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How could a molybdenum metal atom get into biomolecules’ structure: mass spectrometry based version

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Modeling of formation of primary organic molecules in the course of prebiological biochemical evolution usually deals with assembling of H, C, O, N, S chemical elements. However, biomolecules of such importance as enzymes incorporate metal atoms. These could get into the structure of evolving organic molecules through direct contact with early Earth’s minerals. This step of biochemical evolution was proposed in the framework of the “iron world hypothesis”. Enzymatic activity of minerals was considered, whereas direct reactions of metal inclusion into organic molecules, to the best of our knowledge, were not modeled.

In our studies of bionanohybrids of the transition metal dichalcogenide MoS2, we have considered combinations of this mineral with various organic compounds and biomolecules probed by means of laser desorption/ionization (LDI) mass spectrometry [1]. None of the studied compounds have shown cluster ions or associates with the Mo atom or ion, with the only exception: thio-derivatives of nucleic acid bases 6-thiopurine (TP), 2-thioadenine, and 6-thioguanine. Along with the expected signals corresponding to individual components, products of the bases oxidation and MoS2-related clusters, a new group of peaks appeared in the LDI mass spectra of these three systems. As an example, for the (TP + MoS2) nanohybrid, this group was recorded at m/z 410 418 in the positive ion mode and m/z 408 416 in the negative ion mode. Isotopic distribution in the peak group evidenced the presence of one molybdenum atom, two nitrogen bases, and an oxygen atom in the structure, while the recording of these species in both positive and negative ion modes in the protonated and deprotonated forms, respectively, indicated their molecular nature. The presumed composition of this molecule as {(2TP − 2H) + Mo + O} was proposed. Modeling of possible structures using the DFT quantum chemical approach revealed a set of configurations in which the centered Mo atom binds to two sulfur and two nitrogen atoms of two TP bases, and to one oxygen atom.

Formation of such a molecule implies a step of extraction of the Mo atom from the MoS2 crystalline lattice and its covalent attachment to definite sulfur-containing heterocyclic organic molecules during the direct contact of these compounds in an aqueous medium. We believe this is the first case of observation of such a process, which may occur during the creation of precursors to molybdenum-containing enzymes. Our further studies are directed toward modeling MoS2 systems with the organic components of the present-day enzyme’s molybdenum-containing cofactors.

1. Kosevich M.V., Pashynska V.A., Shelkovsky V.S., Boryak O.A., Kuzema P.O., Karachevtsev V.A. On laser desorption/ionization mass spectrometric probing of nanocomposites of MoS2 with sulfur-containing organic compounds. Journal of Mass Spectrometry. (2025) 60(12) e5191 (pp 1-13).

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Primary authors: Prof. KOSEVICH, M.V. (B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine); Dr BORYAK, O.A. (B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine); Dr PASHYNSKA, V.A. (B. Verkin

Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine); Dr SHELKOVSKY, V.S. (B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine); Dr KUZEMA, P.O. (Chuiko Institute of Surface Chemistry of the National Academy of Sciences of Ukraine); Prof. STEPANIAN, S.G. (B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine); Prof. KARACHEVTSEV, V.A. (B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine)

Presenter: Prof. KOSEVICH, M.V. (B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine)