

two similar ligands at opposite positions (180° apart) is called *trans*-isomer. Thus a square planar complex having two similar ligands at 1-2, 2-3, 3-4 and 1-4 positions is called *cis*-isomer while that having two similar ligands at 1-3 and 2-4 positions is called *trans*-isomer. *cis*- and *trans*-isomers are also named by numbering system. Thus in $[\text{Pd}^2\text{Cl}_2\text{BrI}]^{2-}$ if two Cl⁻ ions are placed *cis* to each other or at 1-2 positions, it is named as *cis*-dichloro bromiodo palladium (II) ion or 1,2-dichloro bromiodo palladium (II) ion. On the other hand, if two Cl⁻ ions are placed *trans* to each other or at 1-3 positions, it is named as *trans*-dichlorobromiodo palladium (II) ion or 1,3-dichlorobromiodo palladium (II) ion (See Fig. 15.2.)

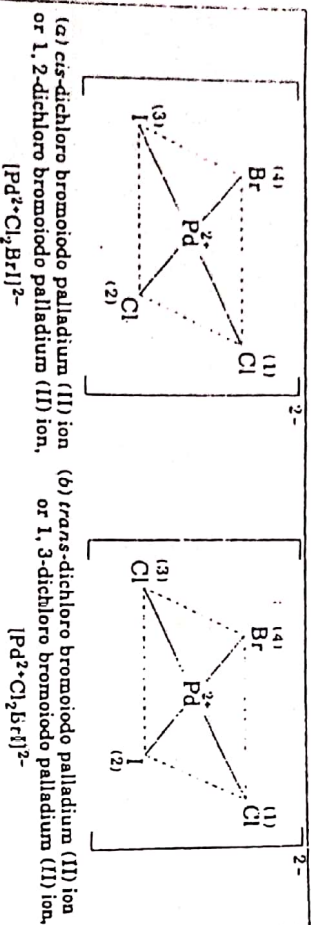


Fig. 15.2. Nomenclature of geometrical (*cis*- and *trans*) isomers of a square planar complex.

Here we shall consider geometrical isomerism in square planar complexes of $[\text{Ma}_2\text{b}_2]$, $[\text{Ma}_2\text{b}_2]$, $[\text{Ma}_2\text{bcd}]$ and $[\text{M}(\text{AB})_2]$ type in which M is the central metal atom; a, b, c and d are monodentate ligands and (AB) is an unsymmetrical bidentate ligand, since it has two different donor atoms namely A and B.

1. **Square planar complexes of $[\text{Ma}_2\text{b}_2]$ and $[\text{Mab}_2]$ type.** Square planar complexes of this type do not show geometrical isomerism, since all the possible spatial arrangement of four ligands round the central metal atom is the same.

2. **Square planar complexes of $[\text{Ma}_2\text{b}_2]$ type.** Important examples of square planar complexes of this type are $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^{2+}$, $[\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2]^{2+}$ etc. These complexes exist in *cis*- and *trans*-isomers. These isomers of $[\text{Pt}^2(\text{NH}_3)_2\text{Cl}_2]^{2+}$ are shown in Fig. 15.3. In (a) since both NH_3 molecules and both Cl^- ions are *cis* to each other, it is called *cis*-isomer. On the other hand, in (b) since both NH_3 molecules and both Cl^- ions are *trans* with respect to each other, it is called *trans*-isomer.

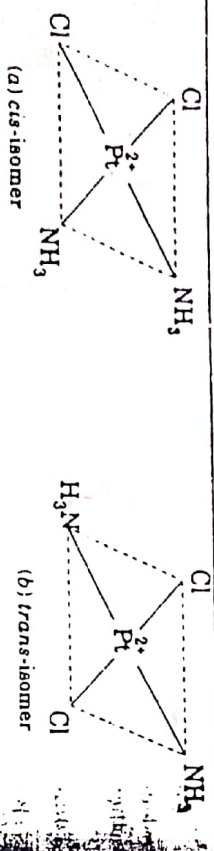
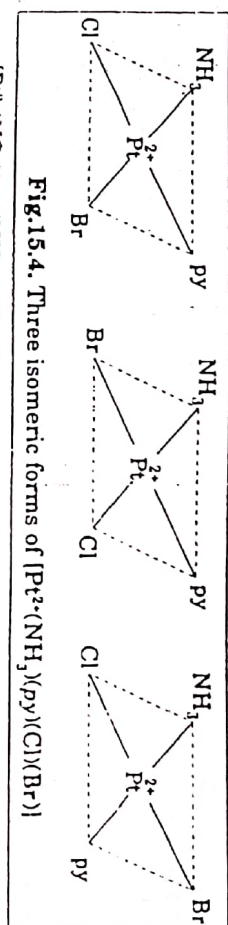


Fig. 15.3. *cis*- and *trans*-isomers of $[\text{Pt}^2(\text{NH}_3)_2\text{Cl}_2]^{2+}$.

Square planar complexes

in three isomeric forms shown below in Fig. 15.4. These isomeric forms can be obtained by selecting one ligand, say NH_3 , and then placing the remaining three ligands, one by one, *trans* to NH_3 .



