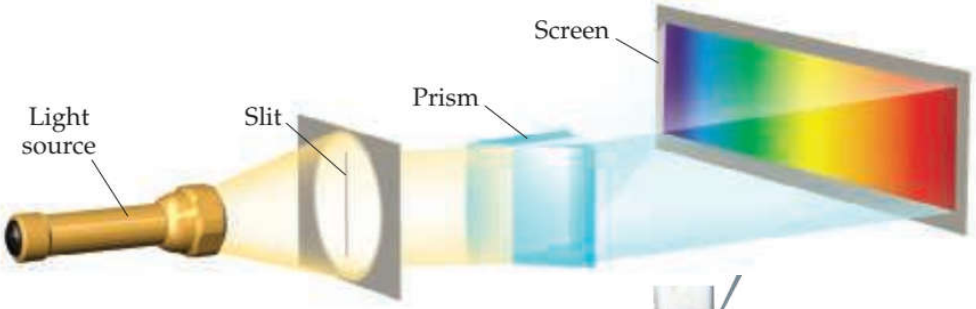
Aula 11 QE

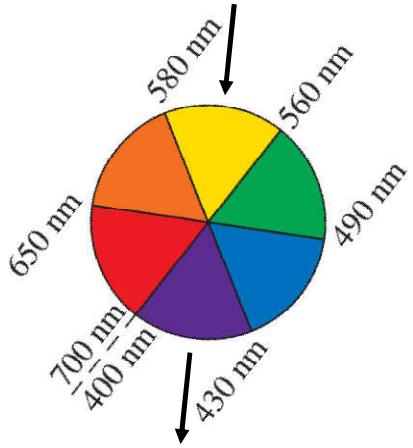
Espectro de absorção e complexos

Espectro de Absorção

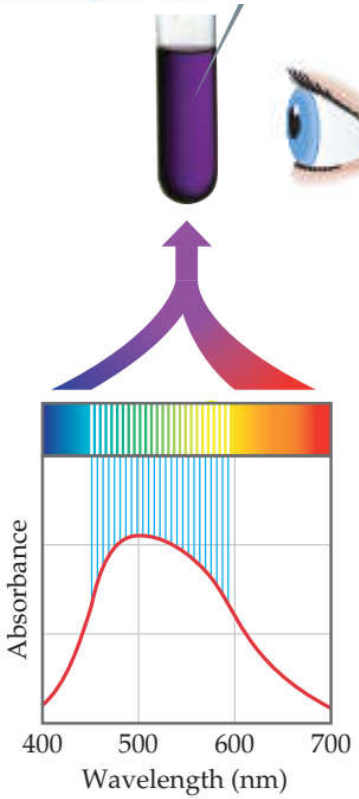
Por quê vemos cores?

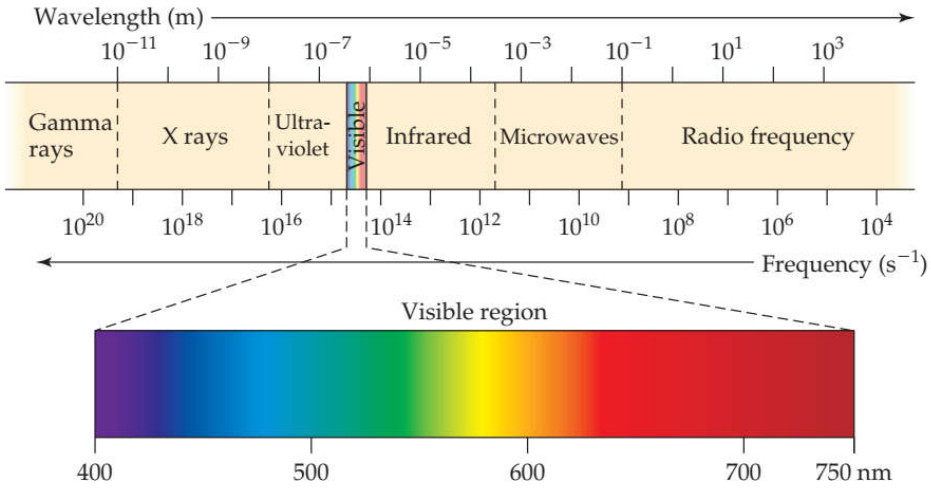


absorve



observa

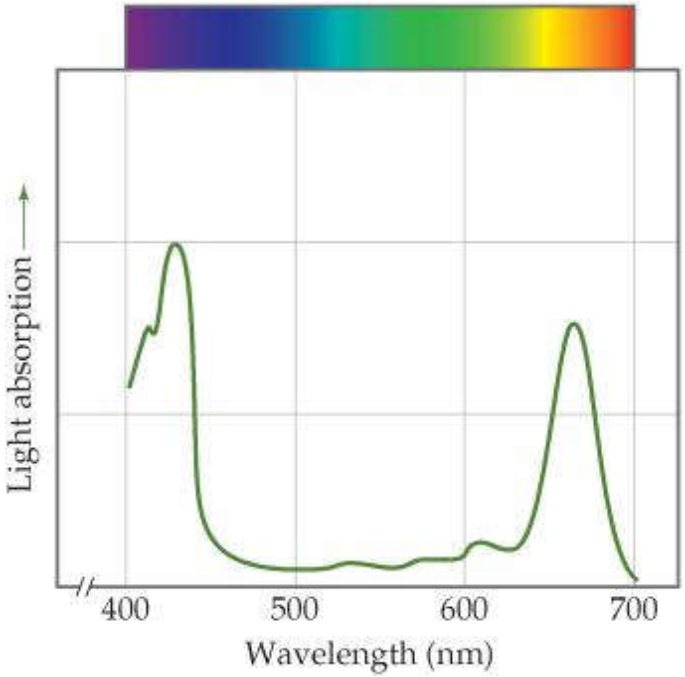


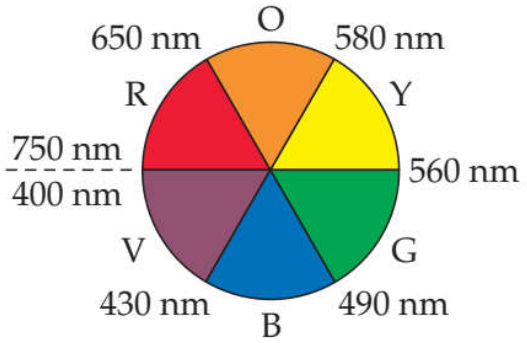


$$E = h\nu \qquad E = \frac{hc}{\lambda}$$

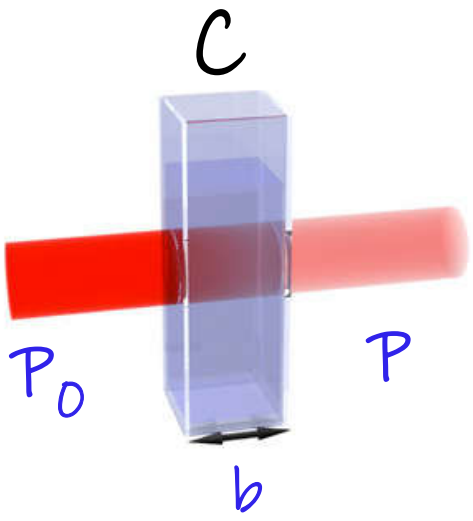
$$c = \lambda . \nu$$

Casca da laranja absorve o azul e o olho enxerga laranja



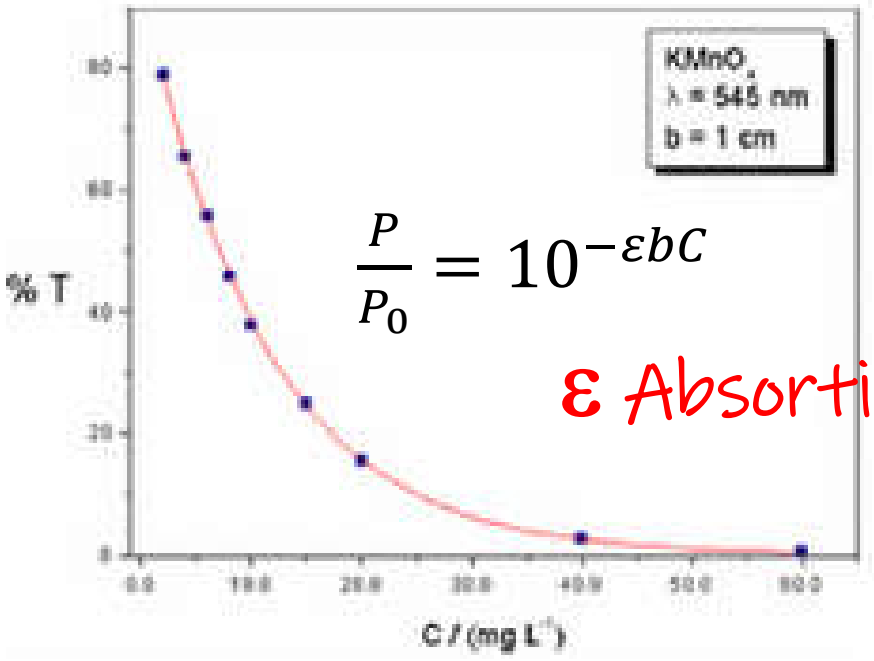


Quanto absorve?



