

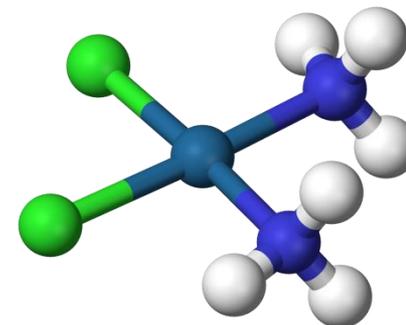
Aula 10 – A

Compostos de Coordenação

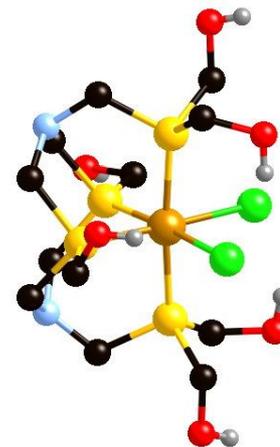
Configurações eletrônicas

Ligação metal-ligante

Estruturas e Geometrias / Isomeria



Alfred Werner



Metais



Prata



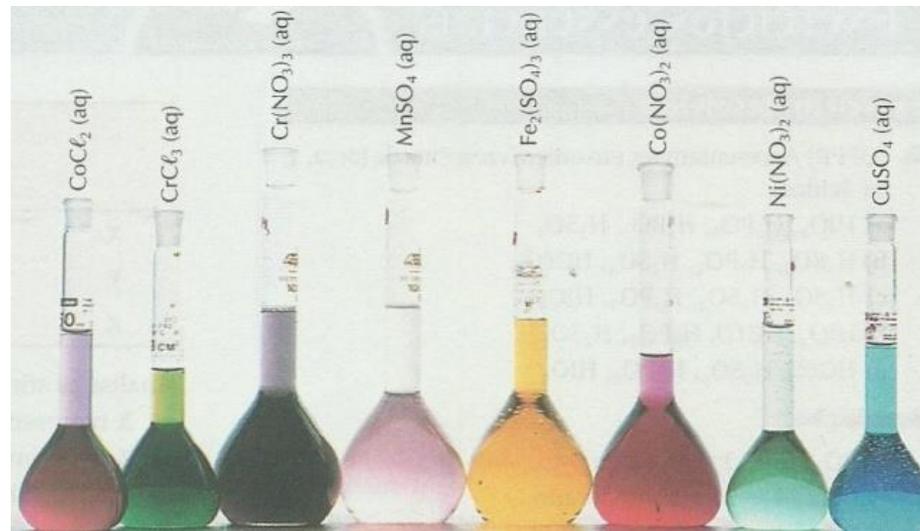
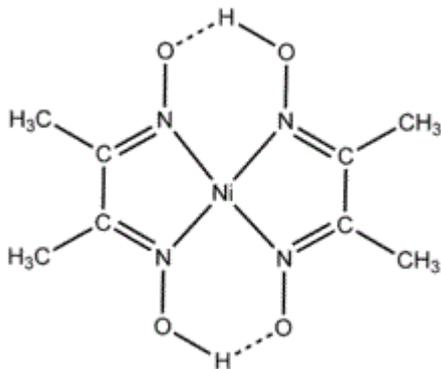
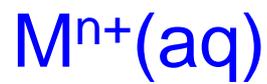
Ouro



Cobre

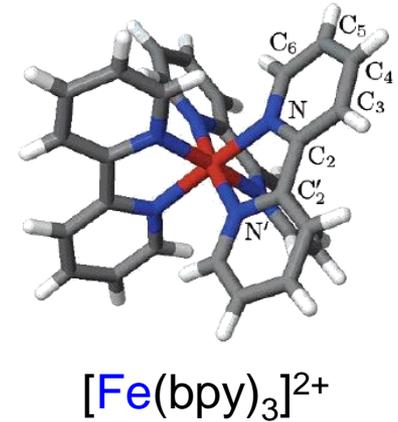
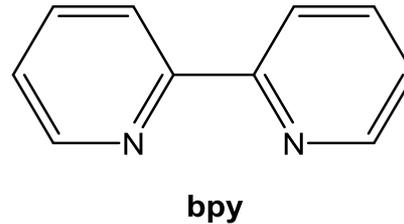
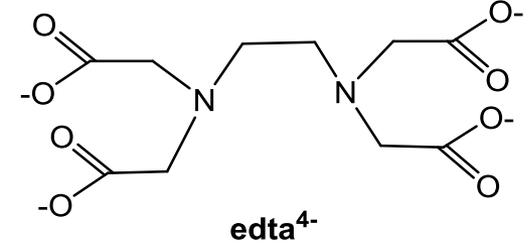
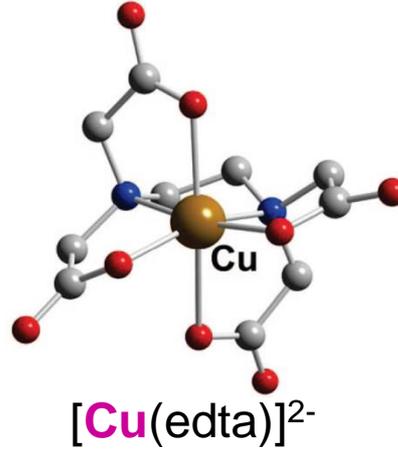
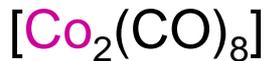
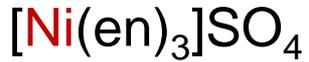
Elementos no estado metálico

Metais em Solução



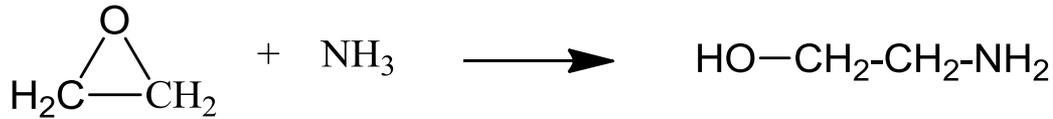
Metais de transição

Como explicar as **ligações químicas** em compostos como:

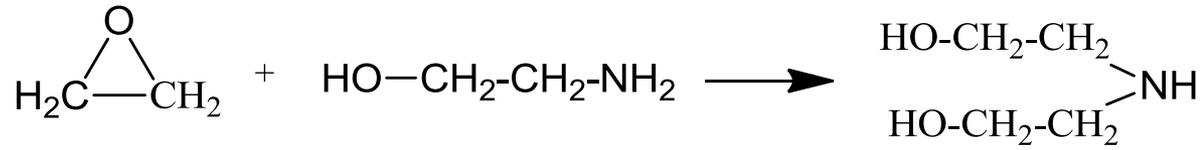


Por que Compostos de Coordenação são importantes para engenheiros?

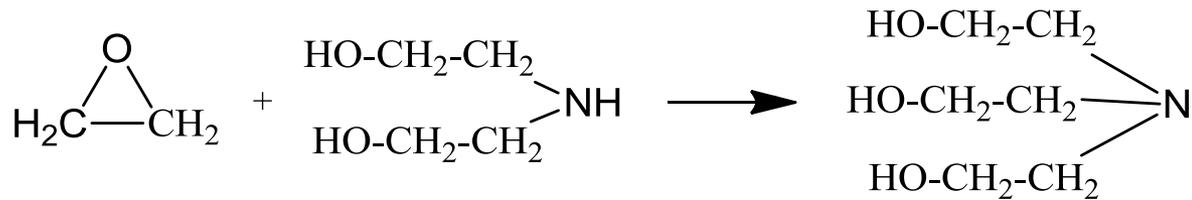
Oxiteno – produz **óxido de eteno**, a partir do etileno, e a partir dele diferentes produtos de importância industrial são obtidos, entre eles as **etanolaminas**, Usadas como agentes alcalinizantes e neutralizantes de emulsionantes aniônicos



MEA **Monoetanolamina**,
2 aminoethanol

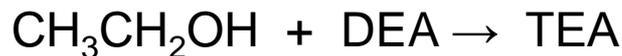
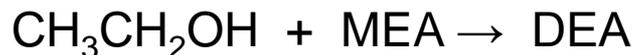


DEA **Dietanolamina**,
2,2 imino dibis (2-hydroxyethyl)
aminoethanol

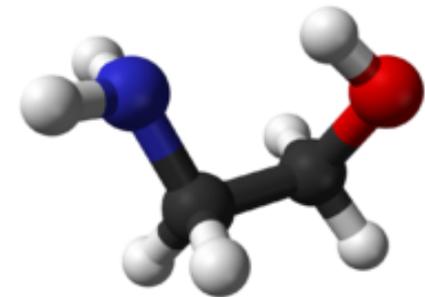


TEA **Trietanolamina**,
2,2',2"-nitrilotriethanol

Adiciona-se **excesso de etanol** para garantir a reação:



e obtém-se uma **mistura das três etanolaminas**

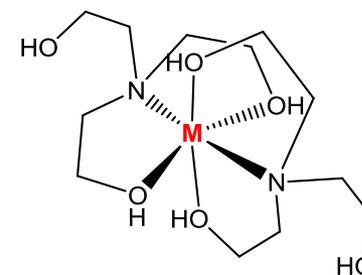
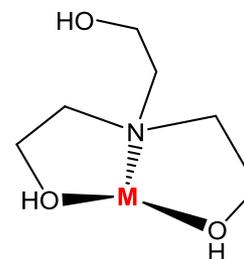
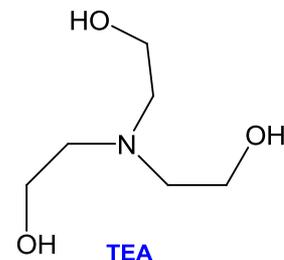


Separação por destilação fracionada

TEA[®] – produto obtido fora das especificações (ligeiramente colorida)

<http://www.oxiteno.com.br/cms/media/27047/etanolaminas-textile-pt.pdf>

	MEA	DEA	TEA
Líquido /cor	15	15	50
Pureza, %	99,2	84,0	99,0
Densidade 20°C, g/ml	1,019	1,100	1,125
PE, °C	170	> 100	340 (d)



Boletim Técnico:

Armazenar em tanques de **aço inoxidável 316 ou 304**, ou em **tanques de aço carbono revestidos com polietileno de alta densidade (PEAD)**.

O **cobre e suas ligas**, como latão, não devem ser utilizados nos equipamentos de armazenamento e transferência, uma vez que formam sais complexos com MEA, DEA e TEA[®], tornando os produtos ligeiramente azulados.

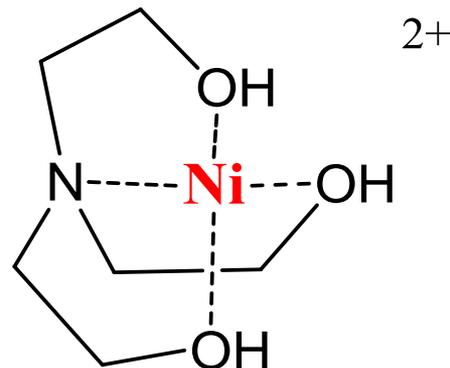
A **separação das etanolaminas** é feita em **três colunas de destilação em série**. No topo da primeira sai o **etanol**, no topo da segunda sai a **MEA**. Na terceira pelo topo sai a **DEA** e no fundo a **TEA**. Este é o ponto de mais alta temperatura.

O que ocorreu é que a **TEA sempre saia de especificação devido à cor avermelhada** ou **azulada** (o produto deve ser incolor).

As análises revelaram presença de **Níquel** ou **Cobre**. Inicialmente pensou-se que o **etanol** estivesse contaminado. Análises revelaram que não. O mistério foi revelado quando uma bateria de análises revelou que só a **TEA** apresentava a contaminação, no fundo da coluna.

O material de construção era o **aço inox 304** (18% de Ni e 8% de Co).

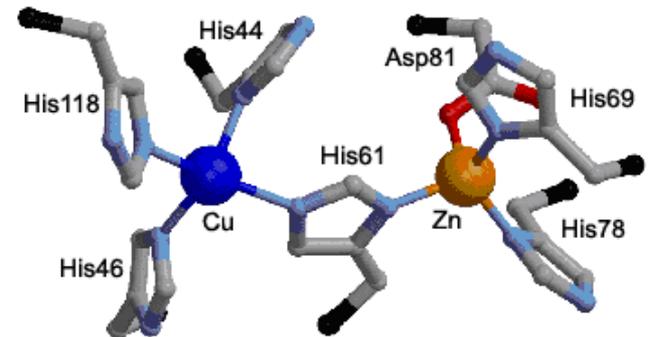
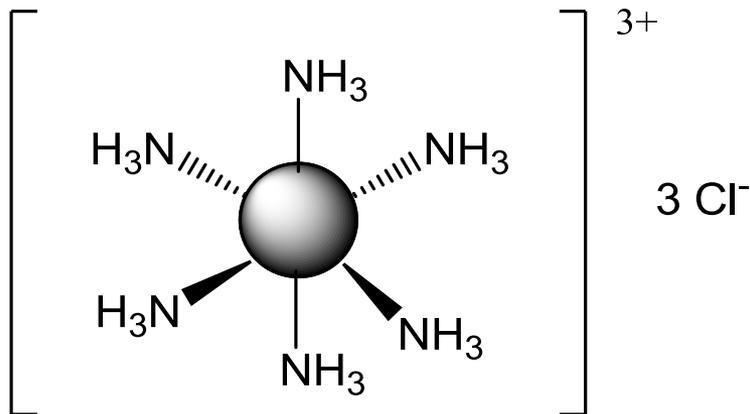
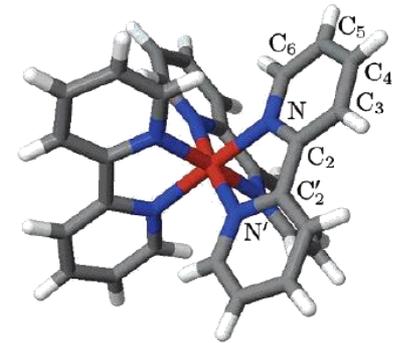
Então **a química revelou o mistério**: na temperatura de operação ($\pm 180^{\circ}\text{C}$) a **TEA** complexava o **Ni presente no aço inox** formando um composto colorido. A reação ocorria em quantidades mínimas, da ordem de **fração de ppm**, mas suficiente para colorir o produto.



O problema foi resolvido inicialmente com aplicação de vácuo mais pronunciado (**diminuição da temperatura de destilação**) e posterior substituição do refulvedor (equipamento de vaporização para a destilação) por **aço-liga sem níquel**.

Conteúdo

1. Compostos de coordenação: histórico e importância
2. Configurações eletrônicas
3. Diferentes ligantes
4. Estruturas e geometrias / Isomeria
5. Teorias de ligação
6. Propriedades espectrais e magnéticas



Conceitos Fundamentais

Para compostos comuns, como: NaCl ou BaSO_4 estamos acostumados a verificar o **estado de valência** ou o estado de oxidação do cátion metálico, que é contrabalançado pelos ânions.



Quando consideramos os **metais do bloco d**, entretanto, nos deparamos com **espécies mais complicadas** ou “complexas”, por exemplo:



Neste caso, tem-se que considerar, além da valência e dos correspondentes contra-íons, a **esfera de coordenação do metal** (isto é, o número de ligantes coordenados ao íon metálico), o átomo através do qual é feita a ligação do **L** ao **M** (**átomo coordenante**), a **geometria** do composto e a possibilidade de formação de **isômeros**.

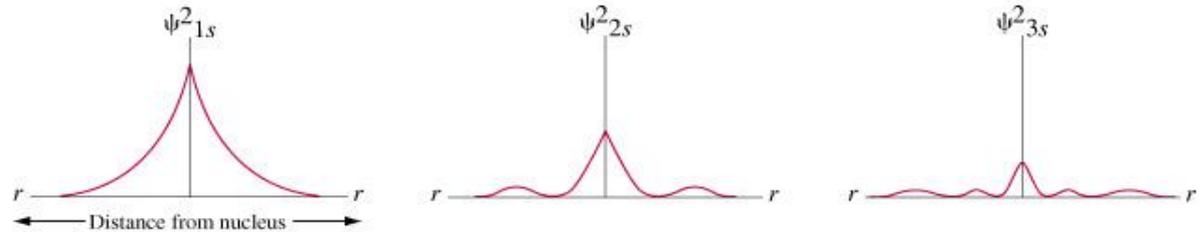
ORBITAIS

$$1s \quad \Psi = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

$$2s \quad \Psi = -\frac{1}{4} \left(\frac{1}{2\pi a_0^3} \right)^{1/2} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

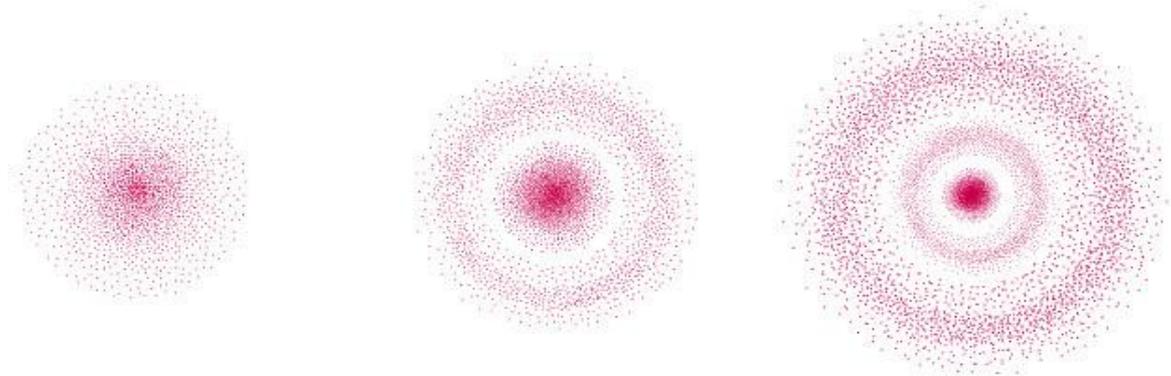
$$3s \quad \Psi = \frac{1}{9} \left(\frac{1}{3\pi a_0^3} \right)^{1/2} \left(3 - \frac{2r}{a_0} + \frac{2r^2}{9a_0^3} \right) e^{-r/3a_0}$$

Obtidos pela resolução da equação de Schrodinger



A forma do orbital s

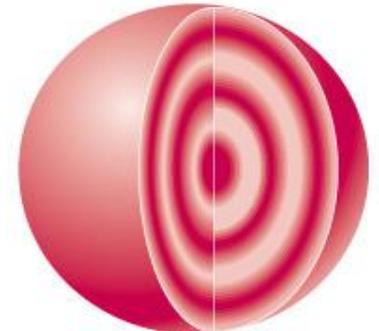
Representa a região no espaço onde é mais provável encontrar o elétron.