$[\text{Pt}^2(\text{NO}_2)(\text{py})(\text{NH}_3)(\text{NH}_2\text{OH})^+]$ and $[\text{Pt}^2(\text{C}_6\text{H}_5)(\text{NH}_3)(\text{Cl})(\text{Br})]$ are other examples of square planar complexes which exist in three isomeric forms.

The existence of three isomeric forms in case of the complexes mentioned above indicates that these complexes have square planar geometry.

4. **Square planar complexes of $[\text{Ma}_2\text{bcl}]$ type.** Square planar complexes of this type also show *cis*-*trans* isomerism. For example, $[\text{Pd}^2\text{Cl}_2\text{BrI}]^{2-}$ ion exists in *cis*- and *trans*-isomers as shown below in Fig. 15.5.

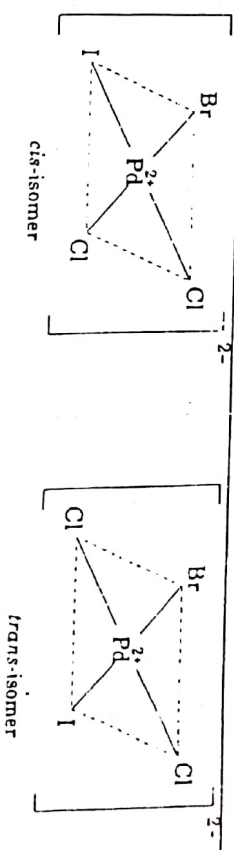


Fig. 15.5. *cis*- and *trans*-isomers of $[\text{Pd}^2\text{Cl}_2\text{BrI}]^{2-}$ ion.

$[\text{Pt}^2(\text{py})_2(\text{NH}_3)\text{Cl}]^{2+}$ is another example of square planar complex of $[\text{Ma}_2\text{bcl}]$ type which exists in *cis*- and *trans*-isomers.

5. **Square planar complexes of $[\text{M}(\text{AB})_2]$ type.** Here M is the central metal ion and (AB) represents an unsymmetrical bidentate ligand in which A and B are two different coordinating (donor) atoms. Square planar complexes of this type also exist in *cis*- and *trans*-isomers. For example, $[\text{Pt}^2(\text{gly})_2]$ exists in *cis*- and *trans*-isomers as shown in Fig. 15.6. Here gly represents the glycinate ligand, $\text{NH}_2\text{CH}_2\text{COO}^-$ which has N and O atoms as its donor atoms (i.e., A = N and B = O).

$[\text{Cu}^{2+}(\text{gly})_2]^{2+}$ is also an example of square planar complex of $[\text{M}(\text{AA})_2]$ type. This complex also exhibits *cis*-*trans* isomerism.

Geometrical Isomerism in 6-coordinated Complexes: Octahedral Complexes

We know that a complex compound having central atom with coordination number equal to 6 is octahedral in shape. Before discussing the geometrical isomerism exhibited by various types of octahedral complexes, we should know how *cis*- and *trans*-isomers of an octahedral complex are named. 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 placed

Important examples of octahedral complexes of M_a,b type. Cis - fac and $trans$ - mer isomers of $[Co(NH_2)_2Cl_3]$ are given in Fig. 15.10.

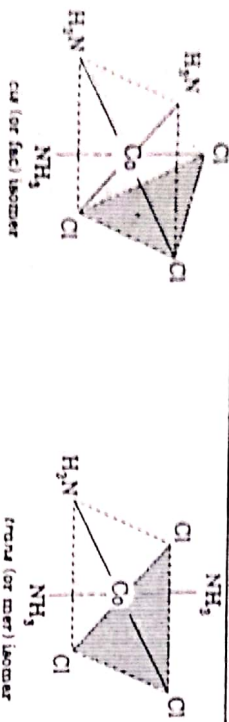


Fig. 15.10. cis - fac and $trans$ - mer isomers of $[Co(NH_2)_2Cl_3]$ octahedral complex.

$[Co(NH_2)_2CH_2COO]_2$ also has two geometrical isomers, viz., facial and meridional. See Fig. 15.11. In the given complex N and O atoms are the donor atoms.

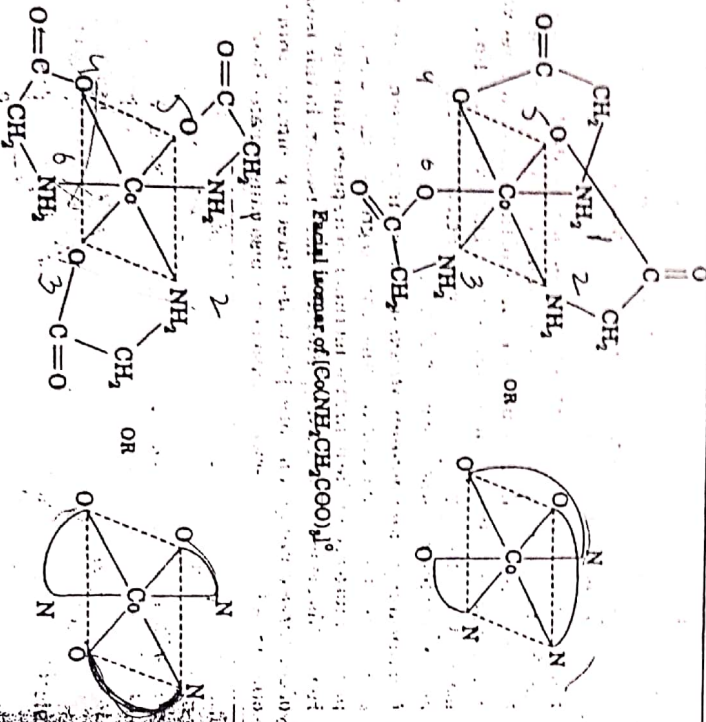


Fig. 15.11. Facial and meridional isomers of $[Co(NH_2)_2CH_2COO]_2$.

4. Octahedral complexes of $[M_a,bcd]$ type. $[Co^{3+}(NH_3)_2(H_2O)Cl]^{2+}$ ion is an important example of octahedral complex of $[M_a,bcd]$ type. This ion has cis - and $trans$ -

cis positions to each other and in $trans$ -form these ligands (i.e. two NH_3 molecules) have $trans$ positions with each other.

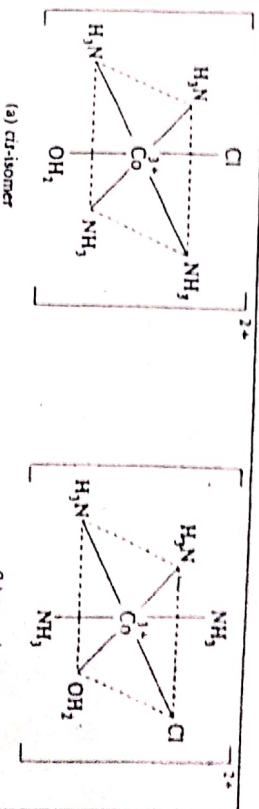


Fig. 15.12. Structure of cis - and $trans$ -isomers of $[Co^{3+}(NH_3)_2(H_2O)Cl]^{2+}$ octahedral complex ion.

5. Octahedral complexes of $[M_a,b_2c_2]$ type. $[Pt^{2+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion is an important example of octahedral complex of $[M_a,b_2c_2]$ type. This ion can exist in only three isomers that have been actually isolated. It may be noted from the figure that (I) form is a cis -form since in this form two identical ligands are occupying adjacent positions. Form (II) is $trans$ -form because in it the two identical ligands are placed at opposite positions.

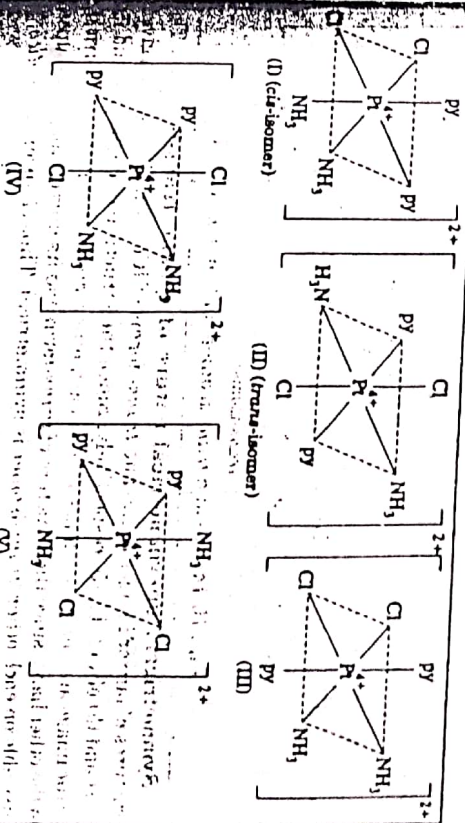


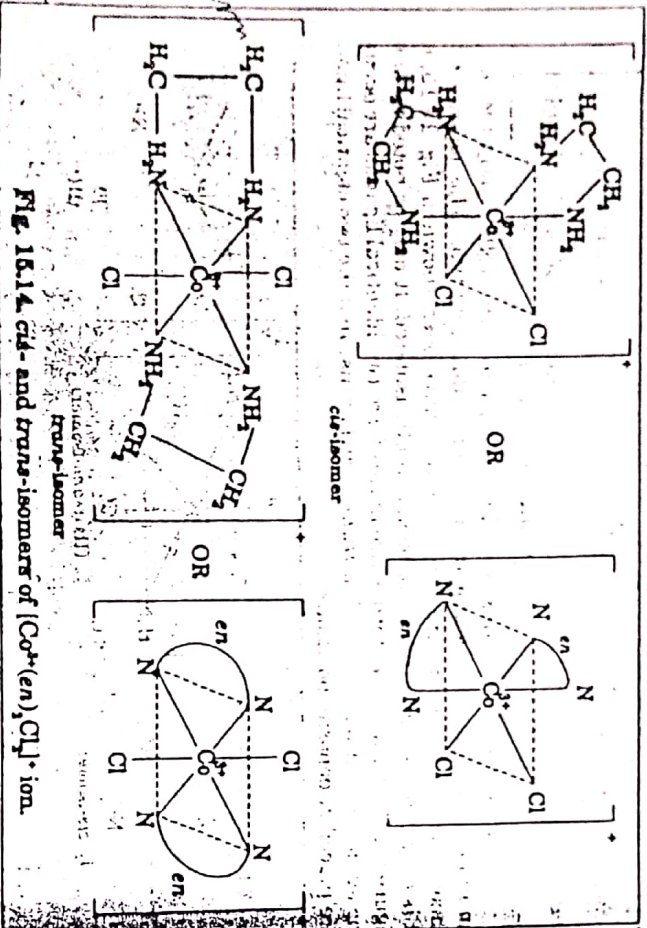
Fig. 15.13. All possible five geometrical isomers of $[Pt^{2+}(NH_3)_2(py)_2Cl_2]^{2+}$ ion.

