Coordination compounds and ligands

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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.

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 Ni(ClO4)2 with the Brønsted base ammonia to form a complex according to equation 4. 1 Ni(ClO4)2 + 6NH3 †’ [Ni(NH3)6](ClO4)2 (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 [Co(NH3)5Cl]Cl2, in which the coordination complex is [Co(NH3)5Cl]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 H2O or NH3, larger molecules such as H2NCH2CH2NH2 or N(CH2CH2NH2)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 [Co(NH3)5Cl]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.

Types of Ligand

Where a ligand is bound to a metal ion through a single donor atom, as with Cl-, H2O or NH3, the ligand is said to be unidentate (the ligand binds to the metal through a single point of attachment as if it had one tooth). Where two donor atoms can be used to bind to a metal ion, as with H2NCH2CH2NH2, the ligand is said to be bidentate, and where several donor atoms are present in a single ligand as with N(CH2CH2NH2)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. A huge variety of ligands appear in coordination complexes, 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. Bidentate ligands may be classified according to the number of atoms in the ligand which separate the donor atoms 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. Bicyclic proligands are also known which can completely encapsulate a metal ion. Some of these systems have given the names cryptand or sepulchrate, Certain polydentate ligands are particularly good at linking together several metal ions and are refered to as polynucleating ligands.

Geometry

In coordination chemistry, a structure is first described by its coordination number, the number of ligands attached to the metal (more specifically, the number of Ïƒ-type bonds between ligand(s) and the central atom). Usually one can count the ligands attached, but sometimes even the counting can become ambiguous. Coordination numbers are normally between two and nine, but large numbers of ligands are not uncommon for the lanthanides and actinides. The number of bonds depends on the size, charge, and electron configuration of the metal ion and the ligands. Metal ions may have more than one coordination number.

Typically the chemistry of complexes is dominated by interactions between s and p molecular orbitals of the ligands and the d orbitals of the metal ions. The s, p, and d orbitals of the metal can accommodate 18 electrons (see 18-Electron rule; for f-block elements, this extends to 32 electrons). The maximum coordination number for a certain metal is thus related to the electronic configuration of the metal ion (more specifically, the number of empty orbitals) and to the ratio of the size of the ligands and the metal ion. Large metals and small ligands lead to high coordination numbers, e. g. [Mo(CN)8]4-. Small metals with large ligands lead to low coordination numbers, e. g. Pt[P(CMe3)]2. Due to their large size, lanthanides, actinides, and early transition metals tend to have high coordination numbers.

Different ligand structural arrangements result from the coordination number. Most structures follow the points-on-a-sphere pattern (or, as if the central atom were in the middle of a polyhedron where the corners of that shape are the locations of the ligands), where orbital overlap (between ligand and metal orbitals) and ligand-ligand repulsions tend to lead to certain regular geometries. The most observed geometries are listed below, but there are many cases which deviate from a regular geometry, e. g. due to the use of ligands of different types (which results in irregular bond lengths; the coordination atoms do not follow a points-on-a-sphere pattern), due to the size of ligands, or due to electronic effects (see e. g. Jahn-Teller distortion):

Linear for two-coordination,

Trigonal planar for three-coordination,

Tetrahedral or square planar for four-coordination

Trigonal bipyramidal or square pyramidal for five-coordination,

Octahedral (orthogonal) or trigonal prismatic for six-coordination,

Pentagonal bipyramidal for seven-coordination,

Square antiprismatic for eight-coordination, and

Tri-capped trigonal prismatic (Triaugmented triangular prism) for nine coordination.

Some exceptions and provisions should be noted:

The idealized descriptions of 5-, 7-, 8-, and 9- coordination are often indistinct geometrically from alternative structures with slightly different L-M-L (ligand-metal-ligand) angles. The classic example of this is the difference between square pyramidal and trigonal bipyramidal structures.

Due to special electronic effects such as (second-order) Jahn-Teller stabilization, certain geometries are stabilized relative to the other possibilities, e. g. for some compounds the trigonal prismatic geometry is stabilized relative to octahedral structures for six-coordination.

Isomerism

The arrangement of the ligands is fixed for a given complex, but in some cases it is mutable by a reaction that forms another stable isomer.

There exist many kinds of isomerism in coordination complexes, just as in many other compounds.

Stereoisomerism

Stereoisomerism occurs with the same bonds in different orientations relative to one another. Stereoisomerism can be further classified into:

Cis-trans isomerism and facial-meridional isomerism

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.

