NOVEL OXIDATION DEGREE – Zn^{+3} IN THE MACROCYCLIC COMPOUND WITH *TRANS*-DI[BENZO]PORPHYRAZINE AND FLUORIDE LIGAND: QUANTUM-CHEMICAL CONSIDERATION

Oleg V. Mikhailov[a]* and Denis V. Chachkov[b]

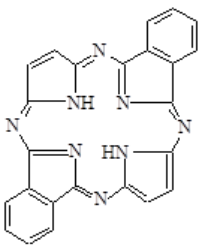
Keywords: zinc(III), fluoride ligand, di[benzo]porphyrazine, DFT method.

Based on the results of a quantum chemical calculation using two variants of the DFT method, the possibility of the existence of a zinc heteroligand complex with *trans*-dibenzoporphyrazine and fluoride ion where oxidation degree of zinc is +3 that is unusual for the given chemical element, have been shown. The data on the key structural parameters and multiplicity of the ground state of this complex have been presented, too.

* Corresponding Authors
E-Mail: olegmkhlv@gmail.com
[a] Kazan National Research Technological University, K. Marx Street 68, 420015 Kazan, Russia
[b] Kazan Department of Joint Supercomputer Center of Russian Academy of Sciences – Branch of Federal Scientific Center"Scientific Research Institute for System Analysis of the RAS", Lobachevski Street 2/31, 420111 Kazan, Russia

INTRODUCTION

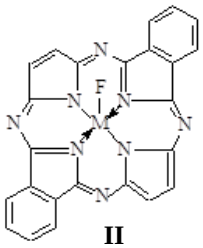
As it is well known for long time, the lightest of the d-elements of the Group II (XII) of the Mendeleev Periodic System of Chemical Elements, zinc, in all its chemical compounds, simple as well as coordination, has oxidation state of +2. The existence of compounds of Zn with higher oxidation states remains unproved in the experiment up to now.[1,2] A non-empirical quantum-chemical calculation revealed a very small probability of their existence, at least for ZnF_4, where this element has an oxidation state of +4.[3] Nevertheless, based on these data, we cannot exclude the possibility of the existence of zinc compounds with an intermediate oxidation state between +2 and +4, namely +3, which, in principle, may be realized in any macrocyclic coordination compounds containing ligands with fluorine donor atoms having a sufficiently high electronegativity.[4] On the other hand, such macrocyclic (NNNN)-donor atomic ligands as porphyrazine derivatives, in particular *trans*-di[benzo]porphyrazine (**I**), are capable of stabilizing the most diverse oxidation states of *d*-elements low as well as high. [5-9]



I

Figure 1. Strucutre of t*rans*-di[benzo]porphyrazine**.**

Therefore, it seems appropriate to use for the stabilization of the above oxidation state of zinc namely the combination of these two ligands which takes place in complexes of type **II** containing one F^- anion and double deprotonated form of *trans*-di[benzo]porphyrazine (where M is the atom of the *d*-element, in particular, Zn). At the present time, there is no information about such coordination compounds in the literature; however, it is possible to estimate the probability of their existence using modern quantum chemical calculation methods. This paper has been devoted to theoretical consideration of the given question.



II

Figure 2. Proposed structure of Zn(III) complex.

CALCULATION METHOD

Quantum-chemical calculations were performed by the two versions of DFT method. In the first of them (OPBE/TZVP), combining the common TZVP extended triple zeta split-valence basis set[10,11] and the OPBE non-hybrid functional,[12,13] which as shown earlier,[13–17] predicts in the case of 3*d* elements more adequately the relative energy stabilities of high-spin and low-spin states, and reliably characterizes key geometric parameters of corresponding molecular structures. In the second, B3PW91/TZVP, combining the common TZVP and B3PW91 functional,[18,19] which according to data,[20] has minimal value of so-called "normal error" in comparison with other variants of DFT method. This conclusion is in full harmony with the data of structural parameters of macrocyclic complexes of various 3*d*-elements with phthalocyanine obtained as a result of various DFT

quantum-chemical calculations and in experiment (see Supplemental material). Calculations were performed with the Gaussian09 program package.[21] The correspondence of the found stationary points to energy minima was proved in all cases by the calculation of second derivatives of energy with respect to atom coordinates. All equilibrium structures corresponding to minima of the potential energy surfaces had only real positive frequency values. Zn^{+3} has $3d^9$ electronic configuration, and, in this connection, spin multiplicities 2 and 4 were considered in calculation. Among the structures optimized at these multiplicities, the lowest-lying structure was selected. Parameters of molecular structures with the given multiplicities were calculated by the unrestricted methods (UOPBE and UB3PW91, respectively).

