

### ❖ Formation of Complexes from Aquo Ions

The complex formation from the aquo ions yields the assembly containing metal ions with only water as ligands. These complexes are the major components in aqueous solutions of many metal salts, like metal sulphates, perchlorates and nitrates. The formula for metal-aquo complexes  $[M(H_2O)_n]^{z+}$  where the value of  $z$  generally varies from +2 to +4. The metal-aquo complexes play some very important roles in biological, industrial and environmental aspects of chemistry. Now though the homoleptic aquo complexes (only with  $H_2O$  as the ligands attached) are very common, there are many other complexes that are known to have a mix of aquo and other ligand types.

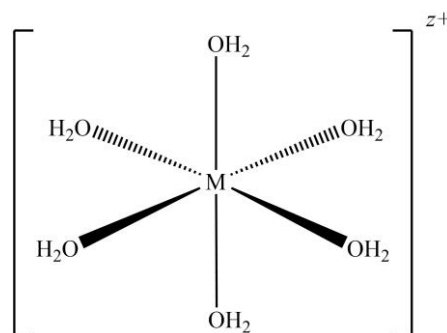


Figure 13. Structure of an octahedral metal aquo complex.

The most common stereochemistry for metal-aquo complexes is octahedral with the formula  $[M(H_2O)_6]^{2+}$  and  $[M(H_2O)_6]^{3+}$ ; nevertheless, some square-planar and tetrahedral complexes with the formula  $[M(H_2O)_4]^{2+}$  are also known. A general discussion on the different types and other properties is given below.

#### ➤ *Six-Coordinated Metal-Aquo Complexes*

Most of the transition metal elements from the first transition series and some alkaline earth metals form hexa-coordinated complexes when their corresponding salts are dissolved in water. Some of the most studied hexa-coordinated complexes are given below.

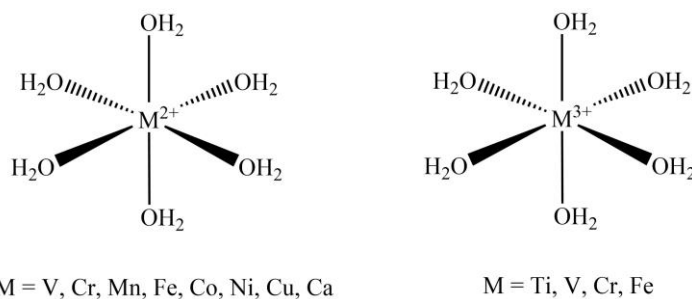


Figure 14. Structure of six-coordinated metal-aquo complexes.

➤ **Four-Coordinated Metal-Aquo Complexes**

The metal-aquo complexes that exist with coordination numbers lower than six are very uncommon but not absent from the domain. For instance,  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  form  $[\text{M}(\text{H}_2\text{O})_4]^{2+}$  complexes with the square-planar stoichiometry; and a rare tetrahedral aquo complex  $[\text{Ag}(\text{H}_2\text{O})_4]^+$  is also known. Some of the most studied hexa-coordinated complexes are given below.

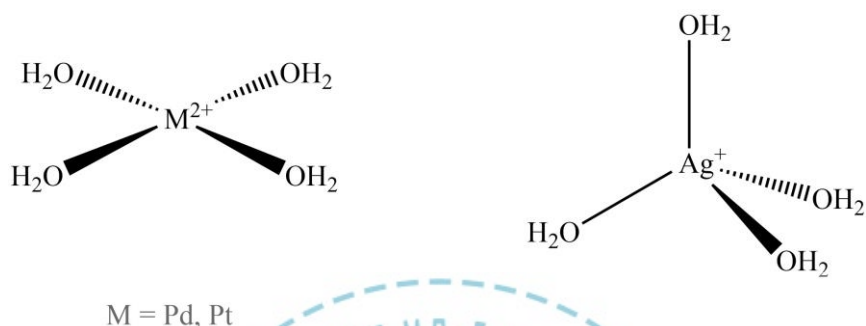


Figure 15. Structure of four-coordinated metal-aquo complexes.

➤ **Eight and Nine Coordinated Metal-Aquo Complexes**

The metal-aquo complexes of the trivalent lanthanides are eight- and nine-coordinated, which is obviously due to the large size of the metal ions. In past, the coordination number of  $\text{Ln}^{3+}$  ions in their aquo complexes was somewhat more or less controversial; however, nowadays, advanced characterization techniques like  $\text{O}^{17}$  NMR or density functional studies number of coordinated water molecules decreases from nine to eight with the decrease of the ionic radius i.e  $\text{La}^{3+}$  to  $\text{Lu}^{3+}$ . Some of the most studied eight and nine-coordinated complexes are given below.

