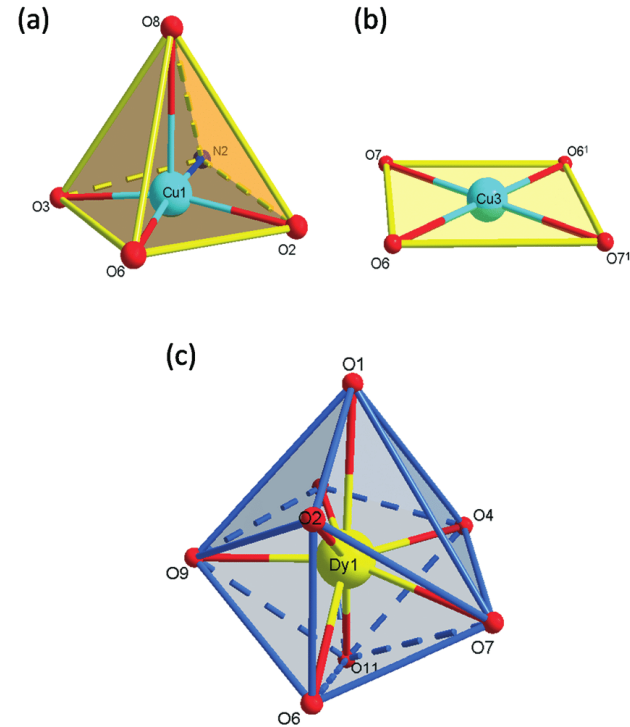
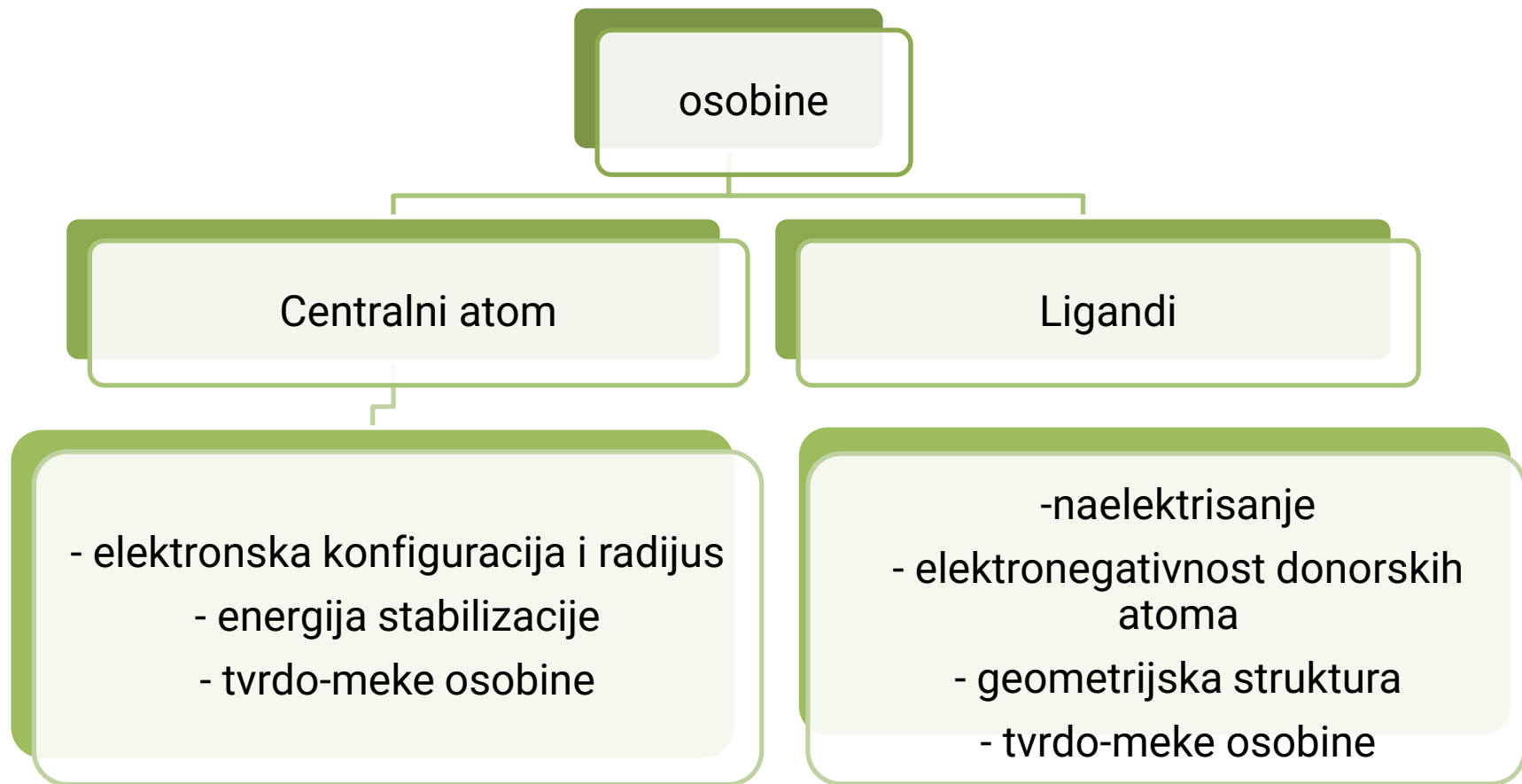


GEOMETRIJSKA STRUKTURA KOMPLEKSNIH JEDINJENJA

Koliko veza metal-ligand treba formirati i kako te veze treba prostorno rasporediti da bi se dobila najveća moguća stabilizacija?



GEOMETRIJSKA STRUKTURA KOMPLEKSNIH JEDINJENJA



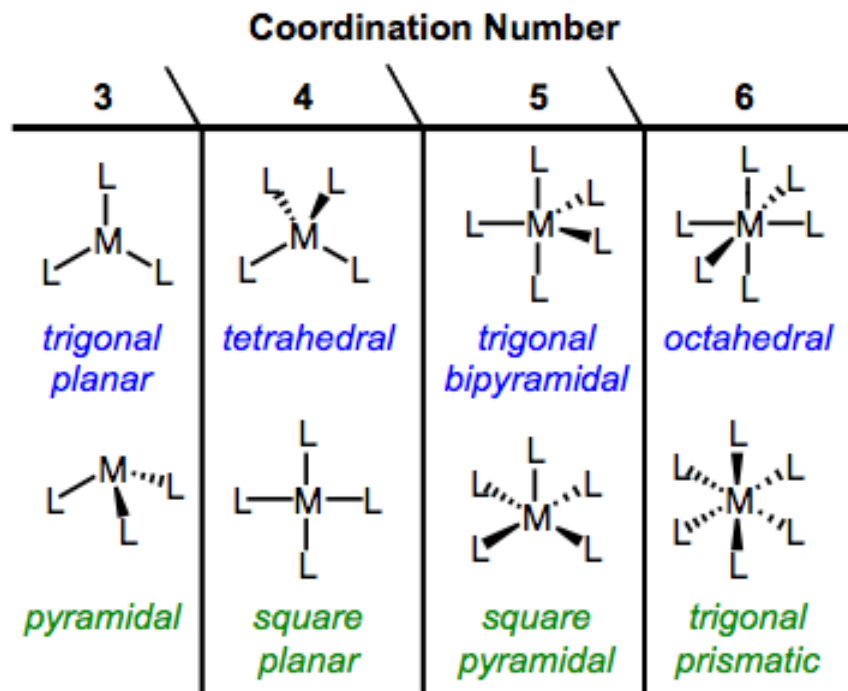
- Mnogi metali imaju tendenciju da ispoljavaju poželjne koordinacione brojeve, koji zavise od njihovog oksidacionog stanja i radijusa

Radius Ratio	Coordination number	Type of void	Example
< 0.155	2	Linear	
0.155 - 0.225	3	Triangular Planar	B ₂ O ₃
0.225 - 0.414	4	Tetrahedral	ZnS, CuCl
0.414 - 0.732	6	Octahedral	NaCl, MgO
0.732 - 1.000	8	Cubic	CsCl, NH ₄ Br
1	12	Close packing (ccp and hcp)	metals

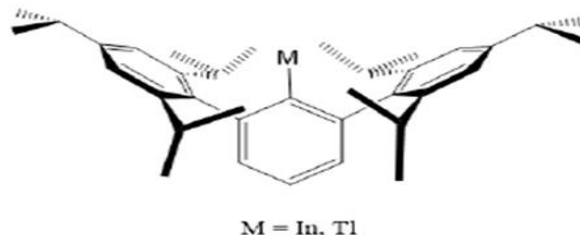
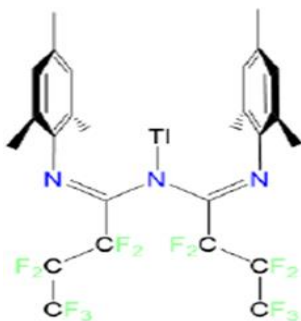
Relationship between Radius Ratio and Coordination Number

