The earlier history of coordination chemistry is full of individual contributions both in the experimental as well as theoretical aspects. But it was the monumental work of Dr Alfred Werner which put coordination chemistry to its sound scientific footing and paved the way to future development in this field.

Ever since 1891 when Werner put forward his theory of coordination compounds, their study has been gaining increasing momentum. Application of the knowledge derived from the electronic structure of the atom, and the theory of quantum mechanics, aided by the varieties of physical methods of measurements that have been developed in recent times, has helped to create interest in the study of coordination chemistry. These development have made it possible to reveal the shape and configuration of coordinated molecules as a whole, based on the findings about the nature of the interatomic force, or the chemical bond involved in their formation, the directions in which such forces act, the strength of the valence bond and the magnitude of the intervalency angles, and the interatomic distances.

Before elaborating on the modern concepts of coordination chemistry it is worthwhile making a passing reference to the pioneering work done in this field. The nineteenth century heralded the growth of knowledge regarding the molecular structure
of compounds. The views regarding the constancy of valency which were successful in explaining the structure of organic compounds were extended to include inorganic compounds like the hydrates, double salts and metal ammonia compounds. Of these the ammonia compounds received relatively kaener attention. The study of complex compounds thus began side by side with the study of the ammoniates or ammines. The discovery of these substances is usually attributed to Taessert, who observed in 1798 that cobalt salts combined with ammonia. Among the predecessors of Werner, who attempted to explain the formation and behaviour of metal ammoniates, were Berzelius, Graham, Claus, Blomstrand and Jorgensen. Their explanations fell short of giving a comprehensive postulate, which only Werner could give.

Werner's coordination theory:

Werner classified chemical compounds under two main heads:

(1) Complexes of the first order or simple compounds, and
(2) Complexes of the second or higher order including double, molecular, or complex compounds.

His view was that the affinity or the binding power of an atom was not completely satisfied by union with another atom; a certain amount of residual affinity remained unsaturated on
each after this preliminary combination. Consequently Werner suggested the possibility of there being two types of valency, namely, the primary or principal valency and secondary, residual or auxiliary valency. The primary valency was satisfied when a simple compound was formed, and the compounds of second order were formed by virtue of the auxiliary valency. The valence force was, therefore, found to be variable. Werner also introduced a new measure for the binding power of the atom, which was expressed in integral units and called the coordination number. Each atom or ion had a definite coordination number.

The compounds formed as a result of the combination of an atom or ion with other ions, groups or molecules with the satisfaction of the secondary valency were known as coordination complexes. The groups, molecules or ions held around the central atom were said to be coordinated with the latter and their number gave its coordination number. The coordinated units were oriented symmetrically around the central atom giving a planar, tetrahedral, octahedral or cubical configurations as the case may be and could not appear as ions in solution, though they might be otherwise ionizable. The binding force of the central atom was believed to be gravitational in nature and exerted uniformly in all directions. The coordination number of the central atom, giving the number of coordinated units, was, therefore, supposed to be determined only by geometrical
consideration depending on the amount of space available around it. This aspect of Werner's theory found no justification. Moreover, the existence of two types of valence bonds, namely, the primary and secondary was also not theoretically justified.

The electronic theory of valency helped to remove the inherent weaknesses of Werner's theory.

Electronic theory of valency:

Kossel in 1916 attributed chemical combinations between atoms and ions to transferring of electrons from one atom to the atom, resulting in the attainment of a stable configuration akin to inert gases. The resultant compounds were called heteropolar or ionic compounds. The binding force attracting the combined atoms or ions was electrostatic in nature. The valency involved was known as electro-valency and the linkage between the atoms was known as ionic linkage or ionic bond though there was no actual bond of any kind between them. The other type of substances is distinguished as homopolar compounds. An explanation regarding their formation was offered by Lewis also in 1916. His view was that the assumption of the configuration of the nearest inert gas could be achieved by the sharing of electrons between the bonded atoms. Lewis based his postulates on the classical electromagnetic theory of atomic structure. Having known that the valency of carbon atom in its
compounds acts in definite directions in space, Lewis assumed that these electrons were distributed symmetrically at the eight corners of the cube around the atomic core. Lewis' theory was consequently called the octet theory of valency. Langmuir\textsuperscript{10} gave the name 'covalency' to this type of valency and further developed this theory. The type of linkage involved was called covalent or atomic bond, each bond being represented by a pair of shared electrons.

With the development of the concepts about the structure of the atom, Lewis' assumption regarding the static model of the atom and his octet theory were abandoned. The directional nature of the valency forces was established by the facts of stereochemistry, was then accounted for by Knorr\textsuperscript{11} on the assumption of the orientation of the shared orbits in definite directions in space.