RESULTS AND DISCUSSION

According to the data obtained by us as a result of the quantum-chemical calculation carried out using the DFT OPBE/TZVP method as well as the DFT method B3PW91/TZVP, the Zn(III) complex of type **II** is capable to self-existence, at least in the gas phase. Molecular structure of this complex obtained by DFT B3PW91/TZV method, is shown in figure 1.

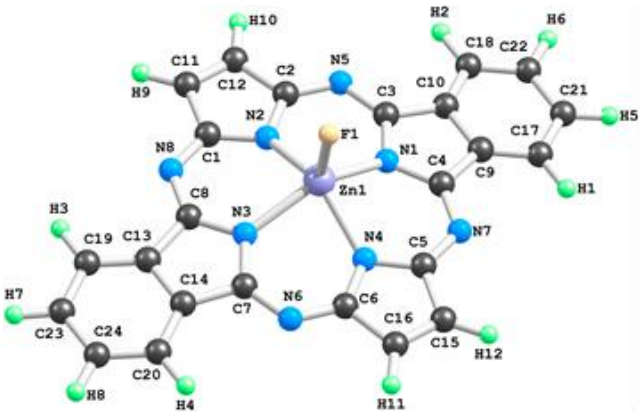


Figure 3. Molecular structure of Zn(III) complex of type **II** obtained by means of DFT B3PW91/TZVP quantum-chemical calculation.

Its molecular structure obtained by the DFT OPBE/TZVP method looks similar. The calculated chemical bond lengths between atoms and bond angles for this compound are presented in Table 1. It is apparent from these data that both the methods used by us give almost identical data for all structural parameters indicated above. As it can be seen from figure 3, the complex under examination has a tetragonal-pyramidal structure of the ZnN_4 chelate node with identical bond angles (NZnN), but rather such a significant (almost 30º) deviation from co-planarity. However, the grouping of nitrogen atoms (N1N2N3N4), which is part of the chelate node, is almost flat (deviation from coplanarity is only 0.2º). The Zn–N bond lengths in the chelate node are equal to each other only in pairs, but the difference between them is insignificant (Table 1). All four 6-membered metal-chelate rings are completely identically to each other in the lengths of bonds between the corresponding atoms as well as in the range of bond angles in them.

Table 1. Bond lengths and bond angles in the Zn(III) complex of type **II.**

Structural parameter	Calculated	
	DFT OPBE/TZVP	DFT B3PW91/TZVP
Zn–N bond lengths in chelate node, pm		
Zn1N1	210.1	210.0
Zn1N2	210.8	207.6
Zn1N3	210.1	210.0
Zn1N4	210.8	207.6
Bond angles in chelate node ZnN_4, *deg*		
(N1Zn1N2)	83.1	83.2
(N2Zn1N3)	83.1	83.2
(N3Zn1N4)	83.1	83.2
(N4Zn1N1)	83.1	83.2
Bond angles sum (BAS), *deg*	332.4	332.8
Non-bond angles between N atoms in N_4 grouping, *deg*		
(N1N2N3)	87.7	91.2
(N2N3N4)	91.9	88.8
(N3N4N1)	87.7	91.2
(N4N1N2)	91.9	88.8
Non-bond angles sum (NBAS), *deg*	359.2	360.0
Bond angles in 6-numbered ring (Zn1N1C4N7C5N4), *deg*		
(Zn1N1C4)	121.5	124.6
(N1C4N7)	127.2	127.7
(C4N7C5)	123.1	123.0
(N7C5N4)	127.3	127.8
(C5N4Zn1)	125.5	124.5
(N4Zn1N1)	83.1	83.2
Bond angles sum (BAS^6), *deg*	707.7	710.8
Bond angles in 5-numbered ring (C3N1C4C9C10), *deg*		
(C3N1C4)	106.8	109.2
(N1C4C9)	110.3	109.4
(C4C9C10)	106.3	106.0
(C9C10C3)	106.3	106.0
(C10C3N1)	110.3	109.4
Bond angles sum (BAS^5), *deg*	540.0	540.0
C–N bond lengths in 6-numbered chelate rings, *pm*		
N1C3	135.8	135.4
N1C4	135.8	135.4
N2C1	135.8	135.2
N2C2	135.8	135.2
N7C4	133.1	132.7
N7C5	133.1	132.6
C–C bond lengths in 5-numbered ring, *pm*		
C4C9	147.1	146.9
C9C10	135.2	140.0
C10C3	147.1	146.9
Zn–F bond length, *pm*		
Zn1F1	186.2	185.4
Bond angles between fluorine, copper and nitrogen atoms, *deg*		
F1Zn1N1	113.1	109.5
F1Zn1N2	108.0	110.8
F1Zn1N3	113.1	109.5
F1Zn1N4	107.9	110.9

A similar situation occurs for four 5-membered non-chelate rings with one nitrogen atom and four carbon atoms adjoining to 6-membered metal chelate rings. Besides, the 5-membered rings are coplanar, while the 6-membered ones are non-coplanar, the deviation from coplanarity in them depending used calculation method and is 12.3° (OPBE/TZVP) and 9.2° (B3PW91/TZVP) (Table 1). As can be seen when comparing the data obtained in the calculations using the above-listed DFT method variants (Table 1), each of the DFT method variants we used gives own individual (although slightly different) sets of bond angles in chelate nodes, metal chelate rings as well as non-chelate 5-membered cycles. However, the sums of these angles in each of these calculation methods are fully identical to each other.

