

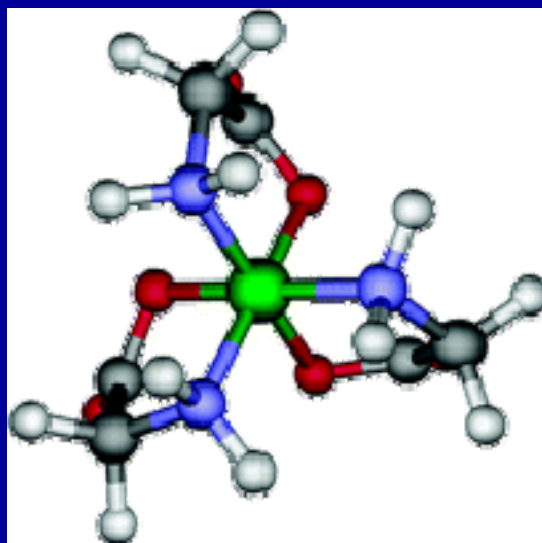
Koordinační chemie



Alfred Werner
(1866-1919)

NP za chemii 1913

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



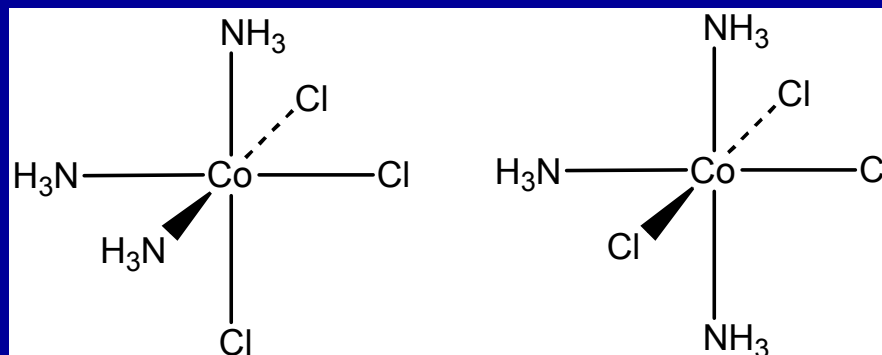
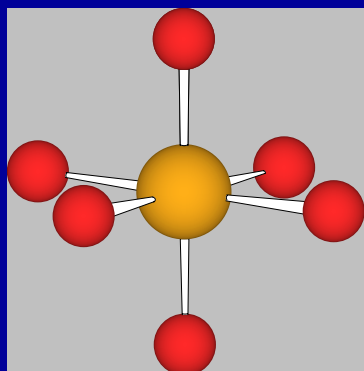
Koordinální sloučeniny

Experimentální výsledky nesouhlasí s dosavadní teorií

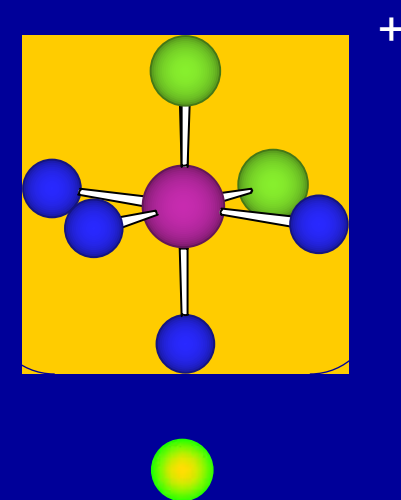
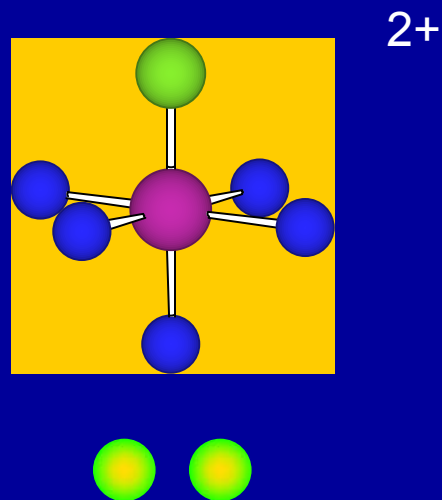
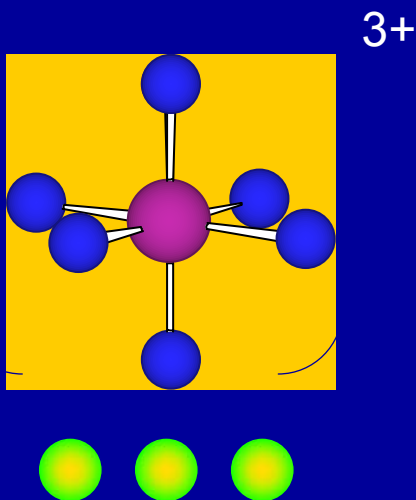
→ nová teorie (model)

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



Koordinační sloučeniny



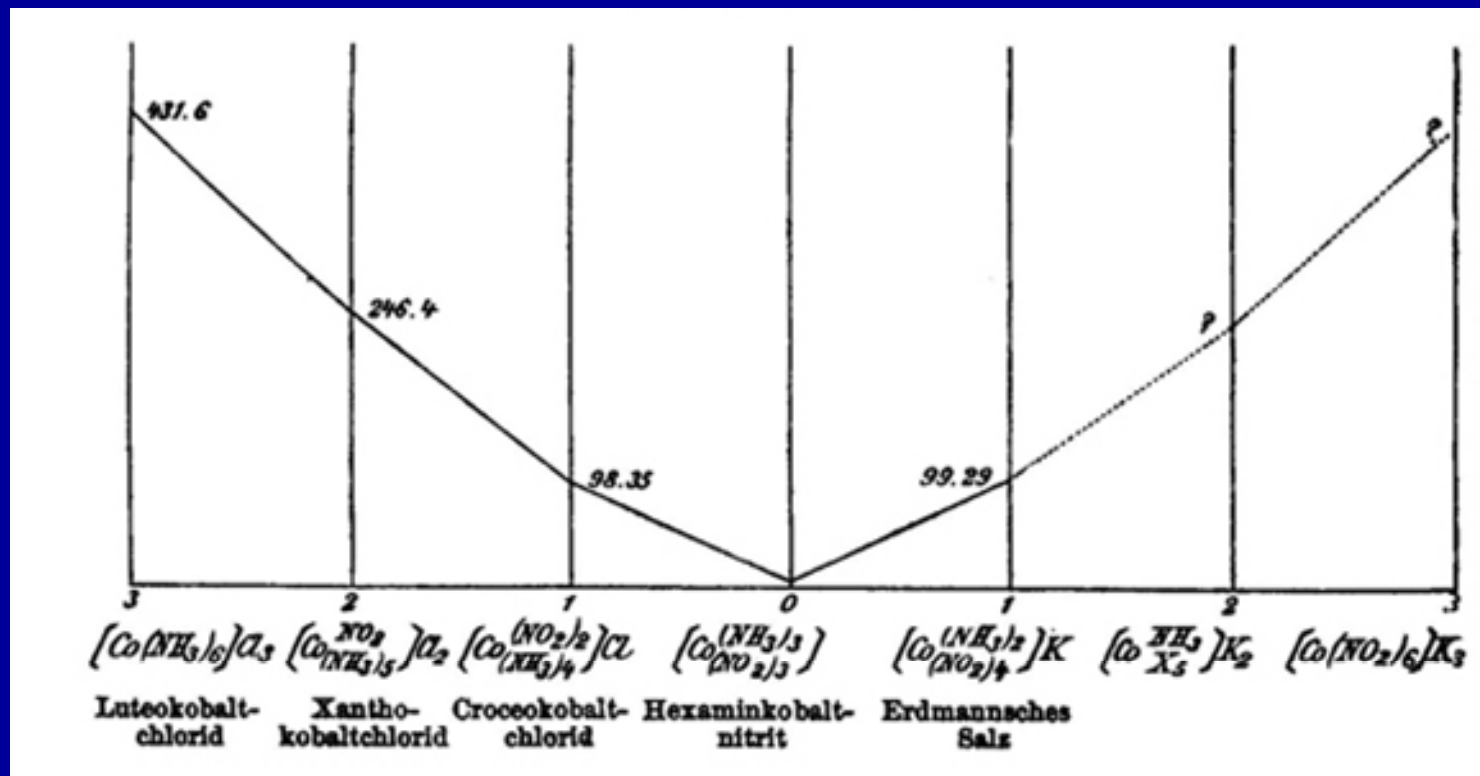
Kov v oxidačním stavu $n+$ (primární valence)

Komplex má koordinační číslo m (sekundární valence)

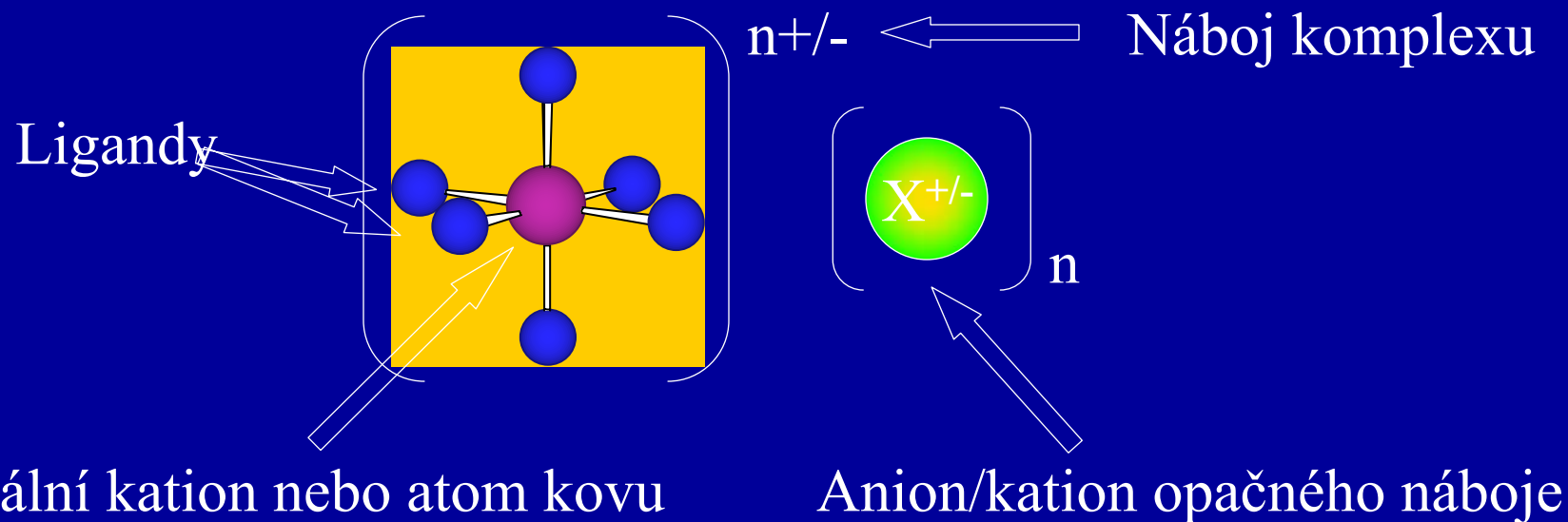
Ligandy vázány k centrálnímu atomu donor-akceptorovými vazbami

