

4

Coordination Compounds

Aims

By the end of this chapter you should understand the terms:

- Coordination compound
- Coordination number
- Coordination geometry
- Uni-, bi- and poly-dentate as applied to ligands
- Homo- and hetero-leptic as applied to complexes

and have a knowledge of:

- The structures of the regular coordination polyhedra of coordination compounds
- The types of isomerism possible in transition element complexes
- Some representative types of ligand which may appear in transition element complexes

When considering the **structures** of coordination compounds it is worth noting that transition element complexes are usually formed from reactions between their salts and Brønsted bases in solution. However, the structures of the compounds formed are usually determined in the solid state using samples crystallized from solution. While it may usually be assumed that the solid state structures are similar to the solution structures, this may not always be so, and some complexes may adopt different structures in solution and the solid state.

4.1 Introduction

In order to explain the formulae and structures of the complex compounds, or **complexes**, formed by transition metal salts with molecular species such as ammonia, Werner coined the terms *primary valence* and *secondary valence*, as explained in Chapter 1. These concepts remain valid today except that the term **oxidation state** has replaced ‘primary valence’ and the term **coordination number** has replaced ‘secondary valence’. Werner had recognized that a transition metal salt could form a complex compound in which the metal ion became bonded to a number of groups which need not necessarily be the counter anions originally present in the salt. The orientations in space of these metal-bound groups would lead to the complex having a particular geometric

structure. In this chapter the structures of transition element complexes are examined in more detail and some definitions of key terms are provided.

4.2 Coordination Compounds

4.2.1 Complexes

One definition of a metal complex or **coordination compound** is ‘a compound formed from a Lewis acid and a Brønsted base’, a Lewis acid being an electron pair acceptor and a Brønsted base a proton acceptor. Thus the interaction of the Lewis acid metal centre in $\text{Ni}(\text{ClO}_4)_2$ with the Brønsted base ammonia to form a *complex* according to equation 4.1



provides an example of the formation of a coordination compound. In writing the formulae of metal complexes it is conventional to include the complete coordination complex within square brackets, an example being provided by $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, in which the coordination complex is $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ with two chloride counterions. The Brønsted bases attached to the metal ion in such compounds are called **ligands**. These may be simple ions such as Cl^- , small molecules such as H_2O or NH_3 , larger molecules such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ or $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, or even macromolecules, such as proteins.

The coordination number (CN) of a metal ion in a complex can be defined as *the number of ligand donor atoms to which the metal is directly bonded*. In the case of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ this will be 6, the sum of one chloride and five ammonia ligands each donating an electron pair. Although this definition usually works well for coordination compounds, it is not always appropriate for organometallic compounds. An alternative definition of CN would be *the number of electron pairs arising from the ligand donor atoms to which the metal is directly bonded*. To apply this definition, it is necessary to assume an ionic formulation and a particular oxidation state for the metal ion, so that charges can be assigned to the ligands as appropriate and the number of electron pairs determined.

4.2.2 Types of Ligand

Where a ligand is bound to a metal ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be **unidentate** (the ligand binds to the metal through a single point of attachment as if it had one

Strictly speaking, the term ‘ligand’ only applies to groups attached to a metal ion. The term **proligand** may be used to refer to a species which may become a ligand through being bound to a metal ion but is not presently in a complex. In this text the symbols X, Y, Z will be used to represent ligands such as F, Cl, NH_3 or H_2O in which one donor atom is bound to the metal ion. The symbol L–L will be used to denote a ligand such as $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ which is bound to a metal ion through two donor atoms. The general symbol L will be used to represent a ligand of any type.

tooth). Where two donor atoms can be used to bind to a metal ion, as with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, the ligand is said to be **bidentate**, and where several donor atoms are present in a single ligand as with $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$, the ligand is said to be **polydentate**. When a bi- or polydentate ligand uses two or more donor atoms to bind to a single metal ion, it is said to form a **chelate** complex (from the Greek for claw). Such complexes tend to be more stable than similar complexes containing unidentate ligands for reasons which will be explored in Chapter 5. A huge variety of ligands appear in coordination complexes and, to illustrate this point, some examples of common types of ligand are shown in Figures 4.1–4.4. Any of a variety of elements may function as donor atoms towards metal ions, but the most commonly encountered are probably nitrogen, phosphorus, oxygen, sulfur and the halides. In addition, a large number of compounds are known which contain carbon donor atoms; these are known as *organometallic* compounds (see page 11). Bidentate ligands may be classified according to the number of atoms in the ligand which separate the donor atoms (Figure 4.1) and hence the size of the chelate ring formed with the metal ion. Thus 1,1-ligands form a four-membered chelate ring when bound to a metal ion, 1,2-ligands a five membered ring, and so on. Cyclic compounds which contain donor atoms oriented so that they can bind to a metal ion and which are large enough to encircle it are known as **macrocyclic** proligands and some examples are shown in Figure 4.4. Bicyclic proligands are also known which can completely encapsulate a metal ion. Some of these systems have given the names **cryptand** or **sepulchrate**, which reflect their ability to wrap up and entomb the metal ion (Figure 4.4).

