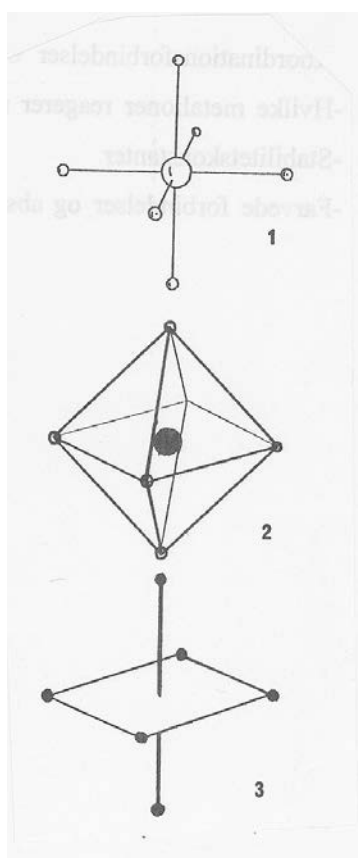


## Coordination compounds and coordination geometry.

Metal ions in aqueous solution are hydrated, which means that they are surrounded by water molecules in a regular way. Most metal ions have a fixed number of water molecules as nearest neighbours in a well defined geometric arrangement. In such cases one could think of a number of sites around the metal ion, where the water molecules “sit”. Such sites are called coordination sites. The hydrated metal ion with its well defined coordination sites is a coordination compound and may also be called a complex. In a coordination compound the metal ion is called the central atom (irrespective of its charge) and the coordination sites are occupied by ligands. Ligands may be molecules or simple or complex anions.

Most metal ions prefer a geometric arrangement with 6 ligands around it in the very regular structure where the 6 ligands are placed closest to the metal ion and with ligand to ligand distances as long as possible. This arrangement is called octahedral and may be represented in several ways.

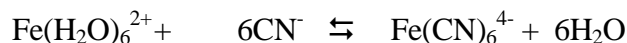


With the metal ion in (0,0,0) of a cartesian coordinate system and the oxygen atoms (of the water molecules) in (1,0,0), (-1,0,0), (0,1,0), (0,-1,0), (0,0,1) and (0,0,-1) at equal distances from the centre we get a picture as in figure 1. If the axes are removed and the four nearest neighbours of each oxygen atom are connected with straight lines we get figure 2 which is called an octahedron (coming from Greek for eight faces). Often the figure 3 is used instead: here each of the four oxygen atoms in the x-y plane are connected with straight lines to its nearest neighbours, while the z- axis is drawn as if the four oxygen atoms defined a solid square in the x-y plane without the metal ion visible.

Such a hydrated metal ion comes from dissolving a metal ion in water and the solution therefore also contains anions.

Thus a simple iron(II) salt as iron(II) sulphate in water will exist in solution as a hydrated iron(II) ion (a coordination compound) and sulphate independent of each other in the solution.

If potassium cyanide is added to this faintly green solution of iron(II) sulphate the solution turns yellow. By partial evaporation a yellow solid may be isolated. This is due to the replacement of each of the 6 water molecules in the hydrated iron(II) ion by a cyanide ions



Cyanide competes rather effectively with a water molecule - cyanide is far more tightly bonded to iron(II) than water in spite of the very high concentration of water molecules in water (>55M). With less than 6 cyanide ions to each iron(II) ion in the solution some of the iron(II) ions are surrounded with less than 6 cyanide ions and therefore with the rest of the 6 sites occupied by water molecules as ligands. The resulting coordination compounds may be described by the formula  $\text{Fe}(\text{H}_2\text{O})_n(\text{CN})_{6-n}^{(n-4)+}$

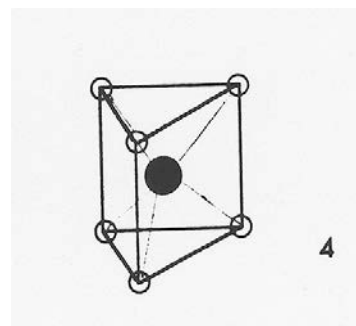
Here n may vary from 0 to 6. In general terms “mixed” complexes  $\text{MA}_n\text{B}_{6-n}^{x+}$  are found, where A and B are two different ligands taking up a site each. A ligand occupying one site is called a monodentate ligand (from Greek: one toothed)

Draw sketches like in figure 3 of all 10 different  $MA_nB_{6-n}^{x+}$  while charges are omitted and only A and B are placed on the coordination sites.

An octahedral complex with 6 monodentate ligands, 4 of which are different, may be found in several isomeric forms. Draw the geometrical isomers

If it was not known that the octahedral arrangement was prevailing one could imagine that the arrangement of ligand was prismatic (cf. fig.4) instead. The prism has two parallel regular triangles separated by a height with the same size as each of the sides of the triangle.

Draw sketches like in figure 4 of all different  $MA_nB_{6-n}^{x+}$  in a prismatic arrangement. (In this case there are more than 10 possible geometries - be systematic)

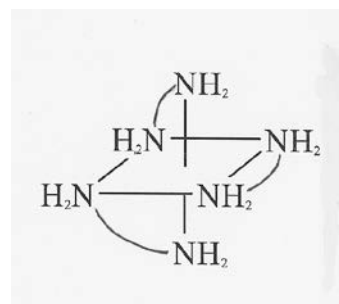


$H_2O$  and  $CN^-$  are examples of small and rather simple ligands each occupying one coordination site. Also  $NH_3$ ,  $F^-$ ,  $Cl^-$ ,  $OH^-$ ,  $SH^-$  and organic counterparts such as  $RNH_2$ ,  $RO^-$ , and  $RS^-$  form coordination compounds with metal ions as monodentate ligands; size and the chain length of R- e.g. in methyl, octyl or phenyl is as such no obstacle to coordination.

When the organic part R- contains other heteroatom, which might potentially coordinate to the metal ion we have a new situation. If the two ligating atoms in the same molecule are relatively close to each other there is a greater chance that they might bind to two neighbouring coordination sites. For example, 1,2-ethanediamine -  $NH_2-CH_2-CH_2-NH_2$  - coordinates better than two molecules of methylamine -  $CH_3-NH_2$ . Also 1,3-propanediamine coordinates better.

Facts demonstrate that the distance between the two N-atoms in 1,2-ethandiamine and in 1,3-propanediamine (which is somewhat flexible because of free rotation around C-C and C-N bonds) fit neighbouring coordination sites on most metal ions. The same N-N distance is, however, too small to reach from one coordination site to the opposite one. To simplify drawings such diamines may be symbolised by  $NH_2 \frown NH_2$  and with three of that kind an octahedral complex may be depicted as in the figure to the right.

Aminoacetic acid, glycine, in basic solution is found as the glycinate ion  $NH_2-CH_2-COO^-$ . The distance between the oxygen and the carboxylate group and the amine-nitrogen is about the same as in 1,2-ethanediamine. This is almost also true for the distance between the two oxygen atoms of the oxalate ion,  $^-OOC-COO^-$  while the malonate ion  $^-OOC-CH_2-COO^-$  corresponds to 1,3-propanediamine and to the anion of 3-aminopropionic acid. Short notations like  $^-O-NH_2$  og  $^-O-O^-$  will simplify drawings.



Draw the two different geometric arrangements of an octahedral  $M(A-B)_3$  complex.

Ligands with two ligating atoms in the molecule (or ion) are called bidentate, analogous to the monodentate ligands with only one coordinating atom. Complicated molecules may contain more than two potentially coordinating atoms and may act as tridentate, tetradentate (etc.) ligands to a metal ion.

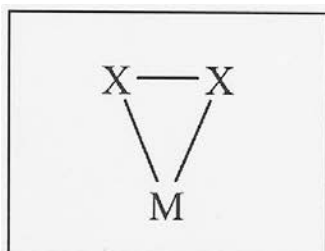
In any case, the mutual distance between ligating atoms and the  $90^\circ$  of an octahedron should be possible to leave a strong bonding with bidentate ligands. It is fairly easy to make some predictions from simple geometric considerations.