Koordinační sloučeniny

Elektrická vodivost roztoků komplexních sloučenin



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 =

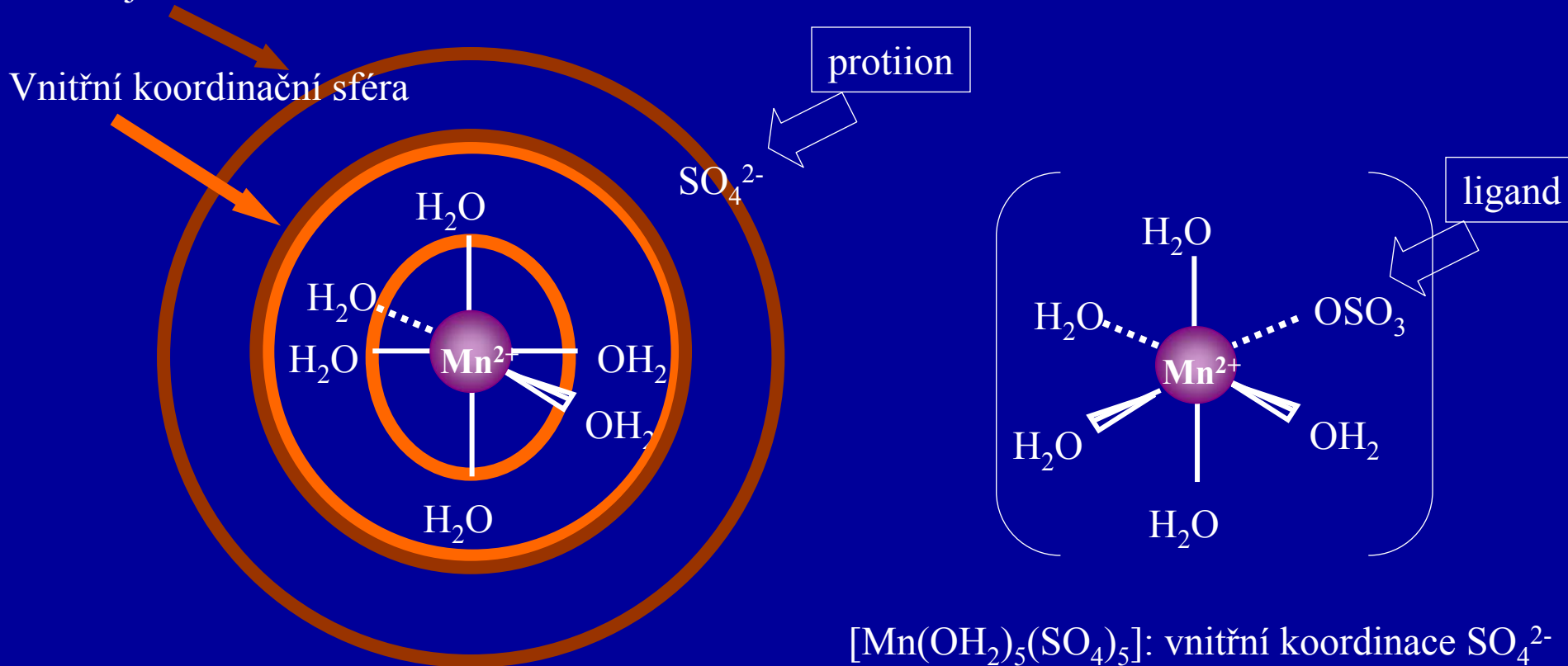
ligandy přímo vázané k centrálnímu atomu

Vnější koordinační sféra =

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

Vnější koordinační sféra

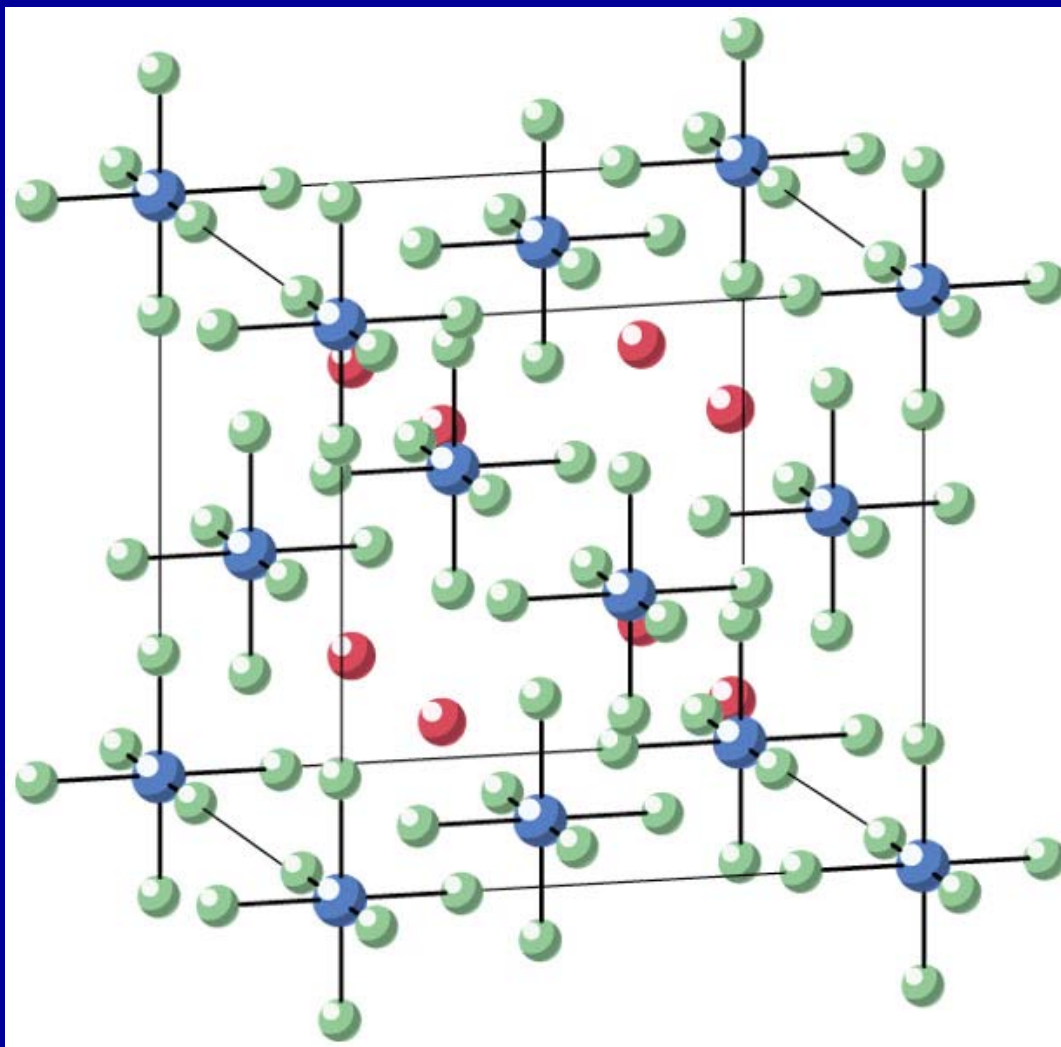
Vnitřní koordinační sféra



$[Mn(OH_2)_5(SO_4)_5]$: 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

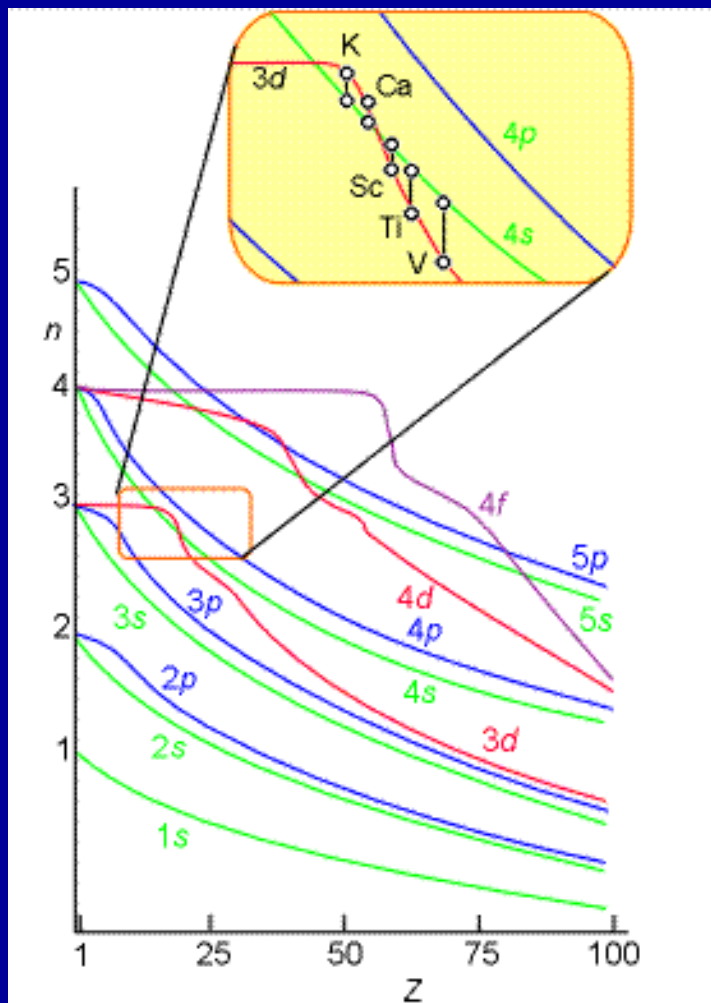
Ar [Ne] 3s² 3p⁶ (4s⁰)

K [Ar] 4s¹ (3d⁰ 4p⁰)

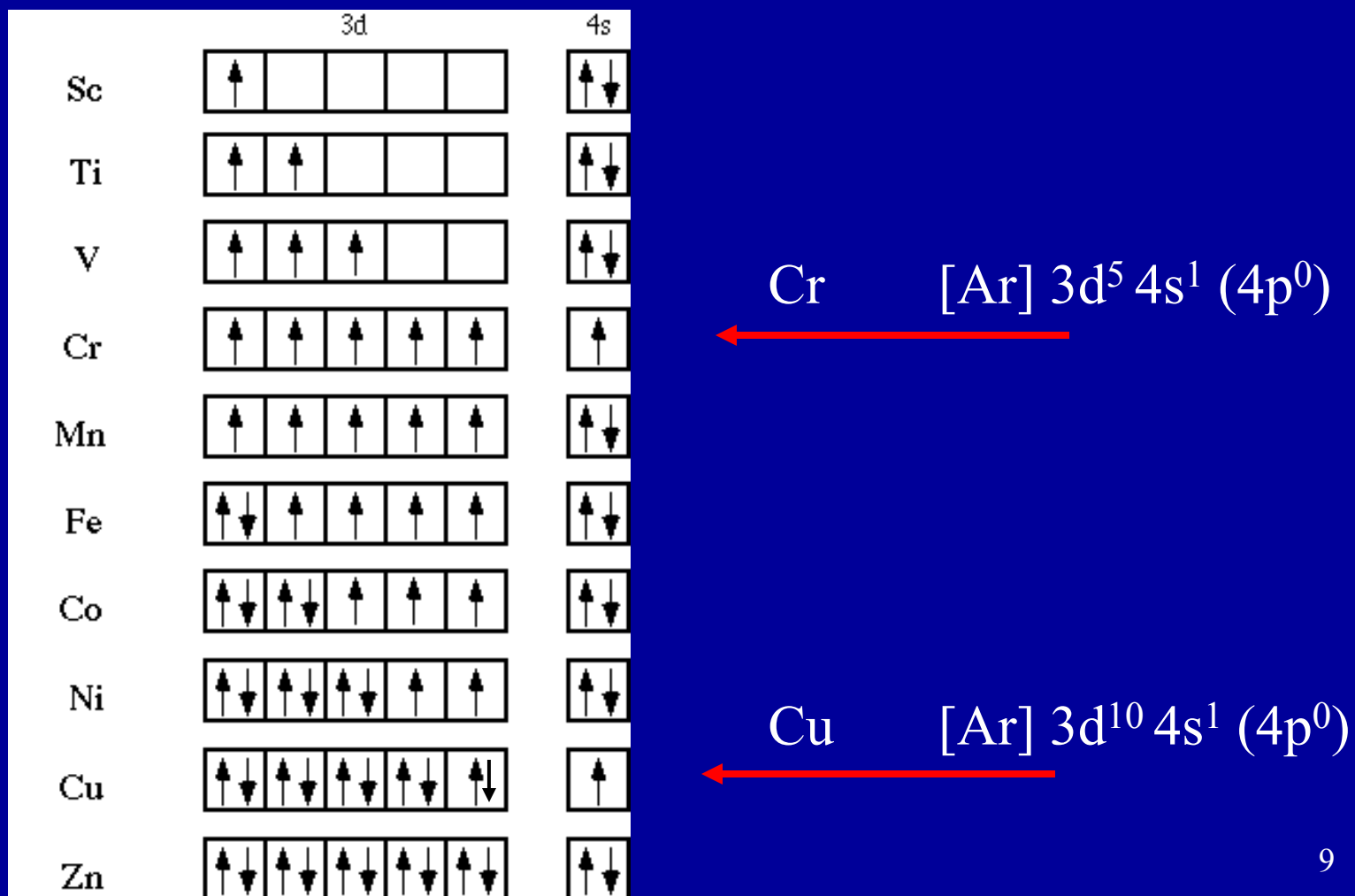
Ca [Ar] 4s² (3d⁰ 4p⁰)

Sc [Ar] 3d¹ 4s² (4p⁰)

Ti [Ar] 3d² 4s² (4p⁰)



Vyšší stabilita zpola zaplněných d-orbitalů

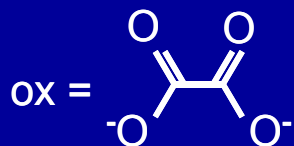


Oxidační stavy přechodných kovů

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										
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

