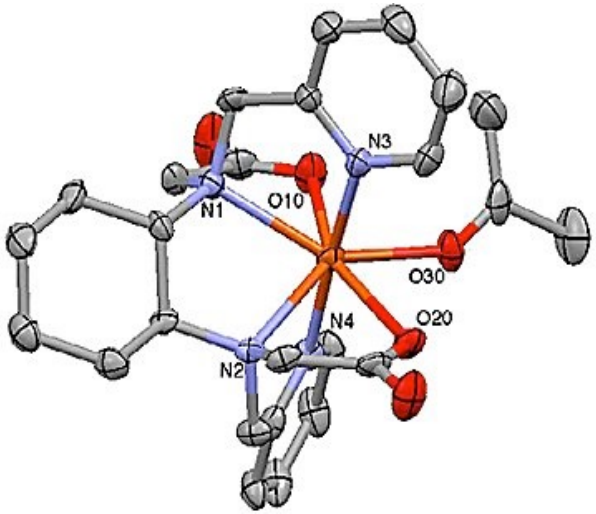
QUÍMICA INORGÂNICA 1

Números de Coordenação e Estruturas



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2020-2021

Química dos Compostos de Coordenação

"COMPLEXOS"

Definição:

Agregados mais ou menos estáveis formados quando um metal ou ião metálico se une directamente a um grupo de moléculas neutras ou iões, sendo o número de ligações simples e independentes superior ao estado de oxidação formal do metal.

Metal ou ião metálico	→	ELEMENTO CENTRAL
Iões ou moléculas que se unem	→	LIGANDOS
Nº de átomos ligados ao elemento central	→	NÚMERO DE COORDENAÇÃO
Ligandos que se unem directamente ao elemento central	→	ESFERA DE COORDENAÇÃO PRIMÁRIA

Números de Coordenação e Estruturas mais Frequentes em Compostos de Coordenação

Para muitos elementos centrais não é possível indicar um número de coordenação característico:

Ni (II), Co (II) e Zn (II), por exemplo formam complexos octaédricos, tetraédricos e até quadrangulares planos, com o número de coordenação N.C. 6 e 4

Co (III), Cr(III) e Pt (IV) formam consistentemente complexos octaédricos (N.C. 6).

Pt (II) e Pd (II) formam complexos quadrangulares planos (N.C. 4).

Na grande maioria dos casos o número de coordenação tem de ser determinado experimentalmente (propriedades físico-químicas, raios-X, momentos dipolares eléctricos, momentos magnéticos, espectroscopia visível/U.V. e infravermelhos.

O número de estruturas possíveis não são muito extensas e algumas são pouco frequentes.

Números de Coordenação e Estruturas mais Frequentes em Compostos de Coordenação

Os nº de coordenação de um complexo dependem de três factores:

1- O tamanho do átomo ou ião central

2- As interacções estereoquímicas entre os ligandos

3- Interacções electrónicas metal-ligando

a) N.C. 2

pouco frequente

Complexos lineares Ag (I), Cu(I), Au(I),

$[Ag(NH_3)_2]^+$ $H_3N \longrightarrow Ag \longleftarrow NH_3$

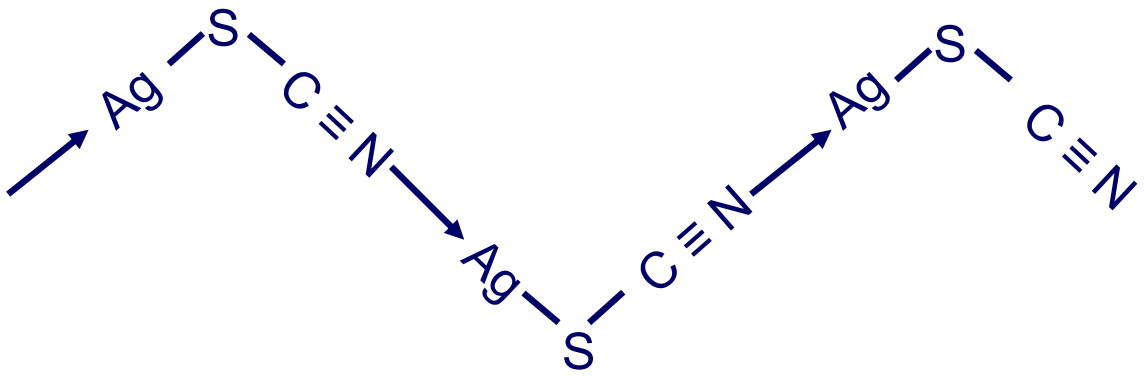
lão diamino prata (I)

$[CuCl_2]^-$ lão dicloro cuprato (I)

O cianeto e o tiocianato de prata podem formar espécies poliméricas.

...- Ag – C ≡ N ⟶ Ag – C ≡ N ⟶ Ag – C ≡ N - ...

LINEAR



ZIG-ZAG

11	12
Cu(I) $[X-Cu-X]^-$ X = Cl, Br	
Ag(I) $[H_3N-Ag-NH_3]^+$	
Au(I) $[R_3P-Au-PR_3]^+$	$H_3C-Hg-CH_3$

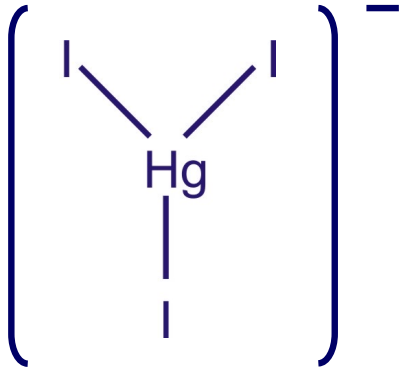
Summary chart 7.1 Linear complexes

b) N.C. 3

pouco frequente

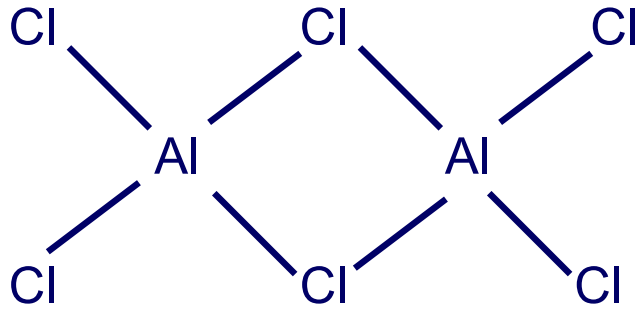
$[HgI_3]^-$

Ião tri-iodo mercurato (II)



Geralmente o composto de fórmula empírica AB_3 não coincide com a fórmula molecular:

$$Al\,Cl_3 \longrightarrow Al_2Cl_6$$

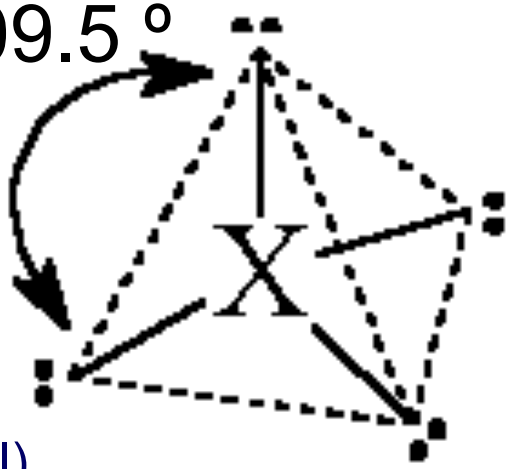


All bond angles = 109.5 degrees

c) N.C. 4

muito frequente

Complexos Tetraédricos

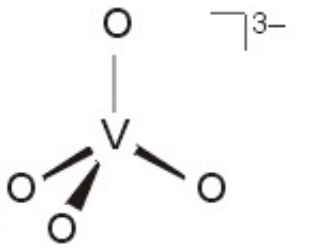
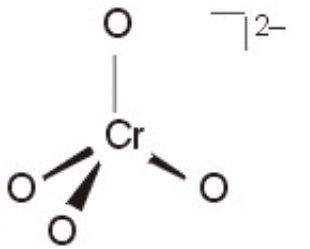
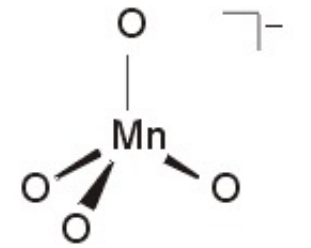


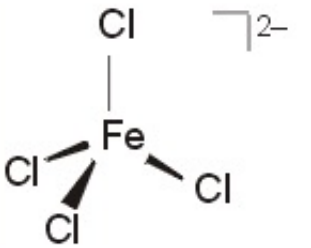
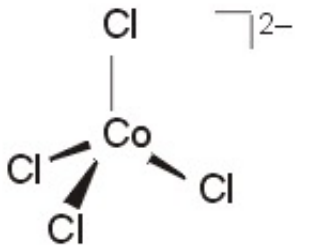
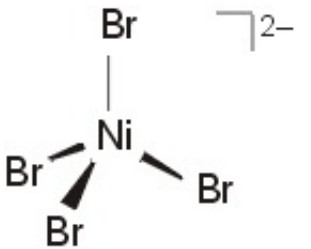
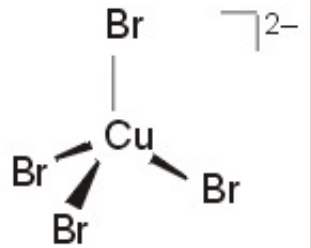
$[ZnCl_4]^{2-}$ lão tetracloro zincato (II)

$[Cd(CN)_4]^{2-}$ lão tetraciano cadmiato (II)

$[FeCl_4]^{-}$

$[Co(NSC)_4]^{2-}$

5	6	7
		

8	9	10	11
			

Summary chart 7.2 Tetrahedral complexes

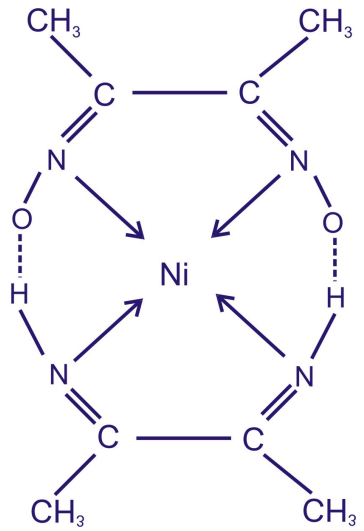
Complexos Quadrangulares Planos

Não são tão comuns como os tetraédricos.

Estrutura característica em complexos de metais com configuração electrónica d^8, Pd (II), Rh (I), Ir (I), Pt (II) e Au (III).

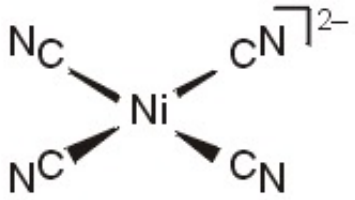
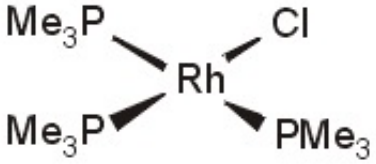
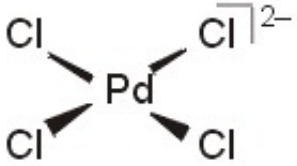
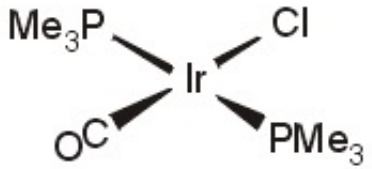
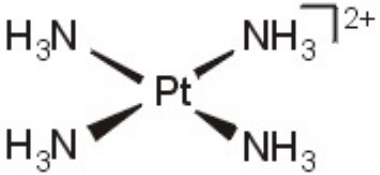
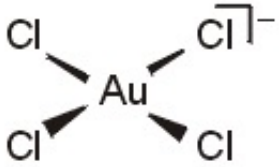
Ni (II) também forma este tipo de complexos.

