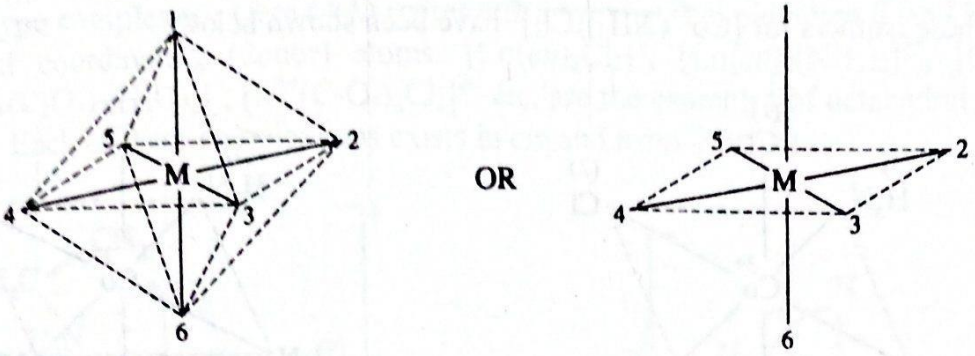
UG PART II
GROUP B, INORGANIC
UNIT – 5
ISOMERISM IN COMPLEXES

Geometrical Isomerism in 6-coordinated Complexes : Octahedral Complexes

A complex compound having central atom with coordination number equal to 6 is octahedral in shape. In an octahedral complex, if two similar ligands are placed on any of the twelve edges of the octahedron, they are said to be in *cis* position. On the other hand, if two similar ligands are lying on a straight line which passes through the centre (where the metal ion is placed), they are said to be in *trans* position.

Thus in an octahedral complex, the two ligands at positions 1-6, 2-4 and 3-5 are *trans* to each other and the two ligands occupying positions 1-2, 1-3, 2-3, 3-6, 6-4 etc. are *cis* to each other.

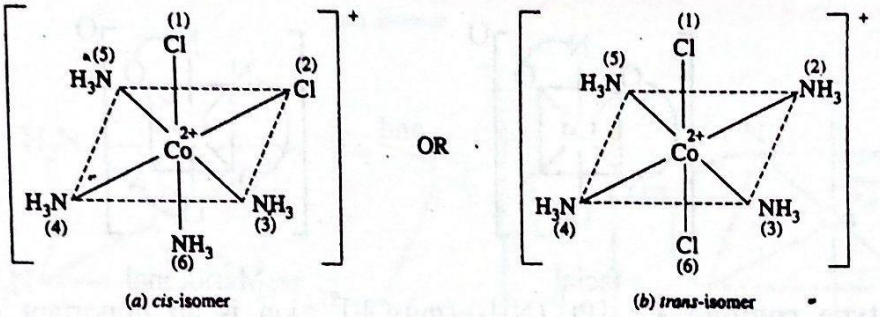


Numbering of six ligands in a regular octahedral complex round the central metal ion, M.

Here we shall discuss the geometrical isomerism in octahedral complexes of the following type:

(1) $[Ma_6]$, $[Ma_5b]$ and $[M(AA)_3]$ type complexes : Octahedral complexes of this type donot exhibit geometrical isomerism.

(2) $[Ma_4b_2]$ type complexes :

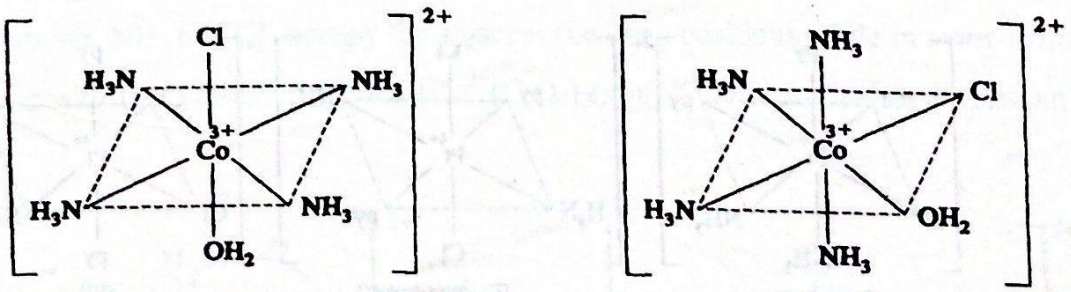


(*a*) *cis*-isomer (*b*) *trans*-isomer

(*a*) *cis*-isomer (1,2-dichlorotetrammine cobalt (III) ion). (yellow-brown)

(*b*) *trans*-isomer (1, 6-dichlorotetrammine cobalt (III) ion). (yellow)

(3) $[Ma_4bC]$ type Complexes : $[Co^{3+}(NH_3)_4(H_2O)Cl]^{2+}$ ion is an important example of octahedral complex of $[Ma_4bC]$ type. This ion has *cis*- and *trans*-isomers whose structures are given below. In *cis*-form two NH_3 molecules have *cis* positions to each other and in *trans*-form these ligands (i.e., two NH_3 molecules) have trans positions with each other.



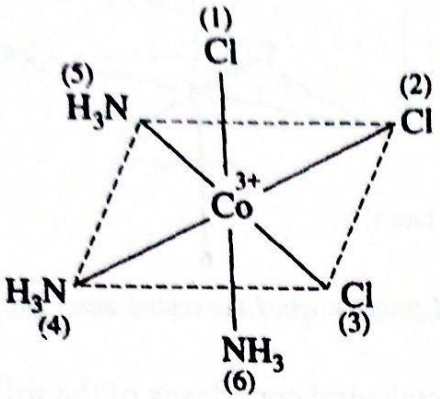
(*a*) *cis*-isomer (*b*) *trans*-isomer

(4) $[Ma_3b_3]$ type complexes : $[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_3(NO_2)_3]$, $[Cr(H_2O)_3F_3]$, $[Cr(NH_3)_3Cl_3]$, $[Rh(py)_3Cl_3]$, $[Ru(H_2O)_3Cl_3]$, $[Ir(H_2O)_3Cl_3]$, $[Pt(NH_3)_3Br_3]^+$, $[Pt(NH_3)_3I_3]^+$ etc. are important examples of octahedral complexes of $[Ma_3b_3]$ type. Two geometrical isomers are for complex Ma_3b_3.

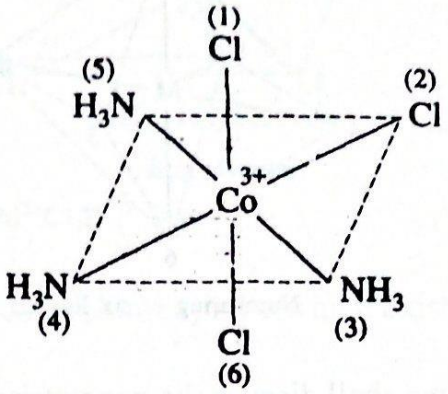
(i) The ligands of one type may form an equilateral triangle on one of the faces (called facial isomer).

(ii) In other isomer, the ligands of one type occupy the positions such that two are opposite (or trans) each other, called meridional isomer.

As an example these isomers for $[Co^{3+}(NH_3)_3Cl_3]^0$ have been shown below.

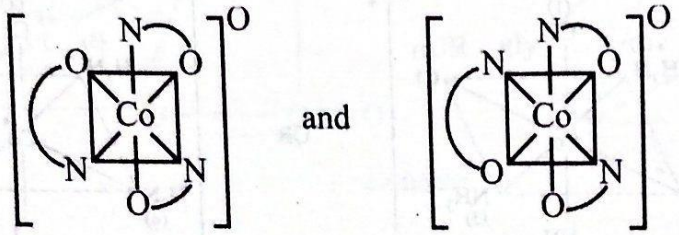


(*a*) *cis*-isomer [1, 2, 3-isomer or facial (*fac*) isomer]



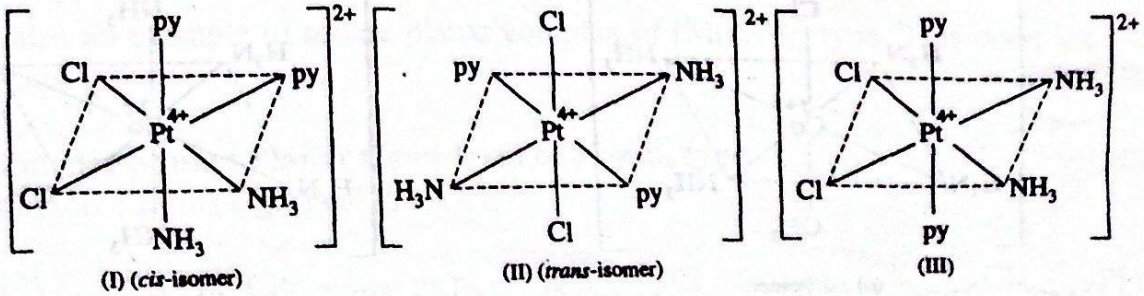
(*b*) *trans*-isomer [1, 2, 6-isomer or meridional (*mer*) isomer].

(5) $[M(AB)_3]^{n\pm}$ type complex e.g. $[Co(gly)_3]$ show fac–meridional isomers.



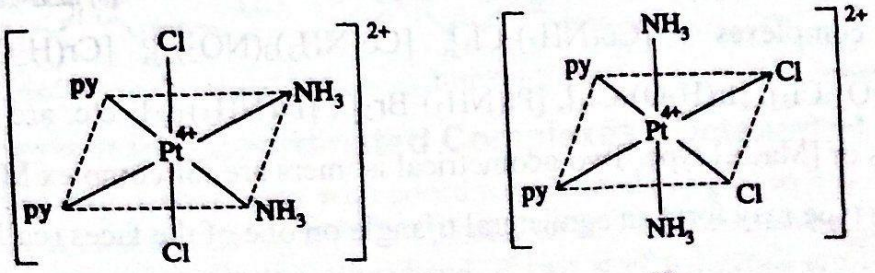
facial Meridional

(6) $[Ma_2b_2c_2]$ type complexes : $[Pt^{4+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion is an important example of octahe complex of $[Ma_2b_2c_2]$ type. This ion can exist theoretically in five geometrical isomers that have b shown below., but it is only three isomers that have been actually isolated. It may be noted from figure that (I) form is a *cis*-form since in this form two identical ligands are occupying adjacent positi Form (II) is a *trans*-form because in it the two identical ligands are placed at opposite positions.



(I) (*cis*-isomer)

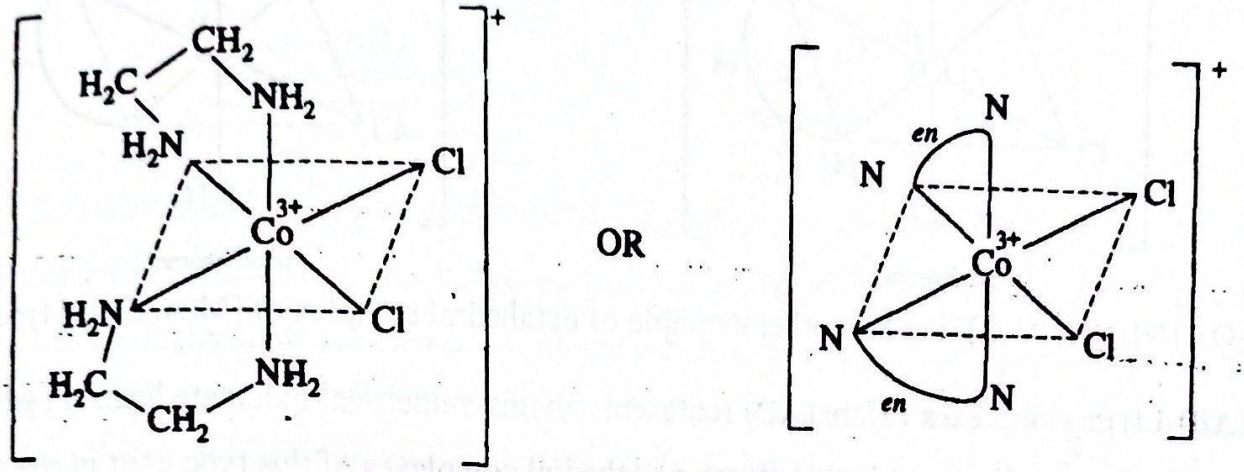
(II) (*trans*-isomer) (III)