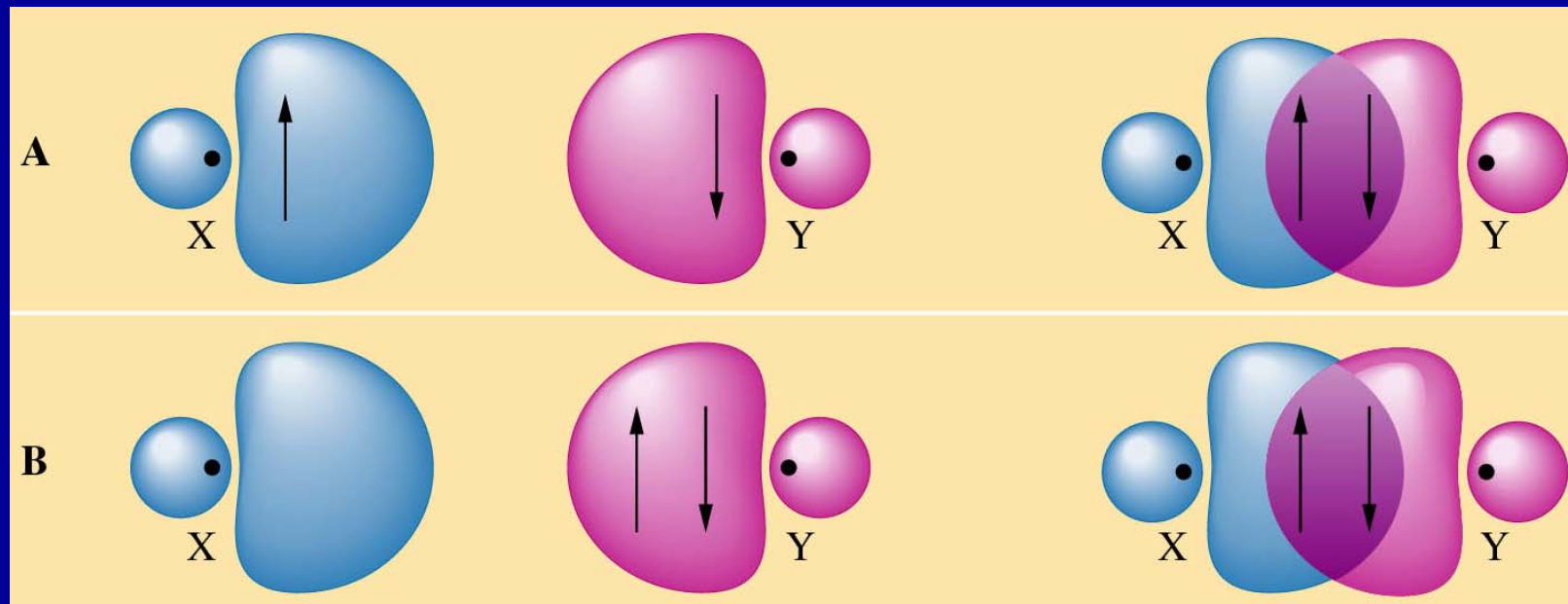


																H	He	
Li	Be												B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	110	111	112		114					
			Ce	Pr	Nd	Pm	Sm	Eu	Gd	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



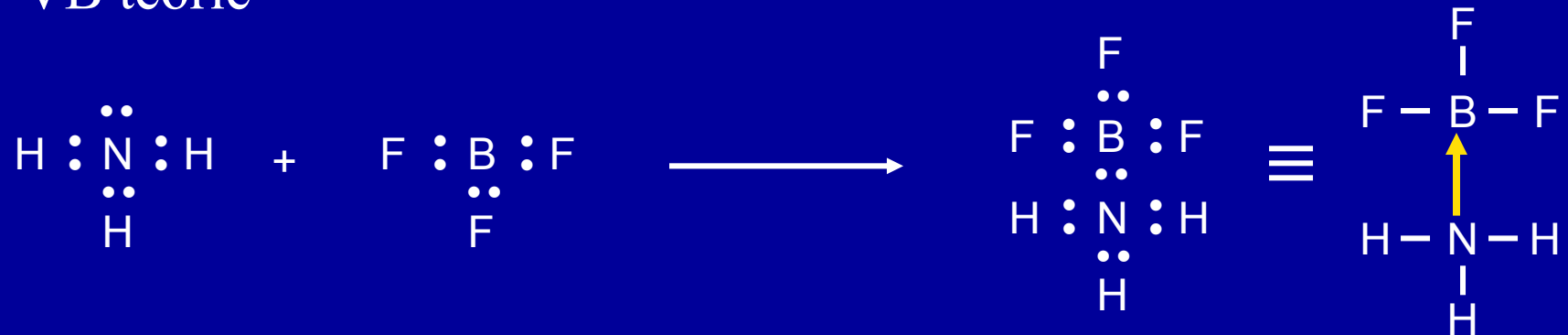
Akceptor
Volný orbital

Donor
Volný e pár

Kovalentní vazba

Donor-akceptorová vazba

VB teorie

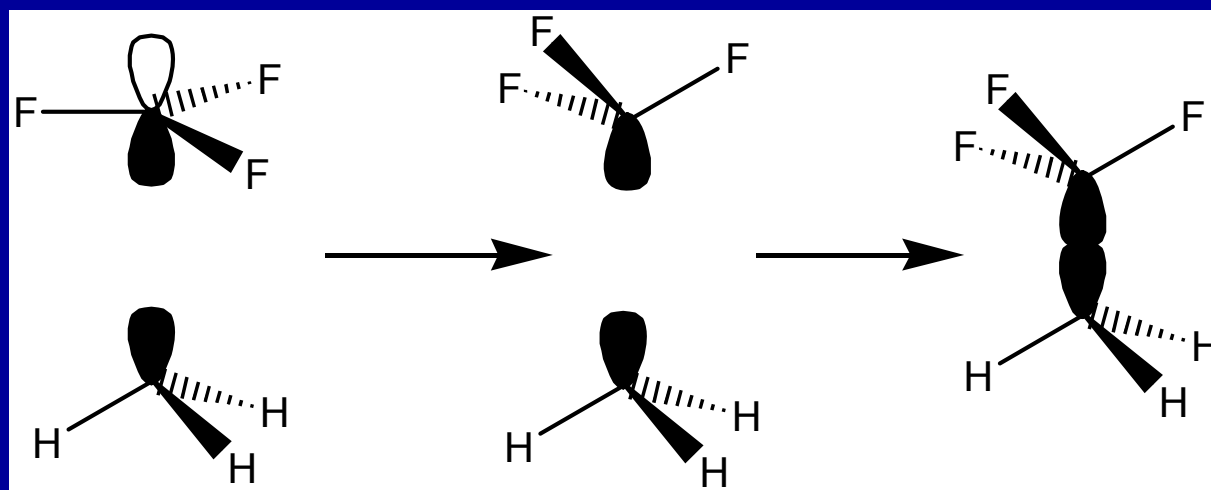


 Donor-akceptorová vazba

Donor-akceptorová vazba

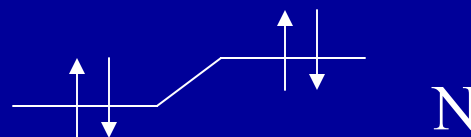


VB teorie



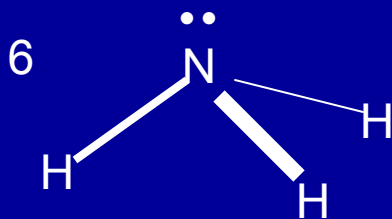
MO teorie

B

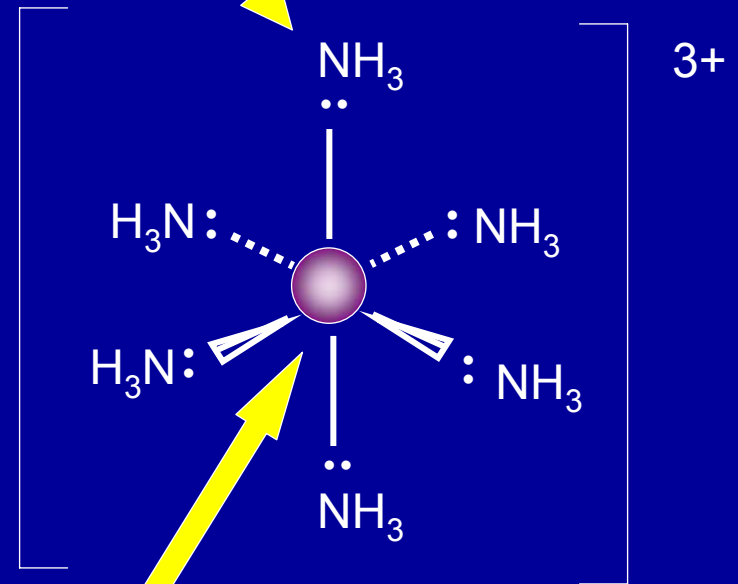


Donor-akceptorová vazba

VB teorie

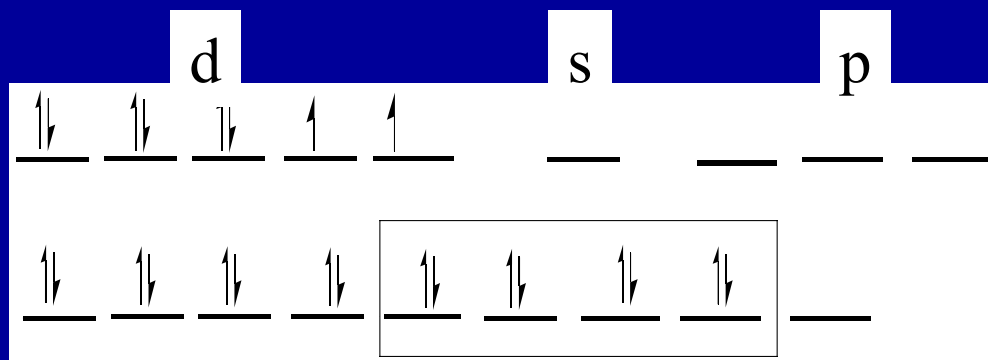


"Lewisovská báze"



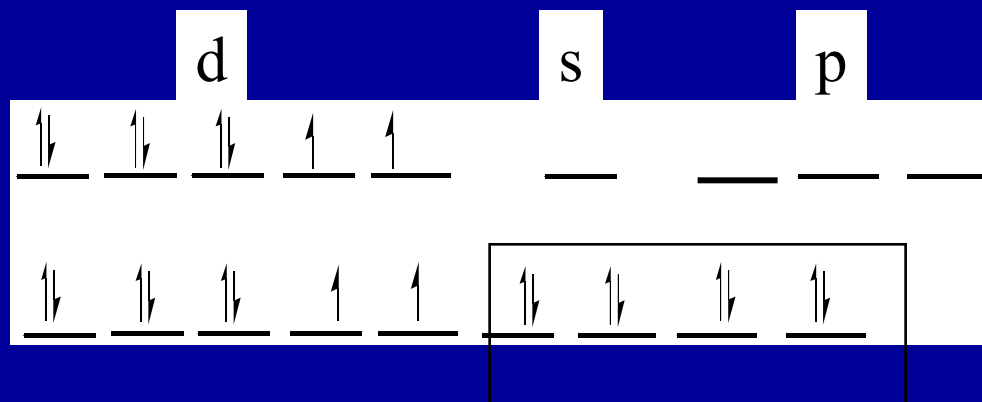
Každý ligand poskytne do vazby 2 elektrony

"Lewisovská kyselina"



