(1)

2019/2020, 1a

What are co-ordination complexes:

They are compounds which consists of a centrally placed metal ion surrounded by a definite number of electron-donating ions or molecules called ligands.

(2) 2019/2020, 1b

Discuss briefly the theories used to explain bonding in transition metal.

A⇒ ① Valence bond theory: In this theory, the ligands are bonded to the ~~complex~~ metal ion by CO-ORDINATE BONDS, to form a co-ordinate complex ion.

Hence, the ligands must have lone pairs of electrons and the metal must have a low-lying d-orbital which can accept electrons from the ligand.

ⓑ Crystal field ~~ligand~~ theory ⇒ This theory Predicts that the bonding between the ligand and the metal is Purely electrostatic. could be ion-ion / ion-dipole interaction.

ⓒ Ligand field Theory ⇒ Explains interaction of ligand with metals using MOLECULAR ORBITAL THEORY that there is always overlapping of atomic orbitals of the metals and ligands.

③ 2019/2020, 4a - 9

ⓐ Using VBT, Predict the shape, hybridisation and Magnetic property of

(i) Sodium tetrabromocobaltate(II)

(ii) Sodium hexanitrocobaltate(III).

A (i) sodium tetrabromocobaltate(II) = $Na_2[Co(Br)_4]$

~~$Na_2[Co$~~ $Na_2[CoBr_4] \longrightarrow 2Na^+ + [Co(Br)_4]^{2-}$

$[Co(Br)_4]^{2-}$

Oxidation state of Co in $[Co(Br)_4]^{2-}$ =

$$x + (-1 \times 4) = -2$$

$$x = -2 + 4 = +2$$

The metal ion is Co^{2+}

$$Co: \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^7}\ \underbrace{\underline{\uparrow\downarrow}}_{4s^2} \qquad Co^{2+}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^7}\ \underbrace{\underline{\ \ }}_{4s^0}$$

- Each Br atom donates 2 electrons (1 Pair) each, we have 4 Bromine atoms, and since Br^- is a weak field ligand, there will be no forced Pairing, for Co^{2+} to accomodade 4 pairs of electrons; it would have to make use of 4-orbitals which will include it's valence 4s orbital and 3 - 4p orbitals to form sp^3 hybrid orbitals.

$$Co^{2+}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^7}\ \ \underbrace{\underline{\ \ }}_{4s}\ \ \underbrace{\underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }}_{4p} \xrightarrow{+8e^-} \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}}_{sp^3}$$

The shape of $[Co(Br)_4]^{2-}$ is tetrahedral, since it has unpaired electrons, it is Paramagnetic.

(ii) Sodium hexanitrocobaltate (III) ⇒ $Na_3[Co(NO_2)_6]$

$$Na_3[Co(NO_2)_6] \rightarrow 3Na^+ + [Co(NO_2)_6]^{3-}$$

$[Co(NO_2)_6]^{3-}$

Oxidation state of Co in the complex: $x + (-1 \times 6) = -3$

$$x = -3 + 6 = +3.$$

The metal ion is Co^{3+}

Co: ⇅ ⇅ ↑ ↑ ↑ ⇅ — $3d^7$, $4s^2$ Co^{3+} ⇅ ↑ ↑ ↑ ↑ __ — $3d^6$, $4s^0$

• NO_2^- is a strong field Ligand, so there will be forced Pairing and in order to accomodate the 6 pair of electrons coming from NO_2 atoms, it would form an hybridization with 6-Orbitals

Co^{3+} ⇅ ⇅ ⇅ __ __ __ __ __ __ — $3d^6$, $4s^0$, $4p$

To form this bond, it would use two of it's internal 3d-Orbital, 1-4s Orbital and 3-4p orbitals to form d^2sp^3 hybrid Orbital.

~~Co^{3+} __ __ __ __ __ __ __ __~~ s

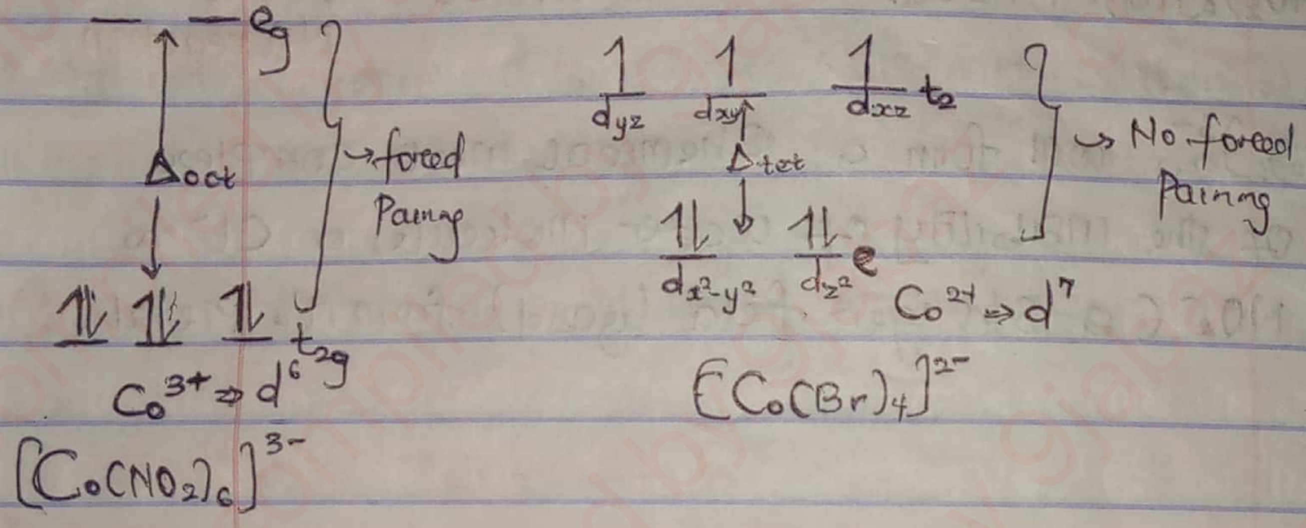
Co^{3+} ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅ — d^2sp^3

Hybridization = Octahedral. Magnetic Property => Dimagnetism, no unpaired electrons

ⓑ Based on crystal field Theory, draw the splitting of the two complex. $[Co(NO_2)_6]^{3-}$

A => The ~~Ligand~~ complex containg NO_2^- will have a Large value for it's CFSE Since it is a strong field Ligand, also Since it has 6 Ligands attached to it, it's in an octahedral environment.

On the Other hand $[Co(Br)_4]^{2-}$ will have a Low weak CFSE due to the weak nature of Br^- Ligand in ~~Octa~~ tetrahedral environment



ⓒ Which one would have the higher molar absorptivity & why?

$[Co(Br^-)_4]^{2-}$ would have a higher molar absorptivity because, it is a tetrahedral complex and hence has no Centre of symmetrical {non-centrosymmetrical ~~centro~~} unlike $[Co(NO_2)_6]^{3-}$ which is an Octahedral. Centrosymmetrical compound/complex with forbidden transitions and hence a reduced molar absorptivity.

ⓓ If each of these complexes were dissolved in water and then concentrated solution of HCl is added. which one would be chemically inert?, give reason(s) for your answer(s).

$[Co(Br)_4]^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Co(H_2O)_6]^{2+}_{(aq)}$

$+ 4Cl^- \rightarrow [Co(Cl)_4]^{2-}_{(aq)}$

$[Co(NO_2)_6]^{3-}_{(aq)} + H_2O_{(l)} \longrightarrow \longrightarrow + HCl \longrightarrow \times$

NO reaction

$[Co(NO_2)_6]^{3-}_{(aq)}$ will form a Chemical inert complex because of the inability of water molecules or Cl^- to displace NO_2^- (a stronger field ligand) from it's metal ion.

(e) Write the molecular Orbital electronic Configuration of Sodium hexanitrocobaltate (III))

$Na_3[Co(NO_2)_6] \longrightarrow 3Na^+ + [Co(NO_2)_6]^{3-}$

$[Co(NO_2)_6]^{3-}$

NO_2^- is a π-acceptor

Oxidation state of Co = +3

$Co^{3+} = 3d^6 4s^0 = 6e^-$

$6NO_2 = 6 \times 2e = 12e^-$

Total = 18e.

