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of structural chemistry of complexes of metal ions. We are certainly interested in complexes as they occur in biology. For example, heme complexes  $\text{Fe}^{3+} / \text{Fe}^{2+}$  and is part of the active transport of oxygen to various parts of the body. Complexes of metal ions are important in enzyme structure and provide an important local symmetry, organizing the surrounding molecular framework. Complexes are also important in metal extraction between aqueous phases and organic phases in which the complex is selectively soluble. Important is the incorporation of complexing agents within membranes so that metal ions selectively penetrate the membrane passing through to a “strip” solution on the other side.<sup>1</sup> This transport is affected by the metal-carrier (complexing agent) and driven by the concentration gradient (Free Energy) across the selective membrane. This technique is used in the food industry for purification and in modern food packaging, in the petrochemical industry for separation, in recycling and in productions of pure chemicals.

## 16.2 Formation of Metal Complexes and some of their Properties

We find that mixtures of metal ions like  $\text{Co}^{3+}$  with ammonia and chloride ion yield stable molecular structures with remarkable properties. Among these properties are a generally octahedral geometry, a characteristic color depending on the number and types of complexing molecules, and an inherent magnetism (or lack of magnetism) and the ability in some cases to rotate the plane of polarized light (optical activity).

First lets look at the atomic structure of cobalt. Co has an argon core, see Table ?? in the Appendix, and valence electrons  $(3d)^7(4s)^2$  leaving three 3d holes (empty orbitals). The  $\text{Co}^{3+}$  ion has electron configuration  $(3d)^6$  and is called a  $d^6$  structure having six electrons available for bonding. The d-electron orbit is one where the orbital angular momentum has the value  $L = 2$  and there are  $2L + 1 = 5$  different orbitals. In a “free state” these five electron orbits have the same energy. Energy states that are the same in this way are called *degenerate* as indicated in Fig. 16.1.

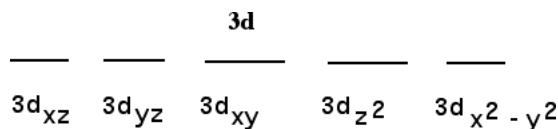


Figure 16.1: Five Degenerate 3d Orbitals

These five orbitals have five different spacial properties as shown in Fig. 16.2.

The way in which the d-electrons fill the available orbits is given by “Hund’s Rule” which states that *everything else being equal, the greatest total spin (multiplicity) is lowest in energy.*

The species complexing the central metal ion are called ligands. Cobalt forms a stable complex with a number of “ligands” one of them being  $\text{Co}[\text{Cl}_6]^{3-}$  and in this case the

<sup>1</sup>Virtually all the salt, NaCl, used in Japan comes from membrane separation technology.

16.2. FORMATION OF METAL COMPLEXES AND SOME OF THEIR PROPERTIES<sup>5</sup>

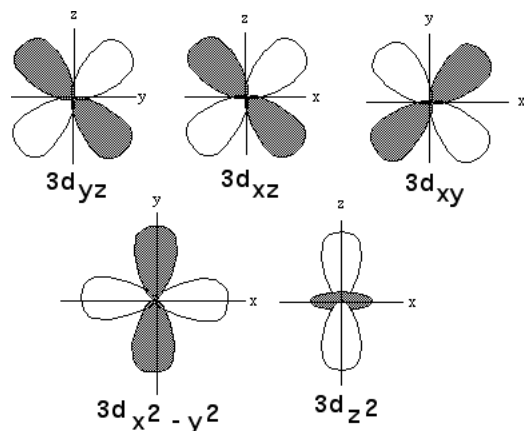


Figure 16.2: Five 3d Orbitals and their Spatial Directions

ligands are the 6 chloride ions. The three dimensional structure of the complex depends on the valence electron orbits available to the ligands. In the case of  $Co[Cl_6]^{3-}$  the structure is *octahedral*.

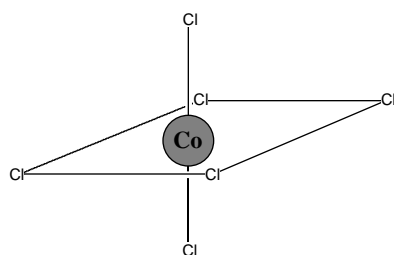


Figure 16.3: An Octahedral Complex of six  $Cl^-$  around  $Co^{3+}$

The number of bonds to the central ion is called the *coordination number* and in this cobalt example the coordination number is 6. Ligands forming one bond to the central ion, as in the case of  $Co[Cl_6]^{3-}$ , are called *monodentate* ligands.

Oxalic acid, which forms a complex with iron  $[Fe(C_2O_4)_3]^{3-}$ , forms two bonds per ligand and is called a *bidentate* ligand complex.

