# Chapter 19

INTRODUCTION TO TRANSITION METAL COMPLEXES

Exercises

19.1   (a) Element belonging to the *d*-block, though usually Groups 3 and 12 are excluded.

(b) Molecules or ions covalently bonded to a central metal ion.

(c) Energy separation between different members of the metal's *d*-orbital set when the metal ion is surrounded by a set of ligands.

19.3   The cyanide ligand stabilizes low oxidation states (in a similar manner to carbon monoxide) and also stabilizes normal oxidation states (as a pseudohalide ion).

19.5 $[Pt(NH_3)_4]^{2+}[PtCl_4]^{2-}$


19.7   The geometric isomers are:
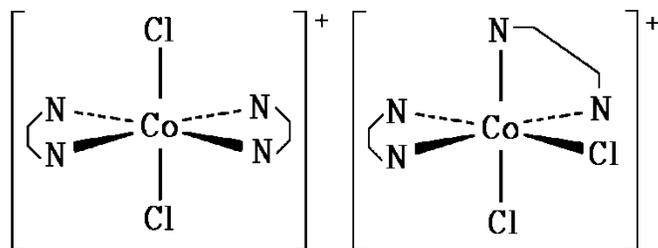
And for one of the geometric isomers, there are two optical (chiral) isomers.
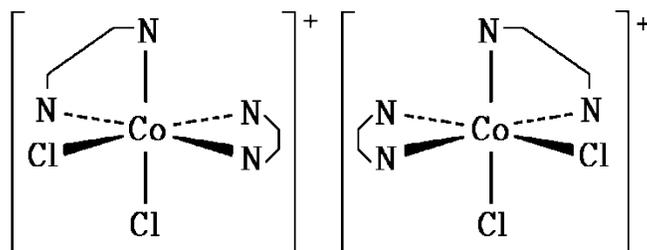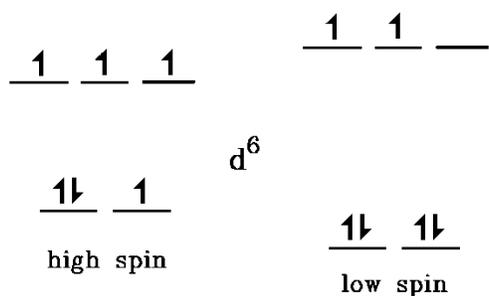
19.9   (a) Ammonium pentachlorocuprate(II); (b) pentaammineaquacobalt(III) bromide; (c) potassium tetracarbonylchromate(-III); (d) potassium hexafluoronickelate(IV); (e) tetraamminecopper(II) perchlorate.

19.11   (a) $[Mn(OH_2)_6](NO_3)_2$.
(b) $Pd[PdF_6]$.
(c) $[CrCl_2(OH_2)_4]Cl \cdot 2\ H_2O$.
(d) $K_3[Mo(CN)_8]$.

19.13   (a) The d^6 configuration in an octahedral field:
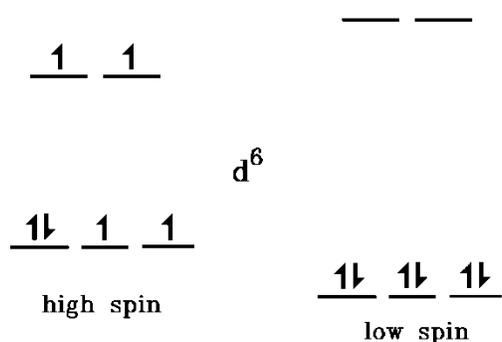
(b) The d^6 configuration in a tetrahedral field:
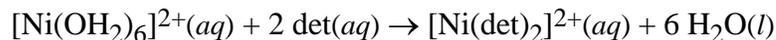

19.15   The largest value of Δ is for the cobalt(III) complex, the others being cobalt(II) because the splitting increases with increase in oxidation state. The smallest value is for cobalt(II) in a tetrahedral environment compared to the middle cobalt(II) in an octahedral environment because Δ_{tet} is only about four-ninths the value of Δ_{oct}.

19.17 (a) $[ReF_6]^{2-}$, because the heavier metal will have the greater crystal
             field splitting.

