60451 - Molecular Design in Inorganic and Organometallic Chemistry

Información del Plan Docente

Academic Year	2017/18
Faculty / School	100 - Facultad de Ciencias
Degree	543 - Master's in Molecular Chemistry and Homogeneous Catalysis
ECTS	6.0
Year	1
Semester	First semester
Subject Type	Compulsory
Module	---

1.General information

1.1.Introduction

Molecular Design in Inorganic and Organometallic Chemistry is a subject dedicated to the study of synthesis, bond systems and models, properties and reactivity of coordination and organometallic complexes, being them mono- or polynuclear, and containing or not metal-metal bonds. This subject also includes the study of clusters and nanoparticles.

A more detailed study will be paid to the organometallic complexes because of their greater involvement in the homogeneous catalysis. process The complexes will be classified for the study in two main groups: complexes with sigma C-M bonds, and complexes with C-M sigma-pi and pi-cyclic bonds. The study pays attention to the structural aspects, the unusual reactivity and also to the current applications: therapeutic properties, luminescent character and possible future developments.

1.2.Recommendations to take this course

The basic knowledge about chemical structure, bonding and reactivity of coordination and organometallic compounds is highly recommended.

Class attendance along with continued work facilitates to pass the course.

1.3.Context and importance of this course in the degree

The subject *Molecular Design in Inorganic and Organometallic Chemistry* is included in the compulsory module of the *Master in Molecular Chemistry and Homogeneous Catalysis*. This subject is taught in the first half term of the course and it has assigned 6 ECTS credits: 4 ECTS for lectures, 1.5 ECTS for solving problems sessions with student participation, and 0.5 ECTS credits to be developed in the laboratory in coordination with other subjets of the module *Molecular Chemistry and Catalysis*. The program of the subject extend the knowledge acquired in the subjects of Inorganic Chemistry along the Degree in Chemistry and is essential for understanding the modifications in the properties and reactivity of molecules or organic fragments caused by the presence of metal, thus influencing processes of Organic Chemistry, Biochemistry and Catalysis.

1.4.Activities and key dates

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The subject *Molecular Design in Inorganic and Organometallic Chemistry* will be taught in the first half term, in addition to the other 3 compulsory subjects of the Master and the optional subjects *Basic methodologies in synthesis* and *Bibliographic resources and databases.* Throughout the course some individual or team-based controls, as well as presentations of some literature works, will be carried out in order to delve into some issues. The presentation dates will be communicated in advance.

The laboratory section of the subject together with those corresponding to other subjects of the module *Molecular Chemistry and Catalysis* constitute an integrated block. Laboratory sessions will be held in the second half of the term. The dates and place will be announced well in advance.

2.Learning goals

2.1.Learning goals

The student must apply basic concepts of coordination chemistry to the synthesis of complexes that contain small molecules.

The student should evaluate the possible modes of coordination, bonding, properties, reactivity and potential applications.

The student must know and apply concepts of metal-metal bonding to di- or polynuclear complexes and clusters.

The student must identify the methods of synthesis, the utility and the applications of nanoparticles.

The student must know the principles and characteristics of the different M-C bonds and recognize the different families of organometallic compounds.

The student must know the usual methods in the synthesis of organometallic complexes and their general properties.

The student must predict the stability and reactivity of the different types of transition metal organometallic complexes and be able to propose methods of synthesis.

The student must be able to use the information provided from spectroscopic and analytical techniques to the characterization of the organometallic complexes.

The student must solve problems and discuss critically questions about structure and reactivity of organometallic complexes.

The student must recognize the utility of some organometallic compounds for the synthesis of organic molecules and as catalysts in chemical processes.

2.2.Importance of learning goals

The learning results of this subject are very important because they will allow the graduate to predict the stability and reactivity of different types of coordination and and organometallic compounds. Also, the learning results will allow the graduate to propose methods of synthesis and get criteria to select the appropriate information from the analytical and spectroscopic techniques for the characterization of complexes. In summary, they will provide tools to the students to

develop their creative ability to perform his job as a researcher and the knowledge to predict the usefulness of inorganic and organometallic complexes in different actual aspects of Science and Technology.

