CH277-15 Inorganic Materials from Complexes to Solids

24/25

Department
Chemistry
Level
Undergraduate Level 2
Module leader
Richard Walton
Credit value
15
Module duration
10 weeks
Assessment
Multiple
Study location
University of Warwick main campus, Coventry

Description

Introductory description

This module will consider chemical bonding in compounds of elements from various parts of the Periodic Table to illustrate how properties arise from their bonding and electronic structure, Complexes of transition-metals will be explored, examining their stability, description of the binding of ligands, mechanism of ligand substitution, and organometallic complexes will be introduced. Solid-state materials will be illustrated using oxides of transition-metals and concepts of crystallographic and diffraction used to how structure of solids is determined. This will lead to consideration of the electronic structure of solids, including band structure and conductivity.

Module web page

Module aims

Building on concepts taught in the first-year modules CH164 and CH166, the module aims to show how useful properties, relevant to industry, biology and technology, arise from chemical bonding and electronic structure, both in molecular complexes and extended solid-state structures. The students will learn how models for chemical bonding can be used to understand the useful properties of inorganic substances.

Outline syllabus

This is an indicative module outline only to give an indication of the sort of topics that may be covered. Actual sessions held may differ.

The module is split into 2 topics and will run over 10 weeks.
Topic 1: Molecular inorganic chemistry – molecules across the Periodic Table (18 lectures)
Topic 2: Solid-state inorganic chemistry – materials across the Periodic Table (12 lectures)

Topic 1: Molecular inorganic chemistry (18 lectures)
Premise: transition-metal complexes do many useful things from carrying O2 around the bloodstream to being catalysts in industrial processes.

Principles 1. What makes metal complexes stable? (thermodynamics) [4 lectures]

- Definition of binding constant and basic statistical effects (decrease in successive K values across series for simple statistical reasons)
- Chelate effect – much higher binding constants – why?
- Matching of hard / soft metals and ligands (taking metal oxidation state into account)
- 'hard' and 'soft' (simple concept) provides an entry into bonding models… basically ionic (CFT) to basically covalent (MO theory) with relevant examples covering the range from essentially ionic model, to an MO model (as covered in Year 1, CH164 and CH166).
- Real world examples of highly stable complexes – siderophores, chelation therapy, extraction of metal ions from ores
- Also mention how this connects to redox states for TM ions: e.g. value of a Cu(I)-Cu(II) redox couple from +1.5V to -1.5V depends on how 'hard / soft' the donor set is; link between ΔG and redox potential.
- Other examples of matching metal ions to appropriate ligands – lithophiles (Ti4+ found as oxide in earth's crust) and chalcophiles (Cd2+ found as sulfide)

Principles 2. What makes metal complexes reactive? (kinetics and mechanisms) [6 lectures]

- Associative / dissociative mechanisms for ligand substitution and the spectrum in between
- Coordinative saturation and unsaturation which connect to associative vs dissociative mechanisms
- Effects of d-electron configuration: kinetically inert vs. labile, replacement of one ligand by another can occur on timescales from nanoseconds to years
- Examples to illustrate to illustrate the value of understanding mechanisms, might include mechanism of action of cis-platin
- Inner-sphere vs outer-sphere electron transfer mechanisms and their rates depending on Franck-Condon factors. Practical example: Plastocyanin has fast Cu(I)-Cu(II) ET because of its rigid geometry intermediate between Cu(I)/Cu(II) which minimises rearrangement
- Lanthanide complexes: Predominance of +3 oxidation state, essentially no covalency due to core nature of 4f orbitals. Hence no CF effects, no geometric preferences, high coordination numbers and highly labile: survey of structures and common ligand types. Real-world important properties… high magnetic moments and strong luminescence. Survey of some important examples: Gd(III) for MRI (high thermodynamic stability with aminocarboxylate

chelating ligands but also high kinetic lability for rapid H2O exchange).

Organometallics: M-C bonded complexes [8 lectures]

- CO as a ligand: π-bonding and spectroscopy
- H2 as a ligand
- Sigma-bonded ligands (hydrides, alkyls)
- Electron counting – 18e rule, relation to earlier ideas of ‘coordinative saturation’
- Some new reaction mechanisms: oxidative addition / reductive elimination reactions
- Pi-bonded ligands (ethene, butadiene, Cp-, benzene) use ferrocene as a case study (still used as redox intermediate in blood glucose sensors for diabetic people)
- Applications: e.g. a simple organometallic catalytic cycle, e.g. Wilkinson’s catalyst, to bring a lot of things together

Topic 2: Solid-state inorganic chemistry (12 lectures)
Premise: fundamental concepts of solid-state chemistry relate to crystal structure, chemical bonding in solids and the electronic and vibrational properties of solids and give rise to properties such as conductivity.

