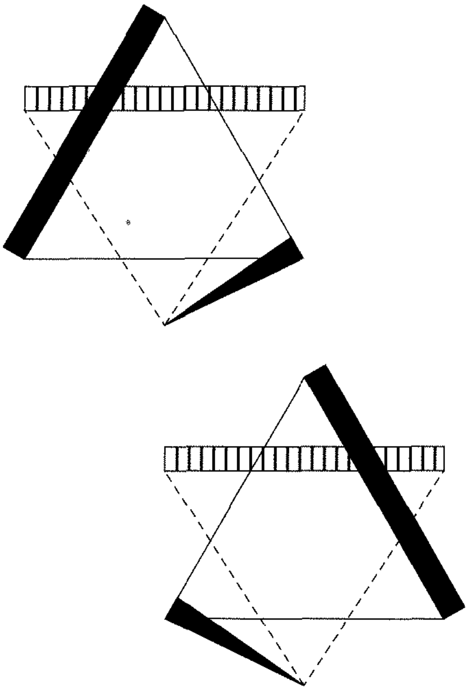


CHAPTER 9

Coordination Chemistry I: Structures and Isomers

Coordination compounds, as the term is usually used in inorganic chemistry, include compounds composed of a metal atom or ion and one or more **ligands** (atoms, ions, or molecules) that formally donate electrons to the metal. This definition includes compounds with metal-carbon bonds, called **organometallic compounds**, which are described in Chapters 13 to 15.

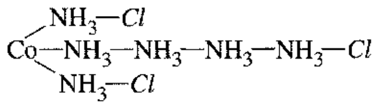
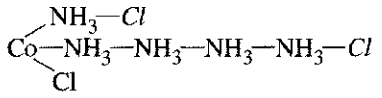
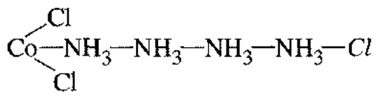
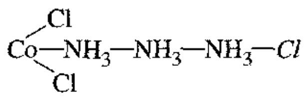
The name coordination compound comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another. Because these compounds are usually formed by donation of electron pairs of ligands to metals, the name is appropriate. Coordinate covalent bonds are identical to covalent bonds formally formed by combining one electron from each atom; only the formal electron counting distinguishes them. Coordination compounds are also acid-base adducts, as described in Chapter 6, and are frequently called **complexes** or, if charged, **complex ions**.

9-1 HISTORY

Although the history of bonding and the interpretation of reactions of coordination compounds really begins with Alfred Werner (1866–1919), coordination compounds were known much earlier. Many coordination compounds have been used as pigments since antiquity. Examples still in use include Prussian blue ($KFe[Fe(CN)_6]$), aureolin ($K_3[Co(NO_2)_6]\cdot 6H_2O$, yellow), and alizarin red dye (the calcium aluminum salt of 1,2-dihydroxy-9,10-anthraquinone). The striking colors of compounds such as these and their color changes on reaction were described in very early documents and provided impetus for further studies. The ion known today as tetraamminecopper(II) (actually $[Cu(NH_3)_4(H_2O)_2]^{2+}$ in solution), which has a striking royal blue color, was certainly known in prehistoric times. With the gradual development of analytical methods, the formulas of many of these compounds became known late in the 19th century, and theories of structure and bonding became possible.

Inorganic chemists tried to use the advances in organic bonding theory and the simple ideas of ionic charges to explain bonding in coordination compounds, but found that the theories were inadequate. In a compound such as hexaamminecobalt(III) chloride, $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$, the early bonding theories allowed only three other atoms to be attached to the cobalt (because of its "valence" of 3). By analogy with ordinary salts, such as $\mathrm{FeCl_3}$, the chlorides were assigned this role. This left the six ammonia molecules with no means of participating in bonding, and it was necessary to develop new ideas to explain the structure. One theory, proposed first by C. W. Blomstrand[1] (1826–1894) and developed further by S. M. Jørgensen[2] (1837–1914), was that the nitrogens could form chains much like those of carbon (and thus could have a valence of 5) as shown in Table 9-1, and that chloride ions attached directly to cobalt were bonded more strongly than those bonded to nitrogen. Alfred Werner[3] (1866–1919) proposed instead that all six ammonias could bond directly to the cobalt ion. Werner allowed for a looser bonding of the chloride ions; we now consider them as independent ions. The series of compounds in Table 9-1 illustrates how both the chain theory and Werner's coordination theory predict the number of ions to be formed by a series of cobalt complexes. Blomstrand's theory allowed dissociation of chlorides attached to ammonia but not of chlorides attached directly to cobalt. Werner's theory also included two kinds of chlorides. The number of chlorides attached to the cobalt (and therefore unavailable as ions) plus the number of ammonia molecules totaled six. The other chlorides were considered less firmly bound and could therefore form ions in solution. We now consider them to be ions in the solid state as well.

TABLE 9-1
Comparison of Blomstrand's Chain Theory and Werner's Coordination Theory

Werner Formula (Modern Form)	*Number of Ions Predicted*	*Blomstrand Chain Formula*	*Number of Ions Predicted*
$[\mathrm{Co(NH_3)_6}]\mathit{Cl}_3$	4	 $\mathrm{Co}\begin{array}{l}\diagup\mathrm{NH_3{-}}\mathit{Cl}\\ \mathrm{{-}NH_3{-}NH_3{-}NH_3{-}NH_3{-}}\mathit{Cl}\\ \diagdown\mathrm{NH_3{-}}\mathit{Cl}\end{array}$	4
$[\mathrm{Co(NH_3)_5Cl}]\mathit{Cl}_2$	3	 $\mathrm{Co}\begin{array}{l}\diagup\mathrm{NH_3{-}}\mathit{Cl}\\ \mathrm{{-}NH_3{-}NH_3{-}NH_3{-}NH_3{-}}\mathit{Cl}\\ \diagdown\mathrm{Cl}\end{array}$	3
$[\mathrm{Co(NH_3)_4Cl_2}]\mathit{Cl}$	2	 $\mathrm{Co}\begin{array}{l}\diagup\mathrm{Cl}\\ \mathrm{{-}NH_3{-}NH_3{-}NH_3{-}NH_3{-}}\mathit{Cl}\\ \diagdown\mathrm{Cl}\end{array}$	2
$[\mathrm{Co(NH_3)_3Cl_3}]$	0	 $\mathrm{Co}\begin{array}{l}\diagup\mathrm{Cl}\\ \mathrm{{-}NH_3{-}NH_3{-}NH_3{-}}\mathit{Cl}\\ \diagdown\mathrm{Cl}\end{array}$	2

NOTE: The italicized chlorides dissociate in solution, according to the two theories.

[1] C. W. Blomstrand, *Berichte*, **1871**, *4*, 40; translated by G. B. Kauffman, *Classics in Coordination Chemistry, Part 2*, Dover, New York, 1976, pp. 75–93.

[2] S. M. Jørgensen, *Z. Anorg. Chem.*, **1899**, *19*, 109; translated by G. B. Kauffman, *Classics in Coordination Chemistry, Part 2*, pp. 94–164.

[3] A. Werner, *Z. Anorg. Chem.*, **1893**, *3*, 267; *Berichte*, **1907**, *40*, 4817; **1911**, *44*, 1887; **1914**, *47*, 3087; A. Werner and A. Miolati, *Z. Phys. Chem.*, **1893**, *12*, 35; **1894**, *14*, 506, all translated by G. B. Kauffman, *Classics in Coordination Chemistry, Part 1*, New York, 1968.

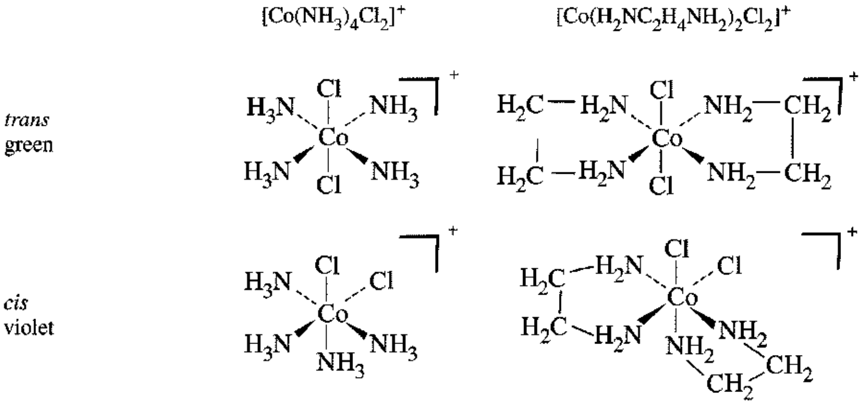


FIGURE 9-1 *Cis* and *Trans* Isomers.

Except for the last compound in the table, the predictions match, and the ionic behavior does not distinguish between them. Even with the last compound, problems with purity and conductance measurements left some ambiguity. The argument between Jørgensen and Werner continued for many years, with each presenting data and explanations favoring his own position. This case illustrates some of the good features of such controversy. Werner was forced to develop his theory further and synthesize new compounds to test his ideas because Jørgensen defended the earlier theory so vigorously. Werner proposed an octahedral structure for compounds such as those in Table 9-1. He prepared and characterized many isomers, including both green and violet forms of $[Co(H_2NC_2H_4NH_2)_2Cl_2]^+$. He claimed that these compounds had the chlorides arranged ***trans*** (opposite each other) and ***cis*** (adjacent to each other) respectively, in an overall octahedral geometry, as in Figure 9-1. Jørgensen offered alternative isomeric structures but finally conceded defeat in 1907, when Werner succeeded in synthesizing the green *trans* and the violet *cis* isomers of $[Co(NH_3)_4Cl_2]^+$, for which there were no counterparts in the chain theory.

However, even synthesis of this compound and the later discovery of optically active coordination compounds did not completely convince all chemists, although such compounds could not be explained directly by the chain theory. It was argued that Werner's optically active compounds still contained carbon, and that their chirality could be due to the carbon atoms. Finally, Werner resolved the compound $[Co(Co(NH_3)_4(OH)_2)_3]Br_6$ (Figure 9-2), initially prepared by Jørgensen, into its two optically active forms, using *d*- and *l*-α-bromocamphor-π-sulfonate as the resolving agents. With this final proof of optical activity without carbon, the validity of Werner's theory was finally accepted. Pauling[4] extended the theory in terms of hybrid orbitals, and later theories[5] have adapted arguments first used for electronic structures of ions in crystals to coordination compounds.

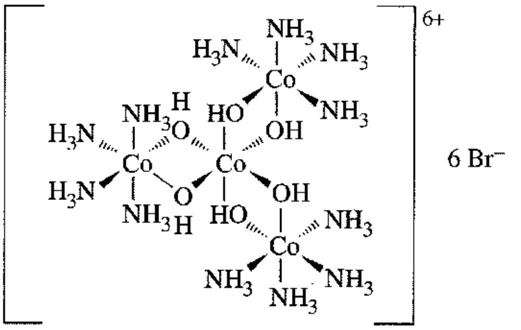


FIGURE 9-2 Werner's Totally Inorganic Optically Active Compound, $[Co(Co(NH_3)_4(OH)_2)_3]Br_6$.

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[4] L. Pauling, *J. Chem. Soc.*, **1948**, 1461; *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960, pp. 145–182.

[5] J. S. Griffith and L. E. Orgel, *Q. Rev. Chem. Soc.*, **1957**, *XI*, 381.

The Werner theory of coordination compounds was based on a group of compounds that is relatively slow to react in solution and thus easier to study. For this reason, many of his examples were compounds of Co(III), Rh(III), Cr(III), Pt(II), and Pt(IV), which are kinetically inert or slow to react. Examination of more reactive compounds over the years has confirmed their similarity to those originally studied, so we will include examples of both types of compounds in the descriptions that follow.

Werner's theory required two kinds of bonding in the compound: a primary one in which the positive charge of the central metal ion is balanced by negative ions in the compound, and a secondary one in which molecules or ions (known collectively as **ligands**) are attached directly to the transition metal ion. The secondary bonded unit has been given many different names, such as the **complex ion** or the **coordination sphere**, and the formula is written with this part in brackets. Current practice considers this coordination sphere the more important, so the words primary and secondary no longer bear the same significance. In the examples in Table 9-1, the coordination sphere acts as a unit; the ions outside the brackets balance the charge and are free ions in solution. Depending on the nature of the metal and the ligands, the metal can have from one up to at least 16 atoms attached to it, with 4 and 6 the most common numbers.[6] Additional water molecules may be added to the coordination sphere when the compound is dissolved in water. We should include the water molecules specifically in the description of the compound, but in some cases they are omitted in order to concentrate on the other ligands. The discussion that follows concentrates on the coordination sphere; the other ions associated with it can frequently vary without changing the bonding between ligands and the central metal.

Werner used compounds with four or six ligands in developing his theories, with the shapes of the coordination compounds established by the synthesis of isomers. For example, he was able to synthesize only two isomers of the $[Co(NH_3)_4Cl_2]^+$ ion. The possible structures with six ligands are octahedral, trigonal prismatic, trigonal antiprismatic, and hexagonal (either planar or pyramidal). Because there are two possible isomers for the octahedral shape and three for each of the others, as shown in Figure 9-3, Werner claimed that the structure was octahedral. Such an argument cannot be conclusive, because a missing isomer may simply be difficult to synthesize or isolate. However, later experiments confirmed the octahedral shape, with *cis* and *trans* isomers as shown in Figure 9-3.

Werner's synthesis and separation of optical isomers proved the octahedral shape conclusively, because none of the other six-coordinate geometries could have similar optical activity.

In a similar way, other experiments were consistent with square-planar Pt(II) compounds, with the four ligands at the corners of a square. Only two isomers are found for $[Pt(NH_3)_2Cl_2]$. Although the two could have had different shapes (tetrahedral and square-planar, for example), Werner assumed that they had the same overall shape and, because only one tetrahedral structure is possible for this compound, he argued that they must have square-planar shapes with *cis* and *trans* geometries. Again, his arguments were correct, although the evidence he presented could not be conclusive. The possible structures are shown in Figure 9-4.

After Werner's evidence for the octahedral and square-planar natures of many complexes, it was clear that any acceptable theory needed to account for bonds between ligands and metals and that the number of bonds required was more than that commonly accepted at that time. Transition metal compounds with six ligands, for example, cannot fit the simple Lewis theory with eight electrons around each atom, and even

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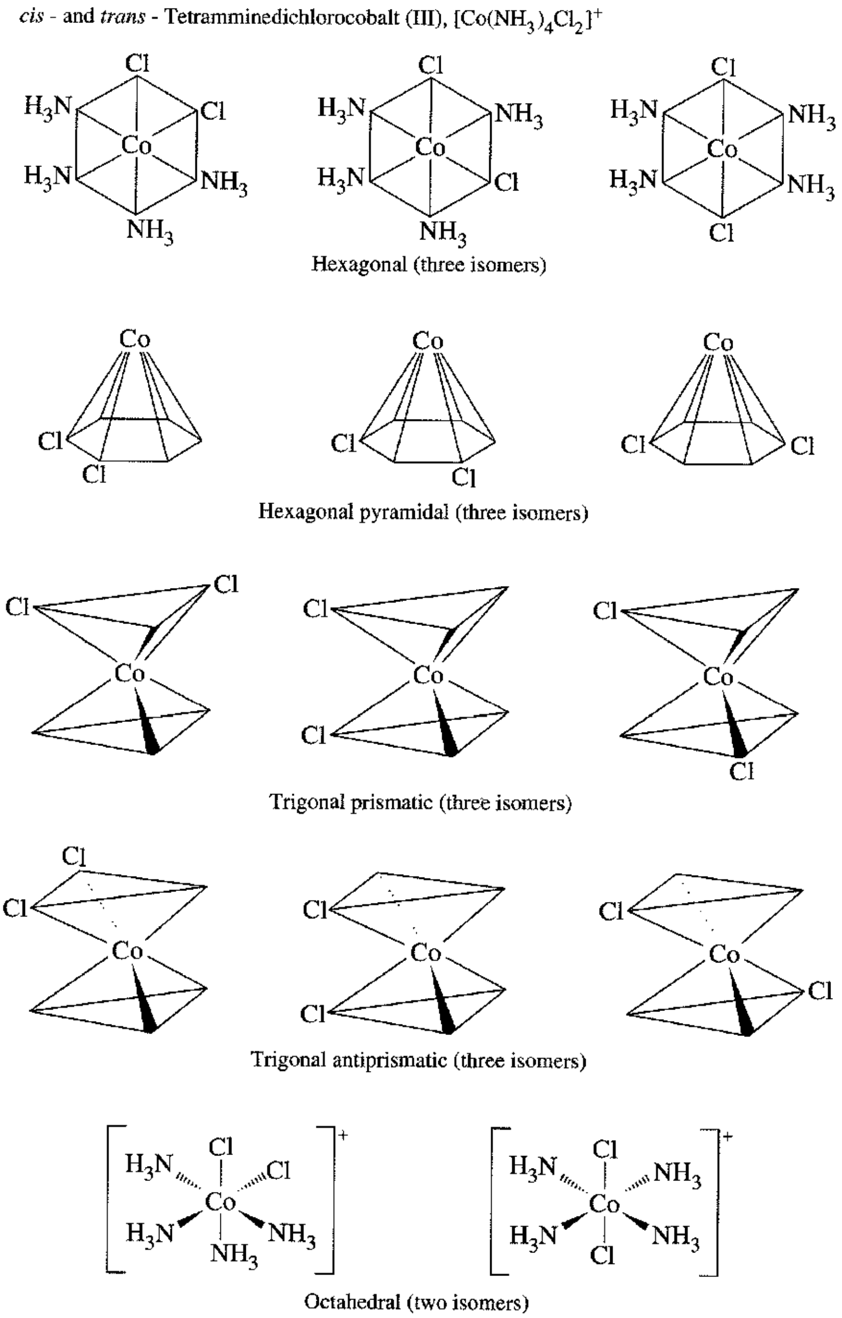
[6] N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Elmsford, NY, 1984, p. 1077. The larger numbers depend on how the number of donors in organometallic compounds are counted; some would assign smaller coordination numbers because of the special nature of the organic ligands.



cis - and *trans* - Tetramminedichlorocobalt (III), $[Co(NH_3)_4Cl_2]^+$

Hexagonal (three isomers)

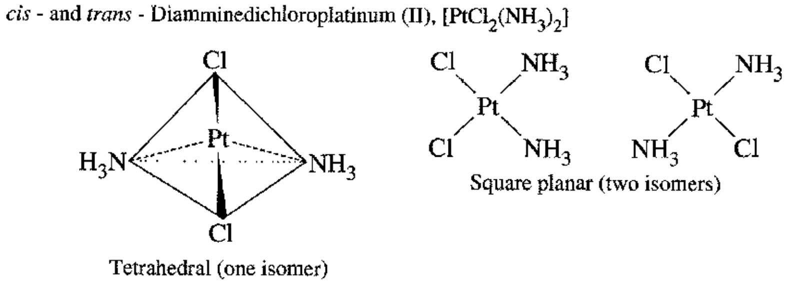
Hexagonal pyramidal (three isomers)

Trigonal prismatic (three isomers)

Trigonal antiprismatic (three isomers)

Octahedral (two isomers)

FIGURE 9-3 Possible Isomers for Hexacoordinate Complexes.



cis - and *trans* - Diamminedichloroplatinum (II), $[PtCl_2(NH_3)_2]$

Tetrahedral (one isomer)

Square planar (two isomers)

FIGURE 9-4 Possible Structures for Tetracoordinate Complexes.

expanding the shell to 10 or 12 electrons does not work in cases such as $[Fe(CN)_6]^{4-}$, with a total of 18 electrons to accommodate. In fact, the **18-electron rule** is sometimes useful in accounting for the bonding in many coordination compounds in a simple way; the total number of valence electrons around the central atom is counted, with 18 as a common result. This approach is more often used in organometallic compounds and is discussed in Chapter 13.

Pauling[7] used his **valence bond** approach to explain differences in magnetic behavior among coordination compounds by use of either 3*d* or 4*d* orbitals of the metal ion. Griffith and Orgel[8] developed and popularized the use of **ligand field theory**, derived from the **crystal field theory** of Bethe[9] and Van Vleck[10] on the behavior of metal ions in crystals and from the molecular orbital treatment of Van Vleck.[11] Several of these approaches are described in Chapter 10, with emphasis on the ligand field theory.

This chapter describes a sampling of the different shapes of coordination compounds. Because of the complex factors involved in determining shapes of coordination compounds, it is difficult to predict shapes with any confidence except when compounds of similar composition are already known. It is possible, however, to relate some structures to the individual factors that interact to produce them. This chapter also describes some of the isomers possible for coordination compounds and some of the experimental methods used to study them. Structures of some organometallic compounds are even more difficult to predict, as will be seen in Chapters 13 through 15.

9-2 NOMENCLATURE

As in any field of study, careful attention to nomenclature is required. The rules for names and formulas of coordination compounds are given here, with examples to show their use, but we need to be aware of changes in nomenclature with time. In many cases, the notation used by those who first prepared a compound is retained and expanded; in other cases, conflicting rules for names are proposed by different people and only after some time is a standard established. The literature naturally includes papers using all the possible names, and sometimes careful research is necessary to interpret those names that had relatively short lifetimes.

Following are the major rules required to name the compounds in this text and those found in the general literature. Reference to more complete sources may be needed to determine the names of other compounds.[12]

Organic (and some inorganic) ligands are frequently named with older trivial names rather than with IUPAC (International Union of Pure and Applied Chemistry) names. The IUPAC names are more correct, but trivial names and abbreviations are still commonly used. Tables 9-2, 9-3, and 9-4 list some of the common ligands. Ligands with two or more points of attachment to metal atoms are called **chelating ligands**, and the compounds are called **chelates** (pronounced key-lates), a name derived from the

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[7] Pauling, *The Nature of the Chemical Bond*, pp. 145–182.

[8] Griffith and Orgel, *op. cit.*; L. E. Orgel, *An Introduction to Transition-Metal Chemistry*, Methuen, London, 1960.

[9] H. Bethe, *Ann. Phys.*, **1929**, *3*, 133.

[10] J. H. Van Vleck, *Phys. Rev.*, **1932**, *41*, 208.

[11] J. H. Van Vleck, *J. Chem. Phys.*, **1935**, *3*, 807.

[12] T. E. Sloan, "Nomenclature of Coordination Compounds,", in G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds., *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, 1987, Vol. 1, pp. 109–134; G. J. Leigh, ed., International Union of Pure and Applied Chemistry, *Nomenclature of Inorganic Chemistry: Recommendations 1990*, Blackwell Scientific Publications, Cambridge, MA, 1990; J. A. McCleverty and N. G. Connelly, eds., International Union of Pure and Applied Chemistry, *Nomenclature of Inorganic Chemistry II: Recommendations 2000*, Royal Society of Chemistry, Cambridge, UK, 2001.

TABLE 9-2
Common Monodentate Ligands

Common Name	*IUPAC Name*	*Formula*
fluoro	fluoro	F^-
chloro	chloro	Cl^-
bromo	bromo	Br^-
iodo	iodo	I^-
azido	azido	N_3^-
cyano	cyano	CN^-
thiocyano	thiocyanato-S (S-bonded)	SCN^-
isothiocyano	thiocyanato-N (N-bonded)	NCS^-
hydroxo	hydroxo	OH^-
aqua	aqua	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS
nitrosyl	nitrosyl	NO^+
nitro	nitrito-N (N-bonded)	NO_2^-
nitrito	nitrito-O (O-bonded)	ONO^-
methyl isocyanide	methylisocyanide	CH_3NC
phosphine	phosphane	PR_3
pyridine	pyridine	py
ammine	ammine	NH_3
methylamine	methylamine	$MeNH_2$
amido	amido	NH_2^-

TABLE 9-3
Common Chelating Amines

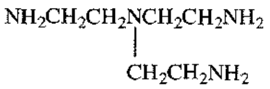
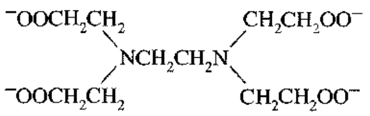
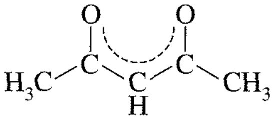
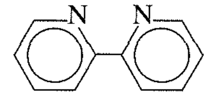
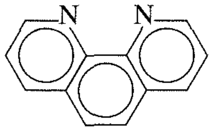
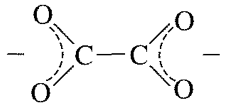
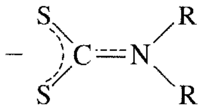
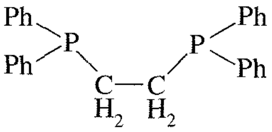
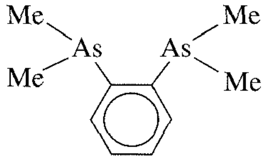
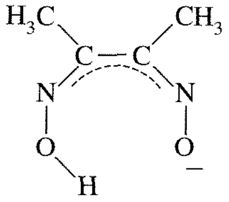
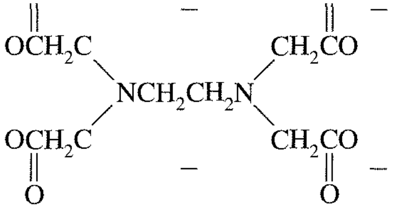
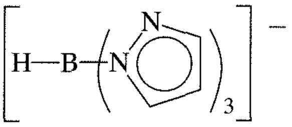
Chelating Points	*Common Name*	*IUPAC Name*	*Abbreviation*	*Formula*
monodentate	ammine, methylamine	ammine, methylamine		NH_3, CH_3NH_2
bidentate	ethylenediamine	1,2-ethanediamine	en	$NH_2CH_2CH_2NH_2$
tridentate	diethylenetriamine	2,2′-diaminodiethylamine or 1,4,7-triazaheptane	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
tetradentate	triethylenetetraamine	1,4,7,10-tetraazadecane	trien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
	β, β′, β″-triaminotriethylamine	β, β′, β″-tris(2-aminoethyl)amine	tren	 $NH_2CH_2CH_2\underset{\underset{CH_2CH_2NH_2}{\vert}}{N}CH_2CH_2NH_2$
pentadentate	tetraethylenepentamine	1,4,7,10,13-pentaazatridecane		$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
hexadentate	ethylenediaminetetraacetate	1,2-ethanediyl (dinitrilo) tetraacetate	EDTA	

TABLE 9-4
Common Multidentate (Chelating) Ligands

Common Name	*IUPAC Name*	*Abbreviation*	*Formula and Structure*
acetylacetonato	2,4-pentanediono	acac	$CH_3COCHCOCH_3^-$ 
2,2′-bipyridine	2,2′-bipyridyl	bipy	$C_{10}H_8N_2$ 
1,10-phenanthroline phenanthroline	1,10-diaminophenanthrene	phen, *o*-phen	$C_{12}H_8N_2$ 
oxalato	oxalato	ox	$C_2O_4^{2-}$ 
dialkyldithiocarbamato	dialkylcarbamodithioato	dtc	$S_2CNR_2^-$ 
1,2-bis (diphenylphosphino)ethane	1,2-ethanediylbis (diphenylphosphane)	dppe	$Ph_2PC_2H_4PPh_2$ 
o-phenylenebis (dimethylarsine)	1,2-phenylenebis (dimethylarsane)	diars	$C_6H_4(As(CH_3)_2)_2$ 
dimethylglyoximato	butanediene dioxime	DMG	$HONCC(CH_3)C(CH_3)NO^-$ 
ethylenediaminetetraacetato	1,2-ethanediyl (dinitrilo)tetraacetato	EDTA	$(^-OOCCH_2)_2NCH_2CH_2N(CH_2COO^-)_2$ 
pyrazolylborato	hydrotris-(pyrazo-1-yl)borato		

Greek (*khele*, claw of a crab). Ligands such as ammonia are **monodentate**, with one point of attachment (literally, one tooth). Other ligands are described as **bidentate** for two points of attachment, as in ethylenediamine ($NH_2CH_2CH_2NH_2$), which can bond to a metal ion through the two nitrogens. The prefixes **tri-**, **tetra-**, **penta-**, and **hexa-** are used for three through six bonding positions, as shown in Table 9-3. **Chelate rings** may have any number of atoms; the most common contain five or six atoms, including the metal ion. Smaller rings have angles and distances that lead to strain; larger rings frequently result in crowding, both within the ring and between adjoining ligands. Some ligands can form more than one ring; ethylenediaminetetraacetate (EDTA) can form five by using the four carboxylate groups and the two amine nitrogens.

Nomenclature rules

1. The positive ion (cation) comes first, followed by the negative ion (anion). This is also the common order for simple salts.

   Examples: diamminesilver(I) chloride, $[Ag(NH_3)_2]Cl$
   potassium hexacyanoferrate(III), $K_3[Fe(CN)_6]$

2. The inner coordination sphere is enclosed in square brackets in the formula. Within the coordination sphere, the ligands are named before the metal, but in formulas the metal ion is written first.

   Examples: tetraamminecopper(II) sulfate, $[Cu(NH_3)_4]SO_4$
   hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$

3. The number of ligands of one kind is given by the following prefixes. If the ligand name includes these prefixes or is complicated, it is set off in parentheses and the second set of prefixes is used.

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis
8	octa	octakis
9	nona	nonakis
10	deca	decakis

   Examples: dichlorobis(ethylenediamine)cobalt(III),
   $[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$
   tris(bipyridine)iron(II), $[Fe(NH_4C_5\text{-}C_5H_4N)_3]^{2+}$

4. Ligands are named in alphabetical order (according to the name of the ligand, not the prefix), although exceptions to this rule are common. An earlier rule gave anionic ligands first, then neutral ligands, each listed alphabetically.

   Examples: tetraamminedichlorocobalt(III), $[Co(NH_3)_4Cl_2]^+$
   (tetraammine is alphabetized by *a* and dichloro by *c*, not by the prefixes)
   amminebromochloromethylamineplatinum(II),
   $Pt(NH_3)BrCl(CH_3NH_2)$

5. Anionic ligands are given an *o* suffix. Neutral ligands retain their usual name. Coordinated water is called *aqua* and coordinated ammonia is called *ammine*.

Examples: chloro, Cl^-
bromo, Br^-
sulfato, SO_4^{2-}
aqua, H_2O
methylamine, CH_3NH_2
ammine, NH_3 (the double m distinguishes NH_3 from alkyl amines)

6. Two systems exist for designating charge or oxidation number:

   a. The Stock system puts the calculated oxidation number of the metal ion as a Roman numeral in parentheses after the name of the metal. This is the more common convention, although there are cases in which it is difficult to assign oxidation numbers.

   b. The Ewing-Bassett system puts the charge on the coordination sphere in parentheses after the name of the metal. This convention is used by *Chemical Abstracts* and offers an unambiguous identification of the species.

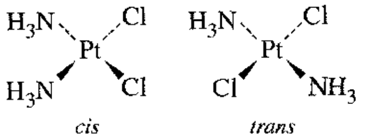
   In either case, if the charge is negative, the suffix *-ate* is added to the name of the coordination sphere.

   Examples: tetraammineplatinum(II) or tetraammineplatinum(2+), $[Pt(NH_3)_4]^{2+}$
   tetrachloroplatinate(II) or tetrachloroplatinate(2−), $[PtCl_4]^{2-}$
   hexachloroplatinate(IV) or hexachloroplatinate(2−), $[PtCl_6]^{2-}$

7. The prefixes *cis-* and *trans-* designate adjacent and opposite geometric locations. Examples are in Figures 9-1 and 9-5. Other prefixes are used as well and will be introduced as needed in the text.

   Examples: *cis-* and *trans*-diamminedichloroplatinum(II), $[PtCl_2(NH_3)_2]$
   cis- and *trans*-tetraamminedichlorocobalt(III), $[CoCl_2(NH_3)_4]^+$

FIGURE 9-5 *Cis* and *Trans* Isomers of Diamminedichloroplatinum(II), $[PtCl_2(NH_3)_2]$. The *cis* isomer, also known as cisplatin, is used in cancer treatment.

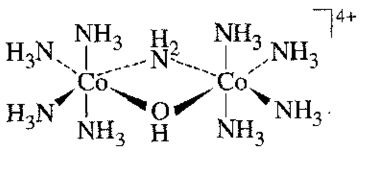


cis *trans*

8. Bridging ligands between two metal ions as in Figures 9-2 and 9-6 have the prefix μ-.

   Examples: tris(tetraammine-μ-dihydroxocobalt)cobalt(6+), $[Co(Co(NH_3)_4(OH)_2)_3]^{6+}$
   μ-amido-μ-hydroxobis(tetramminecobalt)(4+), $[(NH_3)_4Co(OH)(NH_2)Co(NH_3)_4]^{4+}$

FIGURE 9-6 Bridging Amide and Hydroxide Ligands in μ-amido-μ-hydroxobis (tetraamminecobalt) (4+), $[(NH_3)_4Co(OH)(NH_2)Co(NH_3)_4]^{4+}$.



9. When the complex is negatively charged, the names for the following metals are derived from the sources of their symbols, rather than from their English names:

iron (Fe)	ferrate	lead (Pb)	plumbate
silver (Ag)	argentate	tin(Sn)	stannate
		gold (Au)	aurate

Examples: tetrachloroferrate(III) or tetrachloroferrate(1−), $[FeCl_4]^-$
dicyanoaurate(I) or dicyanoaurate(1−), $[Au(CN)_2]^-$

EXERCISE 9-1

Name the following coordination complexes:

a. $Cr(NH_3)_3Cl_3$

b. $Pt(en)Cl_2$

c. $[Pt(ox)_2]^{2-}$

d. $[Cr(H_2O)_5Br]^{2+}$

e. $[Cu(NH_2CH_2CH_2NH_2)Cl_4]^{2-}$

f. $[Fe(OH)_4]^-$

EXERCISE 9-2

Give the structures of the following coordination complexes:

a. Tris(acetylacetonato) iron(III)

b. Hexabromoplatinate(2−)

c. Potassium diamminetetrabromocobaltate(III)

d. Tris(ethylenediamine)copper(II) sulfate

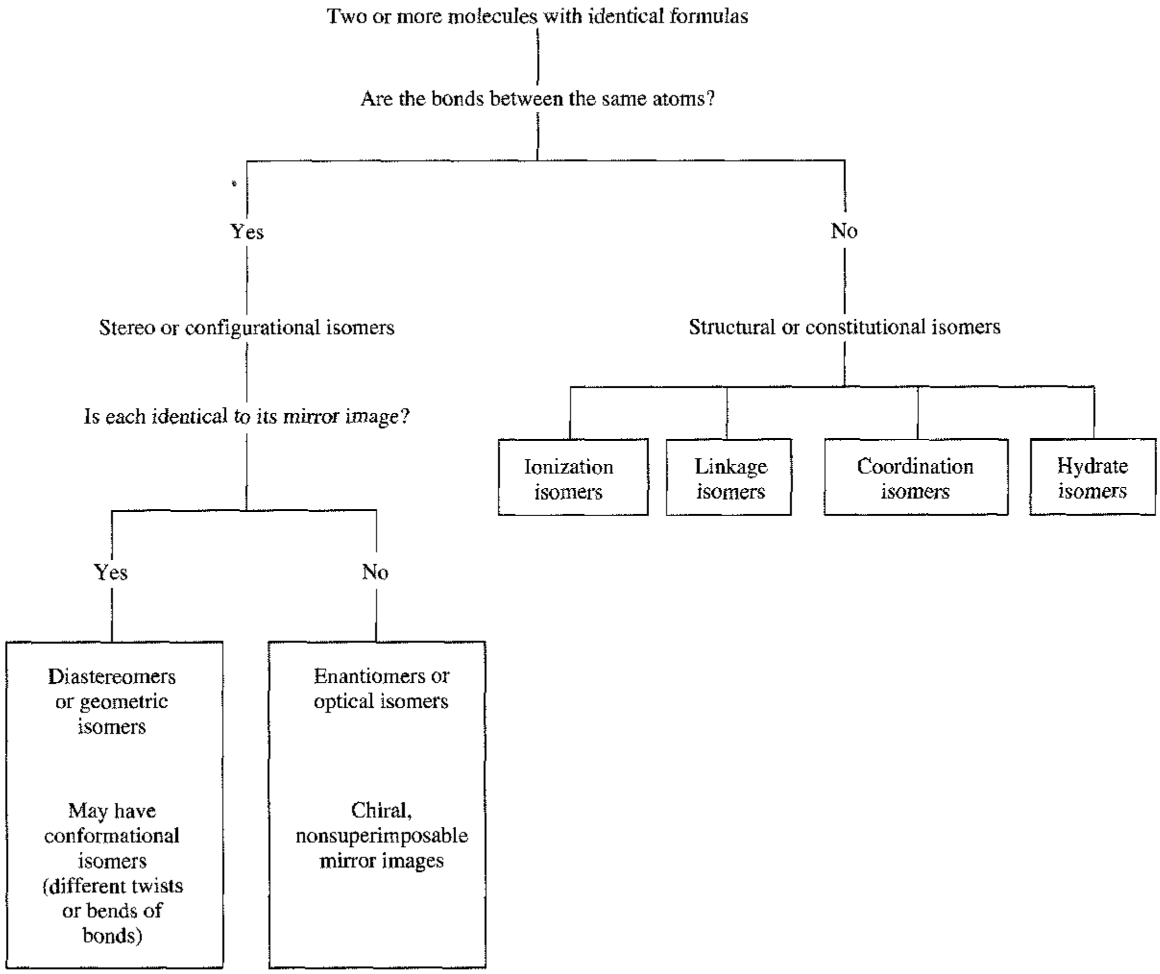
e. Hexacarbonylmanganese(I) perchlorate

f. Ammonium tetrachlororuthenate(1−)

9-3 ISOMERISM

The variety of coordination numbers in these compounds as compared with organic compounds provides a large number of **isomers**, even though we usually keep the ligand the same in considering isomers. For example, coordination compounds of the ligands 1-aminopropane and 2-aminopropane are isomers, but we do not include them in our discussion because they do not change the metal-ligand bonding. We will limit our discussion of isomers to those with the same ligands arranged in different geometries. Naturally, the number of possible isomers increases with coordination number. In the following examples, we also limit our discussion to the more common coordination numbers, primarily 4 and 6, but the reader should keep in mind the possibilities for isomerization in other cases as well.

Isomers in coordination chemistry include many types. **Hydrate** or **solvent isomers**, **ionization isomers**, and **coordination isomers** have the same overall formula but have different ligands attached to the central atom or ion. The names indicate whether solvent, anions, or other coordination compounds form the changeable part of the structure. The terms **linkage isomerism** or **ambidentate isomerism** are used for cases of bonding through different atoms of the same ligand. **Stereoisomers** have the same ligands, but differ in the geometric arrangement of the ligands. The diagram and examples that follow may help make the distinctions clearer.



9-3-1 STEREOISOMERS

Stereoisomers include *cis* and *trans* isomers, chiral isomers, compounds with different conformations of chelate rings, and other isomers that differ only in the geometry of attachment to the metal ion. As mentioned at the beginning of this chapter, study of stereoisomers provided much of the experimental evidence used by Werner to develop and defend his coordination theory. Similar study of new compounds is useful in establishing structures and reactions, even though development of experimental methods such as automated X-ray diffraction can shorten the process considerably.

9-3-2 FOUR-COORDINATE COMPLEXES

Square-planar complexes may have *cis* and *trans* isomers as shown in Figure 9-4, but no chiral isomers are possible when the molecule has a mirror plane (as do many square-planar molecules). In making decisions about whether a molecule has a mirror plane, we usually ignore minor changes in the ligand such as rotation of substituent groups, conformational changes in ligand rings, and bending of bonds. Examples of square-planar complexes that do have chiral isomers are (*meso*-stilbenediamine)(*iso*-butylenediamine)platinum(II) and palladium(II) (Figure 9-7). In this case, the geometry of the

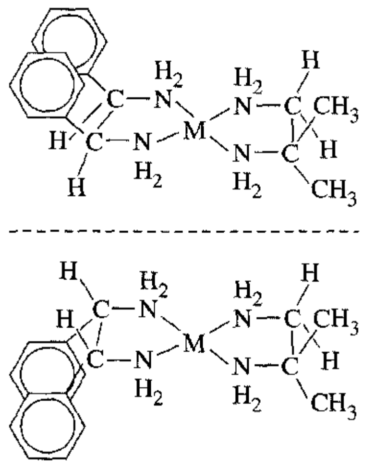


FIGURE 9-7 Chiral Isomers of Square-Planar Complexes: (*meso*-stilbenediamine)(*iso*-butylenediamine)platinum(II) and palladium(II). (From W. H. Mills and T. H. H. Quibell, *J. Chem. Soc.*, **1935**, 839; A. G. Lidstone and W. H. Mills, *J. Chem. Soc.*, **1939**, 1754.)

ligands rule out the mirror planes. If the complexes were tetrahedral, only one structure would be possible, with a mirror plane splitting the molecule between the two phenyl groups and between the two methyl groups.

Cis and *trans* isomers of square-planar complexes are common, with platinum(II) being one of the most common metal ions studied. Examples of $[Pt(NH_3)_2Cl_2]$ isomers are shown in Figure 9-4. The *cis* isomer is used in medicine as an antitumor agent called cisplatin (see Chapter 16). Chelate rings can require the *cis* structure, because the chelating ligand is too small to span the *trans* positions. The distance across the two *trans* positions is too large for all but very large ligands, and synthesis with such large rings is difficult.

9-3-3 CHIRALITY

Chiral molecules (Greek, *kheir*, hand) have a degree of asymmetry that makes their mirror images nonsuperimposable. This condition can also be expressed in terms of symmetry elements. A molecule can be chiral only if it has no rotation-reflection (S_n) axes (Section 4-1). This means that chiral molecules either have no symmetry elements or have only axes of proper rotation (C_n). Tetrahedral molecules with four different ligands or with unsymmetrical chelating ligands can be chiral, as can octahedral molecules with bidentate or higher chelating ligands or with $[Ma_2b_2c_2]$, $[Mabc_2d_2]$, $[Mabcd_3]$, $[Mabcde_2]$, or $[Mabcdef]$ structures (M = metal, a, b, c, d, e, f = monodentate ligands). Not all the isomers of such molecules are chiral, but the possibility must be considered for each.

The only isomers possible for tetrahedral complexes are chiral. All attempts to draw nonchiral isomers of tetrahedral complexes fail because of the inherent symmetry of the tetrahedron.

9-3-4 SIX-COORDINATE COMPLEXES

Complexes of the formula $ML_3L'_3$, where L and L′ are monodentate ligands, may have two isomeric forms called *fac*- and *mer*- (for facial and meridional). *Fac* isomers have three identical ligands on one triangular face; *mer* isomers have three identical ligands in a plane bisecting the molecule. Similar isomers are possible with some chelating ligands. Examples with monodentate and tridentate ligands are shown in Figure 9-8.

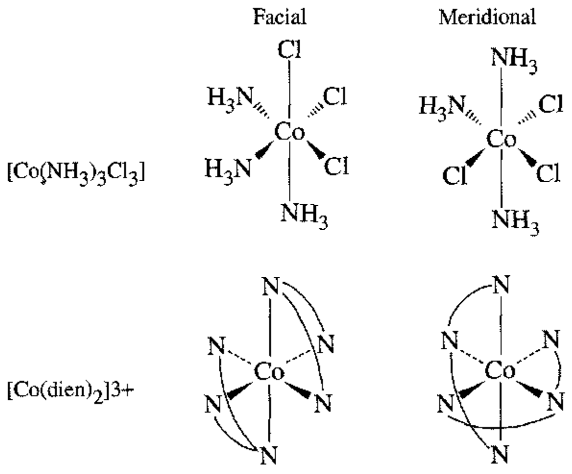
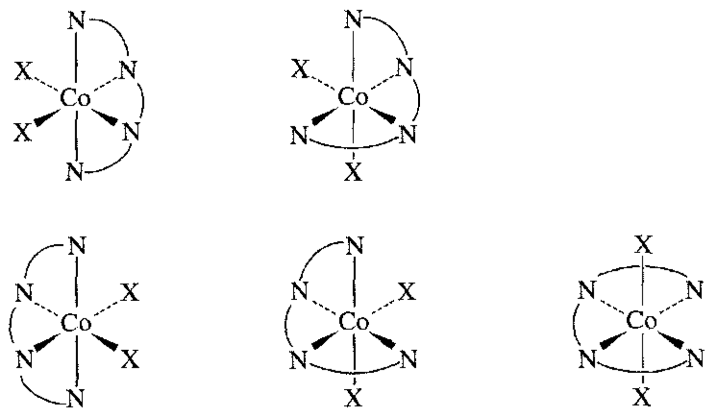


FIGURE 9-8 Facial and Meridional Isomers of $[Co(NH_3)_3Cl_3]$ and $[Co(dien)_2]^{3+}$.

Special nomenclature has been proposed for other isomers of a similar type. For example, triethylenetetramine compounds have three forms: α, with all three chelate rings in different planes; β, with two of the rings coplanar; and *trans*, with all three rings coplanar, as in Figure 9-9. Additional isomeric forms are possible, some of which will be discussed later in this chapter (both α and β have chiral isomers, and all three have additional isomers that depend on the conformations of the individual rings). Even when one multidentate ligand has a single geometry, other ligands may result in isomers. For example, the β, β′, β″-triaminotriethylamine (tren) ligand bonds to four adjacent sites, but an asymmetric ligand such as salicylate can then bond in the two ways shown in Figure 9-10, with the carboxylate *cis* and *trans* to the tertiary nitrogen.

Other isomers are possible when the number of different ligands is increased. There have been several schemes for calculating the maximum number of isomers for each case,[13] although omissions were difficult to avoid until computer programs were used to assist in the process. One such program[14] begins with a single structure, generates all the others by switching ligands from one position to another, and then rotates the new form to all possible positions for comparison with the earlier structures. It is



α
No coplanar rings

β
Two coplanar rings

trans
Three coplanar rings

FIGURE 9-9 Isomers of Triethylenetetramine Complexes.

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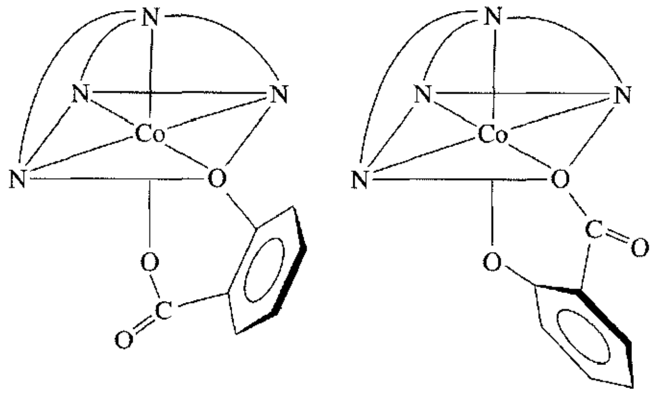
[13] J. C. Bailar, Jr., *J. Chem. Educ.*, **1957**, *34*, 334; S. A. Meyper, *J. Chem. Educ.*, **1957**, *34*, 623.

[14] W. E. Bennett, *Inorg. Chem.*, **1969**, *8*, 1325.



COO$^-$ *trans* to tertiary N

COO$^-$ *cis* to tertiary N

FIGURE 9-10 Isomers of $[Co(tren)(sal)]^+$.

also possible to calculate the number of isomers using group theory, in a procedure developed by Polya.[15]

One approach to tabulating isomers is shown in Figure 9-11 and Table 9-5. The notation <ab> indicates that a and b are *trans* to each other, with M the metal ion and a, b, c, d, e, and f monodentate ligands. The [M<ab><cd><ef>] isomers of $Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)$ are examples,[16] shown in Figure 9-11. The six octahedral positions are commonly numbered as in the figure, with positions 1 and 6 in axial positions and with 2 through 5 in counterclockwise order as viewed from the 1 position.

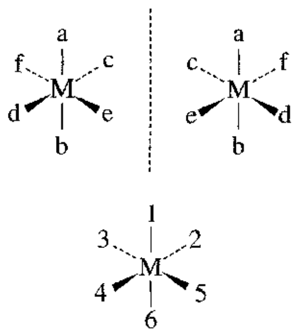


FIGURE 9-11 [M<ab><cd><ef>] Isomers and the Octahedral Numbering System.

If the ligands are completely scrambled rather than limited to the *trans* pairs shown in Figure 9-11, there are 15 different diastereoisomers (different structures that are not mirror images of each other), each of which has an enantiomer (mirror image). This means that a complex with six different ligands in an octahedral shape can have 30 different isomers! The isomers of [Mabcdef] are given in Table 9-5. Each of the 15 entries represents an isomer and its enantiomer, for a total of 30 isomers. Each entry lists the *trans* pairs of ligands; for example, C3 represents the two enantiomers of [M<ad><bf><ce>].

Finding the number and identity of the isomers of a complex is primarily a matter of systematically listing the possible structures and then checking for identical species and chirality. The method suggested by Bailar uses a list of isomers. One *trans* pair, such as <ab>, is held constant, the second pair has one component constant and the other is systematically changed, and the third pair is whatever is left over. Then, the second component of the first pair is changed and the process is continued. The results are given in Table 9-5.

Each isomer (A1, A2, ...) has the trans pairs listed. A1 is shown in Figure 9-11. Each isomer also has a mirror image (enantiomer).

TABLE 9-5
[Mabcdef] Isomers

	A	*B*	*C*
1	ab	ab	ab
	cd	ce	cf
	ef	df	de
2	ac	ac	ac
	bd	be	bf
	ef	df	de
3	ad	ad	ad
	bc	be	bf
	ef	cf	ce
4	ae	ae	ae
	bc	bf	bd
	df	cd	cf
5	af	af	af
	bc	bd	be
	de	ce	cd

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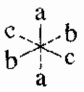
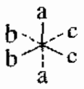
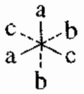
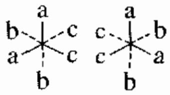
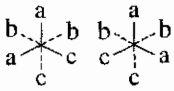
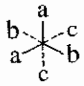
[15] S. Pevac and G. Crundwell, *J. Chem. Educ.*, **2000**, *77*, 1358; I. Baraldi and D. Vanossi, *J. Chem. Inf. Comput. Sci.*, **1999**, *40*, 386.

[16] L. N. Essen and A. D. Gel'man, *Zh. Neorg. Khim.*, **1956**, *1*, 2475.

The same approach can be used for chelating ligands, with limits on the location of the ring. For example, a normal bidentate chelate ring cannot connect *trans* positions.

EXAMPLE

The isomers of $Ma_2b_2c_2$ can be found by this method. In each row, the first pair of ligands is held constant (<aa>, <ab>, and <ac> in rows 1, 2, and 3, respectively). In column B, one component of the second pair is traded for a component of the third pair (for example, in row 2, <ab> and <cc> become <ac> and <bc>).

	A	B
1	aa bb cc  no chirality	aa bc bc  no chirality
2	ab ab cc  no chirality	ab ac bc  chiral
3	ac ab bc  chiral	ac ac bb  no chirality

Once all the *trans* arrangements are listed, drawn, and checked for chirality, we can check for duplicates; in this case, A3 and B2 are identical. Overall, there are four nonchiral isomers and one chiral pair, for a total of six.

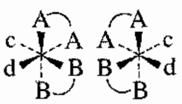
EXERCISE 9-3

Find the number and identity of all the isomers of $[Ma_2b_2cd]$.

After listing all the isomers without this restriction, those that are sterically impossible can be quickly eliminated and the others checked for duplicates and then for enantiomers. Table 9-6 lists the number of isomers and enantiomers for many general formulas, all calculated using a computer program similar to Bennett's.[17]

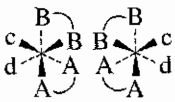
EXAMPLE

A methodical approach is important in finding isomers. AA and BB must be in *cis* positions because they are linked in the chelate ring. For M(AA)(BB)cd, we first try c and d in *cis* positions. One A and one B must be *trans* to each other:



c opposite B
d opposite A

The mirror image is different, so there is a chiral pair.



c opposite A
d opposite B

The mirror image is different, so there is a chiral pair.

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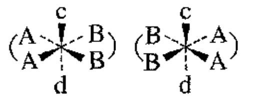
[17] W. E. Bennett, *Inorg. Chem.*, **1969**, *8*, 1325; B. A. Kennedy, D. A. MacQuarrie, and C. H. Brubaker, Jr., *Inorg. Chem.*, **1964**, *3*, 265.

TABLE 9-6
Number of Possible Isomers for Specific Complexes

Formula	*Number of Stereoisomers*	*Pairs of Enantiomers*
Ma_6	1	0
Ma_5b	1	0
Ma_4b_2	2	0
Ma_3b_3	2	0
Ma_4bc	2	0
Ma_3bcd	5	1
Ma_2bcde	15	6
Mabcdef	30	15
$Ma_2b_2c_2$	6	1
Ma_2b_2cd	8	2
Ma_3b_2c	3	0
M(AA)(BC)de	10	5
M(AB)(AB)cd	11	5
M(AB)(CD)ef	20	10
$M(AB)_3$	4	2
M(ABA)cde	9	3
$M(ABC)_2$	11	5
M(ABBA)cd	7	3
M(ABCBA)d	7	3

NOTE: Uppercase letters represent chelating ligands and lowercase letters represent monodentate ligands.

Then, trying c and d in *trans* positions, where AA and BB are in the horizontal plane:



The mirror images are identical, so there is only one isomer. There are two chiral pairs and one individual isomer, for a total of five isomers.

EXERCISE 9-4

Find the number and identity of all isomers of [M(AA)bcde], where AA is a bidentate ligand with identical coordinating groups.

9-3-5 COMBINATIONS OF CHELATE RINGS

Before discussing nomenclature rules for ring geometry, we need to establish clearly the idea of the handedness of propellers and helices. Consider the propellers shown in Figure 9-12. The first is a left-handed propeller, which means that rotating it *counterclockwise* in air or water would move it away from the observer. The second, a right-handed propeller, moves away on *clockwise* rotation. The tips of the propeller blades describe left- and right-handed helices, respectively. With rare exceptions, the threads on screws and bolts are right-handed helices; a clockwise twist with a screwdriver or wrench drives them into a nut or piece of wood. The same clockwise motion drives a nut onto a stationary bolt. Another example of a helix is a coil spring, which can usually have either handedness without affecting its operation.

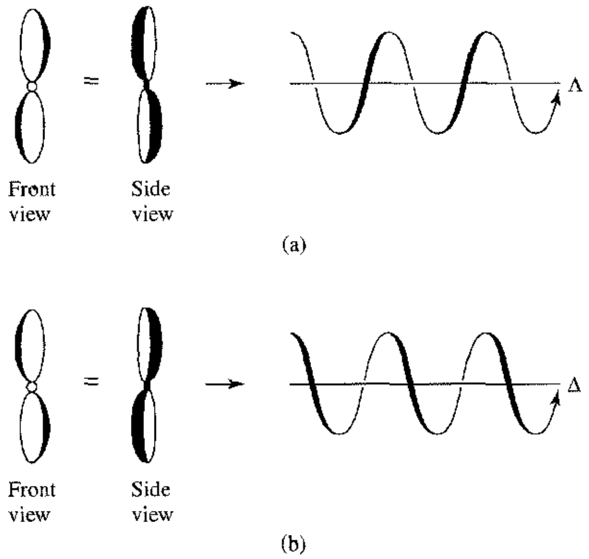


FIGURE 9-12 Right- and Left-handed Propellers. (a) Left-handed propeller and helix traced by the tips of the blades. (b) Right-handed propeller and helix traced by the tips of the blades.

Complexes with three rings, such as $[Co(en)_3]^{3+}$, can be treated like three-bladed propellers by looking at the molecule down a threefold axis. Figure 9-13 shows a number of different ways to draw these structures, all equivalent. The counterclockwise (Λ) or clockwise (Δ) character can also be found by the procedure in the next paragraph.

Complexes with two or more nonadjacent chelate rings may have chiral character. Any two noncoplanar and nonadjacent chelate rings (not sharing a common atom bonded to the metal) can be used to determine the handedness. Figure 9-14 illustrates the process. Rotate the molecule to place a triangular face at the back (away from the viewer), with one ring on the top edge in a horizontal position. Imagine that the second ring was originally at the front, also on the top edge of a triangular face (requiring that the molecule have the shape of a trigonal prism). If it takes a counterclockwise (ccw) twist of the front face to place the ligand as it is in the actual molecule, the rings have a Λ relationship. If it takes a clockwise (cw) twist to orient the front ligand properly, the rings have a Δ relationship.

A molecule with more than one pair of rings may require more than one label, but it is treated similarly. The handedness of each pair of skew rings is determined, and the final description then includes all the designations. For example, an EDTA complex has six points of attachment and five rings. One isomer is shown in Figure 9-15, where the rings are numbered arbitrarily R_1 through R_5. All ring pairs that are not coplanar and are not connected at the same atom are used in the description. The N—N ring (R_3) is omitted because it is connected at the same atom with each of the other rings.

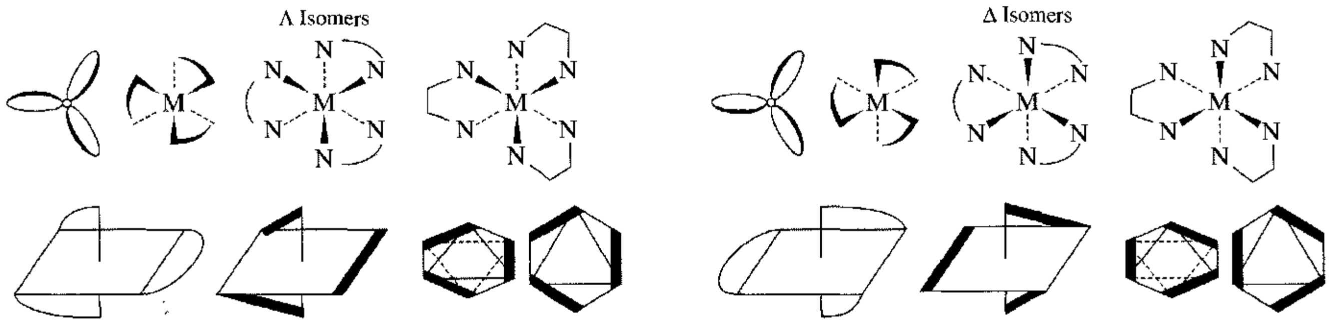


FIGURE 9-13 Left- and Right-handed Chelates.

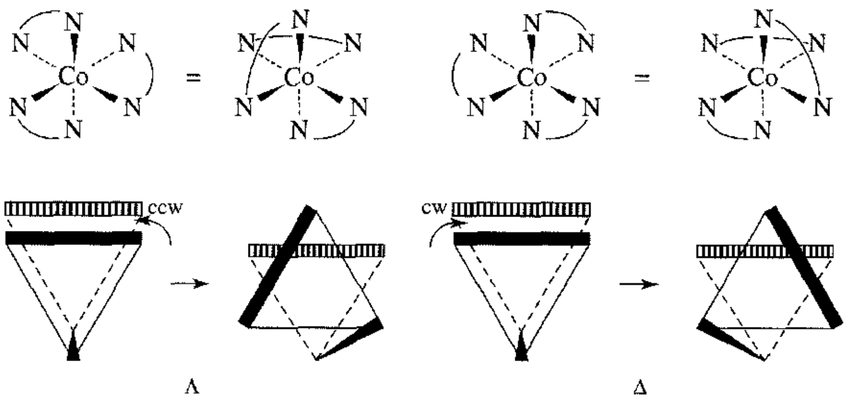


FIGURE 9-14 Procedure for Determining Handedness.

1. Rotate the figure to place one ring horizontally across the back, at the top of one of the triangular faces.
2. Imagine the ring in the front triangular face as having originally been parallel to the ring at the back. Determine what rotation is required to obtain the actual configuration.
3. If the rotation from Step 2 is counterclockwise, the structure is designated lambda (Λ). If the rotation is clockwise, the designation is delta (Δ).

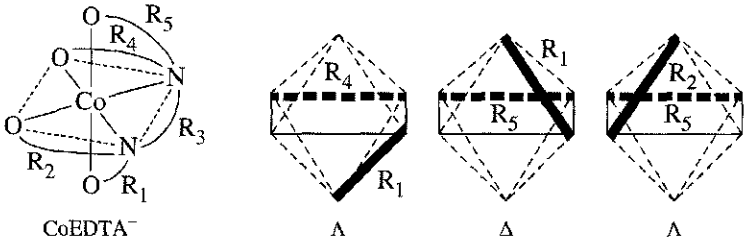
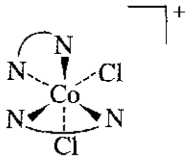


FIGURE 9-15 Labeling of Chiral Rings. The rings are numbered arbitrarily R_1 through R_5. The combination R_1-R_4 is Λ, R_1-R_5 is Δ, and R_2-R_5 is Λ. The notation for this structure is then ΛΔΛ-(ethylenediaminetetraacetato)cobaltate(III).

Considering only the four O—N rings, there are three useful pairs, R_1-R_4, R_1-R_5, and R_2-R_5. The fourth pair, R_2-R_4, is not used because the two rings are coplanar. The method described above gives Λ for R_1-R_4, Δ for R_1-R_5, and Λ for R_2-R_5. The notation for the compound given is then ΛΔΛ-(ethylenediaminetetraacetato)cobaltate(III). The order of the designations is arbitrary, and could as well be ΛΛΔ or ΔΛΛ.

EXAMPLE

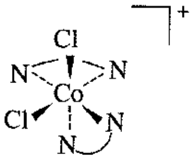
Determine the chirality label(s) for the complex shown:



Rotating the figure 180° about the vertical axis puts one ring across the back and the other connecting the top and the front right positions. If this front ring were originally parallel to the back one, a clockwise rotation would put it into the correct position. Therefore, the structure is Δ-*cis*-dichlorobis(ethylenediamine) cobalt(III).

EXERCISE 9-5

Determine the chirality label(s) for the complex shown:



9-3-6 LIGAND RING CONFORMATION

Because many chelate rings are not planar, they can have different conformations in different molecules, even in otherwise identical molecules. In some cases, these different conformations are also chiral. The notation used also requires using two lines to establish the handedness and the lower case labels λ and δ. The first line connects the atoms bonded to the metal. In the case of ethylenediamine, this line connects the two nitrogen atoms. The second line connects the two carbon atoms of the ethylenediamine, and the handedness of the two rings is found by the method described in Section 9-3-5 for separate rings. A counterclockwise rotation of the second line is called λ (lambda) and a clockwise rotation is called δ (delta), as shown in Figure 9-16. Complete description of a complex then requires identification of the overall chirality and the chirality of each ring.

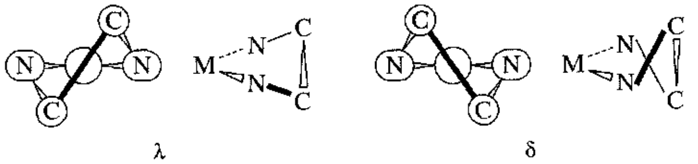


FIGURE 9-16 Chelate Ring Conformations.

Corey and Bailar[18] examined some examples and found the same steric interactions found in cyclohexane and other ring structures. For example, the Δλλλ form of $[Co(en)_3]^{3+}$ was calculated to be 7.5 kJ/mol more stable than the Δδδδ form because of interactions between protons on the nitrogens. For the Λ form, the δδδ ring conformations are more stable. Although there are examples in which this preference is not followed, in general the experimental results have confirmed their calculations. In solution, the small difference in energy allows rapid interconversion of conformation between λ and δ and the most abundant configuration for the Λ isomer is δδλ.[19]

An additional isomeric possibility arises because the symmetry of ligands can be changed by coordination. An example is a secondary amine in a ligand such as diethylenetriamine (dien) or triethylenetetraamine (trien). As a free ligand, inversion at the nitrogen is easy and only one isomer is possible. After coordination there may be additional chiral isomers. If there are chiral centers on the ligands, either inherent in their structure or created by coordination (as in some secondary amines), their structure must be described by the R and S notation familiar from organic chemistry.[20] The trien structures are illustrated in Figures 9-17 and 9-18 and described in the following example. The α, β, and *trans* structures appear in Figure 9-9 without the ring conformations.

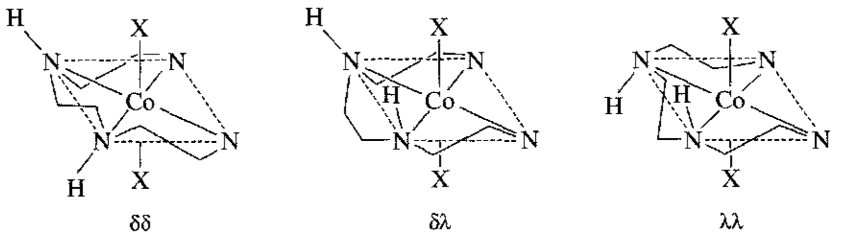


FIGURE 9-17 Chiral Structures of *trans*-$[CoX_2(trien)]^+$.

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[18] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **1959**, *81*, 2620.

[19] J. K. Beattie, *Acc. Chem. Res.*, **1971**, *4*, 253.

[20] R. S. Cahn and C. K. Ingold, *J. Chem. Soc.*, **1951**, 612; Cahn, Ingold, and V. Prelog, *Experientia*, **1956**, *12*, 81.

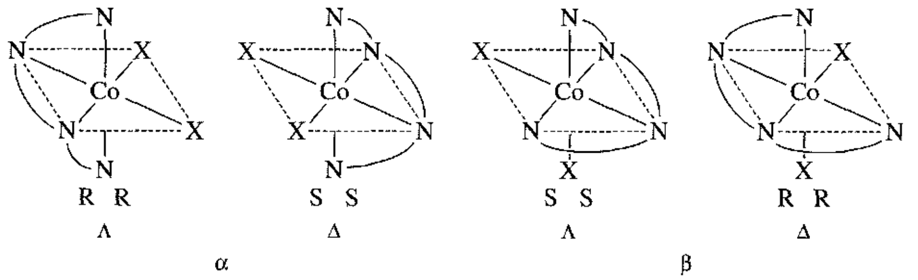


FIGURE 9-18 α and β forms of $[CoX_2(trien)]^+$.

EXAMPLE

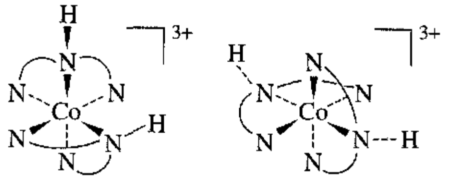
Confirm the chirality of the rings in the *trans*-$[CoX_2trien]^+$ structures in Figure 9-17.

Take the ring on the front edge of the first structure, with the line between the two nitrogens as the reference. If the line connecting the two carbons was originally parallel to the N—N line, a clockwise rotation is required to reach the actual conformation, so it is δ. The ring on the back of the molecule is the same, so it is also δ. The tetrahedral nature of the ligand N forces the hydrogens on the two secondary nitrogens into the positions shown, so the middle ring must be λ. However, it need not be labeled as such because there is no other possibility. The label is then δδ.

The same procedure on the other two structures results in labels of δλ and λλ, respectively. Again, the middle ring has only one possible structure, so it need not be labeled.

EXERCISE 9-6

$[Co(dien)_2]^{3+}$ can have several forms, two of which are shown below. Identify the Δ or Λ chirality of the rings, using all unconnected pairs. Each complex may have three labels.



9-3-7 CONSTITUTIONAL ISOMERS

Hydrate isomerism

Hydrate isomerism is not common but deserves mention because it contributed to some of the confusion in describing coordination compounds before the Werner theory was generally accepted. It differs from other types of isomerism in having water as either a ligand or an added part of the crystal structure, as in the hydrates of sodium sulfate (Na_2SO_4, $Na_2SO_4 \cdot 7\,H_2O$, and $Na_2SO_4 \cdot 10\,H_2O$ are known). More strictly, it should be called solvent isomerism to allow for the possibility of ammonia or other ligands also used as solvents to participate in the structure, but many examples involve water.

The standard example is $CrCl_3 \cdot 6\,H_2O$, which can have three distinctly different crystalline compounds, now known as $[Cr(H_2O)_6]Cl_3$ (violet), $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$ (blue-green), and $[CrCl_2(H_2O)_4]Cl \cdot 2\,H_2O$ (dark green). A fourth isomer, $[CrCl_3(H_2O)_3]$ (yellow-green) also occurs at high concentrations of HCl.[21] The three cationic isomers can be separated by cation ion exchange from commercial $CrCl_3 \cdot 6\,H_2O$, in which the major

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[21] S. Diaz-Moreno, A. Muñoz-Paez, J. M. Martinez, R. R. Pappalardo, and E. S. Marcos, *J. Am. Chem. Soc.*, **1996**, *118*, 12654.

component is $[CrCl_2(H_2O)_4]Cl\cdot 2\,H_2O$ in the *trans* configuration. Other examples are also known; a few are listed below.

$[Co(NH_3)_4(H_2O)Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl\cdot H_2O$

$[Co(NH_3)_5(H_2O)](NO_3)_3$ and $[Co(NH_3)_5(NO_3)](NO_3)_2\cdot H_2O$

Ionization isomerism

Compounds with the same formula, but which give different ions in solution, exhibit ionization isomerization. The difference is in which ion is included as a ligand and which is present to balance the overall charge. Some examples are also hydrate isomers, such as the first one listed below.

$[Co(NH_3)_4(H_2O)Cl]Br_2$ and $[Co(NH_3)_4Br_2]Cl\cdot H_2O$

$[Co(NH_3)_5SO_4]NO_3$ and $[Co(NH_3)_5NO_3]SO_4$

$[Co(NH_3)_4(NO_2)Cl]Cl$ and $[Co(NH_3)_4Cl_2]NO_2$

Many other examples, and even more possibilities, exist. Enthusiasm for preparing and characterizing such compounds is not great at this time, and new examples are more likely to be discovered only as part of other studies.

Coordination isomerism

Examples of a complete series of coordination isomers require at least two metal ions and sometimes more. The total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. This is best described by example.

For the empirical formula $Pt(NH_3)_2Cl_2$, there are three possibilities:

$[Pt(NH_3)_2Cl_2]$	
$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$	(This compound apparently has not been reported, but the individual ions are known.)
$[Pt(NH_3)_4][PtCl_4]$	(Magnus' green salt, the first platinum ammine, was discovered in 1828.)

Other examples are possible with different metal ions and with different oxidation states:

$[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$

$[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2][PtCl_4]$

Pt(II) Pt(IV) Pt(IV) Pt(II)

Linkage (ambidentate) isomerism

Some ligands can bond to the metal through different atoms. The most common early examples were thiocyanate, SCN^-, and nitrite, NO_2^-. Class (a) metal ions (hard acids) tend to bond to the nitrogen of thiocyanate and class (b) metal ions (soft acids) bond through the sulfur, but the differences are small and the solvent used influences the bonding. Compounds of rhodium and iridium with the general formula $[M(PPh_3)_2(CO)(NCS)_2]$ form M—S bonds in solvents of large dielectric constant and

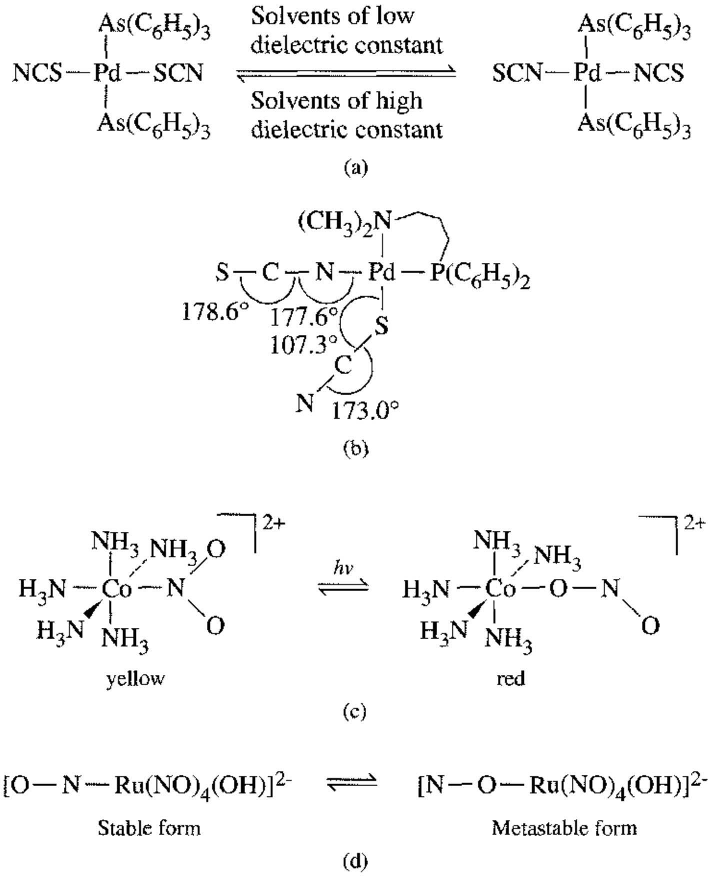

FIGURE 9-19 Linkage (Ambidentate) Isomers.

M—N bonds in solvents of low dielectric constant,[22] as shown in Figure 9-19(a). There are also compounds[23] with both M-SCN (thiocyanato) and M-NCS (isothiocyanato) [isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylaminopropane) palladium(II); Figure 9-19(b)]. M-NCS combinations are linear and M-SCN combinations are bent at the S atom in all thiocyanate complexes. This bend means that the M-SCN isomer has a larger steric effect, particularly if it can rotate about the M—S bond.

The nitrite isomers of $[Co(NH_3)_5NO_2]^{2+}$ were studied by Jørgensen and Werner, who observed that there were two compounds of the same chemical formula but of different colors [Figure 9-19(c)]. A red form of low stability converted readily to a yellow form. The red form was thought to be the M—ONO nitrito isomer and the yellow form the M—NO_2 nitro isomer, based on comparison with compounds of similar color. This conclusion was later confirmed, and kinetic[24] and ^{18}O labeling[25] experiments showed that conversion of one form to the other is strictly intramolecular, not a result of dissociation of the NO_2^- ion followed by reattachment. In a more recent example, the stable O—N—Ru form of $[Ru(NO)_5(OH)]^{2-}$ is in equilibrium with the metastable N—O—Ru form[26] [Figure 9-19(d)].

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[22] J. L. Burmeister, R. L. Hassel, and R. J. Phelen, *Inorg. Chem.*, **1971**, *10*, 2032; J. E. Huheey and S. O. Grim, *Inorg. Nucl. Chem. Lett.*, **1974**, *10*, 973.

[23] D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Am. Chem. Soc.*, **1970**, *92*, 5351; G. R. Clark and G. J. Palenik, *Inorg. Chem.*, **1970**, *9*, 2754.

[24] B. Adell, *Z. Anorg. Chem.*, **1944**, *252*, 277.

[25] R. K. Murmann and H. Taube, *J. Am. Chem. Soc.*, **1956**, *78*, 4886.

[26] D. V. Fornitchev and P. Coppens, *Inorg. Chem.*, **1996**, *35*, 7021.

9-3-8 EXPERIMENTAL SEPARATION AND IDENTIFICATION OF ISOMERS

Separation of geometric isomers frequently requires fractional crystallization with different counterions. Because different isomers will have slightly different shapes, the packing in crystals will depend on the fit of the ions and their overall solubility. One helpful idea, systematized by Basolo,[27] is that ionic compounds are least soluble when the positive and negative ions have the same size and magnitude of charge. For example, large cations of charge 2+ are best crystallized with large anions of charge 2−. Although not a surefire method to separate isomers, this method helps to decide what combinations to try.

Separation of chiral isomers requires chiral counterions. Cations are frequently resolved by using the anions *d*-tartrate, antimony *d*-tartrate, and α-bromocamphor-π-sulfonate; anionic complexes are resolved by the bases brucine or strychnine or by using resolved cationic complexes such as $[Rh(en)_3]^{3+}$.[28] In the case of compounds that racemize at appreciable rates, adding a chiral counterion may shift the equilibrium even if it does not precipitate one form. Apparently, interactions between the ions in solution are sufficient to stabilize one form over the other.[29]

The best method of identifying isomers, when crystallization allows it, is X-ray crystallography. Current methods allow for the rapid determination of the absolute configuration at costs that compare favorably with other, more indirect methods, and in many cases new compounds are routinely examined this way.

Measurement of optical activity is a natural method for assigning absolute configuration to chiral isomers, but it usually requires more than simple determination of molar rotation at a single wavelength. Optical rotation changes markedly with the wavelength of the light used in the measurement and changes sign near absorption peaks. Many organic compounds have their largest rotation in the ultraviolet, and the old standard of molar rotation at the sodium D wavelength is a measurement of the tail of the much larger peak. Coordination compounds frequently have their major absorption (and therefore rotation) bands in the visible part of the spectrum, and it then becomes necessary to examine the rotation as a function of wavelength to determine the isomer present. Before the development of the X-ray methods now used, debates over assignments of configuration were common, since comparison of similar compounds could lead to contradictory assignments depending on which measurements and compounds were compared.

Polarized light can be either circularly polarized or plane polarized. When circularly polarized, the electric or magnetic vector rotates (right-handed if clockwise rotation when viewed facing the source, left-handed if counterclockwise) with a frequency related to the frequency of the light. Plane-polarized light is made up of both right- and left-handed components; when combined, the vectors reinforce each other at 0° and 180° and cancel at 90° and 270°, leaving a planar motion of the vector. When plane-polarized light passes through a chiral substance, the plane of polarization is rotated. This **optical rotatory dispersion** (ORD) or optical rotation is caused by a difference in the refractive indices of the right and left circularly polarized light, according to the equation

$$\alpha = \frac{\eta_l - \eta_r}{\lambda}$$

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[27] F. Basolo, *Coord. Chem. Rev.*, **1968**, *3*, 213.

[28] R. D. Gillard, D. J. Shepherd, and D. A. Tarr, *J. Chem. Soc., Dalton Trans.*, **1976**, 594.

[29] J. C. Bailar, ed., *Chemistry of the Coordination Compounds*, Reinhold Publishing, New York, **1956**, pp. 334–335, cites several instances, specifically $[Fe(phen)_3]^{2+}$ (Dwyer), $[Cr(C_2O_4)_3]^{3-}$ (King), and $[Co(en)_3]^{3+}$ (Jonassen, Bailar, and Huffmann).

where η_l and η_r are the refractive indices for left and right circularly polarized light and λ is the wavelength of the light. ORD is measured by passing light through a polarizing medium, then through the substance to be measured, and then through an analyzing polarizer. The polarizer is rotated until the angle at which the maximum amount of light passing through the substance is found, and the measurement is repeated at different wavelengths. ORD frequently shows a positive value on one side of an absorption maximum and a negative value on the other, passing through zero at or near the absorption maximum, and also frequently shows a long tail extending far from the absorption wavelength. When optical rotation of colorless compounds is measured using visible light, it is this tail that is measured, far from the ultraviolet absorption band. The variance with wavelength is known as the **Cotton effect**, positive when the rotation is positive (right-handed) at low energy and negative when it is positive at high energy.

Another measurement, **circular dichroism**, CD, is caused by a difference in the absorption of right and left circularly polarized light, defined by the equation

$$\text{Circular dichroism} = \varepsilon_l - \varepsilon_r$$

where ε_l and ε_r are the molar absorption coefficients for left and right circularly polarized light. CD spectrometers have an optical system much like UV-visible spectrophotometers with the addition of a crystal of ammonium phosphate mounted to allow imposition of a large electrostatic field on it. When the field is imposed, the crystal allows only circularly polarized light to pass through; changing the direction of the field rapidly provides alternating left and right circularly polarized light. The light received by the detector is compared electronically and presented as the difference between the absorbances.

Circular dichroism is usually observed only in the vicinity of an absorption band, a positive Cotton effect showing a positive peak at the absorption maximum and a negative effect showing a negative peak. This simple spectrum makes CD more selective and easier to interpret than ORD. With improvements in instrumentation, it has become the method of choice for studying chiral complexes. Both ORD and CD spectra are shown in Figure 9-20.

Even with CD, spectra are not always easily interpreted because there may be overlapping bands of different signs.[30] Interpretation requires determination of the overall symmetry around the metal ion and assignment of absorption spectra to specific transitions between energy levels (discussed in Chapter 11) in order to assign specific CD peaks to the appropriate transitions. Even then, there are cases in which the CD peaks do not match the absorption peaks and interpretation becomes much more difficult.

9-4 COORDINATION NUMBERS AND STRUCTURES

The isomers described to this point have had octahedral or square-planar geometry. In this section, we describe some other common geometries. Explanations for some of the shapes are easy and follow the VSEPR approach presented in Chapter 3, usually ignoring the *d* electrons of the metal. In these cases, three-coordinate complexes have a trigonal-planar shape, four-coordinate complexes are tetrahedral, and so forth, assuming that each ligand-metal bond results from a two-electron donor atom interacting with the metal. Some complexes do not follow these rules, and require more elaborate explanations, or have no ready explanation.

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[30] R. D. Gillard, "Optical Rotatory Dispersion and Circular Dichroism," in H. A. O. Hill and P. Day, eds., *Physical Methods in Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 1968, pp. 183–185; C. J. Hawkins, *Absolute Configuration of Metal Complexes*, Wiley-Interscience, New York, 1971, p. 156.

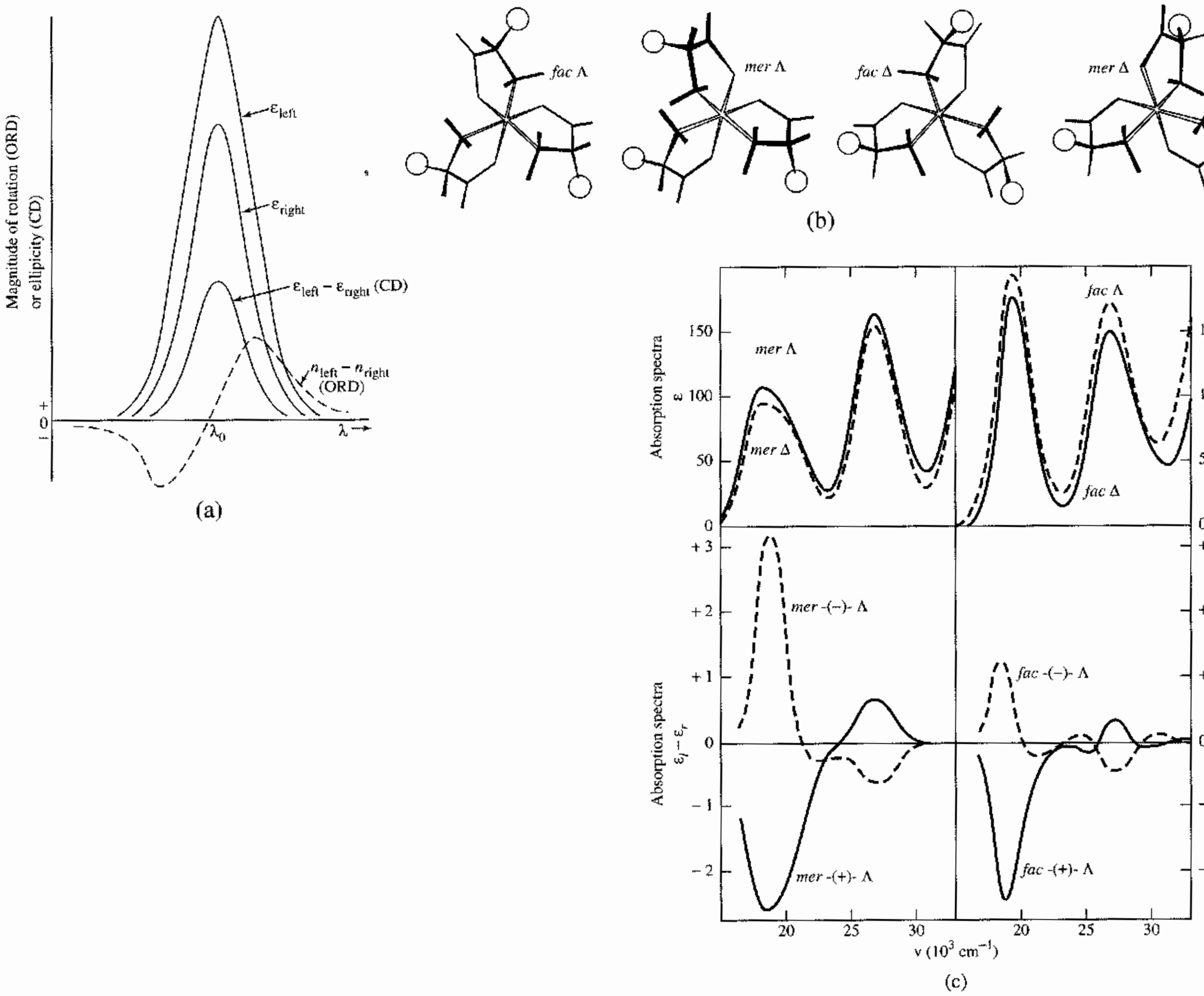

FIGURE 9-20 The Cotton Effect in ORD and CD. (a) Idealized optical rotatory dispersion (ORD) and circular dichroism (CD) curves at an absorption peak, with a positive Cotton effect. (b) Structures of tris-(S-alaninato) cobalt(III) complexes. (c) Absorption and circular dichroism spectra of the compounds in (b). (Data and structures in (b) adapted with permission from R. G. Denning and T. S. Piper, *Inorg. Chem.*, **1966**, 5, 1056. © 1966 American Chemical Society. Curves in (c) adapted with permission from J. Fujita and Y. Shimura, Optical Rotatory Dispersion and Circular Dichroism, in K. Nakamoto and P. J. McCarthy, eds., *Spectroscopy and Structure of Metal Chelate Compounds*, John Wiley & Sons Inc., New York, 1968, p. 193. © 1968 John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

The overall shape of a coordination compound is the product of several interacting factors. One factor may be dominant in one compound, with another factor dominant in another. Some factors involved in determining the structures of coordination complexes include the following:

1. The number of bonds. Because bond formation is usually considered exothermic, more bonds should make for a more stable molecule.
2. VSEPR arguments, as used in the simpler cases of the main group elements.
3. Occupancy of *d* orbitals. Examples of how the number of *d* electrons may affect the geometry (e.g., square-planar versus tetrahedral) will be discussed in Chapter 10.

4. Steric interference by large ligands crowding each other around the central metal.
5. Crystal packing effects. These include the effects resulting from the sizes of ions and the overall shape of coordination complexes. The regular shape of a compound may be distorted when it is packed into a crystalline lattice, and it is difficult to determine whether deviations from regular geometry are caused by effects within a given unit or by packing into a crystal.

The angles in a crystal lattice may fit none of the ideal cases. It is frequently difficult to predict shapes, and all predictions should be addressed skeptically unless backed by experimental evidence.

9-4-1 LOW COORDINATION NUMBERS (CN = 1, 2, AND 3)

Coordination number 1 is rare, except in ion pairs in the gas phase. Even species in aqueous solution that seem to be singly coordinated usually have water attached as well and have an overall coordination number higher than 1. Two organometallic compounds with coordination number 1 are the Tl(I) and In(I) complexes of 2,6-$\text{Trip}_2\text{C}_6\text{H}_3$.[31,32] The thallium compound is shown in Figure 9-21. In spite of the very bulky ligand that prevents any bridging between metals, the indium complex can also complex with $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$. $\text{Ga}[\text{C}(\text{SiMe}_3)_3]$ is an example of a monomeric singly coordinated organometallic in the gas phase.[33] A transient species that seems to be singly coordinated is VO^{2+}.

Coordination number 2 is also rare. The best known example is $[\text{Ag}(\text{NH}_3)_2]^+$, the diamminesilver(I) ion. The silver 1+ ion is d^{10} (a filled, spherical subshell), so the only electrons to be considered in the VSEPR treatment are those forming the bonds with the

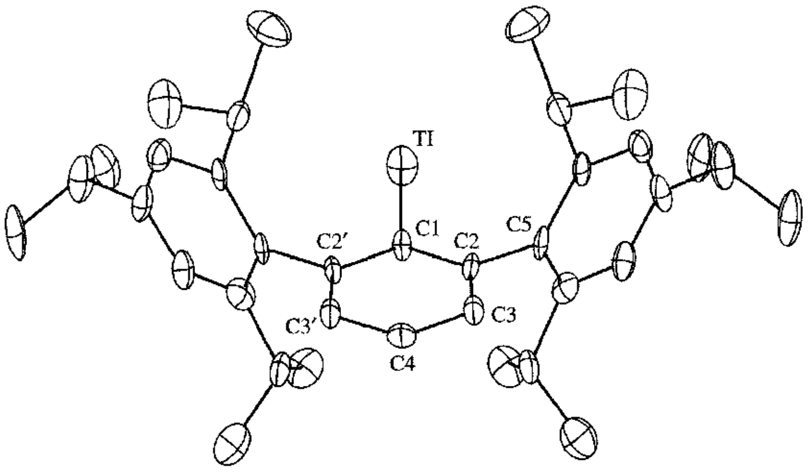

FIGURE 9-21 Coordination Number 1. Shown is 2,6-$\text{Trip}_2\text{C}_6\text{H}_3\text{Tl}$ (Trip = 2,4,6-$i\text{Pr}_3\text{C}_6\text{H}_2$). (Reproduced with permission from M. Niemeyer and P. P. Power, *Angew. Chem., Int. Ed.*, **1998**, *37*, 1277.)

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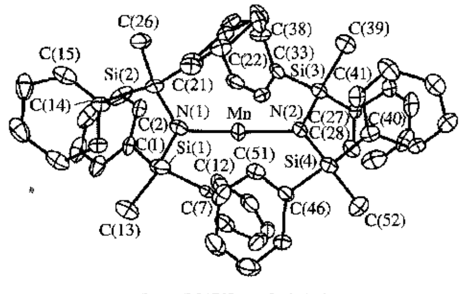
[31] M. Niemeyer and P. P. Power, *Angew. Chem., Int. Ed.*, **1998**, *37*, 1277; S. T. Haubrich and P. P. Power, *J. Am. Chem. Soc.*, **1998**, *120*, 2202.

[32] The earlier editions of this book included Cu(I) and Ag(I) complexes of 2,4,6-$\text{Ph}_3\text{C}_6\text{H}_2^-$ (5′-phenyl-*m*-terphenyl-2′-yl) as having CN = 1. Later analysis made this claim unlikely. (A. Haaland, K. Rypdal, H. P. Verne, W. Scherer, and W. R. Thiel, *Angew. Chem., Int. Ed.*, **1994**, *33*, 2443.)

[33] A. Haaland, K.-G. Martinsen, H. V. Volden, W. Kaim, E. Waldhör, W. Uhl, and U. Schütz, *Organometallics*, **1996**, *15*, 1146.

FIGURE 9-22 Complexes with Coordination Number 2. ($[Mn(N[SiMePh_2]_2)_2]$ reproduced with permission from H. Chen, R. A. Bartlett, H. V. R. Dias, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.*, **1989**, *111*, 4338. © 1989 American Chemical Society.)



$[Mn(N(SiMePh_2)_2)_2]$

$[H_3N—Ag—NH_3]^+$

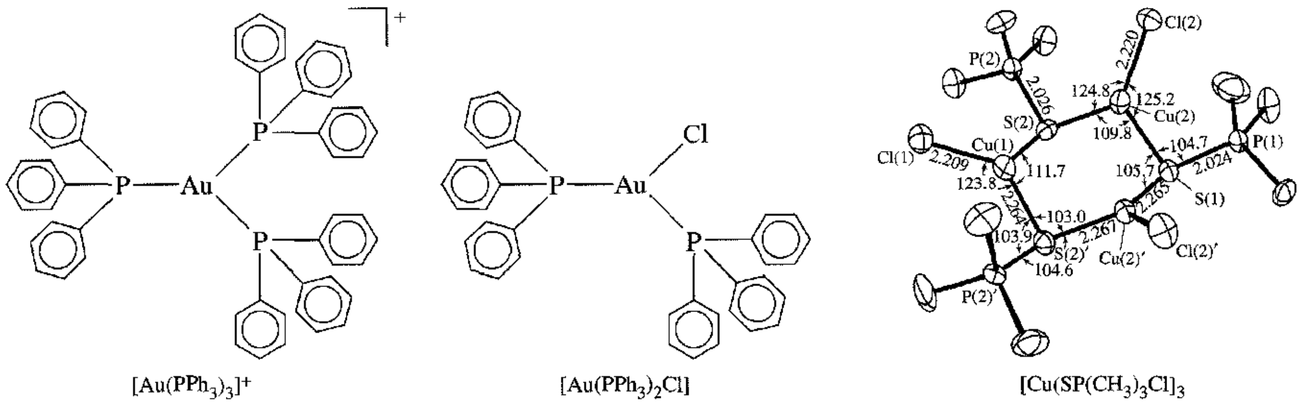
$[Cl—Cu—Cl]^-$

$NC—Hg—CN$

$[CN—Au—CN]^-$

ammonia ligands, and the structure is linear as expected for two bonding positions. Other examples are also d^{10} and linear ($[CuCl_2]^-$, $Hg(CN)_2$, $[Au(CN)_2]^-$), except for d^5 $Mn[N(SiMePh_2)_2]_2$, which is shown in Figure 9-22. Examples of 2-coordinate d^6 and d^7 complexes also exist.[34,35] Large ligands such as the silylamine help force a linear or near-linear arrangement.

Coordination number 3 also is more likely with d^{10} ions, with a trigonal-planar structure being the most common. Three-coordinate Au(I) and Cu(I) complexes that are known include $[Au(PPh_3)_3]^+$, $[Au(PPh_3)_2Cl]$, and $[Cu(SPPh_3)_3]^+$.[36,37] Most three-coordinate complexes seem to have a low coordination number because of ligand crowding. Ligands such as triphenylphosphine, PPh_3, and di(trimethylsilyl)amide, $N(SiMe_3)_2^-$, are bulky enough to prevent larger coordination numbers, even when the electronic structure favors them. All the first-row transition metals except Mn(III) form such complexes, either with three identical ligands or two of one ligand and one of the other. These complexes have a geometry close to trigonal planar around the metal. Others with three ligands are MnO_3^+, HgI_3^-, and the cyclic compound $[Cu(SPMe_3)Cl]_3$. Some of these complexes are shown in Figure 9-23.



$[Au(PPh_3)_3]^+$
(a)

$[Au(PPh_3)_2Cl]$
(b)

$[Cu(SP(CH_3)_3Cl]_3$
(c)

FIGURE 9-23 Complexes with Coordination Number 3. [(c) reproduced with permission from J. A. Tiethof, J. K. Stalick, and D. W. Meek, *Inorg. Chem.*, **1973**, *12*, 1170. © 1973 American Chemical Society.]

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[34] D. C. Bradley and K. J. Fisher, *J. Am. Chem. Soc.*, **1971**, *93*, 2058.

[35] H. Chen, R. A. Bartlett, H. V. R. Dias, M. M. Olmstead, and P. P. Power, *J. Am. Chem. Soc.*, **1989**, *111*, 4338.

[36] F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, **1968**, *7*, 2273.

[37] N. C. Baenziger, K. M. Dittemore, and J. R. Doyle, *Inorg. Chem.*, **1974**, *13*, 805.

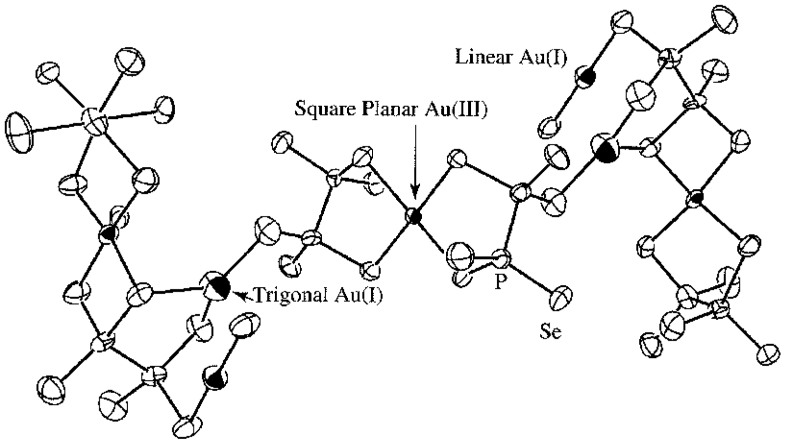

FIGURE 9-24 $K_2Au_2P_2Se_6$, a Gold Complex with Gold in Three Different Geometries. Dark circles, Au; large open circles, Se; small open circles, P. $[P_2Se_6]^{4-}$ ions bridge Au(I) in linear and trigonal geometries and Au(III) in square-planar geometry. The structure is a long chain, stacking to form open channels containing the K^+ ions. (Reproduced with permission from K. Chordroudis, T. J. McCarthy, and M. G. Kanatzidis, *Inorg. Chem.*, **1996**, *35*, 3451. © 1996 American Chemical Society.)

A final example (Figure 9-24) shows gold with three different geometries, linear Au(I), trigonal Au(I), and square planar Au(III).[38]

9-4-2 COORDINATION NUMBER 4[39]

Tetrahedral and square-planar structures are two common structures with four ligands. Another structure, with four bonds and one lone pair, appears in main group compounds such as SF_4 and $TeCl_4$, giving a "seesaw" structure, as described in Chapter 3 (Figure 3-11). Crowding around small ions of high positive charge prevents higher coordination numbers for ions such as Mn(VII) and Cr(VI), and large ligands can prevent higher coordination for other ions. Many d^0 or d^{10} complexes have tetrahedral structures, such as MnO_4^-, CrO_4^{2-}, $[Ni(CO)_4]$, and $[Cu(py)_4]^+$, with a few d^5, such as $MnCl_4^{2-}$. In such cases, the shape can be explained on the basis of VSEPR arguments, because the d orbital occupancy is spherically symmetrical with zero, one, or two electrons in each d orbital. However, a number of tetrahedral Co(II) (d^7) species are also known ($CoCl_4^{2-}$ is one), as well as some for other transition metal complexes, such as $[Co(PF_3)_4]$, $TiCl_4$, $[NiCl_4]^{2-}$, and $[NiCl_2(PPh_3)_2]$. Tetrahedral structures are also found in the tetrahalide complexes of Cu(II). $Cs_2[CuCl_4]$ and $(NMe_4)_2[CuCl_4]$ contain $CuCl_4^{2-}$ ions that are close to tetrahedral, as are the same ions in solution. The Jahn-Teller effect described in Chapter 10 causes distortion of the tetrahedron, with two of the Cl—Cu—Cl bond angles near 102° and two near 125°. The bromide complexes have similar structures. Examples of tetrahedral species are given in Figure 9-25.

Square-planar geometry is also possible for four-coordinate species, with the same geometric requirements imposed by octahedral geometry (both require 90° angles between ligands). The only common square-planar complexes whose structures are not imposed by a planar ligand contain d^8 ions [Ni(II), Pd(II), Pt(II), for example], although

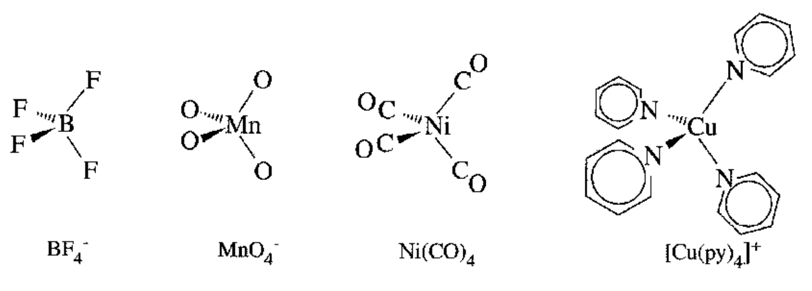

FIGURE 9-25 Complexes with Tetrahedral Geometry.

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[38] K. Chordroudis, T. J. McCarthy, and M. G. Kanatzidis, *Inorg. Chem.*, **1996**, *35*, 3451.

[39] M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem.*, **1980**, *27*, 325.

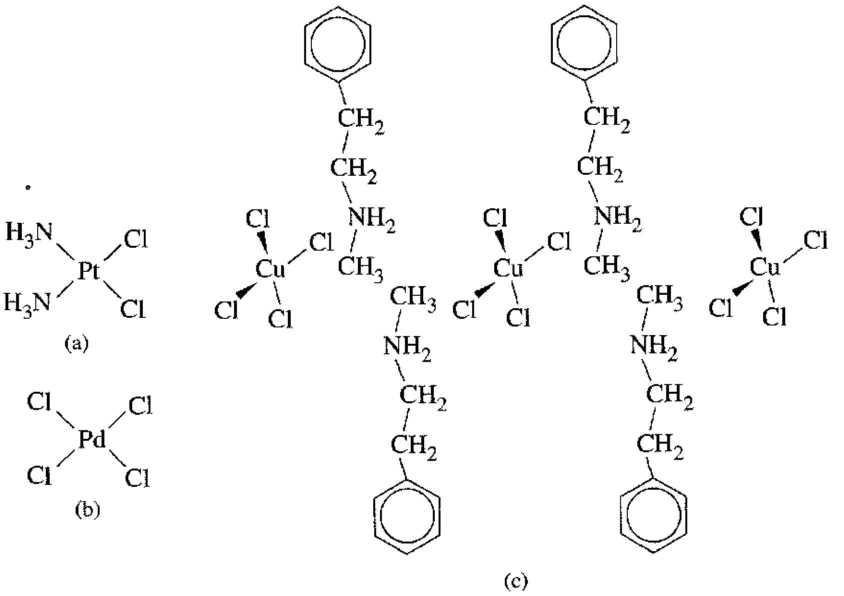

FIGURE 9-26 Complexes with Square-Planar Geometry. (a) $PtCl_2(NH_3)_2$. (b) $[PdCl_4]^{2-}$. (c) N-Methylphenethylammonium tetrachlorocuprate(II) at 25°C. At 70°C, the $CuCl_4^{2-}$ anion is nearly tetrahedral. (Adapted with permission from R. L. Harlow, W. J. Wells, III, G. W. Watt, and S. H. Simonsen, *Inorg. Chem.*, **1974**, *13*, 2106. © 1974 American Chemical Society.)

Ni(II) and Cu(II) can have tetrahedral, square-planar, or intermediate shapes, depending on both the ligand and the counterion in the crystal. Cases such as these indicate that the energy difference between the two structures is small and crystal packing can have a large influence on the choice. Many copper complexes have distorted six-coordinate structures between octahedral and square-planar in shape. Pd(II) and Pt(II) complexes are square-planar, as are the d^8 complexes $[AgF_4]^-$, $[RhCl(PPh_3)_3]$, $[Ni(CN)_4]^{2-}$, and $[NiCl_2(PMe_3)_2]$. At least one compound, $[NiBr_2(P(C_6H_5)_2(CH_2C_6H_5)_2]$, has both square-planar and tetrahedral isomers in the same crystal.[40] Some square-planar complexes are shown in Figure 9-26.

9-4-3 COORDINATION NUMBER 5[41]

The structures possible for coordination number 5 are the trigonal bipyramid, the square pyramid, and the pentagonal plane (which is unknown except for $[XeF_5]^-$, probably because of the crowding that would be required of the ligands). The energy difference between the trigonal bipyramid and the square pyramid is very small. In fact, many molecules with five ligands either have structures between these two or can switch easily from one to the other in fluxional behavior. For example, $Fe(CO)_5$ and PF_5 have nuclear magnetic resonance spectra (using ^{13}C and ^{19}F, respectively) that shows only one peak, indicating that the atoms are identical on the NMR time scale. Because both the trigonal bipyramid and the square pyramid have ligands in two different environments, the experiment shows that the compounds switch from one structure to another rapidly or that they have a solution structure intermediate between the two. In the solid state, both are trigonal bipyramids. $[VO(acac)_2]$ is a square pyramid, with the doubly bonded oxygen in the apical site. There is also evidence that $[Cu(NH_3)_5]^{2+}$ exists as a square-pyramidal structure in liquid ammonia.[42] Other five-coordinate complexes are known for the full range of transition metals, including $[CuCl_5]^{3-}$ and $[FeCl(S_2C_2H_2)_2]$. Examples of five-coordinate complexes are shown in Figure 9-27.

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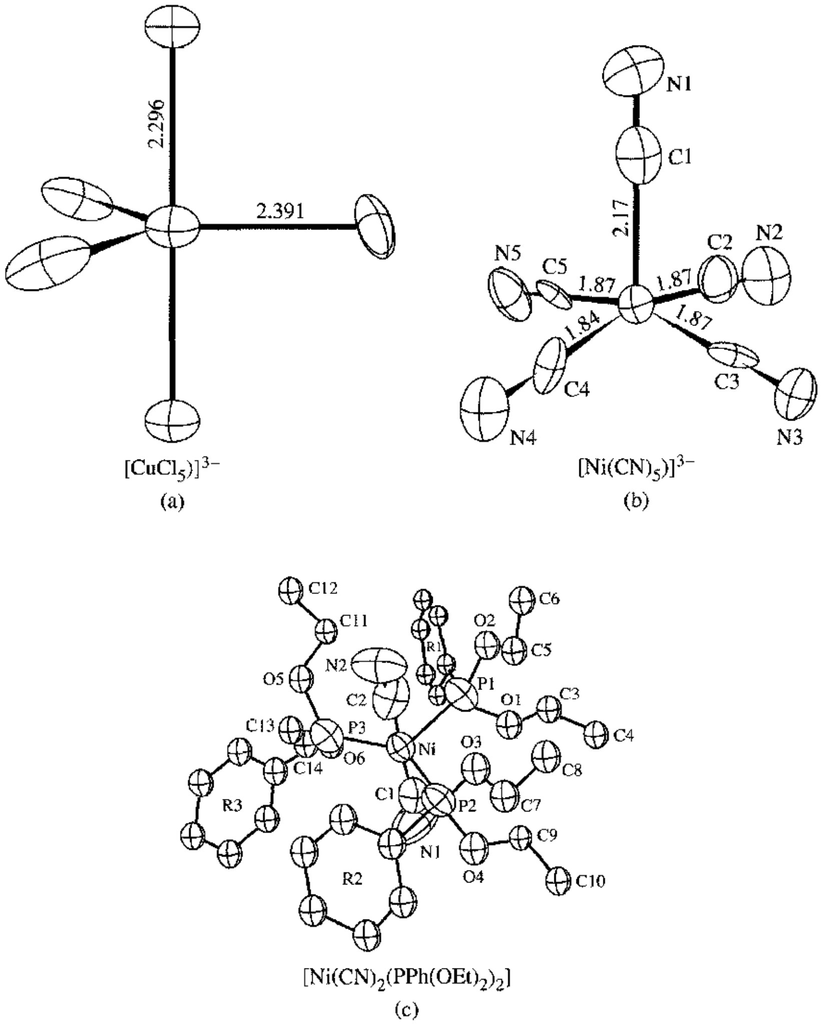
[40] B. T. Kilbourn, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, **1963**, 207.

[41] R. R. Holmes, *Prog. Inorg. Chem.*, **1984**, *32*, 119; T. P. E. Auf der Heyde and H.-B. Bürgi, *Inorg. Chem.*, **1989**, *28*, 3960.

[42] M. Valli, S. Matsuo, H. Wakita, Y. Yamaguchi, and M. Nomura, *Inorg. Chem.*, **1996**, *35*, 5642.



$[CuCl_5)]^{3-}$
(a)

$[Ni(CN)_5)]^{3-}$
(b)

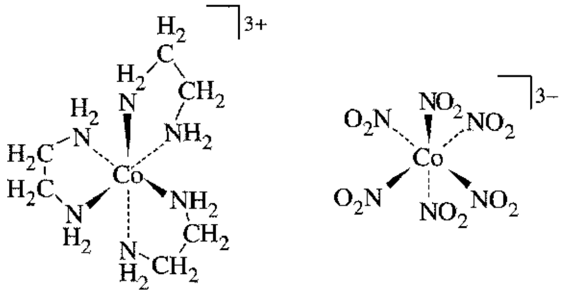
$[Ni(CN)_2(PPh(OEt)_2)_2]$
(c)

FIGURE 9-27 Complexes with Coordination Number 5. (a) $[CuCl_5]^{3-}$. (From $[Cr(NH_3)_6][CuCl_5]$, K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **1968**, *7*, 1111.) (b) $[Ni(CN)_5]^{3-}$. (From $[Cr(en)_3][Ni(CN)_5]$, K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **1968**, *7*, 1362.) (c) $[Ni(CN)_2(PPh(OEt)_2)_3$. (From J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **1969**, *8*, 1084.) (Reproduced with permission of the American Chemical Society. © 1968 and 1969.)

9-4-4 COORDINATION NUMBER 6

Six is the most common coordination number. The most common structure is octahedral; some trigonal prismatic structures are also known. If a metal ion is large enough to allow six ligands to fit around it and the *d* electrons are ignored, an octahedral shape results from VSEPR arguments. Such compounds exist for all the transition metals with d^0 to d^{10} configurations.

Octahedral compounds have been used in many of the earlier illustrations in this chapter and others. Other octahedral complexes include tris(ethylenediamine) cobalt(III), ($[Co(en)_3]^{3+}$), and hexanitritocobaltate(III), ($[Co(NO_2)_6]^{3-}$), shown in Figure 9-28.



$[Co(en)_3]^{3+}$ $[Co(NO_2)_6]^{3-}$

FIGURE 9-28 Complexes with Octahedral Geometry.

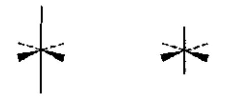


FIGURE 9-29 Tetragonal Distortions of the Octahedron.

For complexes that are not regular octahedra, several types of distortion are possible. The first is elongation, leaving four short bonds in a square-planar arrangement together with two longer bonds above and below the plane. Second is the reverse, a compression with two short bonds at the top and bottom and four longer bonds in the plane. Either results in a tetragonal shape, as shown in Figure 9-29. Chromium dihalides exhibit tetragonal elongation; crystalline CrF_2 has a distorted rutile structure, with four Cr—F distances of 200 pm and two of 243 pm, and other chromium(II) halides have similar bond distances, but different crystal structures.[43]

A trigonal elongation or compression results in a trigonal antiprism when the angle between the top and bottom triangular faces is 60°, and a trigonal prism when the two triangular faces are eclipsed, as shown in Figure 9-30. Most trigonal prismatic complexes have three bidentate ligands (dithiolates, $S_2C_2R_2$, or oxalates are common) linking the top and bottom triangular faces. Although similar in other ways, β-diketone complexes usually have skew conformations and have near-octahedral symmetry around the metal. Trigonal prismatic dithiolate complexes are shown in Figure 9-30. The trigonal structures of complexes such as these may be due to π interactions between adjacent sulfur atoms in the trigonal faces. Campbell and Harris[44] summarize the arguments for stability of the trigonal prismatic structure relative to octahedral.

A number of complexes that appear to be four-coordinate are more accurately described as six-coordinate. Although $(NH_4)_2[CuCl_4]$ is frequently cited as having a square-planar $[CuCl_4]^{2-}$ ion, the ions in the crystal are packed so that two more chlorides are above and below the plane at considerably larger distances in a distorted octahedral structure. The Jahn-Teller effect described in Chapter 10 is the cause of this

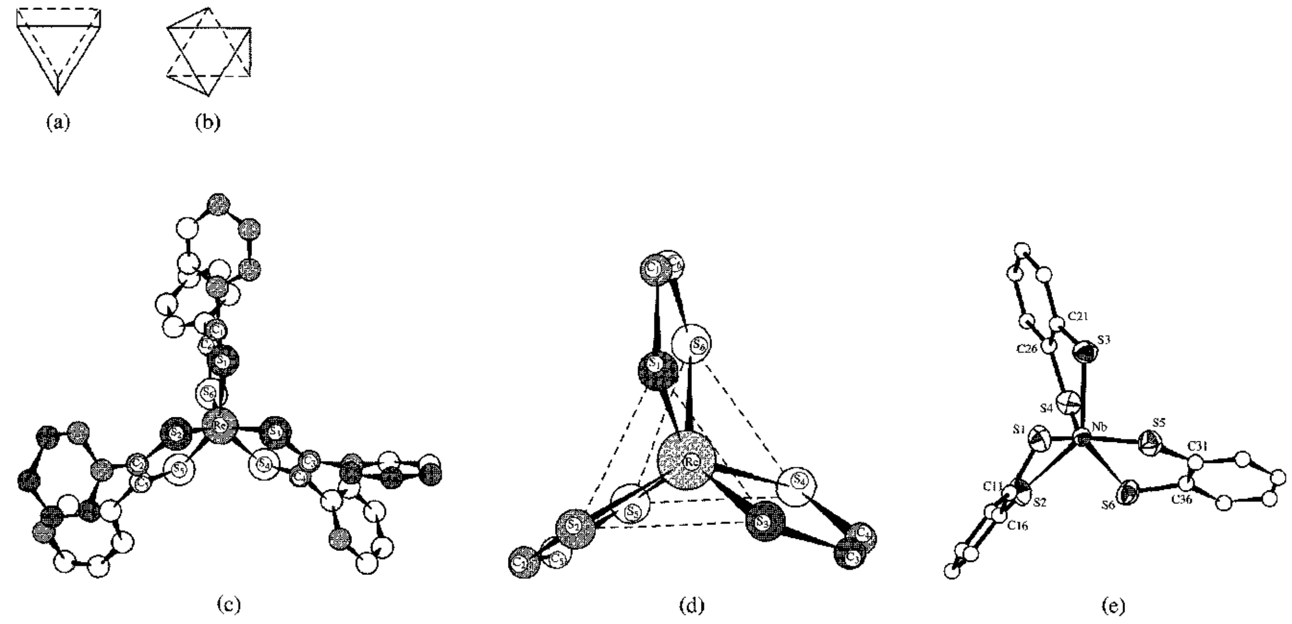


FIGURE 9-30 Complexes with Trigonal Prismatic Geometry. (a) A trigonal prism. (b) A trigonal antiprism. (c), (d) $Re(S_2C_2(C_6H_5)_2)_3$. Part (d) is a perspective drawing of the coordination geometry of (c) excluding the phenyl rings. (Reproduced with permission from R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **1966**, *5*, 411. © 1966 American Chemical Society.) (e) Tris(benzene-1,2-dithiolato) niobate(V), $[Nb(S_2C_6H_4)_3]^-$, omitting the hydrogens. (Reproduced with permission from M. Cowie and M. J. Bennett, *Inorg. Chem.*, **1976**, *15*, 1589. © 1976 American Chemical Society.)

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[43] A. F. Wells, *Structural Inorganic Chemistry*, 5th ed., Oxford University Press, Oxford, 1984, p. 413.

[44] S. Campbell and S. Harris, *Inorg. Chem.*, **1996**, *35*, 3285.

distortion. Similarly, $[Cu(NH_3)_4]SO_4{\cdot}H_2O$ has the ammonias in a square-planar arrangement, but each copper is also connected to distant bridging water molecules above and below the plane.

Another nonoctahedral six-coordinate ion is $[CuCl_6]^{4-}$ in the compound [*tris*(2-aminoethyl)amine$H_4]_2[CuCl_6]Cl_4{\cdot}2H_2O$.[45] There are three different Cu—Cl bond distances, in *trans* pairs at 225.1, 236.1, and 310.5 pm, resulting in approximately D_{2h} symmetry. Many hydrogen-bond interactions occur between the chlorides and the water molecules in this crystal; if the hydrogen bonds are strong, the Cu—Cl bonds are longer.

9-4-5 COORDINATION NUMBER 7[46]

Three structures are possible for seven-coordinate complexes, the pentagonal bipyramid, capped trigonal prism, and capped octahedron. In the capped shapes, the seventh ligand is simply added to a face of the structure, with related adjustments in the other angles to allow it to fit. Although seven-coordination is not common, all three shapes are found experimentally, with the differences apparently resulting from different counterions and the steric requirements of the ligands (especially chelating ligands).

Examples include the following: $[M(trenpy)]^{2+}$ [M = any of the metals from Mn to Zn, and trenpy = $(C_5H_4NCH{=}NCH_2CH_2)_3N$], in which the central nitrogen of the ligand caps a trigonal face of an octahedron; 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaenebis(thiocyanato)iron, $[UO_2F_5]^{3-}$, and $[NbOF_6]^{3-}$, pentagonal bipyramids; $[NiF_7]^{2-}$ and $[NbF_7]^{2-}$, in both of which the seventh fluoride caps a rectangular face of a trigonal prism; and $[W(CO)_4Br_3]^-$, a monocapped octahedron. Some of these complexes are shown in Figure 9-31. An analysis of different geometries and many references has been presented by Lin and Bytheway.[47]

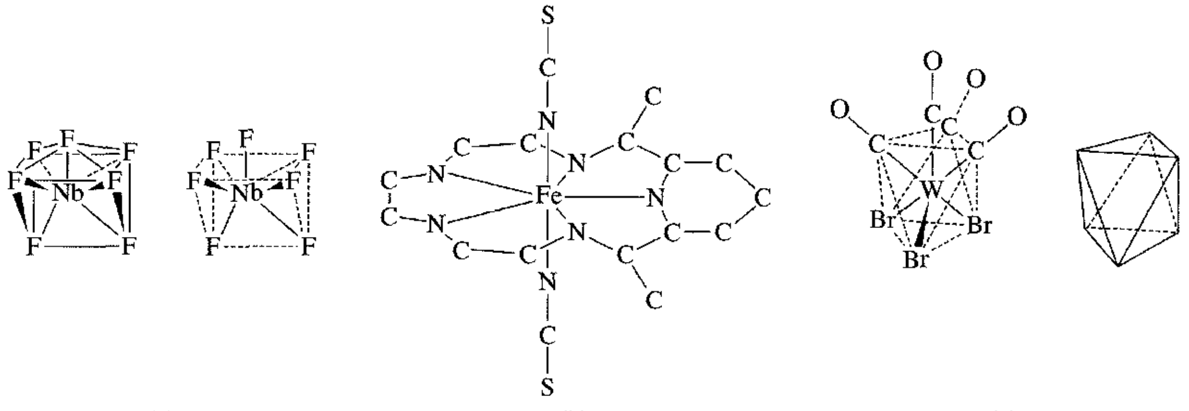

FIGURE 9-31 Complexes with Coordination Number 7. (a) Heptafluoroniobate(V), $[NbF_7]^{2-}$, a capped trigonal prism. The capping F is at the top. (b) 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene complex of Fe(II) with two axial thiocyanates, a pentagonal bipyramid. (From E. Fleischer and S. Hawkinson, *J. Am. Chem. Soc.*, **1967**, 89, 720.) (c) Tribromotetracarbonyltungstate(II) anion, $[W(CO)_4Br_3]^-$, a capped octahedron, and an octahedron in the same orientation. The capping CO is at the top. (From M. G. B. Drew and A. P. Wolters, *Chem. Commun. (Cambridge UK)*, **1972**, 457.)

[45] M. Wei, R. D. Willett, and K. W. Hipps, *Inorg. Chem.*, **1996**, *35*, 5300.

[46] D. L. Kepert, *Prog. Inorg. Chem.*, **1979**, *25*, 41.

[47] Z. Lin and I. Bytheway, *Inorg. Chem.*, **1996**, *35*, 594.

9-4-6 COORDINATION NUMBER 8[48]

Although the cube has eight-coordinate geometry, it exists only in simple ionic lattices such as CsCl. The square antiprism and dodecahedron are common in transition metal complexes, and there are many eight-coordinate complexes. Because the central ion must be large in order to accommodate eight ligands, eight-coordination is rare among the first-row transition metals (although it is likely in $[Fe(edta)(H_2O)_2]^+$ in solution). Solid-state examples include $Na_7Zr_6F_{31}$, which has square antiprisms of ZrF_8 units, and $[Zr(acac)_4]$, a regular dodecahedron. $[AmCl_2(H_2O)_6]^+$ is a trigonal prism of water ligands with chloride caps on the trigonal faces. Three of these complexes are shown in Figure 9-32.

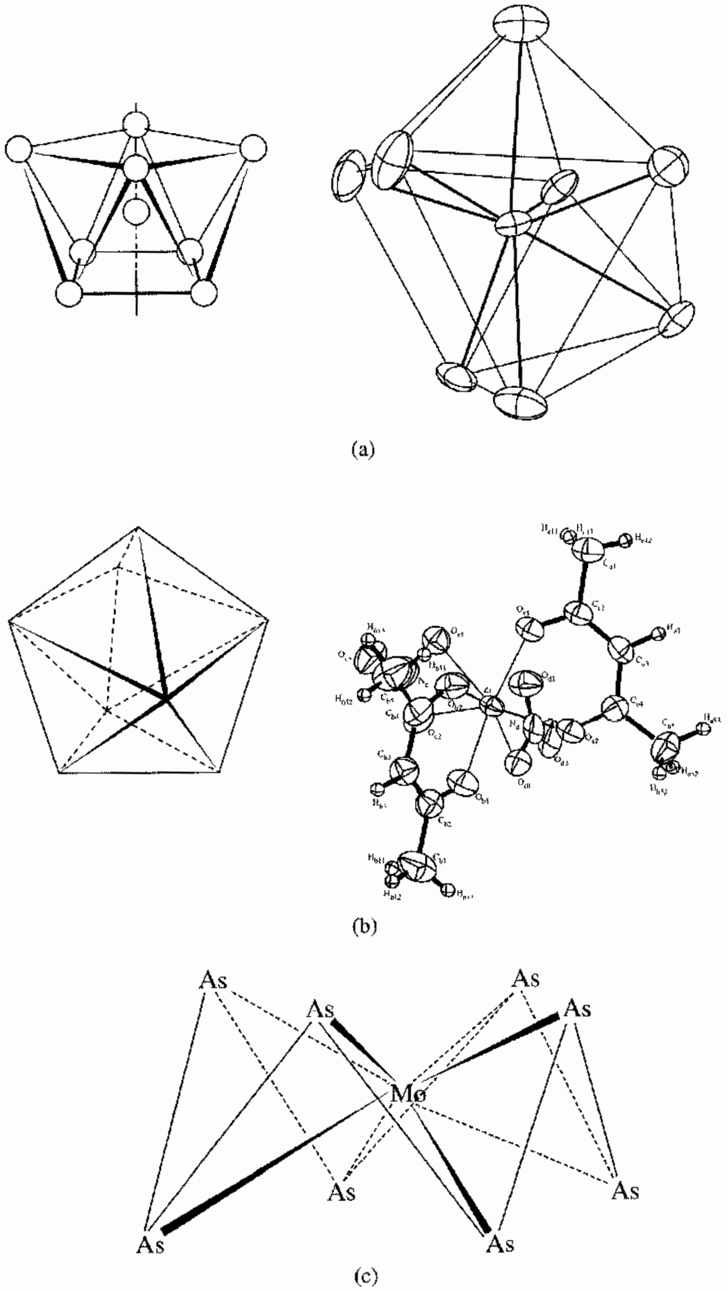

FIGURE 9-32 Complexes with Coordination Number 8.
(a) $Na_7Zr_6F_{31}$, square antiprisms of ZrF_8. (Reproduced with permission from J. H. Burns, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **1968**, *B24*, 230.)
(b) $[Zr(acac)_2(NO_3)_2]$, regular dodecahedron. (Reproduced with permission from V. W. Day and R. C. Fay, *J. Am. Chem. Soc.*, **1975**, *97*, 5136. © 1975 American Chemical Society.) (c) $MoAs_8^{2-}$. (Redrawn from B. W. Eichhorn, S. P. Mattamana, D. R. Gardner, and J. C. Fettinger, *J. Am. Chem. Soc.*, **1998**, *120*, 9708.)

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[48] D. L. Kepert, *Prog. Inorg. Chem.*, **1978**, *24*, 179.

$[Yb(NH_3)_8]^{3+}$ also has a square-antiprism structure.[49] In addition, coordination number 8 is observed in $[Mo(CN)_8]^{4-}$ ions[50] in a compressed square-antiprism structure and when As_8 rings bond to transition metals in a "crownlike" configuration, as in $MoAs_8{}^{2-}$ (also shown in Figure 9-32) and similar complexes.[51]

9-4-7 LARGER COORDINATION NUMBERS

Coordination numbers are known up to 16, but most over 8 are special cases.[52] Two examples are shown in Figure 9-33. $[La(NH_3)_9]^{3+}$ has a capped square-antiprism structure.[53]

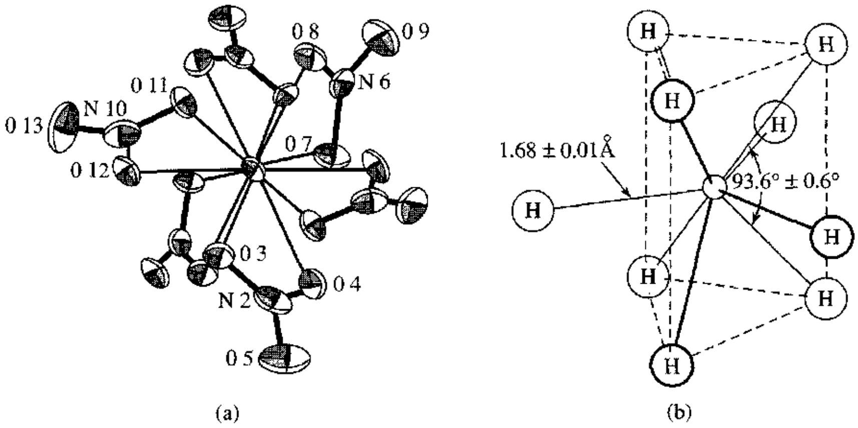

FIGURE 9-33 Complexes with Larger Coordination Numbers. (a) $[Ce(NO_3)_6]^{3-}$, with bidentate nitrates. (Reproduced with permission from T. A. Beinecke and J. Delgaudio, *Inorg. Chem.*, **1968**, *7*, 715. © 1968 American Chemical Society.) (b) $[ReH_9]^{2-}$, tricapped trigonal prism. (Reproduced with permission from S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **1964**, *3*, 558. © 1964 American Chemical Society.)

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The official documents on IUPAC nomenclature are G. J. Leigh, ed., *Nomenclature of Inorganic Chemistry*, Blackwell Scientific Publications, Oxford, England, 1990, and J. A. McCleverty and N. G. Connelly, eds., *IUPAC, Nomenclature of Inorganic Chemistry II: Recommendations 2000*, Royal Society of Chemistry, Cambridge, UK, 2001. The best single reference for isomers and geometric structures is G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds., *Comprehensive Coordination Chemistry*, Pergamon Press, Oxford, 1987. The reviews cited in the individual sections are also very comprehensive.

PROBLEMS

9-1 Name:

- **a.** $[Fe(CN)_2(CH_3NC)_4]$
- **b.** $Rb[AgF_4]$
- **c.** $[Ir(CO)Cl(PPh_3)_2]$ (two isomers)

9-2 Give structures for

- **a.** Bis(en)Co(III)-μ-imido-μ-hydroxobis(en)Co(III) ion
- **b.** Diaquadiiododinitrito Pd(IV) (all isomers)

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[49] D. M. Young, G. L. Schimek, and J. W. Kolis, *Inorg. Chem.*, **1996**, *35*, 7620.

[50] W. Meske and D. Babel, *Z. Naturforsch., B: Chem. Sci.*, **1999**, *54*, 117.

[51] B. W. Eichhorn, S. P. Mattamana, D. R. Gardner, and J. C. Fettinger, *J. Am. Chem. Soc.*, **1998**, *120*, 9708; J. Li and K. Wu, *Inorg. Chem.*, **2000**, *39*, 1538.

[52] M. C. Favas and D. L. Kepert, *Prog. Inorg. Chem.*, **1981**, *28*, 309.

[53] D. M. Young, G. L. Schimek, and J. W. Kolis, *Inorg. Chem.*, **1996**, *35*, 7620.