OPINION

on the dissertation work, for the acquisition of the scientific degree of "Doctor of Sciences"

Author of the dissertation work: Rumyana Zlatinova Yankova-Avramova

Topic of the dissertation work: Structure and functional properties of oxoselenates (IV, VI)

Member of the scientific jury: Prof. DSc Panteley Denev

Relevance of the problem developed in the dissertation in scientific and applied terms

The presented dissertation deals with the structure and functional properties of oxoselenates (IV, VI). Selenium-containing compounds represent a dynamically developing research area with high scientific and applied value. They are characterized by a rich structural diversity, determined by the flexible coordination capabilities of selenate anions and the influence of coordinating metals on the crystal architecture. This structural diversity is the basis of a wide range of functional properties - magnetic, optical, nonlinear-optical, catalytic, thermal and biological.

Modern data indicate that double selenates and selenites with transition metals have significant potential for application both in the field of materials science - as nonlinear optical materials, catalysts and functional nanostructures, and in biomedicine - as sources of biologically active selenium, antioxidants and potential antitumor agents. Of particular note are the complex dependencies between the type of coordinating metal and the manifestation of structural, thermal and optical characteristics, which directly affect the biological activity of these compounds.

The goal and tasks set by Prof. Yankova in this dissertation are fully justified, and the results obtained will contribute to deepening the understanding of the relationship between the structure, physicochemical properties and biological activity of these compounds, as well as to opening up prospects for their application in optoelectronics and medicine.

Degree of knowledge of the state of the problem and the literary material

The first substantial part of the dissertation is a well-structured and developed literature review, dedicated to the current problem with which the dissertationist's scientific research is engaged. This part testifies to the good and in-depth knowledge of the problem by Prof. Rumyana Yankova, which allowed her to further develop the scientific research correctly. 339 literary sources are cited.

The literature review presents the characteristics of selenium and its properties, as well as the properties and applications of selenites and selenates and their double compounds as biologically active substances.

The similarities and differences between the various parameters of selenium in biological systems are examined in detail and compared. The main organic forms and their content in plant and food products, their geographical distribution, the required daily intake are presented in a generalized form. The therapeutic effect, antitumor and antibacterial effects, antioxidant activity and rejuvenating stimuli are noted. Attention is also paid to its toxicity, at increased daily doses of intake.

A detailed analysis of the literature on the progress in synthetic methods in recent decades and the targeted preparation of a wide range of new selenium compounds with diverse physicochemical and biological characteristics, possessing unique structural and functional features, has been made. These materials find application in a number of fields – from the glass and ceramic industries, through semiconductor technology and microelectronics, to the pharmaceutical industry and agrochemistry. The growing interest in oxoselenates (IV, VI) is due not only to their optical, magnetic and catalytic properties, but also to the possibility of structural modification in order to optimize their functional characteristics for specific applications.

The reviewed sources show that nanoforms of selenium compounds, including silver nanoparticles, silver selenate and selenium-containing metal oxides, combine high biological activity with potential for targeted delivery and diagnostic applications.

The review section concludes with a justification of the purpose of the dissertation work and the tasks arising from it.

Compliance of the chosen research methodology with the set goal and objectives of the dissertation work

Prof. R. Yankova knows the state of the problem in detail, which allows her to choose an appropriate methodology for conducting the scientific research and for answering the goal and tasks that she has set for herself. In a logical sequence, 15 selenium compounds were synthesized: selenites, selenates, as well as double salts of alkali metals with d- and f-elements, which were dried, purified and characterized with the known modern methods and equipment.

The formulated goal and the tasks set fully correspond to the used chemical, instrumental methods (X-ray structural analysis (SCXRD), differential scanning calorimetry (DSC), UV-vis and IR spectroscopy) and the methods for determining biological activity: cell survival (Crystal violet), cell morphology (Crystal violet), zeta-potential and size, staining for actin. The obtained experimental data were competently processed by quantum chemical computer calculations: of the molecular electrostatic potential, analysis of frontier molecular orbitals, analysis of the Hirschfeld surface,

Analysis of the Reduced Density Gradient (RDG), DFT calculations of the nonlinear optical properties.