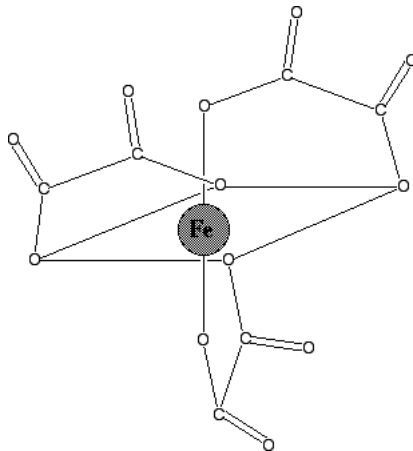


Figure 16.4: The “Bidentate” Complex of Ferric Iron and Oxalic Acid,  $Fe[C_2O_4]^{3-}$

In a crude way we can say that the structure of the complex is determined by the number of d-electrons in the central metal ion. These metal ion valence electrons fill up the available orbitals (3d-orbitals in the case of transition elements) according to Hund’s rule.

### 16.3 The Geometry of Complexes

The geometry of molecules is determined by the organization of valence electrons. Thus, tetrahedral carbon, typified by methane  $CH_4$ , has the configuration  $sp^3$  mixing three differently oriented p-orbitals with s-orbitals to achieve its observed shape. In the case of the 3d electrons in the transition elements the complex ion geometry is also determined by the available electron orbitals.

In the most simple minded way, if we place one of the 3d-orbitals, from Fig. 16.2 so that the lobes are pointing towards the corners of a square then we can have an orbital pointing above and below the plane of the square. This provides six geometrical bonding sites and gives an octahedral geometry. The state of affairs is more complex than this, but we can see that the 3d orbitals contain the elements of octahedral geometry, or in the case of some platinum complexes, a square geometry.

### 16.3.1 Isomers

The dictionary says an isomer is “Any of two or more substances that are composed of the same elements in the same proportions but differ in properties because of differences in the arrangement of atoms.” Complexes provide a rich opportunity to form many isomers. Figures 16.5 and 16.5 show two possibilities. By *cis*- we mean *on the same side* and by *trans*- *on the other side*.

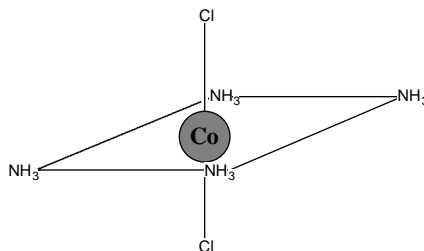


Figure 16.5: A Trans Isomer of Cobalt Complex *trans* –  $[Co(NH_3)_4Cl_2]^+$

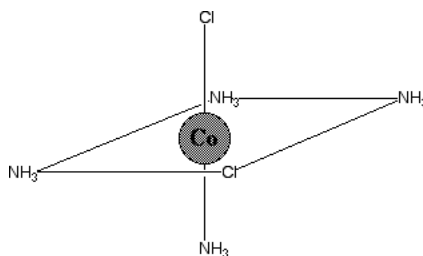


Figure 16.6: A Cis Isomer of Cobalt Complex *cis* –  $[Co(NH_3)_4Cl_2]^+$

### 16.3.2 Optical Activity

Optical activity is the property of some molecules to rotate the plane of polarized light.<sup>2</sup>

Only molecules that have a helical form have this property. The different circular polarizations act differently depending on the handedness of the helical structure relative to the propagation of the light. An optically active molecule thus retards one of these components more than the other. (The index of refraction is different for right and left circularly polarized light.) Molecules that have a helical structure are not superimposable on their mirror image.

The simplest example of a molecule that shows optical activity is a tetrahedral carbon with four different groups. These molecules have an "asymmetric" center that is, not be superimposable on its mirror image. The molecules exist in two mirror image forms, one is dextrorotatory (rotates linearly polarized light to the right) and the other levorotatory.

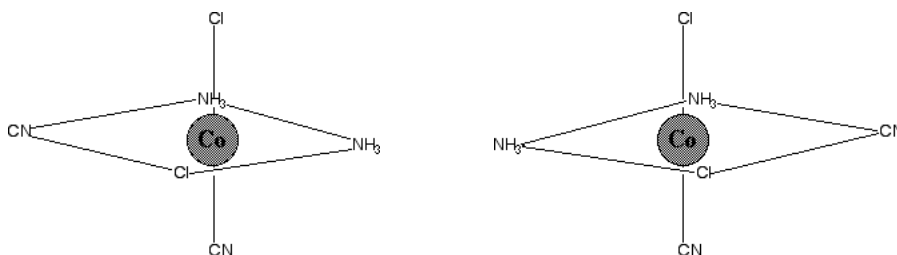


Figure 16.7: Non-superimposable Mirror Images of a Cobalt Complex

It stands to reason that many transition metal complexes are optically active. It is also a fact that chemical and biochemical activity is sensitive to this kind of molecular geometry and this is one of the reasons for introducing this subject.