3.Aims of the course and competences

3.1.Aims of the course

This subject is one of the central topics in the framework of the *Master in Molecular Chemistry and Homogeneous Catalysis*, because provides knowledge of coordination compounds and organometallic complexes, including clusters and nanoparticles, about synthesis, bond models, properties, reactivity and current applications like the catalytic processes that are studied in another subjects as *Catalysis*, *Asymmetric Catalysis*, *Sustainable Chemistry and Catalysis* and *Supramolecular Chemistry*.

One of the main goals of the subject is that students increase their knowledge in Coordination Chemistry to be able to evaluate the effect of different complexes over some small molecules, some of which are widely used in catalytic reactions and processes. In addition, the student will realize how organic compounds change its reactivity when act as ligands bonded to the metal centers. The knowledge of the different types of M-C bond, depending on the organic groups involved, its structure and related properties will provide to the students a global perspective of the Organometallic Chemistry of the transition elements.

3.2.Competences

To know and predict the synthesis and stability of coordination compounds.

Capacity to recognize and make sense to the modifications suffered by the molecules coordinated to a metal center and expect its new reactivity.

Capacity to recognize the presence of metal-metal bonds in polynuclear coordination compounds or clusters.

To be able to select the method for the preparation of metal nanoparticles and for the prediction of potential applications.

To use the nomenclature and specific terminology within the framework of Inorganic Chemistry.

Capacity to recognize the different types of organometallic complexes and predict their stability.

To redict the different reactivity of organometallic complexes.

To be able to select the synthetic methods to prepare organometallic complexes of transition metals.

To be able to design and synthesize new organic, inorganic or organometallic molecules that could be of industrial and technological interest.

To be able to select and use the analytical and spectroscopic data got from standard techniques to elucidate the composition and structure of organometallic complexes.

To understand, explain and study the mechanisms of stoichiometric and catalytic reactions.

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To apply methods, procedures and experimental techniques in advanced synthesis.

To know the applications of organometallic complexes in synthesis and catalysis.

To know the applications of coordination compounds and organometallic complexes in medicine.

To be able to assimilate and critically evaluate research results in Molecular Chemistry relating them with the theoretical knowledge.

4.Assessment (1st and 2nd call)

4.1.Assessment tasks (description of tasks, marking system and assessment criteria)

The evaluation of this course is based on the following activities, weighted as indicated:

1.- A mid-term examination containing theoretical, theoretic-practical questions and problems from the themes 1 to 5 of the program (**P1**). Students who get a mark higher than 5 points will avoid these themes in the final exam.

2.- Elaboration and presentation of a supervised individual or team-based practical work on a scientific paper (**T1**).

There will be a final exam at the end of the term containing theoretical and theoretic-practical questions or problems from the themes 6 to 10 of the program. (**P2**). Students who had not been done the control **P1** or who had not get a 5 points mark, must have an additional exam with questions from themes 1 to 5 (**P1'**), which will represent the 35 % of the final grade.

The final grade will be the best of the following notes:

NOTE 1= 0,35*(**P1** or **P1'**)+ 0,25***T1** + 0,40***P2**

NOTE 2= 0,45***P1'** + 0,55***P2**

The rating of the students in the second annual examination session will consist in a single written exam that cover all themes of theory, problems or laboratory sessions defined as learning activities.

The number of official examination calls per registration and their use will be subjected to the statements of the *Regulation of Permanence in Master Studies* and the *Regulation of the Learning Assessment* (http://www.unizar.es/ice/images/stories/calidad/Reglamento%20Evaluacion.pdf). The latest document will also regulate the general design and scoring criteria of the assessment activities, as well as the exam schedules and timetable for the post-examination review.