6. Octahedral complexes of $[Mabcde]f$ type. Octahedral complexes with have different monodentate ligands have been prepared for Pt (IV). $[Pt(NH_3)(NO_2)(Cl)(Br)(I)]$ is the only complex of this type of complexes.

Theoretically 15 geometrical isomers are possible for this complex compound. In fact only three geometrical isomers have been isolated.

7. Octahedral complexes of $M(AA)_2$ type. Octahedral complexes of this type do not show geometrical isomerism.

8. Octahedral complexes of $[M(AA)_2A_2]$ type. Here (AA) represents a symmetrical bidentate ligand in which A and A are two identical coordinating (donor) atoms. $[Co(en)_2Cl_2]^+$, $[Co(en)_2(NO_2)_2]^+$, $[Cr(en)_2Cl_2]^+$, $[Cr(C_2O_4)_2(H_2O)]^-$, $[Ir(C_2O_4)_2Cl]^-$ etc. are the examples of octahedral complexes of $[M(AA)_2A_2]$ type. Each of these complex ions exists in *cis*- and *trans*-isomers. As an example *cis*- and *trans*-isomers of $[Co^{3+}(en)_2Cl]^{2+}$ ion are shown in Fig. 15.14.



Symmetrical / unsymmetrical nature of *cis*- and *trans*-isomers. The structures of mirror images of *cis*- and *trans*- forms of $[Co^{3+}(en)_2Cl]^{2+}$ ion are given at (a) and (b) of Fig. 15.15 respectively. Since the structure of *cis*-isomer and its mirror image are non-superimposable on each other, *cis*-isomer is unsymmetrical. On the other hand, since the structure of *trans*-form and its mirror image are superimposable on each other, *trans*-isomer is symmetrical. Thus *cis*-isomer is optically active but *trans*-isomer is optically inactive.

9. Octahedral complexes of $[M(AA)_2ab]$ type. $[Co^{3+}(en)_2(NH_3)Cl]^{2+}$ 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 (See Fig. 15.16). $[Ru^{3+}(C_2O_4)_2(py)(NO_2)]^{2-}$ also exists in *cis*- and *trans*-isomers.

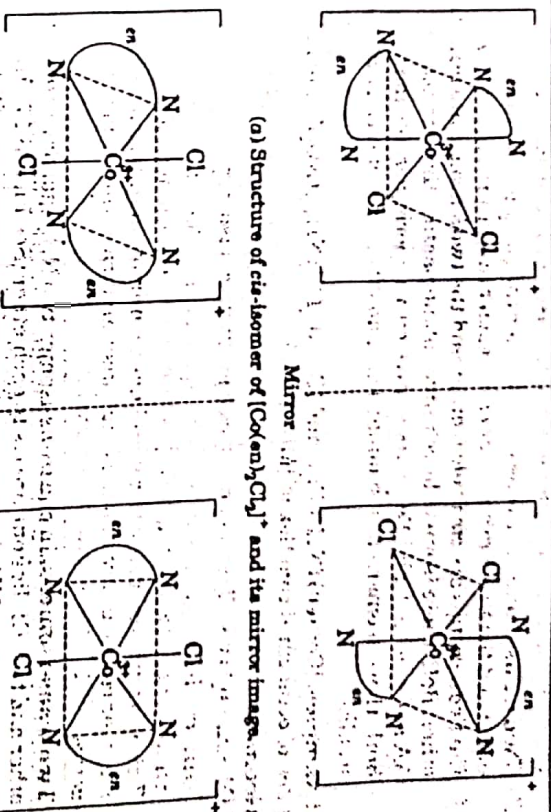
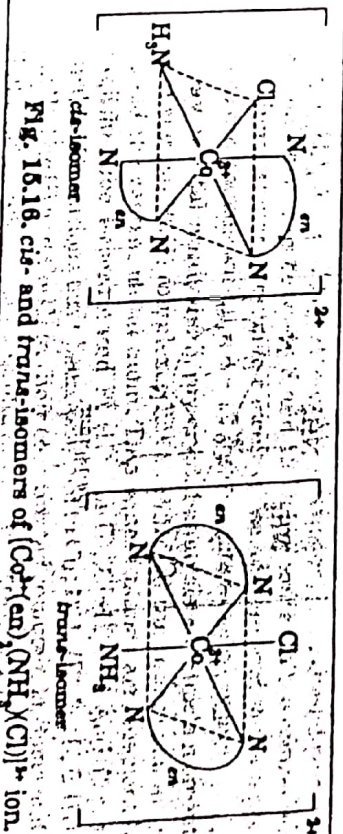


Fig. 15.16. Structure of *cis*- and *trans*-forms of $[Co(en)_2Cl]^{2+}$ ion and their mirror images.



