**Name of the course:** “The theory, structure and magneto-chemistry of coordination compounds”

**Department responsible for the course or equivalent:** Dpt of Chemistry

**Lecturer (name, academic title, e-mail):** Prof. Lukov V.V., vlukov@mail.ru, Dr. Morozov A.N. (mrzv\_61@mail.ru),

**Semester when the course unit is delivered:** 3

**Teaching hours per week:** 6

**Level of course unit:** Master level.

**ECTS credits:** 5

**Admission requirements:** The study of this course requires the following knowledge, skills and abilities that are generated by the preceding disciplines: "General Chemistry", "Physics", "Inorganic chemistry", "Organic chemistry», «Physical methods in chemistry», «Fundamentals of mathematical processing of the information», “Quantum Chemistry”. Course “The theory, structure and magneto-chemistry of coordination compounds**”** is mandatory for studying courses “Advanced Chemistry of the Elements”, “Computational Chemistry”, “General Laws in Chemistry”.

**Course objectives (aims):** The survey of different classes of coordination compounds, their nomenclature and research methods are discussed. The main methods of synthesis of both inert and labile complex compounds, the kinetics and mechanism of ligand substitution, isomerism of complex ions as well as their detailed inner structure are also discussed. A great attention is given to the stability of coordination compounds and determination of main factors that exert influence on it. This course also represents a statement of a current status of study in one of the most important and upcoming methods of physico-chemical research – **magnetochemistry of coordination compounds**. Theoretical models and the laboratory techniques used for interpretation of the data on magnetic susceptibility’s measurement are considered in details. Besides general discussion of the magnetic phenomena such traditional parts of magnetochemistry asthe theory of organic compound’s diamagnetic susceptibility**,** the cooperative magnetic phenomena i.e. ferro-, antiferro-, ferrimagnetism, superparamagnetism etc. have found reflection in the course. However the basic attention is given to the magnetic properties of mono - and polynuclear transition metal complexes – so-called exchange-coupled systems. Recently, interest has grown in the design and in the magnetic properties of polynuclear molecules and molecule-based coordination polymers with mono- or multidimensional frameworks. The main rationale for such studies stems from the understanding of the fundamental science of magnetic interactions and magneto-structural correlations in molecular systems. The metallo-supramolecular synthetic approach makes it possible to assemble a wide range of architectures with defined sizes and shapes; at that the high-nuclearity transition metal complexes are of current importance as new nanometric materials and a single molecule magnets. In this connection the theoretical models and quantum-chemical analysis of polynuclear complexes as well as magneto-structural correlations for these systems are discussed in details.

**Course contents:**

***Education Module 1. "The theory of the structure of coordination compounds"***

* 1. **Introduction to Coordination Chemistry.**
  2. **The main features of coordination compounds. Lability of the coordination bond. Types of ligands. The main approaches to classification of ligands.**
  3. **Coordination bond.**

1.3.1. Consideration of coordination bond with use of approaches by J. Lewis (covalent bond) and Kossel (ionic bond). Reviewing the division of such approaches and their relationship. The basic principles of a simple electrostatic model (approach) in coordination chemistry. Its advantages compared to other approaches. Assumptions for Simple Electrostatic Model approach. Energy of the complex formation and unsaturated character of the bond of ionic type.

1.3.2. Calculation of possible coordination numbers for determination of the structure of single- charged andmulti-charged ion in its interaction with the number of charged ligands. The dependence of the maximum coordination number of the central atom on its charge. Calculation of the energy of complex for determination of most probable coordination number. The Criterion Of Lambert. The consideration of ion-dipole interaction in terms of Simple Electrostatic Model approach. The calculation of attraction/repulsion forces’ balance.

1.3.3. Limitations and disadvantages of Simple Electrostatic Model. Approach developed by K.Fajans to determining the values of refraction of simple ions. Refraction of complex ions. Approach developed by A. Yanshin to determination of refraction of octahedral and planar-square coordination ions. Polarizability and polarizing effects of ions. The mutual ions polarization in the complex and the results of such process. The degree of covalence of coordination bond.

1.3.4. Application of the Polarization Model to an explanation of properties and features of a structure of coordination compounds: reverse of stability of complexes depending on the polarization and electrical properties of the units entering into complex; *trans*-effect, its possible mechanisms and role in complex structure formation.

