McMaster University - Chemistry 3Q03 Inorganic Chemistry (Core)

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Teaching Assistants: TBA

Course Subject: The properties, structures, and reactions of inorganic compounds with emphasis on transition metal chemistry.
Lectures: TBA
Labs: Thursday (R) at 14.30-17.20 in ABB-402.
Exams: TBA (midterms likely in early October and early/mid November).
Prerequisites: CHEM 2I03/2L03 or CHEM 2C03.

Recommended Reading:

- D. Shriver, P. Atkins, *Inorganic Chemistry*, *3rd Ed.*, Freeman, New York, 1999. *– or –*
- C.E. Housecroft, A.G. Sharpe, *Inorganic Chemistry*, Pearson Education, Harlow, 2001 or 2005.

Other Useful References:

- G.L. Miessler, D.A. Tarr, *Inorganic Chemistry*, *3rd Ed.*, Prentice Hall, Upper Saddle River, NJ, 2004.
- J.E. Huheey, E.A. Keiter, R.L. Keiter, *Inorganic Chemistry*, *4th Ed.*, HarperCollins, New York, 1993.
- F.A. Cotton, G. Wilkinson, P.L. Gauss, *Basic Inorganic Chemistry*, *3rd Ed.*, Wiley, New York, 1995.
- F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, *6th Ed.*, Wiley, New York, 1999.
- D.E. Sands, *Introduction to Crystallography*, Dover, New York, 1975. (Titles, ~$12)

Course Contents:

1. General introduction to transition metal chemistry.
2. Coordination complexes and X-ray crystallography.
3. Crystal field (CF) theory.
4. Molecular orbital (MO) theory for transition metal complexes (ligand field theory).
5. CF or MO theory to explain magnetism.
6. CF or MO theory to explain UV-Visible absorption and emission spectra.
7. Reaction mechanisms for (a) substitution reactions and (b) electron transfer.
8. Special topics.

Evaluation:

- 2 Midterms (25 %)
- 1 Final exam (40 %)
- 2 Assignments (15 %)
- Laboratory (20 %). Note: *All experiments must be performed (and submitted before the end of the course) in order to pass.*

Course contents in more detail (may be subject to change)**:**

General introduction to transition metal chemistry

- Position of the transition metals and lanthanides in the periodic table, definitions of common terms.
- Physical properties, basic chemical properties, oxidation state trends (Frost diagrams), occurrence, some applications.
- Electronic configuration for metals and complexes.
- Review of quantum numbers (n, l, m_l, m_s) , effective nuclear charge, radial distribution functions for s-, p-, d- and f-orbitals, shapes of the d- and f-orbitals.
- General trends: atomic radii, ionic radii, ionisation energies.

Coordination complexes

- History – Werner *vs* Blomstrand, definitions of common terms and IUPAC nomenclature.
- Coordination number and geometry.
- X-ray crystallography (2 lectures from Prof. J. Greedan).
- Types of ligand: bridging and chelating (monodentate, bidentate, polydentate etc.).
- Types of isomer: geometric (*cis*, *trans*, *mer*, *fac*), optical, ionization, linkage, coordination, 'polymerization'. Isomerization in 5-,6- and 4-coordinate complexes.
- Thermodynamics: equilibrium constants, formation constants {stepwise (K), overall (β)}, chelate and macrocycle effects, Irving-Williams Series.

Crystal field (CF) theory

- Crystalline lattices – how crystal field theory came about.
- Octahedral CF splitting diagram.
- Crystal field splitting energy (CFSE), Spectrochemical series for both ligands and metals.
- Low spin and high spin complexes, explanation for trends in ionic radii, $\Delta H_{hydration}$ and $\Delta H_{lattice}$.
- Tetrahedral complexes, tetrahedral *versus* octahedral geometry (octahedral site preference energy).
- Jahn-Teller theory, square planar geometry.
- Limitations of crystal field theory.

