

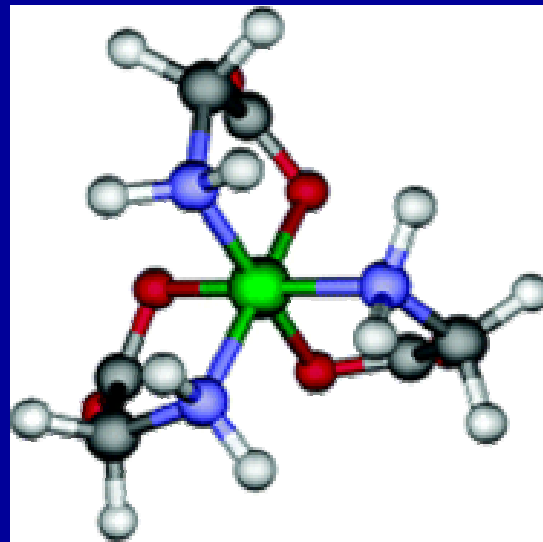
# Koordinační chemie



Alfred Werner  
(1866-1919)

NP za chemii 1913

1893 K centrálnímu atomu může být vázáno více ligandů než odpovídá jeho oxidačnímu číslu.



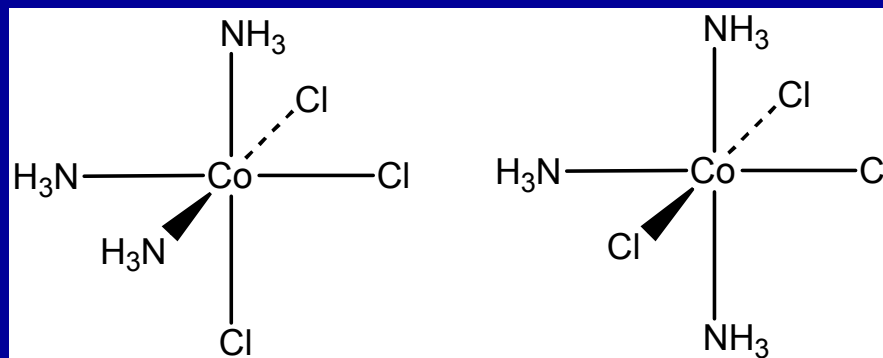
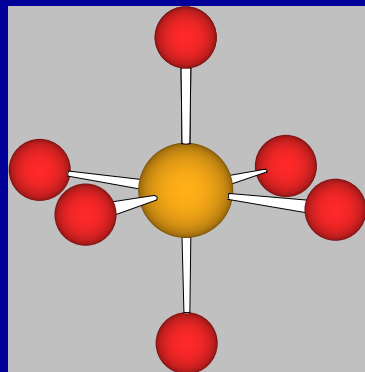
# Koordinační sloučeniny

Experimentální výsledky nesouhlasí s dosavadní teorií

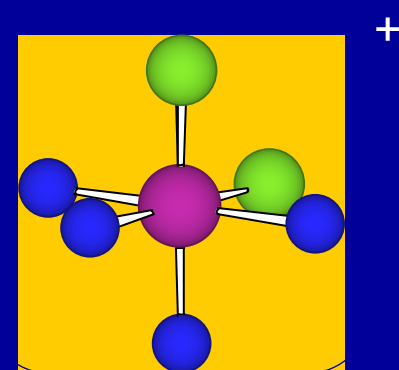
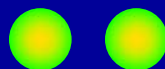
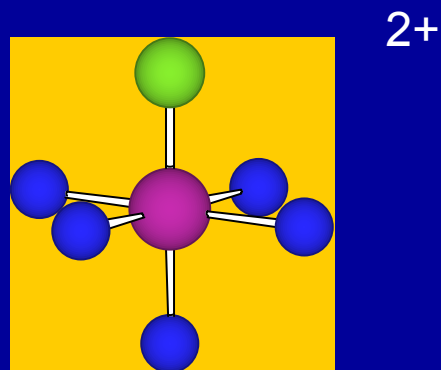
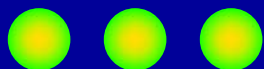
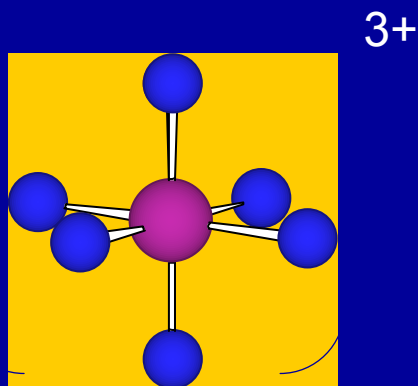
→ nová teorie (model)

Empirický vzorec	Barva	Počet molů iontů na 1 mol látky	Počet molů AgCl, které lze snadno vysrážet z 1 molu látky
$\text{CoCl}_3 \cdot 6\text{NH}_3$	zlatohnědá	4	3
$\text{CoCl}_3 \cdot 5\text{NH}_3$	fialová	3	2
$\text{CoCl}_3 \cdot 4\text{NH}_3$	zelená	2	1
$\text{CoCl}_3 \cdot 3\text{NH}_3$	zelená	0	0

Oktaedr



# Koordinační sloučeniny



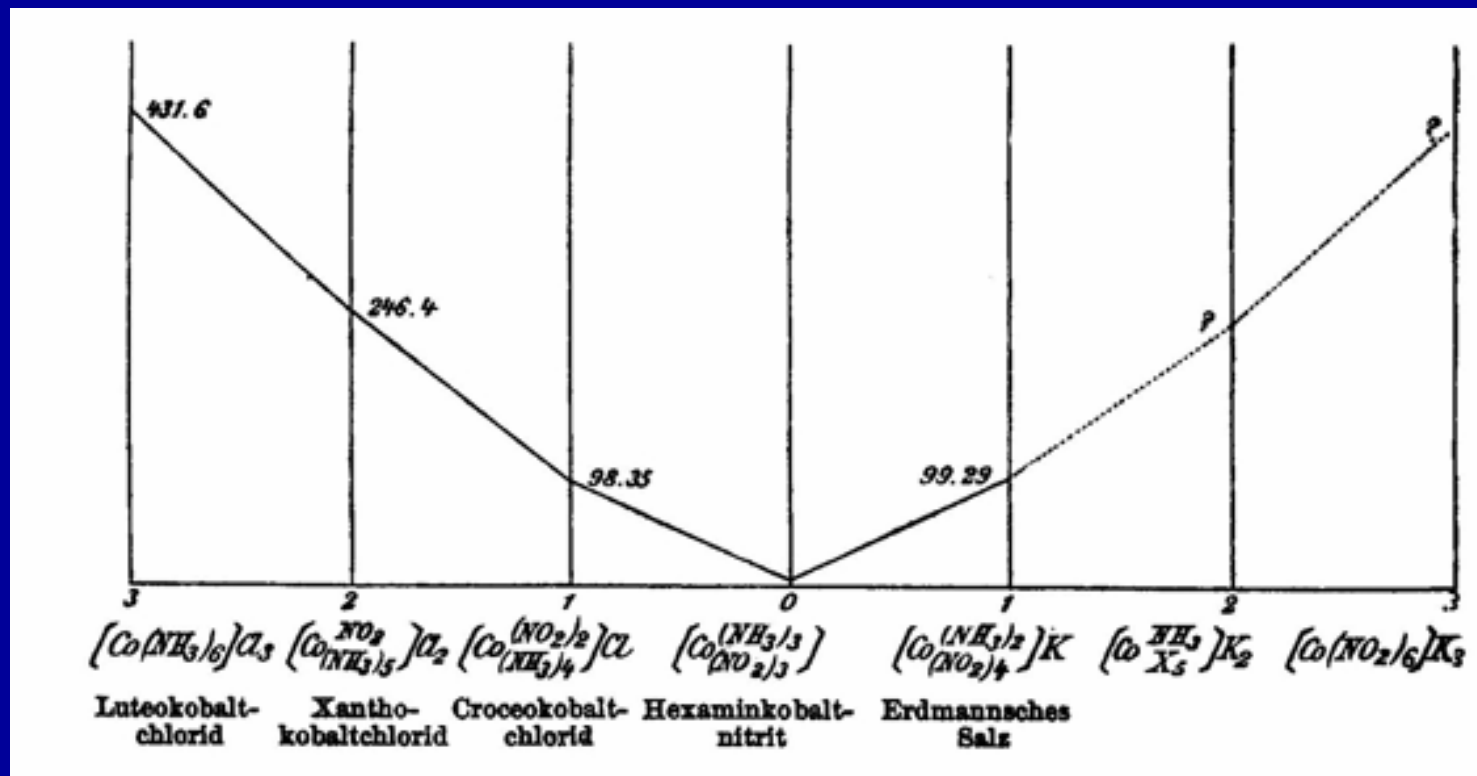
Kov v oxidačním stavu  $n+$  (primární valence)

Komplex má koordinační číslo  $m$  (sekundární valence)

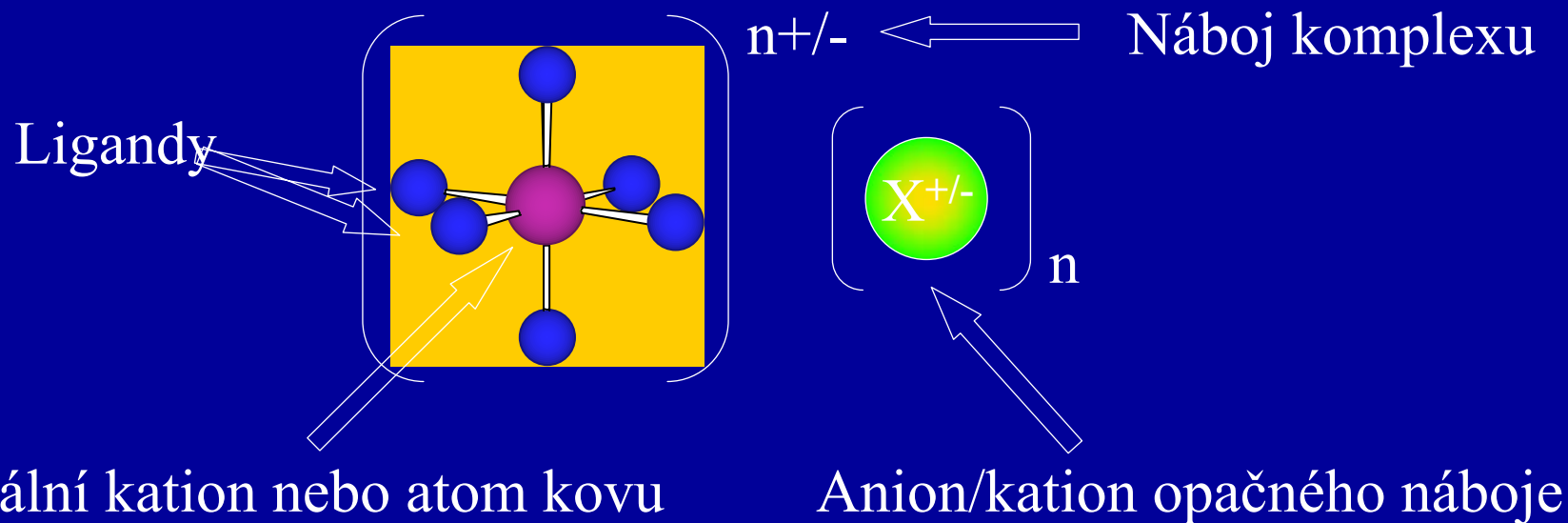
Ligandy vázány k centrálnímu atomu donor-akceptorovými vazbami

# Koordinační sloučeniny

Elektrická vodivost roztoků komplexních sloučenin



# Koordinační sloučeniny



Centrální kation kovu nebo neutrální atom je obklopen souborem ligandů. Každý ligand poskytne 2 elektrony do volných d-orbitalů kovu a vytvoří donor-akceptorovou vazbu.

**Počet ligandů = koordinační číslo**

# Vnitřní a vnější sféra komplexu

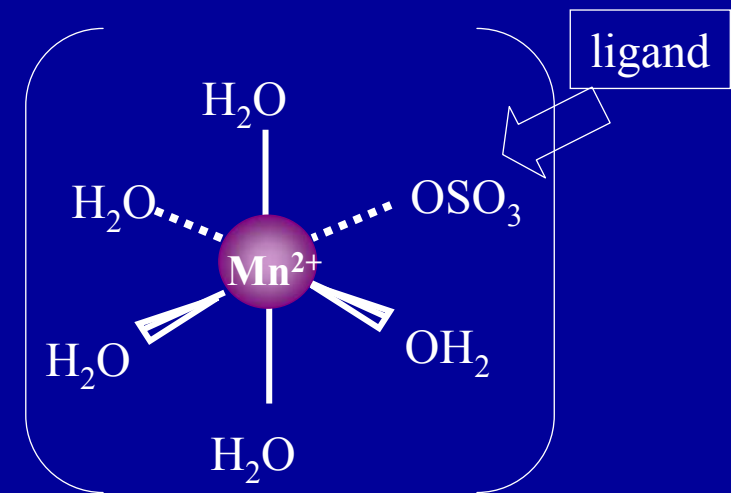
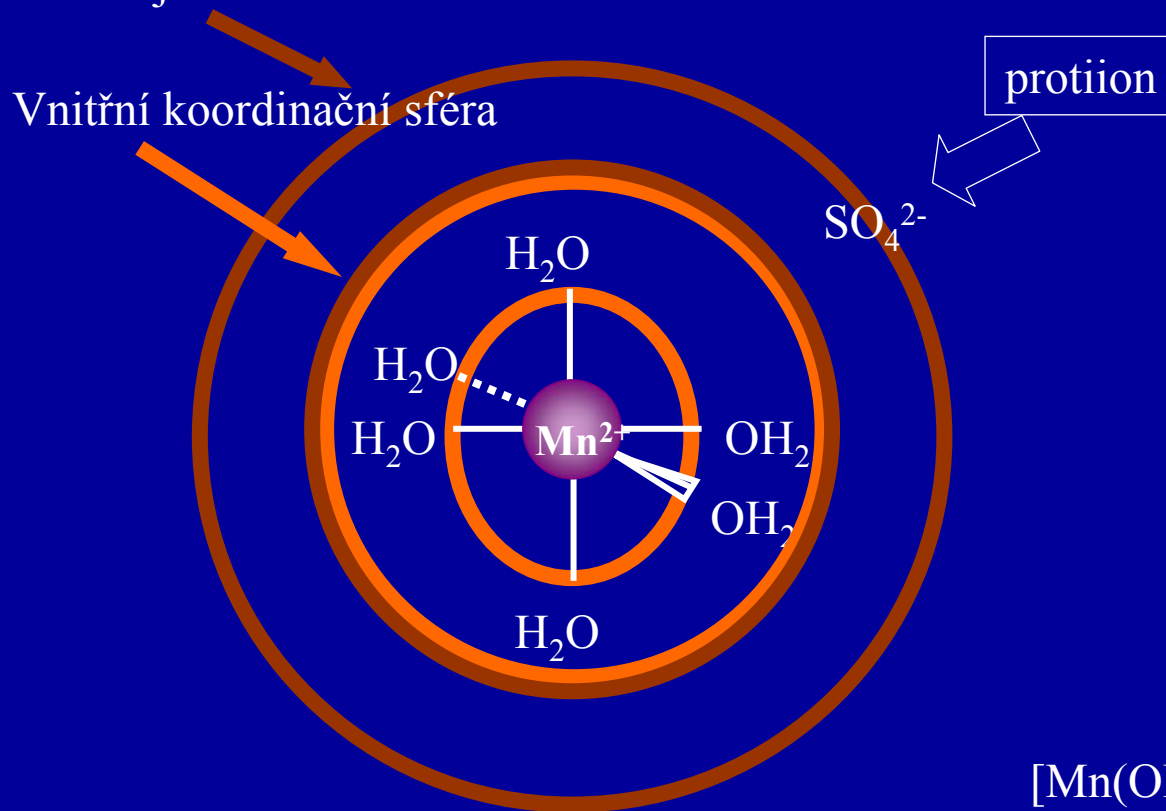
Vnitřní koordinační sféra =

ligandy přímo vázané k centrálnímu atomu

Vnější koordinační sféra =

ionty asociované s komplexem, ale ne přímo vázané k centrálnímu atomu

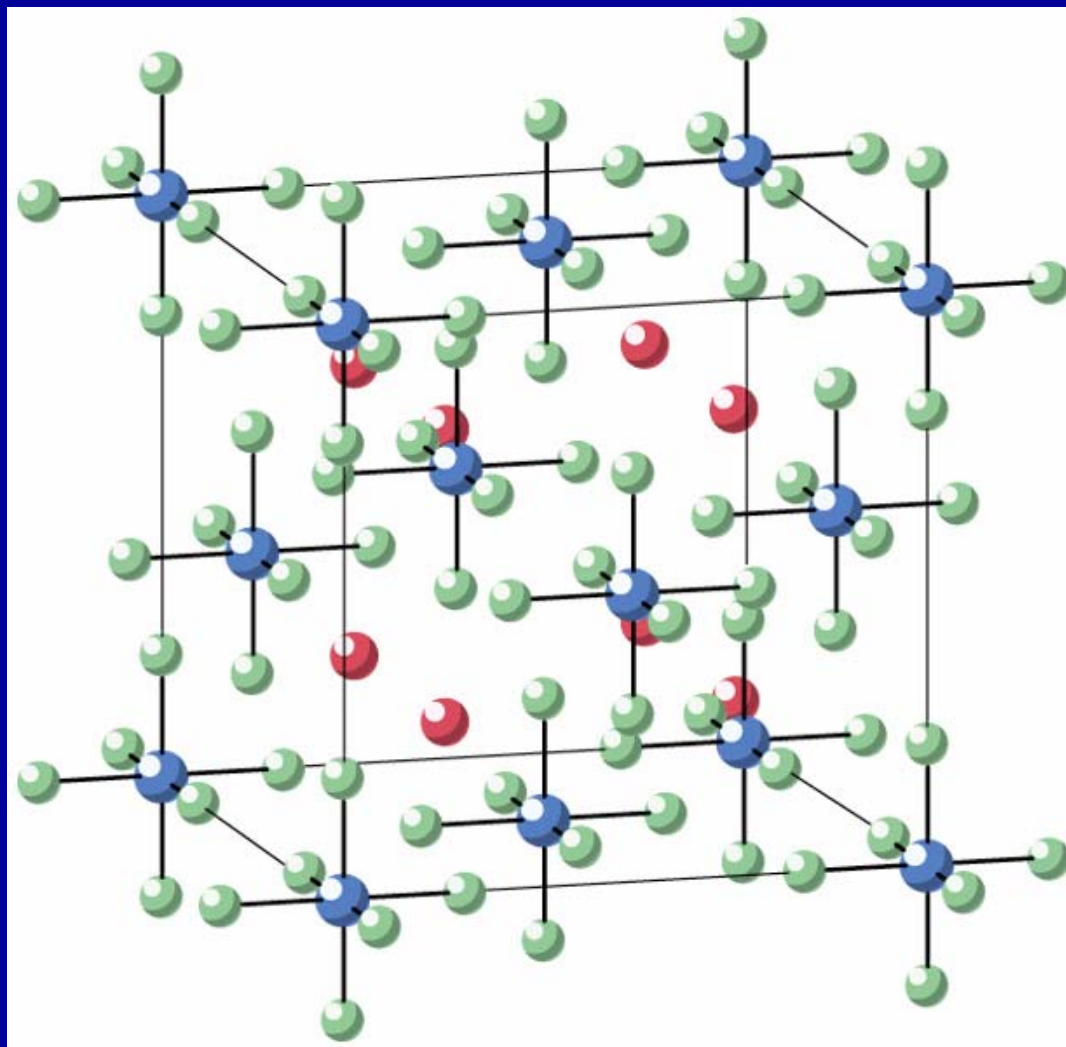
Vnější koordinační sféra



$[\text{Mn}(\text{OH}_2)_5(\text{SO}_4)_5]$ : vnitřní koordinace  $\text{SO}_4^{2-}$

$[\text{Mn}(\text{OH}_2)_6][\text{SO}_4]$ : vnější koordinace  $\text{SO}_4^{2-}$

# Koordinační sloučeniny v pevné fázi



## Změna pořadí energetických hladin

Ar [Ne] 3s<sup>2</sup> 3p<sup>6</sup> (4s<sup>0</sup>)

K [Ar] 4s<sup>1</sup> (3d<sup>0</sup> 4p<sup>0</sup>)

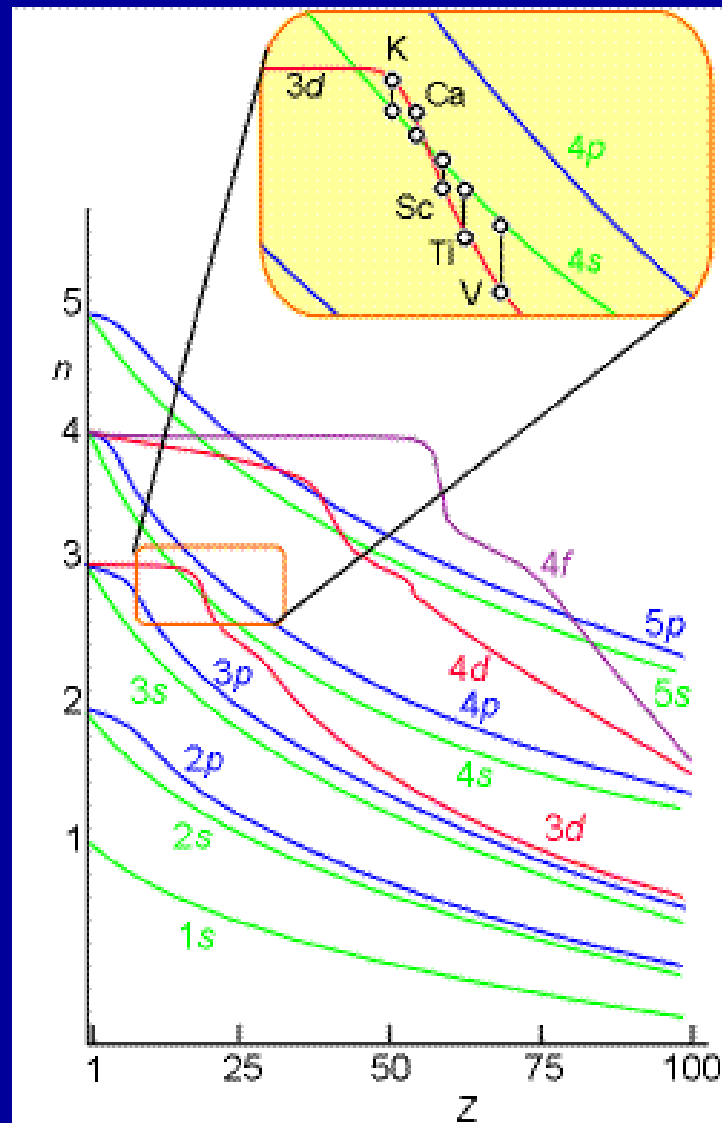
Ca [Ar] 4s<sup>2</sup> (3d<sup>0</sup> 4p<sup>0</sup>)

Sc [Ar] 3d<sup>1</sup> 4s<sup>2</sup> (4p<sup>0</sup>)

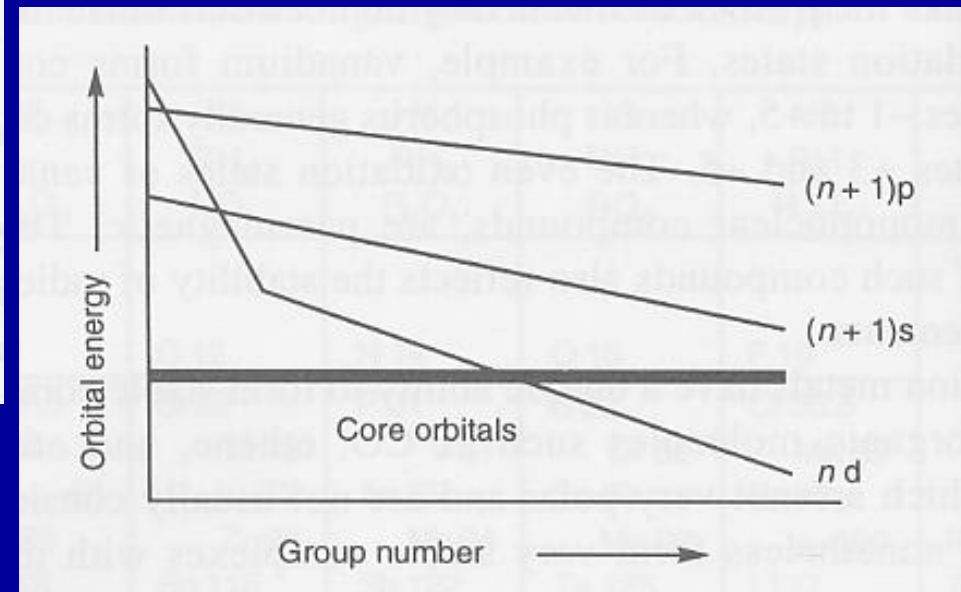
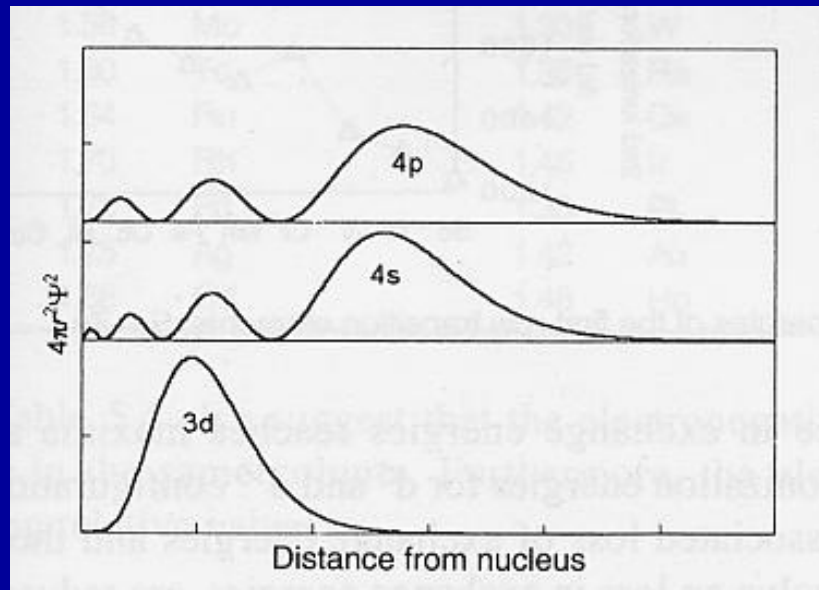
Ti [Ar] 3d<sup>2</sup> 4s<sup>2</sup> (4p<sup>0</sup>)



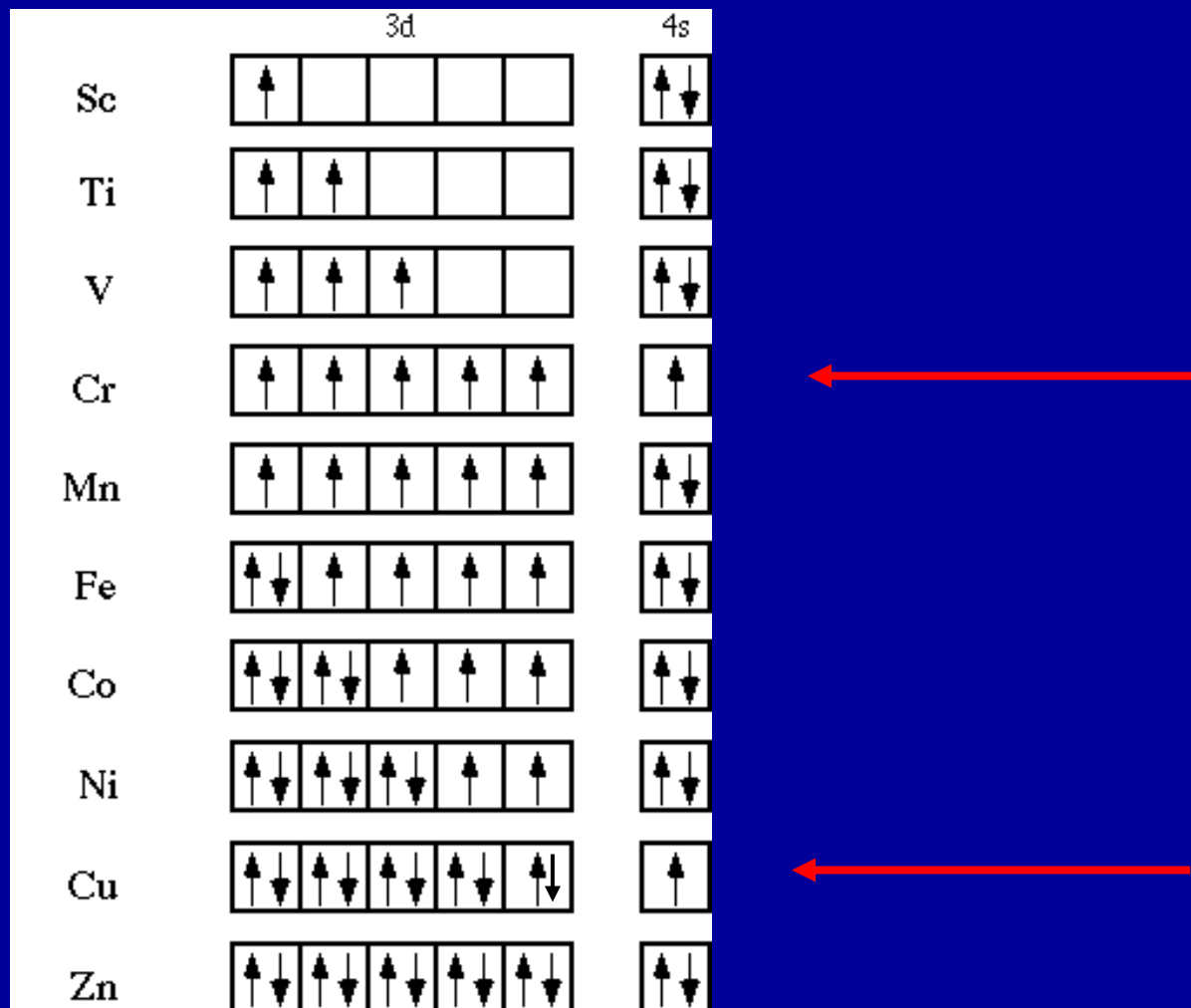
# Změna pořadí energetických hladin



# Elektronové konfigurace přechodných prvků



# Vyšší stabilita zpola zaplněných d-orbitalů



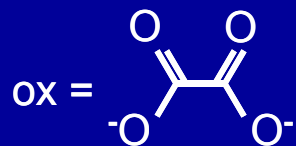
## Oxidační stavy přechodných kovů

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3	2,3 4	1,2,3 4,5	1,2,3 ,4, 5,6	1,2,3 ,4,5,6 ,7	2,3, 4,5,6	1,2,3, 4	1,2 3,4	1,2	2

### First Ionization Energies of the Transition Elements (kJ/mol)

Period	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Fourth	Sc 631	Ti 658	V 650	Cr 652	Mn 717	Fe 759	Co 758	Ni 737	Cu 745	Zn 906
Fifth	Y 616	Zr 660	Nb 664	Mo 685	Tc 702	Ru 711	Rh 720	Pd 805	Ag 731	Cd 868
Sixth	La 538	Hf 680	Ta 761	W 770	Re 760	Os 840	Ir 880	Pt 870	Au 890	Hg 1007

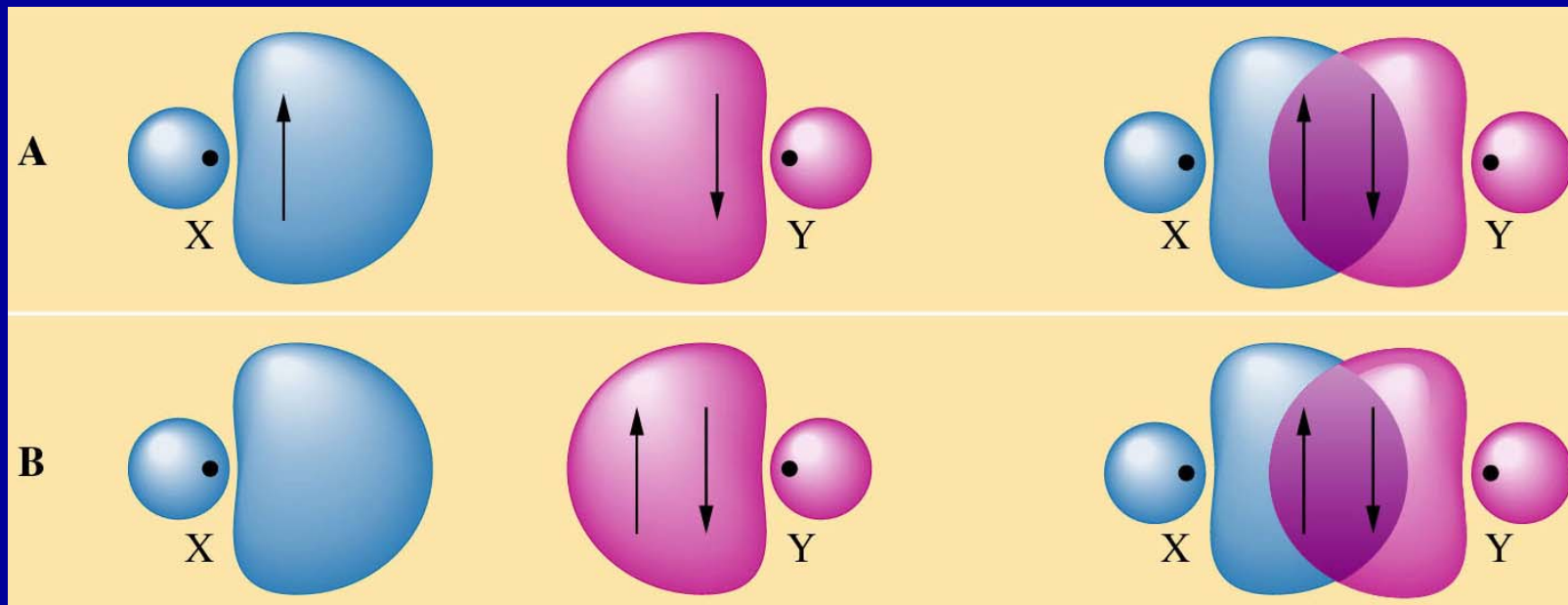




komplex	Ox.č. (Ligand)	Ox.č. (M)	počet d-elektronů
$[\text{Cr}_2\text{O}_7]^{2-}$	-2	+6	$d^0$
$[\text{MnO}_4]^-$	-2	+7	$d^0$
$[\text{Ag}(\text{NH}_3)_2]^+$	0	+1	$d^{10}$
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	0	+3	$d^1$
$[\text{Co}(\text{en})_3]^{3+}$	0	+3	$d^6$
$[\text{PtCl}_2(\text{NH}_3)_2]$	-1, 0	+2	$d^8$
$[\text{V}(\text{CN})_6]^{4-}$	-1	+2	$d^3$
$[\text{Fe}(\text{ox})_3]^{3-}$	-2	+3	$d^5$