VRSTE GEOMETRIJSKIH STRUKTURA

Važno je prepoznati da svaka geometrija ima određeni koordinacioni broj

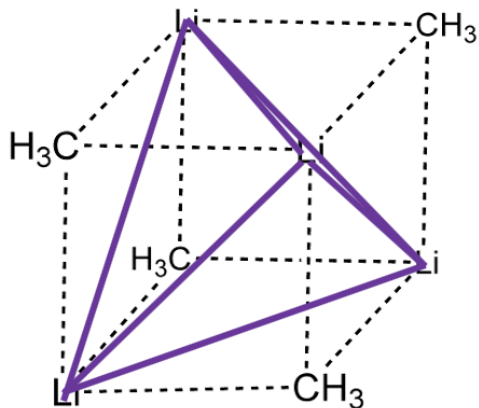
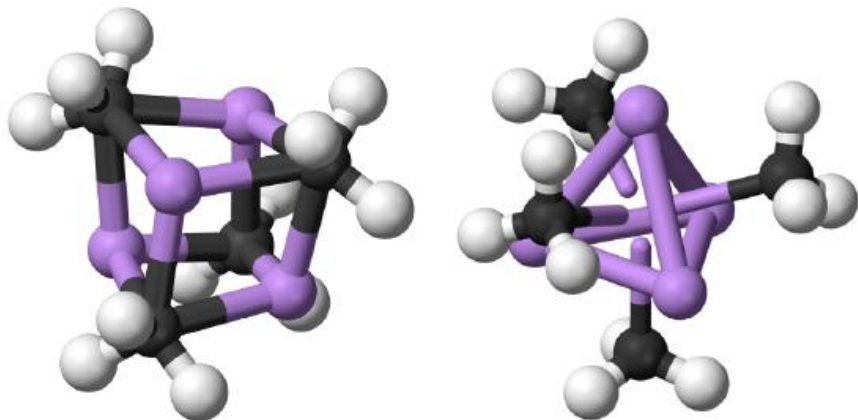


Koordinacioni broj 1



- Izuzetno rijetko se javljaju u praksi
- U gasnoj fazi pod uslovima visokog razblaženja, gde su metal – ligand interakcije ograničene
- Kompleksi indijuma (In) i talijuma (Tl) sa glomaznim ligandima triazapentadienil i 2,6-tris(2,4,6-triizopropilfenil) benzen

Koordinacioni broj 1

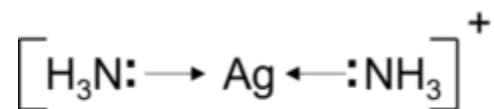


Structure in methyllithium inscribed into a cube.
(<https://commons.wikimedia.org/wiki/File:MeLi.png>)

- Kada postoji jedna tačka vezivanja, tada obično postoje reaktivna koordinaciona mesta na metalnom jonu koja dovode do formiranja klastera.
- Ovo smanjuje energiju i povećava koordinacioni broj
- tetraedarski klaster Li_4Me_4 .

Koordinacioni broj 2

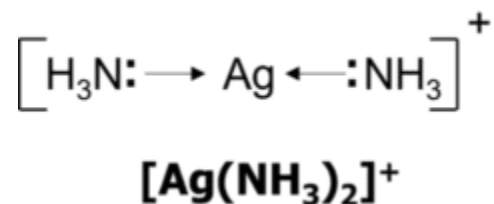
Linearni kompleksi



- posjeduju 2 M-L hemijske veze
 - ugao od 180°
 - sp hibridizacija
- Joni sa d^{10} konfiguracijom
- joni prelaznih metala niskog oksidacionog stanja (+1 i rjeđe +2) poput Cu^+ , Ag^+ , Au^+ , and Hg^{2+} i Be^{2+} , sa NH_3 , Cl^- , CN^- donorskim ligandima

Koordinacioni broj 2

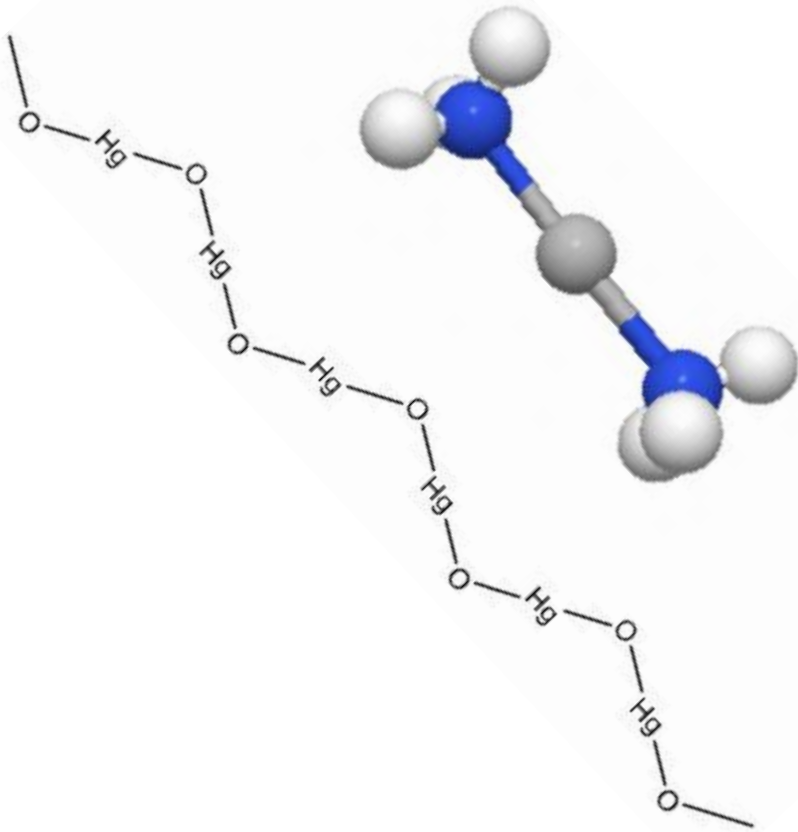
Linearni kompleksi



Predstaviti hibridizaciju orbitala Ag u datom linearnom kompleksu.

Koordinacioni broj 2

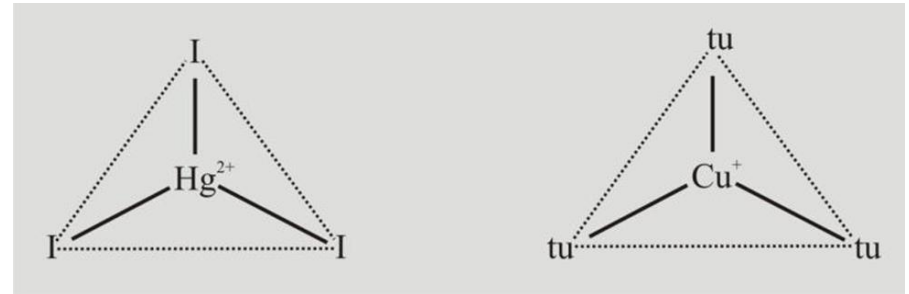
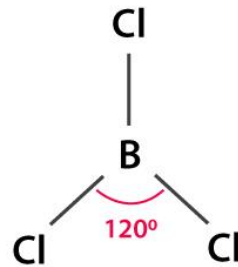
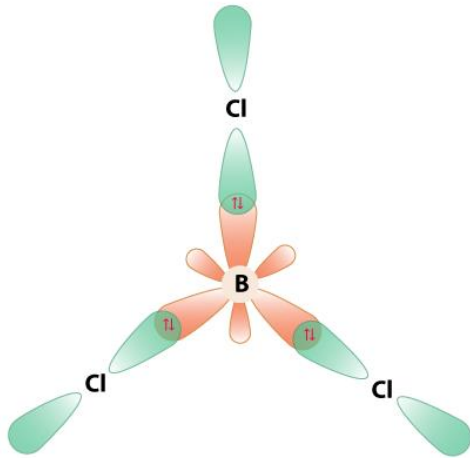
Linearni kompleksi



- Linearna koordinacija se ne nalazi samo u molekularnim jedinjenjima već i u proširenim čvrstim materijama.
- HgO i HgS prave cik-cak lance linearno koordinovanog Hg^{2+} . Savijanje lanca se dešava kod oksidnih anjona, zbog nevezivnih parova elektrona na O.

