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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

GEOMETRY OPTIMIZATION AND COMPARATIVE DFT STUDY OF (DIETHYLENETRIAMINE)BIS(THEOPHYLLINATO)ZINC(II) DIHYDRATE

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ABSTRACT. The paper reports on the molecular modelling of $[Zn(th)_2(dien)] \cdot 2H_2O$, which serves as the model compound for assessing metal–nucleobase interactions. The X-ray crystallographic data was completed by *ab initio* density functional theory. Structural parameters of the complex were investigated by using different methods: the unrestricted Becke three-parameter hybrid exchange functional, combined with the Lee–Yang–Parr correlation functional (B3LYP), the 6-311G(d,p), LANL2DZ, CRENBL, and DZVP basis sets applied for geometry optimizations.

***Keywords**: DFT, diethylenetriamine, theophylline, mixed ligand complexes, molecular modelling*

INTRODUCTION

The chemistry of metal complexes of theophylline (Scheme 1) has been extensively studied, mainly because of the capacity of these complexes to serve as model compounds for assessing the interaction between metal ions and oxopurine bases of nucleic acids. Previous research revealed that theophylline, *i.e.,* 1,3-dimethyl-2,6-dioxo-purine, is able to coordinate metal ions acting as a monodentate ligand *via* N7 in alkaline conditions [1–3] and *via* N9 in neutral conditions [4]; it can also form organometallic compounds *via* the C8 atom [5].

Several compounds in which theophylline acts as a bidentate ligand, forming N7/O6 chelates well also reported [6].

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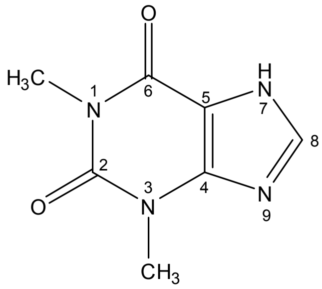


Scheme 1

In our research on coordination compounds with theophylline and various amines we reported the synthesis and characterization of several new mixed ligand complexes of Cu(II), Co(II) and Ni(II), containing the theophyllinato anion and 2-aminoethanol or benzylamine as co-ligands [7–10]. The synthesis of $[Zn(th)_2(dien)]\cdot 2H_2O$ and the corresponding X-Ray structure was also presented [11].

The aim of this work was the calculation of $[Zn(th)_2(dien)]\cdot 2H_2O$, at different levels of theory, in order to evaluate their accuracy by comparing them to experimental data. Results of geometry optimizations were in good agreement with the experimental values.

RESULTS AND DISCUSSION

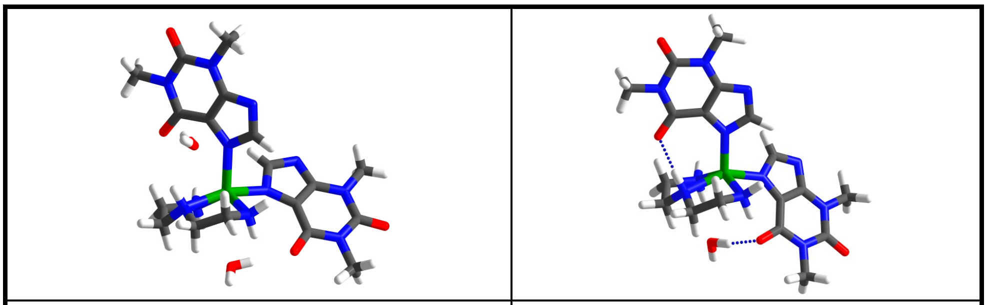
Computational details

Geometry optimizations were performed by using the density functional theory (DFT) using the unrestricted Becke three-parameter hybrid exchange functional, combined with the Lee–Yang–Parr correlation functional (B3LYP). The 6-311G(d,p) [12] full electron and LANL2DZ (Los Alamos National Laboratory 2 Double Zeta) [13, 14] effective core potential (ECP) basis sets are internal, while the CRENBL ECP (Christiansen's effective core potential) [15, 16] and DZVP (Double Zeta Valence with Polarization) [17] full electron basis sets were obtained from the Basis Set Exchange webpage [18]. The *Gaussian09* electronic structure program package was used for calculations [19]. Optimizations were performed with the standard convergency criteria of *Gaussian09*, followed by vibrational analysis to make certain that the obtained geometries are true minima.