# Donor-akceptorová vazba

donor-akceptorová vazba je ekvivalentní kovalentní vazbě



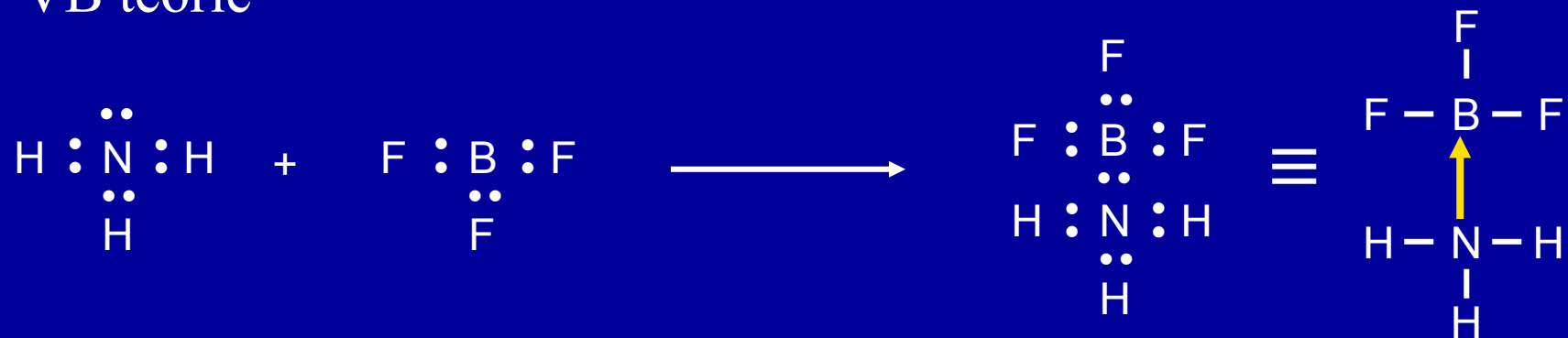
**Akceptor**  
**Volný orbital**

**Donor**  
**Volný e pár**

**Kovalentní vazba**

# Donor-akceptorová vazba

VB teorie



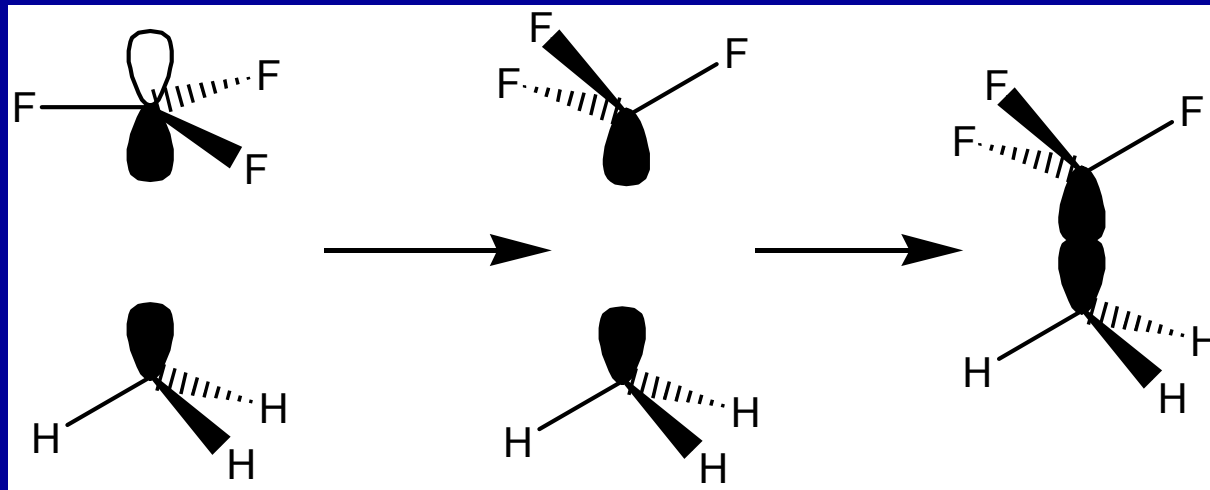
 Donor-akceptorová vazba



# Donor-akceptorová vazba



VB teorie



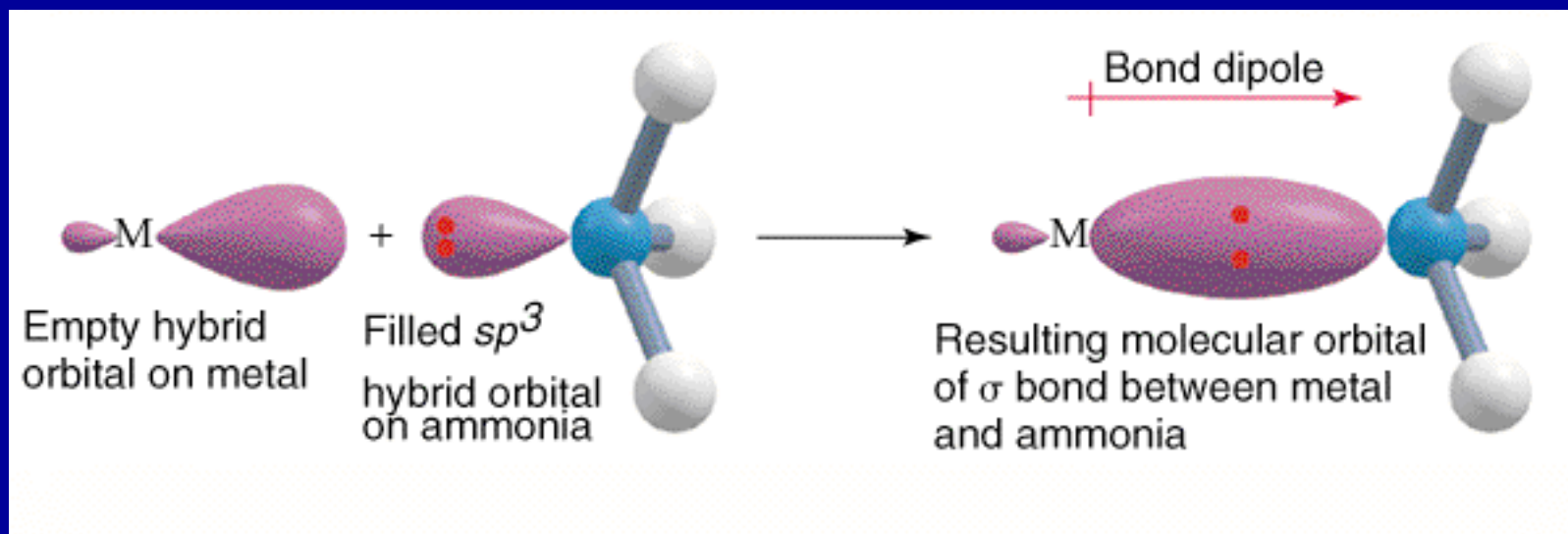
MO teorie

B



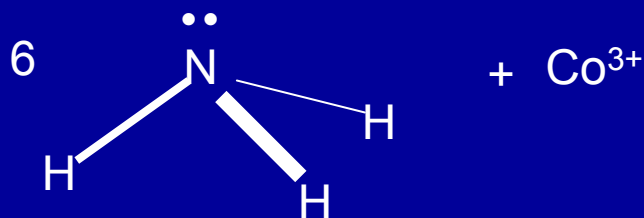
N

# Donor-akceptorová vazba



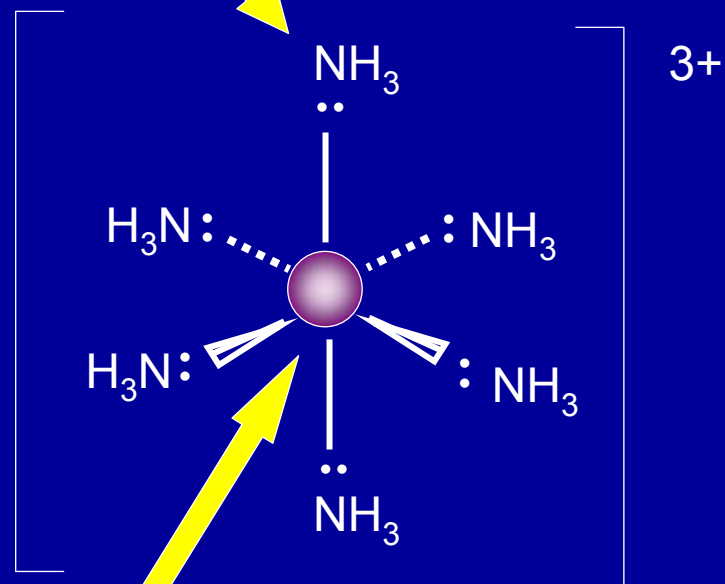
# Donor-akceptorová vazba

VB teorie

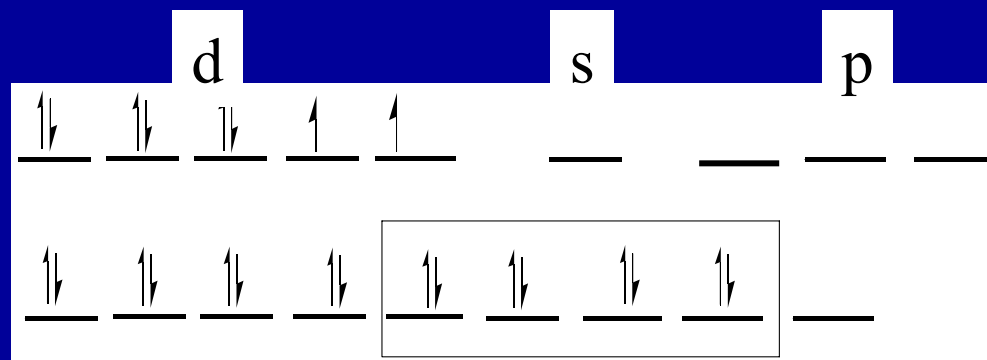


Každý ligand poskytne do vazby 2 elektrony

"Lewisovská báze"

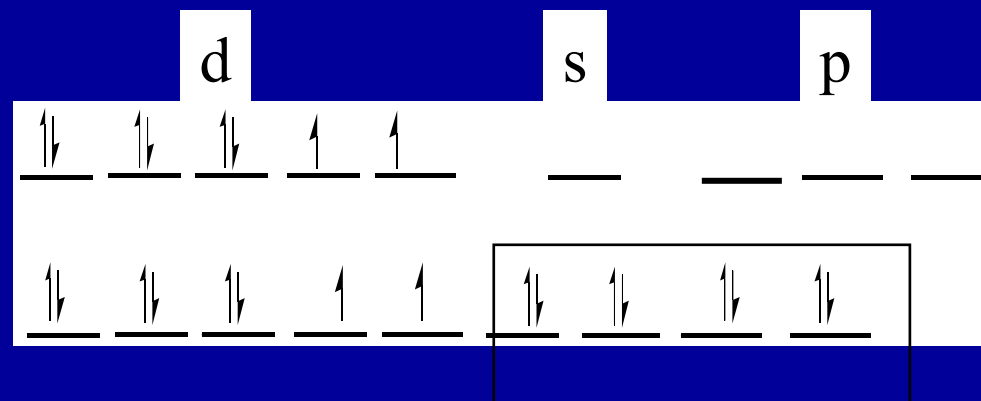


"Lewisovská kyselina"



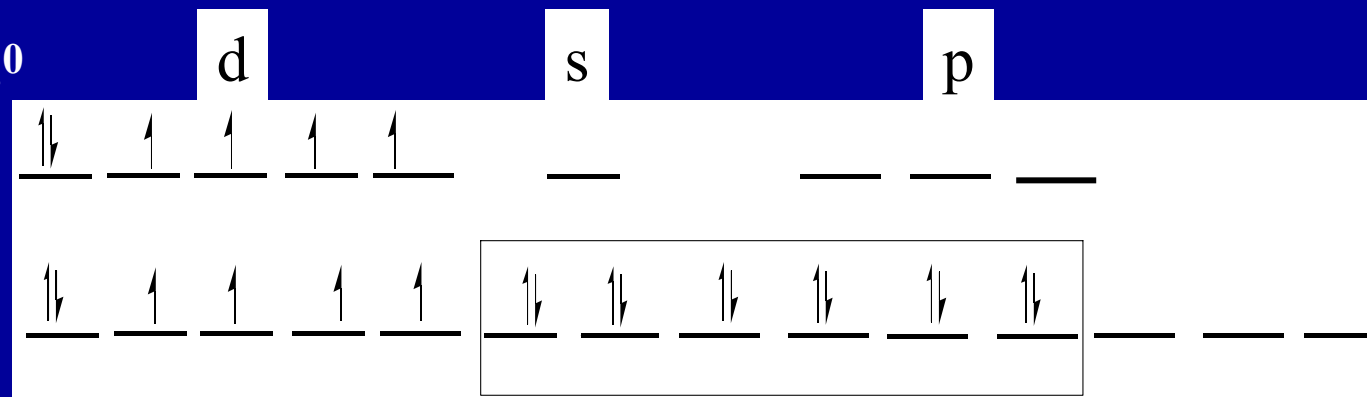
$dsp^2$  hybridní orbitaly

elektrony z Cl<sup>-</sup>, čtvercový



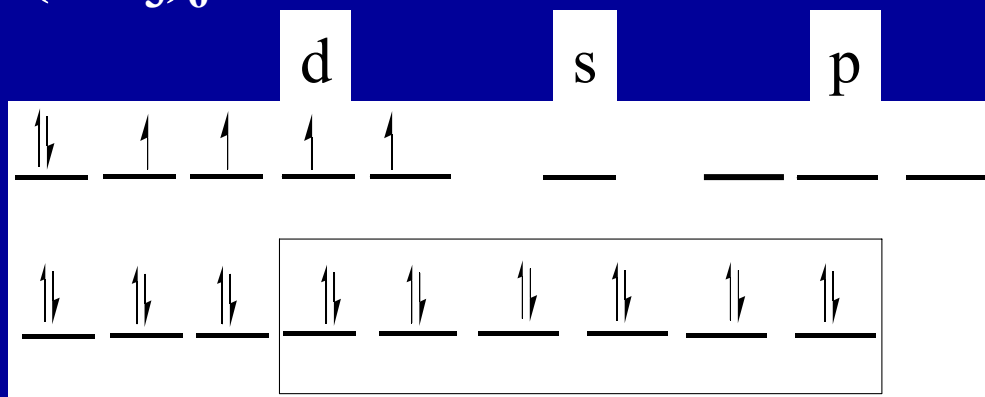
$sp^3$  hybridní orbitaly

elektrony z Cl<sup>-</sup>, tetraedrický



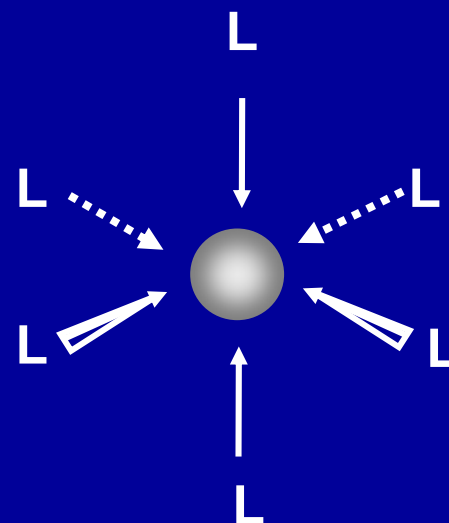
$sp^3d^2$  hybridní orbitály

elektrony z  $\text{F}^-$ , oktaedrický



$d^2sp^3$  hybridní orbitály

elektrony z  $\text{NH}_3$ , oktaedrický



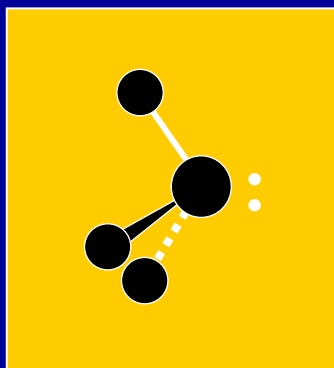
# Monodentátní ligandy

CO  
oxid uhelnatý

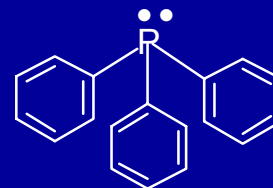
Cr



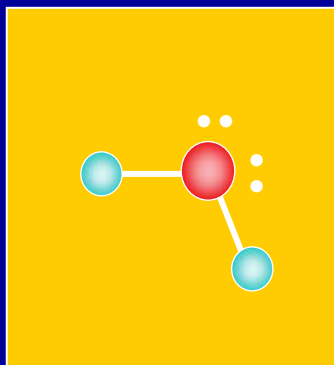
$\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Mo}(\text{CO})_6$



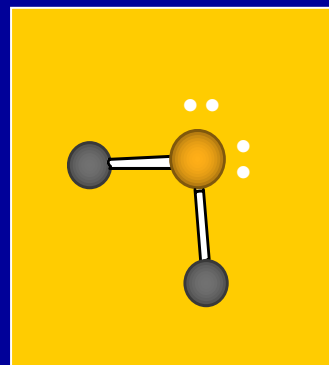
$\text{NH}_3$   
amoniak



$\text{PPh}_3$   
fosfan



$\text{H}_2\text{O}$   
voda



$\text{SR}_2$   
thioether

# HSAB = Teorie tvrdých a měkkých kyselin a bází

R. Pearson 1963

Vysoká oxidační čísla centrálního atomu jsou stabilizována  $F^-$ ,  $O^{2-}$

Nízká oxidační čísla jsou stabilizována  $CO$ ,  $CN^-$

Tvrde donorní atomy

## HSAB

Měkké donorní atomy

$\text{NH}_3$ ,  $\text{F}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$

Malé donorní atomy

Silně elektronegativní

Málo polarizovatelné

stabilní komplexy

Tvrde kovy

$\text{Fe(III)}$ ,  $\text{Mg(II)}$ ,  $\text{Cr(III)}$ ,  $\text{Al(III)}$

Malé atomy (1. přech. řada)

Vysoký náboj

$\text{CO}$ ,  $\text{PPh}_3$ ,  $\text{I}^-$ ,  $\text{C}_2\text{H}_4$ ,  $\text{SRH}$ ,  $\text{CN}^-$ ,  $\text{SCN}^-$

Velké donorní atomy

Málo elektronegativní

Snadno polarizovatelné

stabilní komplexy

Měkké kovy

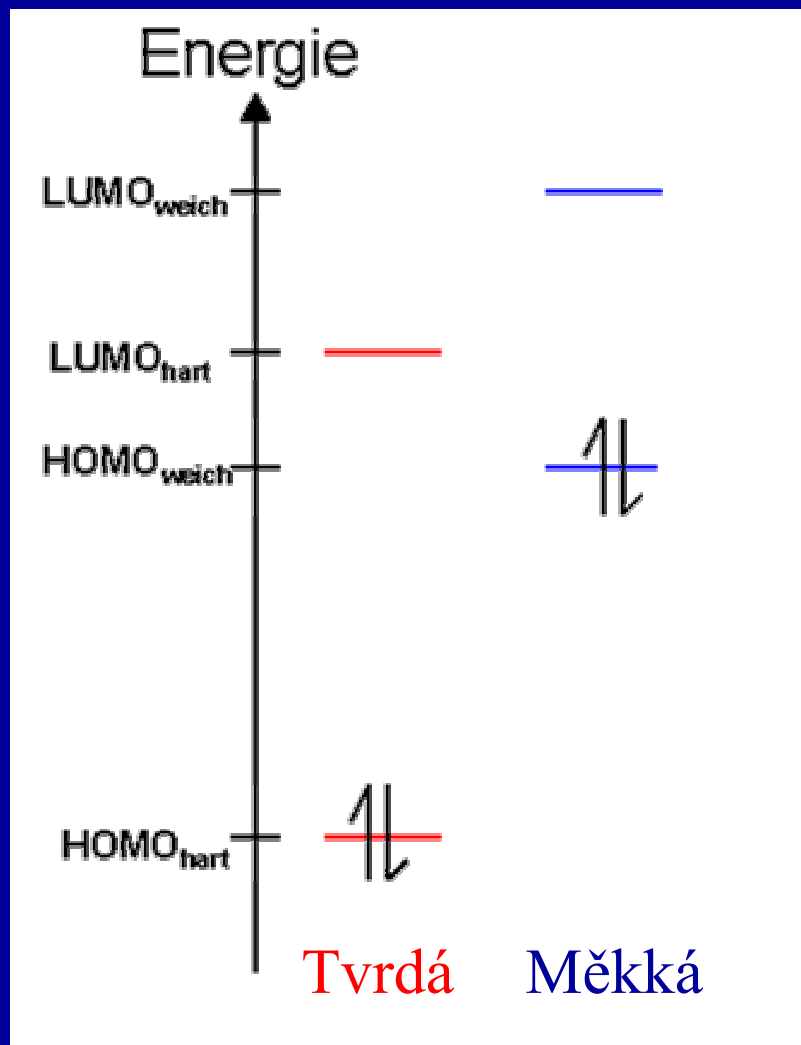
$\text{Ag(I)}$ ,  $\text{Cu(I)}$ ,  $\text{Hg(II)}$ ,  $\text{Au(I)}$

Velké atomy (2. a 3. přech. řada)

Malý náboj



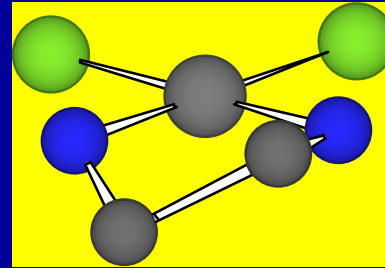
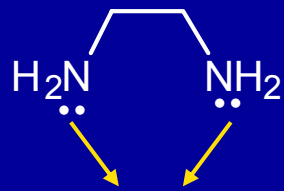




Kyselina

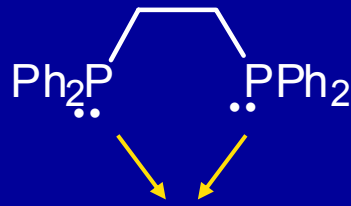
Báze

# Neutrální bidentátní ligandy

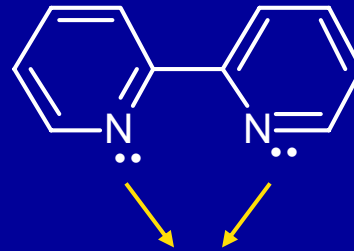


pětičlenný chelátový cyklus  
čtvercově planární komplex

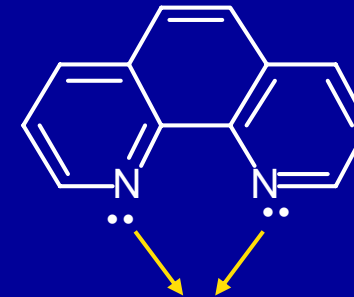
1,2-diaminoethan = ethylendiamin = en



1,2-difenylofosfinoethan  
dppe



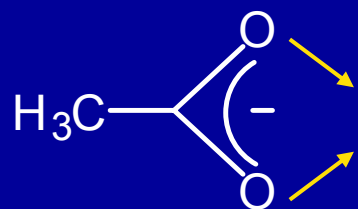
2,2'-bipyridin  
bipy



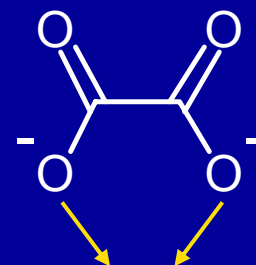
1,10-fenanthrolin  
phen

Chelatace - ligandy jsou vázány velmi pevně k centrálnímu atomu

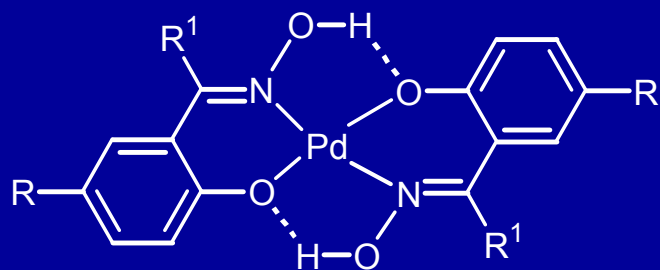
# Aniontové bidentátní ligandy



acetát =  $\text{ac}^-$

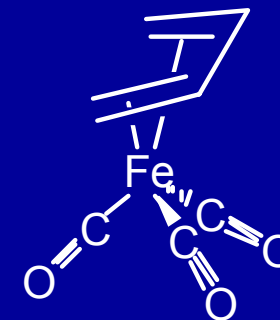


oxalát =  $\text{ox}^{2-}$



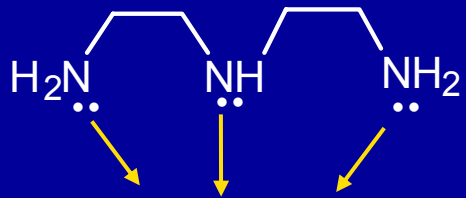
komplex Pd(II)-oxim

$\pi$ -donorní bidentátní ligand



$[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)]$

# Tridentální ligandy



diethylentriamin

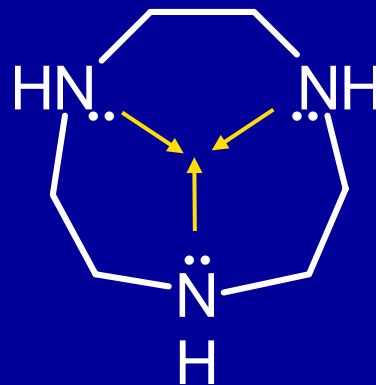
dien



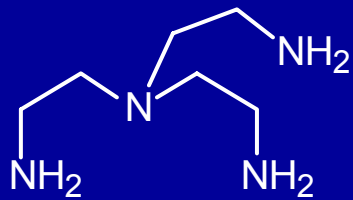
2,2':6',2''-terpyridin

tpy

1,2,4-triazacyklononan  
makrocyclický ligand



# Tetradentátní ligandy

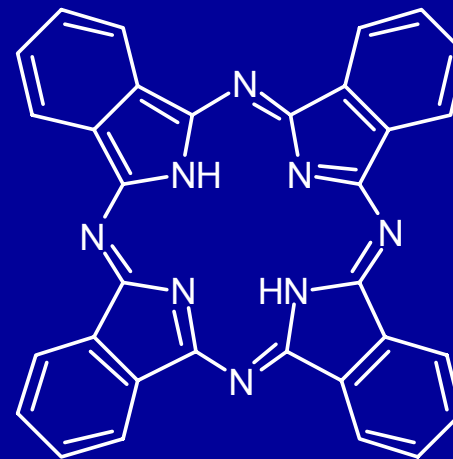


tris(2-aminoethyl)amin

tren



porfyrin



ftalocyanin

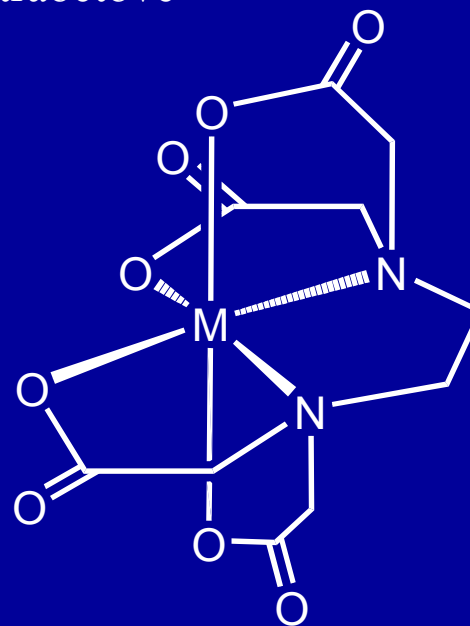
# Multidentátní ligandy

tetraanion kyseliny ethylendiamintetraoctové

EDTA

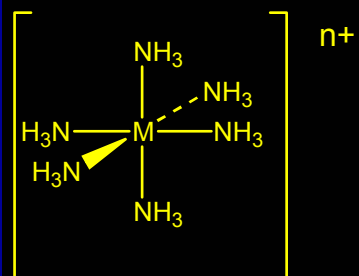


Hexadentátní

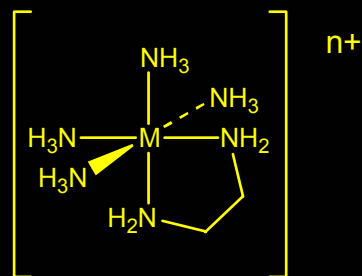


# Topologie komplexů

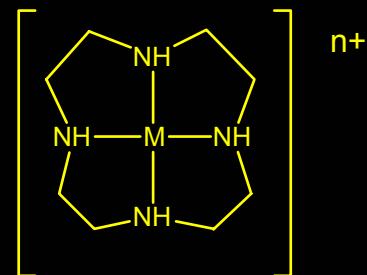
komplexace



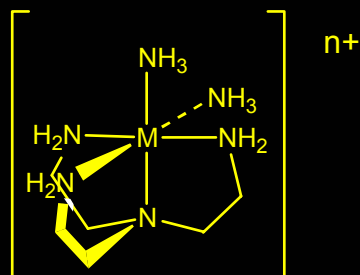
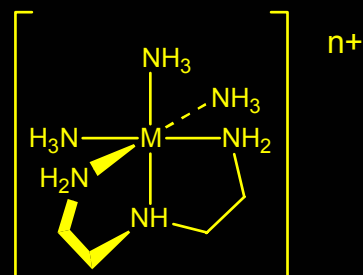
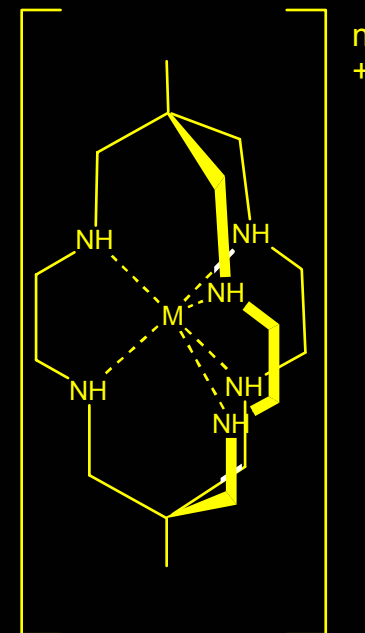
chelatace



makrocyclický efekt



kryptátový efekt



# Názvosloví komplexních sloučenin

$\text{H}_2\text{O}$	voda	aqua-
$\text{NH}_3$	amoniak	ammin-
$\text{CO}$	oxid uhelnatý	karbonyl-
$\text{SO}_4^{2-}$	síran	sulfato-
$\text{S}_2\text{O}_3^{2-}$	thiosíran	thiosulfato-
$\text{PO}_4^{3-}$	fosforečnan	fosfato-
$\text{H}_2\text{PO}_4^-$	dihydrogenfosforečnan	dihydrogefosfato-
$\text{CH}_3\text{COO}^-$	octan	acetato-
$\text{C}_2\text{O}_4^{2-}$	šřavelan	oxalato-
$(\text{CH}_3)_2\text{N}^-$	dimethylamid	dimethylamido-
$\text{F}^-$	fluorid	fluoro-
$\text{O}^{2-}$	oxid	oxo-
$\text{OH}^-$	hydroxid	hydroxo-
$\text{O}_2^{2-}$	peroxid	peroxo-
$\text{HO}_2^-$	hydrogenperoxid	hydrogenperoxo-
$\text{H}^-$	hydrid	hydrido-
$\text{S}^{2-}$	sulfid	thio-
$\text{S}_2^{2-}$	disulfid	disulfido-
$\text{HS}^-$	hydrogensulfid	merkpto-
$\text{CN}^-$	kyanid	kyano-
$\text{SCN}^-$	thiokyanatan	thiokyanato-

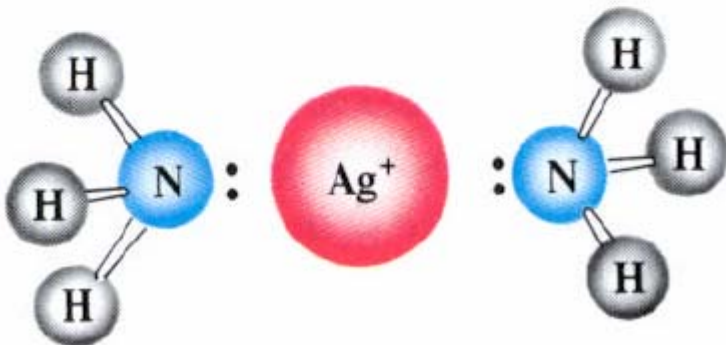
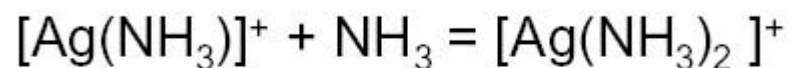
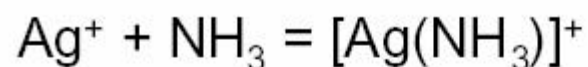


## Názvosloví komplexních sloučenin

$K_3[Fe(CN)_6]$	hexakynoželezitan tridraselný (draselný)
$[Cr(en)_3]Cl_3$	chlorid tris(ethylendiamin)chromitý
$[Pt(NH_3)_4][PtCl_4]$	tetrachloroplatnatan tetraamminplatnatý
$[Co(NH_3)_3Cl_3]$	komplex triammin-trichlorokobaltitý
$[Ni(CO)_4]$	tetrakarbonyl niklu (nebo nikl)
$Na[Co(CO)_4]$	tetrakarbonylkobaltid(1-) sodný
$K_4[Ni(CN)_4]$	tetrakyanonikl(4-) tetradraselný

## Stabilita komplexů

Konstanta stability komplexu = rovnovážná konstanta tvorby



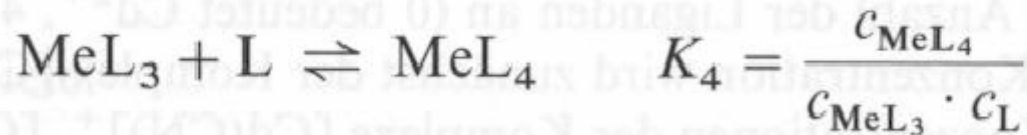
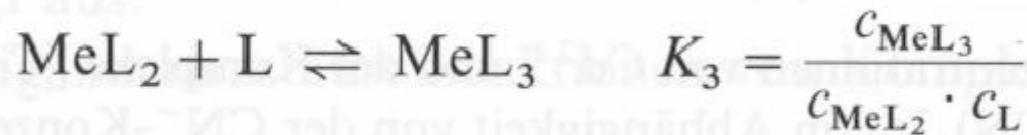
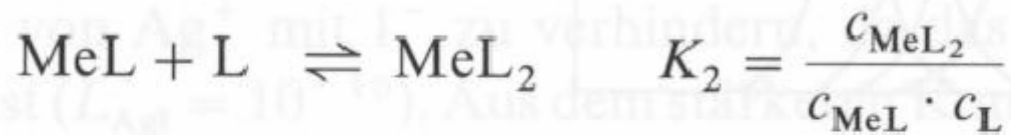
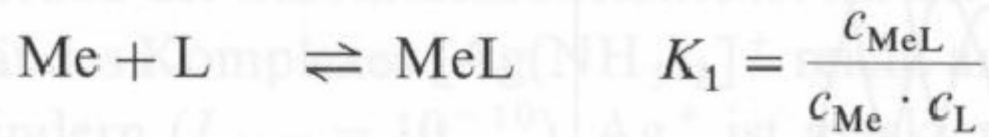
Vysoká hodnota  $K$   
= stabilní komplex

$$K_1 = \frac{[\text{AgNH}_3^+]}{[\text{Ag}^+][\text{NH}_3]}$$

$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{AgNH}_3^+][\text{NH}_3]}$$

# Stabilita komplexů

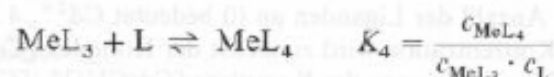
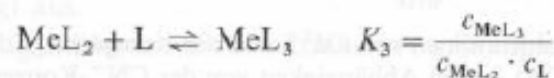
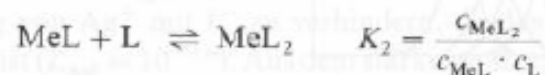
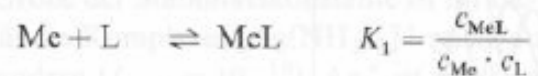
Konstanta stability komplexu  $ML_n$



$$K_1 > K_2 > K_3 \dots > K_n$$

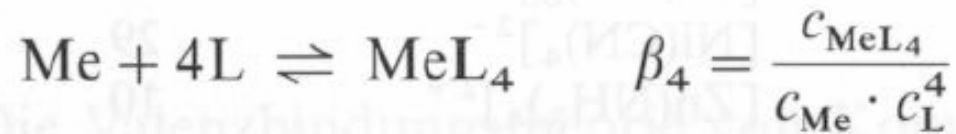
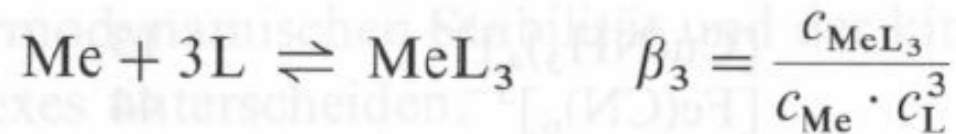
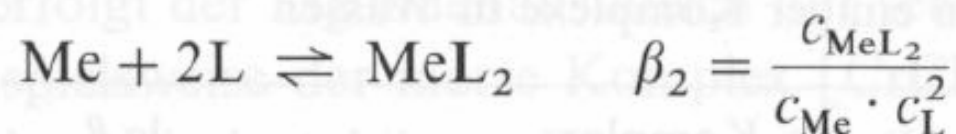
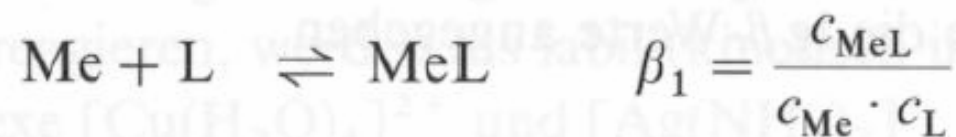
# Stabilita komplexů

## Celková konstanta stability komplexu



$$\beta_n = K_1 \cdot K_2 \dots K_n$$

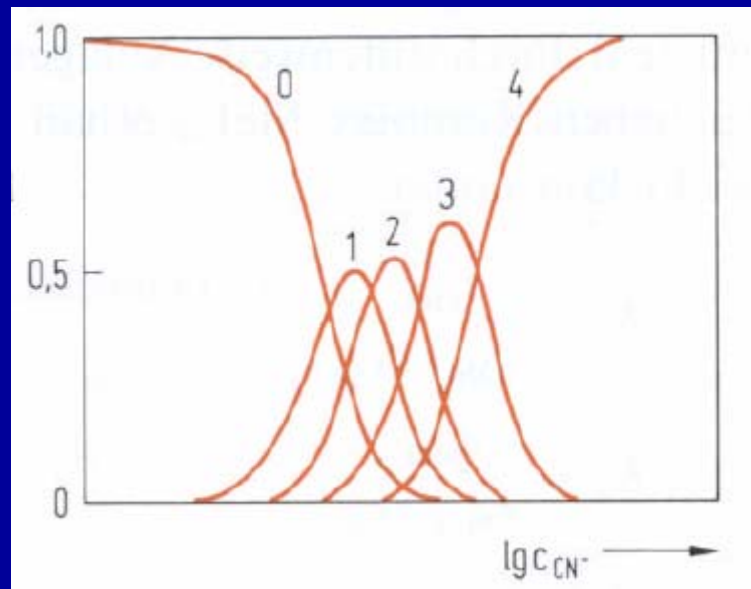
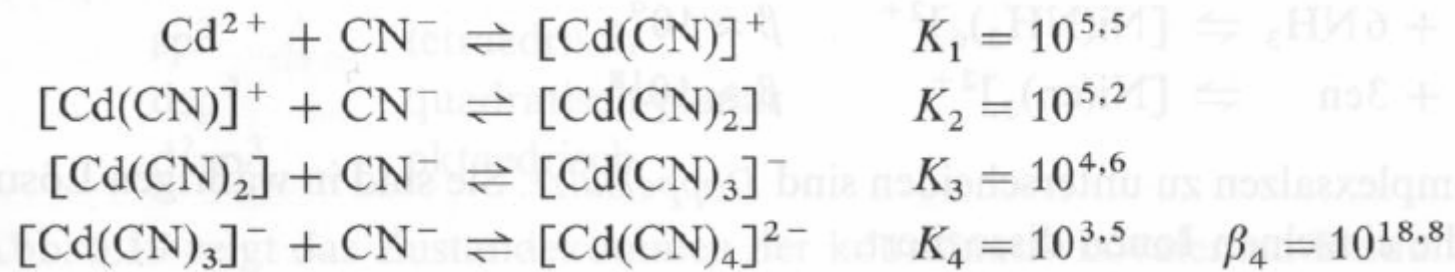
$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$$