## 16.4 Crystal Field Splitting of d Levels

The energy levels of atoms and ions are represented by hydrogenic like orbitals and are denoted by

$$(1s); (2s), (2p_x)(2p_y)(2p_z); (3s), (3p_x)(3p_y)(3p_z), (3d_{xz})(3d_{yz})(3d_{xy})(3d_{z^2})(3d_{x^2-y^2}); \dots$$

The d, energy levels have orbital angular momentum  $L = 2$ , and have  $2L + 1 = 5$  components as indicated by the subscripts on the 3d orbitals above. These, in a free atom or ion, have

<sup>2</sup>Light is electromagnetic radiation having an oscillating electric (and magnetic) field transverse to its direction of propagation. A single wave of this light has its electric vector rotating in a clockwise, or a counter clockwise, manner as it comes towards us. The clockwise rotating light is called righthand circular polarized light and the counterclockwise rotating light is called lefthand polarized light. If two of these are put together in phase then they describe a linearly variation of the light field, or a linear polarization. Ordinary light is composed of many such beams at random orientations and is unpolarized. Passing through a polarizer, or even reflecting from a surface produces linear polarization where the electric field oscillates in a plane perpendicular to the propagation direction. This beam may be considered made up of two counter rotating circular components mentioned above. It is these circular components that interact differently with molecules which have a left or right handedness and retard one of the circular components relative to the other. The resulting combination of circular components is again a linearly polarized light, but with its plane of polarization rotated by an amount characteristic of the molecule.

the same energy. Levels having the identical energy are called “**degenerate.**” Here, for the d-electrons, we have a five-fold degeneracy as in Figure 16.1. It is this energy degeneracy that is broken by surrounding the ion by ligands. This removal of energy degeneracy has a profound effect on the properties of the complexed transition metal ion.

As we said, most of the observed properties of transition metal ion complexes is explained by the behavior of the d-electrons. Crystal Field theory is one view for the removal of the degeneracy of the five d-energy levels by the electrostatic interaction of the surrounding ligands. The idea is that an ion, say  $Fe^{3+}$  is surrounded by negative charges like six  $CN^-$ . These negative charges will cause a removal of the 5-fold degeneracy of the atomic d-orbits. Each of the five orbitals, have a different spacial extent, see Fig. 16.2, and will react differently to the charges assuming different energies.

In the case of the transition metal complexes the d-energy levels have characteristic “crystal field” splittings caused by the ligands. We can understand this by thinking of the ligands ( $CN^-$  for example) as charge densities surrounding the metal ion. The electric field from these ligand charges will split the d-energy levels of the metal ion as mentioned. Some ligands provide a strong splitting, or large energy level separation and others a weak splitting. The degree of this splitting and the number of electrons filling the d-orbits determines the structure, color, and magnetism of the complex. Fig. 16.8 shows one such removal of 3d-electron degeneracy.

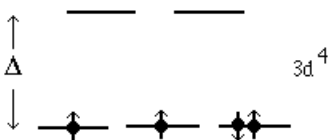


Figure 16.8: Schematic Removal of Degeneracy of 3d-electrons in a Crystal Field

## 16.5 The Colors of Complexes

The absorption of light excites an electron from the “ground” configuration to a higher level as shown in Fig. 16.9. From the wavelength of the absorbed light and the equation  $h\nu = \frac{hc}{\lambda} = \Delta E = (E_2 - E_1)$  we can estimate the d-level splitting,  $\Delta_o$ .

We have a rough understanding of the fundamental processes that occur when light interacts with matter. If we have a beam of white light incident on a metal complex for example, it may absorb a specific wavelength (frequency) from the beam leaving the rest of the wavelengths to pass through the material. Since the complex has removed one color (wavelength) it stands to reason that the material will appear as the complimentary color. We can use the color wheel below to estimate the absorbed wavelengths from the color of the complex.

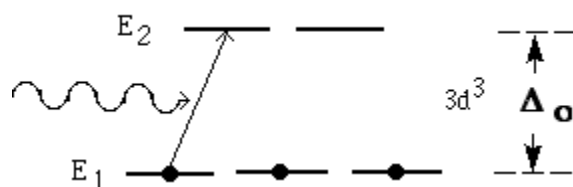


Figure 16.9: Typical d-electron Excitation

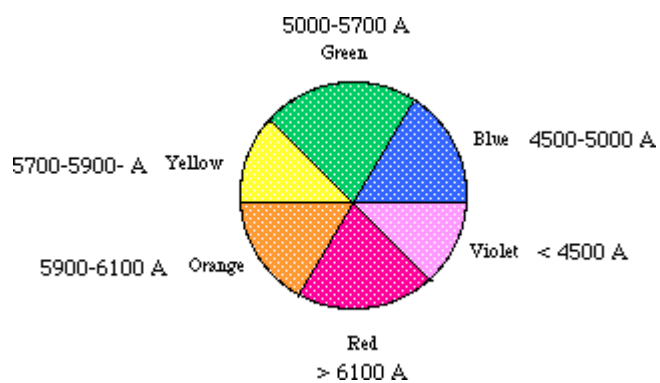


Figure 16.10: Color Wheel

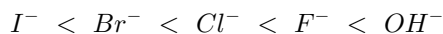
Colors of Some Octahedral Complexes					
complex	absorbed wavelength	absorbed color	complex's color	$\Delta_o$ cm <sup>-1</sup>	total spin
$Co(F)_6^{3-}$	700	red	green	14,300	2
$Co(C_2O_4)_3^{3-}$	600, 420	yellow, violet	dark green	17,000	2
$Co(H_2O)_6^{3+}$	600, 400	yellow, violet	blue-green	18,200	0
$Co(NH_3)_6^{3+}$	475, 340	Blue, UV	yellow	22,900	0
$Co(en)_3^{3+}$	470, 340	Blue, UV	yellow-orange	23,000	0
$Co(CN)_6^{3-}$	310	UV	pale yellow	34,800	0
$Co(SCN)_4^{2-}$	600	orange	blue	~18,000	3/2
$Fe(CN)_6^{3-}$	286	UV	red	35,000	1/2
$Fe(CN)_6^{4-}$	300	UV	red	30,000	0
$Fe(H_2O)_6^{3+}$	570	yellow green	pale violet	~17,500	5/2