(a) 1s



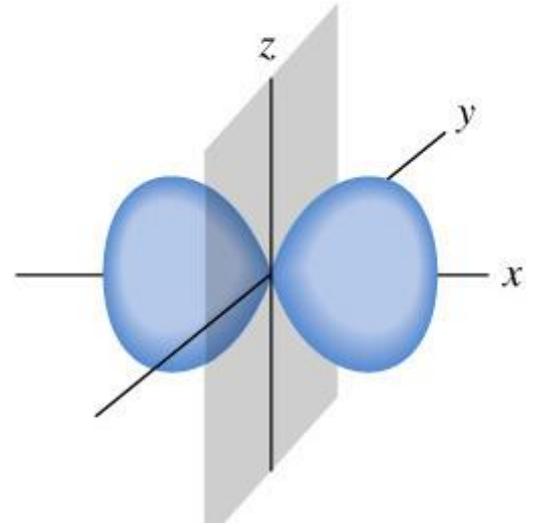
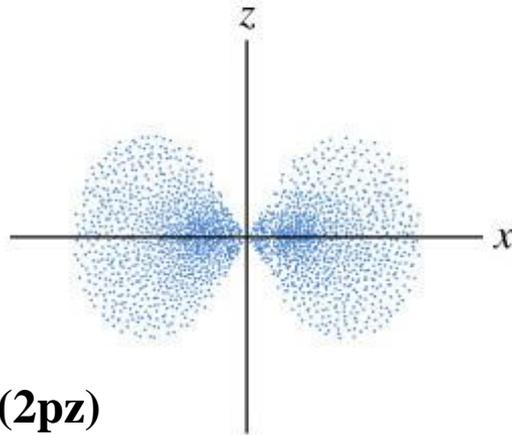
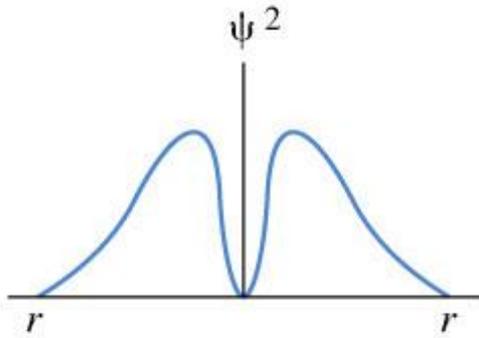
(b) 2s



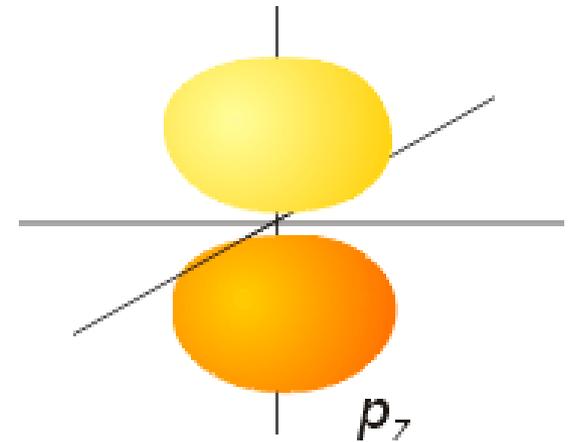
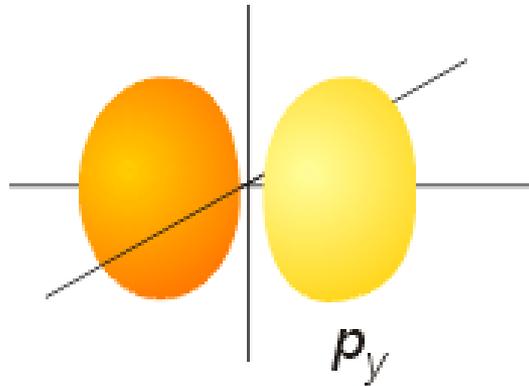
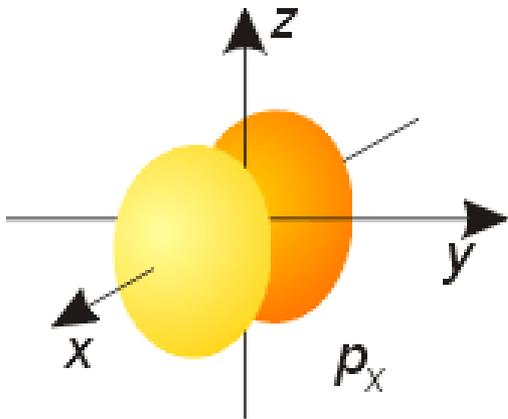
(c) 3s

A LIGAÇÃO QUÍMICA REFLETE AS CARACTERÍSTICAS DOS ORBITAIS USADOS

A forma do orbital p



$$\Psi = \frac{1}{4} \left(\frac{1}{2\pi a_0^5} \right)^{1/2} r e^{-r/2a_0} \begin{cases} \cos \theta & (2pz) \\ \text{sen} \theta \cos \phi & (2px) \\ \text{sen} \theta \text{sen} \phi & (2py) \end{cases}$$

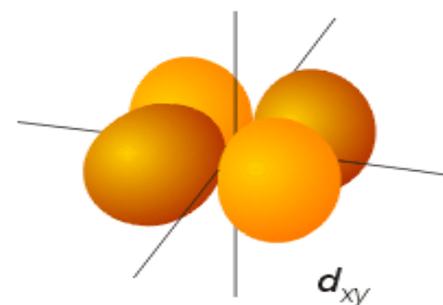
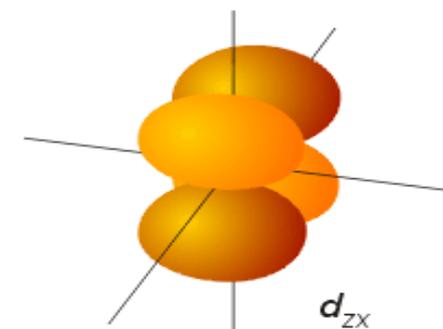
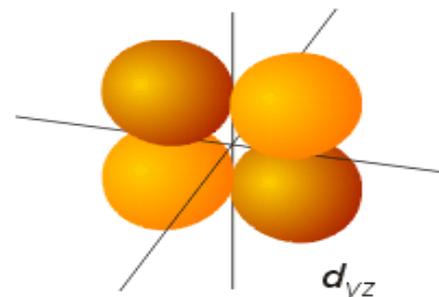
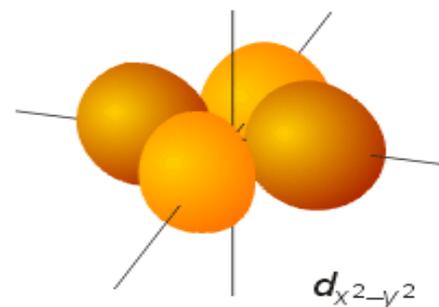
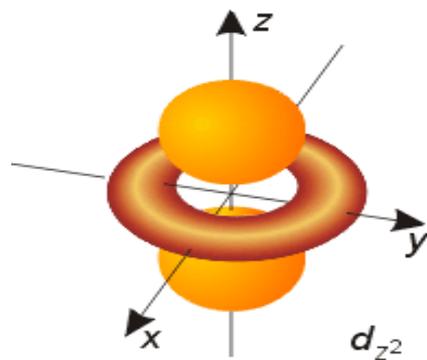


Orbitais d

Metais de Transição

Dependendo do **estado de oxidação do metal**, estes orbitais podem estar **parcialmente preenchidos**, levando a **espécies diamagnéticas ou paramagnéticas**.

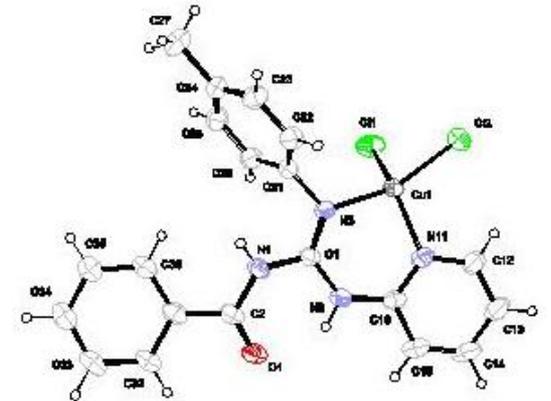
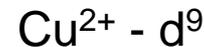
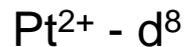
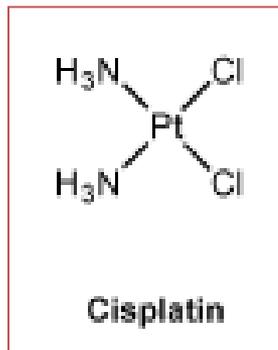
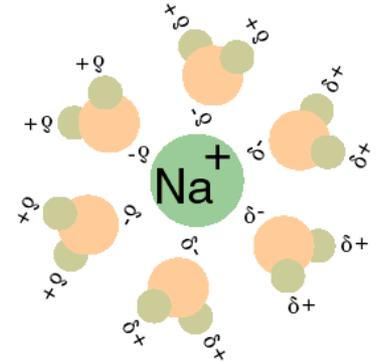
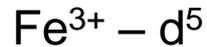
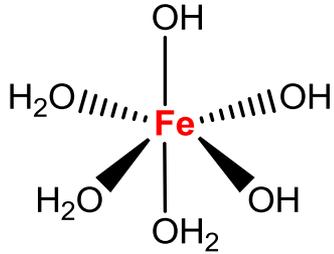
Estas espécies em geral apresentam **propriedades espectroscópicas e magnéticas** interessantes.



Acomodam até 10 elétrons e ao interagir com os orbitais dos ligantes têm sua energia modificada.

Exemplos de Compostos de Coordenação

Tem-se um **íon metálico central**, coordenado a **ligantes** através de átomos que contêm um **par de elétrons disponível para formar uma ligação**. Os ligantes podem ser íons ou moléculas simples, até biomoléculas como aminoácidos ou proteínas.

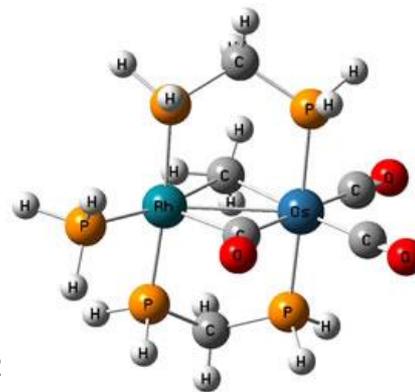




Pd - [Kr] 4s² 4p⁶ 4d⁸ 5s²

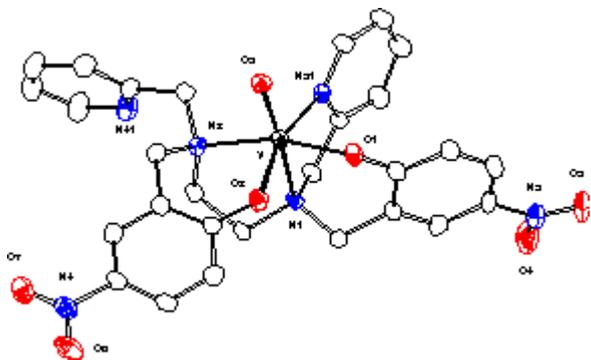
Pd(II) - d⁸

[Pd(pirazol)₃N₃]_n



Rh - [Kr] 4s² 4p⁶ 4d⁷ 5s²

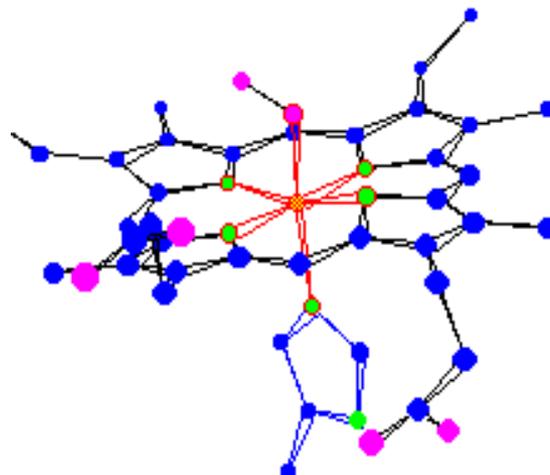
Os - [Xe] 5s² 5p⁶ 5d⁶ 6s²



Fe(II) - d⁶

Fe - [Ne] 3s² 3p⁶ 3d⁶ 4s²

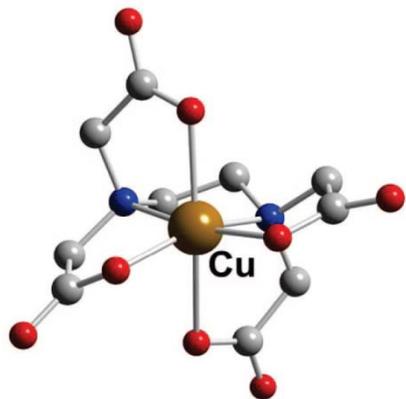
Fe(III) - d⁵



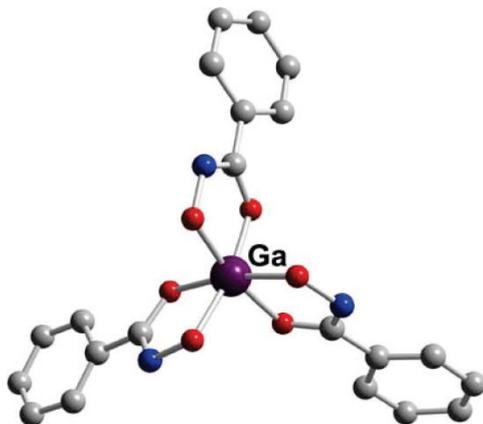
Oxi-hemoglobina

As espécies formadas podem ser:
catiônicas, aniônicas e neutras

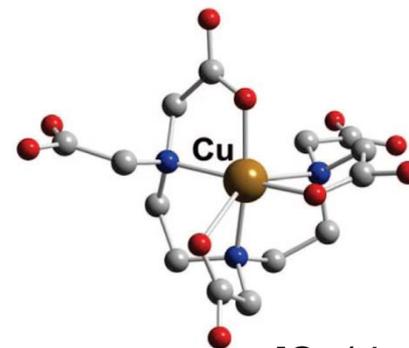
Chem. Rev. 2010, 110, 2858–2902



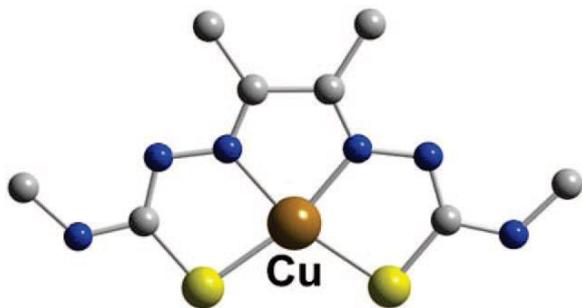
[Cu(edta)]²⁻



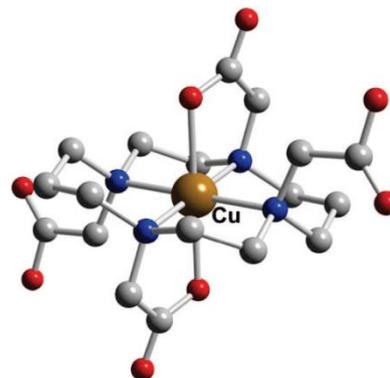
[Ga(tris(benzo-hidroxiato))]



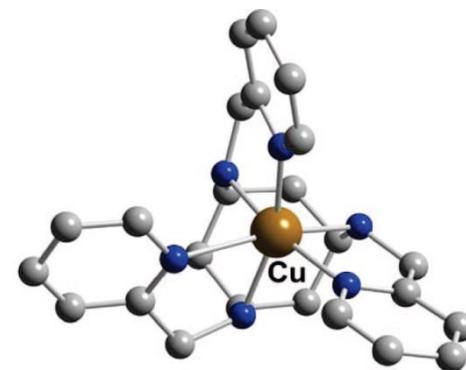
[Cu(dtpa)]³⁻



[Cu(atsm)]



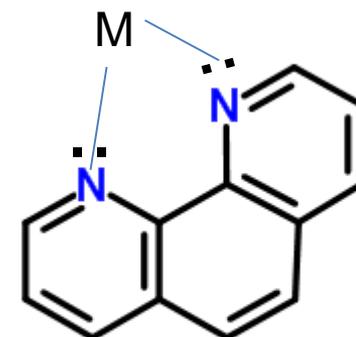
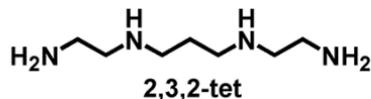
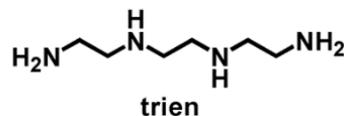
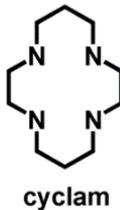
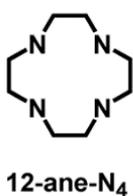
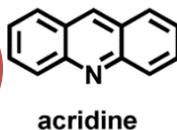
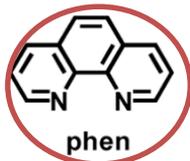
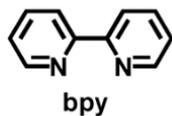
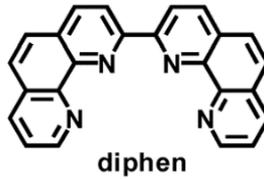
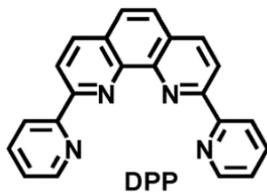
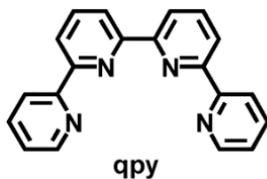
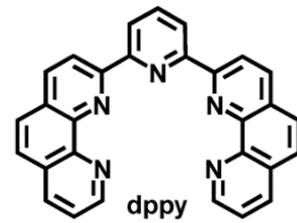
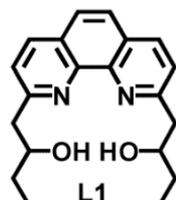
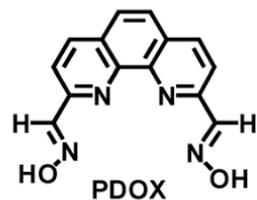
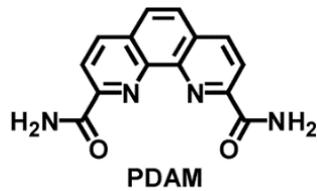
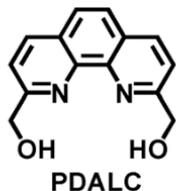
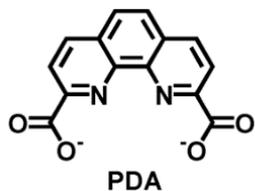
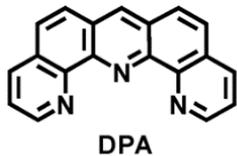
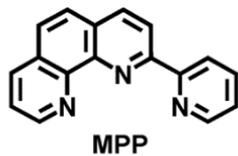
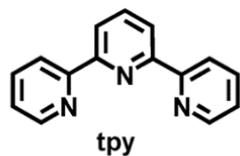
[Cu(H₂teta)]²⁻



[Cu(tachpyr)]²⁺

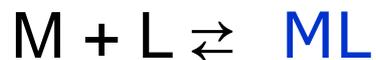
Regras da IUPAC – nomenclatura de comp. de coordenação

Exemplos de ligantes NITROGENADOS

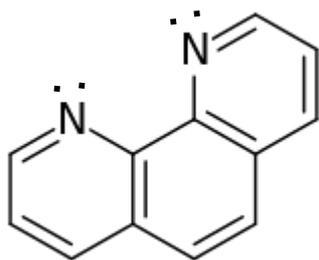


A ligação se dá através de pares de elétrons do ligante

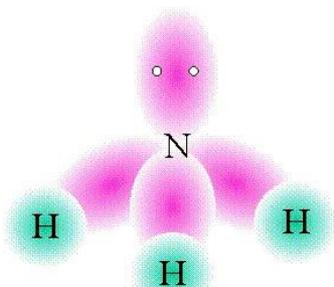
Estabilidade termodinâmica, dependendo do metal e do ligante



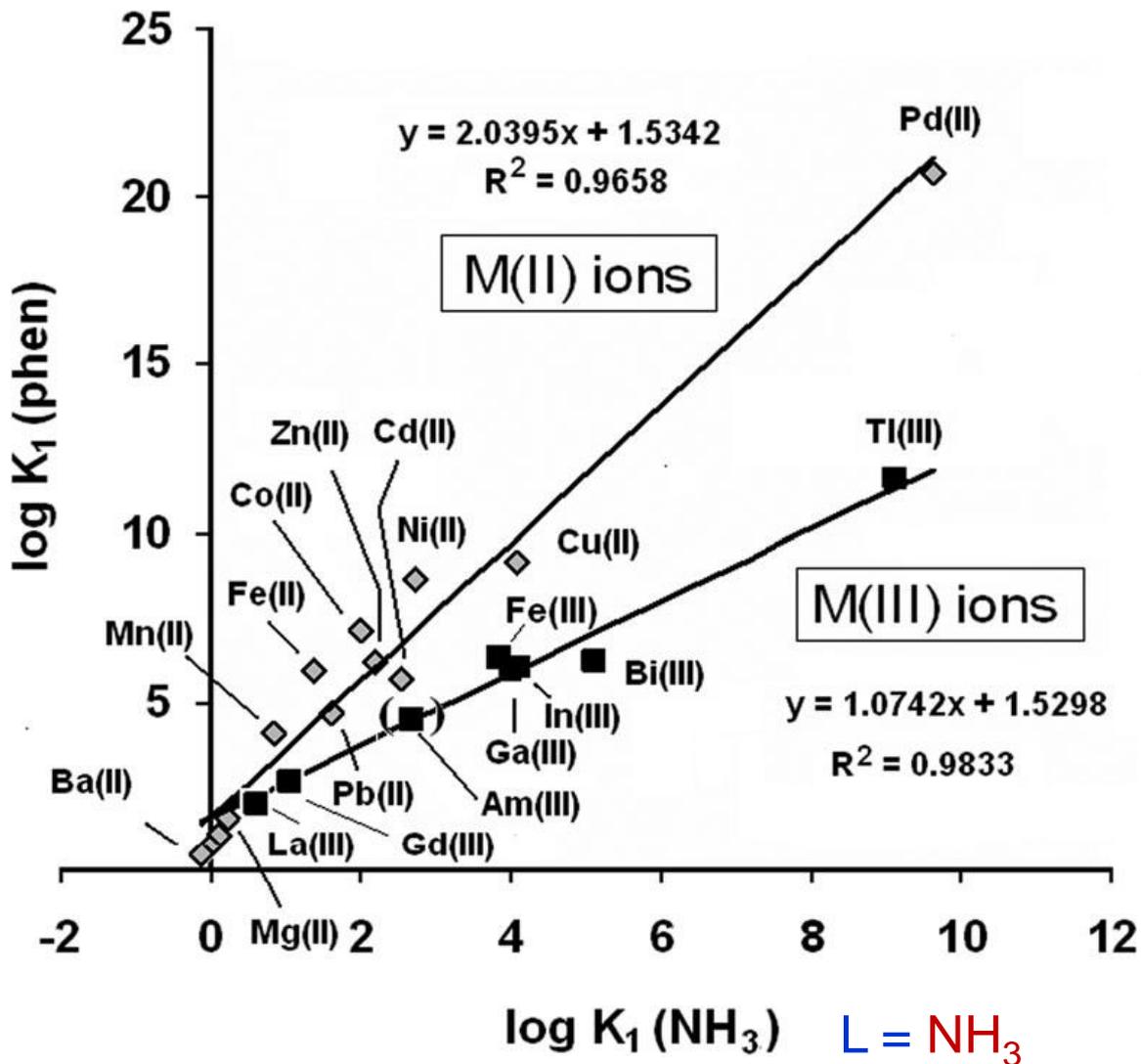
$$K_1 = [ML]/[M][L]$$



L = phen

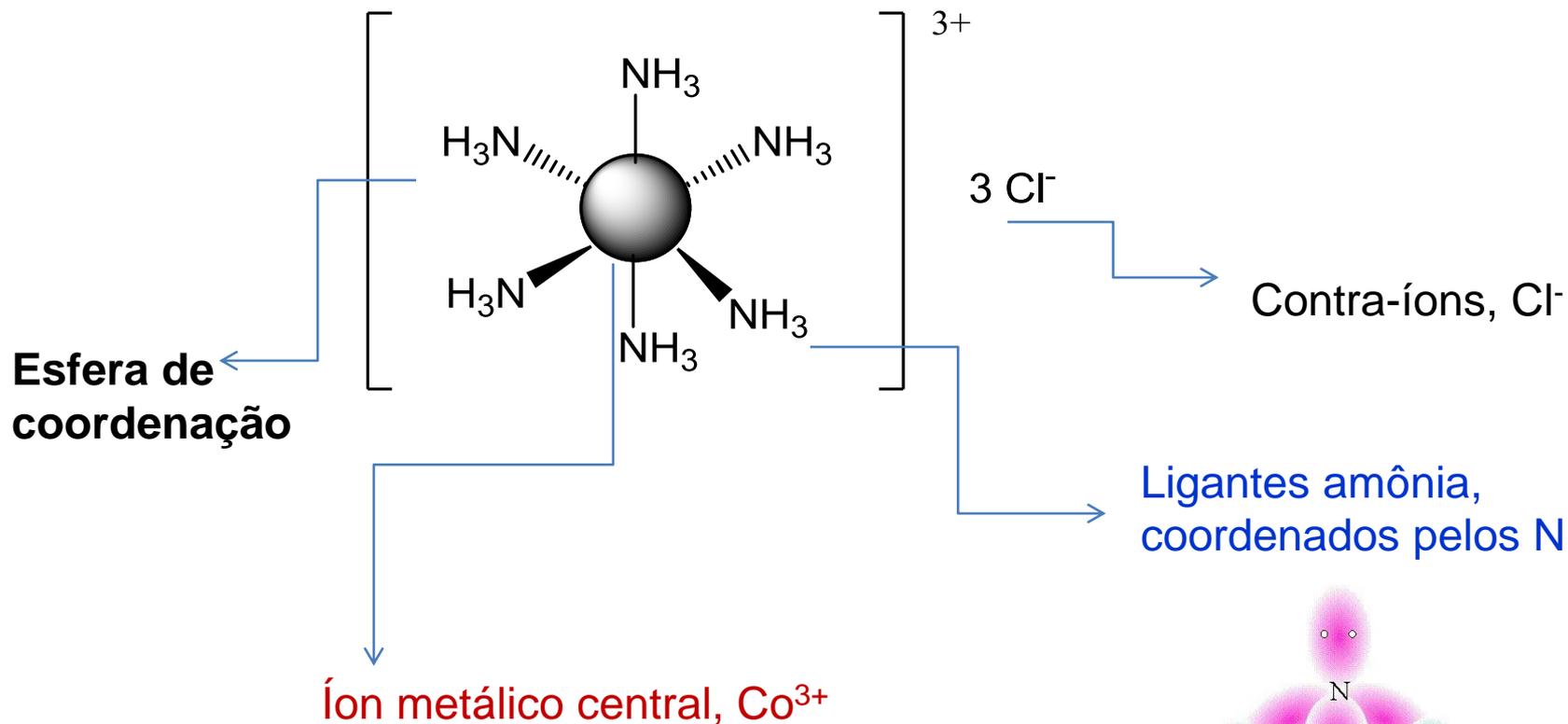


sp³ hybrid orbitals (tetrahedral)



A **Química de Coordenação** nasceu da necessidade de explicar compostos com valência maior do que a esperada.

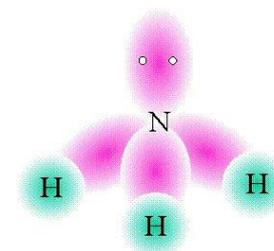
Ex.: $\text{CoCl}_3 \cdot 6\text{NH}_3$



Contra-íons, Cl^-

Ligantes amônia,
coordenados pelos N

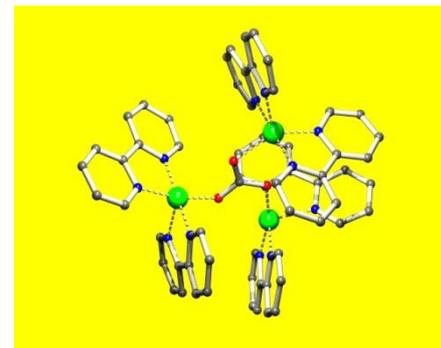
Íon metálico central, Co^{3+}



*sp³ hybrid
orbitals
(tetrahedral)*

Compostos de Coordenação

Características



Caracterizam-se por apresentar **um íon metálico central**, ligado a moléculas neutras ou ânions, denominados **ligantes**. O íon metálico atua como **ácido de Lewis** e os ligantes como **bases de Lewis**.

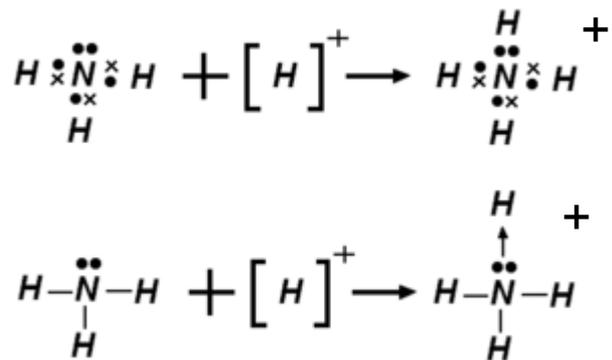
Apresentam **características espectrais** peculiares, com bandas internas do ligantes, bandas d-d e bandas de transferência de carga.

Também apresentam **propriedades magnéticas** características, com espécies diamagnéticas e para magnéticas, dependendo do estado de oxidação do metal e da força do campo ligante, formando complexos de alto spin ou baixo spin.

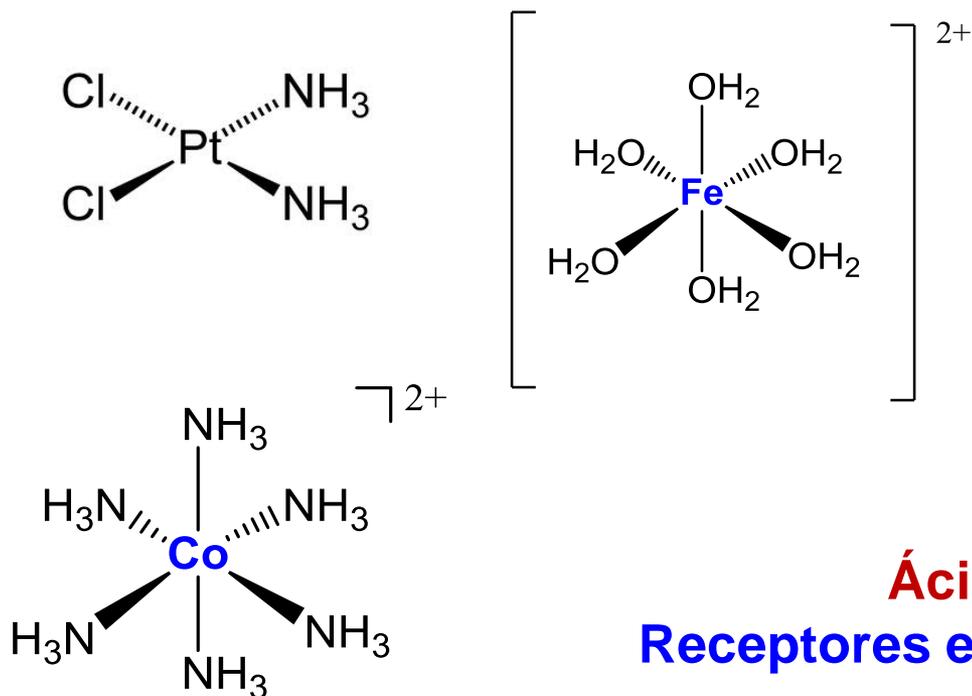
São formados geralmente por **reações de substituição** do ligante **aqua** (solvente) por ligantes de interesse.

Apresentam diversas possibilidades de **isomeria** (geométrica, de ligação, óptica, etc).

Compostos de Coordenação



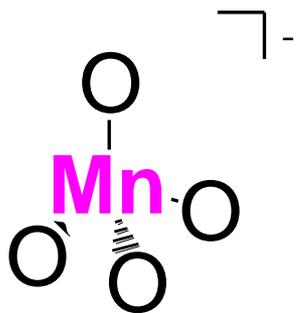
Ligações dativas ou de coordenação ocorrem quando um **ácido de Lewis** (um **receptor** de elétrons) **recebe** um par de elétrons de uma **base de Lewis** (um **doador** de elétrons), para formar um **aduto**.



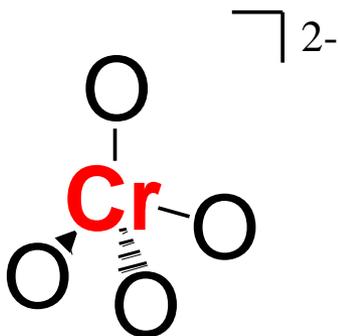
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$
 $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

Ácidos e bases de Lewis
Receptores e doadores de pares eletrônicos

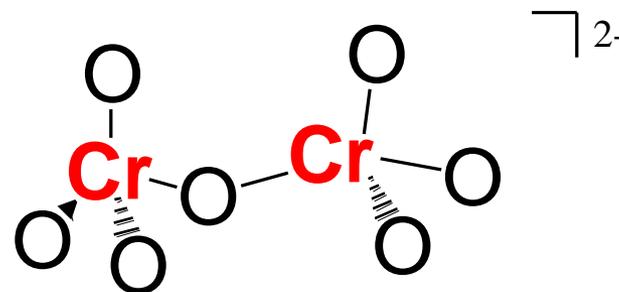
Nestas espécies o **ligante** é um íon **óxido**, O^{2-}



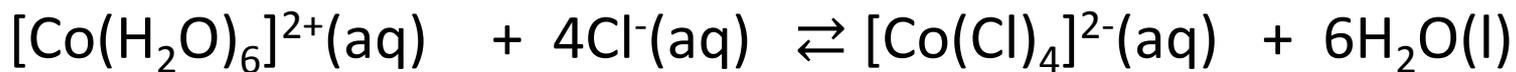
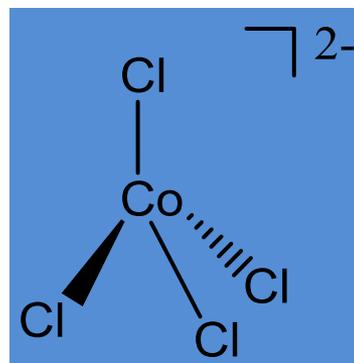
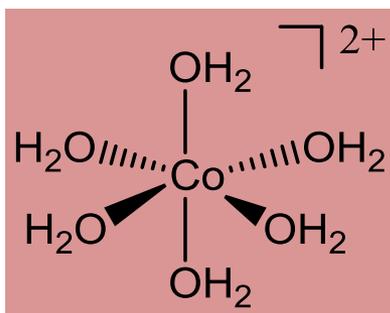
ânion permanganato



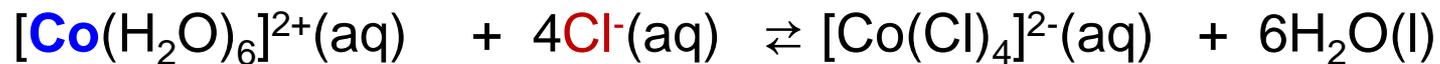
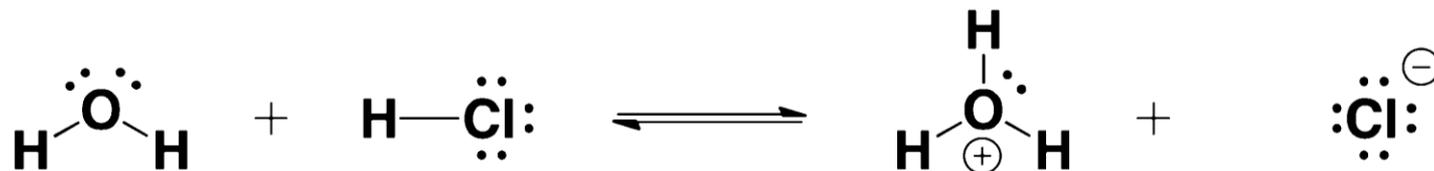
cromato



dicromato

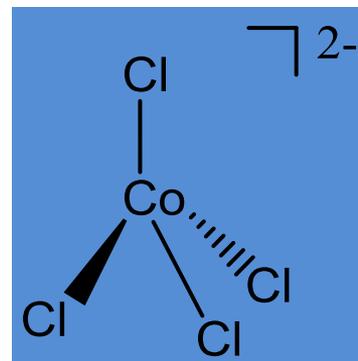
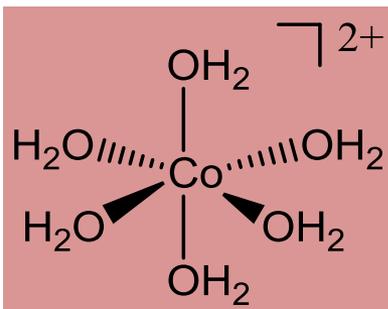


Reações ácido-base

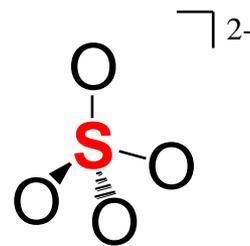
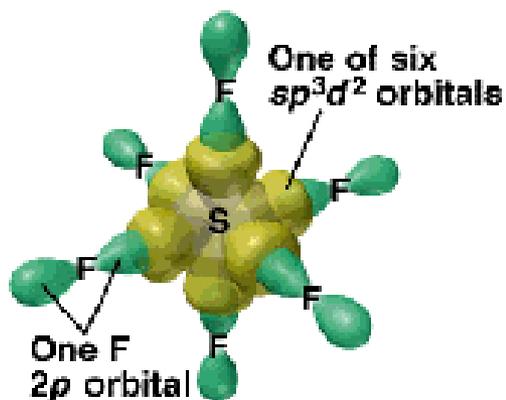


ácido de Lewis

base de Lewis

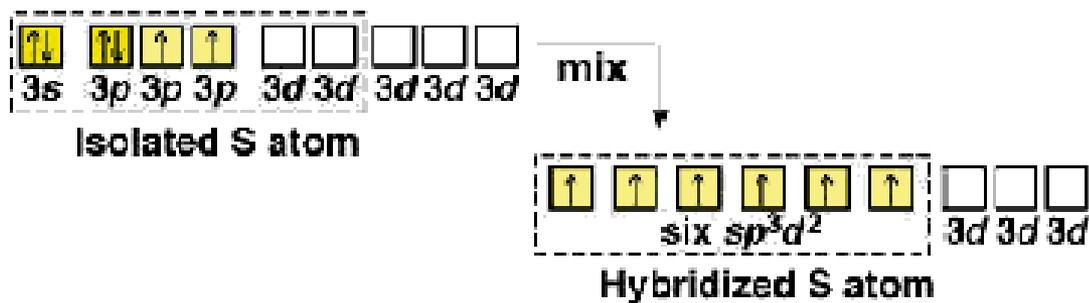


Obs.: pode-se ter também um átomo central não-metálico, como em



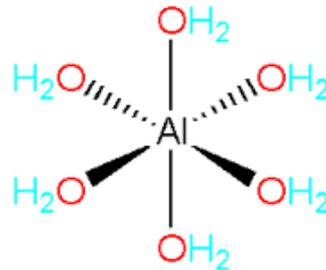
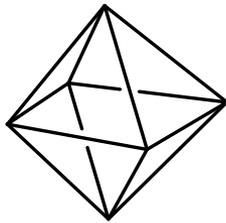
Íon sulfato

octaedro

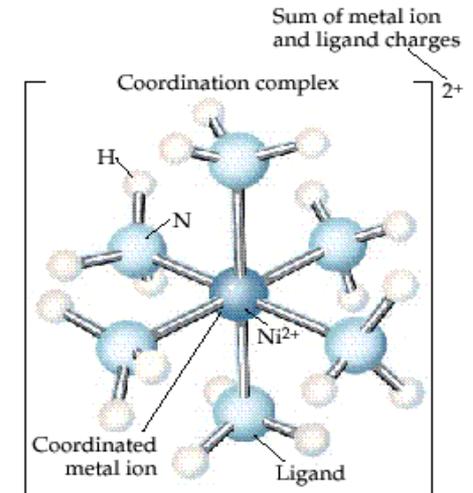


Metal e Ligantes

Ligantes são íons ou moléculas capazes de doar pares de elétrons – são bases de Lewis. Por sua vez o íon metálico central atua como ácido de Lewis

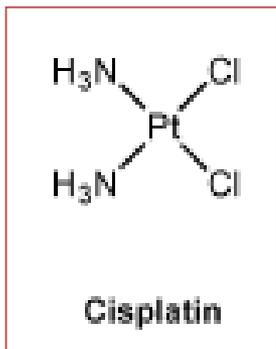


] $3+$



Ácido de Lewis = receptor de pares de elétrons

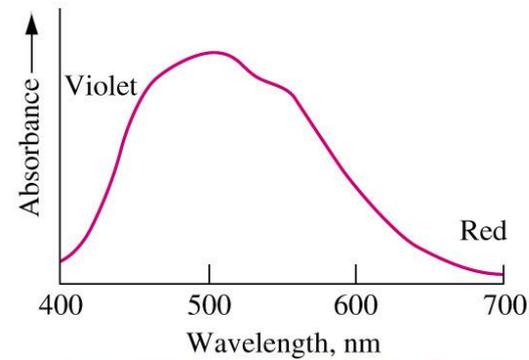
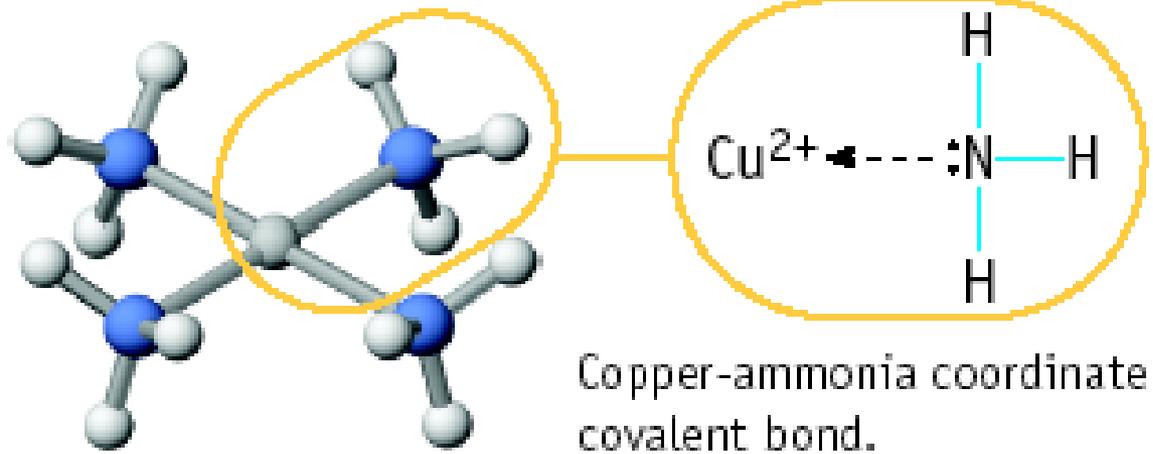
Base de Lewis = doador de pares de elétrons



Estes compostos podem ser **catiônicos**, **aniônicos** ou **neutros**.

Cisplatina foi o primeiro composto preparado com **atividade antitumoral**; é capaz de se intercalar na estrutura do DNA, levando à chamada morte programada da célula ou **apoptose**. É um exemplo de espécie complexa neutra.

Formação:

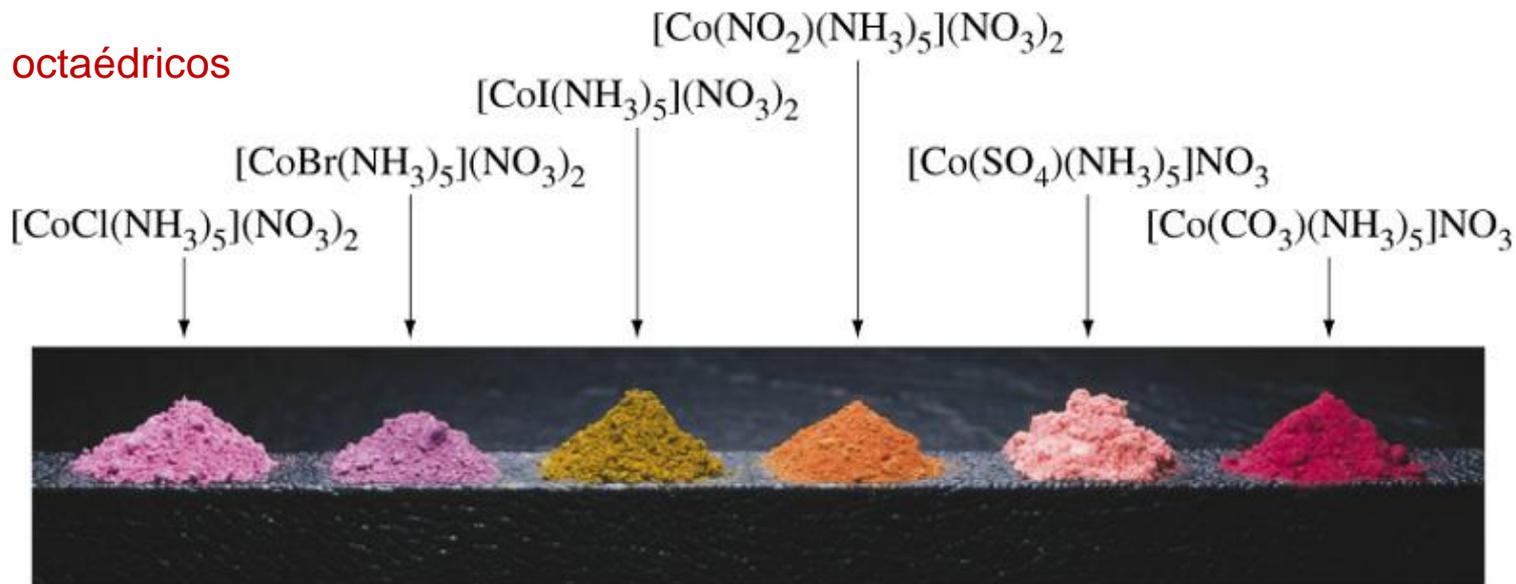


(a)

(b)

Complexos com metais de transição em geral apresentam grande diversidade de cores, em decorrência de suas estruturas eletrônica e geométrica.