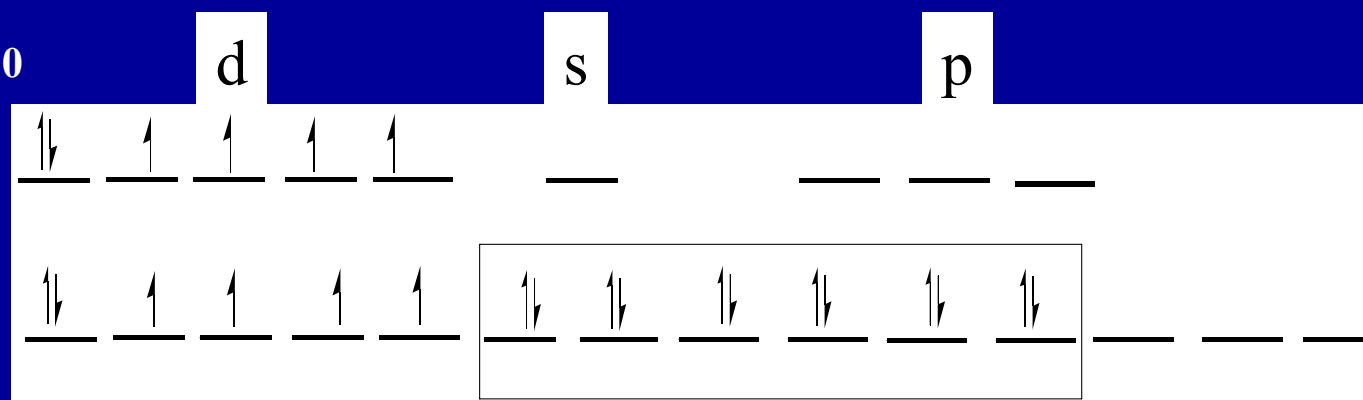
dsp^2 hybridní orbitaly

elektrony z Cl⁻, čtvercový



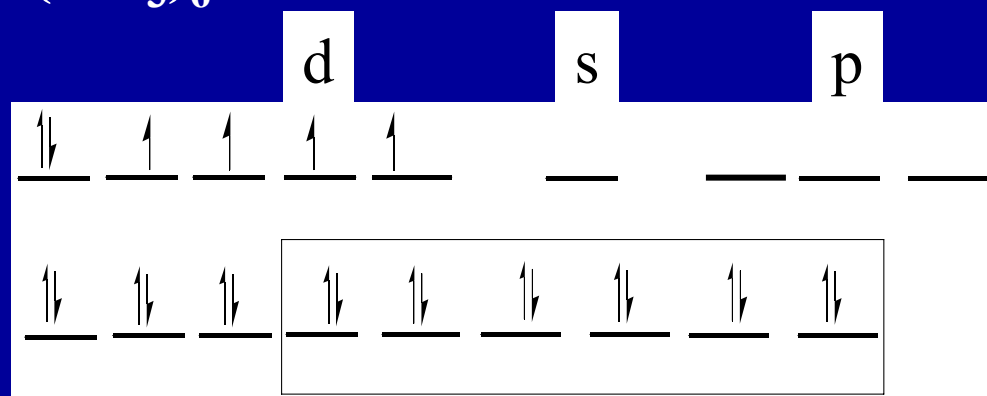
sp^3 hybridní orbitaly

elektrony z Cl⁻, tetraedrický



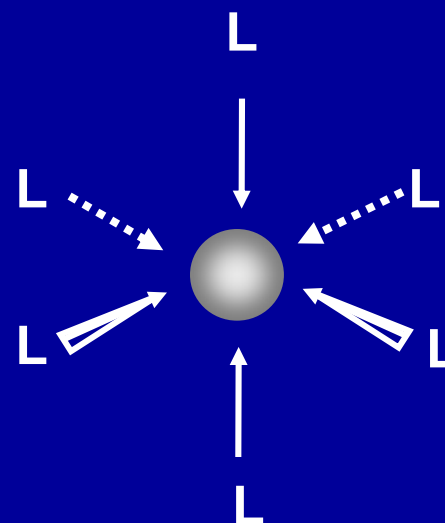
sp^3d^2 hybridní orbitály

elektrony z F^- , oktaedrický



d^2sp^3 hybridní orbitály

elektrony z NH_3 , oktaedrický



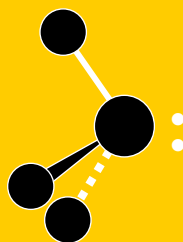
Monodentátní ligandy

CO
oxid uhelnatý

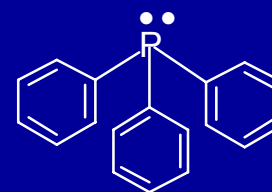
Cr



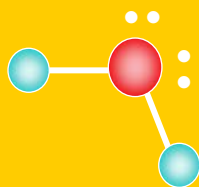
$\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, $\text{Mo}(\text{CO})_6$



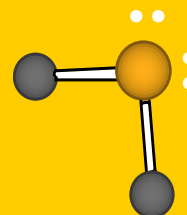
NH_3
amoniak



PPh_3
fosfan



H_2O
voda



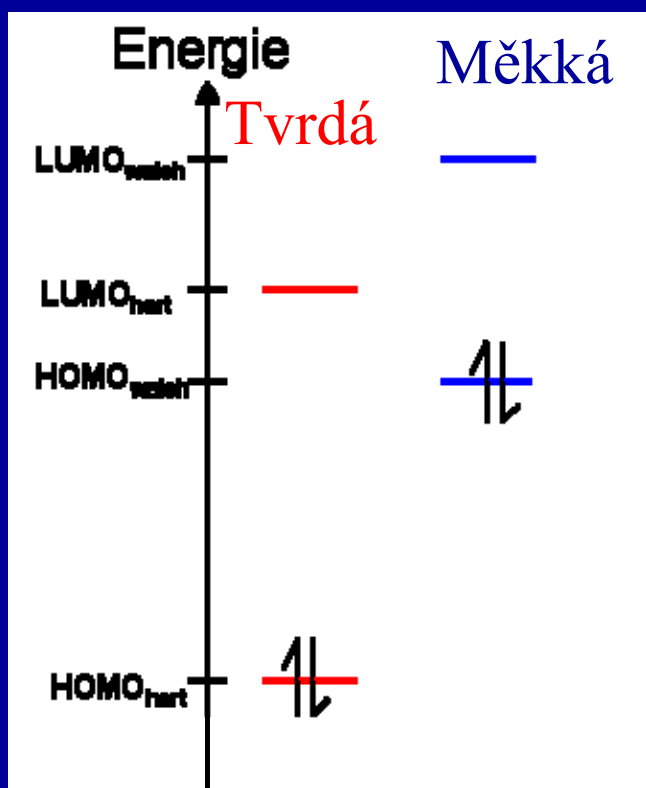
SR_2
thioether

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^-



Kyselina

Báze

Tvrde donorní atomy

NH_3 , F^- , H_2O , OH^- , CO_3^{2-}

Malé donorní atomy

Silně elektronegativní

Málo polarizovatelné

stabilní komplexy

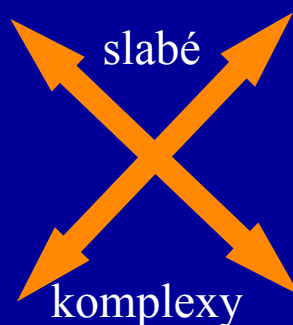
Tvrde kovy

Fe(III) , Mg(II) , Cr(III) , Al(III)

Malé atomy (1. přech. řada)

Vysoký náboj

HSAB



Měkké donorní atomy

CO , PPh_3 , I^- , C_2H_4 , SRH , CN^- , SCN^-

Velké donorní atomy

Málo elektronegativní

Snadno polarizovatelné

stabilní komplexy

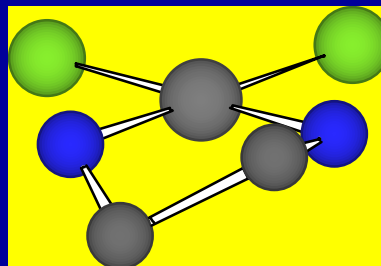
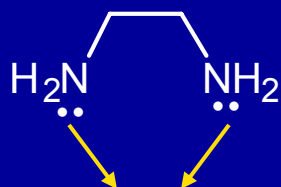
Měkké kovy

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

Velké atomy (2. a 3. přech. řada)

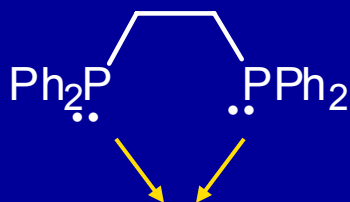
Malý náboj

Neutrální bidentátní ligandy

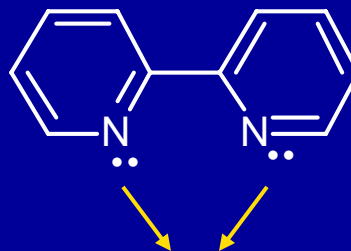


pětičlenný chelátový cyklus
čtvercově planární komplex

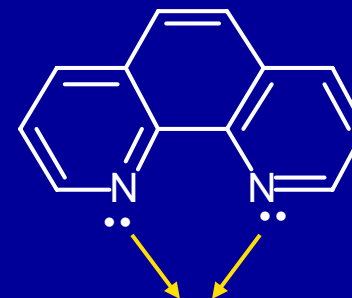
1,2-diaminoethan = ethylendiamin = en



1,2-difenylofosfinoethan
dppe



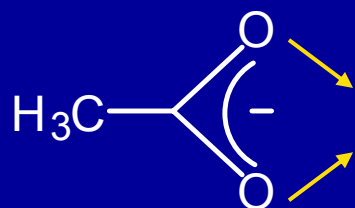
2,2'-bipyridin
bipy



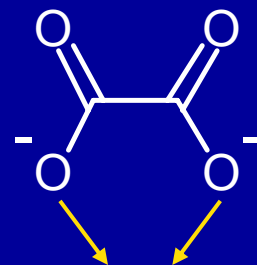
1,10-fenanthrolin
phen

Chelatace - ligandy jsou vázány velmi pevně k centrálnímu atomu

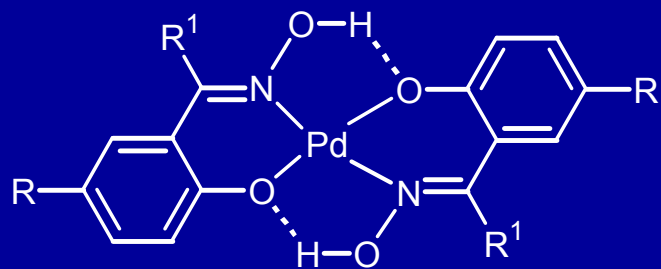
Aniontové bidentátní ligandy



acetát = ac^-

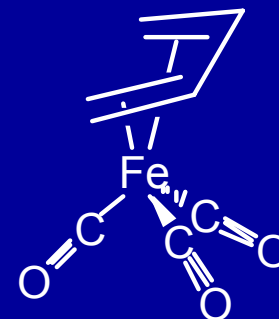


oxalát = ox^{2-}



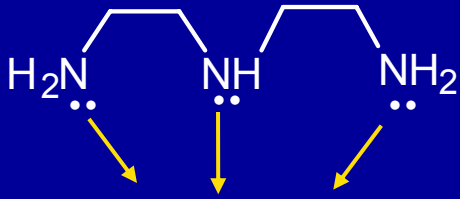
komplex Pd(II)-oxim

π -donorní bidentátní ligand



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

Tridentátní ligandy

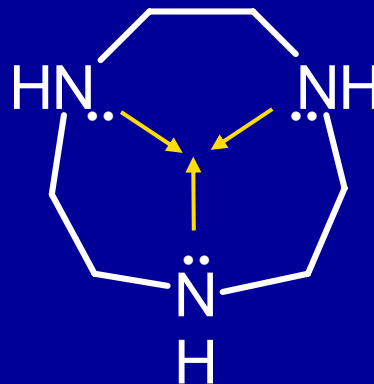


diethylentriamin
dien

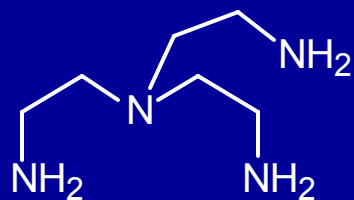


2,2':6',2''-terpyridin
tpy

1,2,4-triazacyklononan
makrocyclický ligand



Tetradentátní ligandy

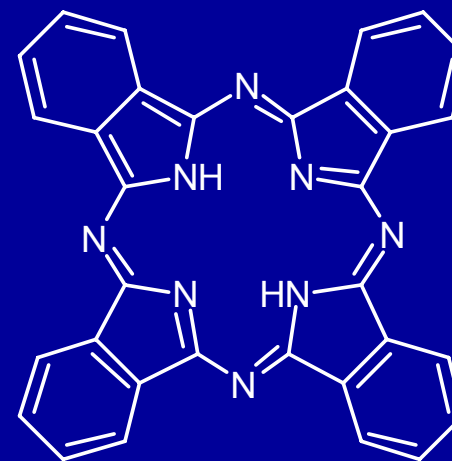


tris(2-aminoethyl)amin

tren



porfyrin



ftalocyanin

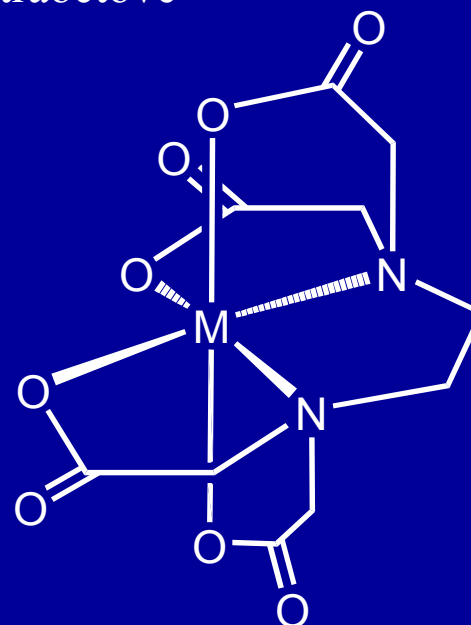
Multidentátní ligandy

tetraanion kyseliny ethylendiamintetraoctové

EDTA



Hexadentátní



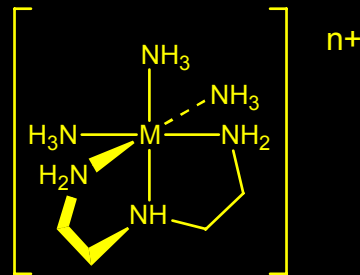
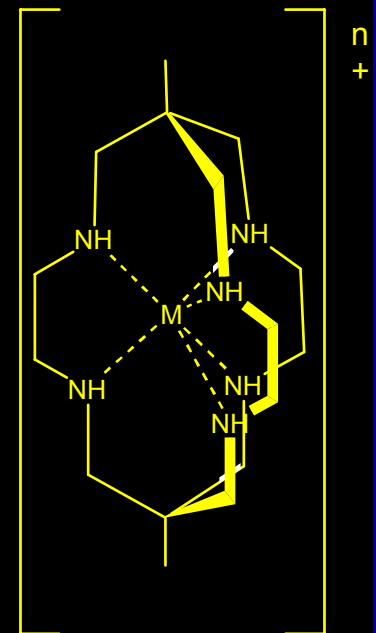
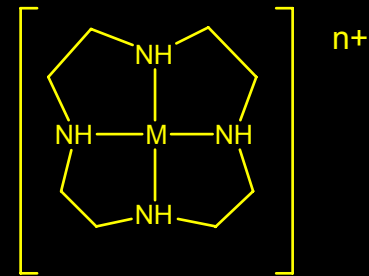
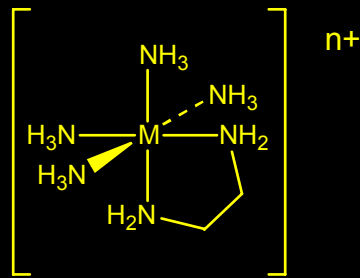
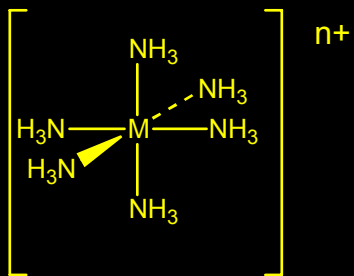
Topologie komplexů

