UNIVERSITÀ
DEGLI STUDI DI MILANO-BICOCCA

SYLLABUS DEL CORSO

Chimica di Coordinazione e Metallorganica

2627-1-F5402Q002

Aims

The aim of the course is to provide an adequate understanding of the properties, structure, electronic configuration, reactivity, and applications of coordination compounds of transition metals and organometallic compounds. At the end of the course, students will have acquired the basic knowledge of coordination chemistry and organometallic chemistry, as well as practical skills regarding the main techniques for the synthesis, isolation, and purification of coordination and organometallic compounds.

Knowledge and understanding skills. Students will complete and deepen their knowledge on the general topics regarding coordination chemistry such as crystal field theory; ligand field theory; the spectrochemical series; the concepts of ? and ? donation, and ?* and ?* backdonation; electronic counting and the d? configuration of the metal ion; UV-Vis spectra and magnetism in coordination compounds; the 18-electron rule, ionic model and neutral atom model; classification of coordination compounds according to the coordination numbers and their geometry; classification of ligands according to the donor atom, the description of coordination compounds according to the d? configuration of the metal ion; isomerism in coordination compounds; reactivity of coordination compounds. Students will complete and deepen their understanding of the general topics of organometallic chemistry, such as the description of the various classes of organometallic compounds and their synthesis mechanisms; the reactivity of organometallic compounds; the application of organometallic compounds in homogeneous catalysis. In the laboratory experiences, experimental methodologies for the synthesis and characterization of coordination and organometallic compounds will be learned.

Ability to apply knowledge and understanding. Students will be able to use the IUPAC nomenclature to identify coordination and organometallic compounds; correctly interpret the formulas of coordination and organometallic compounds in terms of geometry, type of ligand, type of bond, as well as predict the reactivity of coordination and organometallic compounds; synthesize coordination and organometallic compounds, handling chemical reagents safely, and ensure their proper disposal to prevent risks in laboratories.

Autonomy of judgment. Students will be able to predict the reactivity of coordination and organometallic compounds; write a report on laboratory experimental activities, summarizing the experience and providing information obtained from the acquisition and processing of experimental data, critically evaluating the results

obtained.

Learning abilities. Students will be able to understand the basic principles of coordination and organometallic chemistry, applying them correctly to the problem to be solved even in contexts different from those presented in the course, deepening the topics covered also with tools different from those provided.

Communication skills. Students will be able to clearly and succinctly describe orally and with a proper use of language the basic knowledge of coordination and organometallic chemistry, as well as the aims and procedures of the various laboratory experiments. They will also carry out experimental laboratory work in small groups, sharing the organization of the work and communication of information and results, communicating scientific results by drafting written laboratory reports.

Contents

The course on Coordination and Organometallic Chemistry is divided into two parts: (I) coordination chemistry (introduction, descriptive analysis of the different classes of coordination compounds and their synthesis mechanisms, classifying coordination compounds based on their geometry, donor atom of the ligands, and electronic configuration of the metal center, isomerism in coordination compounds, reactivity); (II) organometallic chemistry (descriptive analysis of the different classes of organometallic compounds and their synthesis mechanisms, specifying the nature of the metal-carbon interaction and its particular reactivity, application in homogeneous catalysis).

The Coordination and Organometallic Chemistry Laboratory includes a practical part of the synthesis and reactivity experiments of coordination and organometallic compounds, carried out either individually or in pairs, aimed at experimentally verifying the concepts illustrated in class.