Optimized geometries

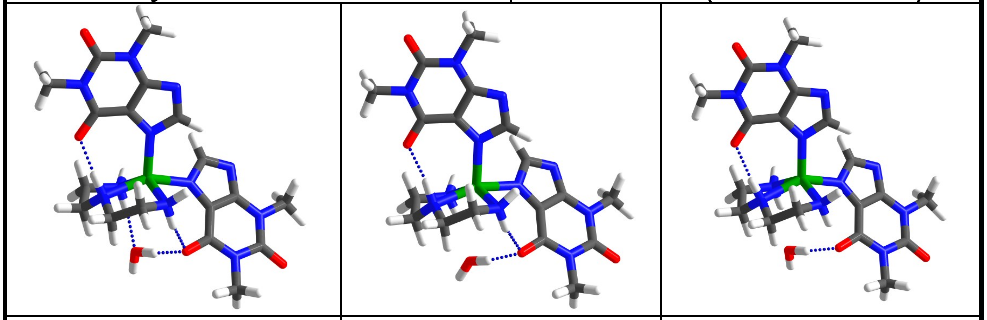
In the complex under study, the geometry around the pentacoordinated Zn(II) is a distorted trigonal bipyramide, consisting of three N atoms of the diethylenetriamine ligand and the N7 atom of each of the two theophyllinate moieties. The Zn–N_a distance found in the complex is longer than the Zn–N_e bond, corresponding to the typical appropriate distances found in trigonal bypiramidal structures. One of the two water molecules is positioned on the coordination axis, but relatively far from the central Zn(II) atom; consequently, it can be considered as being located outside the proper coordination sphere of Zn(II).

The molecular structure of $[Zn(th)_2(dien)]$ with the water molecule, closer to the metal ion, was optimized in the gaseous phase. The final geometries and the structure determined by X-Ray diffraction are displayed in Figure 1. In all cases there are two hydrogen bonds present in the optimized structures; one between the C6=O of the equatorial theophylline and the N_2–H of dien moiety and the other formed between the C6=O of the axial theophylline and the water molecule.



X-Ray molecular structure

Calculated (B3LYP/6-311G)**



Calculated (B3LYP/LANL2DZ)

Calculated (B3LYP/CRENBL ECP)

Calculated (B3LYP/DZVP)

Figure 1. X-Ray molecular structure of $[Zn(th)_2(dien)]\cdot 2H_2O$,
and the corresponding optimized structures.
(Color code: C – grey, N – blue, O – red, H – white, Zn – green)

The main geometrical parameters, optimized at different levels of theory, are listed in Table 1. Theoretical calculations revealed that the majority of optimized bond lengths are slightly longer than the experimental values.

This can be also considered as a consequence of having performed the theoretical calculations for an isolated molecule in gaseous phase, while the experimental results were recorded for the compound in solid state. Hydrogen bonds formation also contributes to the changes in geometry.

Our results suggest that the differences of bond lengths and bond angles between the experimental data and the predicted values are greater when using the DZVP basis set. According to the calculated values, the water molecule considered for optimization is located outside the coordination sphere. This statement is valid for all calculation techniques employed. Therefore, the Zn(II) atom is pentacoordinated, having distorted trigonal bipyramide geometry; hence, it cannot be considered as being hexacoordinated.

The mean error for angle values is greater, when using the DZVP basis set (see Table 1).

Table 1. Experimental and calculated geometry parameters.

	X-Ray	**6-311G(d,p)**	**LANL2DZ**	**CRENBL ECP**	**DZVP**
Distances (Å)					
Zn–N_a	2.120	2.087	2.159	2.127	2.110
Zn–N_e	2.074	2.031	2.097	2.142	2.049
Zn–N_1	2.084	2.161	2.183	2.204	2.199
Zn–N_2	2.220	2.215	2.242	2.246	2.244
Zn–N_3	2.092	2.175	2.201	2.231	2.207
Zn–O_w	3.190	3.735	3.639	3.592	3.819
Angles (°)					
N_a–Zn–N_e	95.5	104.2	102.0	96.1	105.3
N_a–Zn–N_1	93.3	91.2	90.8	92.1	90.8
N_a–Zn–N_2	165.1	151.9	154.1	161.7	149.6
N_a–Zn–N_3	97.2	94.0	92.9	95.2	93.9
N_e–Zn–N_1	119.6	114.9	118.5	116.9	115.5
N_e–Zn–N_3	101.9	101.2	101.8	96.8	101.8
N_1–Zn–N_3	135.9	140.9	137.8	144.6	139.5
N_e–Zn–O_w	171.6	166.7	170.0	171.8	167.0

N_a and N_e represent the N7 donor atom of theophylline ligands. The terminal N_1 and N_3 atoms of the dien ligand are in the equatorial plane, while the middle N_2 atom is located in an axial position. O_w designates the O atom of the nearer water molecule, opposite to the N_e position.

Reported data are in good agreement with the experimental ones, revealing that the CRENBL ECP and the B3LYP/LANL2DZ level of theory are suitable for the theoretical study of the system described above.

Vibrational analysis

Vibrational frequencies, calculated at the B3LYP/6-311G(d,p) level, were scaled by the typical factor 0.96. Several selected primary calculated harmonic frequencies are listed in Table 2, in comparison with the experimental data. The Gabedit program [20] was used for assigning the calculated harmonic frequencies.

