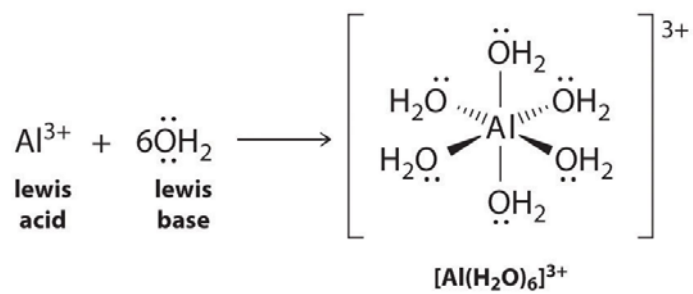
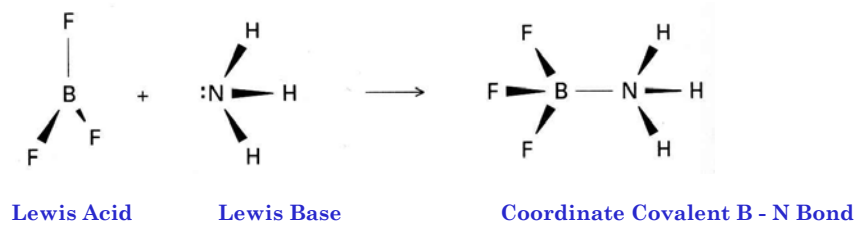
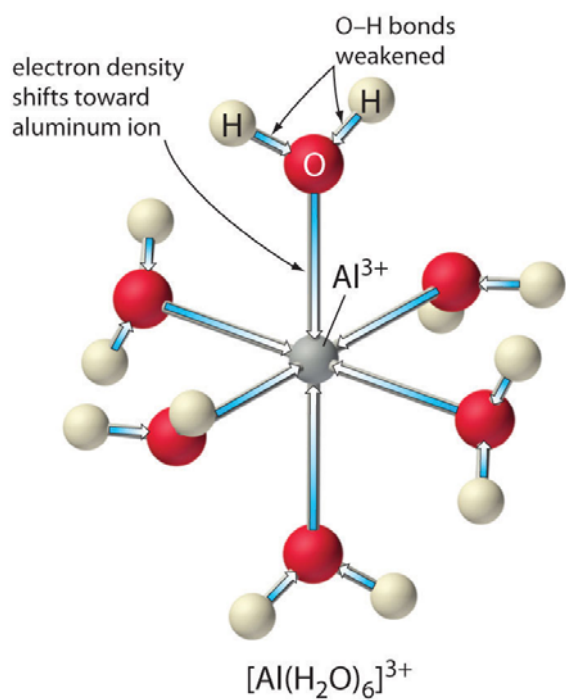


Topic 9C - Coordination Compounds

Lewis Acid-Base Reactions:



(a)



(b)

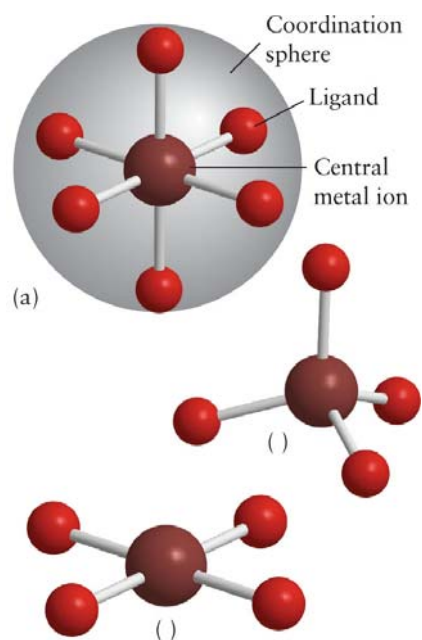


FIGURE 17.18 (a) Almost all six-coordinate complexes are octahedral. Four-coordinate complexes are either (b) tetrahedral or (c) square planar.

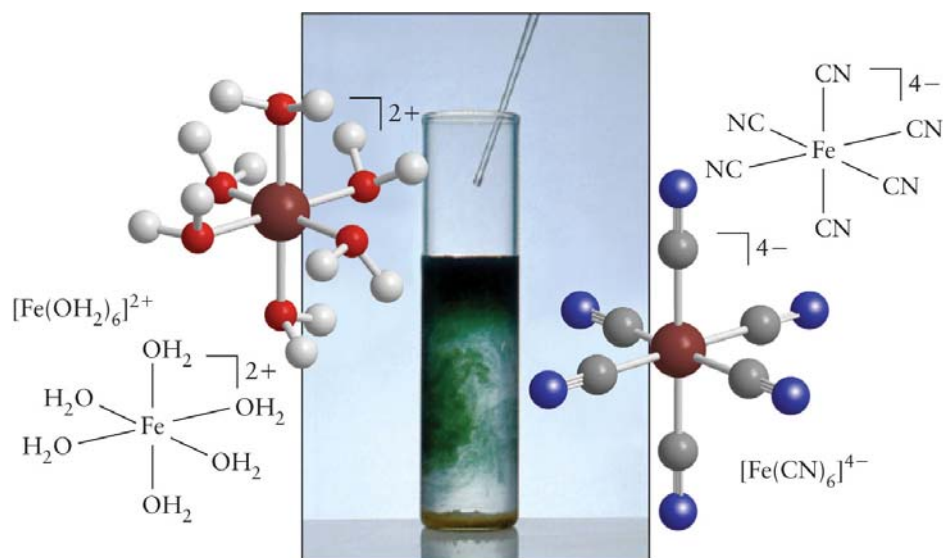
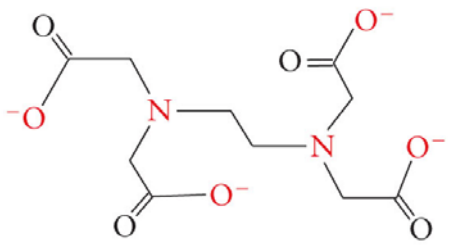


FIGURE 17.19 When potassium cyanide is added to a solution of iron(II) sulfate, the cyanide ions replace the H_2O ligands of the $[\text{Fe}(\text{OH}_2)_6]^{2+}$ complex (left) and produce a new complex, the hexacyanoferrate(II) ion, $[\text{Fe}(\text{CN})_6]^{4-}$ (right). The blue color is due to the polymeric compound called Prussian blue, which forms from the cyanoferrate ion.

TABLE 17.4 Common Ligands

Formula*	Name
Neutral ligands	
OH ₂	aqua
NH ₃	ammine
NO	nitrosyl
CO	carbonyl
NH ₂ CH ₂ CH ₂ NH ₂	ethylenediamine (en) [†]
NH ₂ CH ₂ CH ₂ NHCH ₂ CH ₂ NH ₂	diethylenetriamine (dien) [‡]
Anionic ligands	
F ⁻	fluorido
Cl ⁻	chlorido
Br ⁻	bromido
I ⁻	iodido
OH ⁻	hydroxido
O ²⁻	oxido
<u>C</u> N ⁻	cyanido-κC
<u>C</u> N ⁻	isocyano, cyanido-κN
<u>N</u> CS ⁻	isothionato, thiocyanato-κN
N <u>C</u> S ⁻	thiocyanato-κS
NO ₂ ⁻ as <u>O</u> NO ⁻	nitrito-κO
NO ₂ ⁻ as <u>N</u> O ₂ ⁻	nitro, nitrito-κN
CO ₃ ²⁻ as <u>O</u> CO ₂ ²⁻	carbonato-κO
C ₂ O ₄ ²⁻ as ⁻ O ₂ CCO ₂ ⁻	oxalato (ox) [†]
	ethylenediaminetetraacetato (edta) [§]
SO ₄ ²⁻ as <u>O</u> SO ₃ ²⁻	sulfato

*Ligand atoms that bond to the metal atom are underlined in ambiguous cases.

[†]Bidentate (attaches to two sites).

[‡]Tridentate (attaches to three sites).

[§]Hexadentate (attaches to six sites).

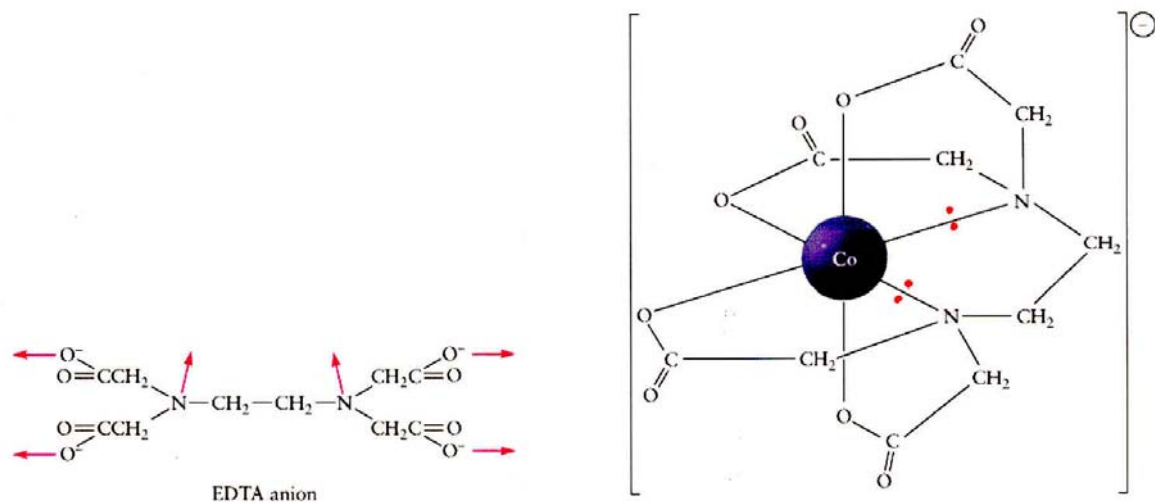


FIGURE 8.21 The chelation complex of EDTA with cobalt(III). Each EDTA ion has six donor sites at which it can bind (by donating lone-pair electrons) to the central metal ion.

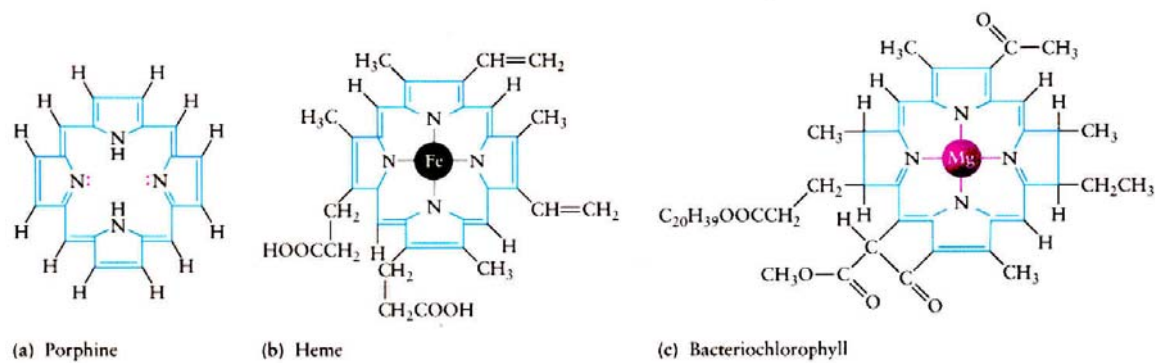


FIGURE 8.22 Structures of (a) porphine, (b) heme, and (c) bacteriochlorophyll. The porphine ring common to the three structures is highlighted in blue.

