CO-ORDINATION COMPOUNDS

PROBLEM 1437 Name the following compounds according to IUPAC convention:

(i) $[Co(NH_3)_6]Cl_3$ (ii) $[CoCl(NH_3)_5]^{2+}$ (iii) $[CoSO_4(NH_3)_4]NO_3$

(iv) $K_2[OsCl_5N]$ (v) $Na_3[Ag(S_2O_3)_2]$ (vi) $K_2[Cr(CN)_2(O)_2(O_2)NH_3]$

(vii) $[Ir(NH_3)_5(ONO)]Cl_2$ (viii) $K_2[PbCl_4]$ (ix) $KCu[Co(CN)_6]$ (x) $K_3[Au(CN)_6]$

(xi) $Li[AlH_4]$ (xii) $Na[BH_4]$ (xiii) $Na_3[AlF_6]$

(xiv) $[CoCl_2(H_2O)_4]Cl \cdot 2H_2O$

PROBLEM 1438 Name the following complexes according to IUPAC convention:

(i) $[Cr(NH_3)_6][Cr(NCS)_6]$ (ii) $[Cu(NH_3)_4][PtCl_4]$ (iii) $[Pt(NH_3)_4][PtCl_4]$

(iv) $[Co(NH_3)_6]_2[Ni(CN)_4]_3$ (v) $[Pt(NH_3)_4Cl_2][PtCl_4]$

(vi) $[Co(NH_3)_6]_4[Co(NO_2)_6]_3$ (vii) $[Cr(NH_3)_5NO_2]_3[Co(NO_2)_6]_2$

(viii) $[Pt(Py)_4][PtCl_4]$ (ix) $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$

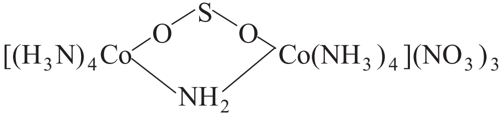
(x) $[Co(NH_3)_6][Cr(NH_3)_2Cl_4]$ (xi) $[Co(NH_3)_4Br_2]_2[ZnCl_4]$

(xii) $[Co(NH_3)_5CO_3]_2[CuCl_4]$ (xiii) $[Ag(NH_3)_2]_4[Fe(CN)_6]$

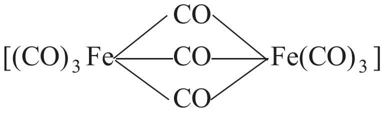
(xiv) $[Cr(en)_2Cl_2]_2[PdCl_4]$

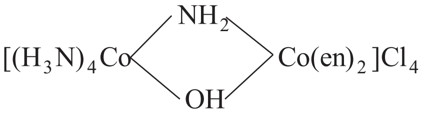
PROBLEM 1439 Name the following complexes according to IUPAC convention:

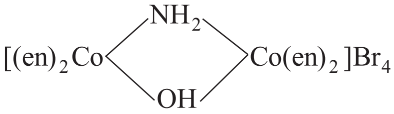
(i) $[(NH_3)_5CoNH_2Co(NH_3)_5](NO_3)_5$

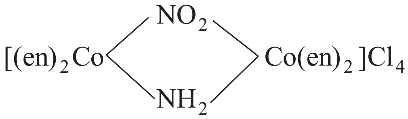
(ii) 

$[(H_3N)_4Co\underset{NH_2}{\overset{O\diagup S\diagdown O}{\quad}}Co(NH_3)_4](NO_3)_3$

(iii) 
$[(\mathrm{CO})_3\mathrm{Fe}\begin{smallmatrix}\mathrm{CO}\\ \mathrm{CO}\\ \mathrm{CO}\end{smallmatrix}\mathrm{Fe}(\mathrm{CO})_3]$

(iv) 
$[(\mathrm{H_3N})_4\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co(en)_2}]\mathrm{Cl_4}$

(v) 
$[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{OH}\end{smallmatrix}\mathrm{Co(en)_2}]\mathrm{Br_4}$

(vi) 
$[(\mathrm{en})_2\mathrm{Co}\begin{smallmatrix}\mathrm{NO_2}\\ \mathrm{NH_2}\end{smallmatrix}\mathrm{Co(en)_2}]\mathrm{Cl_4}$

Problem 1440 Write molecular formula of the following complexes:

(i) pentaaminebromocobalt (III) sulphate
(ii) dichlorobis(ethylendiamine) platinum (IV) sulphate.
(iii) tetrapyridineplatinum (II) tetrachloroplatinate (II).
(iv) potassium carbonylpentacyanoferrate (II).
(v) cesium pentafluorotellurate (IV)
(vi) triammine bromoplatinum (II) nitrate.
(vii) dichlorobis (ethylenediamine) cobalt (III) chloride monohydrate.
(viii) tetraquadibromochromium (III) chloride
(ix) ammonium heptafluorozirconate (IV)
(x) hexaammine nickel (II) hexanitrocobaltate (III).
(xi) dichlorobis (ethylenediamine) chromium (III) tetrachloropalladate (II).
(xii) aluminium tetrachloroacerate (III).
(xiii) Iron (III) hexacyanoberrate (II).

Problem 1441 Two complexes of cobalt have same molecular formula $\mathrm{Co(NH_3)_3(H_2O)_2ClBr_2} \cdot 34.15$ g of *A* loses 1.8 g of weight when heated to 200°C whereas no weight loss was observed on similar treatment with *B*. An aqueous solution of *A* has conductivity equivalent to that of a compound with two ions per formula unit while conductivity of *B* in aqueous solution is equivalent to a compound with three ions per formula unit. Also a 100 mL 0.1 M aqueous solution of *A*, on treatment with excess of $\mathrm{AgNO_3}$ solution produced 1.88 g of precipitate while a 100 mL 0.1 M aqueous solution of *B* on treatment with excess of $\mathrm{AgNO_3}$ solution produced 3.315 g precipitate. Identify *A* and *B*. (Atomic weight : Co = 59, Br = 80).

Problem 1442 A complex salt has molecular formula $\mathrm{Co(NH_3)_5SO_4Br}$ and exist in two isomeric forms *A* and *B*. An aqueous solution of *A* produced a white precipitate on treatment with $\mathrm{BaCl_2}$ solution while *B* did not produce any precipitate on similar treatment. *B* on treatment with aqueous $\mathrm{AgNO_3}$ produced a brown precipitate. Identify *A* and *B* and predict the type of isomerism being exhibited by them.

Problem 1443 An octahedral complex of platinum has molecular formula $\mathrm{Pt(NH_3)_4Cl_2 \cdot Br_2}$ and exist in two isomeric forms *A* and *B*. An aqueous solution of *A* containing 49.4 g of salt give 37.6 g of precipitate on treatment with excess $AgNO_3$ solution whereas an aqueous solution of *B* containing same amount of salt gave 28.7 g of precipitate on treatment with excess of $AgNO_3$ solution. Identify *A* and *B*. [Atomic mass : Pt = 195, Ag = 108, Br = 80].

Problem 1444 *A, B* and *C* are three complexes of chromium (iii) with their formula $H_{12}O_6Cl_3Cr$. Complex *A* does not react with concentrated H_2SO_4 solution whereas complexes *B* and *C* loses 6.75% and 13.5% of their weight, respectively, on treatment with concentrated H_2SO_4 solution. Deduce formula of *A, B* and *C*.

Problem 1445 An aqueous solution of titanium chloride, when subjected to magnetic measurement, measured zero magnetic moment. Deduce formula of complex assuming it to be octahedral in aqueous solution.

Problem 1446 A cobalt (ii) salt when dissolved in excess of concentrated HCl, it forms an octahedral complex whose magnetic moment was found to be 3.87 Bm. Predict shape of complex.

Problem 1447 How $[Co(NH_3)_6][Cr(NO_2)_6]$ and $[Co(NO_2)_6][Cr(NH_3)_6]$ can be distinguished by electrochemical method?

Problem 1448 How $[Cr(NH_3)_6][Cr(NO_2)_6]$ and $[Cr(NH_3)_4(NO_2)_2][Cr(NH_3)_2(NO_2)_4]$ can be distinguished from conductivity measurement in their aqueous solution?

Problem 1449 Two complexes of chromium have empirical formulae corresponding to $Cr(NH_3)_3(NO_2)_3$. In aqueous solution, one of these is non-conducting while other is electrolytic. What is the lowest possible formula weight of conducting reagent? What is the highest possible formula weight of non-conducting reagent?

Problem 1450 Write formula of all possible polymerization isomers of $Pt(NH_3)_2(NO_2)_2$.

Problem 1451 A metal complex having composition $Cr(NH_3)_4Cl_2Br$ has been isolated in two forms *A* and *B*. A reacts with $AgNO_3$ producing a white precipitate which was soluble in dilute ammonia solution. *B* reacts with $AgNO_3$ producing a pale-yellow precipitate soluble in concentrated ammonia solution. Write formula of *A* and *B* and state hybridization of chromium in each. Also calculate their magnetic moment (spin only).

Problem 1452 A metal complex having composition $Cr(NH_3)_4ClBr_2 \cdot H_2O$ has been isolated in three forms *A, B* and *C*. Heating 16.7 gram of either *A* or *C* loses 0.9 gram of its weight whereas no weight loss was observed on heating *B*. Adding 35.35 g of *A* to a concentrated solution of $AgNO_3$ resulted in 14.35 gram of precipitate whereas adding same amount of *C* to a concentrated $AgNO_3$ solution resulted in 18.8 g of precipitate. In another experiment, when 6.67 gram of complex *B* was added to a concentrated aqueous solution of $AgNO_3$, when 7.52 gram precipitate was formed. Deduce formula of complexes *A, B* and *C*.

Problem 1453 An octahedral complex of cobalt has its composition $Co(NH_3)_3(H_2O)_3(SO_4)(NO_3)$ and it exists in four isomeric forms *A, B, C* and *D*. Simple heating of either *A* or *B* loses 5.6% of its original weight whereas similar treatment on *C* causes 11.2% loss in its original weight *D* did not lose any weight on simple heating. Either *A* or *C* did not result in any precipitation if treated with aqueous $BaCl_2$ solution, whereas *B* and *D* resulted a white precipitate when treated with aqueous $BaCl_2$ solution. Also *C* does not conduct electricity in its aqueous solution. Deduce formula of *A, B, C* and *D*.

Problem 1454 An octahedral complex of platinum has its composition $Pt(NH_3)_4Cl_2Br_2$ and exist in three isomeric forms *A, B* and *C*. *A* 4.94 gram of compound *A* on treatment with excess of aqueous

$AgNO_3$ gave 3.76 g of precipitate. 2.47 gram of *B* on treatment with excess of $AgNO_3$ solution gave 1.66 gram of precipitate while 9.88 gram of *C* gave 5.74 gram of precipitate with aqueous $AgNO_3$. Deduce structural formula of *A, B* and *C*. (Atomic weight Pt = 195, Br = 80, Ag = 108)

PROBLEM 1455 A complex of cobalt has composition $Co(NH_3)_3(H_2O)_2ClBr_2$ and exist in two isomeric forms *A* and *B*. *A* on simple heating loses 5.3% of its weight whereas *B* does not lose any weight on simple heating. *A* on treatment with excess of $AgNO_3$ solution gives off precipitate that is 42% by mass of the complex. Similar treatment of *B* gives off another precipitate which is 110% by mass of the complex. Deduce structures of *A* and *B*.

PROBLEM 1456 A solution was prepared by dissolving 0.5 g $CrCl_3 \cdot 6H_2O$ in sufficient water and volume made upto 100 mL. A 10.0 mL position of this solution when treated with excess of $AgNO_3$, gave a precipitate, filtered dried and weighed to be 0.538 gram. Deduce structural formula of the complex.

PROBLEM 1457 A complex $[CoA_6]^{3+}$ is red coloured while $[CoB_6]^{3+}$ is green coloured.

(a) Which ligand produces the lager crystal field splitting.
(b) Which complex is expected to be more easily oxidised.

PROBLEM 1458 In which complex $[Cu(H_2O)_4]^{2+}$ or $[Cu(NH_3)_4]^{2+}$, are the bonds from acceptor to the donor atoms stronger?

PROBLEM 1459 Which complex is more stable $[Cr(NH_3)_6]^{3+}$ or $[Cr(en)_3]^{3+}$?

PROBLEM 1460 Why are complexes of Ti^{4+} and Zn^{2+} are typically white?

PROBLEM 1461 Accounts for the followings :

(a) $Ni(CN)_4^{2-}$ is diamagnetic but $[NiCl_4]^{2-}$ is paramagnetic.
(b) $[Ni(CO)_4]$ is tetrahedral
(c) $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

PROBLEM 1462 Why $[CuCl_4]^{2-}$ exist but $[CuI_4]^{2-}$ does not?

PROBLEM 1463 Both $Fe(CN)_6^{3-}$ and $Fe(H_2O)_6^{3+}$ are colourless in aqueous medium, explain.

PROBLEM 1464 Calculate the magnetic moment of $K_3[Mn(CN)_6]$ and $K_2[MnBr_4]$ and explain the geometries of these complexes.

PROBLEM 1465 Select the complexes which will absorb in visible range :

(a) $[Ti(H_2O)_6]Cl_3$ (b) $[VF_4]$ (c) $[Cu(NH_3)_4]^+$ (d) $[Cu(NH_3)_4]^{2+}$
(e) $[Ni(CN)_4]^{2-}$ (f) $[Ni(CO)_4]$

PROBLEM 1466 CoF_6^{3-} is paramagnetic while $Co(CN)_6^{3-}$ is diamagnetic, explain.

PROBLEM 1467 Use an orbital diagram to show the electron distribution in 3*d*-orbitals of the central metal ion in each of the following complex ion. If more than one distribution seems possible, indicate whether you expect low-spin or high-spin state to be favoured and determine spin-only magnetic moment.

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[FeCl_6]^{3-}$ (c) $[CoCl_4]^{2-}$ (d) $[Mn(CN)_6]^{3-}$

PROBLEM 1468 Of the following two complexes:
$[Cr(H_2O)_6]Cl_3$ and $[Cr(NH_3)_6]Cl_3$, one is yellow coloured while other is violet. Identify them.

PROBLEM 1469 Of the following two complexes :
$[Fe(H_2O)_6](NO_3)_2$ and $K_4[Fe(CN)_6]\cdot 3H_2O$, one is green coloured while other is yellow. Identify them.

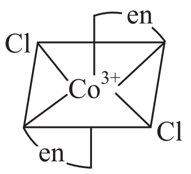
PROBLEM 1470 Explain why one of the *cis-trans* isomers of $[CoCl_2(en)_2]$ exhibit optical isomerism and other does not.

PROBLEM 1471 Would you expect to find optical isomerism in either of the hypothetical tetrahedral complexes : $[ZnA_2B_2]^{2+}$ and $[ZnABCD]^{2+}$? Explain.

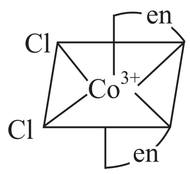
PROBLEM 1472 The complex $[Pt(NH_3)_2Cl_2]$ displays *cis-trans* isomerism but $[ZnCl_2(NH_3)_2]$ does not. Why do you suppose these two cases are different?

PROBLEM 1473 The magnetic properties of octahedral complex ion $[CrL_6]^{3+}$ are independent of identity of the ligand L. How do you account for this fact?

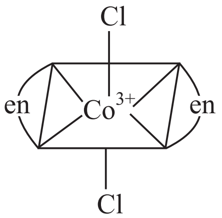
PROBLEM 1474 Four structures are shown in the accompanying sketch. Indicate whether any of these structures are identical, geometrical isomers or optical isomers:



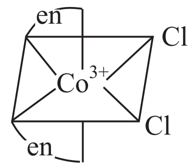
(a)



(b)



(c)



(d)

PROBLEM 1475 When ethylene diamine is added to a solution of cobalt chloride hexahydrate in concentrated HCl, a blue crystalline solid separate out. Analysis of this complex shows : $N = 14\%$, $C = 12\%, H = 5\%, Cl = 53.25\%$. The magnetic moment of the solution was found to be 3.9 Bm. Determine structural formula and shape of this complex.

PROBLEM 1476 Addition of $TiCl_3$ to an aqueous solution of urea followed by addition of KI gives a deep blue crystals of octahedral complex containing Ti, urea and iodine with this magnetic moment (spin-only) $= 1.76$ Bm. Also 1.0 g of this complex on heating in excess of oxygen gives 0.12 g TiO_2. Deduce structures of complex.

PROBLEM 1477 (a) Explain why dissolution of a chromium (III) salt produces an acidic solution?
(b) Explain why the slow addition of hydroxide ions to a solution of Cr(III) ions first produces a gelatinous precipitate that subsequently dissolves with further addition of hydroxide ion.

PROBLEM 1478 Name the following complex ions:
(a) $[Zr(OX)_4]^{4-}$ (b) $[CuCl_4(H_2O)_2]^{2-}$ (c) $[Pt(NH_3)Cl_3]^-$ (d) $[Mo(CN)_4(OH)_4]^{4-}$

PROBLEM 1479 By considering electronic configuration, suggest a reason why iron (III) compounds are readily prepared from iron (II), but conversions of Ni(II) and Co(II) to Ni(III) and Co(III) are much more difficult?

Problem 1480 Suggest a chemical test for distinguishing between:

(a) $[Ni(SO_4)(en)_2]Cl_2$ and $[NiCl_2(en)_2]SO_4$
(c) $[Ni(en)_2I_2]Cl_2$ and $[NiCl_2(en)_2]I_2$

Problem 1481 (a) Sketch the orbital energy-level diagrams for $[MnCl_6]^{4-}$ and $[Mn(CN)_6]^{4-}$. (b) Which complex is expected to transmits the longer wavelengths of incident electromagnetic radiations?

Problem 1482 The complex $[Co(CN)_6]^{3-}$ is pale yellow.

(a) Is short or long wavelength visible light absorbed?

(b) How many unpaired electrons are available?

(c) If ammonia molecules are substituted for cyanide ions as ligands, will the shift in absorbance of radiation be towards the blue or red region of electromagnetic radiation?

Problem 1483 Explain why high spin complex Mn^{2+} are only faintly coloured.

Problem 1484 The relative thermodynamic stability of two complexes can be predicted from a comparison of their standard potentials. Determine which complex of the following pair is the more stable?

$$\text{(i)} \qquad [Co(NH_3)_6]^{3+} + e \longrightarrow [Co(NH_3)_6]^{2+} \quad E^\circ = 0.11\,\text{V}$$

$$\text{(ii)} \qquad [Co(H_2O)_6]^{3+} + e \longrightarrow [Co(H_2O)_6]^{2+} \quad E^\circ = 1.81\,\text{V}$$

Problem 1485 (a) When excess of $AgNO_3$ is added to a 0.001 mol Cr(III) chloride, 0.001 mol AgCl is formed.

(b) When excess of $AgNO_3$ is added to a 0.001 mol Cr(III) chloride, 0.003 mol of AgCl is formed. Discuss the structure of complex based on above information.

Problem 1486 Identify the type of isomers represented by the following pairs :

(a) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$
(b) $[Cr(OH)_2(NH_3)_4]Br$ and $[CrBr(OH)(NH_3)_4]OH$
(c) $[Co(NCS)(NH_3)_5]Cl_2$ and $[Co(SCN)(NH_3)_5]Cl_2$
(d) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ and $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$

Problem 1487 Following is a chelating ligand called nitrilotriacetic (NTA) acid. It act as a tetradentate ligand. Sketch the structures of $[Co(NTA)(H_2O)_2]^{3+}$ ion and propose type of isomerism if present any : $N(CH_2COOH)_3$: Nitrilotriacetic acid.

Problem 1488 The complex shown below is called diethylenetriamine (dien) :

$$H_2\ddot{N}{-}CH_2CH_2{-}\ddot{N}H{-}CH_2CH_2{-}\ddot{N}H_2$$

(a) Sketch the structure of complex $[Co(dien)_2]^{3+}$

(b) Which complex would be expected to be more stable in aqueous solution, $[Co(dien)_2]^{3+}$ or $[Co(NH_3)_6]^{3+}$?

Problem 1489 Arrange the following complexes in order of increasing wavelength of visible light absorbed by them :

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[CrCl_6]^{3-}$ (c) $[Cr(en)_3]^{3+}$ (d) $[Cr(CN)_6]^{3-}$ (e) $[Cr(NH_3)_6]^{3+}$

PROBLEM 1490 Which complex should be expected to absorb light of highest frequency $[Cr(H_2O)_6]^{3+}$, $[Cr(en)_3]^{3+}$ or $[Cr(CN)_6]^{3-}$?

PROBLEM 1491 Which complex should absorb light at longer wavelength?

(a) $[Fe(OH_2)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$
(b) $[Mn(CN)_6]^{3-}$ or $[Mn(CN)_6]^{4-}$

PROBLEM 1492 Sketch the structures of the following complexes indicating any *cis-trans* or optical isomerism:

(a) $[Pt(H_2O)_2Br_2]$ square planar
(b) $[Pt(NH_3)(Py)(Cl)(Br)]$ square planar, Py = Pyridine
(c) $[Zn(NH_3)_3Cl]^+$
(d) $[Ni(H_2O)_4Cl_2]$
(e) $[Co(C_2O_4)_2Cl_2]^{3-}$

PROBLEM 1493 Draw diagrams for any *cis-trans* and optical isomers that could exist for the following complexes:

(a) $[Co(en)_2NO_2(Cl)]^+$
(b) $[Co(en)_2Cl_2]^+$
(c) $[Cr(NH_3)_2(H_2O)_2Br_2]^+$
(d) $[Pt(NH_3)_2Cl_4]$
(e) $[Cr(en)_3]^{3+}$

PROBLEM 1494 Determine the spin only magnetic moment:

(a) $[CoF_6]^{3-}$
(b) $[Co(en)_3]^{3+}$
(c) $[Mn(CN)_6]^{3-}$
(d) $[MnCl_6]^{4-}$

PROBLEM 1495 If trimethylphosphene is added to solution of Ni(II) chloride in acetone, a blue compound of molar mass 280 is isolated. This compound on analysis gave the following composition :

$$Ni = 21.5\%, \quad Cl = 26\%, \quad \text{and} \quad (CH_3)_3P = 52.5\%$$

This blue compound does not have any isomeric forms. What are the geometry and molecular formula of this blue complex? Also determine magnetic moment (spin-only) of the complex.

PROBLEM 1496 The complex $Na_2[Ni(CN)_2Br_2]$ has zero magnetic moment. Predict geometry and draw shape of the complex.

PROBLEM 1497 Draw all geometrical isomers of the following complexes:

(a) $[Co(NH_3)_2Cl_4]^-$
(b) $[Co(NH_3)_3Cl_3]$

PROBLEM 1498 Draw structures of all the geometrical and optical isomers of each of the following complex:

(a) $[Co(NH_3)_6]^{3+}$
(b) $[Co(NH_3)_5Cl]^{2+}$
(c) $[Co(C_2O_4)_3]^{3-}$

PROBLEM 1499 The $[Ni(CN)_4]^{2-}$ ion is diamagnetic while $[Ni(Cl)_4]^{2-}$ ion is paramagnetic. Explain with the help of crystal field splitting diagram.

PROBLEM 1500 Transition metal complexes containing cyanide (CN^-) ligands are often yellow in colour, whereas those containing H_2O ligands are often green or blue in colour. Explain.

PROBLEM 1501 The absorption maximum for complex ion $[Co(NH_3)_6]^{3+}$ occurs at 470 nm. Determine the crystal field splitting energy.

PROBLEM 1502 For each of the following pair, choose the complex that absorbs light of longer wavelengths.

(a) $[Co(NH_3)_6]^{3+}$ and $[Co(H_2O)_6]^{3+}$
(b) $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$
(c) $[Cu(NH_3)_4]^{2+}$ and $[CuCl_4]^{2-}$

PROBLEM 1503 A solution made by dissolving 0.875 g of compound $Co(NH_3)_4 \cdot Cl_3$ in 25 g of water freezes at $-0.56°C$. Deduce structural formula of complex if cryoscopic constant of water is $1.86 \text{ K kg mol}^{-1}$.

PROBLEM 1504 Oxalic acid $H_2C_2O_4$ is sometimes used to clean rust stains from bathtubs. Explain the chemistry underlying the cleaning action.

PROBLEM 1505 When aqueous potassium cyanide is added to a solution of Cu(II) sulphate, a white precipitate is formed in the beginning which dissolves on adding excess of reagent. No precipitate is formed when $H_2S(g)$ is bubbled through this solution at the point. Explain.

PROBLEM 1506 A concentrated aqueous copper (II) chloride solution is bright green in colour. When diluted with water, the solution becomes light blue. Explain.

PROBLEM 1507 In dilute nitric acid solution, Fe^{3+} forms a dark-red complex with thiocyanate ion (SCN^-) according to following reaction :

$$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons H_2O + [Fe(H_2O)_5NCS]^{2+}$$

In one experiment, 1.0 mL of 0.20 M $Fe(NO_3)_3$ was mixed with 1.0 mL of a 10^{-3} M KSCN solution and 8 mL dilute nitric acid was added. Final concentration of $[Fe(H_2O)_5(SCN)]^{2+}$ was found to be 7.3×10^{-5} M. Calculate formation constant of complex.

PROBLEM 1508 A student has prepared a cobalt complex that has one of the following three structures : $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$ or $[Co(NH_3)_4Cl_2]Cl$. Explain how the student would distinguish between these possibilities by an electrical conductance experiment. At the student's disposal are three strong electrolytes—NaCl, $MgCl_2$ and $FeCl_3$.

PROBLEM 1509 Aqueous solution of $CoCl_2$ are generally either light pink or blue. Low concentrations favour the pink form while high concentration favours blue form. Adding HCl to a pink solution of $CoCl_2$ causes the solution to turn blue; the pink colour is restored by addition of $HgCl_2$.Account for these observations.

PROBLEM 1510 Suggest a method that would allow you to distinguish between *cis*-$Pt(NH_3)_2Cl_2$ and *trans*-$Pt(NH_3)_2Cl_2$.

PROBLEM 1511 You are given two solutions containing $FeCl_2$ and $FeCl_3$ at same concentrations. One solution is light yellow and the other is brown. Identify these solutions based on their colours.

Solutions

COORDINATION COMPOUNDS

1437. (i) hexaamminecobalt (III) chloride.
(ii) pentaamminechlorocobalt (III) ion.
(iii) tetraamminesulphatocobalt (III) nitrate.
(iv) potassium pentachloronitridoosmate (VI).
(v) sodium dithiosulphatoargentate (I).
(vi) potassium amminedicyanodioxoperoxochromate (VI).
(vii) pentaamminenitrito irridium (III) chloride.
(viii) potassium tetrachloroplumbate (II).
(ix) copper (II) potassium hexacyanocobaltate (III).
(x) potassium hexacyanoaurate (III).
(xi) lithium tetrahydrido aluminate (III).
(xii) sodium tetrahydridoborate (III).
(xiii) sodium hexafluoroaluminate (III).
(xiv) tetraaquadichlorocobalt (III) chloride dihydrate.

1438. (i) hexaammine chromium (III) hexaisothiocyanatochromate (III).
(ii) tetraammine copper (II) tetrachloroplatinate (II).
(iii) tetraammine platinum (II) tetrachloroplatinate (II).
(iv) hexaammine cobalt (III) tetracyanonickelate (II).
(v) tetraammine dichloroplatinum (IV) tetrachloroplatinate (II).
(vi) hexaammine cobalt (III) hexanitrocobaltate (II).
(vii) pentaamminenitrochromium (II) hexanitrochromate (II).

(viii) tetrapyridylplatinum (II) tetrachloroplatinate (II).
(ix) hexaammine nickel (II) hexanitrocobaltate (III).
(x) hexammine cobalt (II) diamminetetrachlorochromate (II).
(xi) tetraammine dibromocobalt (III) tetrachlorozincate (II).
(xii) pentaammine carbonatocobalt (III) tetrachlorocuperate (II).
(xiii) diammine silver (I) hexacyanoferrate (II).
(xiv) dichlorobis(ethylenediamine) chromium (III) tetrachloro palladate (II).

1439. (i) μ-amidobis (pentaammine cobalt (III)) nitrate.
(ii) μ-amido-μ-sulphurdioxide bis (tetraammine cobalt (II)) nitrate.
(iii) tri-μ-carbonyl bis (tricarbonyl iron (0)).
(iv) μ-amido-μ-hydroxotetraammine cobalt (III) bis(ethylenediamine) cobalt (III) chloride.
(v) μ-amido-μ-hydroxo dibis(ethylenediamine) cobalt (III) bromide.
(vi) μ-amido-μ-nitro dibis (ethylenediamine) (cobalt (III)) chloride.

1440. (i) $[Co(NH_3)_5Br]SO_4$ (ii) $[Pt(en)_2Cl_2]SO_4$ (iii) $[Pt(Py)_4][PtCl_4]$
(iv) $K_3[Fe(CN)_5(CO)]$ (v) $Cs[TeF_5]$ (vi) $[Pt(NH_3)_3Br]NO_3$
(vii) $[Co(en)_2Cl_2]Cl \cdot H_2O$ (viii) $[Cr(H_2O)_6Br_2]Cl$ (ix) $(NH_4)_3[ZrF_7]$
(x) $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$ (xi) $[Cr(en)_2Cl_2]_2[PtCl_4]$ (xii) $Al[AuCl_4]_3$
(xiii) $Fe_4[Fe(CN)_6]_3$

1441. A : $[Co(NH_3)_3(H_2O)ClBr]Br \cdot H_2O$; B : $[Co(NH_3)_3(H_2O)_2Br]Cl \cdot Br$

1442. A : $[Co(NH_3)_5Br]SO_4$, B : $[Co(NH_3)_5SO_4]Br$, Ionization isomerism.

1443. A : $[Pt(NH_3)_4Cl_2]Br$ B : $[Pt(NH_3)_4Br_2]Cl_2$

1444. A : $[Cr(H_2O)_6]Cl_3$, B : $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, C : $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$.

1445. $[Ti(H_2O)_6]Cl_4$

1446. $[CoCl_6]^{4-}$, octahedral, sp^3d^2-hybridization, an outer orbital complex.

1447. In case of $[Co(NH_3)_6][Cr(NO_2)_6]$, cobalt will be discharged at cathode while with $[Co(NO_2)_6][Cr(NH_3)_6]$, chromium will be discharged at cathode.

1448. $[Cr(NH_3)_6][Cr(NO_2)_6]$ will have lower conductivity due to larger hydrated radius.

1449. Conducting reagent : dimer 482, non-conducting reagent : monomer 241.

1450. $[Pt(NH_3)_4][Pt(NO_2)_4]$ and $[Pt(NH_3)_3(NO_2)][Pt(NO_2)_3NH_3]$ only.