A **macrocyclic ligand** may be defined as a cyclic compound comprising a ring of at least nine atoms including at least three donor atoms oriented so as to bind to a metal ion. In this minimum form a macrocyclic ligand would occupy three adjacent coordination sites on one side of a metal ion. However, larger rings such as cyclam or porphine derivatives (Figure 4.4) may have a central cavity large enough for the metal ion to fit into the plane of the macrocycle.

Sometimes ligands can bind to more than one metal ion in a bridging arrangement, for example in $[\text{W}_2\text{Cl}_9]^{3-}$ illustrated in Figure 4.5. Certain polydentate ligands are particularly good at linking together several metal ions and are referred to as **polynucleating ligands**.

4.2.3 Structure and Isomerism

In coordination compounds, or complexes, the transition elements may show CNs ranging from 1 up to 12 or more for some f-block elements. As there are more ways than one of arranging two, or more, ligand donor atoms about a central metal ion, structural isomers are possible. However, in practice, certain structural arrangements are more favourable energetically than others, limiting the range of commonly found structural types. The idealized regular **coordination geometries** of complexes with CNs from 1 to 6 are summarized in Figure 4.6, CNs 7 and 8 in Figure 4.7 and the higher CNs 9–12 in Figure 4.8. Transition metal complexes usually conform to idealized geometries in an approximate sense, although some distortions from ideality are often present.

The term **coordination geometry** refers to the structural arrangement of ligand donor atoms around a metal atom in a complex. Thus, in a four-coordinate metal complex the donor atoms could be arranged at the vertices of a tetrahedron giving a *tetrahedral coordination geometry*, or they could lie in the same plane to give a *square planar coordination geometry* (see margin note on isomers, page 10).

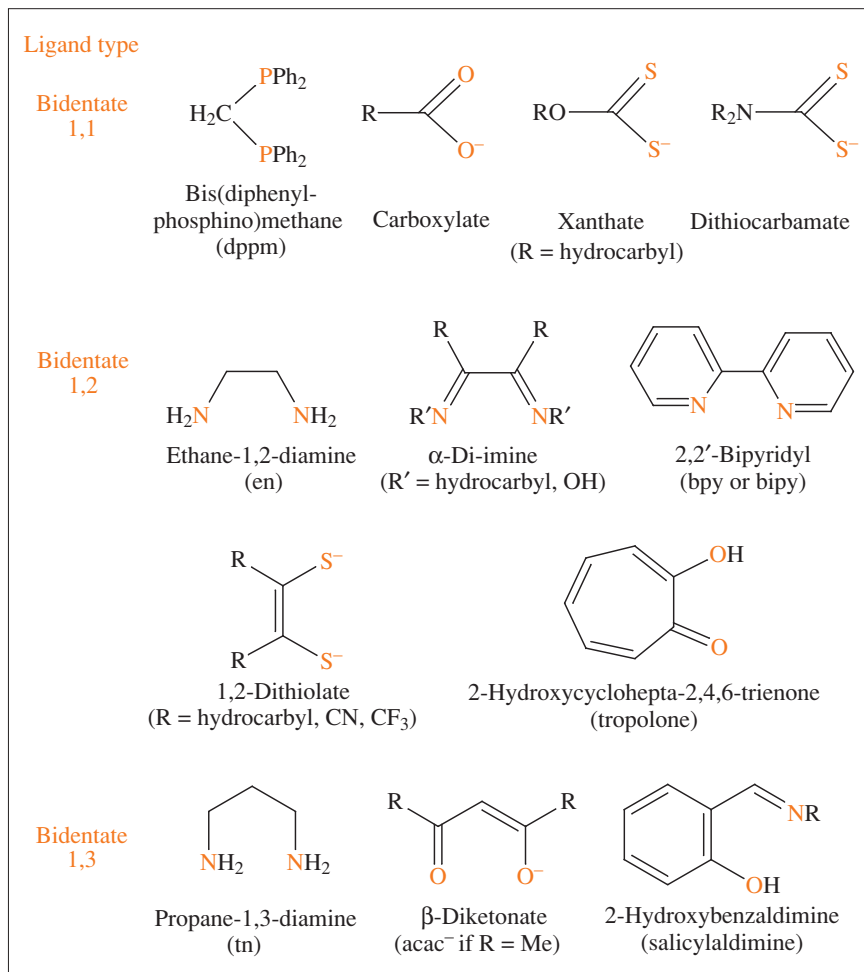


Figure 4.1 Some examples of bidentate ligands

However, the structures of the lanthanide ions tend to be less regular, particularly when more than one type of ligand is present in a **heteroleptic complex**.

The lower CNs are rare among the transition elements. A CN of 1 is very unusual, although not unknown. Its formation depends upon the presence of a very bulky ligand which prevents the binding of additional ligands. A CN of 2 is found in some complexes of d^{10} ions such as Ag^+ or Au^+ , and the geometries of these complexes are normally linear, not bent. A CN of 3 can arise in complexes with sterically demanding ligands such as the bulky amide ligand $\text{N}(\text{SiMe}_3)_2^-$. The d-block metal complexes $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (M = Fe, Cr) have a trigonal planar coordination geometry rather than the T-shaped or pyramidal structures encountered with p-block elements. The f-block metal complex $[\text{La}\{\text{N}(\text{SiMe}_3)_2\}_3]$ is also thought to have a planar structure in solution

Complexes in which a metal is bound to only one kind of donor group, e.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$, are known as **homoleptic**.