The calculated values of the predicted harmonic vibrational frequencies are relatively close to the frequencies found in the experimental FTIR spectrum of the complex. The largest deviations occur for the B3LYP/CRENBL level of the theory.

It can be stated that the scaled frequencies of the DFT calculation are close to the corresponding FTIR vibration values, and that the DFT B3LYP method can predict accurately the vibrational frequencies for the system reported here.

Table 2. Comparison of the observed and calculated vibrational spectra.

Assignment	**Exp. IR (KBr)**	**Calcd. (B3LYP/ 6-311G(d,p))**	**Calcd. (B3LYP/ LANL2DZ)**	**Calcd. (B3LYP/ CRENBL ECP)**	**Calcd. (B3LYP/ DZVP)**
O−H str.	3496.31	3879.32 3528.82	3807.36	4216.31 3595.80	3828.73 3507.71
N−H str.	3353.6 3318.89 3272.61	3398.88 3391.68	3563.28 3559.56 3364.38 3298.10 3275.40	3739.65 3737.18 3492.71 3492.71–3451.96	3548.90 3548.64 3405.40 3393.47 3359.62
C−H str.	2940.91	3232.66–3005.89	3306.03 3296.73 3216.05–3022.41	3207.59–3058.50	3254.30–3027.60
C=O str.	1685.48 1664.27 1635.34	1758.63 1755.57	1668.08 1663.69	1864.99 1861.81 1787.50	1747.37 1744.49

CONCLUSIONS

Our calculations revealed that the utilized techniques were efficient in optimizing structural geometries of systems based on organic molecules and transition metal ions, such as Zn(II). The best calculation precision of the geometry parameters was obtained for the B3LYP/CRENBL ECP and B3LYP/LANL2DZ level of the theory.

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REFERENCES

1. N. S. Begum, H. Manohar, *Polyhedron*, **1994**, *13*, 307.
2. W. J. Birdsall, M. S. Zitzman, *J. Inorg. Nucl. Chem.*, **1979**, *41*, 116.
3. W. J. Birdsall, *Inorg. Chim. Acta*, **1985**, *99*, 59.
4. E. M. Griffith, E. L. Amma, *J. Chem. Soc., Chem. Commun.,* **1979***, 322.*
5. A. Romerosa, J. Suarez-Varela, M. A. Hidalgo, J. C. Avila-Roson, E. Colacio, *Inorg. Chem.*, **1997**, *36*, 3784.
6. D. J. Szalda, T. J. Kistenmacher, L. *G.* Marzilli, *J. Am. Chem. Soc.*, **1976**, *98 (26)*, 8371.
7. P. Bombicz, J. Madarász, E. Forizs, I. Foch, *Polyhedron*, **1997**, *16*, 3601.
8. S. Gál, J. Madarász, E. Forizs, I. Labádi, V. Izvekov, G. Pokol, *J. Therm. Anal. Cal.*, **1998**, *53*, 343.
9. E. Forizs, L. David, O. Cozar, V. Chiş, G. Damian, J. Csibi, *J. Mol. Struct.*, **1999**, *482*, 143.
10. B. Mihály, E. Forizs, I. Silaghi-Dumitrescu, *Studia Univ. Babes-Bolyai, Chemia,* **2007**, *LII*, *4*, 111.
11. B. Mihály, E. Forizs, A.-Z. Kun, I. Silaghi-Dumitrescu, *Acta Cryst.*, **2009**, *E65*, m579.
12. L. A. Curtiss, M. P. McGrath, J-P. Blandeau, N. E. Davis, R. C. Binning, Jr. L. Radom, *J. Chem. Phys.,* **1995**, *103*, 6104.
13. T. H. Dunning Jr., P. J. Hay, “Methods of Electronic Structure Theory”, Ed. H. F. Schaefer III., Plenum, New York, **1977**.
14. P. J. Hay, W. R. Wadt, *J. Chem. Phys.*, **1985**, *82*, 284.
15. M. M. Hurley, L. F. Pacios, P. A. Christiansen, R. B. Ross, W. C. J. Ermler, *Chem. Phys.*, **1986**, *84*, 6840.
16. L. A. LaJohn, P. A. Christiansen, R. B. Ross, T. Atashroo, W. C. J. Ermler, *Chem. Phys.*, **1987**, *87*, 2812.
17. N. Godbout, D. R. Salahub, J. Andzelm, E. Wimmer, *Can. J. Chem.*, **1992**, *70*, 560.
18. K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, *J. Chem. Inf. Model.*, **2007**, *47(3)*, 1045. https://bse.pnl.gov/bse/portal

19. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, **2009**.
20. A. R. Allouche, Gabedit 2.2.11., http://gabedit.sourceforge.net