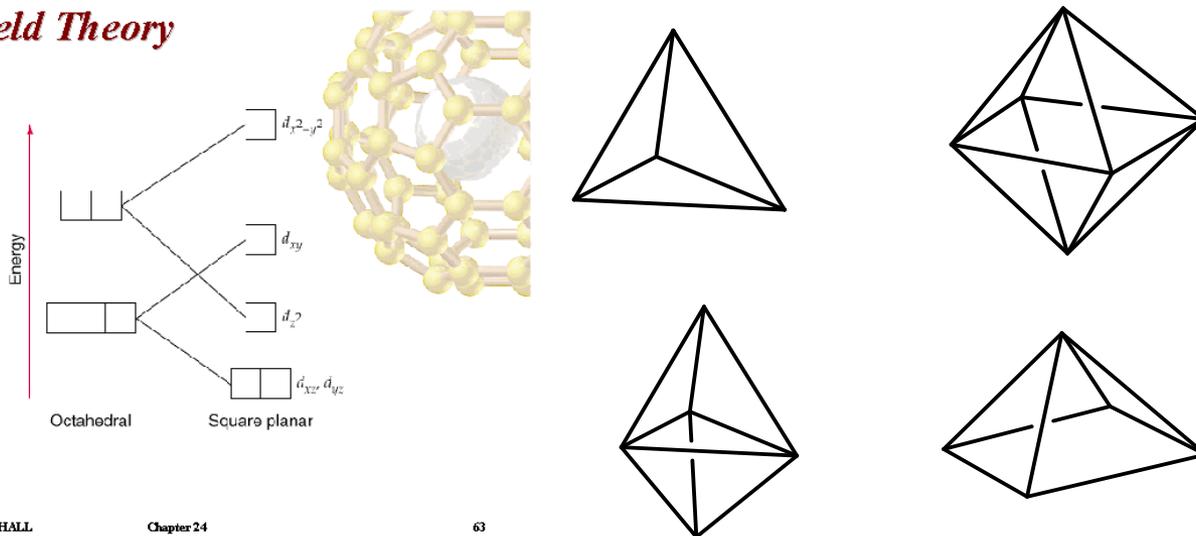
Compostos octaédricos



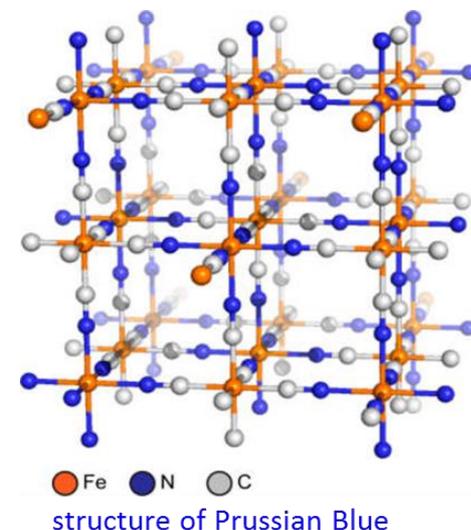
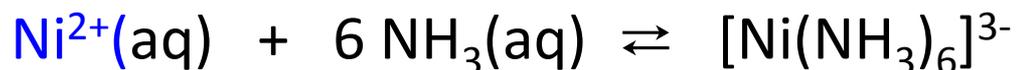
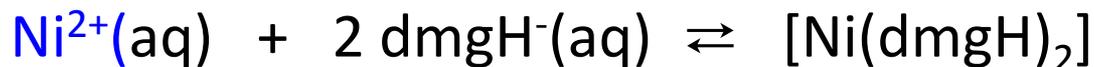
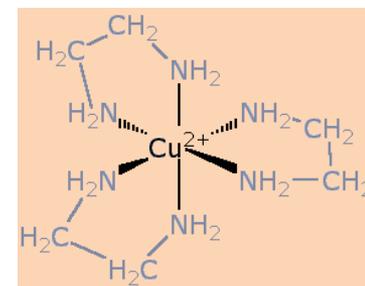
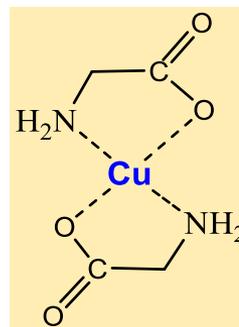
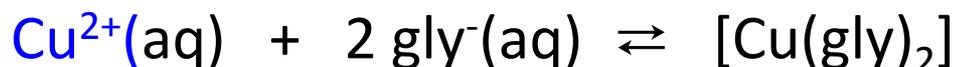
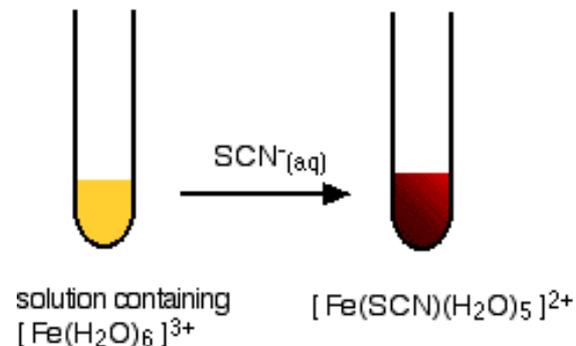
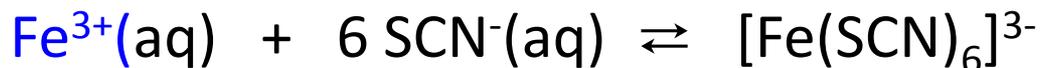
Crystal-Field Theory

Cor = transições eletrônicas na faixa do visível

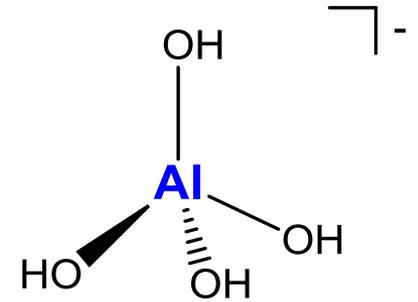
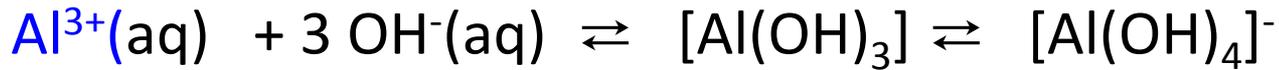
$$\Delta E = h \nu = hc / \lambda$$



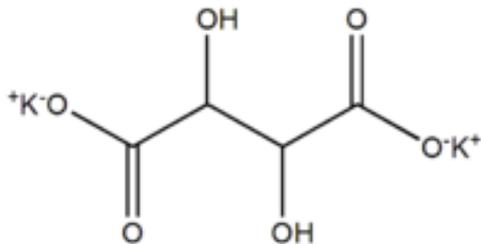
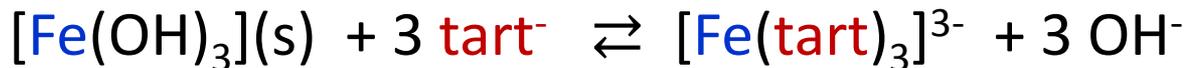
Demonstrações:



Demonstrações:



Íon aluminato

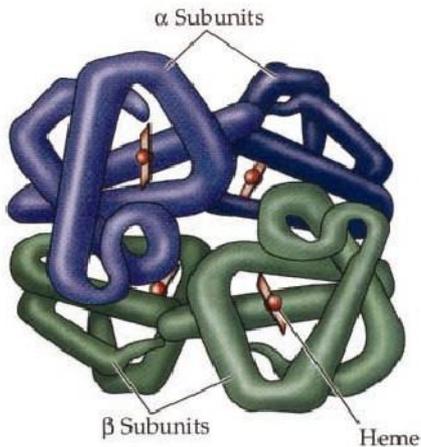
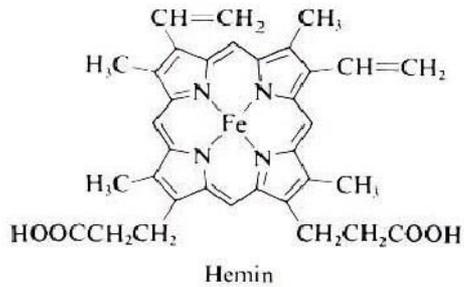


Tartarato de potássio

Ânions **tartarato** consegue manter íons de ferro dissolvidos, mesmo em pH alcalino

As espécies complexas podem ser **catiônicas**, **neutras** ou **aniônicas**. Quando possuem carga são solúveis em água.

Aplicações:



Hemoglobina

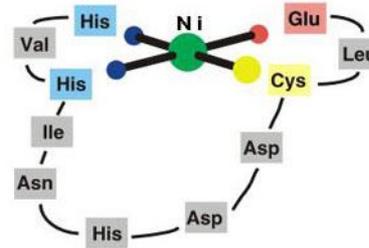
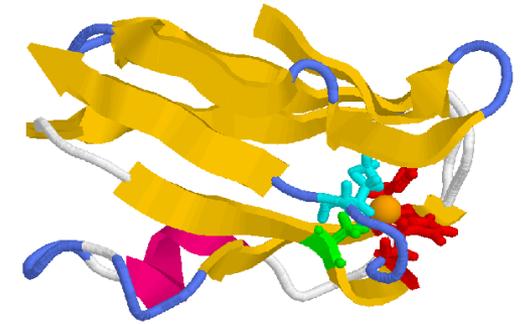


Figure 1. A model of the high-affinity nickel site in NikR based on x-ray absorption spectroscopy (XAS) and mutagenesis results. Residues are colored according to donor atom types (blue: nitrogen; red: oxygen; and orange: sulfur).



Plastocianina

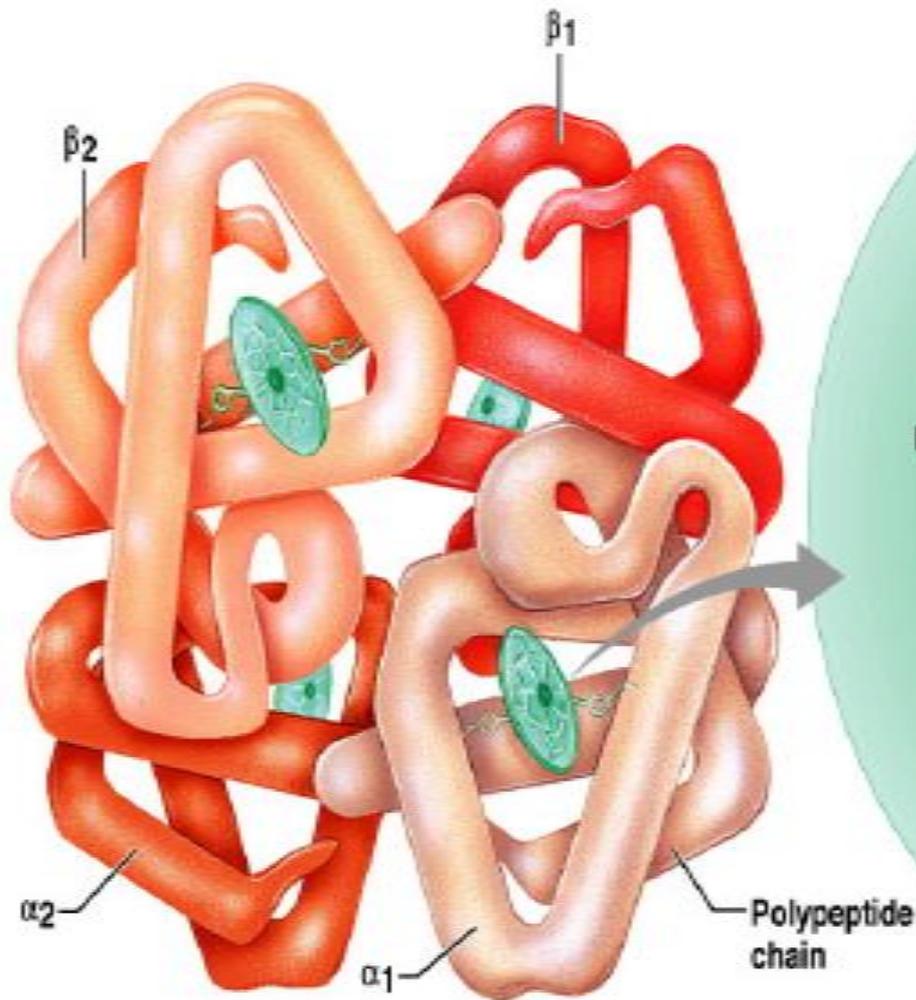
Nas **metaloproteínas**, o ligante é uma proteína e no meio biológico várias biomoléculas podem atuar como ligantes, coordenando íons metálicos.

O **sítio ativo** de metaloproteínas constitui um composto de coordenação, onde um ou mais íons metálicos se ligam a **grupos coordenantes** da proteína, como $-\text{COOH}$, $-\text{NH}_2$, $-\text{SH}$, etc.

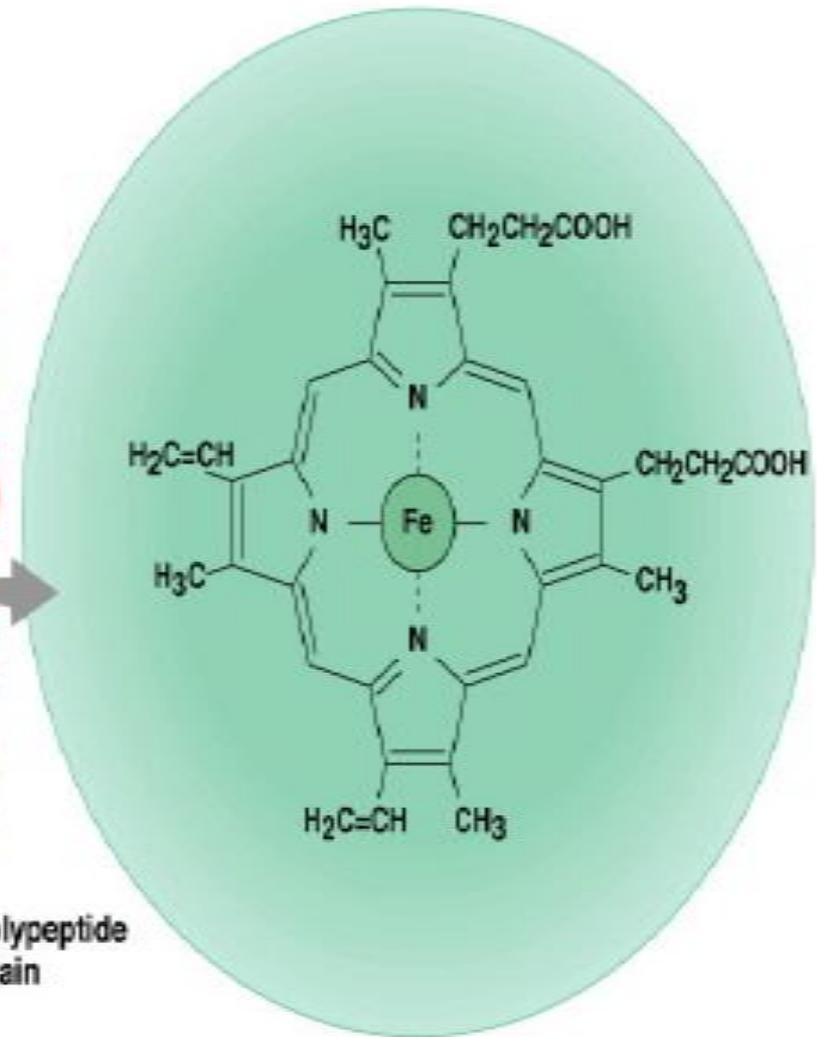
Estes grupos definem e modulam as **propriedades estruturais** e de **reatividade** do íons metálico.

Pode-se **mimetizar** o sítio ativo de enzimas com ligantes mais simples, para desenvolver catalisadores mais seletivos.

Grupo prostético da Hb (grupo onde está coordenado o íon de ferro)

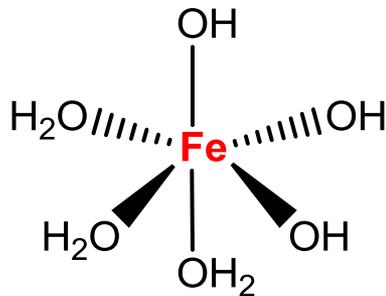


(a) Hemoglobin



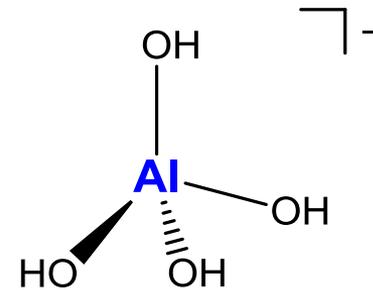
(b) Iron-containing heme group

Extração do alumínio da bauxita



Espécie octaédrica

Espécies complexas



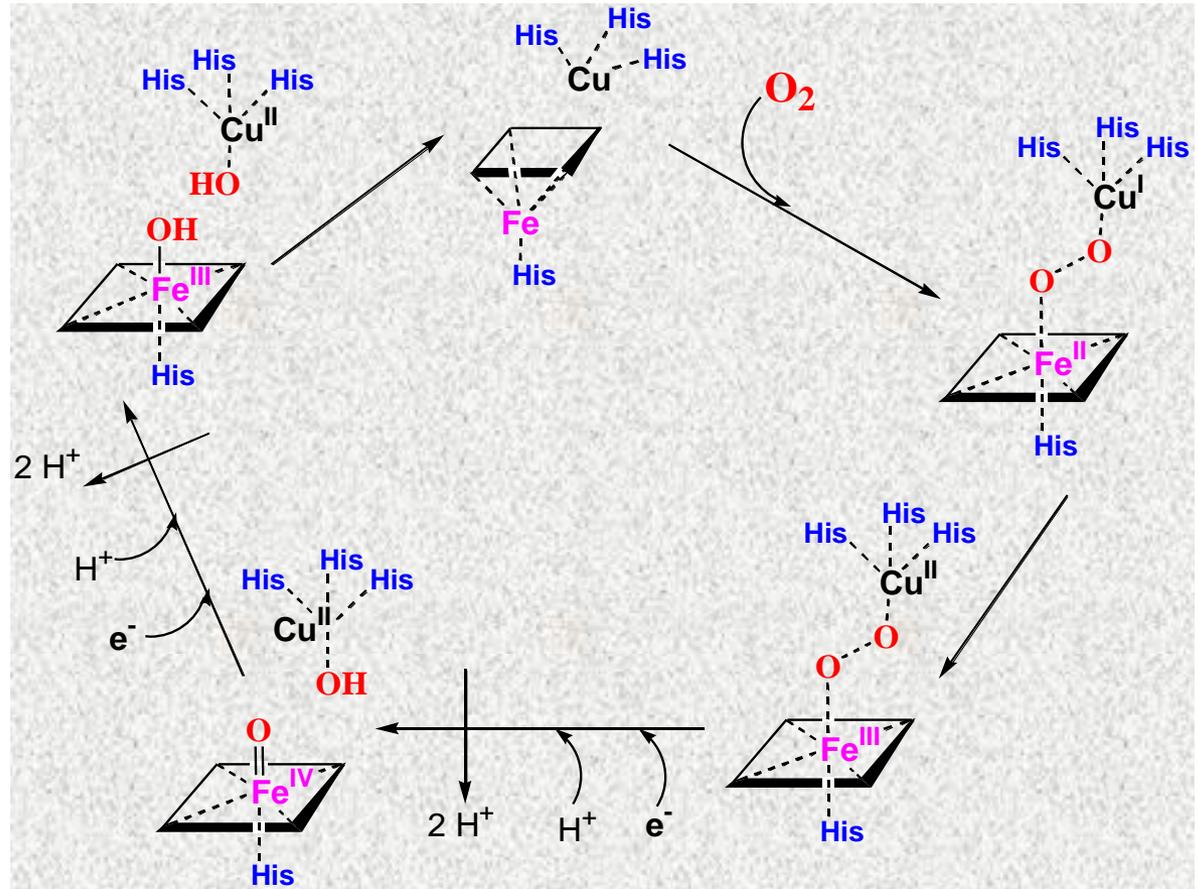
Espécie tetraédrica

Consegue-se dissolver o **alumínio** com excesso de hidróxido, mantendo o **ferro** precipitado, através da formação de diferentes compostos de coordenação.

Catalisadores

Muitos deles constituem compostos de coordenação, garantindo a **interação entre o agente oxidante e o substrato**, por exemplo.

