

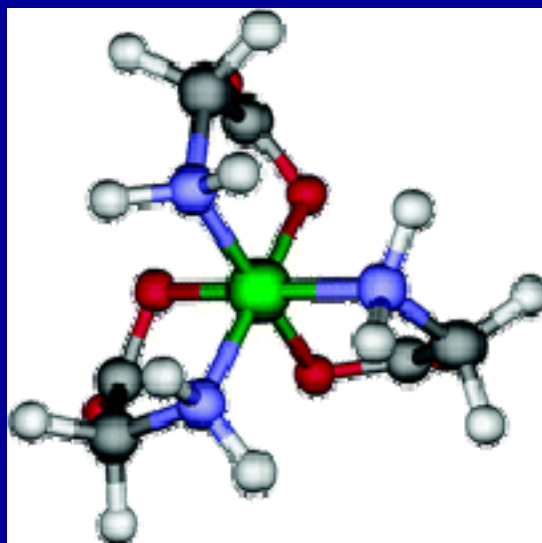
# Koordinační chemie



Alfred Werner  
(1866-1919)

NP za chemii 1913

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



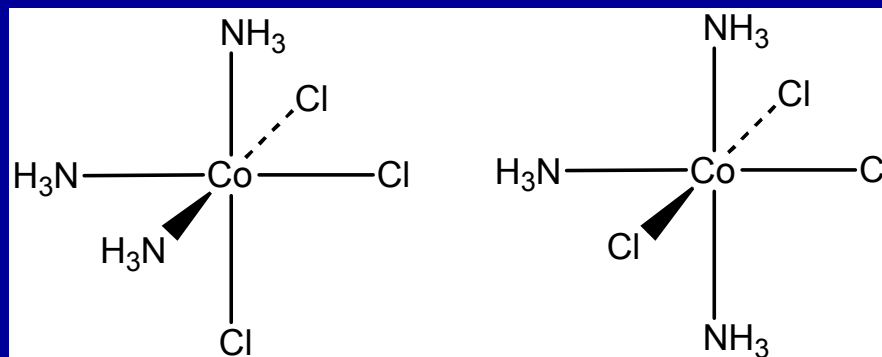
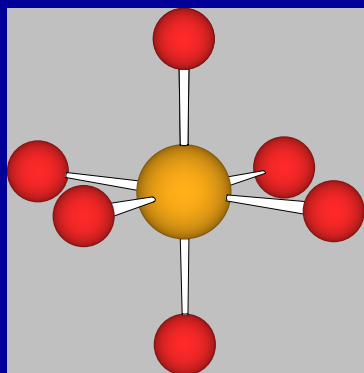
# Koordinální sloučeniny

Experimentální výsledky nesouhlasí s dosavadní teorií

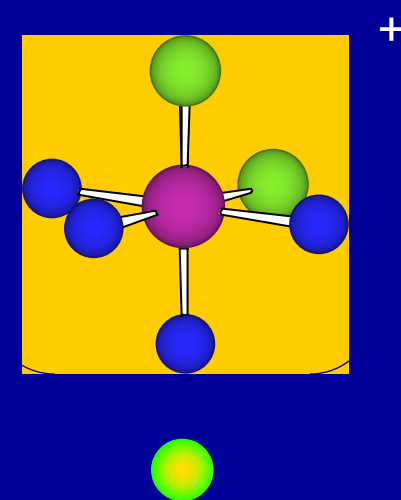
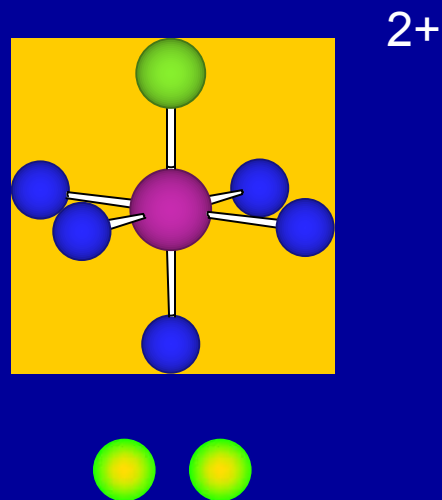
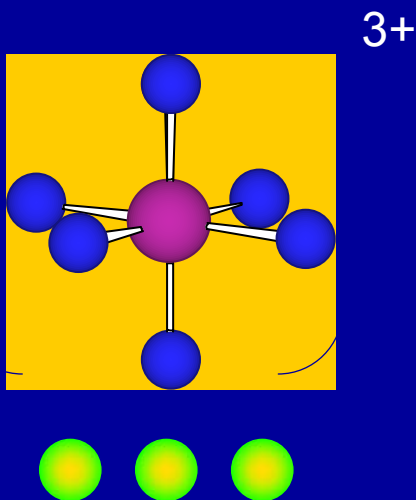
→ nová teorie (model)

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



# Koordináční sloučeniny



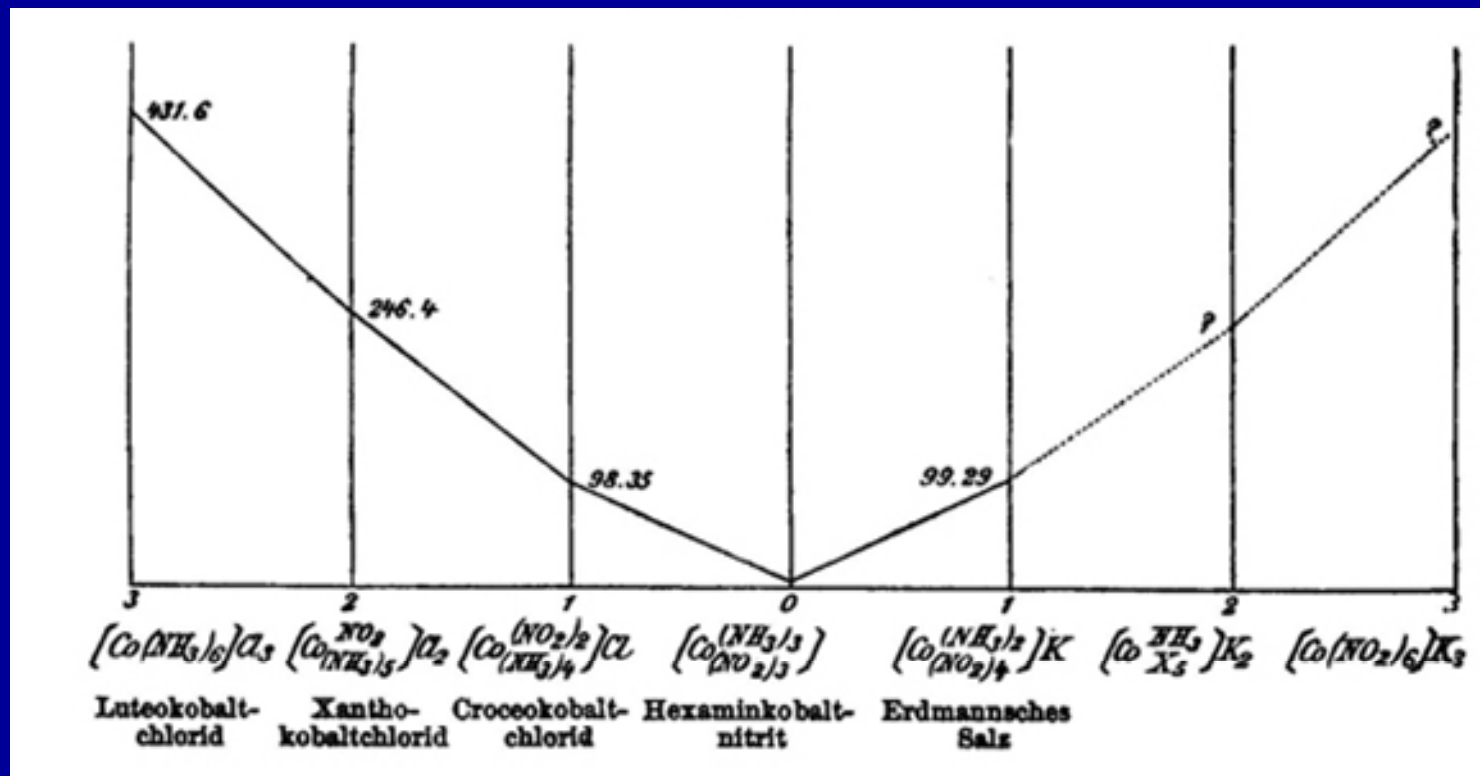
Kov v oxidačním stavu  $n+$  (primární valence)

Komplex má koordinační číslo  $m$  (sekundární valence)

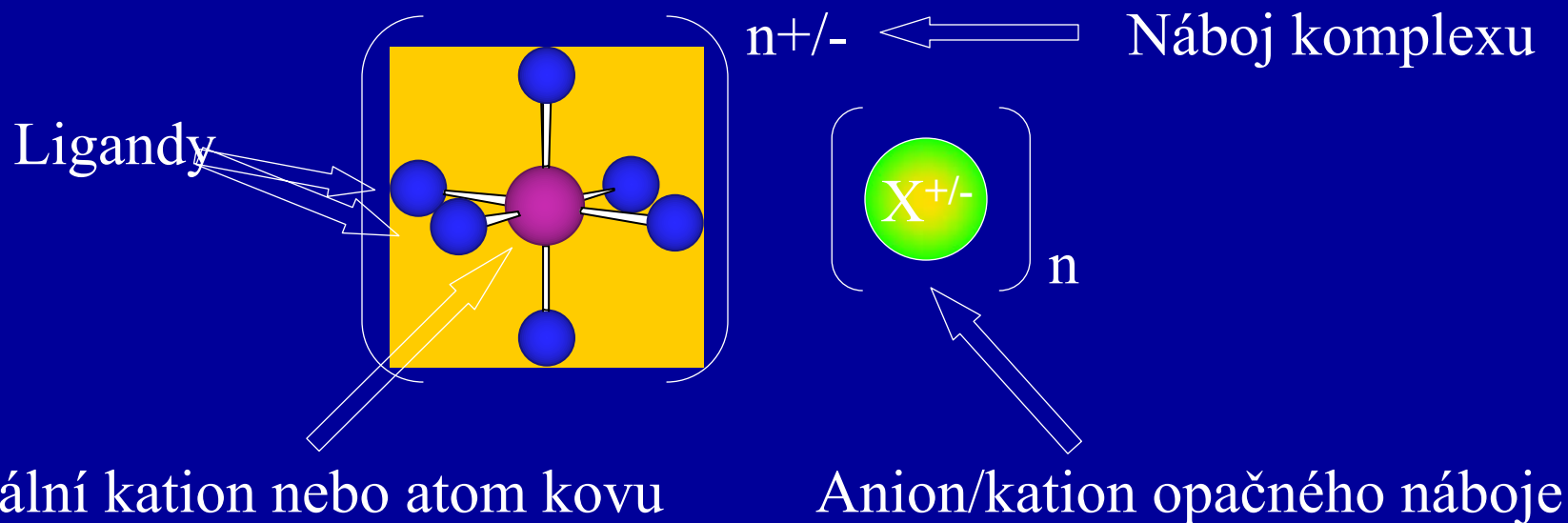
Ligandy vázány k centrálnímu atomu donor-akceptorovými vazbami

# Koordinační sloučeniny

Elektrická vodivost roztoků komplexních sloučenin



# Koordináční 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 =

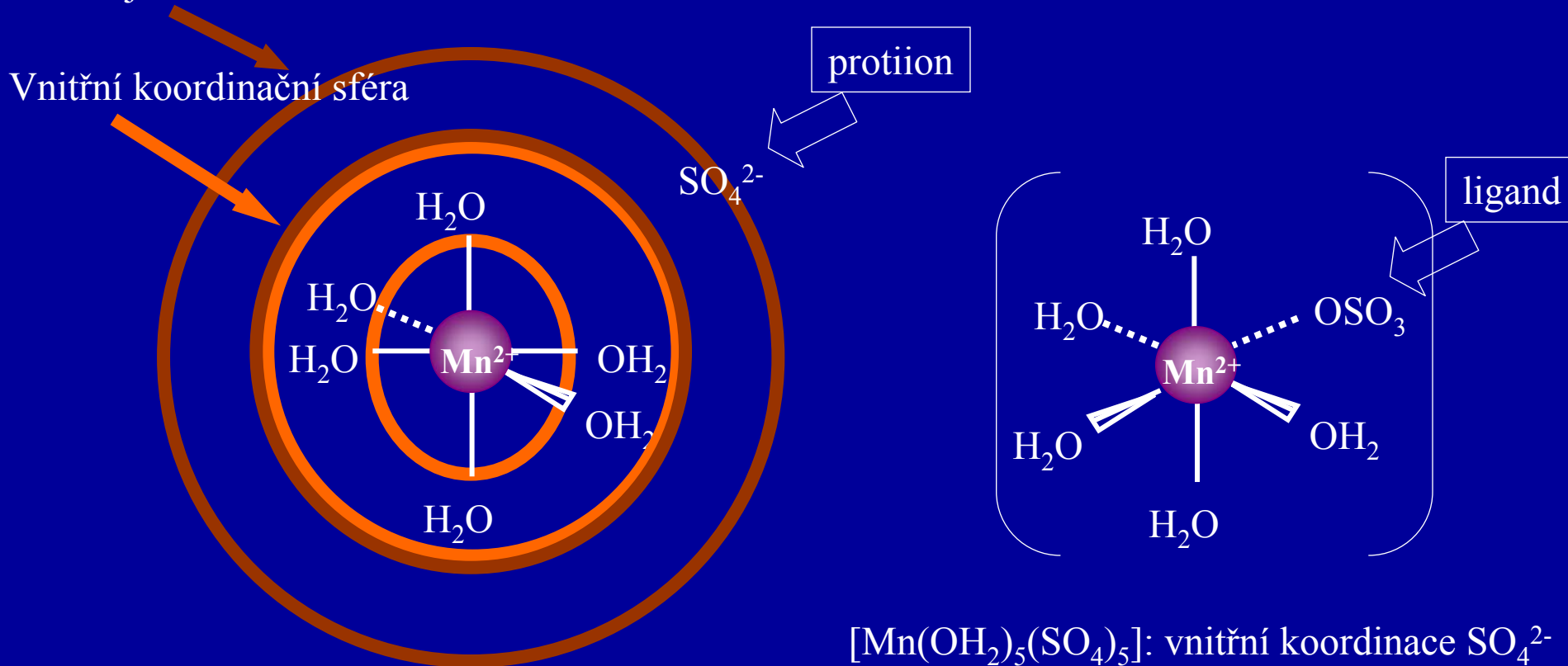
ligandy přímo vázané k centrálnímu atomu

Vnější koordinační sféra =

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

Vnější koordinační sféra

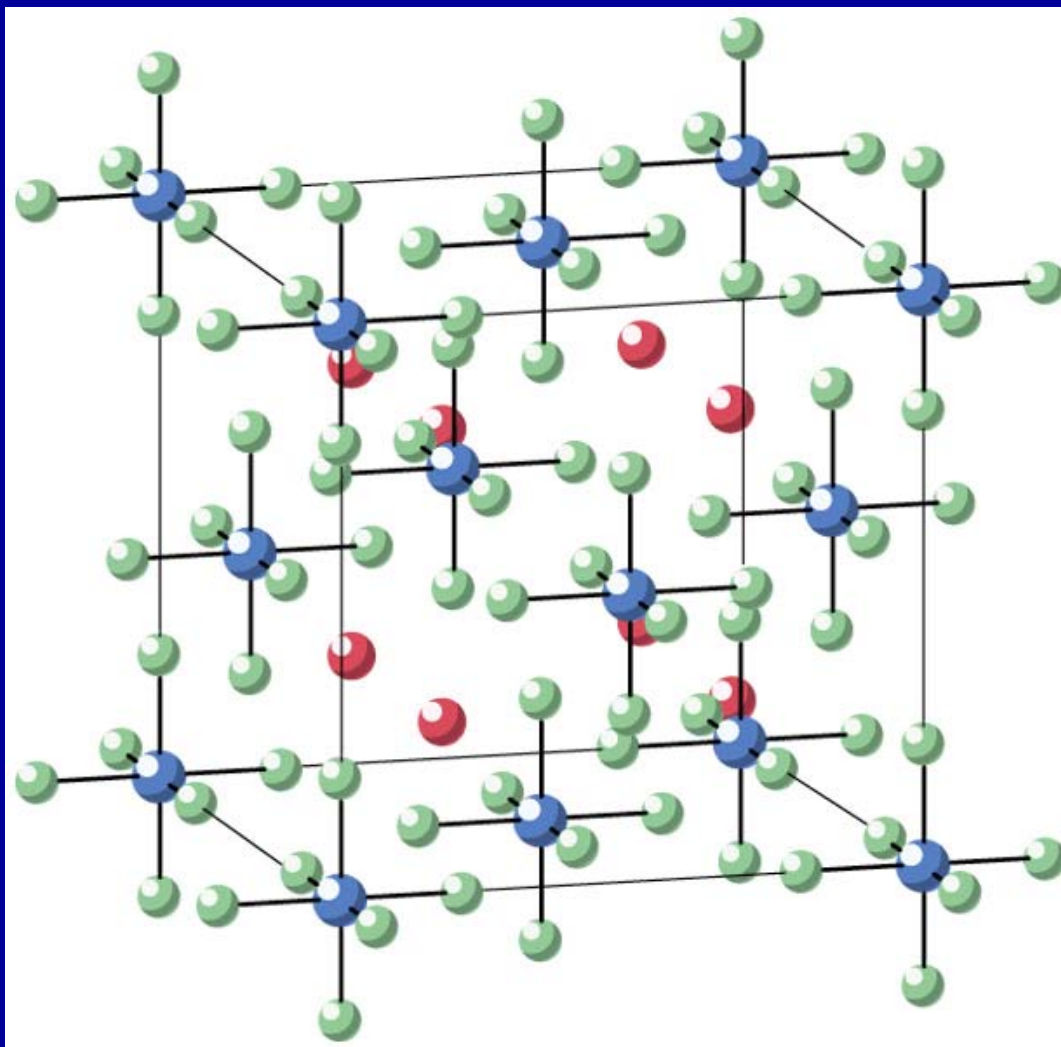
Vnitřní koordinační sféra



$[Mn(OH_2)_5(SO_4)_5]$ : vnitřní koordinace  $SO_4^{2-}$

$[Mn(OH_2)_6][SO_4]$ : vnější koordinace  $SO_4^{2-}$

# Koordinační sloučeniny v pevné fázi



## Změna pořadí energetických hladin

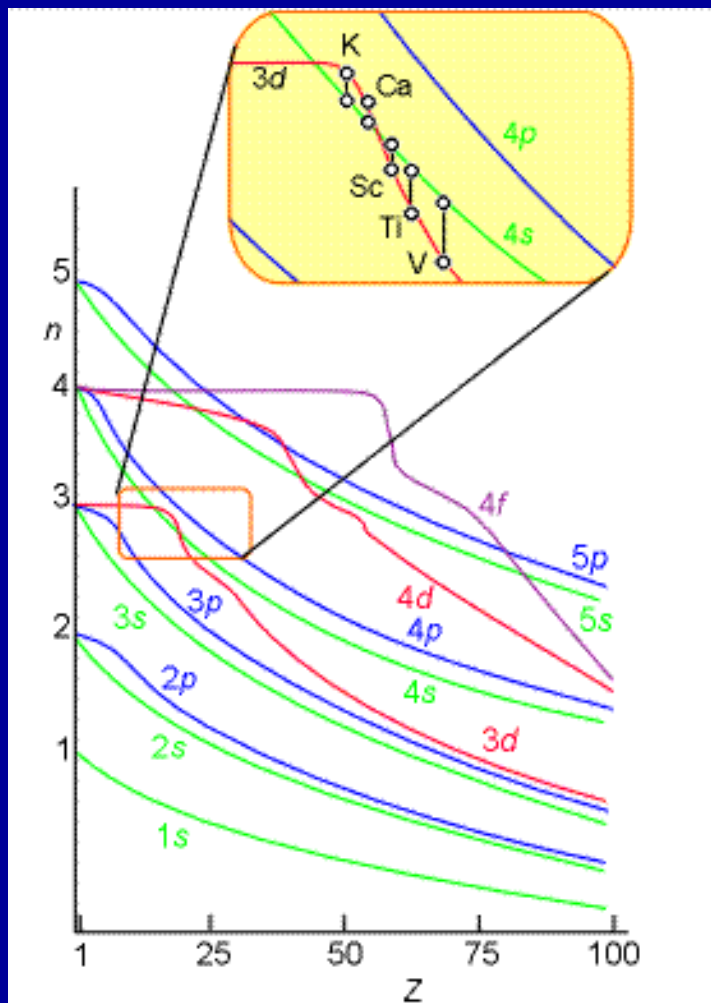
Ar [Ne]  $3s^2 3p^6 (4s^0)$

K [Ar]  $4s^1 (3d^0 4p^0)$

Ca [Ar]  $4s^2 (3d^0 4p^0)$

Sc [Ar]  $3d^1 4s^2 (4p^0)$

Ti [Ar]  $3d^2 4s^2 (4p^0)$





## Vyšší stabilita zpola zaplněných d-orbitalů

	3d	4s
Sc		
Ti		
V		
Cr		
Mn		
Fe		
Co		
Ni		
Cu		
Zn		

Cr [Ar] 3d<sup>5</sup> 4s<sup>1</sup> (4p<sup>0</sup>)



Cu [Ar] 3d<sup>10</sup> 4s<sup>1</sup> (4p<sup>0</sup>)



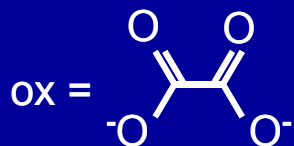
## Oxidační stavy přechodných kovů

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



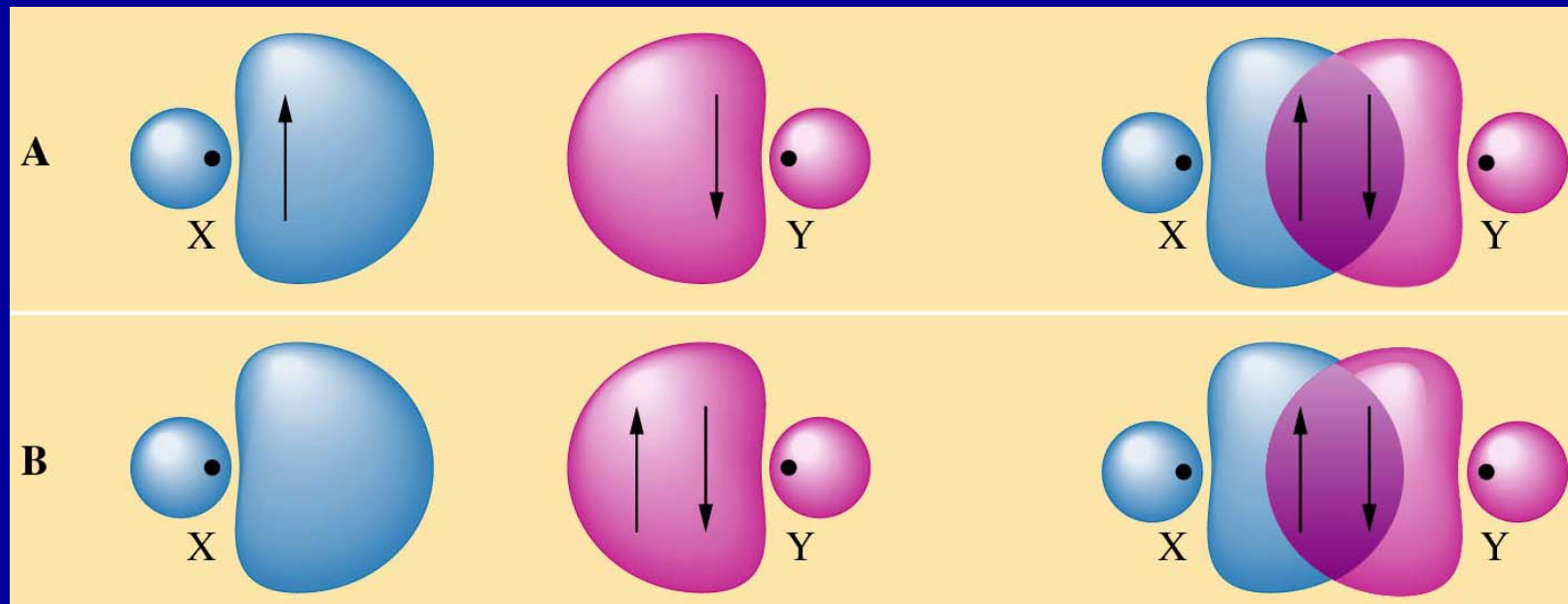


																	H	He
Li	Be												B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	110	111	112		114					
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

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



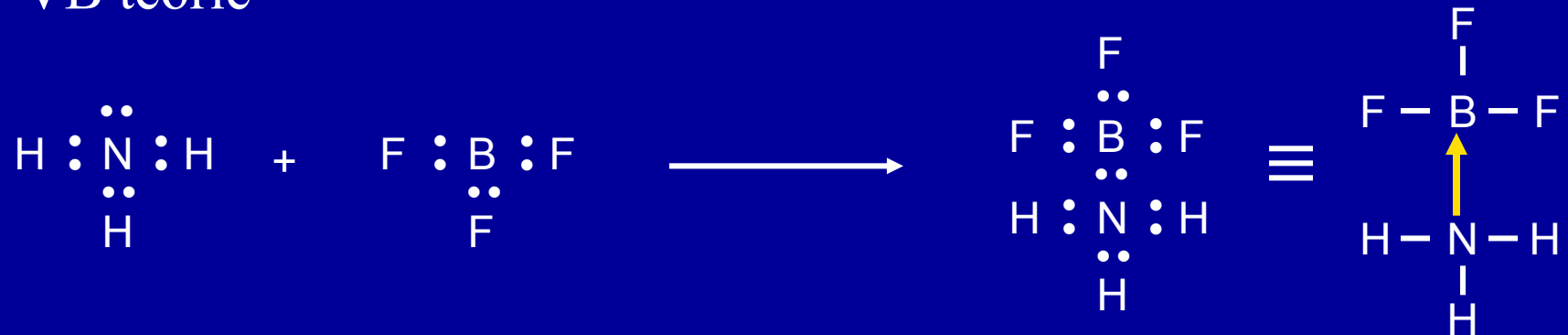
**Akceptor**  
**Volný orbital**

**Donor**  
**Volný e pár**

**Kovalentní vazba**

# Donor-akceptorová vazba

VB teorie

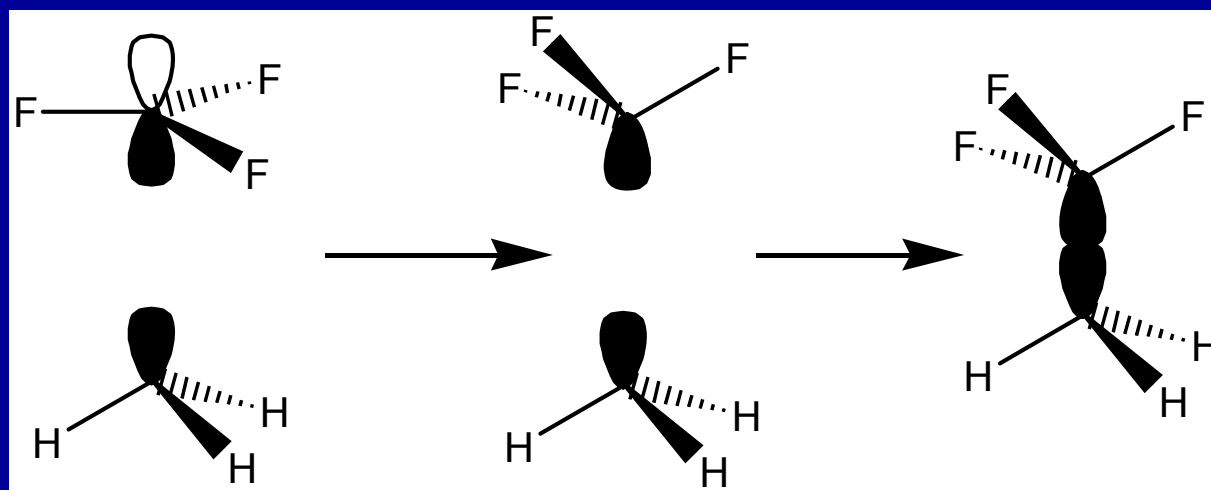


 Donor-akceptorová vazba

# Donor-akceptorová vazba

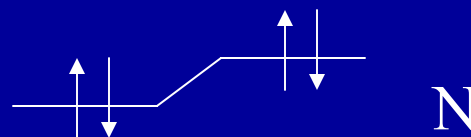


VB teorie



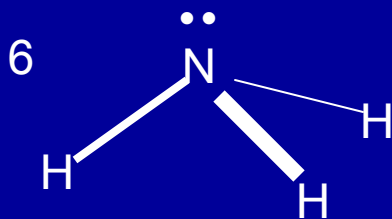
MO teorie

B

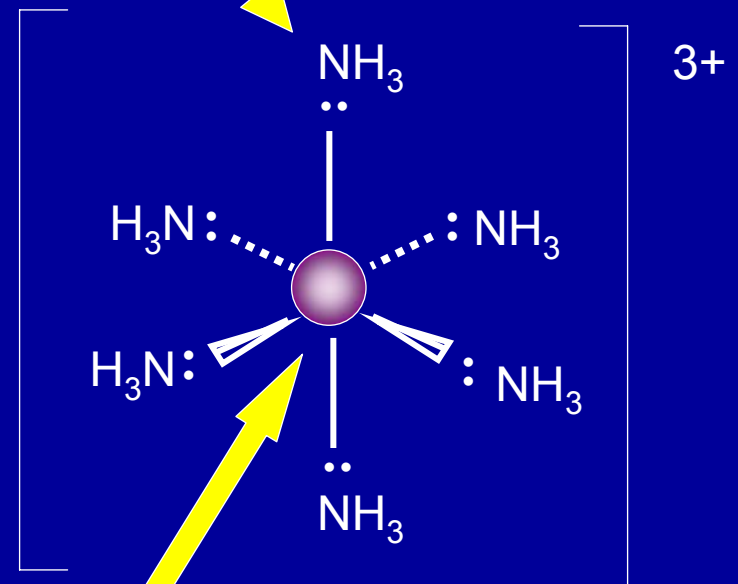


# Donor-akceptorová vazba

VB teorie



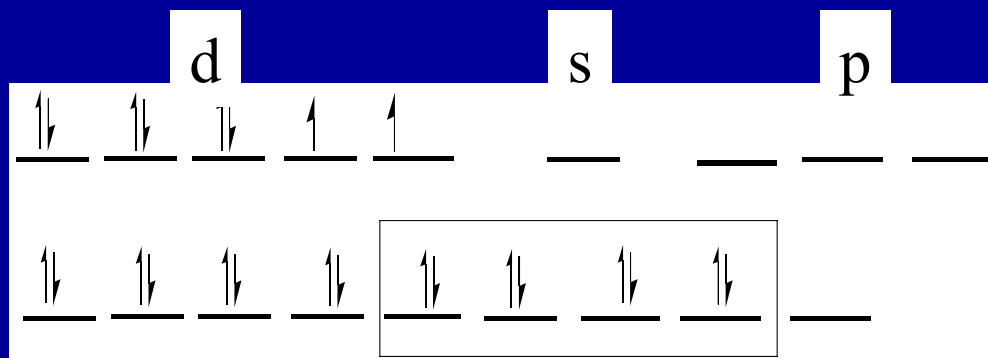
"Lewisovská báze"