Molecular orbital (MO) theory for transition metal complexes (ligand field theory)

- Recap – MO diagrams for simple organic molecules (H_2, HF, N_2, O_2, CO, H_2O, NH_3).
- Constructing MO diagrams for octahedral and tetrahedral complexes (considering σ-bonding only) – symmetry of valence s-, p- and d-orbitals, linear combinations of ligand orbitals.
- Incorporating π-interactions → explanation for spectrochemical series of ligands.

CF or MO theory to explain magnetism and UV-Visible absorption / emission spectra

- Magnetism: paramagnetism, diamagnetism, magnetic susceptibility, χ *vs* T, measuring magnetic susceptibility, ferromagnetism, antiferromagnetism, ferrimagnetism.
- UV-Visible absorption spectra: (a) position and number of transitions: d^1 complexes, d^2 complexes far more complicated, Tanabe-Sunago diagrams, microstates, m_L *vs* m_S tables, terms, transitions between terms, assigning the ground state term, Racah parameters (A, B and C) to assign relative energies to all the terms, metal ions in the gas phase *vs* metal complexes, correlation diagrams, the principal Racah parameter (B), back to Tanabe-Sunago diagrams (E/B vs $\Delta o/B$), non-crossing rule,

high spin to low spin transitions, nephelauxetic effect; (b) intensities of transitions: forbidden transitions, spin and parity (Laporte) selection rules, vibronic coupling; (c) MLCT and LMCT bands, solvatachromism.

- Luminescence, fluorescence, phosphorescence, lasers.

Reaction mechanisms for substitution reactions and electron transfer

- Substitution reactions : (a) Kinetics, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$, types of reaction mechanism (A, D, I_a, I_d), (b) square planar complexes, the trans-effect (A mech), (c) octahedral complexes, A *vs* D mechanism, Taube's rules (D mech) → 'inert' and 'labile' complexes, (d) exceptions.

PLAIN LANGUAGE OVERVIEW OF 3Q03

In CHEM 3Q03, you will learn about molecules and solids containing transition metals [the transition metals are the elements in the centre of the periodic table (Sc→Zn, Y→Cd, Lu→Hg)].

The types of molecules and solids you will learn about in 3Q03 have a wide variety of uses. A selection of these are given below:

Catalysis – A wide variety of both soluble and insoluble transition metal compounds are effective as catalysts. [A catalyst is a chemical that is able to promote a particular reaction but is not itself used up. Therefore, a tiny amount of catalyst can be used to make a huge amount of product]. Some catalysts are used to make small amounts of research chemicals in the lab, others are used to make chemicals such as pharmaceuticals on a multi-tonne scale, and others are used to make widely used chemicals and materials on a giant scale (*e.g.* Ti and Zr are used in alkene polymerization catalysts, Rh containing molecules are used to make millions of tones of acetic acid and aldehydes every year, Fe and V are used to make > 120 million tonnes of NH_3 and SO_3 every year, and the precious metals such as Pt and Rh are used in catalytic converters in our cars).

Green Chemistry – Considerable numbers of researchers are involved in green chemistry. Such research includes the use of transition metal complexes to produce biodegradable polymers, to remove sulphur containing organic impurities from oil and gas, or to harvest solar energy. Many researchers are also involved in the development of catalysts which use O_2 as an oxidant instead of corrosive H_2O_2, catalysts which work in water or ionic liquids instead of organic solvents, catalysts that can be recycled more easily, catalysts that will allow reactions to run at lower temperatures and pressures (making them more energy efficient), catalysts based on less toxic and more abundant metals (*e.g.* iron), catalysts that produce fewer unwanted bi-products, or catalysts that are required in even smaller amounts to promote a particular reaction.

Metal Extraction, Mining and Industrial Waste Treatment – The ability to selectively complex one metal and not another is of huge importance in this area.

Electronics Industry – Transition metals are used extensively in the microelectronics industry, and the type of metal containing molecules that we learn about in 3Q03 are often used to deposit uniform thin films of metals or metal compounds (e.g. for circuit wiring or as insulation in memory and logic chips). As with much of inorganic chemistry, this work is typically carried out under strictly air-free conditions [vacuum line techniques for handling air-sensitive complexes are introduced in the 3Q03 labs and then further developed (including glove box techniques) in 3P03].