1451. A : $[Cr(NH_3)_4BrCl]Cl$ B : $[Cr(NH_3)_4Cl_2]Br$

1452. A : $[Cr(NH_3)_4Br_2]Cl \cdot H_2O$ B : $[Cr(NH_3)_4BrCl] \cdot Br \cdot H_2O$ C : $[Cr(NH_3)_4(H_2O)Cl]Br_2$.

1453. A : $[Co(NH_3)_3(H_2O)_2SO_4]NO_3 \cdot H_2O$, B : $[Co(NH_3)_3(H_2O)_2NO_3]SO_4 \cdot H_2O$
C : $[Co(NH_3)_3(H_2O)(NO_3)(SO_4)] \cdot 2H_2O$ D : $[Co(NH_3)_3(H_2O)_3]SO_4 \cdot NO_3$.

1454. A : $[Pt(NH_3)_4Cl_2]Br_2$ B : $[Pt(NH_3)_4ClBr]BrCl$ C : $[Pt(NH_3)_4Br_2]Cl_2$

1455. A : $[Co(NH_3)_3(H_2O)Br_2]ClH_2O$, B : $[Co(NH_3)_3(H_2O)_2Cl]Br_2$

1456. $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$

1457. (a) Red is complement colour of green wavelength and *vice-versa*. Hence, ligand *B* is producing smaller crystal field splitting.
(b) $[CoA_6]^{3+}$

1458. $[Cu(NH_3)_4]^{2+}$ **1459.** $[Cr(en)_3]^{3+}$

1460. Due to lack of *d-d*-electronic transition.

1461. (a) CN^- is a strong ligand, $d^8(Ni^{2+})$ has all paired electrons in $Ni(CN)_4^{2-}$, while Cl^- is a weak ligand $Ni^{2+}(d^8)$ has two unpaired electrons.

(b) Ni has d^{10}-configuration in $Ni(CO)_4$ and complex is tetrahedral.

(c) Ni in $[Ni(NH_3)_6]^{2+}$ is sp^3d^2-hybridized.

1462. Iodide ion being a strong reducing agent, reduces Cu^{2+} to Cu^+.

1463. Weak ligand field of H_2O gives five unpaired electrons in *d*-orbitals of Fe in $Fe(H_2O)_6^{3+}$ and no electronic transition from one *d*-orbital to other *d*-orbital can occur.

On the otherhand, CN^- being a very strong ligand, gives a very large crystal field splitting and electronic transition from one *d*-level to other require photons of high energy and absorption occur in UV-region.

1464. $K_3[Mn(CN)_6] : \mu = 2.82$ Bm. Octahedral, inner orbital complex.

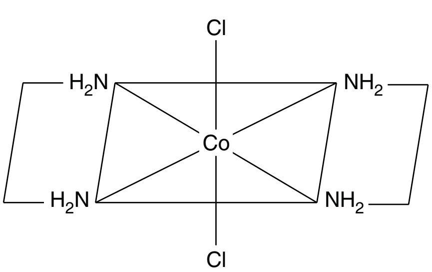
$K_2[MnBr_4] : \mu = 5.92$ Bm, tetrahedral.

1465. (a), (b), (d), (e)

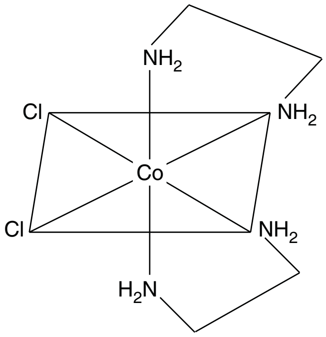
1466. F^- is a weak ligand, forms high spin complex and CoF_6^{3-} has four unpaired electrons in *d*-orbital.

CN^- is a strong ligand and all six electrons in the *d*-orbital of Co^{3+} in $Co(CN)_6^{3-}$ are paired.

1470. The trans-isomer of $[CoCl_2(en)_2]$ possess a plane of symmetry and hence, does not show optical isomerism while cis form is devoid of any symmetry, it shows optical isomerism.

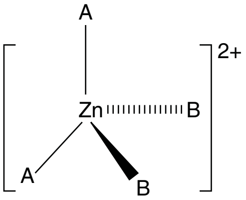


trans $[CoCl_2(en)_2]$
(has plane of symmetry)

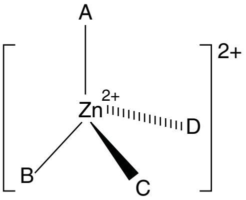


Cis $[CoCl_2(en)_2]$

1471. Complex $[ZnA_2B_2]^{2+}$ will be superimposable on its mirror image due to presence of plane of symmetry while $[ZnABCD]^{2+}$ is optically active.

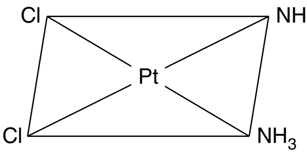


Possess plane of Symmetry

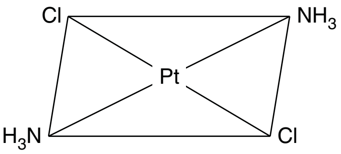


Devoid of Symmetry
(Optically active)

1472. $[Pt(NH_3)_2Cl_2]$ is a square planar complex, therefore, show *cis-trans* isomerism as shown below :



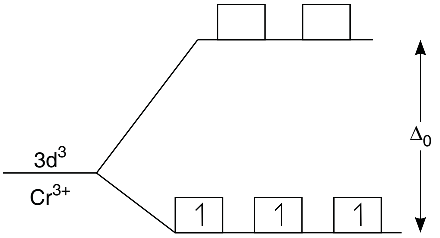
Cis



Trans

On the other hand $[Zn(NH_3)_2Cl_2]$ is tetrahedral and all the positions around metal are equivalent, therefore, no *cis-trans* isomerism is observed.

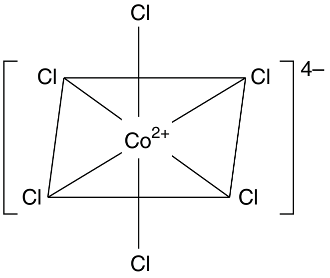
1473. In octahedral complex $[CrL_6]^{3+}$, Cr^{3+} has $3d^3$ configuration. The splitting pattern and electron filling in *d*-orbital of Cr^{3+} can be shown as:



The nature of ligand will affect the (Δ_0) value but not the electronic configuration in the lower level of *d*-orbital. Therefore, magnetic properties, which depends on number of unpaired electrons with central metal, will not be affected by identity of ligand.

1474. "*a*" and "*c*" are identical and both are *trans* isomers. "*b*" and "*d*" are pair of enantiomers and both are *cis*-isomer.

1475. The complex is $[CoCl_6](C_2H_{10}N_2)_2$ and it is octahedral.



1476. The complex has formula $[Ti(H_2NCONH_2)_4I_2]I$.

1477. (a) Cr^{3+} hydrolyses in water according to the following reaction:

$$Cr^{3+} + H_2O \rightleftharpoons Cr(OH)^{2+} + H^+$$

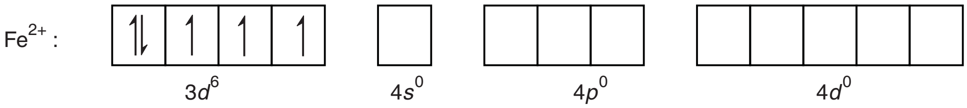
In the above reaction, H^+ is produced which impart acidic nature to the solution.

(b) As OH^- is added, a gelatinous precipitate of $Cr(OH)_3$ is produced at first instant which dissolves on adding excess of OH^- due to formation of complex $[Cr(OH)_6]^{3-}$ as:

$$Cr^{3+} + 3OH^- \longrightarrow Cr(OH)_3\downarrow \xrightarrow{3OH^-} [Cr(OH)_6]^{3-}(aq)$$

1478. (a) tetraoxalatozirconate (IV) ion (b) diaquatetrachlorocupperate (II) ion
(c) amminetrichloroplatinate (II) ion (d) tetracyanotetrahydroxomolybedate (IV) ion

1479. Electronic configuration of Fe(II) is



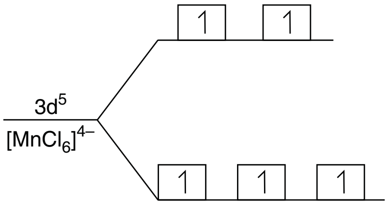
Here Fe^{2+} is readily converted into Fe^{3+} ($3d^5$) due to the reason that Fe^{2+}, after losing an extra electron yields a stable electronic configuration : $3d^5$ where the $3d$-orbital is completely half-filled.

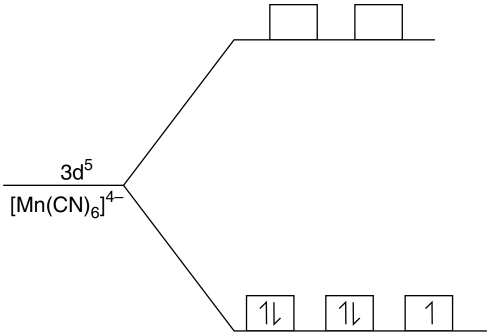
With Ni(II) ($3d^8$) and Co(II) ($3d^7$), no such stable electronic configuration is formed after removing an extra electron from the $3d$-orbitals, therefore, formation of Ni(III) and Co(III) from Ni(II) and Co(II) respectively are very difficult.

1480. (a) An aqueous solution of $[Ni(SO_4)(en)_2]Cl_2$ which produce precipitate with $AgNO_3$ solution and it will not give any precipitate with aqueous $BaCl_2$ solution. However, aqueous solution of $[NiCl_2(en)_2]SO_4$ will form a precipitate with $BaCl_2$.

(b) Aqueous solution of $[Ni(en)_2I_2]Cl_2$ will form a white precipitate with aqueous $AgNO_3$ solution which will be soluble in excess of ammonia solution. However, aqueous solution of $[NiCl_2(en)_2]I_2$ will form an yellow precipitate of AgI which will be insoluble in concentrated ammonia solution.

1481. (a) In $[MnCl_6]^{4-}$, Mn^{2+} has $3d^5$ configuration. Since, Cl^- is a weak ligand, there will be smaller crystal-field splitting. In $[Mn(CN)_6]^{4-}$, Mn^{2+} has again $3d^5$ configuration, but now CN^- is a strong ligand, there will be larger crystal-field splitting as:

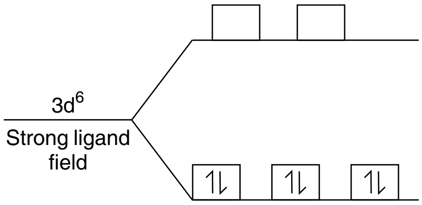




(b) Since, strong ligand field absorb shorter wavelength light, therefore, $[Mn(CN)_6]^{4-}$ will transmits longer wavelengths.

1482. (a) Since, the complex is emitting long wavelength (yellow) light, short wavelength visible light would have been absorbed. This is also evident from the high strength ligand field given by strong ligands-cyanide ion.

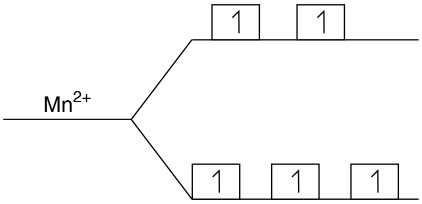
(b) In $[Co(CN)_6]^{3-}$, Co is in $3d^6$ state and ligand is strong, there is no unpaired electrons as:



No unpaired electron, complex is diamagnetic

(c) If NH_3 molecules are substituted for cyanide ions, complex will absorb long wavelength visible light and the shift in absorbance will be towards red region of the spectrum. This is due to the fact that NH_3 is a weaker ligand than CN^-.

1483. In high spin complex of Mn^{2+} ($3d^5$), all the electrons are occupying singly the five-*d*-orbitals as:



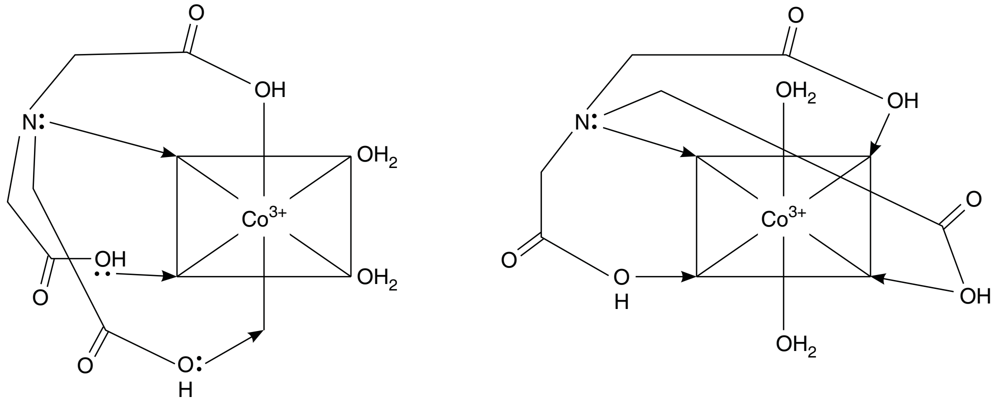
As evident from the above orbital energy diagram for Mn^{2+}, electron transition is not allowed from lower level to higher level since, any electronic transition from low energy level to high energy level will violate "Pauli Exclusion Principle". Therefore, complex of Mn^{2+} is very faintly coloured.

1484. For a spontaneous reaction $\Delta G^\circ < 0$, *i.e.*, $E^\circ > 0$. In the above example, both the reduction reactions are spontaneous. Also reduction potential of reaction (II) is more positive, corresponding ΔG° will be more negative, reaction will be more spontaneous. Therefore, $[Co(NH_3)_6]^{3+}$ is more stable and $[Co(H_2O)_6]^{3+}$ is more reactive.

1485. (a) $[Cr(H_2O)_4Cl_2]Cl$ (b) $[Cr(H_2O)_6]Cl_3$.

1486. (a) Coordination, (b) Ionization, (c) Linkage, (d) Hydrate.

1487.

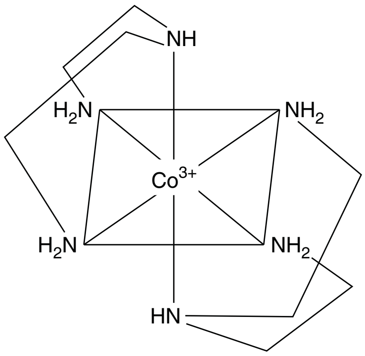


Cis isomer

Trans isomer

Nitrilotriacetic acid [:N($CH_2COOH)_3$]

1488. (a)



1489. Weaker the ligand field strength, smaller will be the crystal field splitting and longer will be the wavelength of absorption. Hence :

$$[Cr(CN)_6]^{3-} < [Cr(en)_3]^{3+} < [Cr(NH_3)_6]^{3+} < [CrCl_6]^{3-} < [Cr(H_2O)_6]^{3+}$$

1490. Stronger the ligand field, greater will be the crystal field splitting and hence, higher will be the frequency of light to be absorbed. Hence, order of frequency of light absorbed by these complexes is :

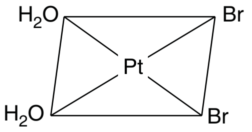
$$[Cr(H_2O)_6]^{3+} < [Cr(en)_3]^{3+} < [Cr(CN)_6]^{3-}$$

1491. (a) Stronger the ligand field, greater will be crystal field splitting, smaller will be the wavelength of light absorbed.

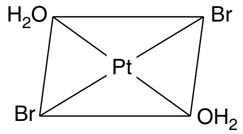
$$\Rightarrow \qquad \lambda : [Fe(CN)_6]^{4-} < [Fe(H_2O)_6]^{2+}$$

(b) Higher the oxidation state of central metal, greater will be the crystal field splitting. Hence, there will be greater crystal field splitting of *d*-orbitals in Mn(III) complex compared to that in Mn(II) complex. Hence, $[Mn(CN)_6]^{4-}$ will absorb at longer wavelength (low energy photons) than $[Mn(CN)_6]^{3-}$.

1492. (a)

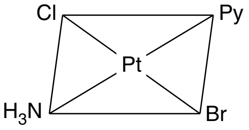


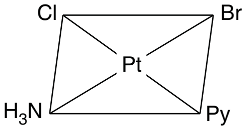
Cis

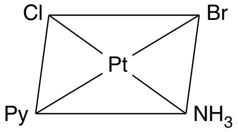


Trans

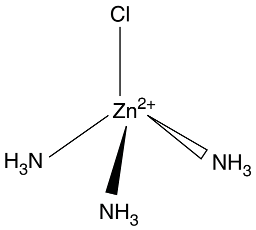
(b)



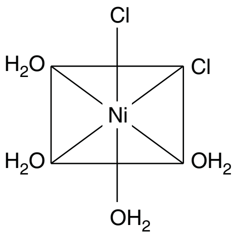




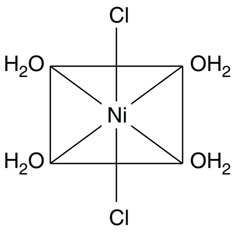
(c) Zn^{2+} has tetrahedral arrangement of ligands around it :



(d)

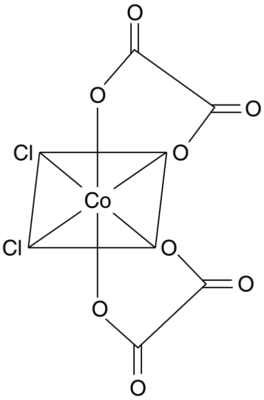


Cis

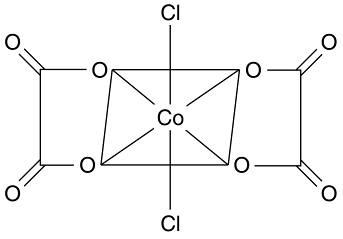


trans

(e)

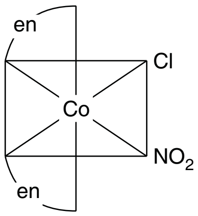


Cis
(Optically active)

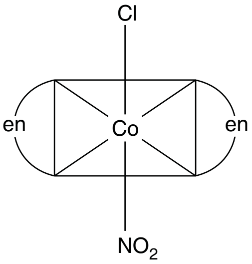


trans

1493. (a)

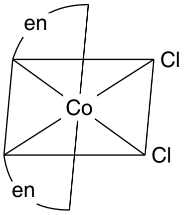


(enantiomeric)

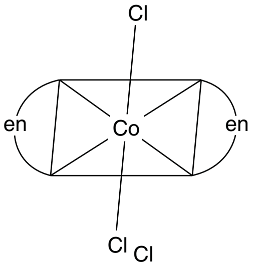


(trans)

(b)

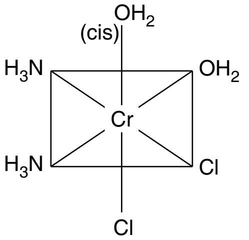


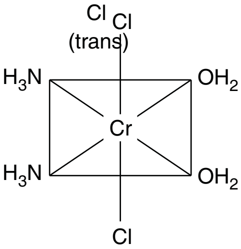
(cis)

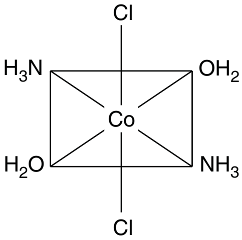


(trans)

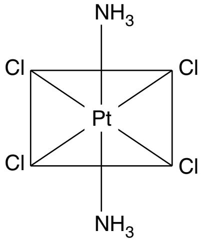
(c)

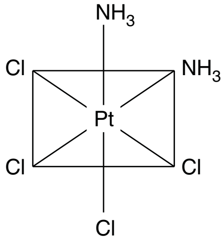




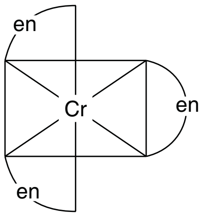


(d)





(e)



1494. Co(III) $= 3d^6$, weak ligand, magnetic moment $= \sqrt{4 \times 6} = \sqrt{24}$ BM $= 4.9$ BM.

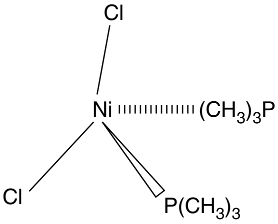
(b) $Co^{3+} : 3d^6$, magnetic moment $= 0$; *en* is a strong ligand.

(c) $Mn^{3+} (3d^4)$ and CN^- strong ligand, two unpaired electron, $\mu = \sqrt{8}$ BM $= 2.82$ BM.

(d) $Mn^{2+} (3d^5)$ and Cl^- is a weak ligand, $\mu = \sqrt{5 \times 7}$ BM $= 5.916$ BM

1495. $NiCl_2 + (CH_3)_3P \longrightarrow$ Compound

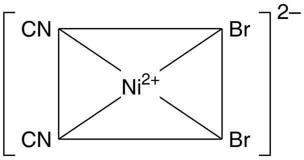
From elemental composition, empirical/molecular formula $= [NiCl_2((CH_3)_3P)_2]$. Since, it has no isomeric forms, complex must be tetrahedral :



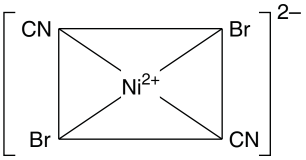
bis (trimethyl phosphine) dichloronickel (II)

Magnetic moment : $Ni^{2+} (3d^8)$ and sp^3 hybridization indicate presence of two unpaired electrons, hence, $\mu = \sqrt{8} = 3.82$ BM.

1496. Zero magnetic moment indicate that there is no unpaired electron and complex is square planar (dsp^2 hybridized Ni).

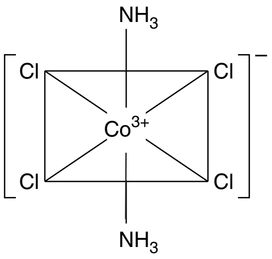


Cis

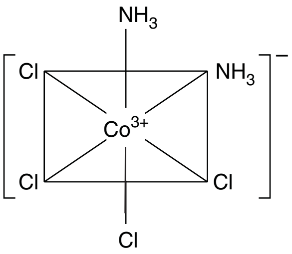


trans

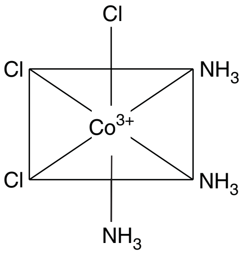
1497. (a)



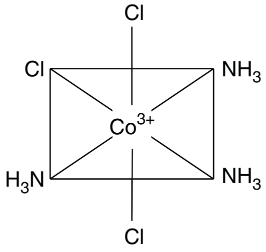
trans



(b)



