Chapter 19
Transition Metals and Coordination Chemistry

6. a)   Ti = [Ar]$4s^2 3d^2$ Ti^{2+} = [Ar]$3d^2$ Ti^{4+} = [Ar]
    b)   Re = [Xe]$6s^2 4f^{14} 5d^5$ Re^{2+} = [Xe]$4f^{14} 5d^5$ Re^{3+} = [Xe]$4f^{14} 5d^4$
    b)   Ir = [Xe]$6s^2 4f^{14} 5d^7$ Ir^{2+} = [Xe]$4f^{14} 5d^7$ Ir^{3+} = [Xe]$4f^{14} 5d^6$

7. a)   Cr = [Ar]$4s^1 3d^5$ Cr^{2+} = [Ar]$3d^4$ Cr^{3+} = [Ar]$3d^3$
    b)   Cu = [Ar]$4s^1 3d^{10}$ Cu^{+} = [Ar]$3d^{10}$ Cu^{2+} = [Ar]$3d^9$
    c)   V = [Ar]$4s^2 3d^3$ V^{2+} = [Ar]$3d^3$ V^{3+} = [Ar]$3d^2$

16. Coordination Compound: A compound composed of a complex ion and counter ion sufficient to give no net charge.
    Complex Ion: A charged species consisting of a metal ion surrounded by ligands.
    Counter Ion: Anions or cations that balance the charge on the complex ion in a coordination complex.
    Coordination Number: The number of bonds formed between the metal ion and the ligands in a complex ion.
    Ligand: A group attached to the central metal ion in a complex.
    Chelate: A complex containing at least one polydentate ligand that forms a ring of atoms including the central metal atom.
    Bidentate: A ligand that can form two bonds to a metal ion.

22. a) hexaamminecobalt(II) chloride   b) hexaquacobalt(III) iodide
    c) potassium tetrachloroplatinate(II)   d) potassium hexachloroplatinate(II)
    e) pentaamminechlorochromium(III) chloride   f) triamminetrinitrochromium(III)

23. a) pentaamminechlororuthenium(III) ion
    b) hexacyanoferrate(II) ion
    c) tris(ethylenediamine)manganese(II) ion
    d) pentaamminenitrocobalt(III) ion

24. a) pentaaquabromochromium(III) bromide
    b) sodium hexacyanocobaltate(III)
    b) bis(ethylenediamine)dinitroiron(III) chloride
    d) tetraamminediiodoplatinum(IV) tetraiodoplatinate(II)
    > Note: The oxidation numbers of platinum where determined by looking at the possible oxidation numbers for platinum, these can be found in slide 8 of your class notes. Platinum is known to have oxidation numbers of +2,+4, +5, and +6 with +2 and +4 being the most common. If the platinum in the cation ($[PtI_2(NH_3)]^{+x}$) had a oxidation state of +2 then the overall charge of the ion would be 0. All of these compounds are ionically bound together. In order for this to happen you need to have positive and negative species. Ionic bonds cannot form if there is not a transfer of electrons therefore, the oxidation state cannot be +2 on platinum in the cation. If the platinum in the cation ($[PtI_2(NH_3)]^{+x}$) had a oxidation state of +4 then the overall charge of the ion would be +2. This would make the oxidation state of the platinum in the anion ($[PtI_4]^{-y}$) be +2 giving

the total anion a charge of -2. Since +2 is also a commonly observed oxidation number for platinum, this gives us the oxidation numbers of both the platinum atoms. The oxidation number of the platinum in the cation is +4 and in the anion is +2. If you do the math for when the oxidation number of the cation +5 or +6 (other observed oxidation numbers of platinum) you will see that you cannot get an oxidation state for the platinum in the anion that is observed.

25.   a) $K_2[CoCl_4]$ b) $[Pt(H_2O)(CO)_3]Br_2$
           c) $Na_3[Fe(CN)_2(C_2O_4)_2]$ d) $[CrCl(NH_3)_3(NH_2CH_2CH_2NH_2)]I_2$

26.   a) $[FeCl_4]^-$ b) $[Ru(NH_3)_5(H_2O)]^{3+}$
           c) $[Cr(OH)_2(CO)_4]^+$ d) $[PtCl_3(NH_3)]^-$

29.   When the $BaCl_2$ is added to the solution, no precipitate forms. Therefore, the sulfate ion must be bound to the cobalt because $BaSO_4$ is not soluble and would have generated a precipitate if not bound to the metal.
           When $AgNO_3$ is added to the solution, a precipitate forms. Therefore, Cl^- must be a counter ion allowing $AgCl_2$ to form.
           SO_4^{2-} must be a bidentate ligand in order for the metal to have a coordination number of 6. Therefore, the compound must be $[Co(SO_4)(NH_3)_4]Cl$

33.   a)   Isomer: One of two or more compounds that contain the same number of the same atoms in different arrangements.
                  Example:

           b)   Structural Isomer: Isomers in which the atoms have different partners or lie in a different order. (Different chemical formulas)
                  Example:

2

c)   Stereoisomers: Isomers in which the atoms have the same partners but are in different arrangements in space. (Same chemical Formulas)

Example:

d)   Coordination Isomers: Isomers that differ by the exchange of one of more ligands between cationic complex and an anionic complex.

Example:

$[CrBr(H_2O)_5]Cl$ and $[CrCl(H_2O)_5]Br$

e)   Linkage Isomers: Isomers that differ in the identity of the atom that a ligand uses to attach to a metal ion.
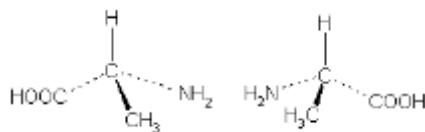
Example:
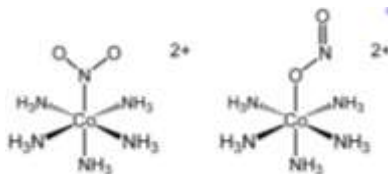
f)   Geometric Isomers: Isomers in which atoms or groups of atoms can assume different positions around a rigid bond.

Example:

g)   Optical Isomers: Isomers in which one molecule is the mirror image of the other molecule.

Example:

34.   a) 2 bonds, one to each of the lone pair of electrons on the oxygen atoms
b) 3 bonds, one to each of the lone pair of electrons on the nitrogen atoms
c) 4 bonds, one to each of the lone pair of electrons on the oxygen or the nitrogen atoms
d) 4 bonds, one to each of the lone pair of electrons on the nitrogen atoms

35.   a)

cis   trans

b)

cis   trans

c)

cis   trans
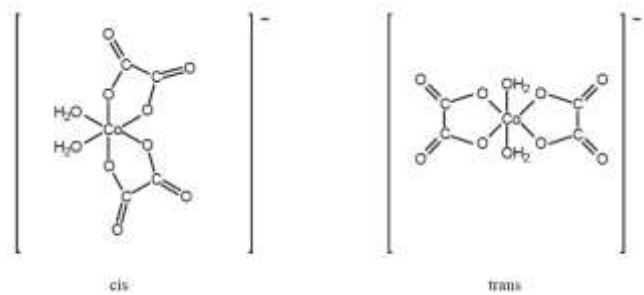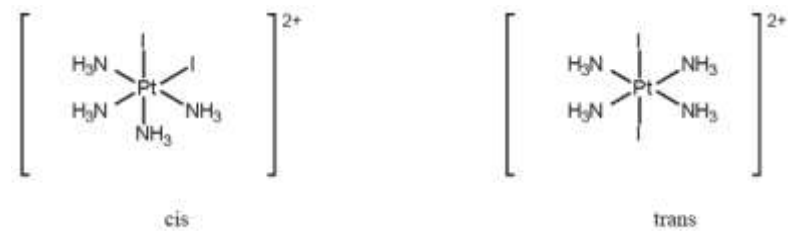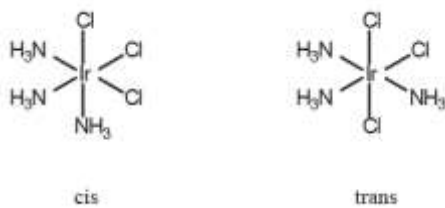
d)
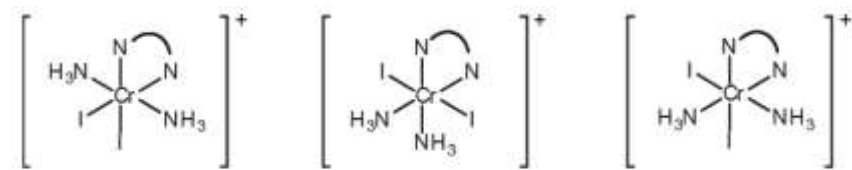
Note: N⌒N is an abbreviation for ethylenediamine (NH₂CH₂CH₂NH₂)

36.   a)   b)
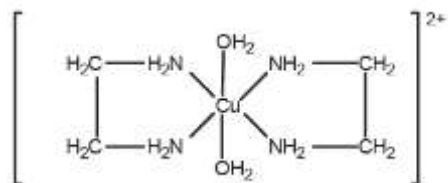

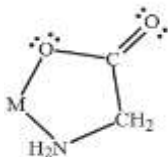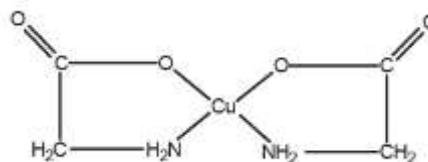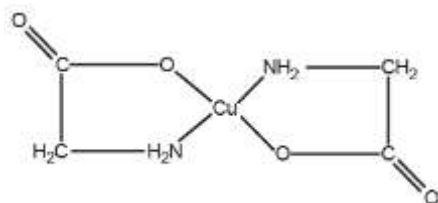c)   d)

4
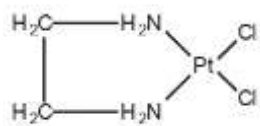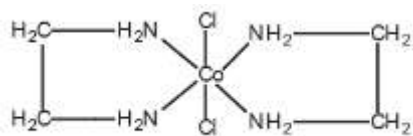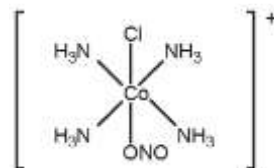
e)

39.

M is a transition metal ion

41.   Linkage Isomer: Isomers that differ in the identity of the atom that a ligand uses to
                    attach to a metal ion.
        In order to form a linkage isomer there needs to be at least 2 different types of atoms in the
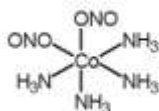   ligand and there needs to be lone pairs on the different types of atoms.
        Capable of forming linkage Isomers
                SCN⁻ (loan pair on both S and N)
                NO_2^- (loan pair on both O and N)
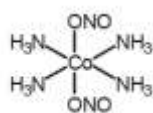   OCN⁻ (loan pair on both O and N)
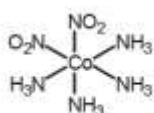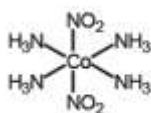   Not Capable of forming linkage Isomers
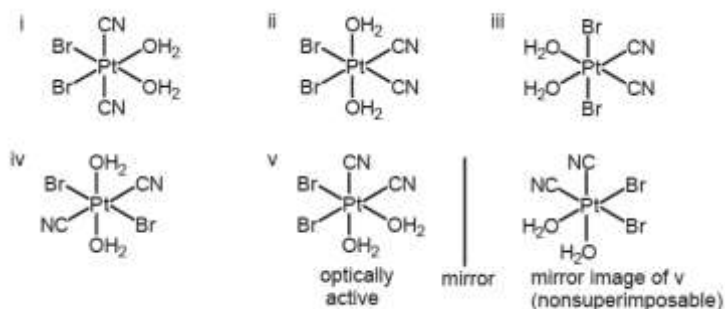 N_3^- (only one type of atom)
                $NH_2CH_2CH_2NH_2$ (only the nitrogen atoms have lone pairs, therefore only 1 bonding site)
                I⁻ (only one type of atom)

42.

5

44.

i

ii

iii

iv

v optically active | mirror | mirror image of v (nonsuperimposable)
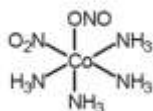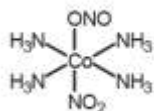
There are 5 geometrical isomers (ligands are attached to different locations (different chemical names)) (i-v)

Note v. (*cis*-diaquadibromodicyanoplatinum(VI)) and its mirror image are both optical isomers (isomers that have the same neighbors but have different locations relative to each other and are not identical to their mirror image (yet they have the same chemical formulas)).

47.   Weak-Field Ligand: A ligand that produces a small ligand field splitting (lies below NH_3 in spectochemical series).

Strong Field Ligand: A ligand that produces a large ligand field splitting (lies above H_2O in the spectochemical series).

Low-Spin Complex: A transition metal complex with the minimum number of unpaired electrons.