Magnetic Materials – Many materials with important magnetic properties incorporate transition metals [*e.g.* $SmCo_5$, $Nd_2Fe_{14}B$, $SrFe_{12}O_{19}$ which have uses in headphones, cell phones and fridge magnets].

Biology and Biochemistry – Transition metals (in particular Mn, Fe, Co, Ni, Cu and Zn) play a very important role in the body (e.g. Iron in hemoglobin in our blood, Cobalt in Vitamin B12, Manganese in antioxidant enzymes). In addition, both transition metals and the lanthanides are also used extensively in biochemistry – for example, to bind with a new protein that has been prepared and separate it from impurities, or as fluorescent tags for biological molecules.

Medicine – Platinum complexes are used as anti-cancer drugs (e.g. cisplatin = $[PtCl_2(NH_3)_2]$), Gold complexes are used as drugs for arthritis (*e.g.* Auranofin), radioactive Technicium is used in radiopharmaceuticals, Vanadium is used as an insulin mimic for the treatment of animals, and various transition metals are used to construct medical implants (*e.g.* titanium, vanadium) or medical devices (*e.g.* shape memory Ni-Ti alloys for use as anchors for tendon fixation, stents or orthodontic wires).

Superconductors – Many superconductors incorporate transition metals (*e.g.* $Tl_2Ba_2CaCu_3O_{10}$).

Thermoelectric Materials – Thermoelectric materials (*e.g.* Zn_4Sb_3 and Te/Ag/Ge/Sb alloy) are materials able to convert heat into electricity. Current uses for thermoelectric materials include cooling devices for research equipment and to generate electricity using the heat produced by the radioactive decay of PuO_2 on the Cassini-Huygens spacecraft.

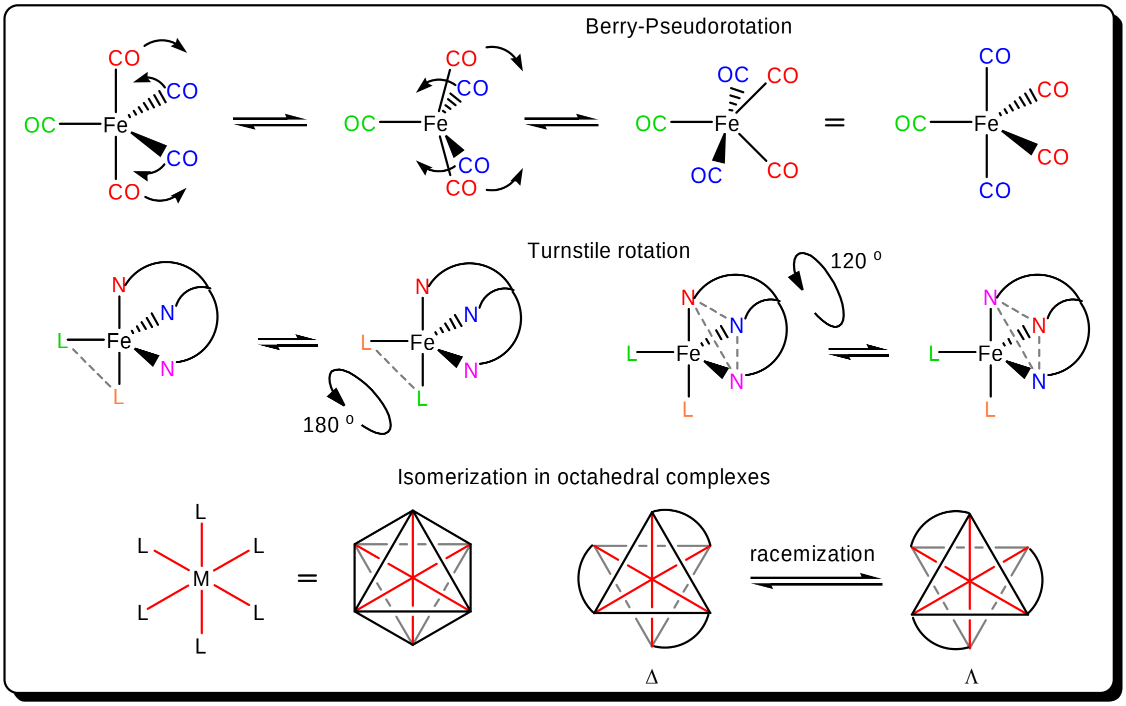
Lasers and Nonlinear Optical Materials – Many lasers rely on the optical transitions that occur in 1st row transition metal compounds – e.g. Cr^{3+} or Ti^{3+} replacing some Al^{3+} ions in Al_2O_3 (ruby or sapphire lasers). Nonlinear optical materials are materials that can be used to manipulate the frequency of light, and are particularly important in the telecommunications industry. A familiar product which relies on nonlinear optical frequency doubling is the green laser pointer: laser light at a wavelength of 1064 nm is generated using a $Nd{:}YVO_4$ crystal, and this is passed through a nonlinear optical crystal of $KTiOPO_4$ which doubles the frequency to produce 532 nm green laser light.