Koordinacioni broj 3

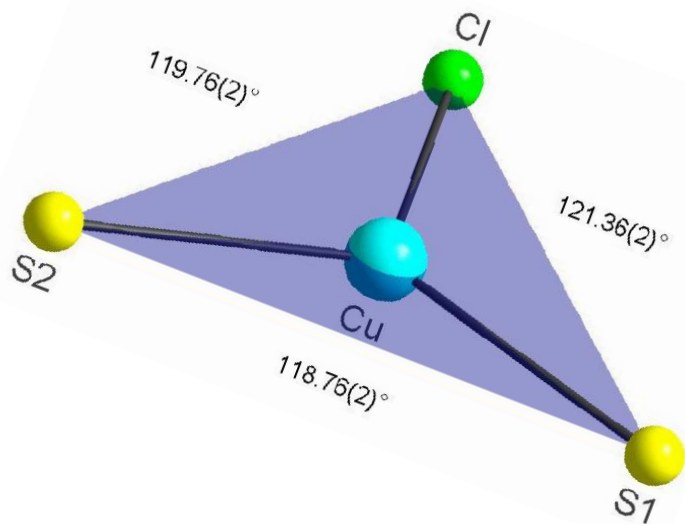
Trigonalno planarni kompleksi



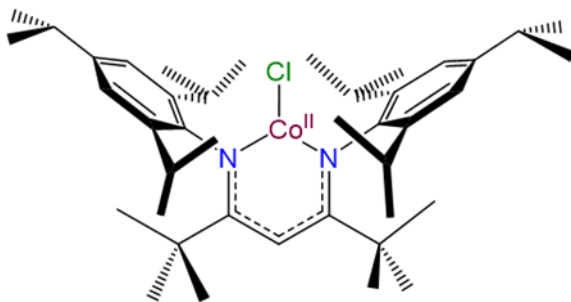
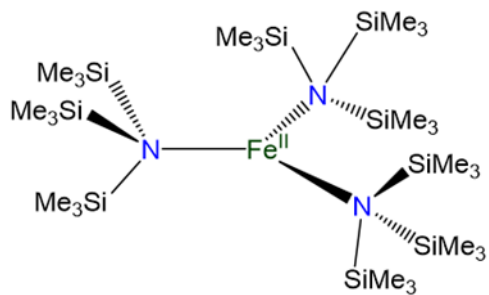
- 3 ML veze koje leže u jednoj ravni
 - zaklapaju ugao od 120°
 - sp^2 hibridizacija
- Ovo je rijetka strukturna grupa kompleksa i uključuje jone prelaznih metala sa mnoštvom d elektrona (d^8 , d^9 i najčešće d^{10}).
 - Grade ih sledeći joni: Cu^+ , Ag^+ , Au^+ , Hg^{2+} i $Pt(0)$.

Koordinacioni broj 3

Trigonalno planarni kompleksi

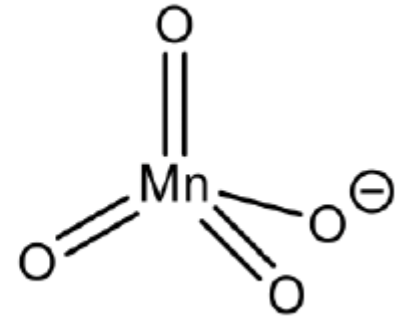
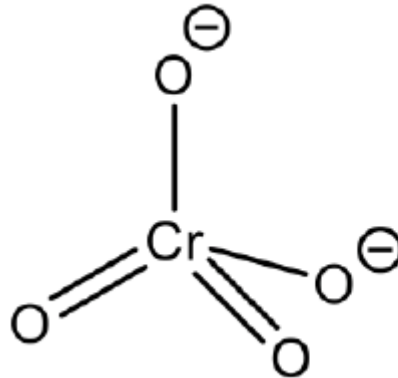
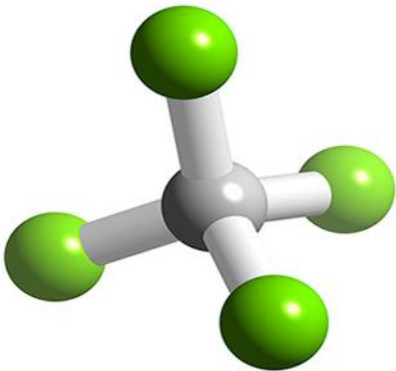


- Kada u sastav kompleksa ulaze složeni ligandi, može doći do pojave sfernih smetnji, koje dovede do odstupanja od pravilne geometrijske strukture.



Koordinacioni broj 4

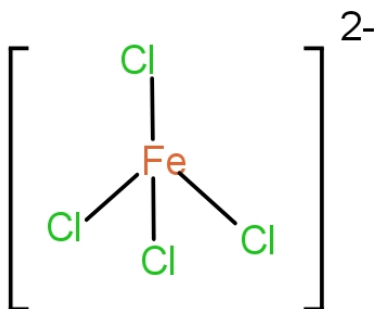
Tetraedarski kompleksi



- zaklapaju ugao od $109^{\circ} 28'$
 - sp^3 hibridizacija
- Veoma zastupljena, spada u stabilnije geometrijske strukture
 - Grade ih elementi p, d i f el. konfiguracije

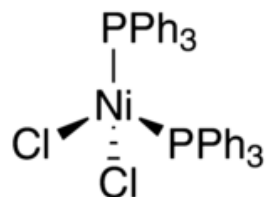
Koordinacioni broj 4

Tetraedarski kompleksi



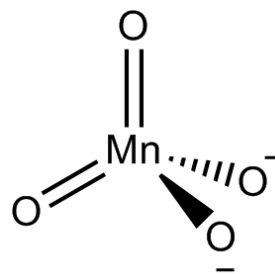
Tip ML_4^{n-}

- $[\text{FeCl}_4]^{2-}$
- $[\text{CoX}_4]^{2-}$
- $[\text{CuX}_4]^{2-}$
- $[\text{NiX}_4]^{2-}$
- $[\text{MnX}_4]^{2-}$



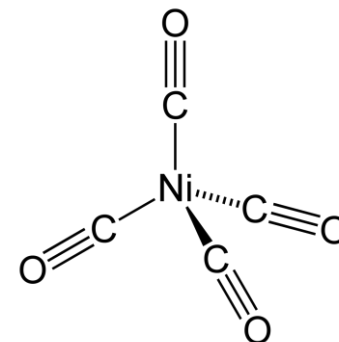
$[\text{Ni}(\text{PPh}_3)_2\text{L}_2]$

fenilfosfinskim
tipom liganda



MnO_4^-

Kompleksi u
obliku okso
anjona

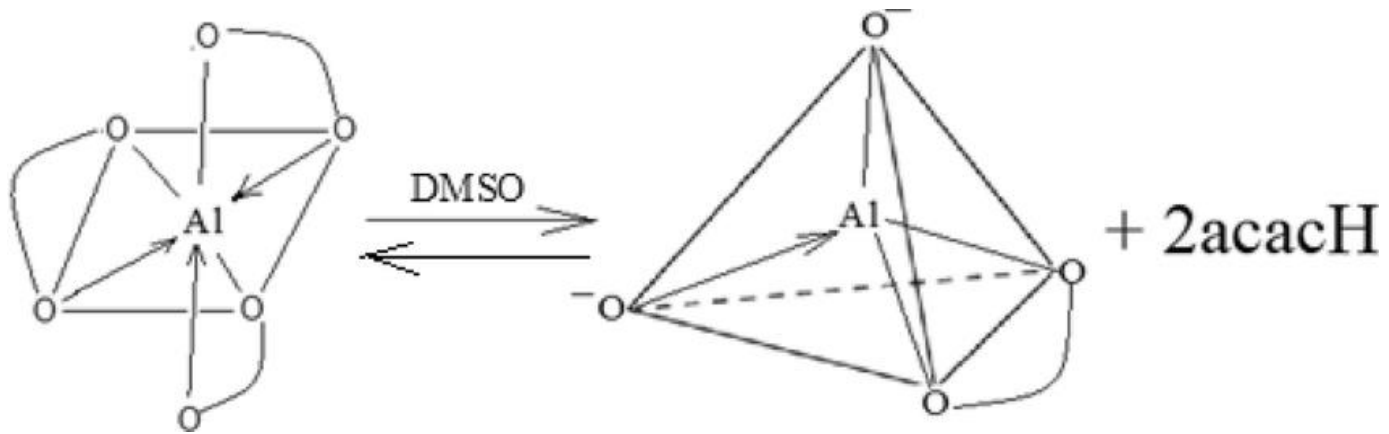


$[\text{Ni}(\text{CO})_4]$

Oksidaciono
stanje
centralnog
atoma je 0

Koordinacioni broj 4

Tetraedarski kompleksi



- Neki tetradarski kompleksi koordinuju molekule rastvarača i prelaze u oktaedarske komplekse.
- Ovaj prelaz se vjerovatno odigrava preko kvadratno planarne strukture.

