



Nomenclature and terminology of Coordination complex : A Review

Surbhi Goyal

Abstract: Discrete coordination compounds and coordination polymers are topical research fields in inorganic chemistry, crystal engineering, solid-state chemistry, and materials science, due to their potential applications in adsorption, separation, catalysis, electrical, magnetic, and optical applications. Beginning with the basic concepts of coordination compounds and coordination polymers, this chapter briefly describes the synthetic methods and rational synthesis of coordination compounds, and the frequently used strategies for the molecular design, the important factors (such temperature, pH, template, additive, solvent, and counter-ion) that have influences on the self-assembly and crystallization, as well as solvothermal/hydrothermal in situ metal/ligand reactions for coordination compounds and coordination polymers, as well as postsynthetic modifications for porous coordination polymers, through selected examples in the literature.

ISSN : 2348-5612 © URR



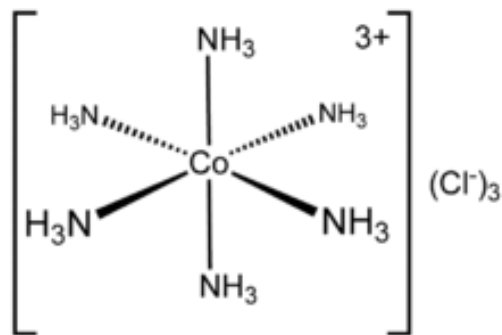
Keywords: Assembly, Coordination compound, Coordination polymer, Linker Modification, Molecular assembly, Molecular design,

Introduction:

In chemistry, a coordination complex consists of a central atom or ion, which is usually metallic and is called the coordination centre, and a surrounding array of bound molecules or ions, that are in turn known as ligands or complexing agents. Many metal-containing compounds, especially those of transition metals, are coordination complexes. A coordination complex whose centre is a metal atom is called a metal complex.

Nomenclature and terminology

Coordination complexes are so pervasive that their structures and reactions are described in many ways, sometimes confusingly. The atom within a ligand that is bonded to the central metal atom or ion is called the donor atom. In a typical complex, a metal ion is bonded to several donor atoms, which can be the same or different. A polydentate (multiple bonded) ligand is a molecule or ion that bonds to the central atom through several of the ligand's atoms; ligands with 2, 3, 4 or even 6 bonds to the central atom are common. These complexes are called chelate complexes; the formation of such complexes is called chelation, complexation, and coordination.



The central atom or ion, together with all ligands, comprise the coordination sphere. The central atoms or ion and the donor atoms comprise the first coordination sphere.

Coordination refers to the "coordinate covalent bonds" (dipolar bonds) between the ligands and the central atom. Originally, a complex implied a reversible association of molecules, atoms, or ions through such weak chemical

bonds. As applied to coordination chemistry, this meaning has evolved. Some metal complexes are formed virtually irreversibly and many are bound together by bonds that are quite strong.

The number of donor atoms attached to the central atom or ion is called the coordination number. The most common coordination numbers are 2, 4, and especially 6. A hydrated ion is one kind of a complex ion (or simply a complex), a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons.

If all the ligands are monodentate, then the number of donor atoms equals the number of ligands. For example, the cobalt(II) hexahydrate ion or the hexaaquacobalt(II) ion $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is a hydrated-complex ion that consists of six water molecules attached to a metal ion Co. The oxidation state and the coordination number reflect the number of bonds formed between the metal ion and the ligands in the complex ion.

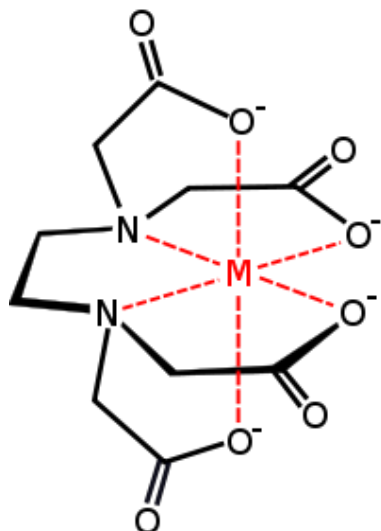
Any donor atom will give a pair of electrons. There are some donor atoms or groups which can offer more than one pair of electrons. Such are called bidentate (offers two pairs of electrons) or polydentate (offers more than two pairs of electrons). In some cases an atom or a group offers a pair of electrons to two similar or different central metal atoms or acceptors—by division of the electron pair—into a three-center two-electron bond. These are called bridging ligands.