Other Uses – batteries, paints (TiO_2, blue cobalt compounds etc.), fuel additives [*e.g.* $Fe(C_5H_5)_2$], corrosion resistant coatings (especially Cr and Zn), alloys for various uses (bronze = Cu/Sn, brass = Cu/Zn, Monel = Cu/Ni), nuclear control rods (*e.g.* Hf or Ag/In/Cd), nuclear fuel rod coatings (*e.g.* Zr) structural metals (stainless steel is typically iron with 10-25% chromium and 0-10% nickel), basic electrical metals (copper and gold wires), metals for jewelry (*e.g.* Au, Pt, Rh, Ag) etc.

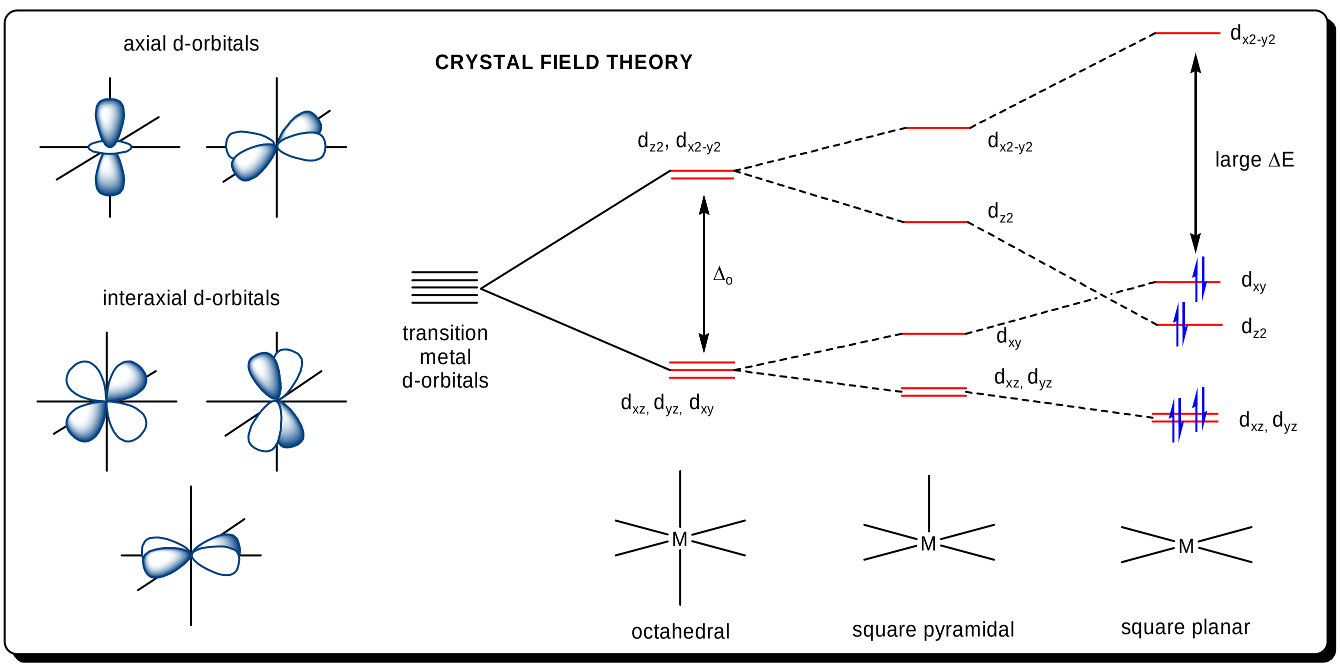
A vast amount of research involving transition metal chemistry is currently going on around the world. Some of this research is directed towards improving/extending existing applications and developing new applications. Other research is directed towards increasing our understanding of transition metal chemistry and advancing the complexity of the structures that chemists are able to make. This more fundamental or exploratory work provides the basic platform of knowledge that allows the development of the future technologies. Given the number of transition metals (30 stable ones), there is still much to be done, and researchers in this area rely on their background in transition metal chemistry (such as that provided in 3Q03, 3P03, 4R03 and 4C03), a knowledge of the current literature, good experimental techniques, persistence, and creativity to be successful. Faculty in our department involved in transition metal research include D. Emslie and G. Schrobilgen (metal containing molecules), J. Greedan, Y. Mozharivskyj and J. Barbier (solid state chemistry), J. Valliant and A. Capretta (inorganic chemistry from a more organic perspective).

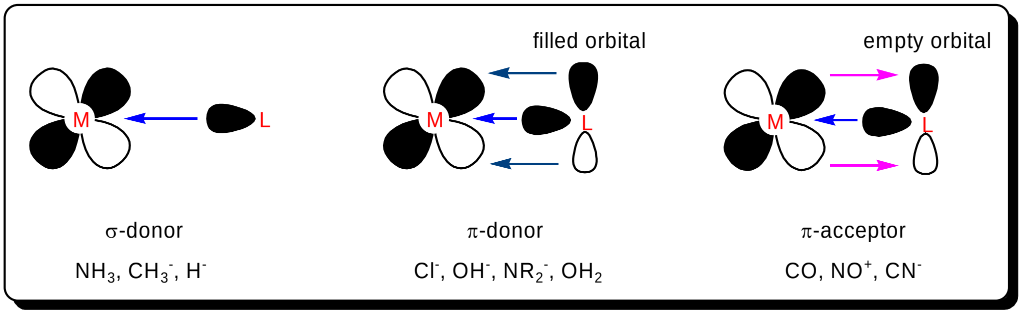
DIAGRAMS / FIGURES TO PROVIDE A FLAVOUR OF 3Q03 COURSE CONTENT

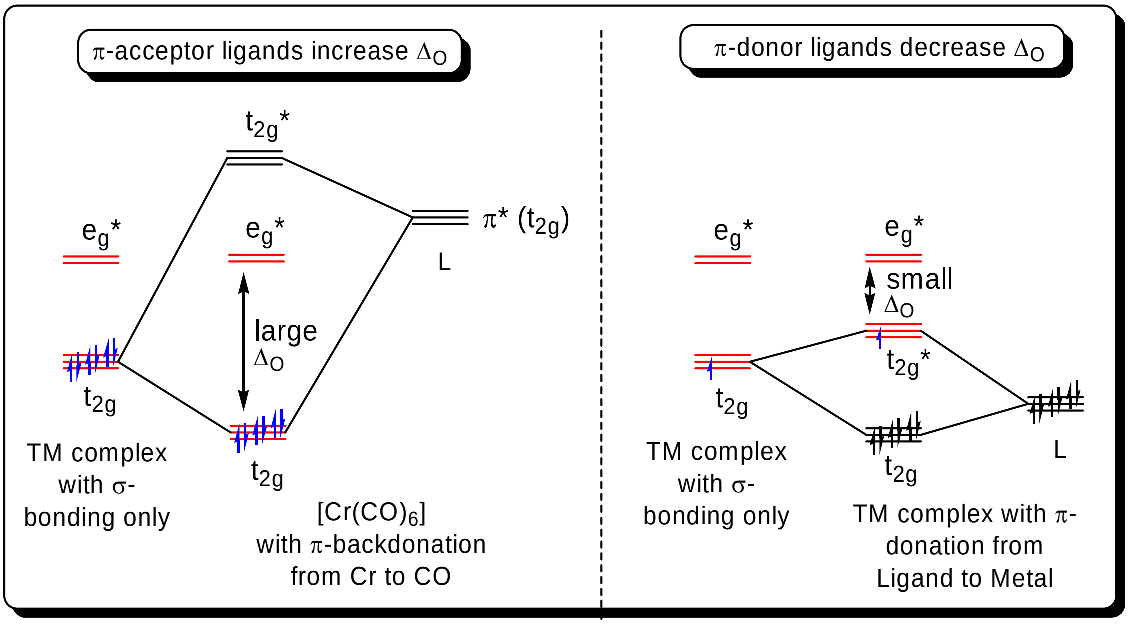
GEOMETRIES AND ISOMERISATION IN COORDINATION CHEMISTRY



