1. What are the geometries of the following two complexes?
(i) $[AlCl_4]^-$
(ii) $[Ag(NH_3)_2]^+$
Ans. tetrahedral, linear

2. What is the respective central-metal oxidation state, coordination number, and the overall charge on the complex ion in $NH_4[Cr(NH_3)_2(NCS)_4]$?
Ans. +3; 6; 1-

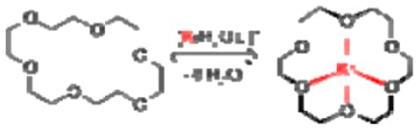
3. The formula for lithium iodotris(trifluorophosphine)nickelate(0) is: (Note: trifluorophosphine is a neutral ligand with the formula $PF_3$.)
Ans. $Li[Ni(PF_3)_3I_3]$

4. Which is more likely to form a high-spin complex—*en*, $F^-$, or $CN^-$?

Ans. $F^-$

5. Name the following compound: $K_2[CrCO(CN)_5]$.
Ans. potassium carbonylpentacyanochromium(III)

6. What is macrocyclic effect?
Ans. Macrocyclic ligands of appropriate size form more stable complexes than chelate ligands. A competition between a noncyclic chelating ligand and a macrocyclic (chelating) ligand having the same number and type of donor atoms will generally lead to complex formation predominantly by the macrocyclic ligand. This is known as the macrocyclic effect.



The entropy term drives this type of reaction to the right. The long noncyclic ligand is more flexible than the corresponding macrocyclic ligand and can adopt many more conformations than the macrocyclic ligand when it is not coordinated.

7. Predict the no. of unpaired electrons, the spin-only magnetic moments at 25 °C for

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each of the following.

a) $[Fe(CN)_6]^{4-}$

b) $[Ru(NH_3)_6]^{3+}$

c) $[Cr(NH3)6]^{2+}$

d) $[EuCl_6]^{4-}$

Ans. a) $Fe^{2+}$ is $3d^6$. Has 0 unpaired electron in l.s. complexes and thus the magnetic moment would be close to 0 $\mu_B$.

b) $Ru^{3+}$ is $4d^5$. Has 1 unpaired electron in l.s. complexes and thus the magnetic moment would be close to 1.73 $\mu_B$.

c) $Cr^{2+}$ is $4d^4$. Have 4 and 2 unpaired electrons in h.s. and l.s. complexes and thus the magnetic moment would be close to 4.90 and 2.83 $\mu_B$, respectively.

d) $Eu^{2+}$ is $4f^7$. Has 7 unpaired electrons in h.s. complexes and thus the magnetic moment would be close to 7.94 $\mu_B$. The magnetic moments deviate considerably from the spin-only values because of strong spin-orbit coupling. The f-orbitals have so little overlap and interactions with ligand orbitals.

8. With reference to the 3d elements in the periodic table identify the elements and associated oxidation numbers that form square planar complexes. Give formulas for three examples of such complexes.

Ans. The square-planar geometry is primarily associated with the $d^8$ electron configuration, and the following elements and oxidation states commonly form the $d^8$ configuration:

| 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | $Ni^{2+}$ | | |
| | | | | | | $Rh^+$ | $Pd^{2+}$ | | |
| | | | | | | $Ir^+$ | $Pt^{2+}$ | $Au^{3+}$ | |

Examples of such complexes: $RhCl(PPh_3)_3$, $IrCl(CO)(PPh_3)_2$, $Ni(CN)_4^{2-}$, $PdCl_4^{2-}$, cis- and trans-$PtCl_2(NH_3)_2$ and $AuCl_4^-$. Note however that $NiCl_4^{2-}$ is not square planar, but is instead tetrahedral. In general, the preference for square planar vs. tetrahedral increases with increasing ligand field strength; the ligand fields for the 2nd and 3rd transition series are intrinsically larger than for the first series metals. Note however, that $Ni(CO)_4$ is also tetrahedral, not square planar, but that is because this complex is d10, rather than $d^8$!

9. Sketch the two structures that describe most six-coordinate complexes. Which is more common?

Ans. Octahedral Trigonal prismatic

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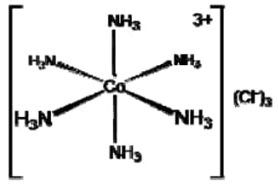
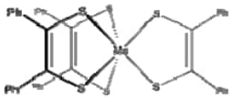
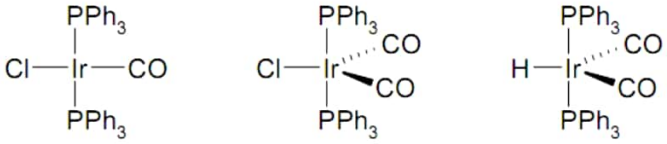




Hexamminecobalt(III) chloride

Trigonal prismatic is an extremely rare geometry, but octahedral is extremely common.

10. The compound $Na_2IrCl_6$ reacts with triphenylphosphine in diethylene glycol under an atmosphere of CO to give *trans*-$[IrCl(CO)(PPh_3)_2]$, known as Vaska's compound. Excess CO produces a five-coordinate species and treatment with $NaBH_4$ in ethanol gives $[IrH(CO)_2(PPh_3)_2]$. Draw and name the three complexes.
Ans.




Names, in oder: Carbonylchlorobis(triphenylphosphine)iridium(I), Dicarbonylchlorobis(triphenylphosphine)iridium(I), and Carbonylhydridobis(triphenylphosphine)iridium(I).

11. Which of the following complexes are chiral? (a) $[Cr(ox)_3]^{3-}$; (b) *cis*-$[PtCl_2(en)]$; (c) *cis*-$[RhCl_2(NH3)_4]^+$; (d) $[Ru(bipy)_3]^{4+}$; (e) $[Co(edta)]^-$; (f) *fac*-$[Co(NO_2)_3(dien)]$; (g) *mer*-$[Co(NO_2)_3(dien)]$. Identify the enantiomers as chiral and achiral complexes.
Ans. (a) $[Cr(ox)_3]^{3-}$ It is definitely chiral; two chelating ligands on an octahedral framework are sufficient do impart chirality to the complex. The two enantiomers provide the left and right of a plane of reflection.
(b) *cis*-$[PtCl_2(en)]$ This molecule would be chiral because of the twist in the en ligand. However, ring inversion in chelate complexes of this type (as in cyclopentane) is very fast at room temperature and well below, so that enantiomers cannot be isolated, and the complex is normally considered to be achiral.
(c) *cis*-$[RhCl_2(NH_3)_4]^+$ This complex is achiral. It has C2v symmetry, and thus has two internal mirror planes, which can be clearly seen in the picture of the molecule, one virtical and one horizontal to the page. Note that the symmetry requires the ammine ligands to be in a specific orientation. In practice, the Rh—N bonds rotate sufficiently fast that the ammine ligands are effectively spherical, so the molecule definitely acts as a $C_{2v}$ species.

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(d) $[Ru(bipy)_3]^{4+}$ This is another example of a tris chelate complex, and therefore will be both chiral and easily resolvable. The stucture is shown with its non-superimposible mirror image below (H atoms omitted for clarity).
(e) $[Co(edta)]^-$ When EDTA chelates a metal such that all six donor atoms coordinate (the most common, but not the only way that this ligand attaches to metals) then the resulting complexes are chiral. The non-superimposable mirror images impart chirality in the system.
(f) *fac*-$[Co(NO_2)_3(dien)]$ (note typo in question!) and (g) *mer*-$[Co(NO_2)_3(dien)]$. If one ignores the conformations of the chelate rings, the complexes are not chiral. The chelates are ethylenediamine linkages, and as discussed for (b) above, such rings interconvert too rapidly to allow the separation of enantiomers of these complexes. The facial isomer has an internal plane of symmetry that includes the central N of dien, the metal and one of the nitro groups. The meridional isomer has a plane through the dien ligand and the metal (as well as one through the metal and the three nitro N atoms.) These planes are vertical to the paper through the middle of the molecules.

12. What is the coordination number of the Fe atom is $K_3[Fe(C_2O_4)_3]$?
Ans. The coordination number is 6. There are three bidentate ligands attached to the central metal, 3 x 2 = 6.

13. What is the coordination number of the Au atom in $K[Au(CN)_2(SCN)_2]$?
Ans. The coordination number is 4. There are four monodentate ligands attached to the central metal.

14. Which of the following can function as a bidentate ligand?
$NH_3$, $C_2O_4^{2-}$, CO, $OH^-$
Ans. Only $C_2O_4^{2-}$, oxalate, is a bidentate ligand. The others are all monodentate.

15. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is commonly referred to as a _____ ligand.
Ans. hexadentate

16. Calculate the oxidation state of the metal and the number of d electrons in the following coordination complexes:
a) $[CoCl_4]^{2-}$ ; b) $[Fe(bpy)_3]^{3+}$; c) $[Cu(ox)_2]^{2-}$; d) $[Cr(CO)_6]$
Ans. a) Each Cl ligand has a charge of -1, so 4 x -1 = -4
Overall charge on the complex is -2, so the oxidation state of Co = +2.
Ground state configuration for Co = [Ar] $3d^7 4s^2$

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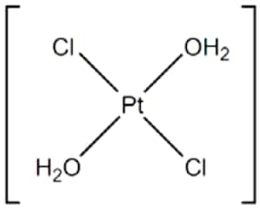
On loss of $2e^-$, $Co^{2+}$ has configuration [Ar] $3d^7$, so seven d electrons.

b) bpy (2,2'-Bipirydyl) is uncharged = neutral
Oxidation state of Fe = +3. Ground state configuration for Fe = [Ar] $3d^6\ 4s^2$
On loss of $3e^-$ $Fe^{3+}$ has configuration [Ar] $3d^5$, so five d electrons.

c) ox (oxalate, $C_2O_4^{2-}$) has charge -2 per oxalate, so total = 2 x -2 = -4
Overall charge on complex = -2, so the oxidation state of Cu = +2.
Ground state configuration for Cu = [Ar] $3d^{10}4s^1$
On loss of $2e^-$, $Cu^{2+}$ has configuration [Ar] $3d^9$, so nine d electrons.

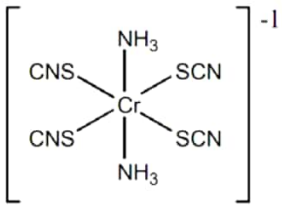
d) CO is uncharged = neutral.
Oxidation state of Cr = 0. In this case, all electrons are in 3d orbitals which are now of lower energy (because filled) than 4s orbitals. Ground state configuration for Cr = [Ar] $3d^5\ 4s^1$. Configuration for $Cr^0$ = [Ar] $3d^6$, so six d electrons.

17. Draw the structure of the following complexes:
a) *trans*-diaquadichloroplatinum (II)
b) diamminetetra(isothiocyanato)chromate (III)
Ans. a)




H2O (aqua) is neutral. Diaqua indicates that there are two of them. Each Cl ligand = -1. Dichloro indicates there are two chlorine ligands. Platinium is in the +2 oxidation state so the complex is uncharged. Trans indicated that the Cl and H2O ligands are located opposite each other.

b)




Ammine is NH3, which is uncharged. There are 2 of them. Isothiocyanato = SCN-, which attaches through the S. Each has a charge of -1 and there are 4. Chromate (III) indicates

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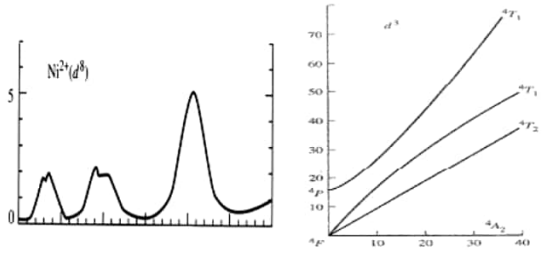
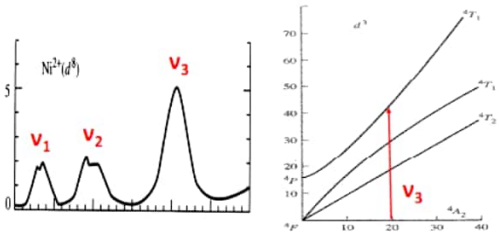
that this is an anion with Cr in the 3+ oxidation state. Charge on SCN- = 4 x -1 = -4. Charge on Cr = +3, so overall charge = -1.

18. For a nickel(II) complex explain the following electronic spectrum with the help of the adjacent Tanabe-Sugano diagram.




Ans. Tanabe-Sugano diagrams are used in coordination chemistry to predict absorptions in the UV and visible electromagnetic spectrum of coordination compounds.
It can be used to assign transitions for the absorptions. The first peak is due to the $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ transition and has an energy equal to $\Delta_o$. The second peak is due to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transition. The third peak is due to the $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition.




19. Explian Hund's rules.
Ans. In atomic physics, Hund's rules refer to a set of rules formulated by German physicist Friedrich Hund around 1927, which are used to determine the term symbol that corresponds to the ground state of a multi-electron atom. In chemistry, rule one is especially important and is often referred to as simply Hund's rules.
The three rules are:
1) For a given electron configuration, the term with maximum multiplicity has the lowest energy. Since multiplicity is 2S+1 equal to, this is also the term with maximum S. S is the spin angular momentum.
2) For a given multiplicity, the term with the largest value of L has the lowest energy, where L is the orbital angular momentum.
3) For a given term, in an atom with outermost sub-shell half-filled or less, the level with the lowest value of J lies lowest in energy. If the outermost shell is more than half-filled, the level with highest value of J is lowest in energy. J is the total angular momentum, J =

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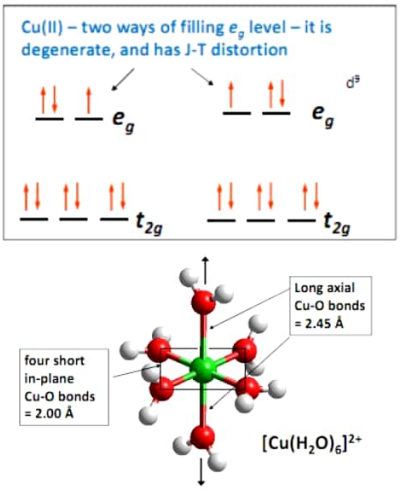
L + S.

20. Explain the Jahn-Teller distortion in $[Cu(H2O)_6]^{2+}$.

Ans. The Jahn-Teller (J-T) theorem states that in molecules/ ions that have a degenerate ground-state, the molecule/ion will distort to remove the degeneracy. This is a fancy way of saying that when orbitals in the same level are occupied by different numbers of electrons, this will lead to distortion of the molecule. For us, what is important is that if the two orbitals of the eg level have different numbers of electrons, this will lead to J-T distortion. Cu(II) with its d9 configuration is degenerate and has J-T distortion.




21. Why the magnetic moment of an octahedral monothiocarbamate complex of Iron (III) dropped from 5.8 $\mu_B$ at 300 K, to 5.8 $\mu_B$ at 150 K, to 4 $\mu_B$ at 78 K?

Ans: In this complex the crystal field splitting $\Delta_O$ is almost exactly equal to the pairing energy (P). A change in temperature can cause a partial spin crossover from high- to low-spin behavior, with unusual magnetic behavior. The magnetic moment value changes as the proportion of molecules in the high- and low-spin states changes with temperature.

22. How complex anions are separated from byproducts and isolated in crystalline form?

Ans: The complex anion such as $[Ni(CN)_5]^{3-}$ can be crystallized using solubility tendency by adding a large counterion of opposite charge. Five coordinate $[Ni(CN)_5]^{3-}$ ion prevented isolation from solution until the matched counterion $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$ was added, whereupon $[Cr(en)_3][Ni(CN)_5].15H_2O$ crystallized out. Evaporating the solvent or adding another solvent that mixes with the first but does not dissolve the product (e.g., adding EtOH to the aqueous solution) can help to crystallize a salt of the product.

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23. How will you prepare $K_3[Rh(ox)_3]$ from kinetically inert $K_3[RhCl_6]$?

Ans: $[RhCl_6]^{3-} + 3\,ox^{2-} \xrightarrow[2h]{100^\circ C} [Rh(ox)_3]^{3-} \xrightarrow[\text{Evaporation}]{K^+}$

Wine red — Yellow

With kinetically inert starting complex, the reaction requires boiling in some high boiling solvent for some hours followed by the supply of appropriate (matching) counterion.

24. How will you prepare inert $[Cr(en)_3]Cl_3$ from inert $[Cr(H_2O)_6]Cl_3$ ?

Ans: $[Cr(H_2O)_6]^{3+} + 3\,en \longrightarrow [Cr(OH)_3(H_2O)_3]\cdot(s) + 3enH^+$

If the ligand is basic in water, and the metal ion is appreciably acidic as well as being a hard acid, the metal ion may prefer to react with the hydroxide ions generated by the ligand in water, rather than the ligand itself.

$d^3$ $Cr^{3+}$ ion is inert and the water molecules do not dissociate as quickly as the basic ligand deprotonates the acidic coordinated water molecules.

$$CrCl_3 \text{ (anhydrous)} + 3\,en \xrightarrow{dry Et_2O} [Cr(en)_3]Cl_3$$

Yellow

25. Give example for substitution of volatile ligands in metal complexes.

Ans: Volatile ligands such as CO, $H_2O$ or $NH_3$ are driven off by heating and then are replaced by a desired ligand in solution or by the counter ions of the starting complex.

$$[Pt(NH_3)_4]Cl_2\,(s) \xrightarrow{250^\circ C} \text{trans-}[PtCl_2(NH_3)_2] + 2NH_3\,(g)$$

White

$$[W(CO)_6] \xrightarrow{h\upsilon} CO\,(g) + W(CO)_5 \xrightarrow{PPh_3} [W(CO)_5(PPh_3)]$$

reactive unsaturated complex

26. What is macrocyclic effect?

Ans: Macrocyclic ligands of appropriate size form more stable complexes than chelate ligands. A competition between a non-cyclic chelating ligand and a macrocyclic (chelating) ligand having the same no. and type of donor atoms will generally lead to

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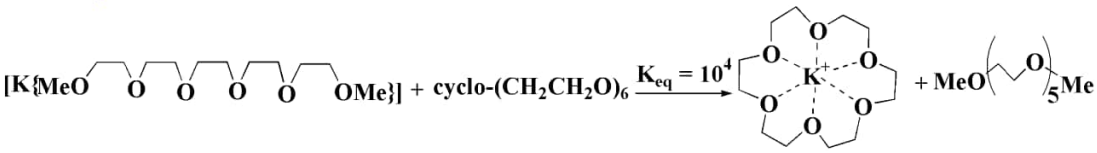
complex formation predominantly by the macrocyclic ligand. This is known as the macrocyclic effect.




The entropy term derives this type of reaction to the right. The long non cyclic ligand is more flexible than the corresponding macrocyclic ligand and can adopt many more conformations than the macrocyclic when it is not coordinated.

27. Predict the number of unpaired electrons, the magnetic moments at 25°C for each of the following

(a) $[Fe(CN)_6]^{4-}$, (b) $[Ru(NH_3)_6]^{3+}$, (c) $[Cr(NH_3)_6]^{2+}$, (d) $[EuCl_6]^{4-}$.

Ans: (a) $[Fe(CN)_6]^{4-} \rightarrow Fe^{2+} \rightarrow 3d^6$.

Low spin complex → o(zero) unpaired electron → $\mu_B$= o

(b) $[Ru(NH_3)_6]^{3+} \rightarrow Ru^{3+} \rightarrow 4d^5$.

Low spin complex → one unpaired electron → $\mu_B$= 1.73 BM.

(c) $[Cr(NH_3)_6]^{2+} \rightarrow Cr^{2+} \rightarrow 3d^4$.

High spin complex → 4 unpaired electrons → $\mu_B$ = 4.90 BM.

Low spin complex → 2 unpaired electrons → $\mu_B$ = 2.83 BM.

(d) $[EuCl_6]^{4-} \rightarrow Eu^{2+} \rightarrow 4f^7$.

High spin complex → 7 unpaired electrons → $\mu_B$ = 7.9 BM.

The f orbitals have so little overlap and interaction with ligand orbitals.

28. Among the following 3d transitionmetal ions which one is kinetically inert?

$Cr^{2+}$, $Co^{3+}$, $Co^{2+}$, $Fe^{3+}$

Ans. $Co^{3+}$

29. Among the following which statement about the *trans*-effect and the *trans*-influence of any square-planar complex is correct?

A. The *trans*-influence is a ground-state effect, whereas the *trans*-effect has a kinetic origin

B. The *trans*-effect is a ground-state effect, whereas the *trans*-influence has a kinetic origin

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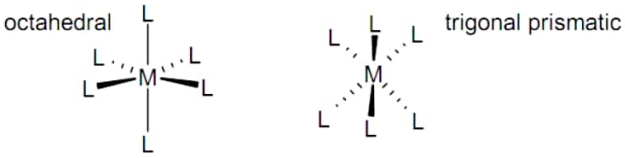
C. Both the *trans*-effect and *trans*-influence are ground-state effects
D. Rates of substitution are affected by the *trans*-effect but have nothing to do with the
Ans. [A]

30. Marcus-Hush theory applies to:
A. any electron transfer reaction of consideration
B. outer-sphere electron transfer in redox reactions
C. inner-sphere electron transfer in redox reactions
D. all biological redox reactions
Ans. The correct answer is B.

31. Show the possible stereoisomers of octahedral $[Mn(H_2O)_2(ox)_2]^{2-}$.

Ans. H2O is monodentate and ox is bidentate oxalate ion and represented by

32. Sketch the two structures that describe most six-coordinate complexes. Which is more common?
Ans.




In coordination chemistry trigonal prismatic is a rare geometry, but octahedral is extremely common.

33. Give formula for three different complexes that have the more common six-coordinate structure.
Ans. Some common examples of six-coordinate complexes are [Cr(NH3)6]3+, [Cr(CO)6], [Cr(OH2)6]2+, [Fe(CN)6]3–, [Fe(CN)6]4–, and [RhCl6]3–. In addition, almost all metal aqua ions (save only Cu2 in the first TM series) have octahedral aqua complexes in water or dilute acid.

34. Name and draw structures of the following complexes: (a) $[Ni(CO)_4]$; (b) $[Ni(CN)_4]^{2-}$; (c) $[CoCl_4]^{2-}$; (d) $[Ni(NH_3)_6]^{2+}$.
Ans.

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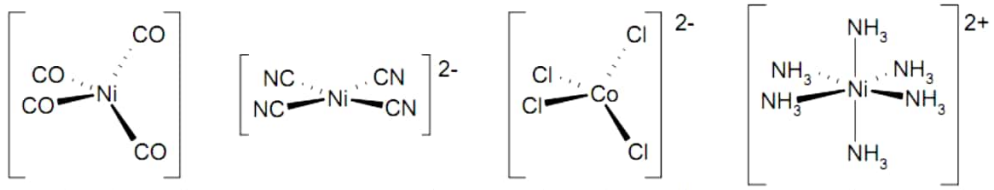


tetracarbonylnickel(0) tetracyanonickelate(2-) tetrachlorocobaltate(2-) hexaamminenickel(II)

35. Determine the configuration (in the form $t_{2g}^{m}e_g^{n}$ or $e^{m}t_2^{n}$, as appropriate), the number of unpaired electrons, and the ligand field stabilization energy as a multiple of $\Delta_o$ or $\Delta_T$ for each of the following complexes using the spectrochemical series to decide, where relevant, which are likely to be strong-field and which weak-field. (a)$[Co(NH_3)_6]^{3+}$; (b) $[Fe(OH_2)_6]^{2+}$; (c) $[Fe(CN)_6]^{3-}$; (d) $[Cr(NH_3)_6]^{3+}$; (e) $[W(CO)_6]$; (f) $[FeCl_4]^{2-}$ and (g) $[Ni(CO)_4]$.

Ans. (a) $[Co(NH_3)_6]^{3+}$

Since the $NH_3$ ligands are neutral, this is a $Co^{3+}$ complex, so we are dealing with a $d^6$ metal ion. Although ammonia is in the middle of the spectrochemical series, a metal in the 3+ oxidation state is past the middle of the metal series, so the combination is very likely to be a low-spin configuration, $t_{2g}^{6}e_g^{0}$. Indeed, octahedral $d^6$ has $S$ = 0 (no unpaired electrons) and is diamagnetic. The LFSE is $6 \times 0.4\Delta_o = 2.4\Delta_o$. Note that this is the largest possible LFSE for an octahedral complex.

(b) $[Fe(OH_2)_6]^{2+}$

The iron ion in this octahedral complex with six neutral water ligands is in the 2+ oxidation state, and water is low on the spectrochemical series. We certainly expect this $d^6$ ion to be in a high spin configuration, $t_{2g}^{4}e_g^{2}$, with $S$ = 2. That is, it has four unpaired electrons and is strongly paramagnetic. The LFSE is $4 \times 0.4\Delta_o - 2 \times 0.6\Delta_o = 0.4\Delta_o$.
Note the much smaller LFSE compared to the low spin d6 case discussed in (a).

