Dr. Zellmer
Time: 7 PM Sun.
40 min

Chemistry 1220
Spring Semester 2023
Quiz XII

All Sections
April 23, 2023

Name ______________KEY__________________ Rec. TA/time ____________________________________

1. (2 pts) Explain the chelate effect and the main driving force behind it (i.e. what this is, the types of ligands involved and what is the main reason why it occurs).

Bidentate (such as ethylenediamine, en) and polydentate (such as EDTA) ligands bind very strongly to metal ions. Metal ions in solution (a hydrated metal cation) react with these types of ligands to form complexes with very large associated K_f values. These large K_f values indicate these types of metal complexes are very stable. These types of ligands easily replace monodentate ligands to form much more stable complexes. Also, when bidentate and polydentate ligands displace monodentate ligands this usually leads to a relatively large increase in entropy (disorder), $\Delta S > 0$. This increase in entropy is generally the primary driving force for the displacement of monodentate ligands by the bi and polydentate ligands.

See section 23.3 and the Closer Look box about this.

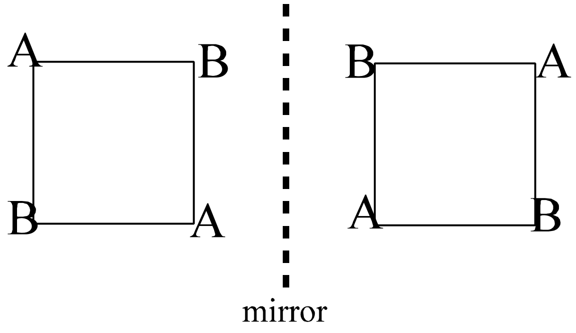
2. (2 pts) From the following pairs of coordination compounds which pair are coordination-sphere isomers and which are linkage isomers? (More than one answer possible.)

A. $K_2[CuBr_2Cl_2]$ and $Na_2[CuBr_2Cl_2]$	Not isomers, same complex.
B. $K_4[Fe(Cl)_2(NO_2)_4]$ and $Na_4[Fe(Cl)_4(NO_2)_2]$	Not isomers, different numbers of same ligands
C.* $[Ni(NH_3)_3Br]Br$ and $[Ni(NH_3)_2Br_2](NH_3)$	Coord. sphere isomers
D.* $K_4[Pd(Cl)_2(SCN)_4]$ and $K_4[Pd(Cl)_2(NCS)_4]$	Linkage isomers, SCN bonded via S or N.
E.* $[Ni(NH_3)_3Br]Cl$ and $[Ni(NH_3)_3Cl]Br$	Coord. sphere isomers (Br or Cl in sphere)

Coordination sphere isomers differ in what ligands are actually coordinated with the metal and those which are outside this “sphere”. Look to see what’s inside the square brackets (coordination sphere) and what’s outside the brackets (counter ions).

Linkage isomers occur when the same ligand can bind via two different sites in the ligand. While not limited to these, there are two listed in the textbook and notes that are most common, SCN^- (via S or N) and NO_2^- (via N or O).

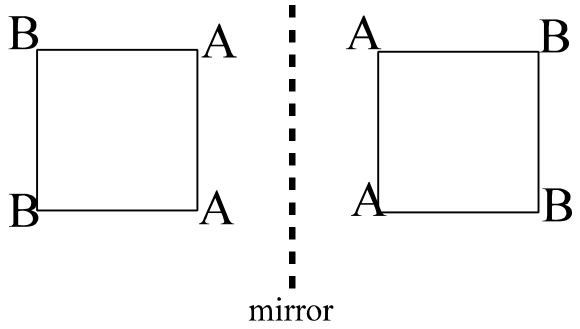
3. (3 pts) The ligands A and B are monodendate ligands. Draw all the possible stereoisomers of a square-planar metal complex of the following form, [MA_2B_2], and label them if appropriate (e.g. cis, trans, fac, mer, etc.). Indicate if any of them are enantiomers (label them clearly as enantiomers, optical isomers). Are any of them polar? **Show work!**



Trans - the two A atoms are trans (**opposite**) to each other, as are the B atoms.

The mirror image **IS superimposable** on the first molecule . Just rotate the mirror image 90° and it can superimpose on the original. So these are actually the same molecule and **NOT enantiomers**. The molecule is **not optically active**.