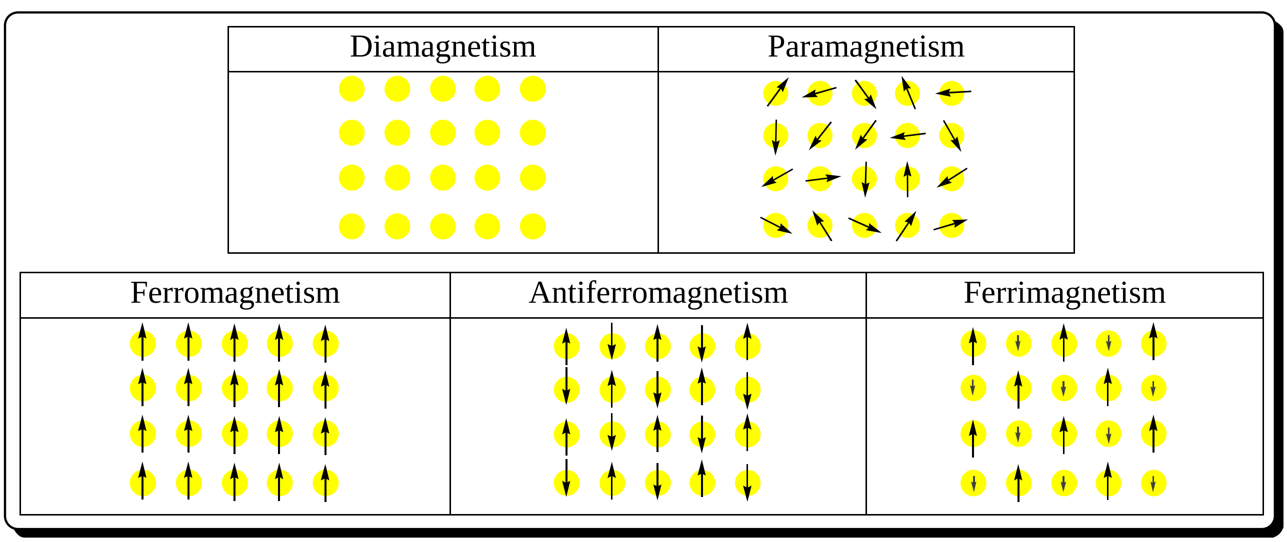
CRYSTAL FIELD THEORY and LIGAND FIELD THEORY




filled orbital
empty orbital
M
L
σ-donor
NH3, CH3-, H-
π-donor
Cl-, OH-, NR2-, OH2
π-acceptor
CO, NO+, CN-