The zinc-donor nitrogen atom and zinc-fluorine interatomic distances (Table 1) correspond in their size to single bonds Zn–N and Zn–F. The facts noted above, as well as the fact that the lengths of Zn–N and Zn–F bonds are different among themselves, allow us to assign the compound Zn(III) under study to the category of tetragonal pyramidal complexes (Figure 3). Besides, the bond angles formed by the fluorine, zinc atoms and the donor nitrogen atoms of the chelate site are slightly different from each other (although they are equal to each other in pairs). The given complex does not have a center of symmetry and therefore, for it a priori one can expect a sufficiently large value of the electric moment of the dipole. Indeed, the data for calculating this parameter (5.61 Debye units according to DFT OPBE/TZVP and 5.51 Debye units according to DFT B3PW91/TZVP) are in full accordance with such an expectation.

According to the data of our calculations, the ground state of the Zn(III) heteroligand complex containing *trans*-di[benzo]porphyrazine and F^- ion under examination according to both calculation methods used here is a spin doublet. It is quite expected for tetragonal-pyramidal complexes with $3d^9$ configuration, and a coordination number of a metal ion equal to 5. Besides, according to the data of both these methods, the nearest excited quartet state has much higher energy (by 157.4 kJ mol^{-1} in the case of DFT OPBE/TZVP and 192.8 kJ mol^{-1} in the case of DFT B3PW91/TZVP), which apparently, makes it impossible an availability of spin-crossover in this complex.

CONCLUSION

As can be seen from the data presented above, both variants of the DFT method used by us in this work, namely OPBE/TZVP and B3PW91/TZVP, quite definitely give evidence about the possibility of the existence of Zn(III) complex, namely [Zn**L**F] containing fluorine anion (F^-) and double deprotonated form ($\mathbf{L}^{2-}$) of *trans*-dibenzoporphyrazine ($H_2\mathbf{L}$). It should be noted in this connection that, according to our calculations of standard thermodynamic parameters $\Delta H^0_{f,\,298}$, $S^0_{f,\,298}$ and $\Delta G^0_{f,\,298}$ of the complex under study using described method,[22] all they are positive (298.7 kJ mol^{-1}, 959.0 kJ mol^{-1} K^{-1} and 515.4 kJ mol^{-1}, respectively) and hence, the given compound cannot be obtained from simple substances formed by chemical elements containing in its composition (zinc, fluorine, nitrogen, carbon and hydrogen). Nevertheless, both variants of the DFT method used by us, namely OPBE/TZVP and B3PW91/TZVP, predict the possibility of the existence of this complex, and the point is now to prepare it experimentally.

FUNDING INFORMATION

All quantum-chemical calculations were performed at the Kazan Department of Joint Supercomputer Center of Russian Academy of Sciences, Branch of Federal Scientific Center “Scientific Research Institute for System Analysis of the RAS”. Contribution of author D. V. Chachkov was funded by the state assignment to the Federal State Institution "Scientific Research Institute for System Analysis of the Russian Academy of Sciences" for scientific research.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest, financial or otherwise.

REFERENCES

[1]Wikipedia. Compounds of zinc. Web-site https://en.wikipedia.org/wiki/ Compounds_of_zinc

[2]Kiselev, Yu. M, Tretiyakov, Yu. D. The problem of oxidation state stabilisation and some regularities of a Periodic system of the elements, *Russ. Chem. Revs.*, **1999**, *68(5)*, 365-379. https://doi.org/10.1070/RC1999v068n05ABEH000496

[3]Kaupp, M., Dolg, M., Stoll, H., Von Schnering, H. G. Oxidation State +IV in Group 12 Chemistry. Ab Initio Study of zinc(IV), cadmium(IV), and mercury(IV) Fluorides, *Inorg. Chem*., **1994**, *33(10)*, 2122–2131. https://doi.org/10.1021/ic00088a012

[4]Grannec, J., *J. Fluorine Chem*. Some physical properties of d-transition metal fluorides in unusual oxidation states, **1984**, *25(1)*, 83-90. https://doi.org/10.1016/S0022-1139(00)81198-7

[5]Thomas, A. L. *Phthalocyanines. Research & Applications*, CRC Press, 1990.

