Cumhuriyet Üniversitesi Fen Fakültesi
Fen Bilimleri Dergisi (CFD), Ciltl 36, No. 2 (2015)
ISSN: 1300-1949

Cumhuriyet University Faculty of Science
Science Journal (CSJ), Vol. 36, No. 2 (2015)
ISSN: 1300-1949

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

Koray SAYIN[1*], Duran KARAKAŞ[2]

[1]*Cumhuriyet University, Institute of Science, Department of Chemistry, 58140 Sivas, Turkey*

[2]*Cumhuriyet 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)$_2$C=NO}{(CH$_3$)$_2$C=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.

* Corresponding author. *Email address*: krysayin@gmail.com

2. COMPUTATION METHODS

The input files of the complex were prepared with GaussView 5.0.8 [35].[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-Plessent (MP2) and density functional theory (DFT) methods (B3LYP [37], B3PW91 [38], MPW1PW91 [39], BHandLYP [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 valance, triple-split valance, 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.

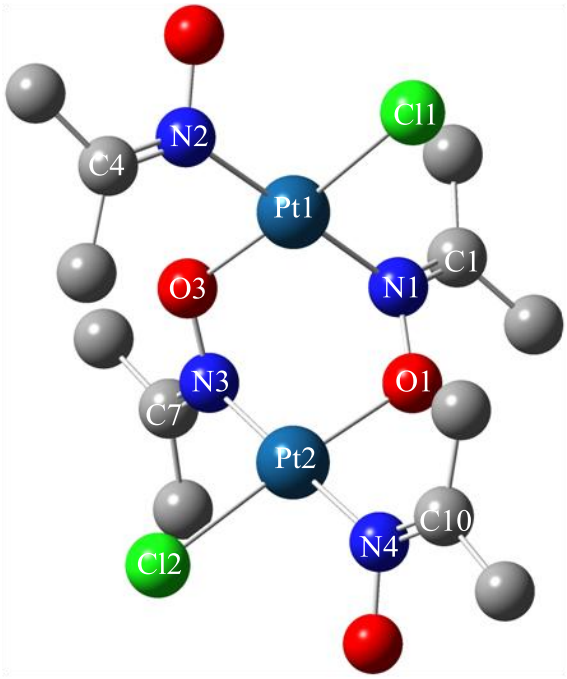

Figure 1. The optimized molecular structure of Pt (II) oxime complex with atomic number scheme in HF/CEP-31G level. Hydrogen atoms were omitted for clarity.

Table 1. Correlation coefficients at bond lengths of different levels

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

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

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

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.

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

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.

Lengths (Å)	Calc.	Exp.[a]	Angles (°)	Calc.	Exp.[a]
Pt1 - N1	2.063	2.009	N1 - Pt1 - N2	173.6	177.0
Pt1 - N2	2.096	2.019	N1 - Pt1 - Cl1	89.8	90.9
Pt1 - Cl1	2.410	2.296	N2 - Pt1 - Cl1	95.5	91.1
Pt1 - O3	2.071	2.030	N3 - Pt2 - N4	173.1	176.0
Pt2 - N3	2.055	2.012	N3 - Pt2 - Cl2	90.5	90.3
Pt2- N4	2.093	2.026	N4 - Pt2 - Cl2	96.2	92.0
Pt2 - Cl2	2.410	2.298	-	-	-
Pt2 - O1	2.063	2.016	-	-	-
N1 - C1	1.284	1.294	-	-	-
N2 - C4	1.285	1.273	-	-	-
N3 - C7	1.284	1.289	-	-	-
N4 - C10	1.286	1.272	-	-	-

[a] Experimental values were taken from *Ref. 28*.

3.2. IR Spectra

Calculated and experimental stretching frequencies and average linear scale factors ($\lambda_{Average}$) 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).

$$\lambda = \frac{\nu_{\text{exp.}}}{\nu_{theo.}} \tag{1}$$

$$\lambda_{Average} = \frac{\sum \lambda_n}{n} \tag{2}$$

where n, $\nu_{exp.}$, $\nu_{theo.}$ 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 ν_{O-H} (3340), ν_{C-H} (3151-2978), $\nu_{C=N}$ (1614, 1581), ν_{C-C} (1321-1255), ν_{N-O} (926), ν_{Pt-O} (646) and ν_{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 ($\lambda_{Average}$).