(note: check these spin values and find missing wavelengths)

### Spectrochemical Series

The ranking of ligands in order of their approximate crystal field strengths from weak field (high spin values) to strong field (low spin values) is

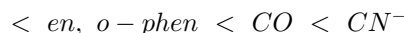
weak field



intermediate field



strong field



where en = ethylenediamine =  $H_2N-CH_2-CH_2-NH_2$  and o-phen = orthophenanthroline. Ligands like en complex a central metal ion by means of the nitrogen atoms and can be represented by N—N in diagrams. Similarly, oxalate,  $C_2O_4^{2-}$ , complexes by means of oxygen and may be represented by O—O in complex diagrams. A powerful chelating agent is EDTA, or ethylenediamine tetra-acetic acid.

## 16.6 Origin of Magnetism in 3d Octahedral Complexes

Operationally, we can think of the magnetic behavior of matter by how it reacts to the effects of an applied, inhomogeneous magnetic field. Material that is repelled by the field, showing an apparent loss in weight, is called diamagnetic, while material that is drawn into

an inhomogeneous magnetic field is called paramagnetic as illustrated in Fig. 16.11.<sup>3</sup>

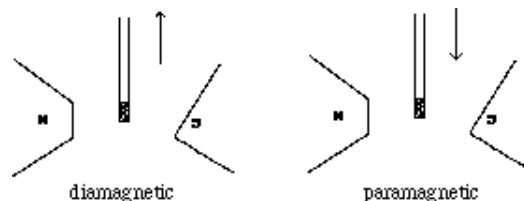


Figure 16.11: Diamagnetic and Paramagnetic behavior of Matter in an Inhomogeneous Magnetic Field

In the diamagnetic case, this behavior is due to the complete pairing of electron spins. The apparent weight loss is due to the “diamagnetic” circulation of the electron density within the molecule as it reacts to reduce the magnetic field. This is an analog of Lenz Law in physics and might be thought of as an example of LeChatlier’s principle; the electrons circulating in a manner to create a small field in opposition to the applied field. In the paramagnetic case the apparent weight gain is due to the presence of unpaired electrons in the molecule.

In metal complexes the valence electrons fill the available energy levels according to the Pauli principle, building up the electronic structure as in any molecule.<sup>4</sup> In these cases the d-orbitals are the last filled and give rise to magnetic properties. The electron population of energy levels also obeys Hund’s rule which states that everything being equal the greatest number of unpaired electrons in degenerate<sup>5</sup> orbitals will be the configuration of lowest energy. Depending whether these levels are widely separated or closely spaced and on the number of electrons, the complex will be diamagnetic (no net electron magnetism) or paramagnetic (net electron magnetism). The following figure, Fig. 16.12, shows the case for four 3d electrons in a strong field splitting with total spin  $S = 1$ . The four electrons fill up the lowest available levels in a manner that creates the largest spin according to Hund’s rule and the Pauli principle.

The next figure, Fig. 16.13, shows the case for four 3d electrons in a weak field splitting with total spin  $S = 2$ .

Both complexes are paramagnetic, but one of them has a greater magnetism than the other.

<sup>3</sup>Ferromagnetism and antiferromagnetism might be considered special cases of “paramagnetic” behavior.

<sup>4</sup>The Pauli Principle states that no two electrons can be in the same quantum state. Since electrons are endowed not only by mass and charge, but also by spin-magnetism, everything can be the same so long as the spin orientation is different. For electrons the spins may be “up” ( $M_s = \frac{1}{2}$ ), or “down” ( $M_s = -\frac{1}{2}$ ).

<sup>5</sup>Orbital degeneracy means orbital of equal energy.

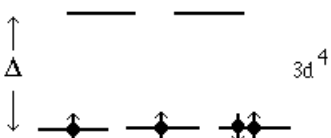


Figure 16.12: Strong field Splitting Octahedral Complex  $3d^4$

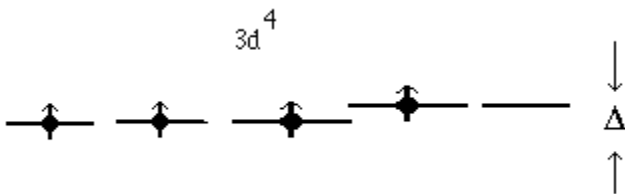
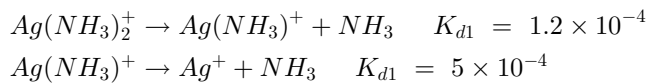


Figure 16.13: Weak field Splitting Octahedral Complex  $3d^4$

## 16.7 Complex Ion Equilibria

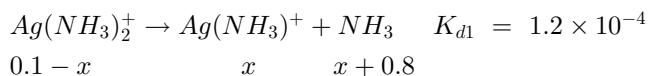
Complex ions undergo many-step dissociations and these are treated in the usual way in chemical equilibrium calculations. As an example consider the dissociation of the silver ammonia complex,  $Ag(NH_3)_2^+$ .<sup>6</sup> The complex dissociates in two steps.



