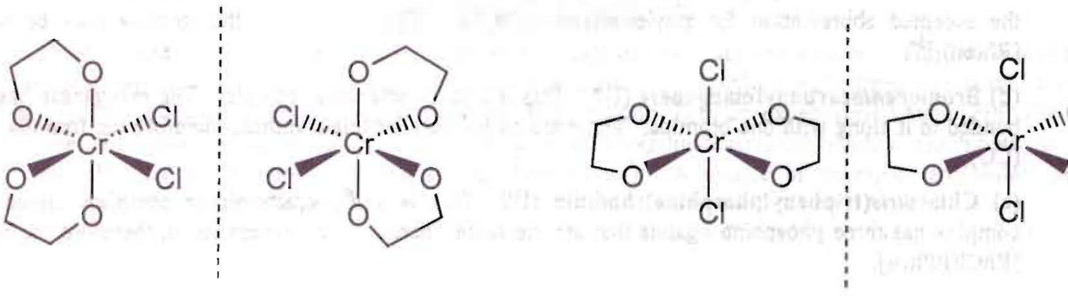
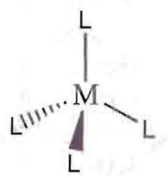


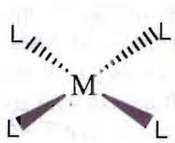
*cis* *trans*

**(c) *cis*-[RhH(CO)(PR$_3$)$_2$]?** This is a complex of Rh(I), which is a $d^8$ metal ion. Four-coordinate $d^8$ complexes of period 5 and period 6 metal ions are almost always square-planar, and [RhH(CO)(PR$_3$)$_2$] is no exception. The bulky PR$_3$ ligands are *cis* to one another. This compound has $C_s$ symmetry, with the mirror plane coincident with the rhodium atom and the four ligand atoms bound to it. A planar complex cannot be chiral, whether it is square-planar, trigonal planar, etc.

8.1 **Four-coordinate complexes? (a) Sketch the two observed structures?** With four-coordinate complexes, the two possible geometries are tetrahedral or square planar. Most of the the first-row divalent transition metal halides are tetrahedral, while metals that have a d$^8$ electronic configuration tend to be square-planar.

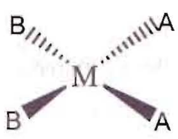


tetrahedral

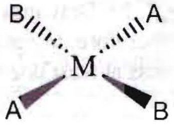


square planar

**(b) Isomers expected for MA$_2$B$_2$?** For a tetrahedral complex there are no isomers for MA$_2$B$_2$; however, for a square-planar complex, there are two isomers, *cis* and *trans*, shown below.

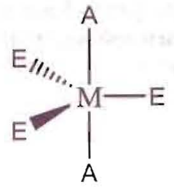


cis



trans

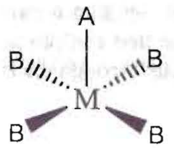
8.2 **Five-coordinate complexes? (a) Sketch the two observed structures?** With five-coordinate complexes, the two possible geometries are trigonal bipyramidal and square-based pyramidal, as shown below.



Trigonal Bipyramidal

A = axial ligands

E = equatorial ligands

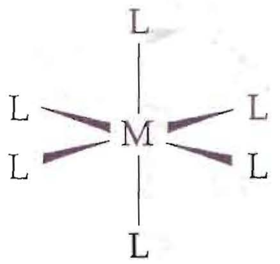


Square based pyramid

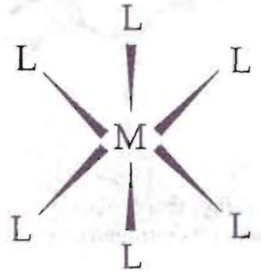
A = axial

B = basal

**8.3** **Six-coordinate complexes? (a) Sketch the two observed structures?** Most six-coordinate complexes are either octahedral or trigonal-prismatic. Drawings of these are shown below.



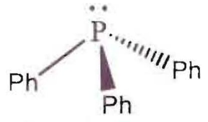
octahedron



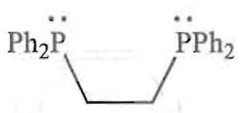
trigonal prism

**(b) Which one of these is rare?** The trigonal prism is rare. Nearly all six-coordinate complexes are octahedral.

**8.4** **Explain the difference between monodentate, bidentate, and quadridentate?** These terms describe how many Lewis bases you have on your ligand and whether they can physically bind to the metal. A monodentate ligand can bond to a metal atom only at a single atom, a bidentate ligand can bond through two atoms, a quadridentate ligand can bond through four atoms. Examples of monodentate and bidentate ligands are shown below.



monodentate

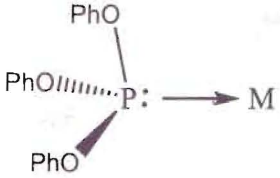


bidentante

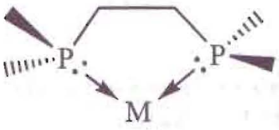
**8.5** **What type of isomers do you get with ambidentate ligands?** Ambidentate ligands are ligands that have two different atoms within the molecule that can serve as a Lewis base. An example is the thiocyanide anion $NCS^-$. It can bond to a metal either through the nitrogen's lone pair or through the sulphur's lone pair, depending on the electronics of the metal. If the metal is soft, then the softer-base sulphur is preferred; if the metal is hard, then the hard-base nitrogen is preferred. These two isomers are known as linkage isomers.

NCS–M (thiocyanato) SCN–M (isothiocyanato)

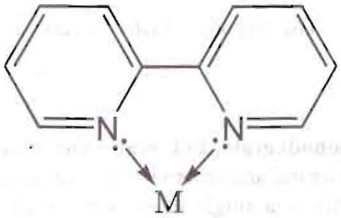
8.6 **Which ligand could act like a chelating ligand?** A chelating ligand has to have at least two Lewis basic sites on the molecule that can physically bond to the metal. **(a)** Triphenylphosphite is a monodentate ligand, which bonds to a metal through the lone pair on the phosphorous atom.



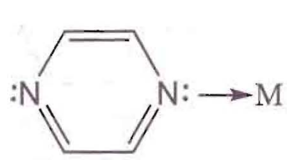
**(b)** Bis(dimethyl)phosphino ethane (dmpe) is a chelating ligand; it is able to bond to a metal through both phosphorous atoms.



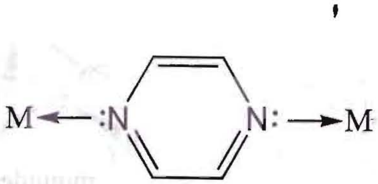
**(c)** Bipyridine (biby) is a chelating ligand that, like bis(dimethyl)phosphino ethane, is able to bond to a metal through both of its nitrogen atoms.



**(d)** Pyrazine is a monodentate ligand even though it has two Lewis basic sites. Because of the location of the nitrogen atoms, the ligand can only bond to one metal; it can, however, bridge two metals, as shown below.

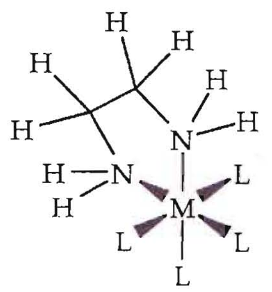


monodentate ligand

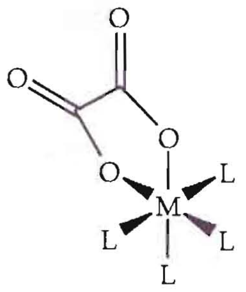


bridging ligand

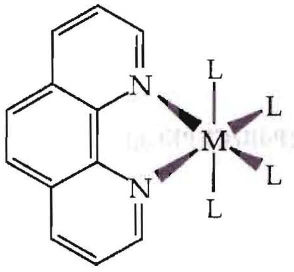
8.7 **Draw structures of complexes that contain the ligands (a) en, (b) ox, (c) phen, and (d) edta?** Generic drawings of octahedral complexes of metal M for (a), (b), and (c) are shown below. In (a), the bidentate ligand ethylenediamine (en = $H_2NCH_2CH_2NH_2$) takes up two coordination sites. For clarity, the carbon atoms of the ethylene bridge are not explicitly shown. The five-membered ring that is formed is not planar—one carbon atom is above and one is below the plane formed by M and the two N atoms. In (b), the bidentate ligand oxalate dianion (ox = $C_2O_4^{2-}$) also takes up two coordination sites. Once again, the carbon atoms of the ligand are shown simply as vertices. Due to the delocalized *p* system of the ligand, the five-membered ring in this case *is* planar. In (c), the bidentate ligand phenanthroline takes up two coordination sites. An example of a complex of ethylenediaminetetraacetate (edta$^{4-}$ = $(O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2)_2^{4-}$) is shown below. Note that the complex $Mg(edta)(OH_2)^{2-}$ is seven-coordinate.



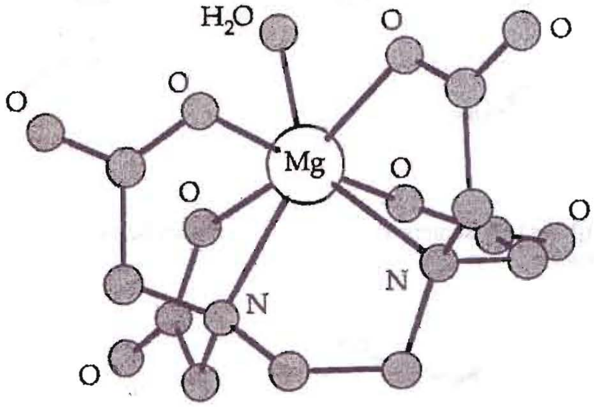
$ML_4(en)$



$ML_4(ox)$



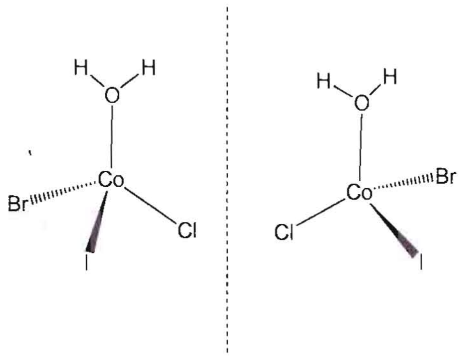
$ML_4(phen)$



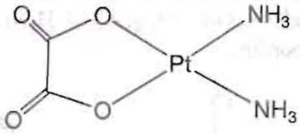
The structure of the $[Mg(edta)(OH_2)]^{2-}$ dianion. Hydrogen atoms have been omitted for clarity, and the carbon atoms of the edta$^{4-}$ ligand are left unlabeled. The hexadentate edta$^{4-}$ ligand nearly surrounds the metal ion.

8.8 **What types of isomers are $[RuBr(NH_3)_5]Cl$ and $[RuCl(NH_3)_5]Br$?** These complexes differ as to which halogen is bonded, and as to which one is the counter ion. These types of isomers are known as ionization isomers. When dissolved into solution, $[RuBr(NH_3)_5]Cl$ will release chloride ions, while $[RuCl(NH_3)_5]Br$ will release bromide ions.

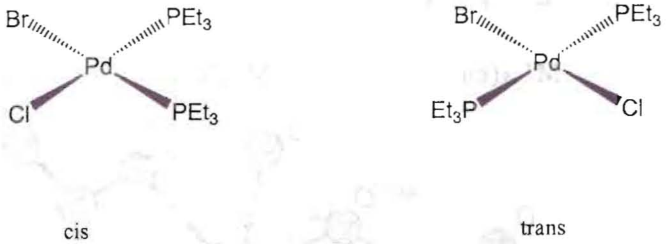
8.9 **Which complexes have isomers?** For tetrahedral complexes, the only isomers found are when you have four different ligands bound to the metal. Therefore, $[CoBr_2Cl_2]^-$ and $[CoBrCl_2(OH_2)]$ have no isomers. However, $[CoBrClI(OH_2)]$ has an optical isomer shown below.



8.10 **Which complexes have isomers?** For square-planar complexes, depending on the ligands, several isomers are possible. **(a) $[Pt(ox)(NH_3)_2]$** has no isomers because of the chelating oxalato ligand. The oxalate forces the ammonia molecules to be *cis* only.



**(b) $[PdBrCl(PEt_3)_2]$** has two isomers, *cis* and *trans*, as shown below.



cis

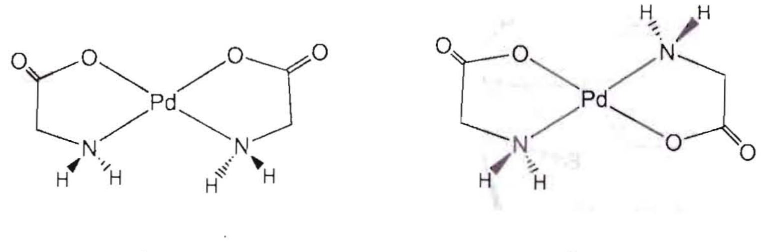
trans

**(c) $[IrHCO(PR_3)_2]$** has two isomers, *cis* and *trans*, as shown below.

cis

trans

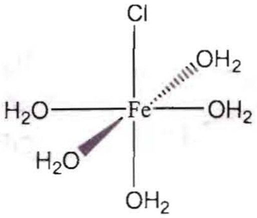
**(d) $[Pd(gly)_2]$** has two isomers, *cis* and *trans*, as shown below.



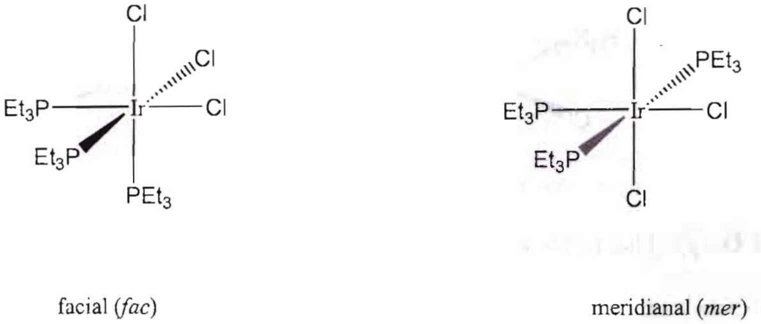
cis

trans

8.11 **How many isomers are possible for the following complexes? (a) $[FeCl(OH_2)_5]^{2+}$?** This complex has no isomers.

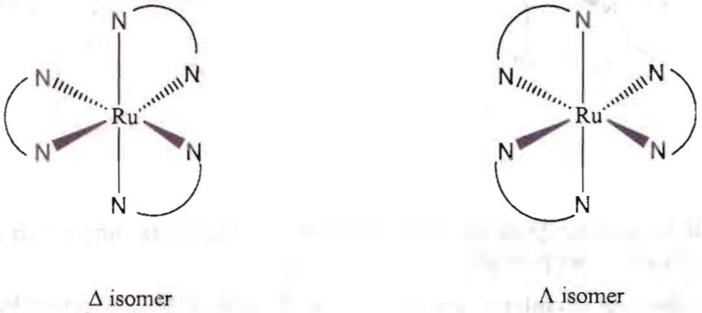


**(b) $[IrCl_3(PEt_3)_2]$?** There are two isomers for this complex, shown below.



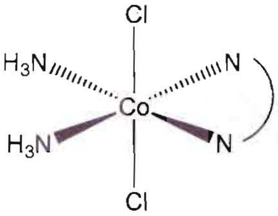
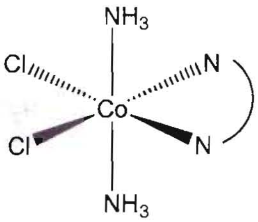
facial (*fac*) meridianal (*mer*)

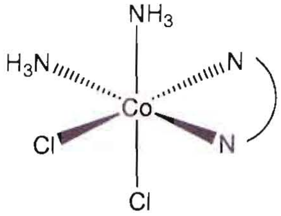
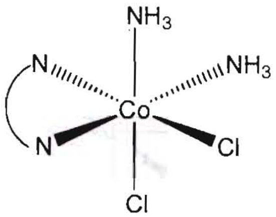
**(c) $[Ru(biby)_3]^{2+}$?** This complex contains optical isomers, shown below.