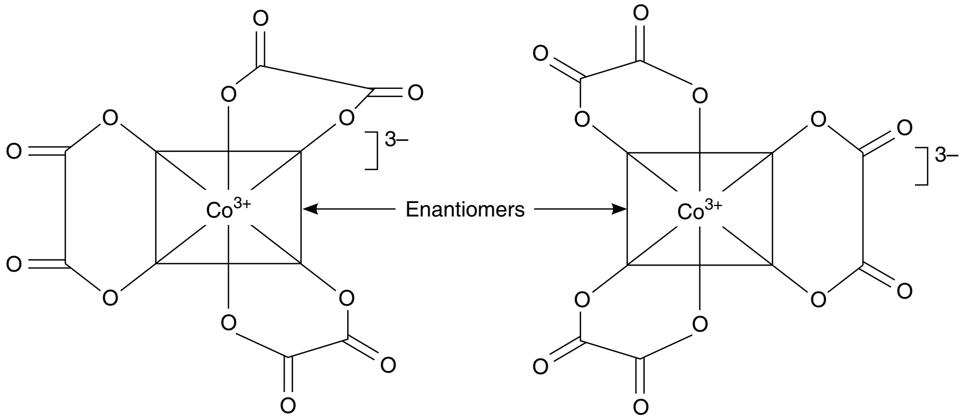
(Facial)



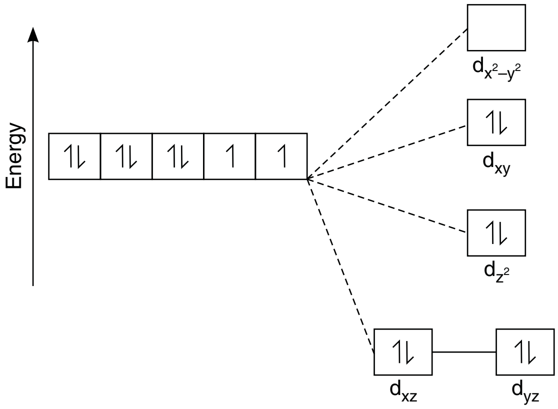
(Meridional)

1498. (a) No isomers (b) No isomers.

(c)

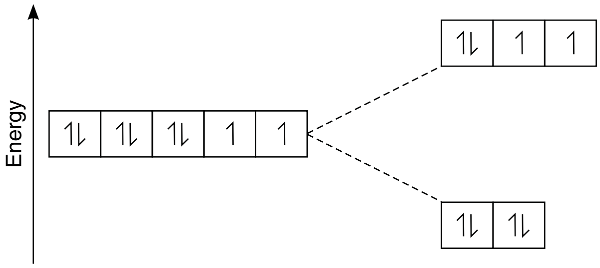


1499. Cyanide ion is a strong ligand and in $3d^8$ (Ni^{2+}) it gives square planar geometry:



$[Ni(CN)_4]^{2-}$ crystal field splitting.

There is no unpaired electron, complex is diamagnetic.
Chloride ion is weak ligand, in $3d^8$ (Ni^{2+}), it produces tetrahedral ligand field.



$[NiCl_4]^{2-}$ crystal field splitting.

There are two unpaired electrons and complex is paramagnetic.

$$\mu = \sqrt{8}\ \text{BM} = 2.82\ \text{BM}.$$

1500. When a substance absorbs a particular colour when bathed in white light, the perceived colour of the reflected or transmitted light is the complementary colour. Also, wavelengths of absorbed and transmitted lights are inversely related.
Cyanide ion being stronger ligand than H_2O, former absorbs light of shorter wavelength than later and wavelengths of transmitted light is longer for cyanide ion (yellow) and shorter for H_2O (blue or green).

1501. The crystal field splitting energy is equal to the energy of photon causing absorption maximum.

$$\Rightarrow \qquad \Delta = \frac{hc}{\lambda} = \frac{6.625\times10^{-34}\times3\times10^{8}}{470\times10^{-9}} = 4.23\times10^{-19}\ \text{J}$$

1502. Stronger the ligand field, shorter the wavelengths of photon absorbed.
(a) $[Co(H_2O)_6]^{3+}$ (b) $[FeF_6]^{3-}$ (c) $[CuCl_4]^{2-}$

1503. $-\Delta T_f = 0.56 = i\times1.86\times\frac{0.875}{233.5}\times\frac{1000}{25}$; i = vant Hoff's factor
$\Rightarrow i = 2$. Hence, formula of complex is $[Co(NH_3)_4Cl_2]Cl$.

1504. Rust consists of mixture of $Fe(OH)_3$ and $Fe_2O_3\cdot nH_2O$. Oxalic acid, being a bidentate, chelating, strong ligand, forms stable complex with iron, removing rust as:

$$Fe^{3+} + 3C_2O_4^{2-} \longrightarrow [Fe(C_2O_4)_3]^{3-}$$

1505. $$Cu^{2+} + 2CN^- \longrightarrow \underset{\text{White}}{Cu(CN)_2}\downarrow \xrightarrow[\text{excess}]{CN^-} \underset{\text{Soluble}}{Cu(CN)_4^{2-}}$$

The complex $Cu(CN)_4^{2-}$ is highly stable and it ionizes very feebly as:

$Cu(CN)_4^{2-} \rightleftharpoons Cu^{2+} + 4CN^-$: K_d is very small and equilibrium lies predominantly to left side.

If H_2S gas is bubbled at this time, no precipitate of CuS is formed due to presence of very small amount of Cu^{2+} ion in the solution (less than required to exceed the solubility limit).

1506. The initial green colouration is due to presence of $[CuCl_4]^{2-}$ in concentrated solution. On dilution, solution turned blue due to conversion of $[CuCl_4]^{2-}$ into $[Cu(H_2O)_6]^{2+}$.

1507. K_f (Formation constant)

$$= \frac{[Fe(H_2O)_5NCS]^{2+}}{[Fe(H_2O)_6]^{3+}[SCN^-]} = \frac{7.3\times10^{-5}}{(0.2)\,(10^{-3} - 7.3\times10^{-5})} = 0.393$$

1508. Electrical conductance of electrolyte depends on number of ions available. By comparison with the conductance of standard electrolyte, nature of unknown electrolyte can be established. In the given experiment, conductance of unknown will match as :
$[Co(NH_3)_6]Cl_3 = FeCl_3, [Co(NH_3)_5Cl]Cl_2 = MgCl_2$ and
$[Co(NH_3)_4Cl_2]Cl = NaCl$.

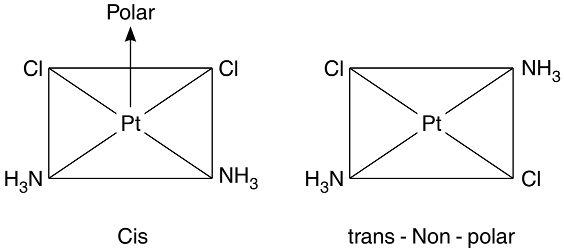
1509. $CoCl_2$ at low concentration appear pink coloured due to its existence as $[Co(H_2O)_6]Cl_2$. On adding HCl, following reaction occurs :

$$[Co(H_2O)_6]Cl_2 + HCl \longrightarrow \underset{\text{blue-coloured}}{[Co(Cl)_6]^{4-}}$$

Adding $HgCl_2$, pink colour is restored due to the following reaction:

$$[CoCl_6]^{4-} + HgCl_2 + H_2O \longrightarrow \underset{\text{pink}}{[Co(H_2O)_6]^{2+}} + \underset{\text{colourless}}{[HgCl_4]^{2-}}$$

1510. The complex is square planar and exhibit *cis*-trans isomerism in which *cis*-form is polar while *trans*-form is non-polar. Dipole moment measurement can allow distinction between these two forms :



1511. Both solutions contain hydrated iron $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ ions. Higher the oxidation state of transition metal, greater will be the crystal field splitting and shorter will be the absorption wavelength. The wavelength of emitted light is inversely related to absorption wavelength. On this basis, transmitted light from $[Fe(H_2O)_6]^{3+}$ will have longer wavelength-will appear yellow, while $[Fe(H_2O)_6]^{2+}$ solution will be brown. This can also be explained on the basis of electronic configurations :

Fe^{3+} $(3d^5)$ and weak ligand field, completely half-filled *d*-orbital. Difficult *d*-*d*-transitions.

Fe^{2+} $(3d^6)$ and weak ligand field, less than full-filled *d*-orbital, easier *d*-*d*-transition.