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COORDINATION COMPOUNDS AND COMPLEX IONS

By

Carole Nelson, 1965

Honors Paper #6

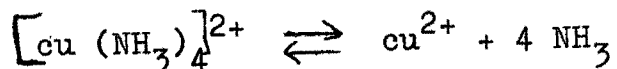
Coordination Compounds and Complex Ions

Thesis: Coordination compounds and complex ions are an important and practical part of fundamental chemistry. Their composition and formation should be understood by a chemistry student.

- I. Early development of coordination chemistry.
 - A. Early theories of the structure of amines.
 - B. Werner's coordination theory.
- II. Modern developments of coordination chemistry.
 - A. Electrostatic theory.
 - B. Electron Bond pairs.
 - C. Dig and Field theory.
- III. Types of coordination compounds and complex ions.
 - A. General types of complex ions.
 - B. Special types of coordination compounds.
 - C. Chelates
- IV. Isomerism
 - A. Stereoisomerism.
 - B. Other types.
- V. Factors affecting stability.
- VI. Nomenclature as set up by the I.U.C.
- VII. Importance of complexes.

A coordination compound is a substance in which atoms or groups of atoms have been added to a metal beyond the number predicted possible on the basis of electrovalent or covalent binding. Both electrons of the additional linkages are furnished by the linked atom of the coordinated groups called ligands. Ligands are negative ions or neutral polar molecules which have unshared electron pairs. The resulting ions are called complex ion is usually limited to those ions which are capable of some dissociation of ions into their component part at ordinary temperature.

An example:



square brackets are used to indicate a complex ion.

The history of chemistry in the 19th century is largely an account of the growth of knowledge of molecular structure. The study of inorganic "complex compounds" antedated the rise of organic chemistry by over fifty years.

The early history of the theory of complex compounds is mainly a study of amines (before Werner called ammonates) because they lent themselves to study by classical methods and attracted the most attention. The discovery of these substances is usually attributed to Tassaert, who observed in 1798 that cobalt salts combine with ammonia.¹

The first logical attempt to explain metal ammonia compounds was made by Berzelius. He observed that metal ammonia compounds did not lose their capacity for combination with other substances.

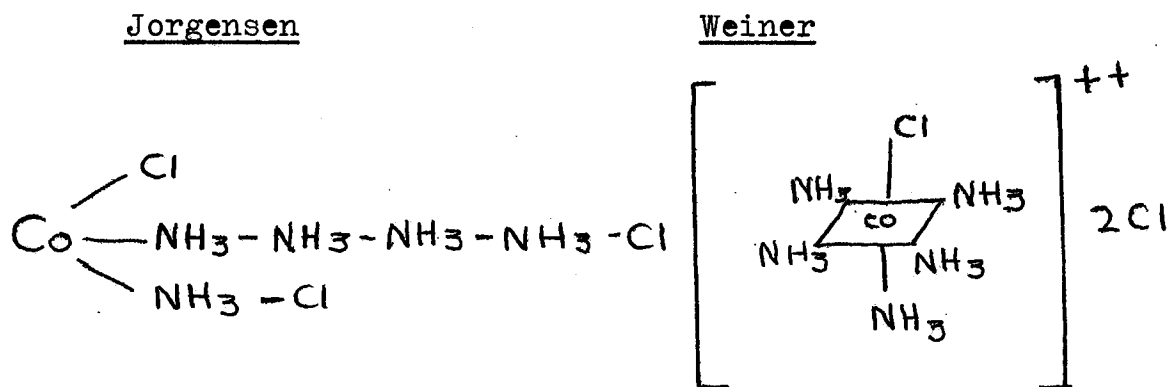
According to Graham's "ammonia" theory, metal ammonals are considered to be substituted ammonium compounds. This view was generally accepted until the time of Weiner. Jorgensen was the one who showed this theory and its modifications were fallacious.¹

The theory of Claus met with vigorous opposition, but ironically, the parts of it most vigorously attacked appeared in only slightly modified form in Weiner's theory. Claus believed that when combined with metallic oxides NH_3 not only does not affect the Saturation capacity (number of ligands a metal can take up) of the metal, but becomes "passive" as regards its own basicity.

Odling suggested that metallic atoms can substitute for the hydrogen atoms just as organic radicals can do. Blomstrand made this the basis of his famous chain theory. According to Blomstrand, the stability of the ammonia chain is not dependent on its strength. Blomstrand's formulas for cobalt ammonia compounds became a center of a long controversy between Jorgensen and Weiner.

Jorgensen extended the chain theory of Blomstrand. Weiner and Jorgensen differed in the way they wrote the

formulas.



Weiner's views seemed a little too radical for Jorgensen, because Weiner's ideas marked a sharp break in the classical theory of valency and structure.

The most important work in this field was done by Alfred Weiner.

The fundamental postulate of his theory can be outlined as the following:⁶

1. Metals possess two types of valency, so-called principal, or ionizable valency and auxiliary or nonionizable valency. Even when the principal valency is satisfied the auxiliary valency can be used to form complex species.

2. Every metal has a fixed number of auxiliary valencies referred to as the coordination number of that metal. Coordination numbers of 4 and 6 are the most common.

3. Principal valencies are satisfied by negative groups (ions) whereas auxiliary valencies may be satisfied by either negative or neutral molecules.

4. The auxiliary valencies are directed in space about the central metal ion.

Weiner won the Nobel prize in Chemistry in 1913 for his work with coordination compounds.

There are several modern developments which add to the ideas brought forth by Weiner. One of these is the electrostatic theory of coordination compounds. This theory was developed to give a self-consistent explanation of the types of valency - to explain Weiner's postulate concerning principal and auxiliary valencies. Some of the men doing research in this field were G. N. Lewis, Kossel, Langmuir, Sidgwick, Fajans, and Pauling.

This theory says that ions in a complex are held together by an attraction of the opposite charges. This theory accounts for the fact in cases of nontransitional elements, but not in transitional elements. It doesn't explain the relative acidity of the hydrated ferric ion and the hydrated aluminum ion.

Weiner's view's were incorporated into the electronic concept of valency in 1923 by N. V. Sidgwick and T. M. Lowry. This introduced the idea of coordinate bond or a special form of covalent bond in which the paired electrons of the bond are furnished by one and only one of the atoms concerned. This is not entirely satisfactory because the donation of electron pairs to a central cation

would produce an improbable accumulation of negative charge on this ion.

Geometry and electron interaction hold the key to the behavior of coordination compounds. Understanding starts with knowledge of the orbitals of the central atom. The Ligand Field theory - also called Crystal Field theory is applicable to any orderly arrangement of interacting particles such as a complex or polyatomic molecule even though it originally applied to crystals. The theory can be defined as the theory of the origins and the consequences of the splitting of electronic energy levels due to the surroundings of the atoms.²

Among physicists this theory is quite old, having been developed by Bethe, Van Vleck, and others in the 1930's. Chemists are just beginning to use it.

This theory is an extension of the electrostatic theory and considers only electrical forces, ignoring covalent bonding.⁸

This theory says that the 5 d orbitals which are equal in energy in the gaseous metal ion, acquire different energies in the presence of the electrostatic field due to ligands. If a negative or a neutral polar molecule approaches with an electron pair pointing toward a corner of the octahedral structure of the central metal ion, the 3 d electrons of the metal will be repelled by the electron pair and will tend to seek nonbonding orbitals with

pointing in between the corners of the octahedral. This causes the nonbonding orbitals to become somewhat lower in energy than the antibonding orbitals.

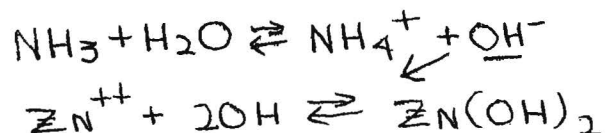
Those orbitals pointing toward ligands are raised in energy with respect to those pointing away from it.

If a complex has more of the electrons in the lower energy levels it is more stable than other complexes in which all the d orbitals are equally filled.

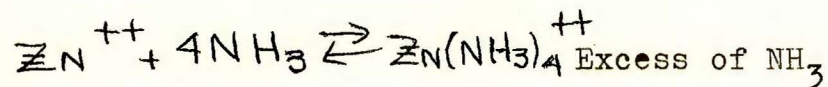
This theory estimates the energies of electrons in the various atomic orbitals of the metal atom that has these features: 1) allows quantitative calculations of energy, 2) predicts stability of complexes of different metals with different ligands, 3) explains visible absorption spectra, 4) explains magnetic properties in detail, 5) predicts structure of complexes, 6) predicts rate of mechanism of reaction, 7) correlates redox potentials, and revitalizes the old electrostatic theory of chemical bonding.⁸

There are three general types of complex ions.³

1. Complex ions formed by the union of cations with inorganic molecules. The majority of ions are hydrated to some extent in aqueous solution. Examples include hydronium ion H_3O^+ and hydrated aluminum ion $Al(H_2O)_6^{3+}$. Also, many of the cations form coordination compounds with ammonia—the compound depending upon the amount of NH_3 .

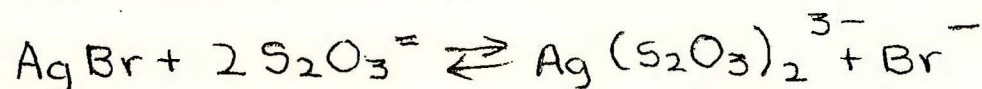


Low concentrations
of NH_3



2. Complexes formed by the union of cations with inorganic anions in which anions are usually in excess of the number to satisfy the electrovalence of the cations. Among the many anions which, in excess, may produce such complex ions are the cyanide, hydroxide, thiocyanate, sulfide, thiosulfite and halide ions.

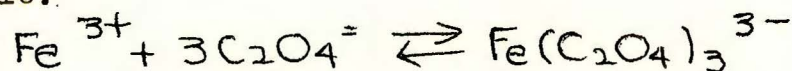
An example of this is:



(This reaction is important in photography.)

3. Complexes resulting from the union of inorganic cations with organic anions or molecules.

Example.

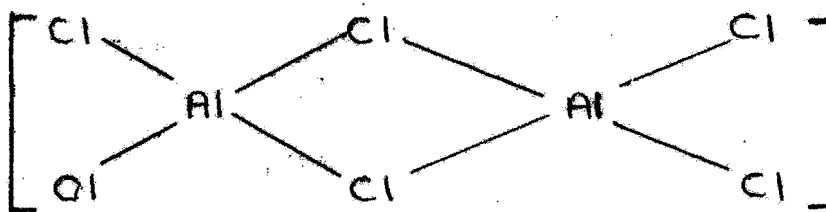


Two specific types of complexes are also worth mentioning. Inner complexes are formed when the organic group of an appropriate types can satisfy both the oxidation number and coordination number of a given cation. They are non-ionic in character and are useful in effecting separations among the metal ions.

In a few instances the cation and anion of a particular compound may associate with each other to give a complex species. They are called auto complexes.

An example of this is mercury chloride. Even though it is apparently salt-like in composition, its aqueous solutions are poor conductors of electricity. It is logical to think of the compound as forming a complex which explains why there is a limited no. of ions in solution. Some special types of coordination compounds include Polynuclear complexes and polyacids and their salts.

Polynuclear complexes contain more than a single center of coordination. Anhydrous aluminum chloride is dimeric in the vapor state and can be diagrammed as



Polyacids are oxygen containing acids (also their derived salts) in which apparent condensation of numbers of simple acid molecules has given materials containing more than a single mole of acid anhydride. If a single type of anhydride is involved, the acid is an isopoly acid, whereas if more than a single type of anhydride is present, the acid is a heteropoly acid.

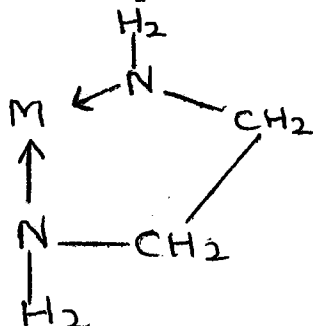
Examples

<u>Isepoly acid</u>	<u>Heteropoly acid</u>
polychromic acid	polymolybdophosphoric acids
$H_2O \cdot y CrO_3$ $y > 1$	$m H_2O \cdot P_2O_5 \cdot y MoO_3$ y is 12 or 24 most commonly

An important division of the coordination compounds are the chelates. The first chelate was recognized and described by Weiner, but development of chelate chemistry has taken place in recent years.

A chelate is a complex containing a ring structure with a single group or molecule occupying two or more coordinate positions in the same atom. Chelate is from a Greek word - Chele - meaning claw

An example of one chelate ring is the bidentate ligand-

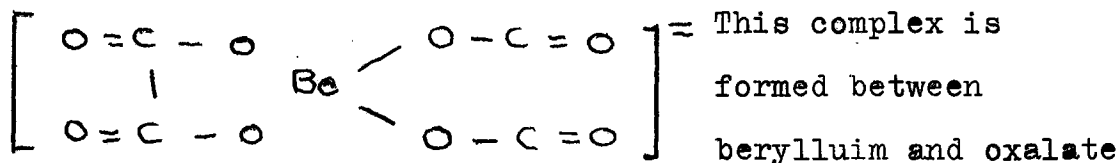


There can be more than one point of attachment

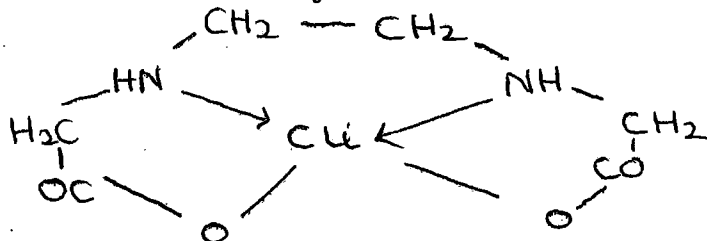
The ring usually with five or six members is closed by the formation of covalent linkages, coordinate bonds, or a combination of the two. This formation with a particular bond is one of the ways of classifying chelates.

Example:

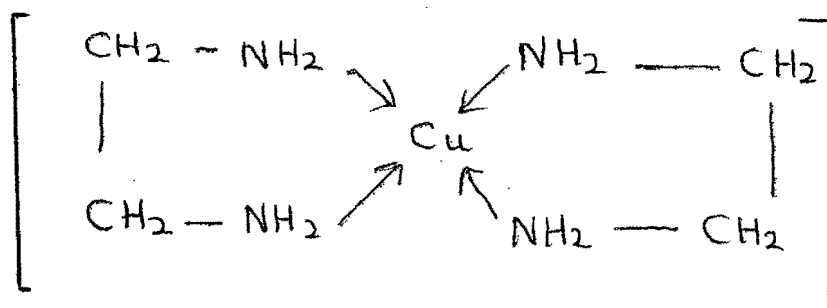
Combined by covalent bonds only-



Combined by both covalent and coordinate bonds - these



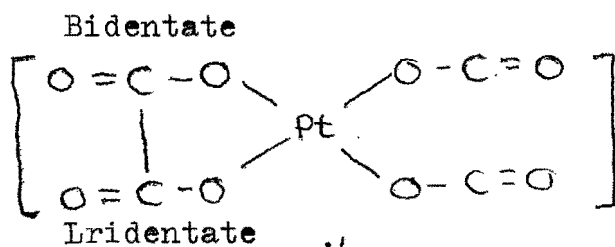
are non-electrolytes and insoluble in H_2O



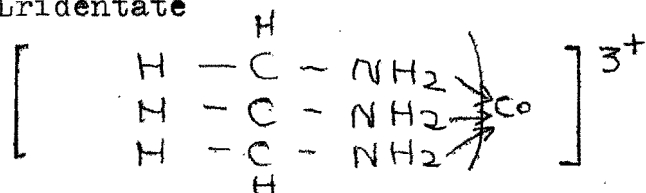
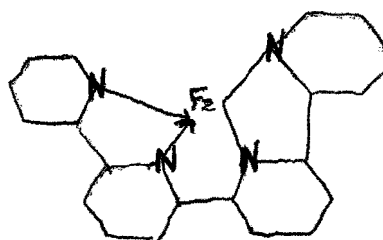
Combined by coordinate bonds only

Another system of classification was devised when it was discovered that ligands of some compounds can combine with metal in three or more coordinate positions.

The names of these classes are Bidentate, Tridentate, Quadridentate, etc. The names show the number of points of attachment. The names Tridentate and Quadridentate literally mean three-tooth and four-tooths respectively.



Quadridentate



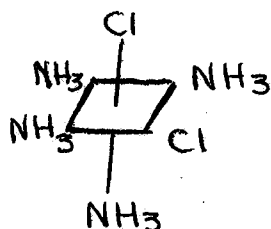
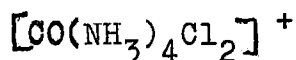
Isomerism was commonly considered to be characteristic only of organic compounds, but it is a phenomenon of position and cannot be limited to the compounds of one

element or to any one class of compounds.

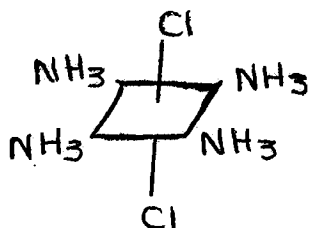
Stereoisomerism by far the most interesting and important of the types of isomerism noted among coordination compounds. Its existence was one of the fundamental postulates of Weiner's theory.

Stereoisomerism is the form of isomerism in which two substances of the same composition and constitution differ only in the relative positions in space assumed by certain of their constituent atoms or groups. It is also called geometrical isomerism.

An example to illustrate this is the isomeric configuration of ions produced by two ions with formula



This is a cis isomer because the one of the substituents (Cl) occurs in the edgewise position.

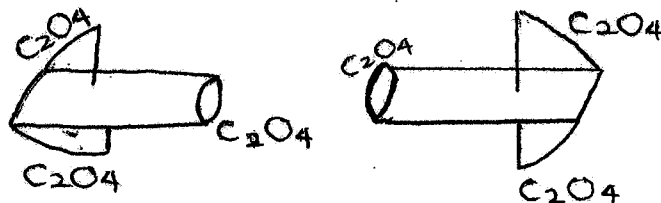


This is a trans isomer because the two differing components occur in the axis position.

Also included in stereoisomerism is optical isomerism or enantiomorphism. This arises when two compounds exist which have configurations of atoms or groups in space around the central atom such that one structure is the mirror image of the other. Mirror-image isomerism is possible only when 2 nonchelated coordinating groups occur in a Cis configura-

tion

An example of this is $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$



There are several types of isomerism other than stereoisomerism.

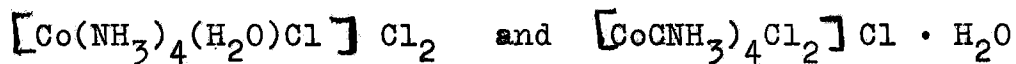
One of these is ionization isomerism. This occurs when two compounds have the same empirical formula, but different ionic groupings.