It is convenient to write the following overall equilibrium constant expression

$$K_{instability} = K_1 \times K_2 = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = 6 \times 10^{-8}$$

Suppose that we have a solution 0.1 mole  $AgNO_3$  in 1 liter of 1.0M  $NH_3$ . What are the concentrations of all the species in solution? Silver nitrate completely dissociates so that  $[NO_3^-] = 0.1M$ . The silver ion reacts with ammonia to form complexes. Since the  $K_{inst}$  is a small number we can consider that “all” the silver is in the complex  $Ag(NH_3)_2^+$  and therefore  $[Ag(NH_3)_2^+] \approx 0.1M$ . Looking at the stoichiometry we find that 2 moles of  $NH_3$  are used for each mole of the  $Ag(NH_3)_2^+$  complex. Thus,  $[NH_3] \approx 1.0 - 2 \times 0.1 = 0.8$ . Now look at the dissociation of  $Ag(NH_3)_2^+$ .



So,

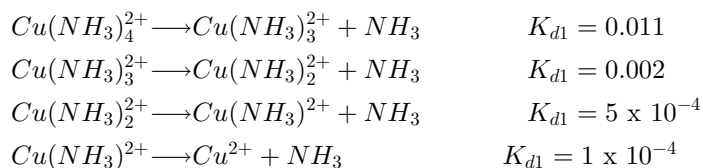
$$K_{d1} = 1.2 \times 10^{-4} = \frac{x(x + 0.8)}{0.1 - x} \approx \frac{x(0.8)}{0.1}$$

and  $x = [Ag(NH_3)^+] = 1.5 \times 10^{-5}$ . From the  $Ag(NH_3)^+$  dissociation equilibrium expression

$$[Ag^+] = \frac{K_{d2}[Ag(NH_3)^+]}{[NH_3]} \approx \frac{5 \times 10^{-4} \times 1.5 \times 10^{-5}}{0.8} = 9.4 \times 10^{-9}$$

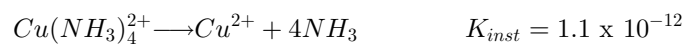
ion	concentration
$[Ag^+]$	$9.4 \times 10^{-9}$
$[Ag(NH_3)^+]$	$1.5 \times 10^{-5}$
$[Ag(NH_3)_2^+]$	0.1

In the case of some copper complexes



<sup>6</sup>Silver chloride,  $AgCl$ , is an insoluble substance with  $K_{sp} = 1.8 \times 10^{-10}$ . On the addition of ammonia the  $AgCl$  ppt. dissolves forming the silver ammonia complex.

The sum of these steps gives an overall reaction



where  $K_{inst} = K_{d1}K_{d2}K_{d3}K_{d4} = 1.1 \times 10^{-12}$  is called the “instability” constant for the complex and gives us a measure of the stability of the complex.

## Appendices

## Appendix A

# Some Electron Configurations of Metal Atoms

Electron Configuration of Some Elements							
atom	no. e's	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f 5g	6s
Ti	22	2	2 6	2 6 2	2 - - -	- - - - -	-
V	23	2	2 6	2 6 3	2 - - -	- - - - -	-
Cr	24	2	2 6	2 6 5	1 - - -	- - - - -	-
Mn	25	2	2 6	2 6 5	2 - - -	- - - - -	-
Fe	26	2	2 6	2 6 6	2 - - -	- - - - -	-
Co	27	2	2 6	2 6 7	2 - - -	- - - - -	-
Ni	28	2	2 6	2 6 8	2 - - -	- - - - -	-
Cu	29	2	2 6	2 6 10	1 - - -	- - - - -	-
Zn	30	2	2 6	2 6 10	2 - - -	- - - - -	-
Y	39	2	2 6	2 6 10	2 6 1 -	2 - - - -	-
Rh	45	2	2 6	2 6 10	2 6 8 -	1 - - - -	-
Pd	46	2	2 6	2 6 10	2 6 10 -	- - - - -	-
Ag	47	2	2 6	2 6 10	2 6 10 -	1 - - - -	-
Ce	58	2	2 6	2 6 10	2 6 10 1	- - 1 - -	2
Pt	78	2	2 6	2 6 10	2 6 10 14	2 6 9 - -	1