$[Pt(NH_3)_4]^{2+}$ $[PdCl_4]^{2-}$



bis (dimetilglioxina) níquel (II)

$[Ni(dmg)_2]$

9	10	11
	 Ni(II)*	
 Rh(I)	 Pd(II)	
 Ir(I)	 Pt(II)	 Au(III)

Summary chart 7.3 Planar complexes

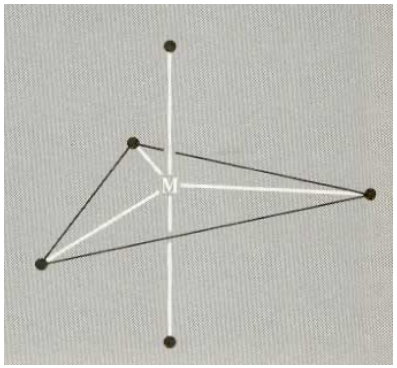
d) N.C. 5

pouco frequente

Bipirâmide Trigonal

(mais corrente)

A

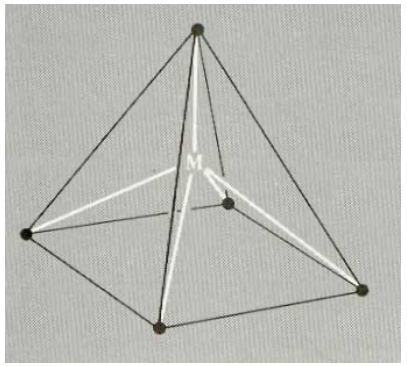


$[Fe(CO)_5$

Pentacarbonilo ferro (0)

Pirâmide Quadrangular

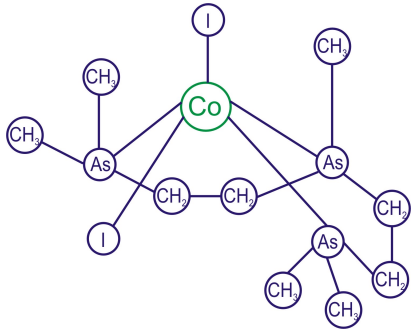
B



$[CoI_2(triarsina)]$

$[Cu(Cl)_5]^{3-}$

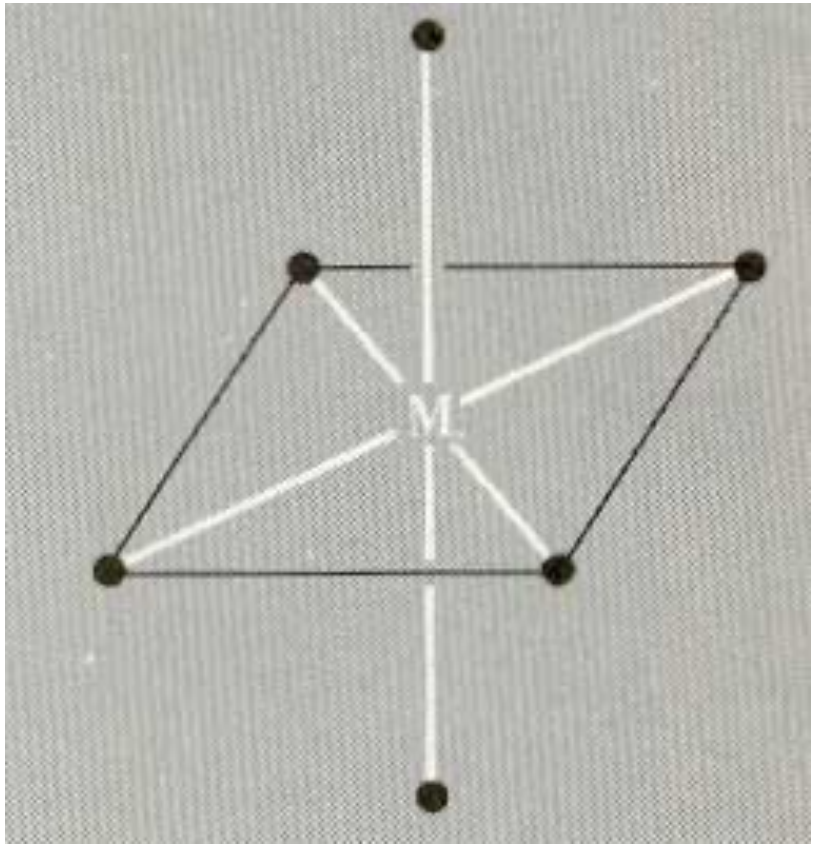
Ião pentaclorocuprato (II)



e) N.C. 6

muito frequente

Complexos Octaédricos



Co (III), Cr (III) e Pt (IV)

e muitos outros

$[Fe(CN)_6]^{4-}$

$[Co(NO)_6]^{3-}$

$[CrCl_2(en)_2]^{+}$

ião dicloro bis (etilenodiamina) **crómio** (III)

O arranjo mais comum para configurações electrónicas de d^0 a d^9 (i.e. complexos de M^{3+}da série de transição 3d)

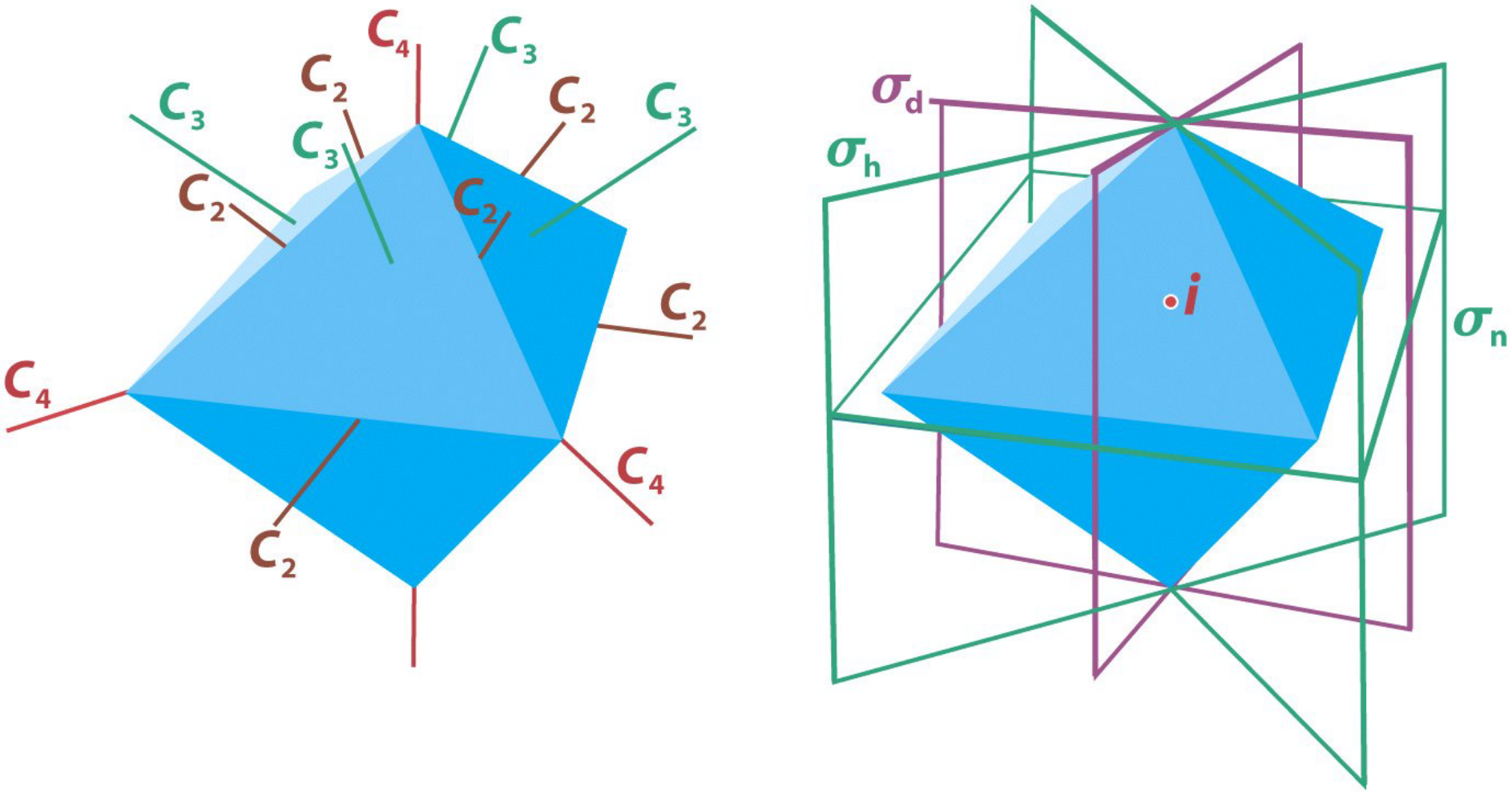
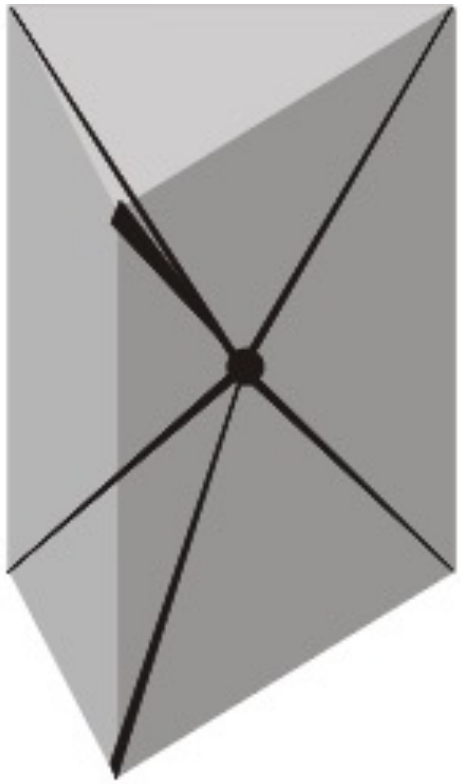
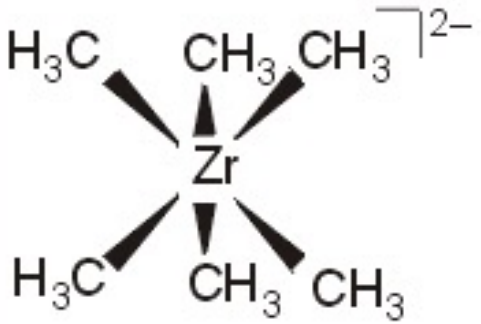
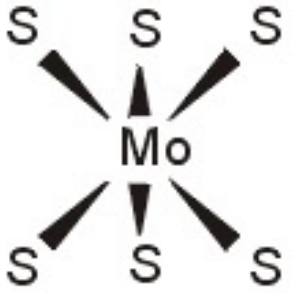
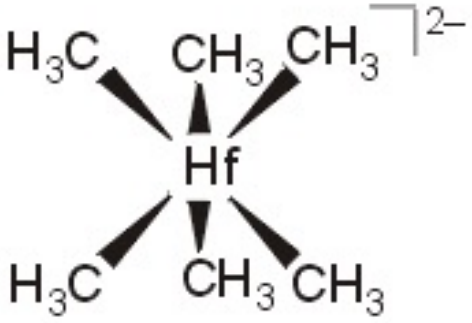
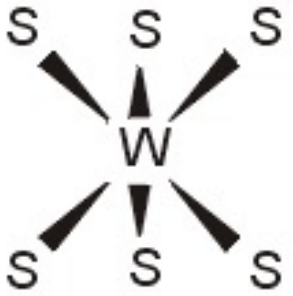


Figure 8-4
Shriver & Atkins Inorganic Chemistry, Fourth Edition

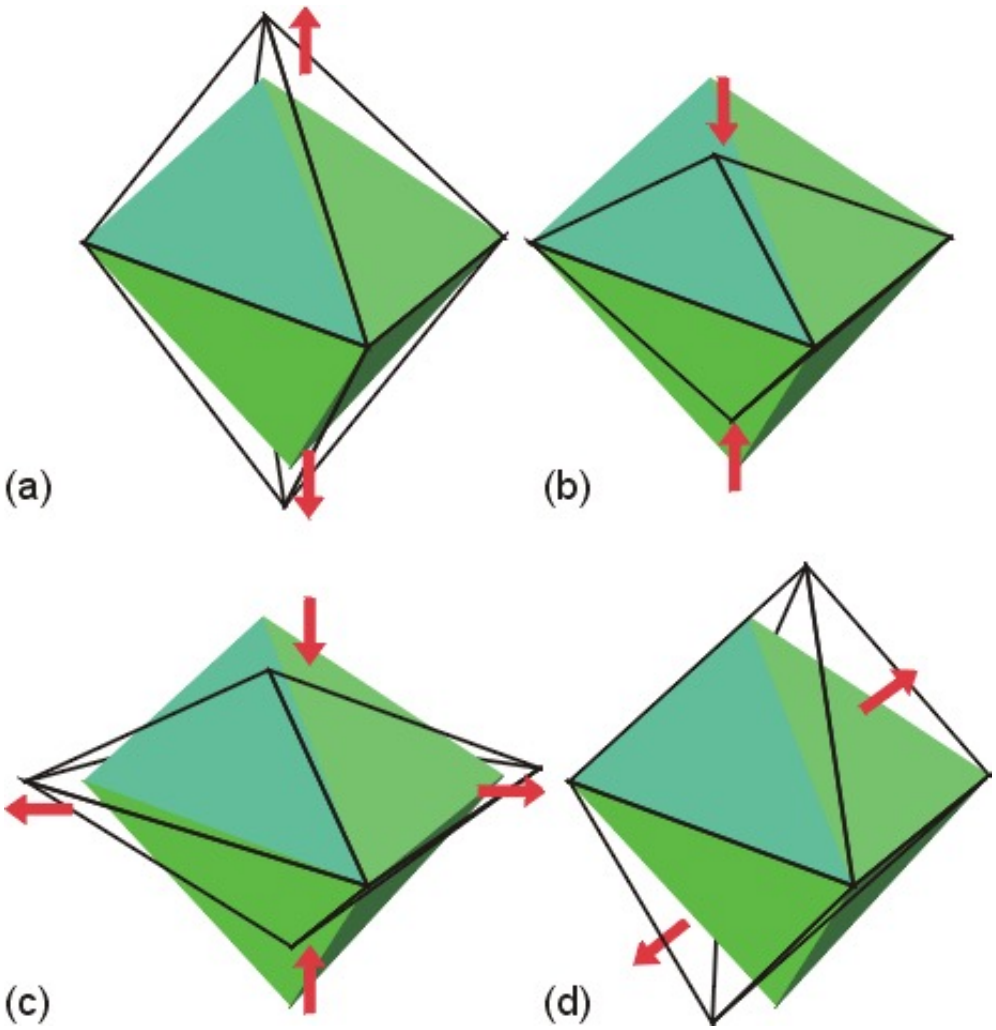
Elementos de simetria do octaedro



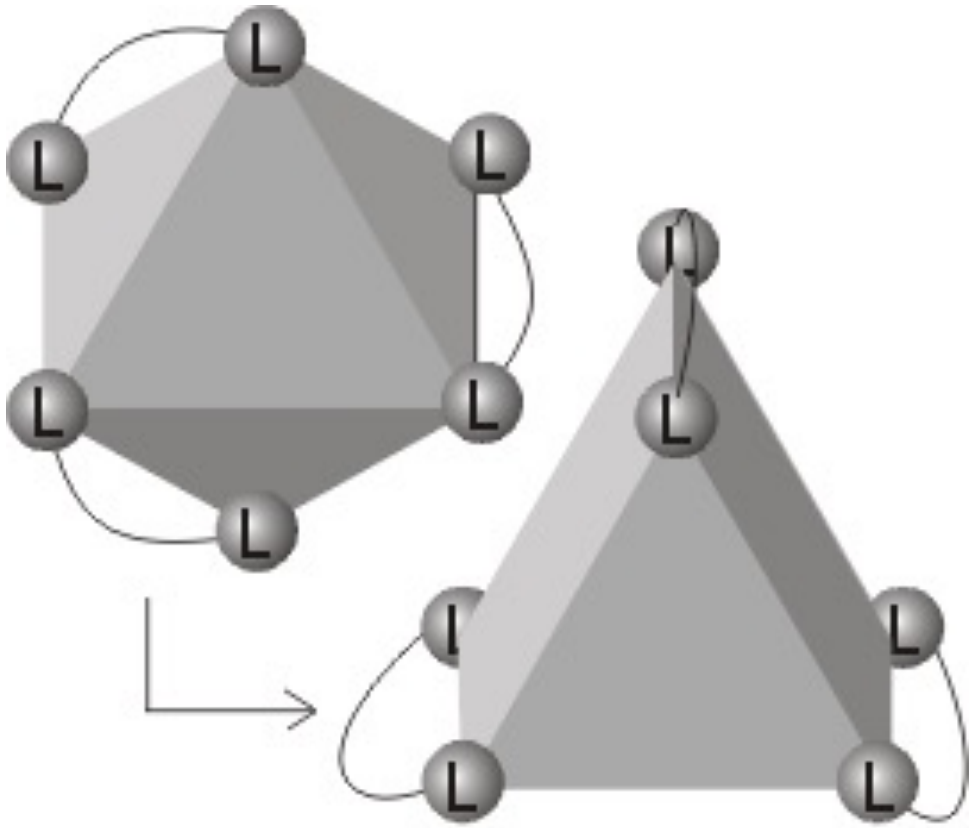
11 Trigonal-prismatic complex, D_{3h}

4	5	6
 Zr(IV)		 Mo(VI)
 Hf(IV)		 W(VI)

Summary chart 7.4 Trigonal–prismatic complexes

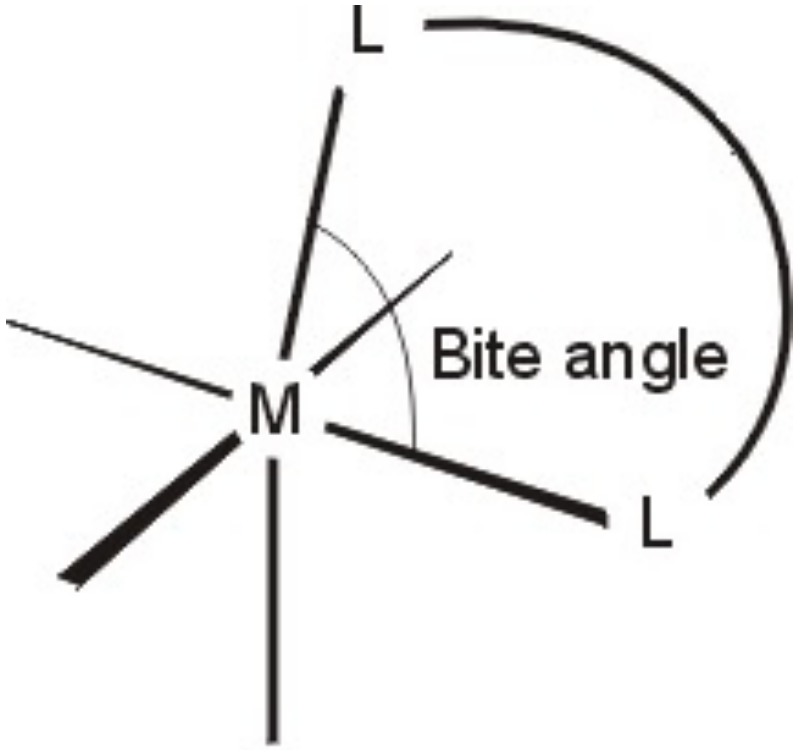


a) e b) Distorção tetragonal dum octaedro regular
c) Distorção rômbica d) Distorção trigonal (pode ser obtido o prisma trigonal através da rotação um ângulo de 60º das faces.



32

Distorção do octaedro para um prisma trigonal

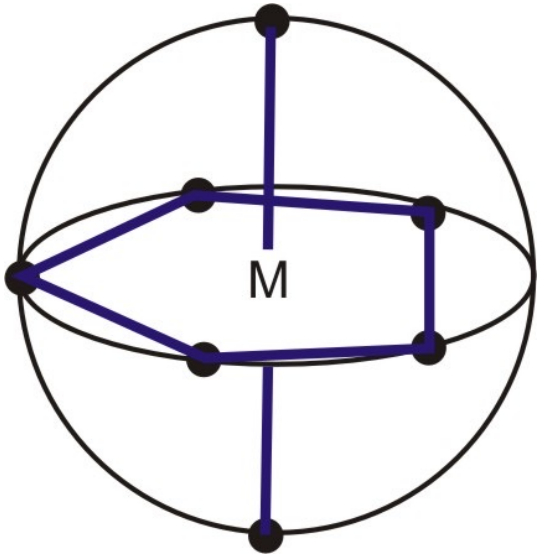


31 Bite angle

A distorção ocorre quando o “bite angle” é pequeno

f) N.C. 7

raro



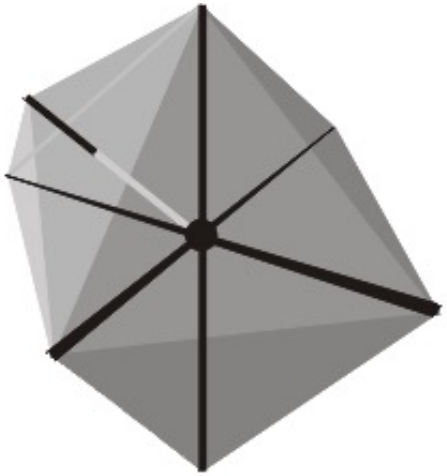
$[ZrF_7]^{3-}$ heptaflúor zirconato (IV)

$[UO_2F_5]^{3-}$ pentafluoro di-oxo uranato (IV)