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

[a]Frequencies were given in cm^{-1}

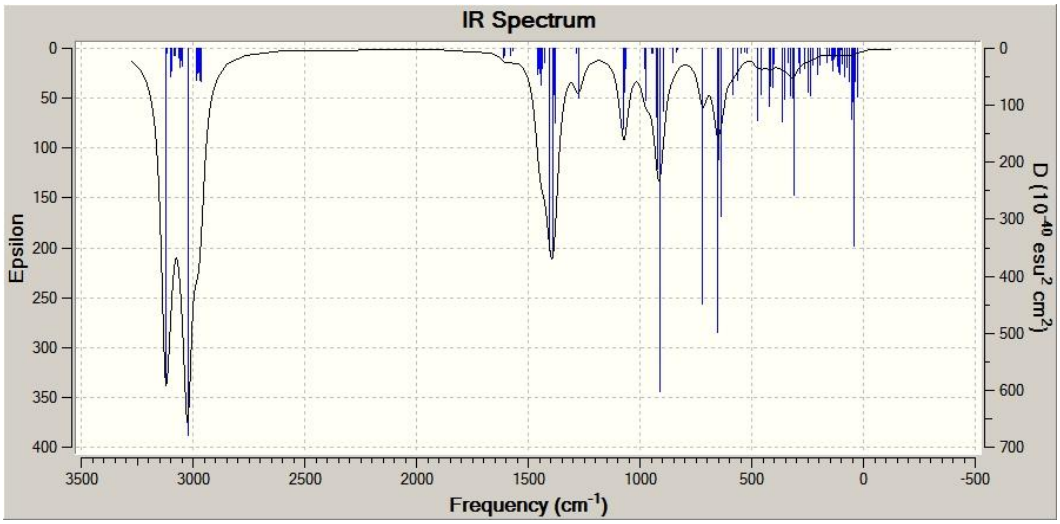

Figure 2. IR Spectrum of Pt(II) oxime complex in BP86/CEP-31G level.

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.

5. 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

[1] Raymond, E., Faivre, S., Chaney, S., Woynarowski, J., Cvitkovic, E., 2002. Cellular and Molecular Pharmacology of Oxaliplatin. Mol Cancer Ther. 1, 227-238.

[2] Raymond, E., Chaney, S. G., Taamma, A., Cvitkovic, E., 1998. Oxaliplatin: A review of preclinical and clinical studies. Ann. Oncol. 9, 1053-1071.

[3] Fuertes, M. A., Castilla, J., Alonso, C., Perez, J. M., 2003. Cisplatin Biochemical Mechanism of Action: From Cytotoxicity to Induction of Cell Death Through Interconnections Between Apoptotic and Necrotic Pathways. Curr. Med. Chem. 10, 257-266.

[4] Ong, S. T., Vogelzang, N. J., 1996. Chemotherapy in malignant pleural mesothelioma. A review. J. Clin. Oncol. 14, 1007-1017.

[5] Weiss, R. B., Christian, M. C., 1993. New Cisplatin Analogues in Development. Drugs. 46, 360-377.

[6] Cleare, M. J., Hoeschele, J. D., 1973. Antilt umour Platinum Compounds. Platinum Met Rev. 17, 2-13.

[7] Cleare, M. J., Hoeschele, J. D., 1973. Studies on the antitumor activity of group VIII transition metal complexes. Part I. Platinum (II) complexes. Bioinorg Chem. 2, 187-210.

[8] Endresi, H., 1985. A hydrogen-bridged dimeric stacked structure in a dioximato complex: (oxamide oximato)(oxamide oxime) platinum (II) iodide dihydrate, [Pt(C2H5N4O2)(C2H5N4O2)]I.2H2O. Acta Cryst. C41, 1047-1049.

[9] Guedes da Silva, M. F. C., Izotova, Y. A., Pombeiro, A. J. L., Kukushkin, V. Y., 1998. Manifestation of redox duality of 2-propanone oxime: Pt(II)-assisted reduction versus Pt (IV) - mediated oxidation of Me2O= NOH species. Inorg. Chim. Acta. 277, 83-88.

