COORDINATION COMPOUNDS

INISOMERISM IN COORDINATION COMPOUNDS

❖ ISOMERISM IN COMPLEXES

Complex compounds that have the same molecular formula but have different structural /special arrangements of ligands are called isomers. These are of two types, namely structural and stereo isomers.

Type of isomerism

- Structural isomerism
  - –Ionisation isomerism
  - –Hydrate isomerism
  - –Linkage isomerism
  - –Coordination isomerism
  - –Coordination position isomerism
- Space / stereo isomerism
  - –Geometrical isomerism
  - –Optical isomerism

STRUCTURAL ISOMERISM

(i) **Ionisation Isomerism** This type of isomerism is due to the exchange of groups between the complex ion and ions outside it. $[Co(NH_3)_5Br]SO_4$ is red -violet. An aqueous solution of it gives a white precipitate of $BaSO_4$ with $BaCl_2$ solution, thus confirming the presence of free SO_4^{2-} ions. In contrast $[Co(NH_3)_5SO_4]Br$ is red. A solution of this complex does not give a positive sulphate test with $BaCl_2$. It does give a cream-coloured precipitate of AgBr with $AgNO_3$, thus confirming the presence of free Br^- ions. Other examples of ionisation isomerism are $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ and $[Co(en)_2NO_2.Cl]SCN$, $[Co(en)_2NO_2.SCN]Cl$ and $[Co(en)_2Cl.SCN]NO_2$.

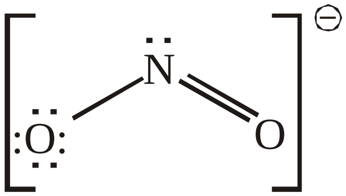
(ii) **Hydrate isomerism** These isomers arise by the exchange of groups in the complex ion with water. Three isomers of $CrCl_3.6\ H_2O$ are known. From conductivity measurements and quantitative precipitation of the ionised Cl^-, they have been given the following

$$[Cr(H_2O)_6]Cl_3$$

$$[Cr(H_2O)_5Cl]Cl_2.H_2O$$

$$[Cr(H_2O)_4Cl_2]Cl.2H_2O$$

(iii) **Linkage Isomerism** This type of isomerism arises when the ligand attached to the central metal ion of a complex in different ways. Such ligands are called ambident ligands. Nitrite ion has electron pairs available for co-ordination both on N and O atoms.

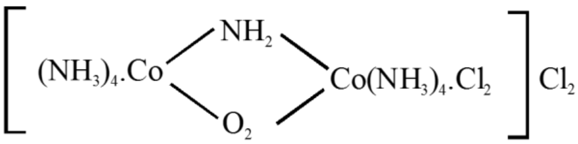


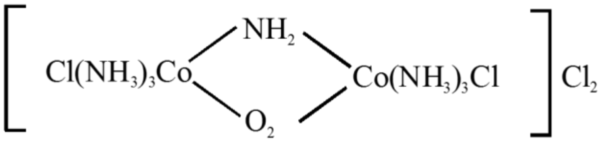
Ex.

(a)	$[Co(NH_3)_5\ ONO]Cl_2$	and	$[Co(NH_3)_5\ NO_2]\ Cl_2$
	pentaamminenitrito-o-cobalt(III) chloride		pentaamminenitrito-N-cobalt-(III)-chloride
	(red)		(yellow)
(b)	$[Mn(CO_5).SCN]^+$	and	$[Mn(CO_5)\ (NCS)]^+$
	pentacarbonylthiocyanto –S-manganese (II) ion		pentacarbonylthiocyanato –N-manganese (II) ion

(iv) **Co-ordination Isomerism** When both the cation and anion are complex ions, then isomerism may be caused by the interchange of ligands between the anion and cation. For example $[Pt(NH_3)_4]\ [PtCl_4]$ and $[PtCl(NH_3)_3]\ [PtCl_3(NH_3)]$. These isomers are called co-ordination isomers.

(v) **Co-ordination Position Isomerism** In polynuclear complexes, an interchange of ligands between the metal nuclei gives rise to co-ordination position isomerism, for example.





