

## Chemistry 475

### Transition Metal Chemistry 2: Bonding

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## Thermodynamics in Coordination Compounds

- Metal-Ligand Interactions are Equilibria between Independent Species
  - Replace solvent molecules in metal's coordination sphere by ligand (omitted)
- Equilibria described by
  - *Stepwise stability constants* ( $K$ ) indicates a stable step
  - *Overall stability constants* ( $\beta_{m/h}$ ) indicates a stable complex

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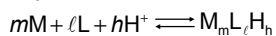
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## More on Overall Stability Constants

- For the Equilibrium



$$\beta_{m/h} = \frac{[M_m L_\ell H_h]}{[M]^m [L]^\ell [H^+]^h}$$

- Treatment of  $H^+/OH^-$

- For  $K_i$ ,  $H^+/OH^-$  included directly
- For  $\beta_{m/h}$ ,  $h = +1$  for  $H^+$ , but  $h = -1$  for  $OH^-$
- Need to use  $K_w = [H^+][OH^-]$

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## Determination of Overall Stability Constants

- Have a Series of Linear Equations
- Solve for  $\log\beta_{mth}$  by Non-Linear Least Squares Routine, but must
  - Measure independently  $\log\beta_{01h}$ ,  $\log K_w$
  - Know  $[L]_{total}$  and  $[M]_{total}$
  - Measure  $[H^+]$  as a function of added standard titrant (potentiometric titration)
  - Or measure change in spectra as a function of added standard titrant

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## Relationship between Stability Constants

- Adding Reactions:  $K_{new} = K_1 \cdot K_2$
- Subtracting Reactions:  $K_{new} = K_1 / K_2$
- Overall Stability Constant is related to Stepwise Stability Constants by

$$\beta_i = \prod K_i$$

- Both are related to  $\Delta G$ 
  - Find  $\Delta H$  and  $\Delta S$  from temperature dependence

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## Thermodynamics with Monodentate Ligands

- Entropy not usually Important
  - No net change in number of particles when solvent molecule replaced by ligand
  - Exception: extensive ordering of solvent molecules about ligand or metal
- Stability of Complexes ( $\Delta G$ ) dominated by  $\Delta H$  from Bonds
  - For most complex ions bonds range from polar covalent to ionic

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## Stability of Complexes with Monodentate Ligands

- Charge of Ligand and Metal
  - Charge neutralization very important
- Match of Lewis Acidity/Basicity between Donor Atoms and Metal
- Electronic Demands of Metal
- Number of Ligands
  - Stability increases with number of ligands
- Ligand Steric Requirements

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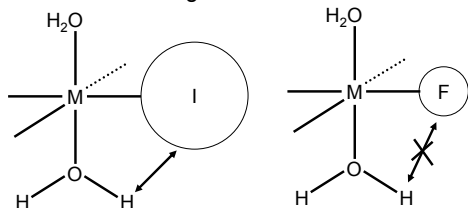
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## Ligand Steric Requirements

- Large Ligands introduce Strain into Complex
  - Lowers bonding interaction




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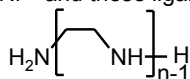
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## Chelate Effect

- Increased Stability of Complexes with Polydentate Ligands relative to Monodentate Analogs
  - Consider  $\text{Ni}^{2+}$  and these ligands



Polyamine	en	dien	trien	tetren
Denticity (n)	2	3	4	5
$\log \beta_{1n0} (\text{NH}_3)$	5.08	6.85	8.12	8.93
$\log \beta_{110} (\text{polyamine})$	7.47	10.7	13.8	17.4

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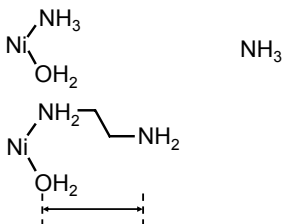
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## Schwarzenbach's Rationale

- Chelate increases Effective Concentration of second Donor when first Donor binds




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## Thermodynamics and the Chelate Effect

Complex	$\Delta G$ (kcal/mol)	$\Delta H$ (kcal/mol)	$\Delta S$ (cal/mol·K)
$\text{Ni}(\text{NH}_3)_2(\text{H}_2\text{O})_4^{2+}$	-6.93	-7.8	-3
$\text{Ni}(\text{NH}_3)_4(\text{H}_2\text{O})_2^{2+}$	-11.08	-15.6	-15
$\text{Ni}(\text{NH}_3)_6$	-12.39	-24	-39
$\text{Ni}(\text{en})(\text{H}_2\text{O})_4^{2+}$	-10.03	-9.0	+4
$\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$	-18.47	-18.3	+3
$\text{Ni}(\text{en})_3^{2+}$	-24.16	-28.0	-10

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## Thermodynamics and the Chelate Effect

- Source of Chelate Effect not Clear
  - Compare differences in thermodynamic quantities (e. g.  $\Delta(\Delta S) = \Delta S_{\text{en}} - \Delta S_{\text{NH}_3}$ )

Complex	$\Delta(\Delta G)$ (kcal/mol)	$\Delta(\Delta H)$ (kcal/mol)	$\Delta(\Delta S)$ (cal/mol·K)
$\text{Ni}(\text{en})(\text{H}_2\text{O})_4^{2+}$	-3.1	-1.2	+7
$\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2^{2+}$	-7.4	-2.7	+18
$\text{Ni}(\text{en})_3^{2+}$	-11.8	-4	+29