Optical isomerism

Optical isomerism occurs when the mirror image of a compound is not superimposable with the original compound. It is so called because such isomers are optically active, that is, they rotate the plane of polarized light. The symbol Î› (lambda) is used as a prefix to describe the left-handed propeller twist formed by three bidentate ligands, as shown. Similarly, the symbol Î” (delta) is used as a prefix for the right-handed propeller twist.[7]

Structural isomerism

Structural isomerism occurs when the bonds are themselves different. Linkage isomerism is only one of several types of structural isomerism in coordination complexes (as well as other classes of chemical compounds). Linkage isomerism occurs with ambidentate ligands which can bind in more than one place. For example, NO2 is an ambidentate ligand: it can bind to a metal at either the N atom or at an O atom. http://t2. gstatic. com/images?q= tbn: ANd9GcRKxYHqV_eczrlInNE3ZAbZOBh-Q1JBpMbyWoRehkKI8y1KEuk&t= 1&usg= __PClvZyGR5yoOsiA5HEgW1Zjyvko=

Naming Coordination Compounds

A complex is a substance in which a metal atom or ion is associated with a group of neutral molecules or anions called ligands. Coordination compounds are neutral substances (i. e. uncharged) in which at least one ion is present as a complex. You will learn more about coordination compounds in the lab lectures of experiment 4 in this course.

The coordination compounds are named in the following way. (At the end of this tutorial we have some examples to show you how coordination compounds are named.)

A. To name a coordination compound, no matter whether the complex ion is the cation or the anion, always name the cation before the anion. (This is just like naming an ionic compound.)

B. In naming the complex ion:

1. Name the ligands first, in alphabetical order, then the metal atom or ion. Note: The metal atom or ion is written before the ligands in the chemical formula.

2. The names of some common ligands are listed in Table 1.

For anionic ligands end in “-o”; for anions that end in “-ide”(e. g. chloride), “-ate” (e. g. sulfate, nitrate), and “-ite” (e. g. nirite), change the endings as follows: -ide http://www. chemistry. wustl. edu/~edudev/LabTutorials/arrow. jpg-o; -ate http://www. chemistry. wustl. edu/~edudev/LabTutorials/arrow. jpg-ato; -ite http://www. chemistry. wustl. edu/~edudev/LabTutorials/arrow. jpg-ito

For neutral ligands, the common name of the molecule is used e. g. H2NCH2CH2NH2 (ethylenediamine). Important exceptions: water is called ‘ aqua’, ammonia is called ‘ ammine’, carbon monoxide is called ‘ carbonyl’, and the N2 and O2 are called ‘ dinitrogen’ and ‘ dioxygen’.

3. Greek prefixes are used to designate the number of each type of ligand in the complex ion, e. g. di-, tri- and tetra-. If the ligand already contains a Greek prefix (e. g. ethylenediamine) or if it is polydentate ligands (ie. can attach at more than one binding site) the prefixes bis-, tris-, tetrakis-, pentakis-, are used instead. (See examples 3 and 4.) The numerical prefixes are listed in Table 2.

4. After naming the ligands, name the central metal. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is call cobalt and Pt is called platinum. (See examples 1-4). If the complex ion is an anion, the name of the metal ends with the suffix -ate. (See examples 5 and 6.). For example, Co in a complex anion is called cobaltate and Pt is called platinate. For some metals, the Latin names are used in the complex anions e. g. Fe is called ferrate (not ironate).

5. Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses.

C. To name a neutral complex molecule, follow the rules of naming a complex cation. Remember: Name the (possibly complex) cation BEFORE the (possibly complex) anion. See examples 7 and 8.

For historic reasons, some coordination compounds are called by their common names. For example, Fe(CN)63ï€ and Fe(CN)64ï€ are named ferricyanide and ferrocyanide respectively, and Fe(CO)5 is called iron carbonyl.

Examples Give the systematic names for the following coordination compounds:

1. [Cr(NH3)3(H2O)3]Cl3

Answer: triamminetriaquachromium(III) chloride

Solution: The complex ion is inside the parentheses, which is a cation.

The ammine ligands are named before the aqua ligands according to alphabetical order.

Since there are three chlorides binding with the complex ion, the charge on the complex ion must be +3 (since the compound is electrically neutral).

From the charge on the complex ion and the charge on the ligands, we can calculate the oxidation number of the metal. In this example, all the ligands are neutral molecules. Therefore, the oxidation number of chromium must be same as the charge of the complex ion, +3.

K4[Fe(CN)6]

Answer: potassium hexacyanoferrate(II)

Solution: potassium is the cation and the complex ion is the anion.