Koordinacioni broj 4

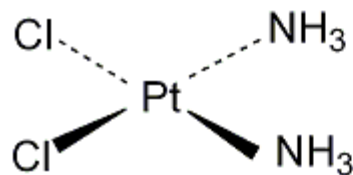
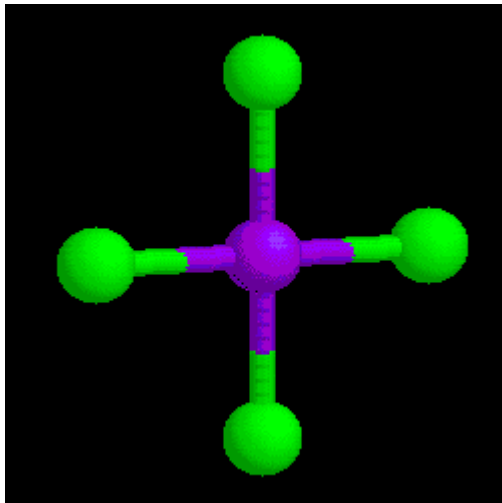
Tetraedarski kompleksi



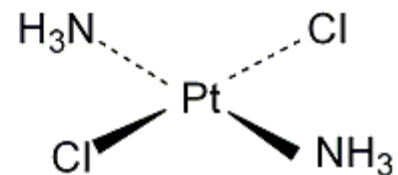
Na primjeru vodenog rastvora tetraakvakobalt(II)-jona predstaviti mogućnost vezivanja molekula rastvarača za CA. Kako se mijenja geometrijska struktura kompleksa u tom slučaju?

Koordinacioni broj 4

Kvadratno planarni kompleksi



Cisplatin



Transplatin

- 4 veze ML zaklapaju ugao od 90°
 - dsp^2 hibridizacija
- Grade ih elementi d^4 (Mn(III)), d^8 (Pt (II), Pd(II), Ni(II)), d^9 (Cu(II), Ag(II), Au(II))
 - Neki zemnoalkalni metali sa helatnim ligandima

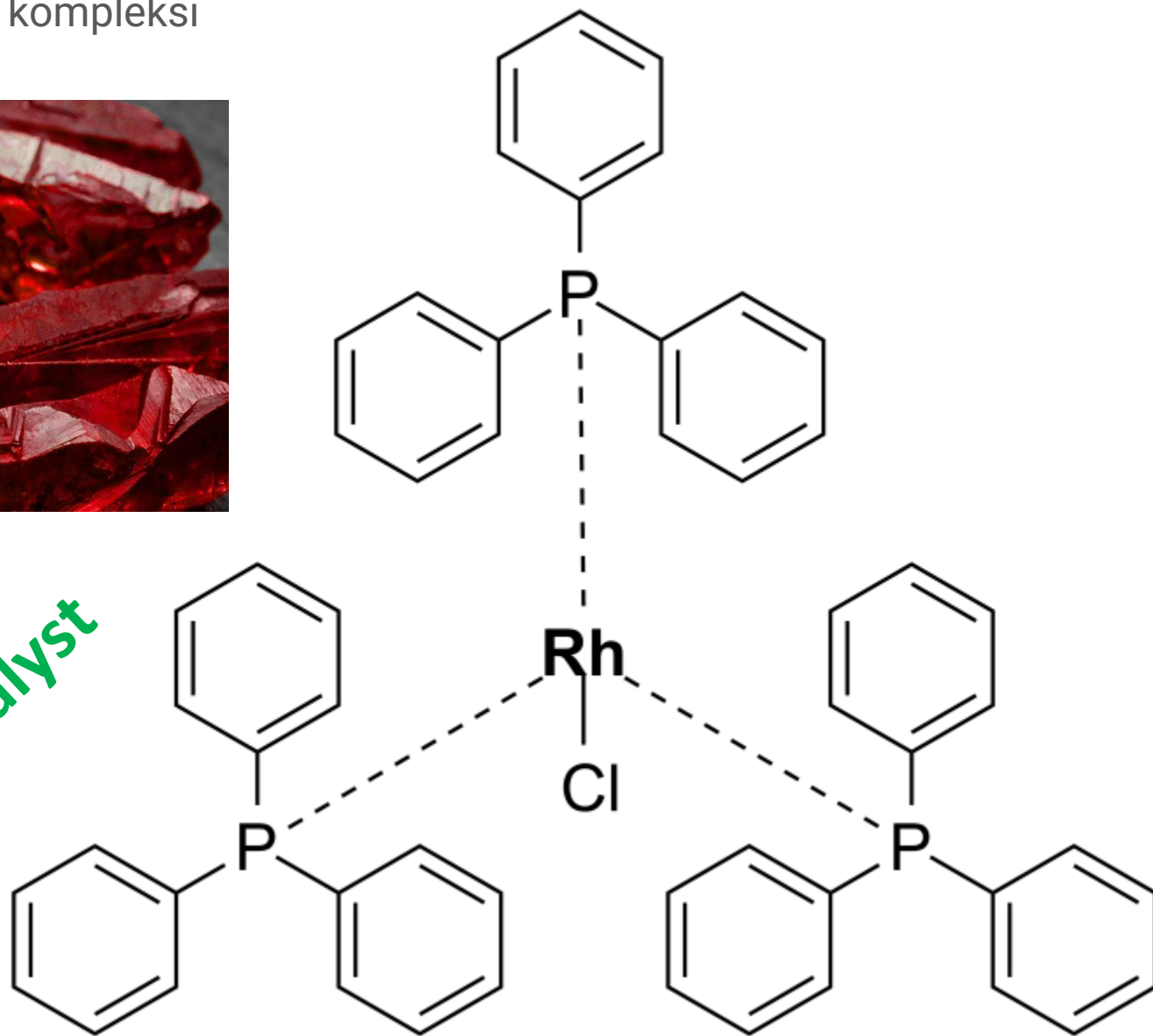
Koordinacioni broj 4

Kvadratno planarni kompleksi



$\text{Rh}(\text{PPh}_3)_3\text{Cl}$

Wilkinson's catalyst



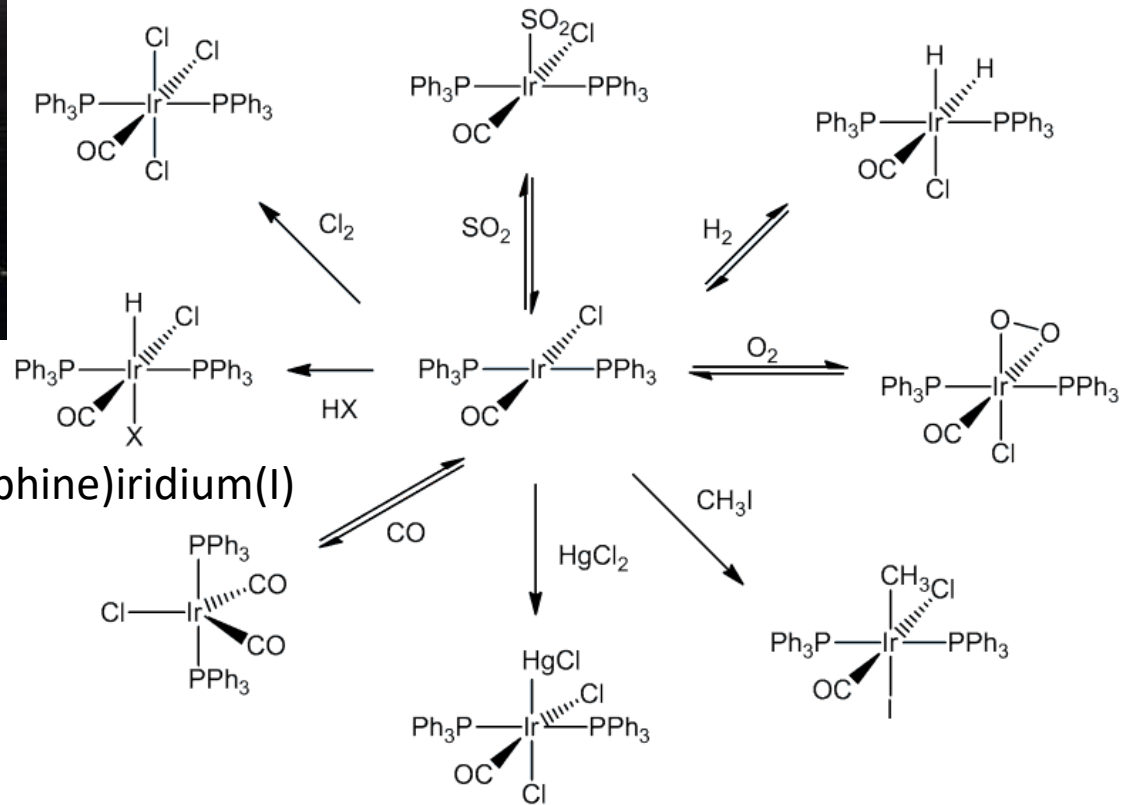
Koordinacioni broj 4

Kvadratno planarni kompleksi



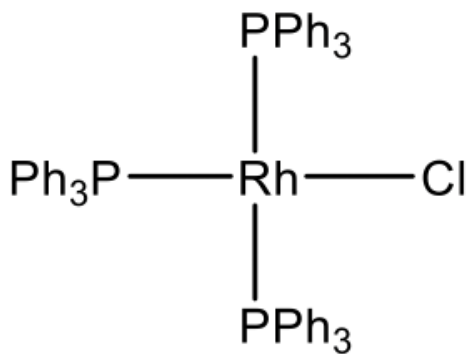
Trans chlorocarbonylbis(triphenylphosphine)iridium(I)