The M.O.T = $a_{1g}^2, t_{1u}^6, e_g^4, \underbrace{t_{2g}^6, e_g^*}, t_{2g}^*, a_{1g}^*, t_{1u}^*$

Space here is wide

$t_{2g} - e_g^*$ {dep. the transition}

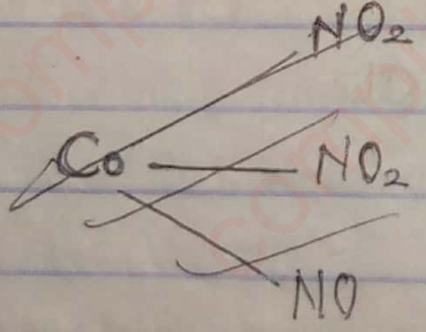
(f) Which of the two Complexes is Likely to have just one Peak in its electronic spectra.

$[Co(NO_2)_6]^{3-}$ will have just one Peak due to the transition from $^5T_{2g} \rightarrow {}^5E_g$ when it absorbs electro-magnetic energy of the right wavelength being a d^6 ion

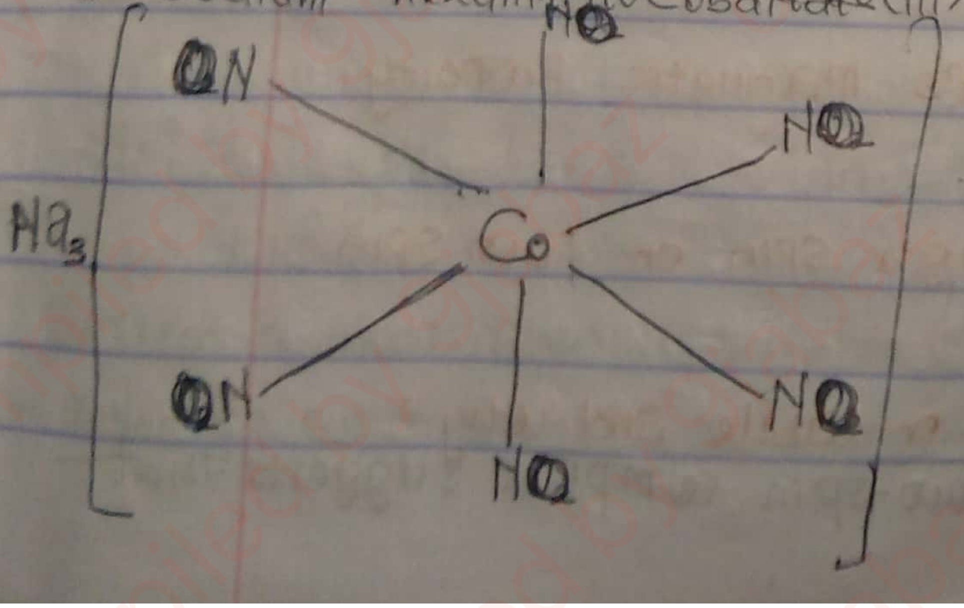
(g) $^5T_{2g} \rightarrow {}^5E_g \Rightarrow {}^5E_g \leftarrow {}^5T_{2g}$

2019/2010; Test 2a, b

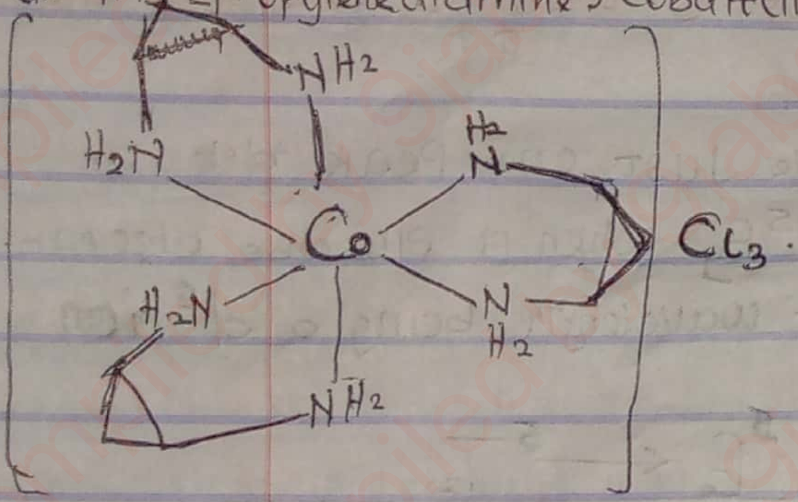
④ Draw the structure of these complexes;



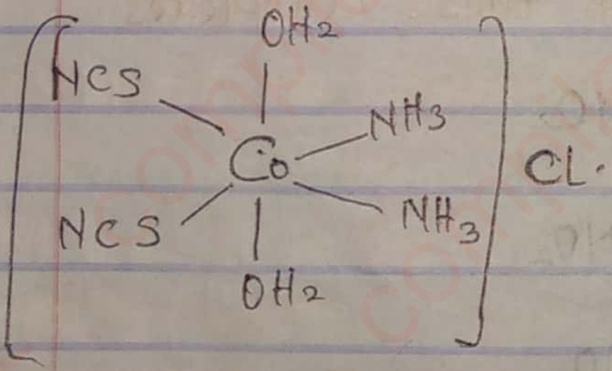
(i) Sodium hexanitritoCobaltate(III)



(ii) Tris [Propylenediamine] cobalt(III) chloride-



(iii) Diamminediaquodiisothiocyanatocobalt(III) chloride



b. The Orbitals of cobalt in complex (iii) above is d^2sp^3 hybridised

(i) what would be it's magnetic property

Dimagnetic.

(ii) would it be high spin or low spin

low spin

(iii) Would it be inert or labile and why?

Inert; a low-spin complex suggests that

a strong field ligand is bonded to the metal and hence such complexes cannot be displaced and as such are INERT.

5) ~~Who~~ 2018/2019 Test

ⓐ What is the IUPAC name of the compounds below?

(i) $Ca[Ni(Br)_4]$ - Calcium tetrabromonickelate (II)

(ii) $[Ni(en)_2(Br)_2]Br_2$ - Dibromo bis(ethylenediammine)nickel(IV) Bromide.

(iii) $[Ni(CO)_4]Br_2$ - ~~Te~~tracarbonyl nickel(II) bromide.

ⓑ Predict the hybridization, shape and magnetic property of the complexes (i) and (ii).

(i) $Ca[Ni(Br)_4] \longrightarrow Ca^{2+} + [Ni(Br)_4]^{2-}$

$[Ni(Br)_4]^{2-}$

find the oxidation state of Ni:

$x + (-1 \times 4) = -2$; $x = -2+4 \Rightarrow x = +2$

The Metal ion is Ni^{2+}

Ni^{0} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}$ $\underbrace{\uparrow\downarrow}_{4s^2}$ Ni^{2+} $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}$ $\underbrace{\ \_\ }_{4s^0}$

Br^- is a weak field ligand, hence no forced pairing, In order to accomodate the 4 pairs of e's from Bromine atom, it will need ~~to~~ 4 hybrid orbitals. To form this, it would use it's 4s orbital and 3-4p orbitals to form sp^3 hybrid orbitals.

$$Ni^{2+}\ \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}\quad \underbrace{\_}_{4s}\quad \underbrace{\_\ \_\ \_}_{4p}\ \xrightarrow{+8e^-}\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow\quad \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{sp^3}$$

Shape: tetrahedral.

Presence of unpaired e's hence Paramagnetic.