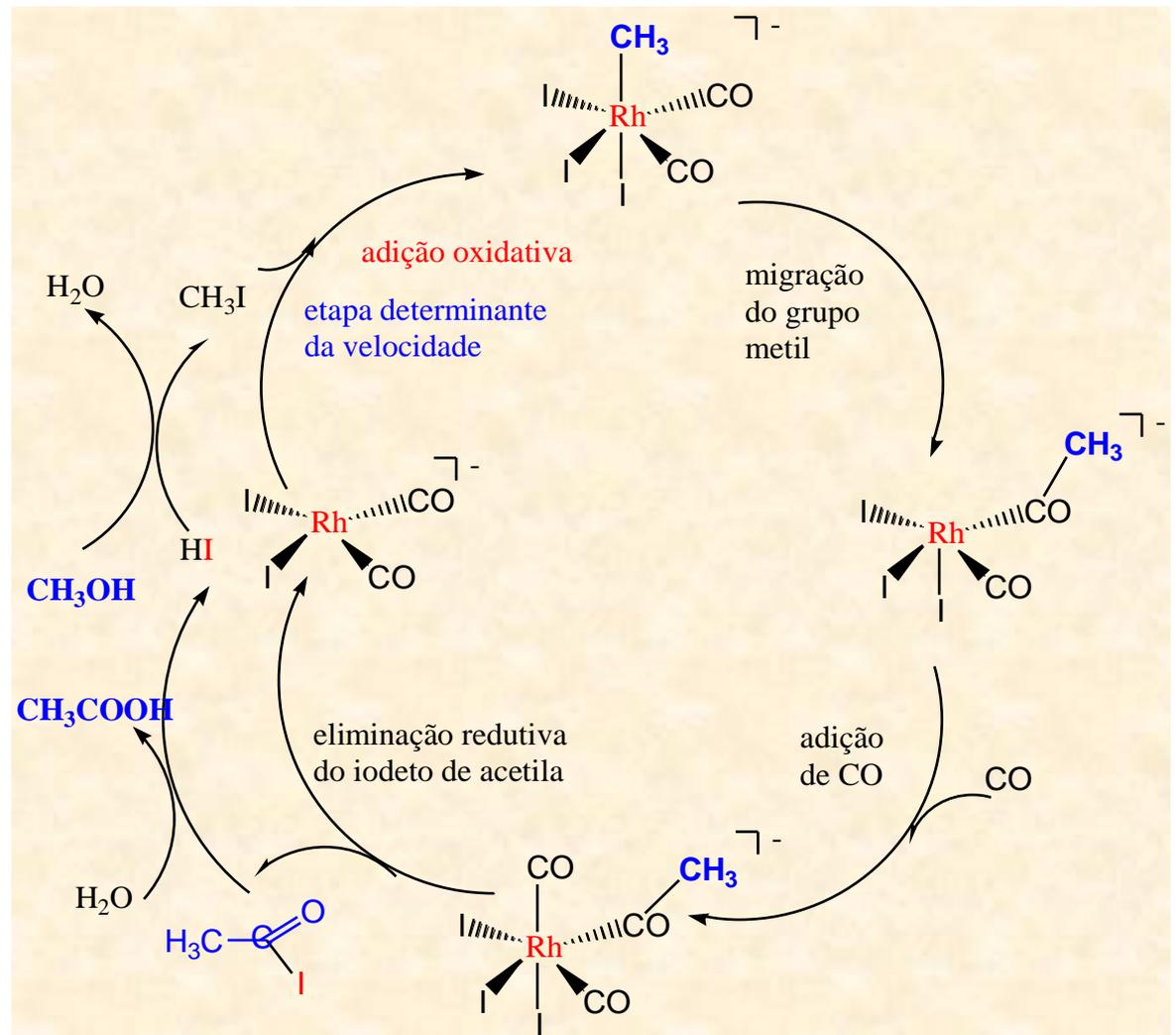
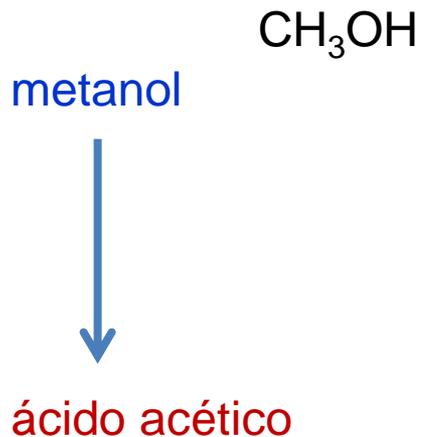
Ciclo catalítico da **citocromo c oxidase**, enzima atuante em nossa cadeia respiratória, que catalisa a redução do oxigênio molecular a duas moléculas de água



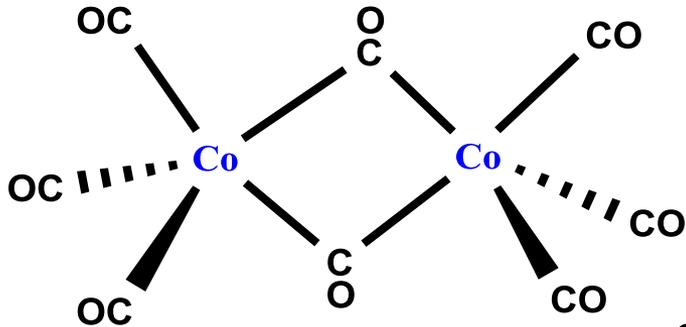
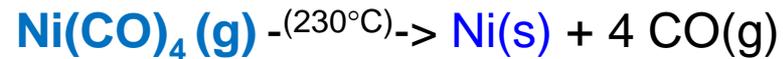
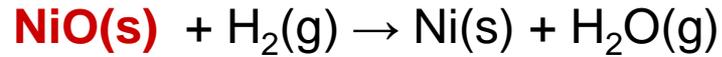
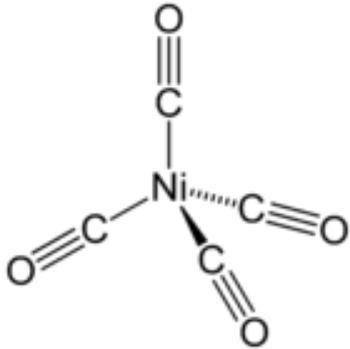
Carbonilação do metanol



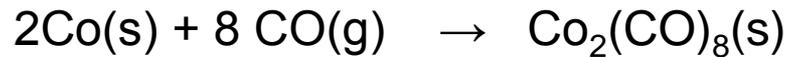
Reação catalisada por um complexo de ródio, catalisador desenvolvido pela **Monsanto**.



Muitos Catalisadores são **compostos organometálicos**
apresentam **ligação metal-carbono**



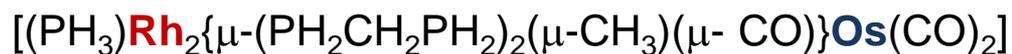
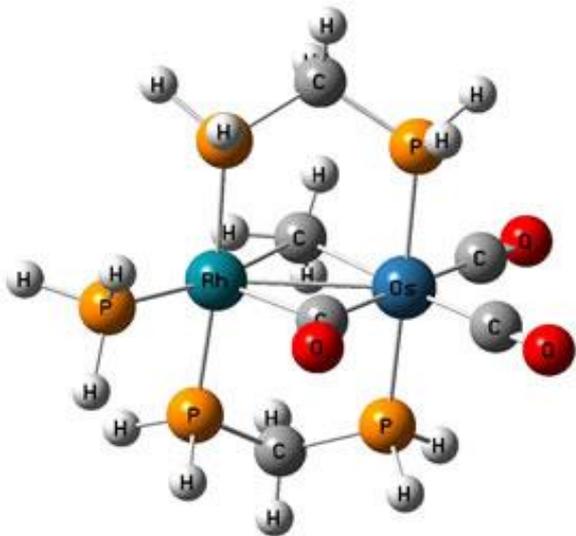
150°C, 35 atm



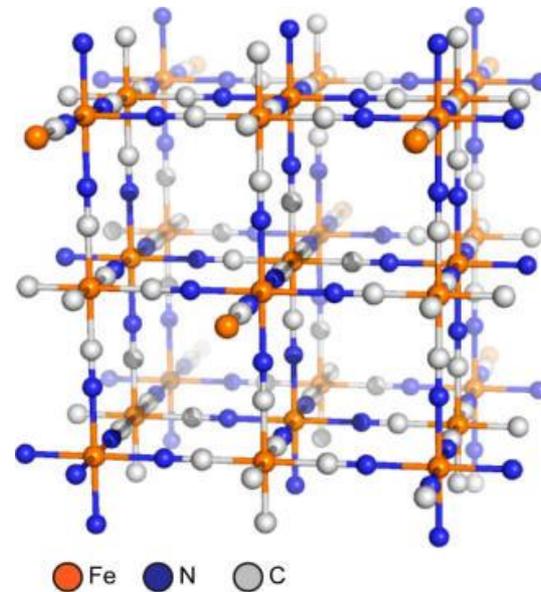
forma-se mais lentamente

Compostos Organometálicos

apresentam **ligação metal-carbono**

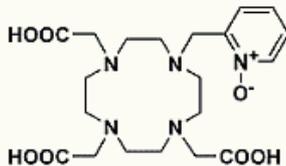
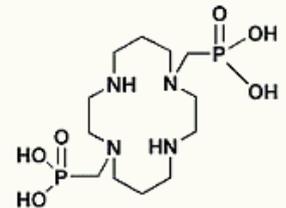
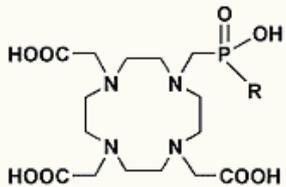


Ligante que pode ligar dois centros metálicos em ponte



Aplicações Radiofarmacêuticas

Contrast agents for MRI tomography



complexos de **Gadolínio** como agentes de contraste

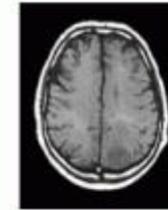
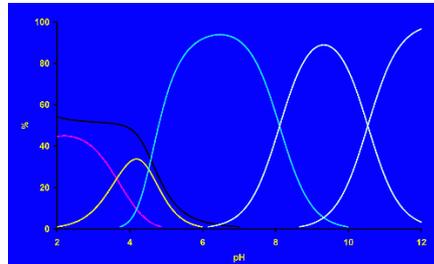
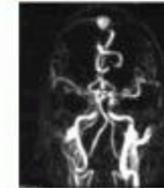


Image without contrast agent



With extracellular contrast agent

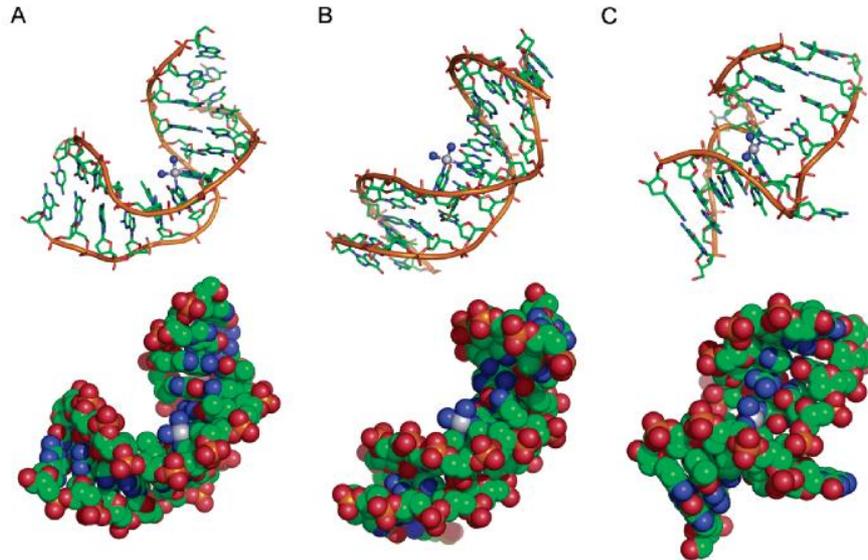
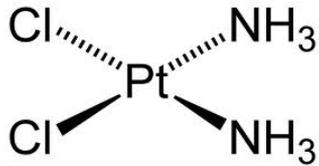


With angiographic contrast agent

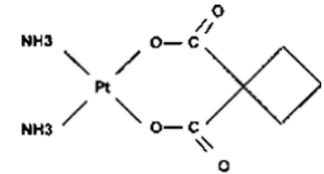
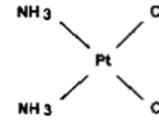
Complexes of transition metal and lanthanide ions for biomedical applications should exhibit a **high kinetic** and **thermodynamic stability** to avoid their decomposition and an intoxication of the organism.

The **radioisotopes** are used for **diagnosis** as well as for a **treatment of mostly cancerous diseases**. The most commonly used isotope is ^{99m}Tc . Technetium ions form stable complexes in low oxidation states with nitrogen-, sulphur- or trivalent phosphorus-containing ligands. On the other hand, there are only few suitable ligands for many radioisotopes of other metal isotopes (e.g. $^{64/67}\text{Cu}$, ^{68}Ga , ^{111}In , ^{90}Y , ^{153}Sm , ^{166}Ho , ^{177}Lu , ^{201}Tl , ^{212}Pb , $^{212/213}\text{Bi}$, etc.).

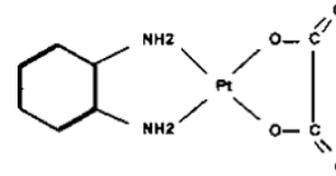
Metalofármacos - antitumorais



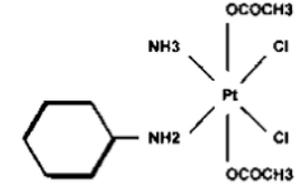
Estes complexos **se intercalam no DNA** e provocam a deformação da dupla hélice, induzindo a chamada **apoptose** ou morte celular programada.



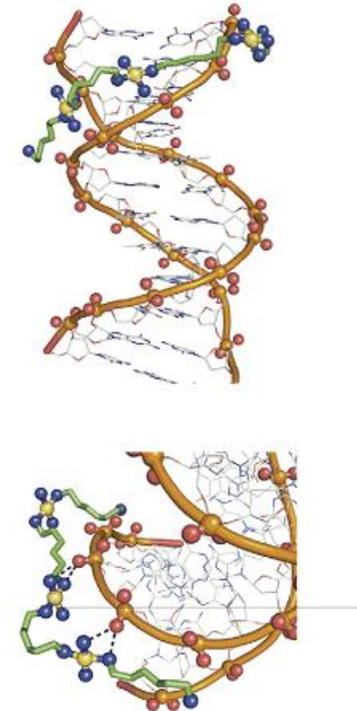
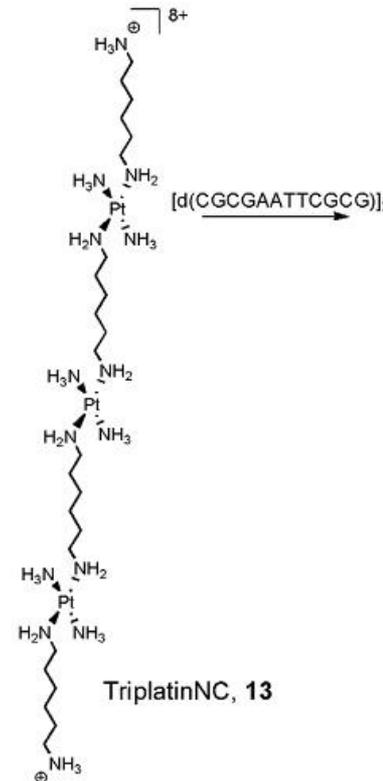
Carboplatin



Oxaliplatin

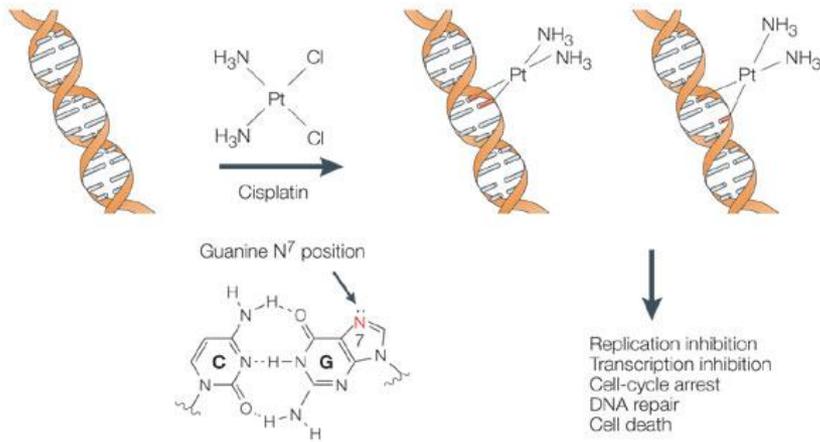


JM216

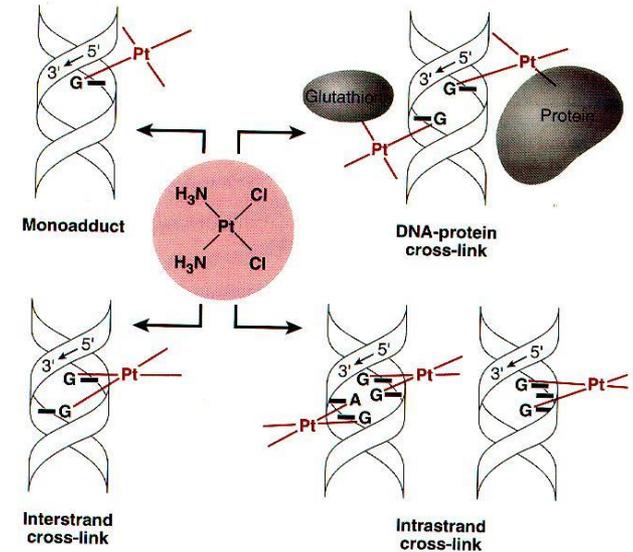
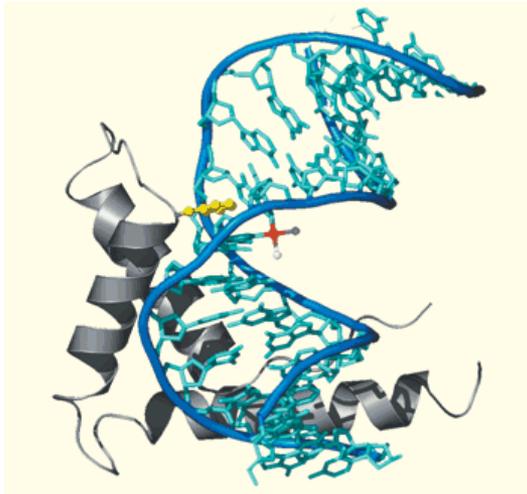


Ligações da cisplatina com bases do DNA

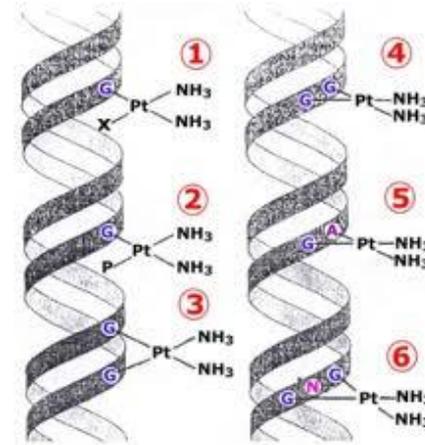
Conhecido composto com **atividade antitumoral**

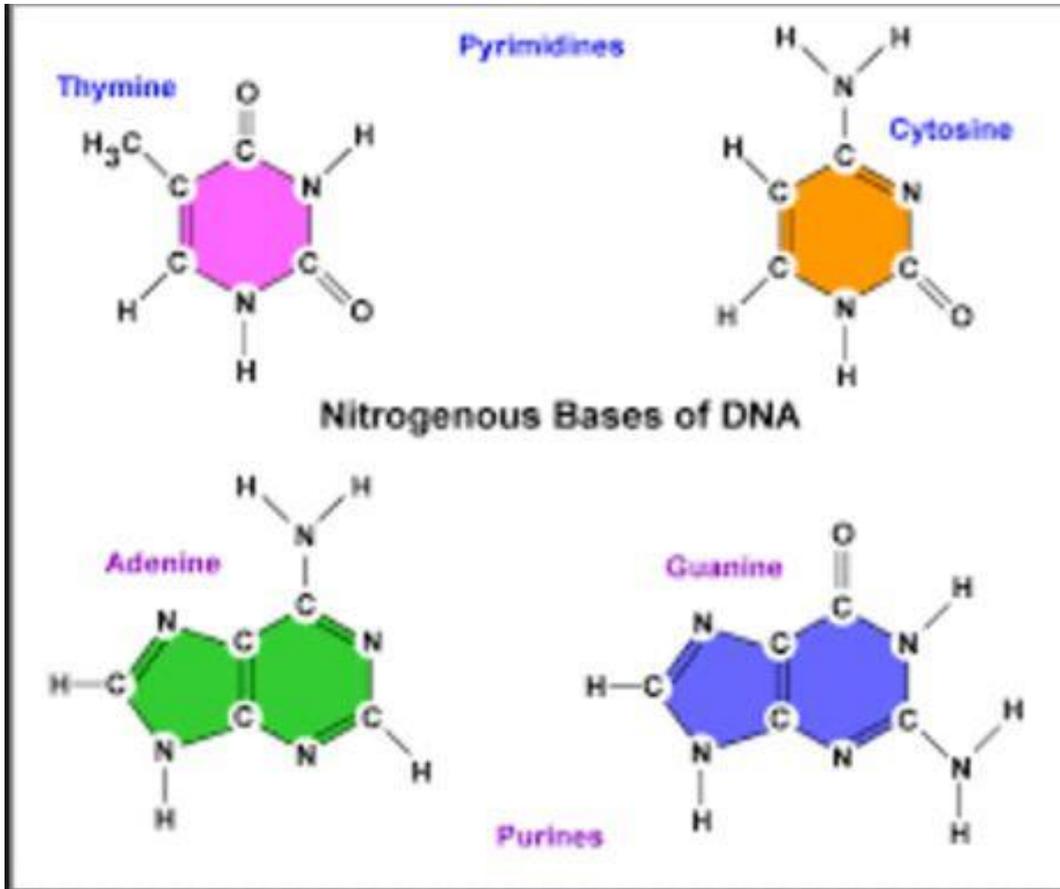


Nature Reviews | Drug Discovery



Seu **mecanismo de ação** no meio biológico envolve ligação às bases do DNA.