High-Spin Complex: A transition metal complex with the maximum number of unpaired electrons.

50.   Cu = $[Ar]4s^1 3d^{10}$ (lower energy when 3d orbital is full)

Cu^{2+} = $[Ar]3d^9$

Cu^+ = $[Ar]3d^{10}$

Complex appear colored because electrons are able to transition between the split d orbitals. Since Cu^+ has a full d shell, no electrons can transition, therefore, Cu^+ compounds tend to be colorless. Cu^{2+} has space for an electron to be promoted, therefore, Cu^{2+} compounds are expected to be colored.
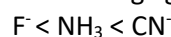
$Cd(NH_3)_4Cl_2$ Cd^{2+} = $[Kr]4d^{10}$

Since Cd^{2+} has a filled d orbital, compounds formed from Cd^{2+} would not be expected to have color.

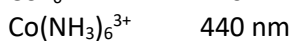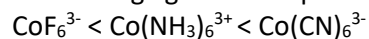54.   Order of increasing energy absorbed $\left(E = \frac{hc}{\lambda}\right)$

   770 nm < 440 nm < 290 nm

Order of increasing ligand field strength
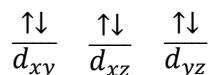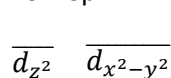
   $F^- < NH_3 < CN^-$

The stronger the field ligand, the greater the ligand field splitting.

Order of increasing ligand field splitting

   $CoF_6^{3-} < Co(NH_3)_6^{3+} < Co(CN)_6^{3-}$

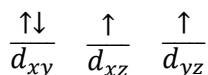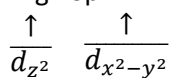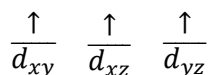|	
CoF_6^{3-}	770 nm
$Co(NH_3)_6^{3+}$	440 nm
$Co(CN)_6^{3-}$	290 nm

55.   a) $Fe^{2+} = [Ar]3d^6$ b) $Fe^{3+} = [Ar]3d^5$

Low Spin   High Spin

$\overline{}$ $\overline{}$ $\overline{\uparrow}$ $\overline{\uparrow}$ $\overline{\uparrow}$ $\overline{\uparrow}$

d_{z^2} $d_{x^2-y^2}$ d_{z^2} $d_{x^2-y^2}$ d_{z^2} $d_{x^2-y^2}$

$\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow}$ $\overline{\uparrow}$ $\overline{\uparrow}$ $\overline{\uparrow}$ $\overline{\uparrow}$

d_{xy} d_{xz} d_{yz} d_{xy} d_{xz} d_{yz} d_{xy} d_{xz} d_{yz}

c) $Ni^{2+} = [Ar]3d^8$ d) $Zn^{2+} = [Ar]3d^{10}$

$\overline{\uparrow}$ $\overline{\uparrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$

d_{z^2} $d_{x^2-y^2}$ d_{z^2} $d_{x^2-y^2}$

$\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$

d_{xy} d_{xz} d_{yz} d_{xy} d_{xz} d_{yz}
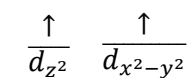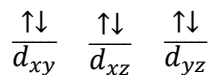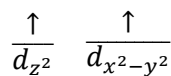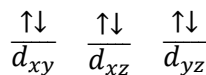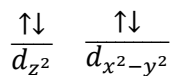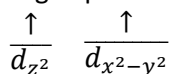
e) $Co^{2+} = [Ar]3d^7$

Low Spin   High Spin

$\overline{\uparrow}$ $\overline{}$ $\overline{\uparrow}$ $\overline{\uparrow}$

d_{z^2} $d_{x^2-y^2}$ d_{z^2} $d_{x^2-y^2}$

$\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow}$

d_{xy} d_{xz} d_{yz} d_{xy} d_{xz} d_{yz}
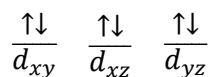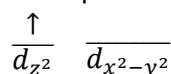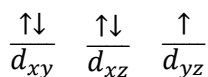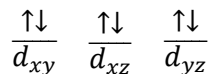
56. $[Co(NH_3)_6]^{3+}$, therefore, Co^{3+} $[Fe(H_2O)_6]^{2+}$, therefore, Fe^{2+}

$Co^{3+} = [Ar]3d^6$ (Low Spin) $Fe^{2+} = [Ar]3d^6$ (High Spin)