Distinction was made between the molecular or double compounds and complex compounds depending on their chemical and physical behaviour as determined from a study of their chemical reactions, migration, conductivity, solubility, distribution ratio, electrode potential, absorption spectrum, freezing point of aqueous solution, and magnetic susceptibility. But as a matter of fact, there is no sharp line of demarcation between the two.
Furthermore, the complex compounds are also found to show a certain gradation of properties among themselves. Complex compounds are accordingly distinguished into two types and termed 'perfect' and 'imperfect' complexes. The latter are partially dissociated in solution into their components and hence more or less respond to the qualitative tests. Their coordination number is often variable depending upon external conditions. A large number of metallic ammnes like CuSO₄·5NH₃, NiCl₂·6NH₃, NiCl₂·4NH₃ etc., belongs to this class. Anionic complexes of the type K₂BeF₄, K₃FeF₆, KHgI₃, K₂HgI₄ etc., also come under the same category.

The perfect complexes give no reactions characteristic of the constituent atoms or groups inside the complex zone, and in them the coordination number for any given central atom of a given charge has always a fixed value. Ammnes of cobalt (III), ferro and ferric cyanides are the typical examples of this class.

In a molecular compound, it is known, that the constituent ions are held by electrostatic force in the solid crystal. But views regarding the nature of the binding force in complexes are varied.

According to Kossel (loc. cit.), in complexes of the type K₂PtCl₆ or [Pt(NH₃)₆]Cl₄, a powerfully positive Pt (IV) ion of small size attracts and hold around itself six negative
chlorine ions or six dipole molecules of ammonia. In molecules of the type ammonia and water it is assumed that the negative charge of the nitrogen or oxygen atom is not completely neutralized by the positive hydrogen atoms. A residual negative charge thus remains on them which is then attracted by the powerfully positive Pt (IV) ion of small size, while the positive hydrogen atoms are somewhat repelled outwards. In K₂PtCl₆, a Pt (IV) ion, holding six negative univalent chlorine around it, renders the entire complex molecule trivalent negative. Kossel, therefore, satisfactorily accounts for the different electrical behaviour of the various complexes with one and the same central atom.

Lewis and Langmuir (loc. cit.), on the other hand, suggests that in coordination complexes the units are held to the central atom by covalent bonds. In some of these complexes, the octet can extend its shell to accommodate twelve electrons or six pair of shared electrons, which give the coordination number of the central atom. Sidgwick¹₂ also shared this view. Lewis' suggestion is that, an electron pair bond may be formed in two ways: (a) each of the two bonded atoms contributing one electron to the shared pair as they normally do; or (b) both the electrons of the shared pair may originate from one of the combining atoms. In the formation of coordination complex the latter type of the electron pair bonds are involved. Thus this type of linkage has been called coordinate covalent bond.
Only atoms with a lone or unshared pair of electrons can form such bonds with an atom which can accept or share such a pair. The numerical value of covalency of the atoms concerned in coordination compounds, no longer depends on the periodic groups to which they belong. Lowry\textsuperscript{13} described this type of bond as 'semipolar' or 'mixed double bond'. In a simple or complex compound, the total number of electrons around an atom after combination was termed, the Effective Atomic Number (E.A.N.) by Sidgwick (loc. cit.). This effective atomic number of the central atom in a complex is either equal to, or very nearly equal to, the atomic number of the nearest inert gas.

P. Ray\textsuperscript{14}, after carrying out an extensive study of the magnetic properties of a number of complex compounds found, that the classification of the latter into perfect and imperfect categories was unjustified. Based on their magnetic behaviour the complex compounds are classified as 'Penetration' and 'Associated' complexes. In the former type the inner d-level of the central ion is more or less filled up or there is a coupling of electrons originally unpaired in the level. In the latter type the binding occurs outside the inner d-level of the central atom. Pauling's theory of quantum mechanics for complex compound\textsuperscript{15} is in full agreement with the above definitions. This magnetic phenomenon gave rise to the so called
Atomic Orbital or Valence Bond Theory, which can be described as follows: The magnetic moment of many paramagnetic ions suffers profound alteration when the latter become centres of coordination complexes. Such alteration is possible only when there is a coupling of unpaired electrons. In the ions of transitional elements, which are most effective in forming coordination complexes, the inner d-level is more or less incompletely filled up with electrons, some of which may remain unpaired. In cases, where they are paired or the d-level is more or less filled during complex formation, there is a change in the magnetic moment of the central ion. The magnetic moment remains unaltered when the number of electrons in the inner d-level of the central atom also remains unaltered after complex formation.

This theory presents a quite simple picture of the coordination complexes and has been widely applied by many authors. But it suffers somewhat from a lack of precision in quantitative interpretations and has for that reason been criticized by many workers.

