CHIMICA INORGANICA SUPERIORE

CHIM/03 - 6 CFU - 1° Semester

Teaching Staff

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LEARNING OBJECTIVES

The course aims to deepen the knowledge on metallic and ionic solids and the properties of coordination compounds. The polyelectronic atom, electronic states, Crystal Field and MO theories, magnetic properties and optical spectra of inorganic complexes will be studied in depth. Furthermore, syntheses, electronic structures and properties of inorganic materials will be studied in depth. We will also provide basic knowledge on the main spectroscopic techniques. Finally, the basic concepts of inorganic photochemistry and homogeneous inorganic catalysis (knowledge and understanding) will be studied. The aim of the course is to acquire reasoning skills to rationalize the properties of solids and inorganic systems in solution (applying knowledge and understanding). At the end of the course students should have their own judgment: ability to propose appropriate inorganic systems for specific electrical, optical or magnetic properties (making judgments).

In particular:

The specific training objectives of this course are:

To understand the atomic structure in detail;

To understand the mechanisms of chemical bonding in solids and in coordination complexes in solution;

Understanding solid crystal structures and the main coordination polyhedra both in solid phase and in solution;

to know the relationships between electronic structures and the properties of insulators, semiconductors and metals and optical and magnetic properties;

Understanding the polyelectronic atom, the configurations, the electronic states and terms, the Russell-Saunders coupling, and the spin-orbit coupling;

to know the magnetic properties;

to know the characteristics of the transition element complexes;

to know the symmetry elements and operations;

to know the basics of group theory and its use in chemistry;

to know the CFT, LFT and MO theories;

Learning the treatment of optical spectra of inorganic complexes through the group theory;

to know the basic concepts of inorganic photochemistry;

to know the basics of the main spectroscopic techniques;

to discuss all proposed activities with scientific method and appropriate language.

Furthermore, in reference to the so-called Dublin Descriptors, this course helps to acquire the following transversal skills:

Knowledge and understanding:

• Capacity of inductive and deductive reasoning.

• Ability to rationalize property-structure correlations;

• Ability to set the prediction of a given optical spectrum of a given inorganic complex, using molecular symmetry and group theory and to interpret the related experimental spectrum.

Ability to apply knowledge:

• Ability to apply the acquired knowledge for the description of the properties of solids and complexes in solution, rigorously using the scientific method.

• Ability to interpret electrical, optical and magnetic phenomena;

• Ability to predict the chemical reactivity of transition metal systems

Autonomy of judgment:

• Ability to critical reasoning.

• Ability to identify the most appropriate solutions to confer particular properties to inorganic materials;

• Ability to identify the predictions of a theory or a model.

• Ability to evaluate the need for the use of complex models with respect to simple theories, in the description of the properties of inorganic materials.

• Communication skills:

• Ability to describe a scientific topic in oral form, with properties of language and terminological rigor, illustrating the reasons and results.

COURSE STRUCTURE

The course includes 6 credits (42 hours) of lectures. Students will actively be involved during the lessons in the classroom.

DETAILED COURSE CONTENT

1. SOLID STATE

Crystal structures: chemical and crystallographic repetitive unit, connection and coordination numbers, coordination polyhedra; structures attributable to the octahedron and the tetrahedron. Crystallographic parameters. Classification of solids; metallic solids, symmetry elements, packing of spheres, compact structures: hexagonal (hcp) and compact cubic (ccp) structures, cubic structure with centered body. Non-compact structures. Elements of band theory; insulators, semiconductors and metals. Ionic radii and binary and ternary ionic solids. Important crystal structures: sodium chloride, cesium chloride, fluorite, rutile, zinc blende and wurtzite. Interstitial systems in compact structures: perovskites and spinels. Lattice energy, Madelung's constant, Born-Haber cycle. Covalent solids; molecular solids. Outline of defects in solids.

2. POLYELECTRONIC ATOM

Particles and waves, the structure of the hydrogen atom, electronic configurations of atoms and ions; ionic radii. Polyelectronic atom, configurations, states and electronic terms, Russell-Saunders coupling, spin-orbit coupling. Magnetic properties. General characteristics of the transition elements.

3. CFT-LFT-MO THEORIES

Classification of ligands: per atom donor; mono and polydentate; s and/or p ligands. Symmetry elements and operations. Overview of group theory. Character tables. Theories of the crystalline field and the ligand field. MO theory. Octahedral, tetrahedral and planar complexes. Spectrochimic series of ligands. Rule of 18 electrons. High spin and low spin complexes.

4. OPTICAL SPECTRA OF INORGANIC COMPLEXES

Optical spectra of inorganic complexes and Lambert-Beer law. Dipolar electric mechanism of optical transitions. Moment of transition. Orbital, spin, vibrational, rotational and translational wave functions. Gerade and ungerade functions. Rules for the evaluation of direct products in symmetry groups. Rule of Laporte. Direct product in octahedral complexes. Consequences of the absence of the inversion element in tetrahedral geometry. Deviations from cubic symmetry. Jahn-Teller effect. Intensity and width of the absorption bands. Vibrations. Franck-Condon principle. Tanabe Sugano diagrams and Racah parameters.

Study of ion spectra $[M(H_2O)_6]^{n+}$. Examination of high and low spin $[ML_6]^{n+}$ ion spectra. Spectra of ion complexes of the II and III transition series. Spectra of distorted octahedral complexes and spectra of tetrahedral complexes. Spectrochemical and nefelauxetic series. Charge transfer spectra.

5. MAGNETIC PROPERTIES OF INORGANIC COMPLEXES.

Diamagnetism, paramagnetism and ferromagnetism. Magnetic measurements and correlations between magnetic properties and electronic structures of compounds.

6. CONCEPTS OF INORGANIC PHOTOCHEMISTRY.

7. NOTES ON THE MAIN SPECTROSCOPIC TECHNIQUES

TEXTBOOK INFORMATION

1) F. ALBERT COTTON, GEOFFREY WILKINSON, CARLOS A. MURILLO, MANFRED BOCHMANN, Advanced Inorganic Chemistry, 6th Edition, Wiley

2) N. N. GREENWOOD, A. EARNSMAW, Chimica degli Elementi, Piccin

3) W. W. PORTERFIELD, Chimica Inorganica, Zanichelli

4) D.F. SHRIVER, P.W. ATKINS, C.H. LANGFORD, Chimica Inorganica, Zanichelli

5) F. A. COTTON, La teoria dei gruppi in chimica, Tamburini