## Appendix B

# Pasteur and Optical Activity

“Pasteur, in 1848, while working with tartaric acids, first demonstrated the phenomenon of optical isomerism in which two forms of a substance are identical in properties with the exception that one form rotates polarized light to the right (dextrorotatory) and the other rotates it equally to the left (levorotatory). When Pasteur began his work on the tartaric acids, two forms were known. Biot had shown the tartaric acid from wine to be dextrorotatory. Kastner had discovered another form of tartaric acid which did not rotate the plane of polarized light or was optically inactive. This form he called racemic tartaric acid (racemic from Latin *racemus* meaning bunch of grapes). Pasteur studied the crystalline forms of the salts of these two tartaric acids and expected to find them to be different. When he crystallized the sodium-ammonium salt of the optically inactive racemic tartaric acid below 28°C, the crystals upon casual inspection looked like those of the sodium-ammonium salt of d-tartaric acid. However, when Pasteur examined the crystals of the racemic tartrate more closely, he observed two kinds of crystals which had exactly the same structures, except they were reversed in space so that one kind of crystal structure was the mirror image of the other, just as the left hand has the same form as the right but is exactly reversed in space to it (mirror images). He also noted that the crystals were asymmetrical in form. Pasteur then separated the two forms of crystals, dissolved them in water, and observed their effects upon polarized light. The solution of one form of crystals rotated to the right and the other to the left. This observation of Pasteur demonstrated that crystalline form must depend upon molecular form, because when the crystals were dissolved only molecular form remained. Just as the crystals of the two tartaric acid salts were asymmetric, one type of molecule rotating polarized light to the right and the other to the left. This work demonstrated three forms of tartaric acid, the dextro- and levorotatory forms, and the racemic form which is optically inactive because it is composed of equal amounts of the dextro and levo acids. Pasteur later discovered meso-tartaric acid which was also inactive, but could not be broken up or resolved into dextro and levo forms. Accordingly, while the molecules of d- and l-tartaric acid are asymmetric, the molecule of meso-tartaric acid must be symmetric since it is optically inactive.”

Quote from the Textbook of Biochemistry, by West and Todd, First Ed., Macmillan, New York, 1951.



## Appendix C

# Problems: Transition Metal Ions and Complexes

These were Homework Problems from Chapter 23 Klotz & Treichel. The answers are on our web page.

15. Give the electron configuration for each ion listed here assuming strong ligand fields, and tell whether it is paramagnetic or diamagnetic.

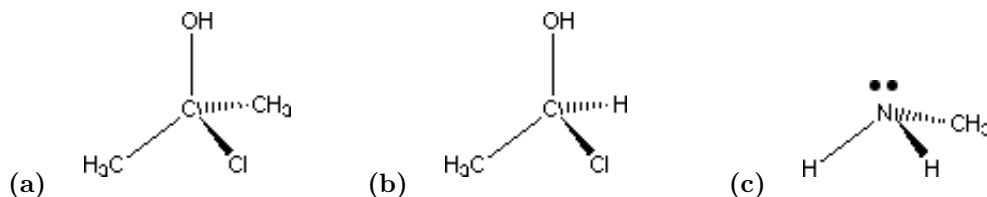
(a)  $Y^{3+}$  (b)  $Pt^{2+}$  (c)  $Rh^{3+}$  (d)  $V^{2+}$  (e)  $Ce^{4+}$  (f)  $U^{4+}$

25. Only one of the following nitrogen compounds or ions,  $NH_4^+$ ,  $NH_3$ , or  $NH_2^-$ , is incapable of serving as a ligand. Identify this species and explain your answer.

37. Which of the following complexes can have geometrical isomers? (If isomers are possible, draw the structures of the isomers and label them as cis or trans, or as fac or mer if appropriate).

(a)  $[Co(H_2O)_4Cl_2]^+$  (b)  $Co(H_2O)_3F_3$  (c)  $[Pt(NH_3)Br_3]^-$  (d)  $[Co(en)_2(NH_3)Cl]^{2+}$

39. Decide whether each of the following molecules has an enantiomer:<sup>1</sup>



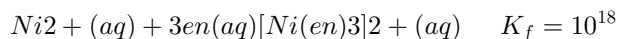
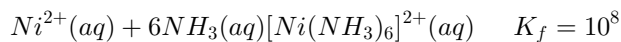
<sup>1</sup>An enantiomer is a stereoisomeric pair consisting of a “chiral” compound and its mirror image isomer.

41. Draw all possible isomers (geometric and optical) for the ion  $[Cr(C_2O_4)_2(H_2O)_2]^-$ .

46. From experiment we know that  $[CoF_6]^{3-}$  is paramagnetic and  $[Co(NH_3)_6]^{3+}$  is diamagnetic. Using the crystal field model, depict the electron configuration for each ion. What can you conclude about the effect of the ligand on the magnitude of  $D^o$ ?

49. In water, the titanium (III) ion,  $[Ti(H_2O)_6]^{3+}$ , is violet. (Its broad absorption band occurs at about 500 nm.) What color light is absorbed by the ion?

61. In this equation, we wish to explore the differences between metal coordination by monodentate and bidentate ligands. Formation constants,  $K_f$ , for  $[Ni(NH_3)_6]^{2+}(aq)$  and  $[Ni(en)_3]^{2+}(aq)$  follow.