$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ are ionization isomers—these compounds are different and give different reactions with chemicals.

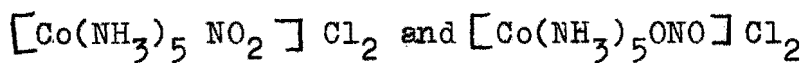
Coordination isomerism results in compounds containing both coordinated cations and anions when differences in the distribution of the groups occurs.

ex. $[\text{Co}(\text{NH}_3)_6]^{2+} [\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{NH}_3)_6]^{3+} [\text{Co}(\text{CN})_6]^{4-}$

Axonate isomers are produced when combined H_2O may coordinate to metal ions in much the same fashion as NH_3 —or lattice position without close association. There is a difference in the number of water molecules in the coordination sphere.



Structural or salt isomerism occurs when more than a single atom in a coordinating group functions as a donor. Examples of isomeric forms resulting from two modes of linkage are



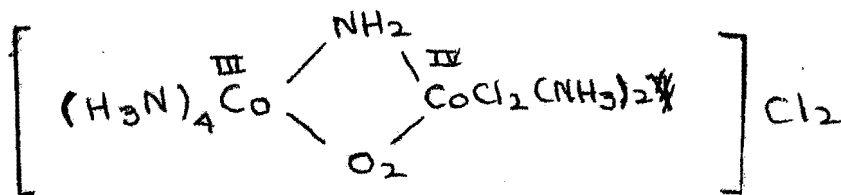
Nitropentammine

nitropentammine

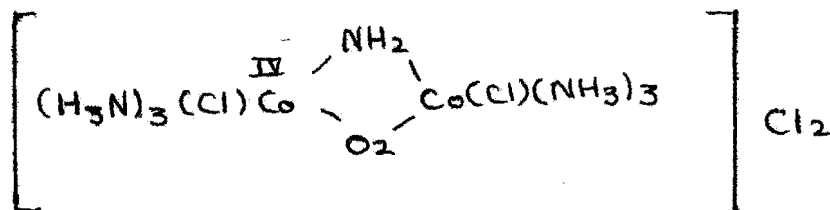
(yellow-brown)

(red)

In polynuclear complexes, coordinate groups maybe present in the same numbers but may arrange themselves differently with respect to the different metal nuclei present. This is called coordinate position isomerism.



Unsymmetrical



Symmetrical

Valence isomerism refers to materials in which the same grouping maybe held by different types of valence bonds-sometimes principal, sometimes auxiliary.

There are several important factors influencing the formation of complex ions and coordination compounds. The stability of the compounds varies widely depending on the stability constant also called dissociation constant.

Environmental factors must be considered such as the temperature and pressure of the solution containing the compound. Concentration is also important. While some complexes occur only in the solid state, others exist in water solutions. Some exist in solution only in the presence of high concentration of coordinating groups.

The nature of the metal ion is of primary concern. Transition elements form more stable complexes than do those ions which are isoelectric with the inert gases.

In complexes containing ion-dipole linkages the size of the central ion is well as the magntude of the charge determines stability.

The nature of the coordining group is also a stability factor. Some complexes are largely ionic in nature rather than covalent. This depends on the donor groups. The nature of the ion outside the coordining sphere must also be considered. Flouride complexes are largely covalent.

The greatest of the facts as influencing this complex formation is ring formation or cyclization. When a

complex is chelated it is generally more stable than a similar compound not chelated.

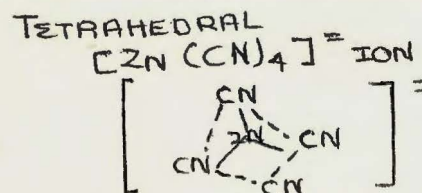
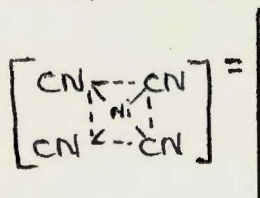
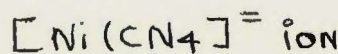
The formation of complex ions by coordinate bonds follow 2 general rules.³

1. The central ion tends to accept electrons to fill incomplete stable orbitals, and each completed orbital contains a pair of electrons of opposite spins.