Co-ordination position isomers

Polymerisation Isomerism

This is not true type of isomerism because it occurs among compounds having the same empirical formula, but different molecular formula. Thus, $[Pt(NH_3)_2Cl_2]$,$[Pt(NH_3)_4][PtCl_4]$, $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$ and $[Pt(NH_3)_3Cl]_2[PtCl_4]$ all have the same empirical formula.

STEREOISOMERISM

The isomers in which atoms are bonded to each other in the same order but that differ in the arrangement of these atoms in the space are called as stereoisomers and the phenomenon as stereoisomerism.

GEOMETRICAL ISOMERISM

This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands. Geometrical isomerism is common among coordination compounds with coordination numbers 4 and 6.

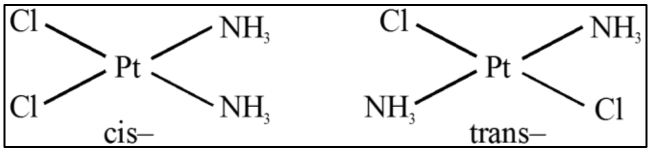
Coordination Number Four:

Tetrahedral Complex:

The tetrahedral compounds cannot show geometrical isomerism as we all know that all four positions are equivalent in tetrahedral geometry.

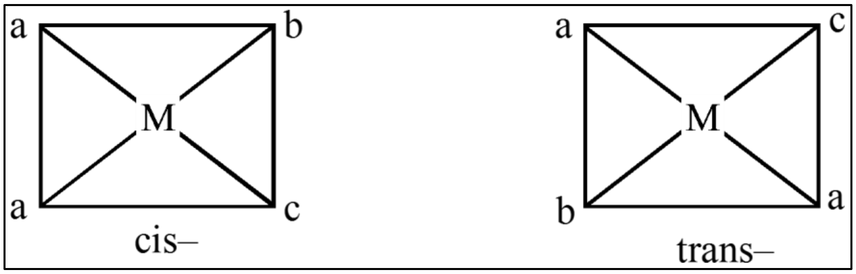
Square Planar Complex:

In a square planar complex of formula $[Ma_2b_2]$ [a and b are unidentate], the two ligands ‘a’ may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer as depicted.

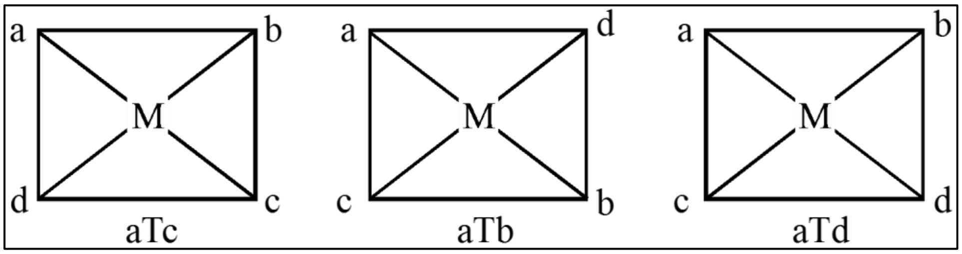


Geometrical isomers (cis and trans) of $Pt(NH_3)_2Cl_2$.

Square planar complex of the type Ma_2bc (where a,b,c are unidentate) shows two geometrical isomers.



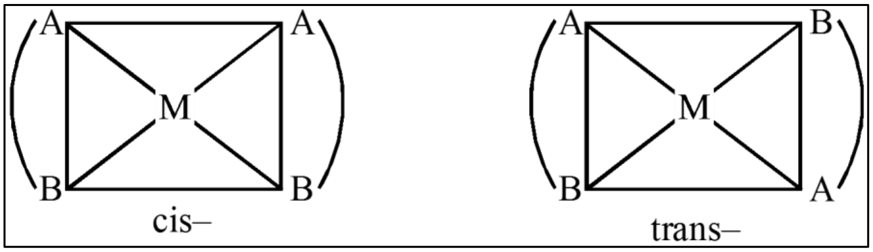
Square planar complex of the type Mabcd (where a,b,c,d are unidentates) shows three geometrical isomers.



Example is $[Pt(NH_3)BrCl(py)]$. Three isomers of the complex

$[Pt(NH_3)(NH_2OH)(py)(NO_2)]^+$ have been isolated and identified.

Square planar complex of the type $M(AB)_2$ (where AB are unsymmetrical bidentates) shows two geometrical isomers. Example is $[Pt(gly)_2]$ in which gly is unsymmetrical ligand.