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## Thermodynamics and the Chelate Effect

- $\text{Ni(en)}_x^{2+}$  Complexes are more Stable than Complexes with  $2x \text{ NH}_3$  Donors
  - Negative  $\Delta(\Delta G)$
- Bond Energies (from  $\Delta(\Delta H)$ ) make only a Small Contribution
- Increased Stability dominated by  $\Delta(\Delta S)$  Term
  - Chelate effect is an entropic effect

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## Source of Large $\Delta S$

- One  $\text{NH}_3$  replaces one  $\text{H}_2\text{O}$ 
  - No change in number of particles,  $\Delta S \approx 0$
- Each en displaces two  $\text{H}_2\text{O}$ 
  - Expect  $\Delta(\Delta S) = R \ln(55.5)$  or  $+7.9 \text{ cal/K}$  per mole extra  $\text{H}_2\text{O}$  liberated (translations)

Complex	$\Delta(\Delta S)$ (cal/mol·K)	n	+7.9 n
$\text{Ni(en)(H}_2\text{O)}_4^{2+}$	+7	1	+7.9
$\text{Ni(en)}_2(\text{H}_2\text{O)}_2^{2+}$	+18	2	+15.8
$\text{Ni(en)}_3^{2+}$	+29	3	+23.7

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## Contribution of $\Delta H$

- Recall  $\text{Ni}^{2+}$  Data for en/ $\text{NH}_3$  Binding
  - There is a small, but real,  $\Delta(\Delta H)$
  - Small differences in ligand Lewis basicity

Complex	$\Delta(\Delta G)$ (kcal/mol)	$\Delta(\Delta H)$ (kcal/mol)	$\Delta(\Delta S)$ (cal/mol·K)
$\text{Ni(en)(H}_2\text{O)}_4^{2+}$	-3.1	-1.2	+7
$\text{Ni(en)}_2(\text{H}_2\text{O)}_2^{2+}$	-7.4	-2.7	+18
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## Extending the Chelate Effect

- Two Donor Atoms in one Ligand increases Complex Stability
  - Increase donors = increased stability?

L	NH <sub>3</sub>	en	trien
p	4	2	1
# links	0	2	3
logβ <sub>1p0</sub>	8.12	13.54	13.8

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## Contribution of ΔH

L	trien	2, 3, 2	tren
p	1	1	1
# links	3	3	3
logβ <sub>1p0</sub>	13.8	16.4	14.6

- CH<sub>2</sub>CH<sub>2</sub> bridge too small, *ring strain*
- *Topology* of donor atoms important

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## Contribution of ΔH

- Bond Energies
  - Hard/soft differences
  - Charge neutralization
- Steric Demands of Ligand and Metal
  - *Bite angle* of chelating groups vs. metal's size (*ring strain*) ⇒ coordination number
  - Steric hindrance within the chelate
  - Topology

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## Related Effects

- Macrocycle Effect: Increased Stability of Cyclic Polydentate Ligands over Acyclic Analogs
- Cryptate Effect: Increased Stability of Ligands containing Multiple Macrocycles
- Result of Ligand *Preorganization*
  - Donor atoms locked in position (rigid ligand) to bind metal
  - Minimal rearrangement for binding (entropy)

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## Enthalpy in Macrocycle and Cryptate Effects

- Strain induced by from Mismatch of
  - Cavity/metal size
  - Preferred geometries
- Ligand is too Organized
  - Strained introduced by bending ligand to fit metal in (kinetic effect seen in rate of ligand binding)

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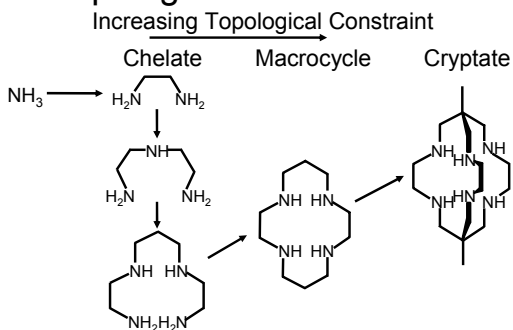
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## Topological Constraints



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## Predisposed Ligands

- Ligands that Bind Strongly, but Donor Atoms are not Highly Preorganized
  - Example: EDTA<sup>4-</sup>
- Have Features that Lead to Strong Binding (*Complementarity*)
  - Charge neutralization
  - Hard/soft donor/acceptor match
  - Preferred geometries match
  - Size match

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## Selectivity

- Relative Preference of a Ligand to bind only One Metal Ion
  - Perfect selectivity is never attained
- Consider Ligand [2.2.2]
  - Relatively selective for Ba<sup>2+</sup> over Na<sup>+</sup>, K<sup>+</sup> and Rb<sup>+</sup>
  - Not so selective for Ba<sup>2+</sup> over Sr<sup>2+</sup>

	Sr <sup>2+</sup>	Ba <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>
log K [2.2.2]	8.0	9.5	3.9	5.4	4.35

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## Maximizing Stability of Coordination Compounds

- Complementarity gives Recognition
  - Electronics
  - Geometry
  - Size
- Constraint/Preorganization optimizes Affinity
  - Topology
  - Rigidity

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## Electronic Structure of Transition Metals

- Contributes to Complex Stability
- Gives rise to Magnetism
  - Identification tool
  - Applications in magnetic materials
- Colors of Transition Metal Complexes
  - Indicative of ligands present and geometry
  - Identification tool
  - Applications in paints, electronics

