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Coordination and Organometallic Compounds

19.1 Introduction

The three series of elements arising from the filling of the 3d, 4d and 5d shells, and situated in the periodic table following the alkaline earth metals, are commonly described as "transition elements", though this term is sometimes also extended to include the lanthanide and actinide (or inner transition) elements. They exhibit a number of characteristic properties which together distinguish them from other groups of elements:

(i) They are all metals and as such are lustrous and deformable and have high electrical and thermal conductivities. In addition, their melting and boiling points tend to be high and they are generally hard and strong.

(ii) Most of them display numerous oxidation states which vary by steps of 1 rather than 2 as is usually the case with those main-group elements which exhibit more than one oxidation state.

(iii) They have an unparalleled propensity for forming coordination compounds with Lewis bases.

(i) and (ii) will be dealt with more fully in later chapters but it is the purpose of the present chapter to expand the theme of (iii).
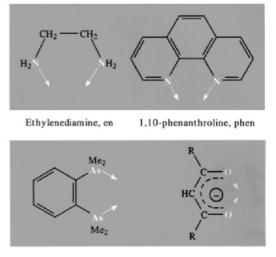
A coordination compound, or complex, is formed when a Lewis base (ligand)[1] is attached to a Lewis acid (acceptor) by means of a "lone-pair" of electrons. Where the ligand is composed of a number of atoms, the one which is directly attached to the acceptor is called the "donor atom". This type of bonding has already been discussed (p. 198) and is exemplified by the addition compounds formed by the trihalides of the elements of Group 13 (p. 237); it is also the basis of much of the chemistry of the

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[1] W. H. Brock, K. A. Jensen, C. K. Jørgensen and G. B. Kauffman, *Ambix* **27**, 171–83 (1981).

transition elements. The precise nature of the bond between a transition metal ion and a ligand varies enormously and the term "donor atom" is often used in situations where its literal meaning should not be assumed. Although inevitably the line of demarcation is rather ill-defined, it is conventional to distinguish two extremes. On the one hand, are those cases in which the bond may be considered profitably as a single σ bond, or even a purely electrostatic interaction, and in which the metal has an oxidation state of $+2$ or higher. On the other hand, are those cases where the bonding is multiple, the ligand acting simultaneously as both a σ donor and a π acceptor (p. 922) and in which the metal usually has a formal oxidation state of $+1$ or less, though the significance of such values is often unclear. Compounds of the former type are commonly described as "classical" or "Werner" complexes since it was through the investigation of such materials that A. Werner in the period 1893–1913 laid the foundations of coordination chemistry[2] (see also p. 912). Compounds of the latter type are exemplified by the carbonyls and other organometallic compounds.

19.2 Types of Ligand

Ligands are most conveniently classified according to the number of potential donor atoms which they contain and are known as uni-, bi-, ter-, quadri-, quinqi- and sexi-dentate accordingly as the number is 1, 2, 3, 4, 5 or 6. Unidentate ligands may be simple monatomic ions such as halide ions, or polyatomic ions or molecules which contain a donor atom from Groups 16, 15 or even 14 (e.g. CN⁻). Bidentate ligands are frequently chelating ligands (from Greek χηλή, crab's claw) and, with the metal ion, produce chelate rings[3]

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[2] G. B. KAUFFMAN, *Alfred Werner Founder of Coordination Theory,* Springer, Berlin, 1966, 127 pp. G. B. Kauffman (ed.) *Coordination Chemistry: A Century of Progress,* ACS Symposium Series **565**, Washington DC, 1994, 464 pp.

[3] C. F. BELL, *Principles and Applications of Metal Chelation,* Oxford University Press, Oxford, 1977, 147 pp.

Ethylenediamine, en   1,10-phenanthroline, phen

o-phenylenebis(dimethylarsine), diars: [1,2-bis(dimethylarsino) benzene] β-diketonates (e.g. R = Me: acetylacetonate, acac)
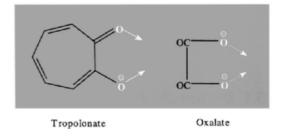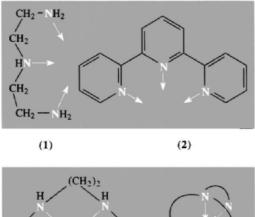

Tropolonate   Oxalate

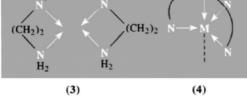**Figure 19.1**   Some bidentate ligands.

which in the case of the most commonly occurring bidentate ligands are 5- or 6-membered, e.g.: see Fig. 19.1. Terdentate ligands produce 2 ring systems when coordinated to a single metal ion and in consequence may impose structural limitations on the complex, particularly where rigidity is introduced by the incorporation of conjugated double bonds within the rings. Thus diethylenetriamine, dien (1), being flexible is stereochemically relatively undemanding, whereas terpyridine, terpy (2), can only coordinate when the 3 donor nitrogen atoms and the metal ion are in the same plane.

Quadridentate ligands produce 3, and in some cases 4, rings on coordination, and so even greater restrictions on the stereochemistry of the complex may be imposed by an
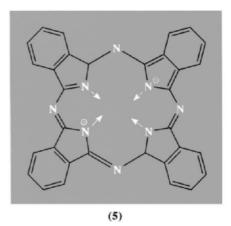
(1)   (2)

(3)   (4)

(5)

(6)   (7)

appropriate choice of ligand. The open-chain ligand triethylenetetramine, trien (3), is, like dien, flexible and undemanding, whereas tri-ethylaminetriamine, tren, i.e. $N(CH_2CH_2NH_2)_3$, is one of the so-called "tripod" ligands which are quite unable to give planar coordination but instead favour trigonal bipyramidal structures (4). By contrast, the highly conjugated phthalocya-nine[4] (5), which is an example of the class of macrocyclic ligands of which the crown ethers have already been mentioned (p. 96), forces the complex to adopt a virtually planar structure and has proved to be a valuable model for the naturally occurring porphyrins which, for instance, are involved in haem (p. 1100), B_{12} (p. 1138) and the chlorophylls (p. 125). Another well-known ligand, which has been used to synthesize oxygen-carrying molecules, is bis(salicylaldehyde)ethylenediimine, salen (6). Quinquidenate and sexidentate ligands are most familiarly exemplified by the anions derived from ethylenediaminetetraacetic acid, edtaH$_4$ i.e. $(HO_2CCH_2)_2N(CH_2)_2N(CH_2CO_2H)_2$, which is

used with remarkable versatility in the volumetric analysis of metal ions. As the fully ionized anion, edta^{4-}, it has 4 oxygen and 2 nitrogen donor atoms and has the flexibility to wrap itself around a variety of metal ions to produce a pseudo-octahedral complex involving five 5-membered rings as in (7).

In the incompletely ionized form, edtaH^{3-}, one of the oxygen atoms is no longer able to coordinate to the metal and the anion is quinquidentate.

Ambidentate ligands possess more than 1 donor atom and can coordinate through either one or the other. This leads to the possibility of "linkage" isomerism (p. 920). The commonest examples are the ions NO$_2^-$ (p. 463) and SCN$^-$ (p. 325). Such ligands can also coordinate via both donor sites simultaneously, thereby acting as bridging ligands.

In the case of organometallic compounds the most satisfactory way of classifying the ligands

[4] C. C. LEZNOFF and A. B. P. LEVER (eds.), *Phthalocyanines, Properties and Applications,* V.C.H., Weinheim, 1990, 336 pp.

is by the number of C atoms attached to (or closely associated with) the metal atom. This essentially structural criterion can be established by several techniques and is more definite than other features such as the presumed number of electrons involved in the bonding. The number of attached carbon atoms is called the *hapticity* of the organic group (Greek ηαπτειν, *haptein*, to fasten) and hapticities from 1 to 8 have been observed. Monohapto groups are specified as η^1, dihapto as η^2, etc. This classification will form the basis of the later discussion of organometallic compounds (pp. 924).