Každý ligand poskytne do vazby 2 elektrony

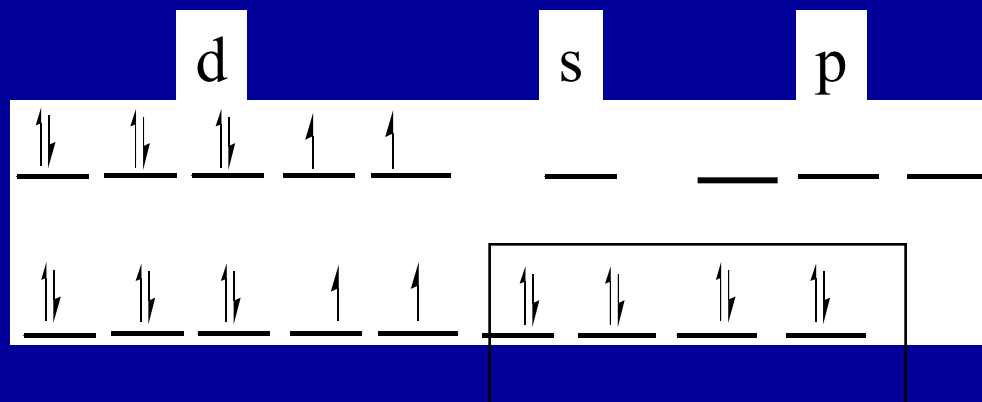
"Lewisovská kyselina"





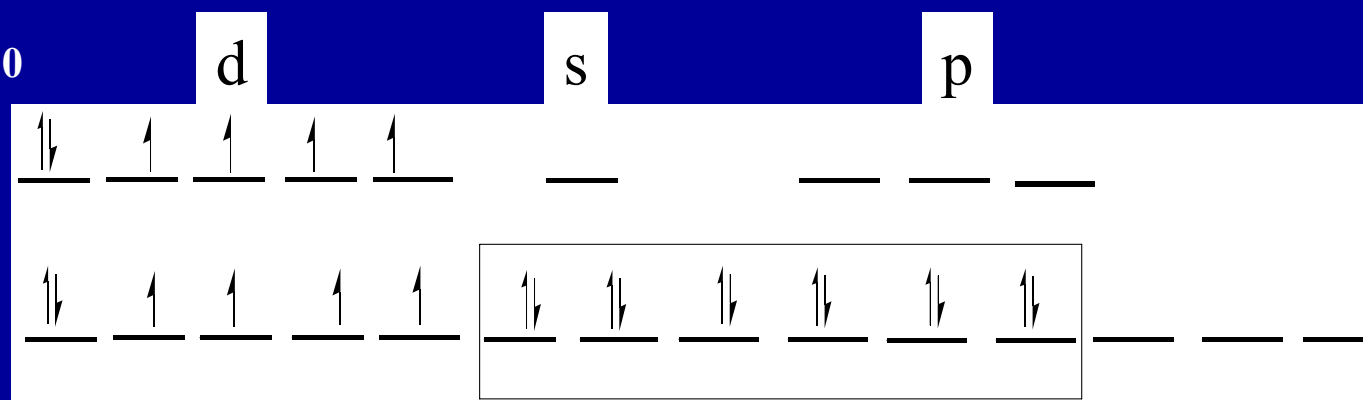
$dsp^2$  hybridní orbitaly

elektrony z Cl<sup>-</sup>, čtvercový



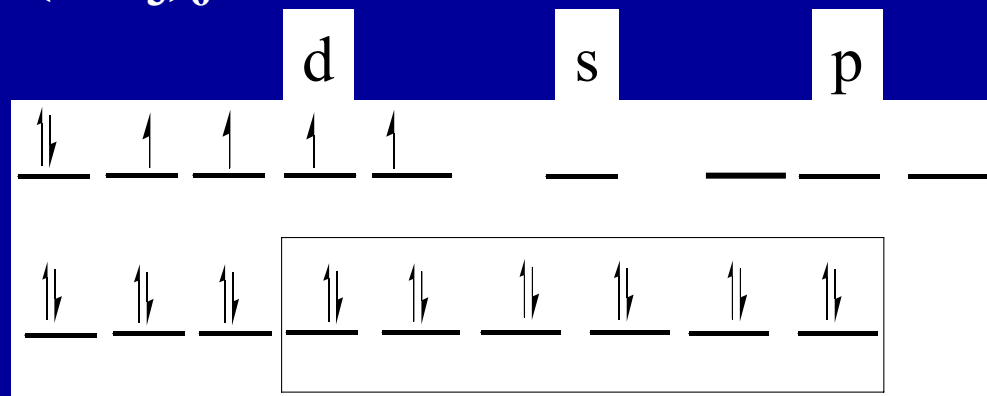
$sp^3$  hybridní orbitaly

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



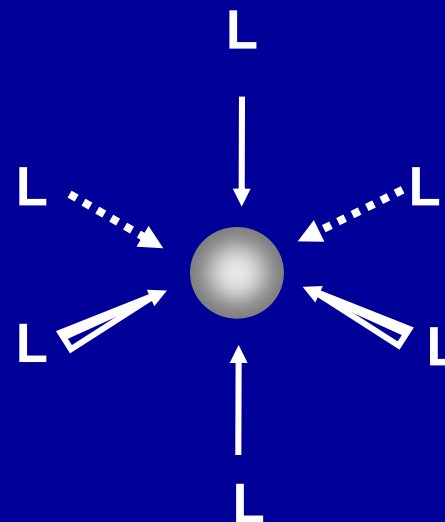
$sp^3d^2$  hybridní orbitály

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



$d^2sp^3$  hybridní orbitály

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



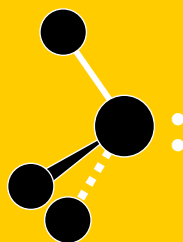
# Monodentátní ligandy

CO  
oxid uhelnatý

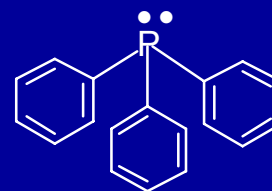
Cr



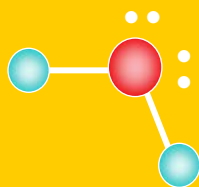
$\text{Ni}(\text{CO})_4$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{Mo}(\text{CO})_6$



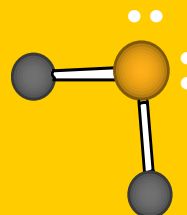
$\text{NH}_3$   
amoniak



$\text{PPh}_3$   
fosfan



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



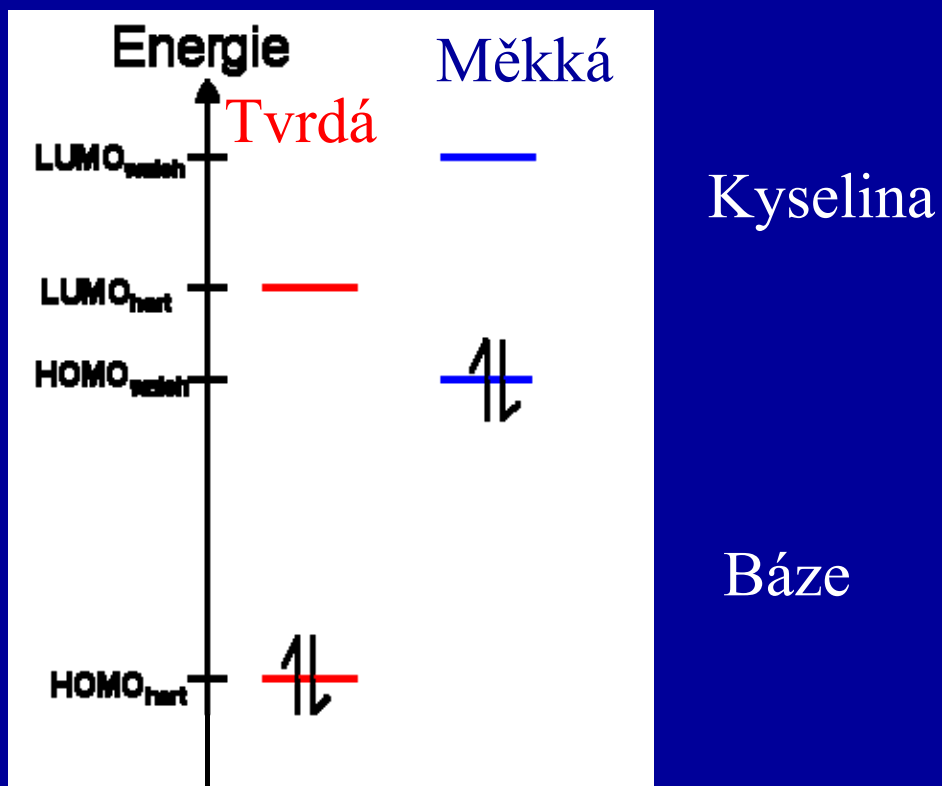
$\text{SR}_2$   
thioether

# 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

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

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

## HSAB



Měkké donorní atomy

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

Velké donorní atomy

Málo elektronegativní

Snadno polarizovatelné

stabilní komplexy

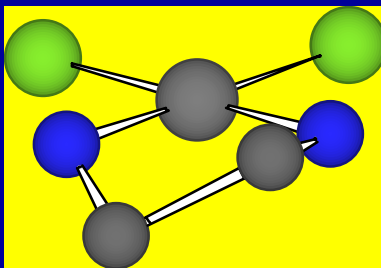
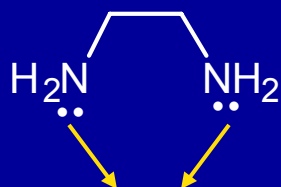
Měkké kovy

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

Velké atomy (2. a 3. přech. řada)

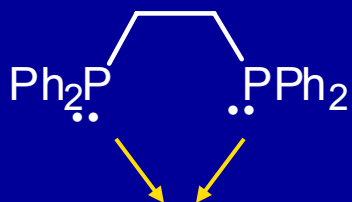
Malý náboj

# Neutrální bidentátní ligandy

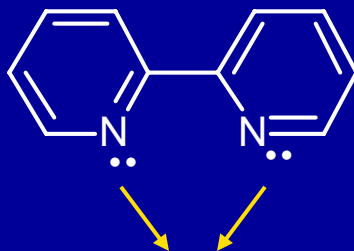


pětičlenný chelátový cyklus  
čtvercově planární komplex

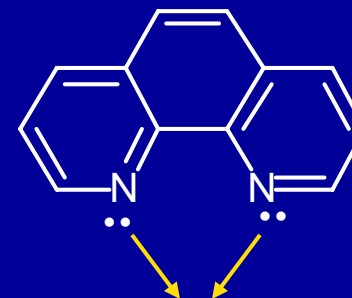
1,2-diaminoethan = ethylendiamin = en



1,2-difenylofosfinoethan  
dppe



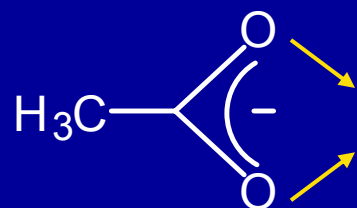
2,2'-bipyridin  
bipy



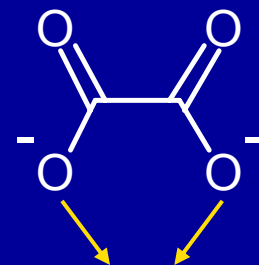
1,10-fenanthrolin  
phen

Chelatace - ligandy jsou vázány velmi pevně k centrálnímu atomu

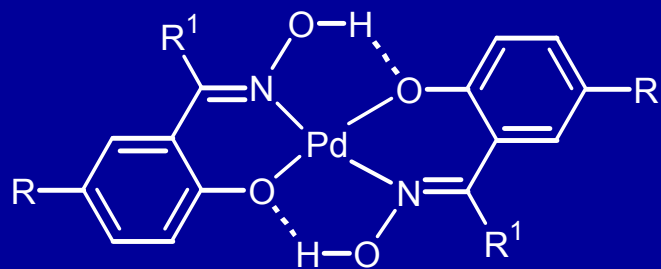
## Aniontové bidentátní ligandy



acetát =  $\text{ac}^-$

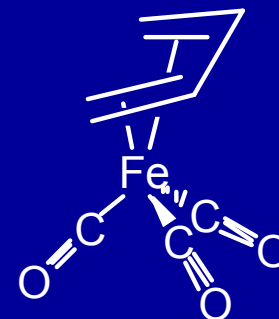


oxalát =  $\text{ox}^{2-}$



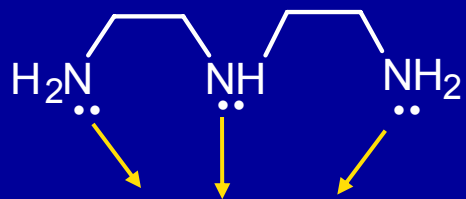
komplex Pd(II)-oxim

$\pi$ -donorní bidentátní ligand



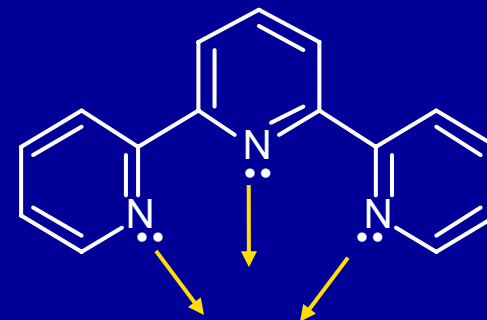
$[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_6)]$

# Tridentátní ligandy



diethylentriamin

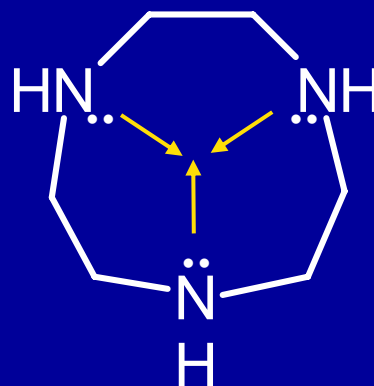
dien



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

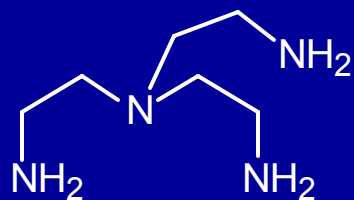
tpy

1,2,4-triazacyklononan  
makrocyclický ligand





# Tetradentátní ligandy

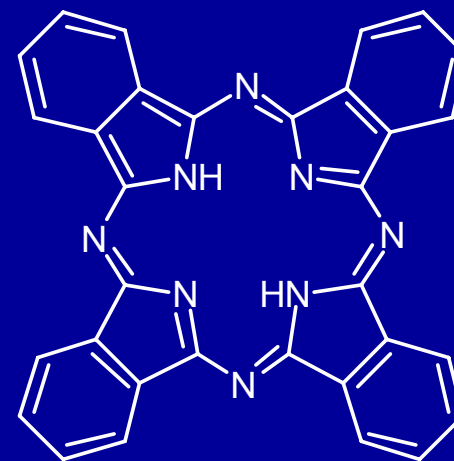


tris(2-aminoethyl)amin

tren



porfyrin



ftalocyanin

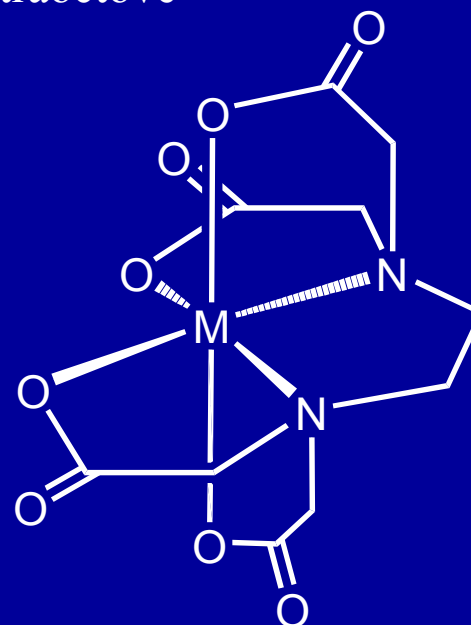
# Multidentátní ligandy

tetraanion kyseliny ethylendiamintetraoctové

EDTA



Hexadentátní



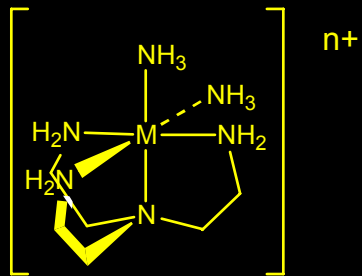
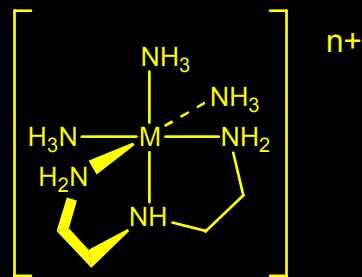
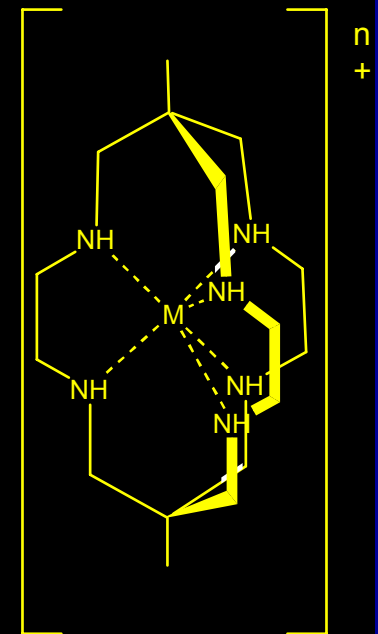
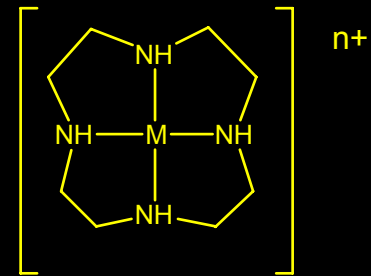
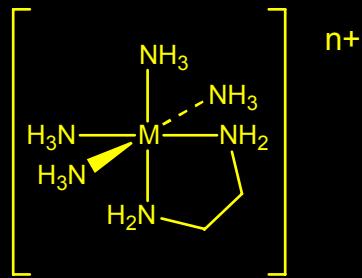
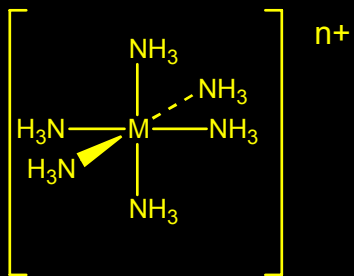
# Topologie komplexů

komplexace

chelatace

makrocyclický efekt

kryptátový efekt



# Názvosloví komplexních sloučenin

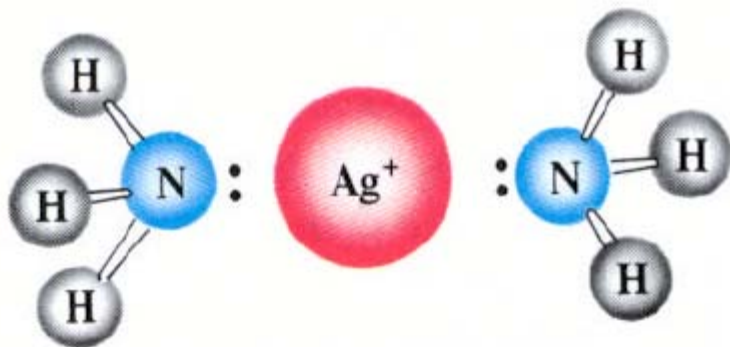
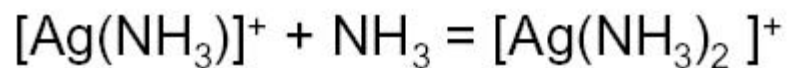
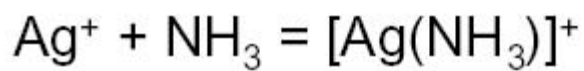
$\text{H}_2\text{O}$	voda	<b>aqua-</b>
$\text{NH}_3$	amoniak	<b>ammin-</b>
$\text{CO}$	oxid uhelnatý	<b>karbonyl-</b>
$\text{SO}_4^{2-}$	síran	sulfato-
$\text{S}_2\text{O}_3^{2-}$	thiosíran	thiosulfato-
$\text{PO}_4^{3-}$	fosforečnan	fosfato-
$\text{H}_2\text{PO}_4^-$	dihydrogenfosforečnan	dihydrogefosfato-
$\text{CH}_3\text{COO}^-$	octan	acetato-
$\text{C}_2\text{O}_4^{2-}$	šťavelan	oxalato-
$(\text{CH}_3)_2\text{N}^-$	dimethylamid	dimethylamido-
$\text{F}^-$	fluorid	<b>fluoro-</b>
$\text{O}^{2-}$	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	<b>kyano-</b>
$\text{SCN}^-$	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
$[Co(NH_3)_3Cl_3]$	<b>komplex</b> 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



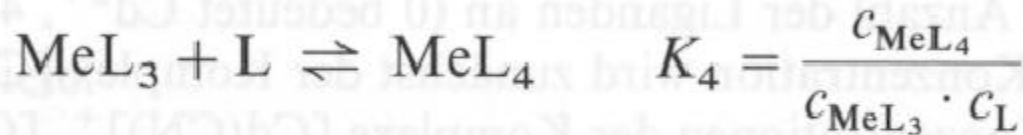
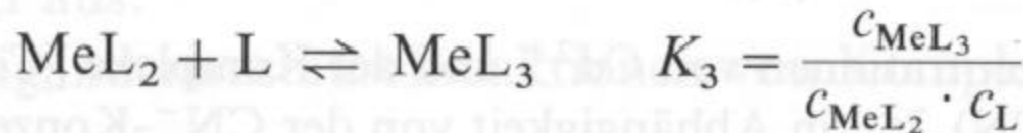
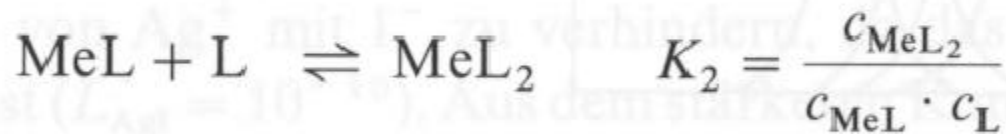
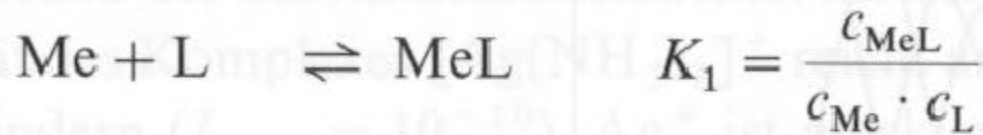
Vysoká hodnota  $K$   
= stabilní komplex

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

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

# Stabilita komplexů

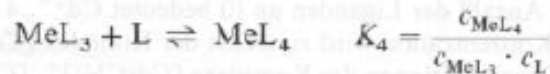
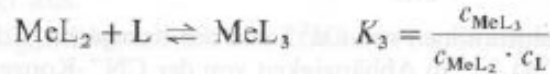
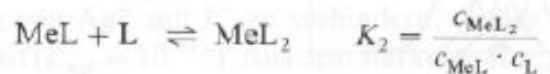
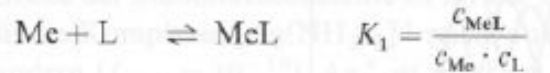
Konstanta stability komplexu  $ML_n$



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

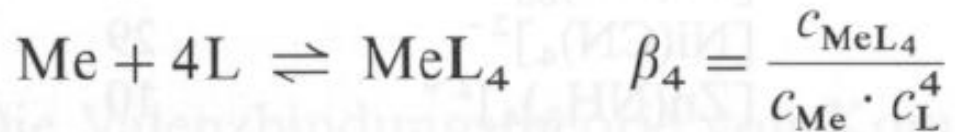
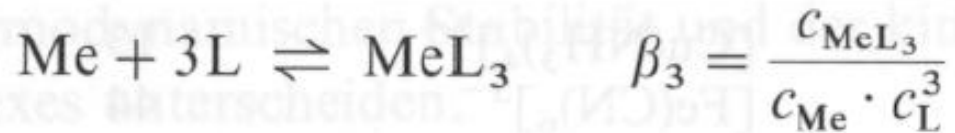
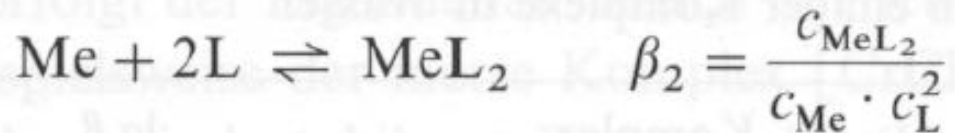
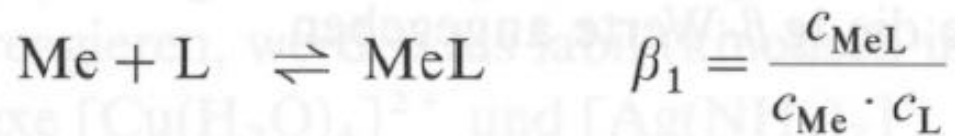
# Stabilita komplexů

## Celková konstanta stability komplexu



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

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

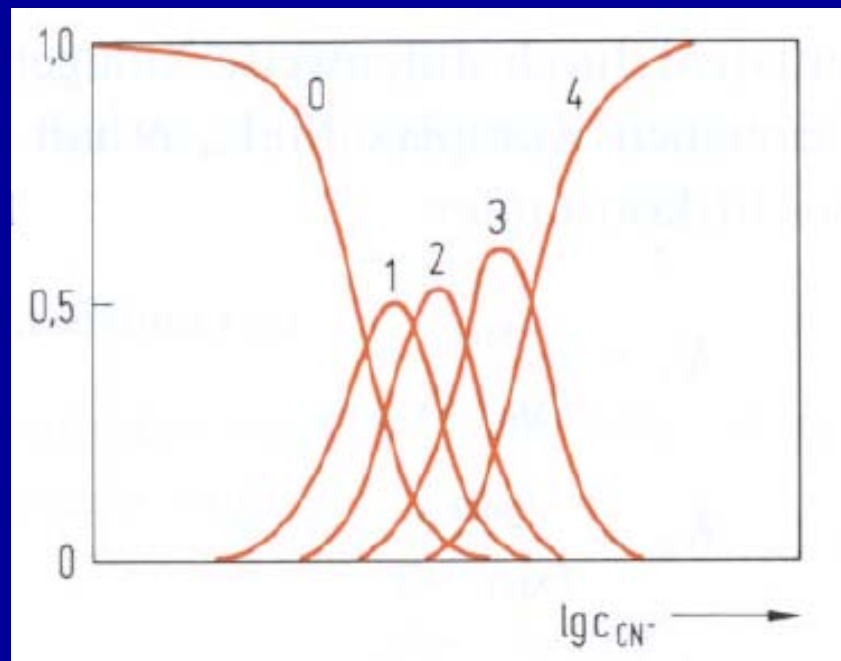
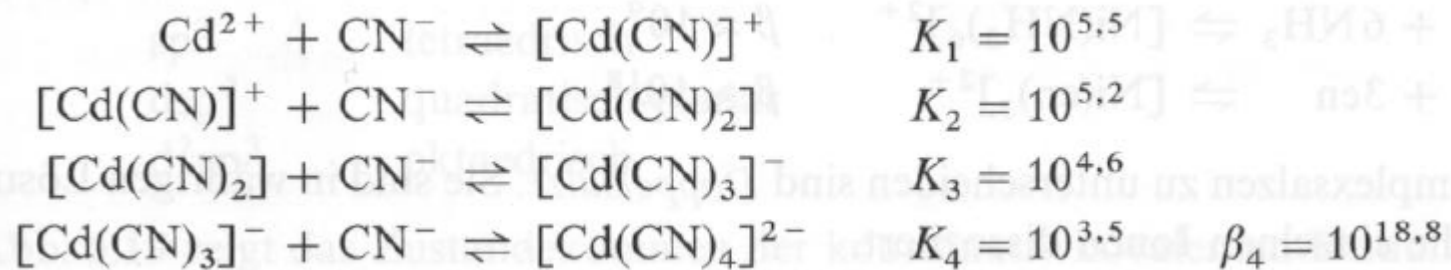




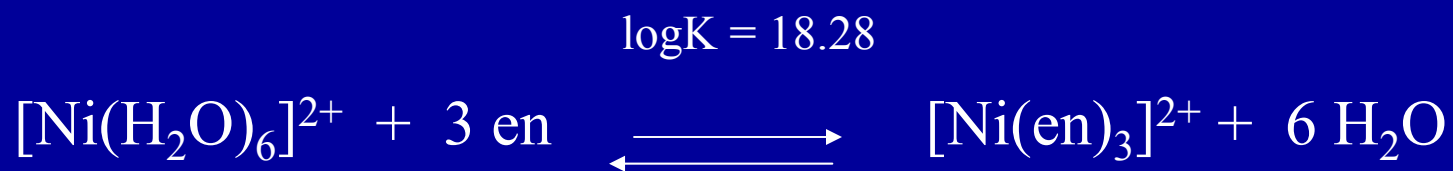
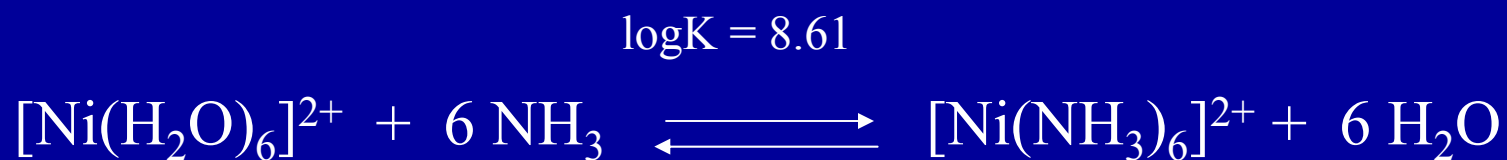
## Stabilita komplexů

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

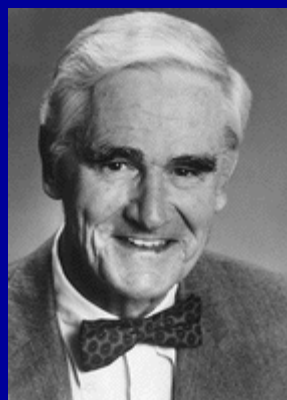


$$\Delta G = -RT \ln K = \Delta H - T\Delta S$$

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

# Cheláty, makrocykly, kryptáty

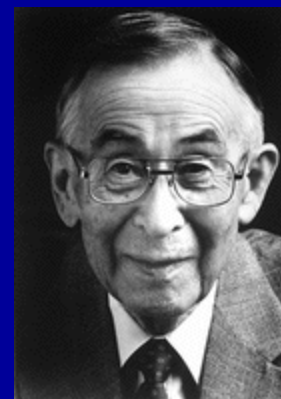
Nobelova cena za chemii 1987



**Donald J. Cram**



**Jean-Marie Lehn**

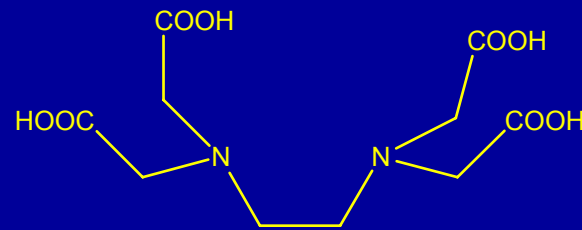


**Charles J. Pedersen**

# Cheláty, makrocycly, kryptáty

EDTA

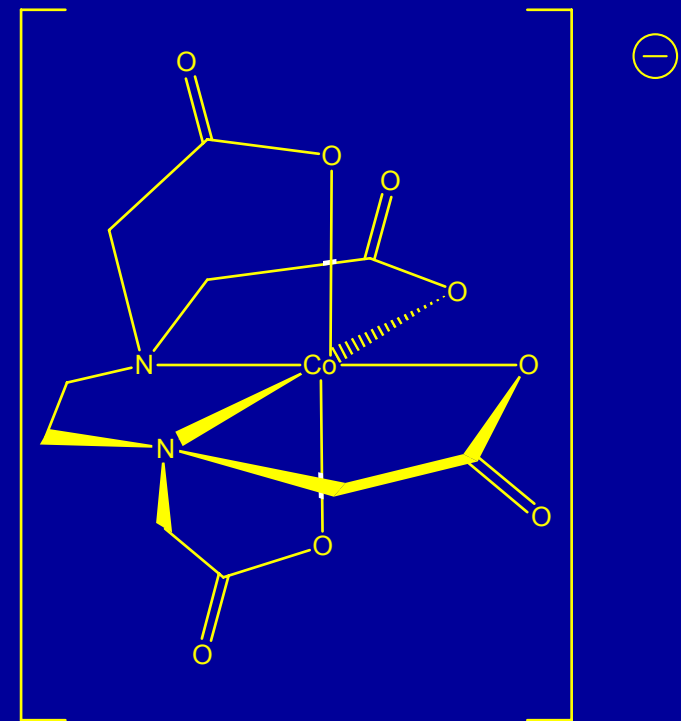
kyselina ethylendiamintetraoctová



Chelatační terapie Pb otravy

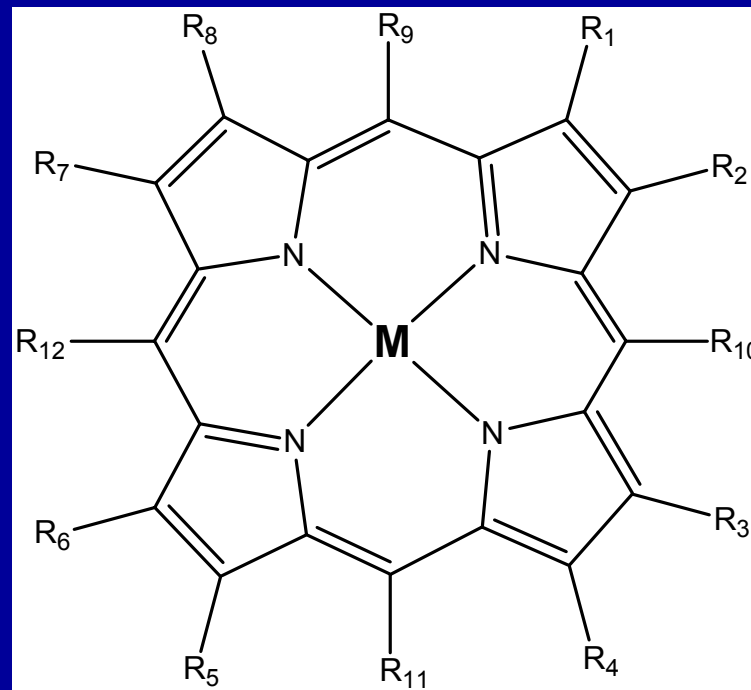
Chelatometrie

Rozpouští  $\text{CaCO}_3$

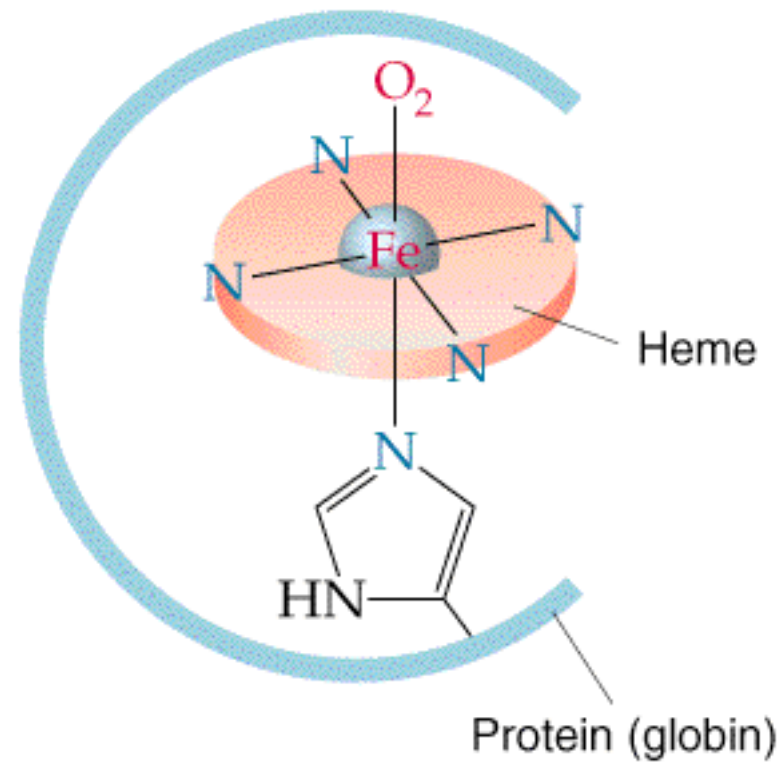
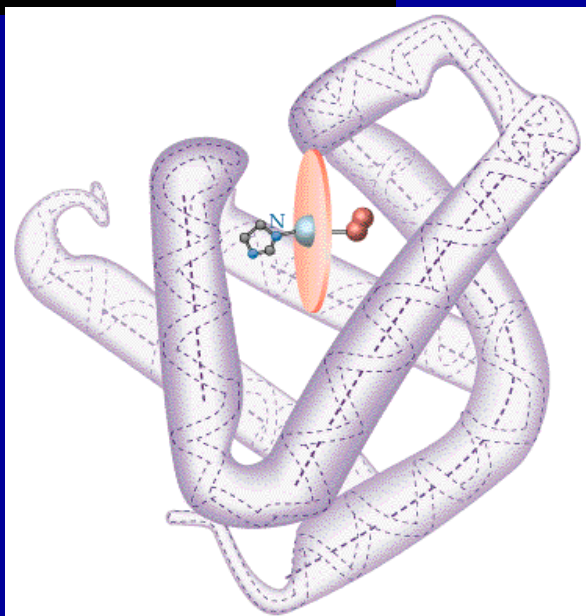
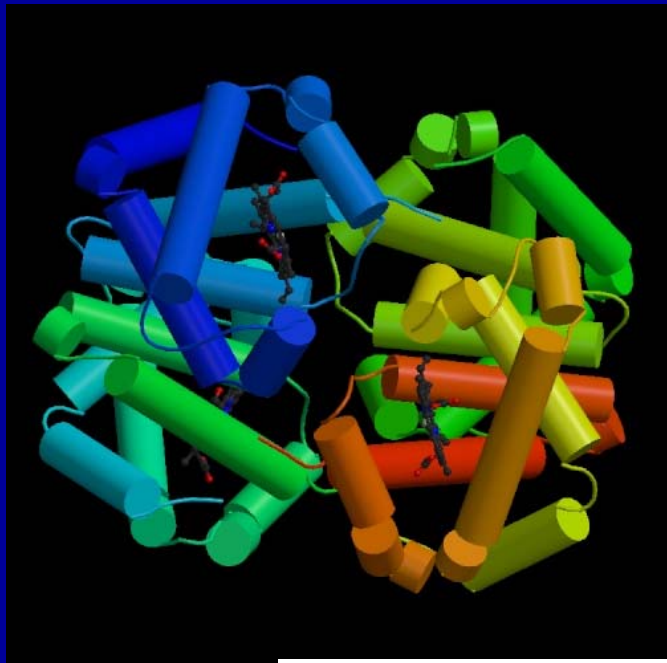


# Cheláty, makrocykly, kryptáty

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

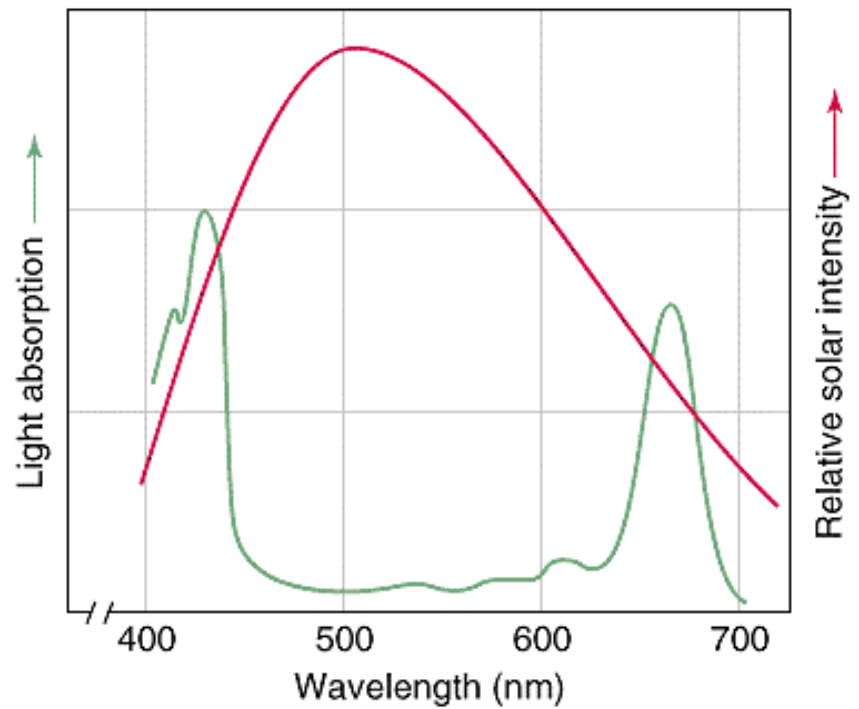
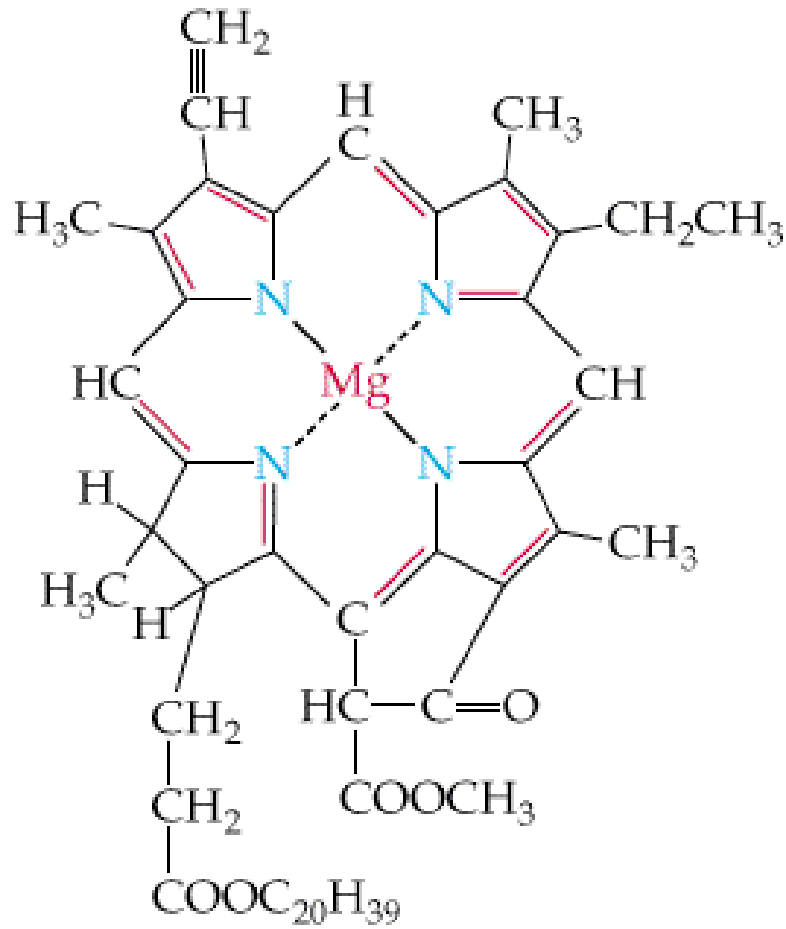


# Hemoglobin





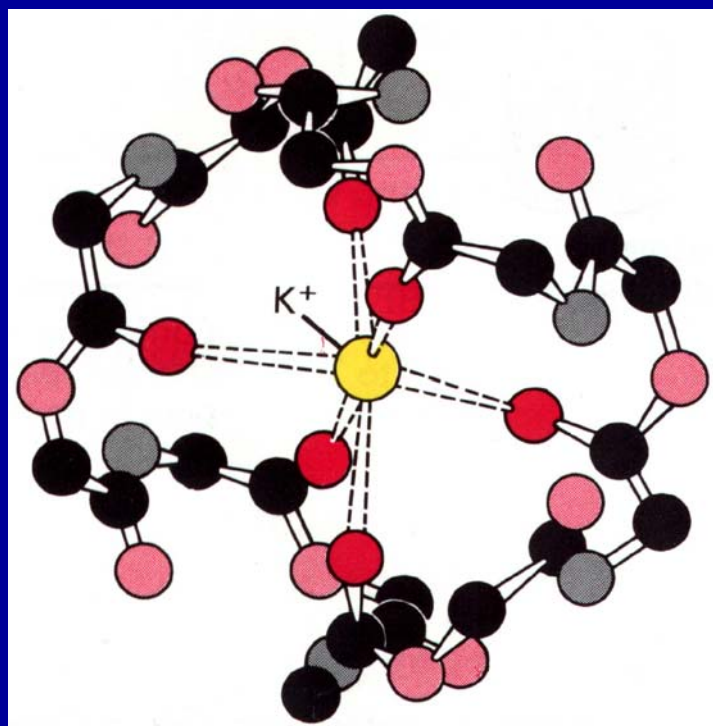
Mg chlorofyl





# Cheláty, makrocycly, kryptáty

Valinomycin



# Tvary komplexních molekul a iontů

Prvky hlavních skupin

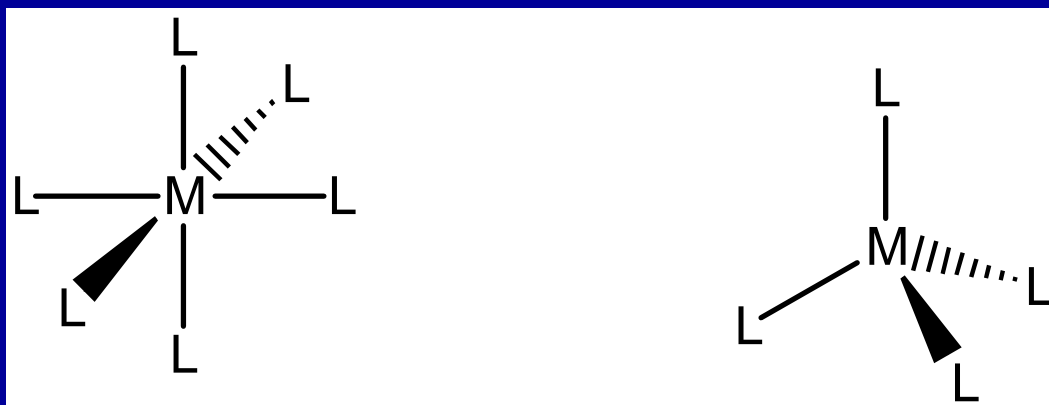
a přechodné prvky s  $d^0$  nebo  $d^{10}$  >>>> VSEPR

(kulově symetrické rozložení d-elektronové hustoty)

Přechodné prvky s  $d^n$  >>>>>>>>> **Teorie ligandového pole**

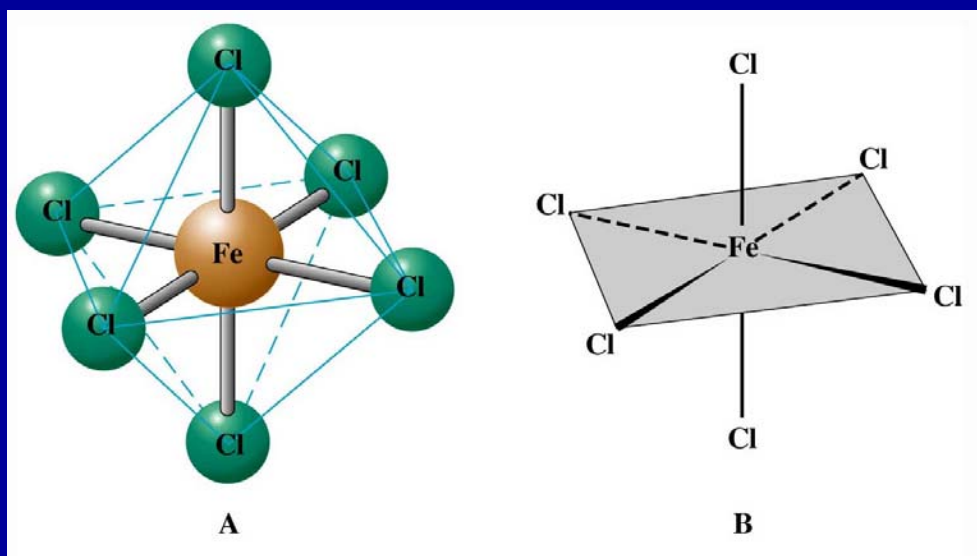
(Ne VSEPR - nesymetrické rozložení d-elektronové hustoty)

## Nejdůležitější tvary komplexních částic



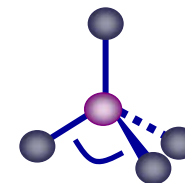
Oktaedrické komplexy  $O_h$

Tetraedrické komplexy  $T_d$

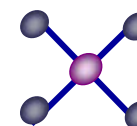


## Nejdůležitější tvary komplexních částic

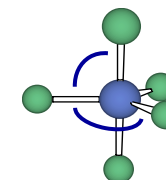
Tetraedrický  $109^{\circ} 28'$  C.N. 4



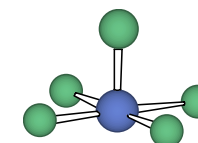
Čtvercově planární  $90^{\circ}$  C.N. 4



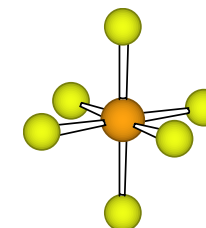
Trigonálně bipyramidální  $120^{\circ} + 90^{\circ}$  C.N. 5



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



Oktaedrický  $90^{\circ}$  C.N. 6



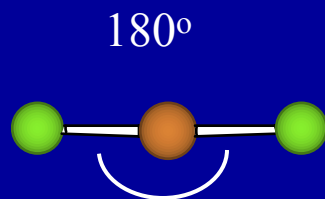
## Nejdůležitější tvary komplexních částic

### Koordinační číslo 2

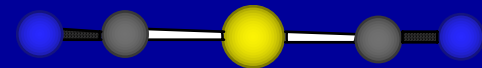
Cu(I), Ag(I), Au(I), Hg(II)

lineární

$[\text{CuCl}_2]^-$



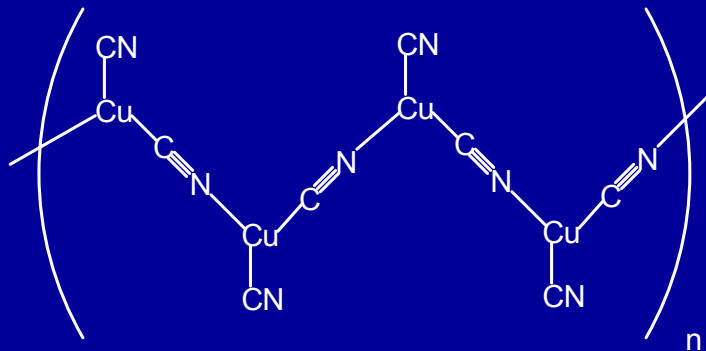
$[\text{Au}(\text{CN})_2]^-$



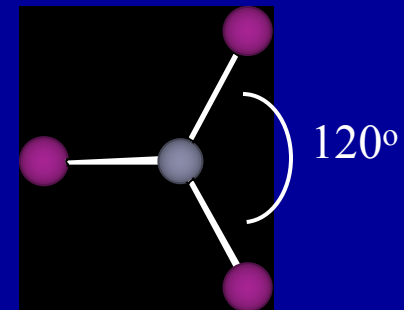
### Koordinační číslo 3

trigonálně planární

$[\text{Cu}(\text{CN})_2]^-$



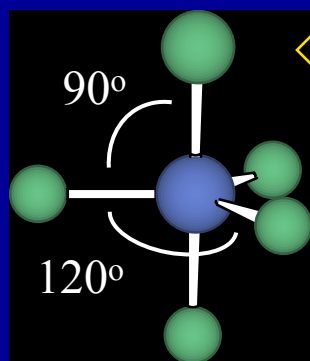
$[\text{HgI}_3]^-$



# Nejdůležitější tvary komplexních částic

Koordinační číslo 5

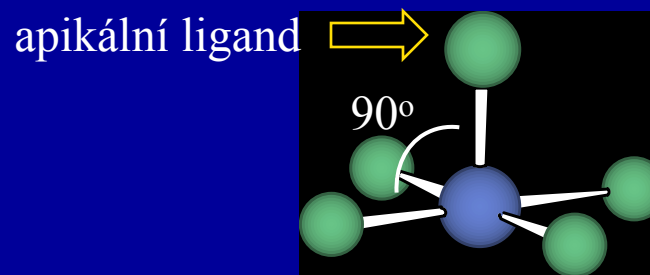
Trigonálně bipyramidální



axiální ligandy

ekvatoriální ligandy

Čtvercově pyramidální

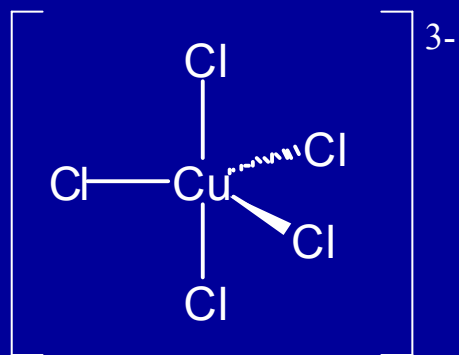


apikální ligand

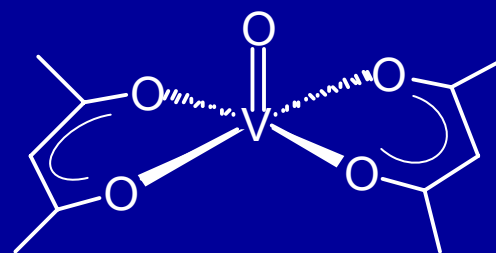
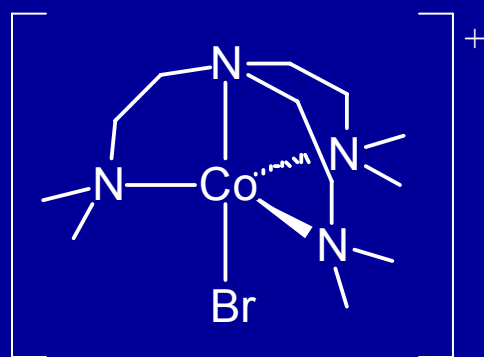
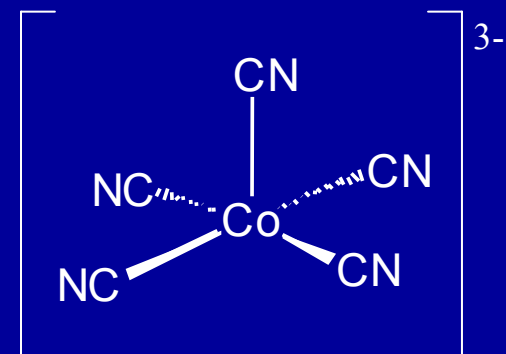
bazální ligandy

Tyto dvě struktury mají velmi podobnou energii

## Trigonálně bipyramidální



## Čtvercově pyramidální



# Izomerie komplexních sloučenin

## Konstituční (strukturní) izomerie

Vazebná

Koordinační

Ionizační

## Prostorová (stereo) izomerie

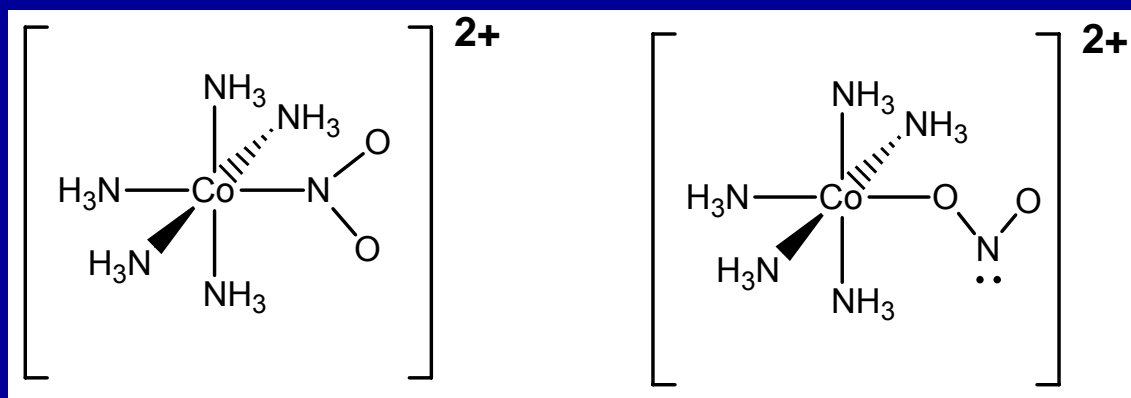
Geometrická

Optická



# Konstituční (strukturní) izomerie

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

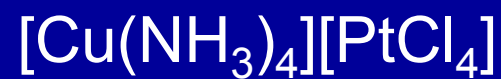
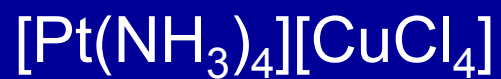


nitro-

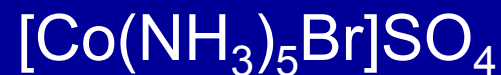
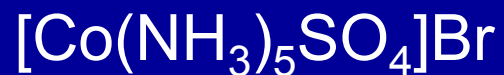
nitrito-

## Konstituční (strukturní) izomerie

Koordinační:

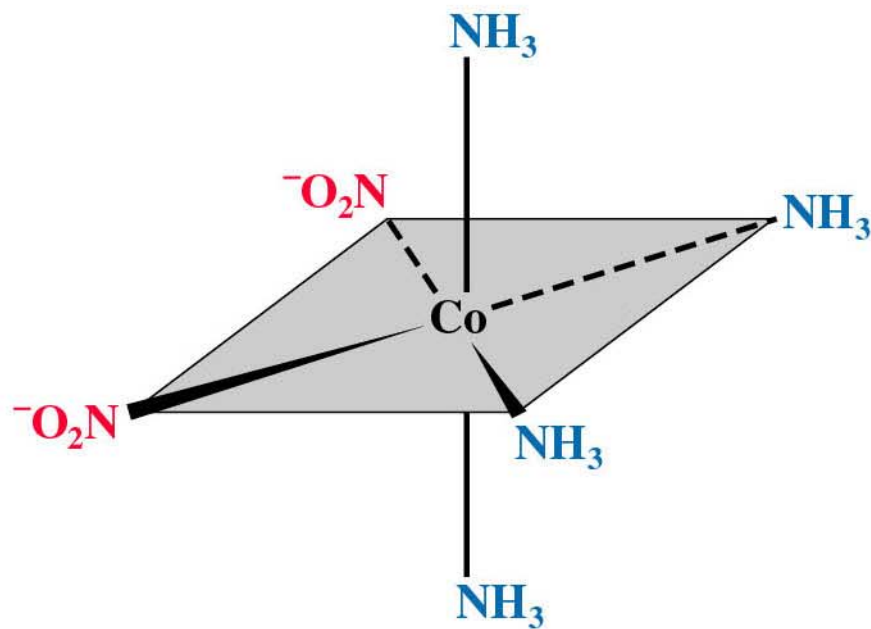


Ionizační:

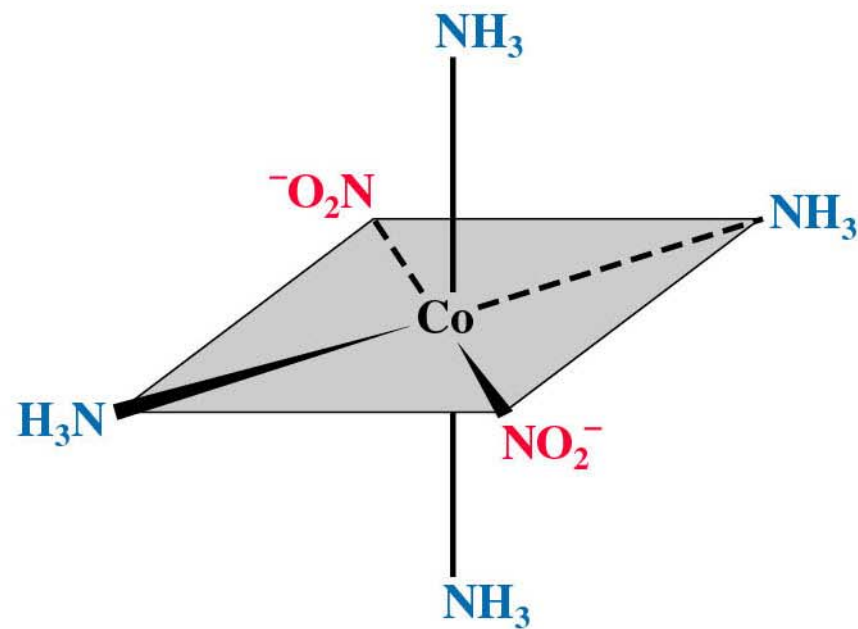


# Prostorová (stereo) izomerie

Geometrická: cis-trans, diastereomery



*cis*



*trans*

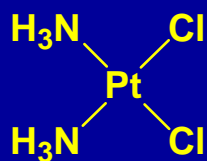
# Prostorová (stereo) izomerie

Geometrická:  
cis-trans,  
diastereomery

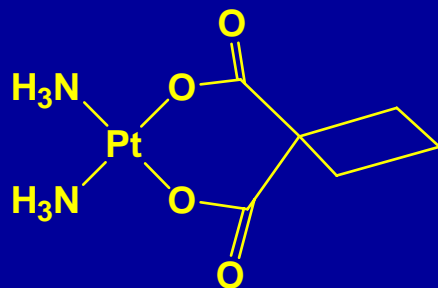
	<i>cis</i>	<i>trans</i>
Ball-and-stick model		
Structural formula	<p><i>cis</i></p>	<p><i>trans</i></p>
Color	Orange-yellow	Pale yellow
Solubility	0.252 g/100 g H <sub>2</sub> O	0.037 g/100 g H <sub>2</sub> O



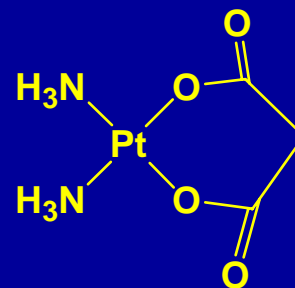
# Protinádorové léky



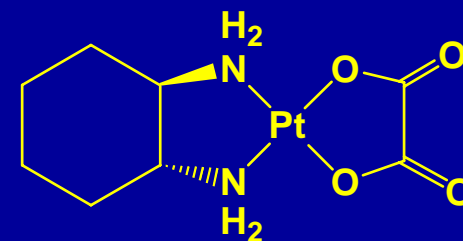
Cisplatin



Carboplatin

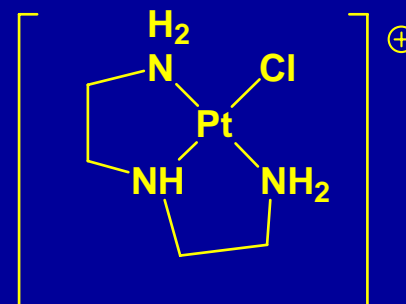
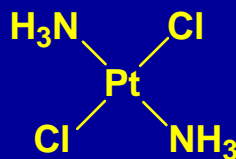


Nedaplatin



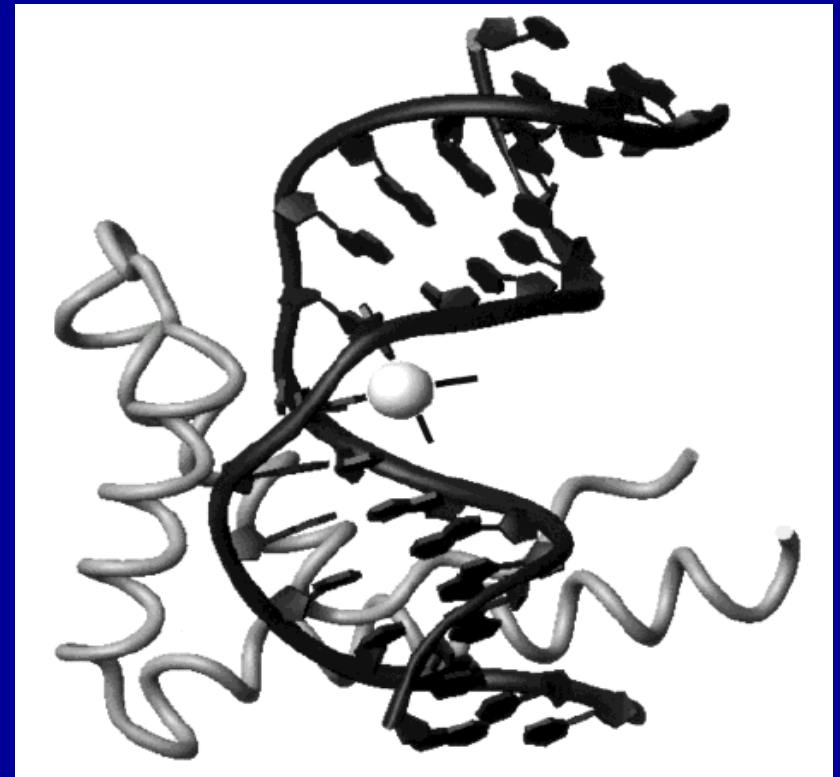
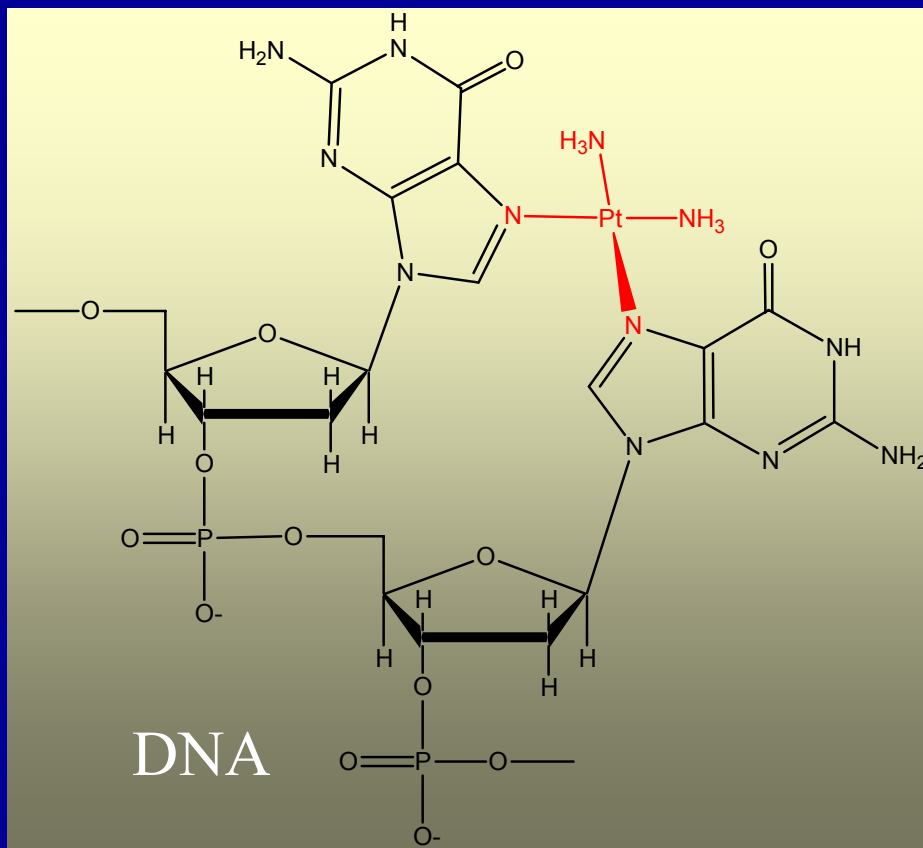
Oxaliplatin

## Neaktivní látky



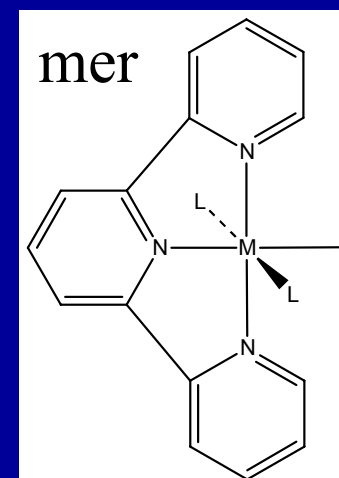
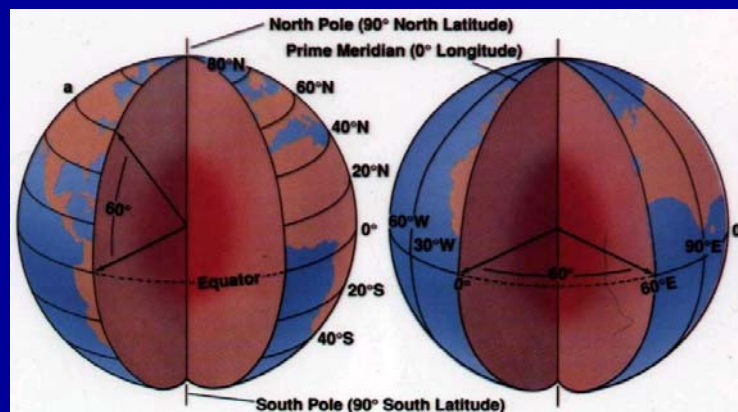
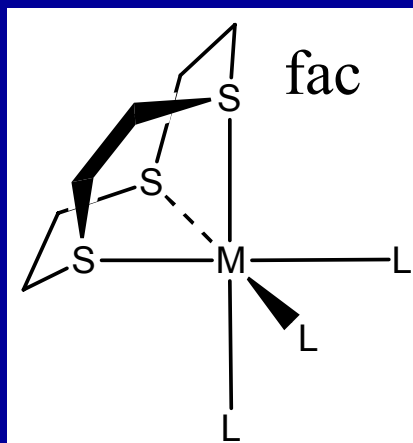
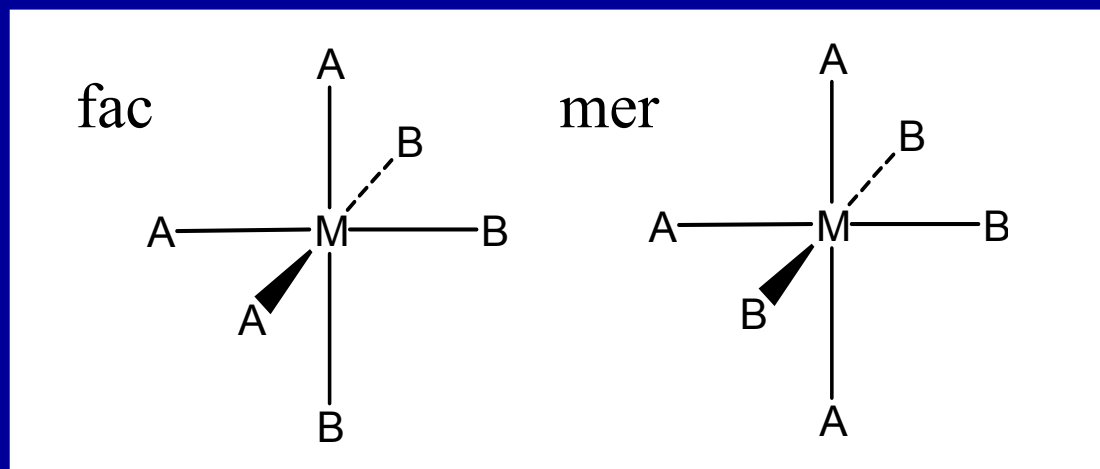
# Prostorová (stereo) izomerie

Cisplatina = kancerostatikum



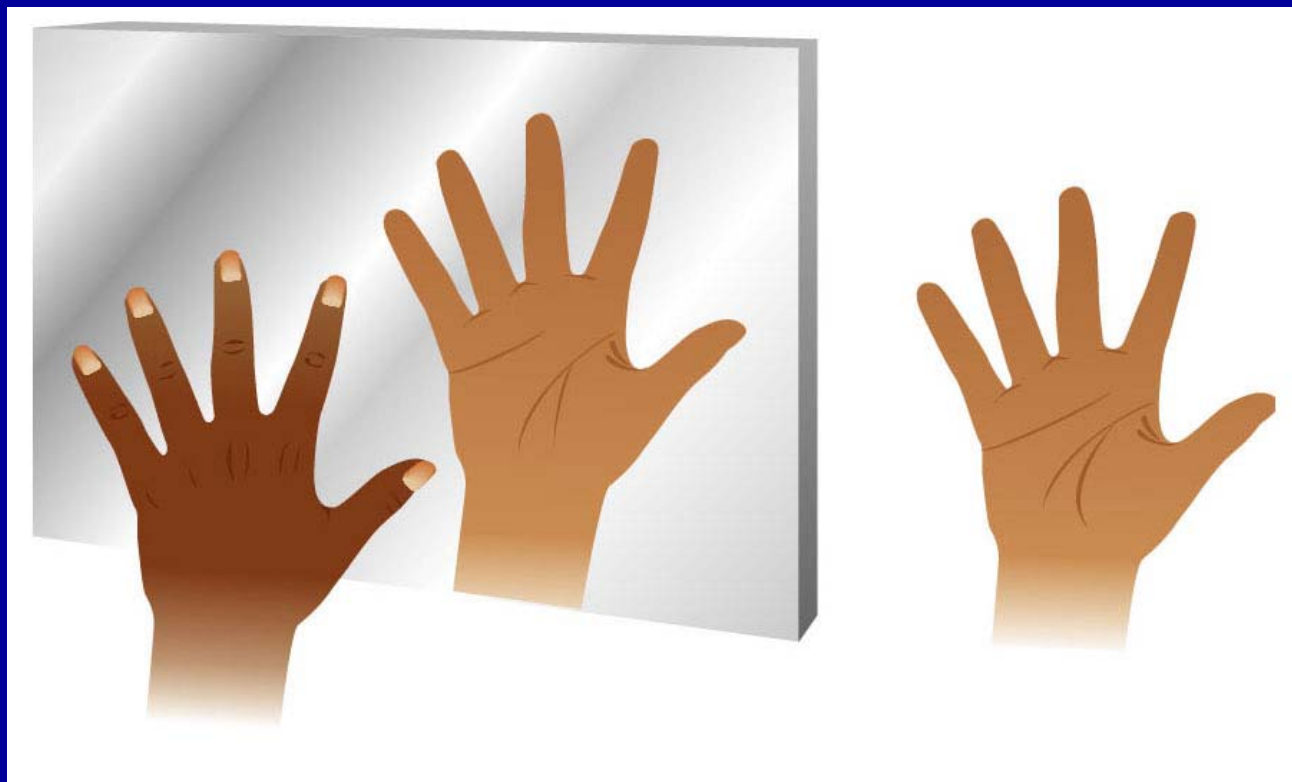
# Prostorová (stereo) izomerie

Geometrická: mer-fac, diastereomery



# Prostorová (stereo) izomerie

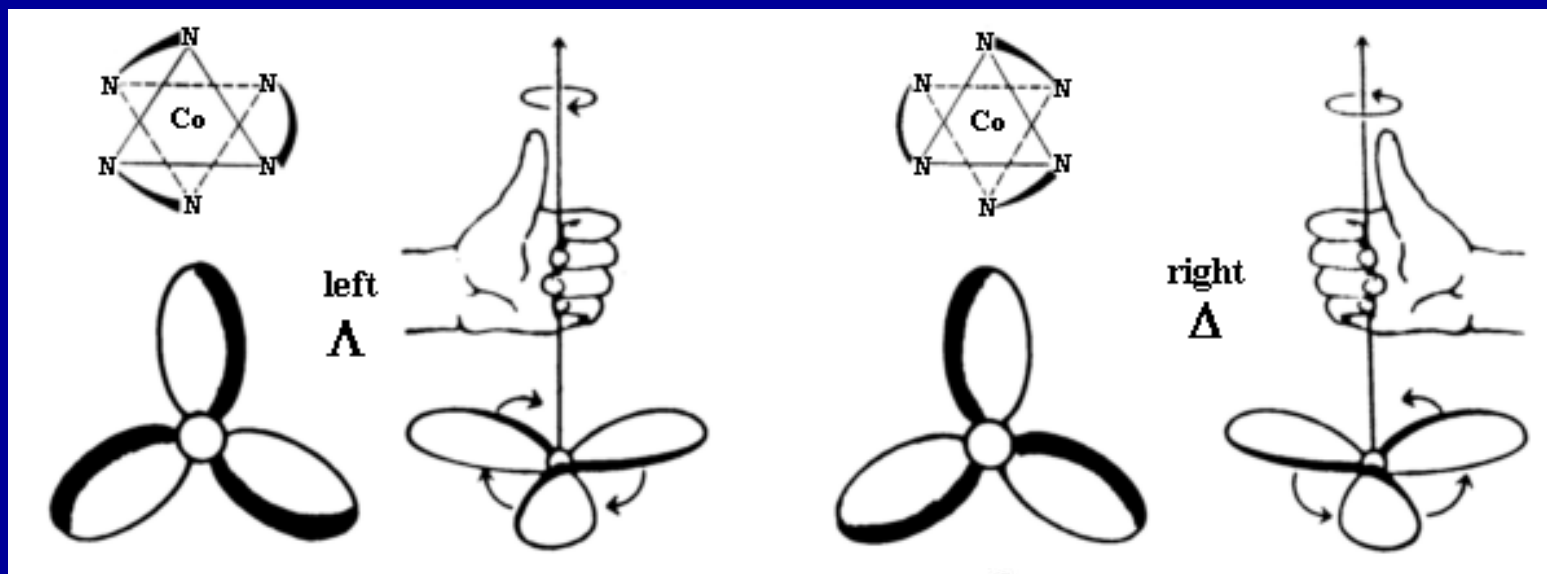
Optická: enantiomery





# Prostorová (stereo) izomerie

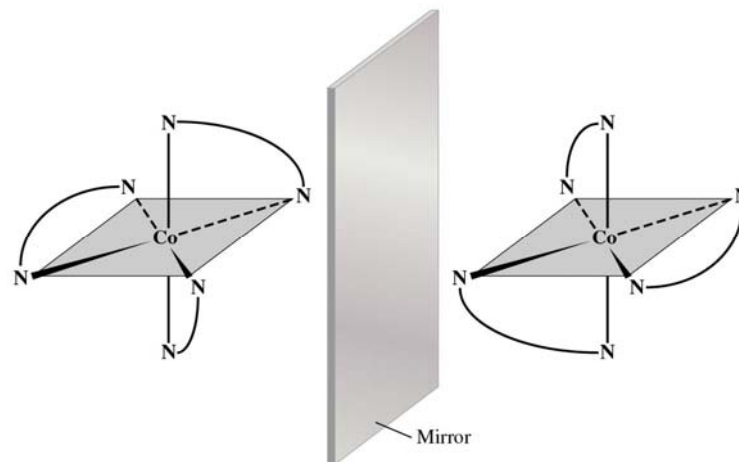
Optická: enantiomery



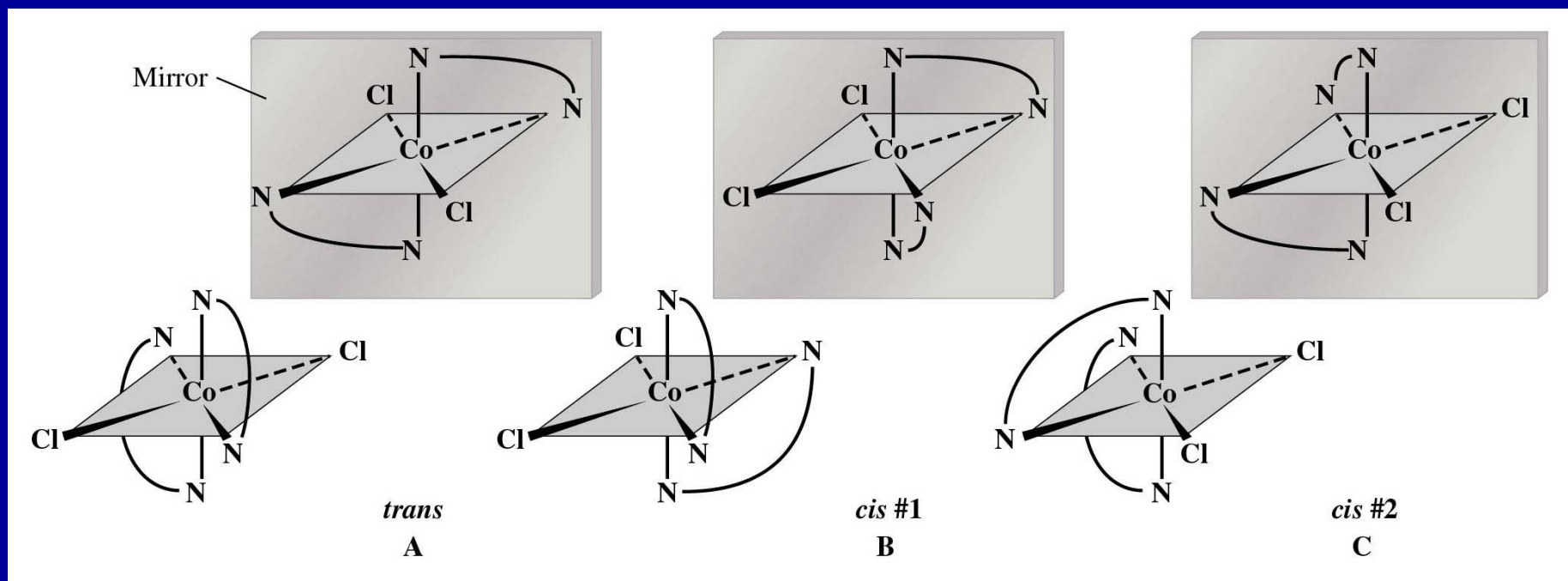
Nemá  $S_n$

$S_1$  = rovina symetrie

$S_2$  = střed symetrie



# Prostorová (stereo) izomerie



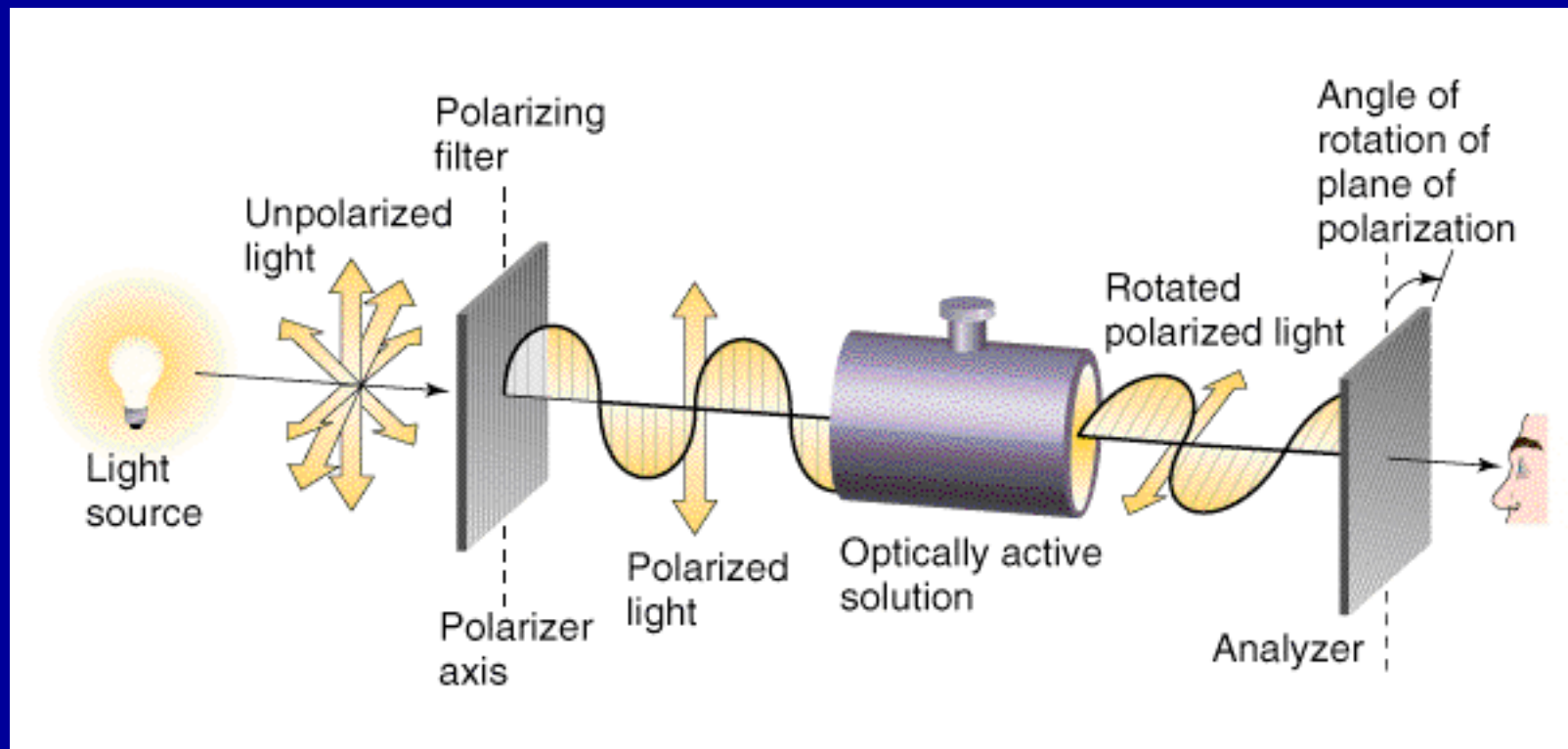
# Optická rotace

Nepolarizované světlo – šíření vln s vektory el. pole v mnoha směrech

Polarizované světlo – filtrem vybrán jen jeden směr

Opticky aktivní látka stáčí rovinu polarizovaného světla o určitý úhel

Měření úhlu stočení analyzátozem – druhý filtr



## 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)

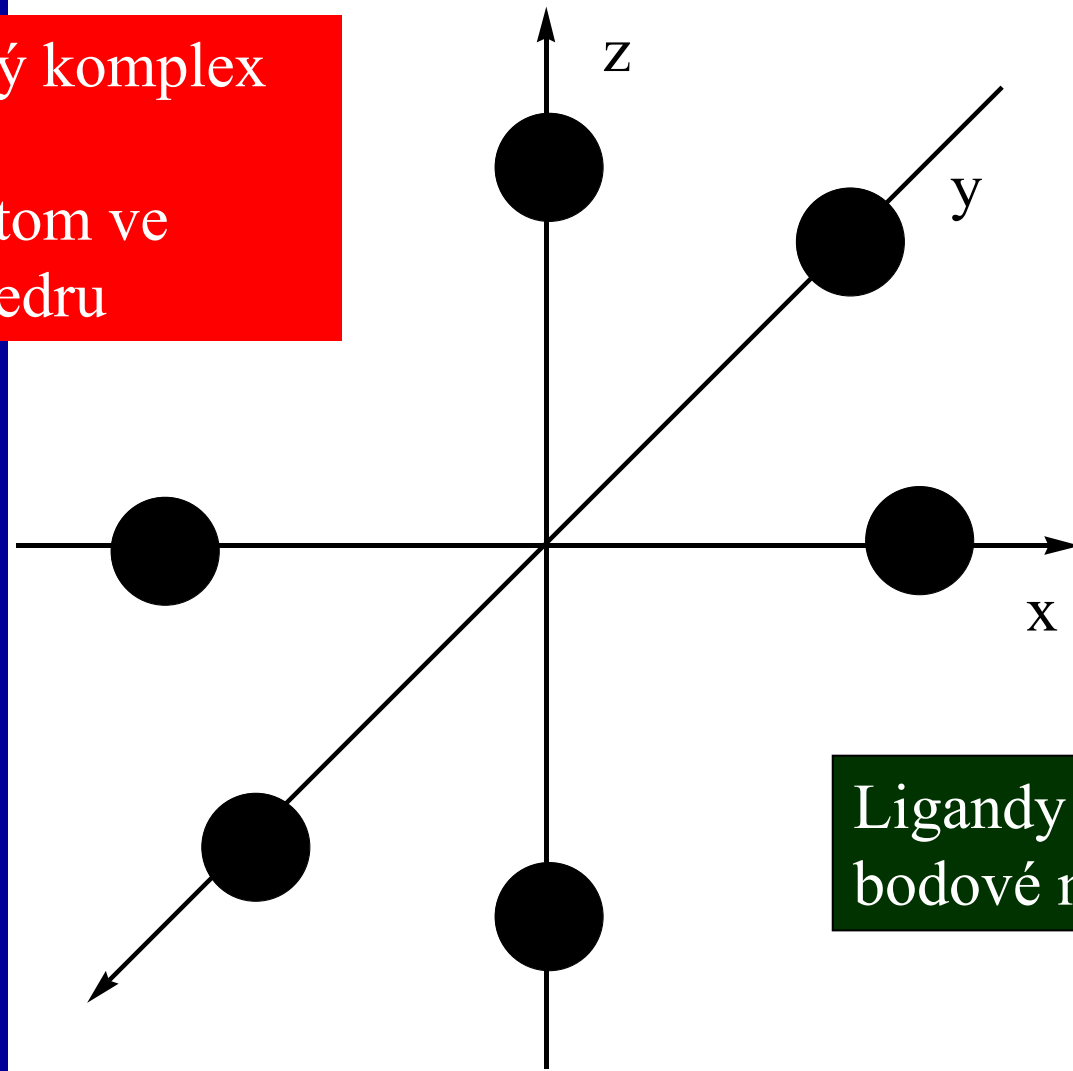
1935, modifikace J. H. Van Vleck Podíl kovalence

4) MO

# Teorie ligandového pole

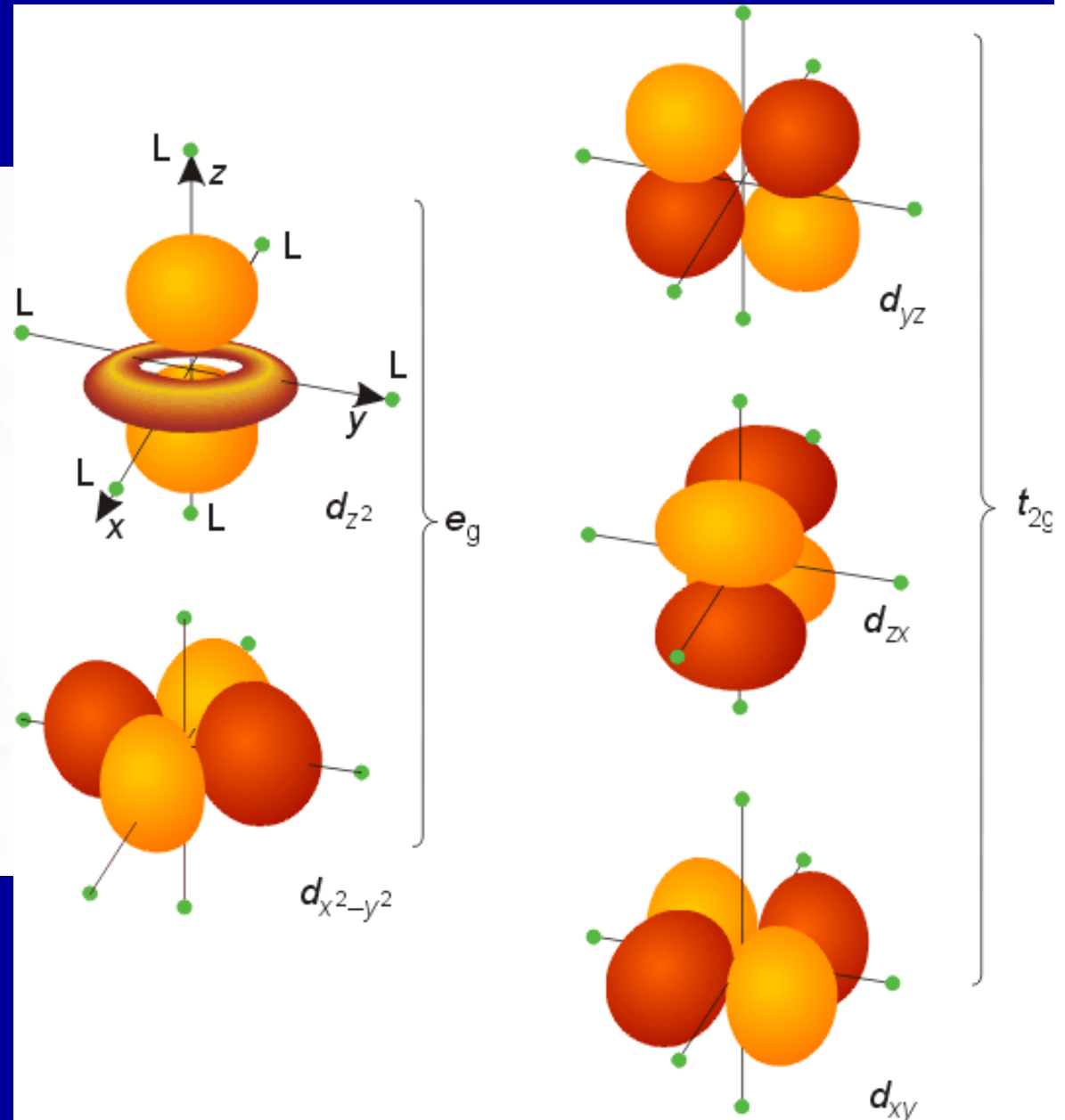
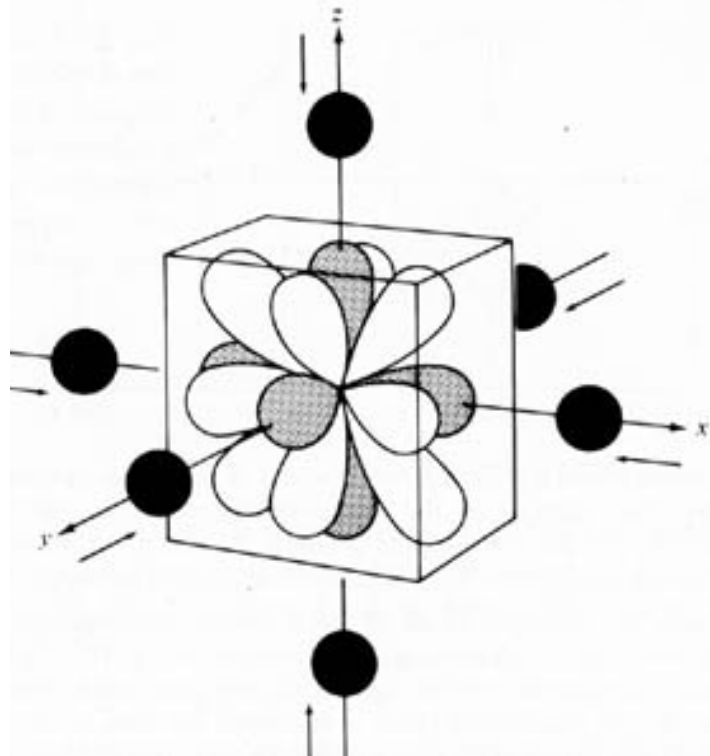
Oktaedrický komplex