5.Methodology, learning tasks, syllabus and resources

5.1.Methodological overview

The methodology followed in this course is oriented towards achievement of the learning objectives. A wide range of

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teaching and learning tasks are implemented, such as:

1. Theoretical classes (4 ECTS)

2. Problem-solving sessions and seminars (1.5 ECTS)

3. Laboratory sessions (0.5 ECTS)

5.2.Learning tasks

The course includes the following learning tasks:

- Lectures (4 ECTS: 40 hours). Students will acquire advanced knowledge of Inorganic and Organometallic Chemistry. This activity is based on interactive teaching in the classroom in a large group.
- Seminars and problem-solving sessions (1.5 ECTS: 15 hours). Students will work, individually or in small groups, with several case studies and scientific papers related to the course contents.
- Laboratory sessions (0.5 ECTS: 5 hours). Laboratory sessions take place in the chemistry laboratory and the attendance is compulsory, as happens with the other courses of the *Chemistry and Molecular Catalysis* module.
- Guided assignments.
- Tutorials: students will have 3 hours per week for individualized tutoring.

5.3.Syllabus

The course will address the following topics:

Topic 1. **Fundamental concepts in Coordination Chemistry.**

- General considerations of transition metals. Structure and properties of coordination compounds. Electronic structure and bonding. Synthesis and reactivity of coordination compounds.

Topic 2. **Activation of small molecules by coordination to metal centers.**

- Coordination of CO2 to metal centers, reactivity. Carboxylation reactions. Complexes with NO and N2O, coordination modes of nitrogen and reduction processes. Coordination and activation of diatomic molecules. Inter - and intramolecular hydrogen bonds.

Topic 3. **Metal-metal bonds in coordination compounds.**

- Introduction and bonding types. Multiple metal-metal bond: bond order, strength and M-M distance. Preparation and reactivity of complexes with quadruple bond. Preparation and reactivity of complexes with triple bond. Complexes with quintuple bond. Other types of metal-metal bonds.

Topic 4. **Clusters Compounds.**

- Carbonyl Clusters of high and low nuclearity. The CO bond in metal carbonyls. Application of NAE and Wade rules to the structure of the clusters. Isolobular concept. Halide clusters. Synthesis of clusters and reactivity.

Topic 5. **Huge clusters and nanoparticles.**

- Classification of the nanoparticles according to the size and shape. Preparation, properties and applications of nanoparticles.

Topic 6. **Types of ligands.**

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- Transition metal organometallic complexes: sigma-donor ligands. Preparation of transition-metal-alkyl and -aryl compounds. Thermodinamic versus kinetic lability. Reactivity: Insertion reactions. Alkenyl and alkynyl complexes: synthesis, properties and applications.

Topic 7. **Transition metal complexes with M-C multiple bonds**.

- Transition metal carbene complexes. Types of carbenes: preparation, structure, binding and reactivity. Alenylidene and vinylidene complexes. Transition metal carbyne complexes: preparation, structure, bonding and reactivity. Applications.

Topic 8. **Transition metal complexes with sigma-pi M-C bonds (linear or cyclic but non aromatic ligands).**

- Synthesis, structure, bonding, reactivity and applications of complexes with olefins and conjugated di-olefins. Alkyne complexes. Allyl and enyl derivatives. Synthesis, structure, bonding and reactivity. Applications.

Topic 9. **Transition metal complexes with sigma-pi M-C bonds (aromatic ligands).**

- Transition metal complexes with aromatic rings. Sandwich and semisandwich complexes. Complexes with three or four membered aromatic rings. Cyclopentadienyl derivatives. Binary cyclopentadienyl complexes. Metal complexes with benzene or its derivatives as ligands. Bis(arene) metal complexes. Semisandwich arene metal carbonyls. Complexes with seven or eight membered aromatic rings. Synthesis, properties and applications.

Topic 10. Medical therapies with metal complexes.

- Essential elements. Chelation therapy. Diagnostic agents. Radiopharmaceuticals. Therapeutic agents (anticancer, antibiotic, anti-arthritis).

5.4.Course planning and calendar

Further information concerning the timetable, classroom, assessment dates and other details regarding this course, will be provided on the first day of class or please refer to the Faculty of Science website https://ciencias.unizar.es/calendario-y-horarios, and the Master's http://masterqmch.unizar.es.

