The University of British Columbia

Sessional Examination - December 1995

Chemistry 202 - Inorganic and Analytical Chemistry

Time: 2 hours

Last Name: Lee **First Name:** Kenjie

PLEASE PRINT

Signature:

Student number:

Lecture section (please circle): WF 8:30 AM TTh 2:30 PM

Instructor's name: **Dr. Chris Orvig**

Answer all parts of all **9** questions in the appropriate spaces in this exam booklet.
The exam consists of **13** pages and a periodic table; check to make sure that it is complete.
The exam is worth 55 of the 100 marks for the course.
Non-programmable calculators are permitted.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$; $\ln = 2.303 \log_{10}$

Some useful information:

the gas constant R = 8.31 J K^{-1} mol^{-1}; $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K$; $\ln = 2.303 \log_{10}$

the gas constant R = 8.31 J K^{-1} mol^{-1}

the freezing point depression constant for water = 1.86 deg mol^{-1} kg

some molar conductivities (Λ_M) in water: NaCl, 118; $BaCl_2$, 260; $CeCl_3$, 408

Trans Effect series: $CN^- \sim CO \sim C_2H_4 > PH_3$ $(PR_3) \sim SH_2$ $(SR_2) > NO_2^- > I^- > Br^- > Cl^-$ $> NH_3$ $(NR_3) \sim py > OH^- > H_2O$

Spectrochemical Series: $CO \sim CN^- >$ phen $> NO_2^- >$ en $> NH_3 \sim$ py $> NCS^- > H_2O \sim C_2O_4^{2-} > F^- > RCO_2^- > OH^- > Cl^- > Br^- > I^-$

Question	1	2	3	4	5	6	7	8	9	Total
Grade										
Maximum	12	30	12	13	8	18	21	21	8	143

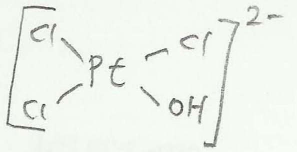
RULES GOVERNING EXAMINATIONS:

1. EACH CANDIDATE SHOULD BE PREPARED TO PRODUCE, UPON REQUEST, HIS/HER LIBRARY/AMS CARD.
2. READ AND OBSERVE THE FOLLOWING RULES:
   - No candidate shall be permitted to ask questions of the invigilators, except in the cases of supposed errors or ambiguities in examination questions.
   - CAUTION - Candidates guilty of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action:
   - Making use of any books, papers, memoranda, other than those authorized by the examiners
   - Speaking or communicating with other candidates
   - Purposefully exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.
3. SMOKING IS NOT PERMITTED DURING EXAMINATIONS.

Q1. **Draw a structure, and write the proper name, for each of products A, B, and C below. Assume the substitution reactions follow the *trans*-effect as shown on the cover page.**

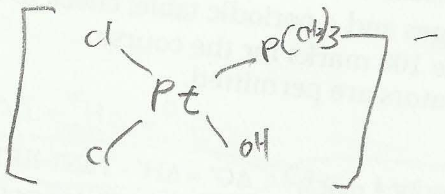
$[PtCl_4]^{2-} \xrightarrow{OH^-} A \xrightarrow{P(CH_3)_3} B \xrightarrow{py} C$

A

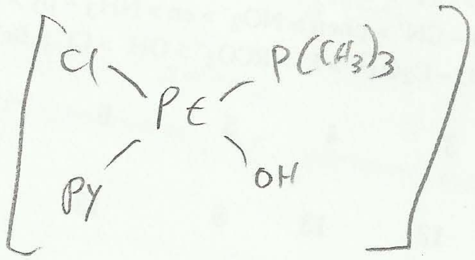


[12 marks]

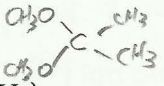
B



C



Q2. In the chemical equations given below, one or two of the reactants or products are given as m moles of X or n moles of Y. For each question identify the unknown(s) (including number of moles) by formula and, where appropriate, stereochemistry. For each equation, describe the reaction type using an appropriate word or two (such as "dissociation reaction").



[30 marks]

(a) $CoCl_2{\cdot}6H_2O \xrightarrow[\Delta]{xs\ (CH_3O)_2C(CH_3)_2} CoCl_2 + mX + nY$

12 CH_3OH 6 $(CH_3)_2CO$

dissociation rxn.

(b) $CoCl_2{\cdot}6H_2O + NH_4Cl + 5NH_3 + 1/4\ O_2 \xrightarrow[catalyst]{H_2O} mX + nY$

$[Co(NH_3)_5Cl](Cl)_2 + NH_3$

redox reaction & substitution.

(c) $[Cr(en)_3]Cl_3 \xrightarrow{\Delta} mX + en$

$CrCl_3$ dissociation rxn.

(d) $K_2[NiCl_4] + 2K \xrightarrow{NH_3\ (l)} nY$

$K_2[NiCl_4] + 2K \xrightarrow{NH_3(l)} nY$

$K_4[Ni(CN)_4]$

redox reaction.