Centrální atom ve  
středu oktaedru



Ligandy jako záporné  
bodové náboje

# d-orbitaly v oktaedrickém poli ligandů



Izolovaný kation

Interakce  
ligandy-kation

Interakce  
ligandy-d elektrony

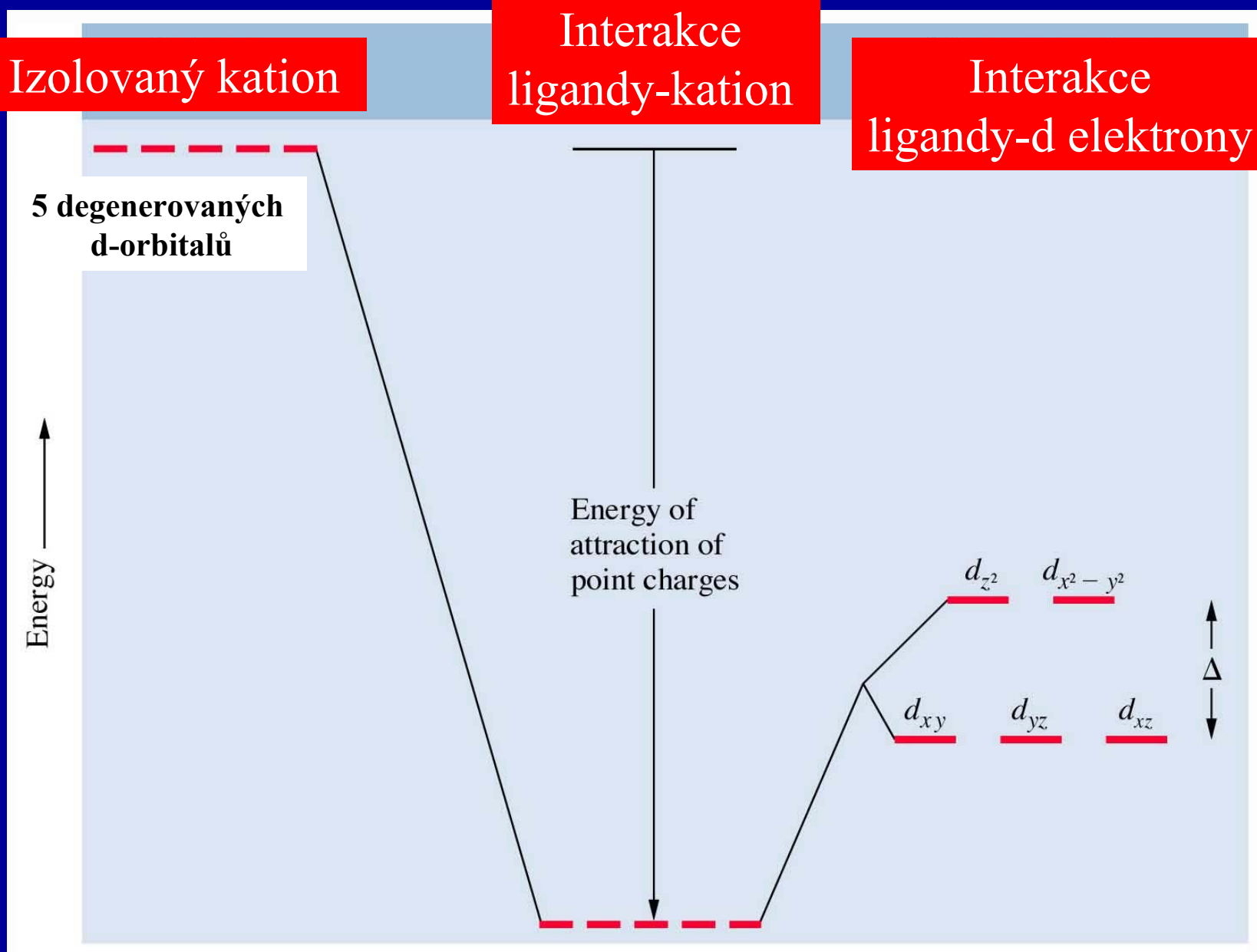
5 degenerovaných  
d-orbitalů

Energy ↑

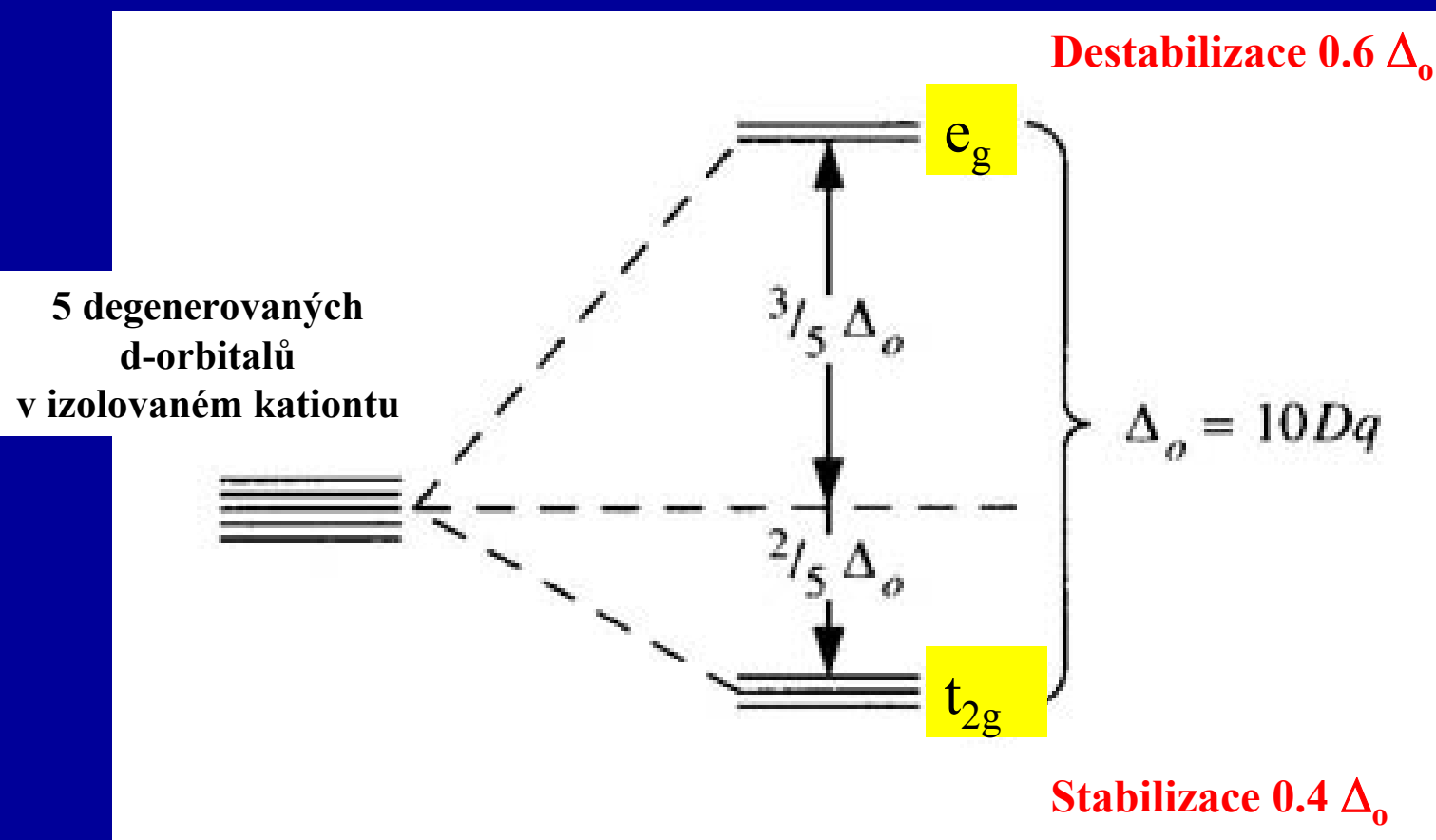
Energy of  
attraction of  
point charges

$d_{z^2}$   $d_{x^2-y^2}$   
 $d_{xy}$   $d_{yz}$   $d_{xz}$

↑ Δ ↓

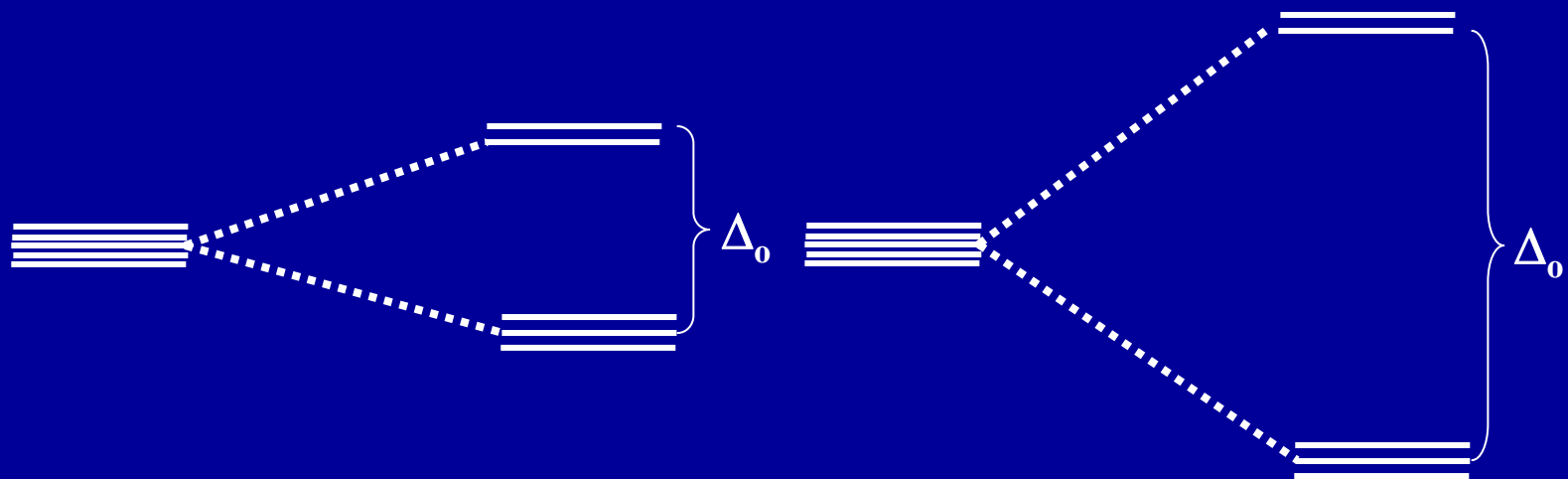


# Rozštěpení d-hladin v $O_h$ poli





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



## Slabé pole

$\Delta_o < P$  (párovací energie)

Vysokospinové komplexy

## Silné pole

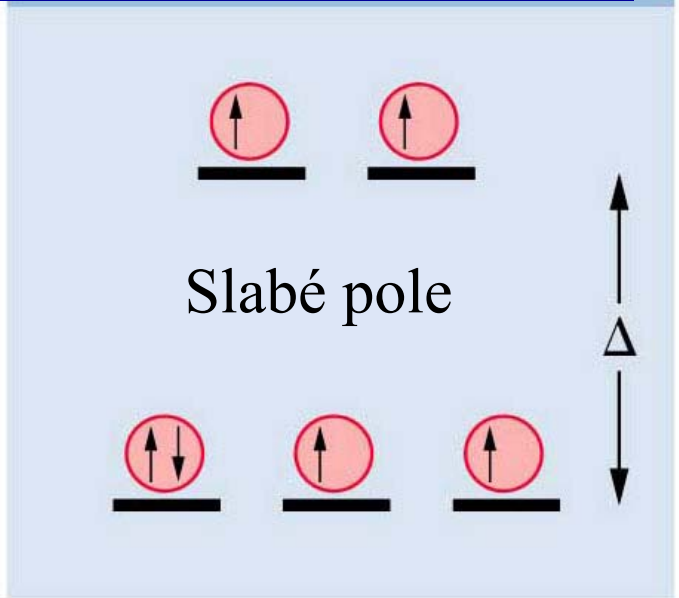
$\Delta_o > P$  (párovací energie)

Nížkospinové komplexy

# Stabilizační energie ligandového pole, CFSE

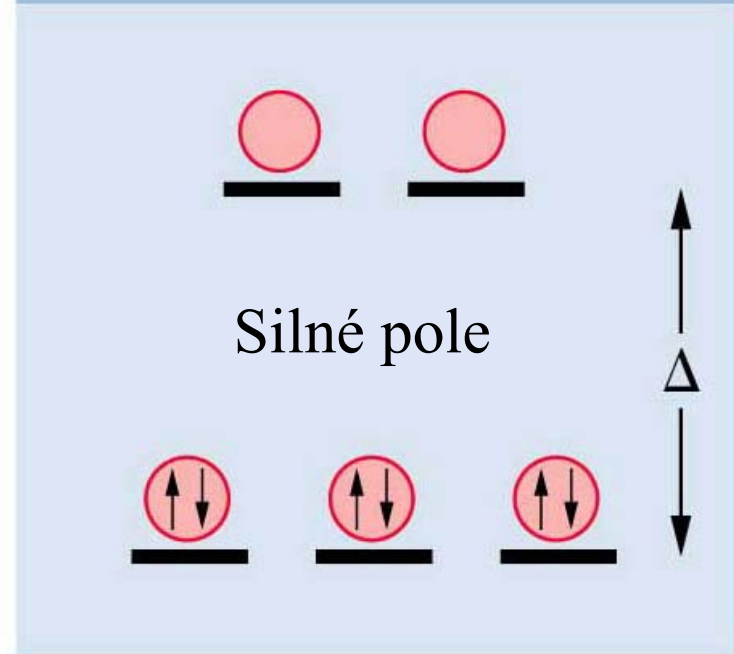
## Vysokospinové komplexy

Energy ↑



## Nízkospinové komplexy

Energy ↑



$\Delta_o$  roste

## Slabé pole

## Silné pole

		e	CFSE		e	CFSE
d <sup>1</sup>	t <sub>2g</sub> <sup>1</sup>	1	0.4 Δ <sub>o</sub>	t <sub>2g</sub> <sup>1</sup>	1	0.4 Δ <sub>o</sub>
d <sup>2</sup>	t <sub>2g</sub> <sup>2</sup>	2	0.8 Δ <sub>o</sub>	t <sub>2g</sub> <sup>2</sup>	2	0.8 Δ <sub>o</sub>
d <sup>3</sup>	t <sub>2g</sub> <sup>3</sup>	3	1.2 Δ <sub>o</sub>	t <sub>2g</sub> <sup>3</sup>	3	1.2 Δ <sub>o</sub>
d <sup>4</sup>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>1</sup>	4	0.6 Δ <sub>o</sub>	t <sub>2g</sub> <sup>4</sup>	2	1.6 Δ <sub>o</sub>
d <sup>5</sup>	t <sub>2g</sub> <sup>3</sup> e <sub>g</sub> <sup>2</sup>	5	0.0 Δ <sub>o</sub>	t <sub>2g</sub> <sup>5</sup>	1	2.0 Δ <sub>o</sub>
d <sup>6</sup>	t <sub>2g</sub> <sup>4</sup> e <sub>g</sub> <sup>2</sup>	4	0.4 Δ <sub>o</sub>	t <sub>2g</sub> <sup>6</sup>	0	2.4 Δ <sub>o</sub>
d <sup>7</sup>	t <sub>2g</sub> <sup>5</sup> e <sub>g</sub> <sup>2</sup>	3	0.8 Δ <sub>o</sub>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>1</sup>	1	1.8 Δ <sub>o</sub>
d <sup>8</sup>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup>	2	1.2 Δ <sub>o</sub>	t <sub>2g</sub> <sup>6</sup> e <sub>g</sub> <sup>2</sup>	2	1.2 Δ <sub>o</sub>

$$\text{CFSE} = (n \text{ t}_{2g}) 0.4 \Delta_o - (n \text{ e}_g) 0.6 \Delta_o$$

e = počet nepárových elektronů

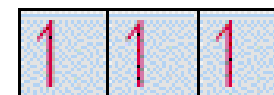
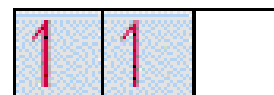
## Rozštěpení d-hladin v $O_h$ poli

Obsazení energetických hladin elektrony:

**Výstavbový princip**

**Hundovo pravidlo**

**Pauliho princip**



# Rozštěpení d-hladin v $O_h$ poli

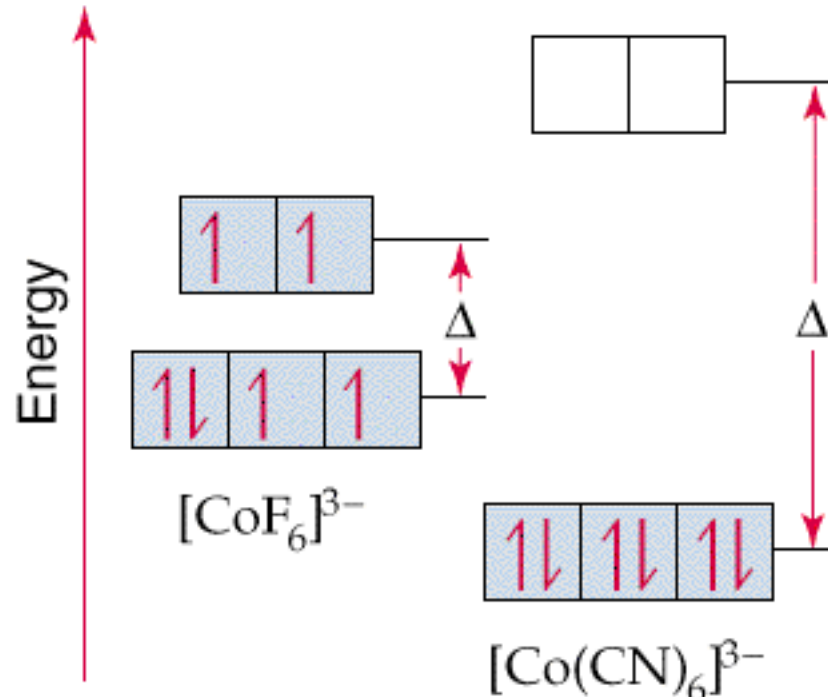
Vysokospinový komplex

Nízkospinový komplex

Slabé pole

Malé štěpení

Slabý ligand



Silné pole

Velké štěpení

Silný ligand

$\Delta_o$  roste

# Stabilizační energie ligandového pole

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

$$\frac{1}{+3/5 \Delta} \text{ ---}$$

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

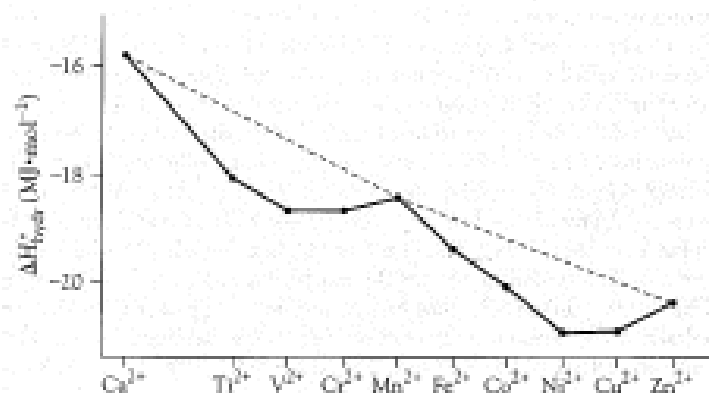


Table 18.3 Crystal field stabilization energies (CFSE) for the dipositive, high spin ions of various Period 4 metals

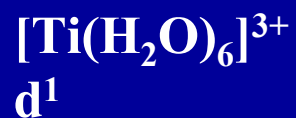
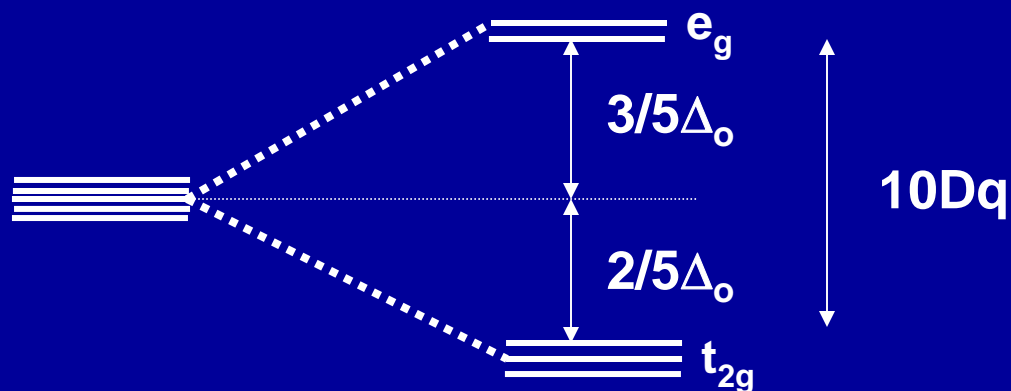
Ion	Configuration	CFSE
Ca <sup>2+</sup>	$d^0$	$-0.0 \Delta_{oct}$
—	$d^1$	$-0.4 \Delta_{oct}$
Ti <sup>2+</sup>	$d^2$	$-0.8 \Delta_{oct}$
V <sup>2+</sup>	$d^3$	$-1.2 \Delta_{oct}$
Cr <sup>2+</sup>	$d^4$	$-0.6 \Delta_{oct}$
Mn <sup>2+</sup>	$d^5$	$-0.0 \Delta_{oct}$
Fe <sup>2+</sup>	$d^6$	$-0.4 \Delta_{oct}$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

$d^0$

$d^5$

$d^{10}$

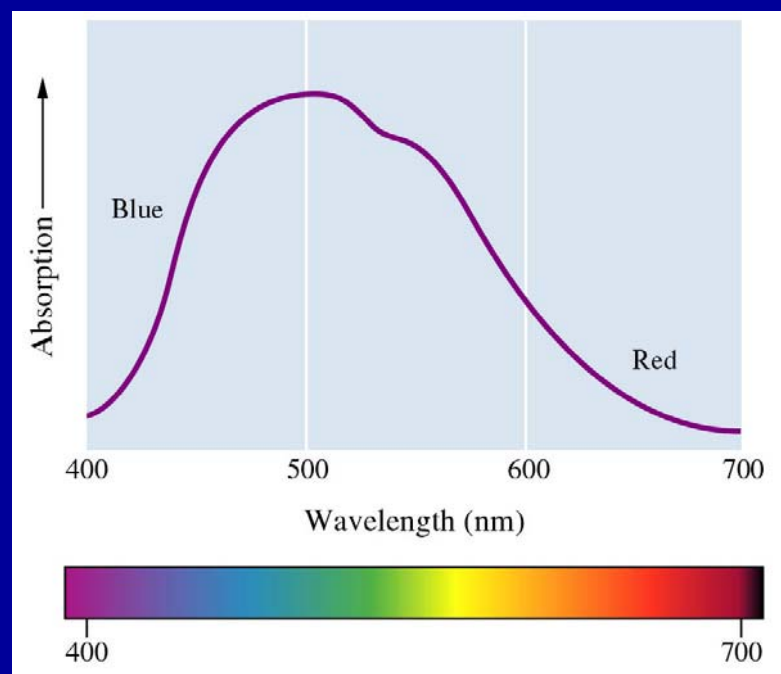
# Rozštěpení d-hladin v $O_h$ poli



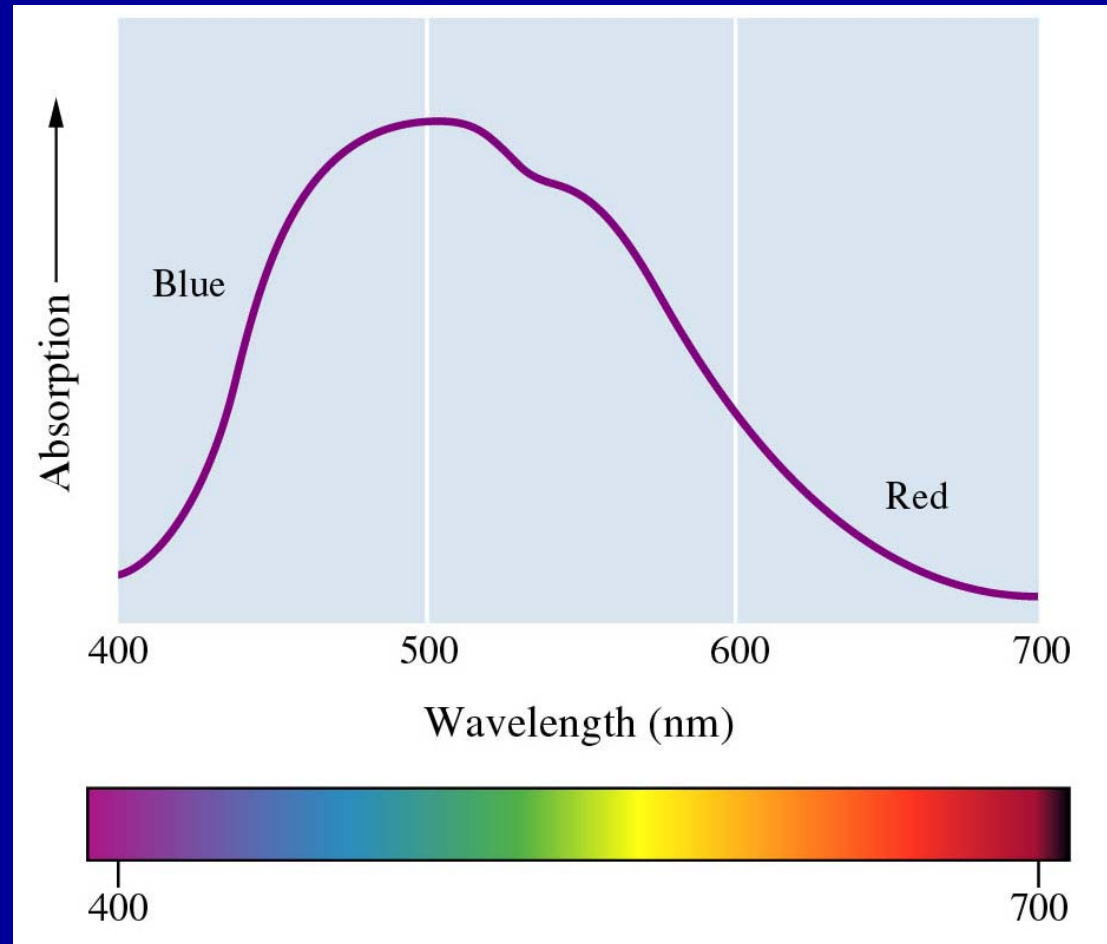
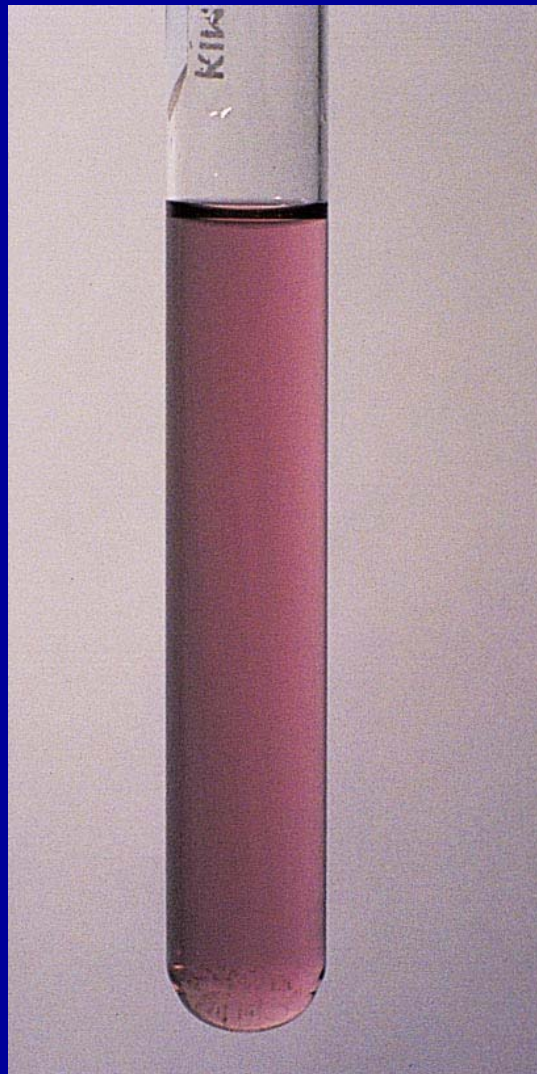
růžový

