Chem 354 Test 2

Date: March 20, 2002

10 1. Thiocyanate anion can bind to a metal atom in two different ways.
   (i) What name is given to this kind of monodentate ligand?
   (ii) What name is given to the complex isomers of thiocyanate?
   (iii) What are the factors that influence the manner in which thiocyanate can bind to a metal ion?

5 2. In aqueous solution, the measured heat of formation $\Delta H_f = -5.1$ kcal/mol, when ethylenediamine binds to Ni (II). In contrast, when malonate binds to Ni(II) in aqueous solution, the measured $\Delta H_f = +1.88$ kcal/mol. Explain the change in sign of ΔH_f.

5 3. What is the thermodynamic explanation of the chelate effect?

10 4. Consider just the d-orbitals in an octahedral complex, draw a simple MO scheme that illustrates π bonding interaction between the metal and its π-donor ligands. Be careful to symmetry label, and show Δ_o and the LMCT transition in your diagram.

5 5. Draw a qualitative Curie-Weiss plot, which illustrates intermolecular ferromagnetic exchange for a complex in the solid state. Draw a qualitative plot that obeys Curie Law behaviour.

5 6. Determine the crystal field stabilization energy for the following complexes using the spectrochemical series to decide whether these are strong or weak field cases: (a) $Fe(CN)_6^{4-}$, (b) $Cr(CO)_6$, (c) $Cu(NCS)_4^{2-}$, (d) $Mn(Cl)_4^{2-}$ and (e) $Ru(2,2\text{-bipyridine})_3^{2+}$

10 7. For the VCl_6^{4-} complex, the following spectral data (in cm^{-1}) were obtained:

ν_1	ν_2	ν_3
20,000	13,000	8,000

i) Assign the transitions and determine Δ_o and B.
ii) Compare the value of B to the V(II) free ion value of $B_0 = 765$ cm^{-1} and explain the difference.

1. i) ambidentate

ii) linkage isomers

iii) a) nature of metal hard or soft character

b) nature of ligand e.g. S ATOM SOFT; NITROGEN atom hard

c) solvent system and d) steric effects

2. ΔH_f FOR en IS < 0 because the bonds that it makes with the metal are stronger than the bonds it makes with the solvent.

FOR malonate, the opposite occurs

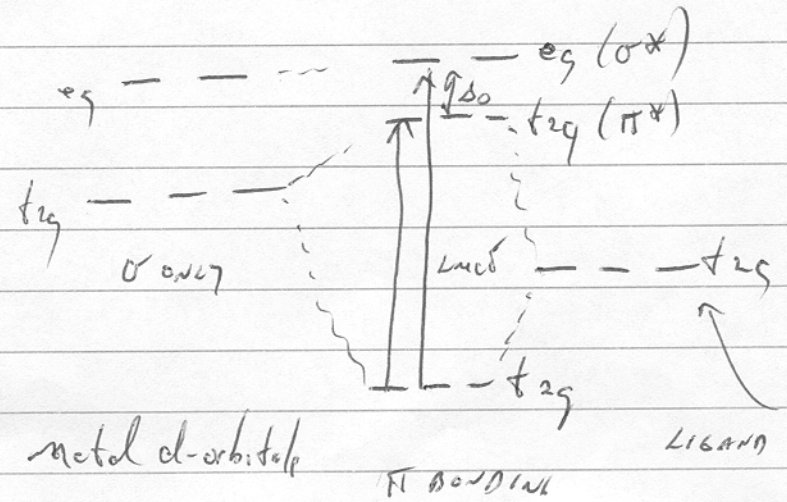
3. Chelate effect is increasing entropy

ie $M(H_2O)_6^{2+} + L_2 \rightarrow M(H_2O)_4L_2 + 2H_2O$

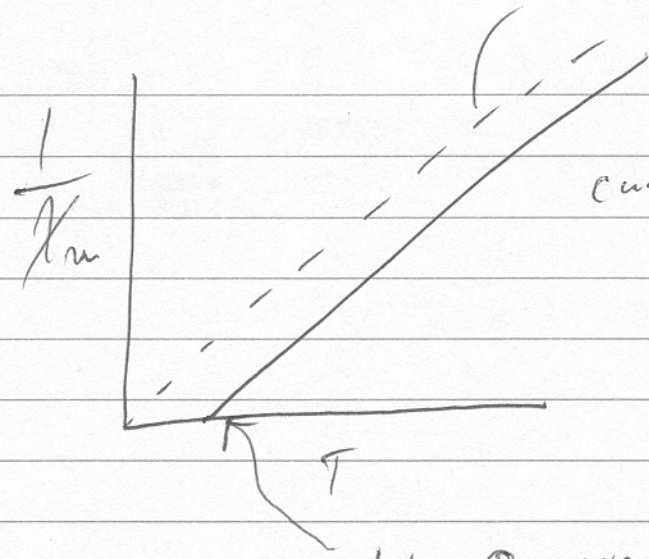
2 SPECIES ——— 3 SPECIES

increasing disorder means $\Delta S > 0$

4.



5.



+ve Θ INDICATES FERROMAGNETIC

6. a) $Fe(CN)_6^{4-}$ ⇒ d^6 LOW SPIN

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↿ ↿ ↿

CFSE = 6 × 4 D_q

= 24 D_q

= 2.4 Δ_o

(ALSO 3 PAIRING ENERGY)

b) $Co(CO)_6$ · d^6 LOW SPIN

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↿ ↿ ↿

SAME AS ABOVE

c) $Cu(NCS)_4^{2-}$ Cu^{2+} d^9 Tetrahedral

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↿ ↿

CFSE = 0.4 Δt

(d) $MnCl_4^{2-}$ Mn^{2+} d^5 high spin

$\uparrow\uparrow\uparrow$ $\uparrow\uparrow$ CFSE = 0

e) $Ru(bpy)_3^{2+}$ d^6 low spin

$\downarrow\downarrow$ $\downarrow\downarrow$ $\downarrow\downarrow$ same as (a)

7. ν_1 $^4A_{2g} \rightarrow {}^4T_{1g}$ 20,000 cm^{-1}

ν_2 $^4A_{2g} \rightarrow {}^4T_{1g}$ 13,000 cm^{-1}

ν_3 $^4A_{2g} \rightarrow {}^4T_{2g}$ 8,000 cm^{-1}

expt ratio $\frac{20000}{8000} = 2.5 = \frac{\nu_1}{\nu_3}$

good match as 15 = Δ_o/B ($\frac{43.5}{18} \approx 2.42$ close enough)

for ν_1 $\frac{E}{B} = 37$ or $B = \frac{20000}{37} = 540 cm^{-1}$

$\frac{D_0}{n} = 15$ OR $D_0 = 15 \times 540 = 8100$

$\beta = \frac{540}{765} \times 100 \simeq 70\%$

ONLY 70% repulsion in d-orbitals of complex compared to free ion: electrons from ligands shield d-orbital electrons from nuclear charge (Z_{eff} decreases). d-orbitals expand (nephelauxetic effect) and repulsion decreases