$[Fe(H_2O)EDTA]^-$

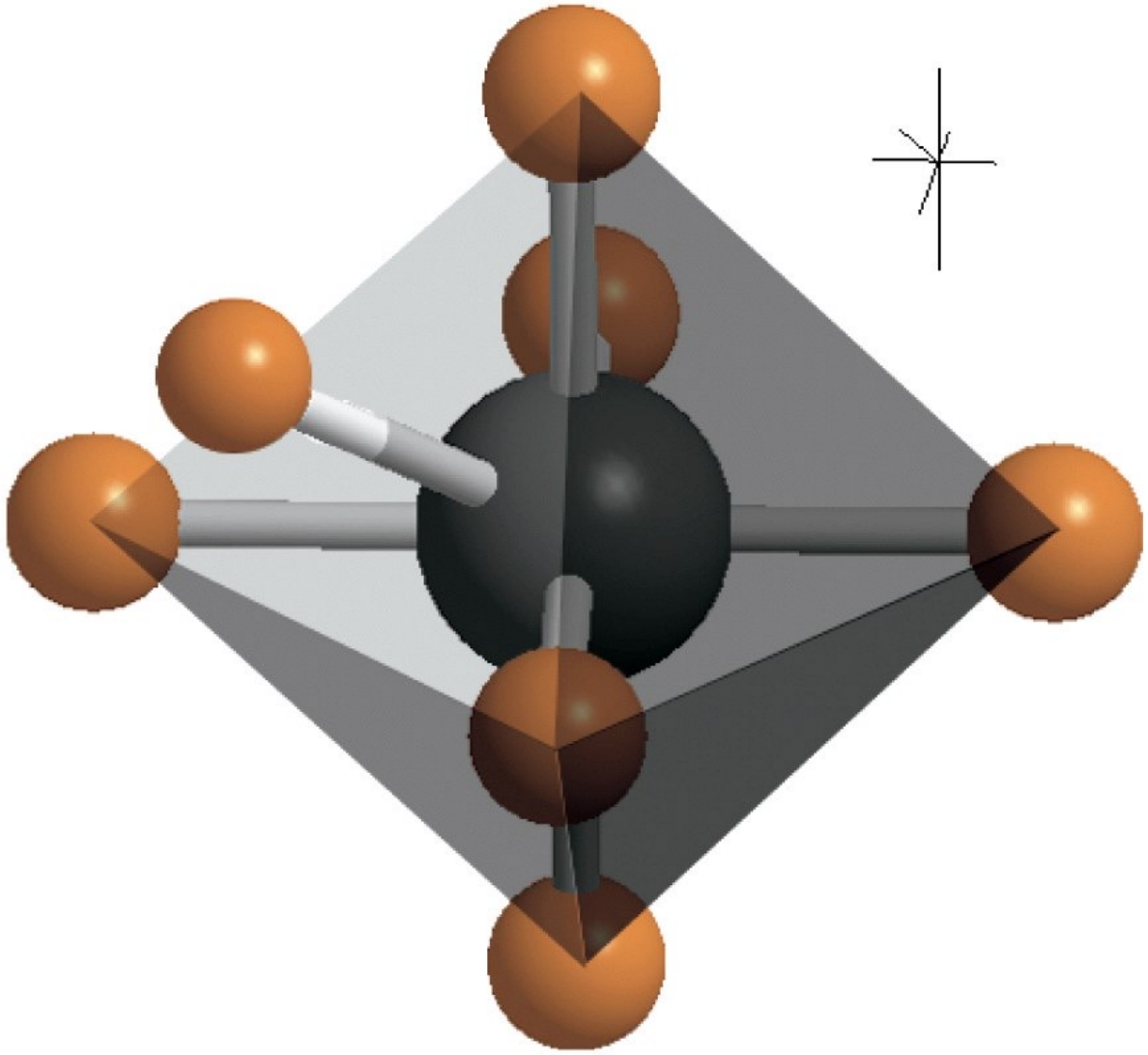
13 Pentagonal-bipyramidal complex, D_{5h}

N.C. 7



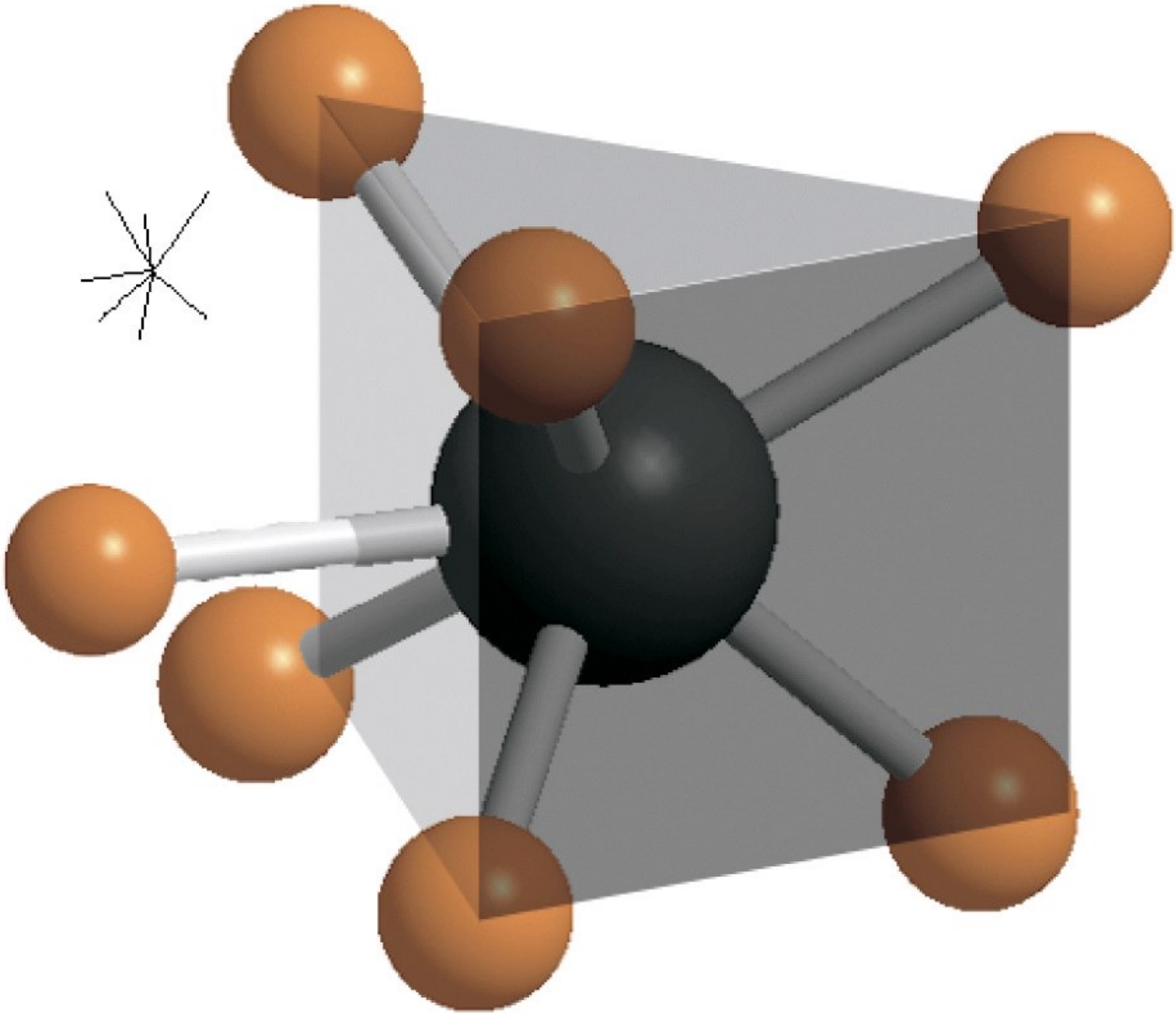
14 Capped octahedral complex

15 Capped trigonal prism



17 Capped octahedron

Structure 8-17
Shriver & Atkins Inorganic Chemistry, Fourth Edition



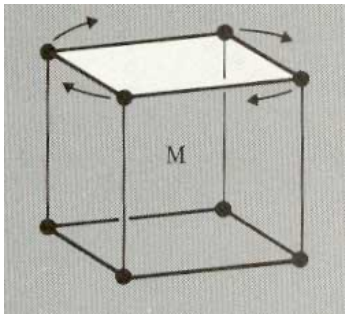
18 Capped trigonal prism

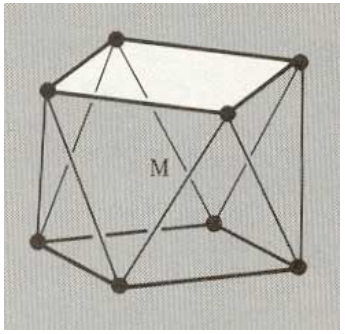
Structure 8-18
Shriver & Atkins Inorganic Chemistry, Fourth Edition