NONPolar



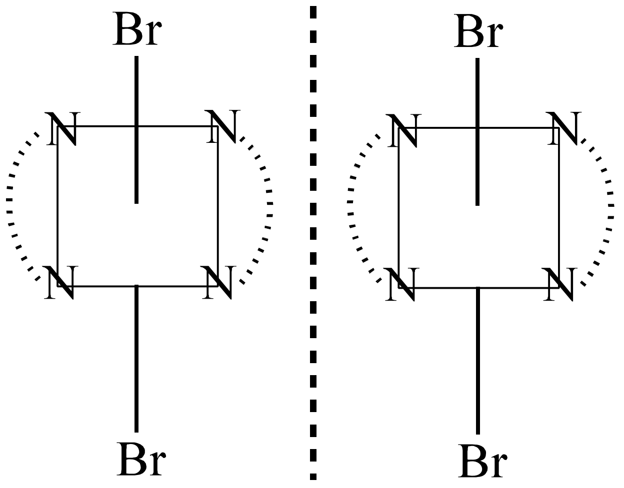
Cis - the two A atoms are cis (**adjacent**) to each other, as are the B atoms.

The mirror image **IS superimposable** on the first molecule . Just rotate the mirror image 180° and it can superimpose on the original. So these are actually the same molecule and **NOT enantiomers**. The molecule is **not optically active**.

POLAR

Square planar structures can have geometric isomers (cis-trans) but NO optical isomers.

4. (3 pts) Draw all the possible stereoisomers of $[Cr(en)_2Br_2]^+$ and label them if appropriate (e.g. cis, trans, fac, mer). **Indicate** if any of them are **enantiomers** (label them clearly as enantiomers). **Show work!**

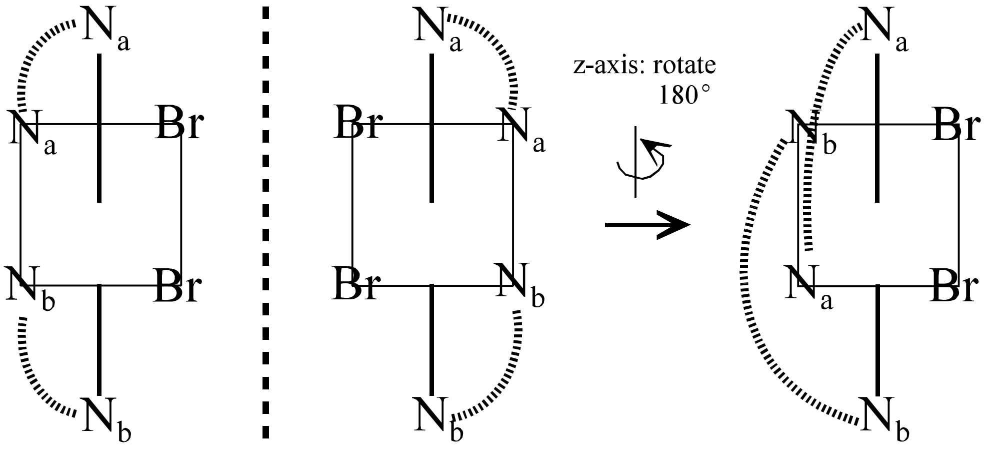


mirror

Trans - the two Br atoms are trans (**opposite**) to each other

The mirror image **IS superimposable** on the first molecule so these are actually the same molecule. These are **NOT enantiomers**. The molecule is **not optically active**.

Cis - the two Br atoms are cis (**adjacent**) to each other



mirror

Label the N atoms connected by the ribbons so you can keep track of them while you draw the mirror image and rotate the molecule. Remember, in the end the only thing which sets the N atoms apart from each other is which ones are connected to each other by the ribbon. Rotate to match up the Br atoms and see if the N atoms, along with the ribbons match up. Once you rotate and try to superimpose forget the labels. Above, I've rotated 180° around the z-axis (the vertical axis) to match up the Br atoms. Then you compare that to the original molecule. While the N atoms themselves will superimpose the **ribbons** do **NOT** superimpose. In the original molecule the N atom above the square is connected to the N atom in the back corner and the N below the square is connected to the N atom in the front corner. In the rotated mirror image the N above the ring is connected to the N in the front corner, while the N below the ring is connected to the N in the back corner. You could rotate the molecule around the x-axis (which is coming out of the paper toward you. This would be the same as flipping it upside down. You get the same thing as shown above by which was obtained by rotating 180° around the z-axis.

The mirror image is <u>**NOT**</u> **superimposable** on the first molecule so these are **enantiomers** and the cis isomer is **optically active**.