19.3 Stability of Coordination Compounds

Because complexes are not generally prepared from their components in the gaseous phase, measurements of their stability necessarily imply a comparison with the stability of some starting material. The overwhelming majority of quantitative measurements have been made in aqueous solutions when the complex in question is formed by the ligand displacing water from the aquo complex of the metal ion. If, for simplicity, we take the case where L is a unidentate ligand and ignore charge, then the process can be represented as a succession of steps for which the stepwise stability (or formation) constants K are as shown:[†]

[†] These constants are expressed here in terms of concentrations which means that the activity coefficients have been assumed to be unity. When pure water is the solvent this will only be true at infinite dilution, and so stability constants should be obtained by taking measurements over a range of concentrations and extrapolating to zero concentration. In practice, however, it is more usual to make measurements in the presence of a relatively high concentration of an inert electrolyte (e.g. 3 M NaClO₄) so as to maintain a constant ionic strength, thereby ensuring that the activity coefficients remain essentially constant. Stability constants obtained in this way (sometimes referred to as "concentration quotients" or "stoichiometric stability constants") are true thermodynamic stability constants referred to the standard state of solution in 3 M NaClO₄(aq), but they will, of course, differ from stability constants referred to solution in the pure solvent as standard state.

$$M(H_2O)_n + L \rightleftharpoons ML(H_2O)_{n-1} + H_2O;$$

$$K_1 = \frac{[ML(H_2O)_{n-1}]}{[M(H_2O)_n][L]}$$

$$ML_{n-1}(H_2O) + L \rightleftharpoons ML_n + H_2O;$$

$$K_n = \frac{[ML_n]}{[ML_{n-1}H_2O][L]}$$

$$M(H_2O)_n + nL \rightleftharpoons ML_n + nH_2O;$$

$$\beta_n = \frac{[ML_n]}{[M(H_2O)_n][L]^n}$$

By convention the displaced water is ignored since its concentration is essentially constant. The overall stability (or formation) constant β_n can clearly be expressed in terms of the stepwise constants:

$$\beta_n = K_1 \times K_2 \times \ldots \times K_n$$

These are thermodynamic constants which relate to the system when it has reached equilibrium, and must be distinguished from any considerations of kinetic lability or inertness which refer to the speed with which that equilibrium is attained.

A vast amount of data[5] has been accumulated from which a number of generalizations can be inferred concerning the factors which determine the stabilities of such complexes. Some of these are as follows:

(i) *The metal ion and its charge.* For a given metal and ligand the stability is generally greater if the oxidation state of the metal is +3 rather than +2. Furthermore, the stabilities of corresponding complexes of the bivalent ions of the first transition series, irrespective of the

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5 L. G. SILLÉN and A. E. MARTELL, *Stability Constants of Metal-ion Complexes*, The Chemical Society, London, Special Publications No. 17, 1964, 754 pp., and No. 25, 1971, 865 pp. *Stability Constants of Metal-Ion Complexes, Part A. Inorganic Ligands* (E. Högfeldt, ed.), 1982, pp. 310, *Part B. Organic Ligands* (D. Perrin, ed.), 1979, pp. 1263. Pergamon Press, Oxford. A continually updated database is now provided by: L. D. PETTIT and K. J. POWELL (eds.), *IUPAC Stability Constants Database*, IUPAC and Academic Software.

Figure 19.2   Classification of acceptor atoms in their common oxidation states.

particular ligand involved, usually vary in the Irving–Williams[6] order (1953):

$$Mn^{II} < Fe^{II} < Co^{II} < Ni^{II} < Cu^{II} > Zn^{II}$$

which is the reverse of the order for the cation radii (p. 1295). These observations are consistent with the view that, at least for metals in oxidation states +2 and +3, the coordinate bond is largely electrostatic. This was a major factor in the acceptance of crystal field theory (see pp. 921–3).

(ii) *The relationship between metal and donor atom.*[6a] Some metal ions (known as class-a acceptors or alternatively as "hard" acids) form their most stable complexes with ligands containing N, O or F donor atoms. Others (known as class-b acceptors or alternatively as "soft" acids) form their most stable complexes with ligands whose donor atoms are the heavier elements of the N, O or F groups. The metals of

Groups 1 and 2 along with the inner transition elements and the early members of the transition series (Groups 3 → 6) fall into class-a. The transition elements Rh, Pd, Ag and Ir, Pt, Au, Hg comprise class-b, while the remaining transition elements may be regarded as borderline (Fig. 19.2). The difference between the class-a elements of Group 2 and the borderline class-b elements of Group 12 is elegantly and colourfully illustrated by the equilibrium

$$[CoCl_4]^{2-} + 6H_2O \overset{Zn^{II}}{\underset{Ca^{II}}{\rightleftharpoons}} [Co(H_2O)_6]^{2+} + 4Cl^-$$
$$\text{Blue} \qquad\qquad\qquad \text{Pink}$$

If Ca^{II} is added it pushes the equilibrium to the left by bonding preferentially to H_2O, whereas Zn^{II}, with its partial b character (p. 1206), prefers the heavier Cl^- and so pushes the equilibrium to the right.

