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ORIGINAL ARTICLE

# Theoretical study of *ht*-[(ph)Pt($\mu$-PN)($\mu$-NP)$PtMe_2$]-($CF_3CO_2$) structure as a heavy dimer complex and comparison of results with experimental X-ray data

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**Abstract** DFT calculations performed using Amsterdam Density Functional (ADF 2009.01b) program to estimate best geometry of an unsymmetrical cationic organo-diplatinum complex containing two bridging 2-diphenylphosphinopyridine,(PN), ligands and a platinum-platinum donor–acceptor bond, *ht*-[(ph)Pt($\mu$-PN)($\mu$-NP)$PtMe_2$]($CF_3CO_2$), as a moderately heavy dimer complex of platinum(II). The obtained geometry is in excellent agreement with the crystallographic data.

Energy is in all cases about 12–15 kcal $mol^{-1}$. For the LDA (XC potential in SCF) the DZ and TZ2P basis sets have been used. Furthermore, for the GGA(BLYP), GGA(BP) and GGA(PW91) method, the DZ basis set have been just used, due to the cost of calculations. The result showed that surprisingly the simple LDA(TZP) method has the minimum of energy, comparing the others. All the attempts for optimizing the mentioned dimer using B3LYP and OLYP methods failed.

## 1. Introduction

The basic concepts used to understand the origin of the properties of transition metal complexes were based on the ligand field theory (Figgis and Hitchman, 2000) around 1970. Maybe one of the first reported literatures about computation was the application of LFT to computing the electronic structure of the complexes of symmetry lower than cubic, namely five coordinated $C_{3v}$ complexes, which only the valence metal (nd) electrons are correlated on it (Bencini and Gatteschi, 1976). Some considerations on the proper use of computational tools in transition metal chemistry are reviewed (Bencini, 2008).

The Amsterdam Density Functional (ADF) package that we use, its 2009.01b version is software for first-principles electronic structure calculations and can be used by academic and industrial researchers (ADF, 2009). It is particularly popular in the research areas of homogeneous and heterogeneous

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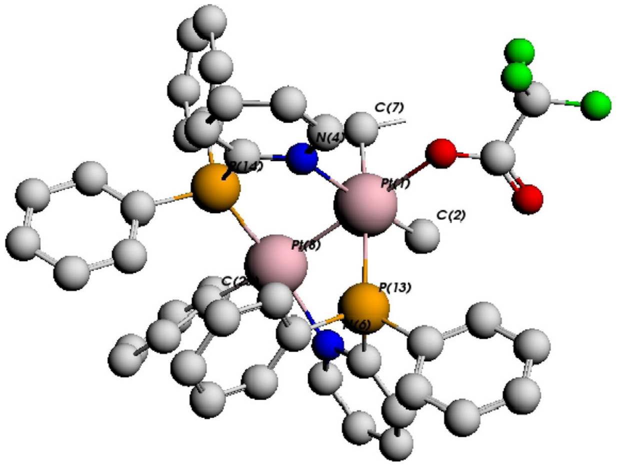

**Figure 1** The PW91/DZ optimized geometry of *ht*-[(ph)Pt($\mu$-PN)($\mu$-NP)PtMe$_2$](CF$_3$CO$_2$) dimer complex. Some nomenclatures in optimized geometry are omitted for clarity.

catalysis, inorganic chemistry, heavy element chemistry, various types of spectroscopy, and biochemistry. Theoretical and technical foundations of the ADF program with a survey of the characteristics of the code (numerical integration, density fitting for the Coulomb potential, and STO basis functions) are reported (Bickelhaupt et al, 2001).

Normally, the investigators prefer to calculate geometries and other properties of small molecules or complexes, due to cost of computations. The amplitude of selected dimmer complex caused to restrict of used basis set or methods.

## 2. Experimental and discussion

### 2.1. Methods

The calculations used the BLYP (Becke, 1988; Lee et al., 1988) from generalized gradient approximation (GGA), with double-$\zeta$ Slater-type orbital basis sets (DZ), all as implemented in the ADF 2009.01b program system mentioned above. All calculations were also repeated with other functionals, including LDA using two difference basis sets, DZ and TZ2P (Vosko et al, 1980), PW91 or BP (with DZ basis set) (Perdew et al., 1992; Perdew et al, 1993).