(e) $TiCl_4 + mX \rightarrow TiCl_4(NH_3)_2$

$2 NH_3$

addition rxn

(f) $[Fe(H_2O)_6]^{3+} + 3\ acac^- \rightarrow mX + nY$

$[Fe(acac)_3]$ $6 H_2O$

substitution rxn.

(g) $Mo(CO)_6 + P(CH_3)_3 \xrightarrow{h\nu} mX + nY$

$[Mo(CO_5) P(CH_3)_3] + CO$

substitution rxn

(h) $[Co(NH_3)_5(CO_3)]^+ + 2H^+ \rightarrow mX + CO_2$

$[Co(NH_3)_5(H_2O)]$

Rxn of coordinated ligand.

Q3. Commercial processes for the electroplating of metals involve the use of complexing agents such as cyanide ion. The amount of such agents affects the concentration of free metal ion dramatically and can therefore affect the potential at which the electrolysis takes place.

(a) Calculate the concentration of "free" [Cd^{2+}] ion present in a solution made up by adding 1.60×10^{-3} mol $Cd(NO_3)_2$ and 2.00 mol KCN to water and diluting to 1.00 L. For this calculation, assume the only complex species present in any significant amount is $[Cd(CN)_4]^{2-}$, for which the overall stability constant is $\beta_4 = 1.00 \times 10^{19}$. (Answer required to two (2) significant figures only.)

[8 marks]

(b) If the solution in part (a) is made more acidic by the addition of a strong acid, what effect would this have on the concentration of "free" [Cd^{2+}]? In considering your answer, ignore volume changes. Also, note that CN^- is the anion of a weak acid.

[4 marks]

Q4. Dark-red prisms of potassium hexacyanomanganate(III) may be prepared by the following reactions:

$$3\,MnCl_2 + HNO_3 + 3\,H_3PO_4 + H_2O \rightarrow 3\,MnPO_4{\cdot}H_2O + NO + 6\,HCl$$

$$6\,KCN + MnPO_4{\cdot}H_2O \rightarrow K_3[Mn(CN)_6] + K_3PO_4 + H_2O$$

$6KCN + MnPO_4{\cdot}H_2O \rightarrow K_3[Mn(CN)_6] + K_3PO_4 + H_2O$

The desired compounds crystallizes upon evaporation of the final mixture.

(a) What types of preparative methods are being utilized in this synthesis?

[2 marks]

Substitution rxn

Redox rxn.

(b) Describe the bonding in $[Mn(CN)_6]^{3-}$ (low spin) in terms of valence bond theory.

d^4

Six ligands require six M acceptor orbitals to bind them.

The six that are used for octahedral metal hybridization are the 4s, 3 & 4p & two of the 3d orbitals. (d_{z^2} & $d_{x^2-y^2}$ orbital)

[3 marks]

Effectively, the lone pairs in the 6 ligand orbitals donate e⁻s into the six empty d^2sp^3 hybrids. Each of the six bonding energy levels represents one dative bond.

(c) Describe the bonding in $[Mn(H_2O)_6]^{3+}$ (high spin) and $[Mn(CN)_6]^{3-}$ (low spin) in terms of crystal field theory.

e_g ↑ —

t_{2g} ↑ ↑ ↑

Weak ligand

e_g — —

t_{2g} ↑↓ ↑ ↑

strong ligand

[4 marks]

(d) What is the Jahn-Teller theorem? Using this theory, which of the two ions in part (c) is likely to have a geometry different from octahedral?

$[Mn(H_2O)_6]^{3+}$.

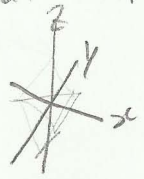
[4 marks]

Jahn-Teller theorem states that tetragonal distortion occurs, elongation or compression of a trans bonds due to an electron being put into d_{z^2} instead of in $d_{x^2-y^2}$ or vice versa, due to unsymmetrical ground state

Q5. Two common geometries for five coordinate transition metal complexes are trigonal bipyramidal and square pyramidal. Draw the d-orbital splitting diagram for the crystal field that corresponds to each of these two stereochemistries. Use the z axis as the unique axis and label each of the d orbitals (d_{xz}, etc.) on the diagram. Provide a qualitative description (a few words) of how you arrived at your diagrams.

[8 marks]

trigonal bipyramidal.



— dz^2

dxy — — dx^2-y^2

— — dxz
dyz

The ligand is directly pointing at the dz^2 orbital and the ring of dz^2 orbital. dxy & dx^2-y^2 are in the plane of equatorial ligands and are destabilized with respect to the other two dxz & dyz which manage to avoid ligands more than the other orbitals

Square pyramidal.

— dx^2-y^2

— dz^2

— dxy

— —
dyz dxz.

dx^2-y^2 points directly at the equatorial ligands causing it to be the highest unstable form. dxy interacts with equatorial ligand as well, being in plane of the ligands.

The "ring" of dz^2 orbital interact with the equatorial ligands and also directly points at dz^2 axial ligand destabilizing more than the remaining 3.

Q6. For each of the following, predict which stability constant is greater and very brie[illegible] explain your choice.