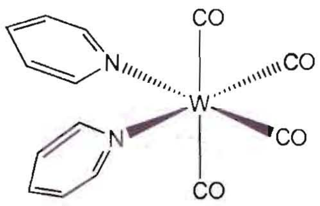
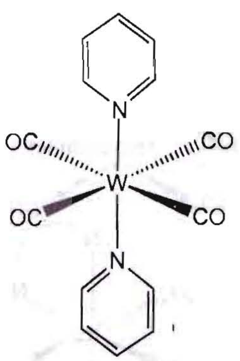
Δ isomer Λ isomer

**(d) $[CoCl_2(en)(NH_3)_2]^+$?** This complex contains *cis* and *trans*, as well as optical isomers, shown below.

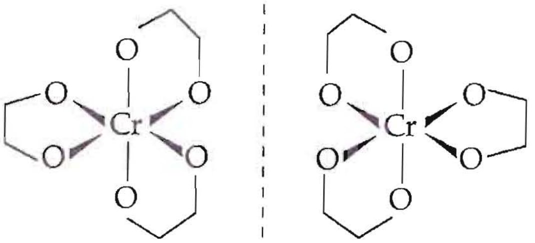



**(e) $[W(CO)_4(py)_2]$** has two isomers, *cis* and *trans*, shown below.

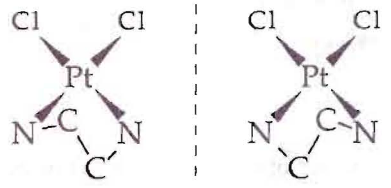



8.12 **Draw all possible isomers for $[MA_2BCDE]$?** Ignoring optical isomers, nine isomers are possible. Including optical isomers, 15 isomers are possible!

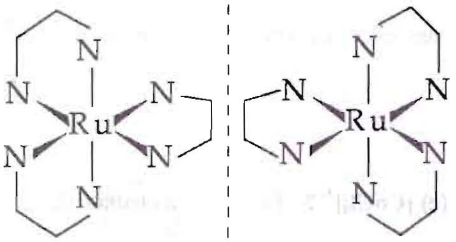
8.13 **Which of the following complexes are chiral? (a) $[Cr(ox)_3]^{3-}$?** All octahedral *tris*(bidentate ligand) complexes are chiral, since they can exist as either a right-hand or a left-hand propeller, as shown in the drawings of the two nonsuperimposable mirror images (the oxalate ligands are shown in abbreviated form and the 3– charge on the complexes has been omitted).



**(b) *cis*-$[PtCl_2(en)]$?** This is a four-coordinate complex of a period 6 $d^8$ metal ion, so it is undoubtedly square-planar. You will recall from Chapter 3 that any planar complex contains at least one plane of symmetry and must be achiral. In this case the five-membered chelate ring formed by the ethylenediamine ligand is not planar, so, strictly speaking, the complex is not planar. It *can* exist as two enantiomers, depending on the conformation of the chelate ring, as shown below. However, the conformational interconversion of the ethylene linkage is extremely rapid, so the two enantiomers cannot be separated.



*d* and *l* $[PtCl_2(en)]$



Δ and Λ $[Ru(bipy)_3]^{3+}$

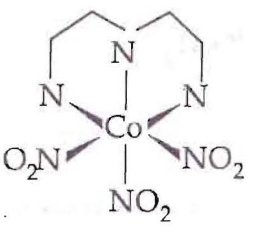
**(c)** ***cis*-$[RhCl_2(NH_3)_4]^+$?** This complex has $C_{2v}$ symmetry, so it is not chiral. The $C_2$ axis is coincident with the bisector of the Cl–Rh–Cl bond angle, one $\sigma_v$ plane is coincident with the plane formed by the Rh atom and the two Cl atoms, and the other $\sigma_v$ plane is perpendicular to the first.

**(d) $[Ru(bipy)_3]^{2+}$?** As stated in the answer to part (a) above, all octahedral *tris*(bidentate ligand) complexes are chiral, and this one is no exception. The two nonsuperimposable mirror images are shown above (the bipyridine ligands are shown in abbreviated form, and the 3+ charge on the complex has been omitted).

