

## Chemistry 475

### Transition Metal Chemistry 1: Structure

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## Structural Methods

- X-Ray Crystallography
  - Bragg diffraction off lattice of electron density ( $n \cdot \lambda = 2 \cdot d \cdot \sin \theta$ )
  - Measure  $\theta$  and spot intensity
  - Reconstruct lattice and refine
- Vibrational and Rotational Spectroscopy
- Useful Methods for Transition Metals
  - Electronic spectroscopy
  - Magnetism

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## Structural Methods

- Nuclear Magnetic Resonance (NMR)
- Based on Nuclear Zeeman Effect
  - Nuclear spin quantum number,  $I$
  - z-Component of  $I$  is  $m_I$
  - Described by Hamiltonian

$$\hat{H} = -\mu_N \cdot \vec{H}_0 \quad \mu_N = \gamma \hbar \vec{I}$$

$\mu_N$  is classical magnetic moment

$\gamma$  is the gyromagnetic ratio (unique for each nucleus)

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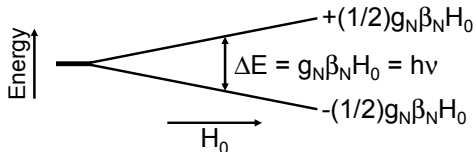
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## Quantum Mechanics

- For Field,  $H_0$ , along z Axis simplifies to

$$\hat{H} = -g_N \beta_N H_0 \hat{I}_z$$

- $\hat{I}_z$  returns original wavefunction times  $m_l$
- For  $I = 1/2$  ( $m_l = \pm 1/2$ ) predicts




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## Further Considerations

- Different Nuclei have different  $\Psi$  due to Chemical Environment
  - Resonance condition is different
  - Chemical shifts (measured in field)
- Nuclear Spins can interact (*couple*)
  - Through space or Fermi contact
  - Hamiltonian is

$$\hat{H} = -\sum_i \sum_j J_{ij} I_i \cdot I_j - \sum_i g_N \beta_N H_0 \hat{I}_{z_i}$$

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## Coupling in NMR

- Signal from Nucleus split into  $(2 \cdot n \cdot I + 1)$  Lines by each  $n$  equivalent Nuclei it is coupled to Intensity of Lines given by
  - Pascal triangle
  - Natural abundance of nuclei
- Equivalence determined by Symmetry
  - Isochronous nuclei (chemically vs. magnetically equivalent)
  - Diastereotopic nuclei
- Quadrupolar Nuclei

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## Coupling in NMR

- J designated by Number of Bonds and Nuclei Coupled
  - ${}^3J_{H,H}$  (usually discussed in organic)
- Resulting Splitting Patterns depend on Magnitude of J's
  - Satellites (Sn lab)
- Consider  ${}^{31}\text{P}$  NMR Spectrum of  $\text{HPF}_2$ 
  - Case 1:  ${}^1J_{P,F} > {}^1J_{P,H}$
  - Case 2:  ${}^1J_{P,H} > {}^1J_{P,F}$

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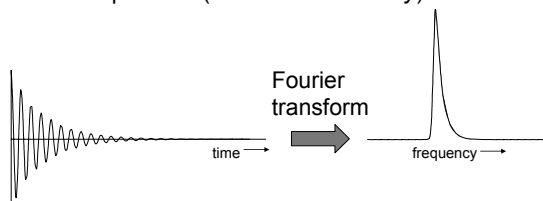
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## Relaxation Effects in NMR

- In NMR Experiment Sample exposed to intense Pulse of Radiation
  - Sample resonates at all its possible frequencies (*free induction decay*)



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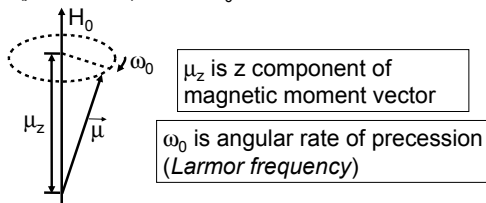
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## Relaxation Effects in NMR

- Alignment of Nuclei in Field stymied by quantization of Angular Momentum
  - Induces a torque and particle spins (*precesses*) about  $H_0$



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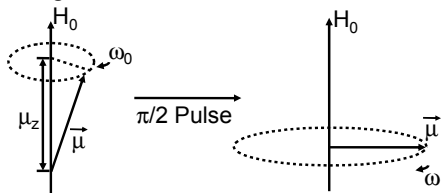
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## Relaxation Effects in NMR

- Apply Magnetic Field Perpendicular to Existing Field



Magnetization vector is transferred from z to x,y plane with a new precessional frequency.

