CHEM.522
Drexel U. Fall Inorganic: MSGT, Sept. 2011.

522Syllabus11D

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Very Useful Course Materials:

1) A. Vincent: *Molecular Symmetry & Group Theory*. 2nd Edn., Wiley, 2001.
2) The course notes will eventually be available on the Bb/Vista website.
3) Molecular model kits – about $22 - contact the DU Student ACS Affiliate ?
4) Shriver & Atkins: : *Inorganic Chemistry*. 5th Edn., Freeman & Co., 2010.

Web Resources:

Look for "CHEM522" after logging on at learning.drexel.edu (no content yet - Sept.18th)
Kettle's *Symmetry in Chemistry* materials are now available on the web, at:
http://www.rsc.org/Membership/Networking/InterestGroups/EducationalTechniques/ChemistryCassettes/index.asp
The Shriver/Atkins textbook website is: www.whfreeman.com/ichem

Reference Materials:

1) F. A. Cotton: *Chemical Applications of Group Theory*. 3rd Edition, Wiley-Interscience 1990. QD461.C65.1990 (Hagerty Reserve)
2) M.F.C. Ladd: *Symmetry in Molecules & Crystals*, Ellis Horwood/Wiley/Halsted, Chichester, 1989: QD461.L23.1989.
3) Housecroft & Sharpe: *Inorganic Chemistry*. 3rd Edn., Prentice-Hall 2009.
4) Miessler & Tarr: *Inorganic Chemistry*, (3rd Edn.) 2003.
5) Huheey, Keiter & Keiter, *Inorganic Chemistry: Principles of Structure & Reactivity*. Fourth Edn., Harper-Collins 1993. (Good chapter on symmetry)
6) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn., Wiley-Interscience, NY, 1997 QD96.I5N33 1997 (or earlier editions): Hagerty Reserve.

Goals:

A primary goal of the GT section of the course is to be able to read and use character tables for solving molecular properties. Be able to translate between name and formula, and sketch corresponding molecular structures. Be able to interpret essentials of X-ray crystallographic results. Know the concept of a group, be able to manipulate/combine elements, using multiplication tables. Be able to use matrix representations of vectors & symmetry operations, generate simpler cases. Understand origins of character values and representations. Be able to use character tables to find classes and subgroups and deduce and combine representations for various properties and objects (*e.g.*, atomic orbitals). Know how to choose basis sets, generate & decompose representations from them & how to use projection operators. Use the Crystal Field Theory model to interrelate stereochemistry, symmetry, configuration, spin state, optical and (the various kinds of) common magnetic properties and crystal field stabilization energy for transition metal compounds; compute magnetic moments for *nd* [and *4f*] ions. Using symmetry methods, be able to derive normalized MO forms for diatomic, cyclic and centric molecules; deduce occupancy of and properties from transition metal complex MO diagrams. Be able to deduce the spin &

orbital multiplicity of ground and excited states. Be able to read Tanabe-Sugano diagrams and recognize *d-d*, LMCT, MLCT & π-π* transitions.

Relationship to other courses and Pre-Requisite Knowledge:
The pre-requisite for CHEM.522 is now your undergraduate preparation in Inorganic Chemistry. The other course in the core graduate sequence is CHEM.523 (Inorganic-III), and the other courses that may be taken include 862, 771 and 772.
Specific things you need to know before entering 522 are: *s,p,d,f*-atomic orbitals; symmetry elements; assignment of molecules to point groups; configurations of *nd* cations; VSEPR & geometries for 2-6-coordination; the Lewis acid/base model; PChem: basis of infrared and electronic (optical) absorption phenomena. We'll do a quick review of *d*-configurations and molecule point group membership before we start the other syllabus material.

Other stuff: Be sure that I have your correct Email address for my exploder. Work on the problem sets !! Attempt to solve the homework problems as soon as we have covered the material in class. There is normally no grade given for attendance or for homework. If you do not do the homework, you will find it hard to pass the exams, and virtually impossible to get a good grade. I suggest that you form a study group with some like-mided students in the course, and collaborate in studying and problem-solving. For help with problem sets or any other concerns, I may be found in my office or lab most of the daytime during the week, though it's probably best to make an appointment. As before, your grade is based on the (usually three) exams: two midterms (20%, 30%) plus a final exam (50%). The grade ranges are: D= 43-45; D+=46-49; C-=50-53; C=54-56; C+=57-59; B-=60-64; B= 65-69; B+=70-75; A-=76-83; A=84-91; A+=92-100. You may bring our periodic table and molecular model kit to the exams (some of the assigned classrooms have no periodic table). If you are not officially registered in the course, no midterms or quizzes will be graded or returned, and you may not receive any distributed materials. Tentative mid-term dates are Oct. 18th & Nov. 15th.

Penalizable misspellings: "flourine", "valance", "assymmetric", "pyrimidal".

Make-Up Exams ?
You don't need an excuse to take the make-up exam if you miss a midterm or final, but you *must* then attend the make-up at the designated time and place or take a zero on it - no excuses. You may make up no more than one mid-term. Make-up exams are never of lesser difficulty than the ones they replace. All make-up exams are tentatively scheduled for the afternoon of Monday Dec. 12th.

The 10-Minute Rule: If I'm more than ten minutes late without prior notice, consider the class cancelled. If you are going to be more than ten minutes late for a class, please don't enter without prior arrangement, until the class takes a break.

Content:
There are three major sections in this course on (mainly transition metal) structure-properties relationships: constitution & structure, CFT, and polyatomic MO's. CFT is the major one, while use of group theoretical methods is an underlying theme.

- Review of metal ion configurations & assigning molecules to point groups.

- Elements of crystal symmetry; interpretation of diffraction articles.
- The Bond Valence Sum method.
- Symmetry elements and groups: combination, matrix usage, characters.
- Classes. Matrix representations of 3D vectors & of operations.
- Irreducible and reducible representations as sets of matrices. Sums. Character tables.
- Mullikan notation. Degeneracy. Application to orbital symmetry.
- Representations for central atom orbitals. The Crystal Field model.
- O_h fields; d-d transitions. The spectrochemical series.
- Jørgensen's *f* & *g*; spin states & dia/para/ferro/antiferro-magnetism of nd^x systems [*4f* systems, spin crossover systems*] dinuclear complexes.
- CFSE & stability, T_d fields, 4d- & 5d-ions; planar/D_{4h} symmetry, Jahn-Teller "distortion".
- Diatomic MO's from a symmetry approach: from basis set to representation.
- Decomposition formula; MO's for cyclic tetraatomic (S_4^{4+} π-system): SALC's.
- Projection operators. Use of PRSG, normalisation & relative energies of MO's.
- Symmetry factoring for centric molecule: LGO's, σ & π MO's for BF_3.
- MO's for octahedral complexes without and with π-bonding.
- Products of representations: spin & symmetry selection rules; splitting of terms by crystal fields, Tanabe-Sugano diagrams, charge-transfer transitions, optical electronegativity.