Detailed program

Part I. Coordination Chimistry.
Introduction: A recap of crystal field theory in coordination compounds with octahedral, tetrahedral, and square planar geometry. Ligand field theory. The spectrochemical series. ? and ? donation, ?* and ?* backdonation. Electron counting and d? configuration of the metal ion. UV-Vis spectra and magnetism in coordination compounds. The 18-electron rule, ionic model and neutral atom model.
Descriptive: Classification of coordination compounds according to coordination numbers and geometry. Classification of ligands according to the donor atom. Classification of coordination compounds according to the d? configuration of the metal ion.
Isomerism in coordination compounds: Conformational, geometric, optical, bonding, and spin isomerism.
Reactivity of coordination compounds:
(a) Substitution in inert and labile coordination compounds: (i) Associative, dissociative, and interchange mechanisms. (ii) Associative substitution in square-planar coordination compounds: trans effect, effect of the incoming ligand (nucleophilicity), the leaving ligand effect, the solvent effect. (iii) Dissociative and interchange substitution in octahedral coordination compounds. (iv) Linear free energy relationship. (v) Catalyzed substitutions.
(b) Redox: (i) Outer sphere mechanism, and Marcus theory. (ii) Inner sphere mechanism, effect of the bridging ligand. (iii) Adjacent attack and remote attack. (iv) Intervalence coordination compounds.
(c) Isomerization: (i) Tetrahedral-square planar isomerization. (ii) Geometric isomerization, racemization. (iii) Bonding isomerization.

Part II. Organometallic Chemistry
Descriptive of organometallic compounds: Historical backgrounds.

Classification of organometallic compounds according to the ligand.
(a) Carbonyl compounds: (i) The Metal-CO bond. (ii) Bridging and terminal carbonyls. (iii) Classification of carbonyl compounds. (iv) Synthesis of carbonyl compounds. (v) Reactions of carbonyl compounds: substitution, nucleophilic attack, electrophilic attack, insertion, reduction.
(b) Reaction with CO analogies: nitrosyl, isonitrile, dinitrogen, substituted phosphines.
(c) Alkyl compounds: (i) Synthesis of alkyl compounds. (ii) Reactions of alkyls: beta-elimination.
(d) Hydride compounds: (i) Synthesis of hydride compounds. (ii) Spectroscopic characterization methods. (iii) Reactions of hydrides. (iv) Non-classical hydrides, and agostic bonds.
(e) Compounds of alkenes, and alkynes.
(f) Allylic compounds, , polyenes and carbocyclic ligands.
(g) Carbenes and carbines.
Specific reactions of organometallic compounds: migratory insertion, oxidative addition, and reductive elimination.
Cycles in homogeneous catalysis: (a) Reaction of hydrogenation: (i) of an alkene, (ii) asymmetric. (b) Reaction of hydroformylation. (c) Reaction of carbonylation of alcohols. (d) Reaction of oxidation of an alkene, Wacker process. (e) Heck process and Suzuki process. (f) Reactions of metathesis.

In-depth lecture: The elements of block f.

Laboratory Activities.
The laboratory activities includes a theoretical part that recalls and deepens the knowledge of coordination and organometallic chemistry underlying the experiments conducted in the laboratory, and a practical part consisting of synthesis and reactivity experiences of coordination and organometallic compounds, also dedicated to learning the main techniques of an experimental laboratory.
The experiences involve the synthesis and physico-chemical characterization of coordination and organometallic compounds of transition metals. In particular:
(a) Synthesis and determination of the magnetic susceptibility of Mn(III) acetylacetonate.
(b) Synthesis of a thermoluminescent tetrameric coordination compound of Cu(I).
(c) Synthesis and characterization of a penta-amminic Co coordination compound containing the di-oxo ligand.
(d) Template synthesis of a macrocycle: Ni(cyclam).
(e) Functionalization and redox reactivity of Ferrocene.
(f) Synthesis and magnetic properties of a coordination polymer of Fe(II).

Prerequisites

Fundamental knowledge acquired from previous courses in General and Inorganic Chemistry, Organic Chemistry, and Physical Chemistry.
Practical laboratory skills acquired from previous courses in General and Inorganic Chemistry, Organic Chemistry, and Physical Chemistry.
To participate to the laboratory activities, it is necessary that students have completed and passed the mandatory safety course (currently valid) provided by the University.

Teaching form

The Coordination and Organometallic Chemistry course of 8 ECTS includes 6 ECTS of lectures corresponding to 48 hours and 2 ECTS of laboratory activities corresponding to 24 hours:
• 24 lectures of 2 hours, in person, Delivered didactics;
• 6 laboratory activities of 4 hours, in person, Interactive teaching.
The lectures are conducted in Italian by the Lecturer, who presents the content of the program using presentations or blackboard demonstrations. Lectures are recorded and made available to students by means of the e-learning

page of the course. Slides are provided by means of the e-learning platform of the course. Although attendance is not mandatory, it is recommended that students regularly attend the lectures for an easier learning of the course content.
Introductory lectures on laboratory activities are made available to students by means of the e-learning page of the course before the execution of the experiments.
The synthesis laboratory activities include laboratory experiences (either individually or in pairs) preceded by recorded introductory lessons shared by means of the e-learning platform of the course, and by brief lectures, also with the aid of slides, before the start of each experience. Attendance at the Laboratory is mandatory (75% of the course, or 5 experiences out of 6).

Textbook and teaching resource

Slides and recordings of the lectures of the Coordination and Organometallic Chemistry course (e-learning platform of the course).
Lecture notes, slides, and recordings of the introductory lectures to the laboratory activities of the Coordination and Organometallic Chemistry course (e-learning platform of the course).

Textbook suggested by the Lecturer:
Mark Weller, Tina Overton, Jonathan Rourke, Fraser Armstrong, *La chimica inorganica di Atkins*, Zanichelli.

Other textbooks:
Geoffrey A. Lawrance, *Introduction to Coordination Chemistry*, John Wiley & Sons Ltd.
Christoph Elschenbroich, *Organometallics*, Wiley-VCH.

Semester

First semester of the first year of the Chemical Sciences and Technologies Master Degree Course.

Assessment method

The student earns ECTSs of the course by passing both a written and an oral exams. There are no intermediate tests planned.
The written exam consists of six laboratory reports in the form of papers that provide a brief description of the experimental procedures, the results obtained, and observations concerning the conducted experimental activities, as well as the processing of characterization data for each experiment. The evaluation of the laboratory reports focuses on the understanding of coordination and organometallic chemistry underlying the experiments, as well as the precision and correctness in reporting numerical results, graphs, and experimental observations. The grades range from 0 to 5 for each report, reaching a maximum of 30/30 for the laboratory module. A positive evaluation of the laboratory reports (minimum 18/30, corresponding to an average score of 3 per laboratory report) and attendance in the laboratory (at least 5 presences out of 6, 75% of the laboratory course) allows the access to the oral exam.
The oral exam with a score out of thirty consists of an interview in which the student must respond clearly and with appropriate language to open-ended questions related to the general aspects of coordination and organometallic chemistry, as well as the experiences conducted in the laboratory. The final grade will take into account the evaluation of the two parts with the following grading scale:
18-21: preparation on a limited number of topics from the course syllabus, with poor ability to discuss and analyze

independently which only emerge in the oral exam as a result of the Lecturer's help and questions; presentation skills occasionally uncertain, vocabulary not always clear and accurate, sometimes incorrect, with very limited critical elaboration;
22-24; preparation on a good number of topics from the course syllabus, although not homogeneous, with sufficient ability to discuss and analyze independently, sometimes prompted by the Lecturer's questions; presentation skills sufficiently clear, generally correct vocabulary, although sometimes not accurate or clear, limited critical elaboration capabilities.
25-27: preparation on a wide range of topics covering the course syllabus, ability to conduct discussions and critical analysis with good autonomy and ability to apply knowledge to real cases, use of correct vocabulary and competence in the use of disciplinary language;
28-30/30L: complete and exhaustive preparation on the subjects of the course syllabus, abiity to independently discuss and critically analyse the principal topics, ability to connect themes to real cases and to different contexts and disciplines, excellent capacity for critical and independent thinking, full mastery of disciplinary vocabulary, rigorous and articulate presentation skills, argumentation skills.

Office hours

From Monday to Friday by appointment.

Sustainable Development Goals

QUALITY EDUCATION | AFFORDABLE AND CLEAN ENERGY | RESPONSIBLE CONSUMPTION AND PRODUCTION | CLIMATE ACTION