The difference in  $K_f$  between these complexes, reflecting a large increase in stability of the chelated complex, is caused by the chelate effect. Recall that  $K$  is related to the standard free energy of the reaction by  $\Delta G^o = -RT \log K$  and  $\Delta G^o = \Delta H^o - T\Delta S^o$ . Here we know from experiment that  $\Delta H^o$  for the  $NH_3$  reaction is -109 kJ/mol, and  $\Delta H^o$  for the en reaction is -117 kJ/mol. Is the difference in  $\Delta H^o$  sufficient to account for the  $10^{10}$  difference in  $K_f$ ? Comment on the role of entropy in the second reaction compared with that in  $NH_3$  reaction.

## Homework Chapter 23 K & T Transition Metal Ions and Complexes

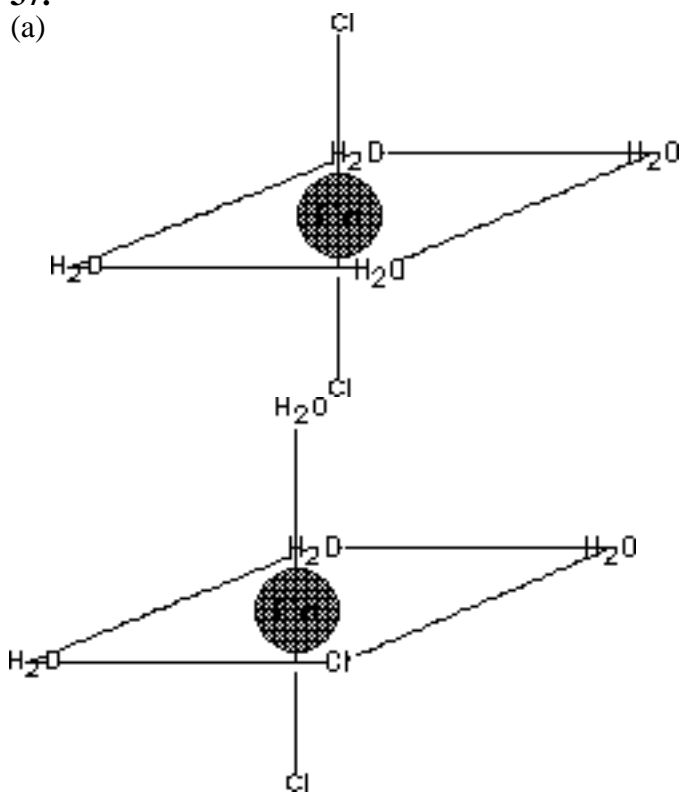
15. Electron configurations for the ions assuming a strong crystal field splitting (d-electron energy level splitting).

- (a)  $\text{Y}^{3+}$  Kr core diamagnetic
- (b)  $\text{Pt}^{3+}$   $5d^8$  paramagnetic
- (c)  $\text{Rh}^{3+}$   $4d^6$  paramagnetic if strong splitting
- (c')  $\text{Rh}^{3+}$   $4d^6$  diamagnetic if weak splitting
- (d)  $\text{V}^{2+}$   $3d^3$  paramagnetic
- (e)  $\text{Ce}^{4+}$  Xe core diamagnetic
- (f)  $\text{U}^{4+}$   $5f^2$  paramagnetic

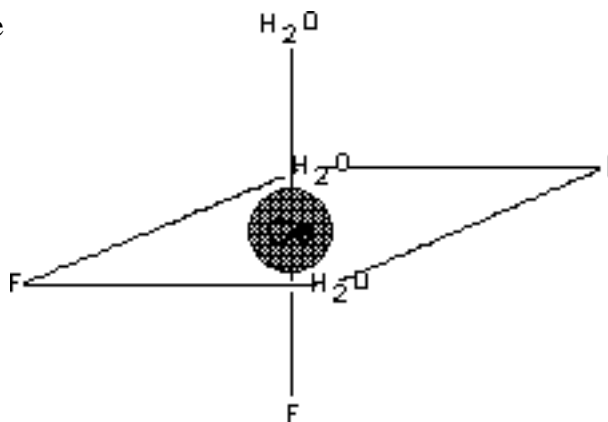
25.  $\text{NH}_4^+$  because the proton,  $\text{H}^+$ , occupies the lone pair electrons of  $\text{NH}_3$ .

37.

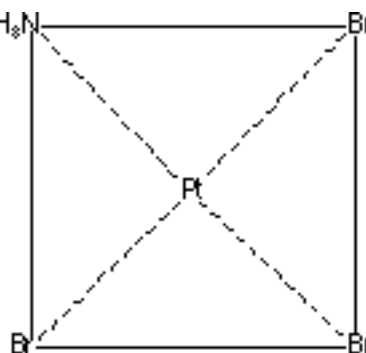
(a)