Bases do DNA:

Timina

Citosina

Adenina

Guanina

têm **propriedades**

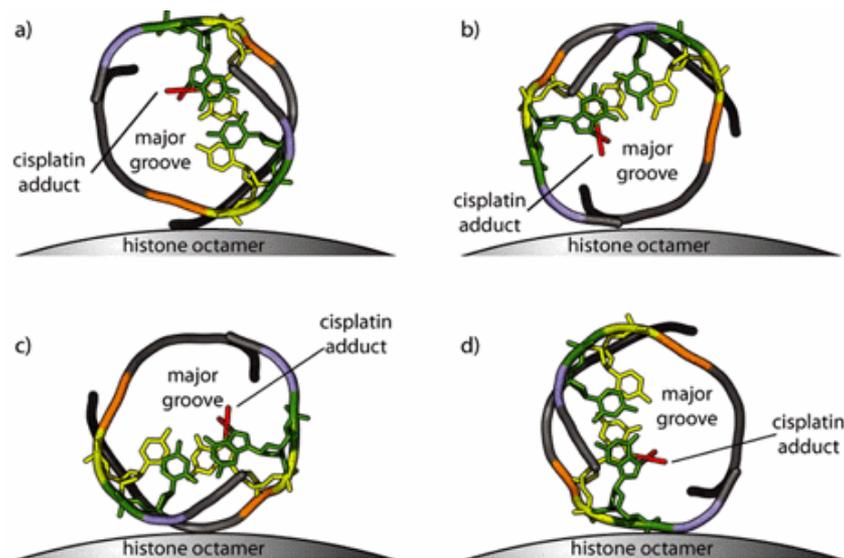
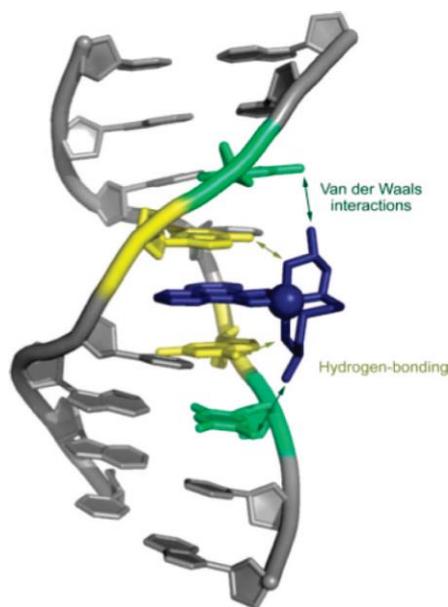
coordenantes, isto é, podem se coordenar a íons metálicos.

Isso possibilita a ação de **metalofármacos antitumorais**.

Application of Metal Coordination Chemistry To Explore and Manipulate Cell Biology

Metalofármacos – agentes antitumorais

Intercalação no DNA



Crystal structure of the **metallo-intercalator 67** bound to target sequence 5'-TGCA-3'. Note the **intercalation of the aromatic phi group**, the **hydrogen-bonding interactions** between the axial amines and the **O6 of guanine**, and the contacts between the pendant methyl groups of the ligand with the methyl groups of thymine. Reprinted with permission from ref 281. Copyright 1993 American Chemical Society.

Estudos acadêmicos que auxiliam na elucidação de mecanismos de atuação e portanto no desenvolvimento de fármacos mais eficientes, com menos efeitos colaterais.

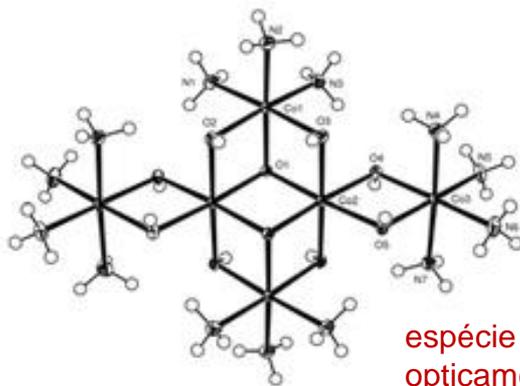
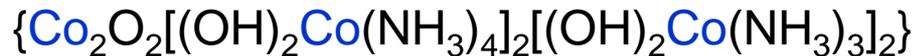
Fundador da Química de Coordenação



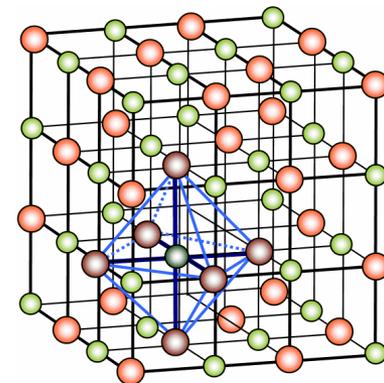
Alfred Werner (1866 - 1919)

Premio Nobel em 1913

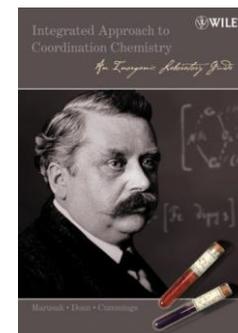
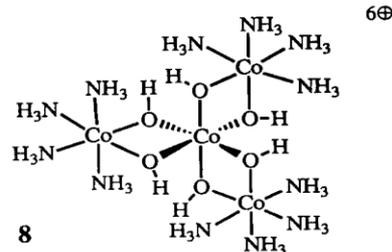
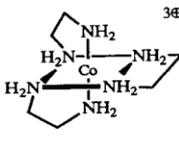
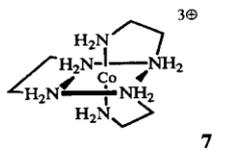
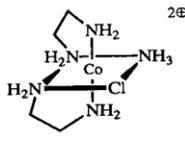
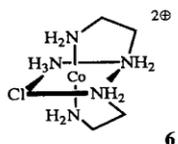
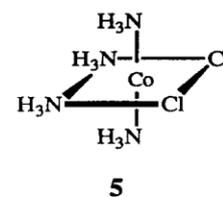
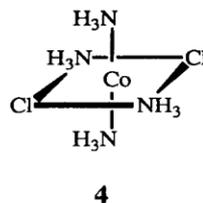
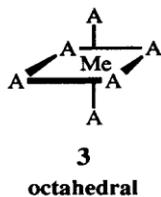
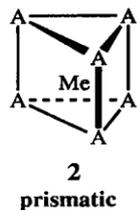
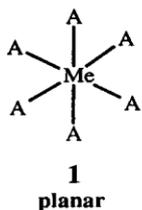
Complexo de cobalto



espécie hexanuclear,
opticamente ativa



Elaborou uma teoria baseada em **características geométricas** (estrutura espacial dessas espécies)



COORDINATION COMPOUNDS

EVAPORATE A SOLN OF CuSO_4

BLUE CRYSTALS

HEAT STRONGLY: WHITE CRYSTALS

" $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ": BLUE

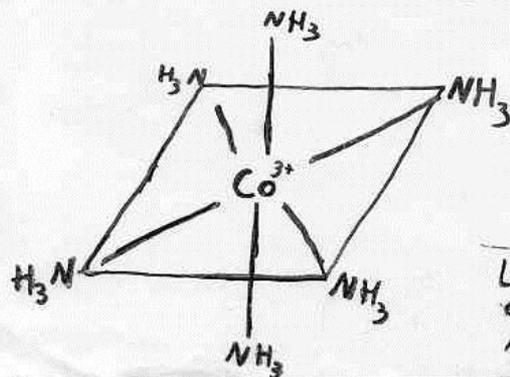
CuSO_4 : WHITE

OTHER EXAMPLES: " $\text{CoCl}_2 \cdot 6\text{NH}_3$ "

" $\text{PtCl}_2 \cdot 4\text{NH}_3$ "

WERNER ~1900: METAL ION SURROUNDED BY "LIGANDS"

" $\text{CoCl}_2 \cdot 6\text{NH}_3$ " really is: $[\text{Co}(\text{NH}_3)_6]^{3+} \text{Cl}_3^-$

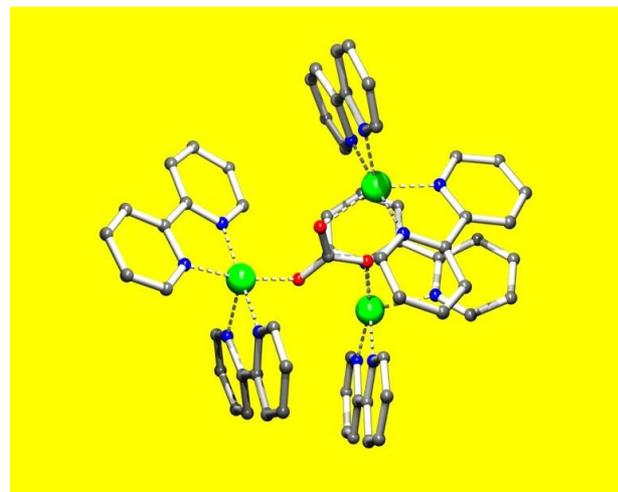


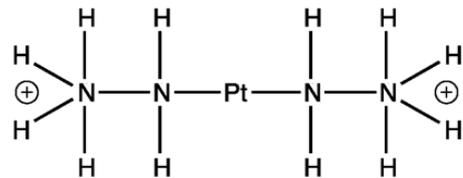
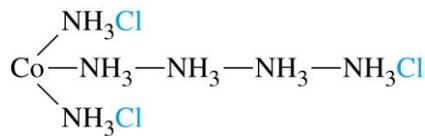
OCTAHEDRAL
COMPLEX

LIGANDS DONATE
 e^- PAIRS INTO
METAL ORBITALS



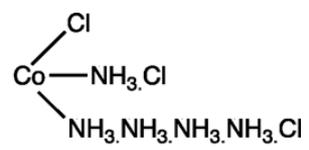
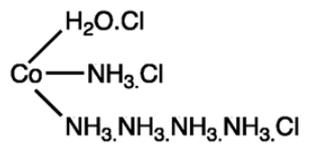
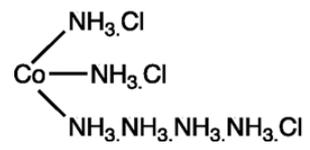
Characterizam-se por um **íon central**, rodeado por **ligantes**, coordenados ao metal através de átomos que apresentam pares de elétrons isolados.



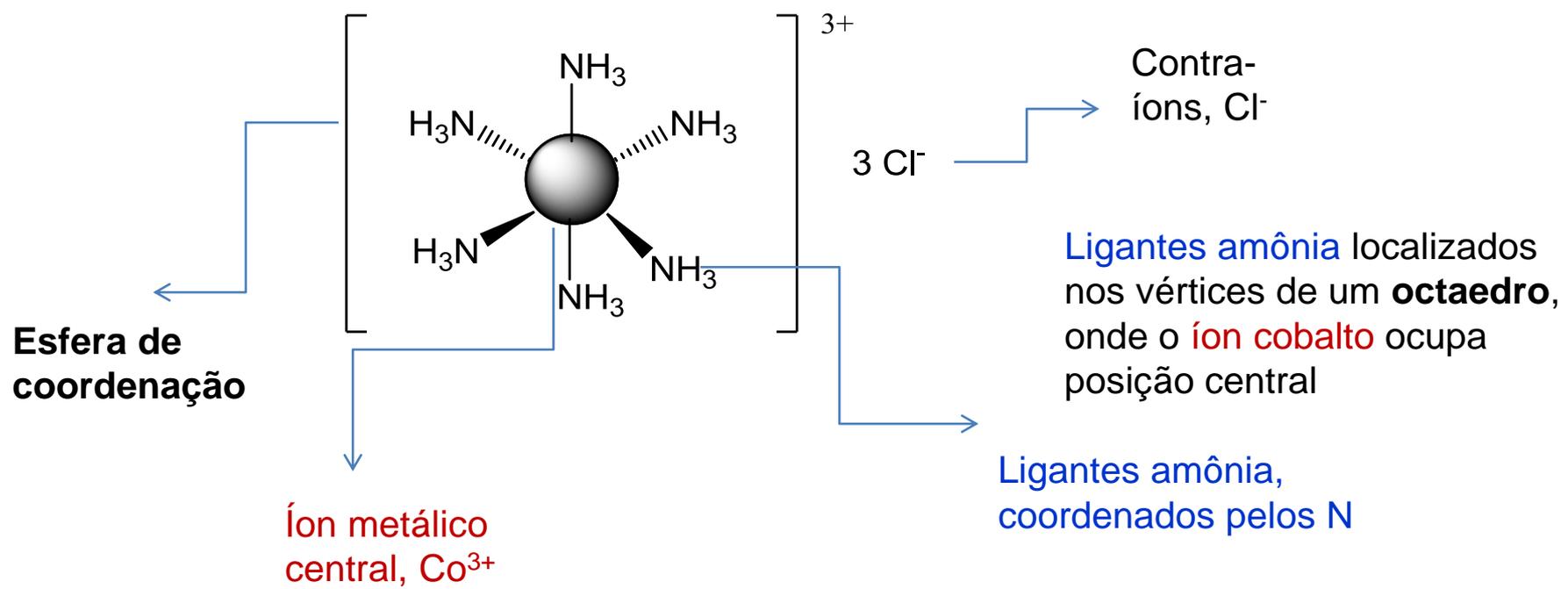


2Cl⁻

Nos primórdios da Química de Coordenação, pensou-se até em cadeias de moléculas de amônia, para explicar a “**valência secundária**” de íons metálicos.



Mas prevaleceu a idéia de A. Werner, levando em conta a **estereoisomeria**, isto é, o **arranjo espacial dos ligantes ao redor do íon metálico central**

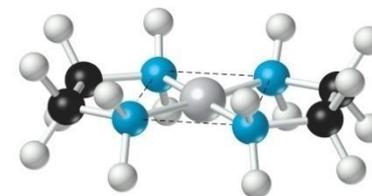


Diferentes tipos de ligantes

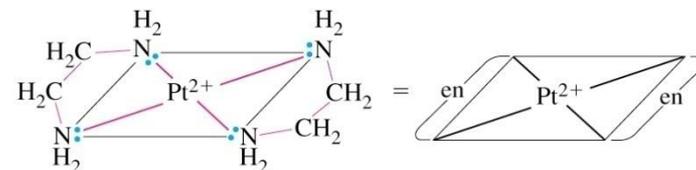
Monodentados: H_2O , OH^- , Cl^- , Br^- , NH_3 , etc.

Bidentados:
en, acac, CO_3^- , $-\text{COOH}$, bpy, phen, etc.

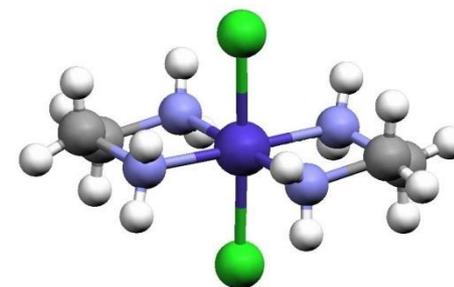
Polidentados:
edta, nta, dtpa, cyclam, etc.



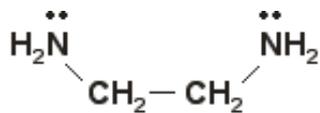
(a)



(b)



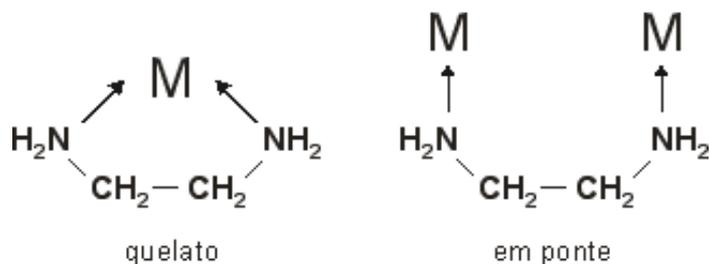
$\text{trans-[Co(en)}_3\text{Cl}_2\text{]}^+$



ligante bidentado (etilendiamina)

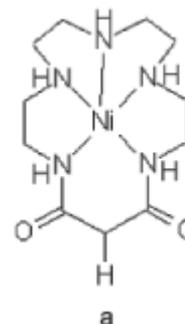


Ni(bipy)2Cl2

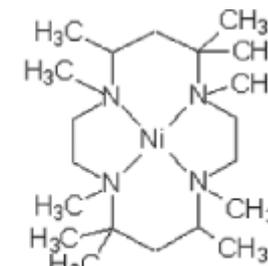


quelato

em ponte

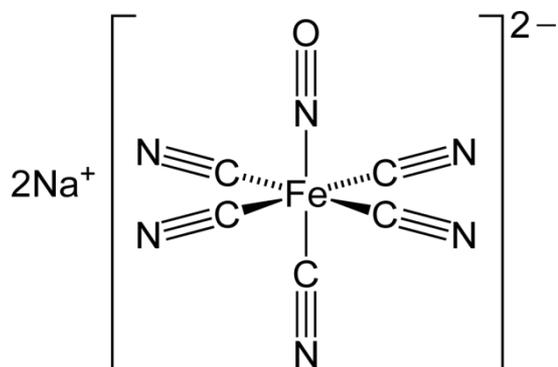


a

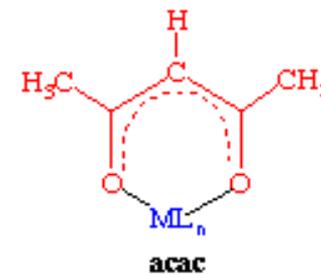
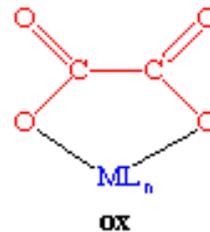
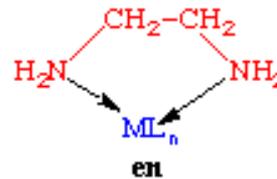
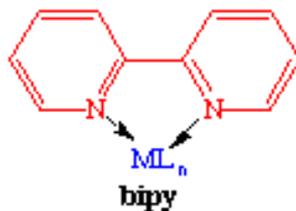


b

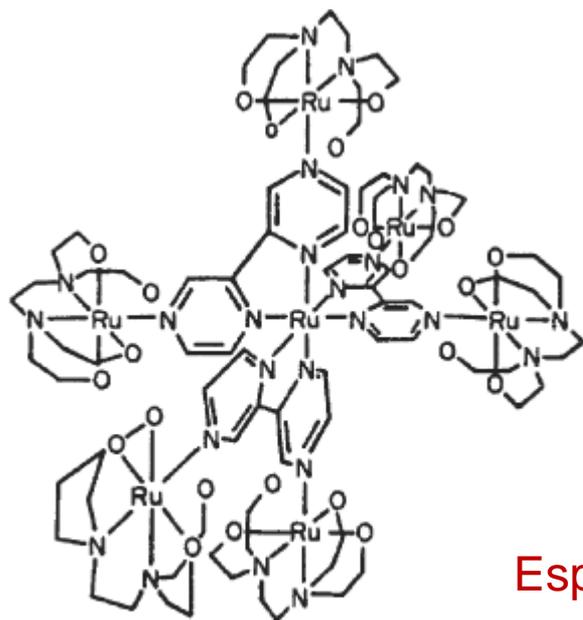
Versatilidade dos ligantes



Espécies **mononucleares** - um único metal central



Ligantes bidentados

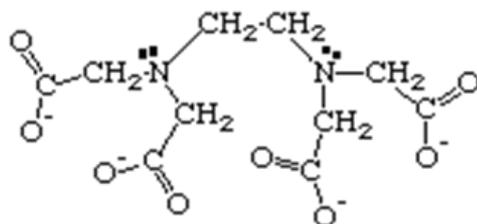


Espécies **polinucleares** – mais de um centro metálico

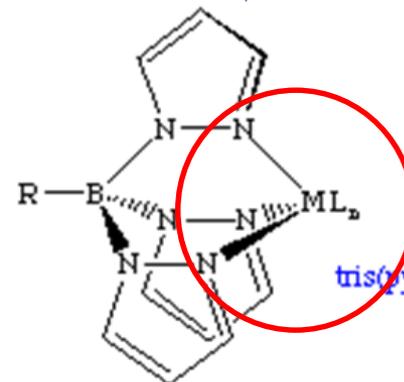
Os ligantes podem ser: **monodentados**, **bidentados**, **tridentados**, etc.

Cl⁻, H₂O, NH₃, etc...

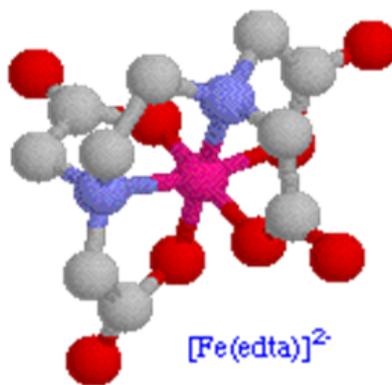
en, bpy, phen, etc..