                                               $\overline{\uparrow}$ $\overline{\uparrow}$

$\overline{}$ $\overline{}$ d_{z^2} $d_{x^2-y^2}$

d_{z^2} $d_{x^2-y^2}$

$\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow\downarrow}$ $\overline{\uparrow}$ $\overline{\uparrow}$

d_{xy} d_{xz} d_{yz} d_{xy} d_{xz} d_{yz}
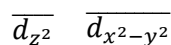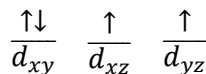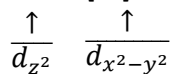
No unpaired electrons (diamagnetic)   Four unpaired electrons (paramagnetic)

NH_3 is a strong field ligand, therefore, it will form a low spin complex. Causing $[Co(NH_3)_6]^{3+}$ to have no unpaired electrons and be diamagnetic. H_2O is a weak field ligand; therefore, it will form a high spin complex. Causing $[Fe(H_2O)_6]^{2+}$ to have four unpaired electrons and be paramagnetic.

57.   a) $[Ru(NH_3)_6]^{2+}$, therefore, Ru^{2+} b) $[Ni(H_2O)_6]^{2+}$, therefore, Ni^{2+}
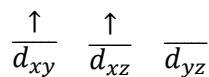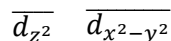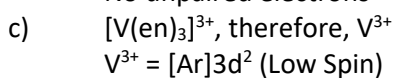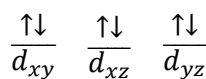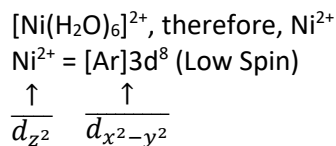 $Ru^{2+} = [Kr]4d^6$ (Low Spin) $Ni^{2+} = [Ar]3d^8$ (Low Spin)

                                                      $\uparrow$ $\uparrow$

              $\overline{d_{z^2}}$ $\overline{d_{x^2-y^2}}$ $\overline{d_{z^2}}$ $\overline{d_{x^2-y^2}}$

                      $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$

                      $\overline{d_{xy}}$ $\overline{d_{xz}}$ $\overline{d_{yz}}$ $\overline{d_{xy}}$ $\overline{d_{xz}}$ $\overline{d_{yz}}$
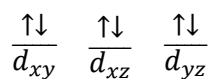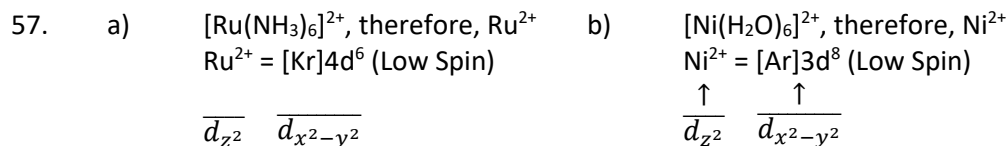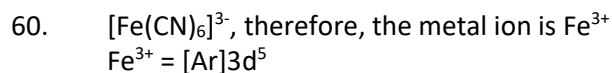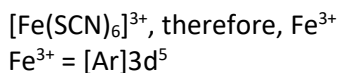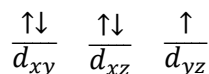
                      No unpaired electrons   2 unpaired electrons
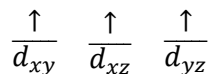
    c) $[V(en)_3]^{3+}$, therefore, V^{3+}
            $V^{3+} = [Ar]3d^2$ (Low Spin)

              $\overline{d_{z^2}}$ $\overline{d_{x^2-y^2}}$

                $\uparrow$ $\uparrow$

              $\overline{d_{xy}}$ $\overline{d_{xz}}$ $\overline{d_{yz}}$

              2 unpaired electrons

60. $[Fe(CN)_6]^{3-}$, therefore, the metal ion is Fe^{3+}
        $Fe^{3+} = [Ar]3d^5$
        If there is only one unpaired electron the complex must be low spin, as seen below.

              $\overline{d_{z^2}}$ $\overline{d_{x^2-y^2}}$

              $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow$

              $\overline{d_{xy}}$ $\overline{d_{xz}}$ $\overline{d_{yz}}$
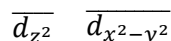
        $[Fe(SCN)_6]^{3+}$, therefore, Fe^{3+}
        $Fe^{3+} = [Ar]3d^5$
        In order to have 5 unpaired electrons the complex must be high spin, as seen below.

              $\uparrow$ $\uparrow$

              $\overline{d_{z^2}}$ $\overline{d_{x^2-y^2}}$

              $\uparrow$ $\uparrow$ $\uparrow$

              $\overline{d_{xy}}$ $\overline{d_{xz}}$ $\overline{d_{yz}}$
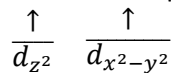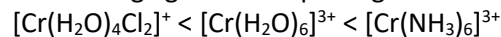
        Therefore, SNC^- must be a weaker field ligand than CN^- causing it to lie below CN^- on the spectrochemical series.

61.   Test Tube #1: Appears: Violet   Absorbs: Yellow
    Test Tube #2: Appears: Yellow   Absorbs: Violet
    Test Tube #3: Appears: Green   Absorbs: Red
    Order of increasing ligand field strength
        $Cl^- < H_2O < NH_3$
    The stronger the field ligand, the greater the ligand field splitting.
    Order of increasing ligand field splitting
        $[Cr(H_2O)_4Cl_2]^+ < [Cr(H_2O)_6]^{3+} < [Cr(NH_3)_6]^{3+}$
    Order of increasing wavelength absorbed
        test tube #2 < test tube #1 < test tube #3
    Order of increasing energy absorbed $\left(E = \frac{hc}{\lambda}\right)$
        test tube #3 < test tube #1 < test tube #2
    $[Cr(NH_3)_6]^{3+}$ test tube #2 (yellow)
    $[Cr(H_2O)_6]^{3+}$ test tube #1 (violet)
    $[Cr(H_2O)_4Cl_2]^+$ test tube #3 (green)

79.   A will have the formula $[CrI_y(NH_3)_x]I_z$
    What we know from the formula
    $x + y = 6$ (the problem told us that A was 6 coordinated)
    $+3 + (-1)y = -((-1)z)$ (the charge of the cation must equal opposite the charge of the anion)
    Calculate the moles of Cr in A (use data i)
        $0.0203\ g\ CrO_3 \left(\frac{1\ mol\ CrO_3}{100.0\ g\ CrO_3}\right)\left(\frac{1\ mol\ Cr}{1\ mol\ CrO_3}\right) = 2.03 \times 10^{-4}\ mol\ Cr$
    Calculate mass percent of Cr
        $2.03 \times 10^{-4}\ mol\ Cr \left(\frac{52.00\ g\ Cr}{1\ mol\ Cr}\right) = 0.0106\ g\ Cr$
        $mass\ \%\ Cr = \left(\frac{m_{Cr}}{m_{total}}\right)100\% = \left(\frac{0.0106\ g}{0.105\ g}\right)100\% = 10.1\%\ Cr$
    Calculate the moles of Cr in 100 g of A
        $10.1\ g\ Cr \left(\frac{1\ mol\ Cr}{52.00\ g\ Cr}\right) = 0.194\ mol\ Cr$
    Calculate the moles of NH_3 in A (use date ii)
        $0.0329\ L\ HCl \left(\frac{0.100\ mol\ HCl}{1\ L\ HCl}\right)\left(\frac{1\ mol\ NH_3}{1\ mol\ HCl}\right) = 0.00329\ mol\ NH_3$
    Calculate the mass percent of NH_3
        $0.00329\ mol\ NH_3 \left(\frac{17.04\ g\ NH_3}{1\ mol\ NH_3}\right) = 0.0560\ mol\ NH_3$
        $mass\ \%\ NH_3 = \left(\frac{m_{NH_3}}{m_{total}}\right)100\% = \left(\frac{0.0560\ g}{0.341g}\right)100\% = 16.4\%\ Cr$
    Calculate the moles of NH_3 in 100 g of A
        $16.4\ g\ NH_3 \left(\frac{1\ mol\ NH_3}{17.04\ g\ NH_3}\right) = 0.962\ mol\ NH_3$
    Calculate x
        $x = \frac{0.962}{0.194} = 4.96 = 5$
    Calculate y
        $x + y = 6$
        $y = 6 - x = 6 - 5 = 1$

Calculate z

$$+3 + (-1)y = -((-1)z)$$
$$z = 3 - y = 3 - 1 = 2$$

[CrI(NH$_3$)$_5$]I$_2$