Coordination Chemistry

Schedule:

Week 1: Basic concepts of coordination chemistry. Complex, ligand, coordination number, etc. Characteristics of ligands (dentiticy, open-chain and macrocyclic ligands, hard-soft classification of donor atoms). Properties of metal ions (hard-soft character, p-, d-, and f-block metals). Recommended literature.

Week 2: Thermodynamics of complex formation. Equilibrium constants (thermodynamic and stoichiometric). Stability product, types of stepwise constants in two- and multi-component systems. Macroconstant, microconstant. Apparent constants (K', pM, KD).

Week 3: Factors influencing the equilibrium constant. Statistical factors, internal and external factors (component-determined factors, solvent effects, ionic strength, and temperature effects).

Week 4: Crystal field and ligand field theory. Crystal field theory for one- and multi-electron systems. Splitting of d-orbitals in regular octahedral, elongated octahedral, and square planar crystal fields (crystal field splitting, crystal field stabilization energy). Ligand field theory. The electron excitation spectra of transition metal complexes.

Week 5: Structural characterization of metal complexes. Basics of spectrophotometry. Effect of coordinating donor atoms on light absorption of complexes. Application of spectrophotometry in equilibrium and structural studies of complexes.

Week 6: pH-potentiometry. Theoretical principles of pH-potentiometry, setup of a pH-potentiometric system. Basic knowledge required for performing pH-potentiometric titrations. Combined glass electrode and its properties. Limitations of pH-potentiometry.

Week 7: Relaxometry. Fundamentals of relaxometry, relaxivity of complexes. Longitudinal and transverse relaxation. Application of relaxometry in mapping equilibrium, kinetic, and relaxation properties of complexes.

Week 8: Calculation of equilibrium constants. Introduction to PSEQUAD and HYPERQUAD softwares, structure and editing of data files. Presentation of problems encountered during constant calculations.

Week 9: Practice exercises I. Calculation of equilibrium constants, discussion of previously assigned examples (calculation of protonation and stability constants from pH-potentiometric, spectrophotometric, ^{1}H-NMR spectroscopic, and relaxometric data).

Calculation of distribution diagrams. Importance of distribution diagrams in interpreting equilibria. Introduction to the MEDUSA software, structure and editing of data files. Application of distribution diagrams in reaction design.

Week 10: Equilibrium databases. Introduction to NIST and SC-Database programs. Data search possibilities.

NMR spectroscopy in coordination chemistry. The phenomenon of magnetic resonance. Primary information obtainable from NMR spectra and their applications in coordination chemistry. Determination of equilibrium constants by NMR techniques. 1D and 2D techniques and their applications. Dynamic processes in NMR spectra of metal complexes.

Week 11: Application of ^{17}O-NMR and NMRD in determining water exchange rates of complexes. Basic concepts. Description of the measurement and evaluation of the relaxation parameters.

EPR spectroscopy of metal complexes. Basics of EPR spectroscopy, structure of the EPR instrument. Information obtainable from EPR spectra: g and A tensors and their temperature dependence. Isotropic and anisotropic parameters. EPR spectra of copper(II), manganese(II), and nickel(III) complexes. Effect of geometry on EPR parameters. 2D EPR techniques and their application in coordination chemistry.

Week 12: Electrochemical and other structural investigation methods. Cyclic voltammetry (CV) and its application in coordination chemistry. High scan rate cyclic voltammetry. Protein-film electrochemistry and coupled techniques. Applications of circular dichroism, Mössbauer spectroscopy, mass spectrometry, and single-crystal X-ray diffraction in determining structures of metal complexes.

Practice exercises II. Evaluation of NMR and ESR spectra.

Week 13: Application of theoretical chemistry methods in coordination chemistry. Fundamentals and applications of density functional theory (DFT) in coordination chemistry. Structures of metal complexes. Approximate calculation of relativistic effects:

effective core potentials methods. Thermodynamic calculations: relative energies of coordination isomers. Calculation of absorption and EPR spectra of transition metal complexes.

Practice exercises III. Introduction to Gaussian software. Structure of input files, geometry optimization, application of effective core potentials (ECP). Frequency calculations. Time-dependent DFT (TD-DFT) calculations and key information obtainable from output files. Generation of absorption spectra.

Week 14: Practice exercises IV. Application of ORCA software for calculation of EPR parameters. Structure of input files, calculation of hyperfine coupling constant. Calculation of magnetic properties of multinuclear metal complexes. Calculation of 17O hyperfine coupling constants.

Substitution and redox reactions of transition metal complexes. Labile and inert complexes. Kinetics of ligand substitution reactions. Fundamentals of the Eigen-Wilkins mechanism. Factors affecting the rate of exchange reactions. Inner- and outer-sphere redox reactions.