As in case of $[Co^{3+}(en)_2Cl]^{2+}$ ion, the *cis*-isomer of $[Co^{3+}(en)_2(NH_3)Cl]^{2+}$ is also unsymmetrical while its *trans*-isomer is symmetrical. Thus *cis*-form is optically active while *trans*-isomer is optically inactive.

10. Octahedral complexes of $[M(AA)_2a_2b_2]$ type. In this complex AA represents a bidentate ligand in which two A atoms are donor atoms. a and b are monodentate ligands. Octahedral complexes of $[M(AA)_2a_2b_2]$ type exist in three geometrical isomers.

(i) **One *cis*-isomer.** In this isomer the two a groups are *cis* to each other. Similarly the two b groups are also *cis* to each other. This isomer is optically active.

metrical and has no mirror plane passing through the metal (M) or centre of inversion. Being unsymmetrical, this isomer is optically active.

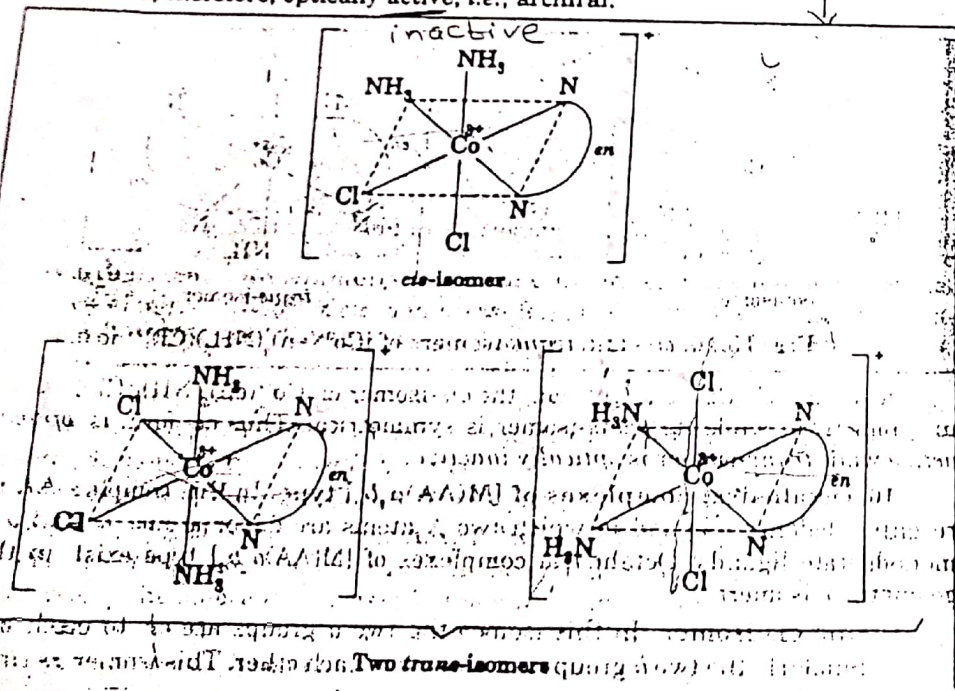
- (ii) **Two trans-isomers.** In one *trans*-isomer the two *a* groups are *trans* to each other and the two *b* groups are *cis* to each other. In the other *trans*-isomer the two *a* groups are *cis* to each other and the two *b* groups are *trans* to each other. Both these isomers have mirror plane passing through the metal (M), AA and a, a / b, b and hence these give only superimposable mirror image. Both these isomers are symmetrical and hence are optically active, i.e., achiral.

Examples: $[\text{Co}^{3+}(\text{en})(\text{NH}_3)_2\text{Cl}]^+$ and $[\text{Co}^{3+}(\text{C}_2\text{O}_4)(\text{NH}_3)_2(\text{NO}_2)_2]^-$ are important examples of octahedral complex of $[\text{M}(\text{AA})_2\text{a}_2\text{b}_2]$.

Geometrical isomers of $[\text{Co}^{3+}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ ion. This ion is an octahedral ion of $[\text{M}(\text{AA})_2\text{a}_2\text{b}_2]$ type. This ion has three geometrical isomers.

- (i) **One cis-isomer.** In this isomer two NH_3 ligands are *cis* to each other. Similarly the two Cl^- ligands are also *cis* to each other. [See Fig. 15.17.]. This isomer is unsymmetrical and has no mirror plane passing through the metal or centre of inversion. Being unsymmetrical this isomer is optically active.
- (ii) **Two trans-isomers.** In one *trans*-isomer two NH_3 ligands are *trans* to each other and two Cl^- ligands are *cis* to each other (See Fig. 15.17). In the other *trans*-isomer two NH_3 ligands are *cis* to each other and two Cl^- ligands are *trans* to each other (See Fig. 15.17). Both these isomers have mirror plane passing through the metal, en and NH_3 , NH_3/Cl , Cl and hence these give only superimposable mirror image. Both these isomers are symmetrical and are, therefore, optically active, i.e., achiral.

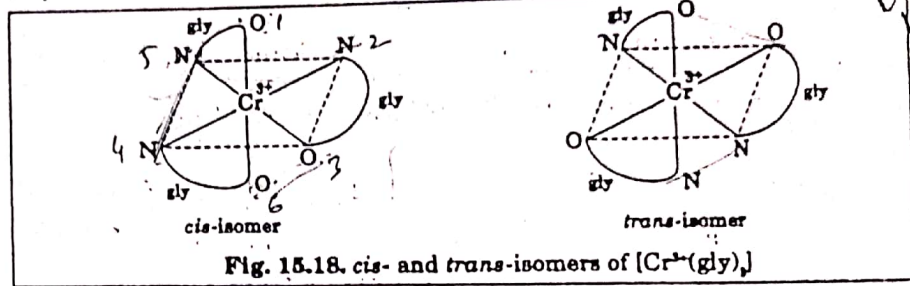
M/A, L, J



important example of octahedral complex

11. Octahedral complexes of $[\text{M}(\text{AB})_3]$ type. 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 $[\text{Cr}^{3+}(\text{gly})_3]$ have been shown in Fig. 15.18. 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

Unsymmetrical bidentate ligand



Since both the forms (i.e. *cis*- and *trans*-forms) are optically active, each of these forms has *d*- and *l*-forms (optical isomers)

To Distinguish Between cis- and trans-isomers

The following methods may be used to distinguish between *cis*- and *trans*-isomers.

1. Dipole moment measurements. Jensen has shown that the Pt (II) complexes of $[\text{Pt}^{2+}\text{A}_2\text{X}_2]$ type, where A = substituted phosphine, arsine or stilbine such as $(\text{C}_2\text{H}_5)_3\text{P}$, $(\text{C}_2\text{H}_5)_3\text{As}$ or $(\text{C}_2\text{H}_5)_2\text{Sb}$ and X = a halogen, have their dipole moments (μ) either equal to zero or between 8 and 12 Debye units. In the compounds with $\mu = 0$, the individual moments have cancelled one another and so these are *trans*-isomers. The compounds with $\mu = 8 - 12$ Debye units are *cis*-isomers.

2. X-ray crystal analysis. X-ray crystal analysis and dipole moment measurements of several Pt(II) complexes have confirmed the square planarity of the bonds around the central metal atom. This square planar arrangement has also been established for 4-coordinated Pt (II), Ag(II), Cu(II) and Au(III) complexes. Tetrahedral configurations have been assigned to Cu (I), Ag(I), Au (I), B(III), Al(III), Zn(II), Cd(II), Hg(II) and Co(II) in their coordinated compounds. Some metals such as Ni(II) appear to show either configuration for 4-coordination.

3. Infra-red spectroscopic technique. In a *trans* octahedral complex such as $[\text{Co}^{3+}(\text{NH}_3)_4\text{Cl}_2]^+$ or in *trans* square planar complex like $[\text{Pt}^{2+}(\text{NH}_3)_2\text{Cl}_2]^0$ the Cl-metal-Cl symmetrical stretching vibration produces no change in the dipole moment of the molecule [Fig. 15.19. (b) and (d)], and thus no band corresponding to this vibration is observed in the infra-red spectrum. However, in the *cis*-form of each compound, the symmetrical stretching vibration [Fig. 15.19(a) and (c)] as well the unsymmetrical stretching vibration produce appreciable changes in the dipole moment; hence the infra-red spectrum of the *cis*-isomer will contain a large number of bands due to Cl-metal-Cl stretching.