g) N.C. 8

depois de N.C. 4 e 6 é talvez o mais frequente

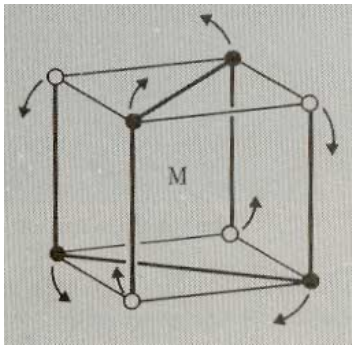
anti-prisma tetragonal

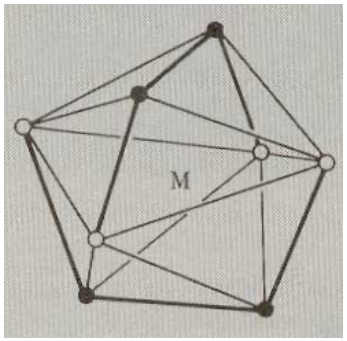




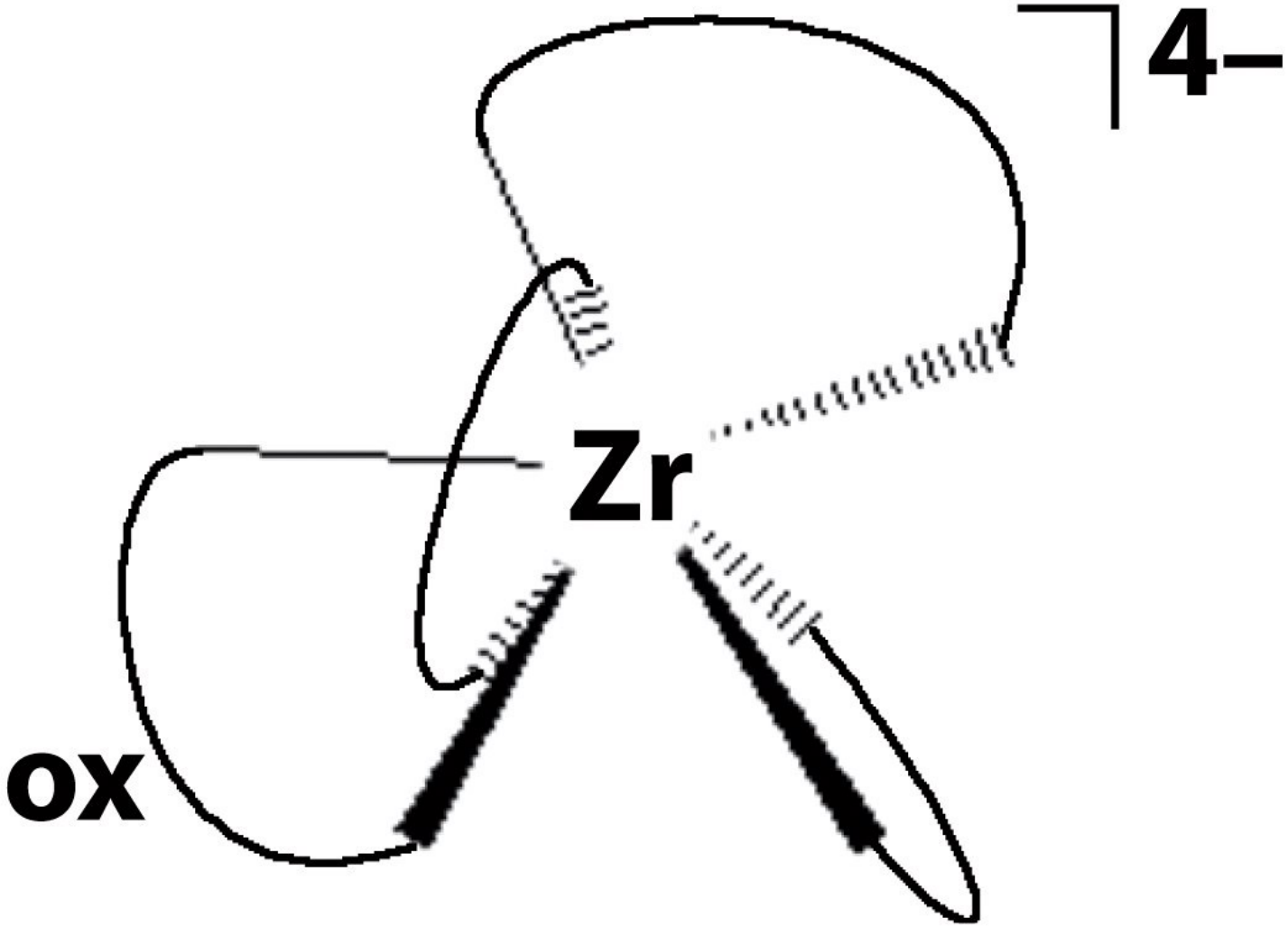
Projecção horizontal

Dodecaédrica de faces triangulares



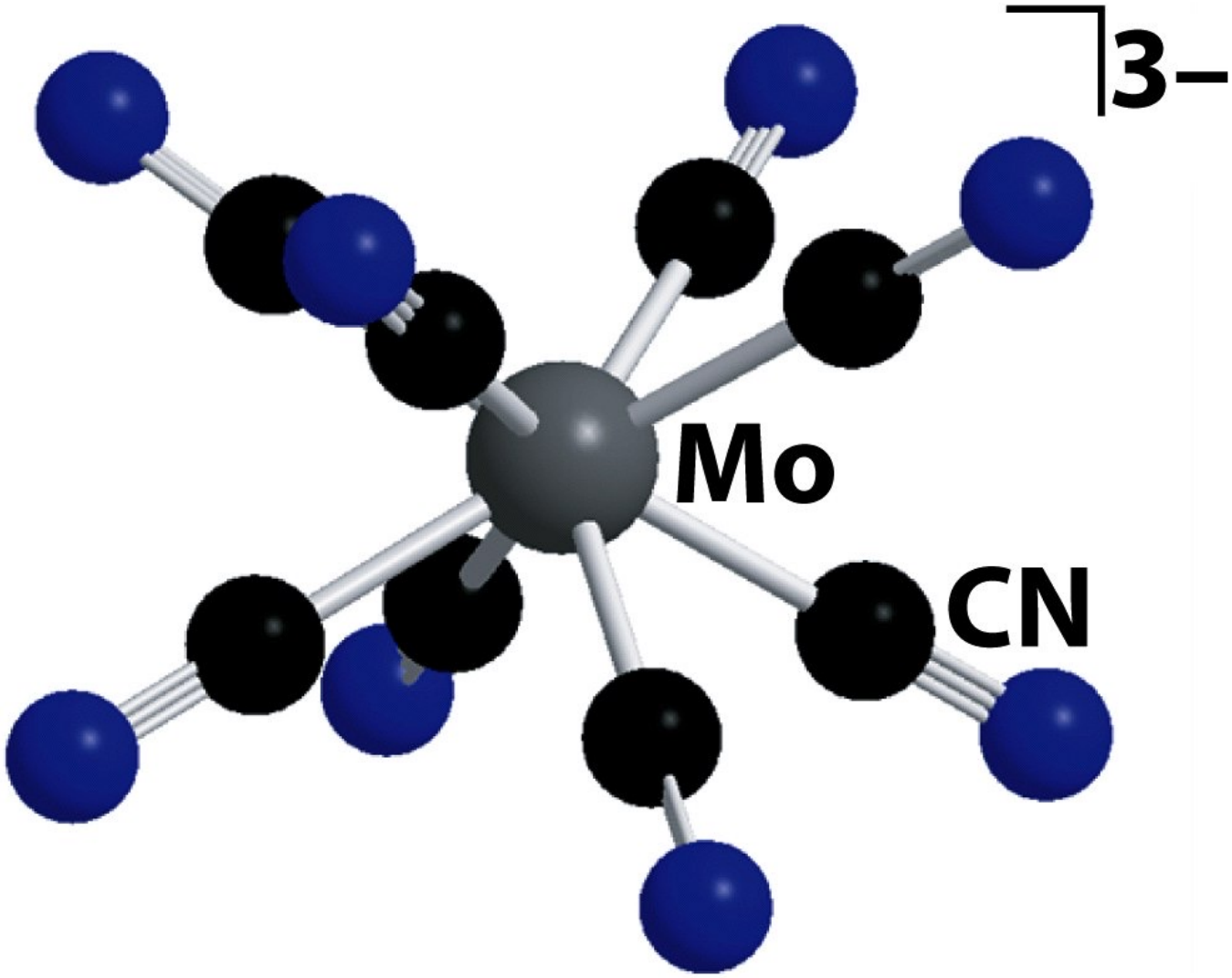


$[TaF_8]^{3-}$ $[Zn(C_2O_4)_4]^{4-}$



23 $[Zr(ox)_4]^{4-}$

Structure 8-23
Shriver & Atkins Inorganic Chemistry, Fourth Edition



22 $[Mo(CN)_8]^{3-}$

Structure 8-22
Shriver & Atkins Inorganic Chemistry, Fourth Edition

N.C.: 8 - 9

Complexing Agents in MRIs

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to "see" each of these separately (Figure 24.8.2). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown in Figure 24.8.2.