(c) $[Fe(CN)_6]^{3-}$

The iron in this octahedral complex with six 1– cyanide ligands is in the 3+ oxidation state, and cyanide is high on the spectrochemical series. This is almost certainly a complex with a low spin configuration. $Fe^{3+}$ is a $d^5$ metal ion, and hence the configuration will be $t_{2g}^{5}e_g^{0}$, with $S$ = ½. The LFSE is $5 \times 0.4\Delta o - 0 \times 0.6\Delta o = 2.0\Delta o$.

(d) $[Cr(NH_3)_6]^{3+}$

The complex contains six neutral ammonia ligands, so it is $Cr^{3+}$, which is a $d^3$ metal ion. There is only one electron configuration for octahedral $d^3$, i.e. $t_{2g}^{3}e_g^{0}$, which means that

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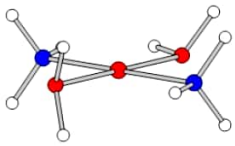
there are three unpaired electrons and $S = 3/2$. The LFSE is $3 \times 0.4\Delta o - 0 \times 0.6\Delta o = 1.2\Delta o$.

(e) $[W(CO)_6]$ Carbon monoxide is neutral and is very high on the spectrochemical series. It is a strong field ligand. The metal is therefore in the neutral oxidation state. However, in the complex we promote the 4s electrons into 3d, so that it is nonetheless a $d^6$ metal atom. We expect a low spin complex, with configuration $t_{2g}^6 e_g^0$, and $S = 0$. The LFSE is $2.4\Delta_o$.

(f) $[FeCl_4]^{2-}$
This is a tetrahedral complex, because the ligands are –1, the metal is therefore 2+, and $Fe^{2+}$ is $d^6$, which is not a candidate for square planar geometry. Remember that all tetrahedral complexes are high spin because $\Delta_T$ is inherently small $\{\Delta_T = (4/9)\Delta_o\}$. Thus the expected electron configuration is $e^2t_2^3$, and $S = 2.0$ for four unpaired electrons, and strongly paramagnetic. The LFSE is $3 \times 0.6\Delta_T - 3 \times 0.4\Delta_T = 0.6\Delta_T$.

(g) $[Ni(CO)_4]$
This is also a tetrahedral complex, because the ligands are neutral, the metal is (after promotion of the 4s electrons) d10, and hence not a candidate for square planar geometry. Of course, regardless of geometry, complexes of d10 metal atoms and ions will always have LFSE = 0, and this complex is no exception.

36. The complex first denoted $\beta$-$[PtCl_2(NH_3)_2]$ was identified as the *trans*-isomer. (The *cis* isomer was denoted α.) It reacts slowly with solid $Ag_2O$ to produce $[Pt(NH_3)_2(OH_2)_2]^{2+}$. This complex does not react with ethylendiamine to give a chelated complex. Name and draw the structure of the diaqua complex.
Ans. The fact that the aqua complex does not react with en suggests that it too must be the trans isomer, since this chelating ligand cannot stretch across a metal to occupy two trans positions on any metal ion; indeed en complexes are always *cis*. The complex is thus trans-diamminediaquaplatinum(II):



37. The 'third isomer' (neither $\alpha$ nor $\beta$, see previous question) of composition $PtCl_2 \cdot 2NH_3$ is an insoluble solid which, when ground with $AgNO_3$, gives a solution containing $[Pt(NH_3)_4](NO_3)_2$ and a new solid phase of composition $Ag_2[PtCl_4]$. Give the structures and names of each of these Pt(II) compounds.

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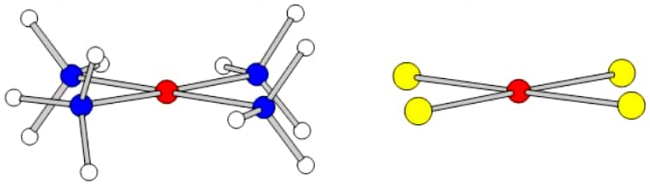
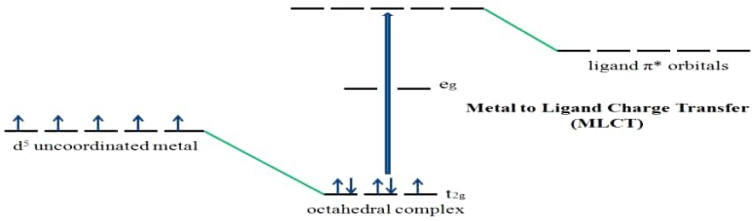
Ans. The overall formula satisfied by the complex salt is $[Pt(NH_3)_4][PtCl_4]$, and this fits the observed reaction:

$$[Pt(NH_3)_4][PtCl_4] + 2AgNO_3 \rightarrow [Pt(NH_3)_4](NO_3)_2 + Ag_2[PtCl_4]\ (s)$$



38. When do we expect MLCT bands in metal complexes?

Ans. If the metal is in a low oxidation state and the ligand possesses low-lying empty orbitals (for example CO or $CN^-$) then a MLCT transition may occur. The transition of an electron from the $t_{2g}$ (pi) and the $e_g$ (sigma*) to the $t_{1u}$ (pi*/sigma*). These transitions arise from pi acceptor ligands and metals that are willing to donate electrons into the orbitals of Ligand character. Examples of pi accepting ligands are as follows: CO, NO, $CN^-$, $N_2$, bpy, o-phen, RNC, $C_5H_5^-$, C=C bonded groups, C≡C bonded groups.




Metal to Ligand Charge Transfer (MLCT) involving an octahedral $d^5$ complex.

39. $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$ both appear blue in solution because of the presence of copper ions. However, the two solutions are not identical. How would the appearance of these solutions differ? If given an unlabeled sample of each, how could the two solutions be distinguished without collecting any spectra?

Ans. $[Cu(NH_3)_4]^{2+}$ is a tetrahedral complex and is therefore non-centrosymmetric. Since it is non-centrosymmetric, it is not Laporte forbidden. $[Cu(H_2O)_6]^{2+}$ is an octahedral complex whose d-d transitions are Laporte forbidden. $[Cu(NH_3)_4]^{2+}$ will be a darker shade of blue in solution because its d-d transitions are not forbidden, and $[Cu(H_2O)_6]^{2+}$ will have a pale shade of blue in solution because its d-d transitions are Laporte forbidden. Coloration and absorption of $[Cu(H_2O)_6]^{2+}$ in the ultraviolet-visible range is attributed to vibronic coupling.

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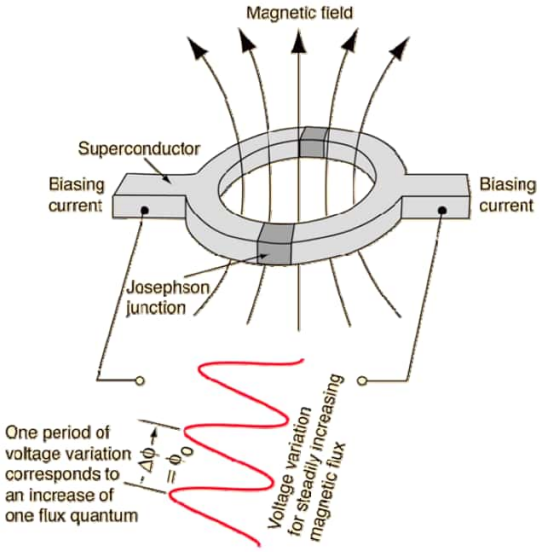
40. What is SQUID?

Ans. SQUID is superconducting quantum interference device. The superconducting quantum interference device (SQUID) consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions. The device may be configured as a magnetometer to detect incredibly small magnetic fields -- small enough to measure the magnetic fields in living organisms. SQUIDs have been used to measure the magnetic fields in mouse brains to test whether there might be enough magnetism to attribute their navigational ability to an internal compass.

The great sensitivity of the SQUID devices is associated with measuring changes in magnetic field associated with one flux quantum. One of the discoveries associated with Josephson junctions was that flux is quantized in units. If a constant biasing current is maintained in the SQUID device, the measured voltage oscillates with the changes in phase at the two junctions, which depends upon the change in the magnetic flux. Counting the oscillations allows you to evaluate the flux change which has occurred.

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