komplexace

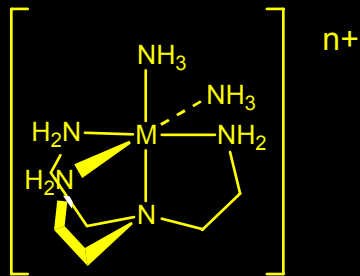
chelatace

makrocyclický efekt

kryptátový efekt



Makrocycklus
> 7 atomů v cyklu



Názvosloví komplexních sloučenin

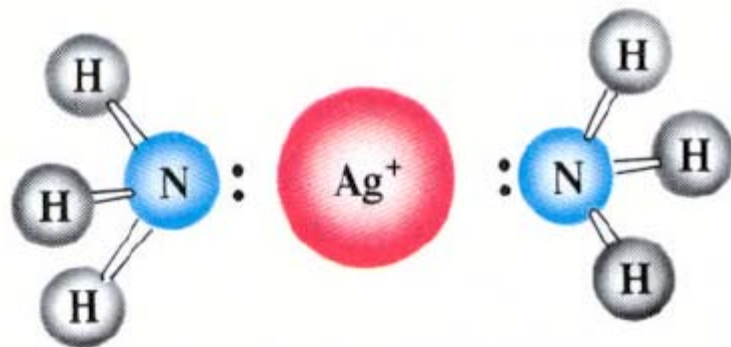
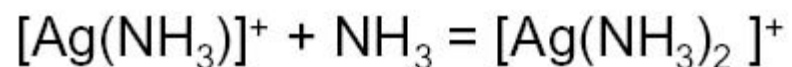
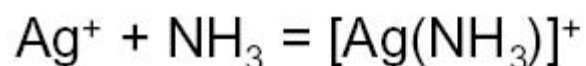
H_2O	voda	aqua-
NH_3	amoniak	ammin-
CO	oxid uhelnatý	karbonyl-
SO_4^{2-}	síran	sulfato-
$\text{S}_2\text{O}_3^{2-}$	thiosíran	thiosulfato-
PO_4^{3-}	fosforečnan	fosfato-
H_2PO_4^-	dihydrogenfosforečnan	dihydrogefosfato-
CH_3COO^-	octan	acetato-
$\text{C}_2\text{O}_4^{2-}$	šťavelan	oxalato-
$(\text{CH}_3)_2\text{N}^-$	dimethylamid	dimethylamido-
F^-	fluorid	fluoro-
O^{2-}	oxid	oxo-
OH^-	hydroxid	hydroxo-
O_2^{2-}	peroxid	peroxo-
HO_2^-	hydrogenperoxid	hydrogenperoxo-
H^-	hydrid	hydrido-
S^{2-}	sulfid	thio-
S_2^{2-}	disulfid	disulfido-
HS^-	hydrogensulfid	merkpto-
CN^-	kyanid	kyano-
SCN^-	thiokyanatan	thiokyanato-

Názvosloví komplexních sloučenin

$\text{K}_3[\text{Fe}(\text{CN})_6]$	hexakynoželezitan tridraselný (draselný)
$[\text{Cr}(\text{en})_3]\text{Cl}_3$	chlorid tris(ethylendiamin)chromitý
$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	tetrachloroplatnatan tetraamminplatnatý
$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	komplex triammin-trichlorokobaltitý
$[\text{Ni}(\text{CO})_4]$	tetrakarbonyl niklu (nebo nikl)
$\text{Na}[\text{Co}(\text{CO})_4]$	tetrakarbonylkobaltid(1-) sodný
$\text{K}_4[\text{Ni}(\text{CN})_4]$	tetrakyanonikl(4-) tetradraselný

Stabilita komplexů

Konstanta stability komplexu = rovnovážná konstanta tvorby

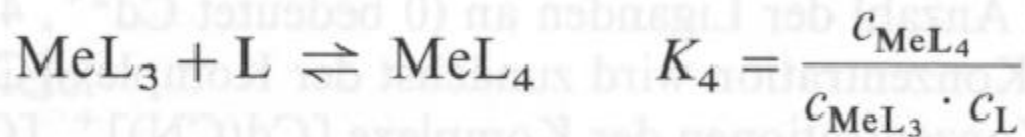
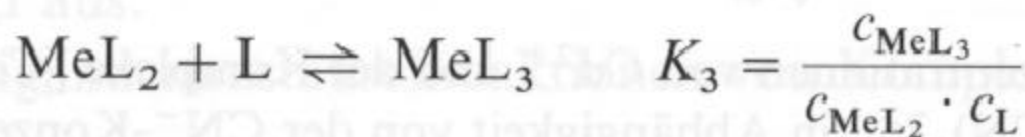
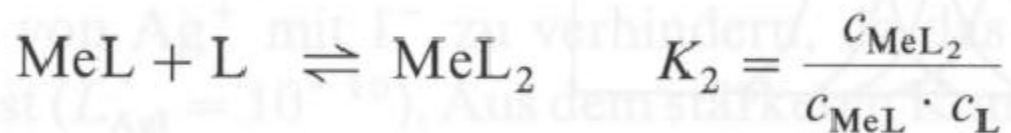
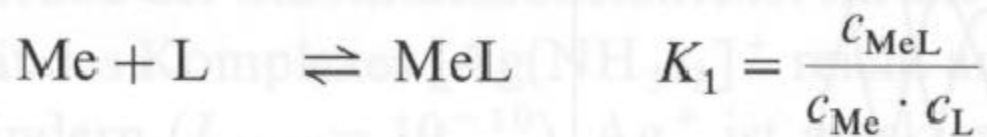


Vysoká hodnota K
= stabilní komplex

$$K_1 = \frac{[\text{AgNH}_3^+]}{[\text{Ag}^+][\text{NH}_3]}$$
$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{AgNH}_3^+][\text{NH}_3]}$$

Stabilita komplexů

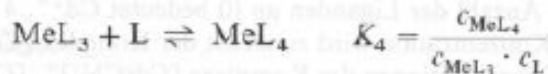
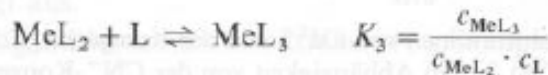
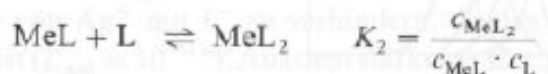
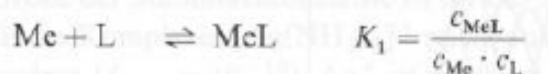
Konstanta stability komplexu ML_n



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

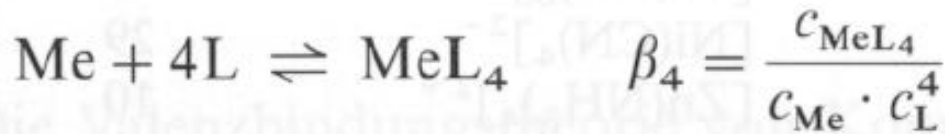
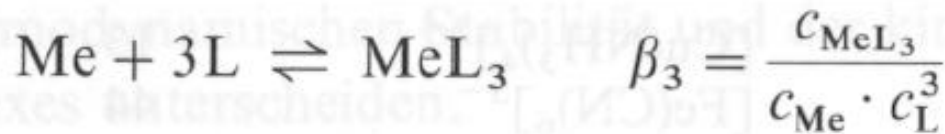
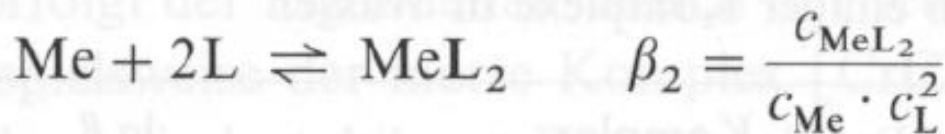
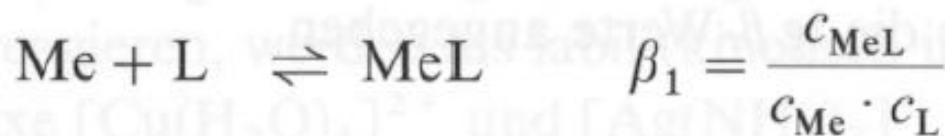
Stabilita komplexů

Celková konstanta stability komplexu



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

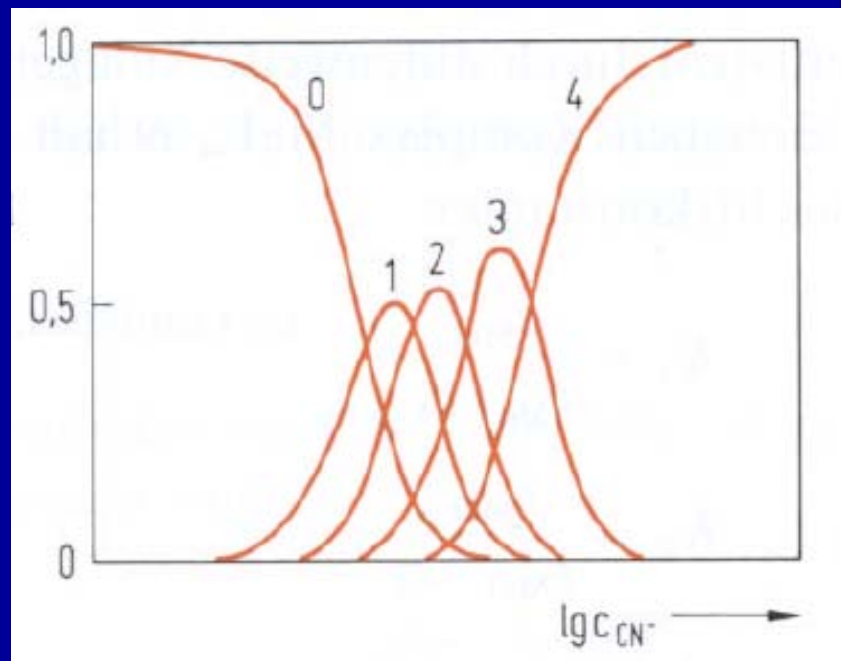
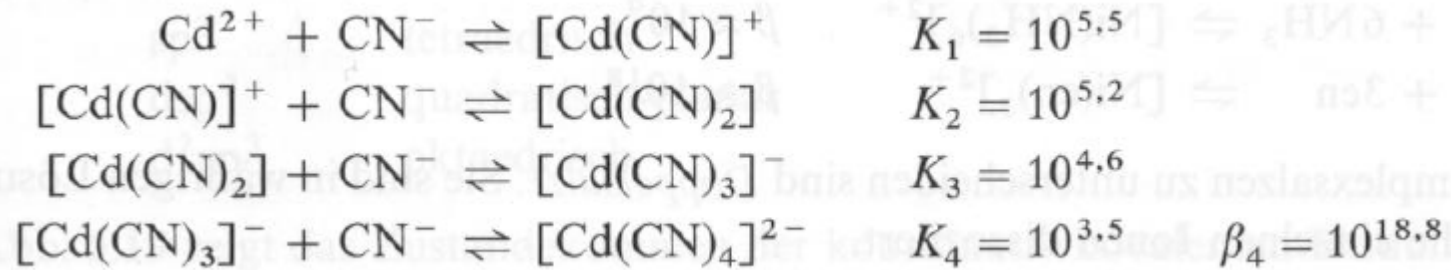
$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$$



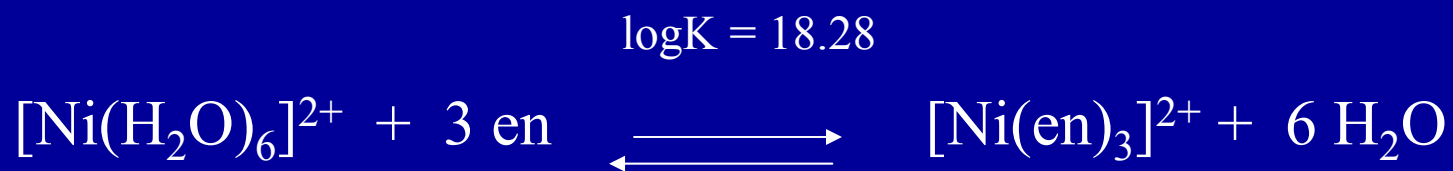
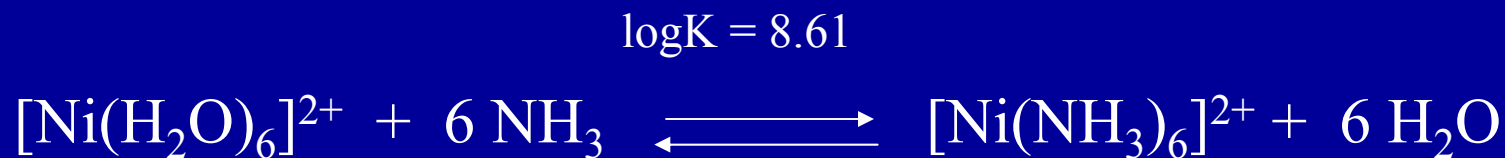
Stabilita komplexů

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

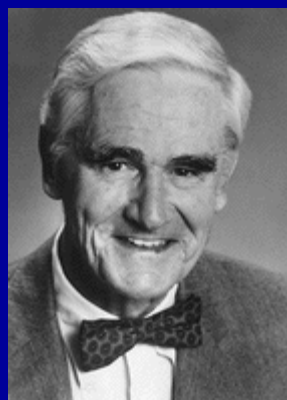


$$\Delta G = -RT \ln K = \Delta H - T\Delta S$$

ΔH stejná pro obě reakce (Ni-O \rightarrow Ni-N)
 ΔS vysoká pro chelataci, vzniká více částic

Cheláty, makrocycly, kryptáty

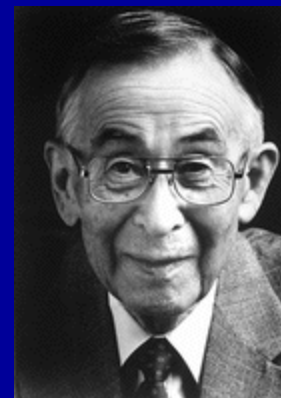
Nobelova cena za chemii 1987



Donald J. Cram



Jean-Marie Lehn

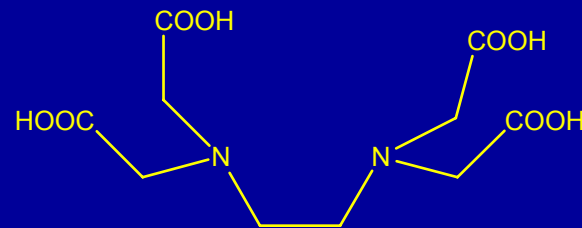


Charles J. Pedersen

Cheláty, makrocycly, kryptáty

EDTA

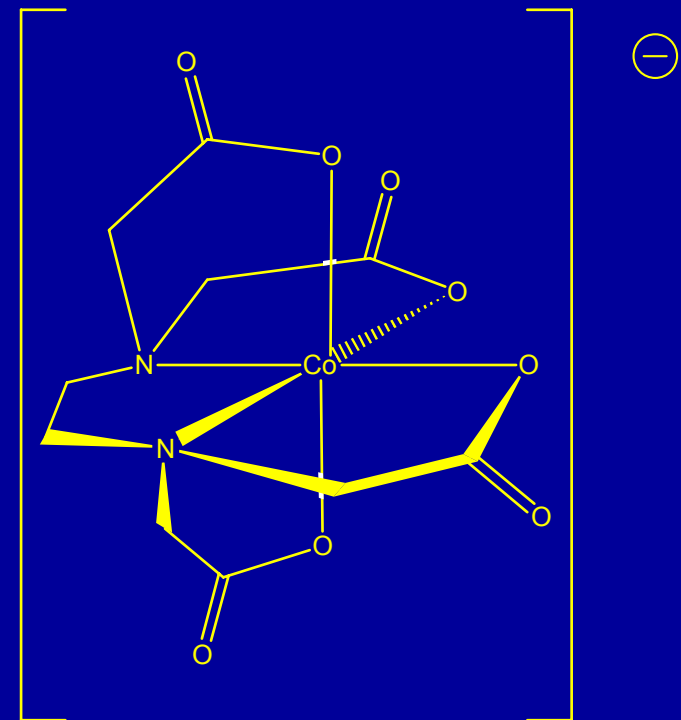
kyselina ethylendiamintetraoctová



Chelatační terapie Pb otravy

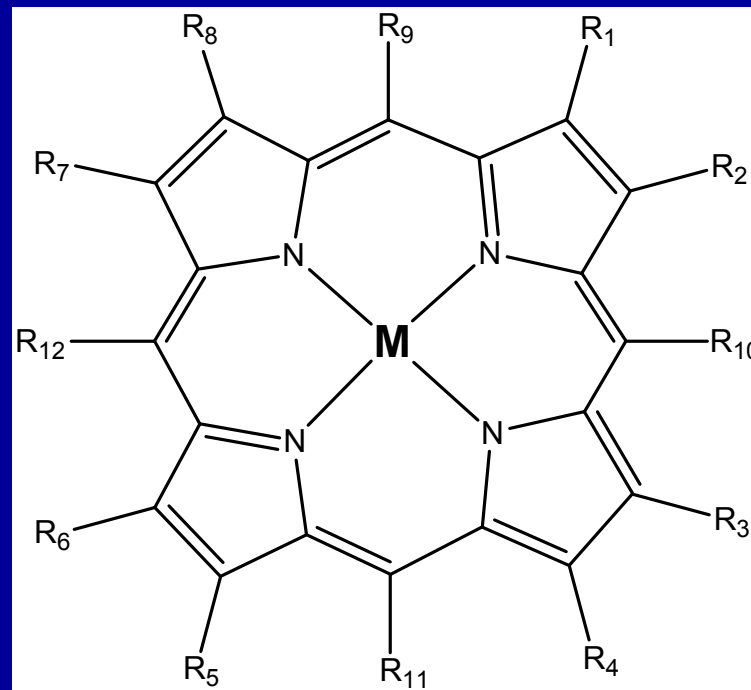
Chelatometrie

Rozpouští CaCO_3

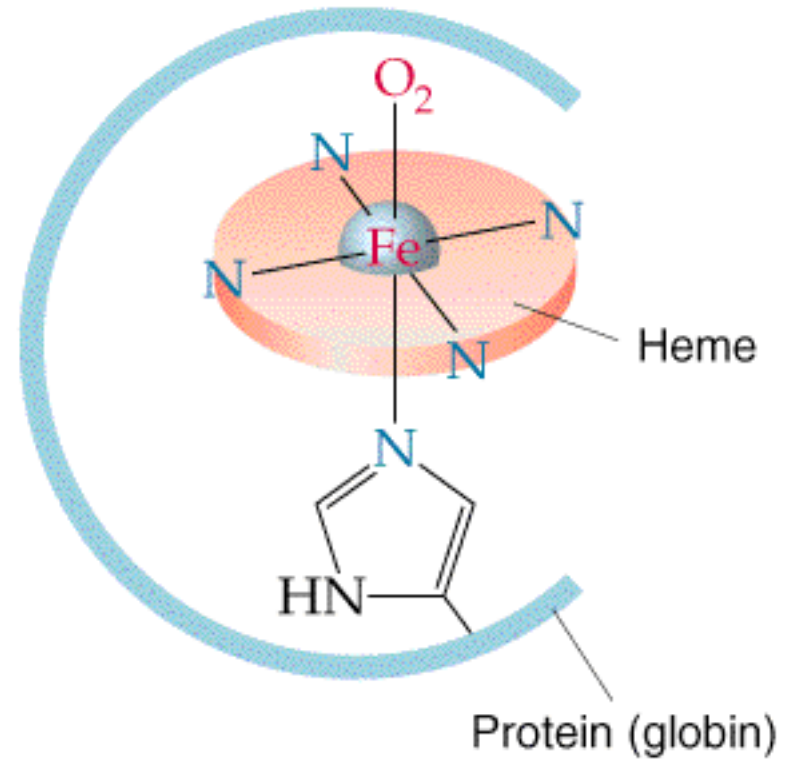
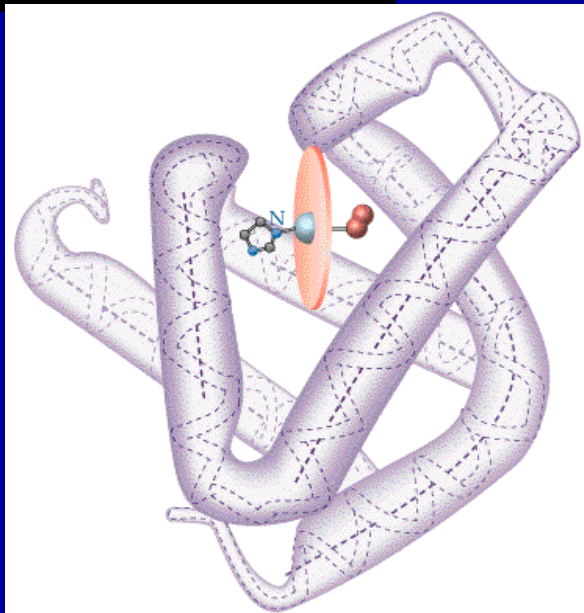
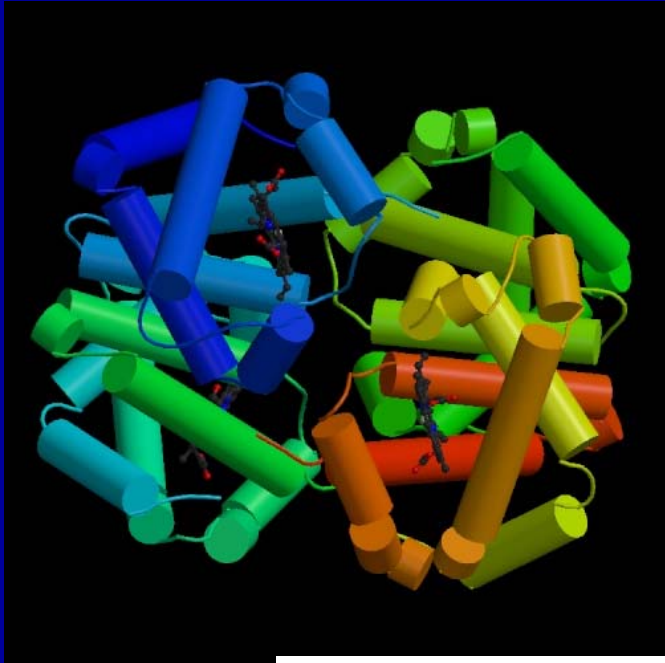


Cheláty, makrocykly, kryptáty

Metaloporfyriny: M = Fe (hem, cytochrom c), Mg (chlorofyl), Co (B₁₂)