[3 marks each]

(a) β_2 for the formation of $[Fe(en)_2(H_2O)_2]^{2+}$ and β_4 for the formation of $[Fe(NH_3)_4(H_2O)_2]^{2+}$.

greater.

chelate effect.

entropy

(b) β_3 for the formation of the tris(trimethylenediamine) and the tris(ethylenediamine)complexes of Co(III).

5 membered ring's more stable than 6-membered ring.

(c) K_2 for the formation of $[Cd(CN)_2(H_2O)_2]$ and K_3 for the formation of $[Cd(CN)_3(H_2O)]^-$.

K_2 $[Cd(H_2O)_4] + 2CN \rightleftharpoons [Cd(CN)_2(H_2O)_2] + 2H_2O$

4 sites, 2 sites.

K_3 $[Cd(H_2O)_4] + 2CN \rightleftharpoons [Cd(CN)_3(H_2O)] + 2H_2O$

4 sites. 3 sites

(d) K_1 for the formation of the triethylenetetraamine and the pentaethylenehexa-amine complexes of Ni(II).

chelate effect

Q6 (continued)

(e) K_1 for $[Fe(EDTA)]^{-}$ or K_1 for $[Fe(EDTA)]^{2-}$.

↑ more + charge ↑ charge/radius more stable

(f) True or false: K_1 for $[Mn(CN)_6]^{4-}$ < K_1 for $[Fe(CN)_6]^{4-}$ < K_1 for $[Co(CN)_6]^{4-}$ < K_1 for $[Ni(CN)_6]^{4-}$

↑ smaller radius.

True.

Q7. Not all of the statements below are true. Comment on the correctness of each statement and in each case justify your comment briefly in a sentence or two.

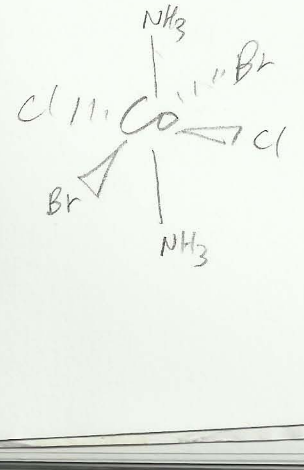
[3 marks each]

(a) If a molecule contains a C_4 axis then rotation by 180° about that axis leaves the molecule unchanged in appearance.

True.

(b) It is not possible for a molecule to possess both a centre of inversion and a two-fold improper rotation axis.

False



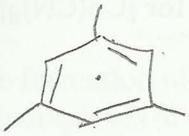
Q7 (continued)

(c) Fe, Zn, Cu, and Mn are necessary metal ions in biological systems.

(d) 1,3,5-trimethylbenzene belongs to the point group ~~D_{3d}~~.

check w/ quiz →

False



D_{3h}

(e) An S_n symmetry operation involves a rotation operation followed by an inversion operation.

True.

(f) Visible d-d transitions in $[MnCl_6]^{4-}$ have low values of ε.

True

(g) EDTA forms very weak metal chelate complexes.

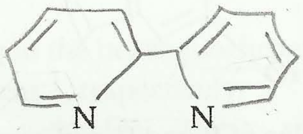
strong

F

Q8. Some complexes of ruthenium were prepared as described below. All complexes involve six-coordinate ruthenium.

(a) Commercial $RuCl_3 \cdot xH_2O$ was refluxed with 2,2'-dimethoxypropane to give anhydrous $RuCl_3$. Dry ruthenium(III) chloride (1.93 mmol) was refluxed in ethanol for 72 hr together with 2,2'-bipyridine (5.67 mmol). The initial green solution turned orange, and when the solution was concentrated and cooled, red crystals of compound A formed. The molecular formula of compound A was found to be $C_{30}H_{36}Cl_2N_6O_6Ru$. A 100 mL portion of a 0.1-M solution of compound A gave 20 mmol of AgCl when treated with $AgNO_3$ solution. Compound A loses six water molecules on gentle heating.

2,2'-bipyridine is



(i) Give the structural formula of compound A and name it.

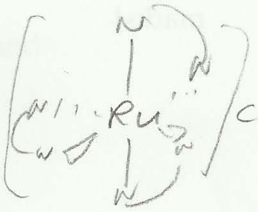
$RuCl_3$ (1.93 mmol) + CH_3CH_2OH + 2,2'-bipyridine (5.67 mmol)

[4 marks]

→ (A) $C_{30}H_{36}Cl_2N_6O_6Ru$ (24)

$6H_2O$ 2Cl outer 3 (bipy)

(A) $[Ru(C_{10}H_8N_2)_3]Cl_2 \cdot 6H_2O$



bis (2,2' bipyridine) ruthenium (II) chloride hexahydrate.

(ii) To which point group does the complex ion in A belong?

[1 mark]

D_3

(iii) If you are given some optically pure (+)-[Co(EDTA)]⁻, suggest how you might resolve any enantiomorphs of compound A.

[2 marks]

React w/ a chiral compd to make diastereomers which can be resolved due to diff. physical properties.