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## Electronic Structure Models

- Lewis Dot Structures, VSEPR and Valence Bond Theory
  - Fail miserably for transition metals
- Crystal Field Theory (CFT)
  - Electrostatic model, reasonably good
- Molecular Orbital Theory
  - Similar to LFT, overestimates covalency
- Ligand Field Theory (LFT)
  - CFT + covalency

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## Crystal Field Theory

- Pure Electrostatic Model where in d Electrons repelled by Ligand Electrons
- Electron Repulsion in terms of
  - Slater-Condon-Shortley parameters ( $F_i$ )
  - Racah parameters (A, B, C)
- Predicts more e<sup>-</sup>-e<sup>-</sup> Repulsion than observed Experimentally
  - Configurational interactions
  - Covalency

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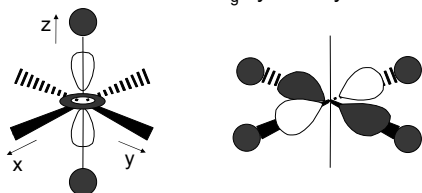
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## CFT for $O_h$ Complexes

- Electrons in  $d_{z^2}$  and  $d_{x^2-y^2}$  Orbitals strongly destabilized
  - These orbitals have  $e_g$  symmetry




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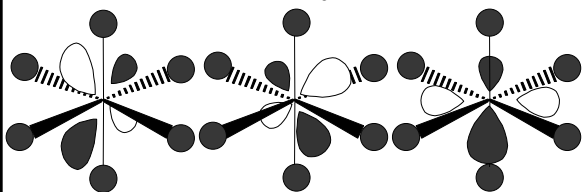
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## CFT for $O_h$ Complexes

- Electrons in  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  Orbitals are less destabilized by  $O_h$  Crystal Field
  - These orbitals have  $t_{2g}$  symmetry




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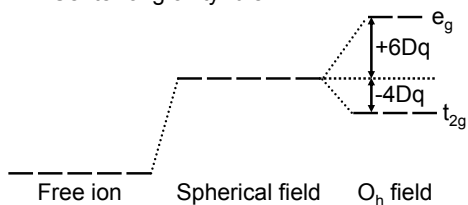
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## CFT for $O_h$ Complexes

- $O_h$  Ligand Field splits d Orbitals
  - Splitting equals  $10Dq$ , where  $Dq = \frac{Z_1 e^2}{6a^5} \bar{r}^4$
  - Center of gravity rule




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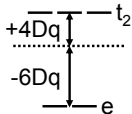
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## CFT for $T_d$ Complexes

- Splitting of d Orbitals is Inverted and Smaller
  - $10Dq_{\text{tetrahedral}} = -4/9 10Dq_{\text{octahedral}}$
  - Center of gravity preserved
  - Note “g” designation has been dropped




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## Molecular Orbital Theory

- Covalent Model
- Correctly predicts
  - Splitting of d orbitals
  - Trends with different metals/ligands
- Overestimates Covalency of Metal-Ligand Bond
  - Interaction mostly ionic with small amount of covalency

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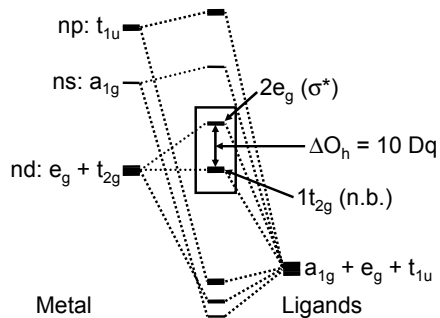
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## MO Diagram $O_h$ $\sigma$ Donors




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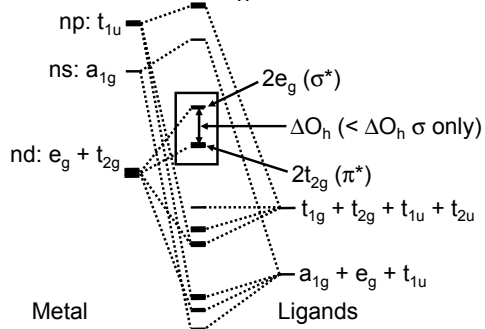
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### MO Diagram $O_h$ $\sigma/\pi$ Donors




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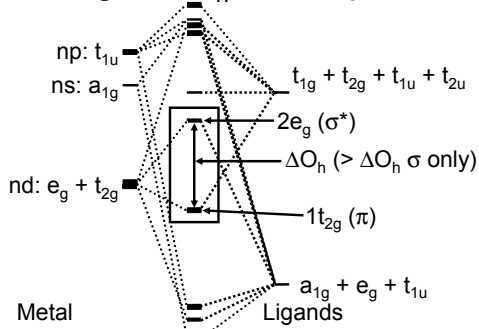
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### MO Diagram $O_h$ $\pi$ Acceptors




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### Ligand Field Theory

- Crystal Field Theory too Ionic, MO Theory too Covalent
- Ligand Field Theory introduces Parameter,  $\lambda$ , that reduces Electron-Electron Repulsion
  - Accounts for covalency
  - 0 (pure CFT) <  $\lambda$  < 1 (pure MO)
  - Most complexes have  $\lambda^2 < 0.3$
  - Not necessarily isotropic