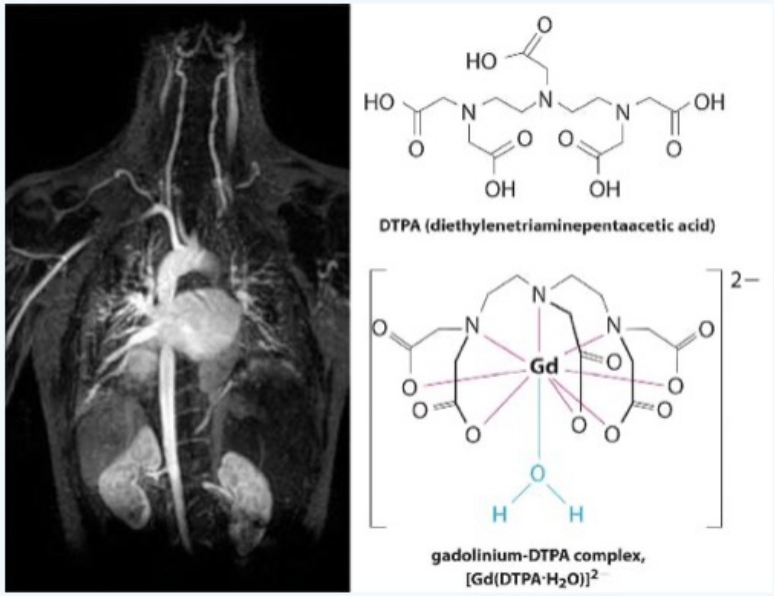


Figure 24.8.2: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

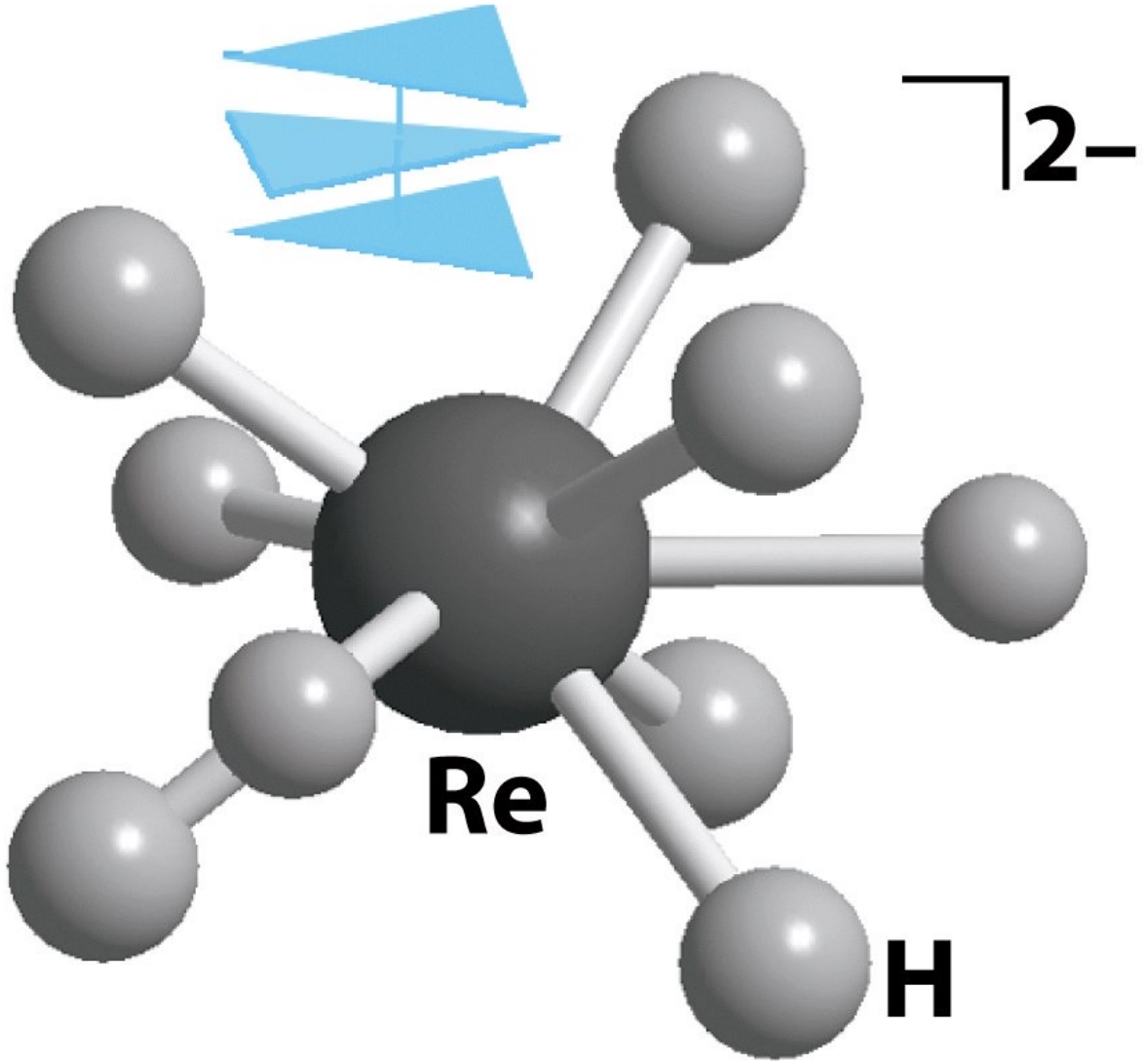
Nº de Coordenação superiores a 8

h) N.C. 9, 10, 11 e 12

são importantes nos elementos do bloco-f

$[Nd(OH_2)_9]^{3+}$

Exemplo do bloco-d $[ReH_9]^{2-}$

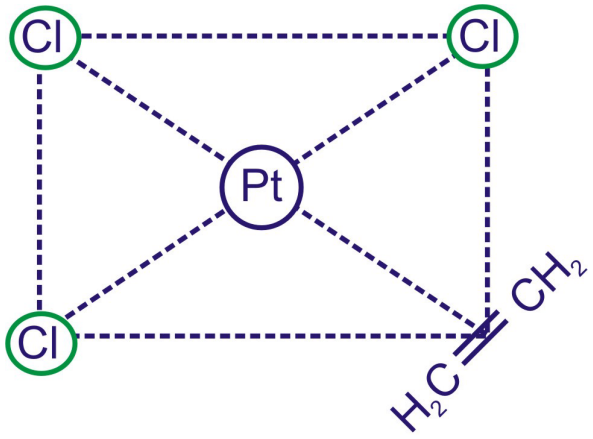


25 $[ReH_9]^{2-}, D_{3h}$

Structure 8-25
Shriver & Atkins Inorganic Chemistry, Fourth Edition

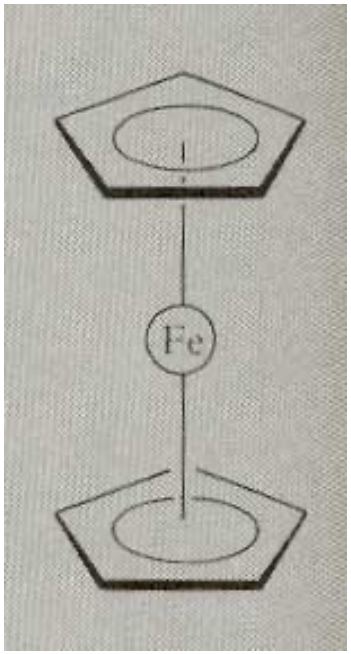
i) Complexos de Nº de Coordenação difícil de visualizar

$K[PtCl_3(C_2H_4)]$



Sal de Zeise

Complexos "Sanduiche"



Bis (ciclopentadienilo) ferro (II)

Ferroceno

Nestes complexos é difícil individualizar qual o átomo do ligando responsável pela coordenação.

Isomerismo em Compostos de Coordenação

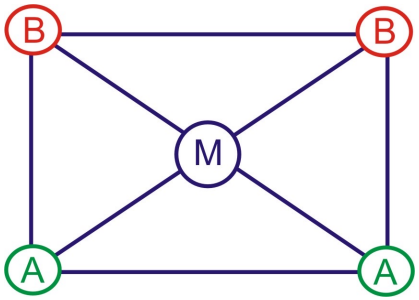
Isómeros Geométricos

Fórmula empírica idêntica. Diferem no arranjo dos ligandos em torno do metal.

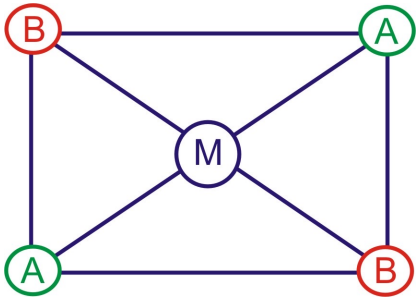
Em geral têm propriedades químicas e físicas diferentes e podem por isso ser separados por diversos métodos.

Isómeros ***Cis*** e ***Trans***

Complexos Quadrangulares Planos

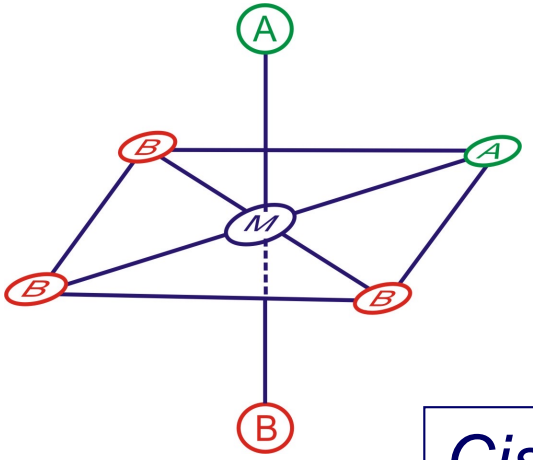


Cis

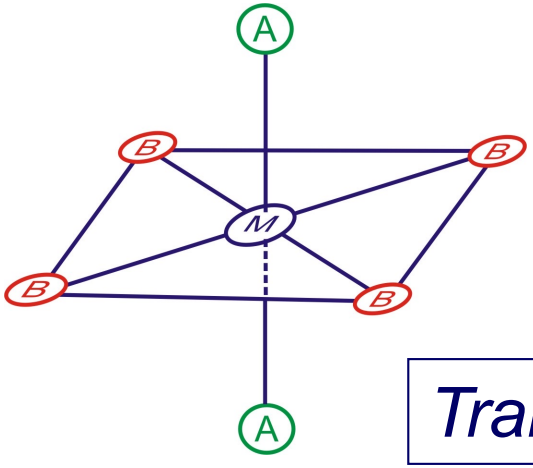


Trans

Complexos Octaédricos

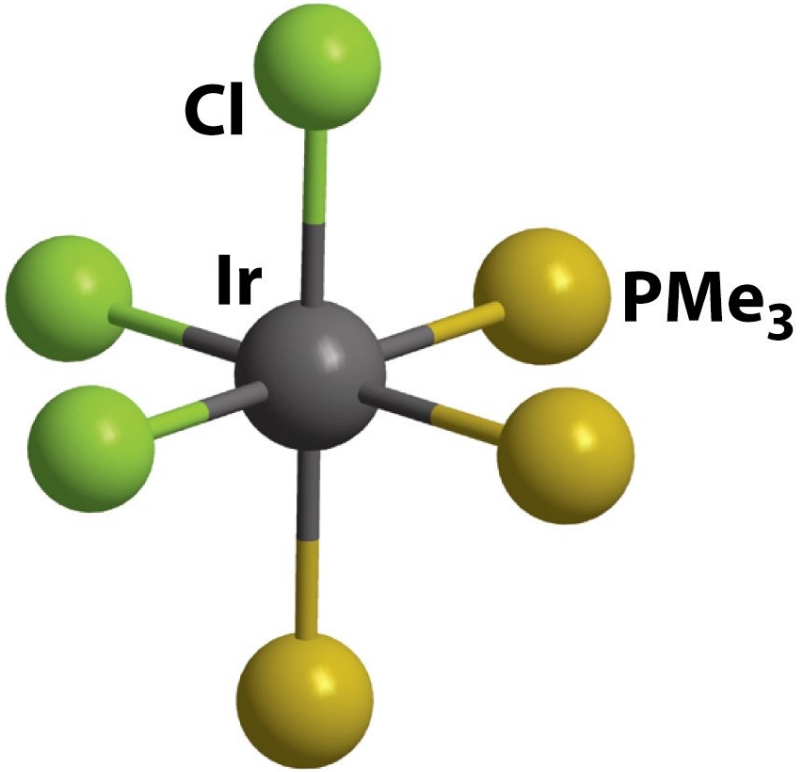


Cis



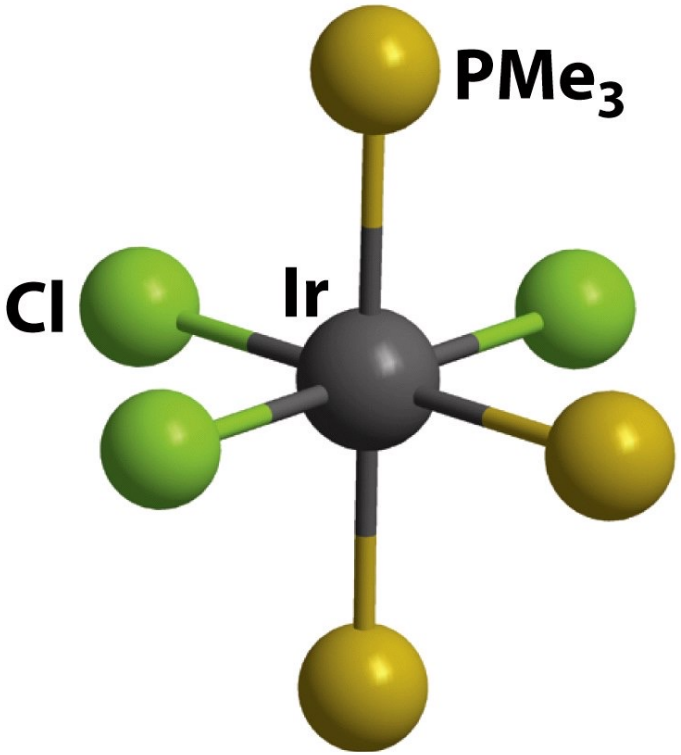
Trans

Isómeros fac- e mer-



68 ***fac*-[In(Cl)$_3$(PMe$_3$)$_3$]**

Structure 8-68
Shriver & Atkins Inorganic Chemistry, Fourth Edition



69 ***mer*-[Ir(Cl)$_3$(PMe$_3$)$_3$]**

Structure 8-69
Shriver & Atkins Inorganic Chemistry, Fourth Edition

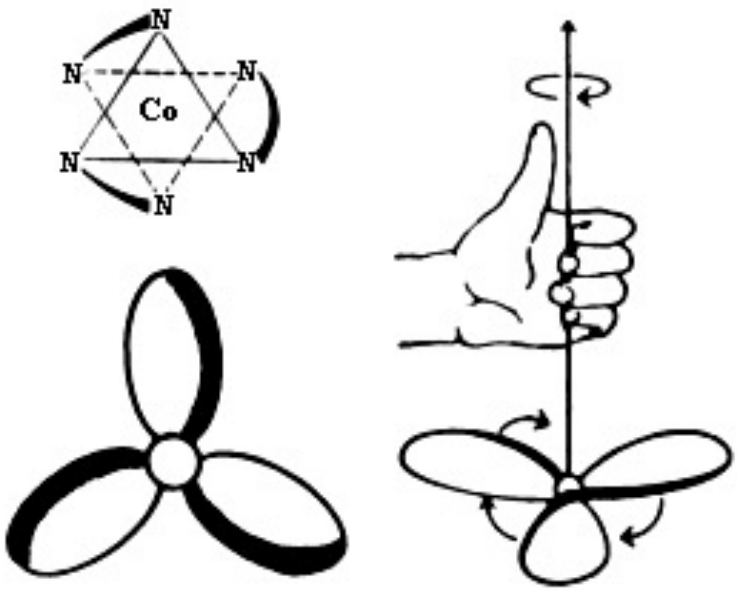
Isómeros ópticos

Substâncias que quando atravessadas por uma radiação polarizada podem *rodar* o plano de polarização dizem-se *Opticamente Activas*.