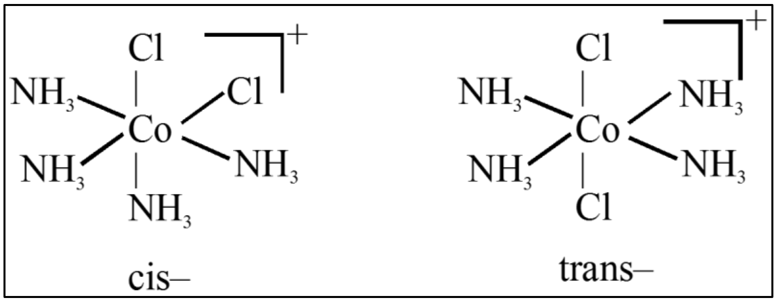


Similarly, M(AB)(CD) also shows two geometrical isomers.

Note: $M(AA)_2$,(where AA are symmetrical bidentates) does not show geometrical isomerism. e.g., $[Cu(en)_2]^{2+}$ $[Pt(ox)_2]^{2-}$, etc.

Coordination Number Six:

Geometrical isomerism is also possible in octahedral complexes.



cis– trans–

Geometrical isomers (cis and trans) of $[Co(NH_3)_4Cl_2]^+$

Number of possible isomers and the spatial arrangements of the ligands around the central metal ion for the specific complexes are given below.

(I) Complexes containing only unidentate ligands

(i) Ma_2b_4 – 2 (aa)(bb)(bb)

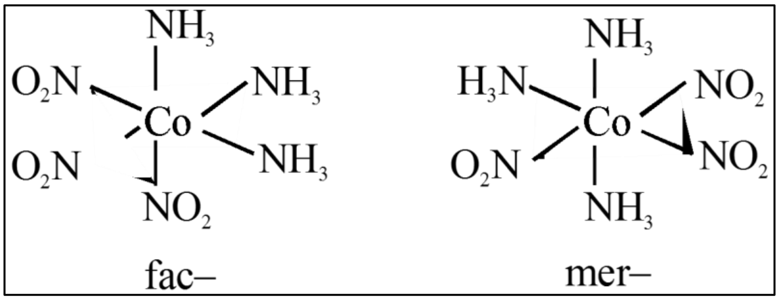
(ab)(ab)(bb)

(ii) Ma_4bc – 2 (aa)(aa)(bc)

(aa)(ab)(ac)

(iii) Ma_3b_3

Complexes of the formula Ma_3b_3, where a and b are monodentate ligands, may show two isomeric forms called fac– and mer–. Facial isomers have three identical ligands on one triangular face where as meridional isomers have three identical ligands in a plane bisecting the molecule. Similar isomers are possible with some chelating ligands.



fac– mer–

The facial(fac) and meridional(mer) isomers of $[Co(NH_3)_3(NO_2)_3]$.

Unsymmetrical bidentate ligands also show fac-mer isomerism.

(iv) Ma_3b_2c – 3 (aa)(ab)(bc)

(aa)(bb)(ac)
(ab)(ab)(ac)

(v) Ma_3bcd – 4
(aa)(ab)(cd)
(aa)(ac)(bd)
(aa)(ad)(bc)
(ab)(ac)(ad)

(vi) $Ma_2b_2c_2$ – 5
(aa)(bb)(cc)
(aa)(bc)(bc)
(bb)(ac)(ac)
(cc)(ab)(ab)
(ab)(ac)(bc)

(vii) Ma_2b_2cd – 6

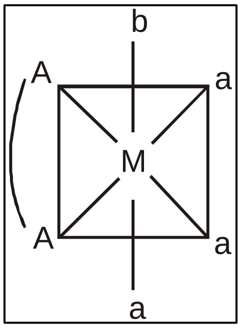
(viii) Ma_2bcde – 9

(ix) Mabcdef, $[Pt(py)(NH_3)(NO_2)(Cl)(Br)(I)]$ – 15

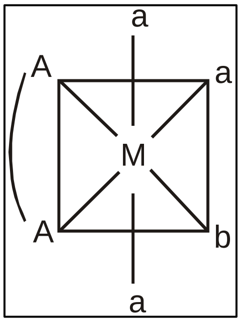
Note: Ma_6 and Ma_5b have only one form.

(II) Compounds containing bidentate ligand and unidentate ligands.

(i) $M(AA)a_3b$ – Two geometrical isomers are possible.

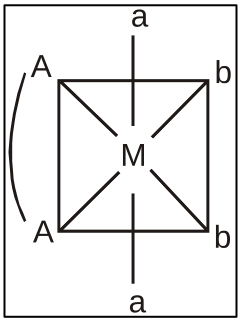


bTa

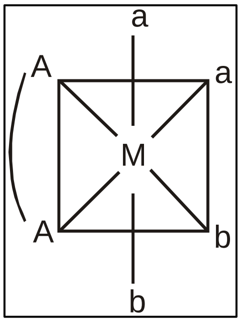


aTa

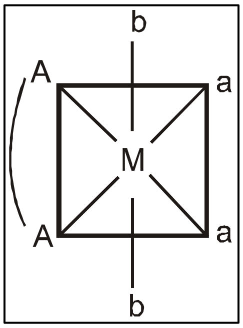
(ii) $M(AA)a_2b_2$ – Three geometrical isomers are possible.



aTa



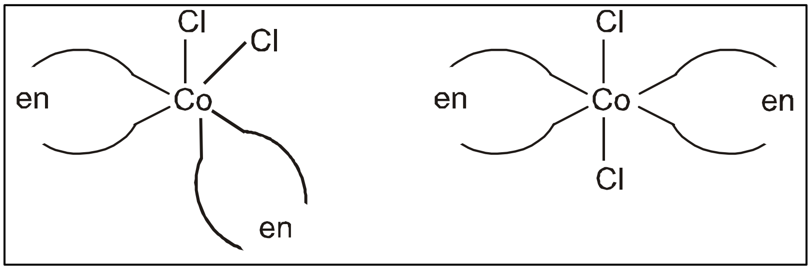
aTb



bTb

Note : With $[M(AA)b_4]$, only one form is possible. M(AA)abcd have six geometrical isomers.

(iii) $M(AA)_2a_2$ – Two geometrical isomers are possible.



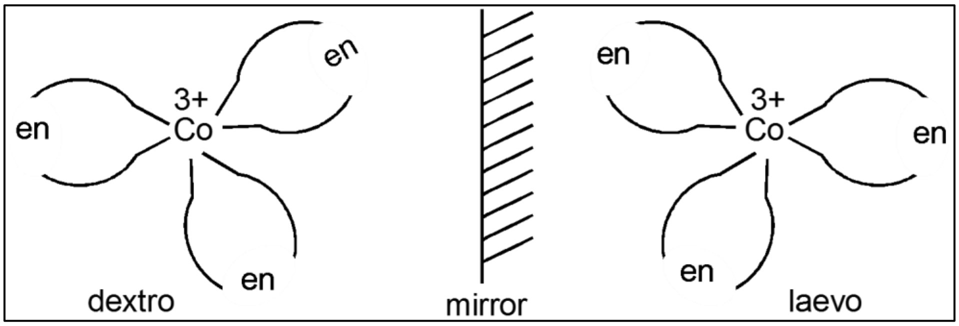
Geometrical isomers (cis and trans) of $[CoCl_2(en)_2]$

OPTICAL ISOMERISM

A coordination compound which can rotate the plane of polarized light is said to be optically active. When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarized light are said to exhibit optical isomerism and the molecules are optical isomers. Optical isomers are mirror images that cannot be superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral. This is due to the absence of elements of symmetry in the complex. The two forms are called dextro(d) and laevo(l) depending upon the direction they rotate the plane of polarised light in a polarimeter (d rotates to the right, to the left).

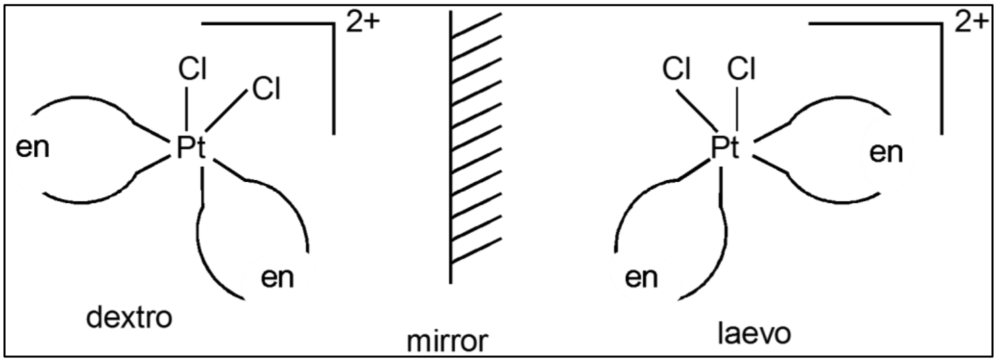
Octahedral complex:

Optical isomerism is common in octahedral complexes involving didentate ligands. For example, $[Co(en)_3]^{3+}$ has d and ℓ forms as given below.



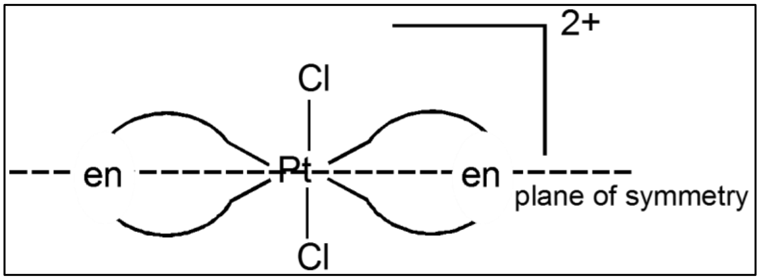
d and ℓ of $[Co(en)_3]^{3+}$

Cis-isomer of $[PtCl_2(en)_2]^{2+}$ show optical isomerism as shown below because of the absence of plane of symmetry as well as centre of symmetry.

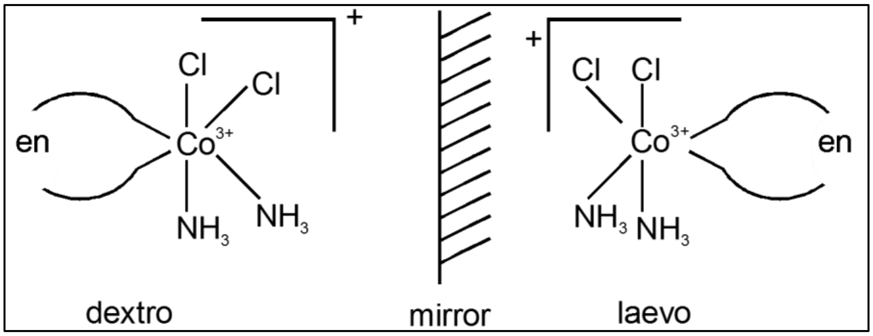


d and ℓ of cis-$[PtCl_2(en)_2]^{2+}$

But trans isomer of $[PtCl_2(en)_2]^{2+}$ does not show optical isomerism.

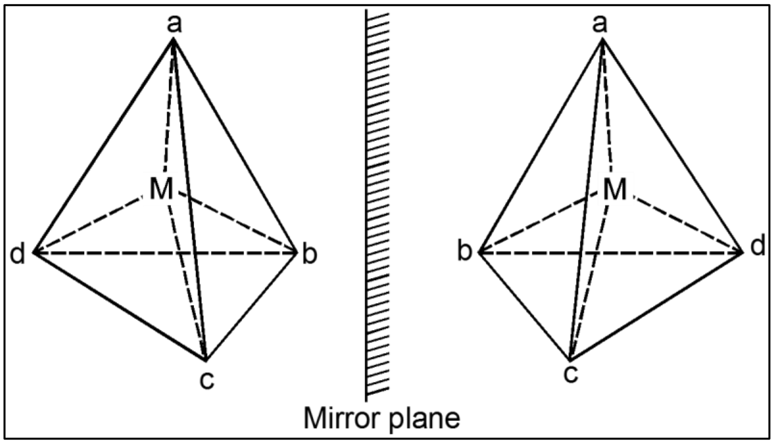


cis-$[Co(NH_3)_2Cl_2(en)]^+$ can show optical isomerism due to the absence of plane of symmetry as well as centre of symmetry.

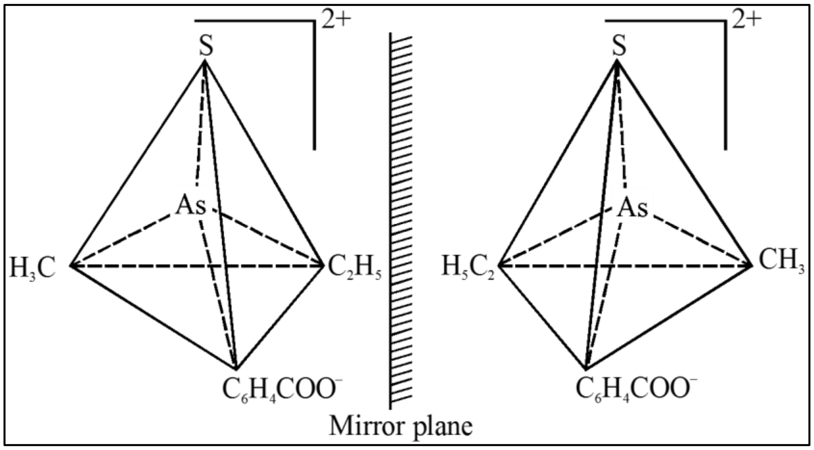


Tetrahedral complex:

Optical isomerism is expected in tetrahedral complexes of the type [Mabcd] analogous to tetrahedral carbon atom.



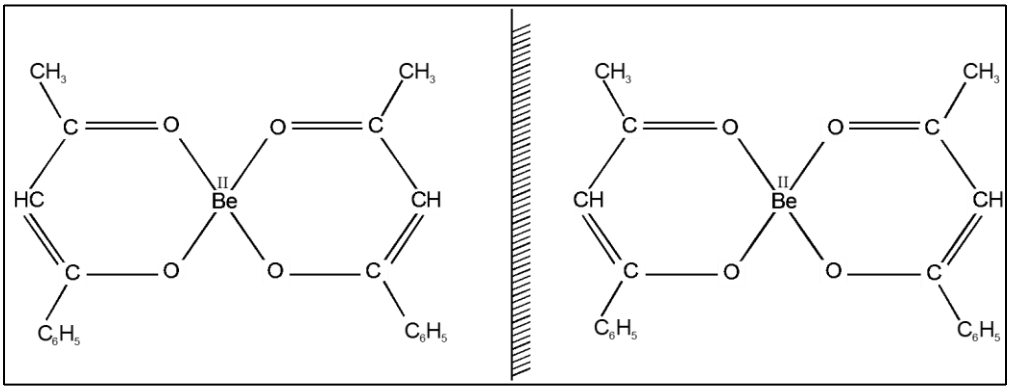
(i) For example $[As(\textbf{III})(CH_3)(C_2H_5)(S)(C_6H_4COO)]^{2+}$, shows optical isomerism as given below.



Here it may be noted that 4 different groups round the central metal ion are not the only requirement to make the complex to show mirror-image isomerism. All that is required is that the molecule should be asymmetric

(i.e., unsymmetrical), i.e., it should have no plane of symmetry so that it can exist in two mirror-image forms.

(ii) Tetrahedral complexes of Be, B, Cu(II) and Zn(II) with unsymmetrical bidentate ligands have been resolved into optical isomers. In order for the complex to be chiral, the chelating ligand must be unsymmetrical (not necessarily asymmetric or chiral, itself). An example is bis(benzoylacetate) Be(II) complex, $[(C_6H_5COCHCOCH_3)_2Be]^0$ whose mirror-image isomers are shown in figure.



Here it may be noted from the figure that the complex has no centre or plane of symmetry and the two forms are not superimposable on each other. This explains the resolution of the complex into d-and ℓ-forms.

Square planar complex:

Square planar complexes are rarely found to show the optical isomerism. The plane formed by the four ligating atoms and the metal ion is considered to be a mirror plane and thus prevents the possibility of chirality. Although, square planar complexes seldom show optical isomerism, yet a four -coordinated complex of Pt (II),

$[Pt\ (II)(NH_2.CH(C_6H_5).CH(C_6H_5NH_2).(NH_2.CH_2.C(CH_3)_2.NH_2)]^{2+}$

which has square-planar shape has been resolved into two forms by Mills and Quibell in 1935.