It seems that, as suggested by Ahrland *et al.*[7] in 1958, this distinction can be explained at least partly on the basis that class-a acceptors are the

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[6] H. M. N. H. IRVING and R. J. P. WILLIAMS, *J. Chem. Soc.* 1953, 3192–210.

[6a] R. G. PEARSON, *Coord. Chem. Revs.* **100**, 403–25 (1990).

[7] S. AHRLAND, J. CHATT and N. R. DAVIES, *Q. Revs.* **12**, 265–76 (1958).

more electropositive elements which tend to form their most stable complexes with ligands favouring electrostatic bonding, so that, for instance, the stabilities of their complexes with halide ions should decrease in the order

$$F^- > Cl^- > Br^- > I^-$$

Class-b acceptors on the other hand are less electropositive, have relatively full d orbitals, and form their most stable complexes with ligands which, in addition to possessing lone-pairs of electrons, have empty π orbitals available to accommodate some charge from the d orbitals of the metal. The order of stability will now be the reverse of that for class-a acceptors, the increasing accessibility of empty d orbitals in the heavier halide ions for instance, favouring an increase in stability of the complexes in the sequence

$$F^- < Cl^- < Br^- < I^-$$

(iii) *The type of ligand.* In comparing the stabilities of complexes formed by different ligands, one of the most important factors is the possible formation of chelate rings. If L is a unidentate ligand and L-L a bidentate ligand, the simplest illustration of this point is provided by comparing the two reactions:

$$M(aq) + 2L(aq) \rightleftharpoons ML_2(aq)$$

for which $\beta_L = \dfrac{[ML_2]}{[M][L]^2}$

and

$$M(aq) + L\text{-}L(aq) \rightleftharpoons ML\text{-}L\ (aq)$$

for which $\beta_{L\text{-}L} = \dfrac{[ML\text{-}L]}{[M][L\text{-}L]}$

or alternatively by considering the replacement reaction obtained by combining them:

$$ML_2(aq) + L\text{-}L(aq) \rightleftharpoons ML\text{-}L(aq) + 2L(aq)$$

for which $K = \dfrac{[ML\text{-}L][L]^2}{[ML_2][L\text{-}L]} = \dfrac{\beta_{L\text{-}L}}{\beta_L}$

Experimental evidence shows overwhelmingly that, providing the donor atoms of L and L-L are the same element and that the chelate ring

formed by the coordination of L-L does not involve undue strain, L-L will replace L and the equilibrium of the replacement reaction will be to the right. This stabilization due to chelation is known as the *chelate effect*[8] and is of great importance in biological systems as well as in analytical chemistry.

The effect is frequently expressed as $\beta_{L\text{-}L} > \beta_L$ or $K > 1$ and, when values of ΔH° are available, ΔG° and ΔS° are calculated from the thermodynamic relationships

$$\Delta G^\circ = -RT \ln \beta \text{ and } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

On the basis of the values of ΔS° derived in this way it appears that the chelate effect is usually due to more favourable entropy changes associated with ring formation. However, the objection can be made that β_L and $\beta_{L\text{-}L}$ as just defined have different dimensions and so are not directly comparable. It has been suggested that to surmount this objection concentrations should be expressed in the dimensionless unit "mole fraction" instead of the more usual mol dm^{-3}. Since the concentration of pure water at 25°C is approximately 55.5 mol dm^{-3}, the value of concentration expressed in mole fractions = conc in mol dm^{-3}/55.5 Thus, while β_L is thereby increased by the factor $(55.5)^2$, $\beta_{L\text{-}L}$ is increased by the factor (55.5) so that the derived values of ΔG° and ΔS° will be quite different. The effect of this change in units is shown in Table 19.1 for the Cd^{II} complexes of L = methylamine and L-L = ethylenediamine. It appears that the entropy advantage of the chelate, and with it the chelate effect itself, virtually disappears when mole fractions replace mol dm^{-3}.