$243 \text{ kJ mol}^{-1}$

$(\Delta_o)$

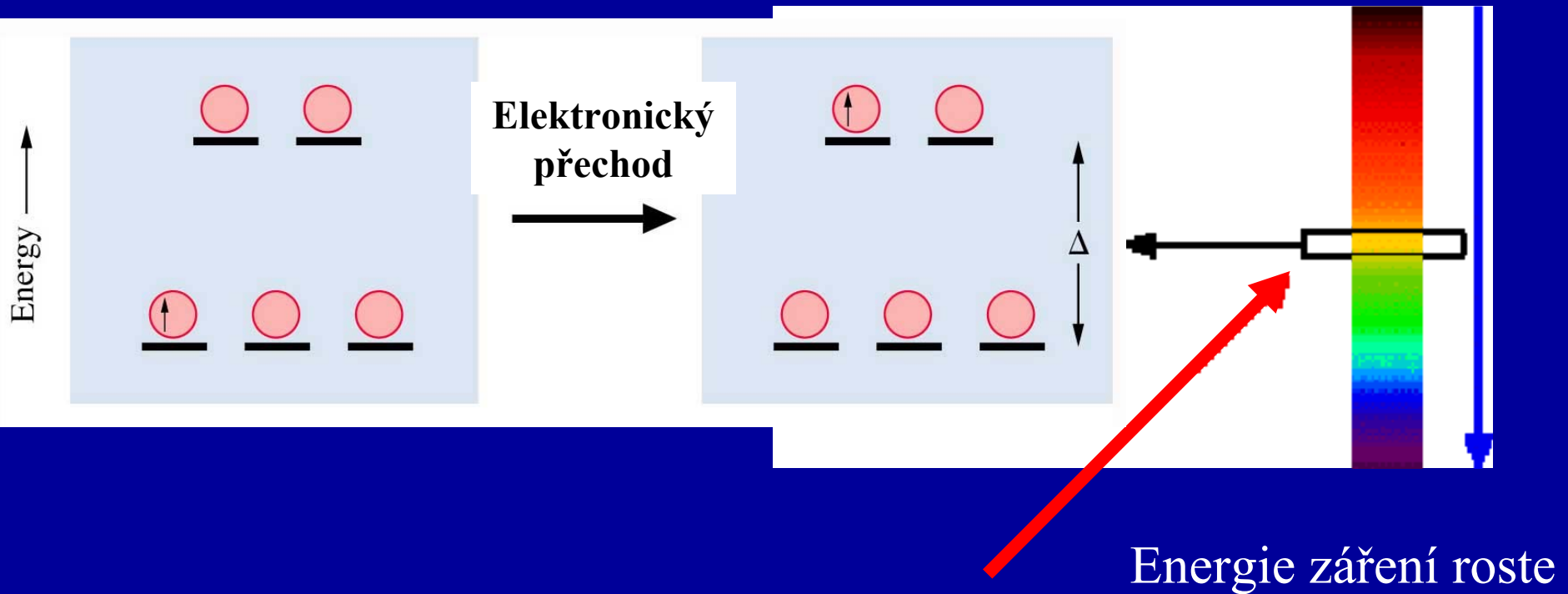


# UV-vis absorpční spektrum $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

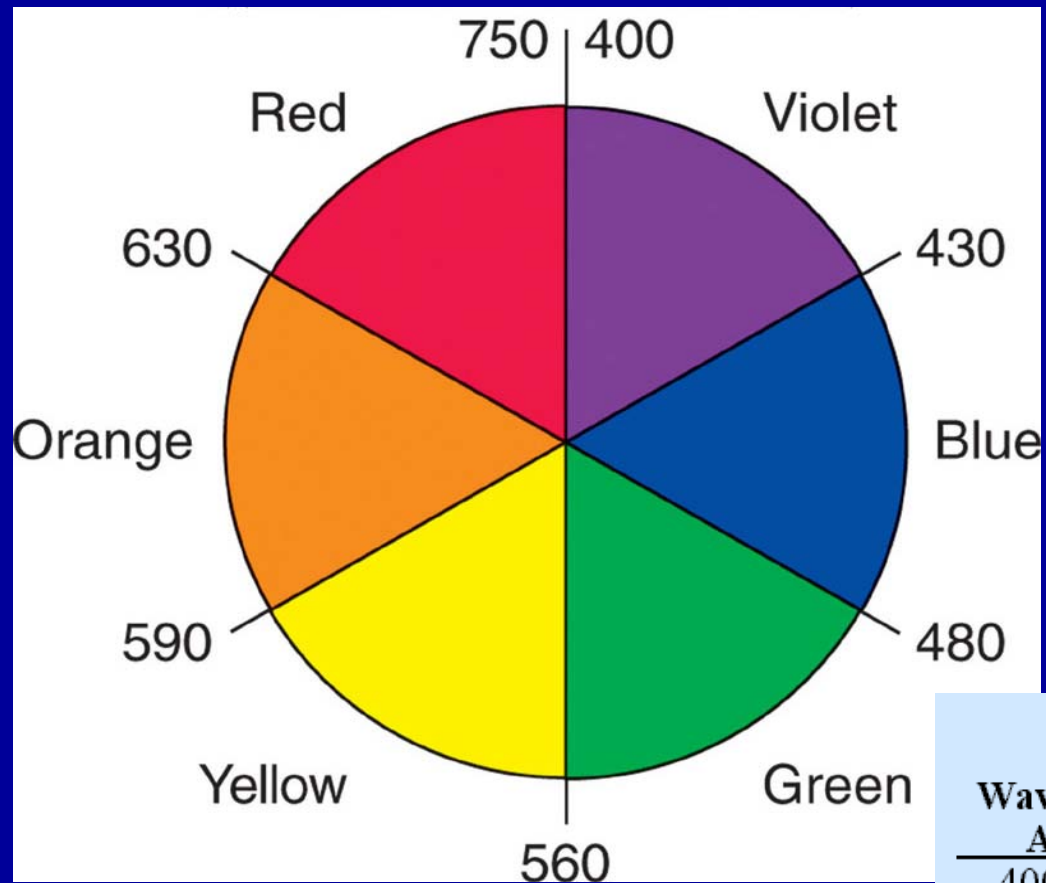




# Elektronické přechody



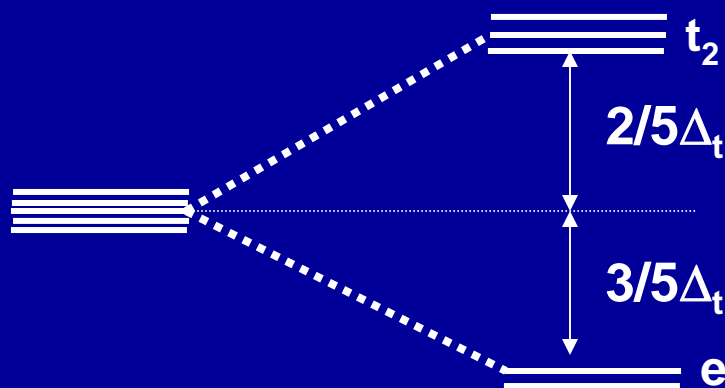
Tato energie je právě dostatečná pro excitaci elektronu



Wavelength (Color) Absorbed	Color Observed
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>

E

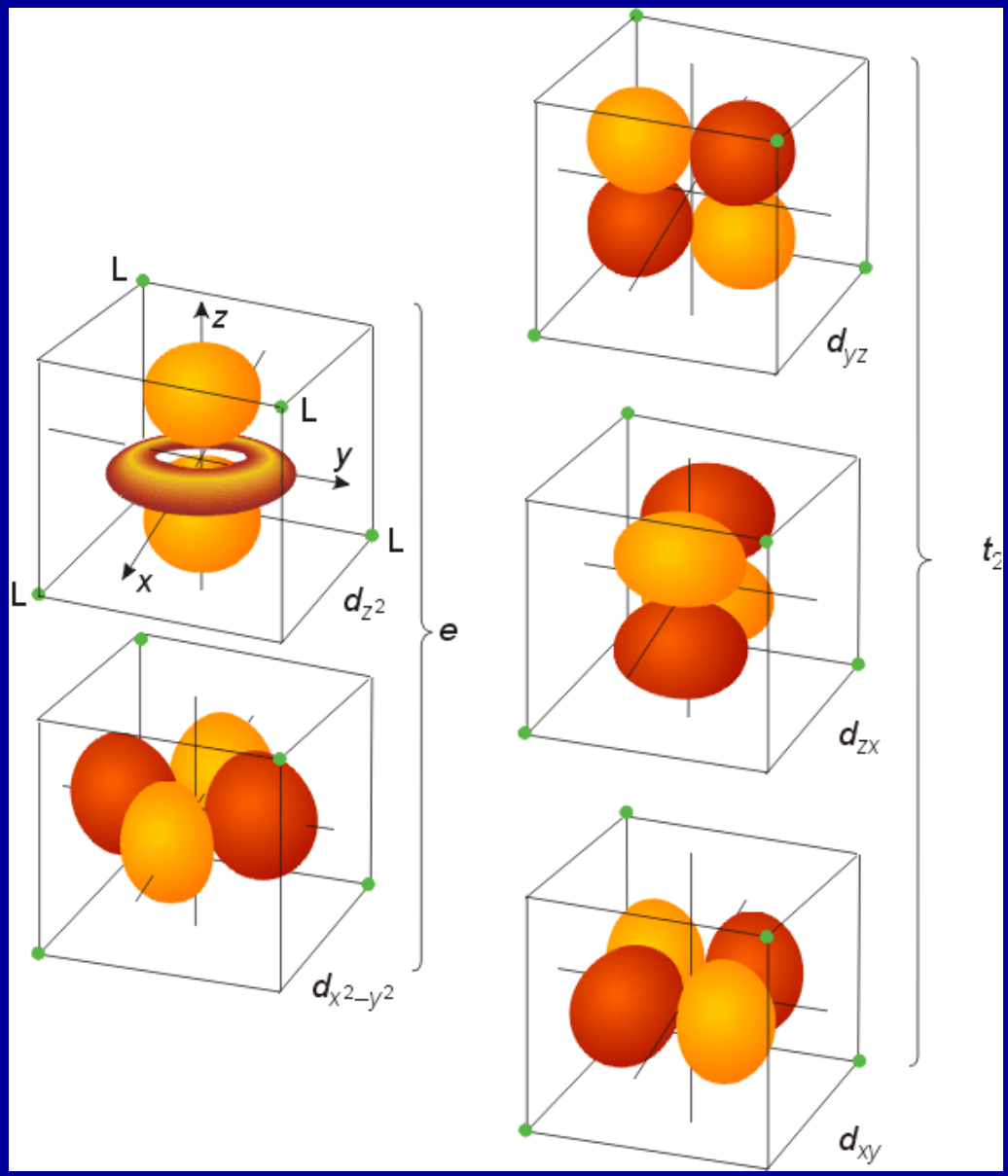
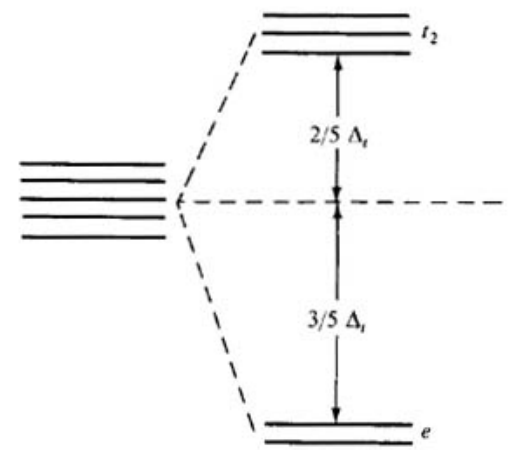
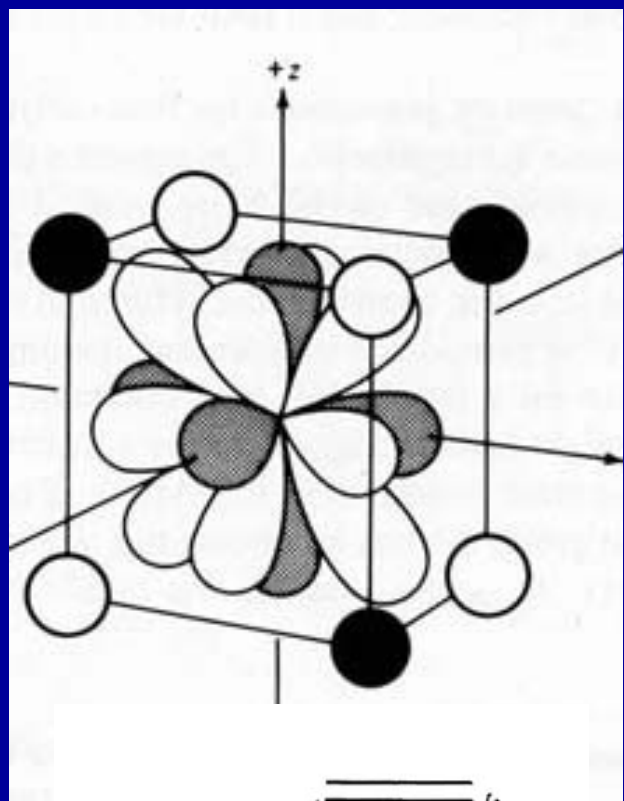
## Rozštěpení d-hladin v $T_d$ poli



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

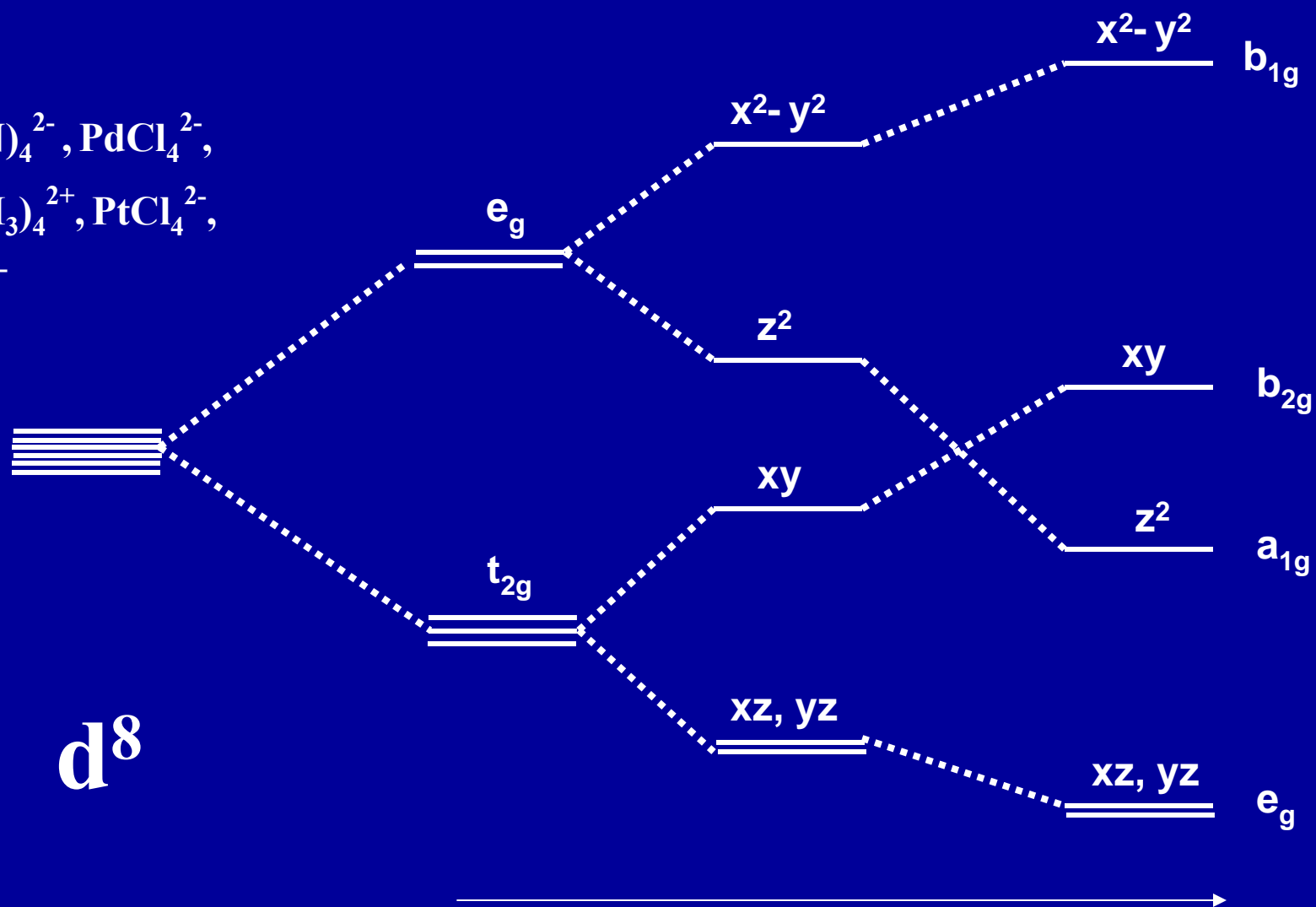
$T_d$  komplexy jsou vždy vysokospinové  
žádný d-orbital nemíří přímo k ligandům (jako u  
 $O_h$ ) slabší interakce

# d-orbitaly v tetraedrickém poli ligandů



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

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



Odtržení ligandů v ose z

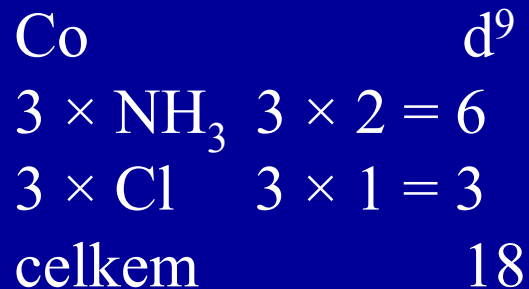
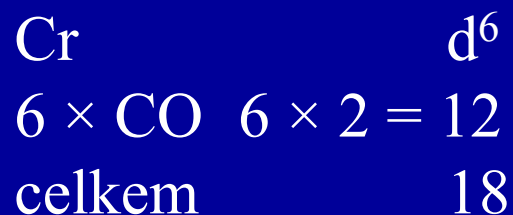
## 18-ti elektronové pravidlo

Počet d-elektronů neutrálního kovu

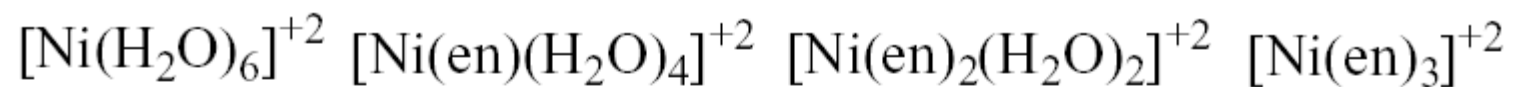
+ 2 e neutrální ligandy

+ 1 e aniontové ligandy

součet 18 pro stabilní komplexy



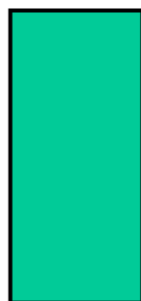
## Vliv ligandů na vlastnosti komplexů



green



green/blue



blue

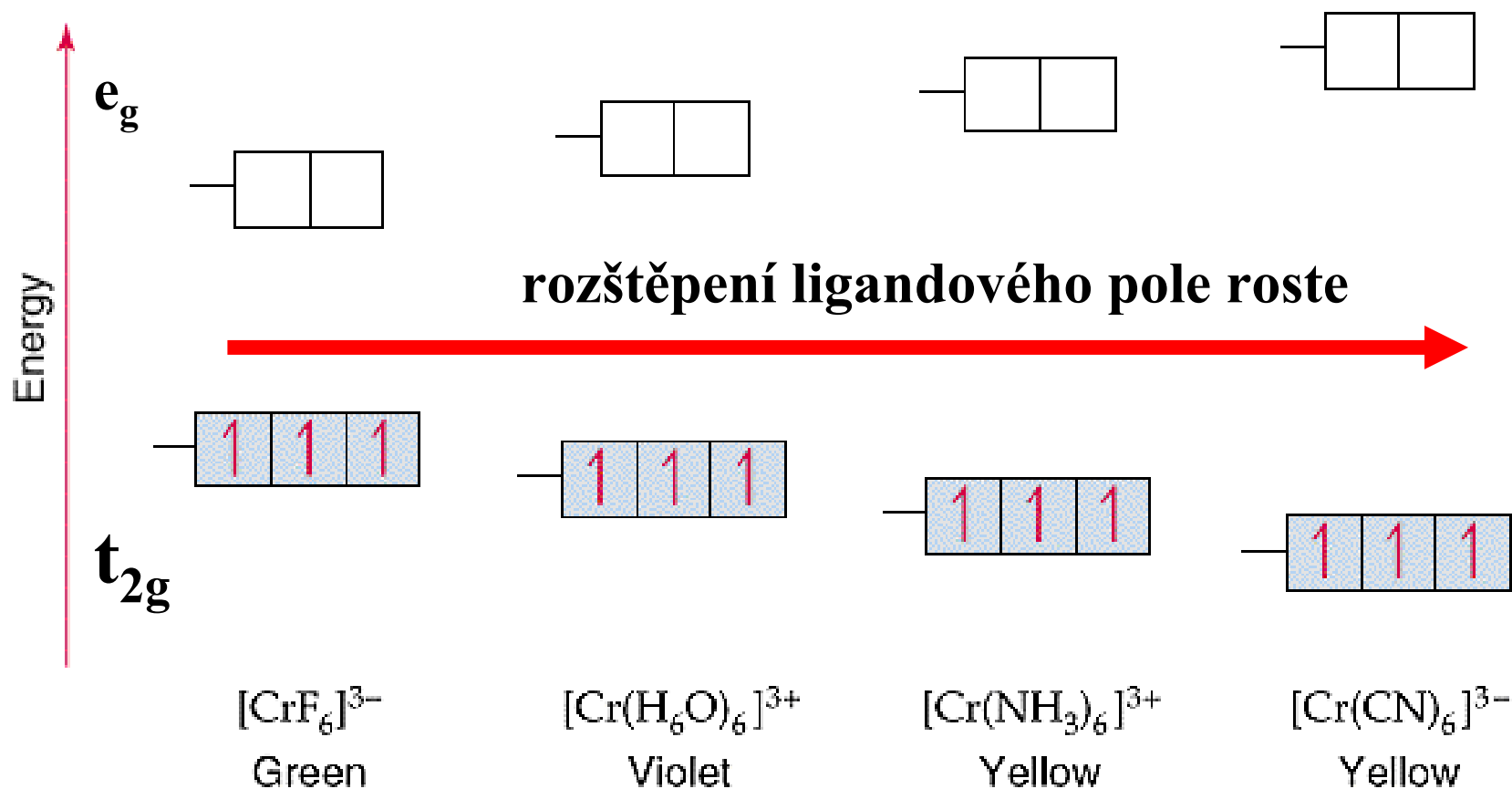


purple



en = ethylendiammin

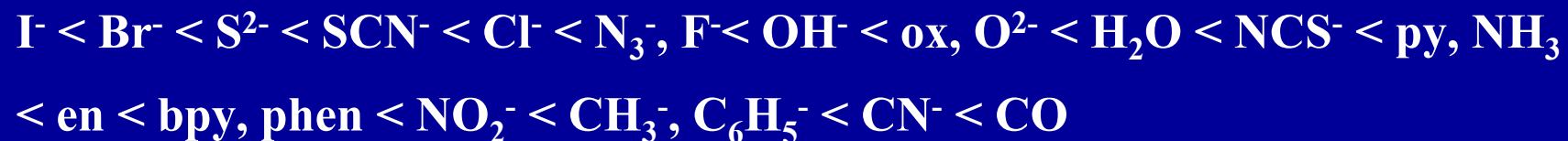
# Vliv ligandů na vlastnosti komplexů





## Faktory ovlivňující velikost rozštěpení ligandového pole

Spektrochemická řada ligandů:



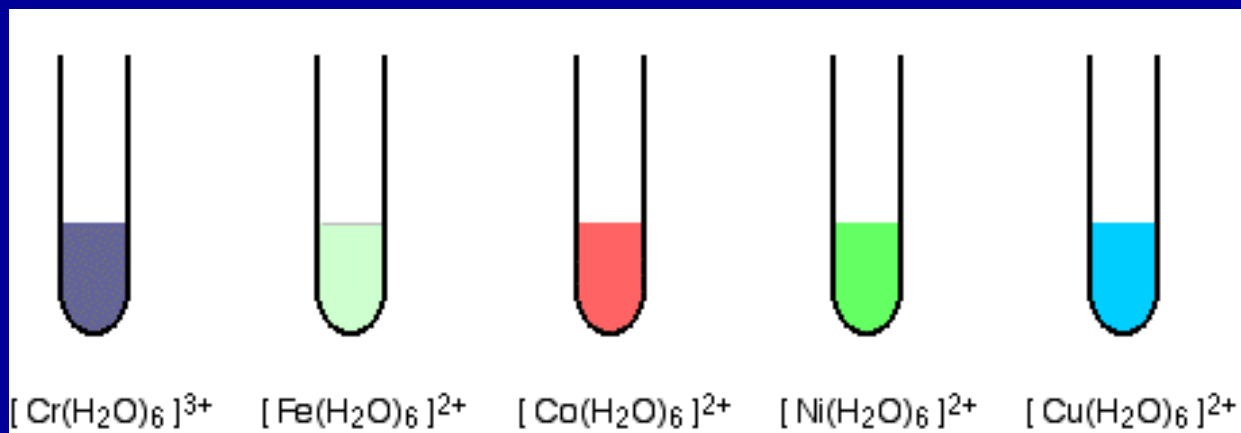
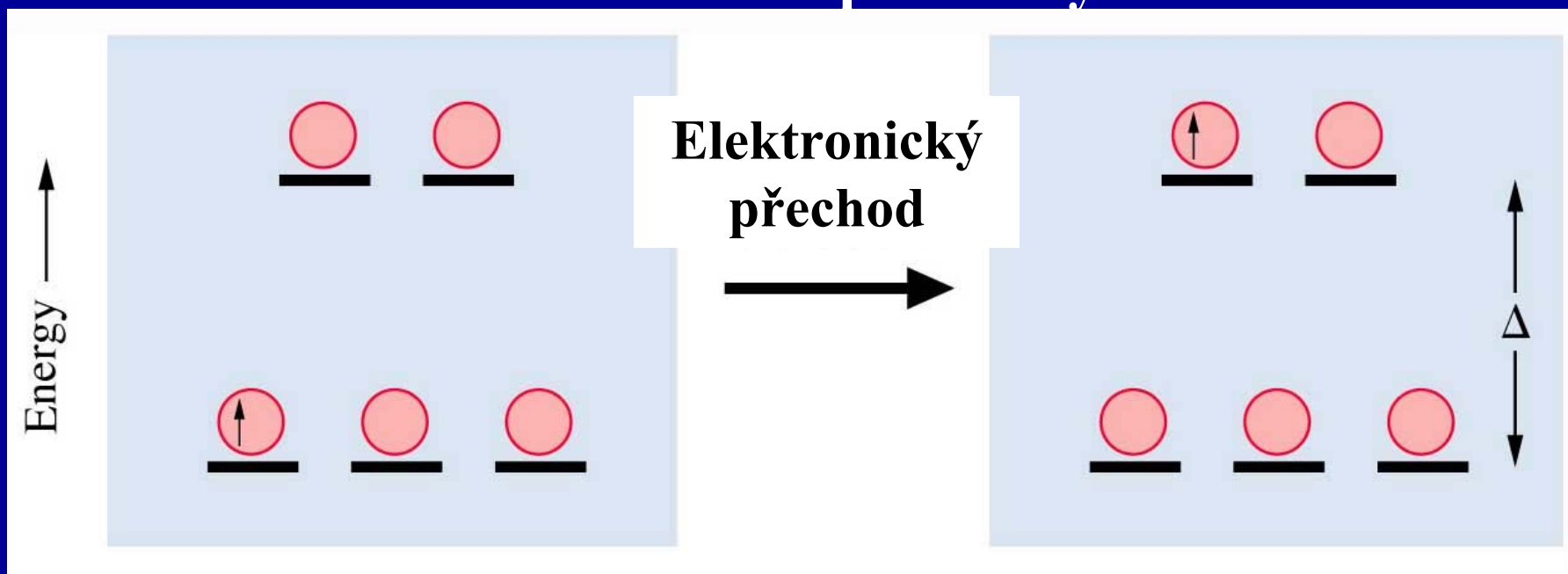
Centrální atom:

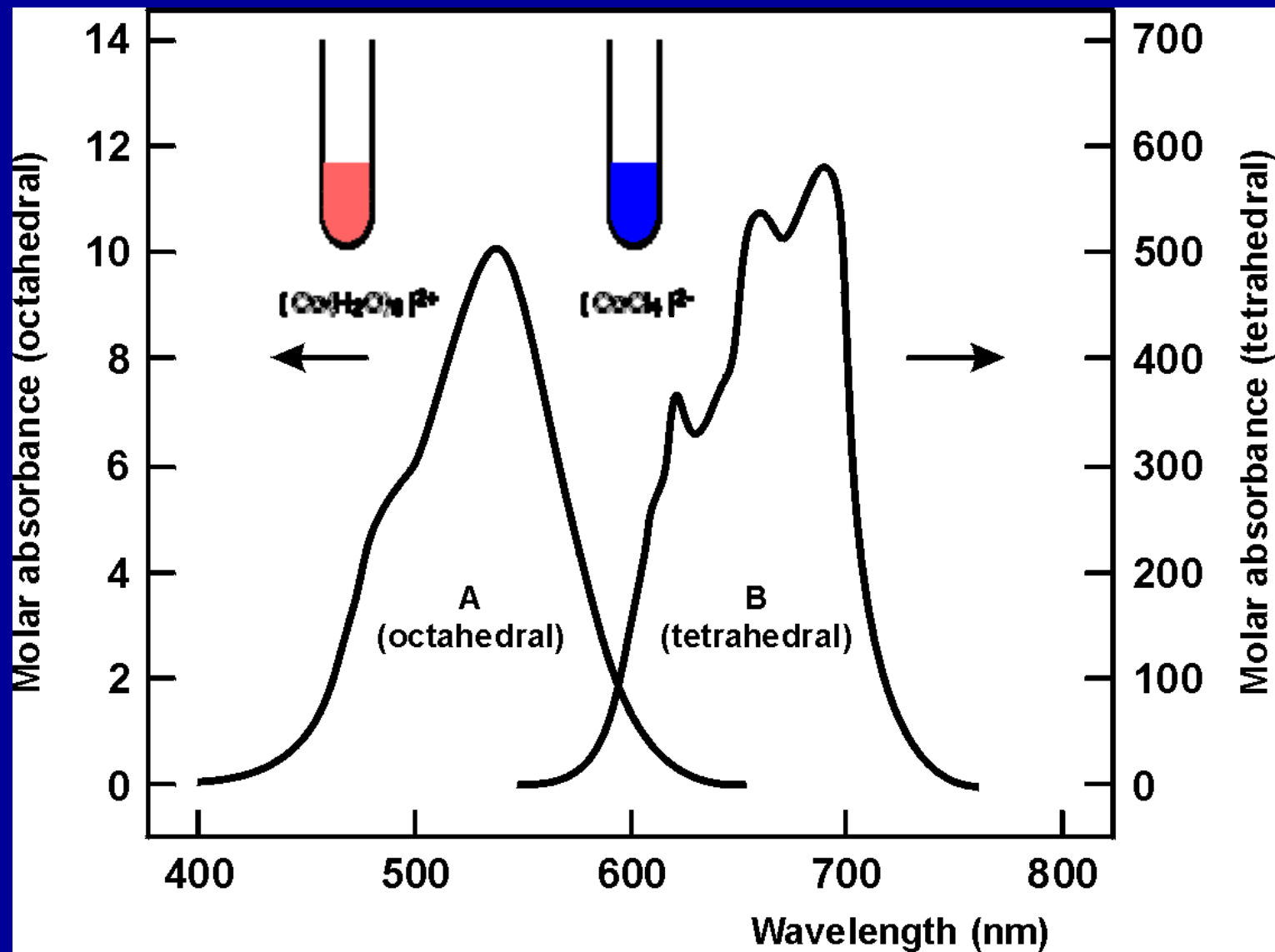


Typ koordinace  $4/9 \Delta_{\text{O}} = \Delta_{\text{t}}$

Síla a délka vazby M-L

# Elektronické přechody





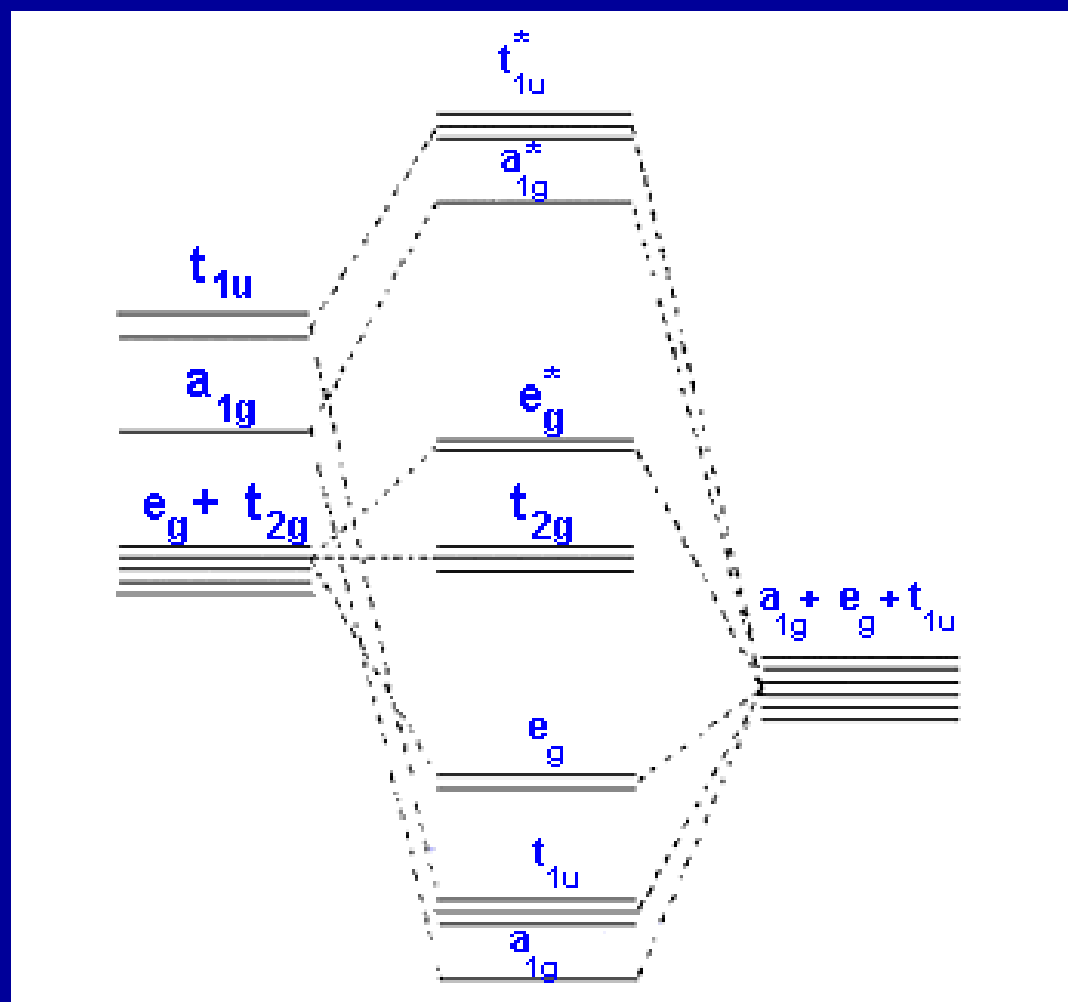
# Popis vazby v komplexech pomocí MO

3 x np

1x ns

5x (n-1) d

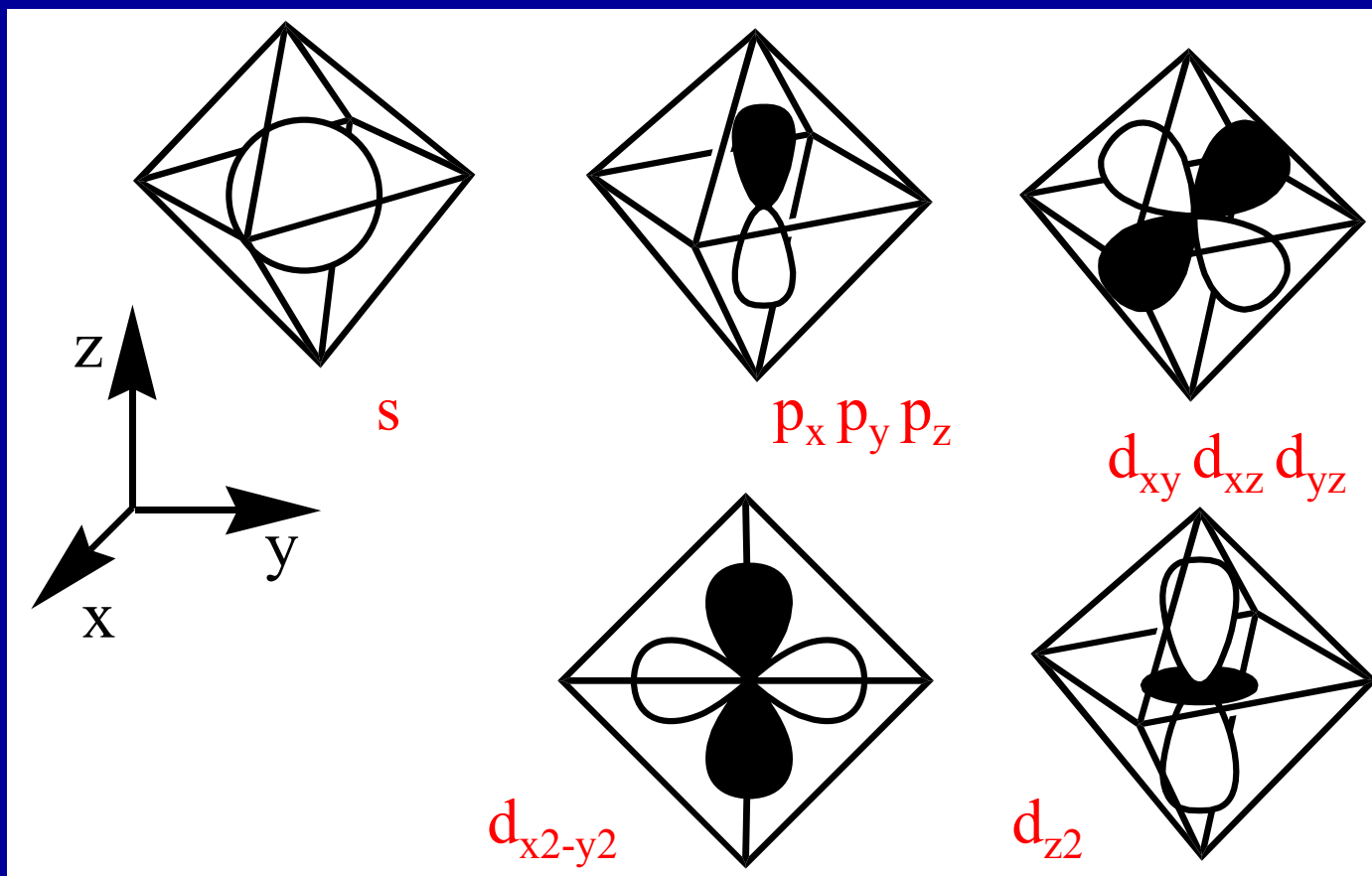
Orbitaly kovu

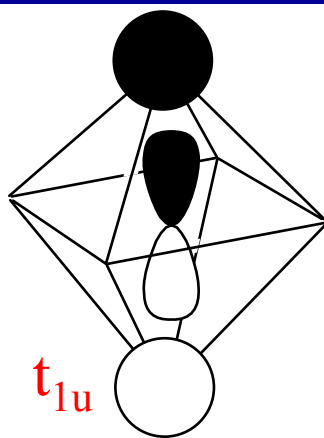
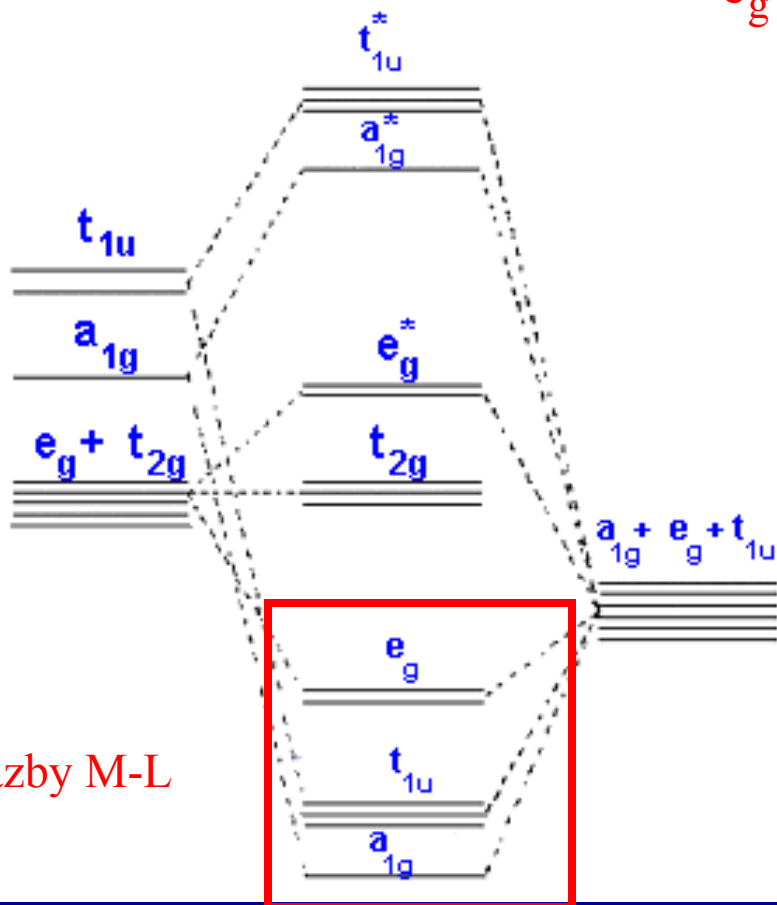
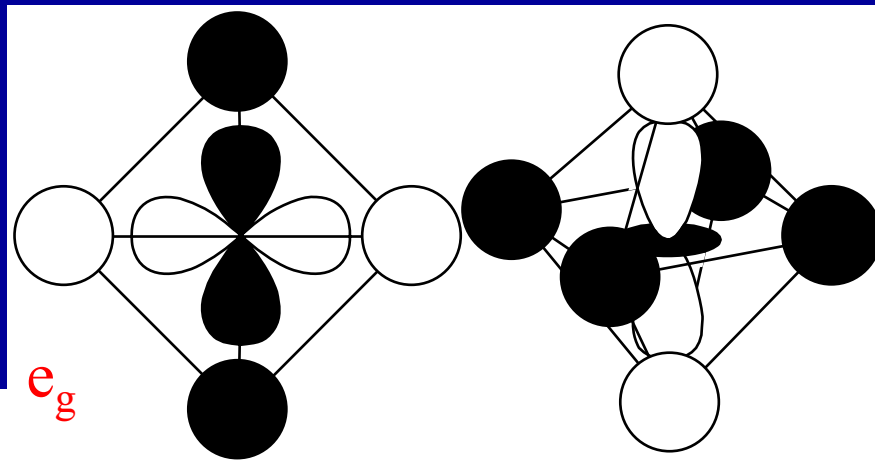


SALCAO

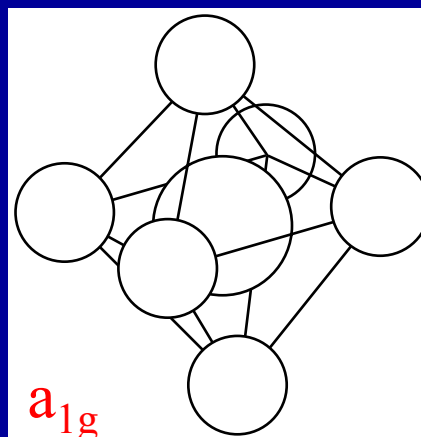
Orbitaly  
ligandů

# Valenční orbitály kovu



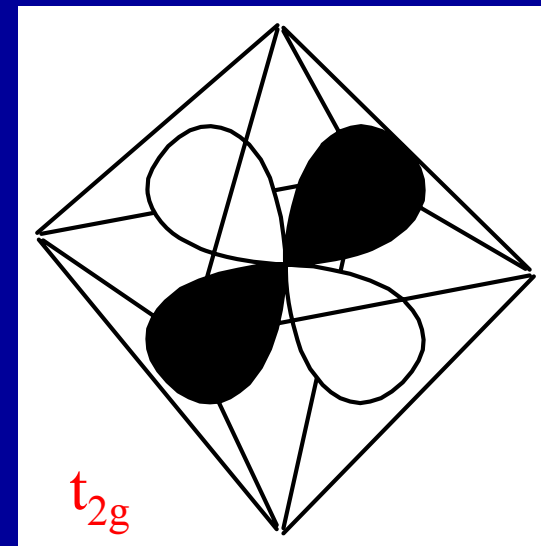
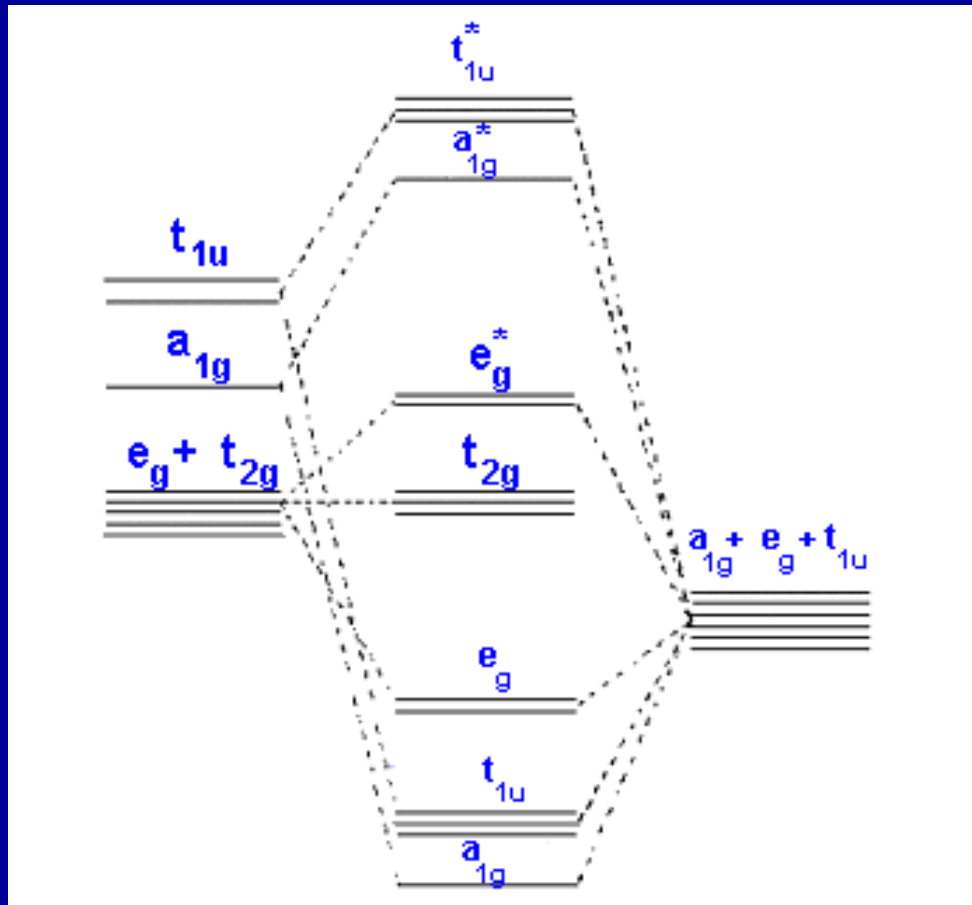


3 x np

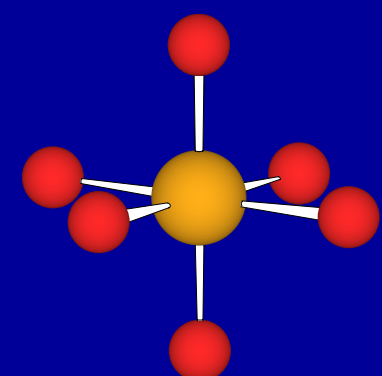
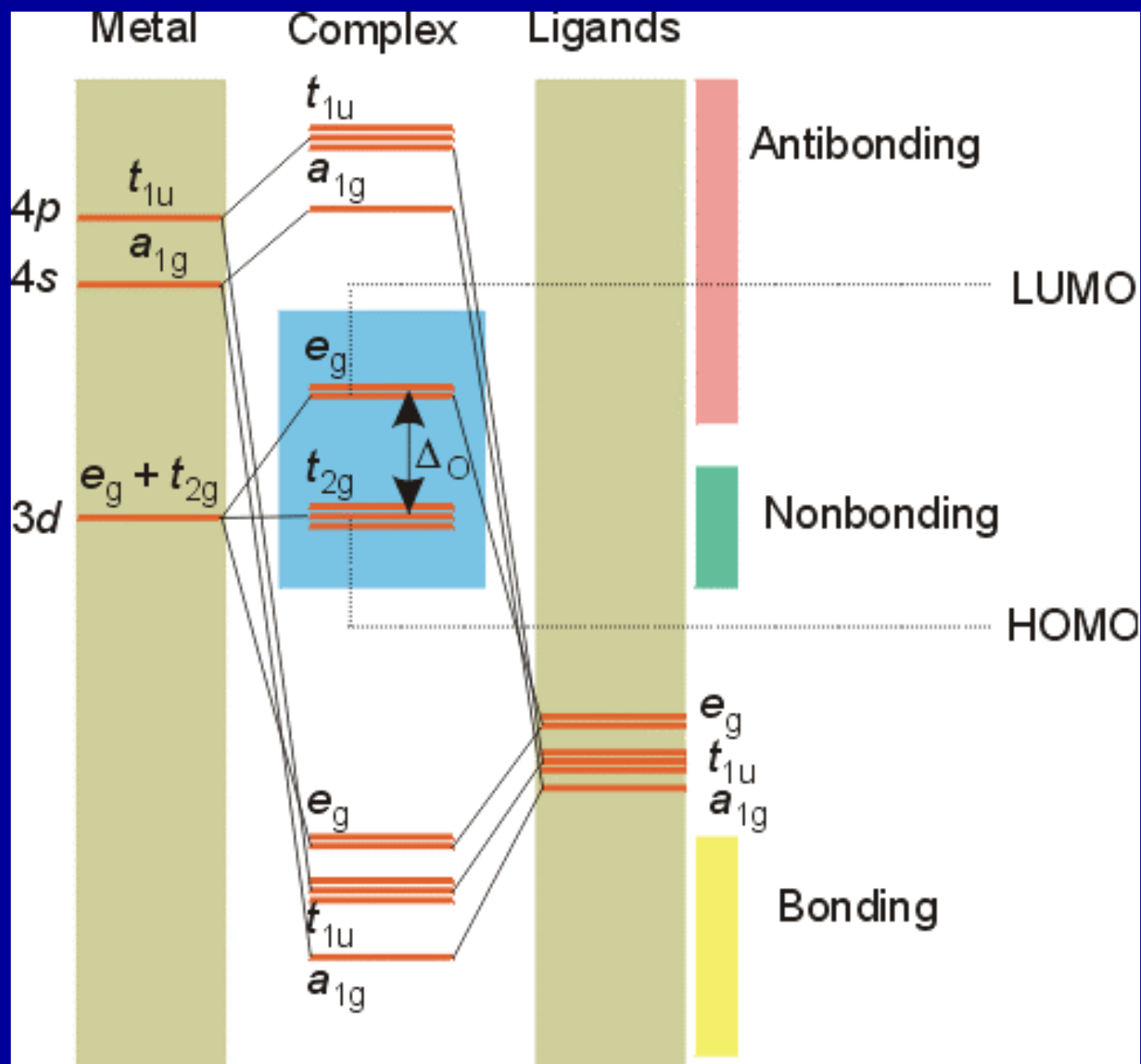


Sigma vazby M-L

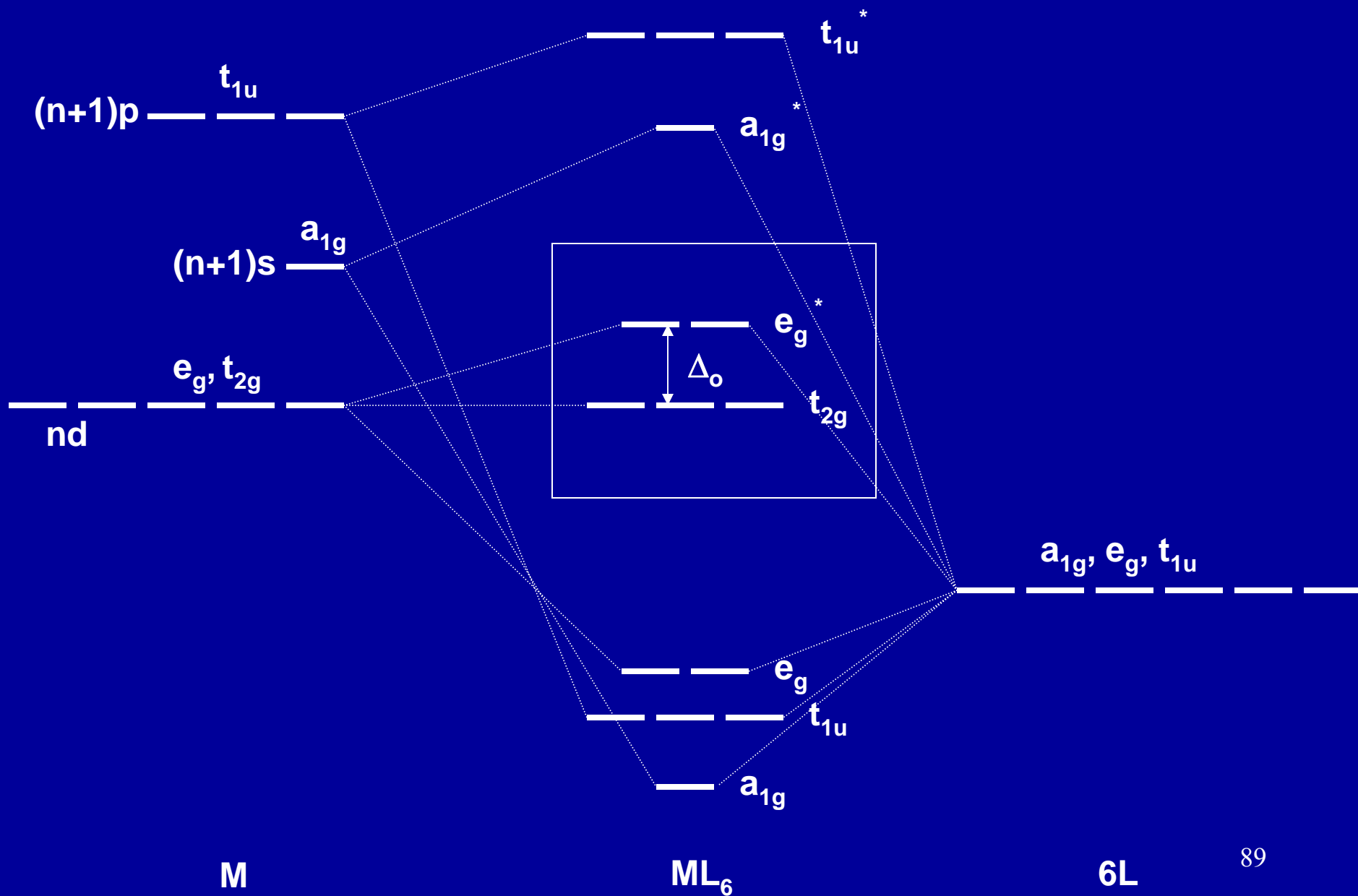
# Nevazebné d-orbitaly

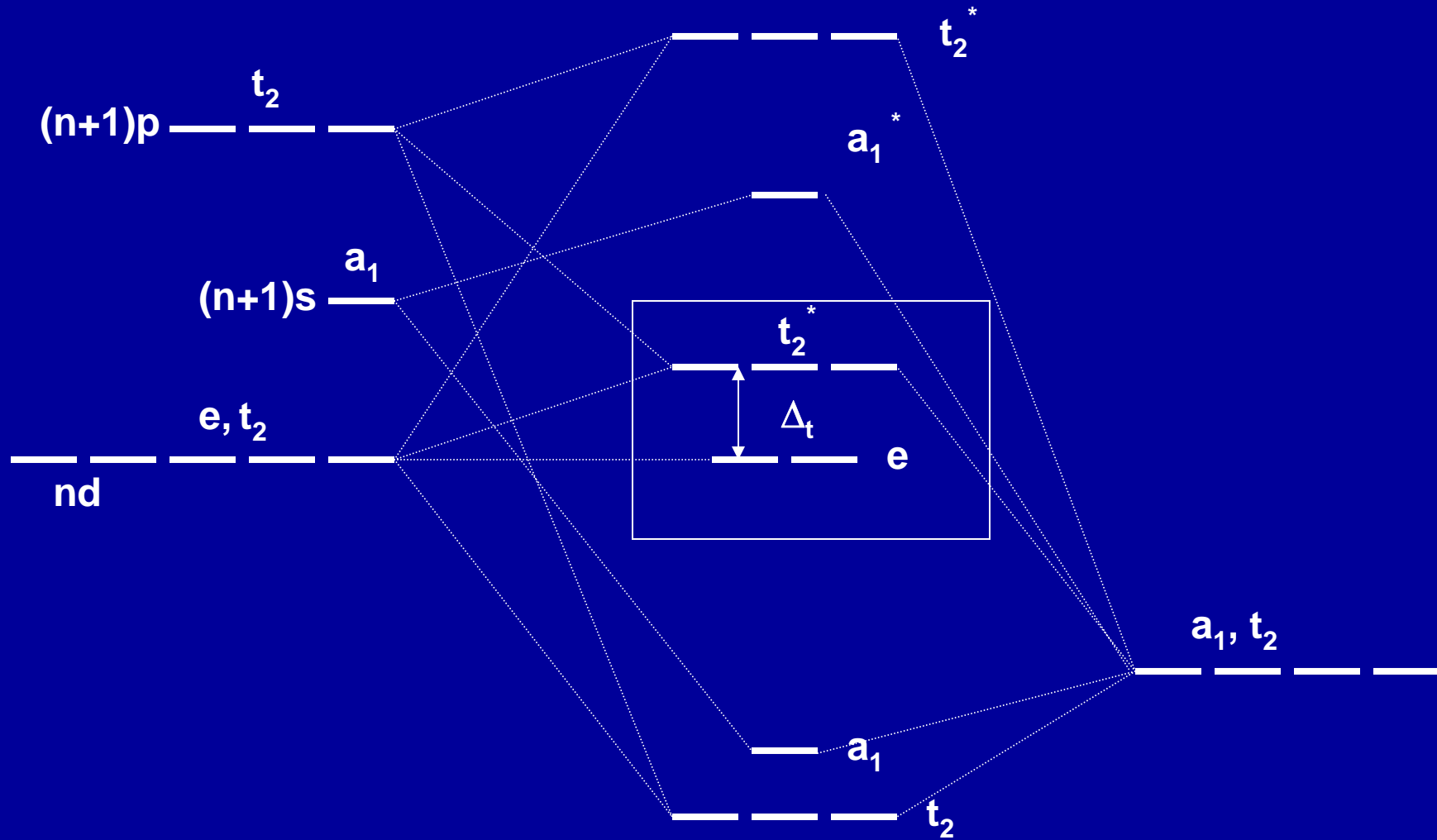


Neexistuje žádná vhodná kombinace AO ligandů (pro sigma vazbu)