LI =

A
Pt
A

A
X

LI =

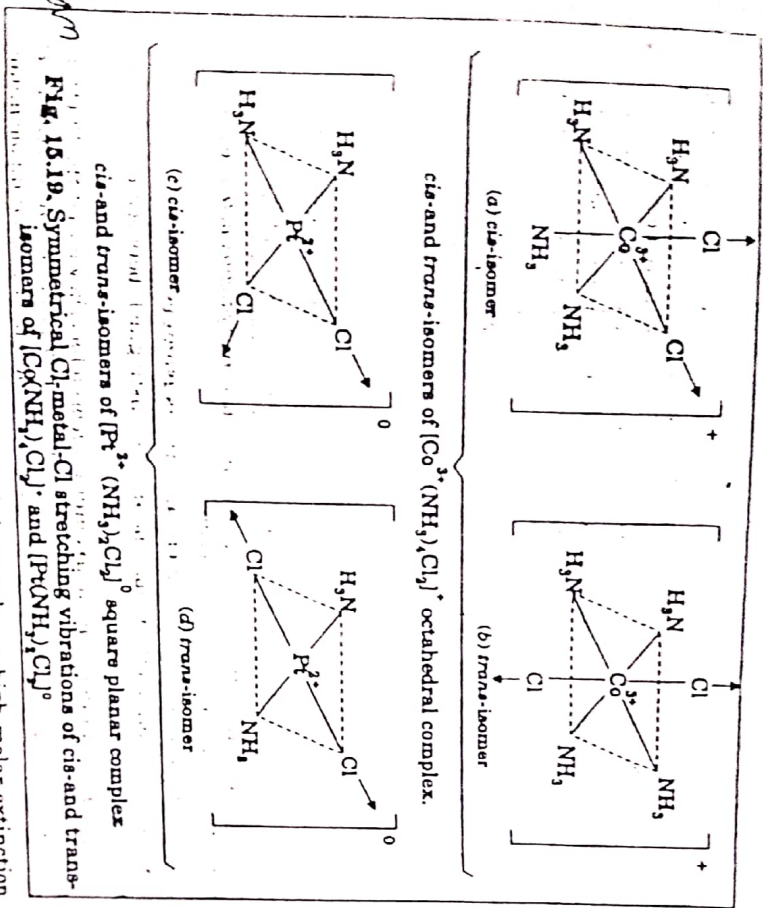


FIG. 15.19. Symmetrical Cl-metal-Cl stretching vibrations of cis- and trans-isomers of $[Co(NH_3)_2Cl_2]^+$ and $[Pt(NH_3)_2Cl_2]^0$

4. **Molar extinction coefficient.** A cis-isomer has a high molar extinction coefficient (absorption) than the corresponding trans-isomer and sometimes the two isomers may differ significantly in their absorption spectra.

5. **To resolve cis-isomer** The technique which consists of attempting to resolve the cis-isomer into the two possible optically active isomers is also commonly used to distinguish it from the trans-isomers.

6. **Grinberg's method.** It is a chemical method and assumes that when a chelating ligand having two donor atoms separated by two to four other atoms reacts with cis- and trans-isomers separately, its two donor atoms coordinate to the central metal ion of the cis-form at two cis-positions and thus form five or six-membered ring, while in the trans-form they coordinate to the central metal ion at trans positions and thus the ligand acts as a monodentate ligand, i.e., the ligand cannot form a ring complex with trans form. Typical chelating ligands used for the purpose are oxalic acid, $(COOH)_2$, glycine (H_2N-CH_2-COOH) and ethylenediamine $(NH_2-CH_2-CH_2-NH_2)$. The application of this method can be explained by considering the reaction of oxalic acid and glycine with cis- and trans-isomers of square planar complex of $Pt(II)$, $[Pt^{2+}(NH_3)_2Cl_2]^0$ (Fig. 15.20). Quite obviously the cis-isomer gives a chelated complex while the trans-isomer yields a non-chelated complex

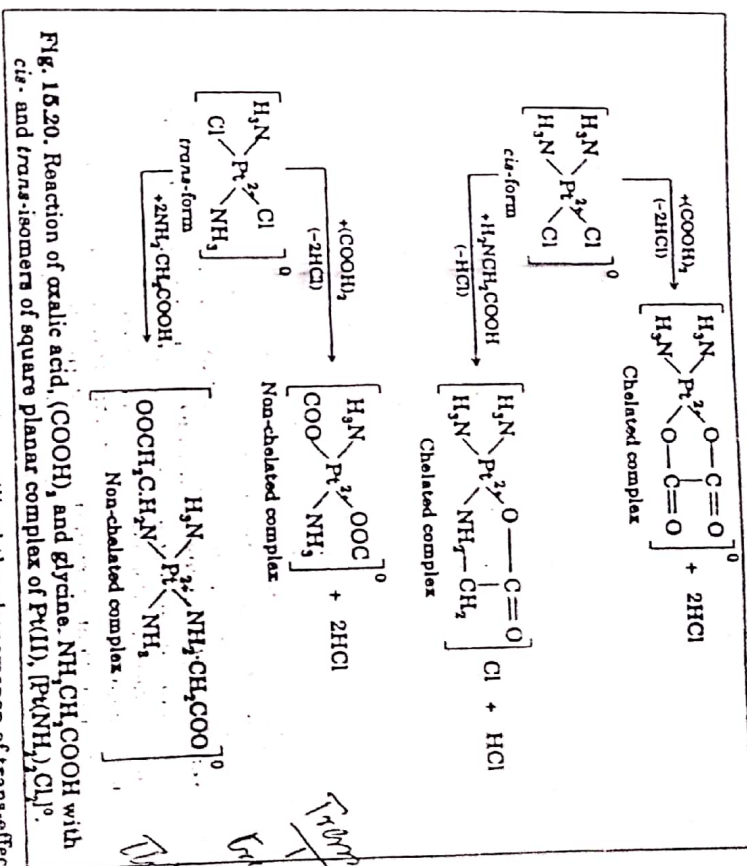


Fig. 15.20. Reaction of oxalic acid, $(COOH)_2$, and glycine, NH_2CH_2COOH with cis- and trans-isomers of square planar complex of $Pt(II)$, $[Pt(NH_3)_2Cl_2]^0$.

7. **Kurnakov's reaction.** Kurnakov utilised the phenomenon of trans-effect in distinguishing the pairs of cis- and trans- isomers of square planar complexes of $[PtAX_2Cl_2]$ type by treating them with thiourea.

Optical (or d-l or mirror-image) Isomerism

Before discussing the optical isomerism shown by various types of complexes we will define some important terms related to this isomerism.