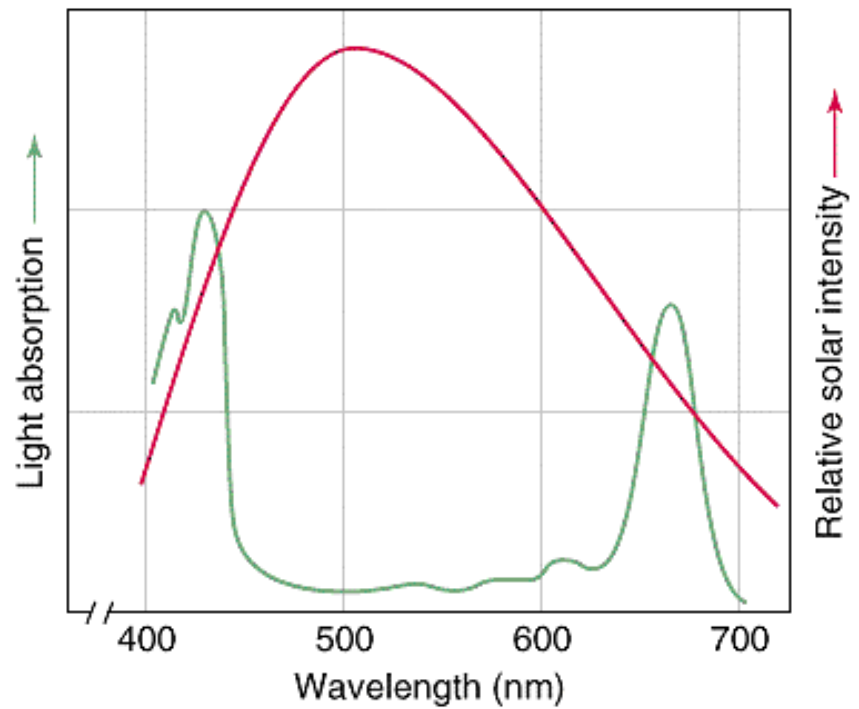
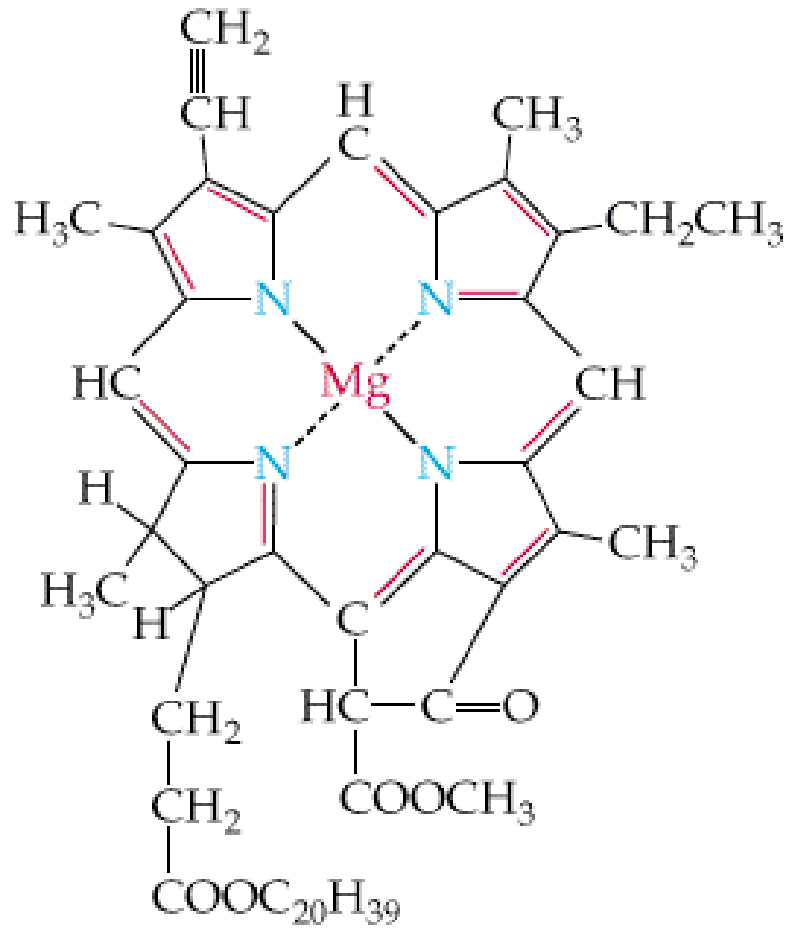


Hemoglobin



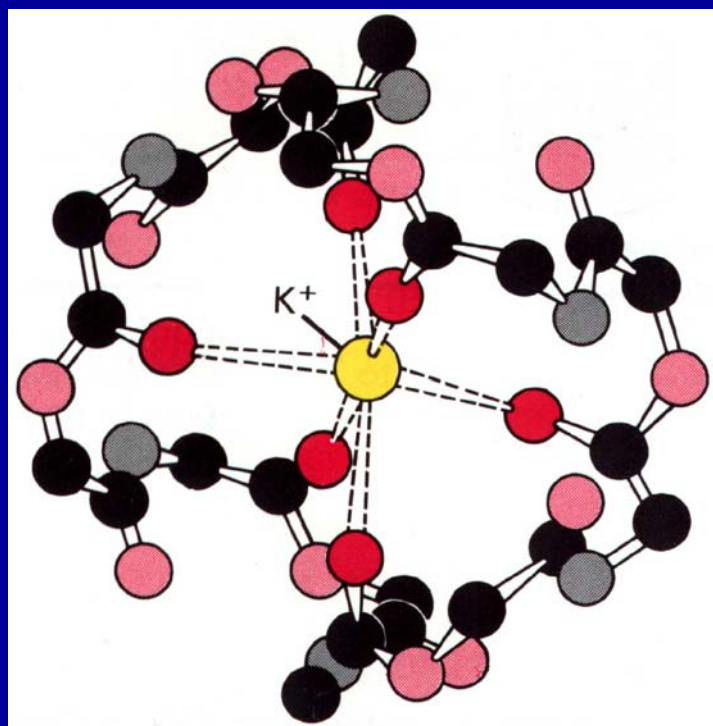


Mg chlorofyl



Cheláty, makrocycly, kryptáty

Valinomycin



Tvary komplexních molekul a iontů

Prvky hlavních skupin

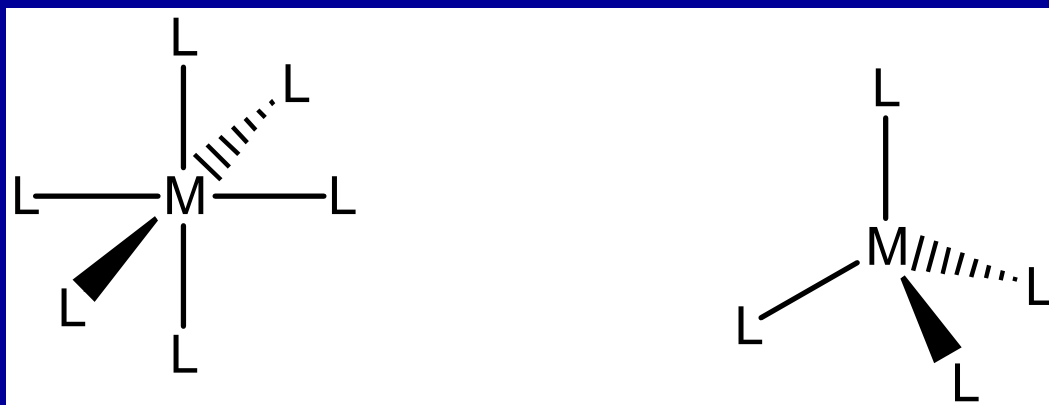
a přechodné prvky s d^0 nebo d^{10} >>>> VSEPR

(kulově symetrické rozložení d-elektronové hustoty)

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

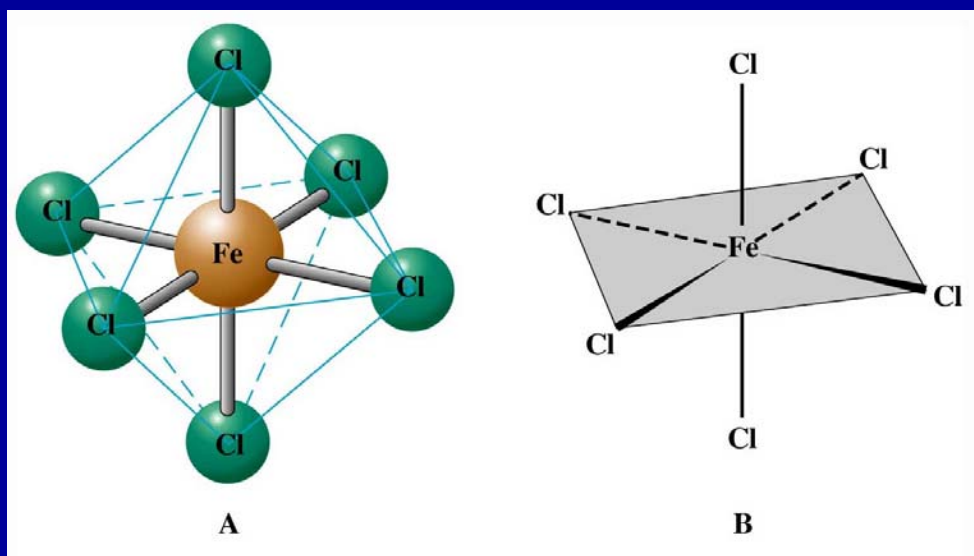
(Ne VSEPR - nesymetrické rozložení d-elektronové hustoty)

Nejdůležitější tvary komplexních částic



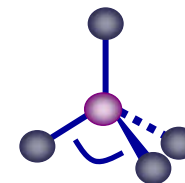
Oktaedrické komplexy O_h

Tetraedrické komplexy T_d

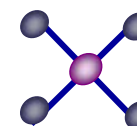


Nejdůležitější tvary komplexních částic

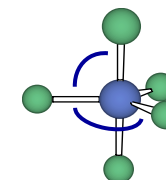
Tetraedrický $109^{\circ} 28'$ C.N. 4



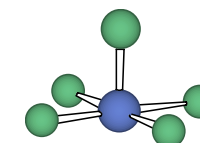
Čtvercově planární 90° C.N. 4



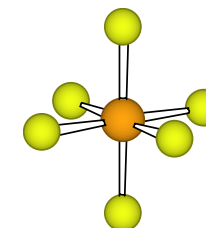
Trigonálně bipyramidální $120^{\circ} + 90^{\circ}$ C.N. 5



Čtvercově pyramidální 90° C.N. 5



Oktaedrický 90° C.N. 6

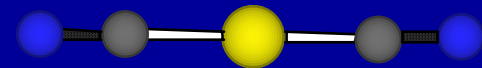
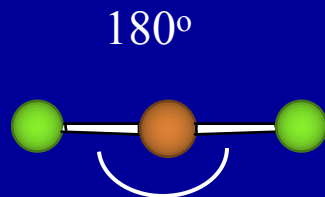


Nejdůležitější tvary komplexních částic

Koordinační číslo 2

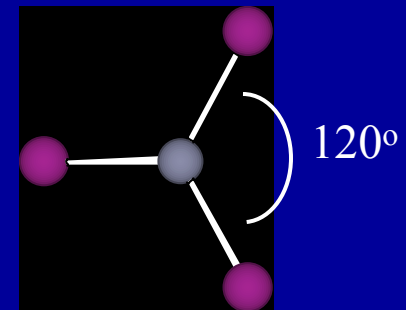
Cu(I), Ag(I), Au(I), Hg(II)

lineární



Koordinační číslo 3

trigonálně planární

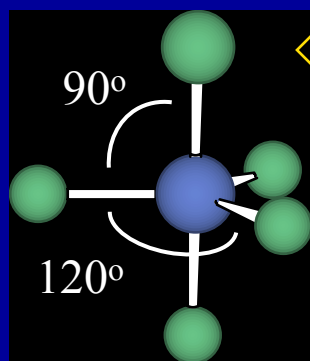


Nejdůležitější tvary komplexních částic

Koordinační číslo 5



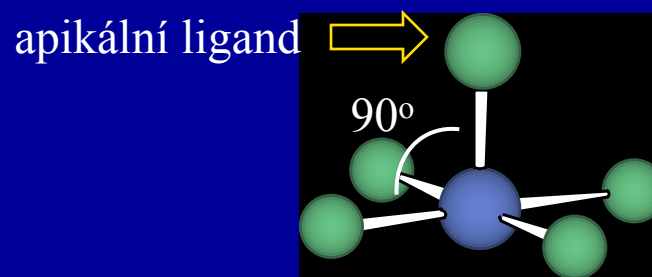
Trigonálně bipyramidální



axiální ligandy

ekvatoriální ligandy

Čtvercově pyramidální

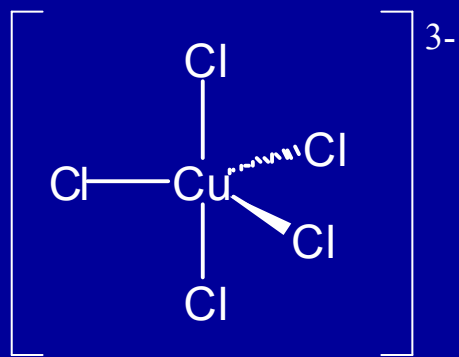


apikální ligand

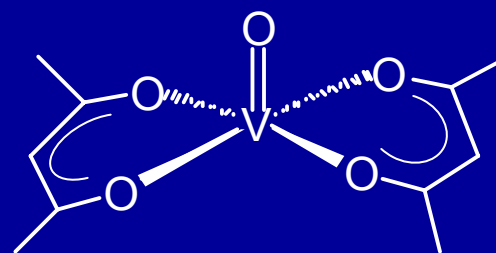
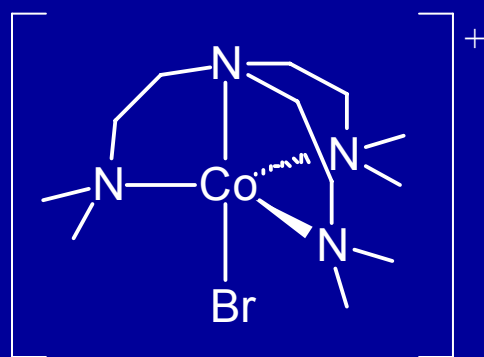
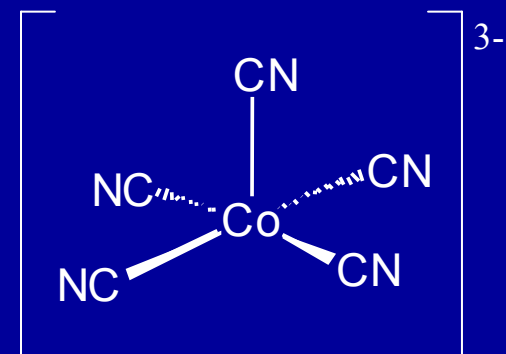
bazální ligandy