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## Spectrochemical Series

- With Fixed Metal  $\Delta O_h$  *generally* increases from  $\sigma/\pi$  Donors to  $\sigma$  Donors to  $\pi$  Acceptors

$I^- < Br^- < Cl^- < SCN^- \sim N_3^- < F^- < urea < OH^- < CH_3COO^- < ox < H_2O < NCS^- < EDTA < NH_3 \sim py < en \sim tren < o\text{-}phen < NO_2^- < H^- \sim CH_3^- < CN^- < CO$

- With Fixed Ligand  $\Delta O_h$  *generally* increases in the Order

$Mn^{2+} < Co^{2+} \sim Ni^{2+} \sim Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Ir^{3+} < Re^{4+} < Pt^{4+}$

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## Nephelauxetic Effect

- Define (for C/B fixed at Free Ion Value)

$$\beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} < 1$$

– Covalency in complex (most  $\beta \sim 0.8$ )

- Decreases for Fixed Metal

$F^- > H_2O > urea > NH_3 > en \sim ox > SCN^- > Cl^- \sim CN^- > Br^- > S^{2-} \sim I^-$

- Decreases for Fixed Ligand

$Mn^{2+} > Ni^{2+} \sim Co^{2+} \sim Mo^{3+} > Cr^{3+} > Fe^{3+} > Rh^{3+} \sim Ir^{3+} > Co^{3+} > Mn^{4+} > Pt^{4+}$

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## Contribution of $10Dq$ to $\Delta H$

- Expect Bond Strength to Follow Spectrochemical Series, but doesn't
  - OK for light  $\sigma$  donors (F, O, N, C)
  - Fails for heavy  $\pi$  donors (S, P)
- Spectrochemical Series includes Effects from both  $\sigma$  and  $\pi$  Bonding
  - Not considered in CFT
  - Need more complete treatment LFT/MO

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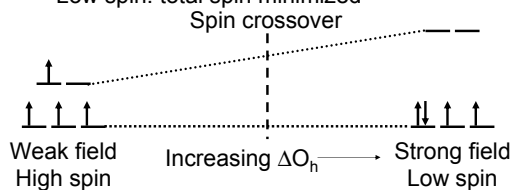
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## Electronic Configuration's Contribution to Stability

- Arrangement of Electrons in d Orbitals depends on  $\Delta O_h$  relative to SPE
  - High spin: total spin maximized
  - Low spin: total spin minimized




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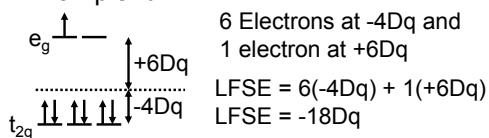
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## Ligand Field Stabilization Energy

- Decrease in Total Energy of Complex caused by Splitting of d Orbitals
  - Depends on number of electrons
  - $d^0$ ,  $d^{10}$  and  $d^5$  (high spin) have no LFSE
- Example:  $d^7$




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## LFSE and $Dq$

- Complexes gain Stability by going Low Spin, but depends on Ligand and Metal
  - Some ligands always give low spin complexes:  $CN^-$ ,  $CO$ ,  $H^-$ ,  $R^-$  (o-phen,  $NO_2^-$ )
  - Heavier transition metals are always low spin
  - Lower oxidation states tend to be high spin (first row only)
- Complex could be stabilized but might not be!

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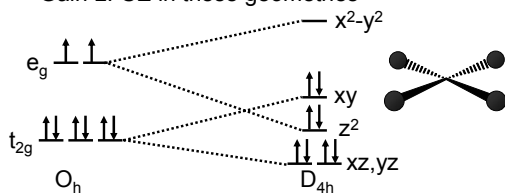
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## LFSE and Geometry

- $T_d$  Complexes always High Spin
  - $Dq$  too small to overcome SPE
- Preference of  $d^7$ ,  $d^8$  and  $d^9$  for  $T_d$  or  $D_{4h}$ 
  - Gain LFSE in these geometries




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## Irving-Williams Series

- Observed Trend in Stability Constants
  - $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$
- LFSE Effect
  - $Mn^{2+}$  (0  $Dq$ ),  $Fe^{2+}$  (-4  $Dq$ ),  $Co^{2+}$  (-8  $Dq$ ),  $Ni^{2+}$  (-12  $Dq$ ),  $Cu^{2+}$  (-6  $Dq$ ),  $Zn^{2+}$  (0  $Dq$ )
- And Increasing Hardness of Metal
  - Charge is constant, ionic radius decreases across the period (shielding constant)

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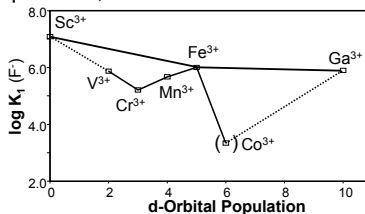
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## LFSE and Complex Stability

- Ligands Below  $H_2O$  in Spectrochemical Series show *inverted* Irving-Williams
  - $Dq$  smaller, net loss of LFSE



After Fig. 2.12b Martell, A. E. and Hancock, R. D. "Metal Complexes in Aqueous Solutions".