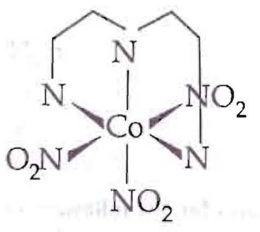
**(e)** ***fac*-$[Co(NO_2)_3(dien)]$?** There is a mirror plane through the metal, bisecting the dien ligand shown below.

**(f)** ***mer*-$[Co(NO_2)_3(dien)]$?** There are two mirror planes: one through all three coordinating N atoms of the dien ligand and the metal atom; the other through all three nitro groups and the metal atom.

If you take into account the various conformations of the ethylene linkages, the stereoisomer possibilities are much more complicated. As explained in the text for en, the ethylene linkages undergo *rapid* conformational interconversion.

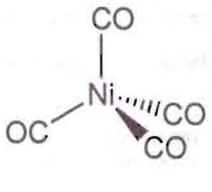


*fac*

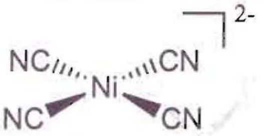


*mer*

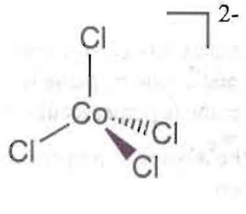
**8.14 Name and draw the structures of the complexes? (a) $[Ni(CO)_4]$?** Nickel tetracarbonly or tetracarbonyl nickel(0) has a tetrahedral geometry, shown below.



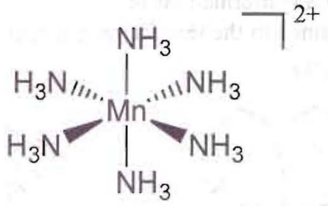
**(b) $[Ni(CN)_4]^{2-}$?** Tetracyanonickelate (II), like most $d^8$ metal complexes with four ligands, has square-planar geometry, shown below.



**(c) $[CoCl_4]^{2-}$?** Tetrachlorocobaltate (II) is tetrahedral, like most of the first-row transition metal chlorides.



**(d) $[Mn(NH_3)_6]^{2+}$?** Hexaamminemanganesium (II) has octahedral geometry, shown below.



**8.15** **Write the formulas for the following complexes?** The key to writing formulas from a name is keeping the balance of charge between the metal and its ligands. To do this, you need to know if the ligands that directly bond to the metal are neutral or ionic; this will help you determine what the oxidation state is on the metal. The chemical name gives the oxidation state of the metal as a roman numeral; simply balance charge with the ligands that directly bond to the metal and the counter-ions, if necessary.

**(a) $[CoCl(NH_3)_5]Cl_2$**, since it is cobalt (III), and the ammonia ligands are neutral and the chloride bond to the metal is anionic, you know that you need two chlorides as your counter-ion.

**(b) $[Fe(OH_2)_6](NO_3)_3$**, again, since the water's ligands are neutral, you need three nitrates as your counter-ion to balance charge.

**(c) *cis*-[~~Fe~~Ru$Cl_2$(en)$_2$]** has a divalent metal center, the chlorides are anionic, and the ethylene diamines are neutral; therefore you do not need a counter-ion to achieve a 2+ charge for the iron atom, rendering the complex neutral.

**(d) $[Cr(NH_3)_5\mu\text{–}OH\text{–}Cr(NH_3)_5]Cl_5$;** the Greek symbol μ means you have a bridging ligand between two metal complexes, so you need to balance charge for the entire dimeric complex. The ammonia's ligands are neutral, and the bridging hydroxide is an anionic ligand, giving one of the chromium atoms a 1+ charge; thus you need five chloride counter-ions to bring each chromium atom up to a 3+ charge. This gives us an overall 6+ charge for the dimeric complex.

**8.16 Name the following complexes?**

**(a)** ***cis*-$[CrCl_2(NH_3)_4]^+$?** *cis*-tetra(ammine)di(chloro)chromium(III)

**(b)** ***trans*-$[Cr(NCS)_4(NH_3)_2]^-$ ?** *trans*-di(ammine)tetrakis(isothiocyanato)chromate (III)

**(c)** **$[Co(C_2O_4)(en)_2]^+$?** bis(ethylenediamine)oxalatocobalt(III), which is neither *cis* nor *trans* but does have one optical isomer, shown below.