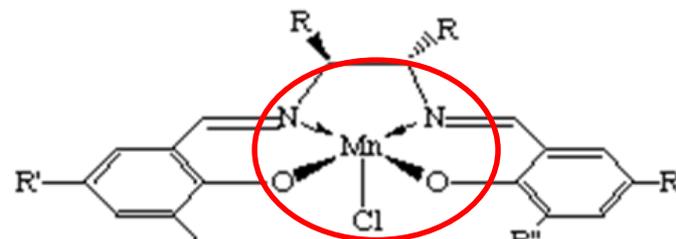
EDTA as a free molecule



tris(pyrazolyl)borate



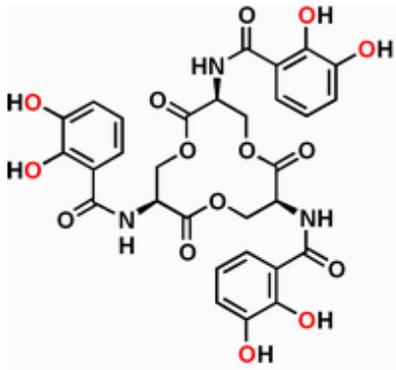
[Fe(edta)]²⁻



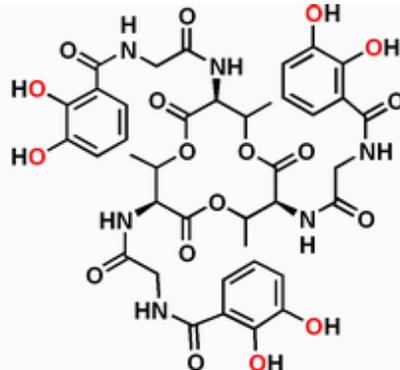
Chiral Mn-salen complex
(Asymmetric epoxidation catalyst)

Ligantes polidentados

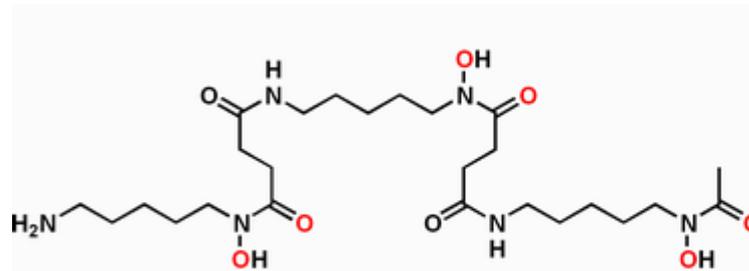
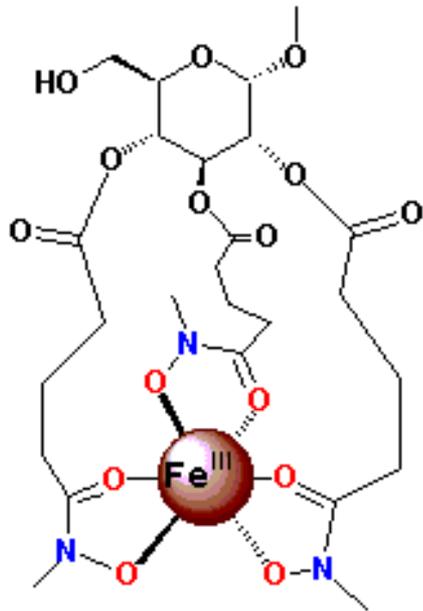
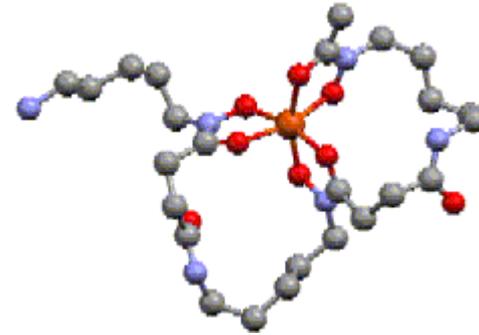
Sideróforos Naturais usados por microorganismos (bactérias) para capturar íons de ferro



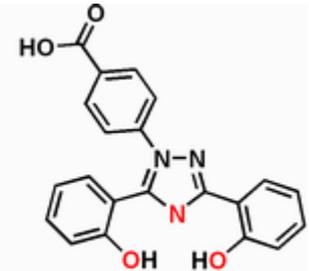
Enterobactin



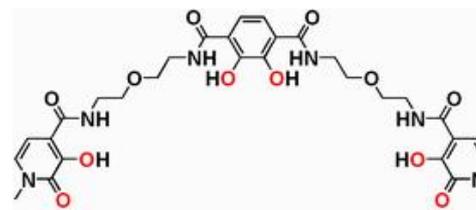
Bacillibactin



Desferal

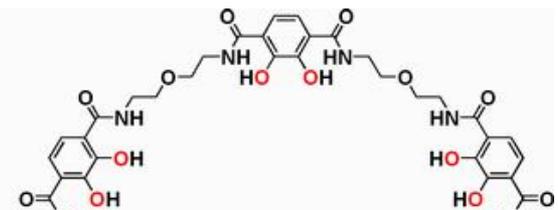


Deferasirox



5-LIO(Me-3,2-HOPO)₂(TAM)

pM(Fe^{III}) = 30.4



5-LIO(TAMmeg)₂(TAM)

pM(Fe^{III}) = 34.4

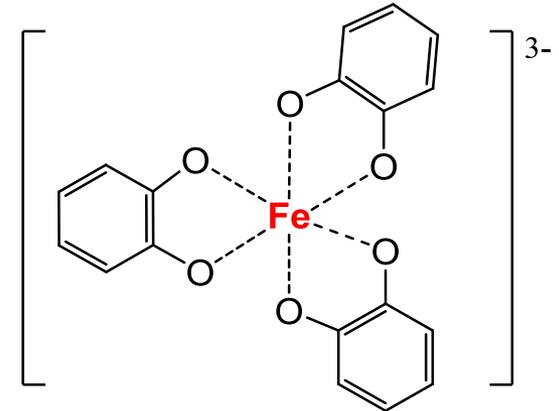
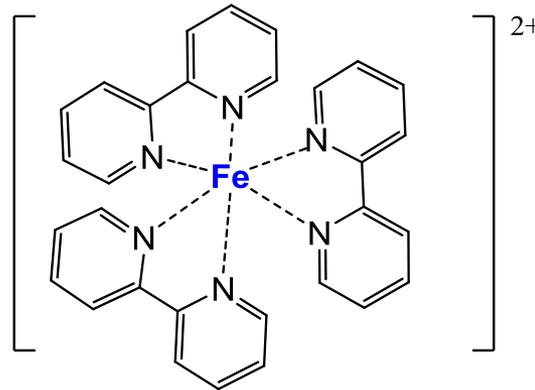
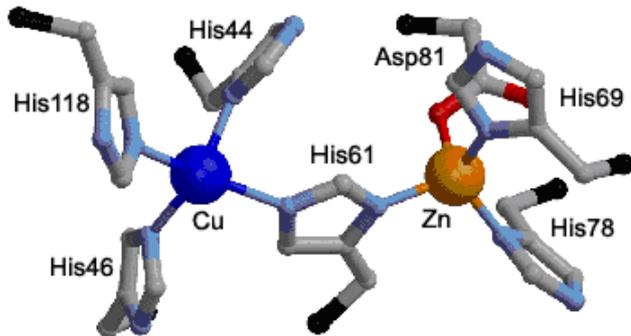
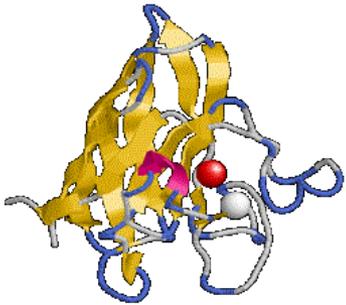
Quelantes de ferro, aprovados para uso em terapia

Dependendo do **metal** e de seu **estado de oxidação** há preferências quanto ao átomo que vai se coordenar.

Exemplos:



No meio biológico:



Proteína Cu,Zn-SOD

superóxido dismutase

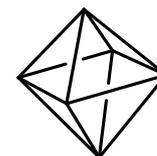
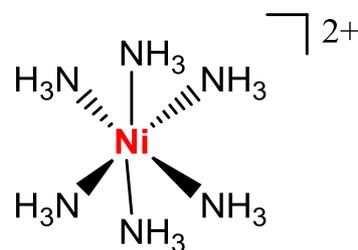
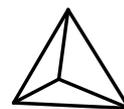
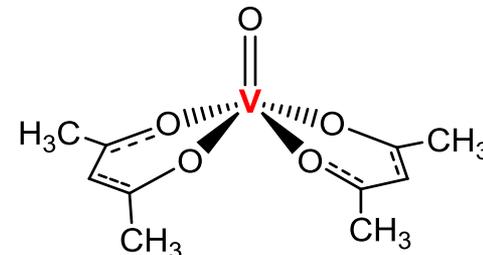
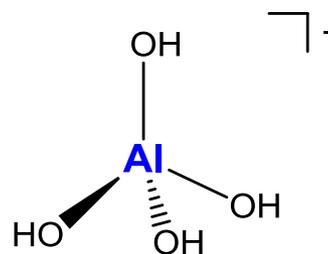
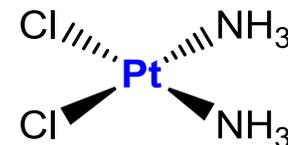
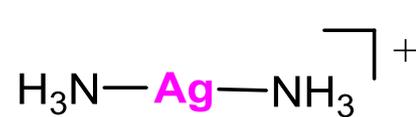
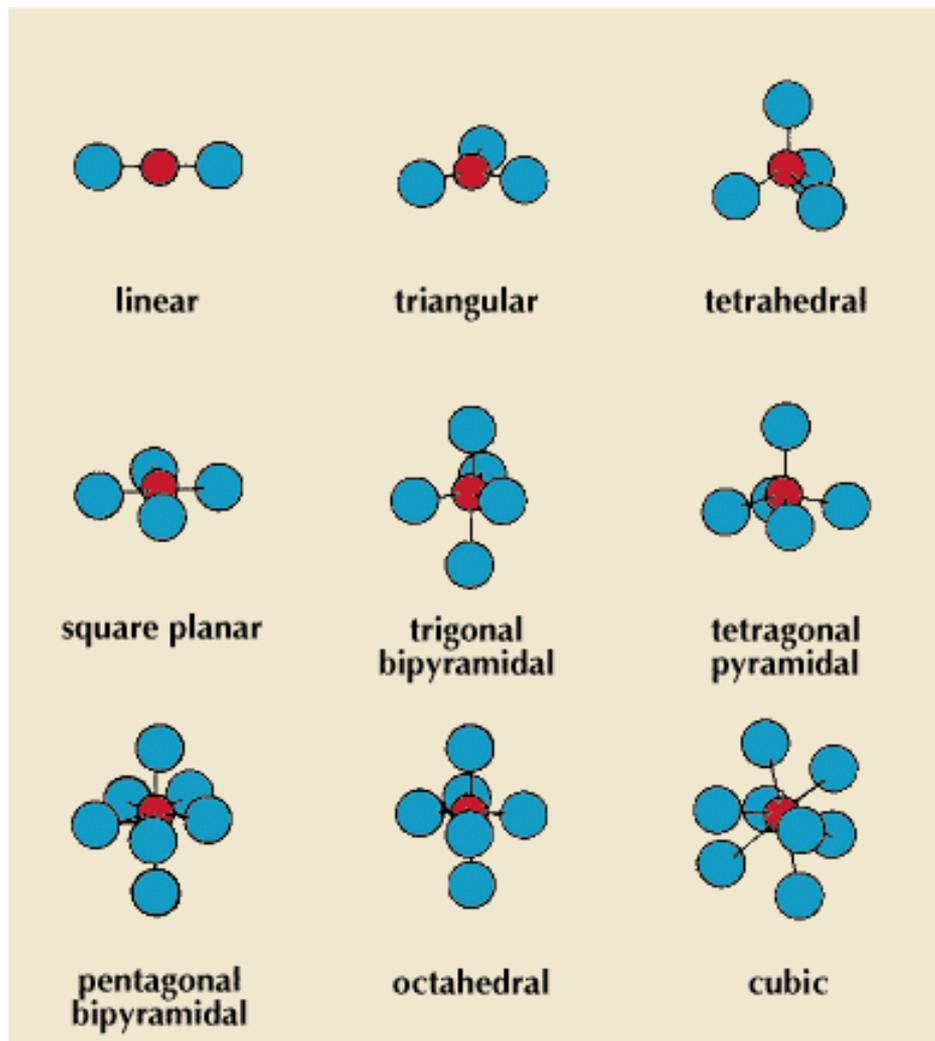
sítio de cobre e sítio de zinco

Catalisa o desproporcionamento (dismutase)

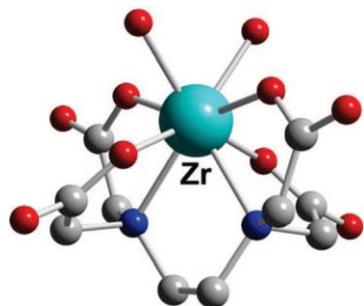


O **zinco** tem papel estrutural e o **cobre** papel catalítico

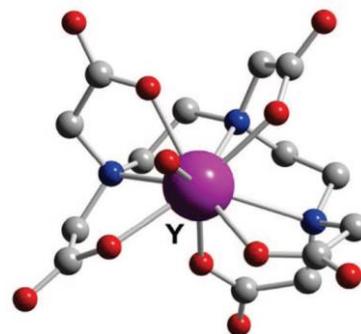
Estruturas mais usuais em compostos de coordenação



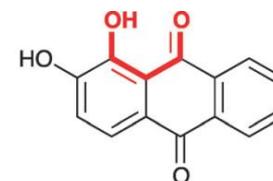
Os átomos maiores (**lantânídios ou actinídios**) apresentam maior número de sítios de coordenação



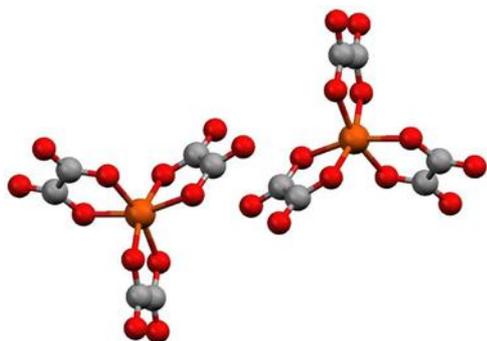
[Zr(edta)]



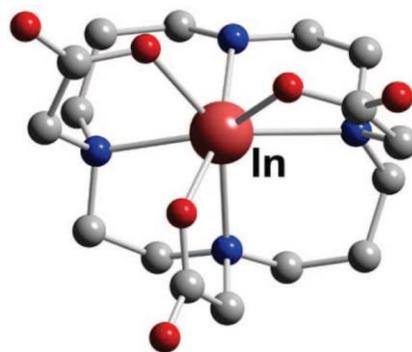
[Y(dtpa)]



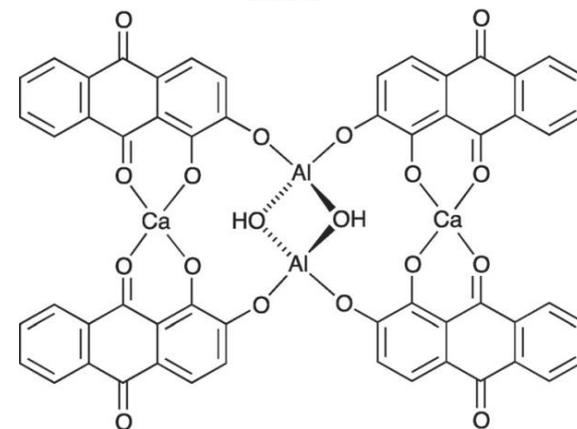
Alizarin



[Fe(ox)₃]³⁻

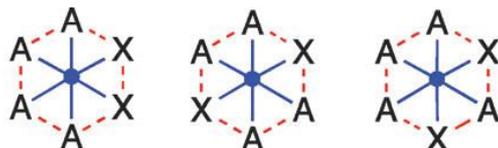
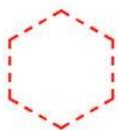


[In-TE3A]



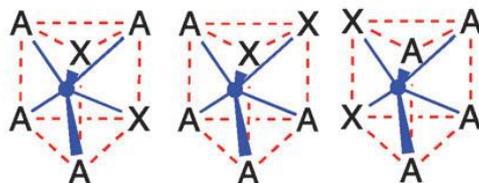
Possibilidades de ISOMERIA

Hexagonal planar



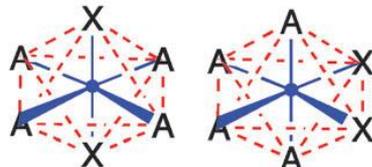
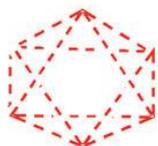
Three geometric isomers

Trigonal prismatic



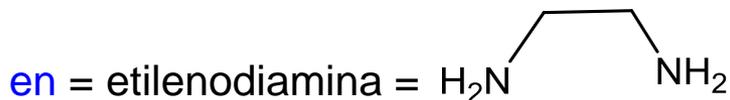
Three geometric isomers

Octahedral

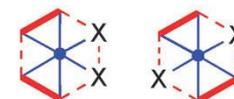


Two geometric isomers

Número de isômeros esperados para várias possíveis geometrias de um complexo hexacoordenado do tipo $[M(NH_3)_4X_2]$.

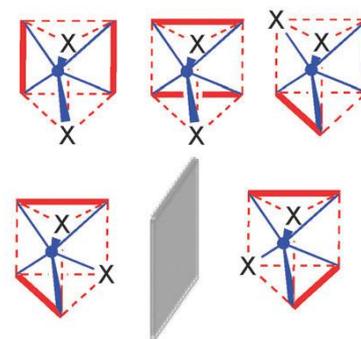


Hexagonal planar



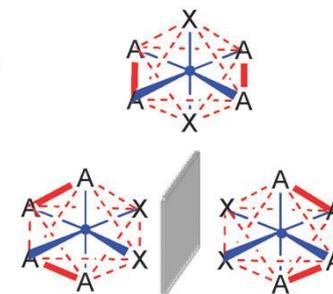
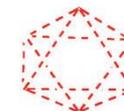
Two geometric isomers

Trigonal prismatic



Four geometric isomers
Two enantiomers

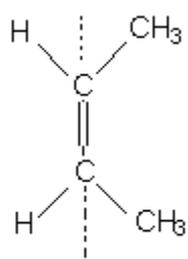
Octahedral



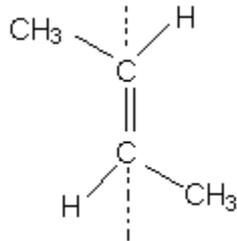
Two geometric isomers
Two enantiomers

Número de isômeros esperados para várias possíveis geometrias de um complexo hexacoordenado do tipo $[M(en)_2X_2]$.

Isomeria geométrica

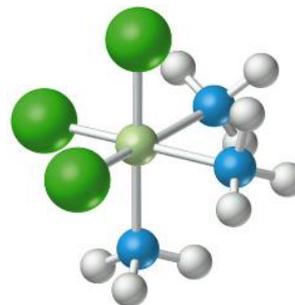
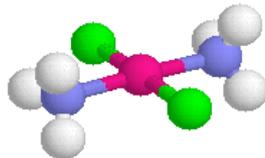
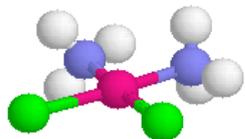
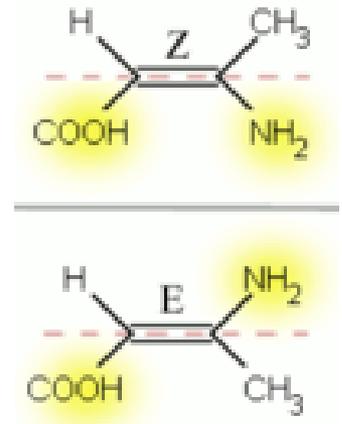


cis

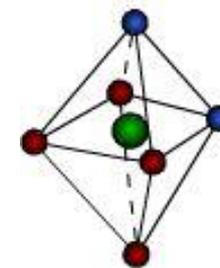


trans

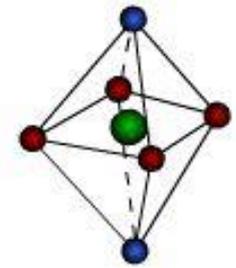
Isômeros geométricos apresentam em geral diferentes propriedades: cor, PF, polaridade, características espectrais, etc.



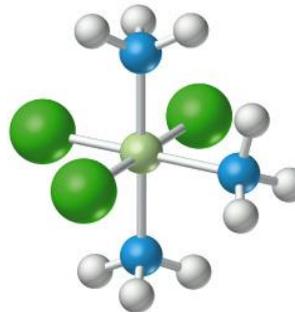
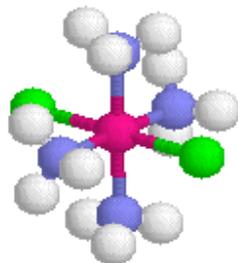
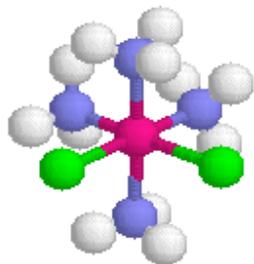
fac-[CoCl₃(NH₃)₃]



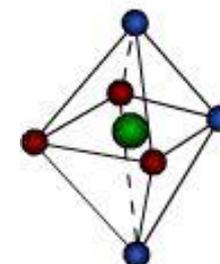
cis



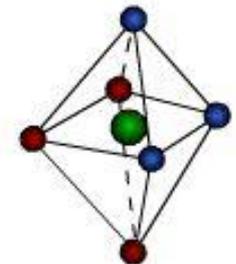
trans



mer-[CoCl₃(NH₃)₃]

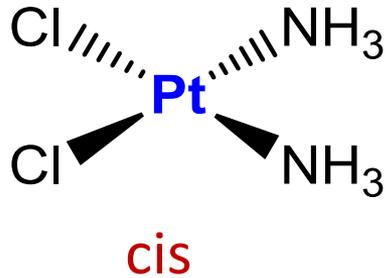


mer

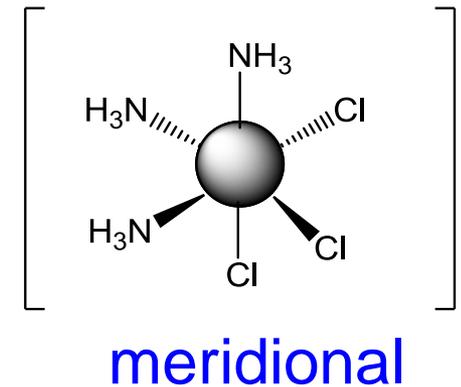
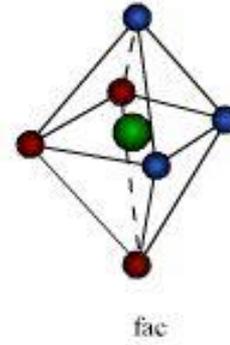
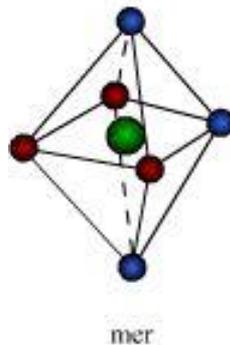
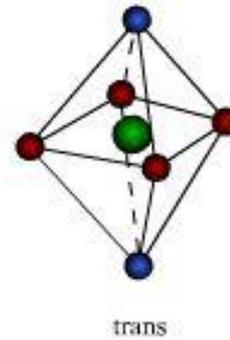
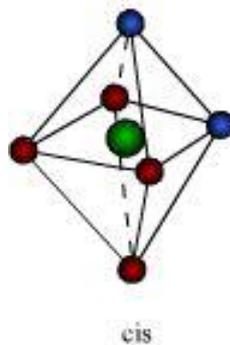
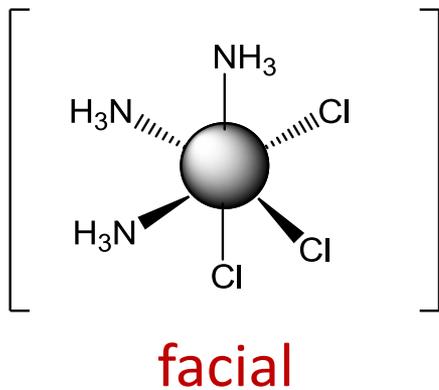
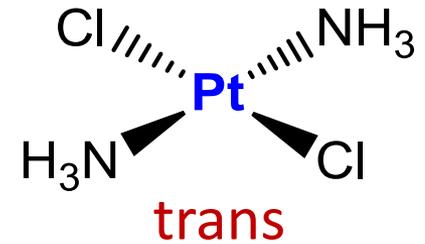


fac

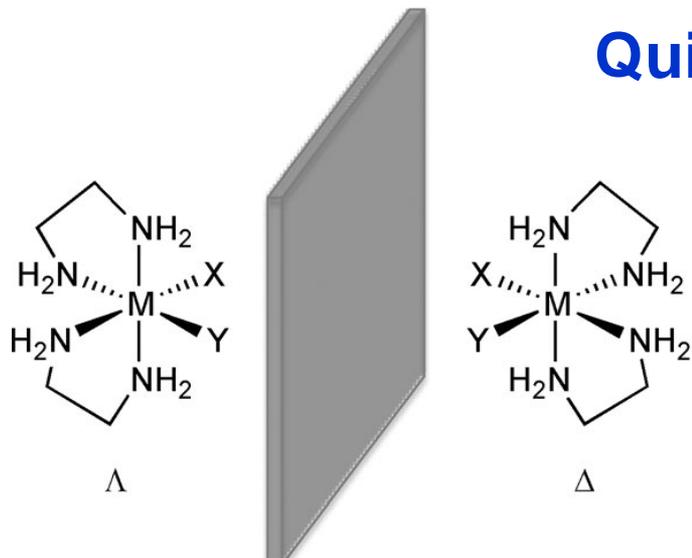
Isômeros geométricos têm propriedades diferentes, que refletem suas estruturas diferentes.