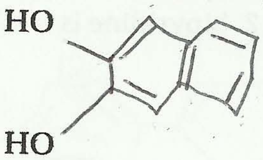
[Ru Cl (NH3)5] Cl + C10 H8 O2

→ (B) C10 H18 Cl (N4) O2 Ru (2 ions)

HCl → (C) H12 Cl3 N4 Ru (C2v) point

Q8 (continued)

(b) A sample of pentamminechlororuthenium(III) chloride (17 mmol) in basic aqueous solution at 55˚C was treated with 2,3-naphthalenediol (H_2dhn, 34 mmol); an intense blue colour rapidly formed. Cooling caused the formation of blue crystals of compound B which analyzed as $C_{10}H_{18}ClN_4O_2Ru$, and an aqueous solution of compound B had a molar conductivity $\Lambda_M = 110$. An aqueous solution of compound B was treated with excess HCl(aq) to give a violet solution that yielded violet crystals of compound C. Compound C had the molecular formula $H_{12}Cl_3N_4Ru$. An aqueous solution of C had a molar conductivity similar to that of B. Spectroscopic studies revealed that the complex ion in C belongs to the C_{2v} point group. Note H_2dhn is:



Ru (NH3)4 Cl3

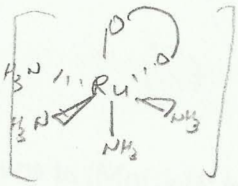
Ru (NH

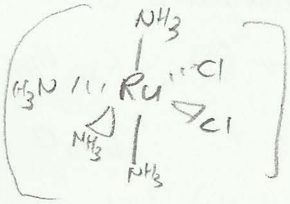
(i) Write the structural formulae of B and C and name them.

[8 marks]

(B) [Ru (C10H6O2) (NH3)4] Cl

(C) [Ru (NH3)4 Cl2] Cl.





cis – tetra ammine di chloro ruthenium (III) chloride

tetra ammine (2,3-naphthalenediol) ruthenium (III) chloride.

(ii) Write balanced chemical equations for the formation of C from the starting material pentamminechlororuthenium(III) chloride.

[4 marks]

[Ru Cl (NH3)5] Cl + C10 H8 O2 + 2 Base⁻

→ [Ru (C10 H6 O2)(NH3)4] Cl + NH3 + 2H Base + Cl⁻

[Ru (C10 H6 O2) (NH3)4] Cl + 2HCl ⟶ [Ru (NH3)4 Cl2] Cl + (C10 H8 O2)

(iii) What would be the freezing point of a 0.01-M aqueous solution of B or C?

[2 marks]

T = kmi = (1.86°C kg mol⁻¹) (0.01 M) (2)

T = 0.037 °C

Q9. Using your knowledge of the factors that affect the magnitude of the crystal field splitting in coordination complexes, give qualitative explanations of the following:

[2 marks each]

Rh Ir

(i) The measured values of 10Dq in the hexachlororhodate(III) and hexachloroiridate(III) anions are 20,300 and 24,900 cm^{-1}, respectively.

Ir is a row below Rh in the periodic table, indicating that Ir is larger atom which cause larger electrostatic attraction, increasing the value of 10Dq.

(ii) The measured values of 10Dq in the hexaaquochromium(II) and hexaaquocobalt(III) cations are 13,900 and 22,000 cm^{-1}, respectively.

Co^{+3} has larger oxidation state than Cr^{+2}.
So, Co^{+3} has larger electrostatic attraction causing higher 10Dq value.

(iii) The measured values of 10Dq in $[Co(py)_4]^{2+}$ and $[Co(py)_6]^{2+}$ are 5,500 and 9,900 cm^{-1}, respectively.

tetrahedral octahedral

$$\Delta_t = \frac{4}{9}\Delta_o$$

(iv) The measured values of 10Dq in $[Mn(H_2O)_6]^{2+}$ and $[Mn(phen)_3]^{2+}$ are 7,800 and 10,800 cm^{-1}, respectively.

Phen is a strong field ligand as compared to H_2O which is a weak field ligand.
A strong field ligand causes larger 10Dq values.

THE END
Happy Holidays from Team 202!!

The University of British Columbia
Sessional Examination - December 1994
Chemistry 202 - Inorganic and Analytical Chemistry
Time: 2 hours

Last Name: Lee **First Name:** Kajira

PLEASE PRINT

Signature:

Student number:

Lecture section (please circle): MW 8:30 AM TTh 2:30 PM

Instructor's name: **Dr. Chris Orvig**

Answer all parts of all **8** questions in the appropriate spaces in this exam booklet.
The exam consists of **13** pages and a periodic table; check to make sure that it is complete.
The exam is worth 55 of the 100 marks for the course.
Non-programmable calculators are permitted.