Complexes in which a metal is bound to more than one kind of donor group, e.g. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, are known as **heteroleptic**.

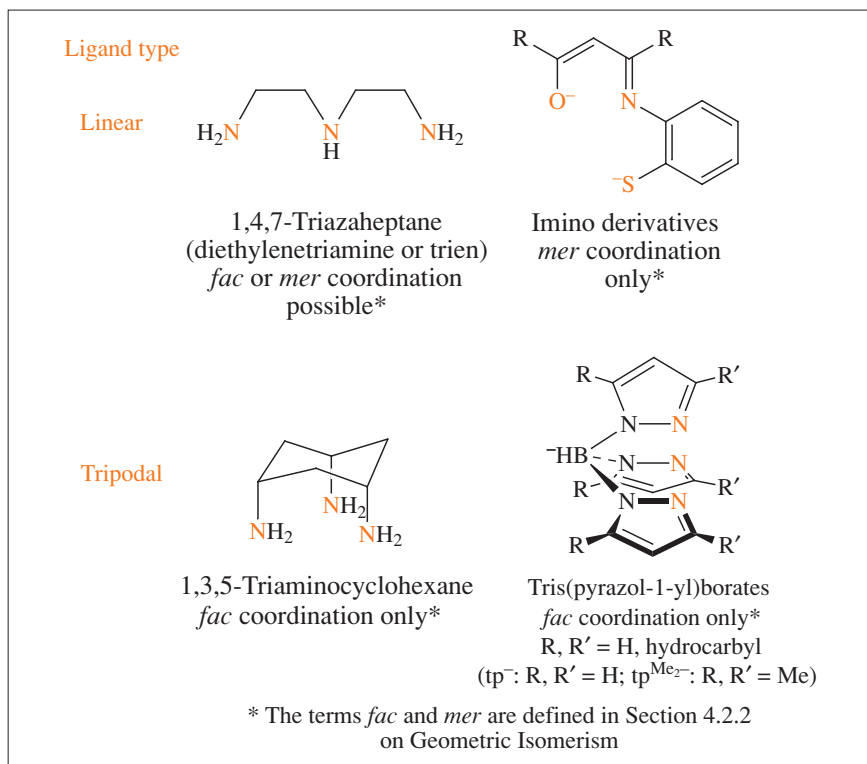


Figure 4.2 Some examples of tridentate ligands

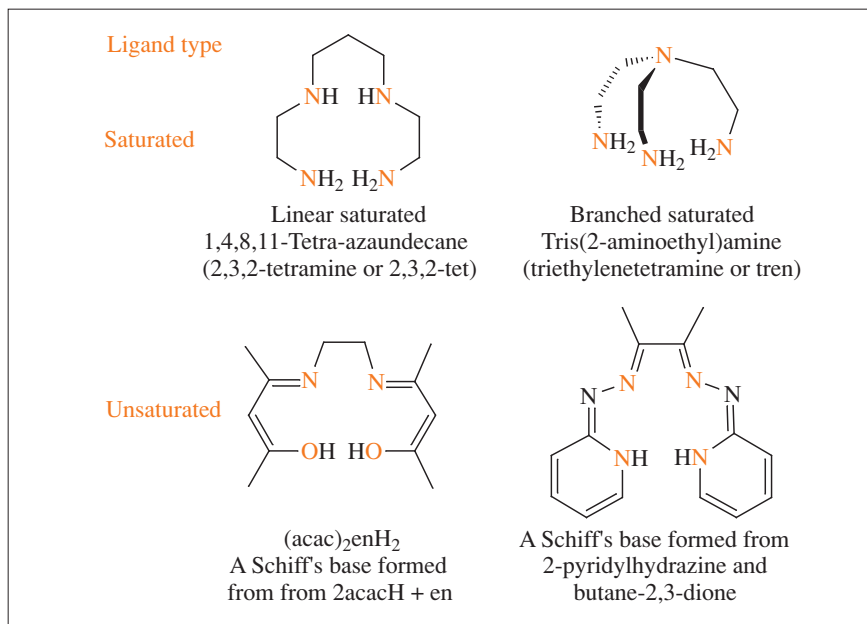


Figure 4.3 Some examples of quadridentate ligands

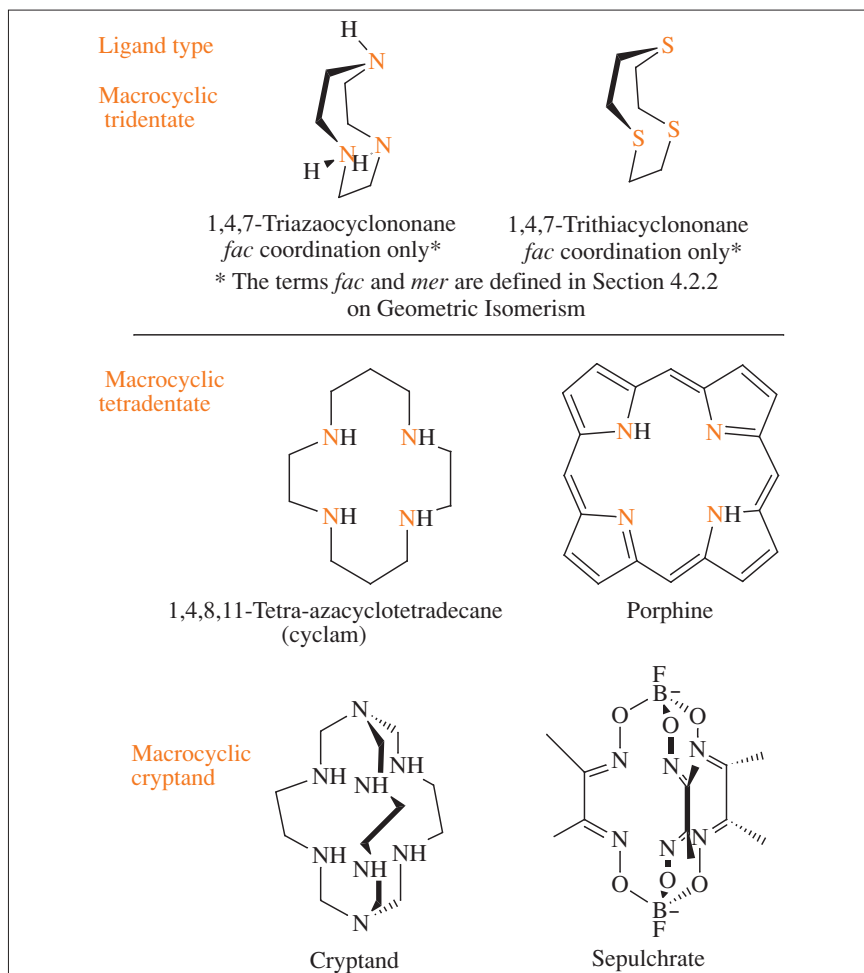


Figure 4.4 Some examples of macrocyclic ligands

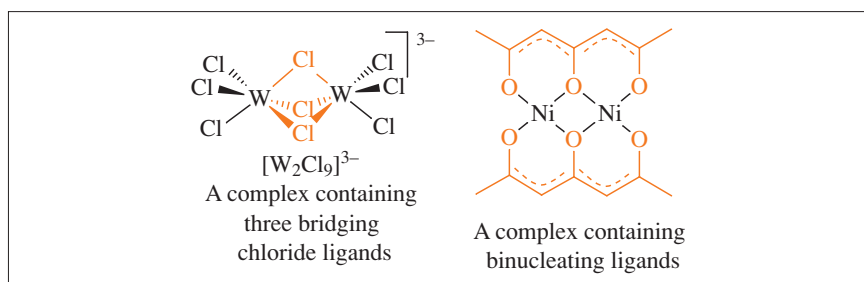


Figure 4.5 Examples of a bridging ligand and a polynucleating ligand

but is pyramidal in the solid state, and provides an extremely rare example of an f-block element with a very low CN. Complexes with CN of 4 are fairly common for certain d-block metals. These complexes may be square planar or tetrahedral in geometry and, for reasons which will be explained in Chapter 6, metal ions with d^8 electron configurations tend

Number	Coordination		Comments
	Geometry	Polyhedron	
1		—	Unimportant
2 Linear		—	Uncommon: found mainly with d ¹⁰ metal ions
3 Trigonal plane			Rare; can be induced by use of sterically bulky ligands
4 Square plane			Common for d ⁸ metal ions otherwise unusual;
4 Tetrahedron			Fairly common, especially for d ¹⁰ and some d ⁵ ions
5 Trigonal bipyramid			Rare } Examples are often similar in structure and energy so may easily interconvert
5 Square pyramid			
6 Octahedron			Very common; usually the most favoured energetically and gives the lowest ligand–ligand repulsions
(Octahedron = trigonal antiprism)			An alternative view of an octahedron down a three-fold rotation axis
6 Trigonal prismatic			Rare, and requires some extra steric or electronic benefit to be favoured over octahedral

Figure 4.6 Idealized structures for coordination numbers 1–6

to be square planar and those with d⁵ or d¹⁰ configurations tetrahedral. A CN of 5 is unusual among transition element complexes and, in a complex which is purely ionically bonded, would be unstable with respect to disproportionation into CN 4 and 6 species. However, covalent contributions to bonding can stabilize CN 5. In the absence of structural demands imposed by the ligands, the two regular structures, trigonal bipyramidal and square pyramidal, are easily interconverted and similar in energy. In the solid state, both structures can be found in slightly distorted form in the salt [Ni(CN)₅]³⁻.

Coordination			Comments
Number	Geometry	Polyhedron	
7 Pentagonal bipyramid			Uncommon
7 Monocapped octahedron			Uncommon
8 Dodecahedron			Most sterically efficient geometric arrangement for eight equivalent ligands
8 Square antiprism			Uncommon
8 Cube			Rare; found only with the largest metal ions
8 Hexagonal bipyramid			Quite common for eight-coordinate complexes of metals with <i>trans</i> -dioxo ligands

Figure 4.7 Idealized structures for coordination numbers 7 and 8

Most regular coordination polyhedra			
C.N. 9	10	11	12
Tricapped trigonal prism	Bicapped square antiprism	Octadecahedron	Icosahedron

Figure 4.8 Idealized structures for coordination numbers larger than 8

The most common CN for d-block transition metal ions is 6, usually with an octahedral geometry. Ligand–ligand interactions make trigonal prismatic structures less energetically favourable so that this geometry is rare, although some examples are known, *e.g.* $[\text{WMe}_6]$ and $[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)]$.