Choosing the BLYP, PW91 and simple LDA functional were due to the amplitude of selected dimmer complex, although there are some recent studies in which OLYP proved to be one of the better functional for transition metal systems (Tangen et al 2007; Conradie and Ghosh, 2007; Wasbotten and Ghosh, 2007). All the attempts for optimizing the mentioned dimer using B3LYP and OLYP methods (Sholl and Steckel, 2009) failed. Due to some restrictions of ADF program, we could not define exact nomenclature for atoms as is in related crystallography.

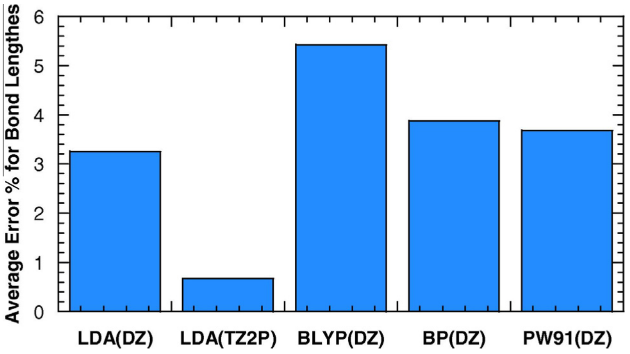

**Figure 2** Comparison of errors of various calculations for bond lengths.

## 3. Results and discussion

There is not too enough available structural information for diplatinum complexes due to their cost of computation. Hence determination of structural parameters of the *ht*-[(ph)Pt($\mu$-PN)($\mu$-NP)PtMe$_2$](CF$_3$CO$_2$) complex could be valuable. One of the optimized structures, using PW91(DZ) functional, with labeling of some atoms are shown in Fig. 1. There is a very well agreement between the theoretically determined parameters of this complex and the experimental values available in the literature (Akbari et al. 2007).

Some selected bond lengths of the diplatinum complex *ht*-[(ph)Pt($\mu$-PN)($\mu$-NP)PtMe$_2$](CF$_3$CO$_2$) which derived from its crystallographic data and various calculations are given in Table 1. Comparison of the errors is shown in Fig. 2.

**Table 1** Selected bond lengths of *ht*-[(ph)Pt($\mu$-PN)($\mu$-NP)PtMe$_2$](CF$_3$CO$_2$) complex, and related errors.

| | Empirical bond length (Å) | | | Calculated bond length (Å) (methods/error) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Crystallographic nomenclature | Bond length (Å) | Cal. nomenclature | LDA (DZ) | %Error | LDA (TZ2P) | %Error | BP (DZ) | %Error | PW91 (DZ) | %Error | BLYP (DZ) | %Error |
| 1 | Pt(1)–C(35) | 2.028 | Pt8–C25 | 2.096 | 3.35 | 2.096 | 3.35 | 2.149 | 5.97 | 2.141 | 5.57 | 2.181 | 7.54 |
| 2 | Pt(1)–N(2) | 2.0912 | Pt8–N6 | 2.127 | 1.71 | 2.173 | 3.91 | 2.206 | 5.49 | 2.204 | 5.39 | 2.251 | 7.64 |
| 3 | Pt(1)–P(1) | 2.1911 | Pt8–P14 | 2.341 | 6.84 | 2.282 | 4.15 | 2.405 | 9.76 | 2.404 | 9.72 | 2.458 | 12.2 |
| 4 | Pt(1)–Pt(2) | 2.6588 | Pt8–Pt1 | 2.719 | 2.26 | 2.715 | 2.11 | 2.793 | 5.05 | 2.782 | 4.63 | 2.837 | 6.70 |
| 5 | Pt(2)–C(41) | 2.064 | Pt1–C2 | 2.120 | 2.71 | 2.118 | 2.62 | 2.167 | 4.99 | 2.165 | 4.89 | 2.194 | 6.30 |
| 6 | Pt(2)–C(42) | 2.089 | Pt1–C7 | 2.123 | 1.63 | 2.135 | 2.20 | 2.169 | 3.83 | 2.166 | 3.69 | 2.195 | 5.07 |
| 7 | Pt(2)–N(1) | 2.1516 | Pt1–N4 | 2.198 | 2.16 | 2.231 | 3.69 | 2.297 | 6.76 | 2.293 | 6.57 | 2.359 | 9.64 |
| 8 | Pt(2)–P(2) | 2.3167 | Pt1–P13 | 2.465 | 6.40 | 2.412 | 4.11 | 2.576 | 11.19 | 2.586 | 11.60 | 2.695 | 16.3 |
| 9 | Pt(2)–O(1) | 2.6263 | Pt1–O3 | 2.361 | −10.09 | 2.394 | −8.85 | 2.473 | −5.84 | 2.449 | −6.75 | 2.528 | −3.74 |