5. (12 pts) Draw the **crystal-field orbital diagrams** for $[FeCl_6]^{3-}$ and $[Fe(CO)_6]^{3+}$. Properly **label** the **orbitals**, **show** the **proper arrangement of electrons**, the **relative crystal-field splitting** (i.e. which is larger) whether they're **high-spin or low-spin** complexes, whether they are **paramagnetic or diamagnetic** and **which** would be expected to **absorb light** of **higher energy**. <u>**Explain**</u> why you've drawn each electron configuration (orbital diagram) as you have and why you get the other results listed in this question (i.e. whether it's high or low spin, paramagnetic or diamagnetic, etc).

Need to determine # electrons on the Fe. To do this you need to first determine the oxidation state of the iron. The oxidation state of Fe in both complexes is a +3.

For iron(III) the electron configuration is [Ar] $3d^5$. There are 5 electrons in the Fe^{3+} d orbitals.

According to the spectrochemical series Cl^- is a **weak-field** ligand and CO is a **strong-field** ligand.

For weak field ligands the crystal-field splitting, Δ, is small enough that the difference in energy between the levels (Δ) is smaller compared to the spin-pairing energy (energy diff. between putting electrons in the same orbital w. opposite spin and putting them in different orbitals w. the same spin). Putting the electrons in separate orbitals lessens the energy of repulsion and this is enough to overcome the small Δ so electrons can go into the higher "e" orbitals w/o a big energy "penalty". This leads to a high-spin case (electrons placed in all orbitals with same spin as much as possible before pairing).

For the strong-field ligand Δ is much larger. Not enough energy is recovered from the spin-pairing energy to overcome this larger Δ. In other words, the system can't gain enough energy by not pairing up the electrons to overcome this larger Δ. Instead the electrons go into the lowest energy orbitals before filling the higher energy orbitals. This leads to a low-spin case.

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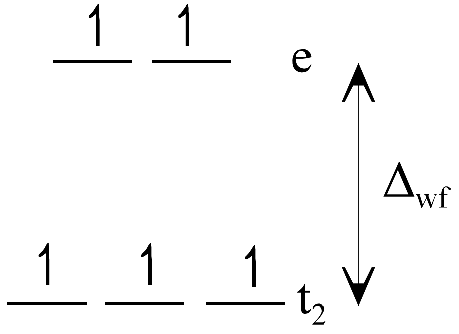
5. (Cont.)

Fe^{3+}: [Ar] $3d^5$



$[FeCl_6]^{3-}$

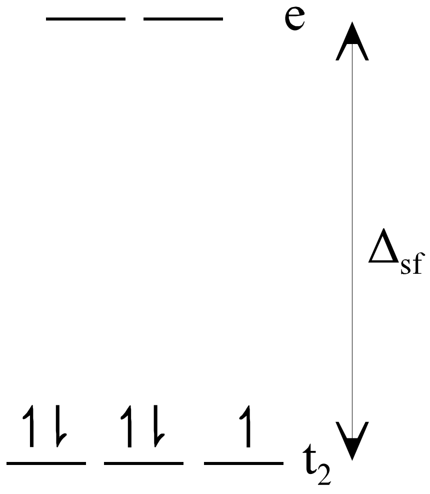
Cl^- wf ligand

Δ small (compared
to SP energy)

high spin

5 unpaired e^-

paramagnetic



$[Fe(CO)_6]^{3+}$

CO sf ligand

Δ large (compared
to SP energy)

low spin

1 unpaired e^-

paramagnetic

The difference in the two spin cases can be seen by the magnetic properties. Both complexes have unpaired electrons making them paramagnetic. Thus they interact w. a magnetic field and are attracted to it. The high-spin case interacts more strongly w. a magnetic field since there are more unpaired electrons. Also, the number of unpaired electrons can be determined since the strength of the interaction w. the magnetic field is a measure of how many unpaired electrons there are.

The **strong-field ligand** case, $[Fe(CO)_6]^{3+}$, will absorb light of **higher energy** (shorter wavelength) since the **crystal-field splitting energy**, Δ, is **larger** for this complex. The light transmitted (color we see) would have less energy (longer wavelength).