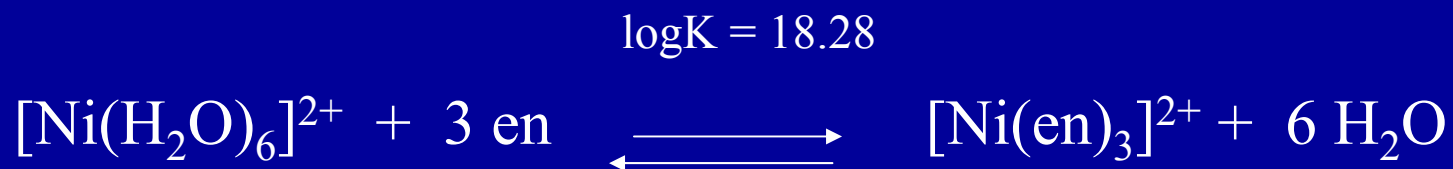
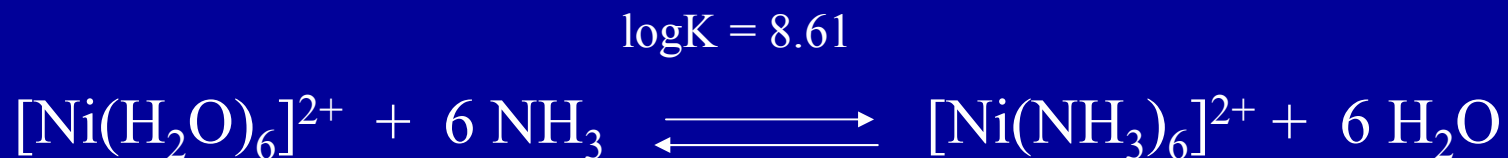
## Stabilita komplexů

Komplex	$\lg \beta$	Komplex	$\lg \beta$
$[\text{Ag}(\text{NH}_3)_2]^+$	7	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	13
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	13	$[\text{Fe}(\text{CN})_6]^{3-}$	44
$[\text{Ag}(\text{CN})_2]^-$	21	$[\text{Fe}(\text{CN})_6]^{4-}$	35
$[\text{Au}(\text{CN})_2]^-$	37	$[\text{Ni}(\text{CN})_4]^{2-}$	29
$[\text{Co}(\text{NH}_3)_6]^{2+}$	5	$[\text{Zn}(\text{NH}_3)_4]^{2+}$	10
$[\text{Co}(\text{NH}_3)_6]^{3+}$	35	$[\text{Cu}(\text{CN})_4]^-$	27

## Stabilita komplexů



## Chelátový efekt

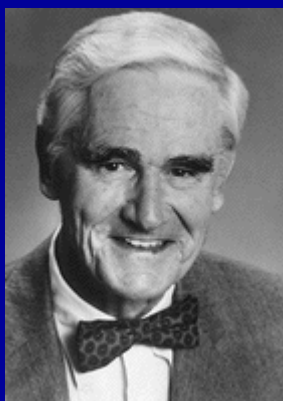


$$\Delta G = -RT \ln K = \Delta H - T\Delta S$$

$\Delta H$  stejná pro obě reakce (Ni-O  $\rightarrow$  Ni-N)  
 $\Delta S$  vysoká pro chelataci, vzniká více částic

# Cheláty, makrocykly, kryptáty

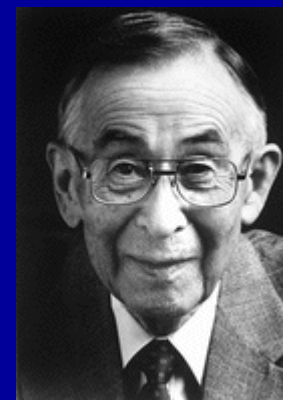
Nobelova cena za chemii 1987



**Donald J. Cram**



**Jean-Marie Lehn**



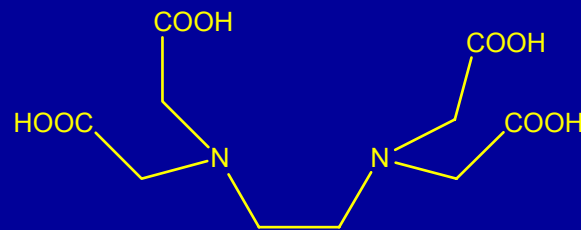
**Charles J. Pedersen**



# Cheláty, makrocikly, kryptáty

EDTA

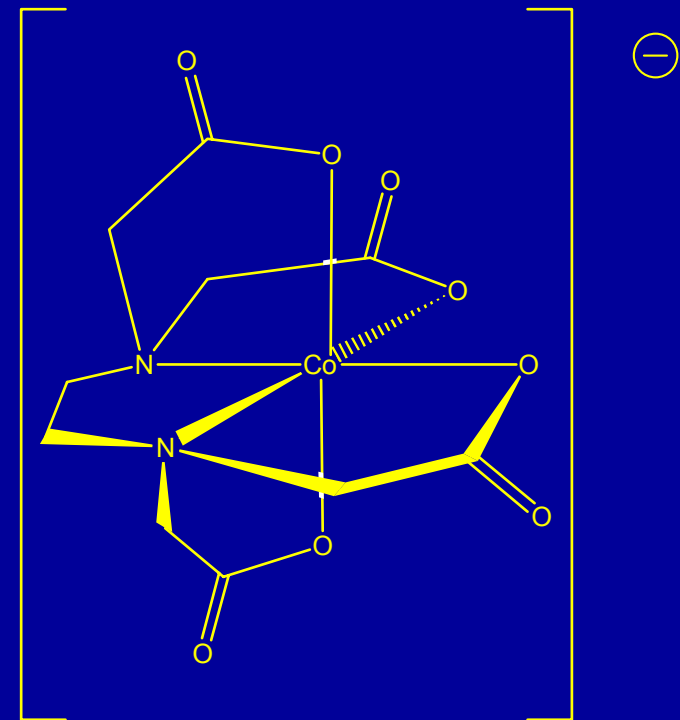
kyselina ethylendiamintetraoctová



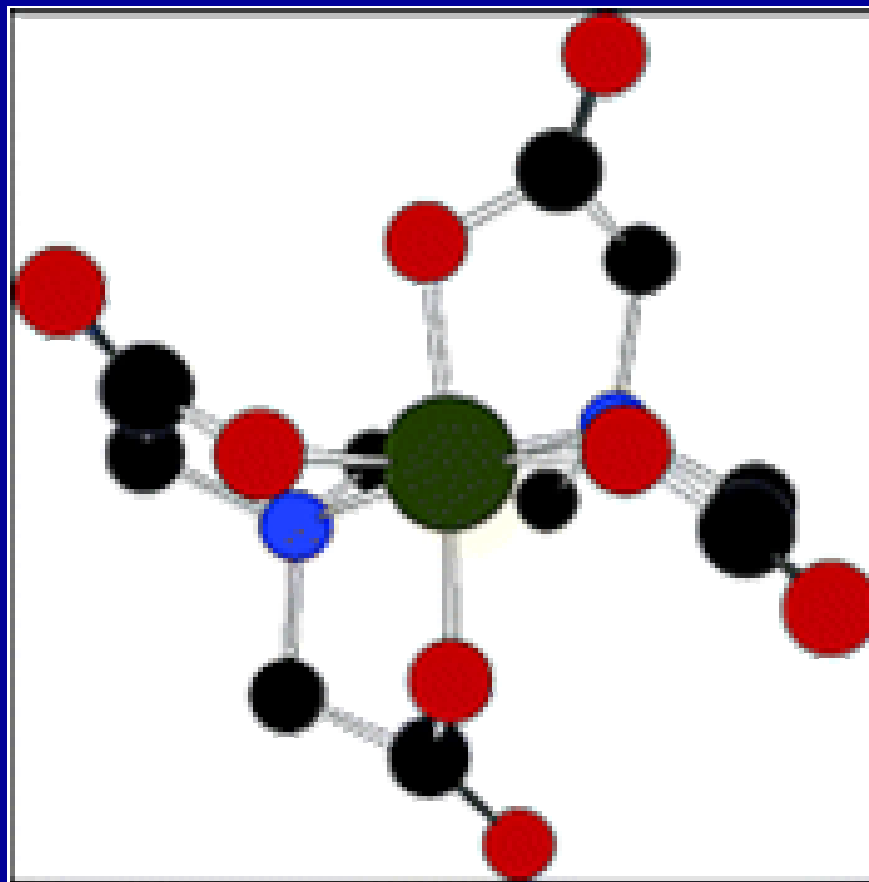
Chelatační terapie Pb otravy

Chelatometrie

Rozpouští  $\text{CaCO}_3$

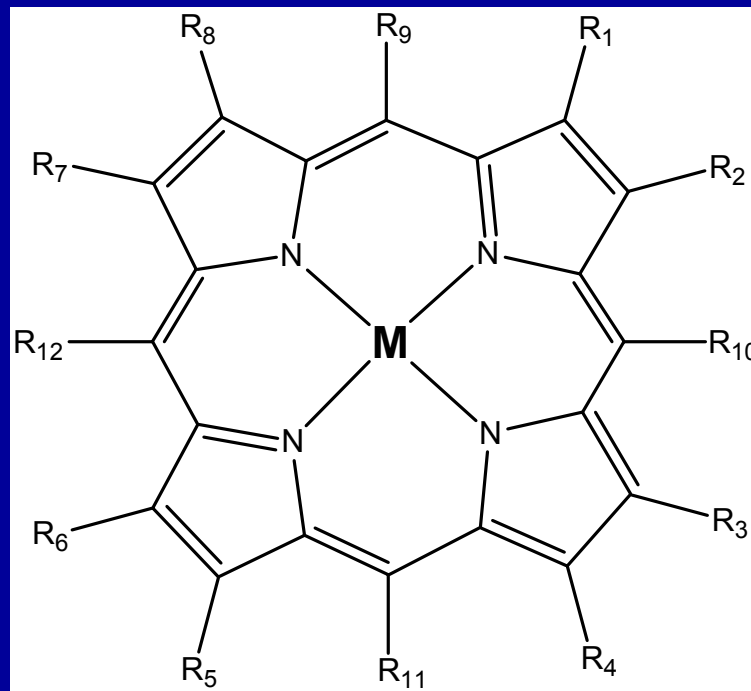


# CaEDTA trans N

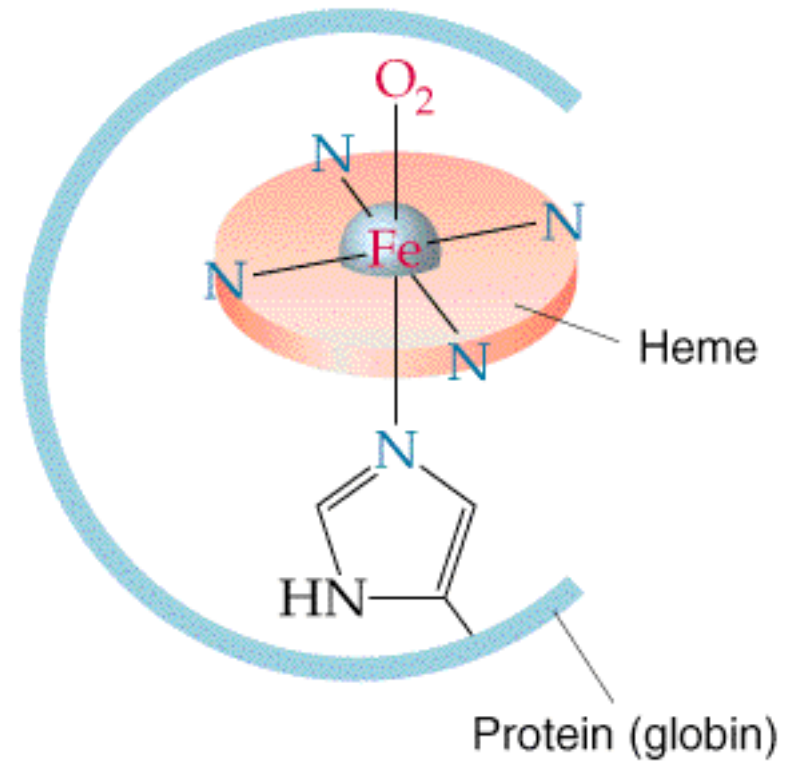
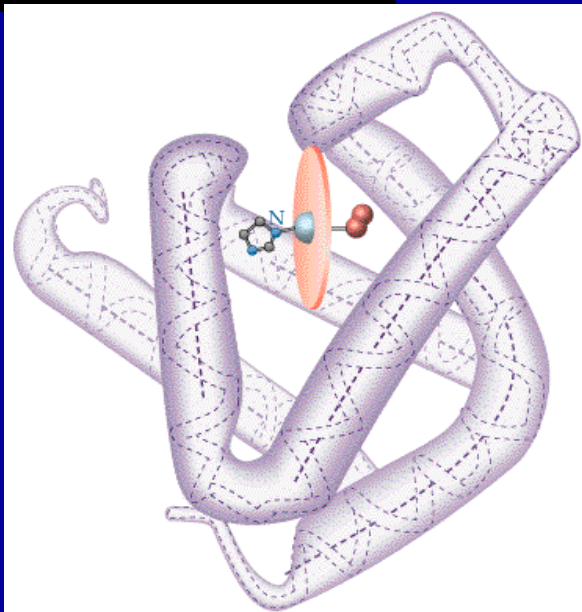
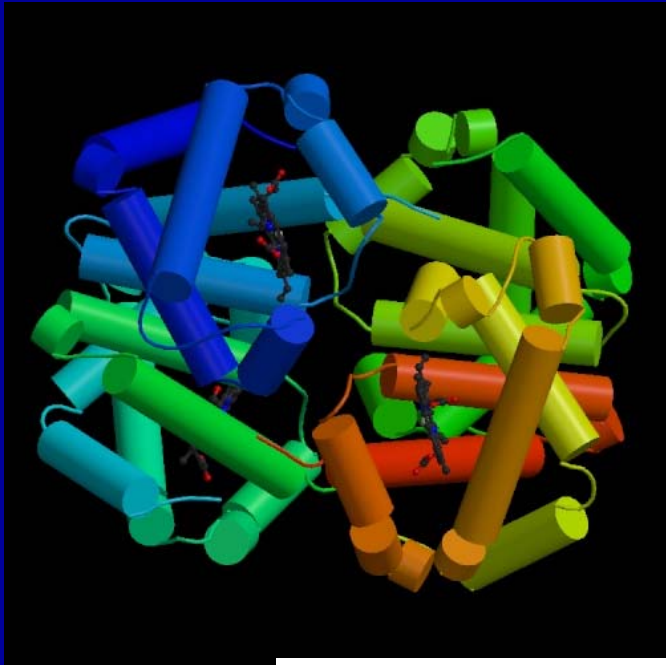


# Cheláty, makrocykly, kryptáty

Metaloporfyriny: M = Fe (hem, cytochrom c), Mg (chlorofyl), Co (B<sub>12</sub>)

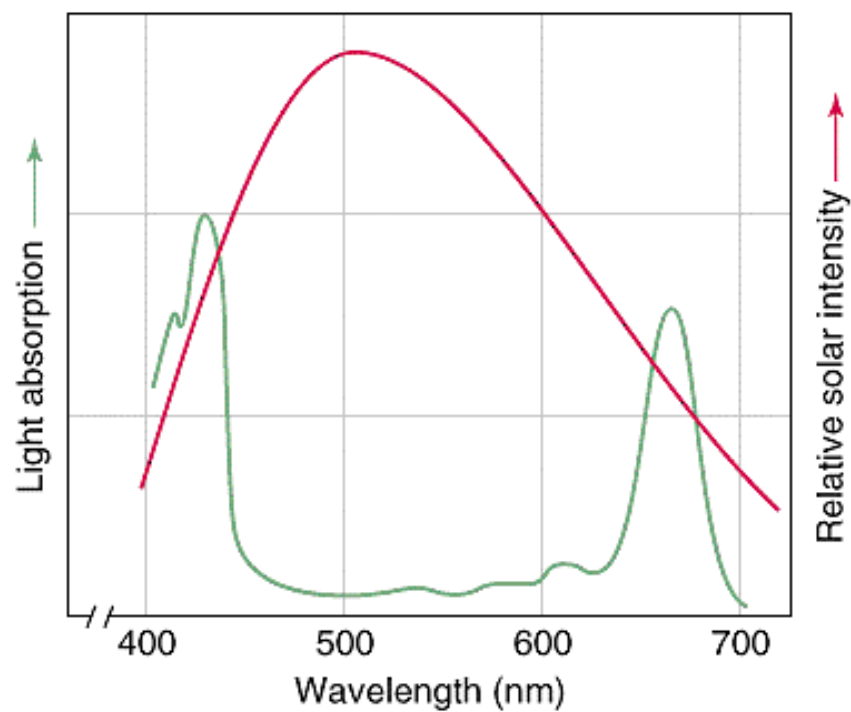
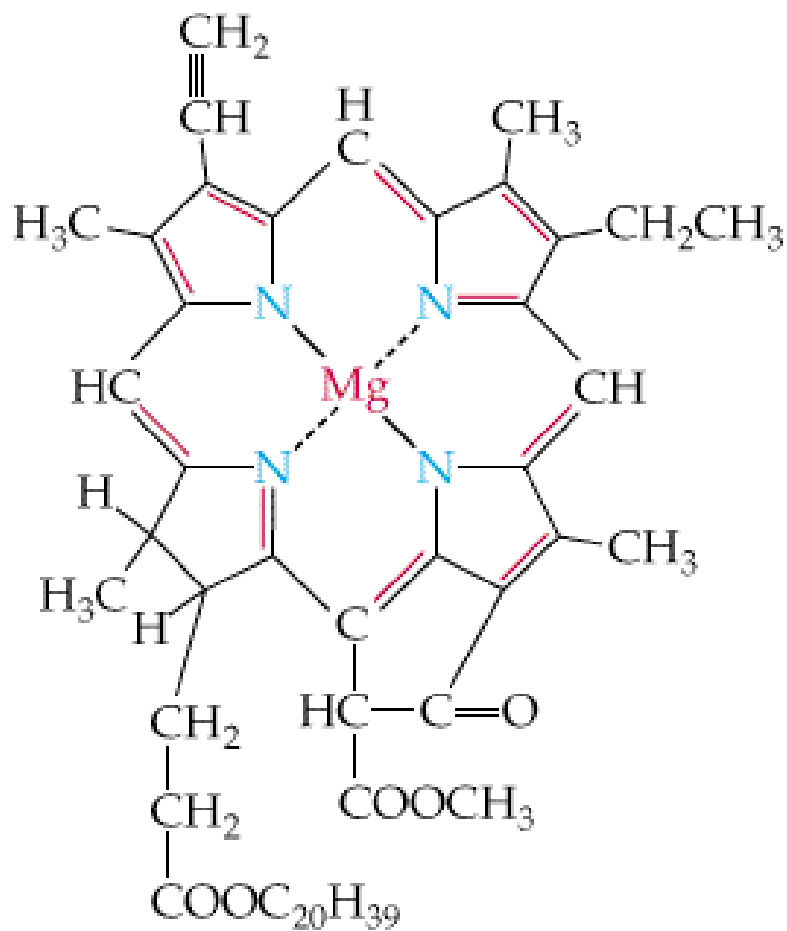


# Hemoglobin



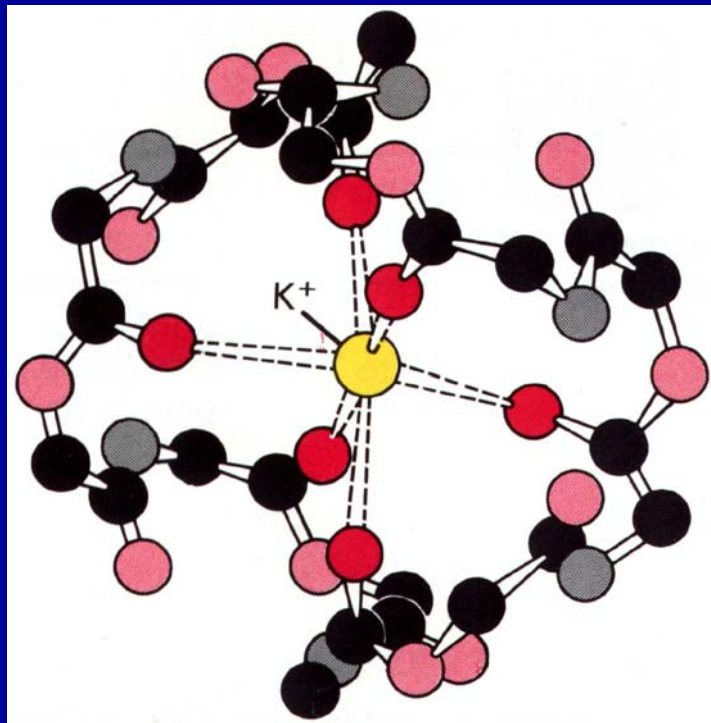


Mg chlorofyl



# Cheláty, makrocikly, kryptáty

Valinomycin

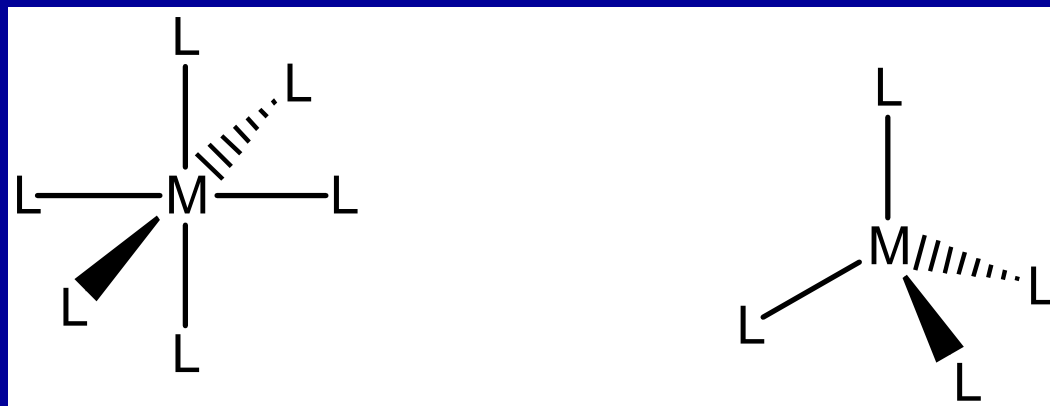


# Tvary molekul a iontů

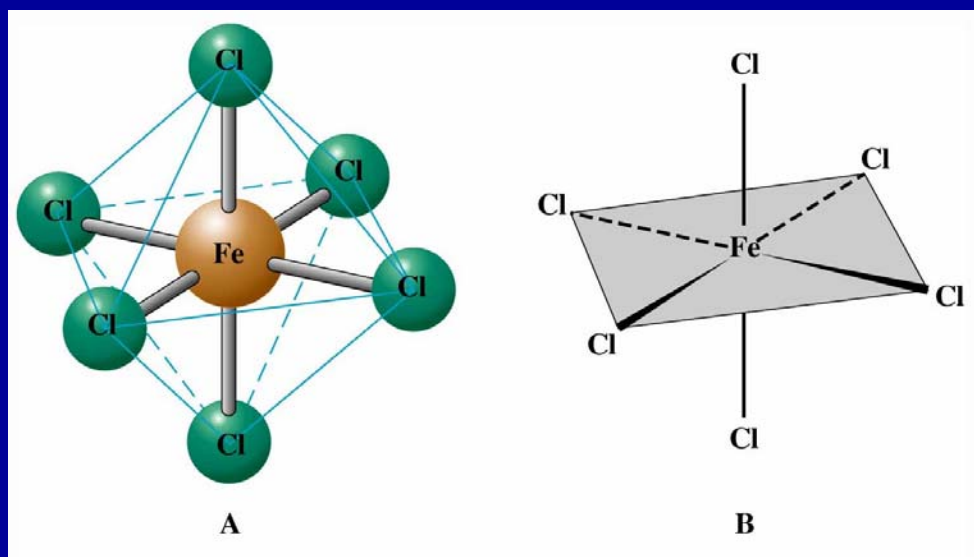
Prvky hlavních skupin >>>> VSEPR

Přechodné prvky >>>>>>>>> Teorie ligandového pole

## Nejdůležitější tvary komplexních částic



Oktaedrické komplexy  $O_h$



Tetraedrické komplexy  $T_d$



## Nejdůležitější tvary komplexních částic

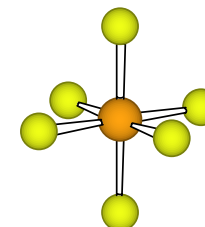
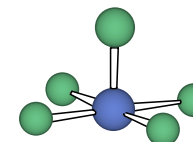
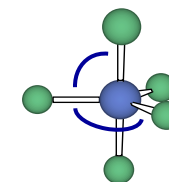
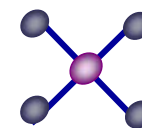
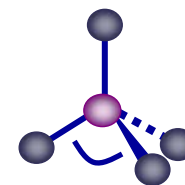
Tetraedrický  $109^{\circ} 28'$  C.N. 4

Čtvercově planární  $90^{\circ}$  C.N. 4

Trigonálně bipyramidální  $120^{\circ} + 90^{\circ}$  C.N. 5

Čtvercově pyramidální  $90^{\circ}$  C.N. 5

Oktaedrický  $90^{\circ}$  C.N. 6

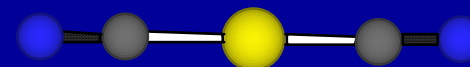
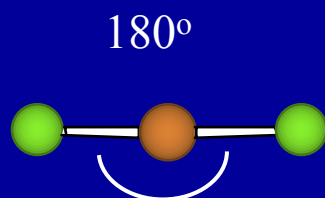


## Nejdůležitější tvary komplexních částic

### Koordinační číslo 2

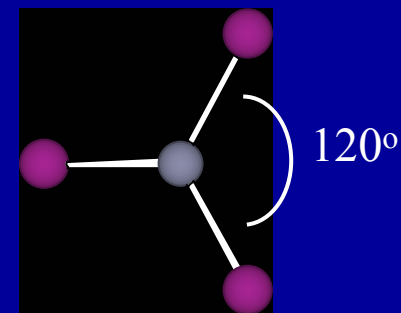
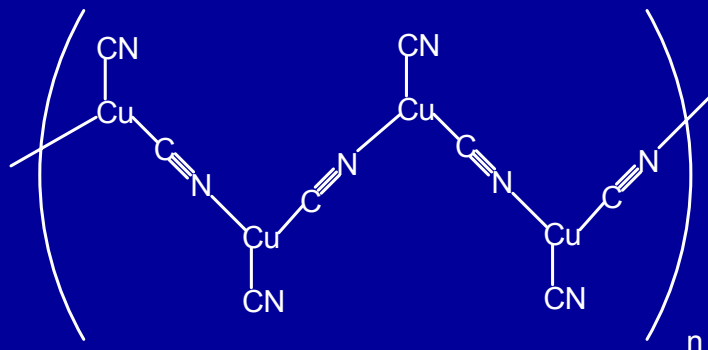
Cu(I), Ag(I), Au(I), Hg(II)

lineární



### Koordinační číslo 3

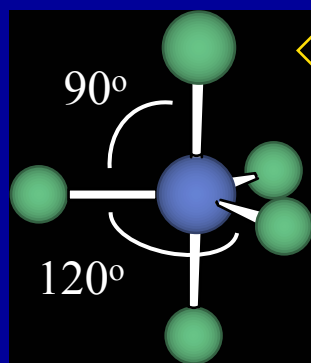
trigonálně planární



# Nejdůležitější tvary komplexních částic

Koordinační číslo 5

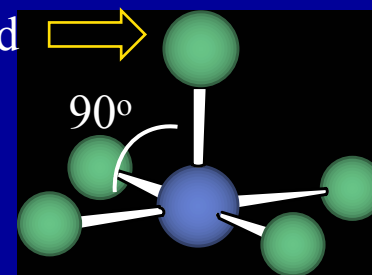
Trigonálně bipyramidální



axiální ligandy

ekvatoriální ligandy

Čtvercově pyramidální

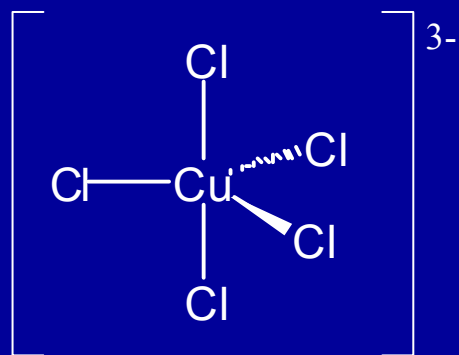


apikální ligand

bazální ligandy

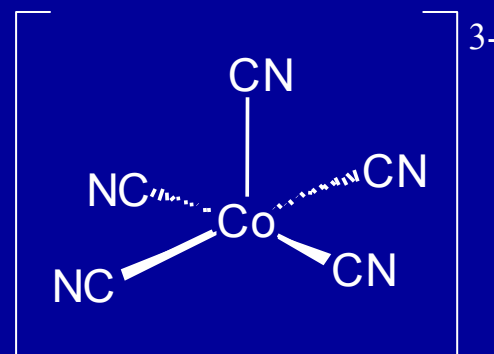
Tyto dvě struktury mají velmi podobnou energii

## Trigonálně bipyramidální

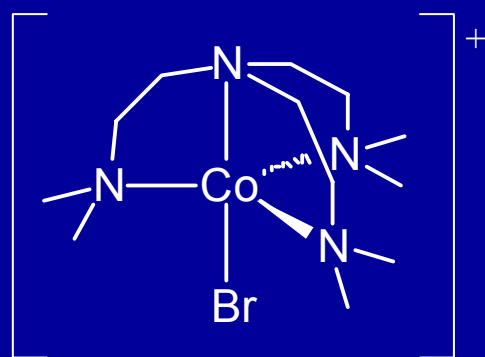


$[\text{CuCl}_5]^{3-}$

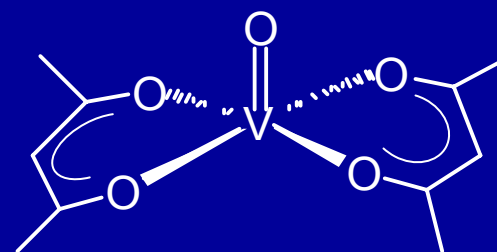
## Čtvercově pyramidální



$[\text{Co}(\text{CN})_5]^{3-}$



$[\text{Co}(\text{Me}_6\text{tren})\text{Br}]^+$



$[\text{VO}(\text{acac})_2]$

# Izomerie komplexních sloučenin

## Konstituční (strukturní) izomerie

Vazebná

Koordinační

Ionizační

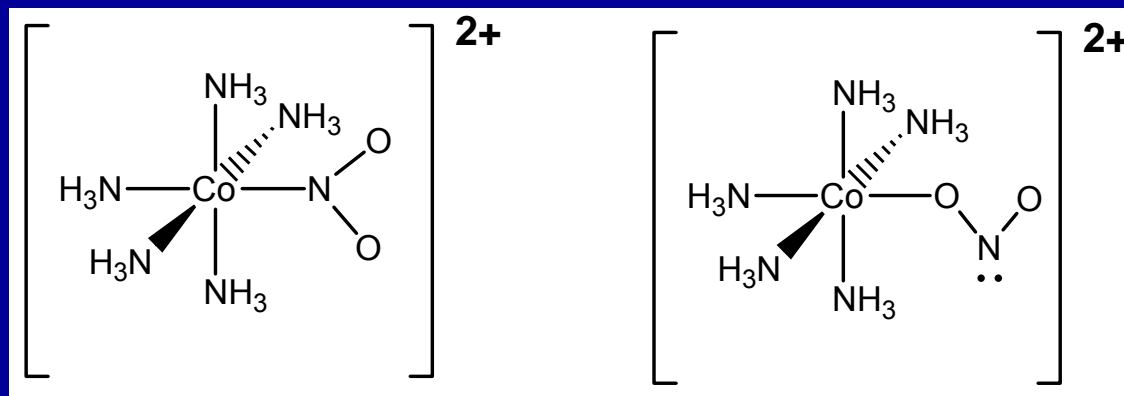
## Prostorová (stereo) izomerie

Geometrická

Optická

# Konstituční (strukturní) izomerie

Vazebná:  $\text{SCN}^-$ ,  $\text{NO}_2^-$ ,  $\text{OCN}^-$

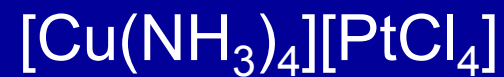
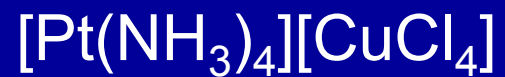


nitro-

nitrito-

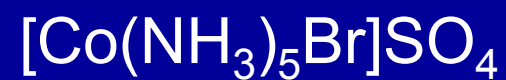
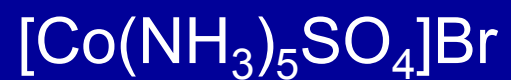
# Konstituční (strukturní) izomerie

Koordinační:



# Konstituční (strukturní) izomerie

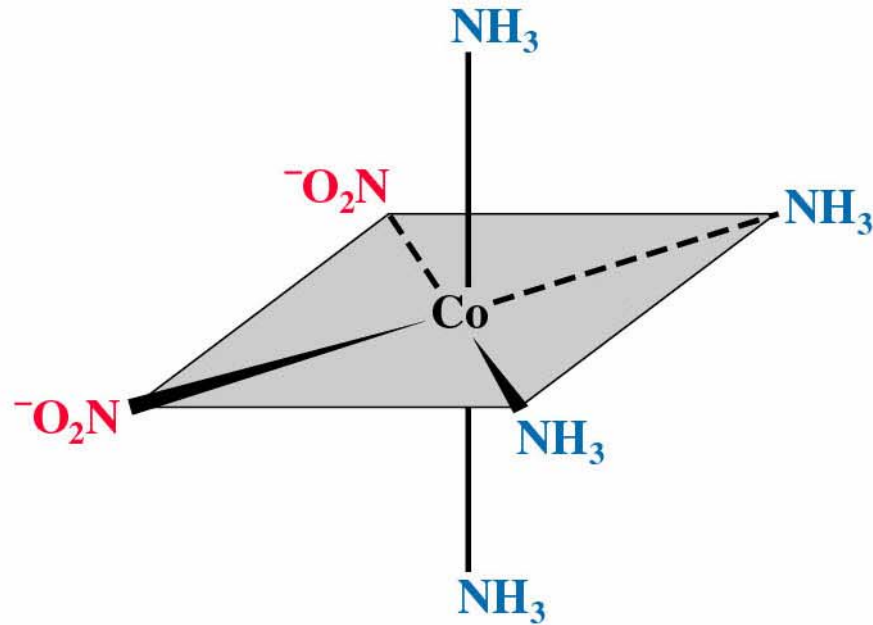
Ionizační:



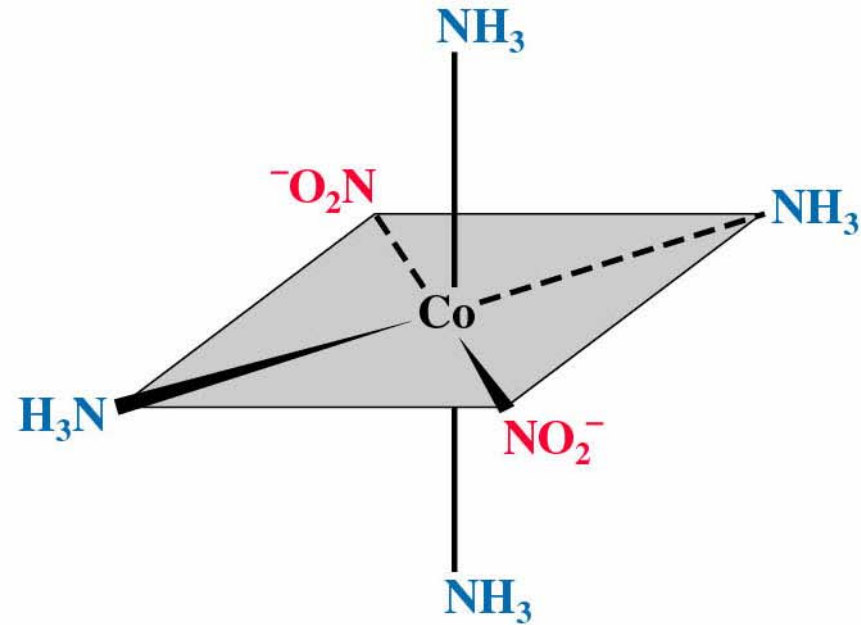


# Prostorová (stereo) izomerie

Geometrická: cis-trans, diastereomery



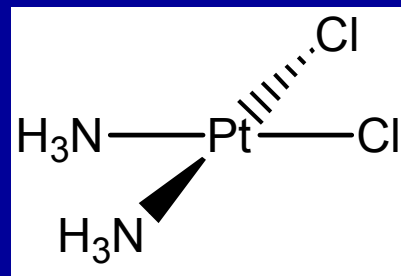
*cis*



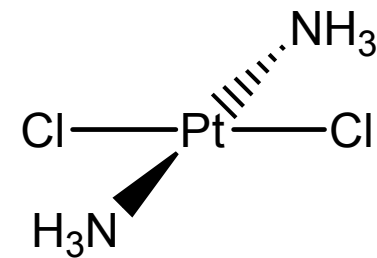
*trans*

# Prostorová (stereo) izomerie

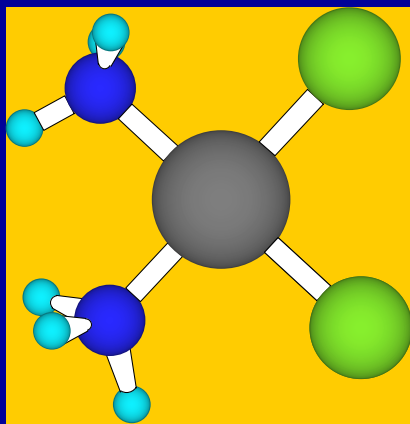
Geometrická: cis-trans, diastereomery



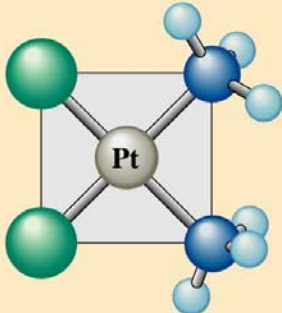
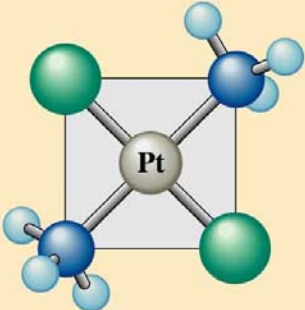
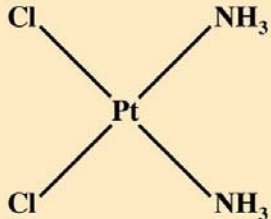
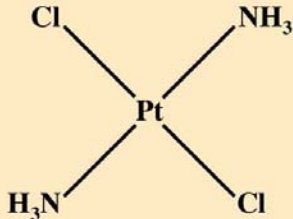


cis



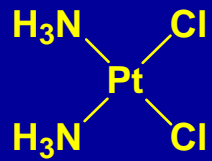
trans



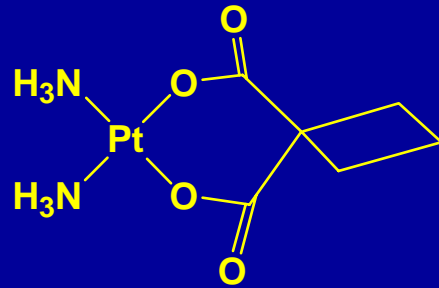
# Prostorová (stereo) izomerie

	<i>cis</i>	<i>trans</i>
Ball-and-stick model		
Structural formula		
		
Color	Orange-yellow	Pale yellow
Solubility	0.252 g/100 g H <sub>2</sub> O	0.037 g/100 g H <sub>2</sub> O

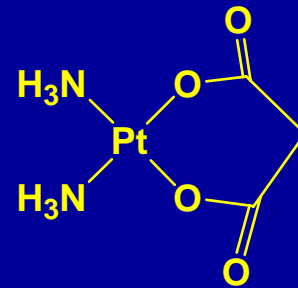
# Protinádorové léky



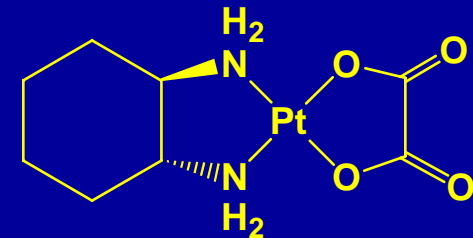
Cisplatin



Carboplatin

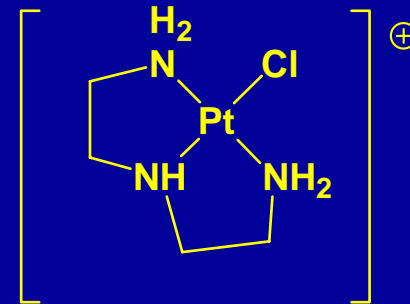
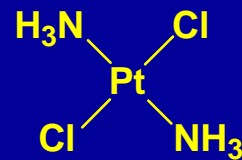


Nedaplatin



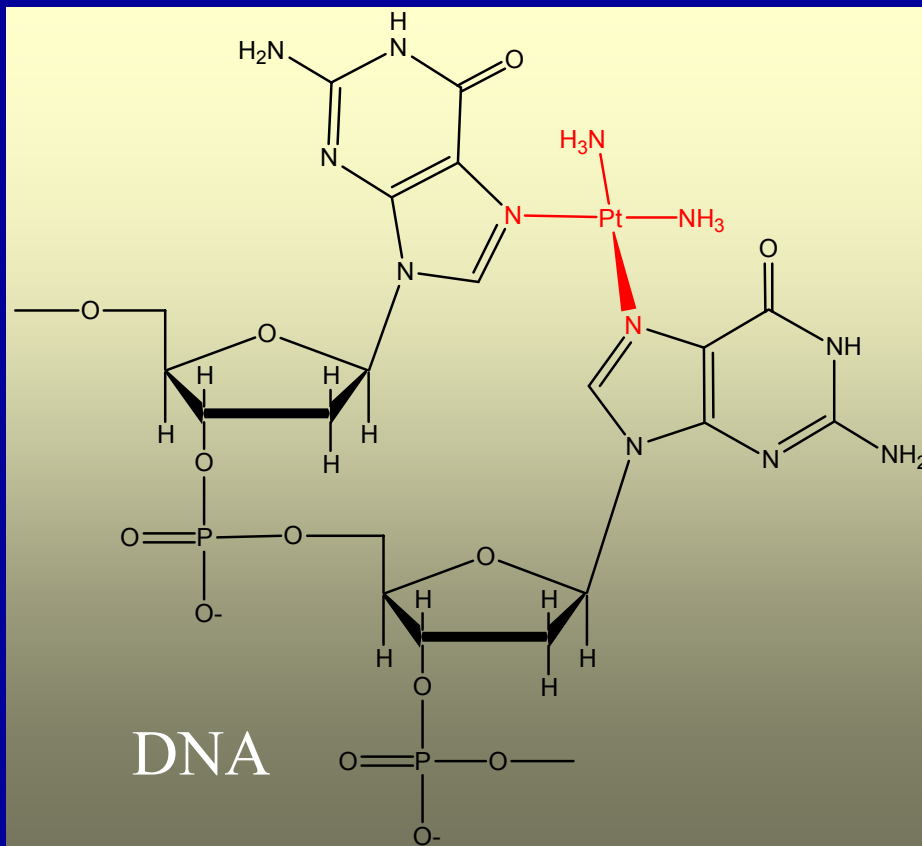
Oxaliplatin

## Neaktivní látky



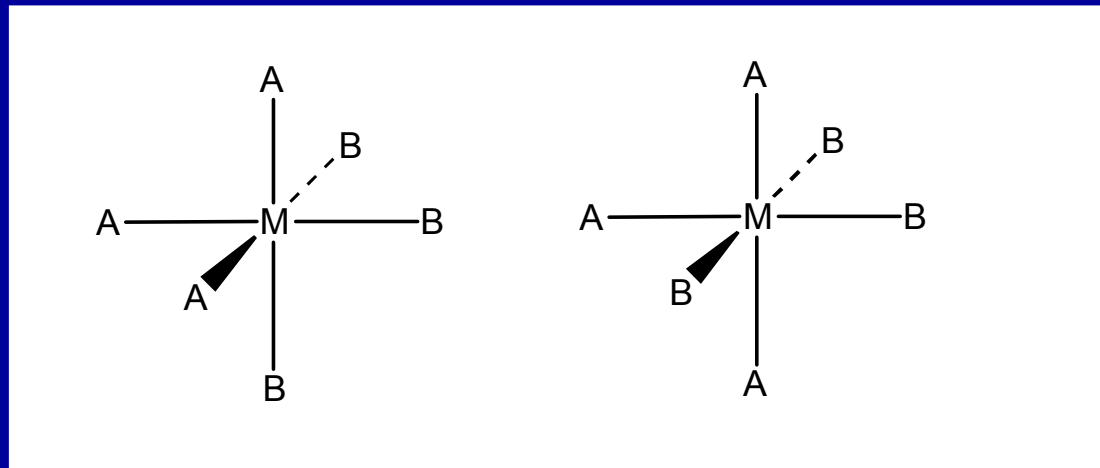
# Prostorová (stereo) izomerie

Cisplatina = kancerostatikum

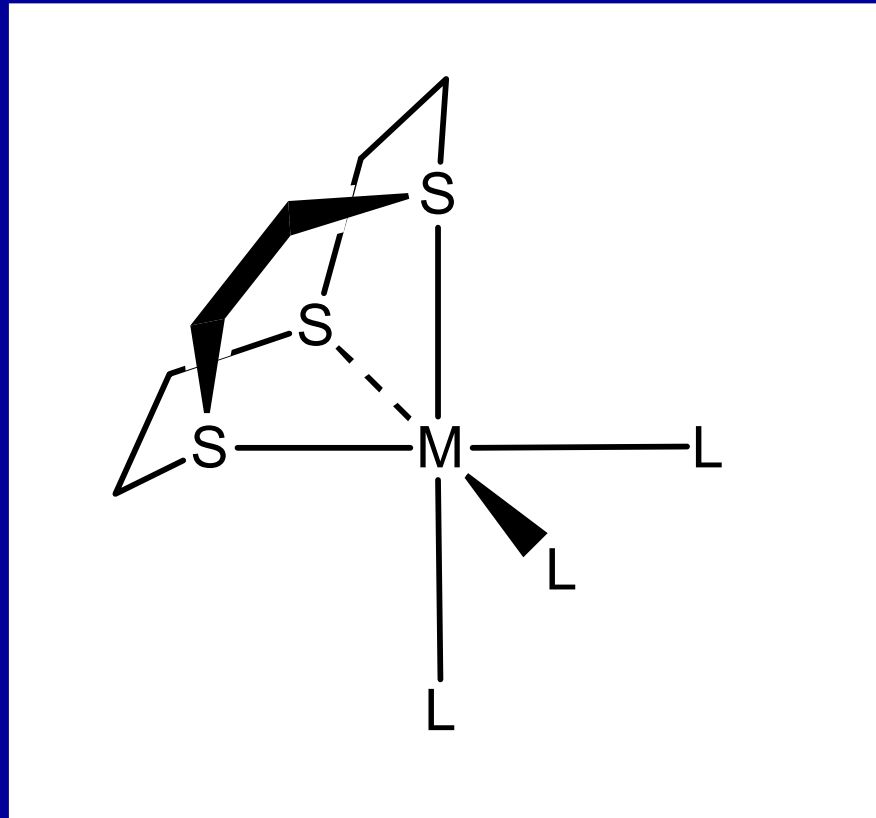


# Prostorová (stereo) izomerie

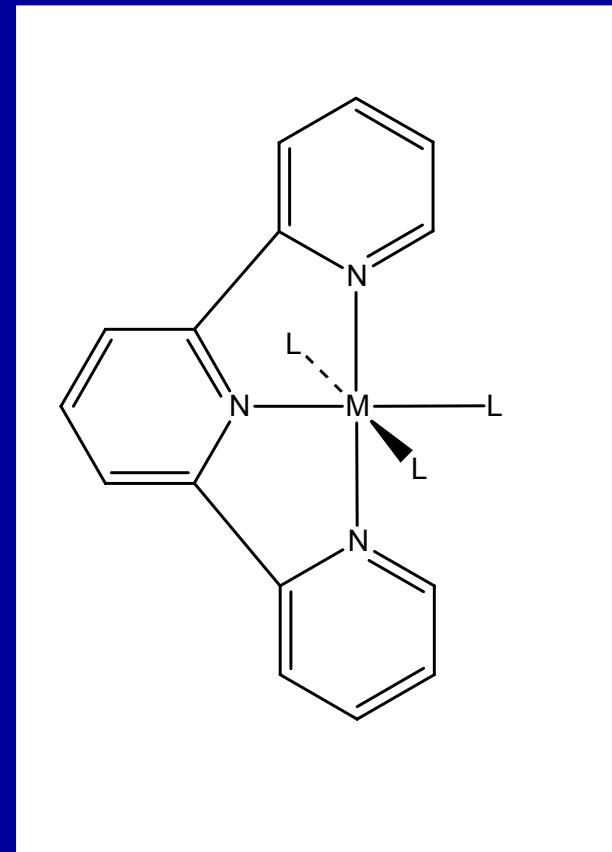
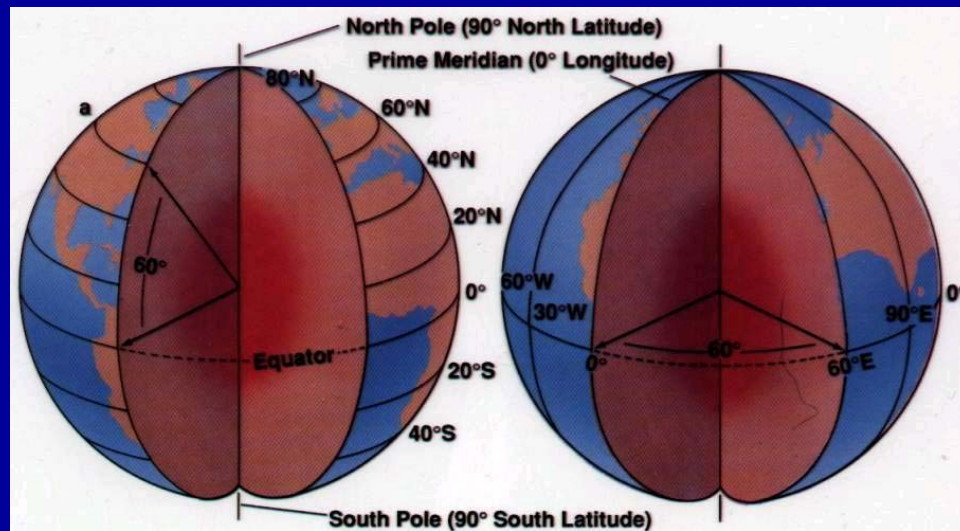
Geometrická: mer-fac, diastereomery



# Prostorová (stereo) izomerie

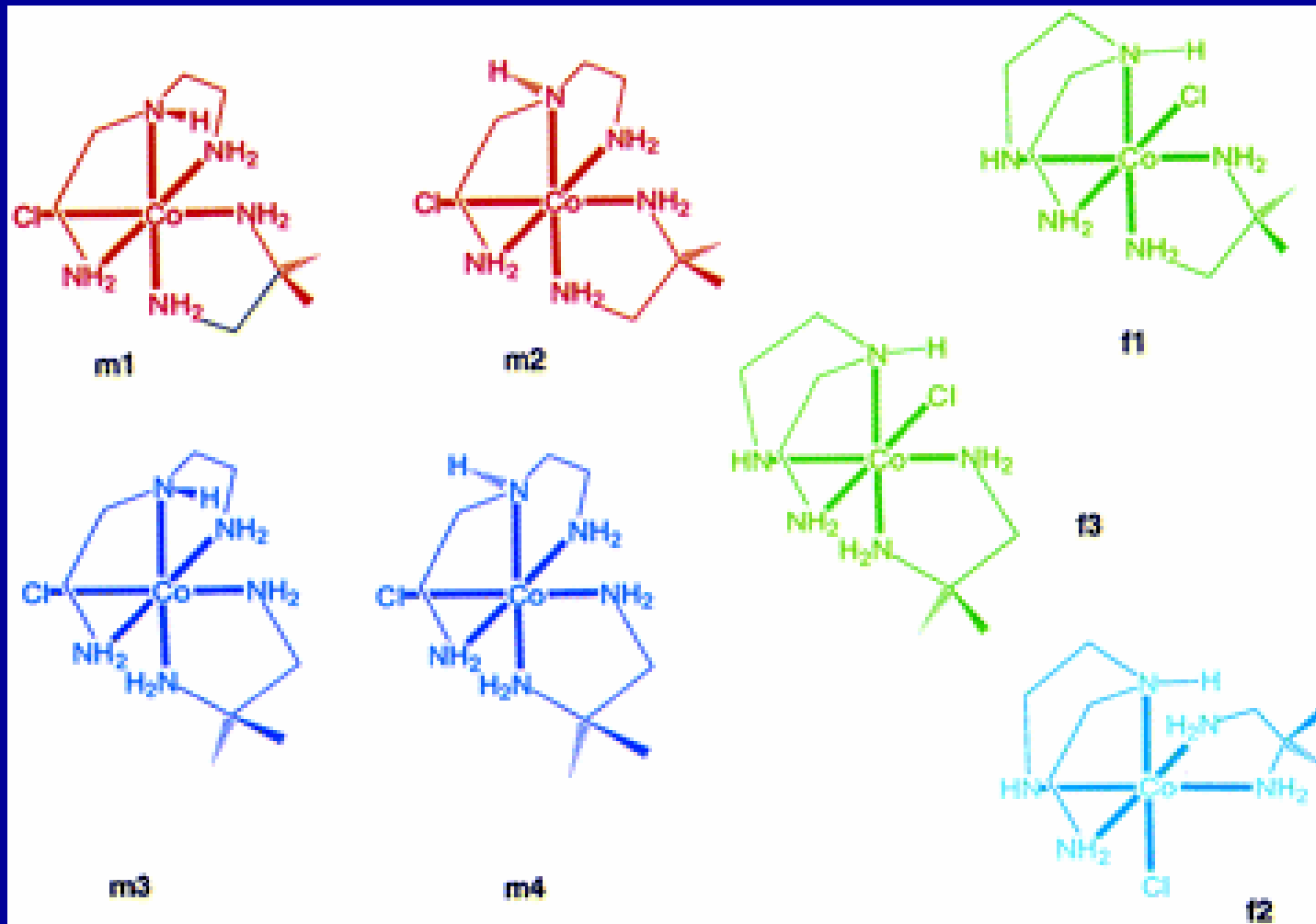


# Prostorová (stereo) izomerie



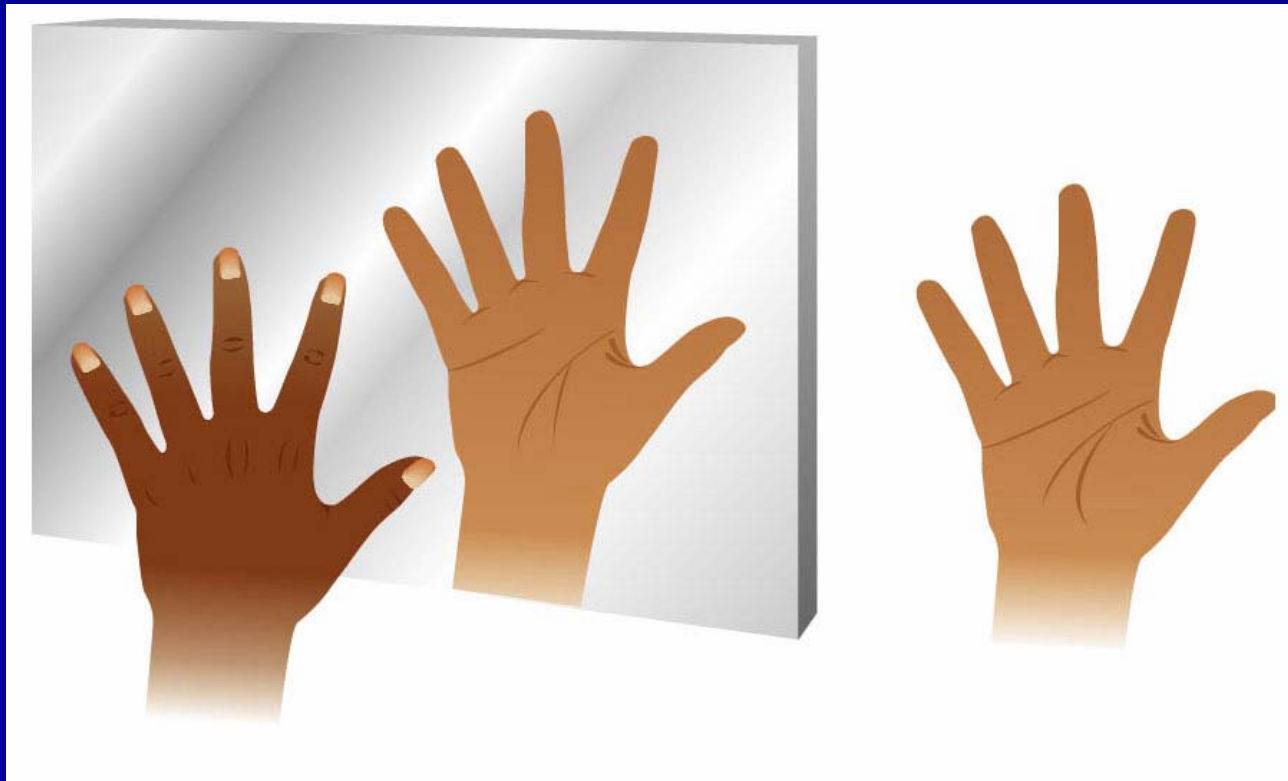


# Prostorová (stereo) izomerie



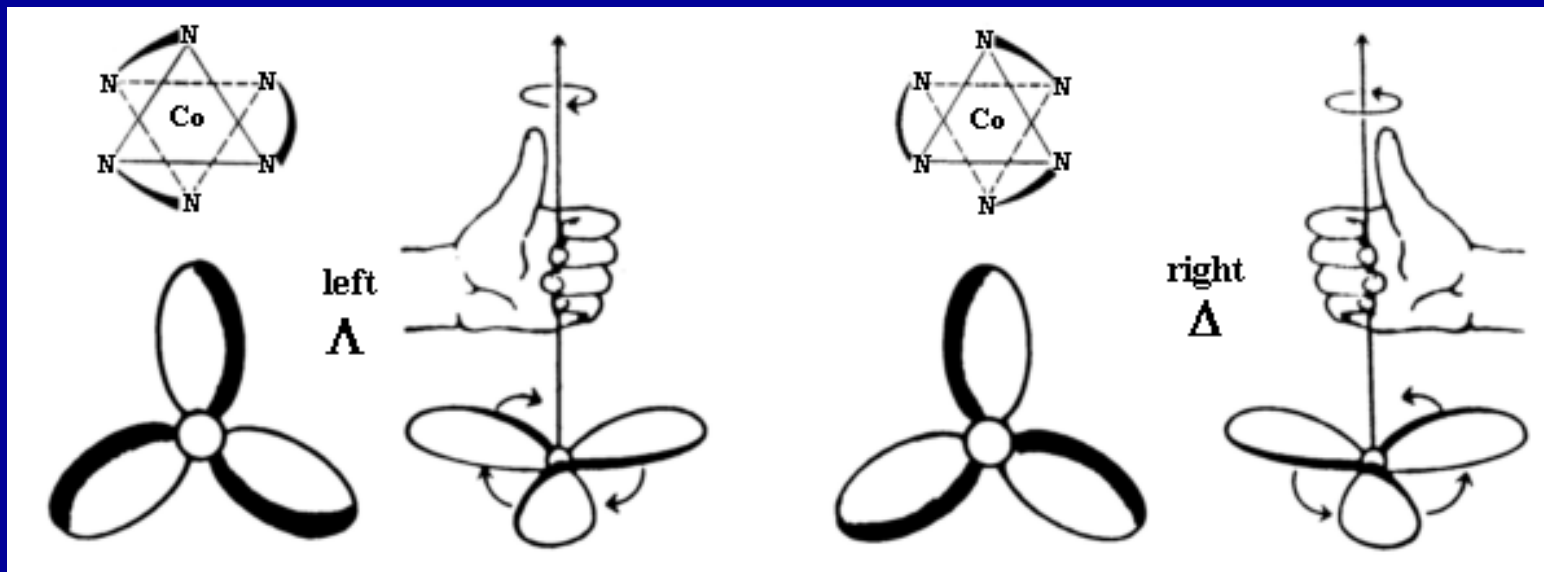
# Prostorová (stereo) izomerie

Optická: enantiomery

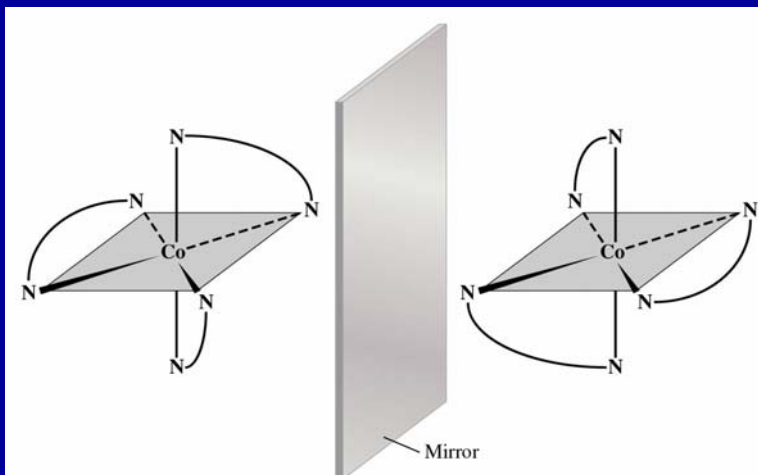


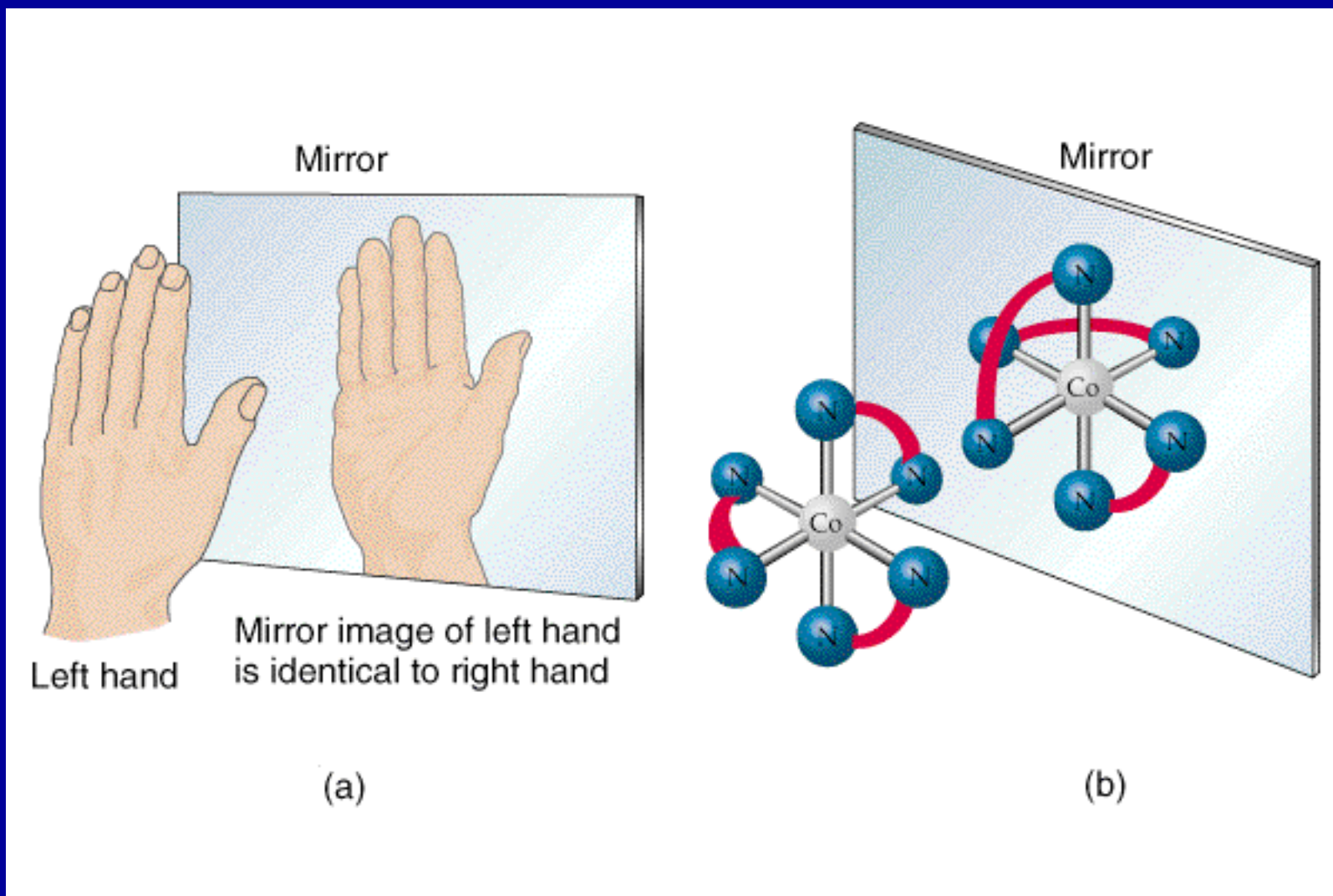
# Prostorová (stereo) izomerie

Optická: enantiomery

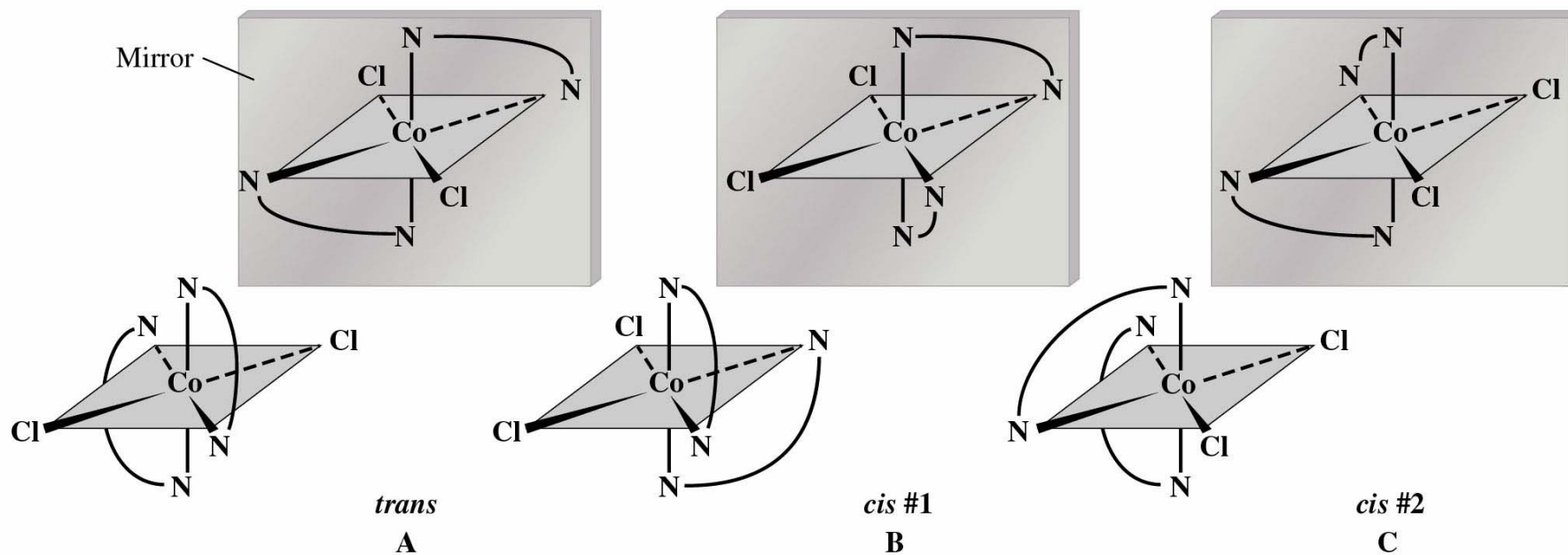


Nemá  $S_n$





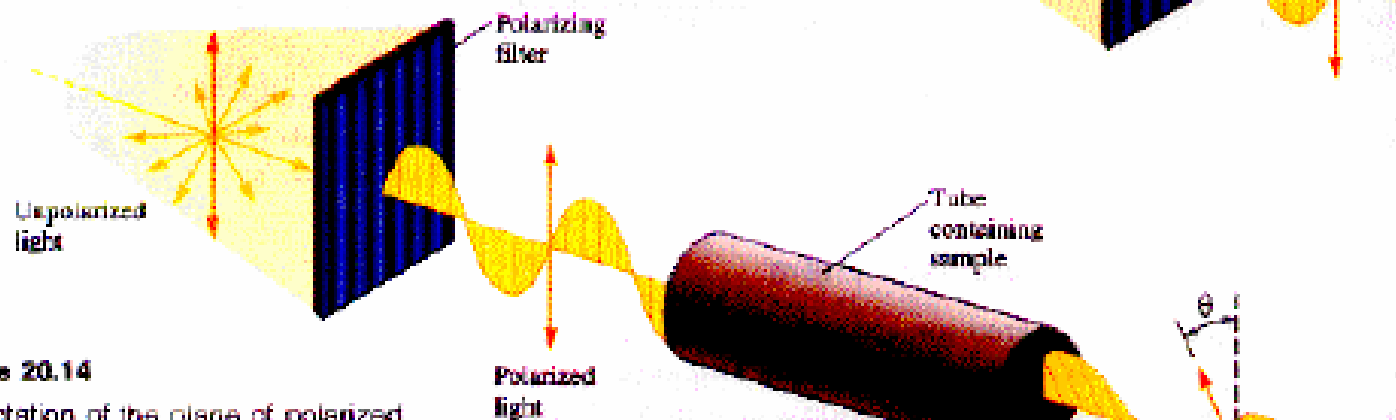
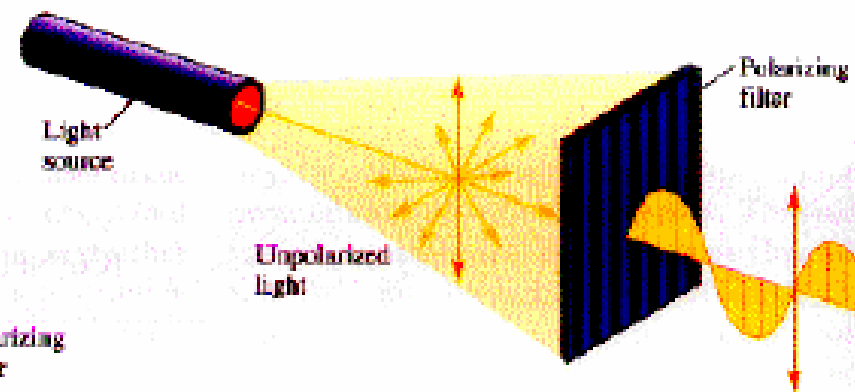
# Prostorová (stereo) izomerie



# Optická rotace

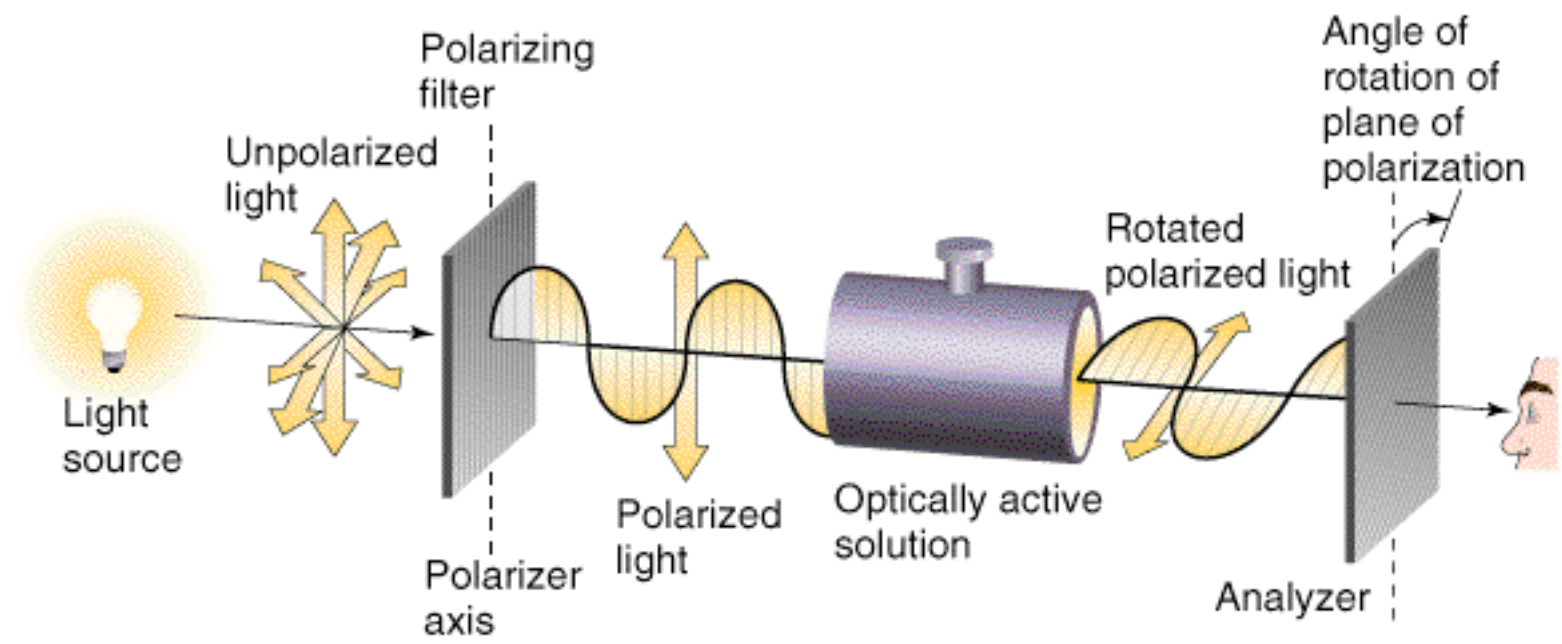
**Figure 20.13**

Unpolarized light consists of waves vibrating in many different planes (indicated by the arrows). The polarizing filter blocks all waves except those vibrating in a given plane.



**Figure 20.14**

The rotation of the plane of polarized light by an optically active substance. The angle of rotation is called theta ( $\theta$ ).



## Popis vazby v komplexech

1) VB

2) Teorie krystalového pole (CFT = Crystal Field Theory)

1929, Hans Bethe Čistě elektrostatické interakce mezi ligandy a kovem

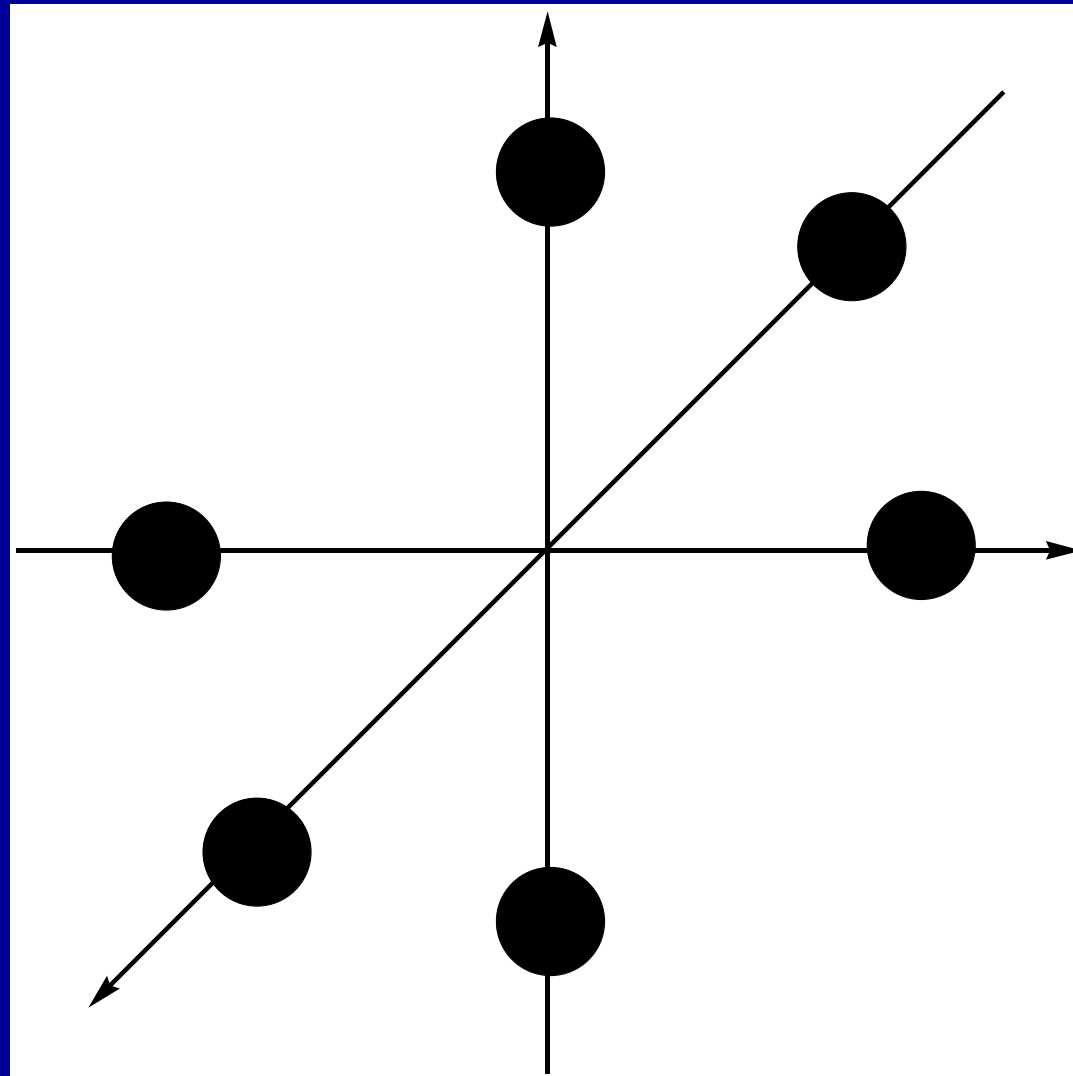
3) Teorie ligandového pole (LFT = Ligand Field Theory)

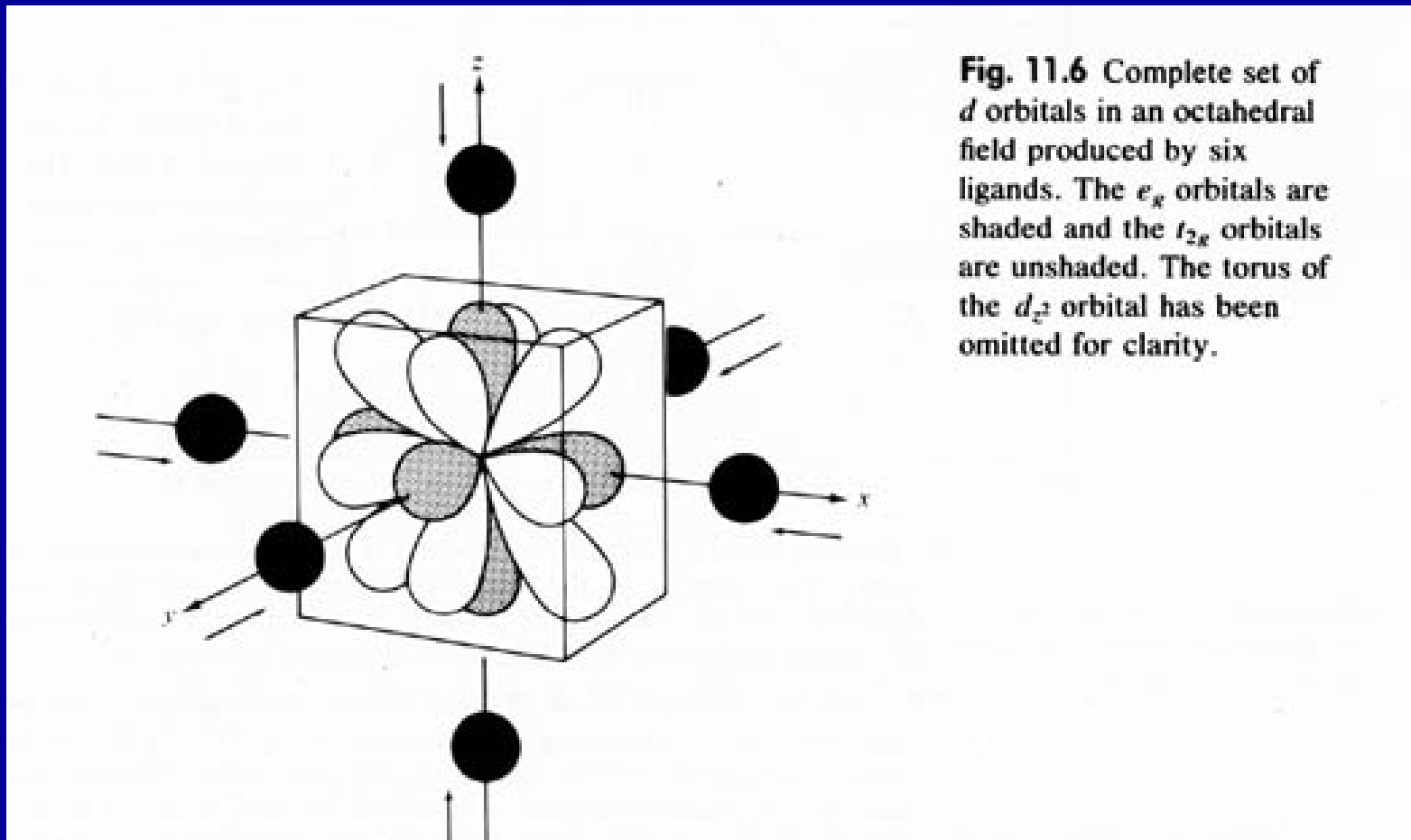
1935, modifikace J. H. Van Vleck Podíl kovalence

4) MO

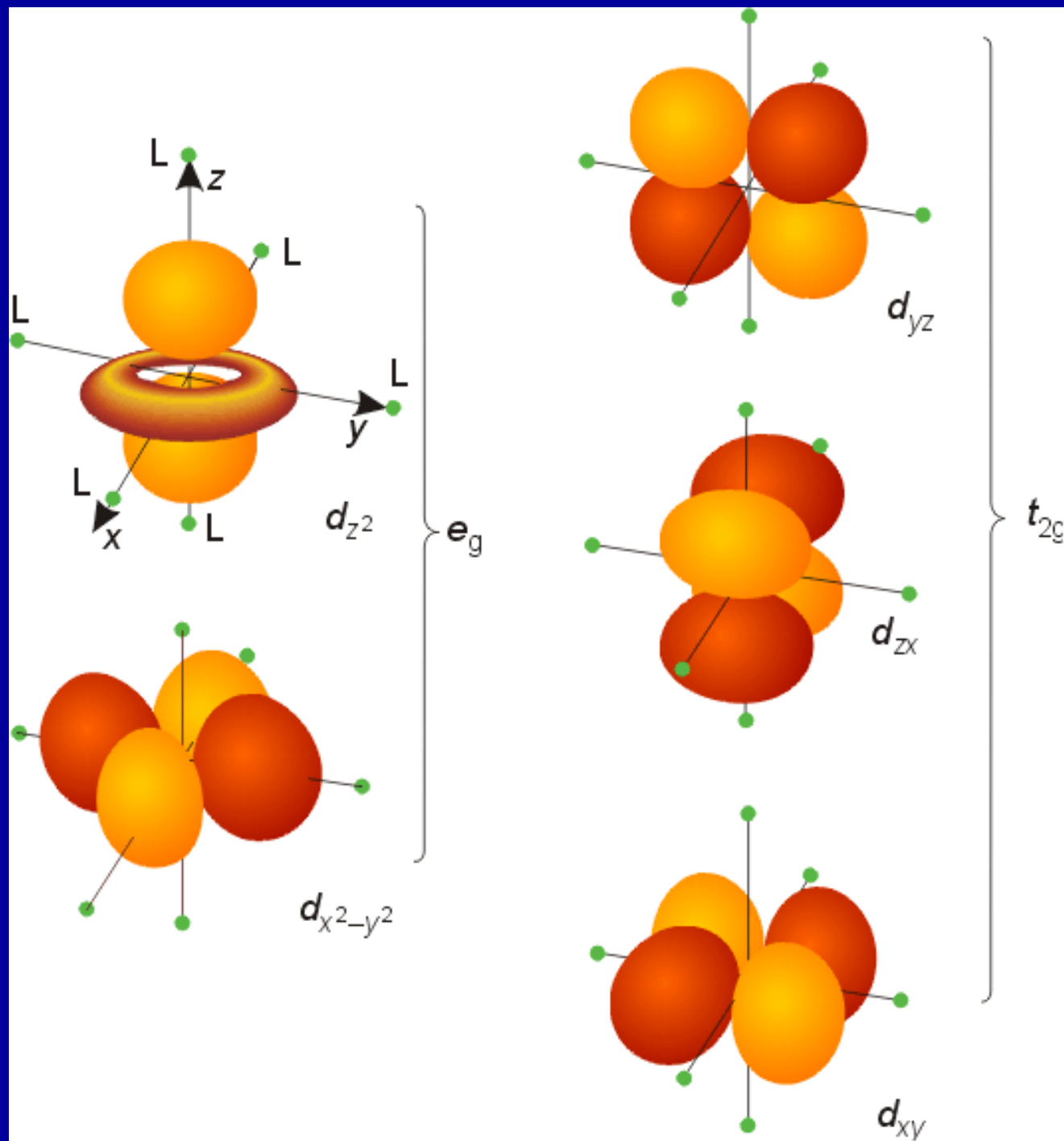


# Teorie ligandového pole





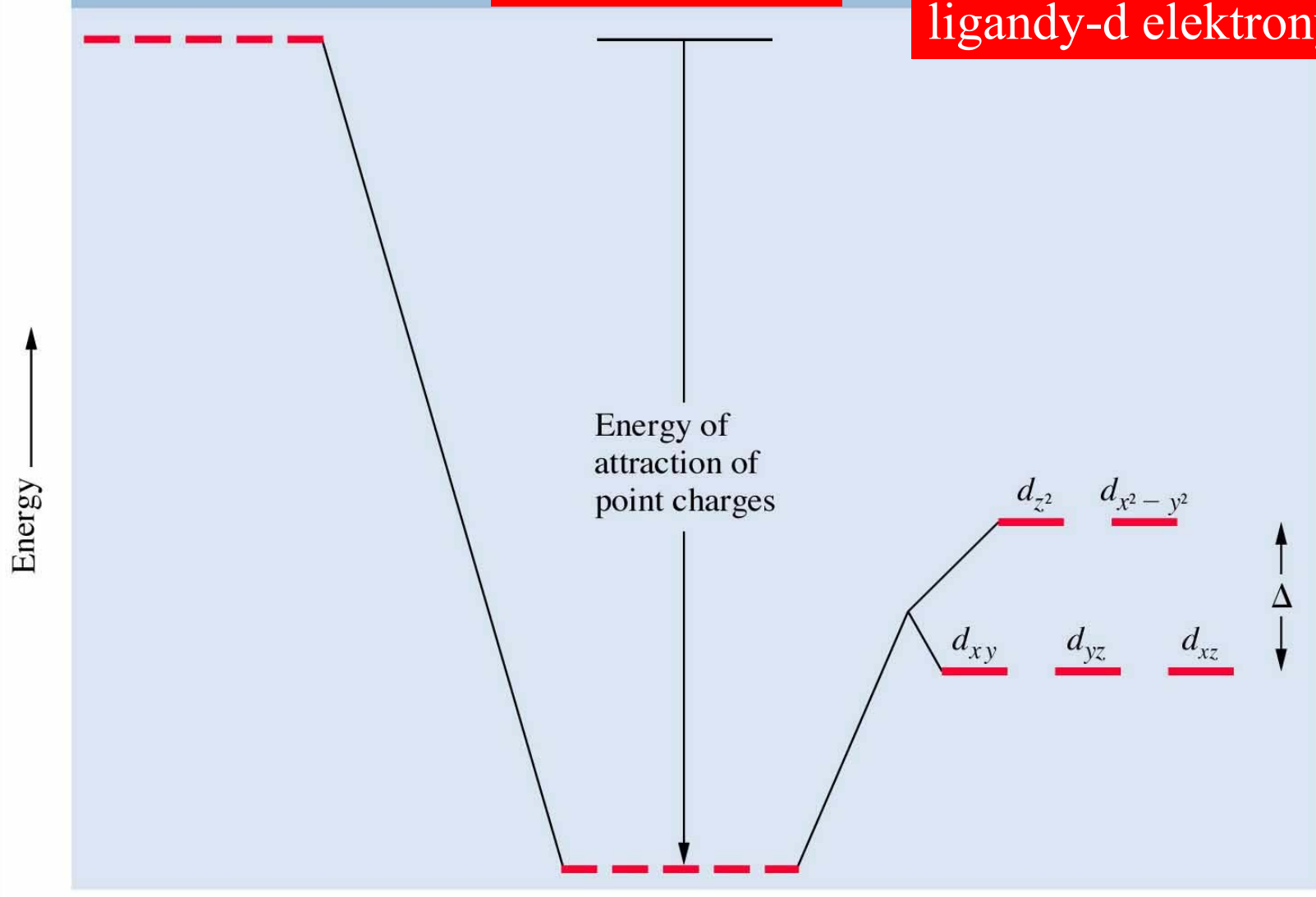
**Fig. 11.6** Complete set of  $d$  orbitals in an octahedral field produced by six ligands. The  $e_g$  orbitals are shaded and the  $t_{2g}$  orbitals are unshaded. The torus of the  $d_{z^2}$  orbital has been omitted for clarity.



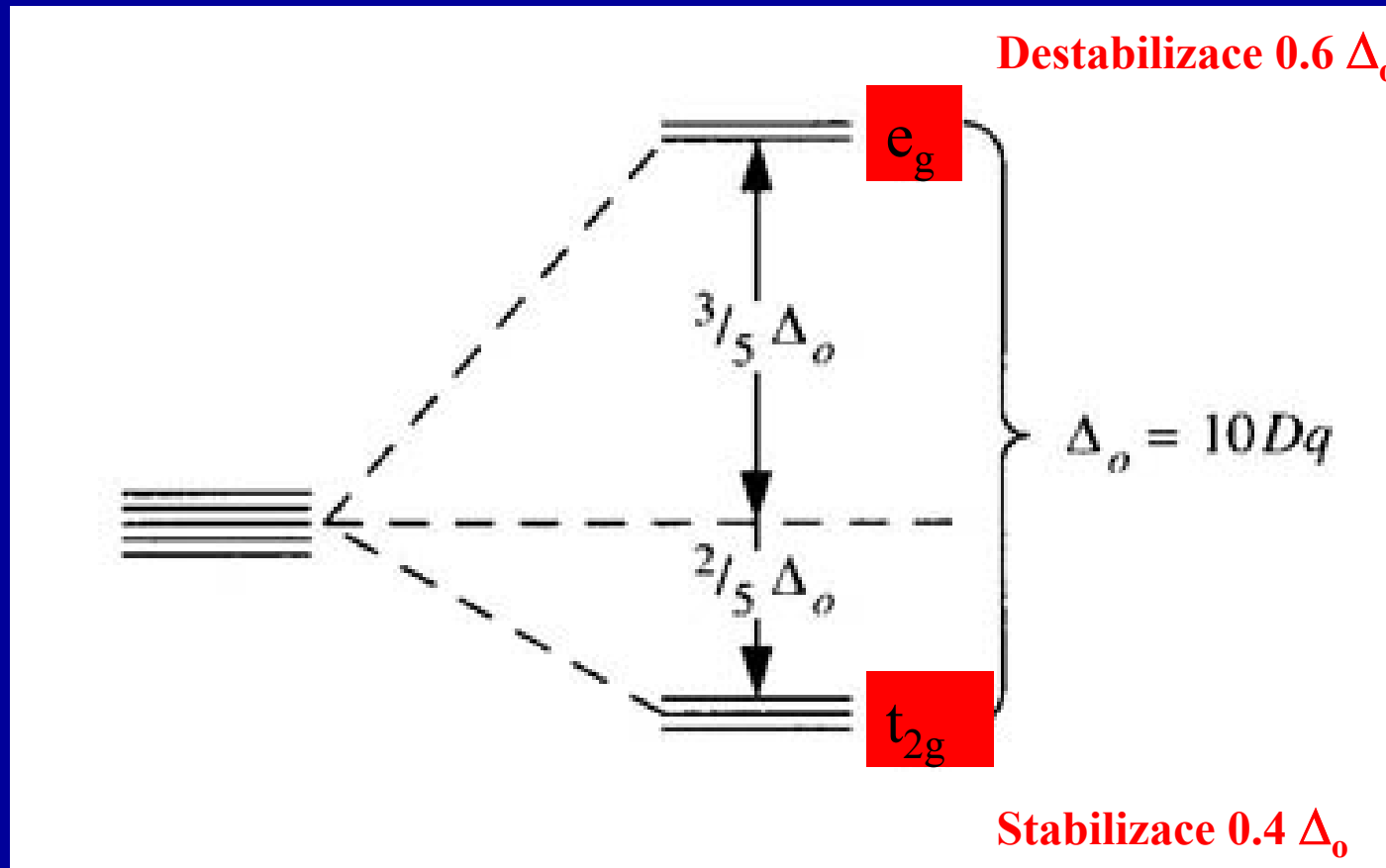
Izolovaný kation

Interakce  
ligandy-kation

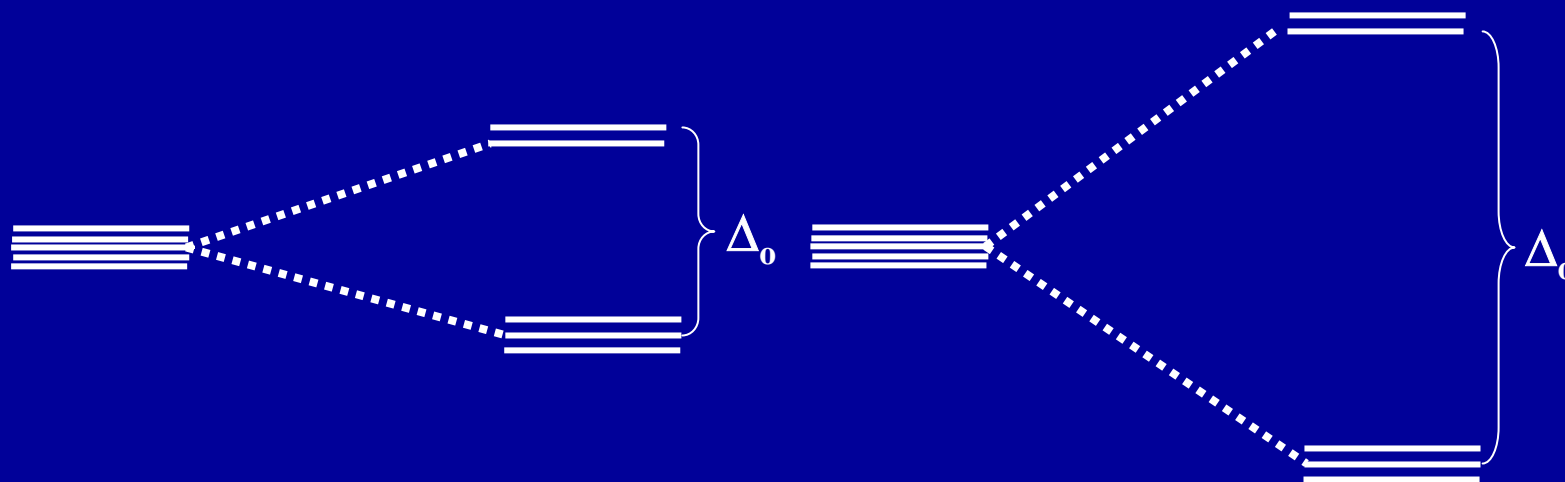
Interakce  
ligandy-d elektrony



# Rozštěpení d-hladin v $O_h$ poli



# Stabilizační energie ligandového pole (CFSE = Crystal Field Stabilization Energy)



Slabé pole

$\Delta_0 < P$  (párovací energie)

Vysokospinové komplexy

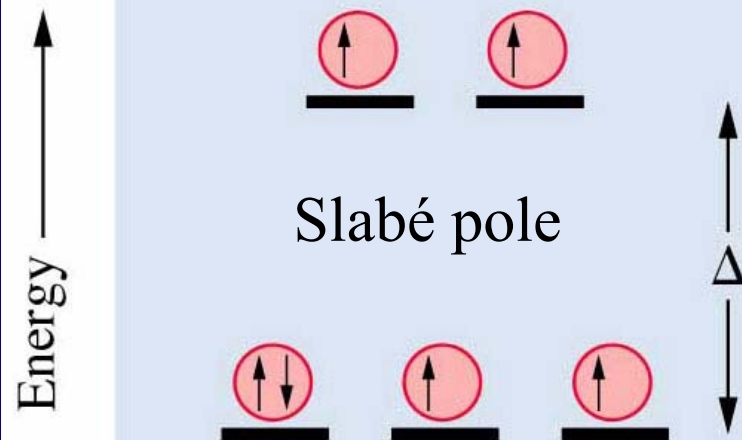
Silné pole

$\Delta_0 > P$  (párovací energie)

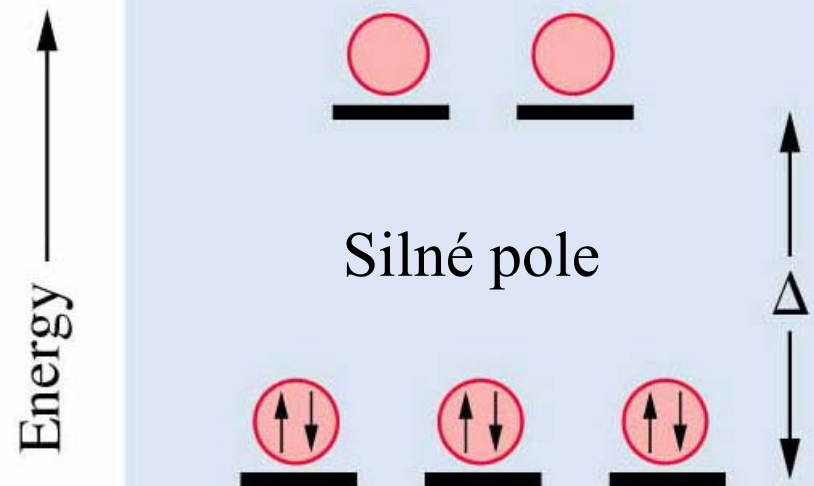
Nízkospinové komplexy

# Stabilizační energie ligandového pole

## Vysokospinové komplexy



## Nízkospinové komplexy



$\Delta_o$  roste

Slabé pole

Silné pole

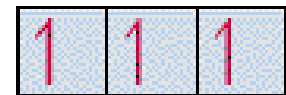
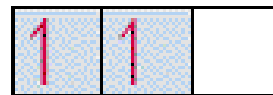
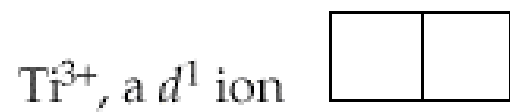
		e	CFSE		e	CFSE
$d^1$	$t_{2g}^1$	1	$0.4 \Delta_0$	$t_{2g}^1$	1	$0.4 \Delta_0$
$d^2$	$t_{2g}^2$	2	$0.8 \Delta_0$	$t_{2g}^2$	2	$0.8 \Delta_0$
$d^3$	$t_{2g}^3$	3	$1.2 \Delta_0$	$t_{2g}^3$	3	$1.2 \Delta_0$
$d^4$	$t_{2g}^3 e_g^1$	4	$0.6 \Delta_0$	$t_{2g}^4$	2	$1.6 \Delta_0$
$d^5$	$t_{2g}^3 e_g^2$	5	$0.0 \Delta_0$	$t_{2g}^5$	1	$2.0 \Delta_0$
$d^6$	$t_{2g}^4 e_g^2$	4	$0.4 \Delta_0$	$t_{2g}^6$	0	$2.4 \Delta_0$
$d^7$	$t_{2g}^5 e_g^2$	3	$0.8 \Delta_0$	$t_{2g}^6 e_g^1$	1	$1.8 \Delta_0$
$d^8$	$t_{2g}^6 e_g^2$	2	$1.2 \Delta_0$	$t_{2g}^6 e_g^2$	2	$1.2 \Delta_0$

$$CFSE = (n t_{2g}) 0.4 \Delta_0 - (n e_g) 0.6 \Delta_0$$

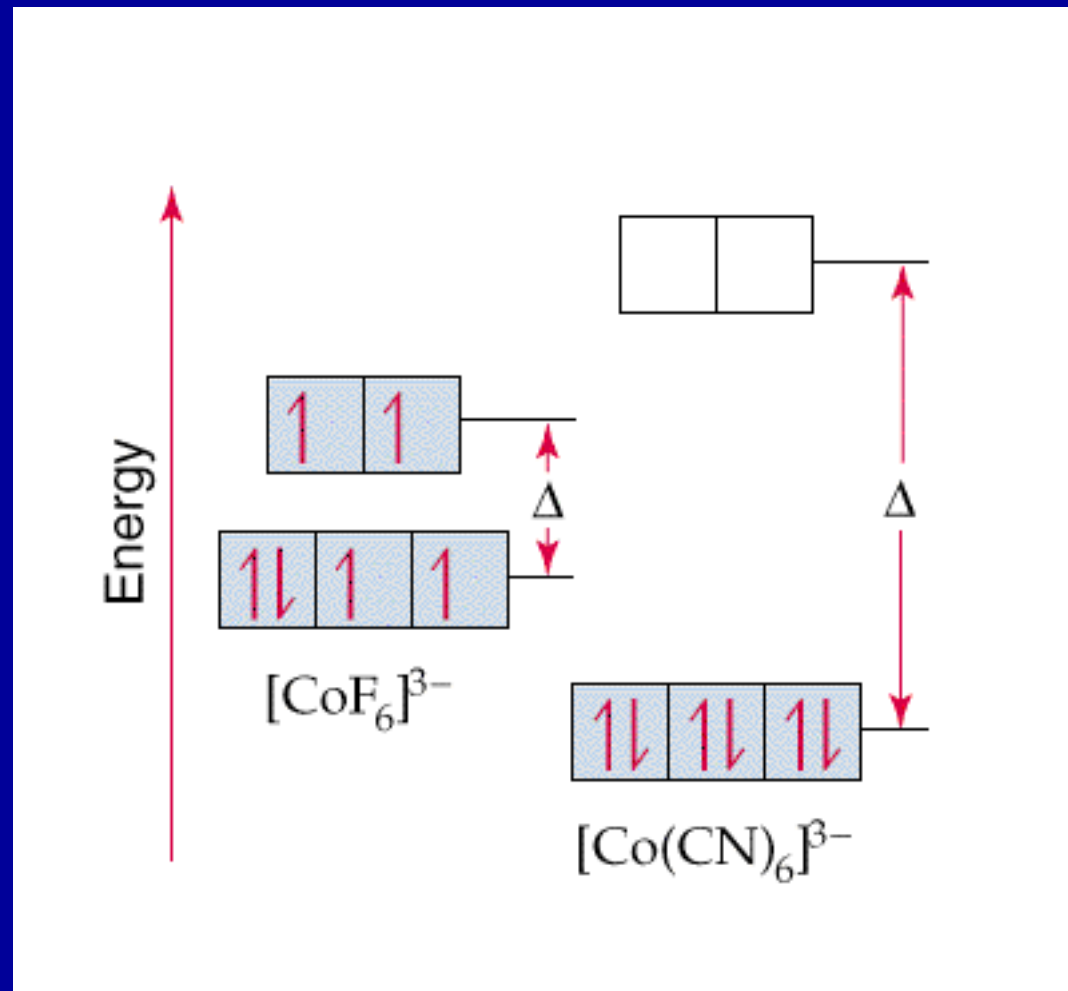
e = počet nepárových elektronů



# Rozštěpení d-hladin v $O_h$ poli



# Rozštěpení d-hladin v $O_h$ poli



# Stabilizační energie ligandového pole

CFSE for high spin  $d^4$  is  
 $= (+3/5 - 2/3 - 2/3 - 2/3)\Delta$

$$\frac{1}{+3/5 \Delta} \text{ ———}$$

$$\frac{1}{-2/3 \Delta} \quad \frac{1}{-2/3 \Delta} \quad \frac{1}{-2/3 \Delta}$$

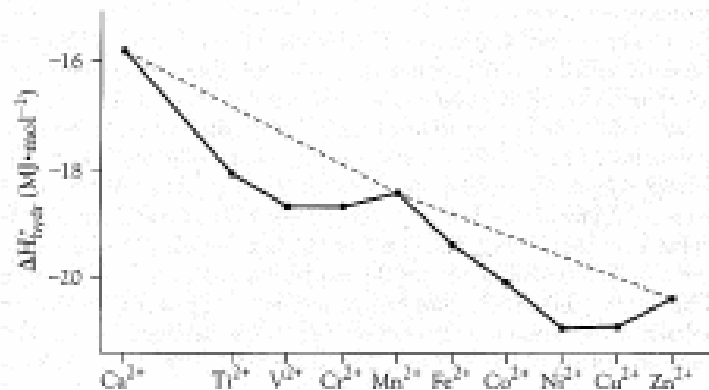


Table 18.3 Crystal field stabilization energies (CFSE) for the dioxo, high spin ions of various Period 4 metals

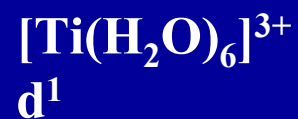
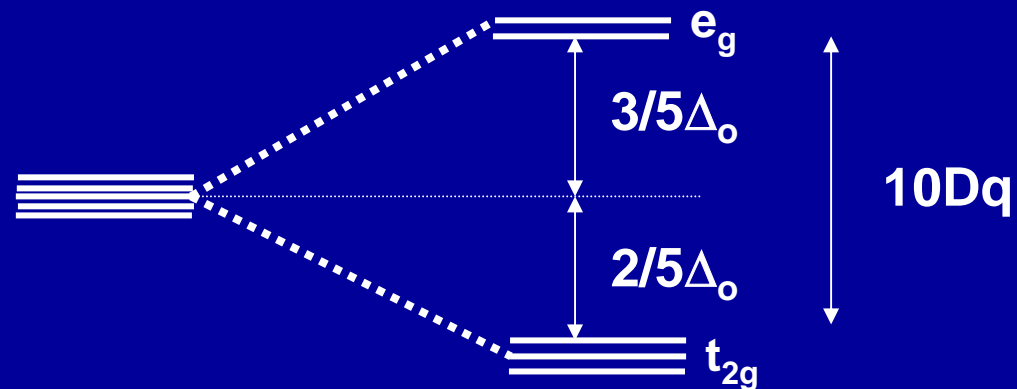
Ion	Configuration	CFSE
Ca <sup>2+</sup>	$d^0$	$-0.0 \Delta_{oct}$
—	$d^1$	$-0.4 \Delta_{oct}$
Ti <sup>2+</sup>	$d^2$	$-0.8 \Delta_{oct}$
V <sup>2+</sup>	$d^3$	$-1.2 \Delta_{oct}$
Cr <sup>2+</sup>	$d^4$	$-0.6 \Delta_{oct}$
Mn <sup>2+</sup>	$d^5$	$-0.0 \Delta_{oct}$
Fe <sup>2+</sup>	$d^6$	$-0.4 \Delta_{oct}$
Co <sup>2+</sup>	$d^7$	$-0.8 \Delta_{oct}$
Ni <sup>2+</sup>	$d^8$	$-1.2 \Delta_{oct}$
Cu <sup>2+</sup>	$d^9$	$-0.6 \Delta_{oct}$
Zn <sup>2+</sup>	$d^{10}$	$-0.0 \Delta_{oct}$

$d^0$

$d^5$

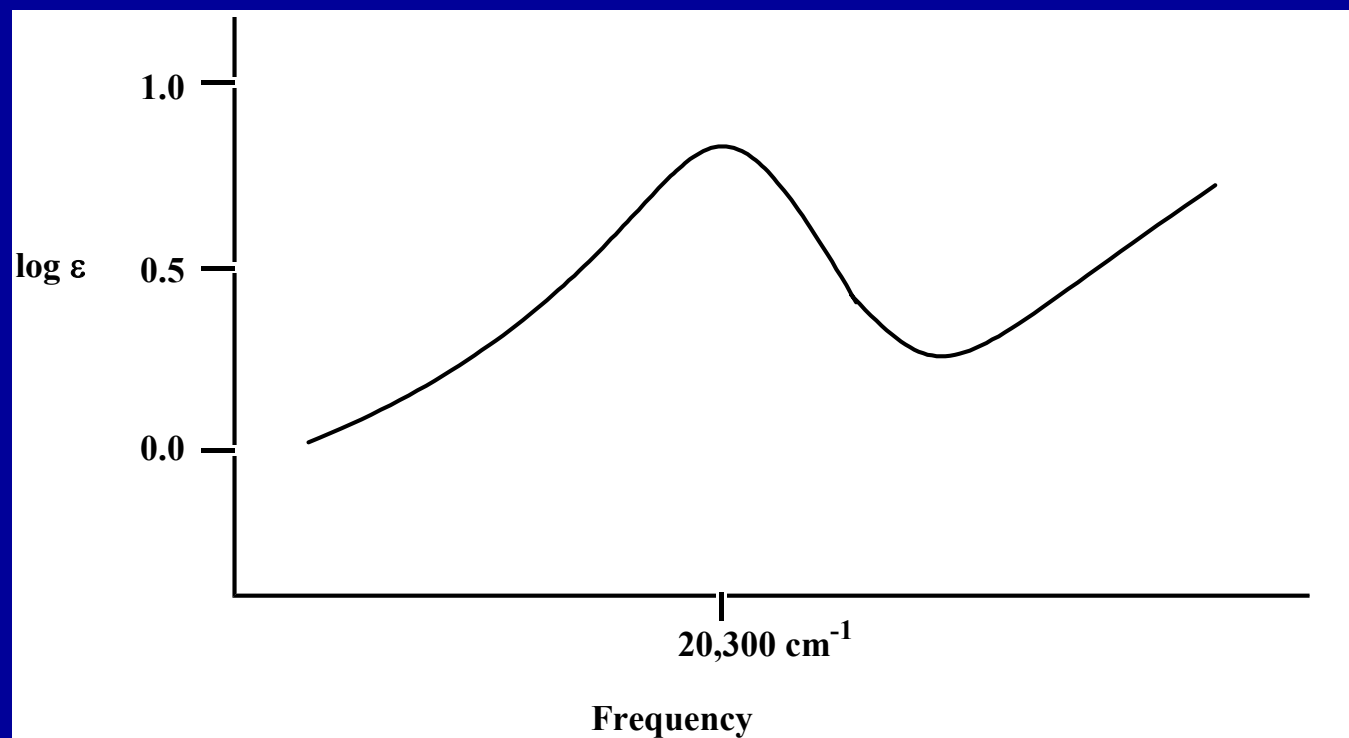
$d^{10}$

# Rozštěpení d-hladin v $O_h$ poli

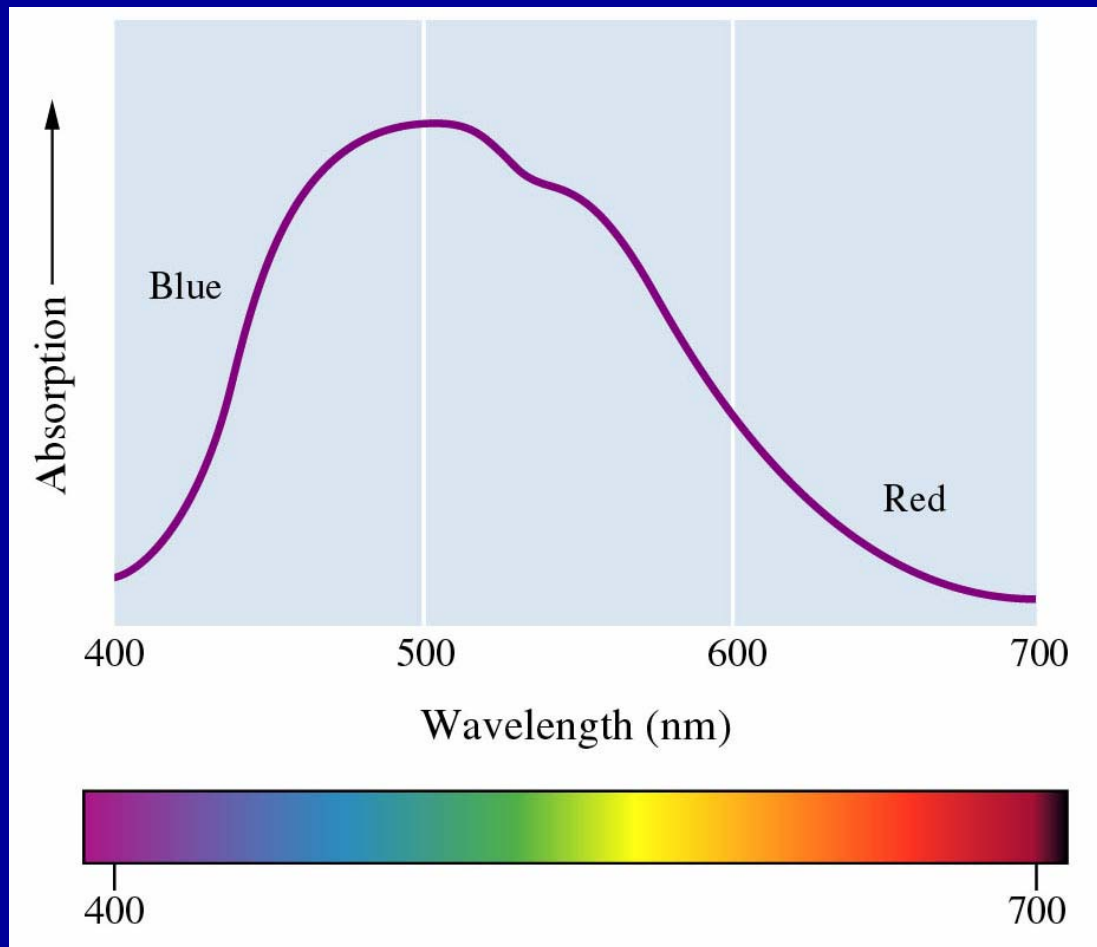
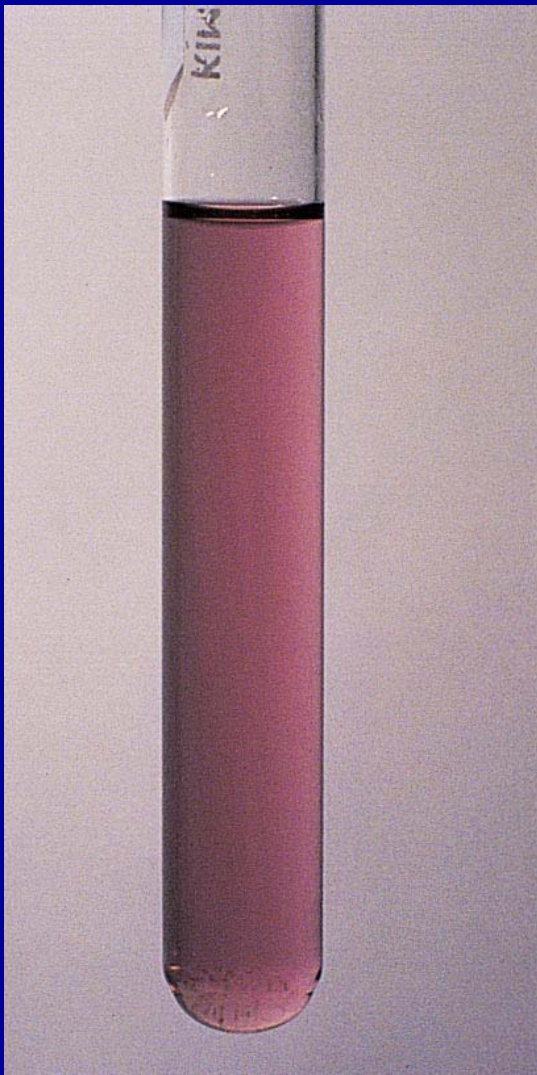


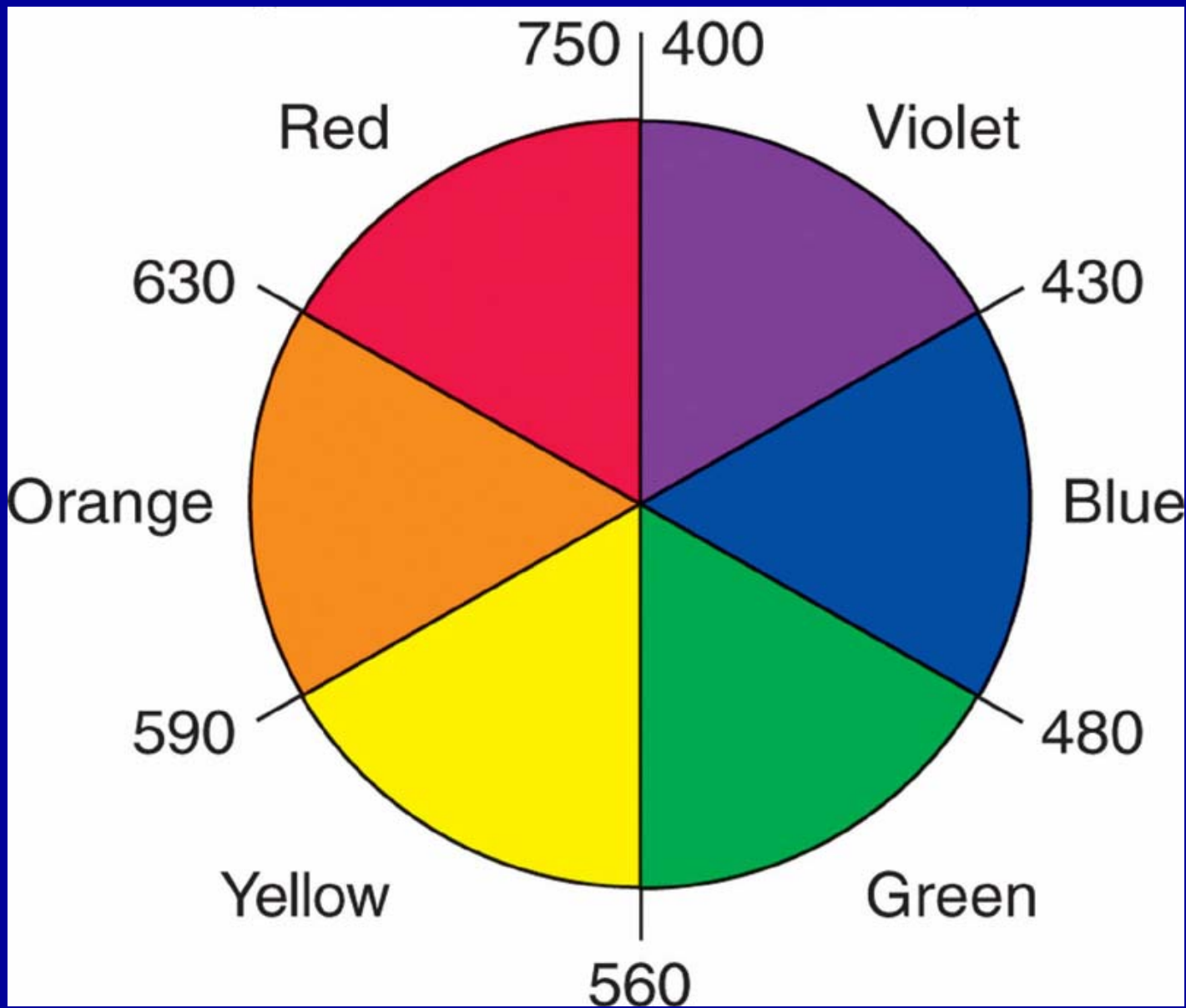
růžový

$243 \text{ kJ mol}^{-1}$   
 $(\Delta_o)$

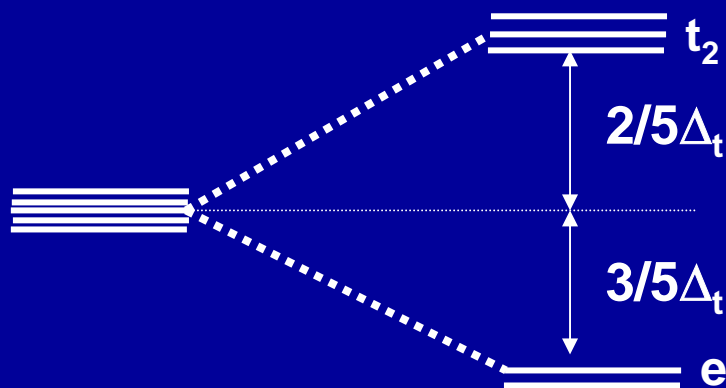


# UV-vis spektrum $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



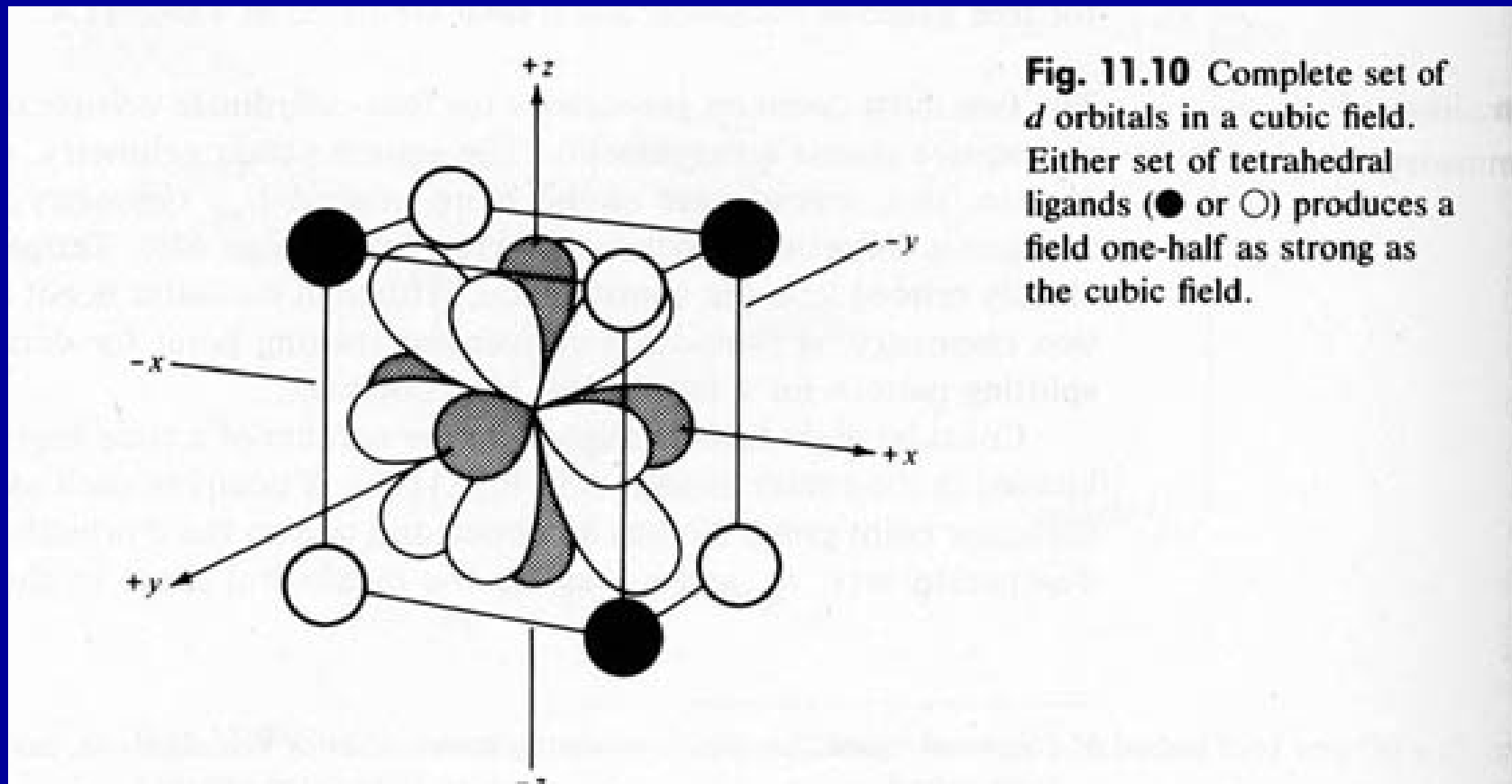


## Rozštěpení d-hladin v $T_d$ poli

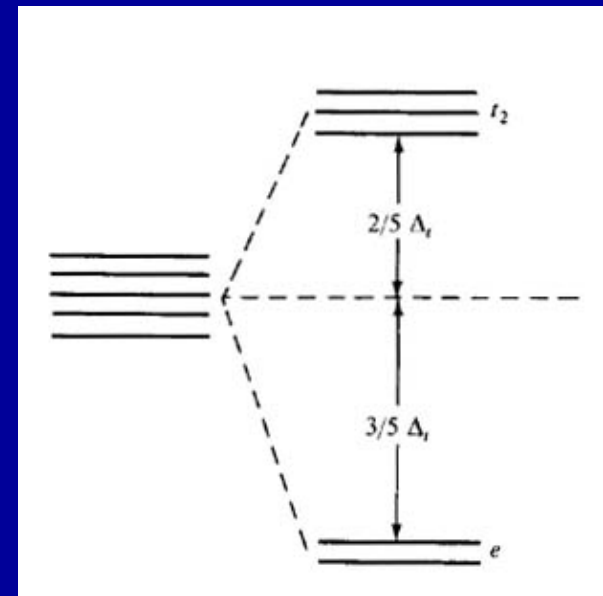
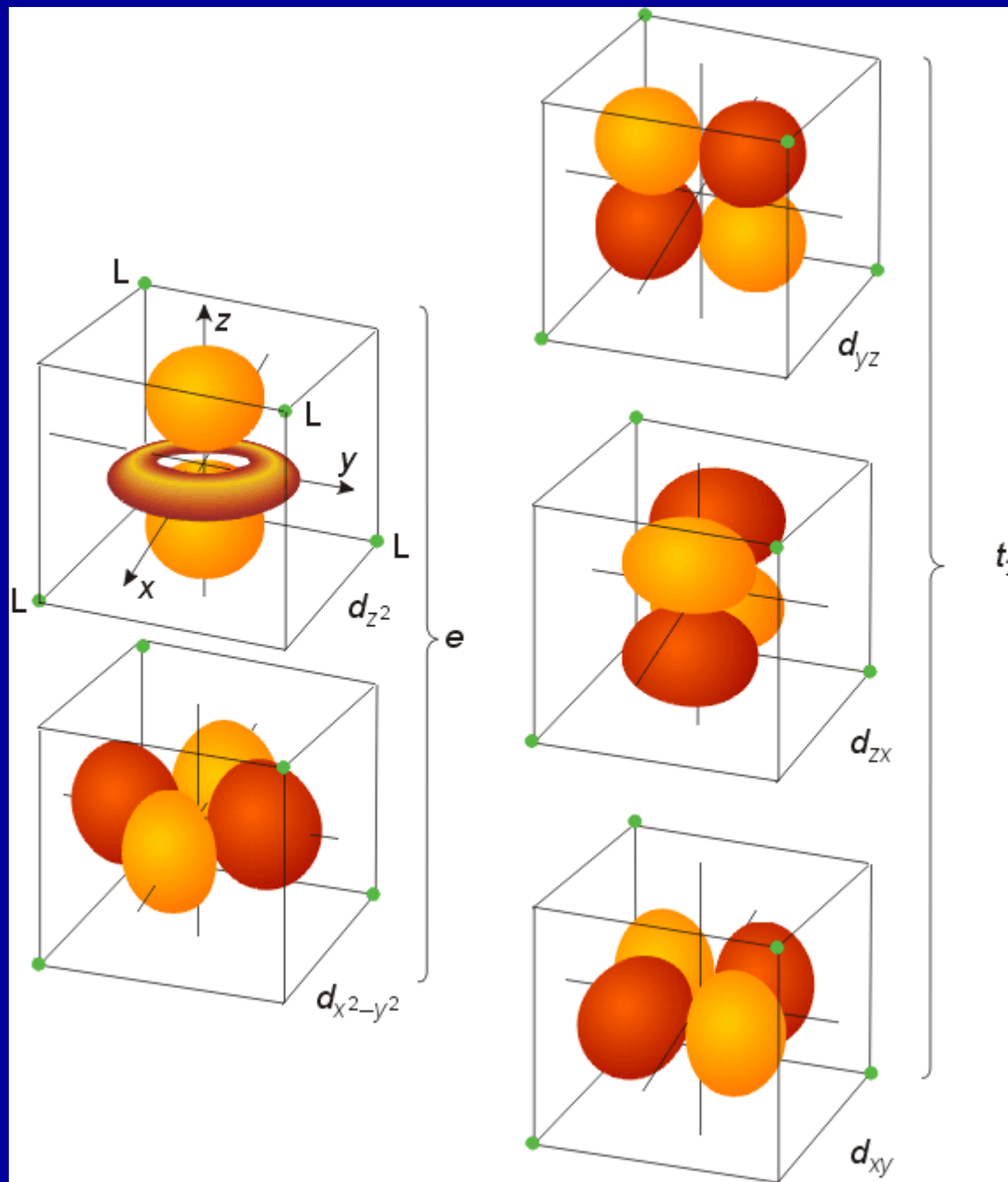


$$\Delta_t = 4/9 \Delta_o$$

$T_d$  komplexy jsou vždy vysokospinové  
žádný d-orbital nemíří přímo k ligandům (jako u  
 $O_h$ ) slabší interakce

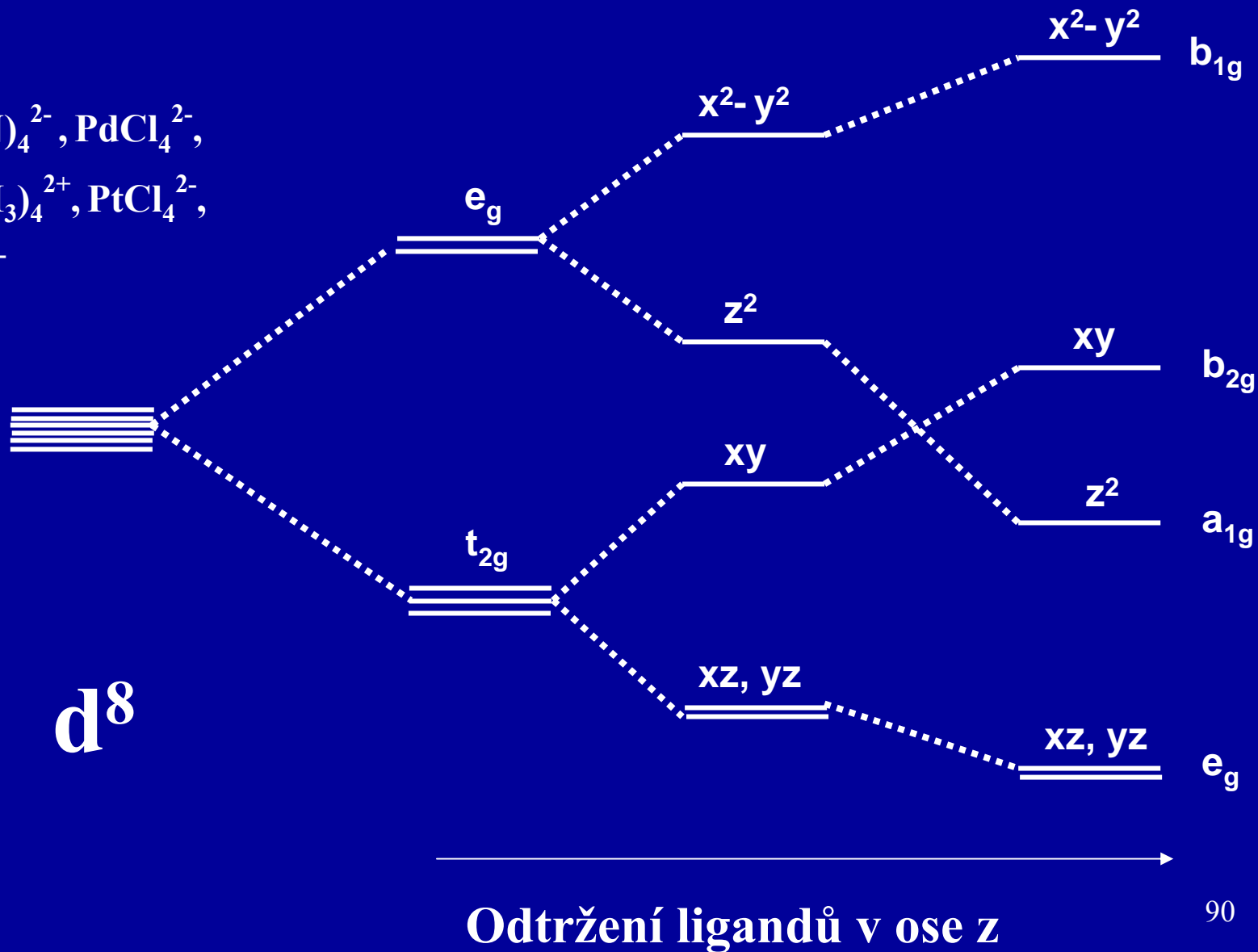


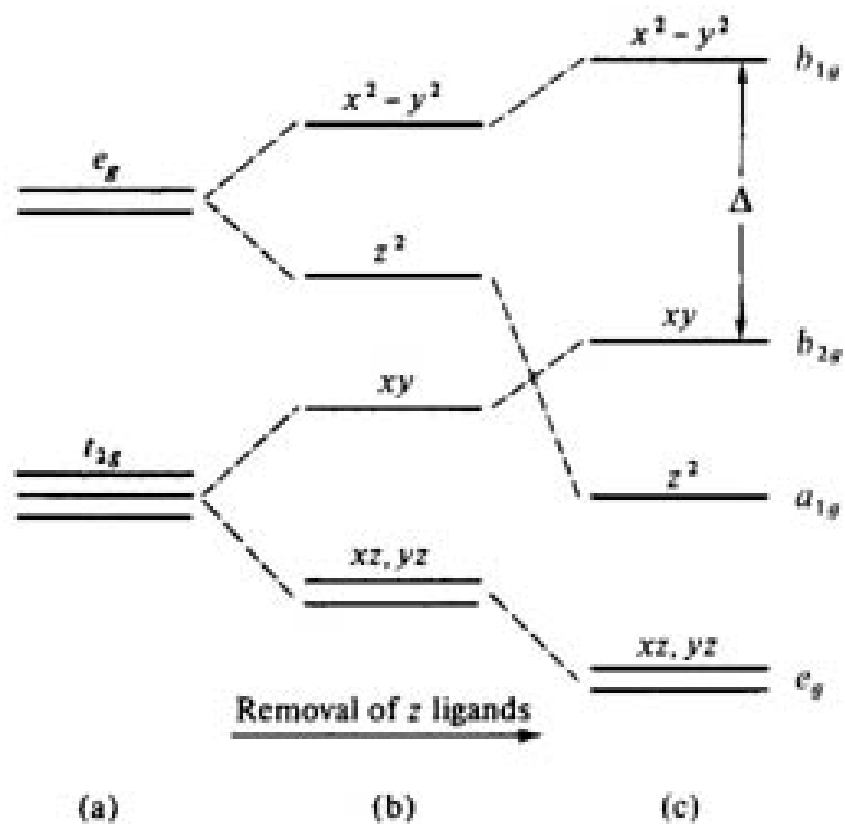




# Rozštěpení d-hladin v čtvercovém poli ( $d^8$ )

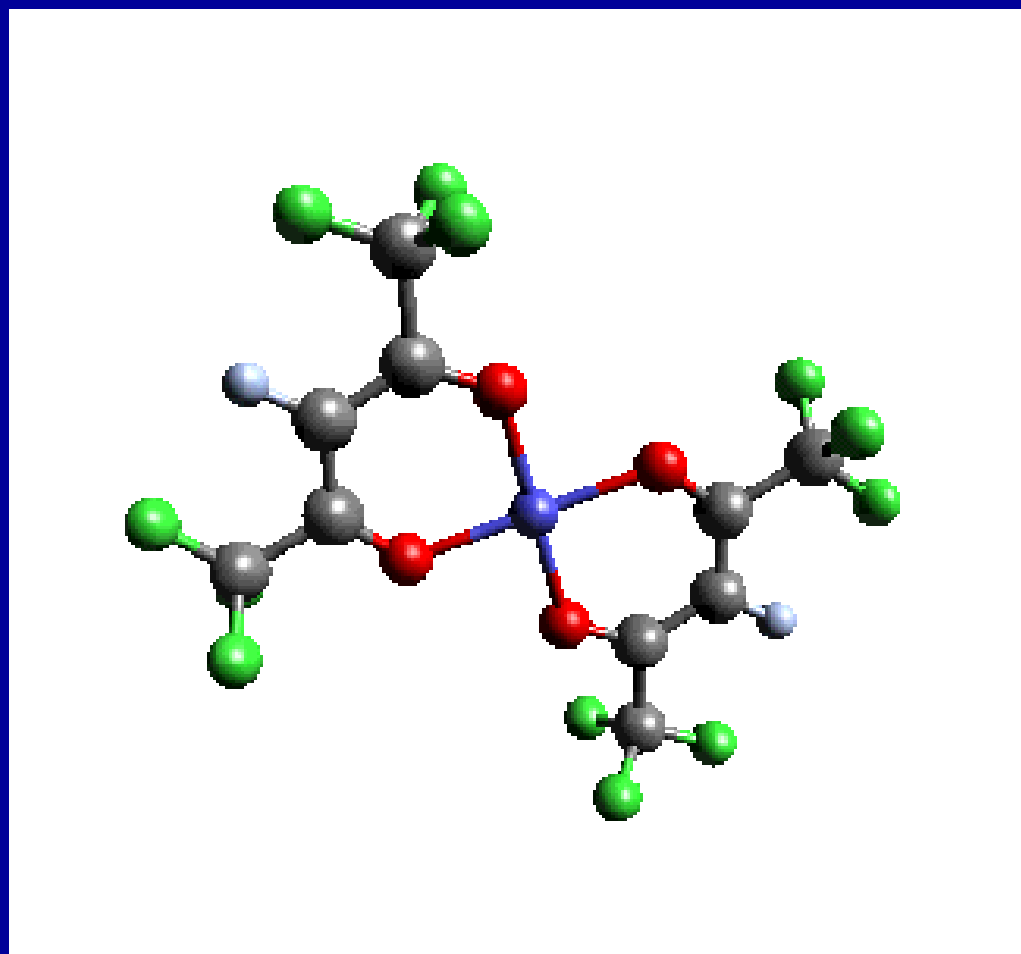
$\text{Ni}(\text{CN})_4^{2-}$ ,  $\text{PdCl}_4^{2-}$ ,  
 $\text{Pt}(\text{NH}_3)_4^{2+}$ ,  $\text{PtCl}_4^{2-}$ ,  
 $\text{AuCl}_4^-$



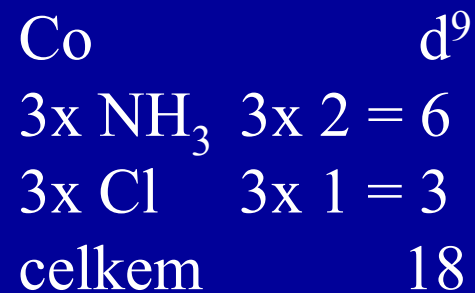
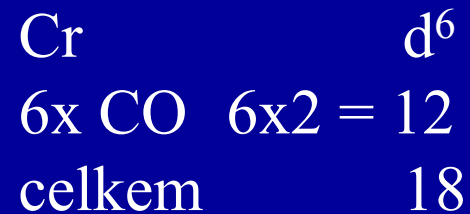


**Fig. 11.12** An octahedral complex (a) undergoing z axis elongation such that it becomes tetragonally distorted (b) and finally reaches the square planar limit (c). The a<sub>1g</sub> (d<sub>z<sup>2</sup></sub>) orbital may lie below the e<sub>g</sub> (d<sub>xz</sub> and d<sub>yz</sub>) orbitals in the square planar complex.

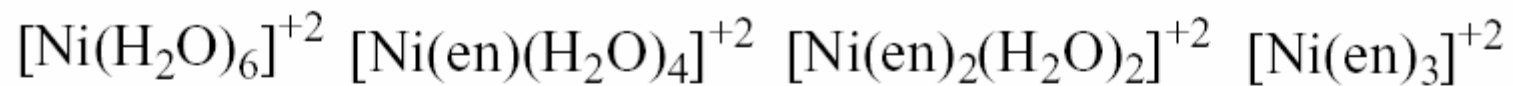
# $\text{Cu}(\text{hfacac})_2$



## 18-ti elektronové pravidlo



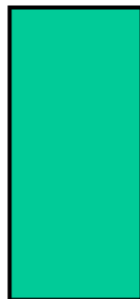
## Vliv ligandů na vlastnosti komplexů



green



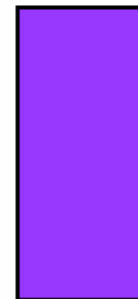
green/blue



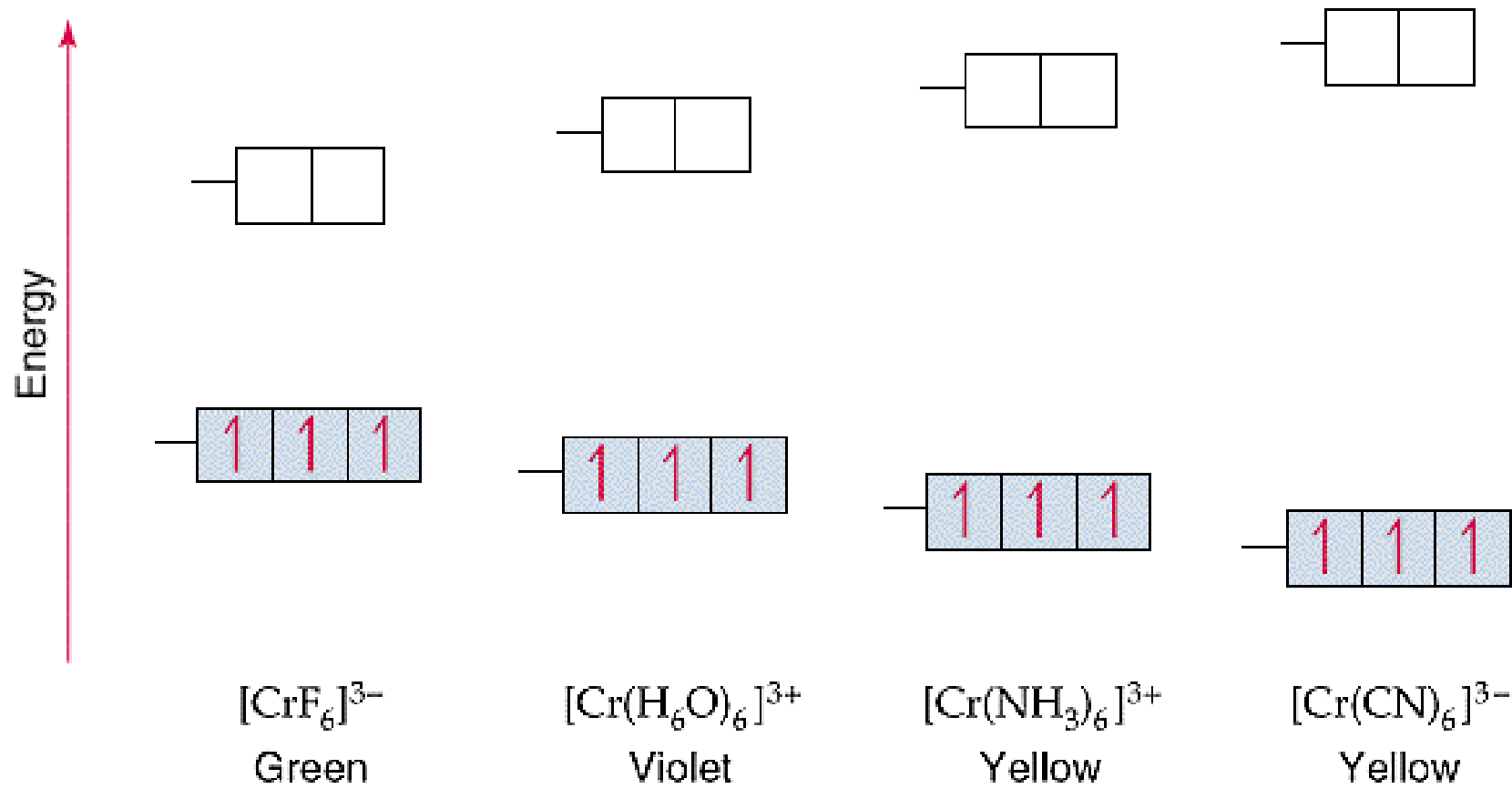
blue



purple

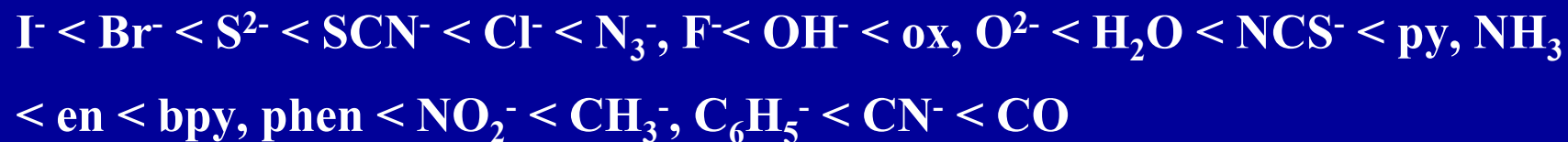


# Vliv ligandů na vlastnosti komplexů



## Faktory ovlivňující velikost rozštěpení ligandového pole

Spektrochemická řada ligandů:



Centrální atom:

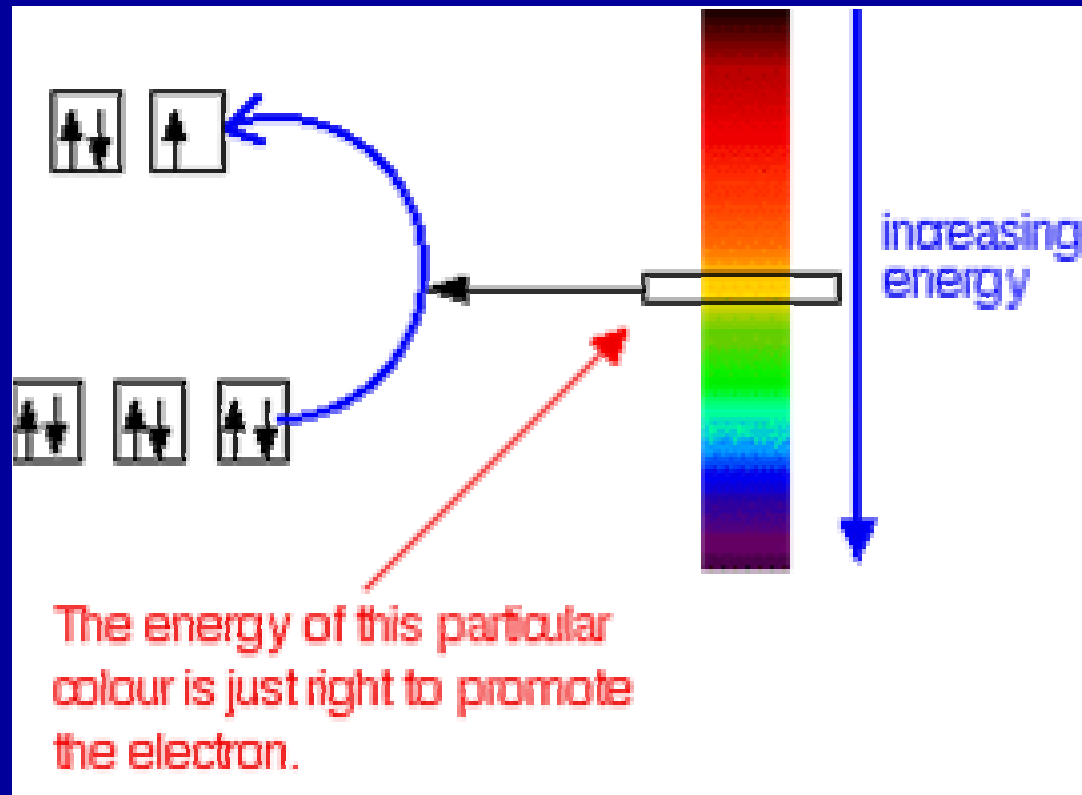


Typ koordinace  $\frac{4}{9} \Delta_{\text{O}} = \Delta_{\text{t}}$

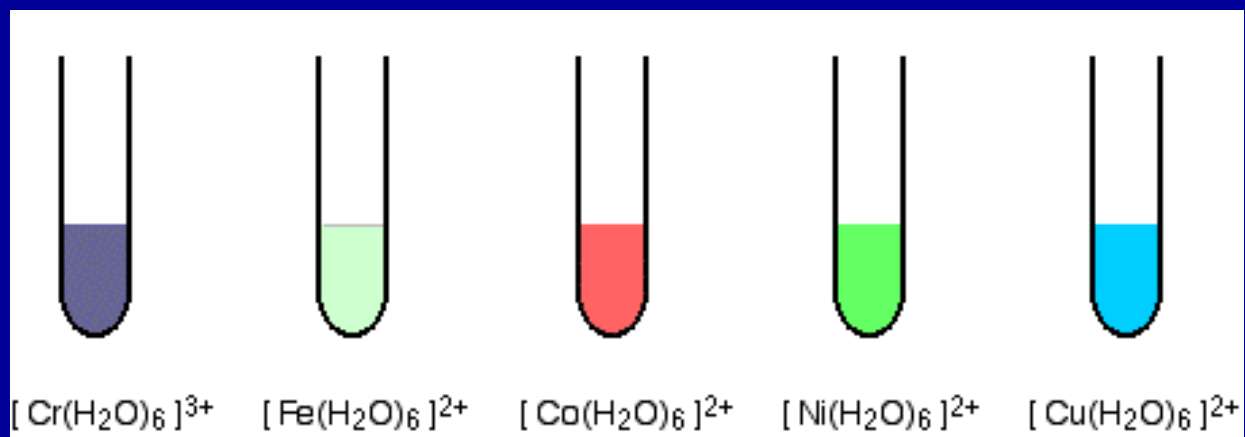
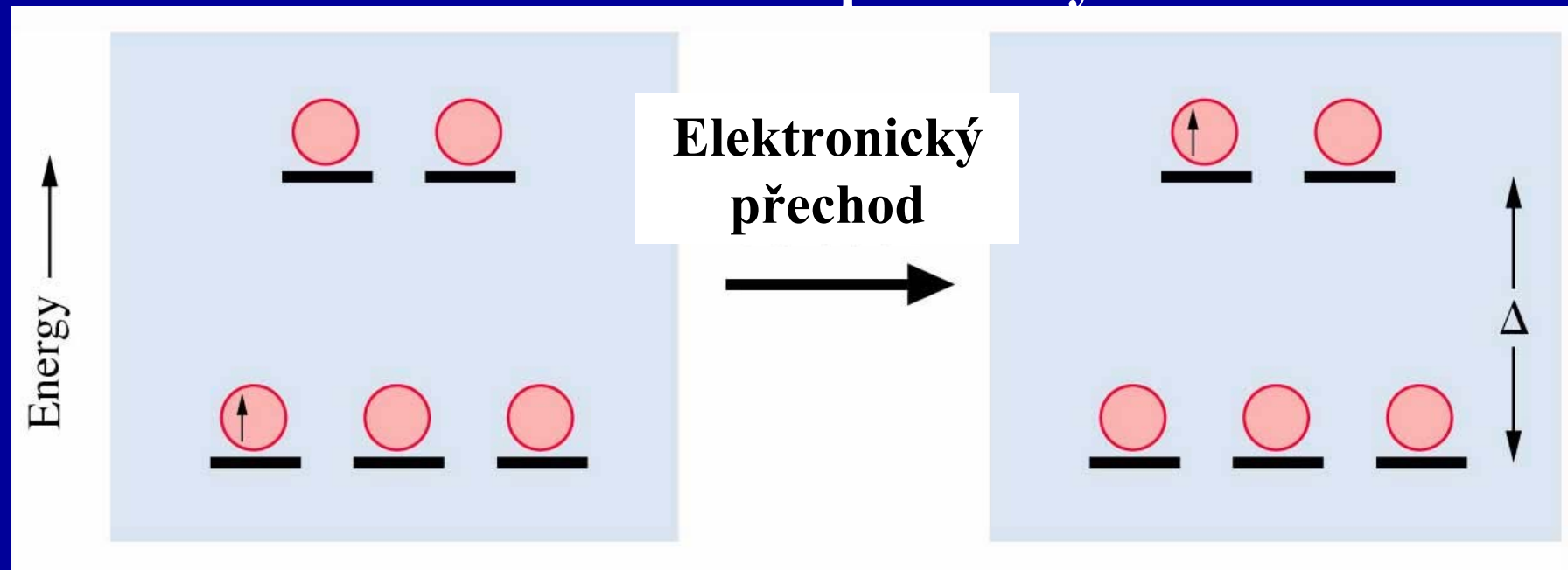
Síla a délka vazby M-L