Transmitância T

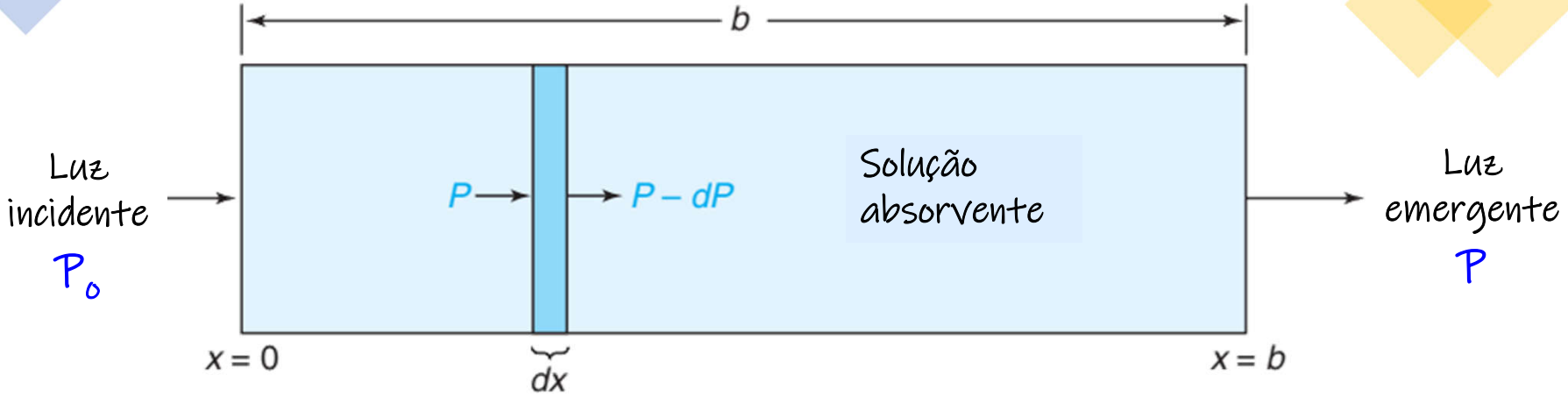
$T = P/P_0$ $\%T = P/P_0 \times 100$



$$\frac{P}{P_0} = 10^{-\varepsilon b C}$$

ε Absortividade molar

Absorção de luz → Lei de Beer-Lambert



$$dP = -\beta PCdx \qquad -\frac{dP}{P} = \beta Cdx \qquad -\int_{P_0}^{P} \frac{dP}{P} = \beta C \int_0^b dx \qquad -lnP - (-\ln P_0) = \beta Cb$$

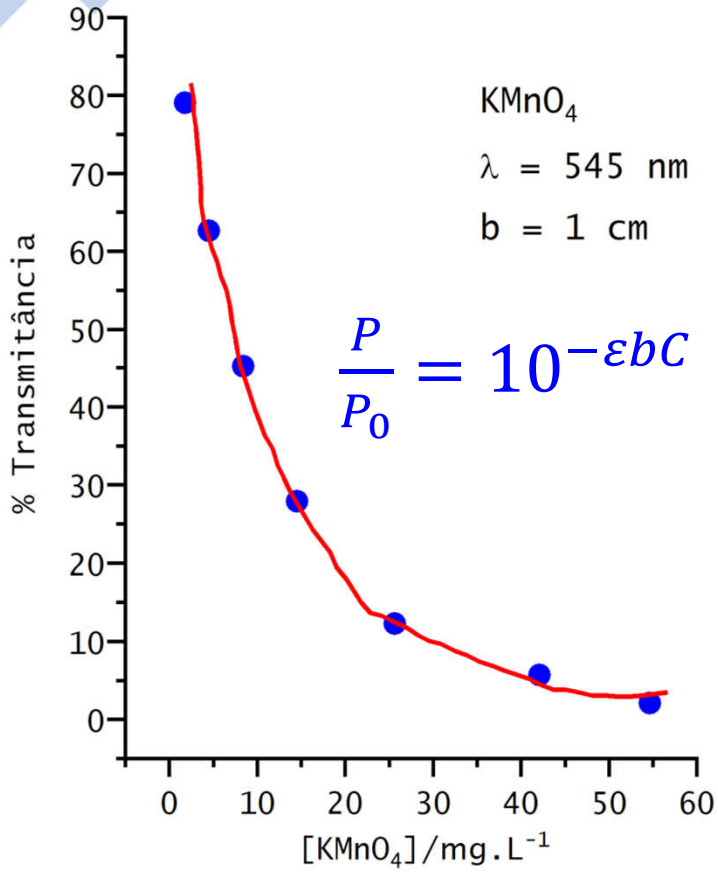
β = constante de proporcionalidade

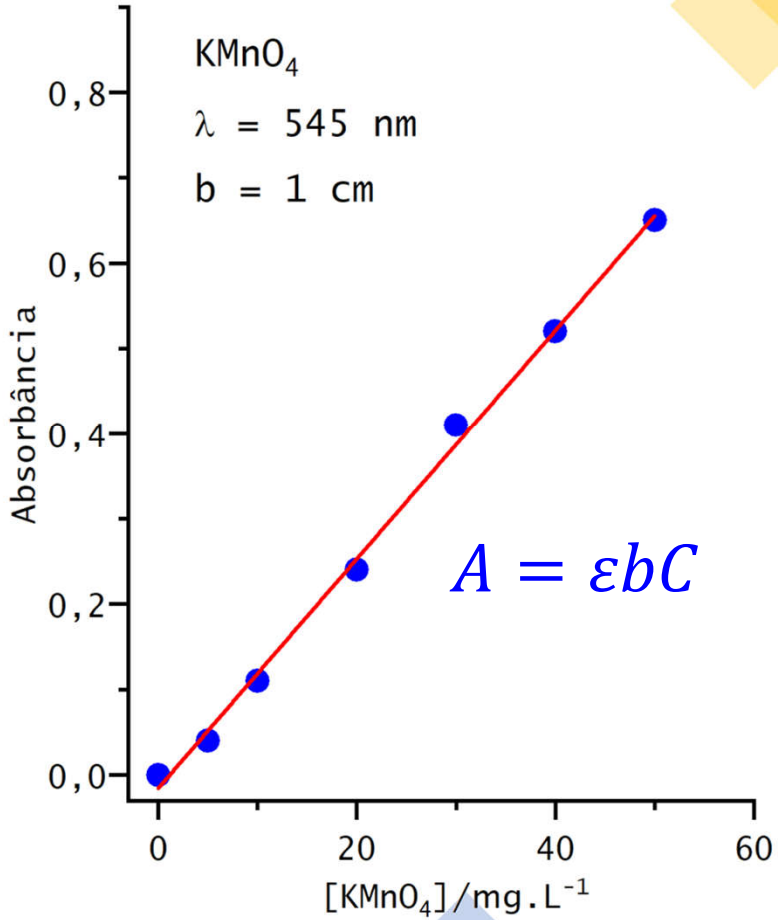
Sinal de menos → intensidade de luz diminui com aumento de x