[6]Sliwa, W., Mianovska, B., Metalloporphyrin arrays, *Transit. Met. Chem*., **2000**, *25(5)*, 491-504. https://doi.org/10.1023/A:1007054025169

[7]Mamardashvili, G. M., Mamardashvili, N. Z., Koifman, O. I., Self-assembling systems based on porphirins, *Russ. Chem. Revs*. **2008**, *77(1)*, 59-75. https://doi.org/10.1070/RC2008v077n01ABEH003743

[8]Lomova, T. N., *Axial coordinated metal porphyrins in science and practice*, URSS, Moscow, **2018**.

[9]Khelevina, O. G., Malyasova, A. S., 40 years with porphyrazines, *J. Porph. Phthalocyanines*, **2019**, *23(11)*, 1261-1264. https://doi.org/10.1142/S1088424619300246

[10]Schaefer, A., Horn, H., Ahlrichs, R., Fully optimized contracted Gaussian basis sets for atoms Li to Kr, *J. Chem. Phys*. **1992**, *97 (4)*, 2571-2577. https://doi.org/10.1063/1.463096

[11]Schaefer, A., Huber, C., Ahlrichs, R., Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr, *J. Chem. Phys*., **1994**, *100(8)*, 5829-5835. https://doi.org/10.1063/1.467146

[12]Hoe, W. M., Cohen, A., Handy, N. C., Assessment of a new local exchange functional OPTX, *Chem. Phys. Lett*., **2001**, *341(3-4)*, 319-328. https://doi.org/10.1016/S0009-2614(01)00581-4

[13]Perdew, J. P., Burke, K., Ernzerhof, M., Generalized Gradient Approximation Made Simple, *Phys. Rev. Lett*., **1997**, *78(7)*, 1396-1396. https://doi.org/10.1103/PhysRevLett.78.1396

[14]Paulsen, H., Duelund, L., Winkler, H., Toftlund, H., Trautwein, A. X., Free Energy of Spin-Crossover Complexes Calculated with Density Functional Methods, *Inorg. Chem*., **2001**, *40(9)*, 2201-2203. https://doi.org/10.1021/ic000954q

[15]Swart, M., Groenhof, A. R., Ehlers, A. W., Lammertsma, K., Validation of Exchange−Correlation Functionals for Spin States of Iron Complexes, *J. Phys. Chem. A*, **2004**, *108(25)*, 5479-5483. https://doi.org/10.1021/jp049043i

[16]Swart, M., Ehlers, A. W., Lammertsma, K., Performance of the OPBE exchange-correlation functional, *Mol. Phys*. **2004**, *102(23)*, 2467-2474. https://doi.org/10.1080/00268970420002750l7

[17]Swart, M., Metal–ligand bonding in metallocenes: Differentiation between spin state, electrostatic and covalent bonding, *Inorg. Chim. Acta*, **2007**, *360(1)*, 179-189. https://doi.org/10.1016/j.ica.2006.07.073

[18]Becke, A. D., Density-functional exchange-energy approximation with correct asymptotic behavior, *Phys. Rev. A*, **1988**, *38(6)*, 3098-3100. https://doi.org/10.1103/PhysRevA.38.3098

[19]Perdew, J. P., Burke, K., Wang, Y., Generalized gradient approximation for the exchange-correlation hole of a many-electron system, *Phys. Rev. B*, **1996**, *54*(23), 16533-16539.https://doi.org/10.1103/PhysRevB.54.16533

[20]Medvedev, M. G., Bushmarinov, I. S., Sun, J., Perdew, J. P., Lyssenko, K. A., Density functional theory is straying from the path toward the exact functional, *Science*, **2017**, *355(6320)*, 49-52. https://doi.org/10.1126/science.aah5975

[21]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., Nakatsuji H., Caricato M., Li H., Hratchian H. P., Izmaylov A. F., Bloino J., Zheng G., Sonnenberg J. L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J. A., Jr., Peralta J. E., Ogliaro F., Bearpark M., Heyd J. J., Brothers E., Kudin K. N., Staroverov V. N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J. C., Iyengar S. S., Tomasi J., Cossi M., Rega N., Millam J. M., Klene M., Knox J. E., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Martin R. L., Morokuma K., Zakrzewski V. G., Voth G. A., Salvador P., Dannenberg J .J., Dapprich S., Daniels A. D., Farkas O., Foresman J. B., Ortiz J. V., Cioslowski J., Fox D. J., Gaussian 09, Revision A.01, Gaussian, Inc., Wallingford CT, **2009**.

[22]Ochterski, J. W., *Thermochemistry in Gaussian*, Gaussian, Inc., Wallingford CT, **2000**.

Received: 02.02.2020.
Accepted: 25.05.2020.