An important distortion of the octahedral structure, found in certain complexes, results from stretching or compressing the octahedron along a fourfold rotation symmetry axis, producing a **tetragonal distortion** (Figure 4.9a). This type of distortion is commonly found among complexes of the d^9 Cu^{2+} ion for reasons which will be explored in Chapter 6. Another, less important, type of distortion results from stretching or compressing the octahedron along a threefold rotation symmetry axis, producing a **trigonal distortion** (Figure 4.9b).

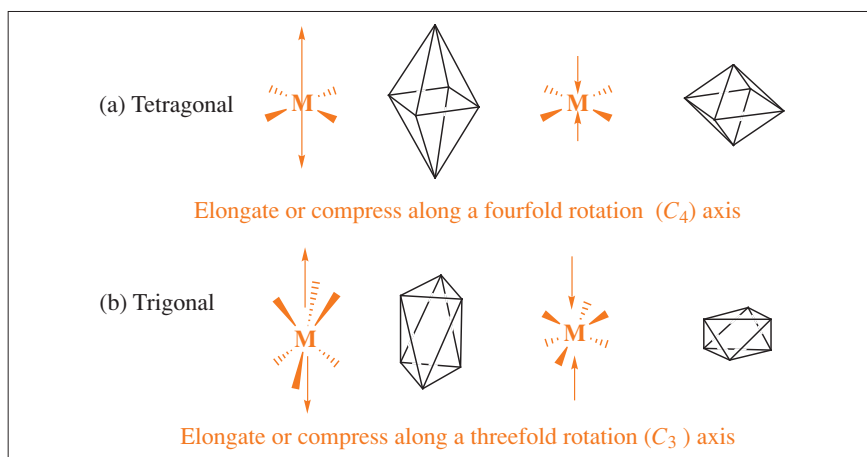


Figure 4.9 Distortions of the octahedral coordination geometry

The higher CNs of 7, 8 and 9 are unusual for d-block metals, although some examples can be found among the complexes of the early second- and third-row metals. The cyano complexes of molybdenum, $[\text{Mo}(\text{CN})_8]^{z-}$ ($z = 3, 4$), provide well-known examples and, in the solid state, can be found with a dodecahedral or a square antiprismatic structure, depending on the counterion present. In contrast, CNs of 8 or 9 are quite typical among the complexes formed by the f-block elements and CNs up to 14 are known. Although regular geometries can be assigned to these higher CNs, the energy differences between the different structures are often small. Since the core-like nature of the f orbitals gives little directional preference in the bonding, the structures of lanthanide complexes tend to be determined by ligand–ligand interactions and distortions from ideal geometries are common. The highest CNs are found with the larger metal ions and the sterically most compact ligands such as NO_2^- or H_2O . An example of 12 coordination is provided by $[\text{Ce}(\text{NO}_3)_6]^{3-}$, in which six octahedrally disposed nitrate groups each bind through two oxygens to the Ce^{3+} ion to give a distorted icosahedral structure. A rare example of a CN of 14 is found in the solid-state structure of $[\text{U}(\text{BH}_4)_4]$ in which the U^{4+} ion is bonded to 14 hydrogen atoms.

In addition to the structural isomerism possible for each CN, several

other types of isomerism (geometric, optical, linkage, coordination, ligand, ionization, solvate) are possible in transition element complexes.

Geometric Isomerism

In heteroleptic complexes the different possible geometric arrangements of the ligands can lead to isomerism, and important examples of this behaviour are found with CNs 4 and 6. In a square planar complex of formula $[MX_2L_2]$ (X and L are unidentate) the two ligands X may be arranged adjacent to each other, in a *cis* isomer, or opposite each other, in a *trans* isomer. Such isomerism is not possible for a tetrahedral geometry but similar behaviour is possible in CN 6 octahedral complexes of formula $[MX_2L_4]$ in which the two ligands X may be oriented *cis* or *trans* to each other (Figure 4.10a). This type of isomerism also arises when ligands L-L (e.g. L-L = $NH_2CH_2CH_2NH_2$) with two donor atoms are present in complexes of formula $[MX_2(L-L)_2]$. A further example of geometric isomerism can occur in octahedral complexes of formula $[MX_3L_3]$, depending on whether the three ligands X, or L, all lie in the same plane giving a meridional, or *mer*, isomer, or whether they are adjacent forming a triangular face of the octahedron in a facial, or *fac*, isomer (Figure 4.10b).

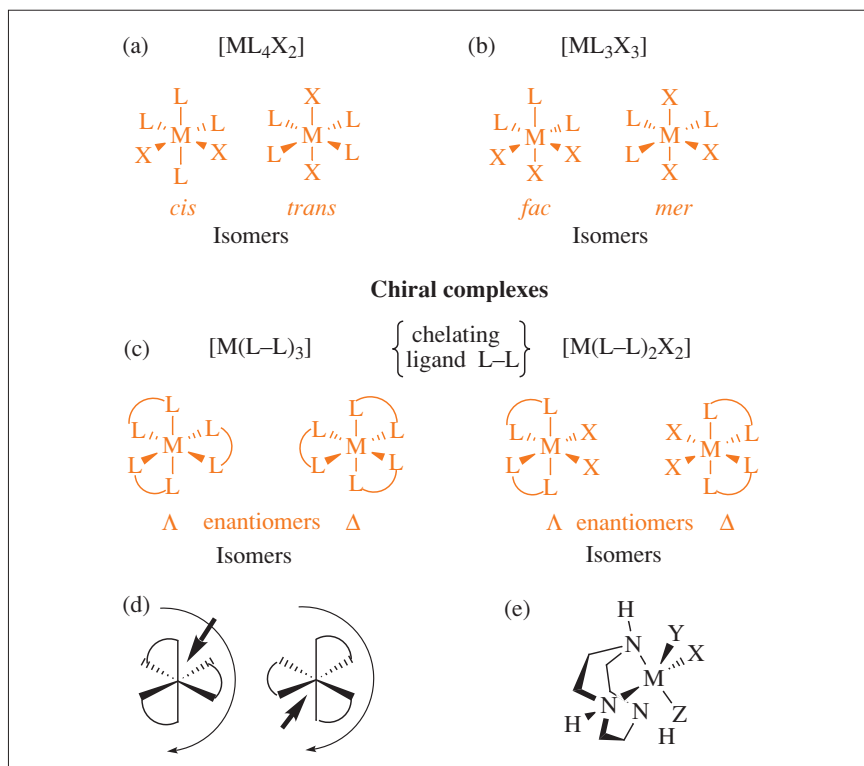


Figure 4.10 Isomers of octahedral complexes

Optical Isomerism

In the octahedral complexes $cis-[MX_2(L-L)_2]$ and $[M(L-L)_3]$ the presence of the ligands L–L leads to a further isomeric possibility since the metal centre is **chiral** (Figure 4.10c). The presence of the L–L ligands gives rise to a propeller shape. When rotated clockwise the Δ isomer appears to screw into the plane while the Λ isomer appears to screw out of the plane (Figure 4.10d). Thus $[Co(en)_3]^{3+}$ is chiral, and can be resolved into its Δ and Λ isomers through fractional crystallization with a chiral counterion such as tartarate. A tetrahedral complex with four different unidentate ligands will also be chiral, just like a carbon atom in a chiral organic molecule. In practice, examples of this type are rare, but an important example of similar structural type arises with heteroleptic CN 6 complexes containing one *fac*-tridentate ligand and three different unidentate ligands (Figure 4.10e). Some compounds of this type have been found to be effective reagents in the asymmetric synthesis of chiral organic molecules and are of importance in the synthesis of certain fine chemicals and pharmaceuticals.

Linkage Isomerism

Linkage isomerism arises when a ligand may bind to a metal ion through either of two or more different donor atoms. A simple example is provided by complexes containing the thiocyanate ligand, NCS^- , which may bind through the nitrogen to give $M-NCS$ or the sulfur to give $M-SCN$. The former may be associated with the valence tautomer $^-N=C=S$ and the latter with $N\equiv C-S^-$. Jørgensen¹ discovered the first example of such behaviour in the complex $[Co(NH_3)(NO_2)]Cl_2$, which can be obtained as a red form, in which the nitrite ligand is bound through oxygen, and as a yellow form, in which the nitrite ligand is bound through nitrogen.

Coordination Isomerism

This form of isomerism arises from the interchange of ligands between cationic and anionic complexes of different metal ions present in a salt. An example is provided by $[Co(NH_3)_6][Cr(CN)_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+} , and its coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$ in which the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+} . A special case of coordination isomerism can arise in which a series of compounds have the same empirical formula but different molecular masses for the salt. This is sometimes referred to as ‘polymerization isomerism’, although it does not involve polymerization according to a conventional definition involving the linking together of a single repeating unit. An example of polymerization

isomerism is provided by the series of salts in which both the cation and the anion contain Co^{3+} and which have the empirical formula $\{\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3\}_x$, e.g.



Ligand Isomerism

As the name implies, ligand isomerism arises from the presence of ligands which can adopt different isomeric forms. An example is provided by diaminopropane, which may have the amine groups in the terminal 1,3-positions ($\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$) or in the 1,2-positions $\{\text{H}_2\text{NCH}_2\text{-CH}(\text{Me})\text{NH}_2\}$.

Ionization Isomerism

This arises when the counterion in a complex salt is a proligand and can, in principle, displace a ligand which can then become the counterion. An example is provided by the ionization isomers $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ and $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{SO}_4)$.

Solvate Isomerism

This form of isomerism, sometimes known as ‘hydrate isomerism’ in the special case where water is involved, is similar in some ways to ionization isomerism. Solvate isomers differ by whether or not a solvent molecule is directly bonded to the metal ion or merely present as free solvent in the crystal lattice or solution. An example is provided by the aqua complex $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and its solvate isomer $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Worked Problem 4.1

Q Draw all the possible isomers of a five-coordinate complex of formula $[\text{M}(\text{L-L})\text{X}_2\text{A}]$. In each case, identify the situations in which optical isomers are possible (A and X represent different unidentate ligands; L-L represents a bidentate ligand).

A In five-coordinate complexes the basic regular geometries to consider are square pyramidal and trigonal bipyramidal. The ligands X and A may occupy apical or basal sites in the former and axial or equatorial sites in the latter. Similarly, L–L may span similar locations or different locations in either geometry. The possibilities which arise are shown in Figure 4.11.

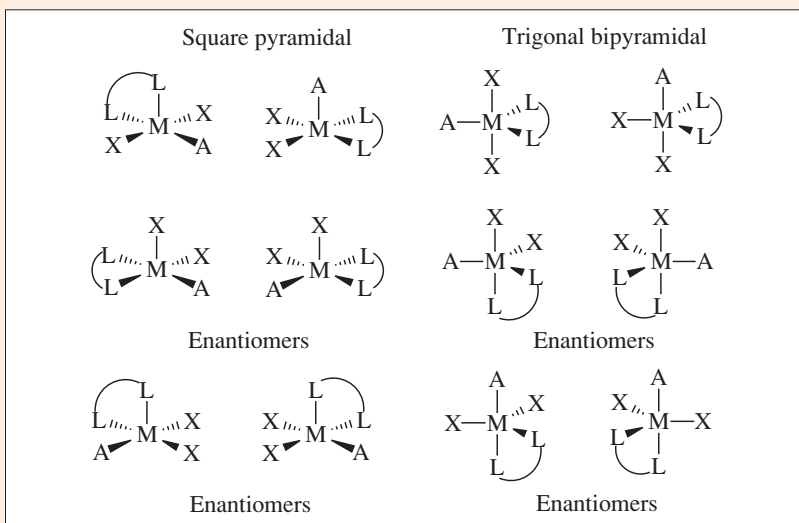


Figure 4.11

4.3 Nomenclature

The systematic naming, or nomenclature, of coordination compounds can be complicated to apply, but it is essential to have some familiarity with the basic rules of nomenclature and to be able to work out the structure of a compound from its systematic name. Only a very brief summary of the rules for naming of coordination compounds can be given here, but more detailed accounts are available elsewhere.^{2,3}

4.3.1 Formulae

The formula of a complete coordination entity (*e.g.* $[\text{Co}(\text{NH}_3)_6]^{3+}$) is written in square brackets. The absence of $[-]$ implies that not all of the ligands in the coordination sphere, typically water or solvent, are given in the formula. As an example, CoCl_2 could refer to anhydrous CoCl_2 , $[\text{CoCl}_2(\text{H}_2\text{O})_4]$ or $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$, although the latter might be written as $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, respectively. The symbol of the central atom is given first followed by the anionic then the neutral ligands, each set in alphabetical order. Where possible the donor atom is written first,

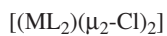
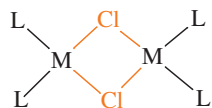
one exception being water which is conventionally written H_2O rather than OH_2 . Within the formula, brackets should be 'nested' as $[\{(\)\}]$ or $\{[(\)]\}$. Where the formulae of salts are given, cations come before anions, *e.g.* $[\text{Co}(\text{H}_2\text{O})_6](\text{NO}_3)_2$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$. The oxidation states of the metal ions may be given as superscript Roman numerals following the ion to which they refer, *e.g.* $[\text{Cr}^{\text{III}}\text{Cl}_6]^{3-}$. Abbreviations may be used in formulae. These include standard abbreviations for functional groups, such as Me, Et and Ph respectively for methyl, ethyl or phenyl groups, and specific abbreviations for ligands, *e.g.* py for pyridine and en for ethane-1,2-diamine. Where protic acid ligands are present it is important to remember that the abbreviation for the neutral ligand must include the proton(s), so that ox^{2-} may represent ethanedioate (oxalate) and H_2ox represents ethanedioic acid (oxalic acid).

4.3.2 Names

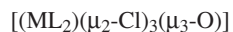
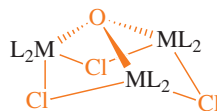
The names of coordination compounds are constructed by listing the ligands in alphabetical order, regardless of charge, before the name of the central atom. Numerical prefixes are used to indicate the numbers of each ligand present, and the oxidation state is given as Roman numerals in parentheses at the end, *e.g.* dichlorobis(trimethylamine)platinum(II) for $[\text{PtCl}_2(\text{NMe}_3)_2]$. Di, tri, *etc.*, are normally used but with more complicated ligand names the prefixes bis, tris, tetrakis, *etc.*, are used to avoid confusion, *e.g.* trichlorotris(trimethylphosphine)rhodium(III) for $[\text{RhCl}_3(\text{PMe}_3)_3]$. In the names of salts, cations come before anions, as with formulae. Anionic coordination compounds are given the suffix -ate. Either the oxidation state of the central atom {Stock system; *e.g.* hexamminecobalt(III) trichloride for $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ }⁴ or the charge on the complex (Ewens–Bassett system)⁵ may be given, *e.g.* tripotassium hexacyanoferrate(3-) for $\text{K}_3[\text{Fe}(\text{CN})_6]$; in the Stock system this is tripotassium hexacyanoferrate(III). Note that ammine in this context refers to NH_3 as a ligand, the term -amine being used for a derivative such as dimethylamine, NHMe_2 . Stereochemical descriptors may precede names or formulae to indicate which isomeric form is present, *e.g.* *cis*-diamminedichloroplatinum(II) for *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$.