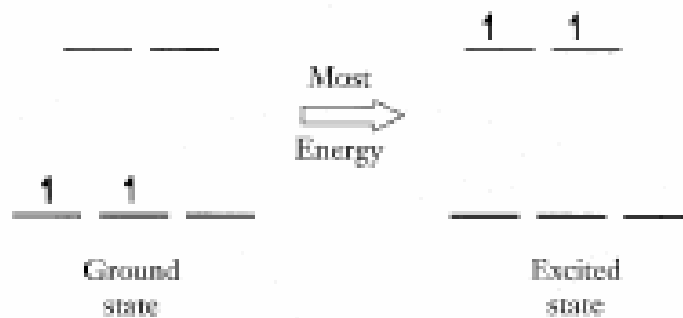
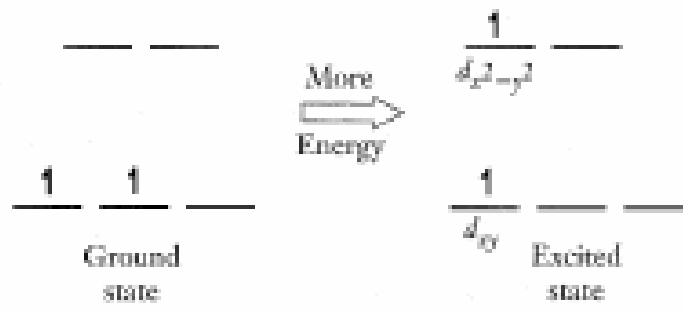
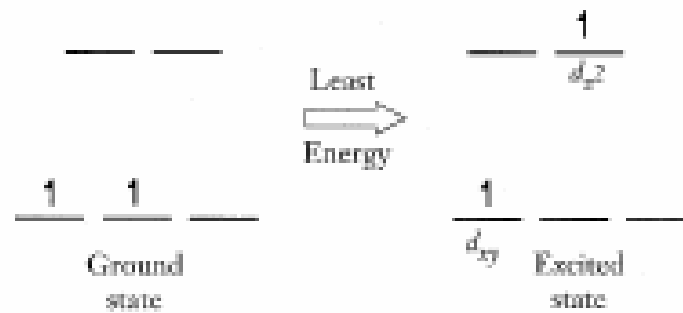
# Elektronické přechody

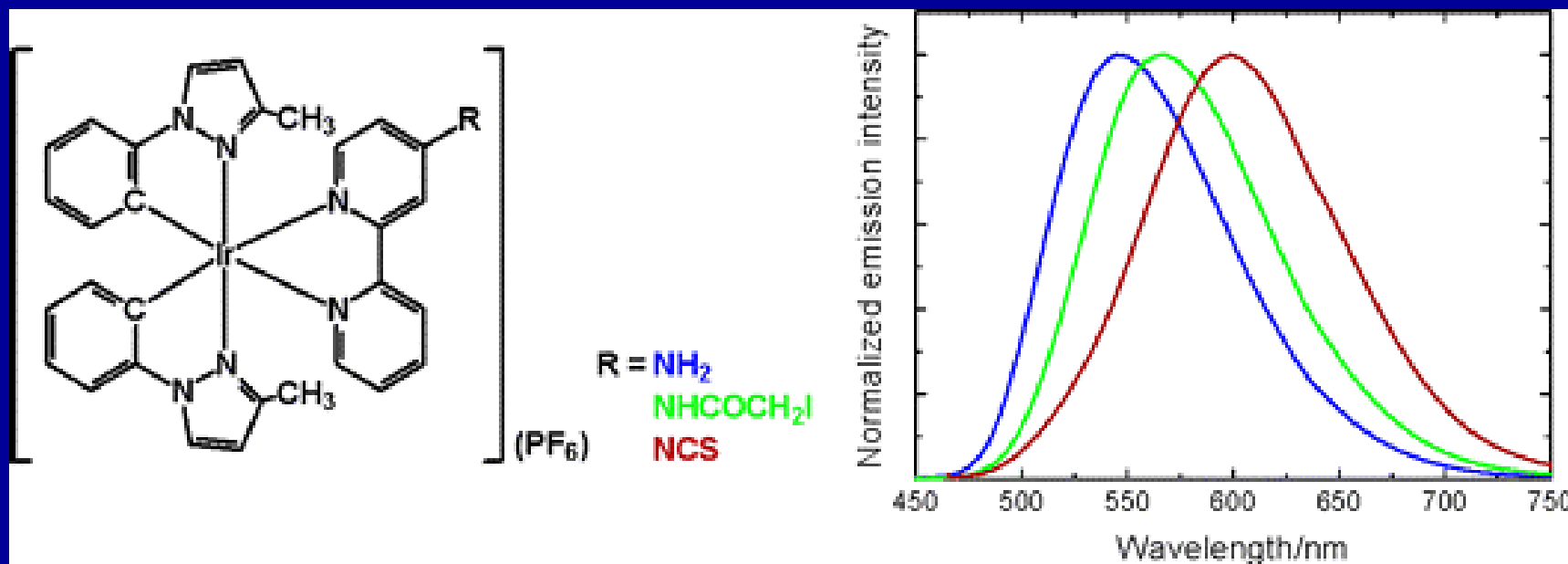


# Elektronické přechody



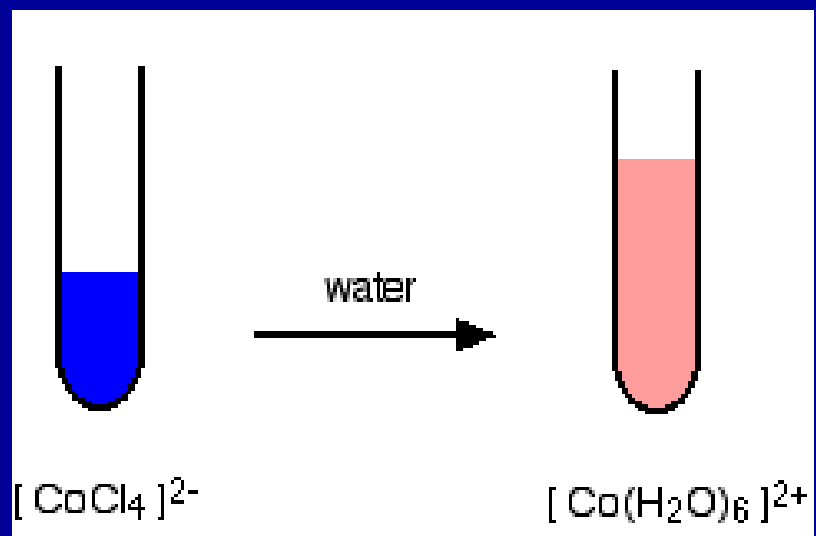
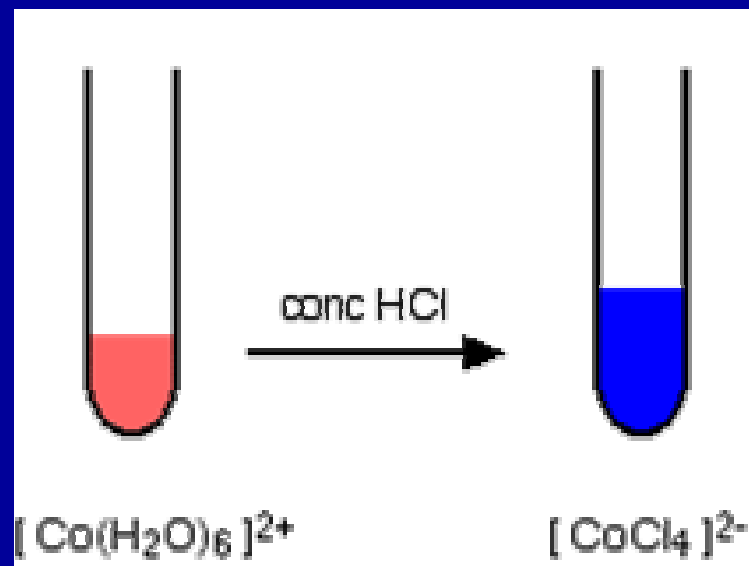
# Elektronické přechody

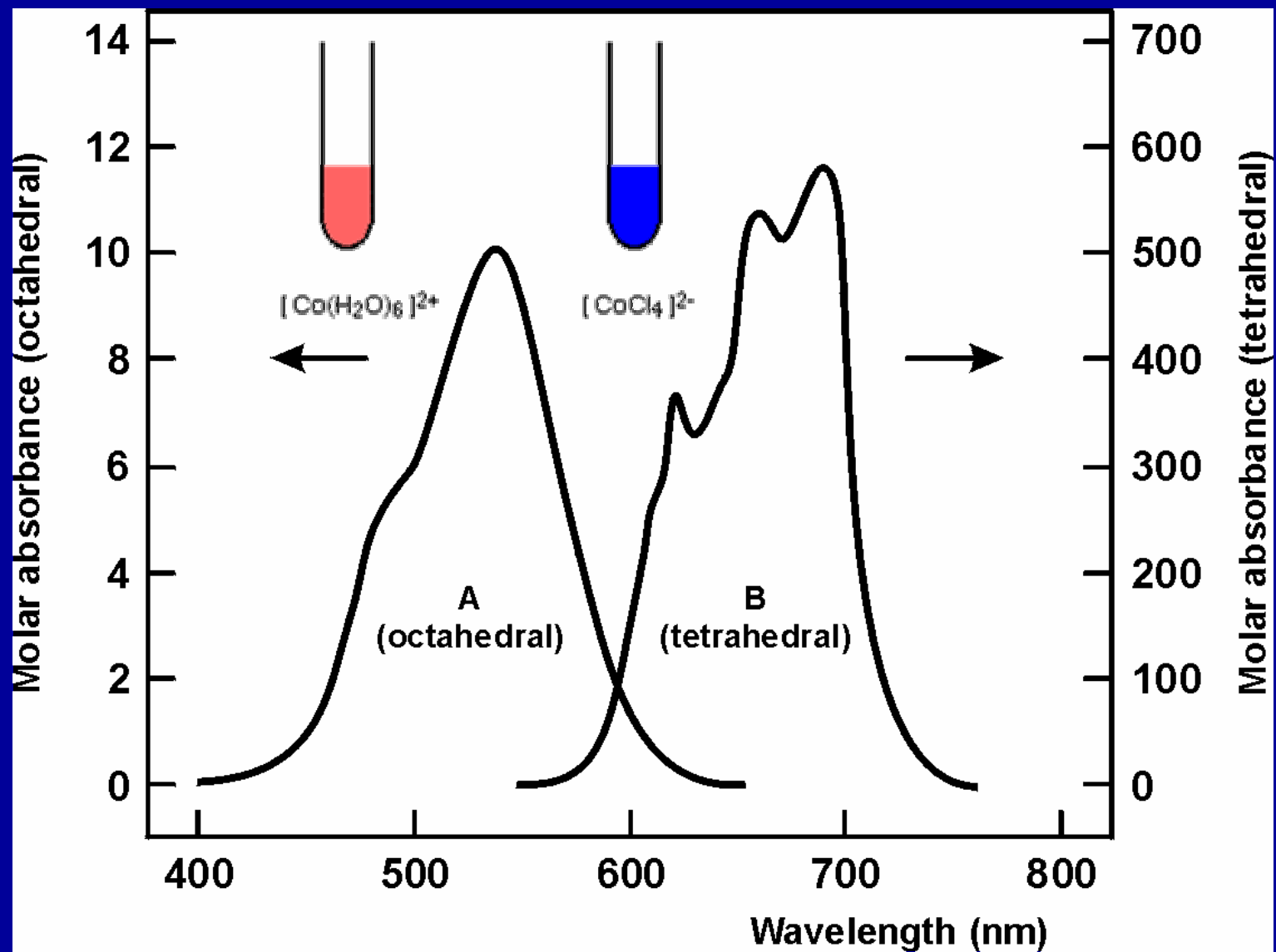




<b>Wavelength (Color) Absorbed</b>	<b>Color Observed</b>
400 nm ( <b>violet</b> )	<b>yellow-green</b>
450 nm ( <b>blue</b> )	<b>orange</b>
490 nm ( <b>blue-green</b> )	<b>red</b>
530 nm ( <b>green</b> )	<b>purple</b>
570 nm ( <b>yellow-green</b> )	<b>violet</b>
580 nm ( <b>yellow</b> )	<b>dark blue</b>
600 nm ( <b>orange</b> )	<b>blue</b>
650 nm ( <b>red</b> )	<b>blue-green</b>
720 nm ( <b>purple</b> )	<b>green</b>

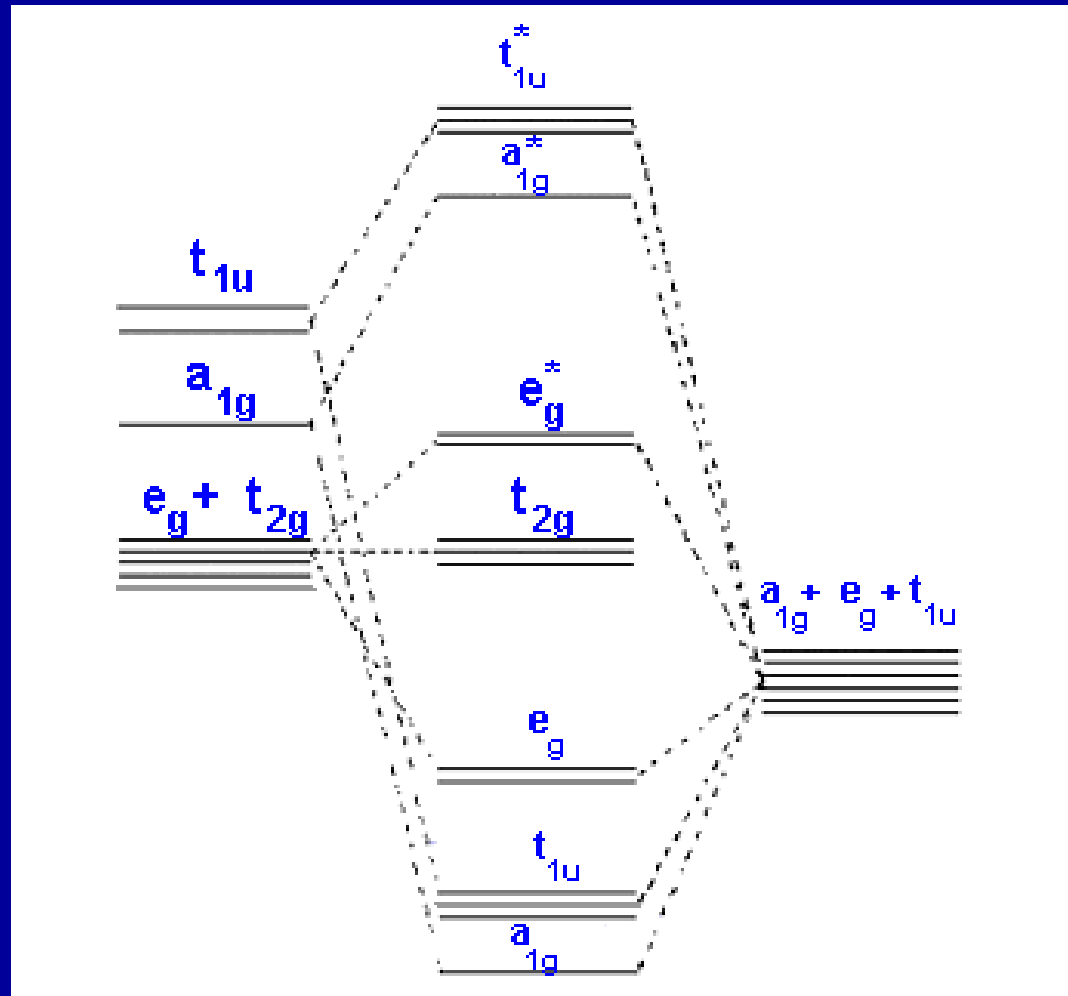






# Popis vazby v komplexech pomocí MO

3 x np  
 1x ns  
 5x (n-1) d  
 Orbitaly kovu

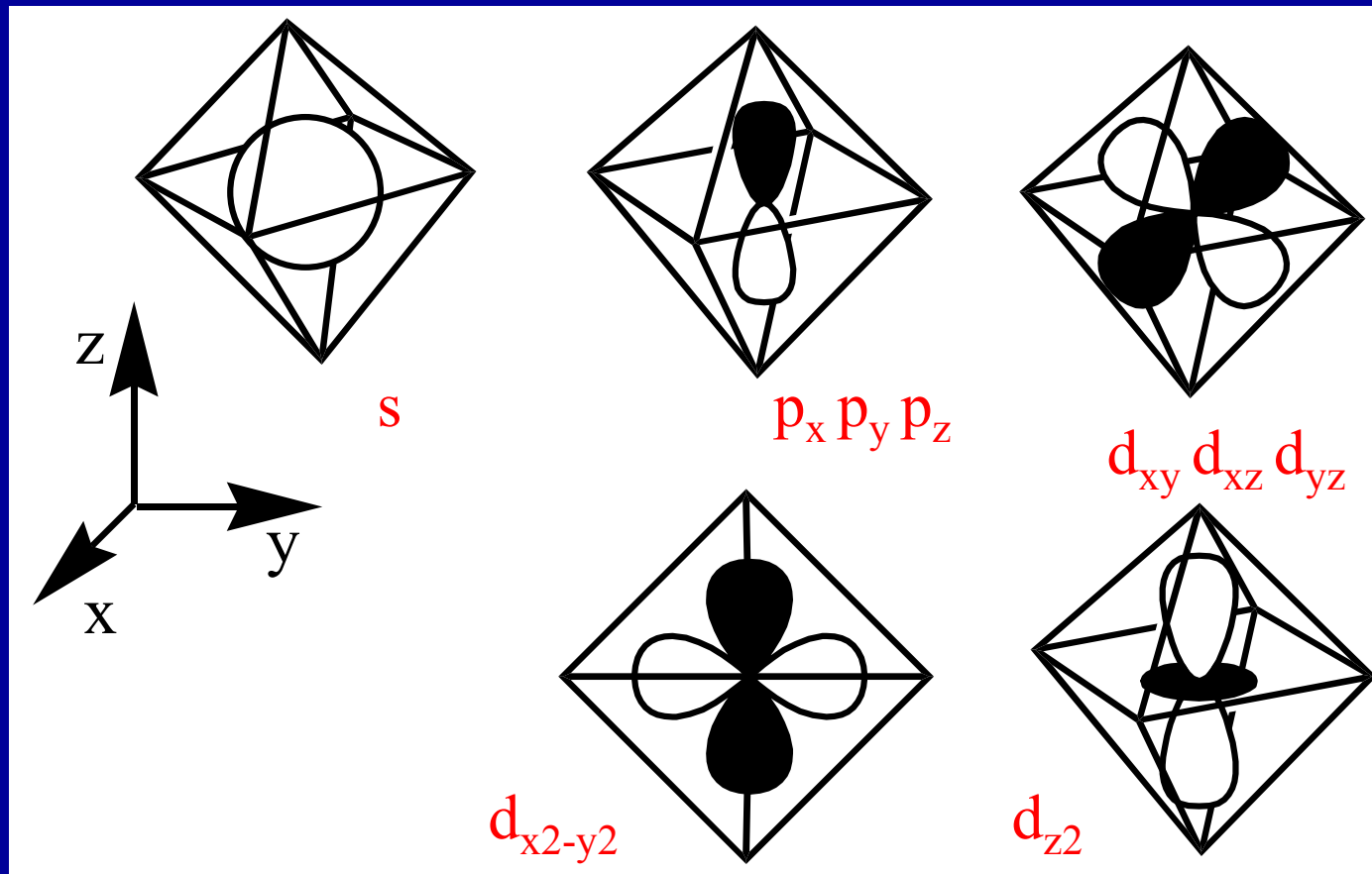


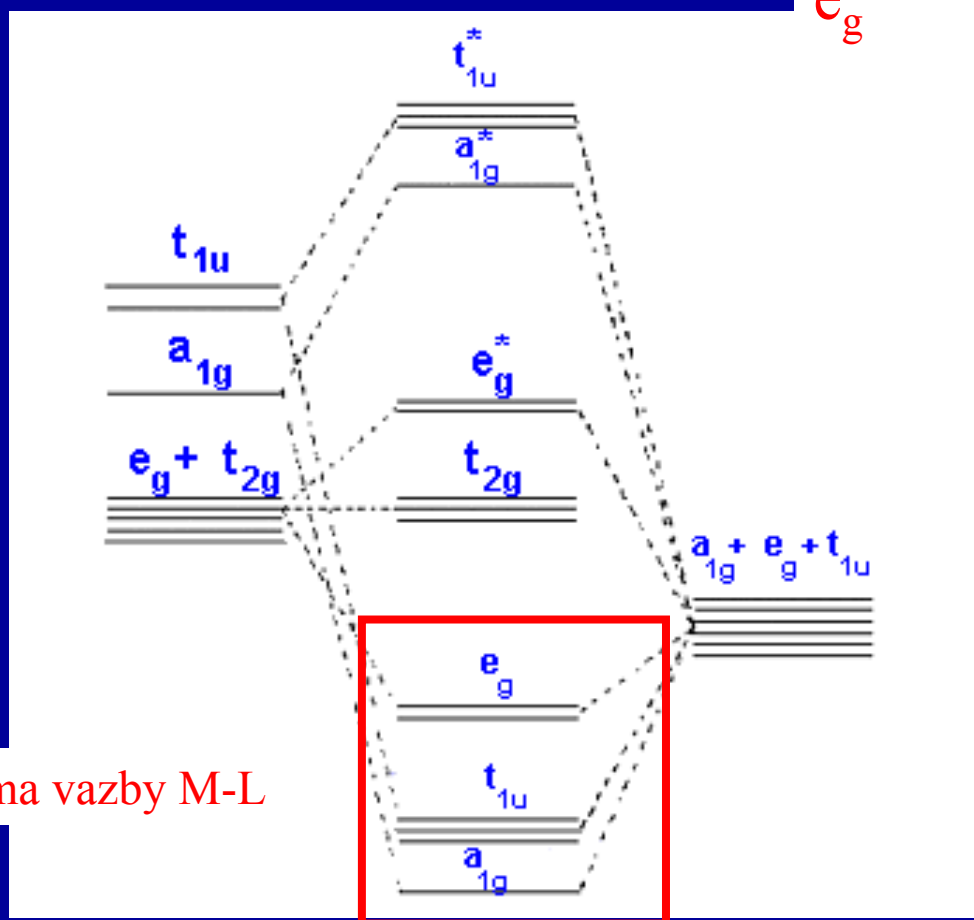
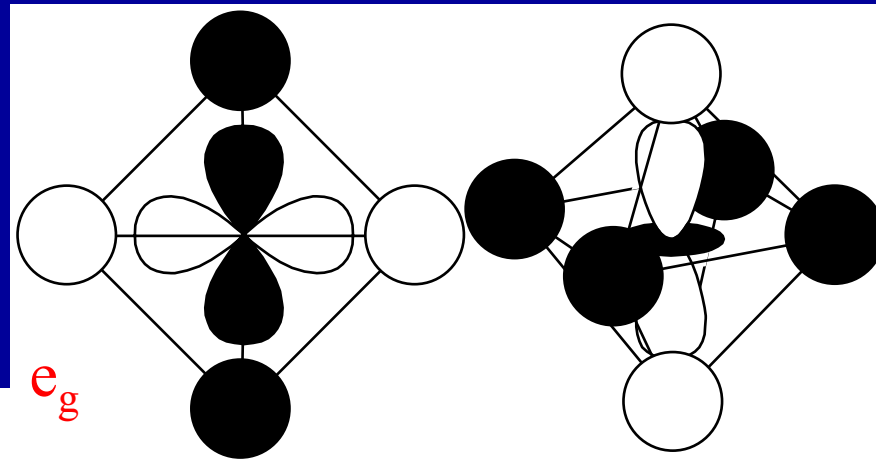
SALCAO

Orbitaly  
 ligandů

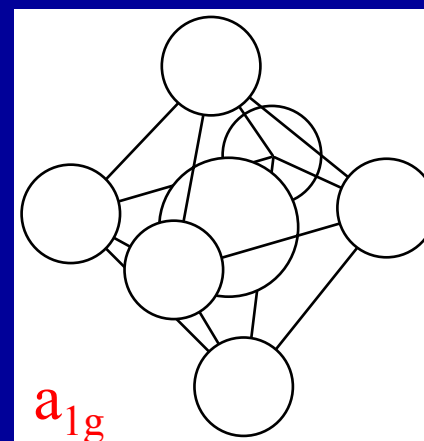
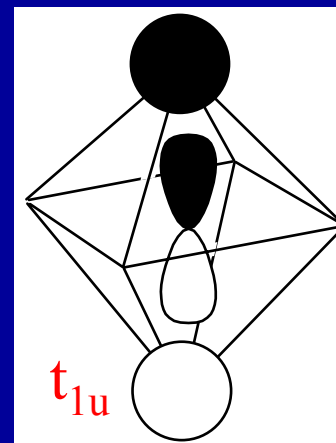


# Valenční orbitály kovu

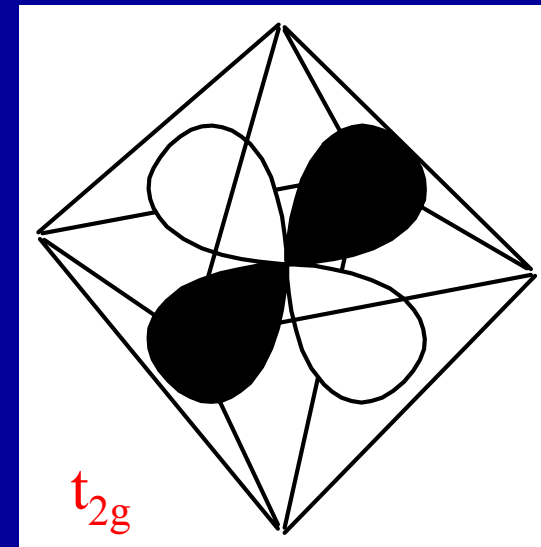
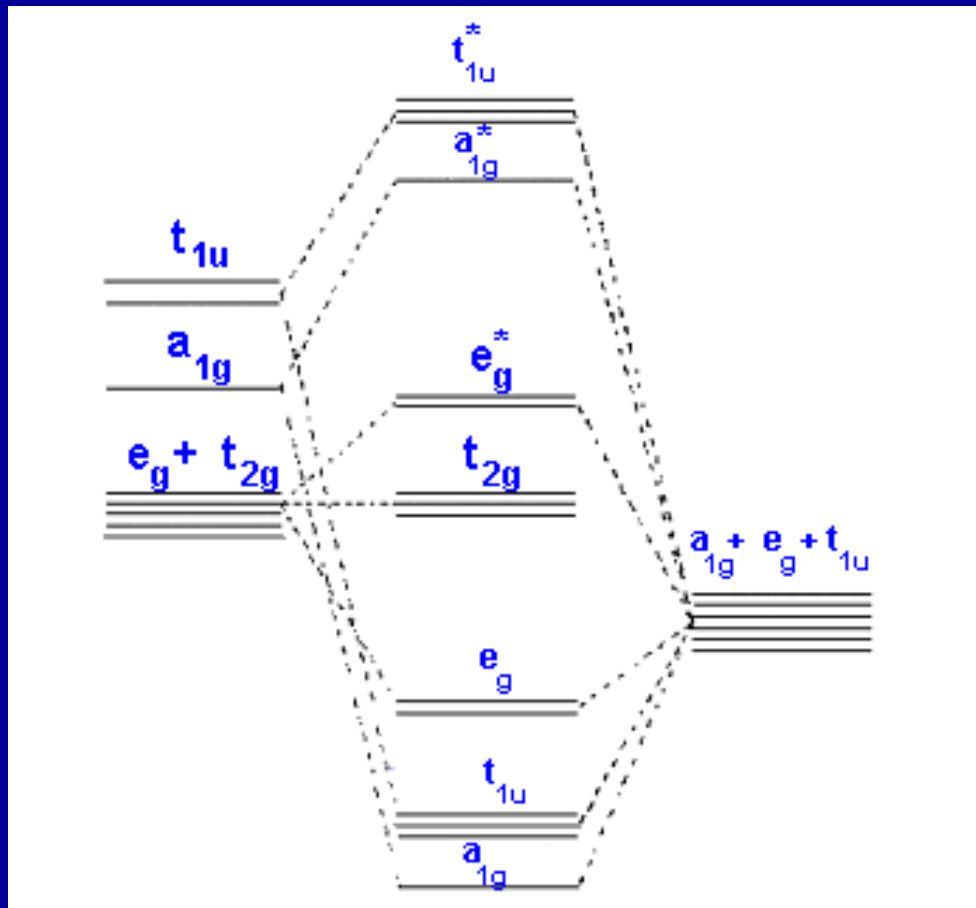




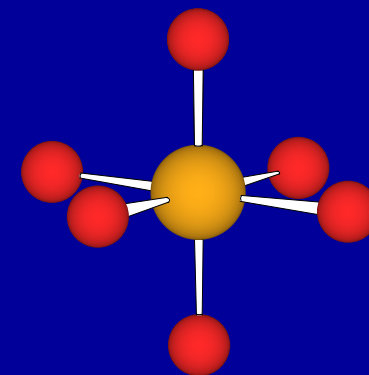
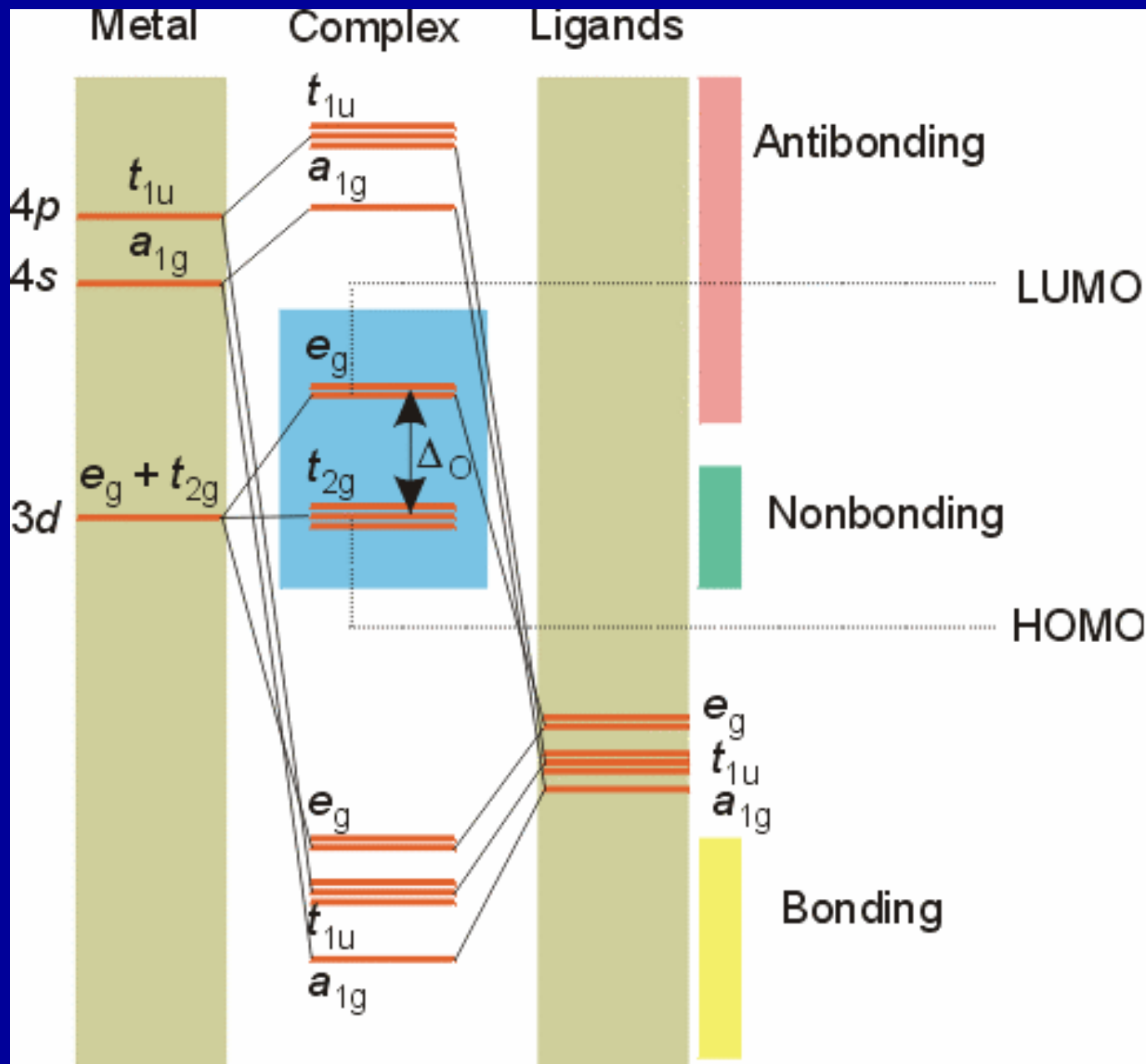
Sigma vazby M-L