Some useful information:

the gas constant R = 8.31 J K^{-1} mol^{-1}; $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$; ln = 2.303 $\log_{10}$

the freezing point depression constant for water = 1.86 deg mol^{-1} kg

some molar conductivities (Λ_M) in water: NaCl, 118; $BaCl_2$, 260; $CeCl_3$, 408

Trans Effect series: $CN^- \sim CO \sim C_2H_4 > PH_3\ (PR_3) \sim SH_2\ (SR_2) > NO_2^- > I^- > Br^- > Cl^-$
$> NH_3\ (NR_3) \sim py > OH^- > H_2O$

Spectrochemical Series: $CO \sim CN^- > phen > NO_2^- > en > NH_3 \sim py > NCS^- >$
$H_2O \sim C_2O_4^{2-} > F^- > RCO_2^- > OH^- > Cl^- > Br^- > I^-$

Question	1	2	3	4	5	6	7	8	Total
Grade									
Maximum	19	20	14	12	30	12	10	28	145

RULES GOVERNING EXAMINATIONS:

1. EACH CANDIDATE SHOULD BE PREPARED TO PRODUCE, UPON REQUEST, HIS/HER LIBRARY/AMS CARD.
2. READ AND OBSERVE THE FOLLOWING RULES:
   - No candidate shall be permitted to ask questions of the invigilators, except in the cases of supposed errors or ambiguities in examination questions.
   - CAUTION - Candidates guilty of the following, or similar, dishonest practices shall be immediately dismissed from the examination and shall be liable to disciplinary action:
   - Making use of any books, papers, memoranda, other than those authorized by the examiners
   - Speaking or communicating with other candidates
   - Purposefully exposing written papers to the view of other candidates. The plea of accident or forgetfulness shall not be received.
3. SMOKING IS NOT PERMITTED DURING EXAMINATIONS.

$c = 2.998 \times 10^8\ ms^{-1}$

$h = 6.626 \times 10^{-34}$ J s.

(planck constant

Q1. In the chemical equations given below, one or two of the reactants or products are given as n moles of A or m moles of B. For each question identify the unknown(s) (including number of moles) by formula and, where appropriate, stereochemistry. For each equation, describe the reaction type using an appropriate word or two (such as "dissociation reaction").

[19 marks]

(a) $[Pt(CN)Cl_3]^{2-} + 2NH_3 \xrightarrow{H_2O} nA + mB$

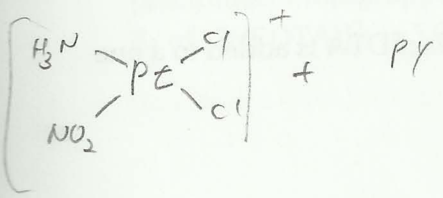
soft, soft, hard, hard

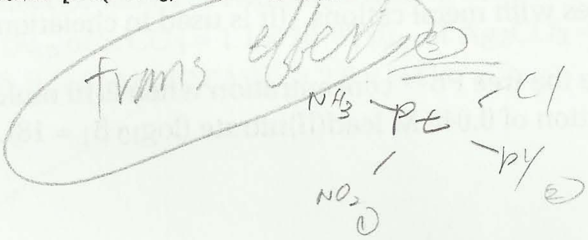
$[Pt(CN)(NH_3)_2Cl]^{+2} + Cl^{-2}$

redox reaction

substitution reaction.

(b) $nA + mB \xrightarrow{H_2O}$ trans-$[Pt(NH_3)Cl(NO_2)(py)] + Cl^-$





(c) $CoCl_2 \cdot 6H_2O \xrightarrow{SOCl_2} CoCl_2 + nA + mB$

$6SO_2$ 12HCL

non-aq. solvents.

(d) $nA + 2K \xrightarrow{NH_3(l)} [Pt(NH_3)_4] + 2KBr$

nA + 2K → [Pt(NH3)4] + 2KBr

reduces

$[Pt(NH_3)_4]Br_2$

Q1 (continued)

(e) $CoCl_2 \cdot 6H_2O + NH_4Cl + 5NH_3 + 1/4\ O_2 \xrightarrow[\text{catalyst}]{H_2O} nA + mB$

$[Co(NH_3)_5Cl]\ 2Cl$ +

redox rxn

substitution

(f) $[Cr(en)_3]Cl_3 \xrightarrow{\Delta} nA + en$

$[Cr(en)_2Cl_2]Cl$

Q2. Ethylenediaminetetraacetate, $EDTA^{4-}$, is a hexadentate ligand that forms very stable complexes with metal cations. (It is used in chelation therapy for the removal of lead.)

(a) Calculate the free Pb^{2+} concentration when 0.10 mole of Na_4EDTA is added to a one litre solution of 0.040 M lead(II)nitrate ($\log_{10} \beta_1 = 18$).

[6 marks]

Q2 (continued)

(b) How much NaCl would it be necessary to add to the lead nitrate-Na_4EDTA solution in (a) in order to precipitate out some $PbCl_2$? (K_{sp} of $PbCl_2$ is 1.6×10^{-5}). Given that the solubility of NaCl in water is about 6M under normal conditions, is it practical to try to precipitate out $PbCl_2$ in this situation?