(ii) $[Ni(en)_2(Br)_2]^{2+}$

Oxidation state of Ni in the complex

$$x + (2\times 0) + (2\times -1) = +2$$

$$x = +2+2 = +4.$$

$$Ni:\ \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}_{3d^8}\quad \underbrace{\uparrow\downarrow}_{4s^2}\qquad Ni^{4+}\ \underbrace{\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{3d^6}\quad \underbrace{\_}_{4s^0}$$

• Although Br^- is a weak field ligand, ethylenediammine (en) is not only a strong field ligand but also a chelating ligand and hence there will be forced pairing. In order to accomodate the 6 lone pairs coming from the ligands, it would form a hybridization that has 6-orbitals, making use of it's vacant 2-3d, 4s and 4p orbitals to form the d^2sp^3 hybrid orbitals

$$Ni^{4+}\ \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \_\ \_}_{3d^6}\quad \underbrace{\_}_{4s^0}\quad \underbrace{\_\ \_\ \_}_{4p^0}\ \xrightarrow{+12e^-}\ Ni^{4+}\ \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{3d^6}\quad \underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{d^2sp^3.}$$

Shape= octahedral

no unpaired electrons = dimagnetic.

(iii) $[Ni(CO)_4]^{2+}$

Oxidation state of Ni in the complex

$x+(4\times0)=+2$

$x+0=+2$; $x=+2$.

Ni° ⇅ ⇅ ⇅ ↑ ↑ ($3d^8$) ⇅ ($4s^2$) Ni^{2+} ⇅ ⇅ ⇅ ↑ ↑ ($3d^8$) _ ($4s^0$)

Since CO is a strong field ligand, it will force pairing and so in order to accomodate 4 lone pairs coming from the CO, it would form hybridization with 4 orbitals making use of it's vacant d-orbitals, ~~4~~s and 2-~~4~~p orbitals to form a dsp^2 hybrid orbital

Ni^{2+} ⇅ ⇅ ⇅ ⇅ _ ($3d^8$) _ ($4s$) _ _ _ ($4p$) $\xrightarrow{+8e^-}$ Ni^{2+} ⇅ ⇅ ⇅ ⇅ ($3d^8$) ⇅ ⇅ ⇅ ⇅ (dsp^2) _ ($4p$)

Shape ⇒ square planar.

no unpaired electrons = dimagnetic.

(C) Calculate the CFSE of (i)

Notice that $[Ni(Br)_4]$ is in a tetrahedral environment and is a d^8 metal, also Br^- is a weak field, so no forced pairing.

$\uparrow\downarrow$ $\uparrow$ $\uparrow$ t_2

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

LF

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

IF

$$CFSE = E_{LF} - E_{IF}$$

where ~~LF =~~ $E_{LF} = n\Delta + mp$

$E_{IF} = mp$.

$$E_{LF} = 4\times(-0.6\Delta_{tet}) + 4(0.4\Delta_{tet}) + 3p$$

$$= -2.4\Delta_{tet} + 1.6\Delta_{tet} + 3p$$

$$E_{IF} = 3$$

$$CFSE = -0.8\Delta_{tet}$$

(d) Briefly explain why ~~the~~ the molar absorptivity of (i) is greater than (ii).

Since (i) is a tetrahedral complex with no centre of symmetry; it is expected that it has a higher Absorbance, hence higher molar absorptivity than (ii) which is an octahedral complex with forbidden d-d transition which lowers it's absorptivity.

⑥ 2016/2017, Exam 1

The oxidation state of nickel in the following complexes $[Ni(H_2O)_6]Cl_2$, $Na_2[NiCl_4]$ and $Na_2[Ni(CN)_4]$ is +2

a) Write the IUPAC name of each complexes

(i) $[Ni(H_2O)_6]Cl_2$ ⇒ hexaquonickel (II)] chloride

(ii) $Na_2[NiCl_4]$ ⇒ Sodium tetrachloronickelate (II)] ion

(iii) $Na_2[Ni(CN)_4]$ ⇒ Sodium tetracyanonickelate (II) ion.

(b) Predict the hybridization and shape of each complex using VBT

(i) $[Ni(H_2O)_6]Cl_2 \longrightarrow [Ni(H_2O)_6]^{2+} + 2Cl^-$

$[Ni(H_2O)_6]^{2+}$

Oxidation state of Ni in the complex is

$x + (0 \times 6) = +2 \Rightarrow x + 0 = 2 \Rightarrow x = +2.$

$Ni^{0}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^8}\quad \underbrace{\underline{\uparrow\downarrow}}_{4s^2}$ $\qquad Ni^{2+}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^8}\quad \underbrace{\underline{\ \ }}_{4s^0}$

(H_2O) is a weak field ligand and hence no forced pairing. To accomodate the 12e's coming from H_2O, it would need 6 hybrid orbitals making use of its empty 4s orbital, 3-4p orbital and 2-4d orbital

$Ni^{2+}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^3}\quad \underbrace{\underline{\ \ }}_{4s}\quad \underbrace{\underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }}_{4p}\quad \underbrace{\underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }}_{4d} \xrightarrow{+12e^-} Ni^{2+}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$

$\underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}}_{sp^3d^2}\quad \underbrace{\underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }}_{4d^3}$

Shape = Octahedral

Hybridization = sp^3d^2

(ii) $[Ni(Cl_4)]^{2-}$

Oxidation state of Ni in the complex

$x+(-1\times4)=-2\ ;\ x=-2+4=+2$

The metal ion is Ni^{2+}

Ni^{0} $\underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}$ $\underset{4s^2}{\uparrow\downarrow}$ Ni^{2+} $\underset{3d^8}{\_\ \_\ \_\ \_\ \_}$ $\underset{4s^0}{\_}$

Cl^- is a weak field ligand, hence no forced pairing, In order to accomodate the 4 pairs of e's from the Cl atom, it will need 4 hybrid orbitals. To form this, it would use its empty 4s orbital and 3-4p orbital to do this

Ni^{2+} $\underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}$ $\underset{4s}{\_}$ $\underset{4p}{\_\ \_\ \_}$ $\xrightarrow{+8e^-}$ $\underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}$ $\underset{sp^3}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}$

(iii) $[Ni(CN)_4]^{2-}$

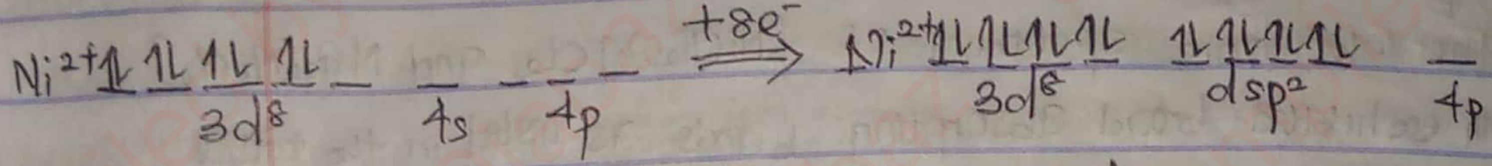
Oxidation state of Ni in the complex

$x+(-1\times4)=-2 \Rightarrow x=-2+4=+2.$

Ni^{0} $\underset{3d^8}{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\ \uparrow}$ $\underset{4s^2}{\uparrow\downarrow}$ Ni^{2+} $\underset{3d^8}{\_\ \_\ \_\ \_\ \_}$ $\underset{4s^0}{\_}$

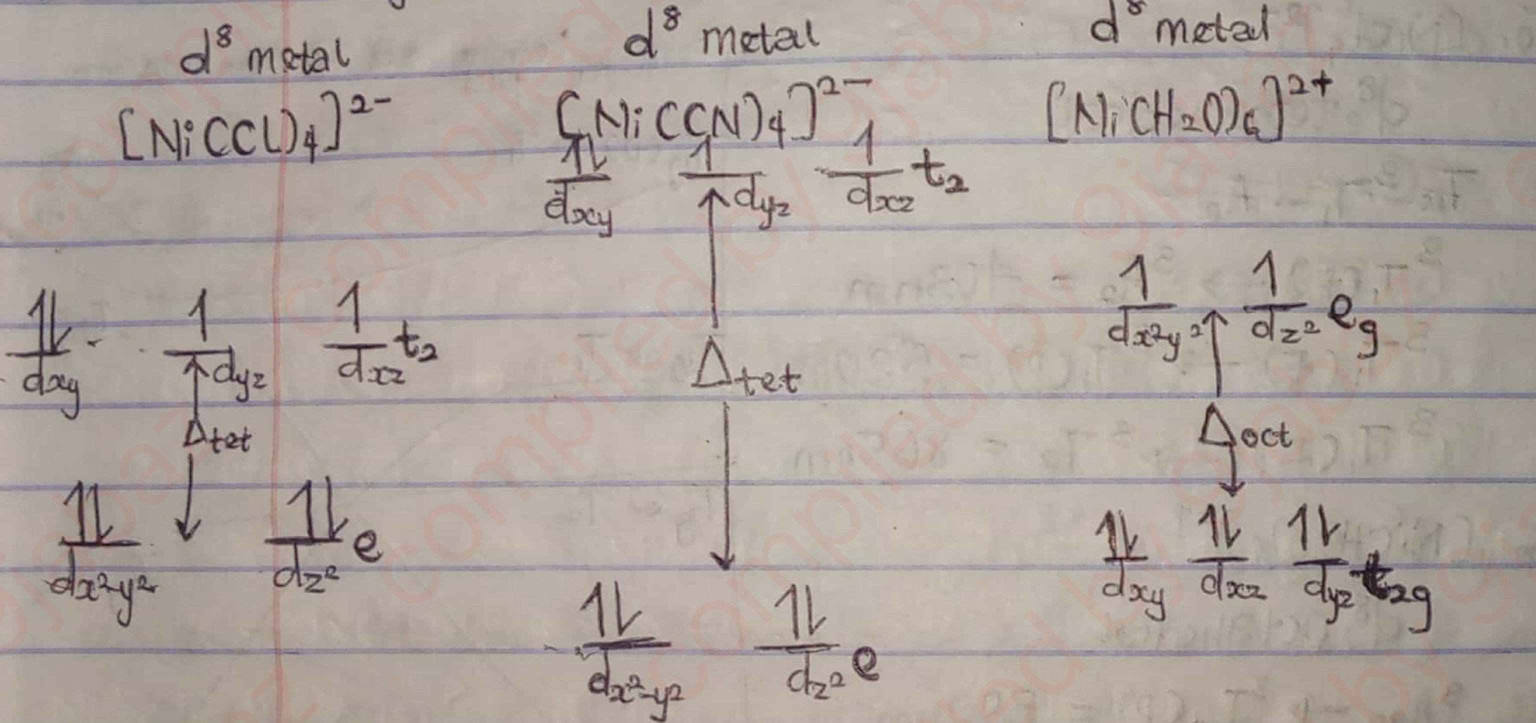
Since CN^- is a strong field ligand, it will force pairing and in order to accommodate 4 pairs of electrons from the ligand it will need to form 4 hybrid orbitals during hybridization making use of it's vacant d-orbital, 1-4s orbital and two 4p orbitals

- Δ_{tet} is less than Δ_{oct}



Shape = Square Planer. Hybridization = dsp².

(c) Draw the Crystal field splitting Pattern of each Complex



ⓓ State for each complex which is centrosymmetric or non centrosymmetric; and which would undergo symmetry allowed or forbidden; spin allowed / spin forbidden electronic trans.

(i) $[Ni(H_2O)_6]^{2+}$ ⇒ Centrosymmetric, Symmetry forbidden, spin allowed

*

(ii) $[Ni(CN)_4]^{2-}$ ⇒ Centrosymmetric, Symmetry forbidden, Spin allowed

(iii) $[Ni(Cl)_4]^{2-}$ ⇒ Non-Centrosymmetric, symmetry allowed, Spin allowed.

$\underbrace{A_{2g}\ T_{2g}\ T_{1g}}_{F}$ $\underbrace{T_{1g}}_{P}$ $d^7 \Rightarrow 3d^{5}4s^2$ ⑯

(e) The electronic spectrum of $[Ni(H_2O)_6]Cl_2$ and $Na_2[NiCl_4]$ both exhibited broad absorption bands as listed in the table below. using LFT, suggest assignments of the electronic transitions

$Na_2[NiCl_4]$	403nm	520nm	865nm
$[Ni(H_2O)_6]Cl_2$	392nm	495nm	800nm

$d^8 = {}^3F$

For $[NiCl_4]^{2-}$

d^8, tetrahedral

~~T_{1} $^3T_1$ — A_2~~

$^3T_1(F) \longrightarrow {}^3A_2 = 403nm$

$^3T_1(F) \longrightarrow {}^3T_1(P) = 520m$

$^3T_1(F) \longrightarrow {}^3T_2 = 865nm$

For $[Ni(H_2O)_6]^{2+}$

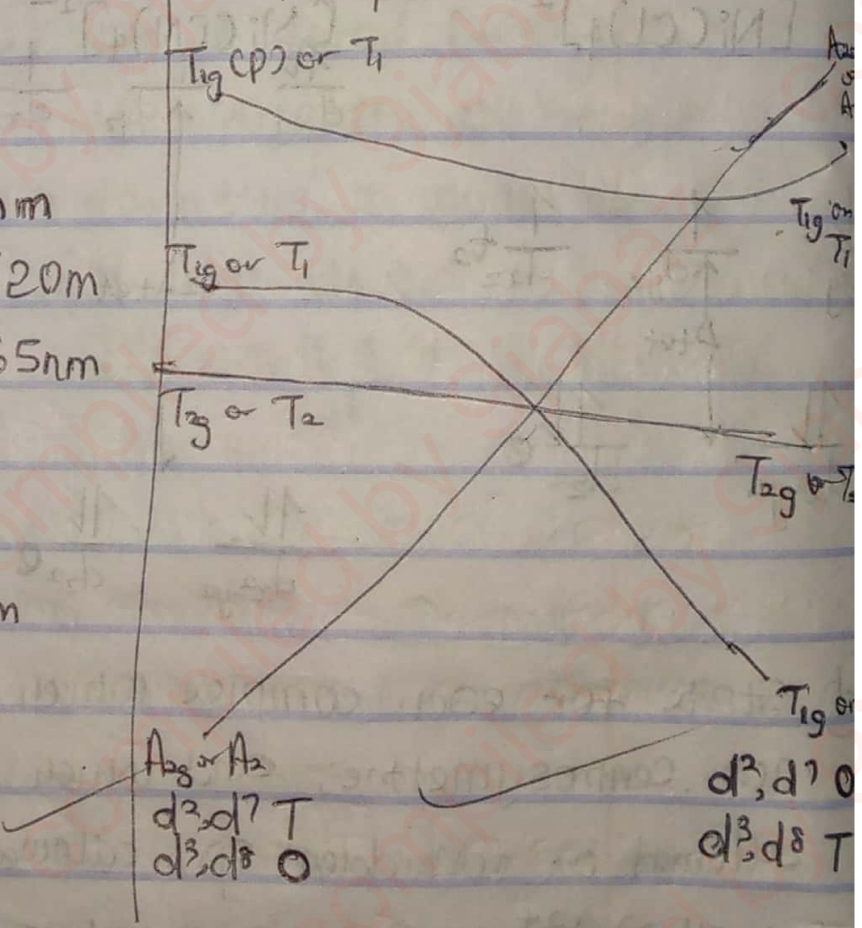
d^8, octahedral

$^3A_{2g} \rightarrow {}^3T_{1g}(P) = 392nm$

$^3A_{2g} \rightarrow {}^3T_{1g} = 495nm$

$^3A_{2g} \rightarrow {}^3T_{2g} = 800nm$

Lemme see if I can remember the plot



[illegible]
[illegible]
[illegible]

2016/2017, 2(a) - 2(b)

Based on ligand field theory, write the molecular electronic configuration of the following complexes:

(i) $Cr(CO)_6$ (ii) $[CoF_6]^{3-}$ (iii) $[Co(en)_3]^{3+}$ (iv) $[CrCl_6]^{3-}$

$[Cr(CO)_6]$ =>

Oxidation of Cr = $x + (0 \times 6) = 0$; $x = 0$

Cr^0 = 6e's $[3d^5, 4s^1]$

6CO = 6 × 2 = 12e's

Total = 18e's

$a_{1g}^2 \, t_{1u}^6 \, e_g^4, t_{2g}^6, e_g^{*0}, t_{2g}^{*0}, a_{1g}^{*0}, t_{1u}^{*0}$

$[CoF_6]^{3-}$

Oxidation state of Co is

$x + (-1 \times 6) = -3$

$x = -3 + 6 = +3$.

$Co^{3+} = [3d^6, 4s^0]$ = 6e's

F is a π-donor

$6F^-$ = 6π electrons + 12e's = 18e's

Total = 24e's

$a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6, t_{2g}^{*4}, e_g^{*2}, a_{1g}^*, t_{1u}^*$

(iii) $[Co(en)_3]^{3+}$

$x+0=+3$

$Co^{3+} = 6e$'s

$3en = 2\times2\times3 = 12e$'s

Total = 18e's

$a_{1g}^{2}, t_{1u}^{6}, e_{g}^{4}, t_{2g}^{6}, e_{g}^{*0}, t_{2g}^{*0}, a_{1g}^{*0}, t_{1u}^{*0}$

(iv) $[Cr(Cl)_6]^{3-}$

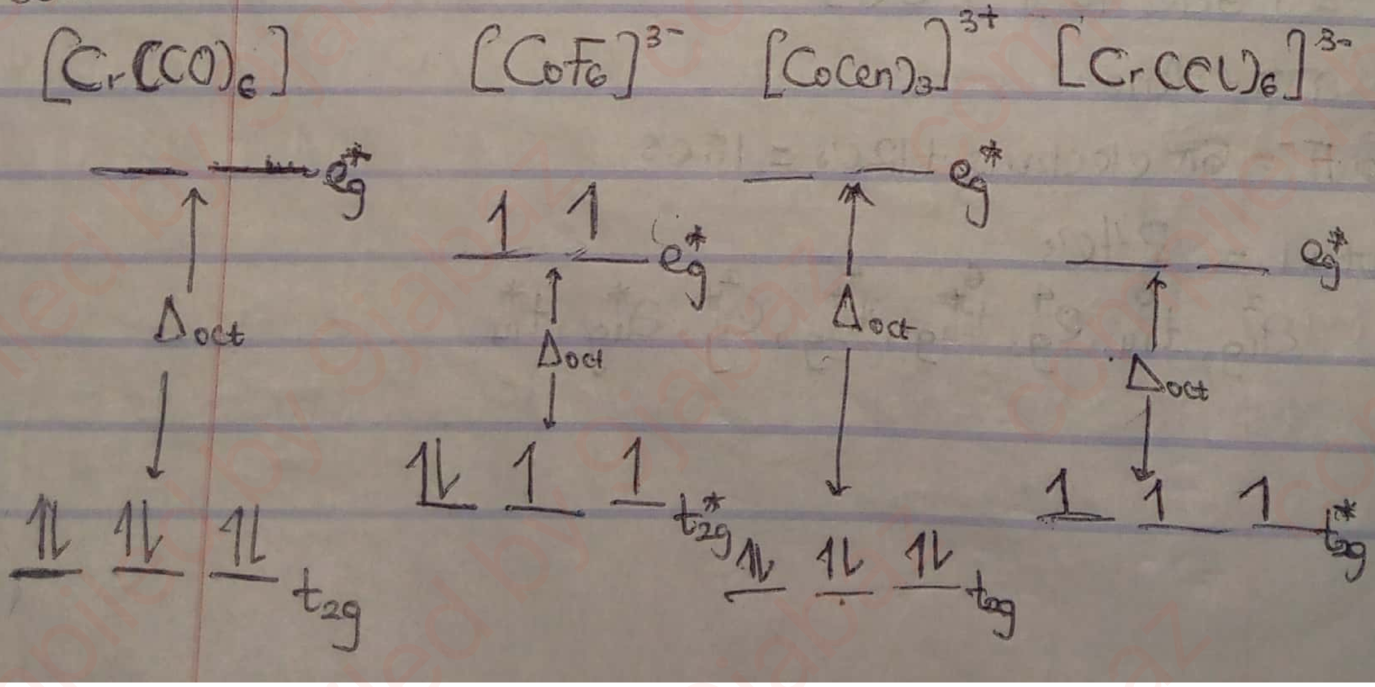
$Cr^{3+} = 3e$'s

$6Cl^{-} = 6\pi e$'s + 12e's = 18e's

Total = 21e's

$a_{1g}^{2}, t_{1u}^{6}, e_{g}^{4}, t_{2g}^{6}, t_{2g}^{*3}, e_{g}^{*}, a_{1g}^{*}, t_{1u}^{*}$

(b) Use simple illustration to show the energy separation between HOMO and LUMO for each complex in (a) above.



2016/2017 – 2c

ⓑ Below are some of the possible arrangements of 2-electrons in the d-orbitals. Derive the term symbols and arrange them in order of increasing energy

-2	-1	0	+1	+2	M_L	M_s
↓	↑				-3	0
↓		↑			-2	0
↓			↑		-1	0
↓				↑	0	0
	↓	↑			-1	0
	↓		↑		0	0
	↓			↑	+1	0
		↓	↑		+1	0
		↓		↑	+2	0
			↓	↑	+3	0
↑↓					~~+4~~ -4	0
	↑↓				-2	0
		↑↓			0	0
			↑↓		+2	0
				↑↓	+4	0

Grouping M_L	L	T. S	Grouping M_s	S	2S+l
-4 → +4	4	G	0	0	1,S
-2 → +2	2	D	0	0	1,S

Term symbol is
^1G, ^1D

To find the J-value
$L+S = 4+0 = 4 \Rightarrow {}^1G_4$
$L+S = 2+0 = 2 \Rightarrow {}^1D_2$

Arranging in order of increasing energy:
$^1D_2$, $^1G_4$
$\xrightarrow{\hspace{4cm}}$
Increasing energy.

- Grouping all the M_L with $M_s = 0$, we have -4,-3,-2,-1,0,1,2,3,4
- Grouping all the M_L with $M_s = 0$, we have -2,-1,0,+1,+2

(Q) 2016/2017; 2d

The electronic spectra of a Cu^{2+} complex in an Octahedral field was observed to consist of one broad band with a shoulder. Explain the reason for this shoulder?

Answer ⇒ Jahn Taller effect is responsible for this effect

$\underline{\uparrow\downarrow}\ \underline{\uparrow}$

$\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$

d^9

The asymmetrical filling of the e_g Orbital causes distortion, ~~thus lowering the energy and there is then a transition from $t_{2g} \rightarrow e_g$ by the electron giving rise to~~ a ~~shoulder [broad]~~ broad band with a shoulder. The broad band is as a result of the d^9 transition from $T_{2g} \leftarrow E_g$ and the shoulder is because of the asymmetrical filling of the e_g Orbital leading to the Jahn Taller effect.

(10) 2018/2019, Section C, b

Ni^{2+} and Pt^{2+} are both d^8 ions but $[NiCl_4]^{2-}$ is tetrahedral in shape and $[PtCl_4]^{2-}$ is square planar. Nickel forms square planar complexes with cyano ligands ($[Ni(CN)_4]^{2-}$). Give a brief explanation for these differences?

Answer:

Using the Valence bond theory, notice that CN^- is a strong field ligand and upon forming a complex with Ni ion, it forces pairing and uses the, d-orbital, s-orbital and 2-4p orbital giving rise to ~~an~~ dsp² hybrid ~~pds~~ ~~p~~ orbital which is square planar in shape; unlike $(NiCl_4)^{2-}$ with a sp³ tetrahedral shape.

Major diff = Strong Vs Weak field ligand ↗ build around it.

(11) 2018/2019, Section C, c

Give a brief explanation on why $[Mn(H_2O)_6]^{2+}$ is pale in color while $[MnO_4]^-$ has a very intense color

A→ $[Mn(H_2O)_6]^{2+}$ is spin forbidden and hence it has a lower absorptivity giving rise to a pale color, but in MnO_4^-, the deep(intense) purple color is as a result of intense LMCT occuring in the visible region of the electromagnetic spectrum. Charge Transfer absorptions are usually very strong and deep color producing

⑫ 2018/2019, Section C, d

Only state the type of bonding that exists in T.M complexes according to (i) Ligand field theory
(ii) Crystal field Theory
(iii) Valence bond Theory

Answer

LFT ⇒ Overlapping of atomic orbitals – M.O.T
CFT ⇒ Electrostatic Bonding
VBT ⇒ Co-ordinate Bonding

(13) 2018/2019, Section C, e

In the table below is the magnetic spin quantum number of a d^7 metal [Ms] and the corresponding orbital quantum number ML

(i) Complete the table below

(ii) combining all the J values obtained, arrange in order of increasing energy.

S/N	Ms	ML	S	L	Multiplicity	J	Term symbols
1	$+3/2$	$-3 \to +3$	$3/2$	3	4	$9/2$	^4F
2	$+1/2$	$-2 \to +2$	$1/2$	2	2	$5/2$	^2D
3	$+1/2$	-5 to $+5$	$1/2$	5	2	$11/2$	^2H
4	$-1/2$	$-1 \to +1$	$1/2$	1	2	$3/2$	^2P
5	$+1/2$	$-3 \to +3$	$1/2$	3	2	$7/2$	^2F
6	$+1/2$	$-4 \to +4$	$1/2$	4	2	$9/2$	^2G

The Term symbols are
^4F, ^2D, ^2H, ^2P, ^2F, ^2G

To find the max J-Values
F ^4F, J-Value = $9/2$, multiplicity = 4, hence allowed J values are $9/2, 7/2, 5/2, 3/2$.
$\Rightarrow {}^4F_{9/2}, {}^4F_{7/2}, {}^4F_{5/2}, {}^4F_{3/2}$
^2D, J-Value = $5/2$, multiplicity = 2, hence allowed J values are $5/2, 3/2$
$\Rightarrow {}^2D_{5/2}, {}^2D_{3/2}$
^2H, J-Value = $11/2$, multiplicity = 2, allowed J values are $11/2, 9/2$
$\Rightarrow {}^2H_{11/2}, {}^2H_{9/2}$
^2P, J-Value = $3/2$, multiplicity = 2, allowed J values are $3/2, 1/2$.
^2F, J-Value = $7/2$, multiplicity = 2 allowed J values are $7/2, 5/2$
$^2G \Rightarrow$ max J Value = $9/2$, multiplicity = 2, allowed J values are $9/2, 11/2$

Arranging in Order of increasing energy
$^2P_{3/2}, {}^2P_{1/2}, {}^2D_{5/2}, {}^2D_{5/2}, {}^2F_{7/2}, {}^2F_{7/2}, {}^2G_{11/2}, {}^2G_{9/2}, {}^2H_{11/2}, {}^2H_{9/2}$, [illegible] ${}^4F_{9/2}, {}^4F_{7/2}, {}^4F_{5/2}, {}^4F_{3/2}$

Primary valence = Oxidation
Secondary valence = Coord

(14) 2018/2019, 6

Anhydrous $CrCl_3$ was dissolved in water to form $[Cr(H_2O)_6]Cl_3$ and dissolved in Conc. Solution of NaOH to yield $Na_3[Cr(OH)_6]$.

ⓐ What is the Correct IUPAC Nomenclature of these Complex

$CrCl_3$ = Chromium (III) Chloride
$[Cr(H_2O)_6]Cl_3$ = hexaaquochromium(III) chloride
$Na_3[Cr(OH)_6]$ = Sodium hexahydroxochromate(III)

ⓑ What is the Primary and Secondary valence of $Na_3[Cr(OH)_6]$

Primary valence = -3
Secondary valence = 6

ⓒ Is $[Cr(H_2O)_6]Cl_3$ an inert or labile complex, give reasones for your answer

Labile complex – H_2O is a weak ligand and hence can be replaced by Stronger field ligand like ^-OH as in the reaction mentioned above.

ⓓ $Na_3[Cr(OH)_6]$ is an octahedral complex, Predict its hybridization and its magnetic properties

~~[Na~~ $Na_3[Cr(OH)_6]^{3+} \longrightarrow 3Na^{+} + [Cr(OH)_6]^{3-}$

$[Cr(OH)_6]^{3-}$

Oxidation state of Cr

$x + (-1 \times 6) = -3$

$x = +3$

The Metal is Cr^{3+}

Cr° 1 1 1 1 1 ($3d^5$) 1 ($4s^1$)

Cr^{3+} 1 1 1 _ _ ($3d^3$) _ ($4s^0$)

^-OH is a ~~strong~~ weak field Ligand and hence it will not force Pairing and in order to accomodate 6 Pairs of electrons from the Ligand, it will need to form 6 hybrid orbitals during hybridisation making use of its empty s orbital, 3-4p-orbitals and two-4d-orbitals to form an sp^3d^2 hybridisation

Cr^{3+} 1 1 1 _ _ ($3d^3$) _ ($4s$) _ _ _ ($4p$) _ _ _ _ _ ($4d$) $\xrightarrow{12e^-}$ Cr^{3+} 1 1 1 _ _ ($3d^3$)

⇅ ⇅ ⇅ ⇅ ⇅ ⇅ (~~4p~~ sp^3d^2)

_ _ _ ($4d^3$)

Shape = Octahedral

Hybridisation = sp^3d^2

Magnetic properties = Paramagnetic - [presence of unpaired electron]

(e) Write the MOE for $[Cr(H_2O)_6]Cl_3$, and underline the molecular orbital orbitals that would determine the Ligand field splitting

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

$Cr^{3+} = 3e^-s$

$6H_2O = 6 \times 2 = 12e^-s$.

Total $= 15e^-s$

$M.O.E = a_{1g}^2, t_{1u}^6, e_g^4, \underline{t_{2g}^3}, \underline{e_g^*}, a_{1g}^*, t_{1u}^*$

d^3 d^8

(f) Calculate the CFSE of $[Cr(H_2O)_6]Cl_3$

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

d^3

CFSE = $E_{LF} - E_{IF}$

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

$\uparrow$ d^8

1 1 1 _ _

IF

_ _

1 1 1

LF

MP = 0

$3x - 0.40\Delta_{oct} = -1.2\Delta_{oct}$

CFSE = $-1.2\Delta_{oct} + 0 + 0$

CFSE = $-1.2\Delta_{oct}$

(g) The ground state term symbol for $[Cr(H_2O)_6]Cl_3$ is ^4F, describe in details the significance of this term symbol

^4F

$2S+1 = 4$

$S = 4 - 1/2 = 3/2$.

This means that the M_s values of $-3/2, -1/2, 1/2, 1/2$

The ~~Hz~~ S value indicates that there are only 3 electrons that are unpaired or 3 holes present hence it is a d^3 or d^7.

F term means $L = 3$

M_L values are $-3, -2, -1, 0, 1, 2, 3$

The J values are $(L+S), (L+S-1), (L+S-2)$ ...

Allowed J values for ^4F are $9/2, 7/2, 5/2$ and $3/2$.

We stop at $3/2$ because it is a quartet so only 4 terms are allowed.

The full term symbol is $^4F_{9/2}, {}^4F_{7/2}, {}^4F_{5/2}, {}^4F_{3/2} \Rightarrow d^7$

$\xrightarrow{\text{Increasing energy}}$

d^4 d^7

For a d^3 Cr^{3+} Cr^{3+}

$$\xrightarrow[\text{Increasing energy.}]{{}^4F_{3/2},\ {}^4F_{5/2},\ {}^4F_{7/2},\ {}^4F_{9/2}}$$

(h) According to LFT, how many bands would the UV-Vis spectra of $Na_3[Cr(OH)_6]$ have and write the full notation electronic transition(s) responsible for these bands in order of increasing wavelengths

$[Cr(OH)_6]^{3-}$

It's a d^3 metal; Octahedral

It will have 3-bands!

The Transitions responsible are

$$\left.\begin{array}{l} {}^4A_{2g} \longleftarrow {}^4T_{1g}(F) \\ {}^4T_{1g}(P) \longleftarrow {}^4T_{1g}(F) \\ {}^4T_{2g}(F) \longleftarrow {}^4T_{1g}(F) \end{array}\right\downarrow \text{Increasing wavelengths}$$

*

(i) Which of the following would complexes would undergo Jahn-Teller distortion? Give reason(s) for your answer

Both of them are d^3 metals so there is assymmetrical filling of e's in the ground state.

Both ~~Meta~~ complexes should undergo Jahn Teller distortion.

(15) 2017/2018, Test.

consider these two complexes (i) $[Fe(H_2O)_6]Cl_2$ (ii) $[Fe(en)_3]Cl_2$

(a) Write the Iupac name

(i) $[Fe(H_2O)_6]Cl_2$ ⇒ hexaaquo Iron(II) chloride.

(ii) $[Fe(en)_3]Cl_2$ ⇒ tris(ethylenediammine) Iron(II) chloride.

(b) Predict the hybridization of Iron in each of the complexes

$[Fe(H_2O)_6]^{2+}$

Oxidation state of Iron

$x + (0 \times 6) = +2 = +2$

The metal is a Fe^{2+}

Fe° $\underbrace{\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{3d^6}$ $\underbrace{\uparrow\downarrow}_{4s^2}$ Fe^{2+} $\underbrace{\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{3d^6}$ $\underbrace{\_}_{4s^0}$

H_2O is a weak field ligand, hence no forced pairing, In order to accomodate the 6 pairs of electrons coming from the ligand, it would need to form 6 hybrid orbitals ~~Make use of its empty~~ making use of ~~its~~ empty 4s Orbital, three 4p-Orbital and two 4d-Orbital forming an sp^3d^2 hybridisation.

Fe^{2+} $\underbrace{\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{3d^6}$ $\underbrace{\_}_{4s^0}$ $\underbrace{\_\ \_\ \_}_{4p}$ $\underbrace{\_\ \_\ \_\ \_\ \_}_{4d}$ $\xrightarrow{+12e^-}$ Fe^{2+} $\underbrace{\uparrow\downarrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow}_{3d^6}$ $\underbrace{\uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow\ \uparrow\downarrow}_{sp^3d^2}$ $\_$ d

Hybridisation = sp^3d^2.

$[Fe(en)_3]^{2+}$

Oxidation state of Iron

$x + (0 \times 3) = +2$

$x = +2$

The metal is Fe^{2+}

$Fe^0 \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^6}\ \underbrace{\underline{\ \ }}_{4s^2}$ $Fe^{2+} \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}}_{3d^6}\ \underbrace{\underline{\ \ }}_{4s^0}$

en (ethylenediammine) is not only a strong field ligad but also a chelating and hence there will be forced pairing. In order to accomodate the 12 lone electrons coming from the 3-en ligands, it would form an hybridisation with 6-orbitals, making use of it's vacant two 3d, 4s and 4p orbitals to form d^2sp^3 hybrid orbitals

$Fe^{2+} \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\ \ }\ \underline{\ \ }}_{3d^6}\ \underbrace{\underline{\ \ }}_{4s^0}\ \underbrace{\underline{\ \ }\ \underline{\ \ }\ \underline{\ \ }}_{4p} \xRightarrow{+12e^-} Fe^{2+} \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}}_{3d^6}\ \underbrace{\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}}_{d^2sp^3}$

Hybridisation = d^2sp^3.

Ⓒ Of the two complexes which would be inert towards ammonia and give one reason why?

$[Fe(en)_3]Cl_2$ will be inert towards ammonia, en is a strong field ligand and since ammonia is less strong than it is; It cannot displace en from it's complex making $[Fe(en)_3]Cl_2$

whenever she says list that means explain too.

Professor Daramola Questions (give her exactly what is in her notes)

1). what are lanthanide elements?
2). why is it difficult to separate lanthanide ions?
3). why were Cerium and Europium the easiest lanthanides to isolate before the develop-ment of ion-exchange chromatography?
4).* Compare and contrast the chemistry of lanthanide elements & actinides under d flg.
1). Oxidation states 2). Magnetic properties 3) Electronic spectral properties.
5. what are actinide elements?
6).* why are the magnetic properties of lanthanide complexes little affected by the ~~[illegible]~~ nature of the ligands.
7). The actinide elements; Thorium, Protactinium and Uranium were the only actinides known before 1940. Then they were thought to be part of the d' series of elements. Justify this assumption.
8). list the various methods for separation of lanthanides. which is most effective?
9).* what are the factors determining the stability of the oxidation states of lanthanides?
*10). The ions americium (III), Am^{3+} ($5f^6$). and europium (III), Eu^{3+} ($4f^6$) are both pink but the absorption bands in the electronic spectra of americium (III) complexes are broader than those in the electronic spectra of europium (III) complexes. suggest explanation for this observation.
11). Compare and contrast the formation of complexes by lanthanides and actinides.
12). Why is the chemistry of lanthanide elements homologous.

Answers

3). Lanthanides have variable oxidation state. Cerium is $4f^1 5d^1 6s^2$, which is the most stable oxidation state. It can exist as +3 and +4. Europium is $4f^7 6s^2$ exist as +2 or +3 so they can exist in other oxidation state apart from the general +3 oxidation state. Therefore, when the lanthanide mixture is oxidized, cerium is precipitated while Europium is passed through reduction process and Europium is gotten. ~~Europium is reduced by reduction to Eu^{2+} and Cerium is precipitated by~~

8). Various methods used in the separation of lanthanides includes;
1). Precipitation method 2). Thermal reaction 3). Fractional Crystallization
4). Complex formation 5). Valency change 6). Ion exchange chromatography.
7). solvent extraction

The Ion exchange chromatography is the most important, rapid and effective general method of separation of the lanthanide.

- The basis of the Principle is the ability to form complex ions.

6). Ion exchange chromatography: The solution of lanthanide ion is introduced at the top of a cation exchange column (It is the Dowex-50, which is a sulfonated polystyrene) The Ln^{3+} ions adsorbed onto ~~the~~ resin ~~onto and eluted~~ using ~~complexing agents~~ displacing H-atoms on the resin.

$$Ln^{3+}_{(aq)} + 3H_{(resin)} \rightleftharpoons Ln^{3+}_{(resin)} + 3H^{+}_{(aq)}.$$

The Ln^{3+} ions are then eluted in a selective manner using an anion complexing agent such as citrate, lactate, which are passed through the column slowly to leave interaction between the elements and the ions. The anionic chelating ligand form complexes with Ln^{3+} and they are displaced from the ion exchange material with the solution

$$Ln^{3+}_{(resin)} + 3H^{+}_{(aq)} + \text{citrate} \longrightarrow Ln(\text{citrate})_3 + 3H_{(resin)}$$

The elution order follows the order of the hydrated lanthanide ion such as lutetium is first eluted then lanthanum.

3). fractional Crystallization: It is used to separate lanthanide salt. The solubility decreases from lanthanum to lutetium. lutetium salt crystallizes out first and is separated. The nitrate salt, sulphate salt, amides and oxalates. have been used because they crystallize out well.

4). Complex formation: The mixture of lanthanide ion is treated with complexes such as EDTA. All lanthanide ion form complexes with EDTA Ions such as Ln^{3+} form the strongest complexes because of the small size and it can be separated. The oxalate of lanthanide ions are insoluble. Therefore, the addition of oxalate ions to solution containing Lanthanide and ~~EDTA does~~. not give a precipitate because all the Lanthanide ions have already complexed with EDTA. If acid is added, the least stable EDTA will be dissociated therefore the lanthanide ions will be available to be a Complex oxalate

7). Solvent extraction: The heavier lanthanide ions are more soluble tri-n-butyl phosphate because it is an organic solvent but in water, solubility is reversed.

LANTHANIDES

No	Elements	Symbols
57	Lanthanum	La
58	Cerium	Ce
59	Praseodymium	Pr
60	Neodymium	Nd
61	Promethium	Pm
62	Samarium	Sm
63	Europium	Eu
64	Gadolinium	Gd
65	Terbium	Tb
66	Dysprosium	Dy
67	Holmium	Ho
68	Erbium	Er
69	Thulium	Tm
70	Ytterbium	Yb
71	Lutetium	Lu

ACTINIDES

No	Elements	Symbols
89	Actinium	Ac
90	Thorium	Th
91	Protactinium	Pa
92	Uranium	U
93	Neptunium	Np
94	Plutonium	Pu
95	Americium	Am
96	Curium	Cm
97	Berkelium	Bk
98	Californium	Cf
99	Einsteinium	Es
100	Fermium	Fm
101	Mendelevium	Md
102	Nobelium	No
103	Lawrencium	Lr

11). If oxalate ions are added to solutions containing Ln ions of EDTA. what happens and why?