Vaska's complex

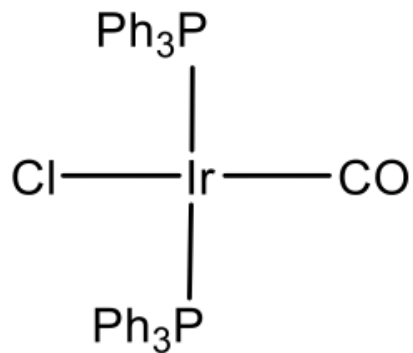


Koordinacioni broj 4

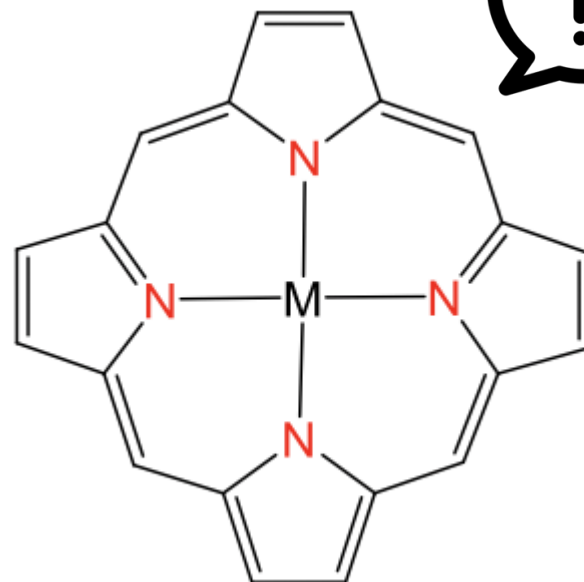
Kvadratno planarni kompleksi



$\text{Rh}(\text{PPh}_3)_3\text{Cl}$

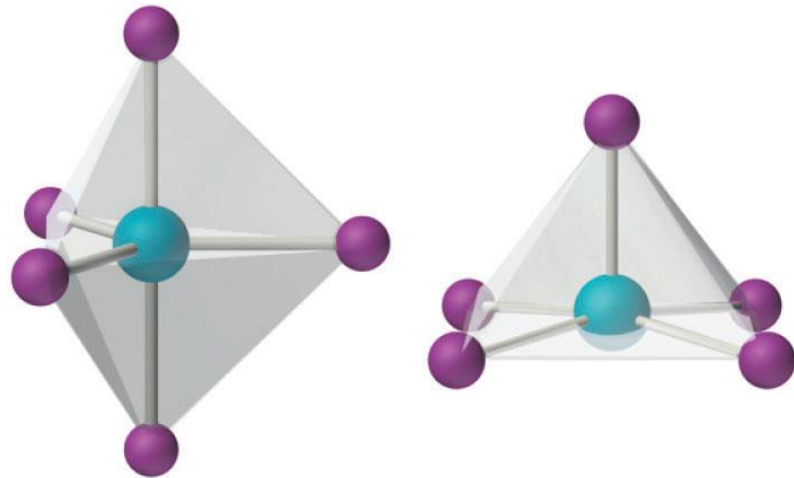
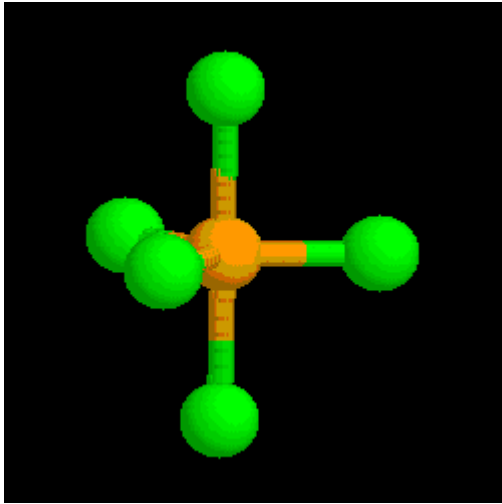


$\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$



Koordinacioni broj 5

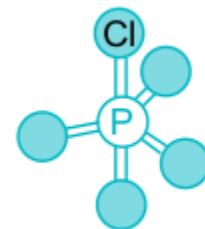
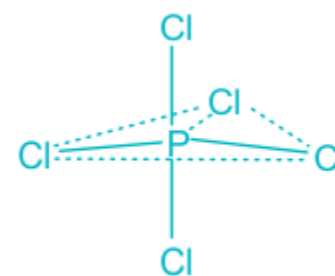
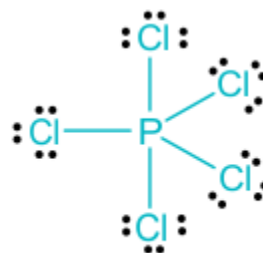
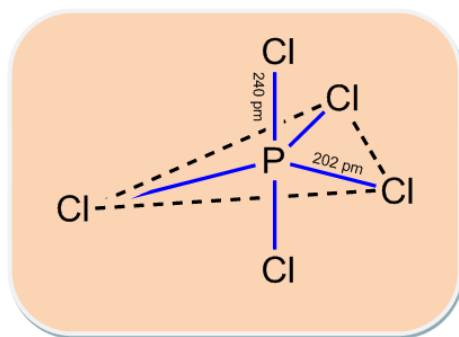
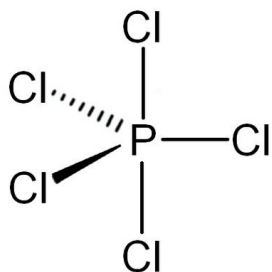
Trigonalno bipiramidalni kompleksi



- 5 vezea ML (3 ekvatorijalne ugao od 120° , 2 aksijalne)
 - $sp^3d_z^2$ hibridizacija
 - Često nije potpuno pravilna

Koordinacioni broj 5

Trigonalno bipiramidalni kompleksi

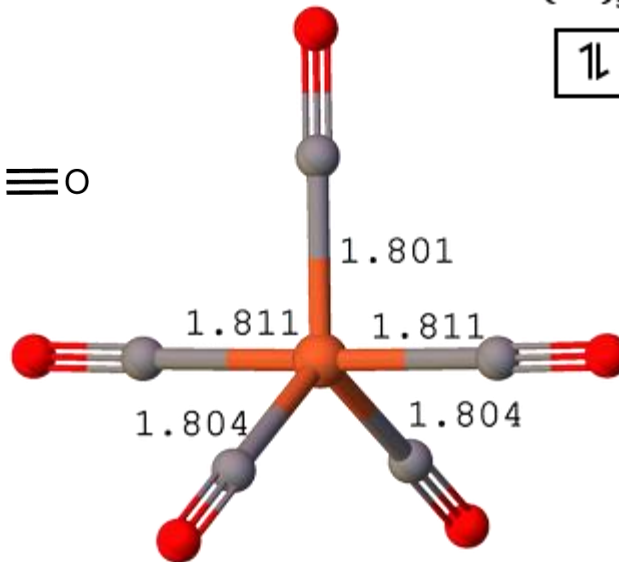
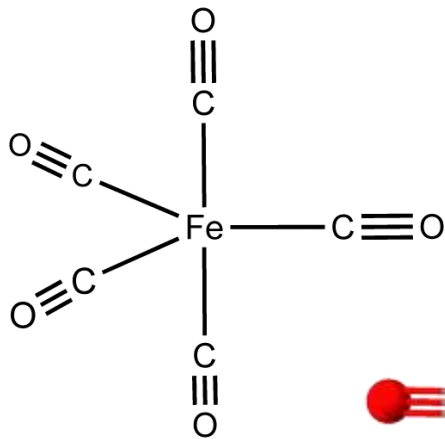


Izdužena trigonalna bipiramida

- Aksijalne veze su duže od ekvatorijalnih
 - Primjeri: PCl_5 i PF_5

Koordinacioni broj 5

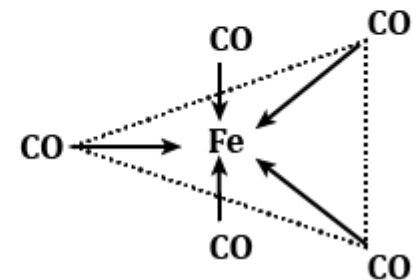
Trigonalno bipiramidalni kompleksi



In $\text{Fe}(\text{CO})_5$ the 'Fe' atom is



dsp^3 - hybridisation

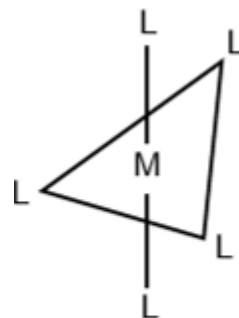
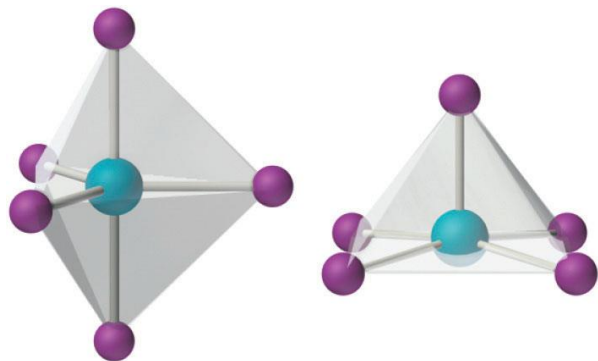


Spljoštena trigonalna bipiramida

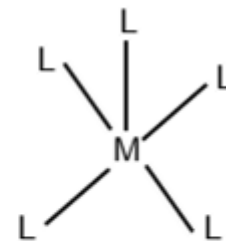
- Aksijalne veze su kraće od ekvatorijalnih
 - Primjeri: $\text{Fe}(\text{CO})_5$ i $[\text{CuCl}_5]^{3-}$
- Trigonalno bipiramidalna struktura sa tetragonalno piramidalnim karakterom

Koordinacioni broj 5

Trigonalno bipiramidalni kompleksi



Trigonal
bipyramidal

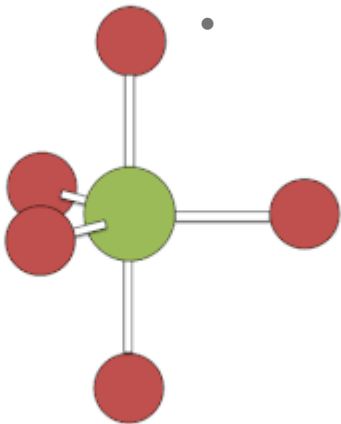
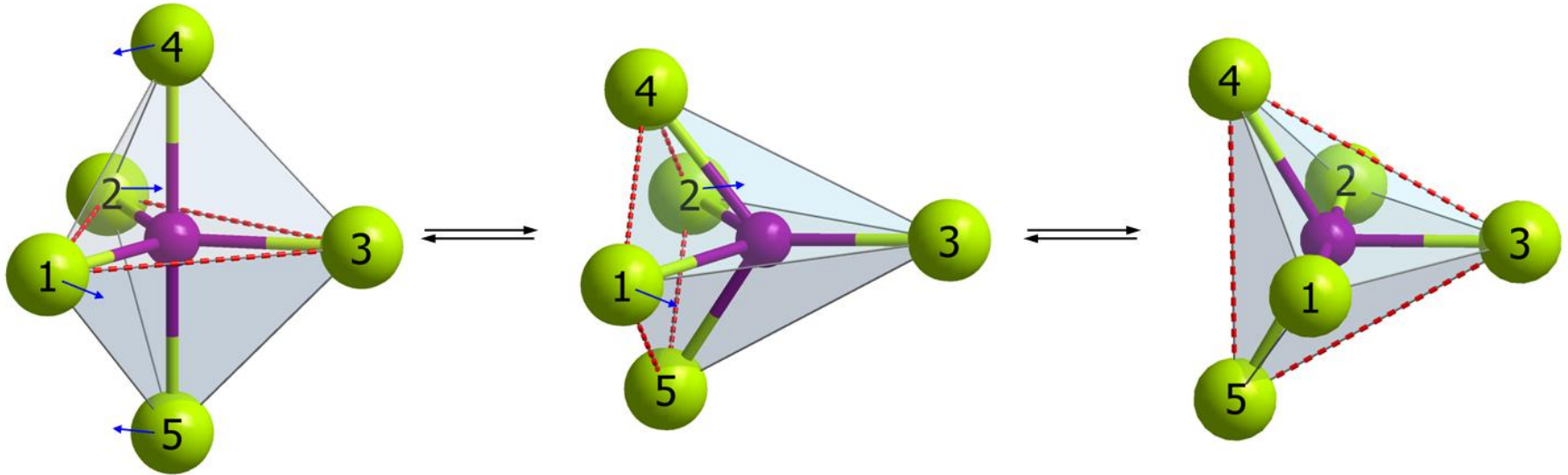


Squae pyramid

- Energetska razlika između strukture trigonalne bipiramide i kvadratne piramide je mala
 - PSEUDOROTACIJA

Koordinacioni broj 5

Trigonalno bipiramidalni kompleksi

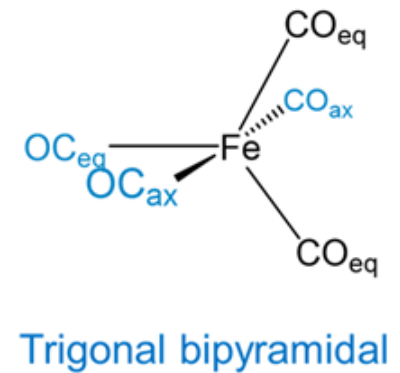
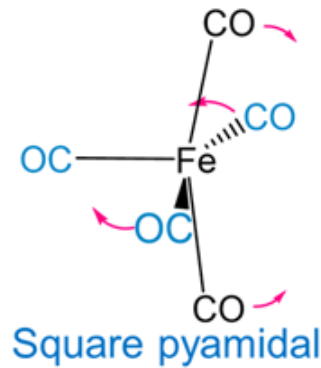
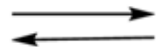
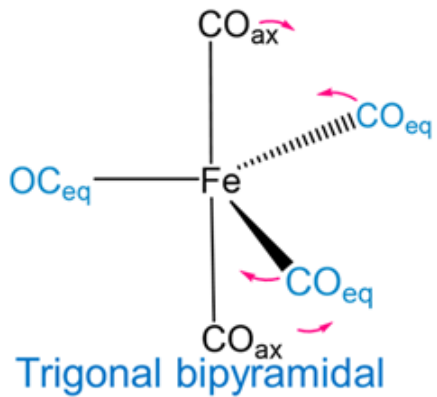
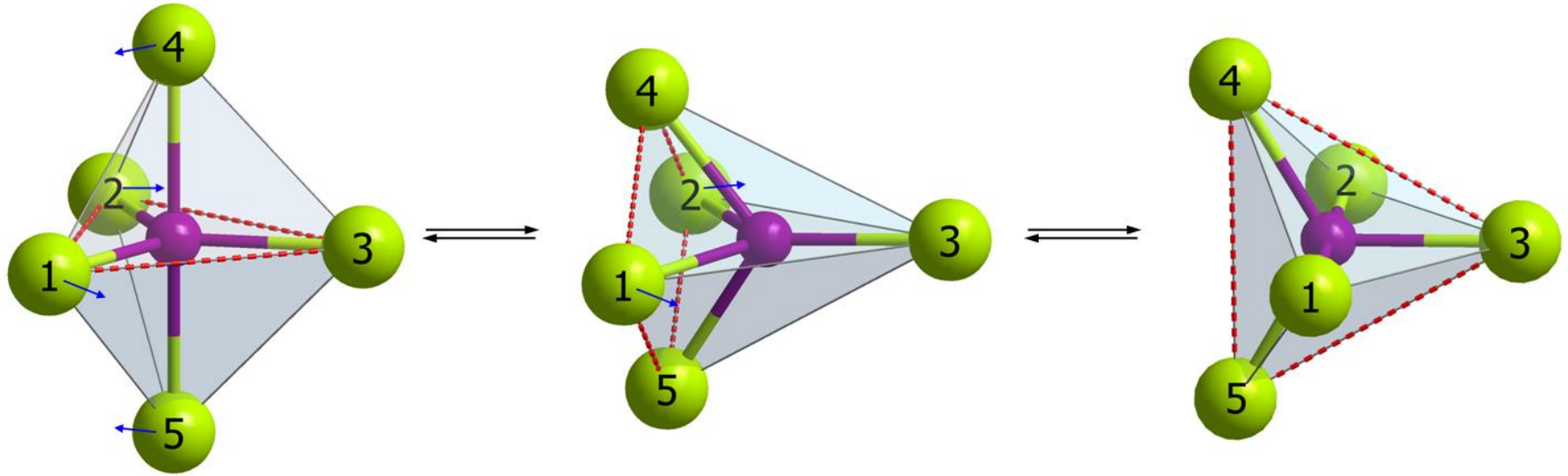


- Eenergetska razlika između strukture trigonalne bipiramide i kvadratne piramide je mala

- PSEUDOROTACIJA

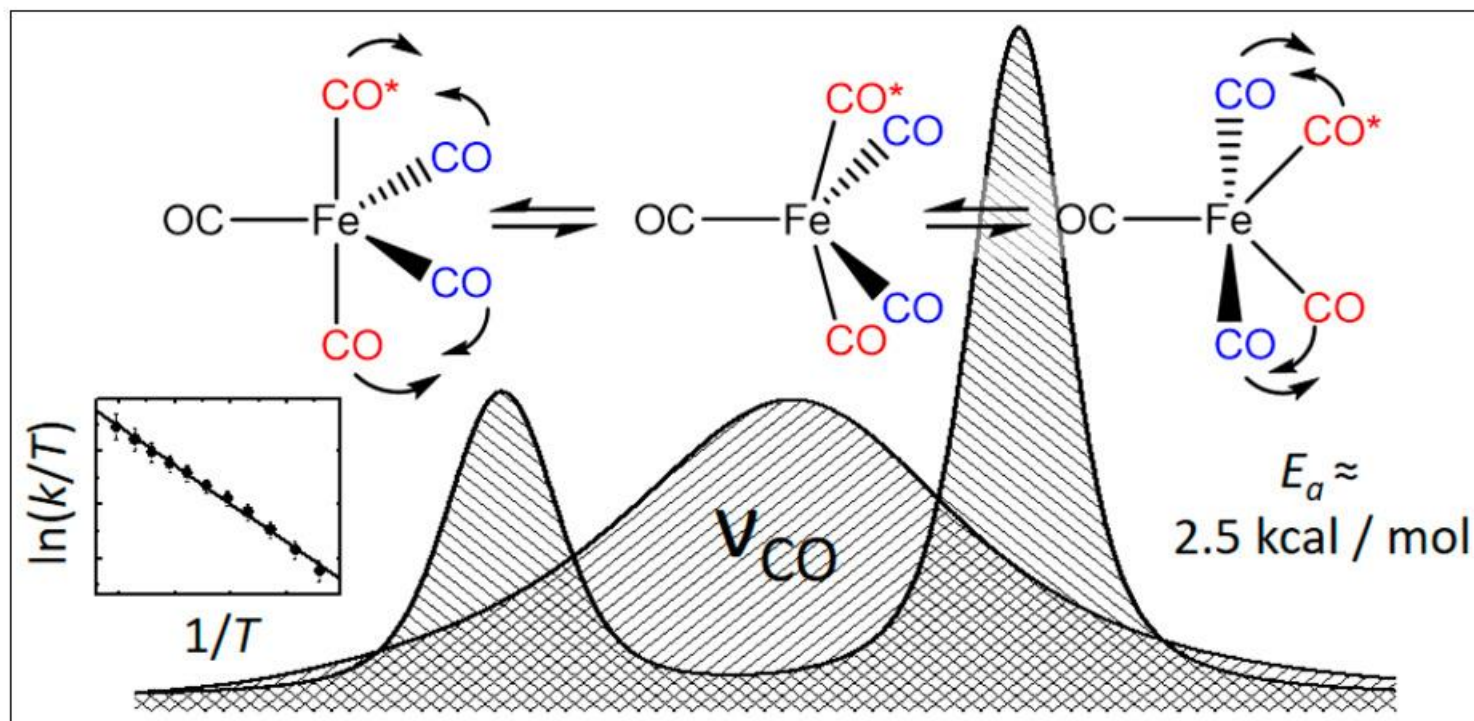
Koordinacioni broj 5

Trigonalno bipiramidalni kompleksi



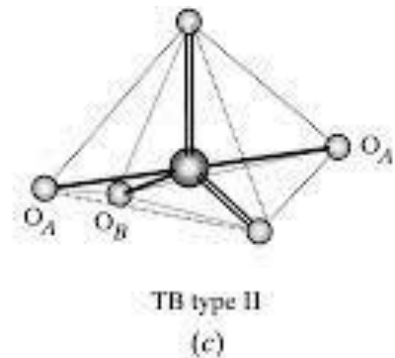
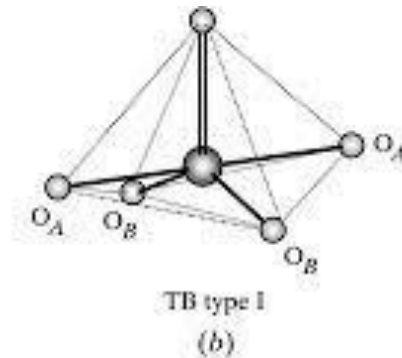
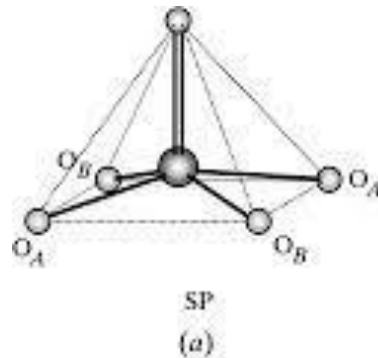
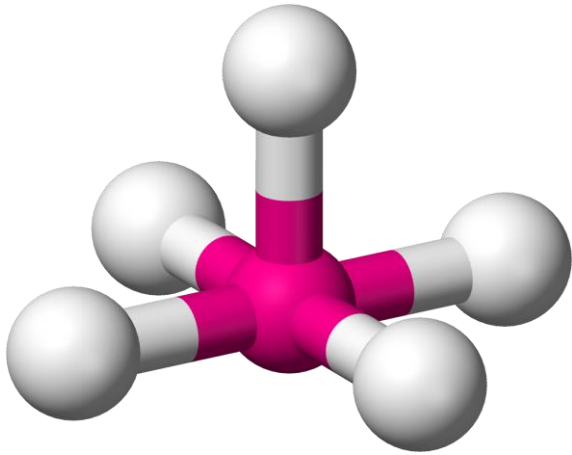
Koordinacioni broj 5

Trigonalno bipiramidalni kompleksi



Koordinacioni broj 5

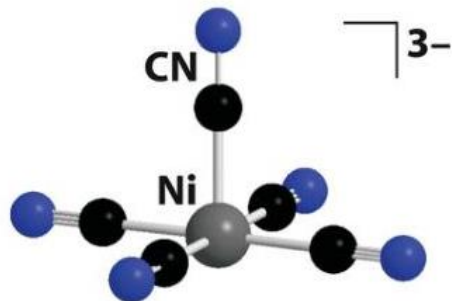
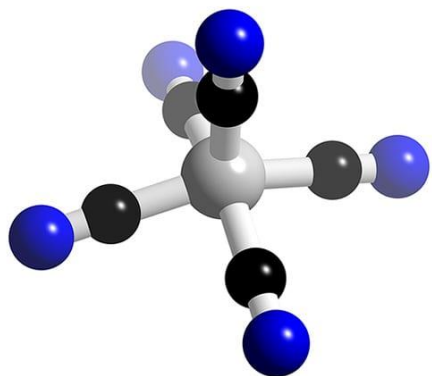
Kvadratno piramidalni kompleksi



- 5 veza ML (4 usmjerene prema uglovima osovice piramide, 1 normalna na tu ravan)
 - $d_{x^2-y^2}$ sp^3 hibridizacija
- Kod većine je dužina aksijalne veze veća

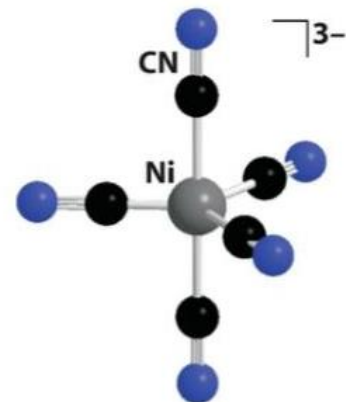
Koordinacioni broj 5

Kvadratno piramidalni kompleksi



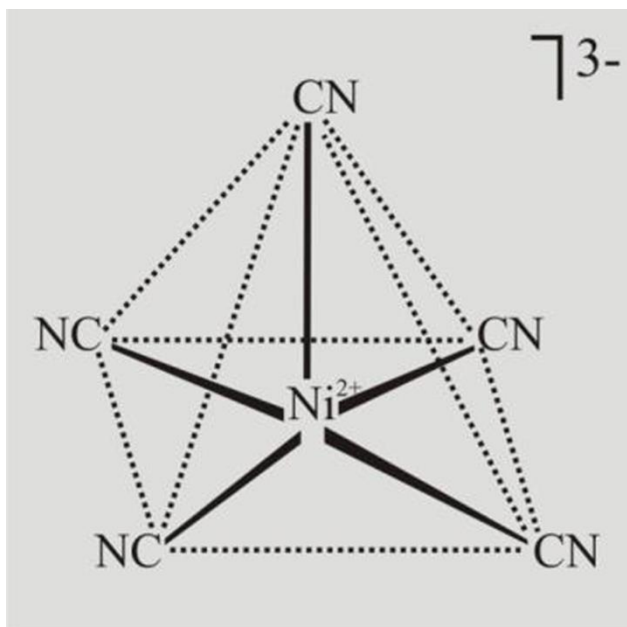
11 $[\text{Ni}(\text{CN})_5]^{3-}$, square pyramidal

Structure 8-11
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D. F. Shriver, F. W. Atkins, T. L. Overton, J. F.ourke, M. T. Wells, and F. A. Armstrong



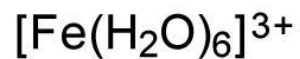
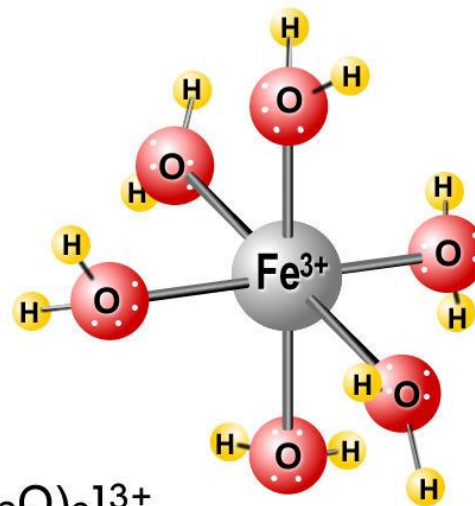
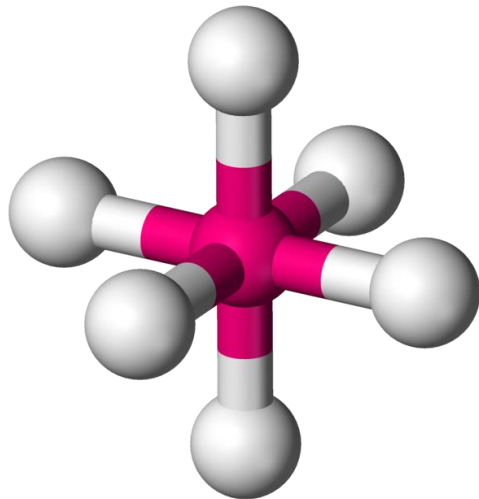
12 $[\text{Ni}(\text{CN})_5]^{3-}$, trigonal bipyramidal

Structure 8-12
Shriver & Atkins Inorganic Chemistry, Fourth Edition
© 2006 by D. F. Shriver, F. W. Atkins, T. L. Overton, J. F.ourke, M. T. Wells, and F. A. Armstrong



Koordinacioni broj 6

Oktaedarski kompleksi



Octahedral

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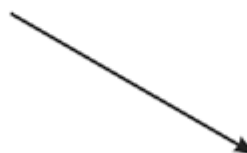
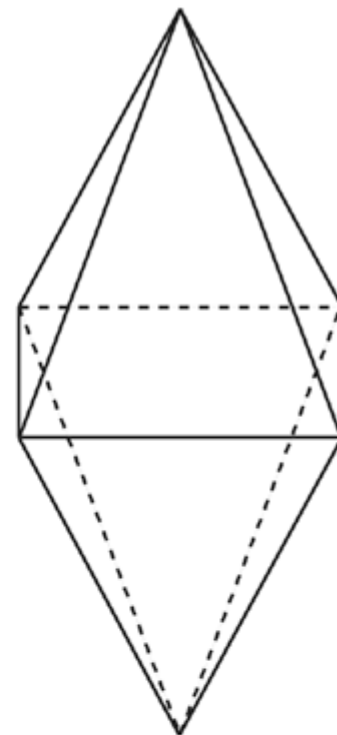
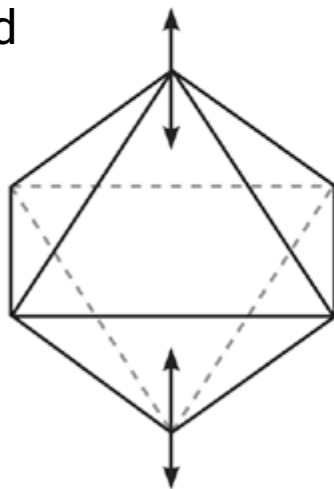
- 6 veza ML (4 u ekvatorijalnoj ravni, 2 aksijalne, normalne na tu ravan sa gornje i donje strane)
 - d^2sp^3 ili sp^3d^2 hibridizacija

Koordinacioni broj 6

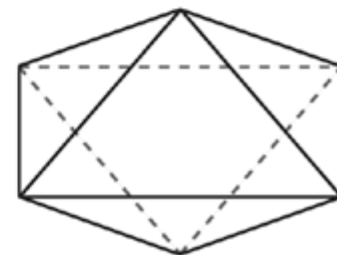
Oktaedarski kompleks

Deformisana oktaedarska struktura

- Do odstupanja dolazi usled nejednake popunjenosti d orbitala



- Tetragonalno (izduženi)
- Trigonalno (spljošteni)

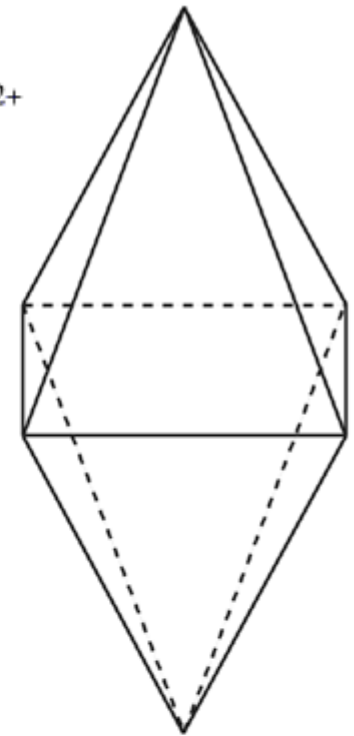
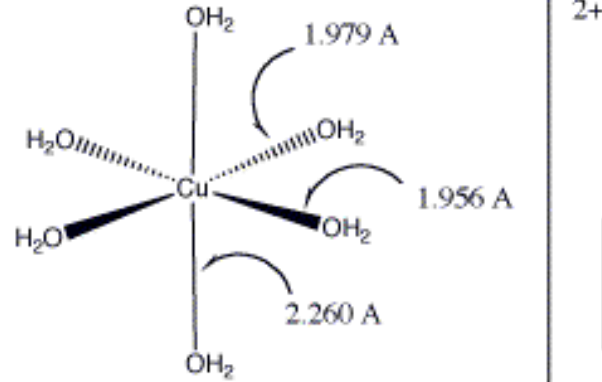
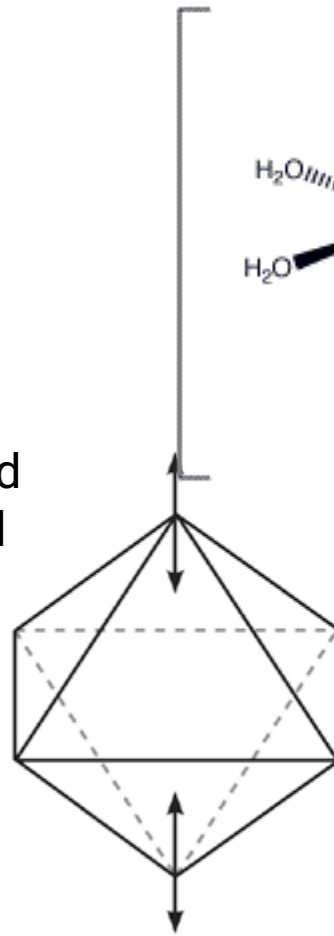


Koordinacioni broj 6

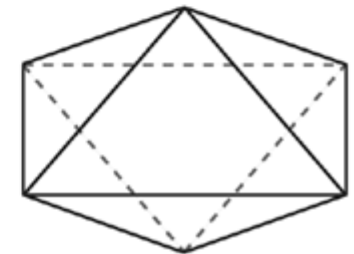
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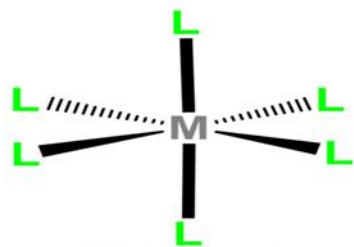


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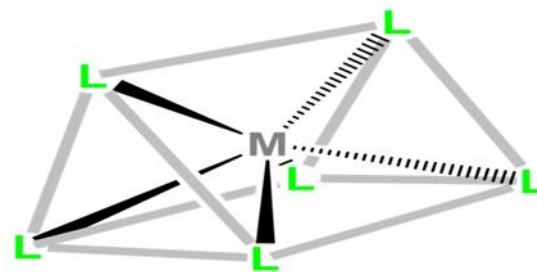


Koordinacioni broj 6

Trigonalno prizmatični kompleksi



Octahedral



Trigonal Prismatic