[10] Makarycheva-Mikhailova, A. V., Haukka, M., Bokach, N. A., Garnovskii, D. A., Galanski, M., Keppler, B. K., Pomberio, A. J. L., Kukushkin, V. Y., 2002. Platinum(IV)-mediated coupling of dione monoximes and nitriles: a novel reactivity pattern of the classic oxime-based chelating ligands. New J. Chem. 26, 1085-1091.

[11] Köcher, S., Lutz, M., Spek, A. L., Walfort, B., Rüffer, T., van Klink, G. P. M., van Koten, G., Lang, H., 2008. Oxime-substituted NCN-pincer palladium and platinum halide polymers through non-covalent hydrogen bonding (NCN = [C6H2(CH2NMe2)2-2,6]−). Journal of Organometallic Chemistry. 693, 2244-2250.

[12] Grabmann, G., Meier, S. M., Scaffidi-Domianello, Y. Y., Galanski, M., Keppler, B. K., Hartinger, C. G., 2012. Capillary zone electrophoresis and capillary zone electrophoresis–electrospray ionization mass spectrometry studies on the behavior of anticancer cis- and trans-[dihalidobis(2-propanone oxime)platinum(II)] complexes in aqueous solutions. Journal of Chromatography A. 1267, 156-161.

[13] Quiroga, A. G., Cubo, L., de Blas, E., Aller, P., Navarro-Ranninger, C., 2007. Trans platinum complexes design: One novel water soluble oxime derivative that contains aliphatic amines in transconfiguration. J. Inorg. Biochem. 101, 104-110.

[14] Zorbas-Seifried, S., Jakupec, M. A., Kukushkin, N. V., Groessl, M., Hartinger, C. G., Semenova, O., Zorbas, H., Kukushkin, V. Y., Keppler, B. K., 2007. Reversion of Structure-Activity Relationships of Antitumor Platinum Complexes by Acetoxime but Not Hydroxylamine Ligands. Mol. Pharmacol. 71, 357-365.

[15] Scaffidi-Domianello, Y. Y., Meelich, K., Jakupec, M. A., Arion, V. B., Kukushkin, V. Y., Galanski, M., Keppler, B. K., 2010. Novel Cis- and Trans-Configured Bis(oxime)platinum(II) Complexes: Synthesis, Characterization, and Cytotoxic Activity. Inorg. Chem. 49, 5669-5678.

[16] Bartel, C., Bytzek, A. K., Scaffidi-Domianello, Y. Y., Grabmann, G., Jakupec, M. A., Hartinger, C. G., Galanski, M., Keppler, B. K., 2012. Cellular accumulation and DNA interaction studies of cytotoxic trans-platinum anticancer compounds. Biol. Inorg. Chem. 17, 465-474.

[17] Karaker, A. J., Hoeschele, J. D., Elliott, W. L., Showalter, H. D., Hollis, L. S., Sercel, A. D., Farrell, N. P., 1992. Anticancer activity in murine and human tumor cell lines of bis(platinum) complexes incorporating straight-chain aliphatic diamine linker groups. J. Med. Chem. 35, 4526-4532.

[18] Wu, P. K., Qu, Y., Van Houten, B., Farrell, N., 1994. Chemical reactivity and DNA sequence specificity of formally monofunctional and bifunctional bis(platinum) complexes. J. Inorg. Biochem. 54, 207-220.

[19] Farrell, N., Appleton, T. G., Qu, Y., Roberts, J. D., Fontes, A. P. S., Skov, K. A., Wu, P., Zou, Y., 1995. Effects of Geometric Isomerism and Ligand Substitution in Bifunctional Dinuclear Platinum Complexes on Binding Properties and Conformational Changes in DNA. Biochemistry. 34, 15480-15486.

[20] Qu, Y., Bloemink, M. J., Reedijk, J., Hambley, T. W., Farrell, N., 1996. Dinuclear Platinum Complexes Form a Novel Intrastrand Adduct with d(GpG), an anti−syn Conformation of the Macrochelate As Observed by NMR and Molecular Modeling. J. Am. Chem. Soc. 118, 9307-9313.