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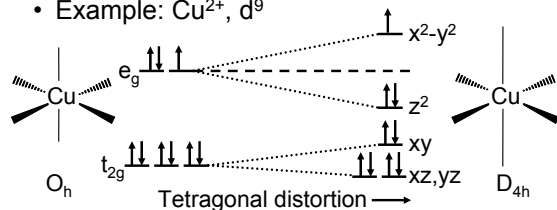
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## Jahn-Teller Theorem

- Complex distorts if it results in Stabilization
  - Relatively small effect  $< 2000 \text{ cm}^{-1}$
  - $10Dq > \sim 10,000 \text{ cm}^{-1}$
- Example:  $\text{Cu}^{2+}$ ,  $d^9$




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## Jahn-Teller Effect and Complex Stability

- Additional Stabilizing Factor with Monodentate Ligands
- Potential Destabilizing Factor with Chelating Ligands
  - Complementarity
  - Ligand design must incorporate Jahn-Teller distortion

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## Electronic States

- Spectroscopy and Magnetism measure Arrangement of all Electrons
- Need to convert one-electron LFT/MO Models to Electronic States
- For Free Ions it is Microstate Problem

Configuration	Terms
$d^1, d^9$	$^2D$
$d^2, d^8$	$^3F, ^3P, ^1G, ^1D, ^1S$
$d^3, d^7$	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P$
$d^4, d^6$	$^5D, ^3H, ^3G, ^3F(2), ^3D, ^3P(2), ^1I, ^1G(2), ^1D(2), ^1S(2)$
$d^5$	$^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2), ^2F(2), ^2D(3), ^2P, ^2S$

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## Molecular Term Symbols

- Derive from Free Ion Term Symbols
  - Descent in symmetry

Configuration	Ground State Term	Molecular Terms ( $O_h$ )
d <sup>1</sup>	<sup>2</sup> D	<sup>2</sup> T <sub>2g</sub> + <sup>2</sup> E <sub>g</sub>
d <sup>2</sup>	<sup>3</sup> F ( <sup>3</sup> P)	<sup>3</sup> T <sub>1g</sub> + <sup>3</sup> T <sub>2g</sub> + <sup>3</sup> A <sub>2g</sub>
d <sup>3</sup>	<sup>4</sup> F ( <sup>4</sup> P)	<sup>4</sup> A <sub>2g</sub> + <sup>4</sup> T <sub>2g</sub> + <sup>4</sup> T <sub>1g</sub>
d <sup>4</sup>	<sup>5</sup> D	<sup>5</sup> E <sub>g</sub> + <sup>5</sup> T <sub>2g</sub>
d <sup>5</sup>	<sup>6</sup> S	<sup>6</sup> A <sub>1g</sub>
d <sup>6</sup>	<sup>5</sup> D	<sup>5</sup> T <sub>2g</sub> + <sup>5</sup> E <sub>g</sub>
d <sup>7</sup>	<sup>4</sup> F ( <sup>4</sup> P)	<sup>4</sup> T <sub>1g</sub> + <sup>4</sup> T <sub>2g</sub> + <sup>4</sup> A <sub>2g</sub>
d <sup>8</sup>	<sup>3</sup> F ( <sup>3</sup> P)	<sup>3</sup> A <sub>2g</sub> + <sup>3</sup> T <sub>2g</sub> + <sup>3</sup> T <sub>1g</sub>
d <sup>9</sup>	<sup>2</sup> D	<sup>2</sup> E <sub>g</sub> + <sup>2</sup> T <sub>2g</sub>

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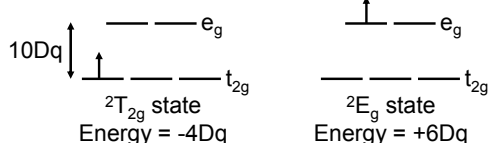
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## Splitting of States

- Group Theory says Free Ion States must split in  $O_h$  Symmetry
  - Can not predict the order of the splitting
  - But CFT, LFT and MO theory do
- Consider d<sup>1</sup> in  $O_h$  (d<sup>9</sup> in  $O_h$ ?)




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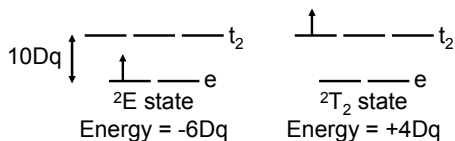
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## Splitting of States

- Now consider d<sup>1</sup> in  $T_d$  (d<sup>9</sup> in  $T_d$ ?)



- Combine into one Diagram describing all possible States arising from d<sup>1</sup> (and d<sup>9</sup>) in  $O_h$  and  $T_d$  Geometries

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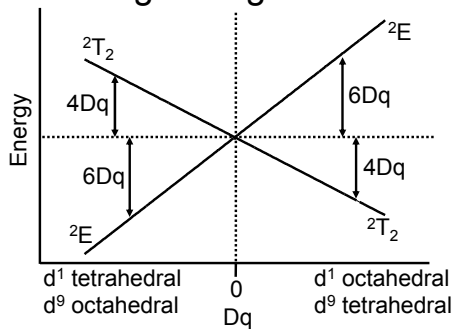
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## Orgel Diagrams




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## Orgel Diagrams

- $d^4$  and  $d^6$  have  $^5D$  Ground State
  - Splitting is the same as other D states
  - Only multiplicity changes
- Through Same Procedure determine Order of States and Energy Splittings
  - Orgel diagram same as  $d^1/d^9$  (multiplicity)
  - Combine into one diagram

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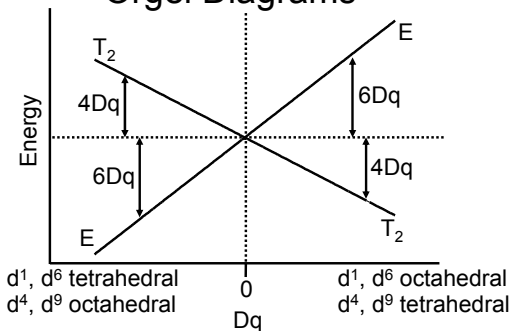
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## Orgel Diagrams




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## Orgel Diagrams

- Additional low-lying Excited State for  $d^2$ ,  $d^3$ ,  $d^7$  and  $d^8$ 
  - F state transforms as  $A_2 + T_1 + T_2$
  - P state transforms as  $T_1$
- *Configurational Interaction* between  $T_1$  States
  - Energy of states depend on  $Dq$  and  $B$
  - Interaction between them depends on  $B$

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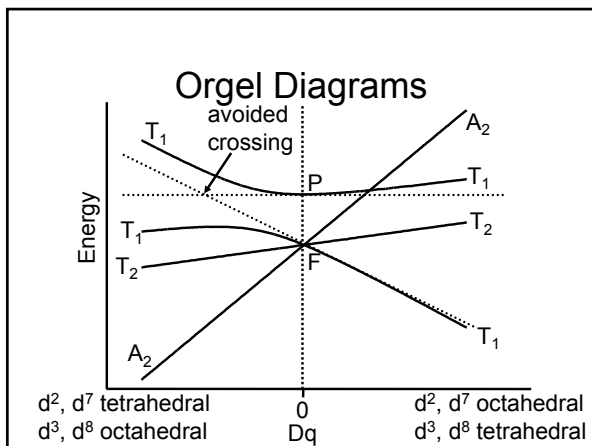
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## Limitations of Orgel Diagrams

- $d^5$  has no Splitting of Ground State
  - ${}^6S$  becomes  ${}^6A_{1g}$  in  $O_h$
  - How to treat transitions in  $d^5$ ?
- How to treat Spin Crossovers?
- What about States with Multiplicities different from Ground State?
- Tanabe-Sugano Diagrams
  - Complete ligand field treatment

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## Determination of Dq and B

### Graphical Method

1. Find ratios of energies for pairs of transitions

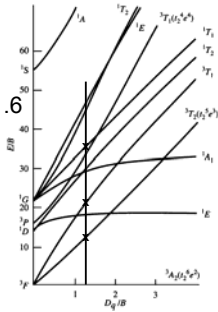
$${}^3T_{1g}(F)/{}^3T_{2g} = 17500/10750 = 1.6$$

$${}^3T_{1g}(P)/{}^3T_{2g} = 2.6$$

2. Using a ruler find place on diagram that matches Dq/B ~ 1.2 reasonable

3. Calculate Dq and B

$$Dq \sim 1100 \text{ cm}^{-1}, B \sim 900 \text{ cm}^{-1}$$




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## Determination of Dq and B

- More Accurate Method is to use Tanabe-Sugano Matrices

- To change  $d^n$  to  $d^{10-n}$ , change sign of Dq
- States that appear in  $1 \times 1$  matrix do not interact with any other state

$$\left. \begin{array}{l} {}^3A_2 e^2 \quad -8B - 20Dq \\ {}^3T_2 et \quad -8B - 10Dq \end{array} \right\} \text{Energies of states}$$

Term symbol  $\uparrow$  Electronic configuration

- In  $d^8$   ${}^3A_{2g} \rightarrow {}^3T_{2g}$  occurs at

$$\Delta E = (-8B - 10Dq) - (-8B - 20Dq) = 10Dq$$

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## Tanabe-Sugano Matrices

- With More than One State

- Diagonalize energy matrix
- If second state is far away in energy, ignore mixing

$$\begin{array}{ccc} & \text{Energy of } {}^3T_1(P) & \\ {}^3T_1 & & \\ t^2 & -5B & 6B \leftarrow \text{Mixing term} \\ et & 6B & 4B - 10Dq \leftarrow \text{Energy of } {}^3T_1(F) \end{array}$$

- Note C occurs only with Multiplicities less than Maximum

- Spin pairing

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## Tanabe-Sugano Matrices

- Diagonalizing a 2 x 2 Matrix

$$\begin{vmatrix} -5B - E & 6B \\ 6B & 4B - 10Dq - E \end{vmatrix} = 0$$

$$(-5B - E)(4B - 10Dq - E) - 36B^2 = 0$$

– Solve for E

- Result

$${}^3A_{2g} \rightarrow {}^3T_{1g}(F) \\ \Delta E = 15Dq + 7.5B - (1/2)(225B^2 + 100Dq^2 - 180DqB)^{1/2}$$

$${}^3A_{2g} \rightarrow {}^3T_{1g}(P) \\ \Delta E = 15Dq + 7.5B + (1/2)(225B^2 + 100Dq^2 - 180DqB)^{1/2}$$

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## Tanabe-Sugano Matrices

- Using Energies of known Transitions can solve for Dq and B
  - $[\text{Ni}(\text{NH}_3)_6]^{2+}$ : Dq = 1075 cm<sup>-1</sup>, B = 897 cm<sup>-1</sup>
- Procedure for T<sub>d</sub>, just change sign of Dq
- In General C can only be determined from Spin Forbidden Transitions
  - Electron pairing only in states with less than maximum spin

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## Tanabe-Sugano Diagrams

- For d<sup>4</sup>, d<sup>5</sup>, d<sup>6</sup> and d<sup>7</sup> Tanabe-Sugano Diagrams have a Discontinuity
  - *Spin crossover*
  - To left is *high spin*
  - To right is *low spin*
- At the Crossover two States are Close in Energy
  - Magnetism

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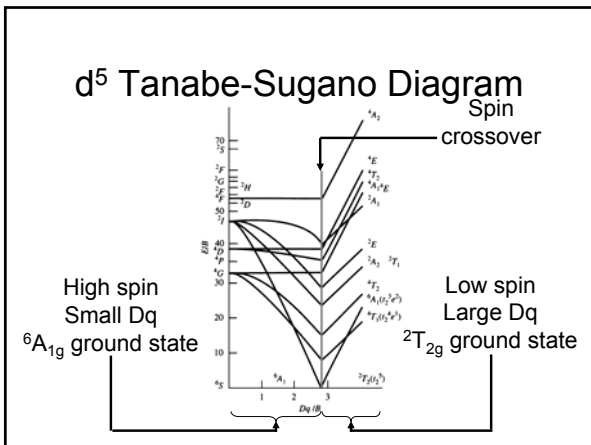
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### Lower Symmetries

- For  $T_d$ , use appropriate Tanabe-Sugano Diagram/Matrix and switch Sign of Dq
  - For others use correlation table
- Example:  $Ni^{2+}$  in  $D_3$ 

$4T_{1g}$	-----	$4A_2$	• Spin does not change
	-----	$4E$	
$4T_{2g}$	-----	$4A_1$	• Single peaks in $O_h$ split into two peaks in $D_3$
	-----	$4E$	
$4A_{2g}$	-----	$4A_2$	• Ordering not always predictable need single crystal polarized experiment
$O_h$	-----	$D_3$	

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### Lower Symmetries

- cis/trans* Isomers often have different Absorbance Spectra and Colors
  - Lower symmetry of *cis*- isomer
- Effective symmetry**
  - Low symmetry complexes behave like higher symmetry complexes
  - Small splittings, large peak widths
  - $[Co(en)_3]^{3+}$  ( $D_3$ ) should shows two peaks in absorbance, not four (resolved in CD)

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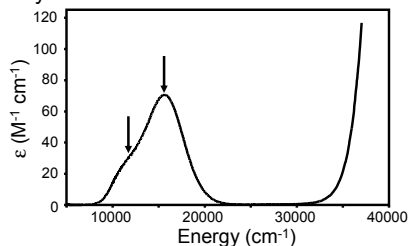
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## The Strange Case of $\text{Cu}^{2+}$

- Expect  $d^9 \text{Cu}^{2+}$  in  $\text{O}_h$  or  $\text{T}_d$  to have a Single Transition in Absorbance

– Why are there two?



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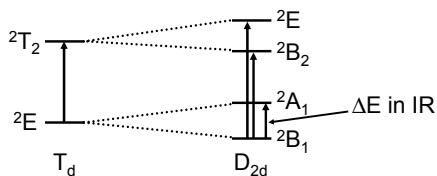
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## Jahn-Teller Effect

- Any Molecule or Ion with an Orbitally Degenerate Ground State will distort to remove the Degeneracy

– Ground state splitting < excited state splitting



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## Charge Transfer

- Usually very Intense ( $\epsilon \gg 1000 \text{ M}^{-1}\text{cm}^{-1}$ )
  - Most are spin and orbitally allowed
  - Some are not, but these are rare
- Ligand to Metal Charge Transfer (LMCT)
  - Metal has higher charge
  - Ligand is easily oxidized
- Metal to Ligand Charge Transfer (MLCT)
  - Metal has lower charge
  - Ligand is easily reduced

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## Charge Transfer

- Energy of CT Transitions depends on Redox Potentials (Electronegativity) of Metal and Ligand
  - Halogens ( $F^- > Cl^- > Br^- > I^-$ )
  - Optical electronegativities
- Large Difference in Potentials leads to
  - Redox reactions
  - Photochemistry
  - Catalysis

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## Magnetism

- Bulk Manifestation of Electron Spin
- Three Types of Magnetic Behavior
  - *Diamagnetic* material repelled by field; electron spins are paired
  - *Paramagnetic* material attracted by field; electron spins are unpaired and randomly oriented in absence of field
  - *Ferromagnetic* material interacts strongly with field; spins are unpaired and oriented

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## Magnetism

- Magnetic Materials contain *Domains*
- Paramagnetic Compounds can become Ferromagnetic below *Curie temperature*
  - Above Curie temperature thermal motions of particles scramble domain alignments
  - Below Curie temperature domain structure maintained
  - Magnets are only “magnetic” below their Curie temperature

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## Experimental Magnetism

- Classically measure Susceptibility ( $\chi$ )  
convert to Magnetic Moment ( $\mu$ )
  - *Gouy Method* measure mass change in field
  - *Evans Method* measure shift of Solvent resonance in presence of compound

$$\chi_{measured} = (477) \frac{\Delta\nu}{Q\nu_i c}$$

- Where  $\Delta\nu$  is shift of solvent resonance,  $\nu_i$  is frequency of instrument,  $c$  is concentration (M),  $Q = 2$  for superconducting magnets