$$ln\frac{P_0}{P} = \beta Cb \qquad log\frac{P_0}{P} = \frac{\beta}{ln10}Cb$$

$$A = \varepsilon bC$$

Absorbância ε


% Transmitância
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
[KMnO4]/mg.L-1
KMnO4
λ = 545 nm
b = 1 cm
P/P0 = 10−εbC


Absorbância
0,8
0,6
0,4
0,2
0,0
0
20
40
60
[KMnO4]/mg.L-1
KMnO4
λ = 545 nm
b = 1 cm
A = εbC

Química dos Metais de Transição

Química de Coordenação

$ns^2(n-1)d$

$_{26}Fe: Ar4s^23d^6$

$_{22}Ti: Ar4s^23d^2$

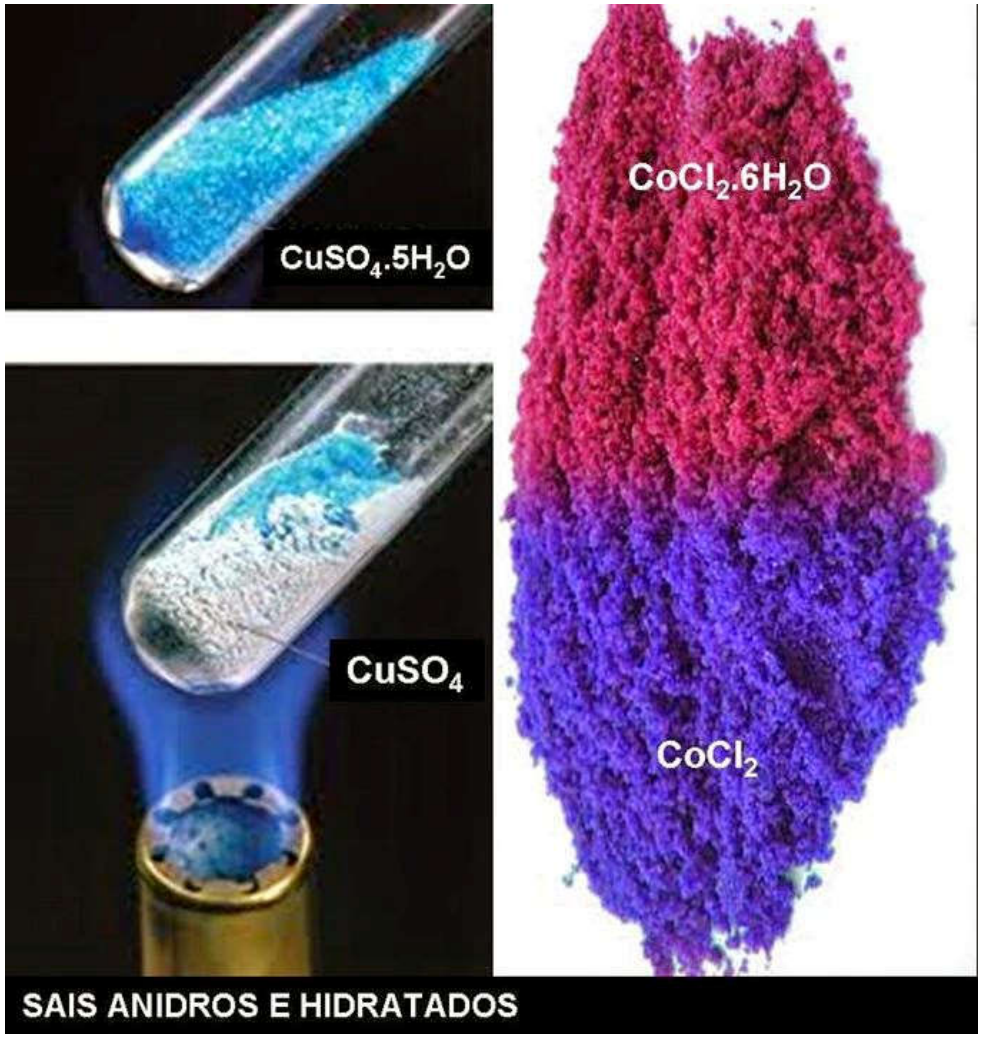
- possuem mais do que 1 E.Ox. estável:
- muitos compostos de metais de transição são coloridos
- muitos compostos de metais de transição exibem propriedades magnéticas

▲ **Figure 23.4** **Aqueous solutions of transition metal ions.** Left to right: Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The counterion is nitrate in all cases.