[21] Farrell, N., Valsecchi, E. M. M., Di Domenico, R., Da Re, G., Manzotti, C., Pezzoni, G., Giuliani, F. C., Spinelli, S., 1997. Chemical and biological properties of a novel bifunctional triplatinum phase I clinical agent. J. Inorg. Biochem. 67, 173.

[22] Qu, Y., Farrell, N., Kasparkova, J., Brabec, V., 1997. DNA binding of properties of trinuclear platinum complex. J. Inorg. Biochem. 67, 174.

[23] Perego, P., Caserini, C., Gatti, L., Carenini, N., Romanelli, S., Supino, R., Colangelo, D., Viano, I., Leone, R., Spinelli, S., Pezzoni, G., Manzotti, C., Farrell, N., Zunino, F., 1999. A Novel Trinuclear Platinum Complex Overcomes Cisplatin Resistance in an Osteosarcoma Cell System. Mol. Pharmacol. 55, 528-534.

[24] Kloster, M. B. G., Hannis, J. C., Muddiman, D. C., Farrell, N., 1999. Consequences of Nucleic Acid Conformation on the Binding of a Trinuclear Platinum Drug. Biochemistry. 38, 14731-14737.

[25] Qu, Y., Rauter, H., Fontes, A. P. S., Bandarage, R., Kelland, L. R., Farrell, N., 2000. Synthesis, Characterization, and Cytotoxicity of Trifunctional Dinuclear Platinum Complexes: Comparison of Effects of Geometry and Polyfunctionality on Biological Activity. J. Med. Chem. 43, 3189-3192.

[26] Cox, J. W., Berners-Price, S. J., Davies, M. S., Qu, Y. Farrell, N., 2001. Kinetic Analysis of the Stepwise Formation of a Long-Range DNA Interstrand Cross-link by a Dinuclear Platinum Antitumor Complex: Evidence for Aquated Intermediates and Formation of Both Kinetically and Thermodynamically Controlled Conformers. J. Am. Chem. Soc. 123, 1316-1326.

[27] Fan, D., Yang, X., Wang, X., Zhang, S., Mao, J., Ding, J., Lin, L., Guo, Z., 2007. A dinuclear monofunctional platinum(II) complex with an aromatic linker shows low reactivity towards glutathione but high DNA binding ability and antitumor activity. J. Biol. Inorg. Chem. 12, 655-665.

[28] Scaffidi-Domianello, Y. Y., Legin, A. A., Jakupec, M. A., Roller, A., Kukushkin, V. Y., Galanski, M., Keppler, B. K., 2012. Novel Oximato-Bridged Platinum(II) Di- and Trimer(s): Synthetic, Structural, and in Vitro Anticancer Activity Studies. Inorg. Chem. 51, 7153-7163.

[29] Giese, B., Deacon, G. B., Kuduk-Jaworska, J., McNaughton, D., 2002. Density functional theory and surface enhanced Raman spectroscopy characterization of novel platinum drugs. Biopolymers. 67, 294-297.

[30] Delp, S. A., Munro-Leighton, C., Khosla, C., Templeton J. L., Alsop N. M., Gunnoe T. B., Cundari T. R., 2009. Combined experimental and computational study of W(II), Ru(II), Pt(IV) and Cu(I) amine and amido complexes using 15N NMR spectroscopy. Journal of Organometallic Chemistry. 694, 1549-1556.

[31] Wysokinski, R., Kuduk-Jaworska, J., Michalska, D., 2006. Electronic structure, Raman and infrared spectra, and vibrational assignment of carboplatin. Density functional theory studies. J Mol Struct.: THEOCHEM. 758, 169-179.

[32] Tornaghi, E., Andreeoni, W., Carloni, P., Hutter, J., Parinello, M., 1995. Carboplatin versus cisplatin: density functional approach to their molecular properties. Chem. Phys. Lett. 246, 469-474.

[33] Adamo, C., Barone, V., 1998. Exchange functionals with improved long-range behavior and adiabatic connection methods without adjustable parameters: The mPW and mPW1PW models. J. Chem. Phys. 108, 664-675.

[34] Gao, H., 2011. Theoretical studies of molecular structures and properties of platinum (II) antitumor drugs. Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy. 79, 687-693.

[35] Dennington II R. D.; Keith T.A.; Millam J.M. GaussView 5.0, Wallingford, CT, 2009.