       (b) $[Fe(CN)_6]^{3-}$, because the higher charge Fe(III) will have the greater
             crystal field splitting.

19.19 Configuration   CFSE

Configuration	CFSE
d^0	$-0.0\ \Delta_{tet}$
d^1	$-0.6\ \Delta_{tet}$
d^2	$-1.2\ \Delta_{tet}$
d^3	$-0.8\ \Delta_{tet}$
d^4	$-0.4\ \Delta_{tet}$
d^5	$-0.0\ \Delta_{tet}$
d^6	$-0.6\ \Delta_{tet}$
d^7	$-1.2\ \Delta_{tet}$
d^8	$-0.8\ \Delta_{tet}$
d^9	$-0.4\ \Delta_{tet}$
d^{10}	$-0.0\ \Delta_{tet}$

19.21 The optimum situation energetically is for the ion with the greater CFSE
       to occupy the octahedral sites. Thus the mixed metal oxide $NiCr_2O_4$ will
       adopt the normal spinel structure, $(Ni^{2+})_t(Cr^{3+})_oO_4$, because the Cr^{3+} ion,
       having the higher oxidation state, will have a greater CFSE than that of the
       Ni^{2+} ion.

19.23 Balanced chemical equation:
             $[Ni(OH_2)_6]^{2+}(aq) + 2\ det(aq) \rightarrow [Ni(det)_2]^{2+}(aq) + 6\ H_2O(l)$
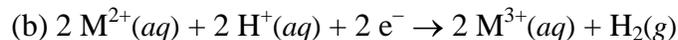   The formation of this product will be favored as a result of the chelate
       effect—the increase in entropy from the increase in moles.

Beyond the Basics

19.25 The ligand tricyclohexylphosphine is probably too large for two of them to
       fit around an iron(III) in addition to the three chloro-ligands.

19.27 (a) M^{2+} should disproportionate as the sum of the potentials
       (0.00 + 0.20) V is positive. The equation would be
             $3\ M^{2+}(aq) \rightarrow M(s) + 2\ M^{3+}(aq)$

(b) $2 \text{ M}^{2+}(aq) + 2 \text{ H}^+(aq) + 2 \text{ e}^- \rightarrow 2 \text{ M}^{3+}(aq) + \text{H}_2(g)$

To find the limit of spontaneity, we can set E = 0.

Because only the hydrogen-ion concentration varies, we can write a simplified Nernst equation:

$$E = 0 = E° - \frac{RT}{2F} \ln\left(\frac{1}{[\text{H}^+]^2}\right) = +0.20 \text{ V} - \frac{8.31 \text{ V}\cdot\text{C}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \times 298 \text{ K}}{2\times(9.65\times10^4 \text{ C}\cdot\text{mol}^{-1})} \ln\left(\frac{1}{[\text{H}^+]^2}\right)$$

$[\text{H}^+] = 4.1\times10^{-4}$

pH = 3.38

19.29 For zinc, with its filled d^{10} orbitals, there is no crystal field stabilization energy; thus geometry is primarily determined by electron-pair repulsions. For nickel, a square-planar geometry will maximize CFSE and it will enable some degree of π bonding to occur between the part-empty d orbitals of the nickel and the filled d orbitals of the selenium.

19.31 (a) $[\text{Cr(OH}_2)_6]^{3+}\cdot3\text{Cl}^-$, hexaaquachromium(III) chloride;
(b) $[\text{Cr(OH}_2)_5\text{Cl}]^{2+}\cdot2\text{Cl}^-$, pentaaquachlorochromium(III) chloride;
(c) $[\text{Cr(OH}_2)_4\text{Cl}_2]^+\cdot\text{Cl}^-$, tetraaquadichlorochromium(III) chloride.

19.33 Fluoride is a weaker field ligand than chloride. Thus the crystal-field splitting for the fluoro- compound will be less than that of the chloro- compound. To give a yellow-orange color, the chloro- compound must be absorbing in the blue (higher energy) portion of the spectrum. To give a blue color, the fluoro- compound must be absorbing in the red (lower energy) portion of the spectrum.