The electrostatic theory of Kossel (loc. cit.) was later elaborated by Cartledge with the use of a single arbitrary parameter called the 'ionic potential'. Fajans showed how the electronic shell of the anion was deformed under
the influence of cationic force. This was a phenomenon akin to polarization. Development of the theory continued through the work of Magnus, Van Arkel and de Boer, Garrick, resulting in the establishment of the Crystal Field Theory, which was set forth in detail by Schlapp and Penny, and Van Vleck. Orgel has made an extensive application of this theory to account for the magnetic behaviour, colour, structure and stability of coordination compounds of the transition elements.

According to this theory, splitting up of the five equivalent d-orbitals of the metal ion occurs under the influence of the electrostatic (crystalline) field due to the ligands, when the field becomes sufficiently strong, as in the case of spectroscopic Stark effect. In the presence of a strong field, the five degenerate d-orbitals may split into two or more sub-levels. The electrons avoid regions of strongest fields due to the attracted ligands, which are either anions or dipoles with their negative ends directed to the positive metal ions. The d-orbitals are split with the result that the orbitals laying in the direction of the ligands are raised in energy, while those lying away from them are characterised by low energy. The nature and number of the levels, as well as their energy difference that results from splitting, depend upon the strength and symmetry of the field, which in its turn
is determined by the geometry or structure of the complex.

As a result of the splitting of the five d-orbitals, the low lying levels are first preferentially filled up with electrons. The absorption bands in the visible spectrum of the complex furnish an estimate of the energy separation between the levels. The magnetic moment of the complex also follows readily from the distribution of electrons in the different levels, some of which consist of doublets or triplets.

The only shortcoming of this theory is that it does not take into consideration directed covalent or electron pair bonds between the ligands and the central atom. As a result of this, the theory fails to explain the formation of complexes with \( \pi \)-bonding and also the resolution of asymmetric complexes into their optically active modifications. Fajans' explanation, based on the concept of polarization and the interpretation of the electronic orbits of the ions, is often utilized to remove this shortcoming. But the main advantage and applicability of this theory over the other two lie in its ability to offer better quantitative interpretation of many properties of the complex, particularly their absorption in the visible region as shown by Orgel (loc. cit.) and others.\(^{28-30}\) The crystal field theory has also been found useful in accounting for the detailed magnetic properties of complexes, as determined by the powerful method of paramagnetic resonance absorption.
Because of the fact that the splitting of the d-orbitals may take place by the formation of covalent bond, some investigators combine the crystal field theory with the molecular orbital theory under the name of ligand field theory. This step facilitates the interpretation of facts. This name is sometimes given to the crystal field theory itself when the latter is applied to single molecules or ions.

The **Molecular Orbital Theory** has been developed by Hund, Mulliken, Herzberg, Lennard-Jones and others. In this theory consideration is made of the electronic orbits in the field produced by several centres of force. Each orbital or wave function in this complex field of force will be characterized by a definite quantum number, with its corresponding energy value, both of which will depend upon the relative positions of these centres of force.

The stability of a molecule depends upon the energy of its electrons. The molecular vibrations and rotations tend to loosen the binding between the nuclei forming the molecule. The strength of the valency bond in a molecule is, therefore, closely associated with the electronic energy or the electronic configuration of the molecule. At the equilibrium position of the two nuclei in a stable molecular state, this electronic energy is minimum. A molecule, like an atom may have a large number of electronic energy levels or terms, which will differ
from the corresponding levels in the atom. The orbital angular momentum of the electron in an atom can not remain constant in a molecule under the influence of the electric field of the neighbouring atom. Hence, there occurs a splitting of the electronic energy level similar to that in an atom under an external electric or magnetic field.

Mulliken (loc. cit.) sums up the fundamental ideas of this theory as follows:

(1) Every nucleus in a molecule tends to be surrounded, by means of sharing or transfer of electrons, by an electron distribution corresponding to some stable configuration having a total charge approximately equal to, or somewhat exceeding, the charge of the nucleus.

(2) Chemical combinations of the homopolar type is a result of the shrinkage and consequent energy decrease of atomic orbitals in the fields of neighbouring nuclei, when such orbitals are shared with little or no premonition.

Van Vleck (loc. cit.) was responsible for the application of the Molecular Orbital Theory to the formation of coordination compounds. The ligand electrons, during complex formation, supply the bonding electrons and the d-electrons originally present in the metal ion are accommodated in the non-bonding d-orbitals and the anti-bonding molecular orbitals.
The energy separation of the non-bonding d-orbitals and the anti-bonding molecular orbitals, as well as the energy required for the pairing of the originally un-paired electrons, determine the formation of electron pairs in the complex. This theory satisfactorily explain all the properties of complex molecules like chemical, stereochemical, magnetic and optical, including those of the unusual coordination compounds such as the metal carbonyls and metal olefines.