[36] Frisch M J, Trucks G W, Schlegel H B, Scuseria G E, Robb M A, Cheeseman J R, Scalmani G, Barone V, Mennucci B & Petersson G A, et al. Gaussian, Inc., Wallingford CT, 2010.

[37] Stephens, P. J., Devlin, F. J., Chabalowski, C. F., Frisch, M. J., 1994. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. J. Phys. Chem. 98, 11623-11627.

[38] Becke, A. D., 1993. Density functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 98, 5648-5652.

[39] Moores, A., Mezailles, N., Ricard, L., Jean, Y., le Floch, P., 2004. η2-Palladium and Platinum(II) Complexes of a λ4-Phosphinine Anion: Syntheses, X-ray Crystal Structures, and DFT Calculations. Organometallics. 23, 2870-2875.

[40] Lee, C., Yang, W., Parr, R. G., 1998. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B. 37, 785-789.

[41] Perdew, J. P., 1986. Density-functional approximation for the correlation energy of the inhomogeneous electron gas. Phys. Rev. B. 33, 8822-8824.

[42] Becke, A. D., 1988. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A. 38, 3098-3100.

[43] Perdew, J. P., Wang, Y., 1992. Accurate and simple analytic representation of the electron-gas correlation energy. Phys. Rev. B. 45, 13244-13249.

[44] Perdew, J. P., Burke, K., Wang, Y., 1996. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. Phys. Rev. B. 54, 16533-16539.

[45] Vosko, S. H., Wilk, L., Nusair, M., 1980. Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys., 58 (1980) 1200-1211.

[46] Ozimiński, W. P., Garnuszek, P., Bednarek, E., Cz Dobrowolski, J., 2007. The platinum complexes with histamine: Pt(II)(Hist)Cl2, Pt(II)(Iodo-Hist)Cl2 and Pt(IV)(Hist)2Cl2. Inorg. Chim. Acta. 360, 1902-1914.

[47] Zhang, L., Zhang, Y., Tao, H., Sun, X., Guo, Z., Zhu, L., 2002. Theoretical calculation on far-infrared spectra of some palladium(II) and platinum(II) halides: effect of theoretical methods and basis sets. J. Mol. Struct.: THEOCHEM. 617, 87-97.

[48] Karakaş, D., Sayin, K., 2013. DFT and TD-DFT studies on copper(II) complexes with tripodal tetramine ligands. Indian J. Chem. 52A, 480-485.

[49] Dunning Jr T H & Hay P J, in: Modern Theoretical Chemistry; Schaefer III H. F., Eds. Plenum, New York, (1976).

[50] Dolg, M., Stoll, H., Flad, H –J., Preuss, H., 1992. Ab initio pseudopotential study of Yb and YbO. J. Chem. Phys. 97, 1162-1173.

[51] Cao, X. Y., Dolg, M., 2002. Segmented contraction scheme for small-core lanthanide pseudopotential basis sets. J. Mol. Struct: THEOCHEM. 581, 139-147.

[52] Collins, J. B., Schleyer, P. V. R., Binkley, J. S., Pople, J. A., 1976. Self-consistent molecular orbital methods. XVII. Geometries and binding energies of second row molecules. A comparison of three basis sets. J. Chem. Phys. 64, 5142-5151.

[53] Hay, P. J., Wadt, W. R., 1985. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys., 82, 270-283.

[54] Kohara, S., Koura, N., Idemoto, Y., Takahashi, S., Saboungi, M. L., Curtiss, L. A., 1998. The Structure of LiKCO3 studied by ab initio calculations and raman spectroscopy. J. Phys. Chem. Solids, 59, 1477-1485.

[55] Stevens, W. J., Basch, H., Krauss, M., 1984. Compact effective potentials and efficient shared-exponent basis sets for the first and second row atoms. J. Chem. Phys. 81, 6026-6033.

[56] Stevens W J, Krauss M, Basch H, & Jasien P G, 1992. Relativistic compaxt effective potential and efficient, shared-exponent basis sets for third-, fourth- and fifth-row atoms. Can. J. Chem. 70, 612-630.

[57] Cundari, T. R., Stevens, W. J., 1993. Effective core potential methods for the lanthanides. J. Chem. Phys. 98, 5555.