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## Bloch Equation

- For Mathematical Simplicity define a *Rotating Frame*
  - Define unit vectors u, v in x, y plane rotating at a frequency  $\omega$
- Precession of Magnetization with Time is then

$$\dot{\vec{M}} = -\gamma \vec{H}_{\text{eff}} \times \vec{M} - \frac{1}{T_2} (M_u \vec{e}_u + M_v \vec{e}_v) - \frac{1}{T_1} (M_z - M_0) \vec{e}_z$$

torque from magnetic field

relaxation effects

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## Relaxation Effects in NMR

- $T_1$  is *Longitudinal Relaxation Time*
  - $1/T_1$  measures rate of return of z component to equilibrium
  - Dominated by *spin-lattice relaxation*
- $T_2$  is *Transverse Relaxation Time*
  - $1/T_2$  measures rate of return of  $\omega$  to equilibrium (dephasing in u, v plane)
  - Mostly *spin-spin relaxation*

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## Importance of $T_1$ and $T_2$

- If  $T_1$  is too Short, No Signal
  - Nuclei return to thermal equilibrium faster than can be measured
  - Paramagnetic centers shorten  $T_1$  for other nuclei in solution or bound to them
- If  $T_2$  is too Short, Broad Signals
  - Linewidth is proportional to  $1/T_2$
  - Paramagnetic centers can shorten  $T_2$

$$\Delta\nu_{1/2} = \frac{1}{\pi T_2}$$

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## More on Linewidths

- *Homogeneous* Broadening
  - Linewidth depends on  $T_2$
- Any additional Broadening caused by *Inhomogeneous Broadening*
  - Imperfections in magnetic field
  - Chemical exchange: fast events show wide peaks if process faster than NMR's timeframe ( $\sim 10^{-1}$  –  $\sim 10^{-9}$  sec)
  - Lower temperature to "freeze out" exchange processes

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## Nuclear Overhauser Effect

- Enhancement of Signal from a Nucleus by Magnetization Transfer from Another
  - Saturate the X nucleus (usually  $^1\text{H}$ )
  - Observe the A nucleus (usually  $^{13}\text{C}$ )

$$\frac{I_A}{I_A^0} = 1 + \frac{\gamma_X}{2\gamma_A} \approx 3 \text{ for } X=^1\text{H} \text{ and } A=^{13}\text{C}$$

- Similar Effect used for 2-D NMR
  - COSY
  - HETCOR

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## Chemistry of the Metals

- Lewis Acid/Base Interactions
  - Metal ion accepts electron pairs from donor atom(s) on a *ligand*
  - Forms a *coordinate covalent (dative)* bond
- Results in *Coordination Compounds* or *Complex Ions (Complexes)*
- Complexes defined by
  - Coordination number (CN) of metal
  - Denticity and hapticity of ligand(s)

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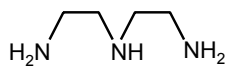
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## Denticity

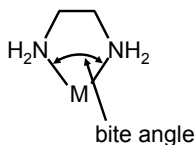
- Number of Donor Atoms a Ligand has to form Coordinate Covalent Bonds

Monodentate



Tridentate

Bidentate



Polydentate: ligand with more than one donor atom

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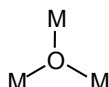
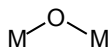
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## Hapticity

- Coordination Number of Donor Atoms
  - Denoted  $\eta$  (eta)
  - Bridging ligands denoted by  $\mu$  (mu)



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## Common Geometries for Transition Metals

- Transition Metals show wide Range of Geometries
  - Only some ions with  $d^0$  and  $d^{10}$  electronic configurations obey VSEPR
- Most Common Geometries are
  - Octahedral (CN = 6)
  - Tetrahedral (CN = 4)
  - Square planar (CN = 4)

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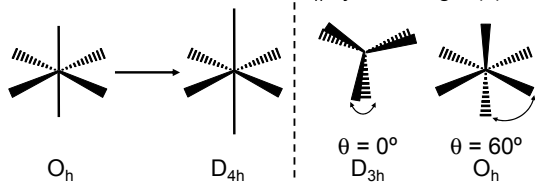
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## Coordination Number Six

- Most Common is Octahedral ( $O_h$ )
  - Often with distortion (Jahn-Teller) to  $D_{4h}$
- Trigonal Prism ( $D_{3h}$ ) is relatively Rare
  - Often distorted toward  $O_h$  by twist angle ( $\theta$ )



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## Coordination Number Four

- Tetrahedral ( $T_d$ )
  - Common with  $d^0$ ,  $d^{10}$ ,  $d^5$  and oxoanions
  - Also for  $d^7$ ,  $d^8$  and  $d^9$  with small  $\pi$  donors
- Square Planar ( $D_{4h}$ )
  - Occurs for  $d^7$ ,  $d^8$  and  $d^9$  with  $\pi$  acceptors
- Bisphenoid, or See-Saw ( $C_{2v}$ )
  - Rare in simple transition metal complexes
  - More common with heavy p-block metals (stereochemically-active lone pair)

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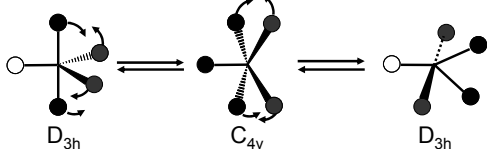
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## Coordination Number Five