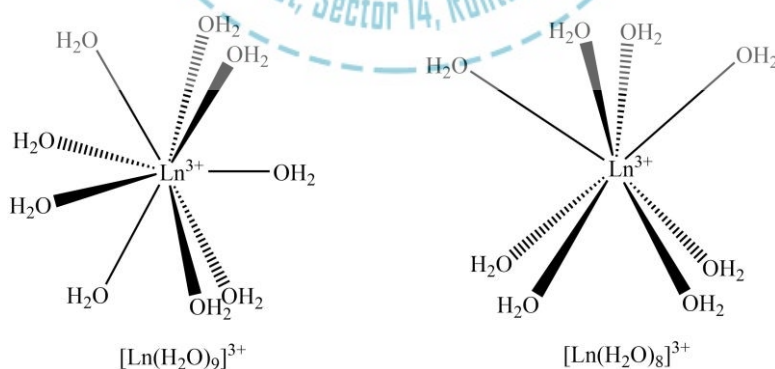


Figure 16. Structure of eight and nine-coordinated metal-aquo complexes.

The  $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$  ions have a trigonal triprismatic geometry with a slightly distorted  $D_3$  symmetry, while the  $[\text{Ln}(\text{H}_2\text{O})_8]^{3+}$  ions possess a square antiprismatic geometry with a slightly distorted  $S_8$  symmetry.

➤ **Metal-Aquo Complexes with Metal-Metal Bond**

There are some metal-aquo complexes which do possess metal-metal bonds. Two of the most studied examples are  $[\text{Mo}_2(\text{H}_2\text{O})_8]^{4+}$  and  $[\text{Rh}_2(\text{H}_2\text{O})_{10}]^{4+}$  which have eclipsed and staggered conformations, respectively. It should also be noted that metal-metal in  $[\text{Mo}_2(\text{H}_2\text{O})_8]^{4+}$  is of quadruple nature (four bond order).

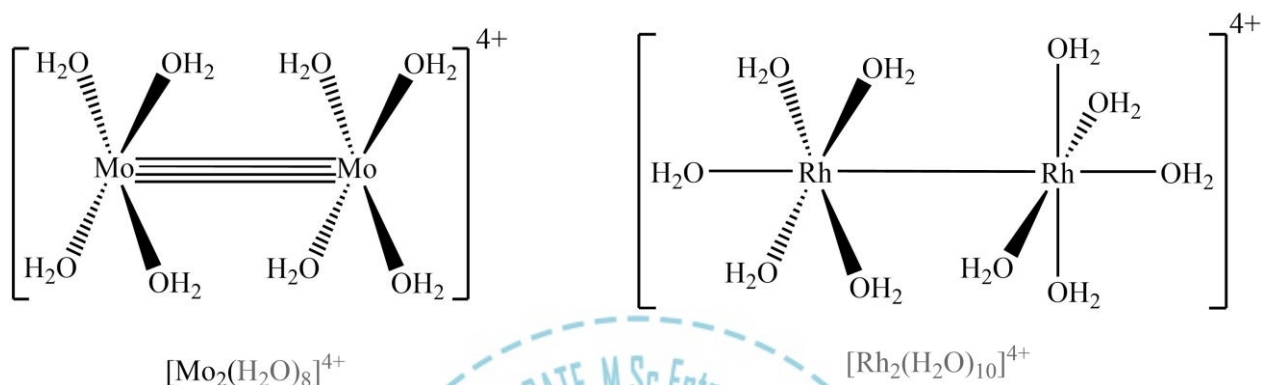
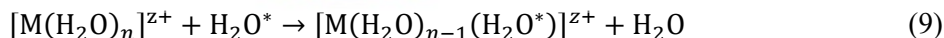


Figure 17. Structure of some representative metal aquo complex with metal-metal bond.

➤ **Important Reactions of Metal-Aquo Complexes**

The main reactions shown by metal-aquo complexes are the electron-transfer, ligand exchange, and acid-base reactions of the O-H bonds. A general discussion on all three is given below.

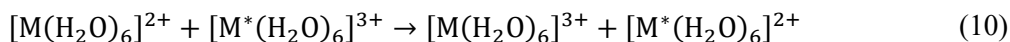
**1. Ligand exchange:** The process of ligand-exchange means the replacement of a previously coordinated  $\text{H}_2\text{O}$  molecule with one from the solution. However, the detection of such phenomena is possible only by labeling the normal  $\text{H}_2\text{O}$  with  $\text{H}_2\text{O}^*$ . The ligand-exchange generally occurs via a dissociative route, which infers that rate constants must be in accordance to the first-order kinetics. The general chemical equation for the ligand-exchange in metal-aquo complexes can be given as follows:



It is also worthy to mention that the above reaction would be of zero free energy change if isotopic labeling is avoided. The rate of ligand-exchange reactions is mainly affected by the charge of the species under consideration. Water-exchange rates are found to be lower for highly charged metal-aquo complexes, while the singly charged species show a much faster rate. For instance, the rates of water exchange in  $[\text{Na}(\text{H}_2\text{O})_6]^+$  is  $10^9$  to what is observed in case of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ . However, the rates of ligand-exchange in  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Ir}(\text{H}_2\text{O})_6]^{3+}$  also differs by a factor of  $10^9$  indicating that electronic configuration is also a major element in deciding the reaction kinetics.

**2. Electron exchange:** The second major types of reaction shown by the metal-aquo complexes are the electron-exchange case of electron transfer reactions. The common electron-exchange or self-exchange

involves the interconversion of trivalent and bivalent metal ions via the exchange of one electron only. To track the metal ions, isotopic labeling in the self-exchange process is used and can be written as:

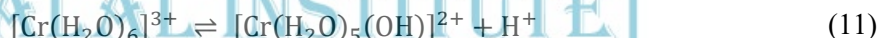


Moreover, the standard redox potentials for different  $M^{2+}/M^{3+}$  redox couples are:

Metal ion	V	Cr	Mn	Fe	Co
Standard redox potential (V)	-0.26	-0.41	+1.51	+0.77	+1.82

It can be clearly seen from the redox potential data that the stability of the lower oxidation state increases with the increase of the atomic number. The exceptionally large magnitude of standard reduction potential for  $Mn^{2+}/Mn^{3+}$  pair is because octahedral complexes of bivalent manganese have zero crystal field stabilization energy (CFSE) but manganese(III) has  $-6Dq$  CFSE. The electron exchange rates depend mainly upon the reorganization energies. In other words, the process of electron-exchange occurs via an outer sphere electron transfer and would be slow if there is a large structural difference between the bivalent and trivalent metal centers. A detailed discussion on this topic is given in the next chapter of this book.

**3. Acid-base reactions:** The ionizable nature of the protons of coordinated ligand makes these metal-aquo complexes as acidic. Consider the case of aquo-complex of trivalent chromium:



Therefore, in comparison to acetic acid (pKa of about 4.8) the Cr(III) aquo complex is a weaker acid (4.3). Moreover, The acidity of these aquo-complexes is also influenced by the electronic configuration; as  $[Ru(H_2O)_6]^{3+}$  (pKa = 2.7) is more acidic than  $[Rh(H_2O)_6]^{3+}$  (pKa = 4), regardless of the fact that trivalent rhodium is expected to be of higher electronegativity. This can be explained in terms of the stabilization of the  $\pi$ -donor hydroxide ligand by the  $Ru^{3+}(t_{2g})$ . It has also been observed that aquo-complex of bivalent metal ions are less acidic than those of trivalent cations. The metal-hydroxo complexes so formed usually undergo olation, a condensation phenomenon that results in formation of polymeric species concentrated solutions. The properties of hydrolyzed species (formed by metal-aquo complexes) are pretty much different from the starting hexa-aquo complexes.; for instance, The rate of ligand-exchange in  $[Al(H_2O)_6]^{3+}$  is twenty thousand times faster than  $[Al(H_2O)_5OH]^{2+}$ .

Finally, about one-third of all transition metals like Zr, Hf, Nb, Ta, W, Tc, Re, Os and Au; the metal-aquo complexes are either unknown or rarely explained in detail. Besides, the metal-aquo complexes of tetravalent metal ions ( $M^{4+}$ ) are expected to be extraordinarily acidic; which in turn, makes their existence highly unfavorable. For instance, the aquo complex  $[Ti(H_2O)_6]^{4+}$  is unknown, but  $[Ti(H_2O)_6]^{3+}$  is well reported in many papers. The stoichiometry of aquo-complexes  $Zr^{4+}$  also controls the acidification as in  $[Zr_4(OH)_{12}(H_2O)_{16}]^{8+}$ . Similarly,  $[VO(H_2O)_5]^{2+}$  is highly stable and well-characterized but  $[V(H_2O)_6]^{5+}$  is still unknown. Monovalent metal ions such as  $Rh^+$  or  $Cu^+$  rarely form isolable complexes with  $H_2O$  as the ligand.

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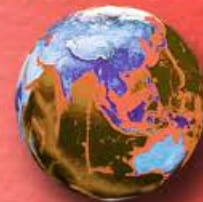
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**Volume I**

**MANDEEP DALAL**



*First Edition*

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