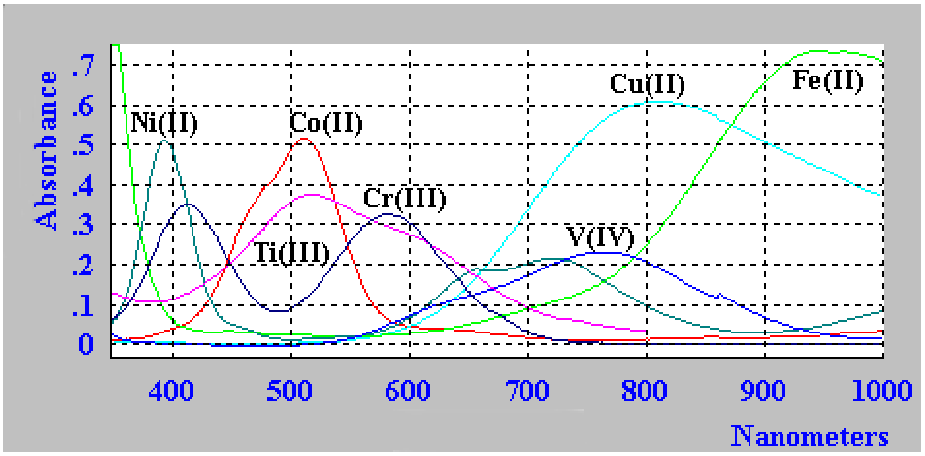

π-acceptor ligands increase ΔO
π-donor ligands decrease ΔO
t2g*
eg*
π* (t2g)
L
large
ΔO
t2g
TM complex with σ-bonding only
[Cr(CO)6]
with π-backdonation from Cr to CO
small
ΔO
TM complex with π-donation from Ligand to Metal

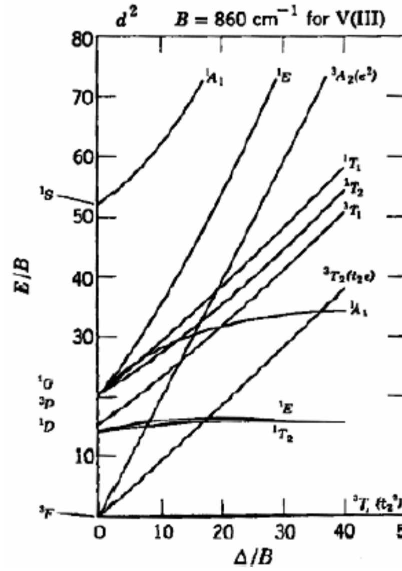
MAGNETISM


Diamagnetism
Paramagnetism
Ferromagnetism
Antiferromagnetism
Ferrimagnetism

ELECTRONIC (UV-VIS) SPECTRA OF TRANSITION METAL COMPLEXES

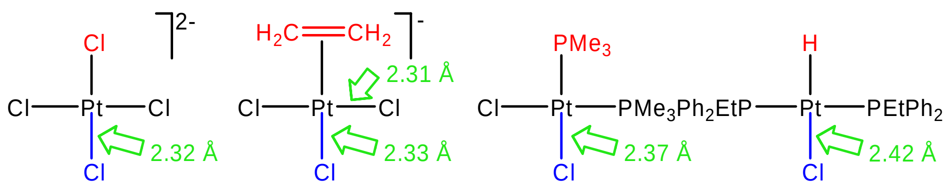
UV-Visible absorption spectra for aqueous solutions of first-row transition metal complexes with the formula $[M(H_2O)_6]^{x+}$





REACTION MECHANISMS

TRANS INFLUENCE
(THE GROUND STATE COMPONENT OF THE TRANS EFFECT)



π-ACCEPTOR ABILITY
(THE TRANSITION STATE COMPONENT OF THE TRANS EFFECT)