G, LANL2DZ, LANL2MB and SDD basis sets were used to determine the best optimized structure, job cpu time and stretching frequencies of Pt(II) oxime complex. Optimized structural parameters and stretching frequencies were subjected to correlation analyses with experimental results. In addition, job cpu times of each level were considered to determine the best method and basis set. According to these evaluations, HF/CEP-31G and BPW91/CEP-31G were found as the best levels for structural parameters and stretching frequencies, respectively.
ACKNOWLEDGEMENTS

We are grateful the office of scientific research projects of Cumhuriyet University (Project No: F-389) for financial supports. This research was made possible by TUBITAK ULAKBIM, High Performance and Grid Computing Center (TR-Grid e-Infrastructure).

REFERENCES


Method and basis set investigation for trans-platinum(II) oxime complex