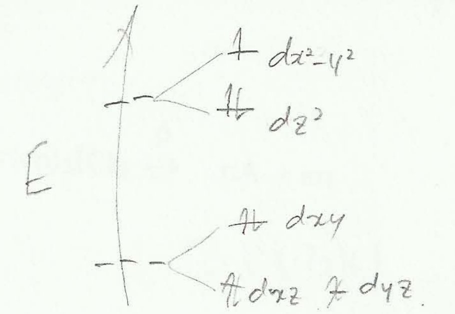
[4 marks]

(c) A one litre solution contains 0.050 moles of $Sr(NO_3)_2$ and 0.030 moles of $AgNO_3$. To this solution is added 0.10 moles of Na_4EDTA. Determine which metal carbonate, $SrCO_3$ or Ag_2CO_3, will precipitate first upon subsequent addition of Na_2CO_3 to this solution. Determine the number of moles of Na_2CO_3 added at the point that this precipitate initially appears. (K_{sp} of $SrCO_3 = 1.1 \times 10^{-10}$; K_{sp} of $Ag_2CO_3 = 8.1 \times 10^{-12}$; β_1 of $[Sr(EDTA)]^{2-}$ is 5.0×10^8; β_1 of $[Ag(EDTA)]^{3-}$ is 2.0×10^7).

[10 marks]

Q3. (a) A common form of distortion from regular octahedral symmetry is the tetragonally elongated octahedron. Draw a d-orbital splitting diagram for a D_{4h} crystal field that corresponds to this stereochemistry. Label the d orbitals (d_{xz}, etc.) on the diagram. Provide a qualitative description of how you arrived at your diagram.

[6 marks]

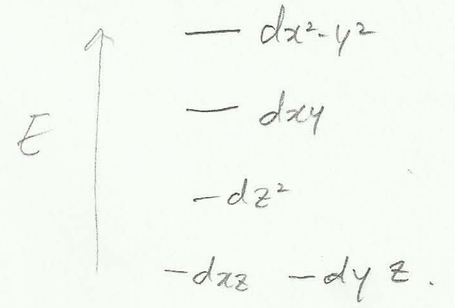


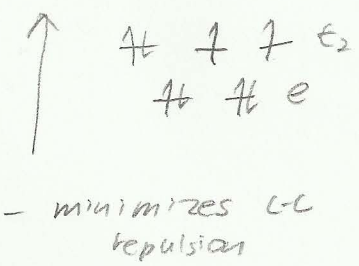
John-Teller distortion occurs due to asymmetrical ground state electronic configuration. As the 9th e⁻ is put into d_{z^2}, the ligands along z axis cannot approach as closely as when the 9th e⁻ was not in d_{z^2} due to larger e⁻ density causing the bond length along z axis to get longer.

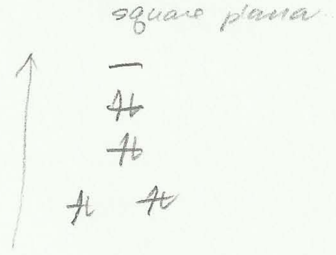
Since the z-axis ligands are further away from the metal, the increase in the energy of the d_z orbital is less. Also the two orbitals d_{xz} & d_{yz} orbitals interact less with the z axis charges as well.

(b) Draw a d-orbital splitting diagram for a four-coordinate square planar complex. Explain how crystal field theory (CFT) can provide a rationale for the observation that for four-coordinate d^8 complexes, some are tetrahedral high spin while others are square planar low spin.

[8 marks]







- minimizes L-L repulsion

- destabilized by L-L repulsion & P
- stabilized by CFSE = −10 Dq.

If 10 Dq is large enough energy cost to go D_{4h} (P & L-L repulsion) can be overcome, and we observe square planar.

Q4. For each of the following, predict which stability constant is greater and very briefly explain your choice.

[3 marks each]

(a) K_3 for the formation of $[Cd(CN)_3(H_2O)]$ and K_4 for the formation of $[Cd(CN)_4]^{2-}$.

K_4

$3CN^- + [Cd(H_2O)_4] \rightleftharpoons [Cd(CN)_3H_2O] + 3H_2O$ ← 3 sites; ↑ 4 sites

$K_3 = 4/3$

$4CN^- + [Cd(H_2O)_4] \rightleftharpoons [Cd(CN)_4]^{2-} + 3H_2O$ (4 sites; 4 sites)

$K_4 = 4/4$

(b) β_3 for the formation of the tris(ethylenediamine) and the tris(trimethylene-diamine) complexes of Co(III).

5-membered ring is more stable.

(c) K_1 for the formation of $[Fe(en)(H_2O)_4]^{2+}$ and β_2 for the formation of $[Fe(NH_3)_2(H_2O)_4]^{2+}$.

chelate effect

entropy.

(d) K_1 for the formation of the diethylenetriamine and the triethylenetetraamine complexes of Ni(II).

chelate effect.

Q5. Not all of the statements below are true. Comment on the correctness of each statement and in each case justify your comment briefly in a sentence or two.

[3 marks each]

(a) It should be possible to resolve the enantiomeric forms of *trans*-$K_3[Co(ox)_2Cl_2]$.

True. rxt w/ a chiral compd → diastereomer

(b) If a molecule contains a C_4 axis then rotation by 180° about that axis leaves the molecule unchanged in appearance.

True

(c) It is not possible for a molecule to possess both a centre of inversion and a two-fold improper rotation axis.

False

(d) Fe, Zn, Cu, and As are necessary metal ions in biological systems.

(e) Octahedral complexes of manganese(III) of the type $[MnL_6]^{3+}$ (where L is a neutral ligand) are expected to show greater distortion from regular octahedral symmetry when the electron configuration is high spin than when the configuration is low spin.