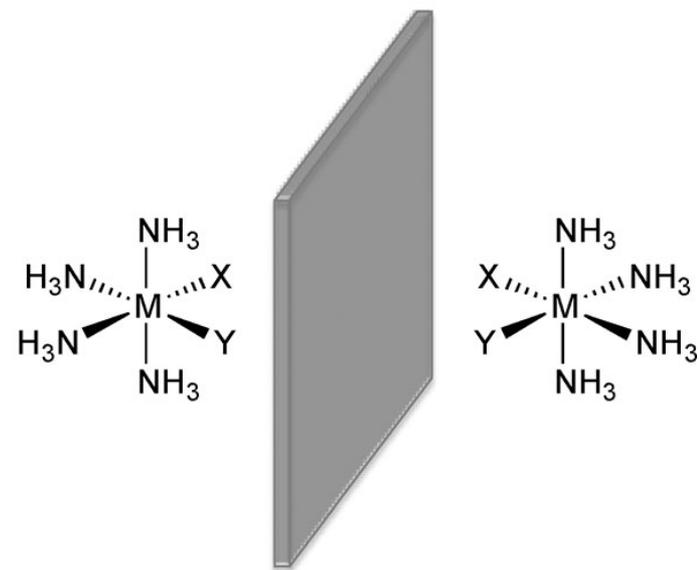
O isômero cis é bem mais ativo como **droga antitumoral**, ligando-se às fitas do DNA.



Quiralidade e Isomeria Óptica

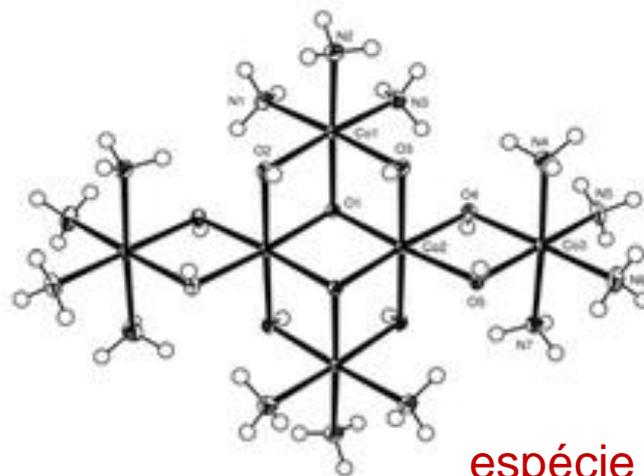
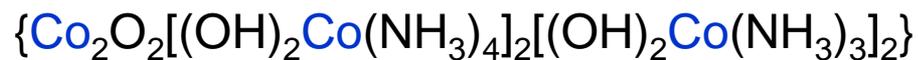


Compostos quirais



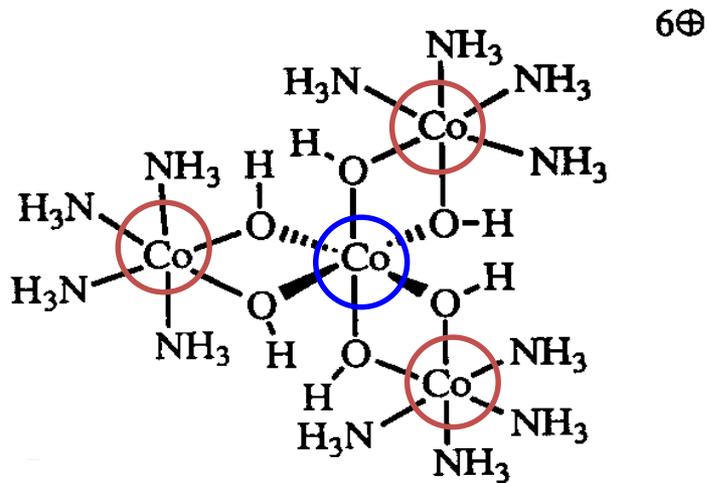
Compostos aquirais (estruturas idênticas)

Complexo de cobalto



espécie hexanuclear,
opticamente ativa
(quiral)

Isômeros ópticos (sem carbono assimétrico)



Apresenta 2 isômeros ópticos

4 íons de cobalto (III)

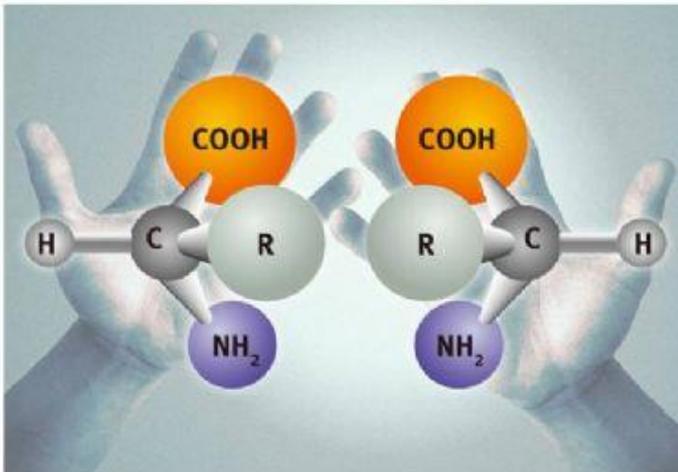
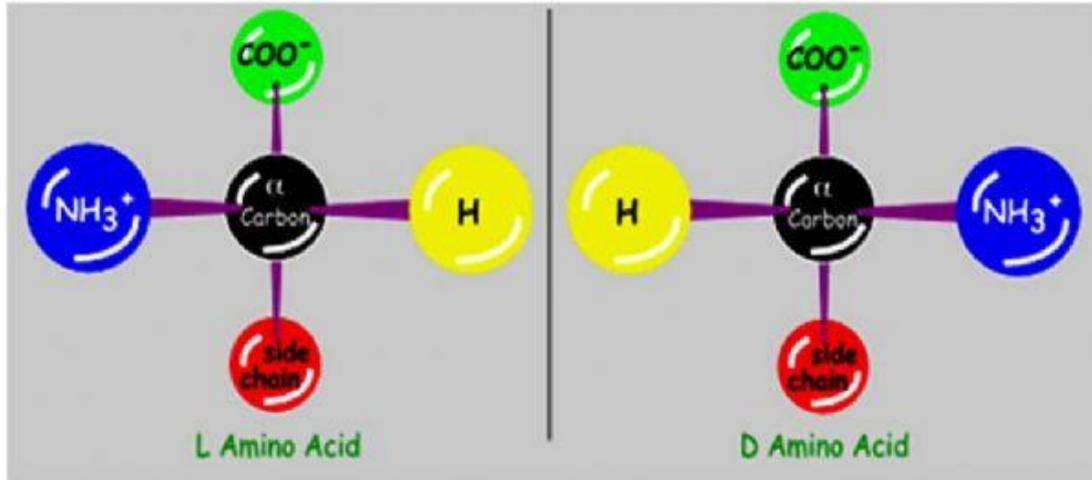
6 ligantes OH⁻

12 ligantes NH₃

3 espécies complexas atuam como ligantes do íon de cobalto(III) central

Quiralidade e Isomeria Óptica

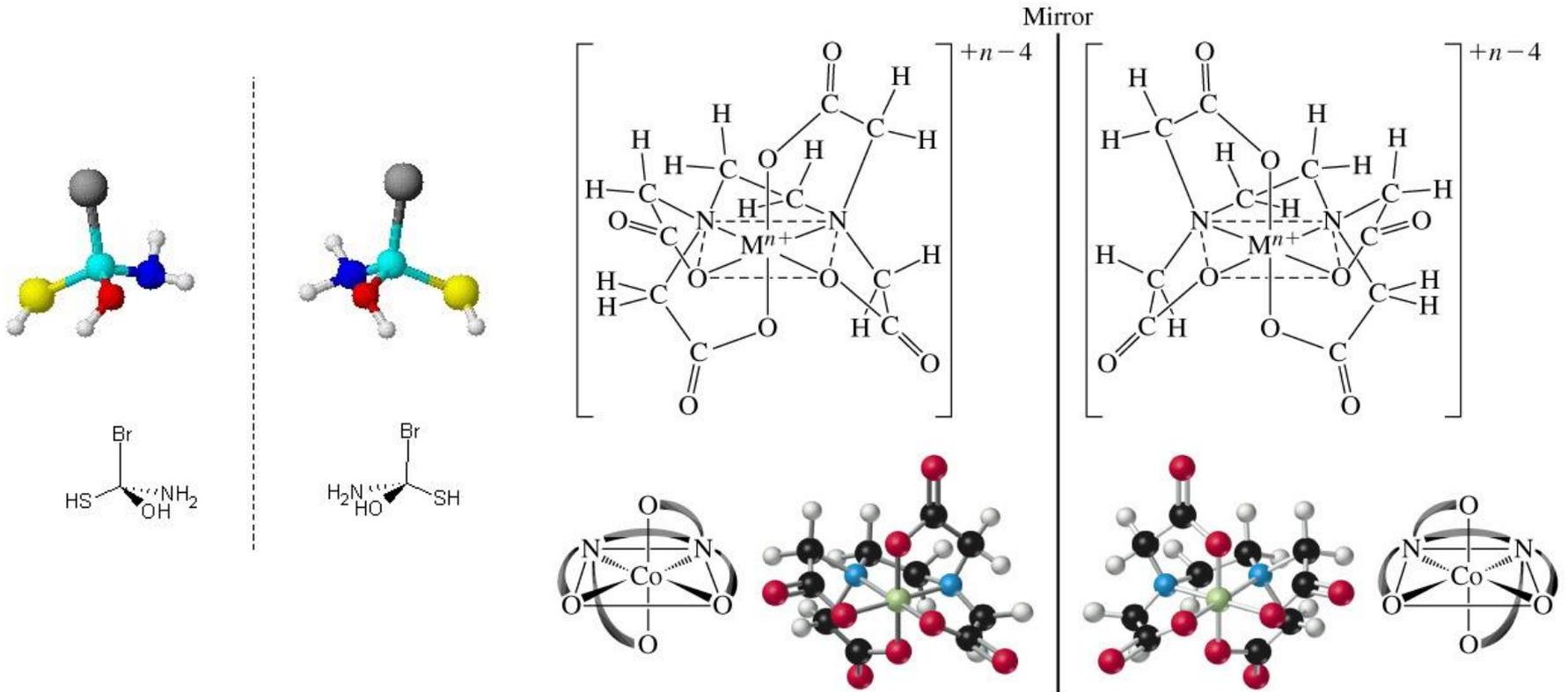
Compostos enantiômeros



Isômeros ópticos ou **enantiômeros** apresentam todas as propriedades físico-químicas iguais. Só podem ser identificados (ou diferenciados) através de sua característica de **girar o plano da luz polarizada**: o isômero **dextrógiro** gira este plano no sentido horário, e o **levógiro** no sentido anti-horário.

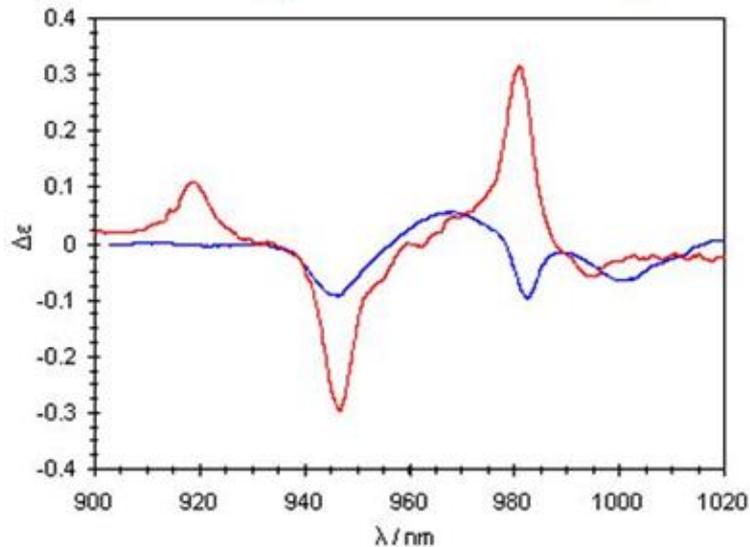
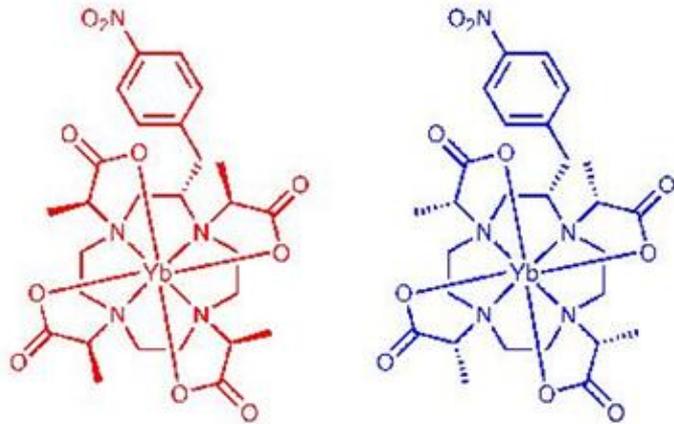
Isomeria óptica

Isômeros ópticos só diferem na propriedade de girar o plano da luz polarizada: um isômero (d-) gira este plano no sentido horário e o outro (l-) no sentido anti-horário.



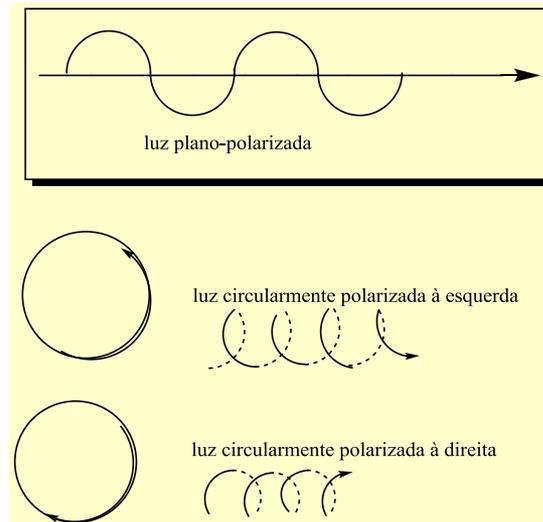
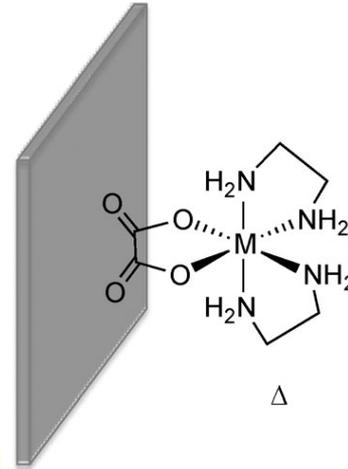
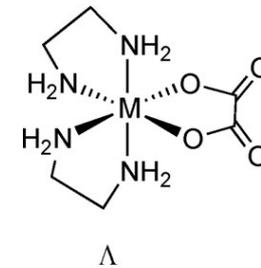
Isômeros: **dextrógiro** e **levógiro**

Espectroscopia: Dicroísmo Circular (CD) ou curvas ORD



Near infrared circular dichroism spectra of two isomeric Yb³⁺ complexes reveal that the ligand field of the lanthanide ion is extremely sensitive to the coordination geometry and thus ligand structure

dois enantiômeros



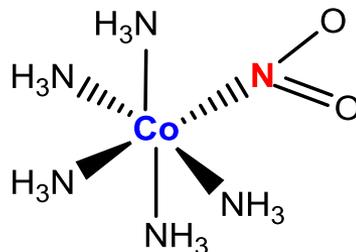
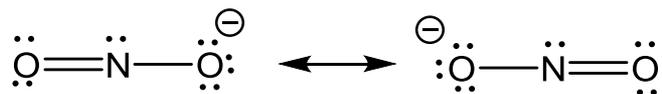
Usando luz circularmente polarizada (CD) ou luz plano polarizada (ORD), é possível distinguir-se os dois enantiômeros.

Esquema 1 – Componentes principais de um polarímetro

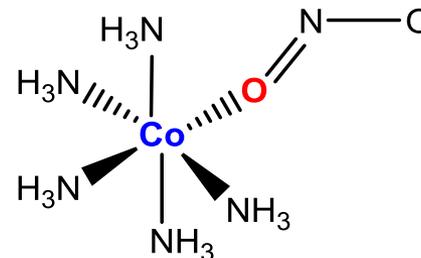


Instrumento para diferenciar enantiômeros (um deles gira o plano da luz polarizada no **sentido horário (d-)** e o outro no **sentido anti-horário (l-)**).

Isomeria de ligação

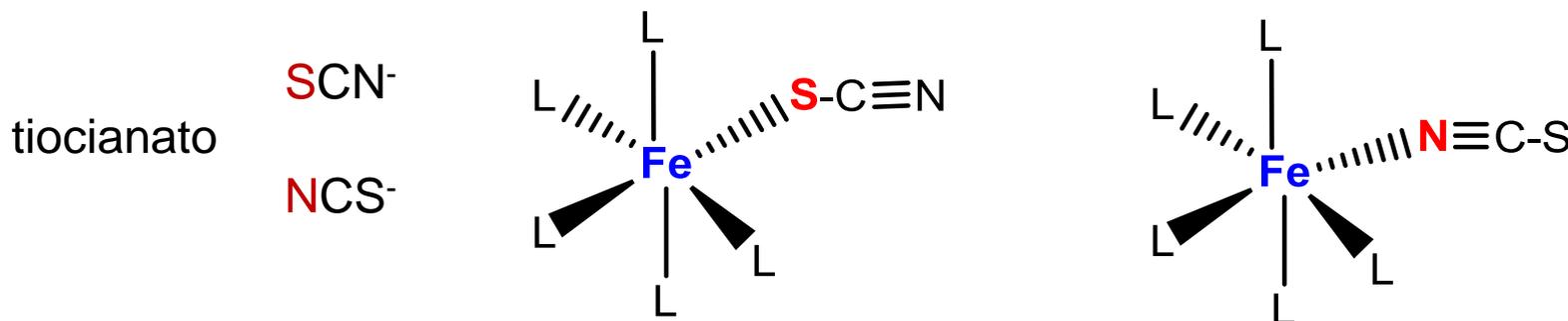
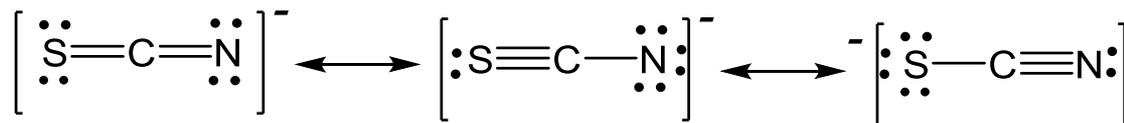


nitro



nitrito

As estruturas de Lewis dos ligantes ajudam a entender as ligações.



Estes ligantes podem também atuar como “pontes” entre dois centros metálicos

Referências:

1. J.C. Kotz e P. Treichel Jr. - *Chemistry and Chemical Reactivity*, Saunders College Publ., Fort Woeth, 1999, 4a. ed., **cap. 23** – The transition elements.
2. Brown, LeMay, Bursten, - *Química: a Ciência Central*, Pearson, 2005, 9ª. Ed., **cap.24** - “Química dos compostos de coordenação”, p. 884-910; Exercícios, p.910-916.
3. Shriver & Atkins – *Química Inorgânica*, Bookman, 2008, 4a. Ed. (Tradução da 4a. ed. - Oxford Univ. Press, 2006 - D.F. Shriver, P.W. Atkins , T.L. Overton, J.P. Rourke, M.T. Weller e F.A. Armstrong), **cap. 18** – “Os metais do bloco d”, p. 455-480; **cap. 19** – “Complexos dos metais do bloco d: estrutura eletrônica e espectro”, p. 481-510.