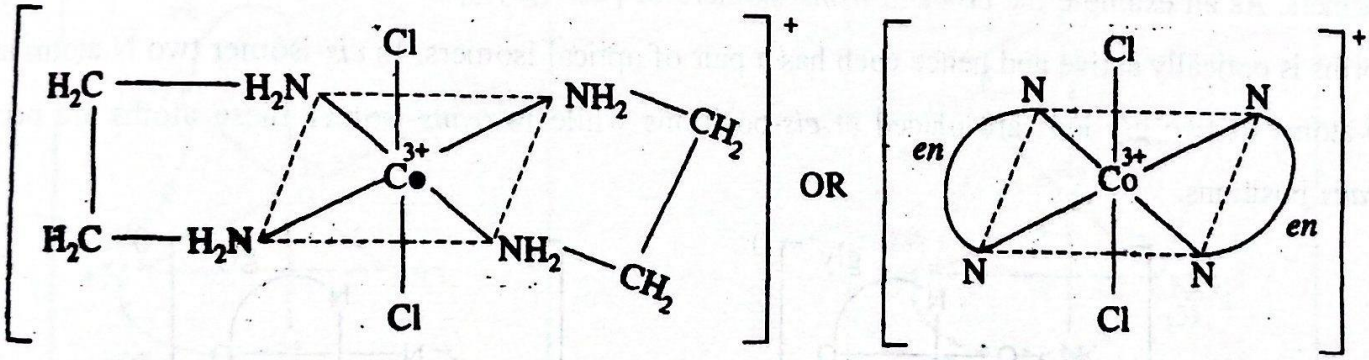
(IV) (V)

(7) $[Mabcdef]^{n\pm}$ type: Such complexes exist in fifteen possible geometrical forms. However all of them have not been isolated e.g. [Pt(py) (NH_3) (NO_2) (Cl) (Br) (I)].

(8) $[M(AA)_2a_2]$ type complexes : Here (AA) represents a symmetrical bidentate ligand in which A and A are two identical coordinating (donor) atoms. $[Co(en)_2Cl_2]^+$, $[Co(en)_2(NH_3)_2]^{3+}$, $[Co(en)_2(NO_3)_2]^+$, $[Cr(en)_2Cl_2]^+$, $[Cr(C_2O_4)_2(H_2O)_2]^-$, $[Ir^{4+}(C_2O_4)_2Cl_2]^{2-}$ etc. are the examples of octahedral complex ions of $[M(AA)_2a_2]$ type. Each of these complex ions exists in *cis*-and *trans*-isomers.

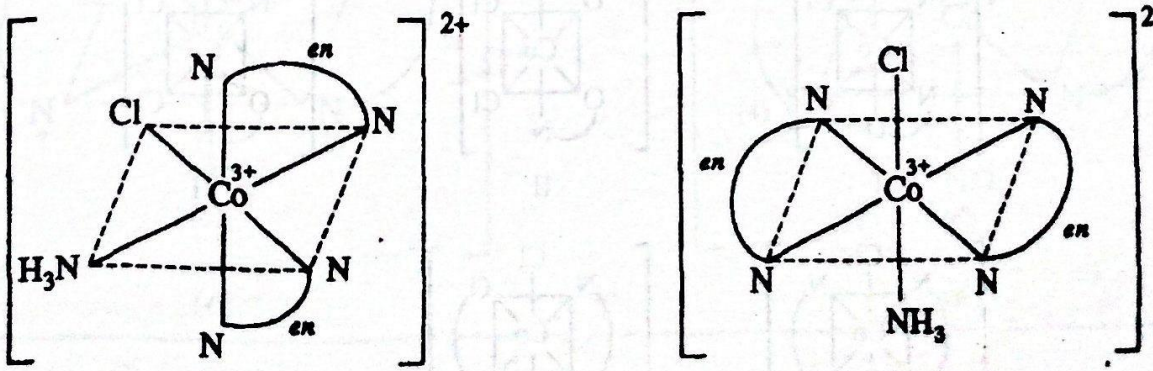


cis-isomer



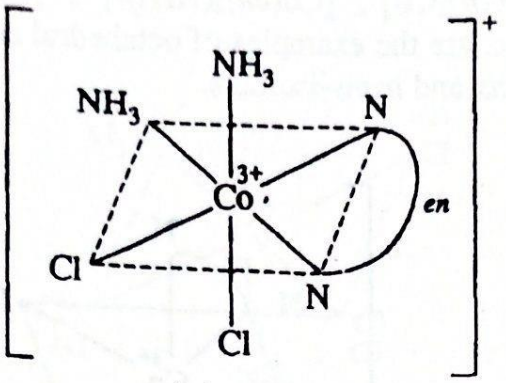
trans-isomer

(9) $[M(AA)_2ab]$ type complexes : $[Co^{3+}(en)_2(NH_3)Cl]^{2+}$ is an important example of octahedral complex of $[M(AA)_2ab]$ type. This complex ion exists in *cis*- and *trans*-isomers. In *cis*-isomer the two monodentate ligands *viz*. NH_3 and Cl^- occupy the adjacent (i.e., *cis*) positions while in *trans*-isomer these ligands occupy opposite (i.e., *trans*) positions $[Ru^{3+}(C_2O_4)_2(py)(NO_2)]^{2-}$ also exists in *cis*- and *trans*-isomers.

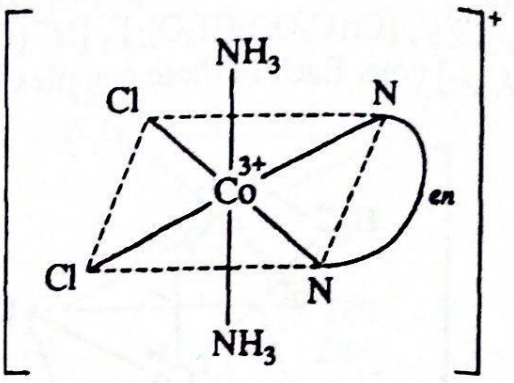


cis-isomer *trans*-isomer

(10) Octahedral complexes of $[M(AA)a_2b_2]$ type : $[Co^{3+}(en)(NH_3)_2Cl_2]^+$ ion is an important example of an octahedral complex ion of $[M(AA)a_2b_2]$ type. In the *cis*-isomer of this ion, both NH_3 group and both Cl^- ions occupy the *cis* positions while in *trans*-isomer both these pairs occupy the *trans* positions.



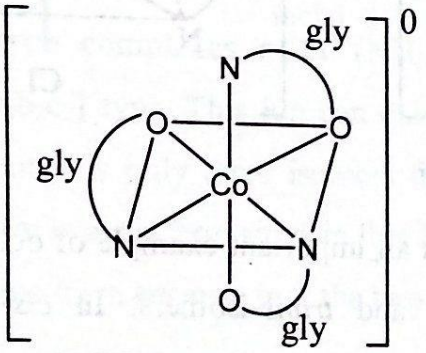
cis-isomer



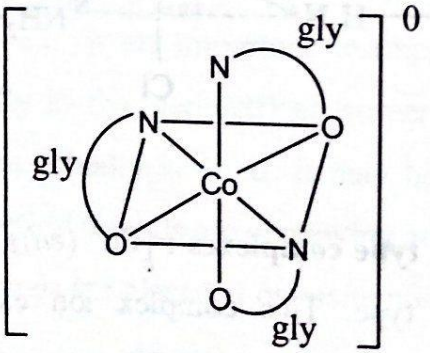
trans-isomer

$[Co^{3+}(C_2O_4)(NH_3)_2(NO_2)_2]^-$ ion is another example of octahedral complex of $[M(AA)a_2b_2]$ type.

(11) $[M(AB)_3]$ type complexes : Here (AB) represents an unsymmetrical bidentate ligand in which A and B are two different coordinating (donor) atoms. Octahedral complexes of this type exist in *cis*- and *trans*-isomers. As an example the *cis*- and *trans*-isomers of $[Cr^{3+}(gly)_3]$ has been shown below. Each of these forms is optically active and hence each has a pair of optical isomers. In *cis*-isomer two N-atoms and two O-atoms of two *gly* ions are placed at *cis*-positions while in *trans*-isomer these atoms are occupying *trans*-positions.

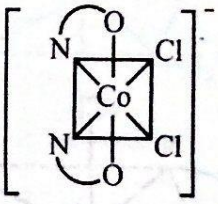


facial-isomer

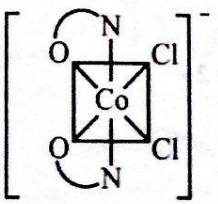


maridonial-isomer

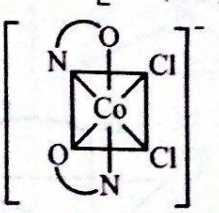
(12) $[M(AB)_2a_2]^{n\pm}$ type: Five geometrical forms have been reported e.g. $\left[Co(gly)_2Cl_2\right]^-$



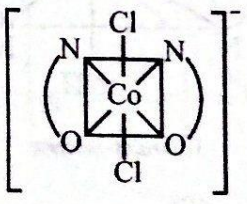
I



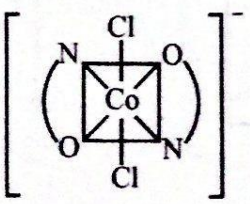
II



III



IV



V