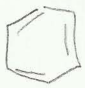
T. d^4

Q5 (continued)

(f) All molecules belonging to D_n point groups are chiral.

F.

(g) Benzene (C_6H_6) belongs to the point group D_{6d}.



F. D_{6h}

(h) An S_n symmetry operation involves a rotation operation followed by an inversion operation.

T.

(i) Visible d-d transitions in $[Mn(H_2O)_6]^{2+}$ have low values of ε.

T.

(j) TPP^{5-} forms very ~~weak~~ metal chelate complexes.

Strong (F.)

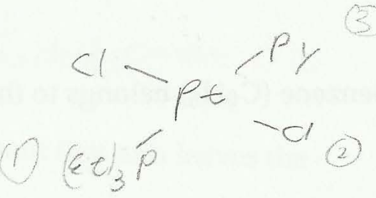
Q6. Complete the reactions below by identifying the reagents A, B, D, and E and by giving the structural formulae and the names of the complex species X and Y. Make use of the trans-effect series (listed on the front page) in answering this question.

(a) $[PtCl_4]^{2-} \xrightarrow{A} X \xrightarrow{B}$ *trans*-dichloro(pyridine)(triethylphosphine)platinum(II)

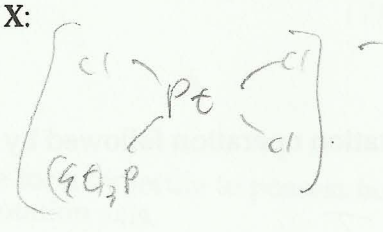
[6 marks]

A is: $(Et)_3P$

B is: Py

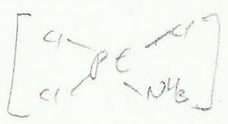


Structure of X:

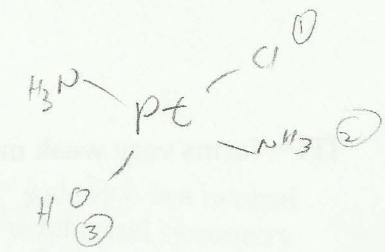


(b) $[PtCl_3(NH_3)]^- \xrightarrow{D} Y \xrightarrow{E}$ *trans*-diamminechlorohydroxoplatinum(II)

[6 marks]

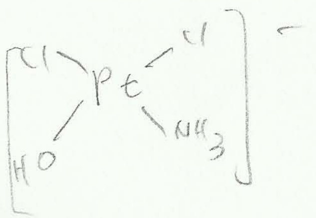


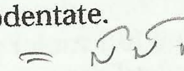
D is: OH

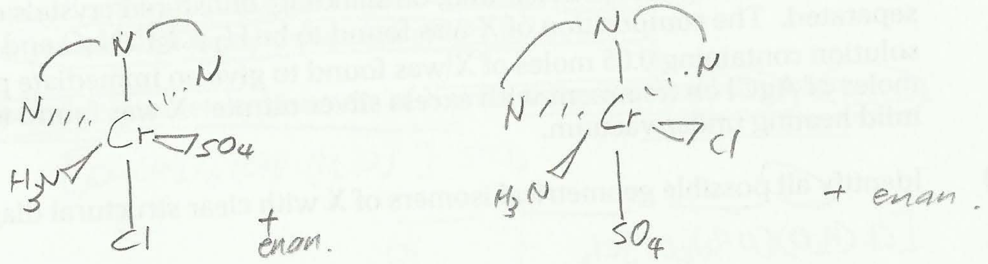


E is: NH_3

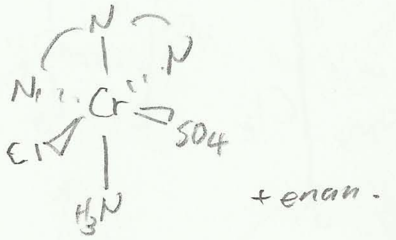
Structure of Y:

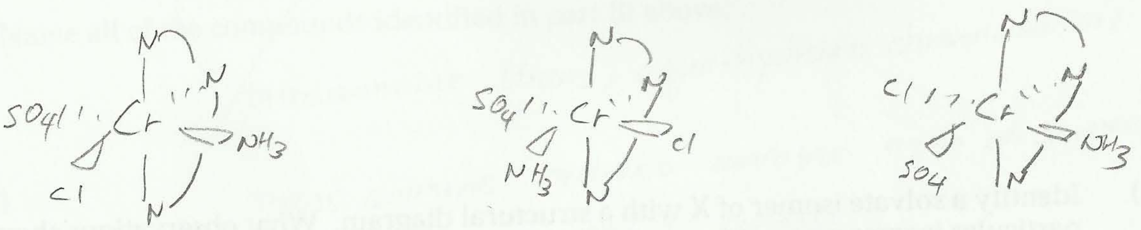


Q7. Identify all geometrical isomers of [Cr(dien)(NH_3)Cl(SO_4)] with clear structural diagrams. Indicate which isomers, if any, are chiral. Consider only six-coordinate complexes in which the sulphate ligand is monodentate.
(Note: dien is $NH_2CH_2CH_2NHCH_2CH_2NH_2$) 



[10 marks]





$[CrSO_4]^+ +_{xs} NH_3 + 3NH_3Cl \rightarrow [Cr\,H_2O\,($ ...

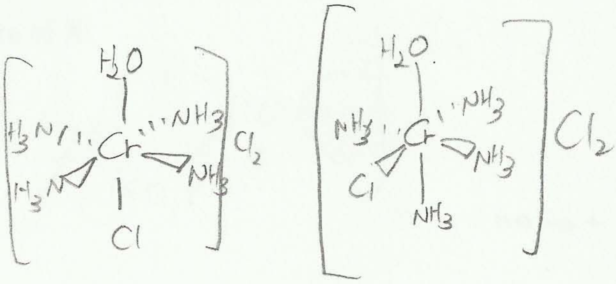
Q8. Some complexes of chromium were prepared as described below. All complexes involve six-coordinate chromium.

(a) Chromium(III) sulfate (0.1 mole) was treated with excess ammonia in the presence of ammonium chloride and the resultant solution was heated to 35°C for one hour. The solution was then cooled in ice, and, on standing, bluish-red crystals of compound X separated. The composition of X was found to be $H_{14}Cl_3CrN_4O$ and an aqueous solution containing 0.05 moles of X was found to give an immediate precipitate of 0.1 moles of AgCl on treatment with excess silver nitrate. X was found to be stable to mild heating under vacuum.

(i) Identify all possible geometrical isomers of X with clear structural diagrams.

$[Cr(H_2O)(NH_3)_4Cl]Cl_2$

[6 marks]



(ii) Identify a solvate isomer of X with a structural diagram. What observations show this particular isomer was not formed in the reaction described above?

$[Cr(NH_3)_4Cl_2]Cl\cdot H_2O$

[4 marks]

0.05 mol of this does not give 0.1 moles of AgCl

but, only 0.05 mole of AgCl.

$[Cr(H_2O)(NH_3)_4Cl]Cl_2$ +  + Na_2SO_4

$\longrightarrow [Cr(NH_3)_4OH \cdot H_2O]SO_4$

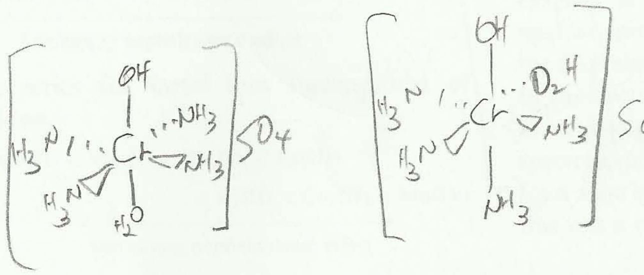
Q8(continued).

(b) An aqueous solution of X (from (a)) was treated with weak base (pyridine) in the presence of excess sodium sulfate. Concentration of the solution followed by cooling in ice led to the formation of an orange precipitate, compound Y. The compound Y had the composition $H_{15}CrN_4O_6S$ and gave a white precipitate when an aqueous solution was treated with aqueous barium chloride.

(i) Identify all possible geometrical isomers of Y with clear structural diagrams.

[6 marks]

$[Cr(NH_3)_4(OH)\cdot(H_2O)]SO_4$.



(ii) Name all of the compounds identified in part (i) above.

[3 marks]

tetraammine (trans) aqua-hydroxo chromium (III) sulfate.

trans ammine hydroxo ammine aqua diammine chromium (III) sulfate.

(iii) What would be the freezing point of a 0.01-M aqueous solution of Y?

[2 marks]

$i = \frac{T}{km}$ $\quad T = ikm$

$= 2(1.86\ ^\circ C\ kg\ mol^{-1})(0.01M)$

$= 0.037\ ^\circ C$

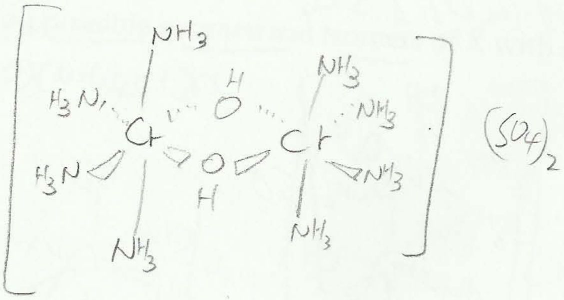
[Cr(NH3)4 OH·H2O] SO4.

Q8(continued).

(c) An aqueous solution of Y (from (b)) was heated to 80˚C and, on cooling, a brown precipitate of compound Z formed. The composition of Z was found to be $H_{26}Cr_2N_8O_{10}S_2$ and the freezing point of a 0.1 M solution of Z was -0.558˚C. An aqueous solution containing 0.026 moles of Z gave, on treatment with excess $BaCl_2$, 0.052 moles of barium sulfate precipitate.

(i) Identify Z with a clear structural diagram.

[4 marks]



(ii) Name Z and give the point group to which the complex cation in Z belongs.

heptaammine-di-μ-hydroxo dichromium (III) sulfate

[3 marks]

D2h

THE END

Happy Holidays from Team 202!!