Chelates:

Morgan and Drew\textsuperscript{35} have introduced a new class of coordination compounds because of their tendency to form cyclic structures. Since the metal ion is entrapped within these ring structures, these compounds have derived their name from the Greek word 'Chela' meaning the claws of lobster or crab. Only those ligands which have more than one point of attachment with the metal ion are capable of forming chelates. The structures of chelates are known as bidentate, tridentate, tetradeutate, and so on, depending on the number of rings involved in their formation, i.e., two, three and four respectively. An unidentate molecule like ammonia can not form chelates.

Contributions to the study of chelates have been made in recent times by Diehl\textsuperscript{36} and Martell and Calvin\textsuperscript{37}.

Chelate formation has found wide application in the field of analytical chemistry\textsuperscript{38}. 


One of the characteristic properties of chelate compounds is their unusual stability. Among the ligands responsible for chelation, there exists a common characteristic. For example, only the salt-forming functional groups have been found useful. These groups have a tendency to replace their acid proton with the metal atom. Those neutral groups containing an atom with a free electron pair suitable for bond formation also form chelates. Considerations based on the Baeyer's Strain Theory attribute the most stable structure to the 5- or 6-membered rings. Existence of chelates having 3-membered rings has not been established, although, chelates having 4, 7, 8 and more rings are known.

Study of coordination compounds in solution:

Various physico-chemical methods for the investigation of complex-formation in solution have been developed during the last couple of decades. There have been two main aspects of this study, namely, the thermodynamic and kinetic. The former evaluates the composition and stability of the complexes, while the latter deals with the rates of reaction of complexes. The various physico-chemical methods available include pH and potentiometric measurements, spectrophotometry, ion-exchange, solvent extraction, and polarography. Application of thermometric, and solubility studies has also proved valuable.
Spectroscopic study involving nuclear magnetic resonance\textsuperscript{46} and study of Raman Spectra\textsuperscript{47} has also been found widely applicable. Optical methods like polarimetry\textsuperscript{48} and refractometry\textsuperscript{49} have been found useful including X-ray and electron diffraction methods\textsuperscript{50} and radioactive tracer techniques.

Job\textsuperscript{52} studied a number of coordination compounds by the method he called 'continuous variations method'. He gave a mathematical treatment to the problem with the derivation of an expression suitable for the use in finding the stoichiometry of the coordination compounds, and in calculating their stability constants.

Vosburgh and Cooper\textsuperscript{53} made an extensive use of this method with modifications of their own. Bjerrum\textsuperscript{54} suggested a method for the determination of stability constants based on pH-titration data.

A number of papers have been published over the years on the physico-chemical study of coordination compounds using a number of their index properties and taking recourse to any of the methods referred to above.

With this background of knowledge at his disposal, the author has made an attempt to study some coordination compounds of Molybdenum and Tungsten with organic acids, with regard to their stoichiometry, stability and structure.
The next three chapters deal with the survey of available literature on the compounds of molybdenum and tungsten, experimental procedures adopted and a critical discussion on the data collected.
REFERENCES


Nyholm, Orgel & Sutton,
20 Cartledge, J. Amer. Chem. Soc., 50, 2855, 2863 (1928); 52, 3076 (1930).
24 Garrick, Phil. Mag., 2, 131 (1930); 10, 171, 76 (1930); 11, 741 (1931); 14, 914 (1932).
29 Jørgensen, ibid., 8, 1502 (1954); 9, 116, 1362 (1955).
31 Hund, Z. Elektrochem., 34, 437 (1928); Z. Physik, 51, 759 (1928); 62, 719 (1930).
32 Mulliken, Rev. Mod. Phys., 2, 60, (1930); 3, 89 (1931); 4, 1 (1932); Chem. Rev., 9, 347 (1931); Phys. Rev., 40, 55 (1932); 41, 49 (1932); 43, 279 (1933).
33 Herzberg, Z. Physik, 57, 601 (1929).

39 Bjerrum, "Metal ammine Formation in Aqueous Solution", P. Hasse and Son, Copenhagen, 1941.

40 Vosburgh et al., J. Amer. Chem. Soc., 62, 437 (1941); 64, 1630 (1942).


49 Spagu & Popper, Bull. Soc. Stiinte Cluj, 8, 5 (1934); 7, 400 (1934); Kolloid Z., 103, 19 (1943); Z. physik. Chem., 182, 154 (1937); 182, 389 (1938).


52 Job, Ann. chim., 9, 113 (1928).


54 Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Hasse and Son, Copenhagen, 1941.