Compositions and Crystal Structures (5 lectures)

- Crystal structures of transition-metal oxides: rock-salt (revision of CH166), rutile, spinel, perovskite, illustrated with examples of their properties/application.
- Examples of crystal field theory to solid state chemistry: CFSE, OSPE and JT distortions.
- Introduction to crystal symmetry: definitions of the unit cell, crystal systems, Bravais lattices, space groups
- Diffraction from crystals: Bragg’s Law. Systematic absences. Indexing diffraction patterns to determine unit cell dimensions and Bravais lattice. (With associated workshop)
- Experimental aspects of the diffraction experiments: X-rays, electrons and neutrons.
- Introduction to reciprocal space

Band structure and electronic conductivity (7 lectures)

- Band structure and electronic conductivity: qualitative introduction.
- QM of solids: the free particle, the particle in a box.
- Electrons in solids: electronic bands; the Fermi-Dirac distribution; density of states; work function, contact potential.
- Conduction: Drude model; effects of band model: metals, insulators and semiconductors; effect of temperature.
- Semiconductors: intrinsic and extrinsic semiconductors; conduction by holes; doping; donor and acceptor levels; p-n junction; introduction to semiconductor devices: photovoltaic cell, light emitting diode.

Learning outcomes

By the end of the module, students should be able to:

- Select the appropriate bonding model (crystal field, ligand field/MO/band theory) for different

molecular and solid-state materials and explain their limitations to explain their properties.
- Apply bonding models to predict thermodynamic trends (e.g. stability of transition-metal complexes and preferred site occupancies in transition-metal oxides)
- Use bonding models to predict and explain trends in kinetics (e.g. labile versus inert) via an appreciation of the energetics associated with likely transition pathways.
- Understand how the structure and hence bonding in molecules can be probed using spectroscopic techniques.
- Understand how the structures of solids can be determined using X-ray diffraction with reference the structures of transition-metal oxides (rock salts, spinels, perovskites) .
- Rationalise the electrical conductivity properties of metals, semiconductors and insulators with reference to band theory
- Practise their communication and team working skills by preparation of a video to highlight the relevance of the fundamental principles learnt in the application of Chemistry.

Indicative reading list

Inorganic Chemistry, Oxford University Press, 7th Edition

Research element

Team video project to produce 5-minute educational video, aimed at A-level students, about some aspect of inorganic chemistry associated with a chemistry Nobel prize.

Subject specific skills

Communication
Critical Thinking
Digital Literacy
Problem Solving
Teamwork

Transferable skills

Communication
Critical Thinking
Digital Literacy
Problem Solving
Teamwork

Study

Study time

Type	Required
Lectures	30 sessions of 1 hour (20%)
Tutorials	2 sessions of 1 hour (1%)
Practical classes	4 sessions of 1 hour (3%)
Private study	84 hours (56%)
Assessment	30 hours (20%)
Total	150 hours

Private study description

N/A

Costs

No further costs have been identified for this module.

Assessment

You do not need to pass all assessment components to pass the module.

Assessment group D

	Weighting	Study time	Eligible for self-certification
Team video project	20%	30 hours	Yes (extension)

In small groups, students must produce an educational video, aimed at A-level students, about some aspect of inorganic chemistry associated with a chemistry Nobel prize.

	Weighting	Study time	Eligible for self-certification
Examination	80%		No

- Answerbook Green (8 page)
- Students may use a calculator
- Graph paper
- Periodic Tables

Assessment group R

	Weighting	Study time	Eligible for self-certification
Examination	100%		No

- Answerbook Green (8 page)
- Students may use a calculator
- Graph paper

Weighting	Study time	Eligible for self-certification

- Periodic Tables

Feedback on assessment

Feedback on assessed work provided via Moodle. Cohort level examination feedback will be provided after the June examination period.

[Past exam papers for CH277]

Availability

Courses

This module is Core for:

- UCHA-4 Undergraduate Chemistry (with Intercalated Year) Variants
  - Year 2 of F101 Chemistry (with Intercalated Year)
  - Year 2 of F122 Chemistry with Medicinal Chemistry (with Intercalated Year)
- UCHA-3 Undergraduate Chemistry 3 Year Variants
  - Year 2 of F100 Chemistry
  - Year 2 of F121 Chemistry with Medicinal Chemistry
- UCHA-F110 Undergraduate Master of Chemistry (with Industrial Placement)
  - Year 2 of F100 Chemistry
  - Year 2 of F110 MChem Chemistry (with Industrial Placement)
  - Year 2 of F112 MChem Chemistry with Medicinal Chemistry with Industrial Placement
- Year 2 of UCHA-F107 Undergraduate Master of Chemistry (with Intercalated Year)
- UCHA-F109 Undergraduate Master of Chemistry (with International Placement)
  - Year 2 of F109 MChem Chemistry (with International Placement)
  - Year 2 of F111 MChem Chemistry with Medicinal Chemistry (with International Placement)
- UCHA-4M Undergraduate Master of Chemistry Variants
  - Year 2 of F100 Chemistry
  - Year 2 of F105 Chemistry
  - Year 2 of F110 MChem Chemistry (with Industrial Placement)
  - Year 2 of F109 MChem Chemistry (with International Placement)
  - Year 2 of F125 MChem Chemistry with Medicinal Chemistry
- Year 2 of UCHA-F127 Undergraduate Master of Chemistry with Medicinal Chemistry(with Intercalated Year)