6. (6 pts) For the following nuclear equations fill in the missing particle and identify the type of process (alpha decay, beta emission, positron emission or electron capture). ${}^{A}_{Z}\text{X}$ may be an element or particle. **Show work!**

a) ${}^{226}_{88}\text{Ra} \rightarrow {}^{222}_{86}\text{Rn} + \mathbf{{}^{4}_{2}He}$ **alpha decay** (alpha emission, α often used instead of ${}^{4}_{2}\text{He}$)
By the way, an α particle is a helium nucleus w/o the 2 electrons of a helium atom and thus technically has a 2+ charge, which is not usually shown.

b) ${}^{191}_{79}\text{Au} + \mathbf{{}^{0}_{-1}e} \rightarrow {}^{191}_{78}\text{Pt}$ **electron capture**

c) ${}^{76}_{36}\text{Kr} \rightarrow \mathbf{{}^{76}_{35}Br} + {}^{0}_{1}\text{e}$ **positron emission** (β^{+} sometimes used instead of ${}^{0}_{1}\text{e}$)

Just remember, **conservation of nucleons (i.e. mass numbers and atomic numbers must be balanced in nuclear equations)**.

7. (4 pts) What element results when ${}^{218}\text{Po}$ undergoes **one alpha** emission, **two beta** emissions and **one alpha** emission (in that order). **Show each step** (4 steps total) in this radioactive series using nuclear equations.

${}^{218}_{84}\text{Po} \rightarrow {}^{214}_{82}\text{Pb} + {}^{4}_{2}\text{He}$ alpha emission (α often used instead of ${}^{4}_{2}\text{He}$ for alpha part.)

${}^{214}_{82}\text{Pb} \rightarrow {}^{214}_{83}\text{Bi} + {}^{0}_{-1}\text{e}$ beta emission (β or β^{-} often used for a beta particle instead of ${}^{0}_{-1}\text{e}$)

${}^{214}_{83}\text{Bi} \rightarrow {}^{214}_{84}\text{Po} + {}^{0}_{-1}\text{e}$ beta emission

${}^{214}_{84}\text{Po} \rightarrow \mathbf{{}^{210}_{82}Pb} + {}^{4}_{2}\text{He}$ alpha emission (α often used instead of ${}^{4}_{2}\text{He}$ for alpha part.)

Remember: **conservation of nucleons**

8. (4 pts) below, what is the missing particle? Show this by writing the balanced nuclear reaction including the missing particle. **Show work!**

$${}^{18}_{8}\text{O} + {}^{1}_{0}\text{n} \rightarrow {}^{19}_{9}\text{F} + ? \qquad \text{Shorthand notation: } {}^{18}_{8}\text{O (n, ?) } {}^{19}_{9}\text{F}$$

$${}^{18}_{8}\text{O} + {}^{1}_{0}\text{n} \rightarrow {}^{19}_{9}\text{F} + {}^{0}_{-1}\text{e}$$

"missing" particle is a **β particle**

$${}^{18}_{8}\text{O (n, }\beta\text{) } {}^{19}_{9}\text{F}$$

9. (5 pts) An animal skin is found to have a ^{14}C activity of 6.5 disintegrations/min•g of carbon compared with living organisms which undergo 16.3 disintegrations/min•g of carbon. The half-life for ^{14}C decay is 5715 yr. Calculate the age of the animal skin.

NOT on Carmen quiz. From Section 21.4, which is on the final exam.

Radioactive decay is a first-order process so we need 1st-order rate law, 1st-order integrated rate eqn and the 1st-order half-life eqn.

$$\text{rate} = k \bullet N \qquad \ln(N_t/N_0) = -\,k \bullet t \qquad t_{1/2} = 0.693/k$$

For this problem, since it's asking for the time (age) we need to use the integrated rate eqn. To do this we need to use the half-life eqn. to get the rate constant since we are given the half-life, $t_{1/2}$ = 5715 yr.

$$k = 0.693/t_{1/2} = 0.693/5715\text{ yr} = 1.2\underline{1}2 \times 10^{-4}\text{ yr}^{-1}$$

Use this in the integrated rate eqn. and solve for **t** (time it takes, the age of the shroud):

N_t = 6.5 disintegrations/min•g $\qquad$ N_0 = 16.3 disintegrations/min•g

$$t = \frac{-1}{1.2\underline{1}2 \times 10^{-4}\text{ yr}^{-1}} \bullet \ln\left(\frac{6.5}{16.3}\right) = 7.\underline{5}81 \times 10^{3}\text{ yr} = 7.6 \times 10^{3}\text{ yr}$$

The animal skin is **7.6 x 10^3 yr** old.

BACON
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Perhaps this is too much bacon. Not possible, there's never too much!