$[Cu(H_2O)_4]^{2+}(aq)$ $NH_3(aq)$ $[Cu(NH_3)_4]^{2+}(aq)$

$CuSO_4.5H_2O$

$CuSO_4$
Anidro

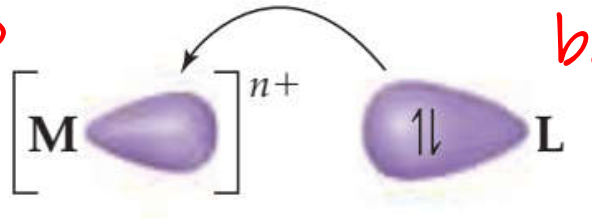

$CuSO_4.5H_2O$
$CuSO_4$
$CoCl_2.6H_2O$
$CoCl_2$
SAIS ANIDROS E HIDRATADOS

Química de Coordenação

$[Cu(H_2O)_4]^{2+}$

Metal — Ligante

Ácido — base

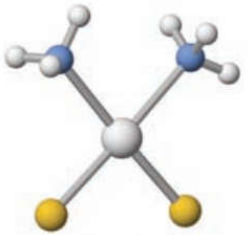


Ligação metal-ligante

Ácido-base de Lewis

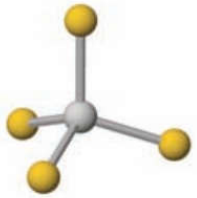
$[Ag(NH_3)_2]^+$

Linear



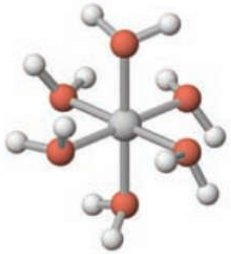
$Pt(NH_3)_2Cl_2$

Square planar



$[NiCl_4]^{2-}$

Tetrahedral



$[Ni(H_2O)_6]^{2+}$

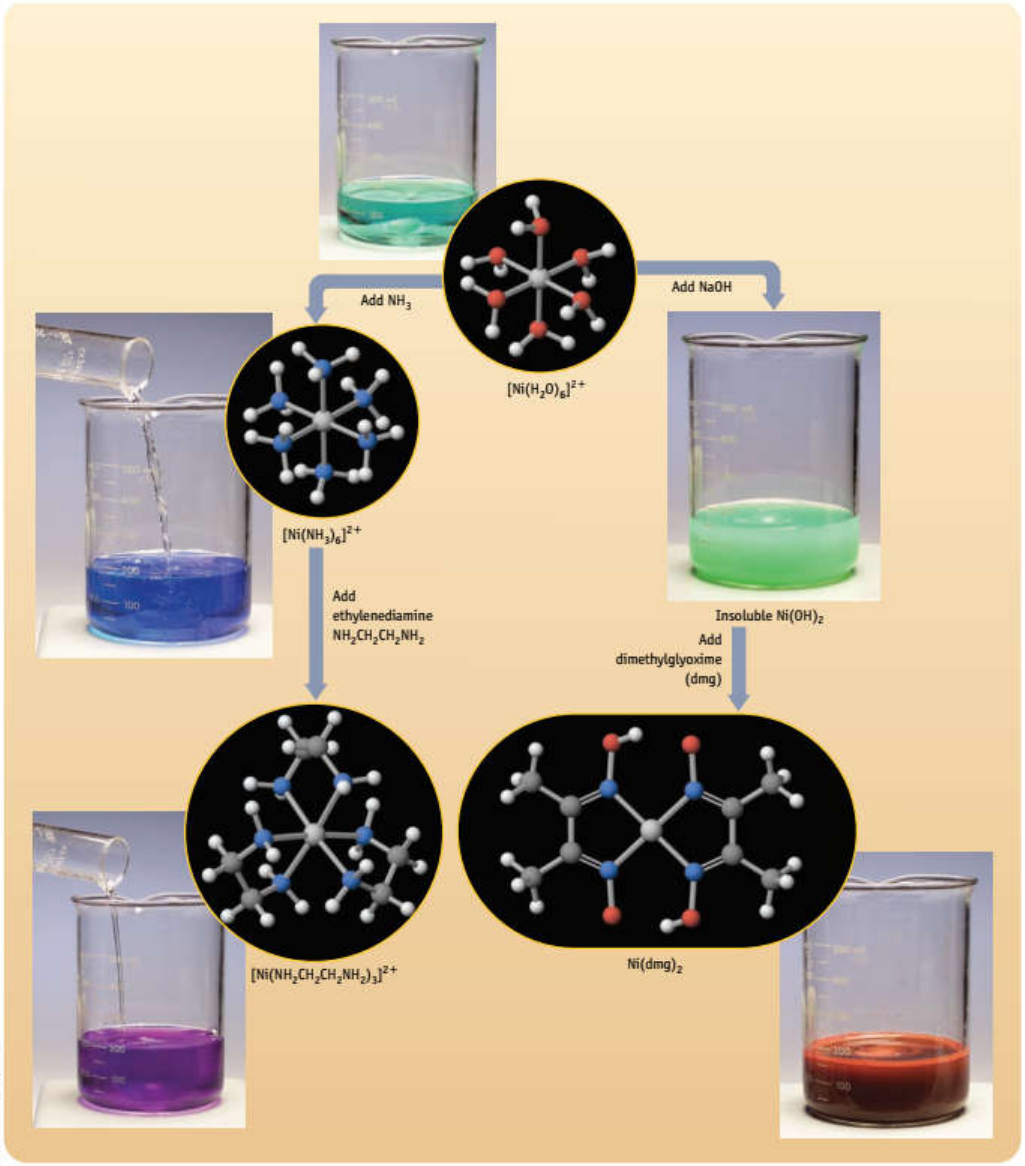
Octahedral

Ligação metal-ligante