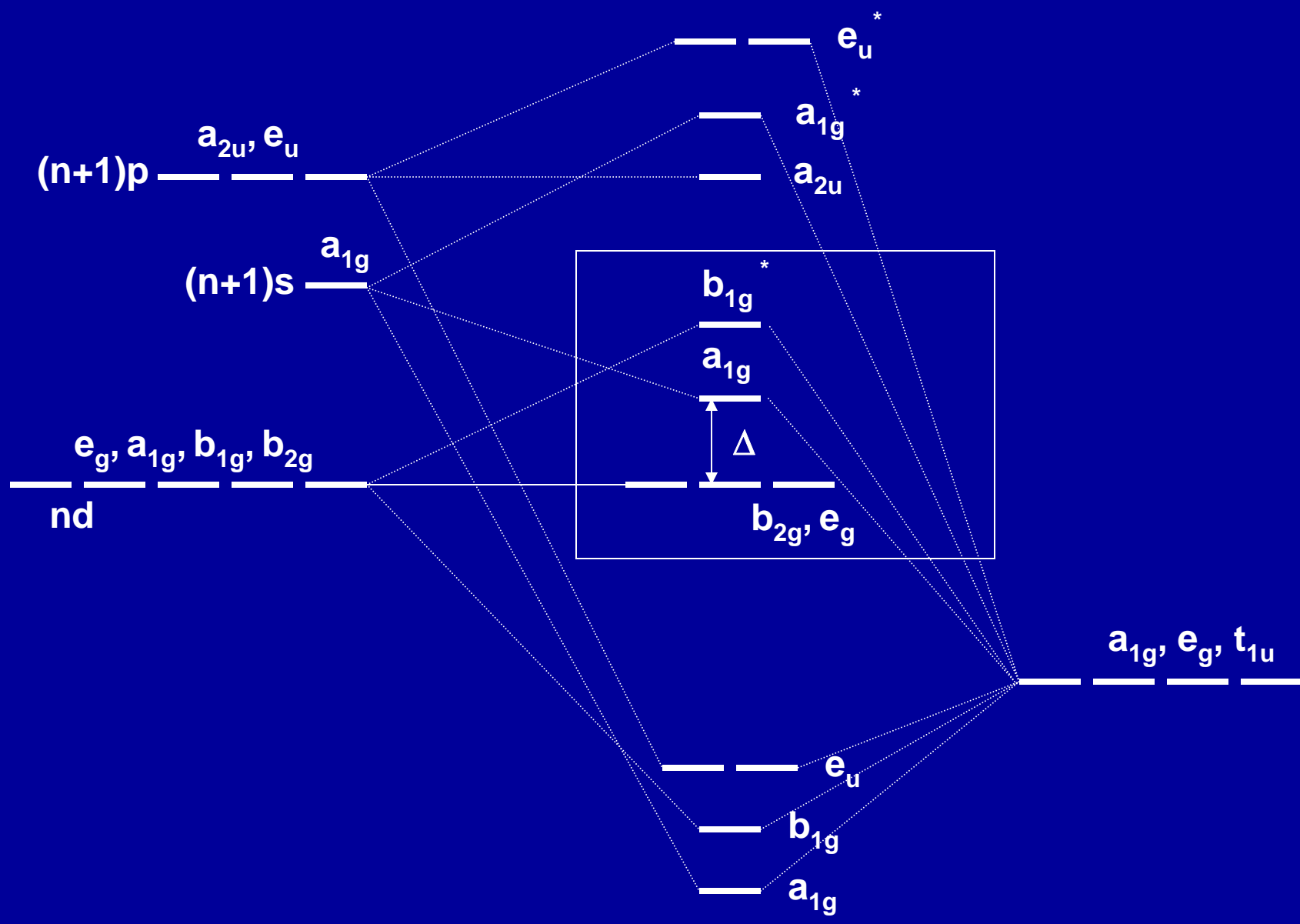




**M**

**ML<sub>4</sub>**

**4L(LGOs)<sub>90</sub>**

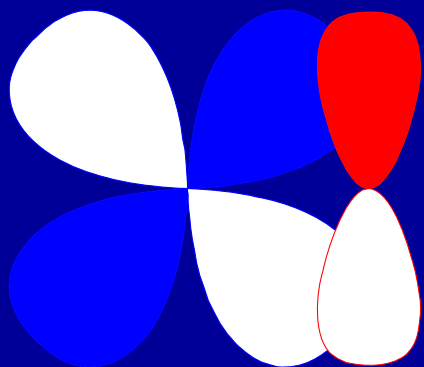


M

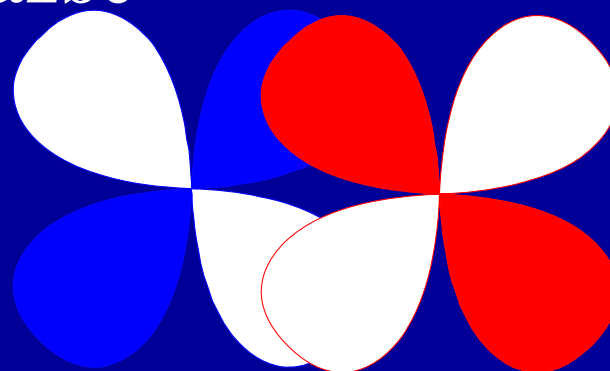
$ML_4 (D_{4h})$

$4L(LGOS)^{91}$

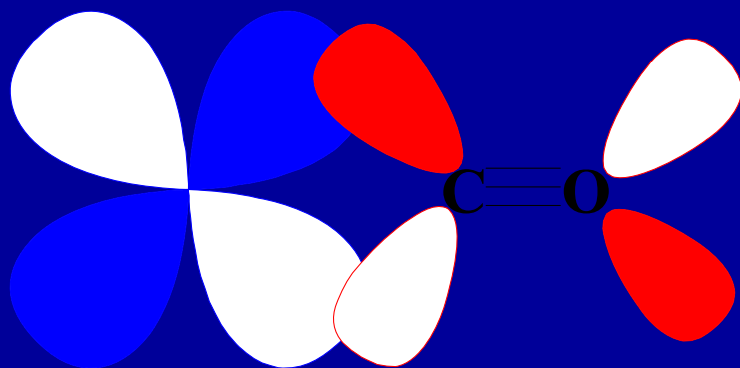
# MO při $\pi$ -vazbě



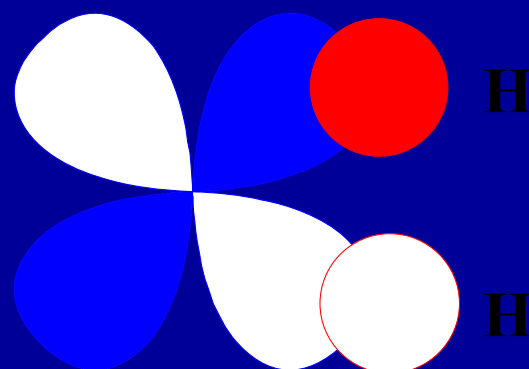
$p\pi-d\pi$   $RO^-$ ,  $RS^-$ ,  $O^{2-}$ ,  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $R_2N^-$



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

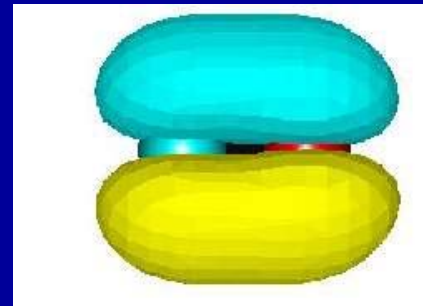
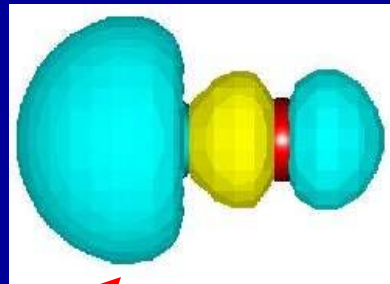
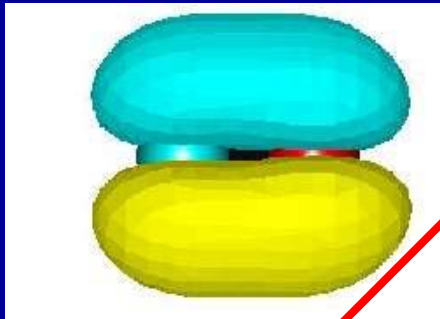
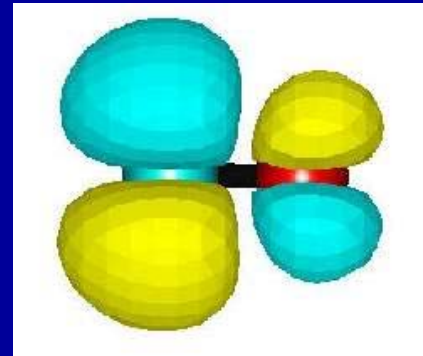
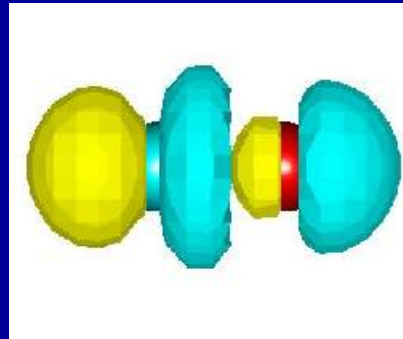
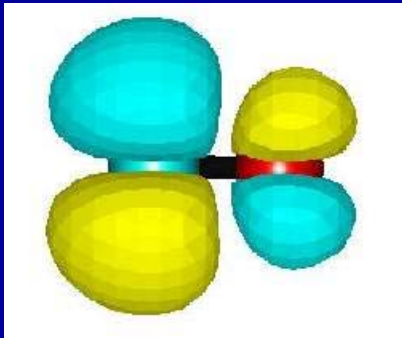


$d\pi-\pi^*$   $CO$ ,  $RNC$ , pyridin,  $CN^-$ ,  $N_2$ ,  $NO_2^-$ , ethylen



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

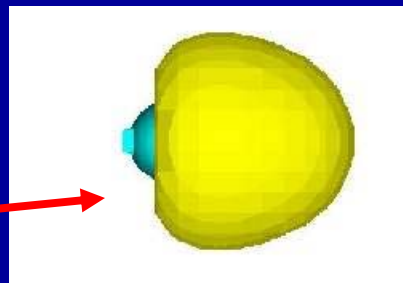
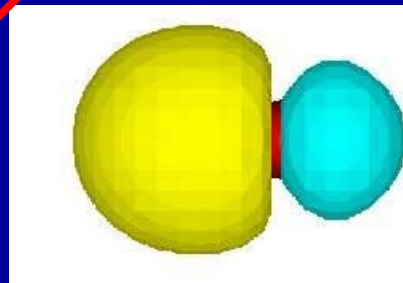
LUMO

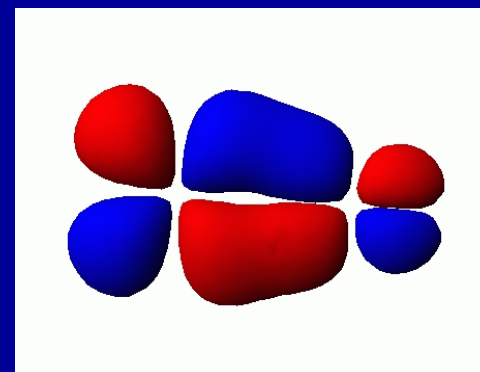
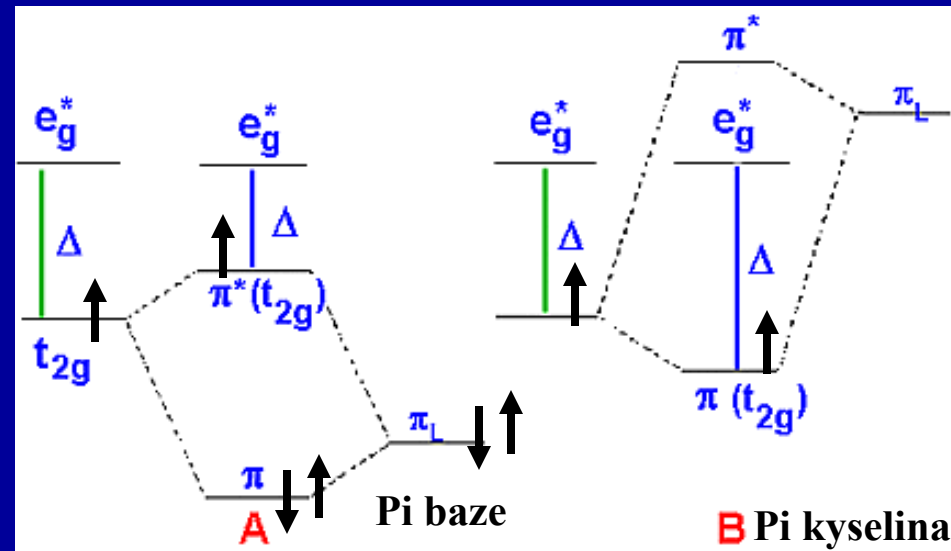
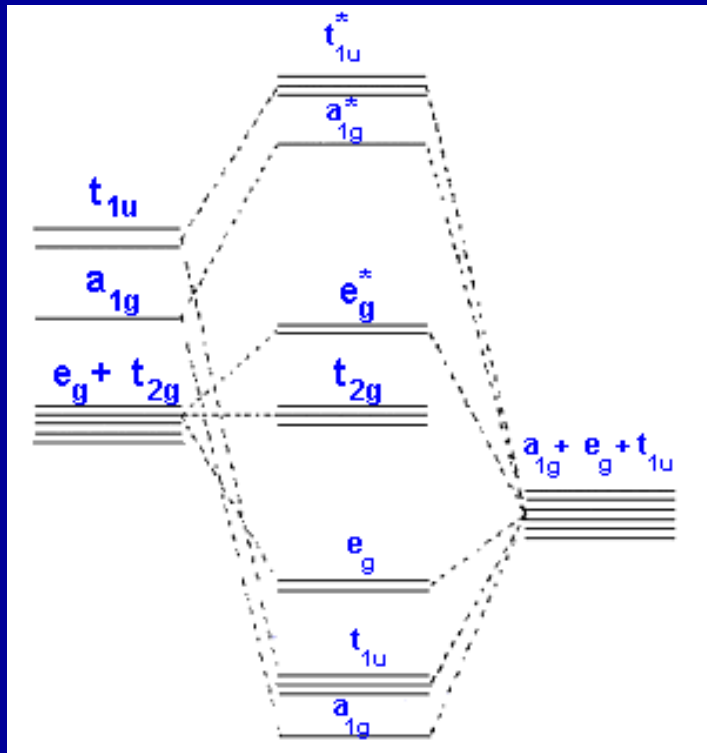
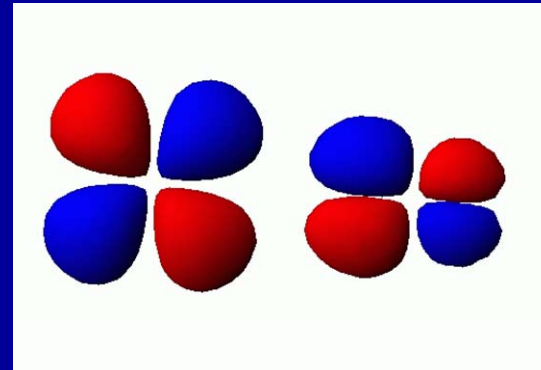


Volný e pár na C  
HOMO

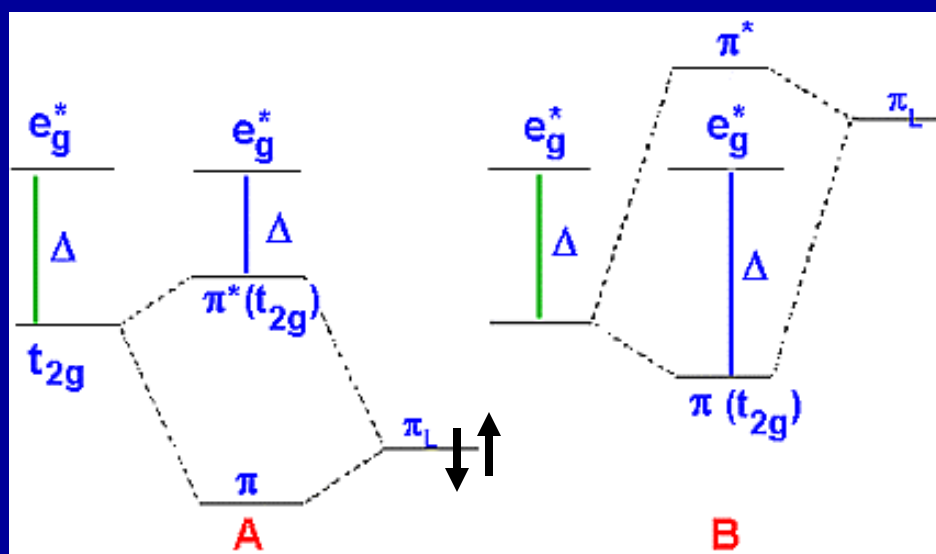


Volný e pár na O





# Ligandy s pi orbitaly



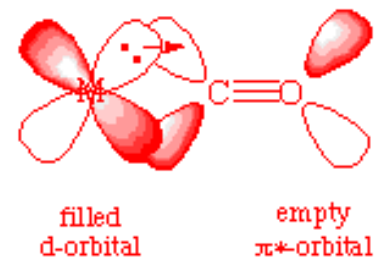
Pi baze

Pi kyselina

$\sigma$  bond:



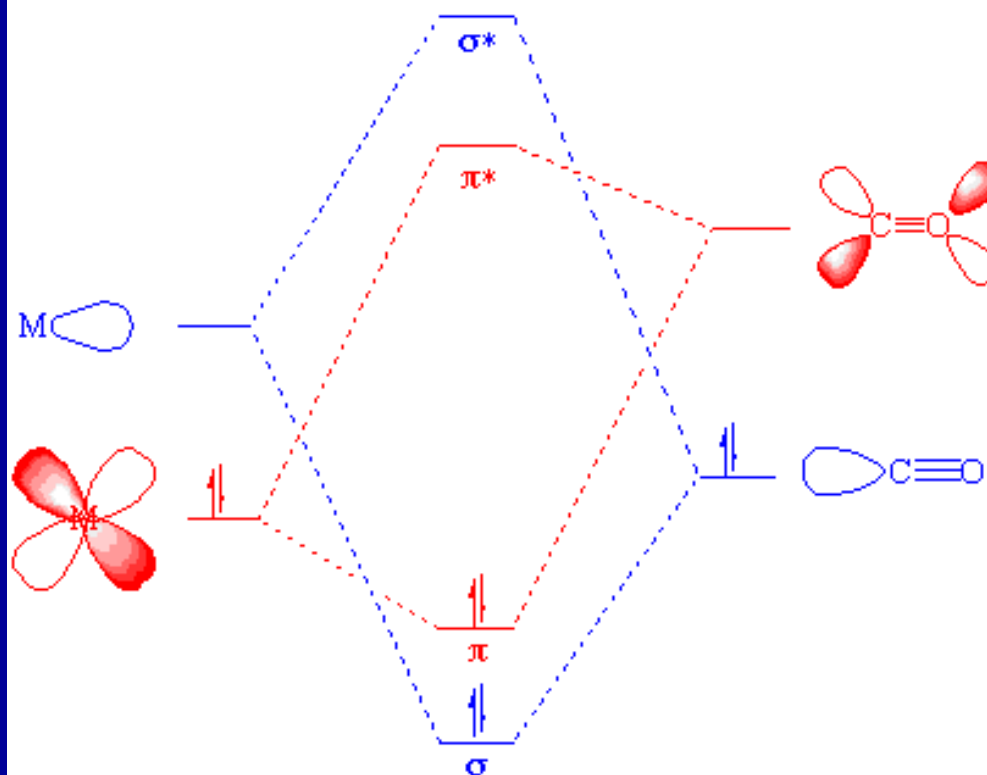
$\pi$  backbond:



$L_{\pi}M$

$L_{\pi}M(CO)$

CO



Zpětná pi donace

$M \rightarrow CO$

Sigma donace

$M \leftarrow CO$



# Jahn-Tellerova distorze

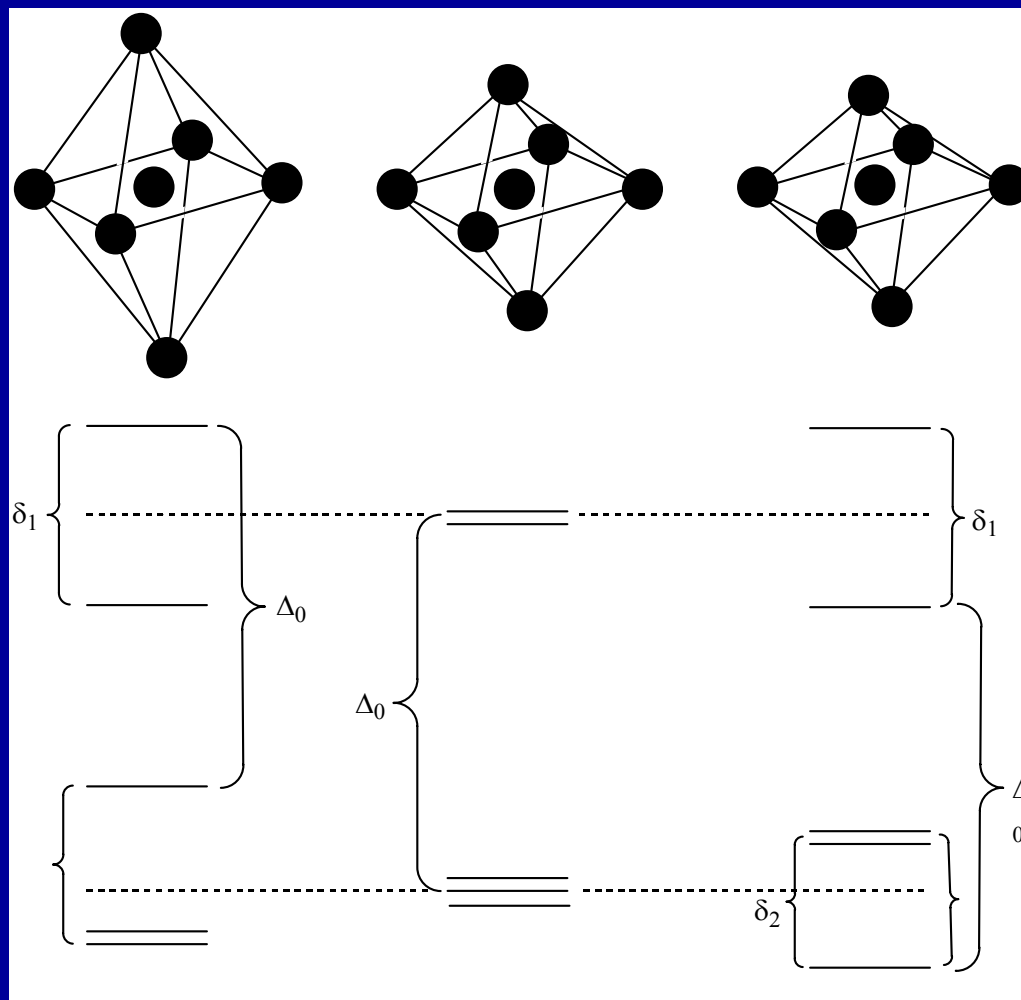
Degenerované hladiny

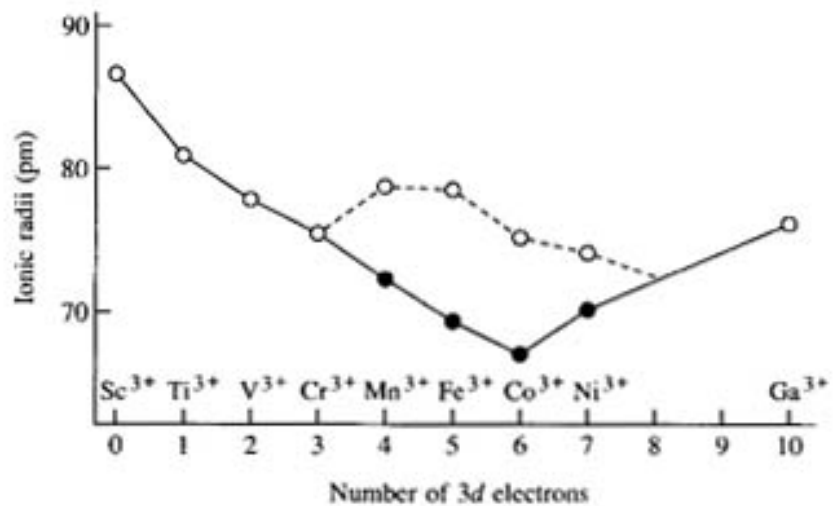
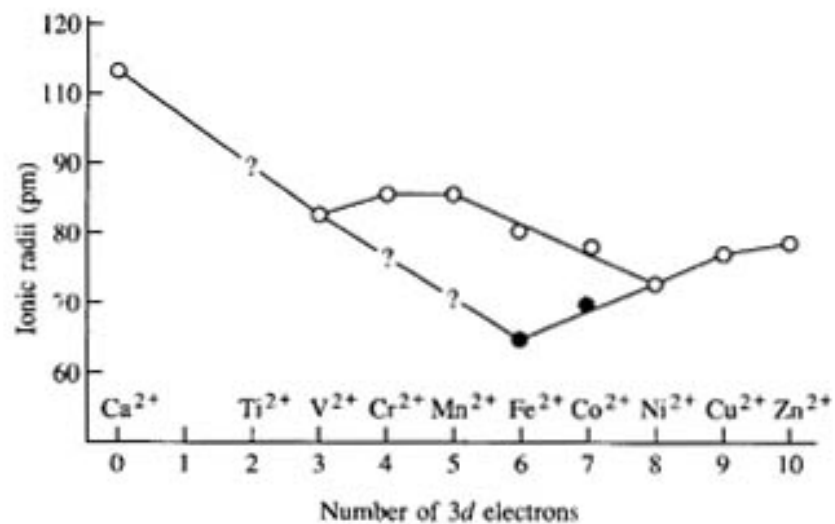
Částečně obsazené

Nelineární molekuly

Degenerace se odstraní

deformací

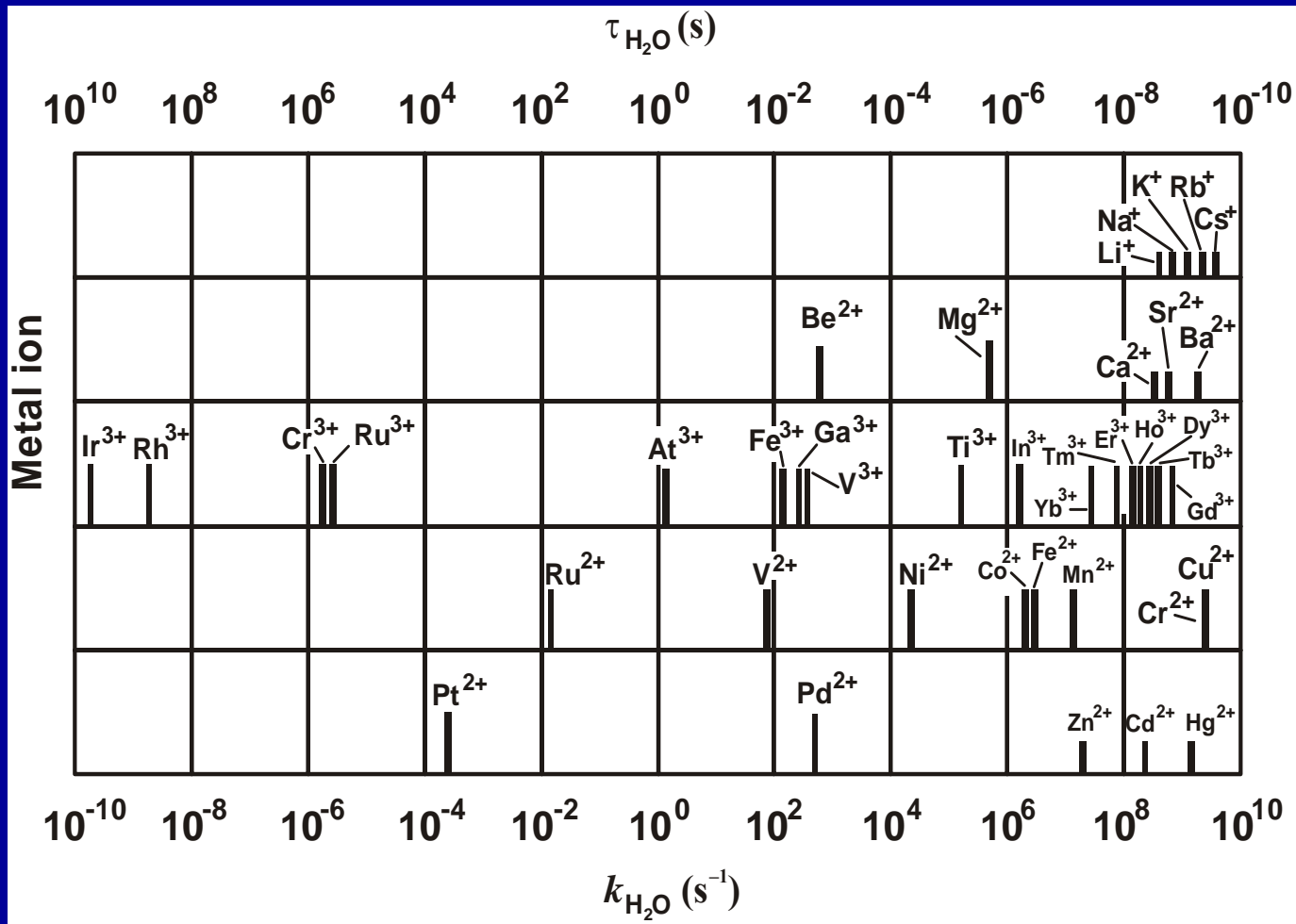




# Kinetika



INERTNÍ



LABILNÍ

# 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)

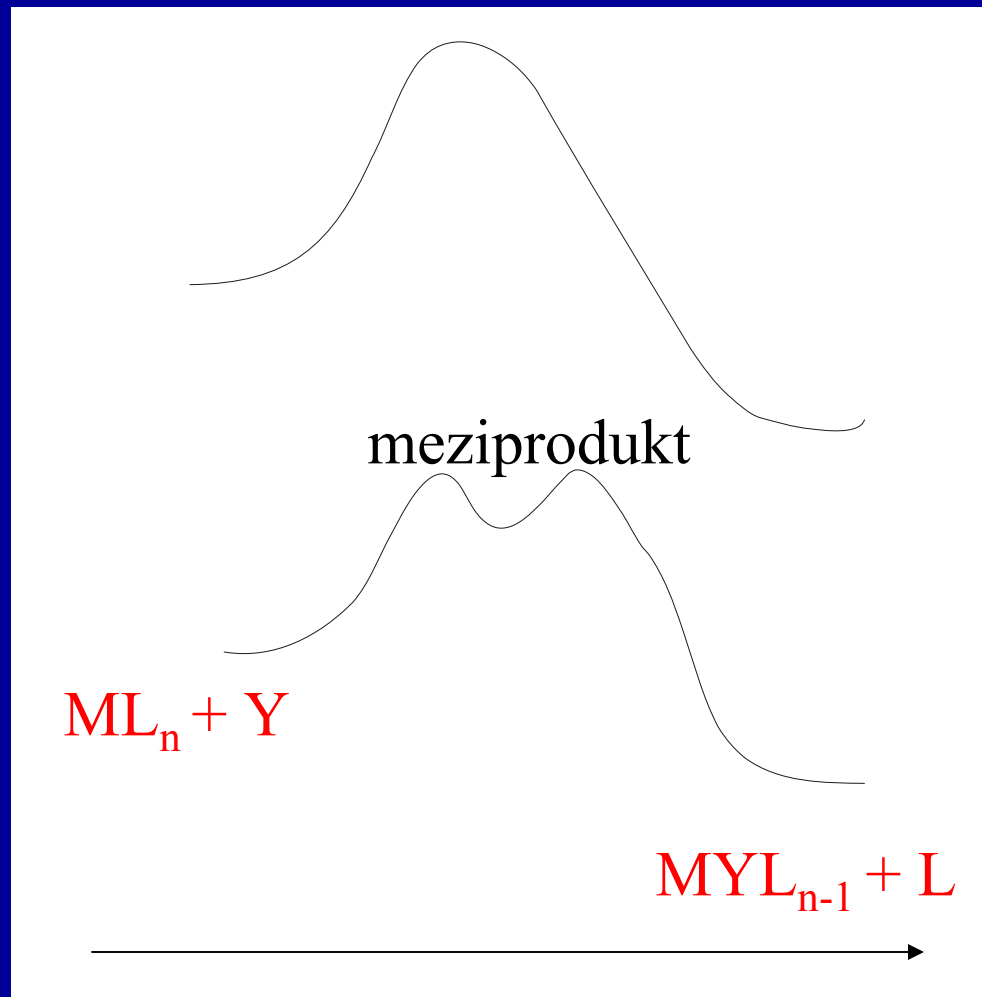
extent to which a ligand effects the rate of exchange of the ligand *trans* to itself

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

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

# Mechanismy reakcí

Výměnný (I)



## Magnetické vlastnosti komplexů

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

Magnetická susceptibilita

M = magnetizace

H = intenzita magnetického 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

