Reference Object Identifier – ROI: jbc-01/17-49-1-21
The Digital Object Identifier – DOI: 10.37952/ROI-jbc-01/17-49-1-21
Submitted on January 17, 2017.

Stability row for heavy-metal complexes (Zn, Co, Cd, and Pb) with phospholipids: a DFT study

© **Sergey A. Peshkov**,[1+] and **Sergey L. Khursan**[2*]
[1] *Department of Chemistry. Orenburg State University. Pobedy Ave., 13. Orenburg, 460018. Orenburg Region, Russia. Phone/fax: +7 (929) 283-23-72. E-mail: Darvin156@mail.ru*
[2] *Laboratory of Chemical Physics. Ufa Institute of Chemistry of Russian Academy of Sciences. Oktyabrya Ave, 71. Ufa, 450054. Republic of Bashkortostan. Russia. Phone/fax: +7 (347) 235-60-66. E-mail: KhursanSL@anrb.ru*

*Supervising author; +Corresponding author

Keywords: phospholipids, metal ions, energy of complexation.

Abstract

A theoretical modelling of complexation of divalent metal ions (Zn, Co, Cd, Pb) with phospholipids has been performed within the all-electron approximation B3LYP/DZP. The optimal structures of the complexes with analogs of phosphatidylserine, phosphatidylethanolamine and phosphatidylcholine have been found (molecules of complexation agents have methyl groups instead of the lipophilic hydrocarbon chains, which do not participate in complexing). The stabilities of the formed compounds are characterized with the total energies including solvation corrections calculated in terms of the continuum model IEFPCM-SMD. The relative energies (ΔE) provide the following series of stability of metal–phospholipid complexes: Cd > Pb > Co ≈ Zn. The calculations show that metal cations are selectively coordinated toward the oxygen atoms bonded with phosphorus. In two possible modes of coordination phospholipid molecules behave as bi- or monodentate ligands. In the first case, the structures of the complexes are close to tetrahedral one of the Zn and Co ions. The bidentate lead complexes have pyramidal structures. In the case of the phosphates as monodentate ligands, the chain structure O-Me-O is formed, nonlinear for the lead complexes and linear for other metals. As found, formation energies of the monodentate Zn and Co complexes are lower than the respective values for the bidentate tetrahedral complexes. An opposite situation is observed in the case of the lead complexes. We find a correlation of the obtained results with experimental regularities of bioaccumulation of the heavy-metal salts by bacteria *Bacillus*. The experimental and theoretical row of activity of heavy metals are consistent except the Cd salts, which reveal strong complexation but low concentration of the metal upon accumulation. A probable reason for this inconsistence has been assumed: accordingly, low level of the cadmium bioaccumulation is caused by its extremal toxicity toward the studied bacillus strains.

References

[1] I.T. Paulsen, Jr M.H. Saier. A novel family of ubiquitous heavy metal ion transport proteins. *The Journal of Membrane Biology*. **1997**. Vol.156. No.2. P.99-103.
[2] A.A. Subakov, E.N. Patova, M.D. Sivkov, E.A. Mikhaylova, L.R. Zubkova. General chemical characteristics of polysaccharides and amino acids of cyanobacterium Nostoc commune Vauch. from the Arctic latitudes. *Butlerov Communications*. **2016**. Vol.47. No.9. P.143-149. DOI: 10.37952/ROI-jbc-01/16-47-9-143
[3] S.A. Peshkov, A.S. Schepin, S.L. Khursan, G.I. Kobzev. Relative stability of the heavy metal (Zn, Cd, Co, Pb) complexes with alanine. *Bulletin of Bashkir University*. **2016**. Vol.21. No.2. P.291-297.
[4] R.R. Kayumova, S.A. Peshkov, S.S. Ostakhov, S.L. Khursan. Concerning the relation of the fluorescence quenching efficiency of tryptophane by heavy metal ions to the efficiency of their bioaccumulation by certain strains of *Bacillus* bacteria. *High Energy Chemistry.* **2017**. Vol.51. No.1. P.80-82.
[5] S.A. Peshkov, A.N. Sizentsov. Bioaccumulation of heavy metals by microorganisms of probiotic pharmaceuticals under *in vitro* conditions. *Bulletin of Orenburg University.* **2013**. No.10. P.142-144.
[6] P.L. Yeagle. Lipid regulation of cell membrane structure and function. *The FASEB Journal.* **1989**. Vol.3. No.7. P.1833-1842.

[7] K.M. Makarulina, I.G. Plaschina, M.V. Kozlov, L.N. Shishkina. Effect of the phospholipid composition on their aggregation in non-polar solvent. *Butlerov Communications*. **2011**. Vol.25. No.7. P.96-100. ROI: jbc-02/11-25-7-96

[8] A.D. Becke. Density - functional thermochemistry. III. The role of exact exchange. The Journal of Chemical Physics. **1993**. Vol.98. No.7. P.5648-5652.

[9] C. Lee, W. Yang, R.G. Parr. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B*. **1988**. Vol.37. No.2. P.785-789.

[10] A. Canal Neto, E.P. Muniz, R. Centoducatte, F.E. Jorge. Gaussian basis sets for correlated wave functions. Hydrogen, helium, first- and second-row atoms. *Journal of Molecular Structure: THEOCHEM.* **2005**. Vol.718. No.1-3. P.219-224.

[11] G.G. Camiletti, S.F. Machado, F.E. Jorge. Gaussian basis set of double zeta quality for atoms K through Kr: Application in DFT calculations of molecular properties. *Journal of Computational Chemistry.* **2008**. Vol.29. No.14. P.2434-2444.

[12] C.L. Barros, P.J.P. de Oliveira, F.E. Jorge, A. Canal Neto, M. Campos. Gaussian basis set of double zeta quality for atoms Rb through Xe: application in non-relativistic and relativistic calculations of atomic and molecular properties. *Molecular Physics*. **2010**. Vol.108. No.15. P.1965-1972.

[13] A. Canal Neto, F.E. Jorge. All-electron double zeta basis sets for the most fifth-row atoms: Application in DFT spectroscopic constant calculations. *Chemical Physics Letters*. **2013**. Vol.582. P.158-162.

[14] R.G. Parr. Density functional theory, in Electron Distributions and the Chemical Bond. *New York.: Plenum Press*. **1982**. P.95-100.

[15] J. Tomasi, B. Mennucci, R. Cammi. Quantum Mechanical Continuum Solvation Models. *Chemical Reviews*. **2005**. Vol.105. No.8. P.2999-3094.

[16] G.A. Andrienko. *ChemCraft, Version 1.8 http://www.chemcraftprog.com*.

[17] 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. Montgomery, J. A., 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, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox Gaussian 09, Revision C.1, Gaussian, Inc., *Wallingford CT.* **2009**.

[18] H.P. McNeil, C.N. Chesterman, S.A. Krilis. Immunology and clinical importance of antiphospholipid antibodies. *Advances in Immunology.* **1991**. Vol.49. P.193-280.