- Todos os ligantes têm pares livres que são doados ao íon metálico.
- A ligação entre o metal e o ligante é uma ligação de 2 elétrons, mas ambos vêm do ligante e nenhum vem do metal.
- A ligação metal-ligante altera as propriedades físicas do metal:

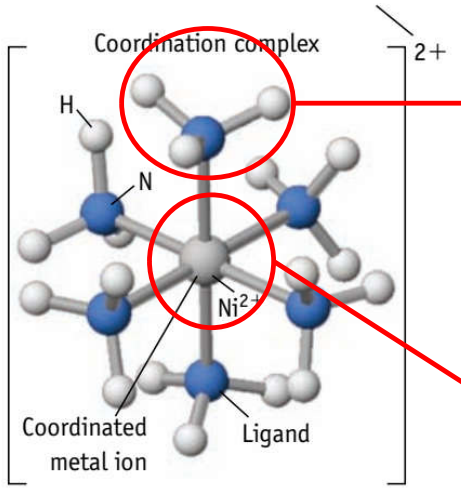
$$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}, \quad E^{\circ} = +0{,}799\ V$$

$$[Ag(CN)_2]^{-}_{(aq)} + e^{-} \rightarrow Ag_{(s)} + 2CN^{-}_{(aq)}, \quad E^{\circ} = -0{,}031\ V$$



Photos: Charles D. Winters

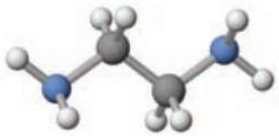
FIGURE 22.12 Coordination compounds of Ni^{2+} ion. The transition metals and their ions form a wide range