**Table 2** Selected bond angles of *ht*-[(ph)Pt($\mu$-PN)($\mu$-NP)PtMe$_2$](CF$_3$CO$_2$) complex and related errors.

| | Empirical bond angles | | Calculated bond angles (methods/error) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Crystallographic nomenclature | Bond angle | Equivalent cal. nomenclature | LDA(DZ) | %Error | LDA(TZ2P) | %Error | BP(DZ) | %Error | PW91(DZ) | %Error | BLYP(DZ) | %Error |
| 1 | C(35)–Pt(1)–N(2) | 88.44 | C25–Pt8–N6 | 92.9 | 5.04 | 89.5 | 1.20 | 92.1 | 4.14 | 91.1 | 3.01 | 91.0 | 2.89 |
| 2 | C(35)–Pt(1)–P(1) | 93.6 | C25–Pt8–P14 | 89.7 | −4.17 | 93.1 | −0.53 | 92.4 | −1.28 | 93.4 | −0.21 | 93.4 | −0.21 |
| 3 | N(2)–Pt(1)–P(1) | 171.25 | N6–Pt8–P14 | 162.3 | −5.23 | 165.4 | −3.42 | 161.8 | −5.52 | 163.3 | −4.64 | 163.5 | −4.53 |
| 4 | C(35)–Pt(1)–Pt(2) | 178.22 | C25–Pt8–Pt1 | 172.0 | −3.49 | 176.0 | −1.25 | 171.7 | −3.66 | 172.7 | −3.10 | 172.4 | −3.27 |
| 5 | N(2)–Pt(1)–Pt(2) | 90.62 | N6–Pt8–Pt1 | 95.1 | 4.94 | 92.3 | 1.85 | 93.5 | 3.18 | 93.1 | 2.74 | 91.7 | 1.19 |
| 6 | P(1)–Pt(1)–Pt(2) | 87.557 | P14–Pt8–Pt1 | 83.0 | −5.20 | 86.1 | −1.66 | 84.3 | −3.72 | 84.2 | −3.83 | 85.5 | −2.35 |
| 7 | C(41)–Pt(2)–C(42) | 84.64 | C2–Pt1–C7 | 84.6 | −0.05 | 83.2 | −1.70 | 83.4 | −1.47 | 83.0 | −1.94 | 82.9 | −2.06 |
| 8 | C(41)–Pt(2)–N(1) | 171.47 | C2–Pt1–N4 | 173.7 | 1.30 | 170.4 | −0.62 | 171.9 | 0.25 | 171.5 | 0.02 | 171.2 | −0.16 |
| 9 | C(42)–Pt(2)–N(1) | 87.24 | C7–Pt1–N4 | 89.2 | 2.25 | 86.8 | −0.50 | 88.5 | 1.44 | 88.6 | 1.56 | 88.3 | 1.22 |
| 10 | C(41)–Pt(2)–P(2) | 90.52 | C2–Pt1–P13 | 89.7 | −0.906 | 88.9 | −1.79 | 90.1 | −0.46 | 90.6 | 0.0884 | 90.2 | −0.35 |
| 11 | C(42)–Pt(2)–P(2) | 173.58 | C7–Pt1–P13 | 167.5 | −3.50 | 166.1 | −4.31 | 167.6 | −3.45 | 167.9 | −3.27 | 166.2 | −4.25 |
| 12 | N(1)–Pt(2)–P(2) | 97.77 | N4–Pt1–P13 | 96.3 | −1.50 | 99.8 | 2.08 | 97.7 | −0.07 | 97.5 | −0.276 | 99.3 | 1.56 |
| 13 | C(41)–Pt(2)–O(1) | 91.39 | C2–Pt1–O3 | 99.0 | 8.33 | 95.4 | 4.39 | 98.2 | 7.45 | 98.3 | 7.56 | 96.3 | 5.37 |
| 14 | C(42)–Pt(2)–O(1) | 89.62 | C7–Pt1–O3 | 90.1 | 0.536 | 88.0 | −1.81 | 88.4 | −1.36 | 89.0 | −0.692 | 89.5 | −0.13 |
| 15 | N(1)–Pt(2)–O(1) | 85.95 | N4–Pt1–O3 | 81.8 | −4.83 | 83.1 | −3.32 | 82.2 | −4.36 | 82.4 | −4.13 | 83.4 | −3.00 |
| 16 | P(2)–Pt(2)–O(1) | 94.72 | P13–Pt1–O3 | 101.3 | 6.95 | 104.9 | 10.7 | 103.0 | 8.74 | 102.0 | 7.69 | 103.4 | 9.16 |
| 17 | C(41)–Pt(2)–Pt(1) | 94.8 | C2–Pt1–Pt8 | 86.7 | −8.54 | 91.6 | −3.38 | 88.0 | −7.17 | 88.0 | −7.17 | 89.9 | −5.17 |
| 18 | C(42)–Pt(2)–Pt(1) | 101.34 | C7–Pt1–Pt8 | 95.2 | −6.06 | 93.9 | −7.34 | 95.3 | −5.96 | 96.1 | −5.17 | 95.0 | −6.26 |
| 19 | N(1)–Pt(2)–Pt(1) | 89.34 | N4–Pt1–Pt8 | 93.1 | 4.21 | 90.3 | 1.07 | 92.1 | 3.09 | 92.0 | 2.98 | 90.9 | 1.75 |
| 20 | P(2)–Pt(2)–Pt(1) | 74.807 | P13–Pt1–Pt8 | 73.3 | −2.01 | 73.9 | −1.21 | 73.9 | −1.21 | 73.3 | −2.01 | 73.4 | −1.88 |
| 21 | O(1)–Pt(2)–Pt(1) | 167.85 | O3–Pt1–Pt8 | 172.6 | 2.83 | 172.9 | 3.01 | 173.1 | 3.13 | 172.3 | 2.65 | 173.0 | 3.07 |