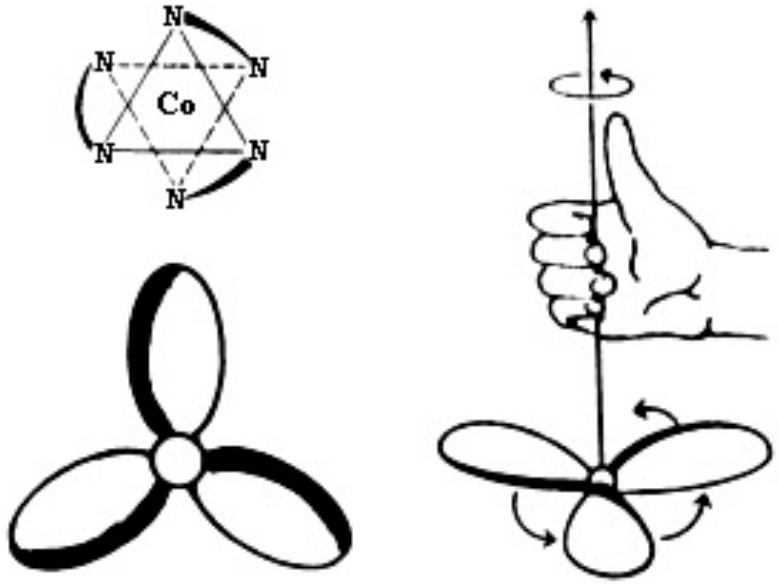
(compostos sem plano de simetria)

Geralmente existem como misturas de dois isómeros que rodam o plano da luz polarizada no sentido *dextrógiro* (isómero d ou (+)) e o outro sentido *levógiro* (isómero l ou (-)).

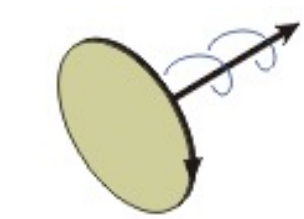
A mistura de dois isómeros – Enantiómeros – designam-se por *mistura Racémica* ou *Racemato*. Os enantiómeros cuja estrutura está relacionada como um objecto para a sua imagem num espelho (e não são sobreponíveis) tem propriedades semelhantes e podem ser separados em condições particulares (*Resolução de Enantiómeros*).



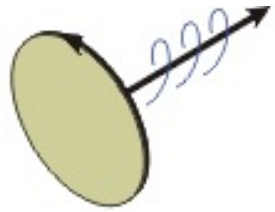
Isómero l ou (-)



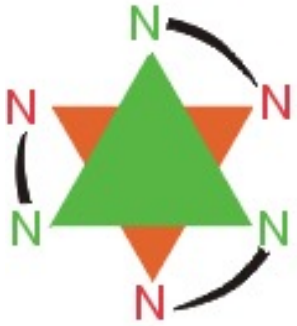
Isómero d ou (+)



Δ



Λ



Δ-[Co(en)$_3$]$^{3+}$

Λ-[Co(en)$_3$]$^{3+}$

Δ-[Co(ox)$_3$]$^{3-}$

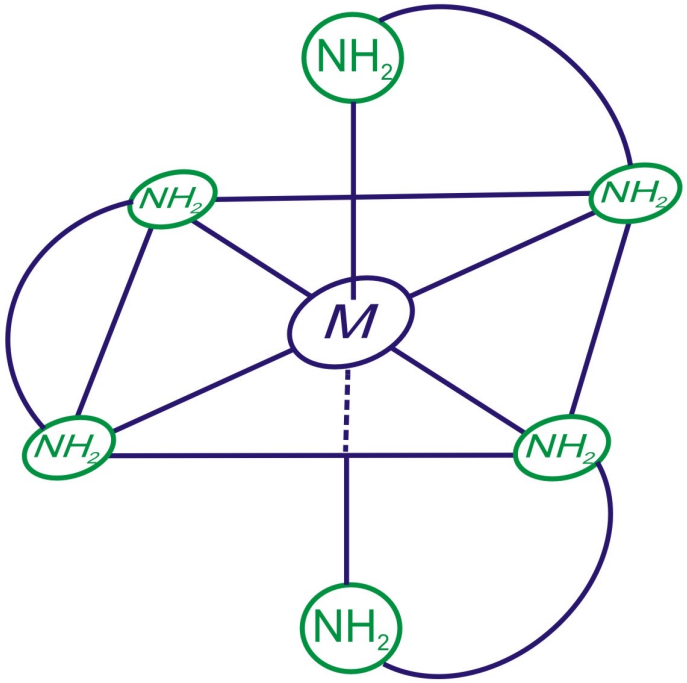
Λ-[Co(ox)$_3$]$^{3-}$

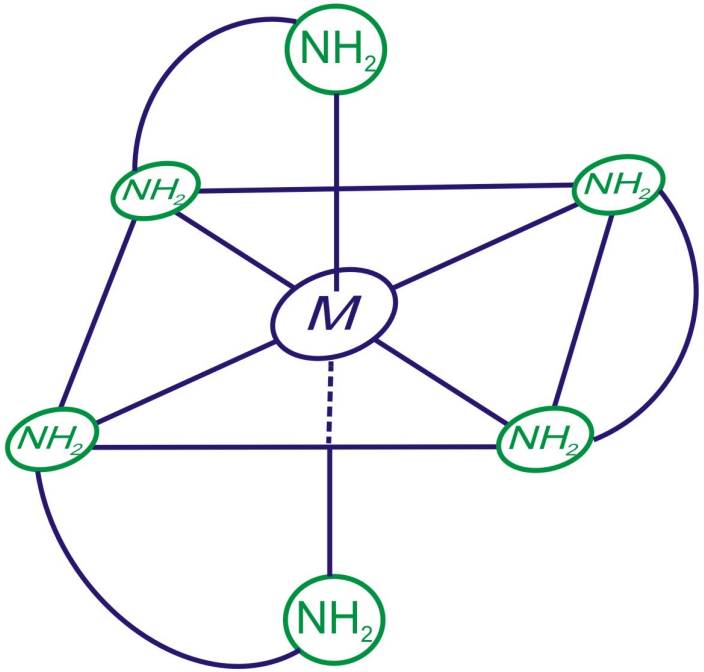
Compostos de Coordenação Opticamente Activos

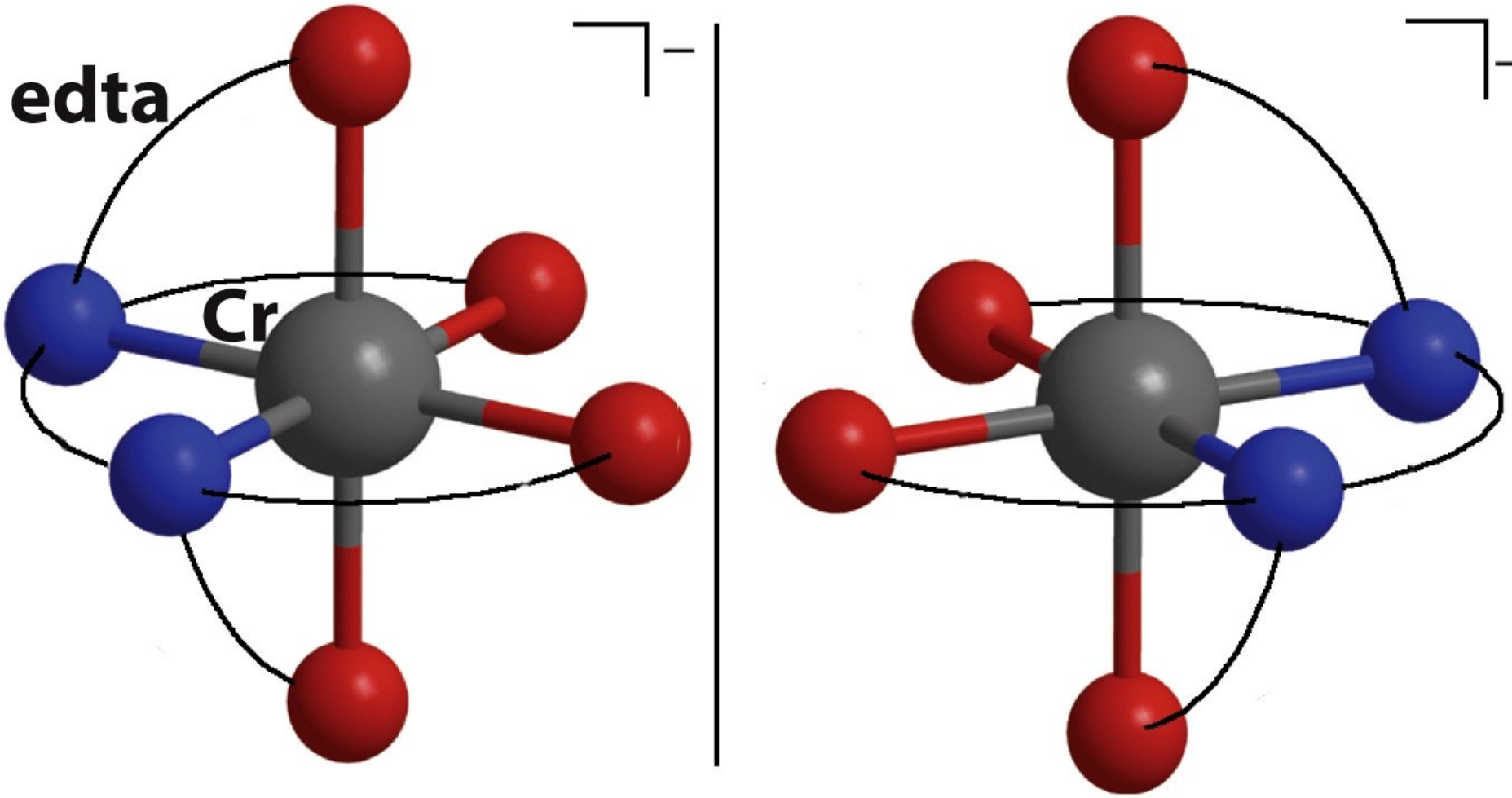
Exemplos:

espelho

$[Co(en)_3]^{3+}$

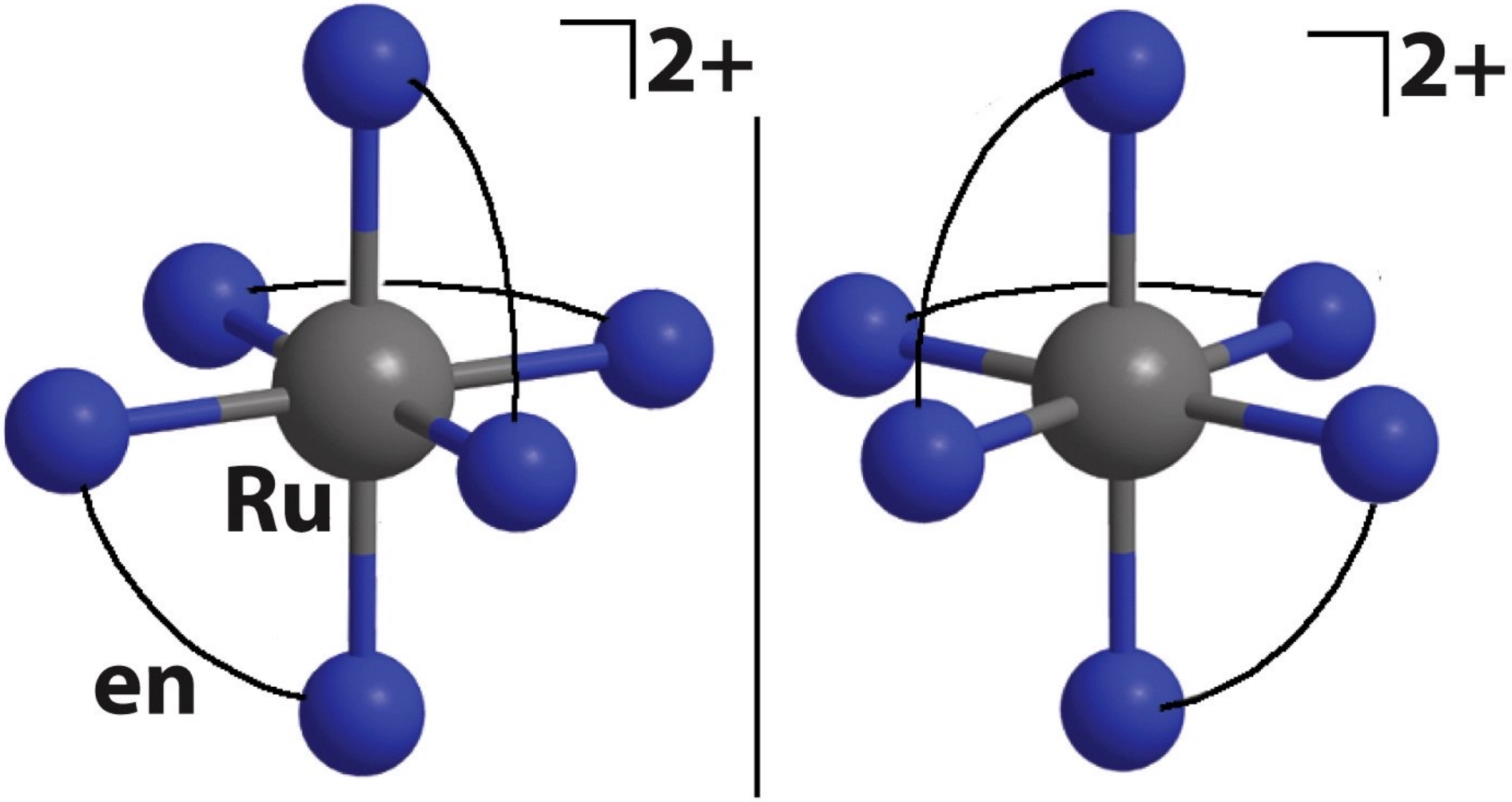






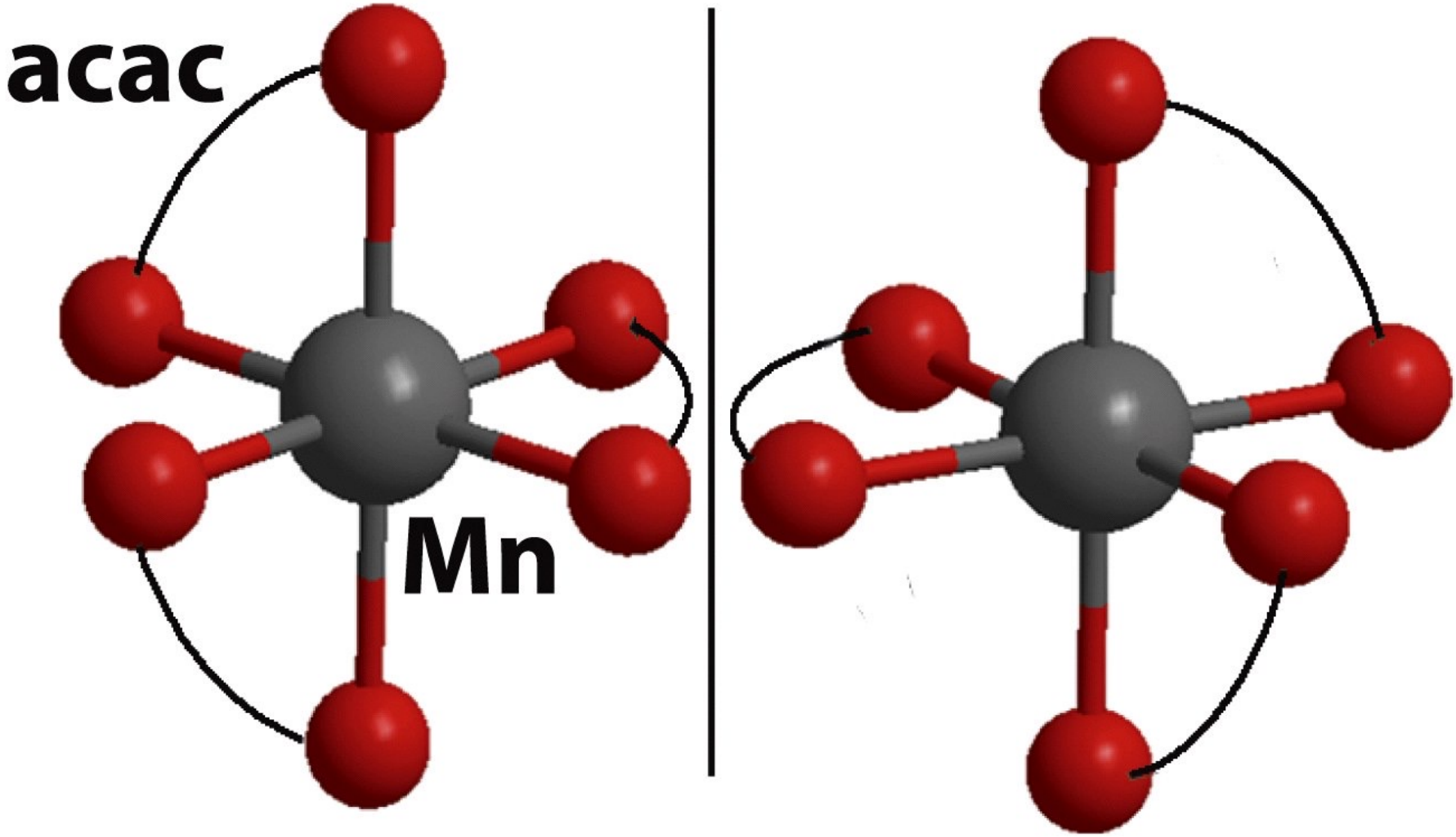
72 $[Cr(edta)]^-$ enantiomers

Structure 8-72
Shriver & Atkins Inorganic Chemistry, Fourth Edition



73 $[Ru(en)_3]^{2+}$ enantiomers

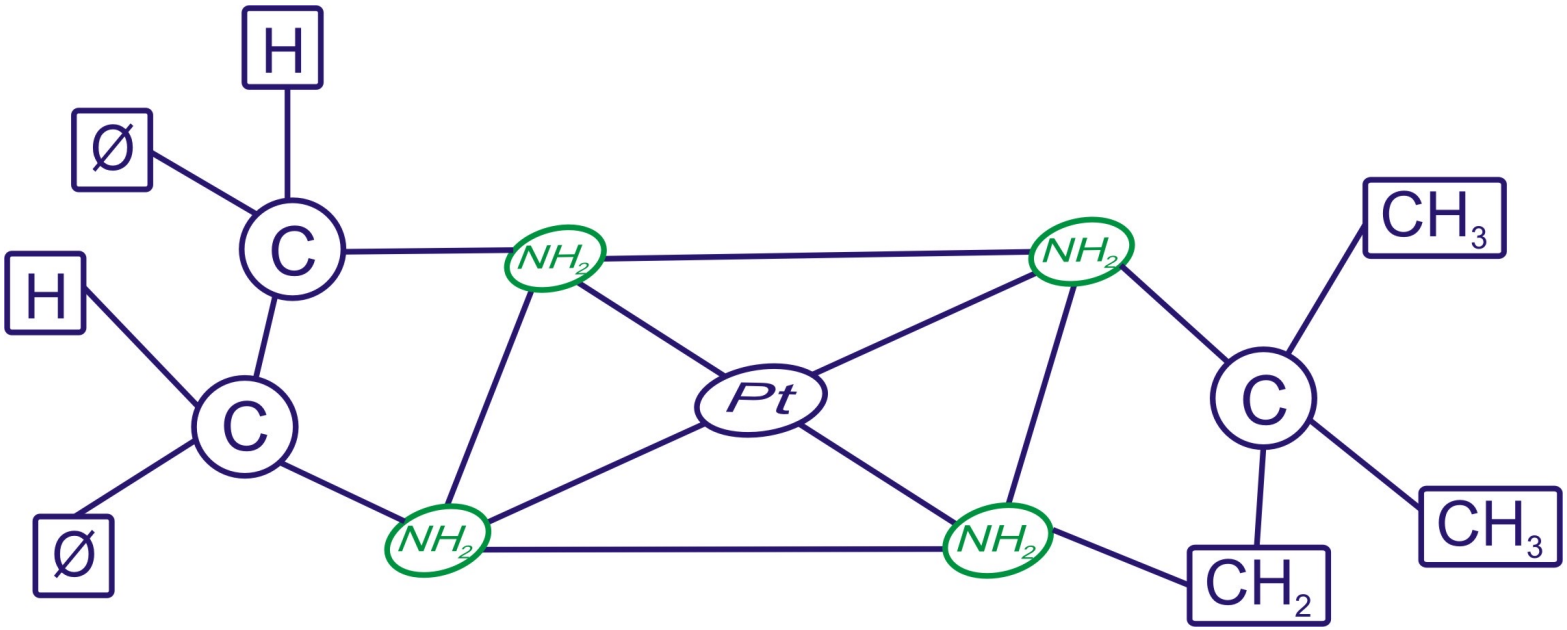
Structure 8-73
Shriver & Atkins Inorganic Chemistry, Fourth Edition



65 $[Mn(acac)_2]$ enantiomers

Structure 8-65
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Tetraédricos do tipo $[M(abcd)]^{4+}$



Quadrangular Plano

(Com ligandos de carbono assimétricos)

Isómeros de ligação

Ocorrem quando existem ligandos que se podem coordenar por diferentes átomos.

$[Cr(NH_3)_5(NO_2)]\,Cl_2$

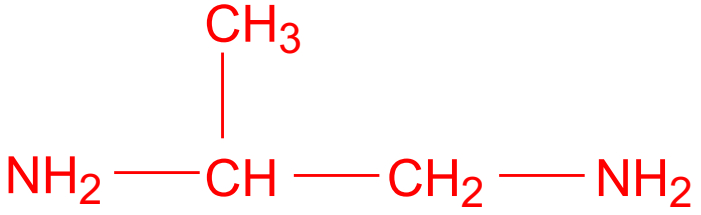
Cloreto de mononitro – N – pentamino cobalto (III)

$[Cr(NH_3)_5(ONO)]\,Cl_2$

Cloreto de mononitro – O – pentamino cobalto (III)

NOTA:

Podem existir isómeros devido à existência de isomerismo nos próprios ligandos.



Isómeros de ionização

Composição idêntica mas diferem no tipo de iões produzidos por ionização.

$[Co(en)_2(NO_2)Cl]\,Cl \longleftrightarrow [Co(en)_2(NO_2)Cl]^+ + Cl^-$

$[Co(en)_2Cl_2]\,(NO_2) \longleftrightarrow [Co(en)_2Cl_2]^+ + (NO_2)^-$

Isómeros de coordenação

Compostos de coordenação com composição idêntica mas a parte aniónica e catiónica são complexos com diferente distribuição de ligandos.

$[Cu(NH_3)_4]\,[Pt(Cl_4)]$ e $[Pt(NH_3)_4]\,[Cu(Cl_4)]$