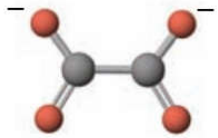
$[Ni(NH_3)_6]^{2+}$

Ligante monodentado

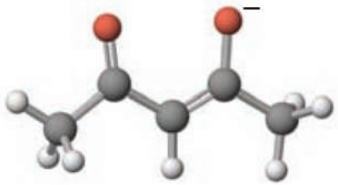
Número de coordenação



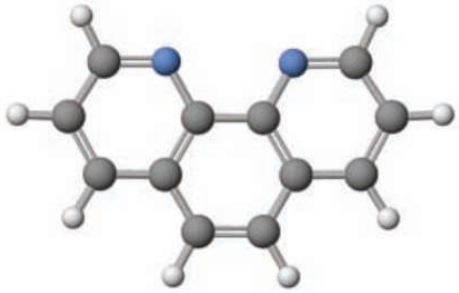
(a) $H_2NCH_2CH_2NH_2$, en



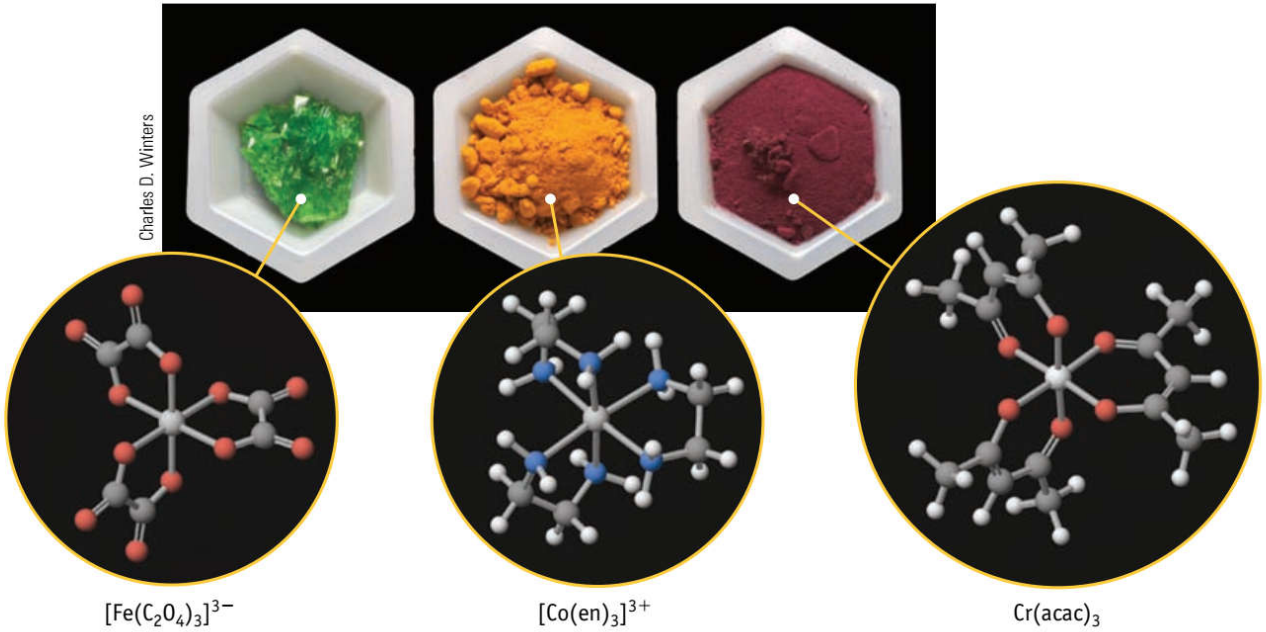
(b) $C_2O_4^{2-}$, ox



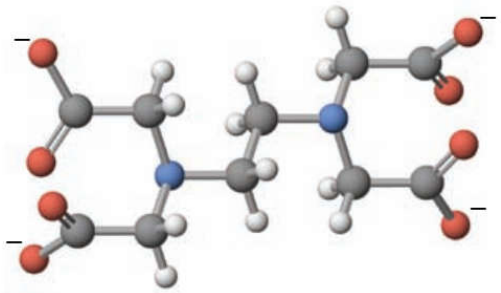
(c) $CH_3COCHCOCH_3^-$, $acac^-$



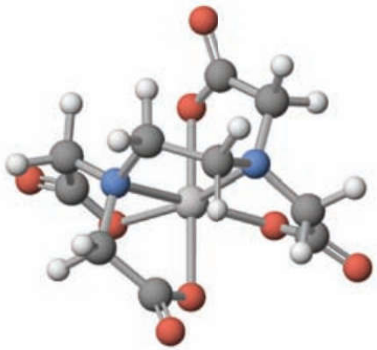
(d) $C_{12}H_8N_2$, phen



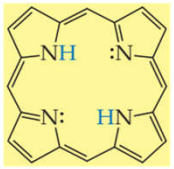
$[Fe(C_2O_4)_3]^{3-}$ $[Co(en)_3]^{3+}$ $Cr(acac)_3$



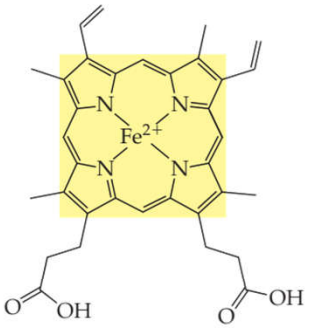
(a) Ethylenediaminetetraacetate, $EDTA^{4-}$



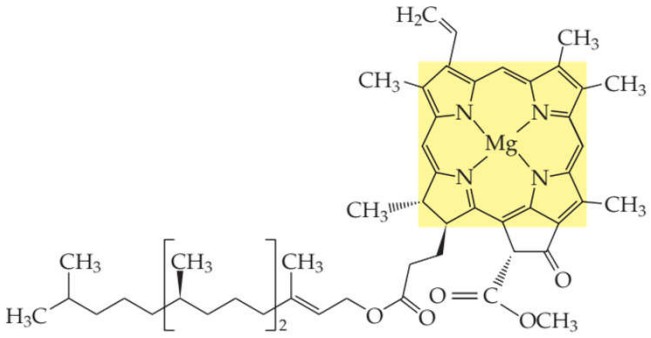
(b) $[Co(EDTA)]^-$



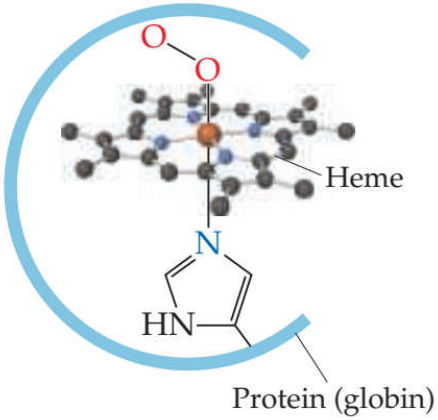
Porphine



Heme b



Chlorophyll a



Complexos de Co(III)