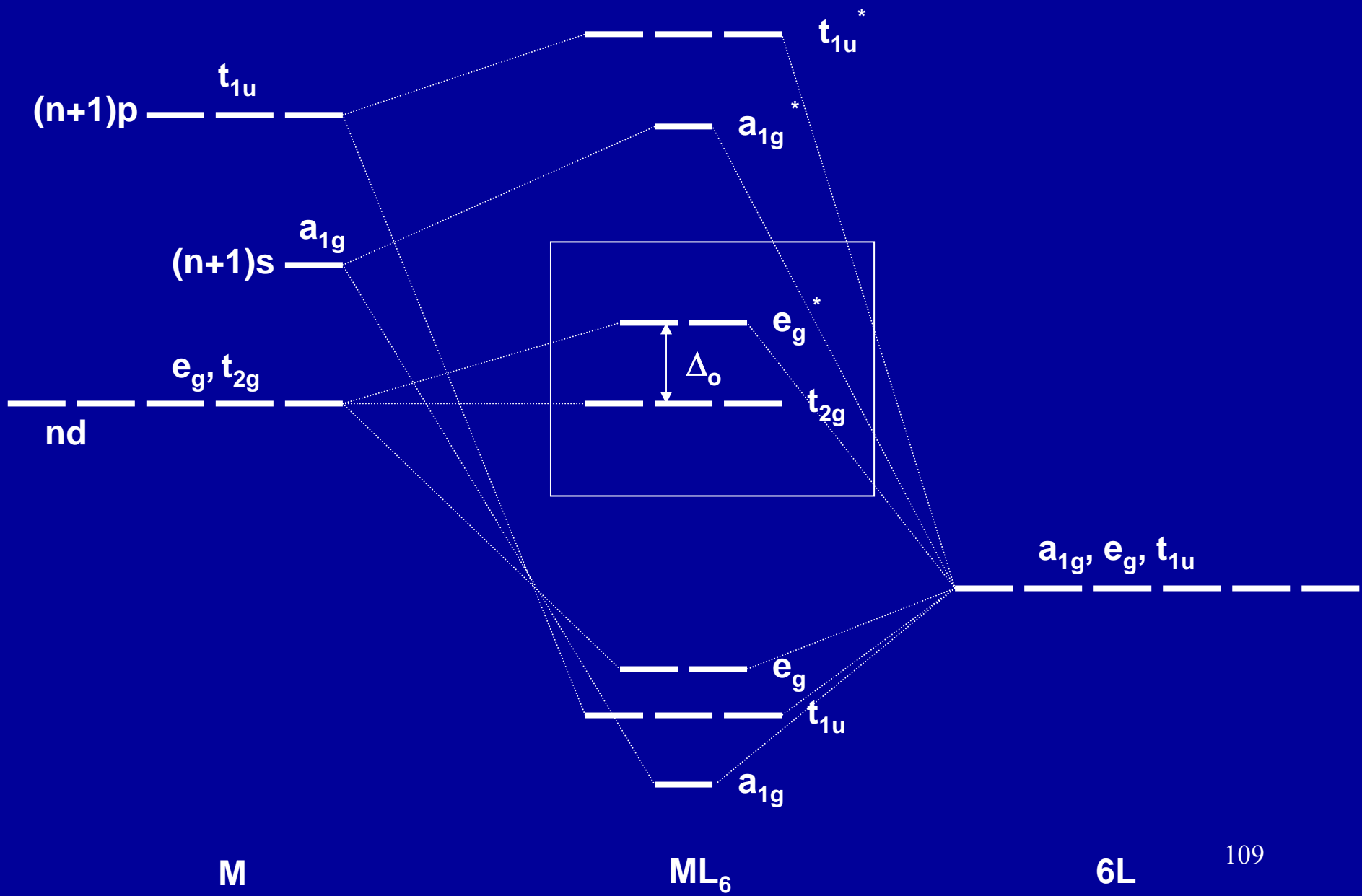


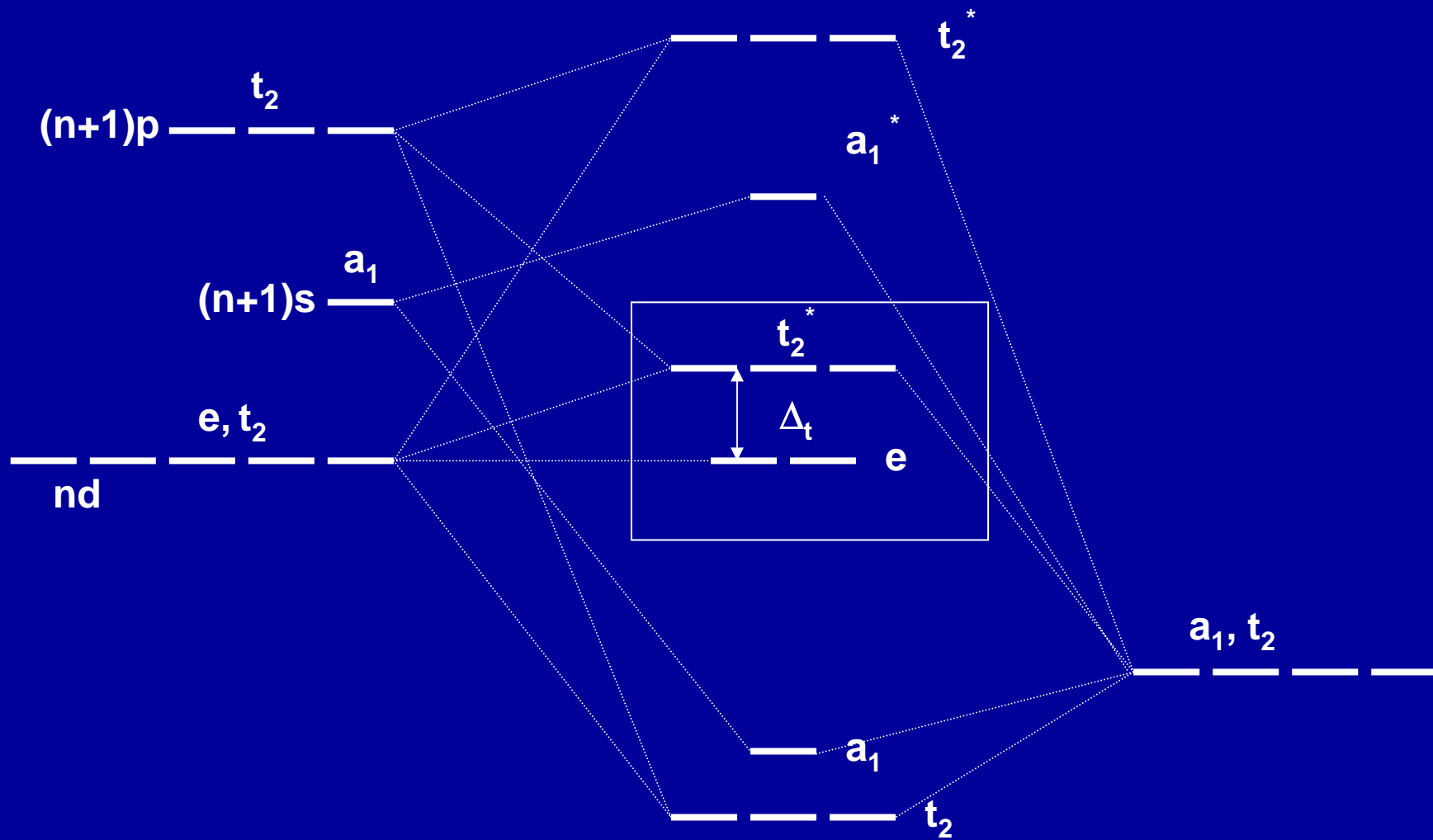
# Nevazebné d-orbitaly



Neexistuje žádná vhodná kombinace AO ligandů



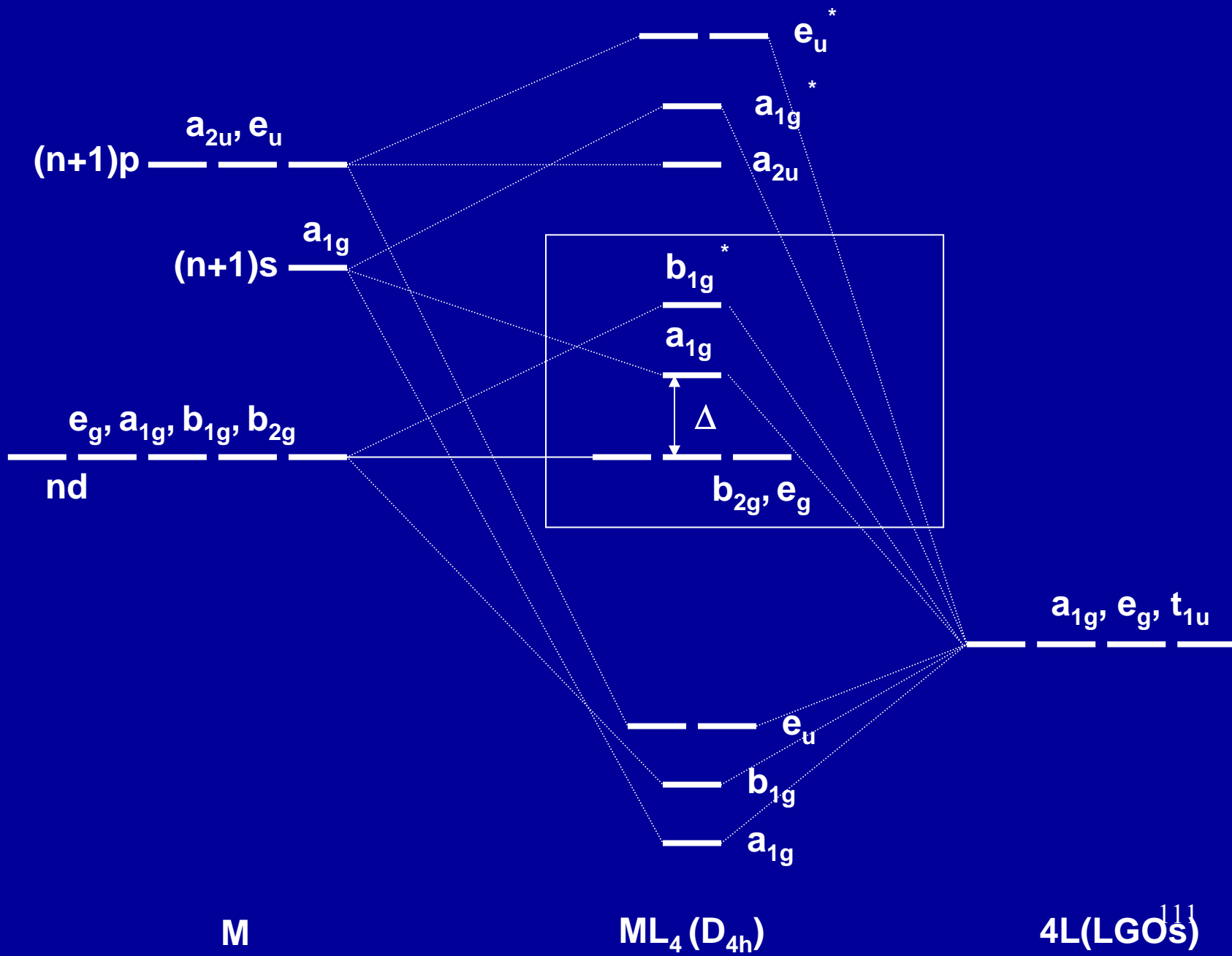




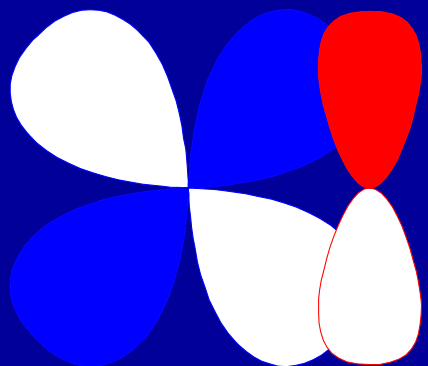
M

$ML_4$

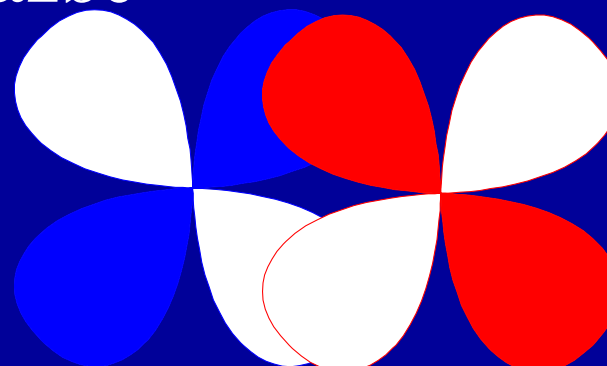
$4L(LGOs)_{110}$



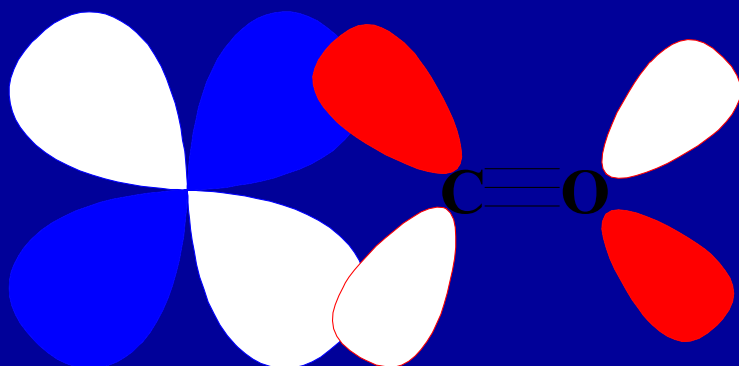
## MO při $\pi$ -vazbě



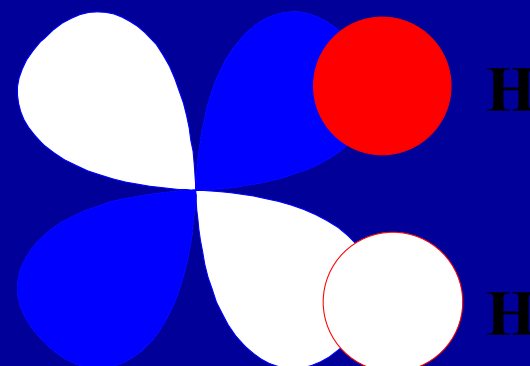
$p\pi-d\pi$   $RO^-$ ,  $RS^-$ ,  $O^{2-}$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $R_2N^-$



$d\pi-d\pi$   $R_3P$ ,  $R_3As$ ,  $R_3S$



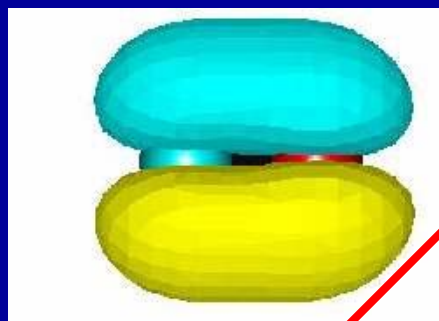
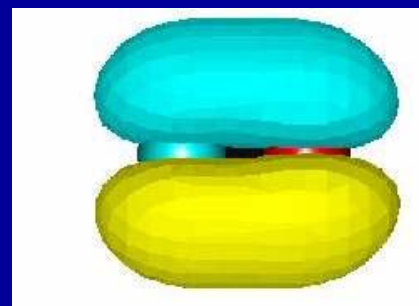
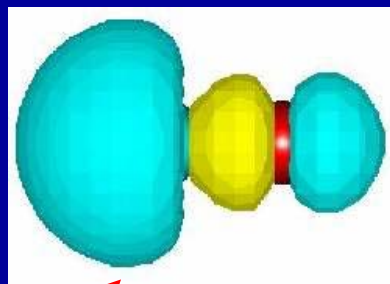
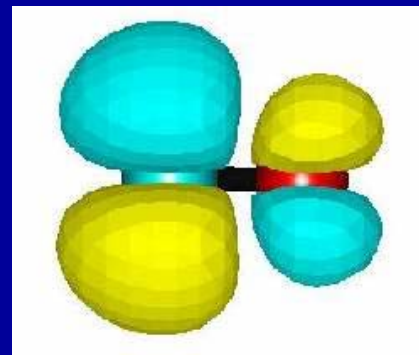
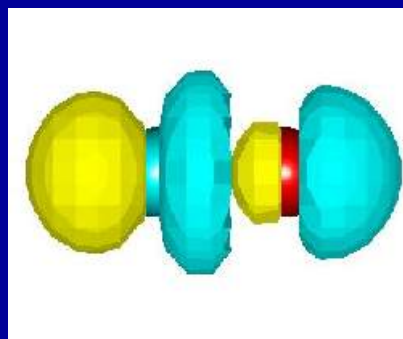
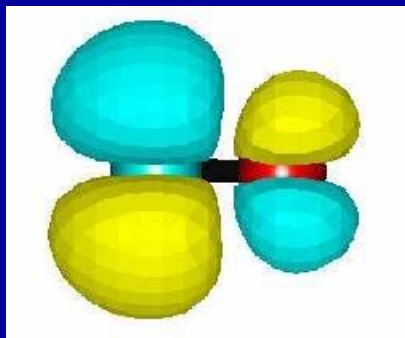
$d\pi-\pi^*$   $CO$ ,  $RNC$ , pyridin,  $CN^-$ ,  $N_2$ ,  $NO_2^-$ , ethylen



$d\pi-\sigma^*$   $H_2$ ,  $R_3P$ , alkany



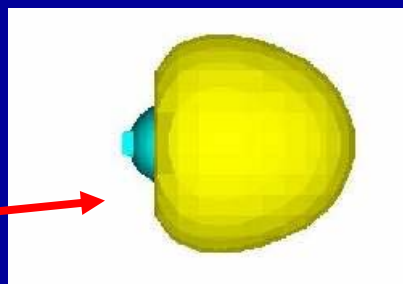
LUMO

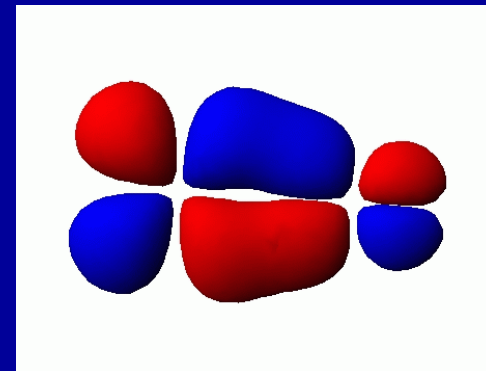
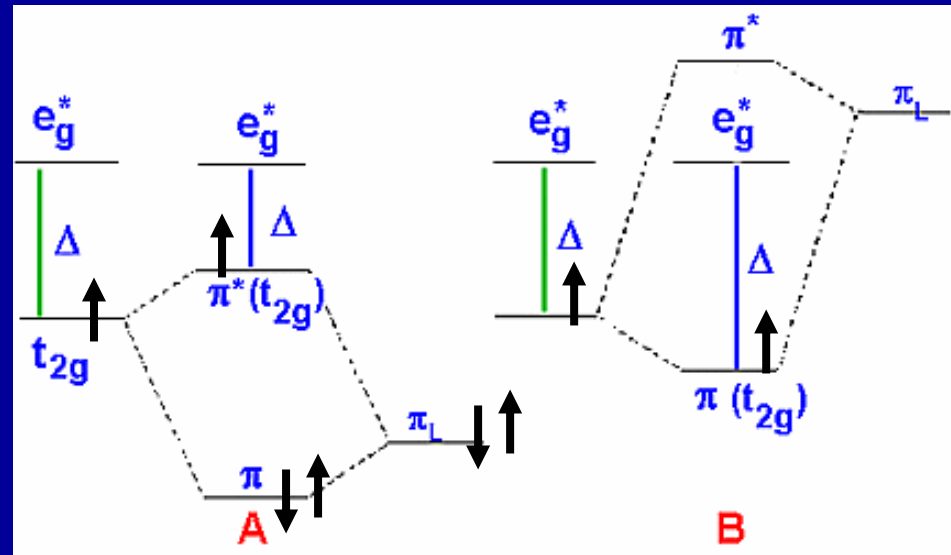
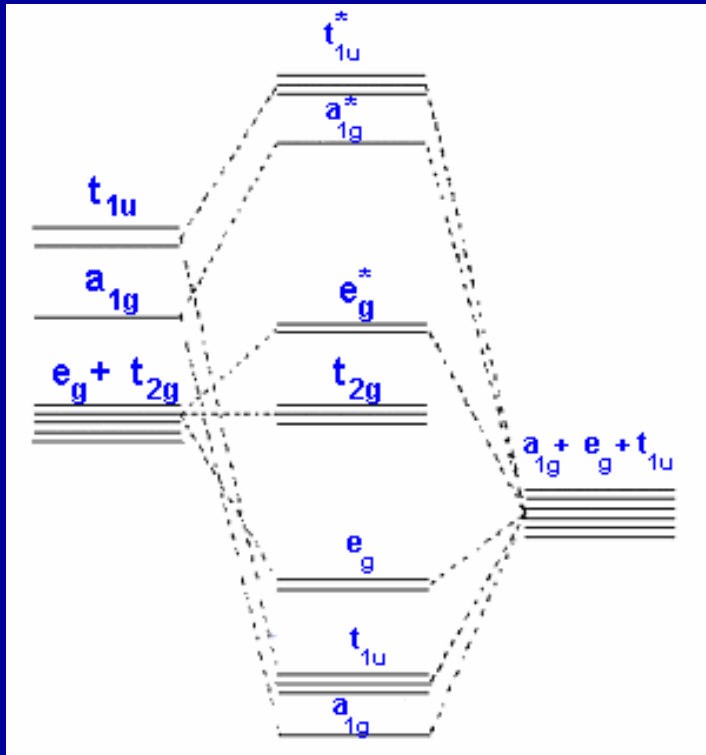
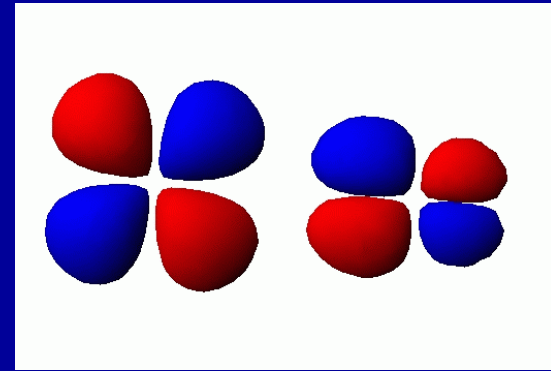


Volný e pár na C  
HOMO

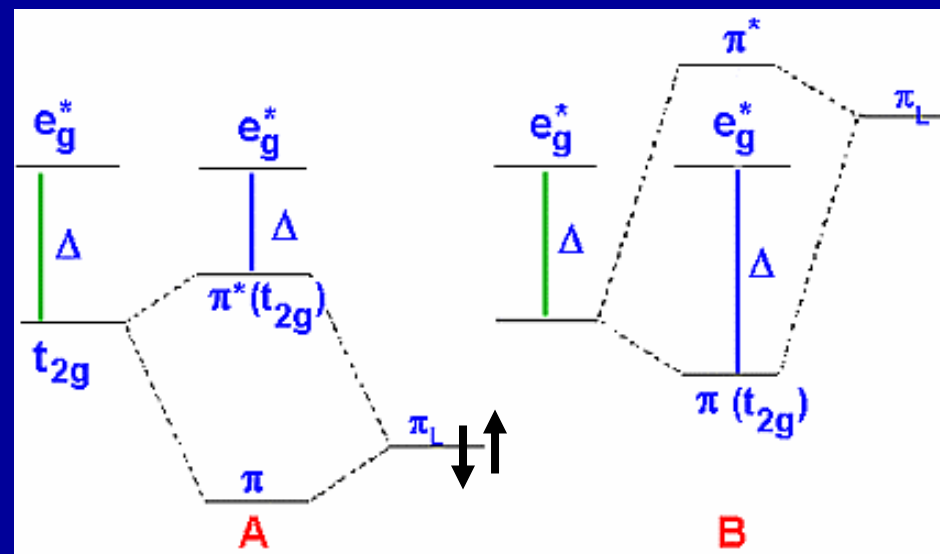


Volný e pár na O





# Ligandy s pi orbitaly

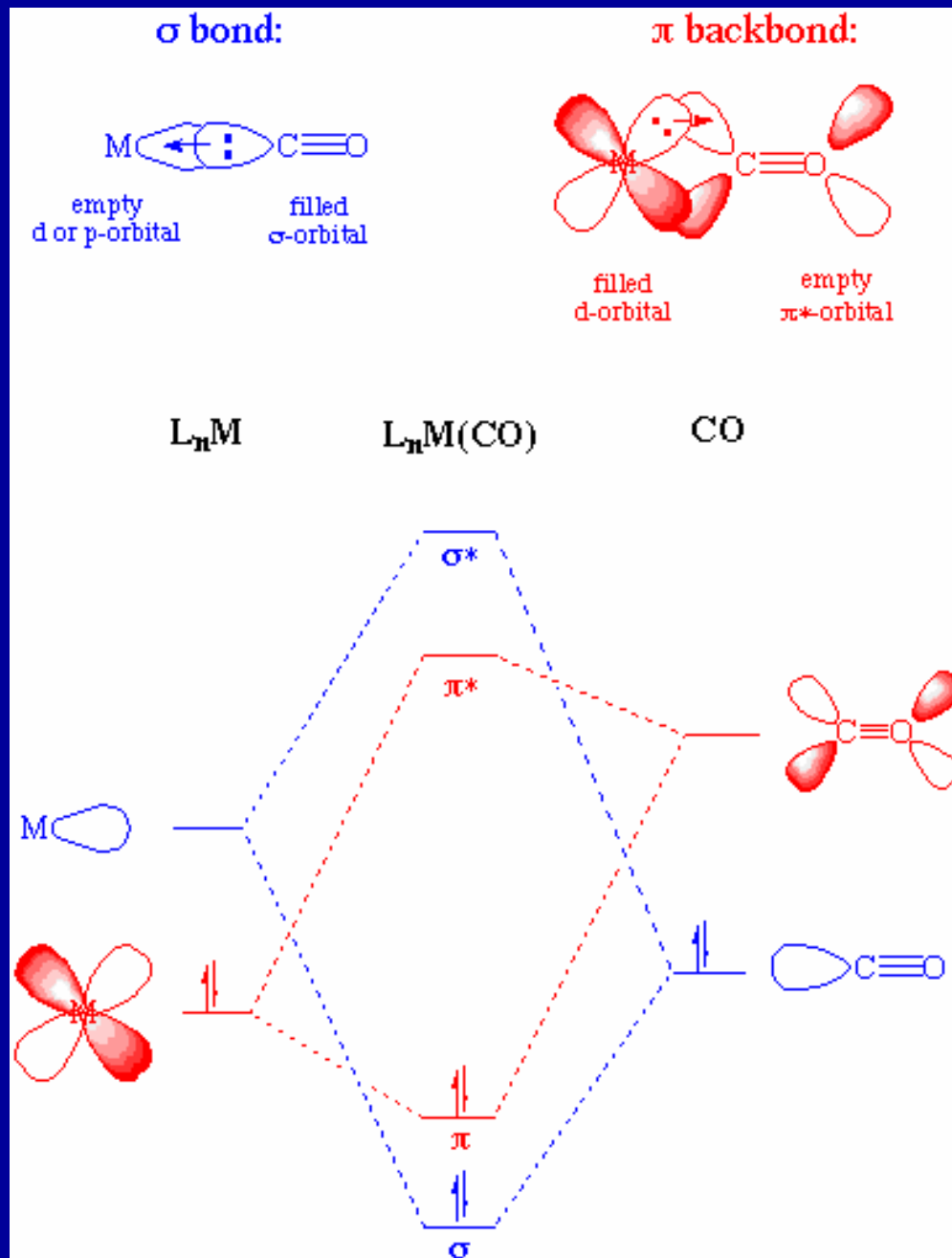


Pi baze

Pi kyselina

Zpětná pi donace  
 $M \rightarrow CO$

Sigma donace  
 $M \leftarrow CO$



# Jahn-Tellerova distorze

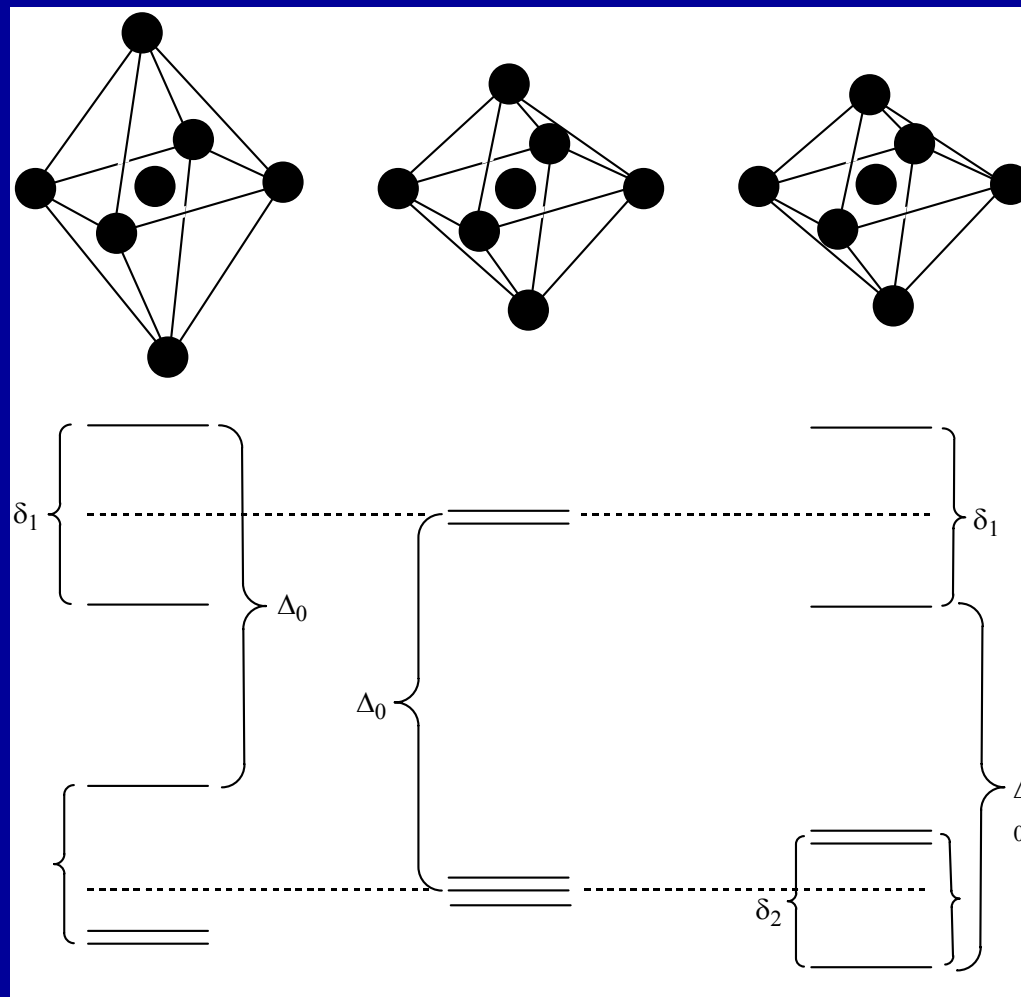
Degenerované hladiny

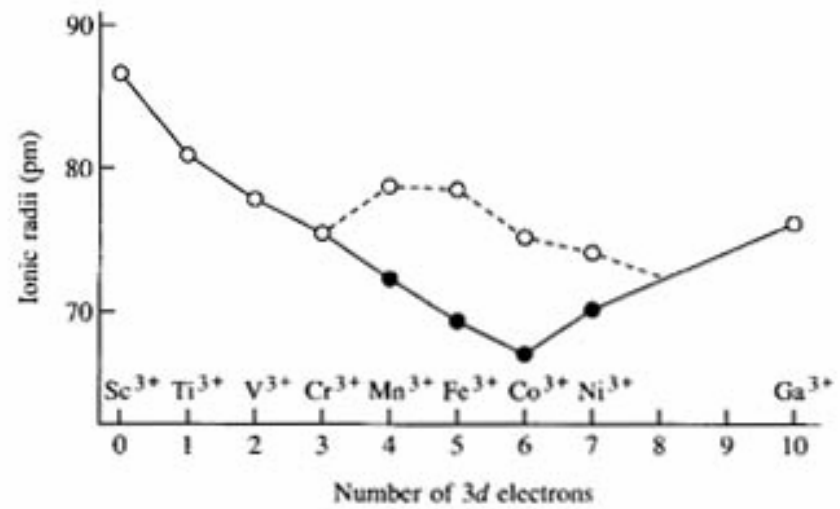
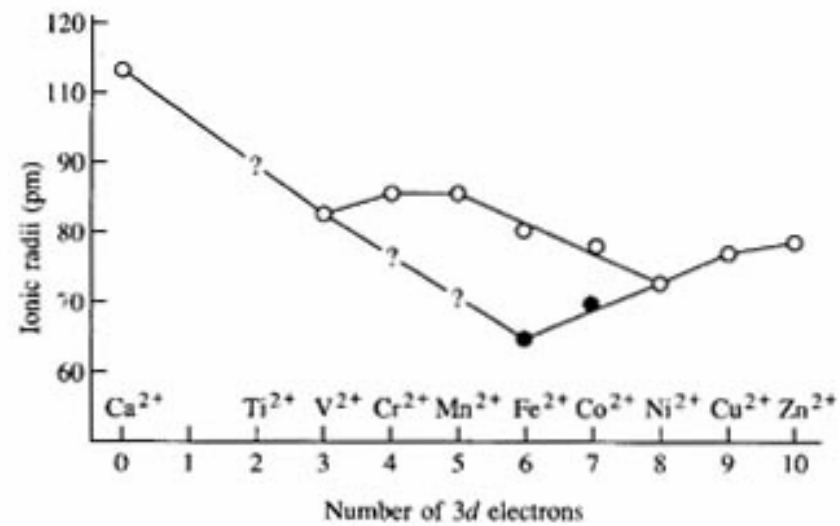
Částečně obsazené

Nelineární molekuly

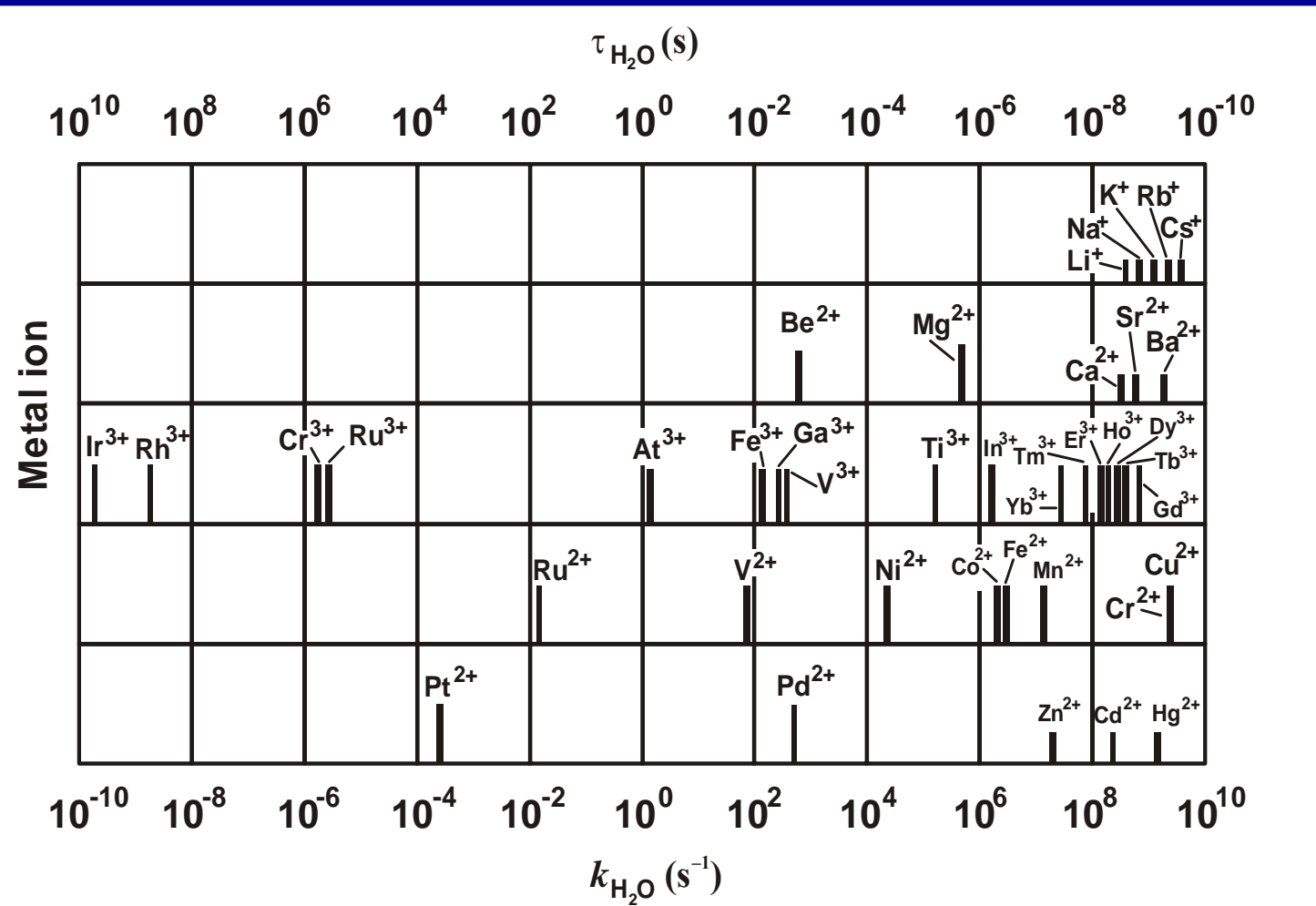
Degenerace se odstraní

deformací





# Kinetika



# Mechanismy reakcí

## Mechanismus

### Disociativní (D)



### Asociativní (A)





## Trans-zeslabení: schopnost ligandu zeslabit vazbu k jinému ligandu v trans poloze

### **Trans-Influence** (thermodynamic effect)

extent to which a ligand weakens the metal-ligand bond of the ligand *trans* to itself

From NMR:  $\text{SiR}_3 > \text{Ph} > \text{R} > \text{P(OR)}_3 > \text{CN} > \text{AsR}_3 > \text{NR}_3 > \text{Cl} > \text{Br} > \text{I}$

From X-ray:  $\text{R} > \text{H} > \text{CR}_2 \approx \text{PR}_3 > \text{AsR}_3 > \text{CO} > \text{C}_2\text{H}_4 > \text{Cl}$

## Trans-efekt: schopnost ligandu urychlit substituci jiného ligandu v trans poloze

### **Trans-Effect** (kinetic effect)

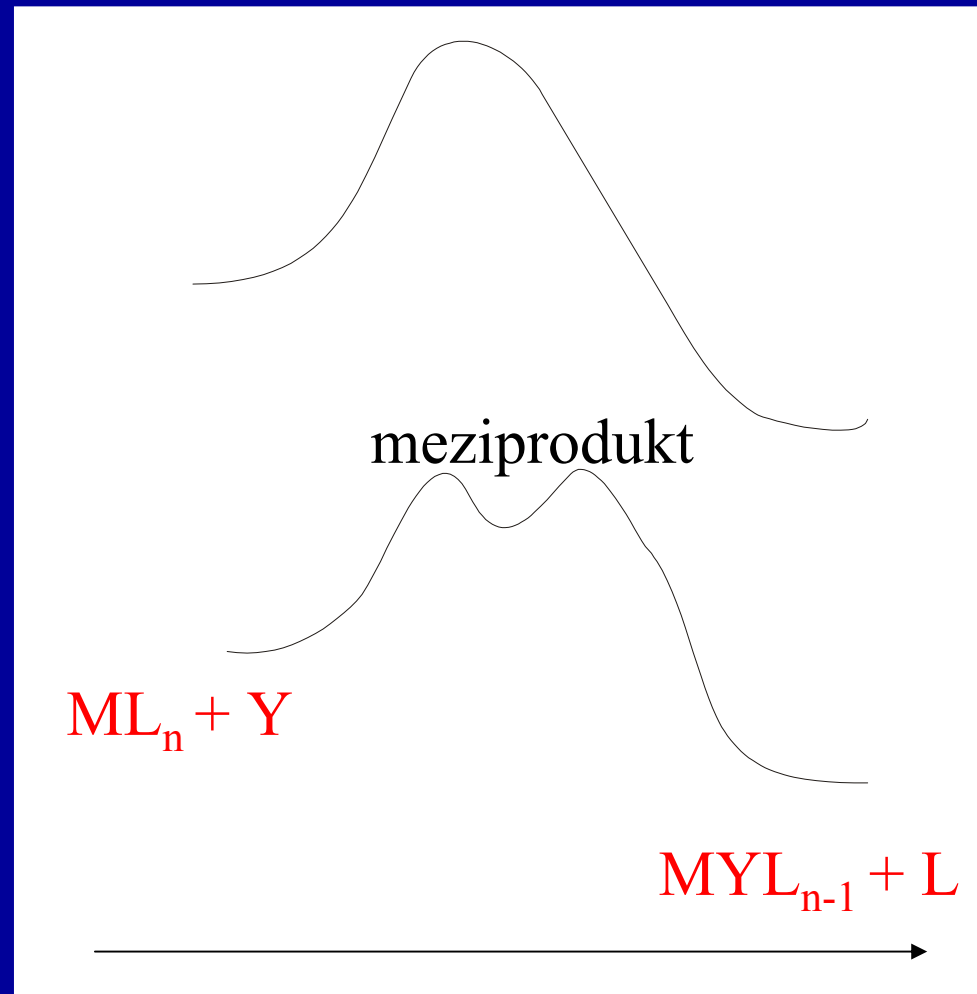
extent to which a ligand effects the rate of exchange of the ligand *trans* to itself

Dissociative mechanism, *trans* effect series = *trans* influence series

Associative mechanism:  $\text{CO}, \text{CN}, \text{C}_2\text{H}_4 > \text{PR}_3 > \text{H} > \text{Me} > \text{Ph} > \text{py} > \text{I} > \text{Br} > \text{Cl} > \text{NH}_3$

# Mechanismy reakcí

Výměnný (I)



# Magnetické vlastnosti komplexů

$$\chi = \frac{M}{H}$$

Magnetická susceptibilita

M = magnetizace

H = intenzita mg pole

Molární magnetická susceptibilita

$$\chi_M = \frac{\chi \cdot M_w}{\rho}$$

$$\chi_M = \frac{N_A \cdot \mu^2}{4kT} = \frac{C}{T}$$

Magnetický moment

$$\mu = 2\sqrt{S(S+1)} = \sqrt{n(n+2)}$$

# Magnetické vlastnosti komplexů