2. The central ion tends to accept sufficient coordinated molecules or ions to produce a symmetrical structure of molecules packed around the central ion. This structure may be planar, tetrahedral, octahedral, or cubic.

Example:

Planar



A comprehensive system of nomenclature was devised by Weiner. Although some modifications of the general system have been found necessary and other modifications have been proposed, all modern systems still contain many points of Weiner's system. The modified Weiner system made by the Nomenclature Committee of the International Union of Chemistry (I.U.C.) overcame some of the cumbersome and non-specific parts of the original postulates. These recommendations differ basically from those of Weiner only in the mode of designating the oxidation state of the central element.

The fundamental postulates offered by the I.U.C.

may be summarized as follows:⁵

1. The cation is named first, followed by the anion.

2. The names of all negative groups end in -o (such as chloro, hydroxo, cyano), whereas those of neutral groups have no characteristic ending (except H₂O - aquo).

3. Coordinated groups are listed in order: negative groups, neutral groups. Then positive groups,

$K[P^+(NH_3)_5Cl_5]$ - Potassium pentachloroammineplatinate (IV).

4. The oxidation state of the central metallic element is designated by a Roman Numeral placed in parenthesis. Ex.

$[Co(NH_3)_6]Cl_3$ - Hexamine cobalt (III) chloride. With complex cations or neutral molecules, this numeral is placed immediately after the name of the element to which it relates, not alteration in the name of the metal being made. With complex ions, the Roman numeral is placed immediately after the name of the complex, with invariably ends in -ate.

$Na[Al(OH)_4]$ Sodium Tetrahydroxodluminate (III)

5. The names of coordinated groups are not ordinarily separated by hyphens or parenthesis.

Later other extensions were adopted to further clarify the naming of coordination compounds. Too often these extensions which are used fairly often are that
1) groups of the same nature (ie. all negative groups)

are listed in alphabetical order without regard to any prefixed designating the number and such groups present and prefixes such as bis-, tris- and tetrakis-, followed by the name of the coordinated groups set off the parenthesis is preferred to that of the old designations di-, tri, and tetra- to indicate number of coordinated groups if the names of those groups are complex.

ex. $[\text{Cu}(\text{en})_2]^{++}$ Bisethylenediamine copper (II) ion
 en - ethylene diamine

The importance of coordination compounds and concepts regarding their formation and constitution cannot be over emphasized. There are a number of general fields in which knowledge and application of coordination compounds have proved of value. Many significant advances have been made during the last several years, and a rapidly expanding number of useful applications have been made and continue to be developed.

Complexes provide an important aid to the farmer in effective soil treatment. Some complexing groups when coordinated to certain metals, made the metals more easily assimilated by the plants, or make it impossible for plant use. The chlorophyll in the plants is a magnesium complex.

Many minerals are coordination compounds. The coloring materials in the blood (such as hemin and hemocyanin) are complexes. Hemoglobin present in the red blood corpuscles of mammals is an iron complex

Complexes are used in industry in pigments (metal phthalocyanins), dyeing (metal lakes) and metallurgy and electrodeposition (cyano complexes). A number of commercial products are in the market which can prevent or control corrosion through coordination. If iron is complexed, it is not free to form iron rust.

Complex ions are used in medicines- Vitamin B₁₂ is a dark-red complex of cobalt. Complexes are also used in diets to make certain metals more or less readily assimilated by the body during metabolism.

Complexes are used extensively in qualitative and quantitative analysis. Many operations are based upon the formation or properties of coordinated derivatives of the metal ions.

These are just a few of the uses of complex ions and coordination compounds in the modern world. Many more new developments will be made in future years.

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