Answer:- The Lanthanide ions would have complexed with EDTA and because EDTA is a stronger complexing agent, the oxalate cannot displace EDTA and ~~the~~ nothing happens.

12). What happens when dil. HCl is added?

Answer:- when dil HCl is added, dissociation of lanthanide complex mixture happens. The 1st one ~~will~~ that disintegrate ~~and~~ is the least stable complex which is the one with the largest size (~~[illegible]~~). (lanthanum).

13). What is lanthanide contraction?

It is the steady decrease in the size of lanthanide atoms and ions with increasing atomic no from lanthanum^{57} to lutetium^{71}. The addition of electrons into an inner shell 4f leads to screening or shielding effect i.e the nucleus reduces its force of attraction on the valence electrons due to the presence of these electrons in the inner shell.

Therefore, there is poor shielding of the 5s and 5p electrons by ~~the~~ 4f el ~~the other~~ The other thing that contributes to the poor shielding ~~of the~~ is th shape of the f orbitals. With the poor shielding, the +vely charged nucleus has greater attraction to the electrons therefore decreasing the atomic size as the atom, which increases the subsequent electrons and goes to the inner 4f orbital leads to p shielding of 5s and 5p electrons

2). It is very difficult because of the similarities in the physical and chemical properties (which is also because of the similar sizes and they have similar trivalent states) ~~It~~ is. to this reason that only classical methods are used. Classical methods are used to exp slight difference in their basic properties such as stability, solubility and then using exchange and valency change. The similarity in ionic radius between adjacent lanthan elements makes it difficult to separate them from each other in naturally occurring and other mixtures.

1). Lanthanide elements are rare earth elements with unfilled f orbitals. It is also inner transition metals. Lanthanides are characterized by the filling of the 4f orbitals and contain the fourteen elements cerium to lutetium and are called lannides because they appear after lanthanum. They are also called lanthde because they exhibit similar chemical properties to lanthanum.

5). ACTINIDE elements are rare earth elements with unfilled f orbitals characterized the filling of the 5f orbitals and are also typical metals. They have the properties of bo the d-block elements & f-block elements. They are radioactive in nature and release a lo energy in radioactive decay. Uranium and Thorium are the most abundant naturally oc ring actinides.

7). They were wrongly thought to be part of the d-series because; of;
i). The chemical similarities with groups of transition metals i.e the titanium & zirconium gr
ii). Increase in the number of oxidation state.
iii). Increase in the stability of higher oxidation state.

11)b Compare and Contrast the formation of complexes by lanthanides & actinides.
Actinides are better complexing agents than lanthanides from the general properties that favours complex formation. i.e due to the smaller size but higher nuclear charge.. Actinides can form Pπ-complexes as well.

Confirmation of why Cerium and Europium are easy to isolate.
They are easy to isolate because they have other stable oxidation states. Cerium can lose all four ($4f^1 5d^1 6s^2$) and still have a stable configuration. Europium can lose two from $6s^2$ and have a stable $4f^7$ half filled orbital.

4). i) Oxidation states :- Actinides have variable oxidation state because of the utilization of the outermost electrons in bonding while lanthanide do not have variable oxidation state due to the buried nature of the 4f orbital.

ii). Magnetic Properties :- Magnetic properties of actinides ions arise from the spin and orbital angular momentum of the 5f electrons while magnetic properties ~~are~~ & of lanthanides are different because of the in-accessibility of the 4f electrons.

iii). Spectral :- The colour of Ln originates from charge transfer transition because the 4f orbital is buried while the colour of actinides originates from the electron transitions within the 5f levels. They are more intense than those of lanthanides

9) factors determining the stability of the oxidation ~~of~~ state of Ln elements.
i). Noble gas configuration f^0 e.g Ce^{4+} ii). Half filled configuration f^7 e.g Eu^{2+}
iii). fully filled configuration f^{14} e.g Yb^{2+} iv). kinetic & thermodynamic factors e.g Sm

6). This is due to the unavailability of the buried 4f orbital of lanthanides which is inaccessible by the ligand.

10). Eu^{3+} ($4f^6$) interacts with ligand environment weakly due to the buried nature of 4f orbital, therefore the absorption bands are sharp. But in Am^{3+} ($5f^6$) the 5f orbital overlap deeply with the ligand metals the absorption band in the electronic spectra are broaden.

Prof Akinyele's Part

Explain why low compound of Mn displays variable O.S.
The valence electron of the transition elements are (n-1)d and ns orbital which a little distinction in energies. Mn has variable oxidation state because of the u
tion of all electrons in the ns orbital and f-electrons in ~~the~~ transition seri
the element. The variable O.S is because of the support of both ns and (n-
orbital in bonding.

Explain giving relevant examples, the catalytic activity | complex formation properties of trans
metals.

Answer

1). Catalytic activity: Transition metals acts as catalysts because they have variable oxidat
states and vacant d-orbitals, which allows them to form temporary intermediat
complexes with reactants and lower activation energy. Eg Fe in Haber process, V_2O_5
contact process, Ni in hydrogenation of alkenes.

2). Complex formation: Transition metals form complexes because their ions are small, hi
availability of vacant low d orbitals donated by the other groups of ligand. this tho
to form multiple bonds. and availability of variable oxidation states. e.g $[Cu(NH)]$
$[Fe(CN)]^{4-}$, $[Co(NH)]^{3+}$.

Lanthanides have homologous chemistry because their outer electron configuration is th
same and 4f electrons do not take part in bonding.

Sources of Lanthanides

1). Monazite sand contain $LnThPO_4$ → 78% e.g Ce & Nd
2). Bastnaesite → mixed fluorocarbonate.
3). Xenotime → The principal source of ~~Ytterbium~~ Yttrium and heavier metals.
4). Samarskite — source of samarium

Prof Akinyele's Part

12). Discuss complex formation in Transition metals.

Answer

Transition metals are found to form complexes due to the following;

1). Small size and high charge of the metal ions.
2). Availability of vacant low d orbitals donated by other groups of ligands.
3). Availability of variable oxidation state
4). Ability to form pi bonds.

Spin – Spin coupling :- Interaction btw Intrinsic spin of one electron and another.
Spin – orbit coupling :- Interaction btw intrinsic spin of electron and orbit ~~of~~ motion of electron

SIMILARITIES BTW NMR & ESR

1). Both obey the resonance condition :- Absorption happens when $\Delta E = h\nu$
2). Both depend on magnetic properties of particles :- the signal depends on intrinsic properties such as spin quantum number and magnetic moment
3). Both involve spin transitions :- In NMR, transition occur btw nuclear spin states while in ESR, transition occur btw electron spin state but the underlying principle of spin flipping is the same.
4). Both require an external magnetic field :- without a strong magnetic field, energy levels do not split (no Zeeman splitting) and resonance cannot occur.
5). Both are non-destructive techniques.

Differences

	Features	NMR	ESR
1).	Sensitivity	Relatively low	Very high
2).	Radiation used	Radio-frequency (RF)	Microwave region.
3).	Magnetic moment source	Nuclear spin	Electron spin
4).	Magnetic field strength	Requires very strong magnetic fields	Requires comparatively weaker magnetic fields
5).	Type of species studied	Diamagnetic and paramagnetic substances	only paramagnetic substances
6).	Energy level splitting	small	large

MEISSNER EFFECT IS USED TO TEST FOR THE PRESENCE OF SUPER CONDUCTING STATE

Applications of lanthanides

1). Nd Fe is used as permanent magnet.
2). Glass polishing and ceramics
3). They are used as phosphorous on TV screen.
4). They are used as petroleum refining catalyst.
5). They are used as catalytic converters.

Consequences of lanthanides.

generally stability attained with an orbital is half or completely filled.

1). They have similar atomic sizes.
2). Ability of complex formation decreases.
3) - Increase in ionization energy.
4). Increase in electronegativity.
5). There are identical properties of the Ln elements.

$Ag = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^9$

$Au = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$ ~~$6p$~~ ~~$5d^1$~~ $6s^2 5d^9$