First consider the distances: The size of the metal ion is of course a determining factor and small and large metal ions exist. The effective radius of  $M^{2+}$ -ions of the 3d-period, (e.g.  $M = Mn, Fe, Co, Ni, Cu$

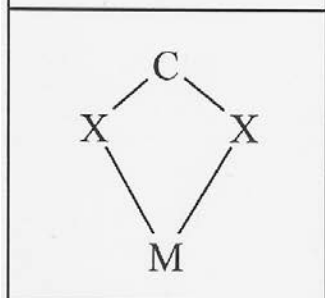
and Zn) is not far from 0.8 Å. In coordination compounds the distance between the centres of the metal ion and the ligating atom is typically around 2 Å (O and N ligands) and a little longer for those with S. Angles of the organic compounds are tetrahedral (around 109°, with single bonds only) or a little larger (120° for the plane groups with double bonds, e.g. C=O, C=N, or C=C). Distances in the ligands may be found from the following table of average distances found in many compounds

	C-C	C=C	C≡C	C-N	C-O	C≡N	C=O
<b>Distance/ Å</b>	<b>1.54</b>	<b>1.33</b>	<b>1.20</b>	<b>1.43</b>	<b>1.43</b>	<b>1.16</b>	<b>1.23</b>

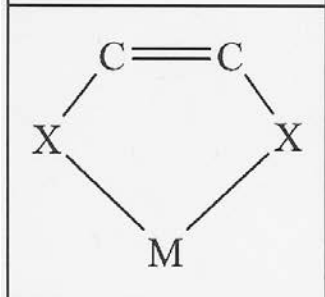
With this data in hand it is possible to make predictions about the suitability of ligands. In the following X is either O or N.



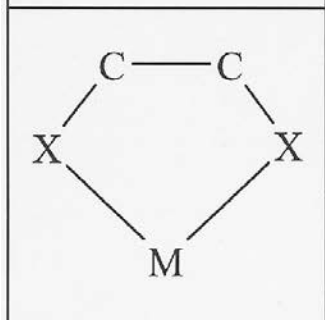
From  $X-X = 1.5$  and  $M-X = 2.0$  Å the angle  $MXM$  may be calculated to be  $44^\circ$ . Since the ideal angle of an octahedral is  $90^\circ$  X-X cannot act as a bidentate ligand.



Here  $X-X$  may be calculated to be  $2 \cdot 1.4 \cdot \sin(109/2)$  or 2.27 Å. The angle  $MXM$  is accordingly  $69^\circ$ . This is rather small compared to the ideal  $90^\circ$  and the strain in this arrangement seems too large. Correction due to a double bond doesn't change the result. Only with smaller metal ions this may be realised. In fact, carbonate may coordinate to cobalt(III) bidentate.

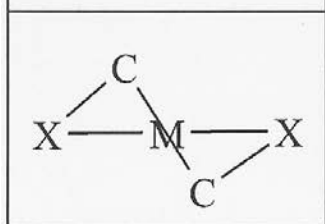


Here  $X-X$  may be calculated to  $1.33 + 2 \cdot 1.4 \cdot \sin 30$  or 2.73 Å and the angle  $MXM$  to be  $86^\circ$ . This is close to  $90^\circ$



Here it should be noticed, that the arrangement isn't planar. The distances will not be very different from the preceding example when considering the possible rotation around a single bond. Now it is even easier to get close to  $90^\circ$  for the angle  $MXM$

This is illustrated in the next drawing which comes from turning the X-C-C-X arrangement  $90^\circ$  around X-X. Additional carbons in the chain, e.g. 3 CH<sub>2</sub>-grupper as in 1,3-propanediamine (X-C-C-C-X) also allows the  $MXM$  to get  $90^\circ$ .



If the carbon chain gets longer the right angle may be achieved, but this may be counteracted to the tendency of two X's bind to two different metal ions.

The main conclusion is in line with experience, namely that ligands with two ligating atoms and a mutual distance as in X-C-C-X or X-C-C-C-X

most often bind in a bidentate mode to metal ions.