Structures

The ions or molecules surrounding the central atom are called ligands. Ligands are generally bound to the central atom by a coordinate covalent bond (donating electrons from a lone electron pair into an empty metal orbital), and are said to be **coordinated** to the atom. There are also organic ligands such as alkenes whose pi bonds can coordinate to empty metal orbitals. An example is ethene in the complex known as Zeise's salt, $\text{K}^+[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$.

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 donor atoms). 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 transition metal complexes is dominated by interactions between s and p molecular orbitals of the donor-atoms in 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). The maximum coordination number for a certain metal is thus related to the

electronic configuration of the metal ion (to be more specific, 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. $[\text{Mo}(\text{CN})_8]^{4-}$. Small metals with large ligands lead to low coordination numbers, e.g. $\text{Pt}[\text{P}(\text{CMe}_3)]_2$. 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 that 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 for five-coordination
- Octahedral for six-coordination
- Pentagonal bipyramidal for seven-coordination
- Square antiprismatic for eight-coordination
- Tricapped trigonal prismatic for nine-coordination



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, e.g. the difference between square pyramidal and trigonal bipyramidal structures.

- Square pyramidal for five-coordination
- Capped octahedral or capped trigonal prismatic for seven-coordination
- Dodecahedral or bicapped trigonal prismatic for eight-coordination
- Capped square antiprismatic for nine-coordination

In systems with low d electron count, due to special electronic effects such as (second-order) Jahn–Teller stabilization, certain geometries (in which the coordination atoms do not follow a points-on-a-sphere pattern) 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.

- Bent for two-coordination
- Trigonal pyramidal for three-coordination
- Trigonal prismatic for six-coordination

References:

- Angelo R. Rossi; Roald. Hoffmann (1975). "Transition metal pentacoordination". *Inorganic Chemistry*. 14 (2): 365–374. doi:10.1021/ic50144a032.
- Compendium of Chemical Terminology, 2nd ed. (the "Gold Book") (1997). Online corrected version: (2006–) "complex". doi:10.1351/goldbook.C01203
- Compendium of Chemical Terminology, 2nd ed. (the "Gold Book") (1997). Online corrected version: (2006–) "coordination entity". doi:10.1351/goldbook.C01330
- Cotton, F. Albert; Wilkinson, Geoffrey; Murillo, Carlos A.; Bochmann, Manfred (1999), *Advanced Inorganic Chemistry* (6th ed.), New York: Wiley-Interscience, ISBN 0-471-19957-5
- Cotton, Frank Albert; Geoffrey Wilkinson; Carlos A. Murillo (1999). *Advanced Inorganic Chemistry*. p. 1355. ISBN 978-0-471-19957-1.
- Cotton, Simon (2006). *Lanthanide and Actinide Chemistry*. John Wiley & Sons Ltd.
- Greenwood, Norman N.; Earnshaw, Alan (1997). *Chemistry of the Elements* (2nd ed.). Butterworth-Heinemann. ISBN 0-08-037941-9.
- Harris, D.; Bertolucci, M. (1989). *Symmetry and Spectroscopy*. Dover Publications.
- Huheey, James E., *Inorganic Chemistry* (3rd ed., Harper & Row 1983), p.524–5 ISBN 0-06-042987-9
- Huheey, James E., *Inorganic Chemistry* (3rd ed., Harper & Row 1983), p.513–24 ISBN 0-06-042987-9
- Jeremy K. Burdett; Roald Hoffmann; Robert C. Fay (1978). "Eight-Coordination". *Inorganic Chemistry*. 17 (9): 2553–2568. doi:10.1021/ic50187a041.