(27) **Today**

Section 10.1 Experimental Data Used in when Describing Bonding in Coordination Compound

Section 10.2 Crystal Field Theory

Next Class (28)

Section 10.2 Crystal Field Theory

Section 10.3 Ligand Field Theory

(29) **Second Class from Today**

Section 10.3 Ligand Field Theory

Section 10.5 The Jan-Teller Effect

Section 10.6 Four and Six-Coordinate Preferences

Third Class from Today (30)

Section 10.6 Four and Six-Coordinate Preferences

What Do We Do when We Study Bonding in Metal Complexes

Formation Constants and Thermodynamic Quantities

See how strongly ligands bind

Magnetic Susceptibility

attraction to magnets

unpaired e^-'s can align with a magnetic field, create their own field and be attracted

paired e^-'s cannot align an will be weakly repelled

Electronic Spectra

as e^-'s move from orbital to orbital the absorb or release E

absorb a photon when goes up in E release photons when e^- goes... Frequency of light absorbed provides info about the energy levels

orbitals are more similar better bonding

			K	
			Cu^{2+}	Ag^{+}
$[M(H_2O)_6]^{Z+}(aq) + NH_3\ (aq)$	$\rightleftharpoons$	$[M(NH_3)(H_2O)_5]^{Z+}(aq) + H_2O\ (l)$	17,000	2,000
$[M(H_2O)_6]^{Z+}(aq) + F^-\ (aq)$	$\rightleftharpoons$	$[M(F)(H_2O)_5]^{(Z+-1)}(aq) + H_2O\ (l)$	8	0.68
$[M(H_2O)_6]^{Z+}(aq) + Cl^-\ (aq)$	$\rightleftharpoons$	$[M(Cl)(H_2O)_5]^{(Z+-1)}(aq) + H_2O\ (l)$	1.2	1,200
$[M(H_2O)_6]^{Z+}(aq) + Br^-\ (aq)$	$\rightleftharpoons$	$[M(Br)(H_2O)_5]^{(Z+-1)}(aq) + H_2O\ (l)$	0.9	20,000

hard Lewis acid — soft acid — soft-soft

For Cu Z = 2, for Ag Z = 1

Ligands bind to different metals with different affinity

rxn with hard acid

$:NH_3$ basic

$:\ddot{F}:^{\ominus}$ slightly less basic } similar in size, more ⊕ nucleus on F

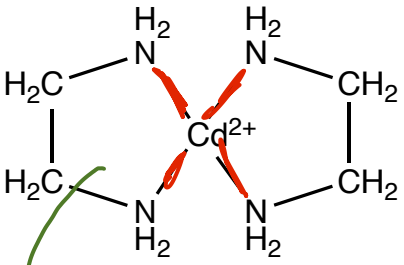
$:\ddot{Cl}:^{\ominus}$ even less basic

$:\ddot{Br}:^{\ominus}$ even less basic } as e^- are more spread out they become less attractive to $H^{\oplus}$

orbitals are more similar better bonding

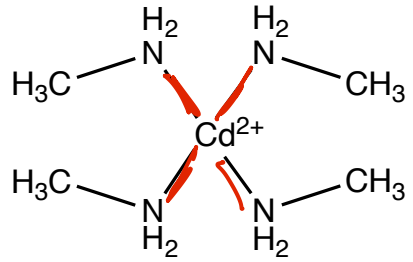
en = $H_2\ddot{N}$ $\ddot{N}H_2$

	ΔH° (kJ/mol)	ΔS° (K kJ/mol)	K
$[Cd(H_2O)_6]^{2+}(aq) + 4\ CH_3\ddot{N}H_2\ (aq) \rightleftharpoons [Cd(NH_2CH_3)_4(H_2O)_2]^{2+}(aq) + 4\ H_2O\ (l)$	–57.3	–67.3	3.3×10^6
$[Cd(H_2O)_6]^{2+}(aq) + 2\ en\ (aq) \rightleftharpoons [Cd(en)_2(H_2O)_2]^{2+}(aq) + 4\ H_2O\ (l)$	–56.5	14.1	4.0×10^{10}



bonds are similar in strength

it's the release of 4 H_2O with the uptake of 2 en



K can be determined experimentally and $\Delta G^\circ = -RT\ln K$

ΔH can be measured using calorimetry (enthalpy)

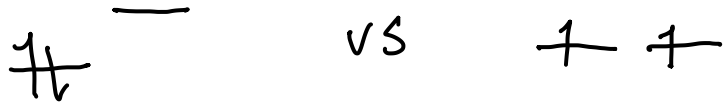
$$\Delta G^\circ = \Delta H - T\Delta S$$

exp exp math

organic most stable ring is cyclohexane C–C–C ∡ ≈ 112°

Metal atoms are larger than C atoms and 5-membered rings are the "magic number".

Hunds rule says that e⁻'s will singly occupy degenerate orbitals before pairing



Diamagnetic compounds are slightly repelled by magnetic fields

paired e⁻'s will not be able to align

Paramagnetic compounds are attracted to magnetic fields

· unpaired e⁻'s will align & be attracted to magnetic fields

related to M_S

related to l of M_l

Magnetic Susceptibility is related to magnetic moment

$$\mu = 2.828\ (\chi T)^{1/2} \qquad \mu_{S+L} = g[S(S+1) + [{}^1/_4\ L(L+1))]^{1/2}$$

or with some approximating.... $\mu_S = (n(n+2))^{1/2}$ (n is the number of unpaired electrons)

and magnetic moment is related to the total spin magnetic moment (the spin quantum number S) S is the sum of the spins of the unpaired e^-'s

S

↑ ↓ $S = \frac{1}{2} + -\frac{1}{2} = 0$

↑ ↑ — $S = +\frac{1}{2} + \frac{1}{2} + -\frac{1}{2}$

↑ $S = 1$

and the orbital angular momentum (L) is the maximum possible sum of the m_l values for an electron configuration

add M_l of occupied orbitals to determine L

$n=2$ $l=1$ $m_l = 1, 0, -1$

$n=3$ $l=2$ $m_l = 2, 1, 0, -1, -2$

fill p + d orbitals starting with $M_l = 1$ for p

$M_l = 2$ for d

for N $1s^2\ 2s^2 2p^3$

$$S = \overbrace{+\tfrac{1}{2} + -\tfrac{1}{2}}^{1s} + \overbrace{+\tfrac{1}{2} + -\tfrac{1}{2}}^{2s} + \overbrace{\tfrac{1}{2} + \tfrac{1}{2} + \tfrac{1}{2}}^{2p} = \frac{3}{2}$$

2p ↑ ↑ ↑

2s ↑↓

$$L = \overbrace{0+0}^{1s} + \overbrace{0+0}^{2s} + \overbrace{1+0-1}^{2p} = 0$$

1s ↑↓

$$S_0 = \overbrace{+\tfrac{1}{2} + -\tfrac{1}{2}}^{1s} + \overbrace{+\tfrac{1}{2} + -\tfrac{1}{2}}^{2s} + \overbrace{\tfrac{1}{2} + \tfrac{1}{2} + \tfrac{1}{2}}^{2p} \cancel{-\tfrac{1}{2}} = 1$$

for Fe

$$L = \overbrace{0+0}^{1s} + \overbrace{0+0}^{2s} + \overbrace{1+0-1+1}^{2p} = 1$$