The resolution of this paradox lies in the assumptions about standard (reference), states which are unavoidably involved in the above definitions of β_L and $\beta_{L\text{-}L}$. In order to ensure that β_L and $\beta_{L\text{-}L}$ are dimensionless (as they have to be if their logarithms are to be used) when concentrations are expressed in units which have dimensions, it is necessary to use the ratios of the actual concentrations to the concentrations of

[8] D. C. MUNRO, *Chem. Br.* **13**, 100–5 (1977).

Table 19.1 Stability constants and thermodynamic functions for some complexes of Cd^{II} at 25°C

Complex	$\log \beta$	$\Delta H°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$T\Delta S°$ (kJ mol^{-1})
(a) $[Cd(NH_2Me)_4]^{2+}$	6.55	−57.32	−37.41	−19.91
	13.53		*−72.20*	*+19.98*
(b) $[Cd(en)_2]^{2+}$	10.62	−56.48	−60.67	+4.19
	14.11		*−80.51*	*+24.04*
Difference (b)−(a)	4.07	+0.84	−23.26	+24.1
	0.58		*−3.31*	*+4.06*

Values in roman type are based on concentrations expressed in mol dm^{-3}. Values in *italics* are based on concentrations expressed in mole fractions. The difference (b)−(a) refers to the replacement reaction

$$[Cd(NH_2Me)_4]^{2+}(aq) + 2en(aq) \rightleftharpoons [Cd(en)_2]^{2+}(aq) + 4NH_2Me(aq)$$

some standard state. Accordingly, the expression for any β should incorporate an additional factor composed of standard state concentrations, and the expression $\Delta G° = -RT \ln \beta$ should have an additional term involving the logarithm of this factor. Not to include this factor and this term inevitably implies the choice of standard states of concentration $= 1$ in whatever units are being used. Only in this way can the factor associated with β be 1 and its logarithm zero. It should be stressed, however, that irrespective of these definitional niceties, it remains true as stated above that chelating ligands which form unstrained complexes always tend to displace their monodentate counterparts under normally attainable experimental conditions.

Probably the most satisfactory model with which to explain the chelate effect is that proposed by G. Schwarzenbach[9]. If L and L-L are present in similar concentrations and are competing for two coordination sites on the metal, the probability of either of them coordinating to the first site may be taken as equal. However, once one end of L-L has become attached it is much more likely that the second site will be won by its other end than by L, simply because its other end must be held close to the second site and its effective concentration where it matters is therefore much

higher than the concentration of L. Because $\Delta G°$ refers to the transfer of the separate reactants at concentrations $= 1$ to the products, also at concentrations $= 1$, it is clear from this model that the advantage of L-L over L, as denoted by $\Delta G°$ or β, will be greatest when the units of concentration are such that a value of 1 corresponds to a dilute solution. Conversely, where a value of 1 coresponds to an exceedingly high concentration, the advantage will be much less and may even disappear. In normal practice even a concentration of 1 mol dm^{-3} is regarded as high, and a concentration of 1 mole fraction is so high as to be of only hypothetical significance, so it need cause no surprise that the choice of the latter unit should lead to rather bizarre results.

The chelate effect is usually most pronounced for 5- and 6-membered rings. Smaller rings generally involve excessive strain while increasingly large rings offer a rapidly decreasing advantage for coordination to the second site. Naturally the more rings there are in a complex the greater the total increase in stability. If a multidentate ligand is also cyclic, and there are no unfavourable steric effects, a further increase in the stability of its complexes accrues. Favourable entropy changes can again be invoked to explain this *macrocyclic effect*. Since a macrocyclic ligand has very little rotational entropy even before coordination, the net increase in entropy when it does coordinate is expected to be even greater than in the case of a comparable non-cyclic ligand.

[9] G. SCHWARZENBACH. *Helv. Chim. Acta* **35**, 2344−59 (1952).