PROBLEM SET 7

Chem 155

5.- IN $Co(CN)_6^{3-}$ WE HAVE Co^{3+}

IN $Co(CN)_6^{4-}$ WE HAVE Co^{2+}

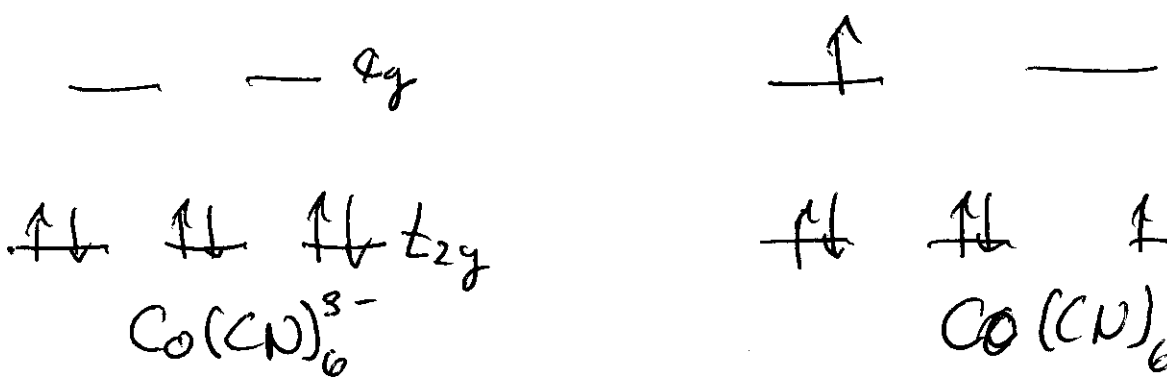
THE INCREASE OF CHARGE OF THE CENTRAL METAL STABILIZES THE COMPOUND

FOR $Co(CN)_6^{3-}$ WE HAVE 6 d e^-

$Co(CN)_6^{4-}$ WE HAVE 7 d e^-

ACCORDING TO CRYSTAL FIELD THEORY

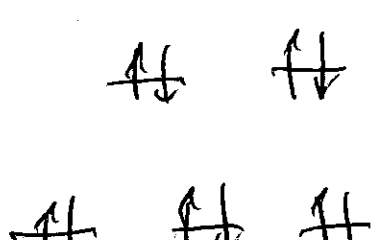
CN^- IS A STRONG FIELD LIGAND SO:



BOTH e_g AND t_{2g} LEVELS ARE ANTIBONDING

THUS $Co(CN)_6^{4-}$ IS LESS STABLE THAN $Co(CN)_6^{3-}$

(6) Zn^{2+} COMPLEXES HAVE 10 d electrons

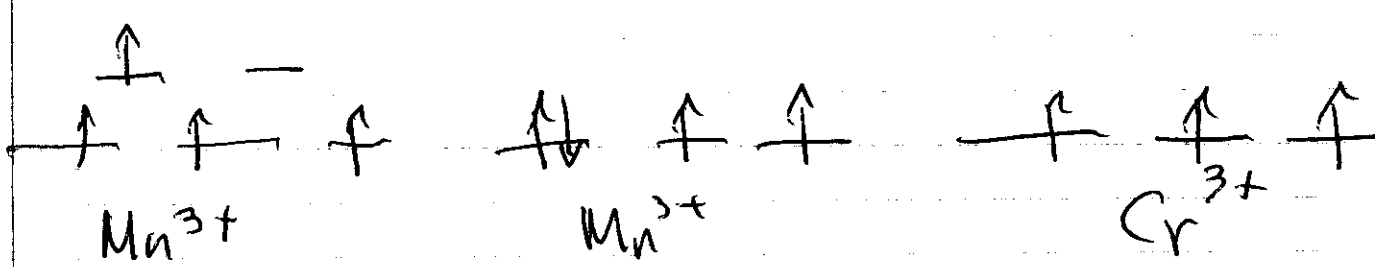


THE 5 d level ARE FULL THUS THE ONLY TRANSITION ARE FROM THE t_{2g} TO HIGHER σ^* OR π^* LEVELS. LARGER GAP IMPLIES MORE ENERGY BEYOND THE VISIBLE.