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## Magnetism

- Measured Susceptibility given by
$$\chi_{measured} = \chi_{diamagnetic} + \chi_{paramagnetic} + \chi_{TIP}$$
- Diamagnetic contribution:  $\chi_{diamagnetic}$ 
  - Associated with all materials
  - Correct with Pascals' constants (tabulated)
- Temperature Independent  
Paramagnetism:  $\chi_{TIP}$ 
  - Field induced mixing of states
  - Corrected for by fitting data

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## Magnetism

- Paramagnetic Contribution:  $\chi_{paramagnetic}$ 
$$\chi_{paramagnetic} = \left( \frac{N\beta^2 \mu_{eff}^2}{3k} \right) \frac{1}{T}$$
- Linear Dependence of Susceptibility on  $1/T$  called *Curie Law*
  - Applicable when energy differences  $\gg kT$
  - Deviations when energy differences  $\approx kT$  or magnetic phase change occurs

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## Curie-Weiss Law

- Corrects for Weak Interactions between Spins above Curie Temperature

$$\chi_{\text{measured}} = \frac{C}{T - \theta}$$

- Where  $\chi_{\text{measured}}$  has been corrected for  $\chi_{\text{diamagnetic}}$  and  $\chi_{\text{TIP}}$
- $C = (N\beta^2\mu_{\text{eff}}^2/3k)$
- Weiss constant,  $\theta$ , determined from fit of susceptibility data

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## Magnetic Moment

- Has contributions from both Spin and Orbital Angular Momentum
- Given by Landé expression

$$\mu = \left[ 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)} \right] \sqrt{J(J+1)}$$

- Or the simplified Landé expression

$$\mu = g\sqrt{S(S+1)}$$

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## Landé g Factor

- Measure of Orbital Angular Momentum's Contribution to Magnetic Moment
  - $g < 2$  for less than half-filled
  - $g > 2$  for greater than half-filled
- Define  $\mu_{\text{spin only}}$  when  $g = 2$ 
  - No orbital angular momentum ( $L = 0$ )

$$\mu_{\text{spin only}} = 2\sqrt{S(S+1)}$$

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## Magnetism of A and E States

- Most Complexes with A or E Ground States in  $O_h$  have  $\mu_{\text{eff}} = \mu_{\text{spin only}}$  ( $g \approx 2$ )
  - Ligand field has quenched orbital angular momentum
- Deviations in g Values caused by
  - Spin-orbit coupling
  - Covalency
- Example: high spin  $\text{Fe}^{3+}$  ( $d^5, {}^6A_{1g}$ )
  - $S = 5/2$  and  $\mu_{\text{spin only}} = 5.92$

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## Magnetism of T States

- In-State Spin-Orbit Coupling leads to an Additional Temperature Dependence of  $T_{1g}$  and  $T_{2g}$  States
  - Curie Law not obeyed
  - $\mu_{\text{eff}} \neq \mu_{\text{spin only}}$
- Important for  $\text{Cr}^{3+}$ ,  $\text{Co}^{2+/3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+/3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  (low spin)
- Treatment beyond the Scope of this Class

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## Electron Paramagnetic Resonance

- Complexes with Non-Singlet Ground States show Zeeman Splitting
  - Energy of each  $m_s$  state given by  $E = g\beta H m_s$
- Small Effect requires Low Temperatures
- Normal EPR measures Half-Integer Spins (Kramers doublets)
  - Selection rule  $\Delta m_s = \pm 1$ , parallel mode
- Integer Spins (non-Kramers) require reconfiguration of Instrument

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## EPR Experimental

- Sweep Field keeping Constant Radio Frequency Radiation
- Measure  $g_{\text{eff}}$  from Spectrum
  - Not necessarily 2.00
- EPR higher Resolution than Susceptibility can see Anisotropic g Values
  - $g_z (g_{\parallel}) \neq g_x, g_y (g_{\perp})$  Axial
  - $g_z \neq g_x \neq g_y$  Rhombic

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## Zero-Field Splitting

- States with  $S > 1/2$  show Zero-Field Splitting caused by mixing other States into Ground State
  - Low symmetry
  - Spin-orbit coupling
- Defined by Two Parameters
  - D axial zero-field splitting
  - E rhombic zero-field splitting ( $E/D \leq 1/3$ )

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## Exchange Coupling

- Multinuclear Clusters show additional Zero-Field Splitting due to Coupling of Electrons on different Metals
- Given Symbol J; in American Convention
  - $J < 0$  antiferromagnetic coupling minimum spin lowest in energy
  - $J > 0$  ferromagnetic coupling maximum spin lowest in energy
- Can give strange EPR and Susceptibility

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## Electron-Nuclear Spin Coupling

- *Hyperfine*: Coupling of Metal Electron Spin to Metal Nuclear Spin
  - Fermi contact
  - Spin polarization of core electrons
  - Dipolar interaction
- *Superhyperfine*: Coupling of Metal Electron to Ligand Nuclear Spin
  - Covalency of metal-ligand bond

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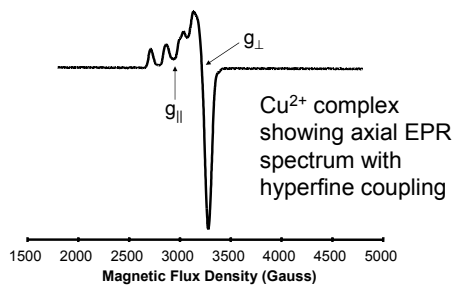
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## Electron Paramagnetic Resonance



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