Since there are 4 K+ binding with a complex ion, the charge on the complex ion must be ï€ 4.

Since each ligand carries -1 charge, the oxidation number of Fe must be +2.

The common name of this compound is potassium ferrocyanide.

Applications of Co-ordination Compounds

(1) Estimation of hardness in water, as Ca++ and Mg2+ ions form complexes with EDTA.

(2) Animal and plant world e. g. chlorophyll is a complex of Mg2+ and haemoglobin is a complex of Fe2+ vitamin B12 is a complex of Co2+.

(3) Electroplating of metals involves the use of complex salt as electrolytes e. g. K[Ag(CN)2] in silver plating.

(4) Extraction of metals e. g. Ag and Au are extracted from ores by dissolving in NaCN to form complexes.

(5) Estimation and detection of metal ions e. g. Ni2+ ion is estimated using dimethyl glyoxime.

(6) Medicines e. g. cis-platin i. e. cis [PtCl2(NH3)2] is used in treatment in cancer

Importance and Applications of Coordination Compounds:

Importance and applications of coordination compounds find use in many qualitative and quantitative chemical analyses. The familiar color reactions given by metal ions with number of ligands. Similarly purification of metal can be achieved through formation and sub sequence decomposition of their coordination compounds.

Inflexibility of water is predictable by simple titration with Na2EDTA. the Ca2+ and Mg2+ ions form stable complex with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes. Some important extraction processes of metals like those of silver and gold, make use of complex formation.

Importance and applications of coordination compounds are of great importance in biological system. The pigment responsible for photosynthesis chlorophyll is a coordinated compound of magnesium. Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron. Coordination compounds are used as catalysts for many industrial processes.

Applications of articles can be electroplating with the silver and gold much more smoothly and evenly from the solution of the complexes. In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the unrecompensed AgBr to from a complex ion
[Ag9S2O3)2]3-

There is growing interest in the user of chelate therapy in medicinal chemistry. An example is the treatment of problem caused by the presence of metal in toxic proportion in plant and animal. Thus, excess of copper and iron are removed by chelating ligands D-penicillamine and desferrioxime B via the formation of the coordination compounds. EDTA is use in the conduct of guide poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours.

Sonochemical Asymmetric Hydrogenation with Palladium

Enantioselective hydrogenation is one of the most versatile methods of asymmetric synthesis, with heterogeneous catalysis, using chiral modifiers, rapidly becoming an alternative to the . traditional. homogeneous methods. The role of modifiers in asymmetric hydrogenations is to enhance catalysis, with the bonding mode and geometry of adsorption being important, as well as the modifier concentration and the type and position of the substituent groups in the aromatic ring. Ultrasonic irradiation (sonication) is known to be beneficial in catalytic asymmetric hydrogenations. Sonication removes catalyst surface impurities, and gives enhanced adsorption to the chiral modifiers. Now a team from Michigan Technological University, Houghton, U. S. A. (S. C. Mhadgut, I. Bucsi, M. Török and B. Török, Chem. Commun., 2004, (8), 984-985; DOI: 10. 1039/b315244h) has revisited the Pd-catalysed, proline-modified, asymmetric hydrogenation of isophorone (3, 3, 5-trimethyl-2-cyclohexen-1-one (with a C= C bond)). They examined the catalyst, the modifier and the effects of sonication. Pd/Al2O3 was found to give a better, thoughlow, enantiomeric excess (ee) than Pd/C. Prolineand its derivatives (isomeric hydroxyl-prolines, prolinols and proline esters) were tested as chiral

modifiers for Pd/Al2O3. Proline was the best modifier, and both enantiomers gave ee £ 35%. Presonication was found to enhance the enantioselectivity when both the Pd/Al2O3 catalyst and the proline modifier were present. . Modifier-free. presonication and the presence of substrate during pretreatment decreased the enantioselectivity. The reaction was performed at 50 bar pressure and 25°C. Presonication for 20 minutes gave the highest optical yields, and increased optical yields across all the H2 pressure range.

Maximum ee occurred at a 1: 2 isophorone: proline ratio, and with optimised conditions and presonication, the ee for the Pd/Al2O3-(S)-proline catalytic system was £ 85%. Ultrasonic cleaning of the catalyst enhanced both the adsorption of the modifier and the modifier- induced surface restructuring of the Pd. The high ee was due to proline adsorption on the Pd surface. New catalysts that can strongly adsorb proline could thus become important in heterogeneous catalysis for C= C double bond hydrogenation of a, b-unsaturated carbonyl compounds.