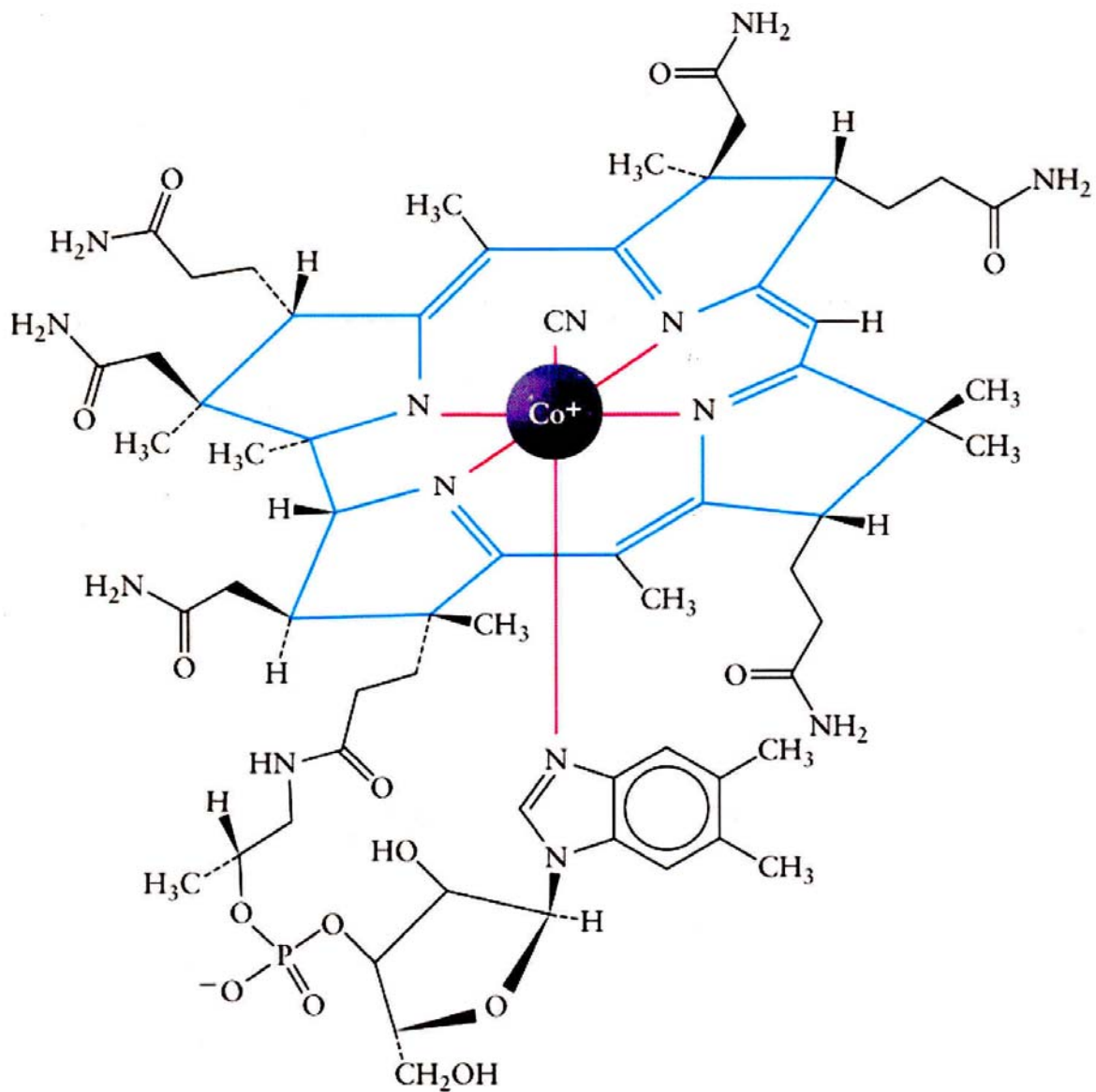


FIGURE 8.23 Structure of vitamin B₁₂.

Toolbox 17.1 HOW TO NAME d-METAL COMPLEXES AND COORDINATION COMPOUNDS

CONCEPTUAL BASIS

The aim of nomenclature is to be succinct but unambiguous. d-Metal complexes are identified by giving the names and numbers of the individual ligands. Because some names can be quite long, interpreting them is rather like eating a large bun: nibble it bite by bite, don't try to swallow it in one gulp. The rules are scrutinized periodically and, when appropriate, changed to achieve greater clarity and consistency. The rules used here are consistent with the latest (2005) IUPAC recommendations. Further information on naming complexes can be found at <http://old.iupac.org/publications/books/seriestitles/nomenclature.html> (refer to the "Red Book").

PROCEDURE

The following rules are adequate for most common complexes; more elaborate rules are needed if the complex contains more than one metal atom. Note that some rules apply to naming the complex (formally, the "coordination entity") and others to writing its chemical formula.

A. Writing the formula

1. The chemical symbol of the central atom (usually a metal) is written first, followed by symbols for the ligands. The entire collection of symbols is placed between square brackets, with the overall charge denoted by a right-superscript.
2. The chemical symbols of ligands are written in alphabetical order; when different ligands contain the same element, those denoted by a single letter (e.g., O) take precedence over symbols represented by two or more letters (e.g., OH). If a particular point needs to be emphasized, then the order may be varied. Water as a ligand is denoted OH₂, to emphasize that the O links to the metal atom.

Examples: [FeCl(OH₂)₅]⁺ [Fe(NH₃)₅(OH₂)₃]³⁺

3. To avoid any ambiguity, the linking atom can be underlined.

Examples: [Fe(NCS)(OH₂)₅]²⁺ [Fe(NCS₂)(OH₂)₅]²⁺

B. Naming the complex

1. Name the ligands first, and then the metal atom or ion. A Roman numeral in parentheses denotes the oxidation number of the central metal ion.
2. Neutral ligands, such as H₂NCH₂CH₂NH₂ (ethylenediamine), have the same name as the molecule, except for H₂O (aqua), NH₃ (ammine), CO (carbonyl), and NO (nitrosyl).
3. Anionic ligands end in -o; for anions that end in -ide (such as chloride), -ate (such as sulfate), and -ite (such as nitrite), change the endings as follows:

-ide → -ido -ate → -ato -ite → -ito

Examples: chlorido, sulfato, and nitrito

4. Greek prefixes indicate the number of each type of ligand in the complex ion:

2	3	4	5	6	...
di-	tri-	tetra-	penta-	hexa-	...

If the ligand already contains a Greek prefix (as in ethylenediamine) or if it is polydentate (able to attach at more than one binding site), then the following prefixes are used instead:

2	3	4	...
bis-	tris-	tetrakis-	...

5. Ligands are named in alphabetical order, ignoring the Greek prefix that indicates the number of each one present.

[FeCl(OH₂)₅]⁺ pentaquachloridoiron(II) ion

[Cr(Cl)₂(NH₃)₄]⁺ tetraamminedichloridochromium(III) ion

(Note that in some cases the order of ligands in the name is not the same as the order in the formula.)

6. If there is an ambiguity in which atom is linked to the metal atom, then κE is added to the name in parentheses, where E denotes the connecting atoms (and κ is kappa):

[Fe(NCS)(OH₂)₅]²⁺ thiocyanato(κN)pentaaqua(III) iron

[Fe(NCS₂)(OH₂)₅]²⁺ thiocyanato(κS)pentaaqua(III) iron

7. If the complex has an overall negative charge (an anionic complex), the suffix -ate is added to the stem of the metal's name. If the symbol of the metal originates from a Latin name (as listed in Appendix 2D), then the Latin stem is used. For example, the symbol for iron is Fe, from the Latin *ferrum*. Therefore, any anionic complex of iron ends with -ferrate followed by the oxidation number of the metal in Roman numerals:

[Fe(CN)₆]⁴⁻ hexacyanidoferrate(II) ion

[Ni(CN)₄]²⁻ tetracyanidonickelate(II) ion

8. The name of a coordination compound (as distinct from a complex cation or anion) is built in the same way as that of a simple compound, with the cation named before the anion:

NH₄[PtCl₃(NH₃)]
ammonium aminetrichloridoplatinate(II)

[Cr(NH₃)₄(OH)₂]Br
tetraamminedihydroxidochromium(III) bromide

This procedure is illustrated in Example 17.1.

Complex	Systematic Name
K ₃ [Fe(CN) ₆]	Potassium hexacyanoferrate(III)
K ₄ [Fe(CN) ₆]	Potassium hexacyanoferrate(II)
Fe(CO) ₅	Pentacarbonyliron(0)
[Co(NH ₃) ₅ CO ₃]Cl	Penta-amminecarbonatocobalt(III) chloride
K ₃ [Co(NO ₂) ₆]	Potassium hexanitrocobaltate(III)
[Cr(H ₂ O) ₄ Cl ₂]Cl	Tetra-aquadichlorochromium(III) chloride
[Pt(NH ₂ CH ₂ CH ₂ NH ₂) ₃]Br ₄	Tris(ethylenediamine)platinum(IV) bromide
K ₂ [CuCl ₄]	Potassium tetrachlorocuprate(II)

TABLE 3.1
Survey of Coordination Sphere Geometries

Coordination number	Structure	Examples
2	Linear	$\text{Ag}(\text{NH}_3)_2^+$, AuCl_2^- , $\text{Hg}(\text{CN})_2$
3	Trigonal	HgI_3^- , $\text{Pt}(\text{PPh}_3)_3$
4	Tetrahedral Square planar	MnO_4^- , CoBr_4^{2-} , ReO_4^- , $\text{Ni}(\text{CO})_4$ PdCl_4^{2-} , $\text{Pt}(\text{NH}_3)_4^{2+}$, $\text{Ni}(\text{CN})_4^{2-}$
5	Trigonal bipyramidal Square pyramidal	CuCl_3^{3-} , CdCl_3^{3-} , $\text{Ni}(\text{CN})_5^{3-}$ $\text{VO}(\text{acac})_2$, $\text{Ni}(\text{CN})_5^{3-}$
6	Octahedral Trigonal prismatic	$\text{Co}(\text{NH}_3)_6^{3+}$ $\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3$
7	Pentagonal bipyramidal Trigonally capped octahedron Tetragonally capped trigonal prism	ZrF_7^{3-} , HfF_7^{3-} , $\text{V}(\text{CN})_7^{4-}$ NbF_7^{2-} , TaF_7^{2-} NbOF_6^{3-}
8	Square antiprism Triangular-faced dodecahedron	ReF_8^{2-} , TaF_8^{3-} , $\text{W}(\text{CN})_8^{4-}$ $\text{Mo}(\text{CN})_8^{4-}$, $\text{Ti}(\text{NO}_3)_4$
9	Tricapped trigonal prism	ReH_9^{2-}

TABLE 2.2
The Number of Actual versus Predicted Isomers for Three Different Geometries of Coordination Number 6

Formula	No. of predicted isomers (numbers in parentheses indicate position of the B ligands)			No. of actual isomers
	Hexagonal planar	Trigonal prism	Octahedral	
MA_5B	One	One	One	One
MA_4B_2	Three	Three	Two	Two
	(1, 2)	(1, 2)	(1, 2)	
	(1, 3)	(1, 4)	(1, 6)	
MA_3B_3	Three	Three	Two	Two
	(1, 2, 3)	(1, 2, 3)	(1, 2, 3)	
	(1, 2, 4)	(1, 2, 4)	(1, 2, 6)	
	(1, 3, 5)	(1, 2, 6)		

Source: From Bodie Douglas, Darl H. McDaniel, and John J. Alexander, *Concepts and Models of Inorganic Chemistry*, 2nd ed. Copyright © 1983. Reprinted by permission of John Wiley & Sons, Inc.

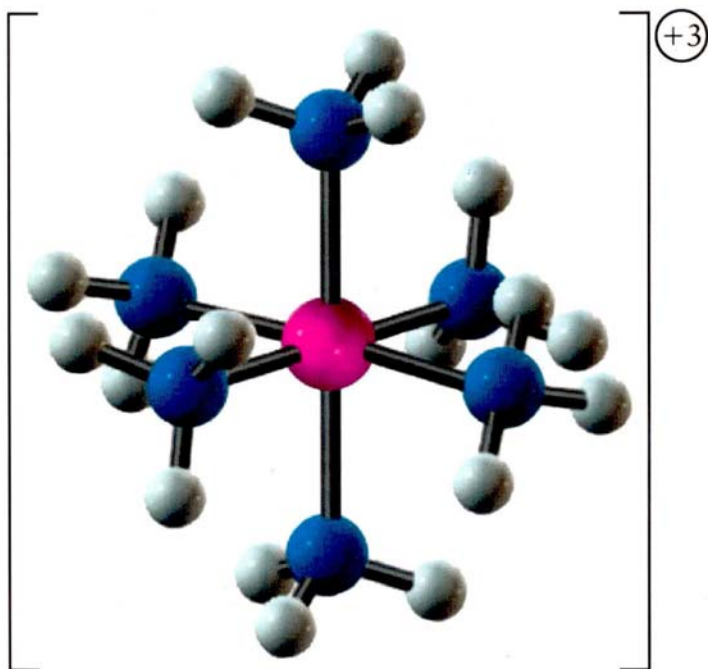
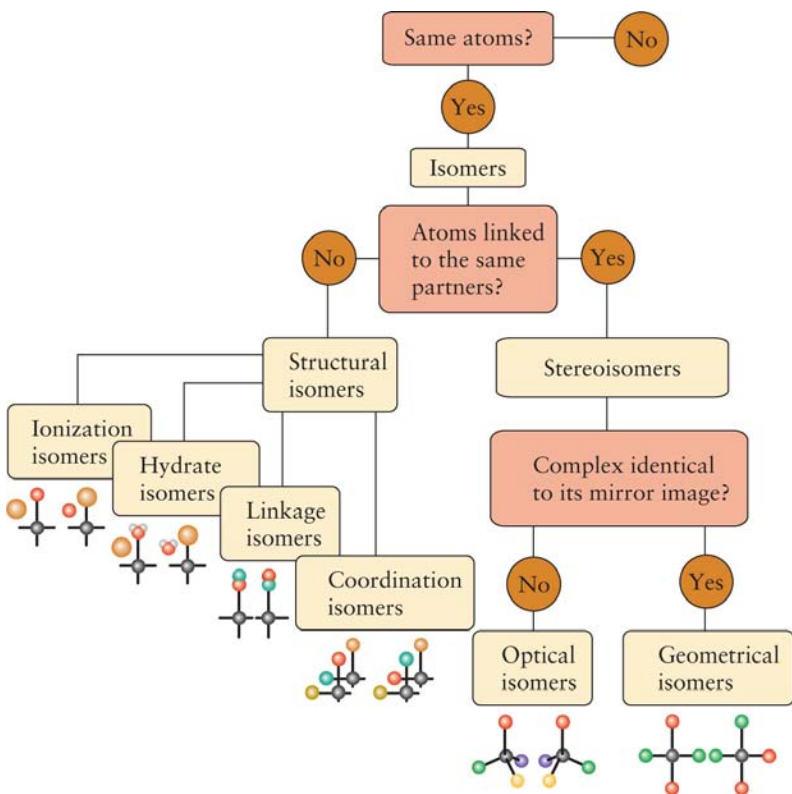


FIGURE 8.14 Octahedral structure of the $\text{Co}(\text{NH}_3)_6^{3+}$ ion. All six corners of the octahedron are equivalent.

FIGURE 17.21 The various types of isomerism in coordination compounds.



ISOMERS

Structural

Ionization



Pentaamminebromidocobalt(III)
sulfate

vs.



Pentaamminesulfatocobalt(III)
bromide

Hydrate



Chromium(III) trichloride hexahydrate

Hexaaquachromium(III) trichloride

Pentaaquachloridochromium(III) dichloride
monohydrate

Tetraaquadichloridochromium(III) chloride
dihydrate

Linkage



Tetraamminechloridonitrocobalt(III)

vs.



Tetraamminechloridonitritocobalt(III)

Coordination



Hexaamminechromium(III)
hexacyanidoferrate(III)



Hexaammineiron(III)
hexacyanidochromate(III)

Stereoisomers

Geometrical



cis-diamminedichloroplatinum(II)

vs.



trans-diamminedichloroplatinum(II)



cis-[bis(ethylenediamine)dichloridocobalt(III)]⁺

vs.



trans-[bis(ethylenediamine)dichloridocobalt(III)]⁺

Optical

Coordination Chemistry

Behaviors of some cobalt (III) chloride + ammonia compounds:



Molar conductivity of aqueous solution is similar to that of $\text{Al}(\text{NO}_3)_3$ (i.e., 4 ions per mole)



Molar conductivity of aqueous solution is similar to that of $\text{Mg}(\text{NO}_3)_2$ (i.e., 3 ions per mole)



Molar conductivity of aqueous solution is similar to that of NaNO_3 (i.e., 2 ions per mole)



Molar conductivity of aqueous solution is similar to that of non-ionized solutes.

Based on the above observations, the four cobalt coordination compounds are:

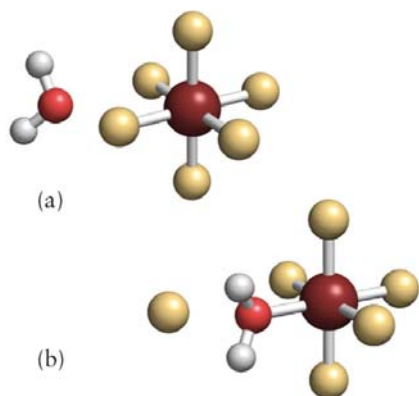


FIGURE 17.22 Hydrate isomers. In part (a), the water molecule is simply part of the surrounding solvent; in part (b), the water molecule is present in the coordination sphere and a ligand (yellow sphere) is now present in the solution.

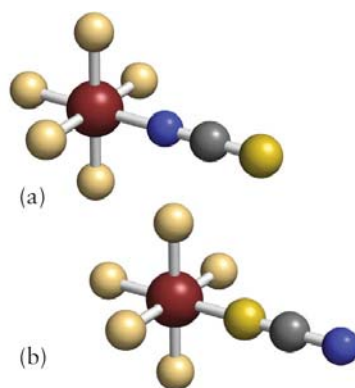


FIGURE 17.23 Linkage isomers. In part (a) the ligand (here NCS^-) is attached through its N atom, but in part (b) it is attached through its S atom.

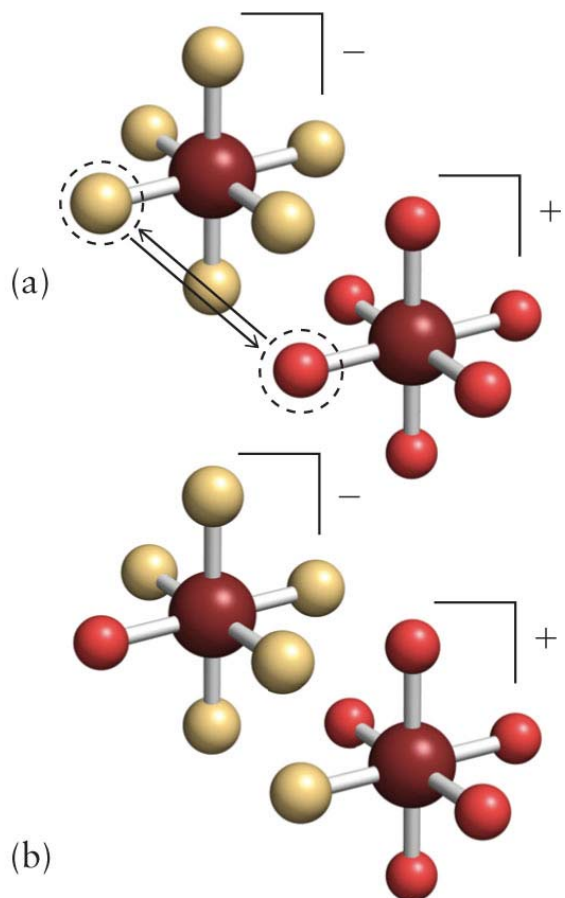
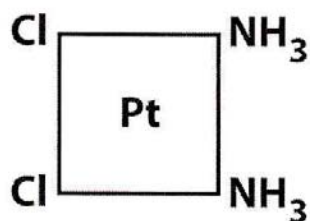
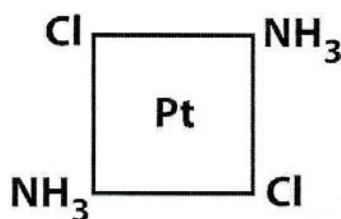


FIGURE 17.24 The compounds in parts (a) and (b) are coordination isomers. In these compounds, a ligand has been exchanged between the cationic and anionic complexes.

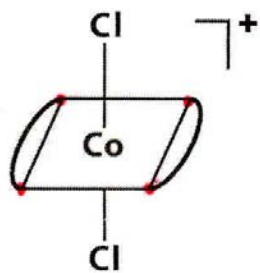
Geometric Isomerism



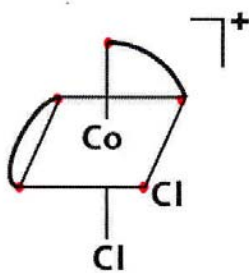
(a) *cis*-[PtCl₂(NH₃)₂]



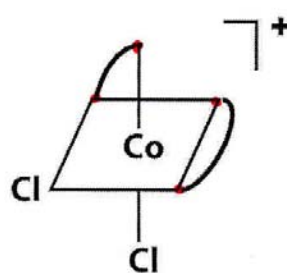
(b) *trans*-[PtCl₂(NH₃)₂]



(a) *trans*-[CoCl₂(en)₂]⁺



(b) *cis*-[CoCl₂(en)₂]⁺



(c) *cis*-[CoCl₂(en)₂]⁺

FIGURE 8.17 Two structural isomers of the coordination compound $\text{Co}(\text{NH}_3)_3\text{Cl}_3$.

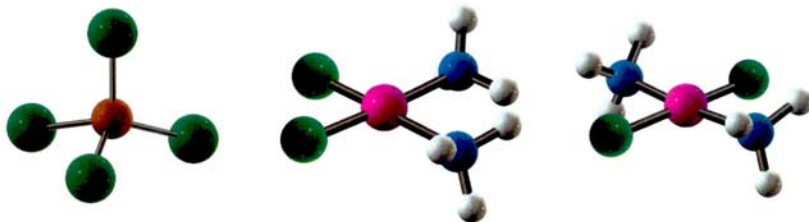
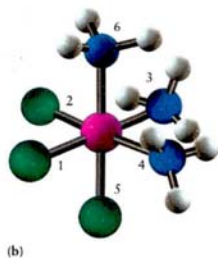
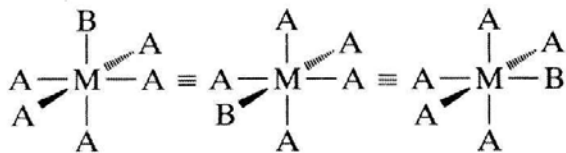


FIGURE 8.18 Four-coordinate complexes. (a) Tetrahedral, $[\text{FeCl}_4]^-$. (b, c) Square planar, illustrating (b) the *cis* and (c) the *trans* forms of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

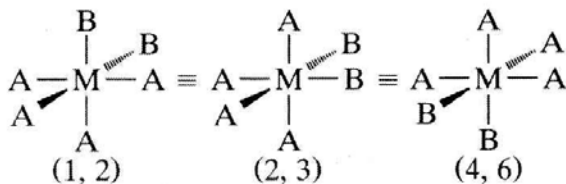
FIGURE 2.4

Equivalent configurations for some octahedral isomers.

(a) MA_5B



(b) MA_4B_2 (Isomer 1)



(c) MA_4B_2 (Isomer 2)

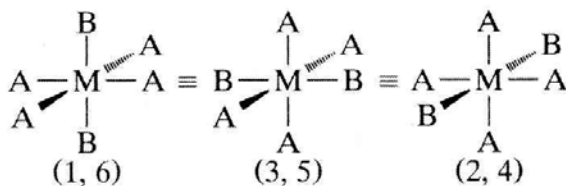


FIGURE 8.15 (a) The *cis*-[Co(NH₃)₄Cl₂]⁺ and (b) *trans*-[Co(NH₃)₄Cl₂]⁺ ions. The *cis* complex is purple in solution, but the *trans* complex is green.

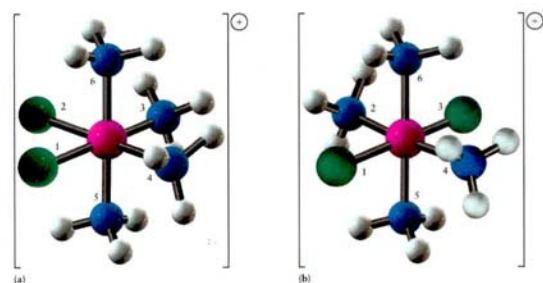
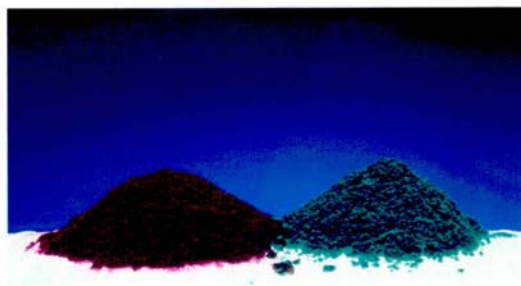
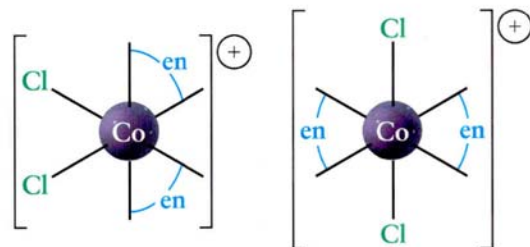


FIGURE 8.16 The complex ion [CoCl₂(en)₂]⁺ is an octahedral complex that has *cis* and *trans* isomers, according to the relative positions of the two Cl⁻ ligands. Salts of the *cis* isomers are purple, and salts of the *trans* isomers are green.



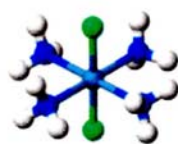
Cis-trans isomerism and facial-meridional isomerism

[edit]

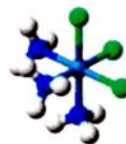
Cis-trans isomerism occurs in **octahedral** and **square planar** complexes (but not tetrahedral). When two ligands are mutually adjacent they are said to be **cis**, when opposite each other, **trans**. When three identical ligands occupy one face of an octahedron, the isomer is said to be **facial**, or **fac**. In a *fac* isomer, any two identical ligands are adjacent or *cis* to each other. If these three ligands and the metal ion are in one plane, the isomer is said to be **meridional**, or **mer**. A *mer* isomer can be considered as a combination of a *trans* and a *cis*, since it contains both *trans* and *cis* pairs of identical ligands.



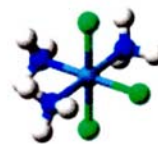
cis-[CoCl₂(NH₃)₄]⁺



trans-[CoCl₂(NH₃)₄]⁺



fac-[CoCl₃(NH₃)₃]



mer-[CoCl₃(NH₃)₃]

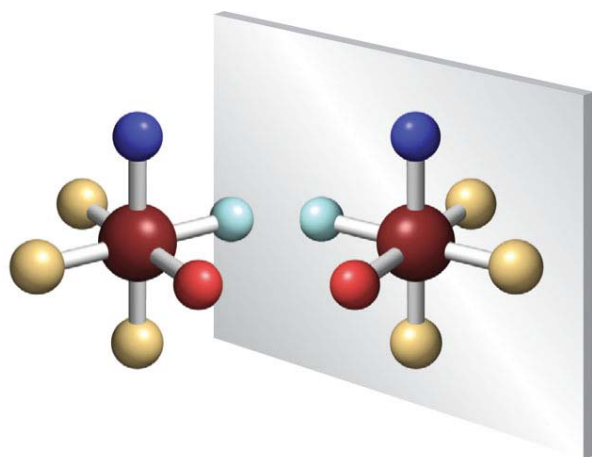


FIGURE 17.25 Optical isomers. The two complexes are each other's mirror image; no matter how we rotate them, one complex cannot be superimposed on the other.

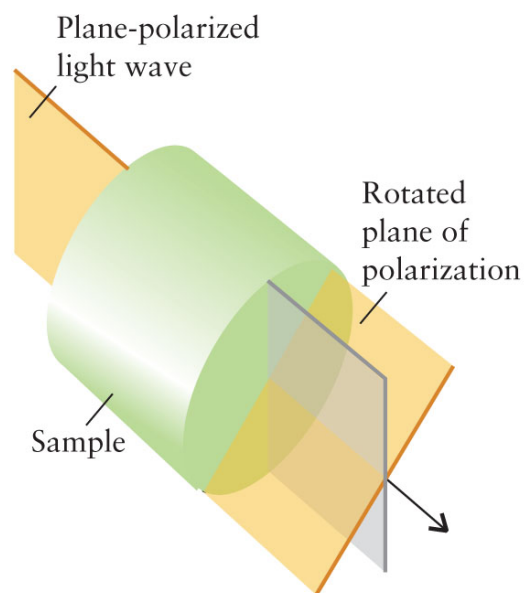


FIGURE 17.26 Plane-polarized light consists of radiation in which all the wave motion lies in one plane (as represented by the plane on the left). When such light passes through a solution of an optically active substance, the plane of the polarization is rotated through a characteristic angle that depends on the identity and concentration of the solute and the length of the path through the sample (right).

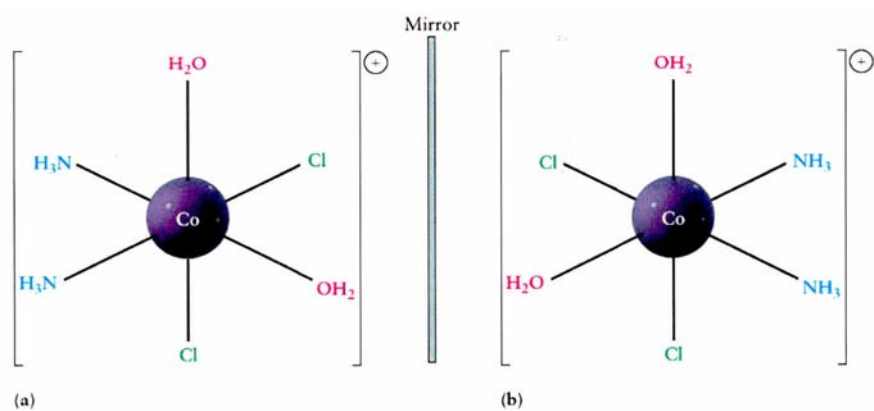


FIGURE 8.20 The structure of (a) the all-*cis* $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$ complex ion, together with (b) its mirror image.

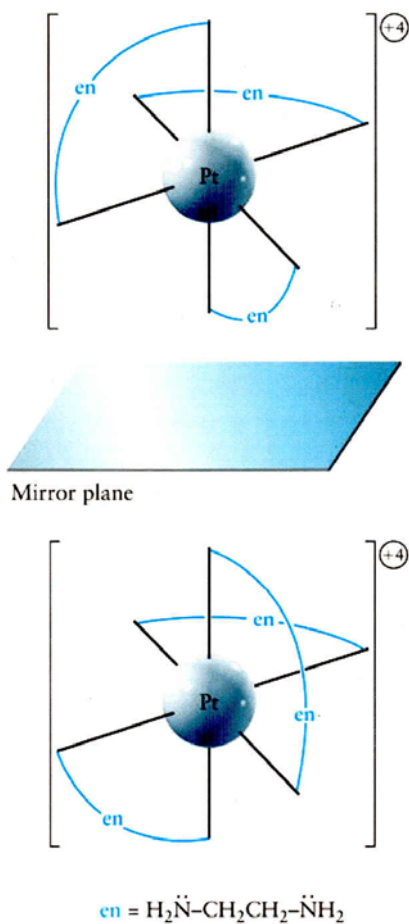
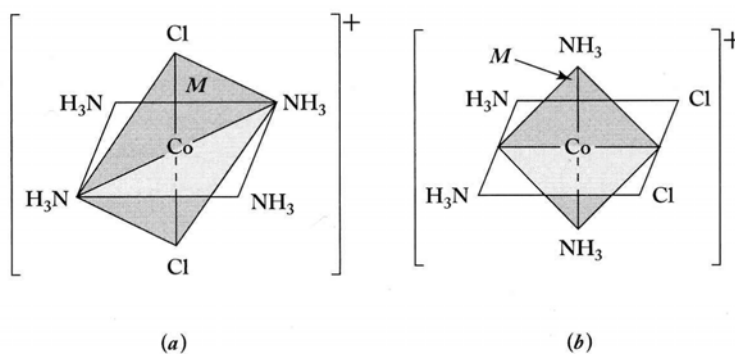


FIGURE 8.19 Enantiomers of the $[\text{Pt}(\text{en})_3]^{4+}$ ion. Reflection through the mirror plane transforms one enantiomer into the other. The two cannot be superimposed by simple rotation.

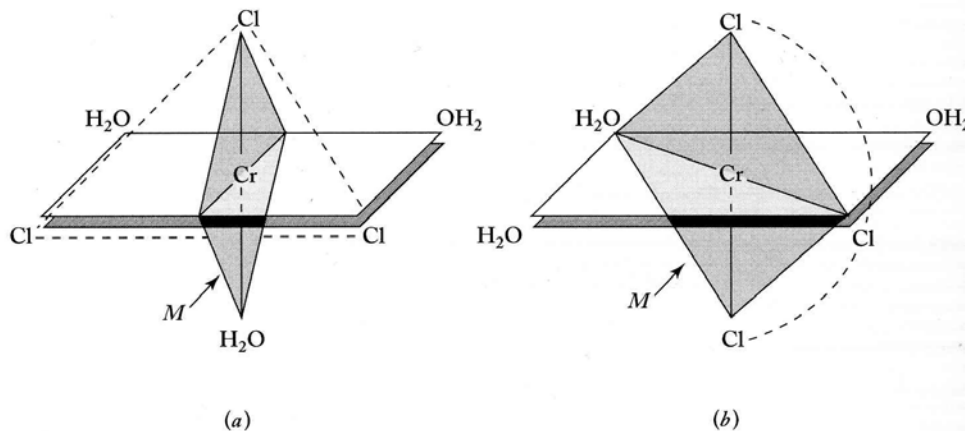
a

FIGURE 3.5

Cis and trans isomers of the tetraamminedichlorocobalt(III) cation. (a) The trans isomer has the two chloride ligands across from each other. (b) The cis isomer has the two chloride ligands adjacent to each other. Both geometric isomers possess an internal mirror plane (*M*) and are nonchiral.

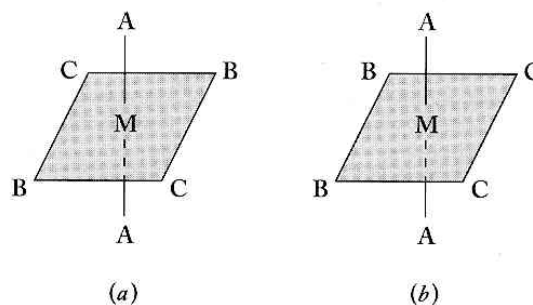
**FIGURE 3.6**

Fac (or cis) and mer (or trans) isomers of triaquatrchlorochromium(III). (a) The fac (or cis) isomer with the triangular face of chloride ligands outlined (dashed lines). (b) The mer (or trans) isomer with the chlorides along half the meridian outlined (dashed lines). Both geometric isomers possess an internal mirror plane (*M*) and are nonchiral.

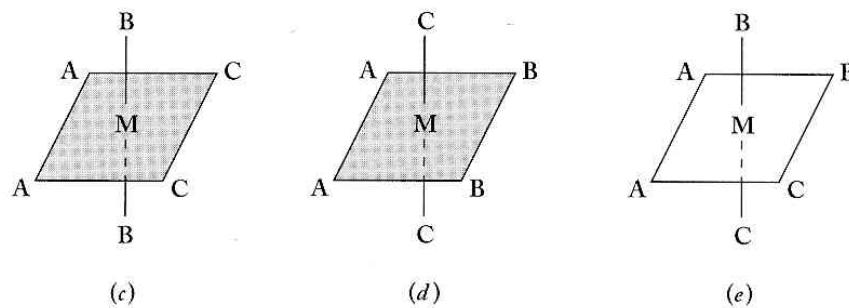
**FIGURE 3.7**

The five geometric isomers of $MA_2B_2C_2$. (a) and (b) have the two A ligands in the trans positions, whereas (c), (d), and (e) have them in the cis positions. (a) to (d) have internal mirror planes, but the all-cis isomer (e) has no mirror plane and is chiral.

trans A's:



cis A's:



Summary of all possible geometric and optical isomers for octahedral complexes that contain six ligands:

Formula	Number of Isomers	Number of Enantiomeric Pairs
MA ₆	1	0
MA ₅ B	1	0
MA ₄ B ₂	2	0
MA ₄ BC	2	0
MA ₃ B ₃	2	0
MA ₃ B ₂ C	3	0
MA ₃ BCD	5	1
MA ₂ B ₂ C ₂	6	1
MA ₂ B ₂ CD	8	2
MA ₂ BCDE	15	6
MABCDEF	30	15

MA₂B₂C₂, for example, has the following six isomers:

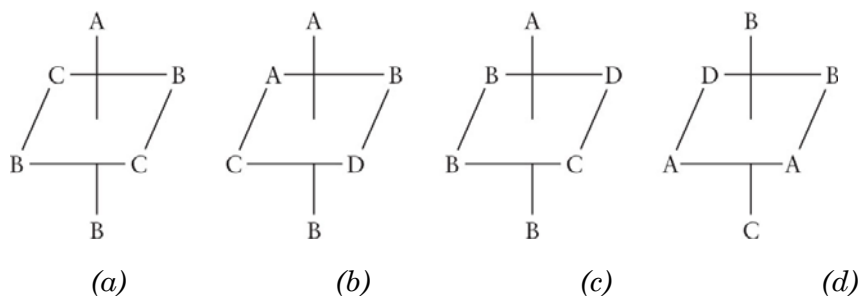
- 1.) A non-chiral isomer in which all of the three pairs of identical ligands are *trans* to each other.
- 2.) Three non-chiral isomers in which one pair of identical ligands (A, B, or C) is *trans*, while the other two pairs are *cis*.
- 3.) An enantiomeric pair of chiral isomers in which all three pairs of identical ligands are *cis* to each other.

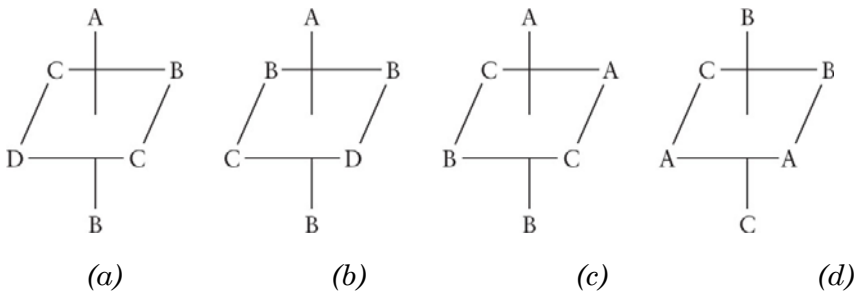
MA₂BCDE has the following 15 isomers:

- 1.) Three non-chiral isomers, in which the two A ligands are *trans* to each other.
- 2.) Twelve chiral isomers, consisting of six enantiomeric pairs.

MABCDEF has 30 possible isomers, all of which are chiral, and consist of 15 enantiomeric pairs.

Which of the following complexes are chiral, and which are pairs of enantiomers?





Useful aids for building models of complex ions:

