Chapter-23

Coordination Chemistry (Geometrical Isomerism)

Arijit Das
Department of Chemistry, Bir Bikram Memorial College, Agartala, Tripura, India
Email: arijitdas78chem@gmail.com

Isomerism in co-ordination compounds (iso-equal, meros – parts):

Two or more compounds having same molecular formula (same molecular weight) but different structural formula and property are known as *isomers* and the phenomenon is called *isomerism*.

Stereoisomerism

1. **Geometrical isomerism**: In metal complex the ligand may occupy different types of positions around the central metal atom which are either adjacent to each other (*cis isomer*) or opposite to one another (*trans isomer*). So geometrical isomerism is also known as '*cis-trans*' isomerism.

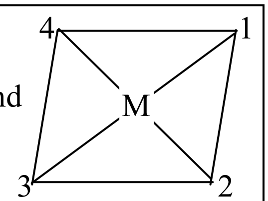
Geometrical isomerism is very much common in coordination compounds for coordination number 4 and 6.

1. Geometrical isomerism in 4-coordination compounds:

A) Tetrahedral complexes: **They do not show geometrical isomerism** due to all four ligands are equidistant to one another.

B) Square planar complexes: Complexes with general formula **Ma_4, Ma_3b, Mba_3 do not show *cis-trans* isomerism** due to equivalent spatial arrangement. *Cis* and *trans* positions in square planar geometry is given below:

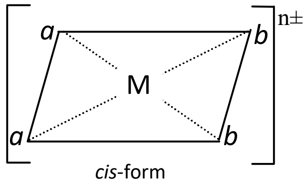
Note : In square planar complexes, there are four cis positions and two trans positions **1-2 = 2-3 = 3-4**
1-3 = 2-4 = *trans* **= 1-4 = *cis***



In the general formula below (a,b) represents monodentate ligands, (aa) represent symmetrical bidentate ligand and (ab) represent unsymmetrical bidentate ligand.

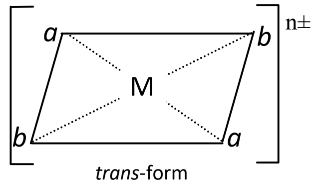
Following type of square planar complexes show cis-trans isomerism.

a) $[Ma_2b_2]^{n\pm}$ type:



cis-form

and

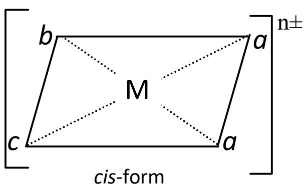


trans-form

(*cis-trans* isomer w.r.t. 'a' and 'b')
(Here *M* = metal ion, *a, b* = monodentate ligand)

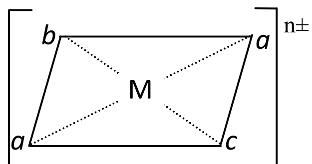
e.g. $[Pt(NH_3)_2Cl_2]$, $[Pd(NH_3)_2(NO_2)_2]$, $[Ni(NH_3)_2Cl_2]$

b) $[Ma_2bc]^{n\pm}$ type:



cis-form

and



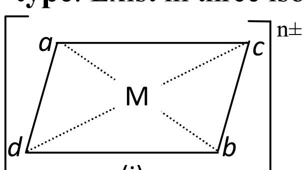
trans-form

Here *M* = metal ion*; a* = neutral ligand (NH_3, Py, H_2O); *b, c* = anionic ligand (Cl^-, Br^-, NO_2^-, SCN^-)

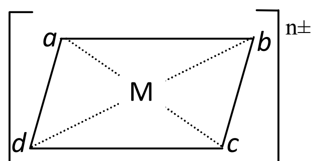
(*cis-trans* isomer w.r.t. 'a')

e.g. $[Pt(Py)_2(NO_2)Cl]$, $[PtCl(NH_3)_2Br]$ etc.

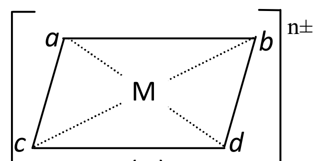
c) $[Mabcd]^{n\pm}$ type: Exist in three isomeric *trans* form.



(i)



(ii)

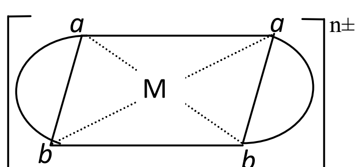


(iii)

The structure of these isomers can be written **by fixing the position of one ligand (a) at one corner and placing the other ligands *b, c, d* trans to it.**

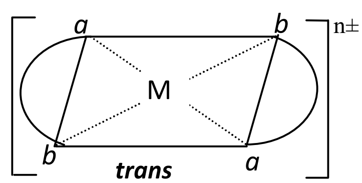
e.g. $[Pt(NO_2)(Py)(NH_2OH)NH_3]^+$, $[Pt(NH_3)(Py)(Cl)(Br)]$ etc.

d) $[M(ab)_2]^{n\pm}$: The square planar complexes having unsymmetrical bidentate ligand also show *cis-trans* isomerism as -



cis

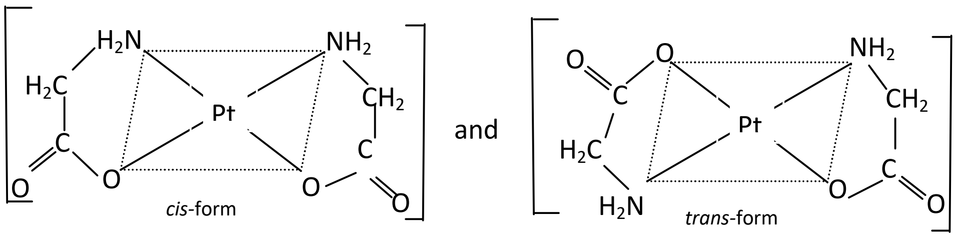
and



trans

Here M = central metal ion; (ab) = unsymmetrical bidentate ligand such as glycinato (gly^{-1}) etc.

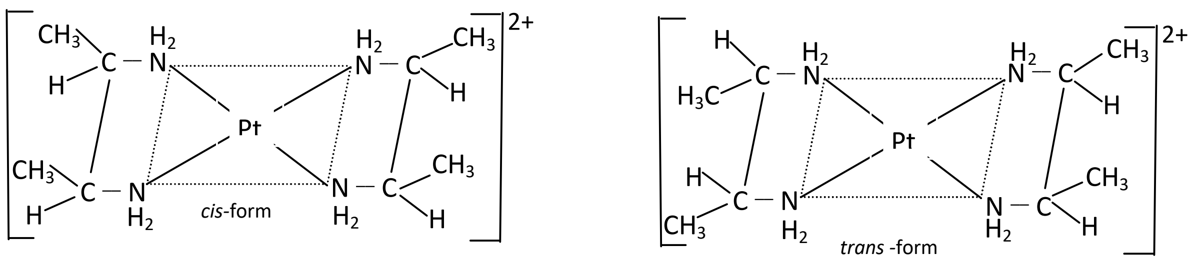
e.g. *cis-trans* isomer of [Pt(gly)$_2$] is given below:



(*cis-trans* isomer w.r.t. donor atom 'N' and 'O')

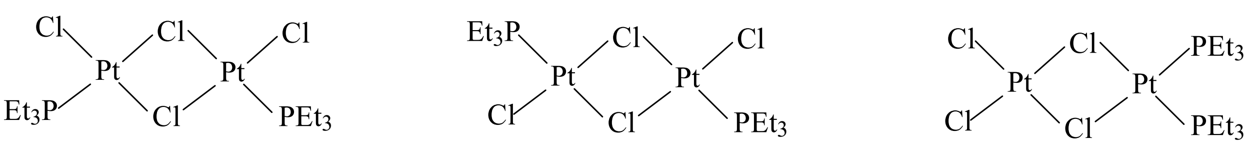
e) [*M*(*aa*)$_2$]$^{n\pm}$ type: Square planar complex having symmetrical bidentate chelating ligand also shows *cis-trans* isomerism.

e.g. *cis-trans* isomer of [Pt(NH$_2$CHCH$_3$.CHCH$_3$NH$_2$)$_2$]$^{2+}$ is shown below.



(*cis-trans* isomer w.r.t. peripheral –CH$_3$ group)

f) [*M$_2$a$_2$X$_4$*] type: Bridged binuclear square planar complexes also show *cis-trans* isomerism as follows –



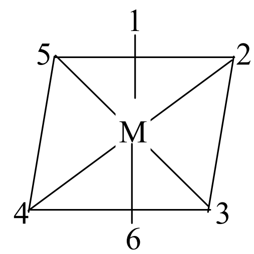
cis-form **(i)** *trans*-form **(ii)** unsymmetrical form **(iii)**

(*cis-trans* isomer w.r.t. peripheral – Cl and PEt$_3$ group)

This molecule also show unsymmetrical isomers which are shown above **(iii)**.

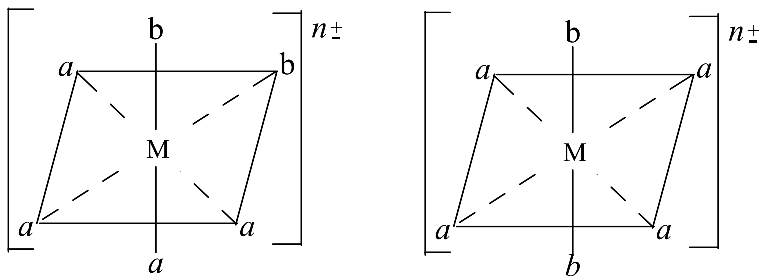
2. Geometrical isomerism in 6-coordination compounds (octahedral compounds):
Complexes with general formula **Ma_6, Ma_5b, Mba_5 do not show *cis-trans* isomerism.**

Note : We know that a regular octahedron has eight faces and six equivalent vertices. In this complex, metal ion is placed at the centre and ligands are placed at the vertices. The position of *cis* and *trans* are
1-2 = 1-5 = 2-5 = 2-3 = 3-4 = 3-6 = 4-6 = 4-5 = *cis*
1-6 = 2-4 = 3-5 = *trans*



Following type octahedral compounds show cis-trans isomerism.

a) $[Ma_4b_2]^{n\pm}$ type: In *cis* isomer two 'b' are adjacent in position while in *trans* two 'b' are opposite to each other.

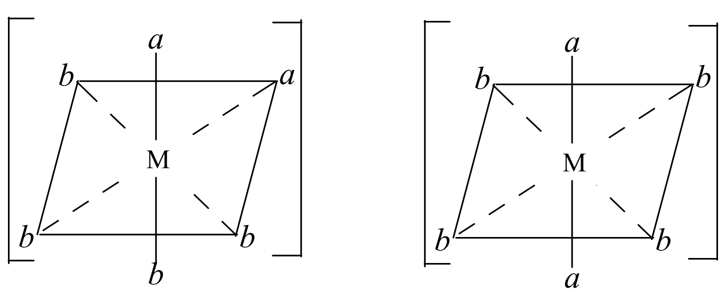


cis-form (1,2-isomer) *trans*-form (1,6-isomer)

(*cis-trans* isomer w.r.t. 'b')

e.g. $[Co(NH_3)_4Cl_2]^+$ and $[Fe(CN)_4(NH_3)_2]^{-1}$

b) $[Ma_2b_4]$ type:

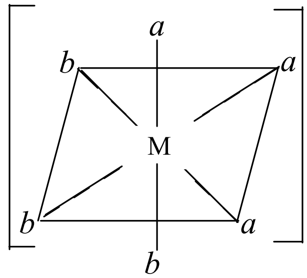


cis-form (1,2-isomer) *trans*-form (1,6-isomer)

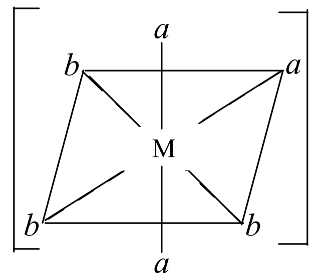
(*cis-trans* isomer w.r.t. 'a')

e.g. $[Co(NO_2)_2(NH_3)_4]$.

c) $[Ma_3b_3]^{n\pm}$ type:



cis-form (facial isomer)

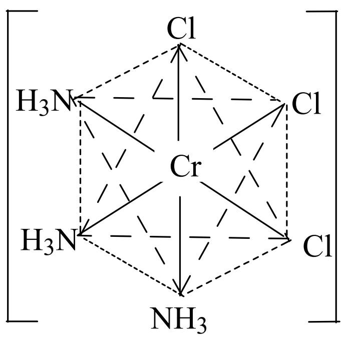


trans-form (peripheral isomer)

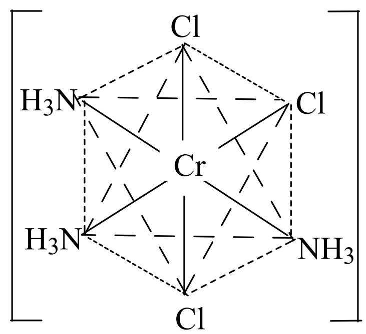
(***same ligands placed in two opposite*** **triangular** ***faces*** **)**

(triangular ***faces disturbed by exchange of one ligand*** **)**

e.g. $[Cr(NH_3)_3Cl_3]$ is found in two forms to one isomer, the three Cl^- ions are on triangular face and the three NH_3 molecules are on the opposite triangular face of the regular tetrahedron. So it is known as facial isomer (*cis* isomer). While in other isomer the Cl^- ions are arranged around on the edge of octahedron and NH_3 on opposite edges. So it is known as *peripheral isomer* (*trans* isomer). **It can also be named as Fac - Mer Isomerism, where 'Fac' denotes *cis* form and 'Mer' denotes *trans* form as** shown below:



facial isomer



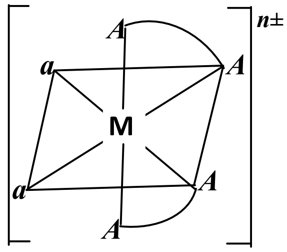
peripheral isomer

(Fac or *cis* form)

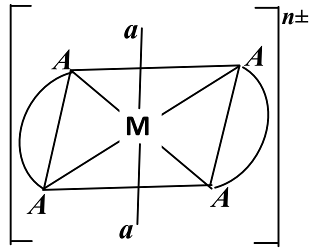
(Mer or *trans* form)

In the 'Fac Isomer' (Fac = Face), the 3 similar ligands are arranged at the 3 corners of a face of the octahedral and in the 'Mer Isomer', the 3 similar ligands are arranged in an arc around the middle of the octahedron (Mer = Meridian).

d) $[M(AA)_2a_2]^{n\pm}$ type: Octahedral complexes having monodentate (a) and symmetrical bidentate ligands (AA) also show *cis-trans* isomerism.



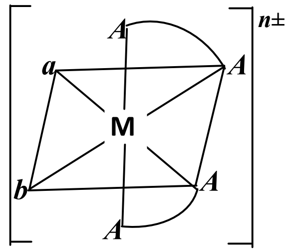
(*a's cis*)



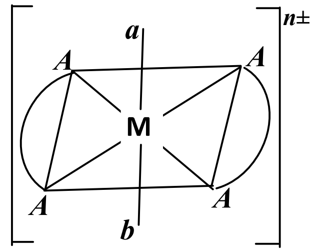
(*a's*

e.g. $[Co(en)_2Cl_2]^+$, $[Co(en)_2(NO_3)_2]^+$, $[Co(C_2O_4)_2Cl_2]^-$ etc.

e) $[M(AA)_2ab]^{n\pm}$ type: The complexes having bidentate ligand (*AA*) and two different monodentate ligands (*a, b*) show *cis-trans* isomerism as follows



(*cis*-form)

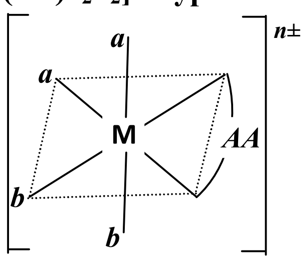


(*trans* -form)

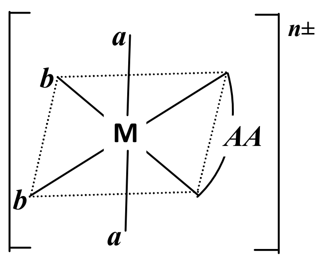
(*cis-trans* isomer w.r.t. symmetrical bidentate ligand 'AA')

e.g. $[Co(en)_2(NH_3)(Cl)]^{2+}$, $[Ru(Py)(C_2O_4)_2(NO)]$ etc.

f) $[M(AA)a_2b_2]^{n\pm}$ type:



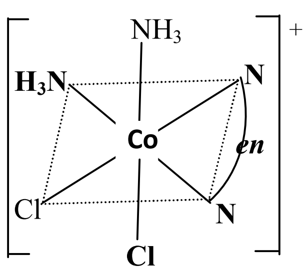
(*cis*-form)



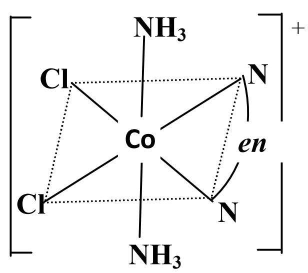
(*trans*-form)

(*cis-trans* isomer w.r.t. monodentate ligand 'a')

e.g. $[Co(en)(NH_3)_2(Cl_2)]^+$ having following *cis-trans* form.

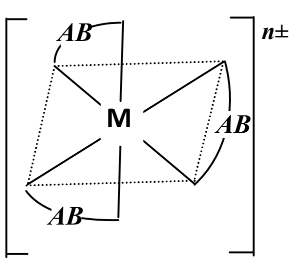


(*cis*-isomer)

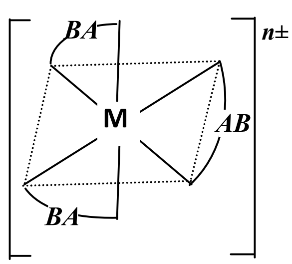


(*trans*-isomer)

g) $[M(AB)_3]^{n\pm}$ type: Octahedral complexes having unsymmetrical bidentate chelating agent '*AB'*, (*A* and *B* show two different co-ordinating atoms of the ligand) show *cis-trans* isomerism.

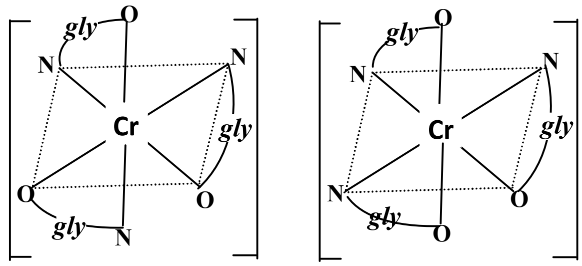


(*cis*isomer)



(*trans*-isomer)

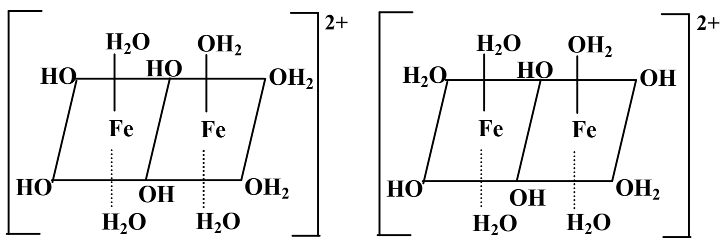
e.g. [Cr(gly)$_3$] → triglycinatochromium (III) have following *cis* and *trans* isomer.



(*cis*- (*trans*-isomer)

(*cis-trans* isomer w.r.t. donor atom)

h) [M$_2$a$_4$b$_6$]$^{n\pm}$ type: In case of polynuclear complex, e.g., $[Fe_2(OH)_4(H_2O)_6]^{2+}$, the geometrical isomers are given below.



***cis* isomer** ***trans* isomer**

(cis w.r.t. left hand side OH and right hand side H_2O; trans w.r.t. diagonally opposite OH and H_2O)

In the above example the two OH groups act as bridges and correct respective octahedral components of the overall structure. **This isomerism is also known as *bridge isomerism*.**

Related Questions

Q.1. The one that is not expected to show geometrical isomerism is
a) $[Ni(NH_3)_4(H_2O)_2]^{2+}$
b) $[Ni(en)_3]^{2+}$
c) $[Ni(NH_3)_2Cl_2]$
d) $[Pt(NH_3)_2Cl_2]$
***Ans*. (c) $[Ni(NH_3)_2Cl_2]$, doesn't exhibit geometrical isomerism because it has tetrahedral geometry.**

Q.2. The complex that can show *fac*- and *mer*-isomers is:
a) $[Pt(NH_3)_2Cl_2]$ **b) $[Co(NH_3)_3(NO_2)_3]$**
c) $[Co(NH_3)_4Cl_2]^+$ **d) $[CoCl_2(en)_2]$**
***Ans*. (*b*)**
Octahedral coordination entities of the type [Ma_3b_3] shows geometrical isomers: *fac* and *mer* isomers. Among the given complexes, the complex with general formula [Ma_3b_3] is $[Co(NH_3)_3(NO_2)_3]$.

Q.3. Among (A) – (D), the complexes that can display geometrical isomerism are

(A) $[Pt(NH_3)_3Cl]^+$ (B) $[Pt(NH_3)Cl_5)^-$

(C) $[Pt (NH_3)_2Cl(NO_2)]$ (D) $[Pt(NH_3)_4ClBr]^{2+}$

a) (D) and (A) b) (C) and (D)

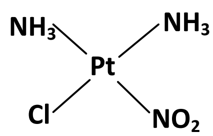
c) (A) and (B) d) (B) and (C)

***Ans*. (*b*)**

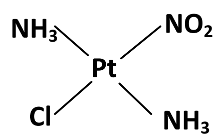
(A) $[Pt(NH_3)_3Cl]^+$: No geometrical isomerism
(B) $[Pt(NH_3)Cl_5]^-$: No geometrical isomerism
(C) $[Pt(NH_3)_2Cl (NO_2)]$: has 2 geometrical isomers
(D) $[Pt(NH_3)_4 ClBr]^{2+}$: exhibit geometrical isomerism.

All Pt^{2+} complexes with coordination number equals to 4 are square planar.

(C) The two NH_3 ligands could arrange in *cis* or *trans* positions.
There are two geometrical isomers.



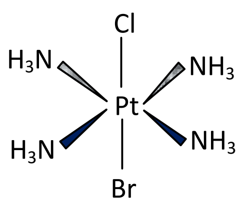
cis



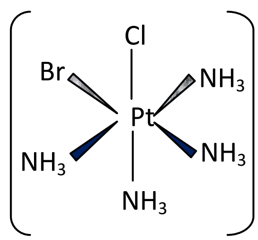
trans

(D) $[Pt(NH_3)_4 ClBr]$: Two geometrical isomers Coordination number = 6,Octahedral geometry.

02 geometrical isomers *cis* or *trans w.r.t. –Cl and Br because they are minimum in number.*



trans



Cis

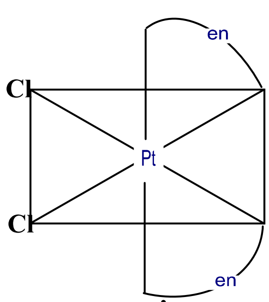
Q.4. The species that can have a *trans*-isomer is (en = ethane–1, 2-diamine, ox = oxalate)

a) $[Pt(en)Cl_2]$ b) $[Cr(en)_2(ox)]^+$

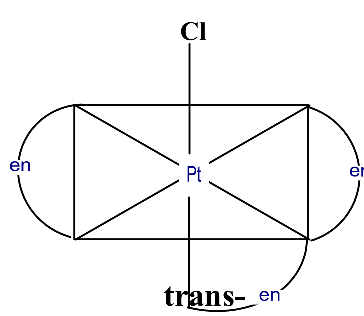
c) $[Pt(en)_2Cl_2]^{2+}$ d) $[Zn(en)Cl_2]$

***Ans*. (*c*)**

$[Pt(en)_2(Cl_2)]^{2+}$ with formula $[M(aa)_2b_2]$ can show geometrical isomerism as follows:



**cis-
(optically
active)
(I)**



**trans-
(optically
inactive)
(II)**

Q.5. The number of geometric isomers that can exist for square planar $Pt(Cl)(py)(NH_3)(NH_2OH)^+$ is (py = pyridine)

a) 2 b) 3 c) 4 d) 6

Ans. b), it belongs to $[Mabcd]^{n\pm}$ type

Q.6. Which one of the following complex ions has geometrical isomers?
a) $[Co(en)_3]^{3+}$
b) $[Ni(NH_3)_5Br]^+$
c) $[Co(NH_3)_2(en)_2]^{3+}$
d) $[Cr(NH_3)_4(en)]^{3+}$
Ans. c), it belongs to $[M(AA)_2a_2]^{n\pm}$ type.

Reference Books:

1. Introduction to Coordination Chemistry, Geoffrey A. Lawrance

2. Coordination chemistry, Joan Ribas Gispert

3. Coordination Chemistry, 20: Invited Lectures Presented at the 20th International Conference on Coordination Chemistry, Calcutta, India, 10-14 December 1979, D. Banerjea

4. Comprehensive Coordination Chemistry III, Gerard Parkin, Edwin C Constable, Lawrence Que

5.https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_and_Websites_(Inorganic_Chemistry)/Coordination_Chemistry/Complex_Ion_Equilibria/Stability_of_Metal_Complexes_and_Chelation

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