1. Optical Activity and Optically Active Complexes

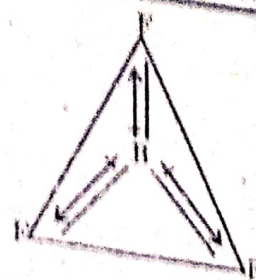
When the solutions of certain complex compounds are placed in the path of a plane polarised light (the waves of the plane-polarised light vibrate only in one direction; vibrations in other directions are cut off), they rotate its plane through a certain angle which may be either to the left or to the right. This property of a complex of rotating the plane of polarised light is called its optical activity and the complex possessing this property is said to be optically active.

2. Different Forms of Optically Active Complexes

(i) $3Cl^- + 3Ag^+ \rightarrow 3AgCl \downarrow$ white ppt.

(ii) (II) is blue-green, loses only one H_2O molecule...

BF_3 has polar bonds but the BF_3 molecule is nonpolar, whose geometry is trigonal planar. The three bond moments are of equal magnitude. They point to the corners of an equilateral triangle. Because of the symmetry of the molecule, the bond moments cancel.



Molecules with symmetrical structures, but different atoms bonded to the central atom, are usually polar. For example, tetrahedral CH_4 molecules are nonpolar, however, tetrahedral CH_3Cl molecules are polar.

2.10 Theories of Chemical Bonding

The bonding theories that are currently accepted allow us to predict structures and properties that are usually accurate (although they are not always entirely satisfactory). As always, we should keep in mind the truism that whatever we propose must be consistent with experimentally determined facts. When there is disagreement between facts and theory, theory must be modified to accommodate all known facts.

We shall discuss three theories. The first is the Valence Shell Electron Pair Repulsion (VSEPR) theory, which assumes that electron pairs are arranged around the central atom in such a way that there is maximum separation (and, therefore, minimum repulsion) among electron pairs. The second theory is the Valence Bond (VB) theory, which explains the bonding in terms of overlapping atomic orbitals. The third theory, is called Molecular Orbital (MO) theory, which assumes that the atomic orbitals of the original unbonded atoms become replaced by a new set of molecular energy levels, called *molecular orbitals*, and the occupancy of these orbitals determines properties of the resulting molecule.

2.11 Valence Shell Electron Pair Repulsion (VSEPR) Theory

Lewis structures provide a very useful method for representing the structures of covalent molecules. Lewis structures, however, do not give any information about the actual geometry (shape) of the molecule. Sidgwick and Powell in 1940 pointed out that the shapes of the molecules can be predicted on the basis of electron pairs present in the valence shell of the central atom. The VSEPR theory explains observed geometry of molecules and polyatomic ions by an electrostatic picture based primarily on the Lewis structure, without reference to orbitals. The main idea of the VSEPR theory is that:

The electron pairs (both lone pairs and shared pairs) surrounding the central atom must be arranged in space as far apart as possible to minimise the electrostatic repulsion between them.

A central atom is any atom that is bonded to two or more than two other atoms. The first and the most important rule of the VSEPR theory is that *the bond angles about a central atom are those that minimize the total repulsion between the electron pairs in the valence shell of the atom.* While working out the shapes of

molecules from this theory, the following rules must be remembered:

1. A lone pair of electrons occupies more space than a bonding pair. This is because the lone pair of electrons is under the influence of only one nucleus of the central atom, they are expected to occupy more space with a greater electron density than the bond pair electrons which are under the influence of two nuclei. Thus decreasing order of repulsion is:
lone pair-lone pair > lone pair-bond pair > bond pair-bond pair
2. Repulsive forces decrease sharply with increasing interpair angle. They are strong at 90° , much weaker at 120° , and very weak at 180° .
3. The influence of a bonding electron pair decreases with the increasing value of electronegativity of an atom forming a molecule.
4. Multiple bonds behave as a single electron-pair for the purpose of VSEPR theory.
5. The two electron pairs of a double bond (or three electron pairs of a triple bond) occupy more space than the one electron pair of a single bond.
6. The lone pairs repel bond pairs giving rise to some distortions in the molecular shape. The distortion may also result due to different atoms in the molecule.

Applications of VSEPR Theory

Let us now apply the valence shell electron pair repulsion theory to predict the shapes of molecules. The first step in the VSEPR method for determining the geometry of the molecule is to write down its Lewis structure in order to determine the number of electron pairs around the central atom. The second step is to determine the total number of electron pairs (lone and bonding) around the central atom. The third step is to determine the number and location of lone pairs. The molecules can be classified according to the number of electron pairs around the central atom.

Gillespie proposed the following rules to explain the shapes of inorganic molecules.

Rule 1. If the central atom of a molecule is surrounded only by bonding electron pairs (bp's) and not by non-bonding electron pair called lone pairs (lp's), the geometry of the molecule will be regular, i.e., it will be linear, triangular planar, tetrahedral, trigonal bipyramid and regular octahedron for 2, 3, 4, 5 and 6 bonding electron pairs.

Rule 2. When the central atom in a molecule is surrounded by both bp's and lp's, the molecule does not have a regular shape. The alternation or distortion in shape is due to the alternation in bond angles which arises due to the presence of lp's on the central atom.

Rule 3. B-A-B bond angle decreases with the increase in electronegativity of atom B in AB molecule wherein A is the central atom. This is due to the fact that with the increase in electronegativity of atom B, the average position of bonding electron-pair moves farther from the central atom A and hence the repulsive