- Square Pyramidal ( $C_{4v}$ ) and Trigonal Bipyramidal ( $D_{3h}$ )
  - Small energy difference between geometries
  - Distorted in solid state, fluxional in solution
  - Berry pseudo-rotation



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## Other Geometries

- Two Coordinate: Linear ( $D_{\infty h}$ ,  $C_{\infty v}$ )
  - $d^{10}$  Heavy metals ( $Hg^{2+}$ ,  $Au^+$ ,  $Ag^+$ )
- Three Coordinate: Trigonal Planar ( $D_{3h}$ )
  - Rare for transition metals ( $d^{10}$ , heavy)
- Seven Coordinate
  - Pentagonal bipyramid ( $D_{5h}$ )
  - Capped trigonal prism ( $C_{2v}$ ) usually distorted due to ligand-ligand repulsion
  - Heavier transition metals or forced by ligand

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## Other Geometries

- Eight Coordinate: Dodecahedron ( $D_{2d}$ ), Square Antiprism ( $D_{4d}$ ) and Cubic
  - Large metals with small ligands
  - Chelates with small bite angles (favors  $D_{4d}$ )
  - Stereochemical non-rigid (distorted in solid, equilibrium in solution (?))
- Higher CN's (9, 10, 12, 14) are known
  - Lanthanides/actinides with monodentate or small bite angle bidentate ligands

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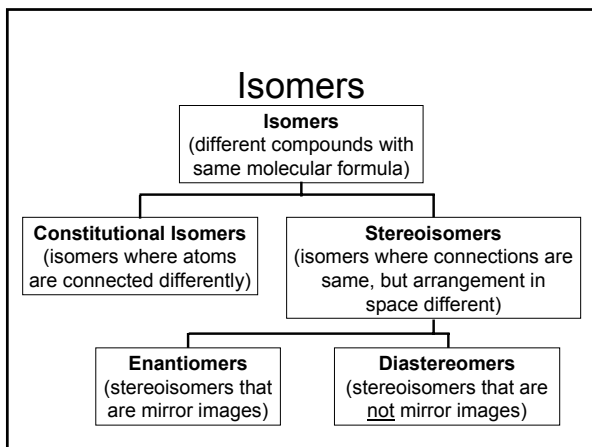
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## Constitutional Isomers

- Hydrate Isomers
  - $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$
- Coordination Isomers
  - $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ ,  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$
- Ionization Isomers
  - $[\text{PtCl}_2(\text{NH}_3)_4]\text{Br}_2$ ,  $[\text{PtBr}_2(\text{NH}_3)_4]\text{Cl}_2$
- Linkage Isomers
  - Ambidentate ligands ( $\text{SCN}^-$ )

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## Stereoisomers

- Molecule must be
  - Stereochemically rigid
  - Substitutionally inert (not *labile*)
- Limited to Square Planar, Tetrahedral and Octahedral Complexes
  - $T_d$  tend to be stereochemically non-rigid
- To have Enantiomers a Complex must lack  $S_n$ 
  - Remember  $S_1 = \sigma$ ,  $S_2 = i$

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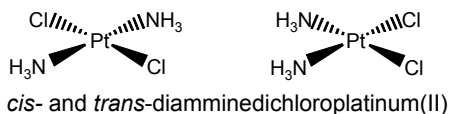
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## Stereoisomers of Square Planar Complexes

- Only Diastereomers Possible for simple  $D_{4h}$  Complexes
  - Mirror plane
  - Chiral ligands can give chiral complexes
- Show *cis/trans* Isomers




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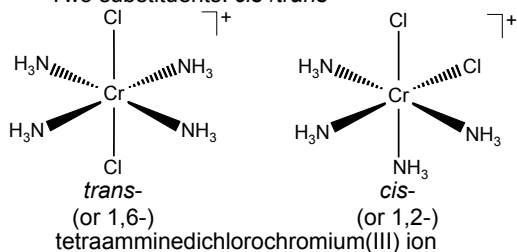
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## Stereoisomers of Octahedral Complexes

- Diastereomers
  - Two substituents: *cis/trans*-




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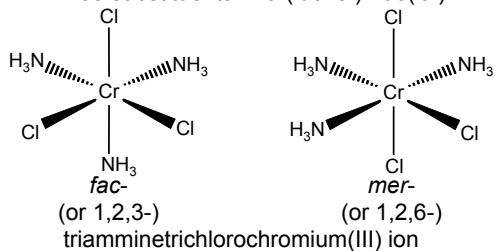
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## Stereoisomers of Octahedral Complexes

- Diastereomers
  - Three substituents: *mer(idonal)/fac(ial)*-




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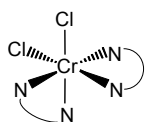
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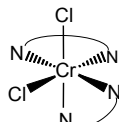


## Designation of Enantiomers in Octahedral Complexes

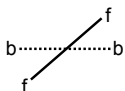
- Example:  $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$



Start with one enantiomer



Rotate to put one ring in back



Determine orientation of rings

$\Delta$ -*cis*-dichlorobis(ethylenediamine)chromium(III) ion

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