(7) Mn^{3+} HAS 4d electrons

Cr^{3+} HAS 3d electrons

HIGH SPIN LOW SPIN



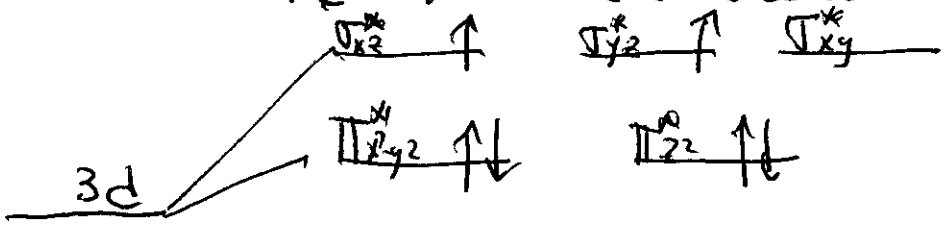
Mn^{3+} COMPLEXES HAVE AND EXTRA e^- IN AN ANTIBONDING ORBITAL. TOTAL OF 4

Cr^{3+} HAS ONE LESS ANTIBONDING ELECTRON

ALSO THE PAIRING OF electrons RAISES THE ENERGY

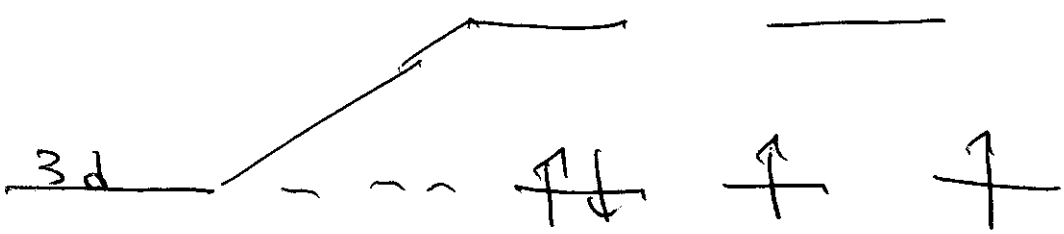
THEREFORE Cr^{3+} COMPLEXES ARE MORE STABLE THAN Mn^{3+} COMPLEXES.

(8) FeO_4^{2-} ASSUMING TETRAHEDRAL Fe^{2+} HAS 6d electrons



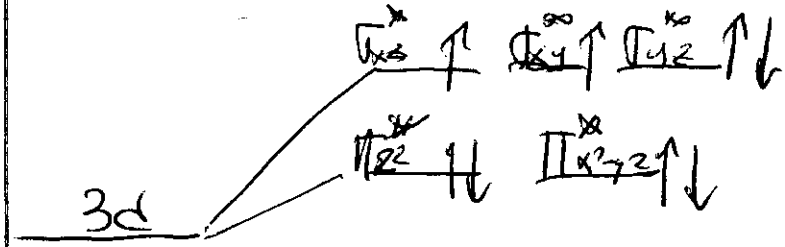
$Mn(CN)_6^{3-}$ OCTAHEDRAL + CN^- STRONG FIELD

Mn^{3+} HAS 4d e⁻



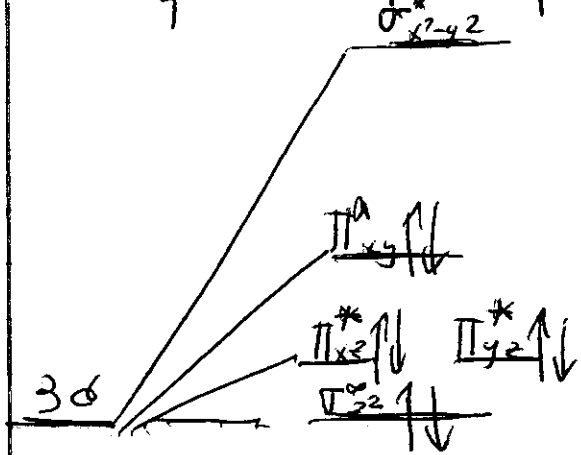
2 UNPAIRED e⁻

$NiCl_4^{2-}$ tetrahedral Ni^{2+} $8\,d\,e^-$



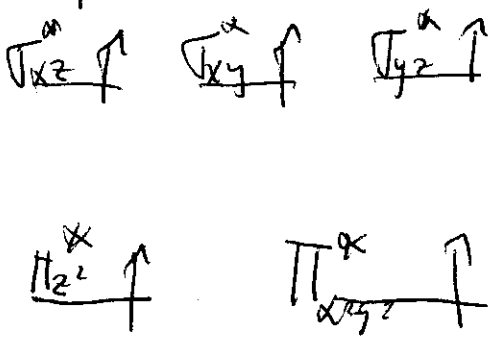
2 UNPAIRED e^-

$PdCl_4^{2-}$ square planar Pd^{2+} $8\,d\,e^-$



NO UNPAIRED e^-

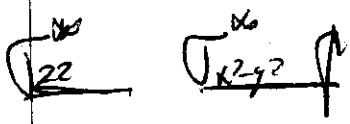
$MnCl_4^{2-}$ tetrahedral Mn^{2+} $5\,d\,e^-$



5 UNPAIRED e^-

Cl^- WEAK FIELD
$\Rightarrow$ HIGH FIELD

$Co(en)_3^{2+}$ Co^{2+} HAS $7d e^-$



octahedral
en STRONG FIELD
⇒ LOW SPIN

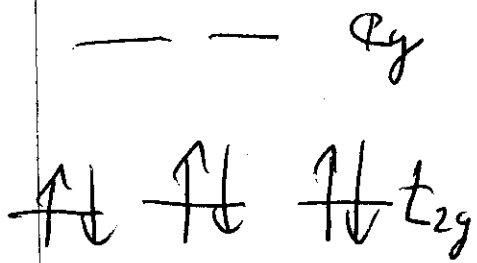
1 UNPAIRED e^-

$Co(en)_3^{3+}$ Co^{3+} — $6d e^-$

0 UNPAIRED e^-

$Rh(NH_3)_6^{3+}$ Rh^{3+} $6d e^-$ octahedral

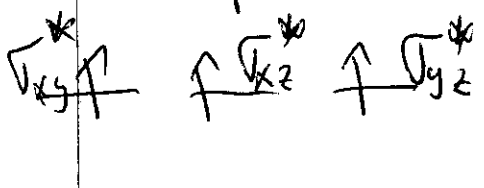
NH_3 STRONG FIELD
LOW SPIN



NO UNPAIRED e^-

$CoBr_4^{2-}$ Co^{2+} tetrahedral $7d e$

Br^- weak field ⇒ HIGH SPIN



$Pt(NH_3)_4^{2+}$ Pt^{2+} $8d e^-$

square planar

NH_3 STRONG FIELD $\Rightarrow$ LOW SPIN

π^*_{xy} ⇅

π^*_{xz} ⇅ π^*_{xy} ⇅

$\sigma^*_{z^2}$ ⇅

NO UNPAIRED e^-

(9) CO STRONG FIELD $V(CO)_6$ octahedral

— — e_g

V 5d elec.

$(t_{2g})^5 (e_g)^0$

⇅ ⇅ ↑ — t_{2g}

$V(CO)_6^- \longrightarrow (t_{2g})^6 (e_g)^0$

$V(CO)_6$ $Cr(CO)_6$ $Mn(CO)_6$

$(t_{2g})^5$ $(t_{2g})^6$ $(t_{2g})^6 (e_g)^1$

BOTH THE t_{2g} AND e_g MO ARE ANTI BONDING

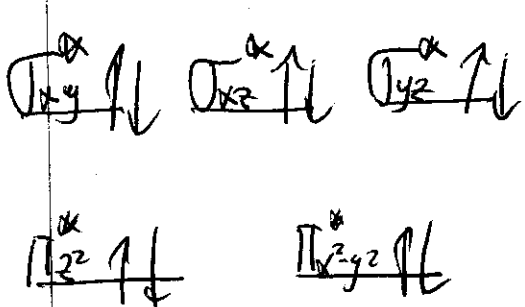
STABILITY

$V(CO)_6 > Cr(CO)_6 > Mn(CO)_6$

(10) $Ni(CO)_4$ tetrahedral (GRAY p 149)

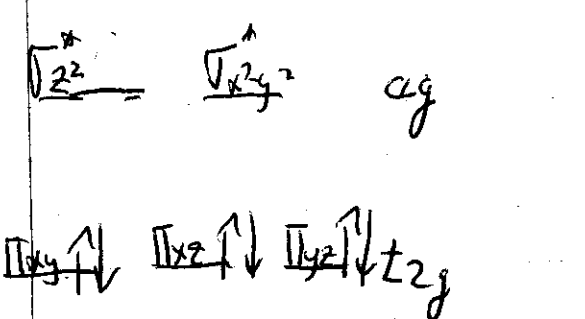
Ni^0 10d elec

CO STRONG FIELD



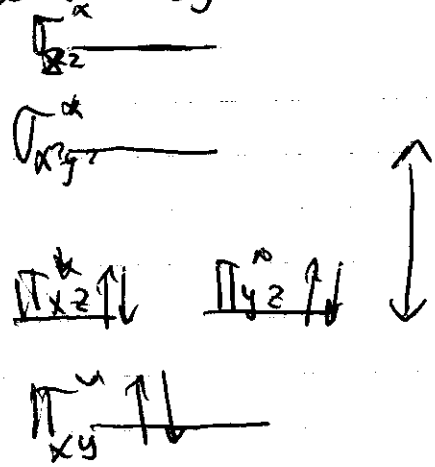
NO d-d transition

(11) $Co(NH_3)_6^{3+}$ 6d elec



d-d $t_{2g} \rightarrow e_g$

$Co(NH_3)_5Cl^{2+}$



FOR $Co(NH_3)_6^{3+}$ $t_{2g} \longrightarrow e_g$

$\lambda = 4300\ \text{Å}$

$Co(NH_3)_5Cl^{2+}$

d-d transition

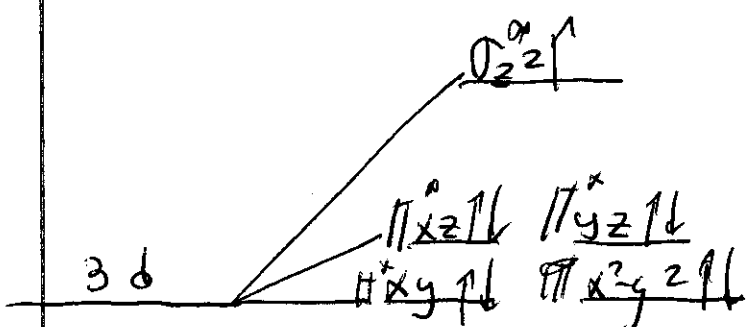
π^*_{xz} or $\pi^*_{yz} \longrightarrow \sigma^*_{x^2-y^2}$

SINCE $\sigma^*_{z^2}$ IS HIGHER IN ENERGY THAN $\sigma^*_{x^2-y^2}$

π^*_{xz} π^*_{yz} ~ ~ ~ π^*_{xy}

THE ORIGINAL t_{2g} e_g GAP IS REDUCED TO $\sigma^*_{x^2-y^2}$ AND π^*_{xz} π^*_{yz}

(16) $CuCl_2$ Cu^{2+} HAS 9d elec.



- CRYSTAL FIELD THEORY SPLITTING

2 d-d transitions

π^*_{xz} or $\pi^*_{yz} \longrightarrow \sigma^*_{z^2}$

π^*_{xy} or $\pi^*_{x^2-y^2} \longrightarrow \sigma^*_{z^2}$

OF HIGHER ENERGY