Medidas de Condutância molar

$[Co(NH_3)_6]^{3+}$ $[Co(NH_3)_6]Cl_3$ $Al(NO_3)_3$

$[Co(NH_3)_5Cl]^{2+}$ $[Co(NH_3)_5Cl]Cl_2$ $Mg(NO_3)_2$

$[Co(NH_3)_4Cl_2]^{+}$ $[Co(NH_3)_4Cl_2]Cl$ $Na(NO_3)$

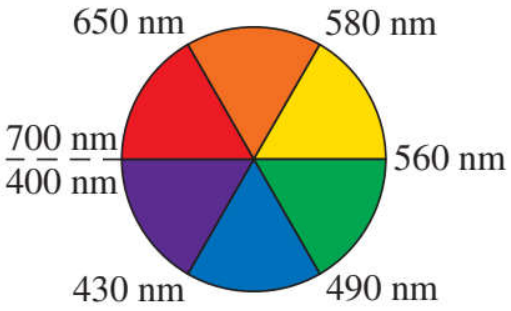
$[Co(NH_3)_3Cl_3]$ → não eletrólito

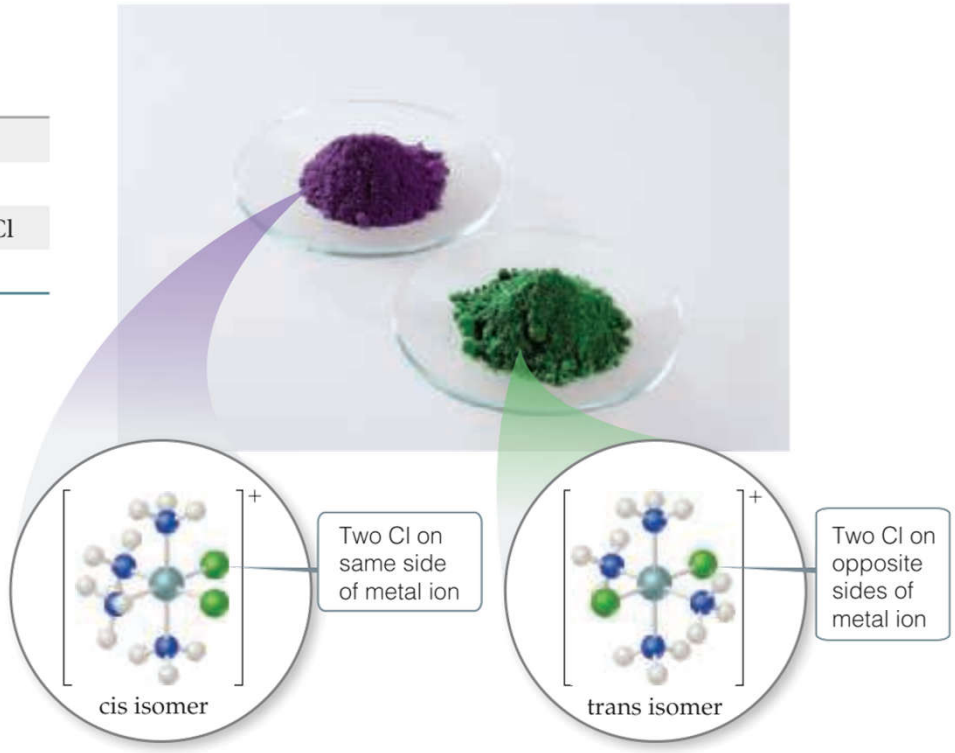
Químico Suiço

1893

Alfred Werner

Original Formulation	Color	Ions per Formula Unit	"Free" Cl^- Ions per Formula Unit	Modern Formulation
$CoCl_3 \cdot 6\,NH_3$	Orange	4	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5\,NH_3$	Purple	3	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4\,NH_3$	Green	2	1	*trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4\,NH_3$	Violet	2	1	*cis*-$[Co(NH_3)_4Cl_2]Cl$





▲ **Figure 23.8** **Isomers of $[Co(NH_3)_4Cl_2]^+$.** The cis isomer is violet, and the trans isomer is green.

NOMENCLATURA DOS COMPLEXOS

eto e ido ⇨ o

Ânion	Nome do Ânion	Nome do Ligante
Cl^-	Cloreto	Cloro
Br^-	Brometo	Bromo
OH^-	Hidróxido	Hidroxo
CN^-	Cianeto	Ciano

ato ⇨ o mesmo

Ânion	Nome do Ânion	Nome do Ligante
SO_4^{2-}	Sulfato	Sulfato
$C_2O_4^{2-}$	Oxalato	Oxalato

Moléculas neutras mantém o nome.
Exceção: H_2O - aquo
NH_3 - amin
CO - carbonil ou carbonila

Repete: bi, tri, tetra, ... quando não há compatibilidade
bis, tris, tetraquis ... ex.: bis(etilenodiamina)

Exemplos

$[Co(H_2O)_6]^{2+}$ íon hexaaquocobalto(II)

$[CoCl_4]^{2-}$ íon tetraclorocobaltato(II)

$[Cr(OH)_4(H_2O)_2]^-$ íon tetrahidroxodiaquocromiato(III)

$[Fe(CN)_6]^{3-}$ íon hexacianoferrato(III)

$[FeF_6]^{4-}$ íon hexafluoroferrato(II)

Escreva o nome dos compostos abaixo

$[Co(H_2O)_6]Cl_2$	cloreto de hexaaquocobalto(II)
$K_2[CoCl_4]$	tetraclorocobaltato(II) de potássio
$K[Cr(OH)_4(H_2O)_2]$	tetrahidroxodiaquocromiato(III) de potássio
$K_3[Fe(CN)_6]$	hexacianoferrato(III) de potássio
$K_4[FeF_6]$	hexafluoroferrato(II) de potássio

Obrigado!!