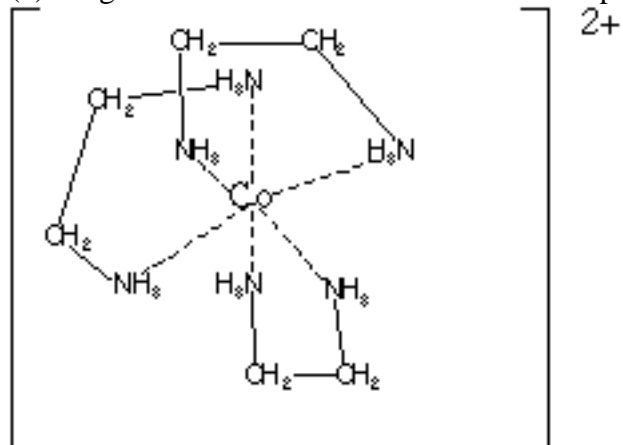
(b) No isomers. The complex looks like



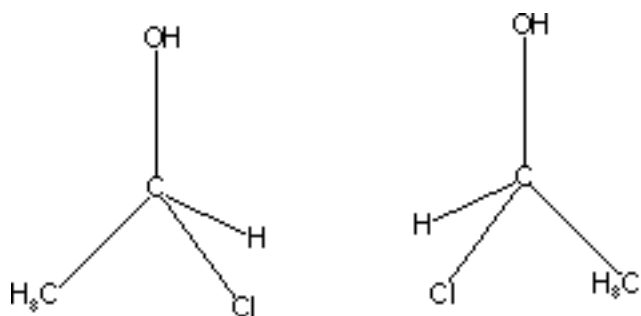
(c) No geometrical isomers. The complex looks like



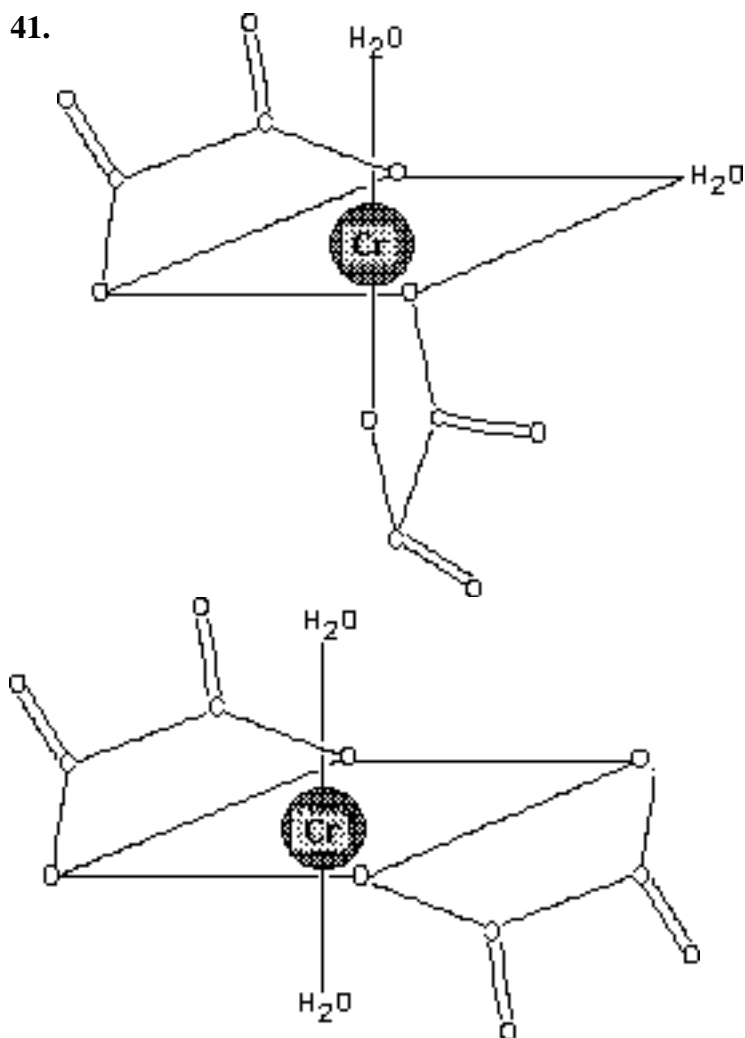
(d) No geometrical isomers. The bidentate complex looks like



**39.** Enantiomer means non-superimposable, mirror images. Only figure (b) with four different groups about the central carbon has a non-superimposable mirror image.



41.



46. In both complexes Co has a valence of 3+ and is therefore  $d^6$ .  $[\text{CoF}_6]^{3-}$  must have a small crystal field splitting (the d-level energy separation must be small) and filling the five d-orbitals with six electrons, following Hund's rule, gives a total electron spin  $S = 2$ .

The ammonia complex, being diamagnetic must have a strong d-level splitting so that the three lowest levels completely fill up with the six electrons and therefore  $S = 0$ .

49. Complex appearing violet must absorb yellowish light of around 580 nm.

61. For the  $\text{NH}_3$  complex reaction the Gibbs Free Energy = -45 kJ/mol, Enthalpy = -109 kJ/mol and Entropy = 212 J/K

For the (en) complex reaction the Gibbs Free Energy = -102.7 kJ/mol, Enthalpy = -117 kJ/mol and Entropy = 48 J/K

It would appear that the great reduction in entropy going from the monodentate complex with ammonia to the bidentate complex with ethylene diamine offers great stability—a high formation constant. Biological complexes are most often bidentate or even higher so it must be that this is an evolutionary advantage living systems have used.

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