4.3.3 Special Symbols

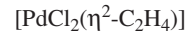
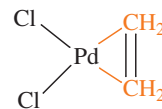
Greek letters are used as special symbols to signify particular structural features in a compound. The character μ is used to denote an atom or group which bridges between two or more metal centres. A subscript denotes the number of atoms bridged as shown in 4.1 and 4.2. The symbol η is used to denote connected atoms in a ligand which bind to the metal atom and a superscript identifies the number involved, as shown



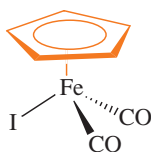
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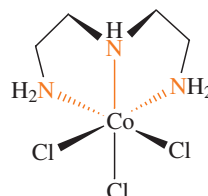
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4.3



4.4

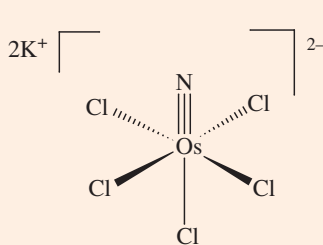


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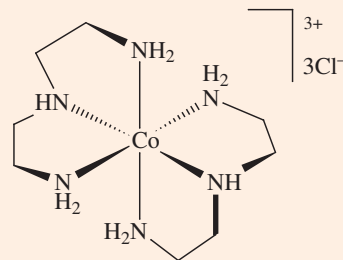
for 4.3 and 4.4. Finally, the symbol κ is used to denote unconnected atoms in a polydentate ligand which bind to the metal centre and again a superscript denotes the number of donor atoms involved and may be followed by the appropriate donor atom symbol italicized, as in 4.5.

Worked Problem 4.2

Q Devise systematic names for the compounds shown in 4.6 and 4.7:



4.6



4.7

A Placing the ligand names in alphabetical order before the metal ion name gives:

4.6: dipotassium pentachloronitridoosmate(VI) (Stock system)
{or dipotassium pentachloronitridoosmate(2-)} (Ewens-Bassett system)};

4.7: bis(1,4,7-triazaheptane- κ^3 - N,N',N'')cobalt(III) trichloride.

Summary of Key Points

1. *The environment of a metal ion in a coordination compound is defined by its coordination number and coordination geometry.*
2. *Any of a wide variety of ligands may be involved in forming coordination compounds with metals.*
3. *Different isomeric structures are possible for many complexes and seven different types of isomerism may be identified.*
4. *A systematic system of nomenclature exists for coordination compounds of metal ions.*

Problems

4.1. Consult text books from the Further Reading section and, for each of the coordination geometries for coordination numbers from 2 to 8, identify at least one known compound which exemplifies that coordination geometry. Draw the structure of each using a notation which reveals the three-dimensional arrangement of the groups.

4.2. List the seven types of isomerism possible for coordination compounds, giving an example of each.

4.3. Draw all the possible isomers of:

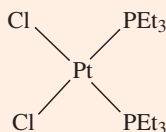
(i) a four-coordinate complex $[\text{ML}_2\text{XY}]$

(ii) an octahedral complex $[\text{MA}_2\text{LXYZ}]$

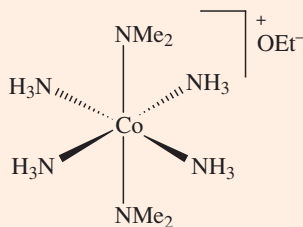
In each case, identify the situations in which optical isomers are possible (A, L, X, Y, Z represent different unidentate ligands)

4.4. Draw the possible isomers of the complex $[\text{Ru}\{\text{S}_2\text{C}_2(\text{CF}_3)_2\}(\text{CO})(\text{PPh}_3)_2]$, in which $\text{S}_2\text{C}_2(\text{CF}_3)_2$ is a bidentate dithiolate ligand (Figure 4.1).

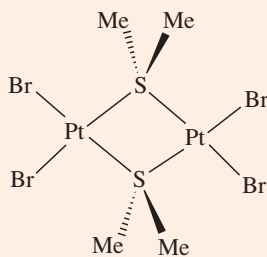
4.5. Devise systematic names for the compounds shown in Formulae 4.8–4.11:



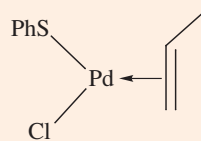
4.8



4.9



4.10



4.11

References

1. S. M. Jørgensen, *Z. Anorg. Chem.*, 1893, **5**, 147; 1899, **19**, 109.
2. J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry*, 4th edn., HarperCollins, New York, 1993, appendix A3.
3. A comprehensive account may be found in the chapter by T. E. Sloane in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R.D. Gillard and J.A. McCleverty, Pergamon Press, Oxford, 1987.
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