* 1. **The theory of Hard and Soft Acids and Bases**

1.4.1. The theory of Hard and Soft Acids and Bases by R. Pearson and its application to coordination process. The main issues of concept. The classification of interacting agents. The main properties of Pearson’s acids and bases. The concept of “Chemical switches”.

* 1. **The main concepts of structural consideration of coordination compounds.**

1.5.1. The Valence Bonds Method (VBM). Types of ligands: those of strong field and low field. High-spin and low-spin complexes and their magnetic properties.

1.5.2. Crystal Field Theory (CFT). The splitting parameter for octahedral and tetrahedral environment of central atom. The spectral properties of complexes in terms of Theory of the Crystal Field. Stabilization energy in coordination compounds.

1.5.3. Ligand Field Theory (LFT). The main issues of the concept and its application to interpretation of coordination compounds structure and properties.

1.5.4. The Molecular Orbitals Method (MO method) and its application to coordination compounds. The interpretation of metallocenes’ properties (magneto-chemical and structural ones) in terms of MO method.

1.5.5. The comparison of VBM, CFT, LFT and MO method, being applied to coordination compounds.

1.5.6. The reactivity of coordination compounds. Types of reactions and factors influencing it.

#### **Education Module 2. “Magneto-chemistry of coordination compounds”**

2.1. The main magneto-chemistry concepts. Macroscopic magnetic effects, temperature-dependent para magnetism, *Curie-Weiss* equation.

2.2. Types of magneto-chemical behaviour of the substances: ferromagnetism, super-para magnetism, *anti*-ferromagnetism, *Langevin*’s diamagnetism and *van Vleck* para magnetism.

2.3. Diamagnetism. Theoretical and experimental bases of *Pascal*’s additive entity scheme.

2.4. Magnetism of paramagnetic ions and complexes. Para magnetism in simple systems with half-one spin.

2.5. The influence of orbital moment of the electron on magneto-chemical behavior of complex compounds. Spin-orbital interaction.

2.6. The use of magnetic susceptibility measurement data of mononuclear complexes of transition metals.

2.7. Magnetic properties of polynuclear complexes. The phenomena of exchange effect. *Heisenberg-Dirac-van-Vleck* model (HDVV Model).

2.8. Exchange parameter in multi-electron ions.

2.9. Mechanisms of exchange process. The theory by Anderson.

2.10. The dependence of super-exchange on angularity.

2.11. Exchange Channels Model.

2.12. The concept of geometric modelling the structure of exchange possessing units in metallo-chelates. Theoretical predictions and examples of experimental data.

2.13. Molecular magnets as a new type of materials.

**Learning outcomes:** *As a result of the development of discipline the student will be* ***able:***

* To make calculations with use of formulas, equations and reference materials;
* To predict the ability of complex formation;
* To predict the complex most probable structure by specified parameters (metal ion charge and charge of ligands, as well as their geometric and electrical parameters;
* To predict the properties of coordination compound of transition metals depending on the electron configuration, the symmetry of the metal environment and strength of ligands’ field, being coordinated;
* To predict the mode of coordination of ligand in terms of HSAB theory concept.
* To determine (experimentally and theoretically) values of effective magnetic moments of mono- and poly-nuclear coordination compounds;
* To carry out an overall analysis of the mechanisms of exchange interactions according to the theory of Anderson;
* To make quantitative description of the angular dependence of super-exchange;
* To explain the features of the electronic and geometrical factors’ influence on the nature and strength of the magnetic exchange interaction in bi- and poly-nuclear metal-chelates of transition metals by using experimental data on the temperature dependence of the molar magnetic susceptibility;
* To calculate magneto-chemical parameters (***2J*** ***g***-factor, medium-quadratic error dimension ***r*** and mass concentration of paramagnetic impurities ***f***) in poly-nuclear systems with exchange interaction.

*As a result of the development of discipline the student will* ***operate*** *with****:***

* The methods of calculating the coordination number of metal ion;
* The experimental methods of physical chemistry being applied to the coordination compounds;
* The modes of orientation in professional information sources (i.e. journals, web-sites, the Internet educational resources).
* The techniques of interpreting the spectral, magnetic, thermodynamic properties of coordination compounds;
* The basic concepts and definitions of "magneto-structural correlations in exchange-related systems" and the issues of the concept of geometric modelling the structure of rate bi-nuclear exchange unit.

**Planned learning activities and teaching methods –** lectures with a variety of examples and practice.

**Assessment methods and criteria:** examination

**Course literature (recommended or required):**

1. Scopenco V.V., Tsivadze A.Yu., Savranskij L.I., Garnovskij A.D. Coordination Chemistry. — Мoscow: ECC “Akademkniga”, 2007.
2. Kostromina N.A., Kumok V.N., Skoryk N.F. Chemistry of coordination compounds. — Moscow: Vysshaya Shkola, 1990.
3. V. Kalinnikov, Rakitin Yu.V. Introduction to magneto-chemistry. M. Nauka, 1980. 302 p.
4. Rakitin Yu.V. Magnetic properties of poly-nuclear complexes of transition metals. "The results of science and technology". The structure of molecules and the chemical bond. Moscow: VINITI. 1986. 95 p.
5. Rakitin Yu.V., Kalinnikov V.T. Modern magnetochemistry. St. Petersburg: Nauka, 1994. 272 p.
6. Khan O. Magnetism of the Heteropolymetallic Systems//Theoret. Approaches. 1987, p. 89.
7. Cairns C.J., Busch D.H. Coord. Chem. Rev. 1986. V. 69. P. 1.
8. Kogan V.A., Lukov V.V. Koordinatsionnaya Chimia. 1993. T. 19. No. 6. p. 476.
9. Kogan V.a., Lukov V.V. Koordinatsionnaya Chimia. 1997. T. 23. No. 1. p. 13.
10. Kogan V.A., Novotortsev V.V., Lukov, V.V. and others. Izvestija Akademii Nauk. Serija Chimicheskaja. 2005. № 3. p. 592.
11. Kogan v.a., Zelentsov V.V., Larin G.M., *and al.* Transition metal complexes with hydrazones. Physico-chemical properties and structure. Moscow: Nauka, 1990. 112 p.
12. Olivier Kahn. Molecular Magnetism.1993 VCH Publishers, Inc.
13. Heiko Lueken. Workshop in Magnetochemistry.Molecular Magnetism (DFG-SPP 1137).Kaiserslautern, 29.09. - 02.10.2003 Foundations. Institut fur Anorganische Chemie, RWTH Aachen.

**7.3. The Internet sources**

http://incampus.ru/ SFedU “Digital campus”

<http://dbs.sfedu.ru/pls/rsu/rsu$iik$.startup> Informational integrated complex unit of SFedU

<http://www.physchem.chimfak.rsu.ru/Sources.html>

<http://scintific.narod.ru/Literature.html> Books on Science.

<http://www.chemport.ru> Electronic copies of books on chemistry. Books and text-books.

<http://www.Chem.net.ru> Site of fundamental chemical education in Russia

<http://www.chem.msu.ru/> Site of chemistry department of Moscow State University.

<http://www.chem.km.ru>/ World of Chemistry.

<http://www.chemworld.narod.ru/internet.html> Literature on chemistry in the Internet.

<http://www.chemweb.com> Site on chemistry.

<http://www.edu.ru/> Educational source.

<http://www.window.edu.ru/window/library> Electronic copies of text-books.

<http://serg.nccom.ru/> Russian Federal educational source.

<http://chemistry-chemists.com/Uchebniki.html> Electronic copies of books on chemistry.

<http://www.ximikat.com/ebook.php..ru> Electronic copies of books on chemistry

<http://freebooks.net.ua/uchebniki/estesstven/khemia> Electronic copies of text-books on sciences on nature.

[ChemicSoft](http://chemicsoft.euro.ru/) — catalogue of Chemical soft;

Chemical Software – chemical soft.

[Научная электронная библиотека](http://www.elibrary.ru) — Electronic copies of 350 journals of Elsevier Publishing.

[Lange and Springer Electronic Resources](http://link.springer.de) — Electronic copies of journals of Lange and Springer Publishings, articles annotations.

***Data banks:***

<http://www.fiz-karlsruhe.de/stn.html> STN International: Databases in Science and Technology

<http://webbook.nist.gov/> NIST WebBook The physical-chemical characteristics of the substances.