The submission of assignments will be held according to the schedule that will be announced in advance.

Students will be provided with extensive scholar material either at reprography or through the University's virtual platform: https://moodle2.unizar.es/add.

5.5.Bibliography and recommended resources

BB Activation of small molecules: organometallic and bioinorganic perspectives / edited by William B. Tolman. Weinheim: Wiley-VCH, cop. 2006

BB Bochmann, Manfred. Organometallics. 2, Complexes with transition metal- carbon [p]-bonds / Manfred Bochmann. - 1st ed. repr. Oxford [etc.]: Oxford University Press, 2000

BB Crabtree, Robert H. The organometallic chemistry of the transition metals / Robert H. Crabtree. 5ª ed. Hoboken, N.J.: Wiley, 2009

BB Elschenbroich, Christoph. Organometallics / Christoph Elschenbroich; translated by Jose Oliveira and Christoph Elschenbroich. 3rd completely rev. and extended ed. Weinheim [etc.]: Wiley-VCH, cop. 2006

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BB Hill, Anthony F. Organotransition metal chemistry / Anthony F. Hill Cambridge: Royal Society of Chemistry, cop. 2002

BB Multiple bonds between metal atoms / edited by F. Albert Cotton, Carlos A. Murillo and Richard A. Walton. - 3rd ed. New York: Springer Science and Business Media, 2005

BB Nanoparticles: from theory to application / edited by Günther Schmid Weinheim: Wiley-VCH, cop. 2004

BB Optoelectronic properties of inorganic compounds / edited by D. Max Roundhill and John P. Fackler, Jr. New York [etc]: Plenum Press, cop. 1999

BB Uses of inorganic chemistry in medicine / edited by Nicholas P. Farrell. - [1st ed.] Cambridge: Royal Society of Chemistry, 1999

BC Astruc, Didier. Química organometálica con ejercicios corregidos / Didier Astruc; traducción, Carmen Claver, Beatriz Alonso Barcelona: Reverté, D.L. 2003

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BC Carriedo Ule, Gabino A. Curso de iniciación a la química organometálica / Gabino A. Carriedo Ule, Daniel Miguel San José. - [1ª ed.] Oviedo: Universidad de Oviedo, Servicio de Publicaciones, D.L.1995

BC Cisplatin: chemistry and biochemistry of a leading anticancer drud / Bernhard Lippert, ed. Weinheim [etc.]: Wiley-VCH, cop. 1999

BC Dabrowiak, James C. Metals in medicine / James C. Dabrowiak Hoboken: Wiley, cop. 2009

BC Elschenbroich, Christoph. Organometallics: a concise introduction / Christoph Elschenbroich, Albrecht Salzer. - 2nd ed., 4ª repr. Weinheim [etc.]: VCH, 2001 (repr.)

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BC Hegedus, Louis S. Transition metals in the synthesis of complex organic molecules / Louis S. Hegedus. - 3rd ed. Sausalito, California: University Science Books, cop. 2010

BC Highly efficient OLEDs with phosphorescent materials / edited by Hartmut Yersin Weinheim: Wiley-VCH, cop. 2008

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BC Metal compounds in cancer therapy / edited by Simon P. Fricker. - 1st ed. London: Chapman & Hall, 1994

BC Nugent, William A. Metal-ligand multiple bonds: the chemistry of transition metal complexes containing oxo, nitrido, imido, alkylidene, or alkylidyne ligands / William A. Nugent, James M. Mayer. - [1st ed.] New York [etc.]: John Wiley & Sons, cop. 1998

BC Pruchnik, Florian P. Organometallic chemistry of the transition elements / Florian P.Pruchnik; translated from polish by Stan A.Duraj. - [1st ed.] New York [etc.]: Plenum Press, cop. 1990

BC Spessard, Gary O. Organometallic chemistry / Gary O. Spessard, Gary L. Miessler New Jersey: Prentice-Hall, cop. 1997

URLs LIST:

Rob Toreki's Organometallic HyperText Book. http://www.ilpi.com/organomet