Contributions of the dissertation work

By the originality of its formulation, the conducted experimental studies can be attributed to the formulation and justification of a new scientific problem, in which the principles of "green chemistry" are applied. In the course of her scientific research, Prof. Yankova has proposed new methods and original scientific approaches, obtained new facts and developed new technological solutions.

Some of the main contributions of the dissertation work are:

• ***Scientific contributions***

• Structural characterization of the alkali and transition metal oxoselenates synthesized by the doctoral candidate was performed, and the influence of the size of the alkali cation and the electronic configuration of the transition metal on the coordination sphere and the stability of the crystal lattice was demonstrated.

• AIM and NBO analyses proved that the studied oxoselenates form stabilizing hydrogen-bonding networks.

• The dependence between the number and nature of water molecules and the initial dehydration temperature was clarified.

• The biological activity of some of the synthesized compounds was determined and it was shown that they have potential applications in oncotherapy as a promising anticancer agent.

• A unified experimental-theoretical methodology has been established, developing a consistent approach including hydrothermal synthesis, X-ray structural analysis, infrared and thermal analysis, combined with quantum chemical modeling (DFT, NBO, AIM, RDG), which provides a complete connection between experimental and theoretical data.

Applied contributions

• Some of the studied compounds have proven potential as nonlinear optical materials due to their high primary hyperpolarizability, which makes them suitable for the development of new photonic and laser devices or can be used to generate nonlinear optical effects.

• Oxoselenates exhibit ionic conductivity, which opens up possibilities for their application as solid-state electrolytes in batteries and ion-conducting materials.

• Iron- and cobalt-containing selenates demonstrate electronic delocalization and redox activity, which makes them promising as catalysts in oxidation-reduction processes, including in organic synthesis and environmentally significant reactions.

• The established high cytotoxic activity and the ability to form negatively charged nanoparticles with a stable zeta potential from some selenates make them potential candidates for inclusion in nanomedical platforms with targeted action.

• Double selenates with alkali and transition metals can find their ecological application as sorbents and stabilizers for selective retention of pollutants (water, heavy metals, polar molecules).

• The proposed regression models and the determined kinetic parameters of decomposition can be used to predict the behavior of selenite and selenate materials upon heating, which has practical significance for ceramic, glass-ceramic and catalyst technologies.

Assessment of dissertation publications

The results of the dissertation work are presented in 20 scientific publications in journals that are referenced and indexed in world-renowned databases of scientific information (Web of Science and Scopus). Prof. Yankova has participated in 9 national scientific projects, is the head of 3 scientific projects of national importance and has published 3 university textbooks.

A list of 96 citations in scientific journals, referenced and indexed in world-renowned databases of scientific information, is presented, which is evidence of the originality of the results obtained.

With the presented 821.4 points for scientometric indicators, Prof. Dr. Rumyana Zlatinova Yankova meets the minimum requirements provided for in the PPRASRB of 350 points, as well as those of the BSU "Prof. Dr. Asen Zlatarov" of 700 points. I declare that I have not identified any element of plagiarism in the presented scientific materials.

Opinions, recommendations and notes

The high scientific level at which the dissertation is presented shows that Prof. Yankova is a scientist with in-depth knowledge both in the field of inorganic chemistry and physical chemistry, and in the chemistry of biologically active substances. The dissertation contains 391 standard pages, 75 tables and 117 figures. The bibliography includes 339 literary sources. This confirms the value of the dissertation, which remains both with the scientific contributions of the studies included in it, and with the precise formulation of the materials related to these studies.

Conclusion

The presented dissertation work examines the current problem of the structure, functional properties and application of oxoselenates (IV, VI). As a result of the research

conducted at a high scientific level, original scientific results have been obtained and significant scientific and applied scientific contributions have been made in the field of chemistry of oxoselenate compounds. I firmly believe that the requirements of the Act on the Development of Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the Regulations of the Bulgarian State University "Prof. Dr. Asen Zlatarov" for the implementation of the Act have been met.

After the analysis, I give a positive assessment of the developed dissertation work and vote for Prof. Dr. Rumyana Zlatinova Yankova-Avramova to acquire the scientific degree "Doctor of Sciences" in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.2. Chemical Sciences, scientific field "Inorganic Chemistry".

Prepared the opinion:

Prof. DSc. Panteley Denev