As one can see from this figure, although all the methods have been shown acceptable results, less than 10% error, the LDA(TZ2P) method has been shown the least error from the X-ray crystallographic data. These results came from nineteen selected bond lengths, which nine of them are collected in Table 1.

The Pt(8) center has a distorted square-planar stereochemistry with Pt(1)P(14)N(6)C(25) coordination. The P(14) atom of one of the 2-diphenylphosphine ligands is in a *trans* arrangement with the N(6) atom of the other one, and the C(25) atom is trans to Pt(1).

Crystallographic data show 2.6588 Å for the donor–acceptor bond of Pt–Pt, while the calculations using LDA(DZ), LDA(TZ2P), BP(DZ), PW91(DZ) and BLYP(DZ) show 2.719, 2.715, 2.793, 2.782 and 2.837 Å, respectively. Clearly, the result of LDA(TZ2P) calculation is the most match with the experimental one, the others also are good too.

The orientation of a plane comprising the carbon atoms of the phenyl ligand [C(25)–C(30)] is almost perpendicular to the Pt coordination plane in both theoretical and experimental results. For example, the LDA(TZ2P) calculation show 176° for C(25)Pt(8)Pt(1) angle instead of 180°. It means that the Pt(1)P(14)N(6)C(25) plan (coordinated atoms around Pt(8)) is perpendicular to the other square plane, N(4)P(13) C(2)C(7), (coordinated atoms around Pt(1)).

As mentioned, the Pt(1) atom is square-pyramidal with N(4)P(13)C(2)C(7) coordination, in which the P atom of one of the PN ligands, P(13), is in a *cis* arrangement with the N atom of the other PN ligand, N(4), and Pt(8) occupying the apical position. The basal coordination plane around Pt(1) is again orienting almost perpendicularly with respect to the Pt(8) coordination plane [P(14)–Pt(8)–Pt(1) = 83.0°; C(7)–Pt(1)–Pt(8) = 95.2°; N(4)–Pt(1)–Pt(8) = 93.1° and C(2)–Pt(1)–Pt(8) = 86.7°, all in LDA–DZ computation].

The coordinated phosphorus atom has more trans influence compared to the N atom, so we expect less bond length for Pt(1)–C(2), comparing to Pt(1)–C(7). The crystallographic data showed 2.064 and 2.089 Å for the first and second respectively. LDA–DZ calculation showed 2.120 and 2.125 Å for the mentioned bonds and confirmed the expectation. The other calculations have shown the similar results.

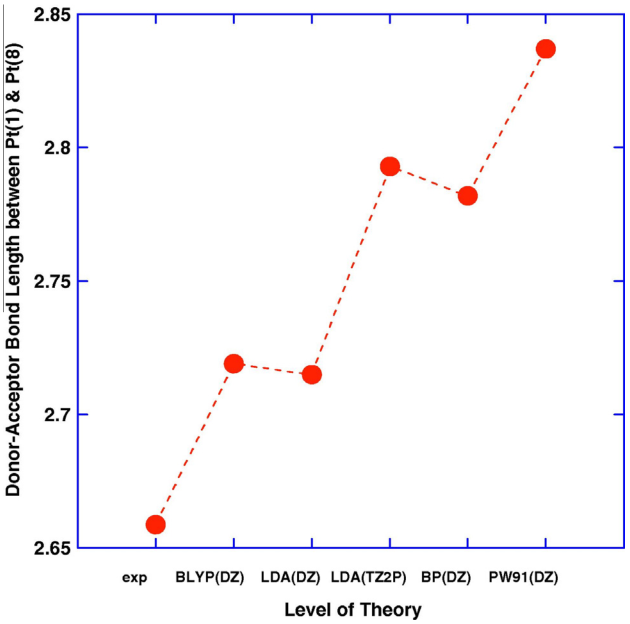

**Figure 3** Comparison of calculated donor–acceptor bonds with experimental datum.

The square-pyramidal coordinated Pt(1) center is also rather weakly connected to the O(3) atom of the trifluoroacetate counter anion [with Pt(1)–O(1) = 2.626 Å (exp), 2.366 Å (cal., LDA–DZ) to form a quasi-octahedral geometry. The donor–acceptor Pt–Pt bond, with a short distance of 2.6588 Å (exp), observed in calculations too [LDA–DZ calculation showed 2.714 Å for example].

The calculated Pt(8)–O(50) bond length in this level (LDA–DZ) is 5.069 Å and suggest that there is notany bonding interaction between these two atoms Table 2.

**Table 3** Calculated Muliken charges of selected atoms.

| Atom | LDA(DZ) | BP(DZ) | LDA(TZP) | BLYP(DZ) | PW91(DZ) |
|---|---|---|---|---|---|
| Pt1 | 0.6496 | 0.6767 | 0.2739 | 0.6393 | 0.6820 |
| C2 | −1.0220 | −0.9855 | 0.0943 | −0.8955 | −0.9877 |
| O3 | −0.6604 | −0.6883 | −0.6646 | −0.6850 | −0.6887 |
| N4 | −0.5511 | −0.5822 | −0.3917 | −0.5724 | −0.5827 |
| N6 | −0.6024 | −0.6104 | −0.4573 | −0.5899 | −0.6055 |
| C7 | −1.0308 | −0.9759 | 0.1187 | −0.8797 | −0.9786 |
| Pt8 | 0.3730 | 0.3954 | 0.4025 | 0.3407 | 0.4128 |
| C12 | −0.1891 | −0.1894 | −0.0893 | −0.1752 | −0.1949 |
| P13 | 0.9627 | 0.9304 | 0.9757 | 0.9182 | 0.9271 |
| P14 | 1.0080 | 0.9899 | 0.9465 | 0.9781 | 0.9823 |
| C16 | −0.1848 | −0.1696 | −0.0989 | −0.1566 | −0.1714 |
| C25 | −0.2692 | −0.2965 | −0.3902 | −0.2674 | −0.2954 |

**Table 4** Total bonding energies calculated in various methods.

| Total bonding energy (kcal/mol) | LDA(DZ) | BP(DZ) | LDA(TZP) | PW91(DZ) | BLYP(DZ) |
|---|---|---|---|---|---|
| | −14259.01 | −13003.14 | −14792.79 | −13246.59 | −12454.87 |

Some selected calculated Muliken charges on related atoms are given in Table 3.

As one can see, the most similar atoms except the Pt(1) and Pt(8) has somehow the same charges. The calculated charge on Pt(1) is moderately more than Pt(8) in all cases (except for LDA(TZP)) which suggest that the donation can occur from Pt(1) to Pt(8) in donor–acceptor Pt–Pt bond. This bond length is obtained as 2.719, 2.715, 2.793, 2.782 and 2.837 using LDA(DZ), LDA(TZP), BP(DZ), PW91(DZ) and BLYP(DZ) levels, respectively. Fig. 3 shows the comparison between these results.

The results of BLYP(DZ) and LDA(DZ) methods show the nearest values to the experimental value for Pt(1)–Pt(8) bond, while the PW91(DZ) method shows the forest.

The total bonding energy for this dimer has also been computed and collected in the Table 4.

As one can find from this table, the minimum obtained total bonding energy is about LDA(TZP) method, which confirms the previous conclusion mentioned in Fig. 2.

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