Tyto dvě struktury mají velmi podobnou energii

Trigonálně bipyramidální



Čtvercově pyramidální



Izomerie komplexních sloučenin

Konstituční (strukturní) izomerie

Vazebná

Koordinační

Ionizační

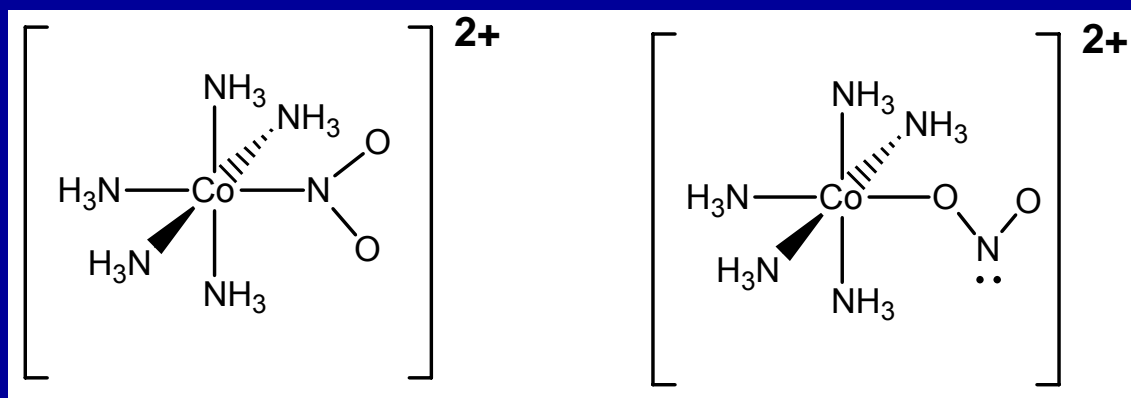
Prostorová (stereo) izomerie

Geometrická

Optická

Konstituční (strukturní) izomerie

Vazebná: SCN^- , NO_2^- , OCN^-

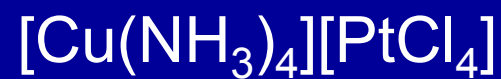
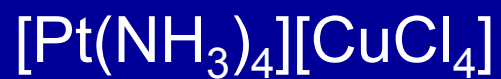


nitro-

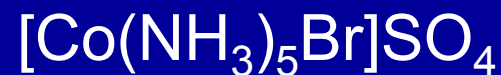
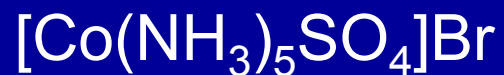
nitrito-

Konstituční (strukturní) izomerie

Koordinační:

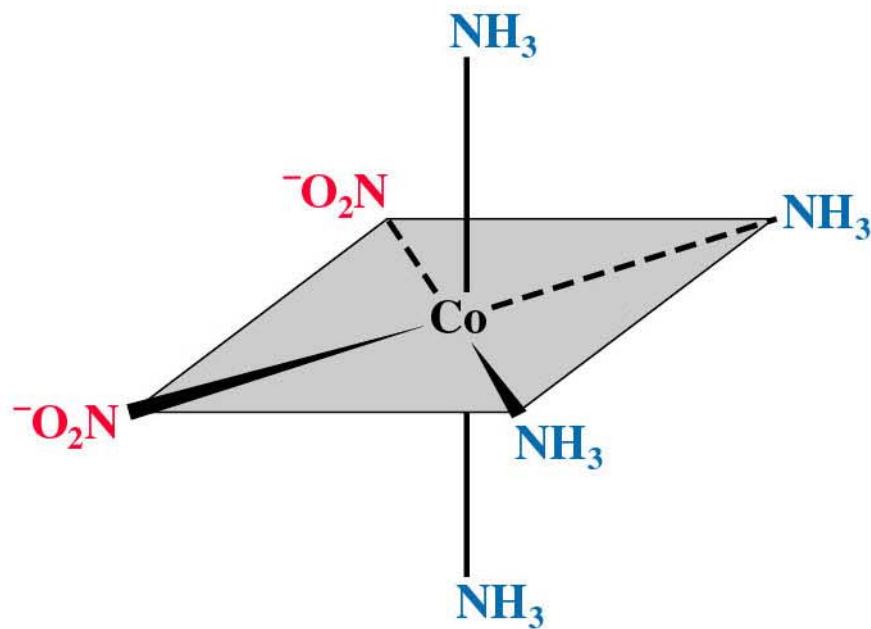


Ionizační:

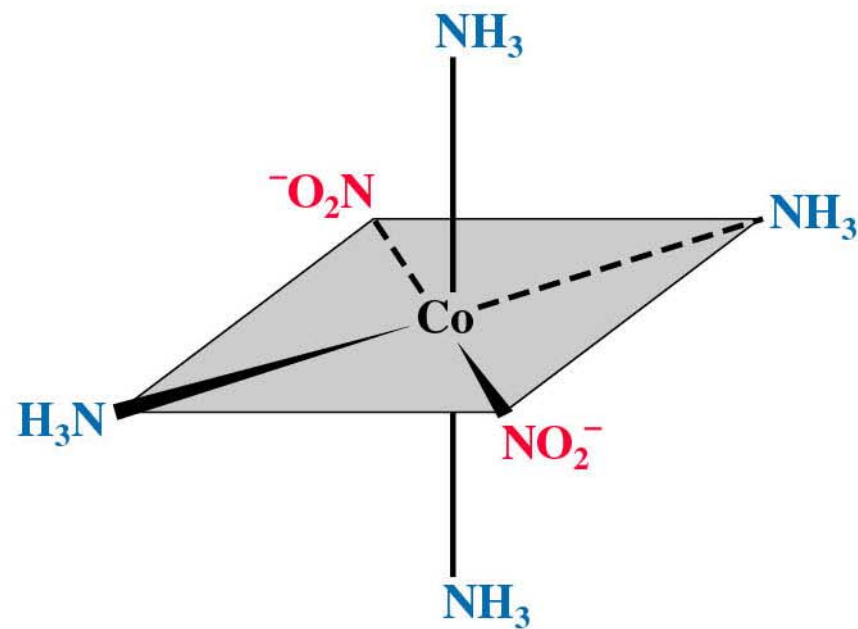


Prostorová (stereo) izomerie

Geometrická: cis-trans, diastereomery



cis



trans

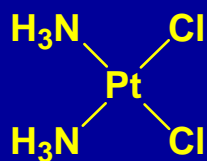
Prostorová (stereo) izomerie

Geometrická:
cis-trans,
diastereomery

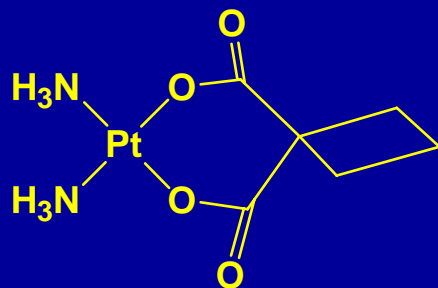
	<i>cis</i>	<i>trans</i>
Ball-and-stick model		
Structural formula		
Color	Orange-yellow	Pale yellow
Solubility	0.252 g/100 g H ₂ O	0.037 g/100 g H ₂ O



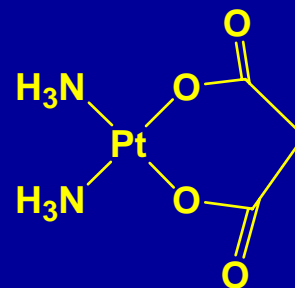
Protinádorové léky



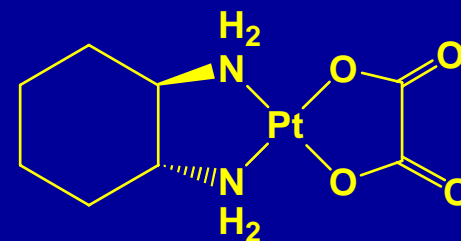
Cisplatin



Carboplatin

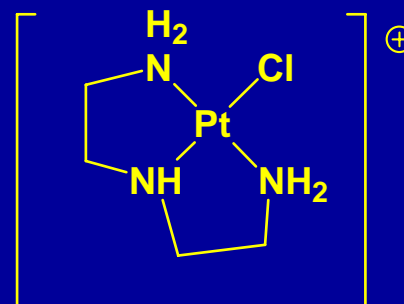
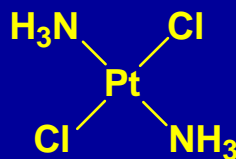


Nedaplatin



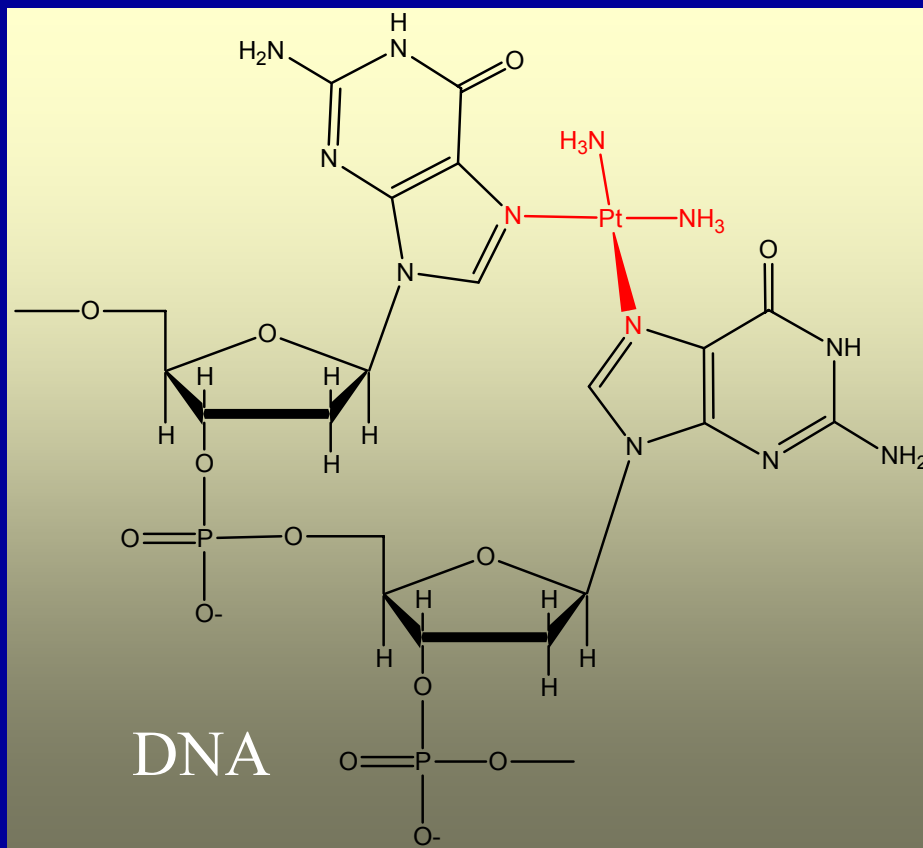
Oxaliplatin

Neaktivní látky



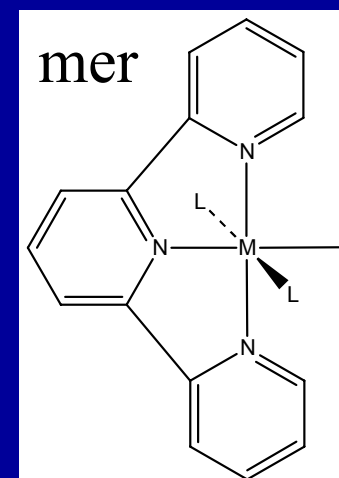
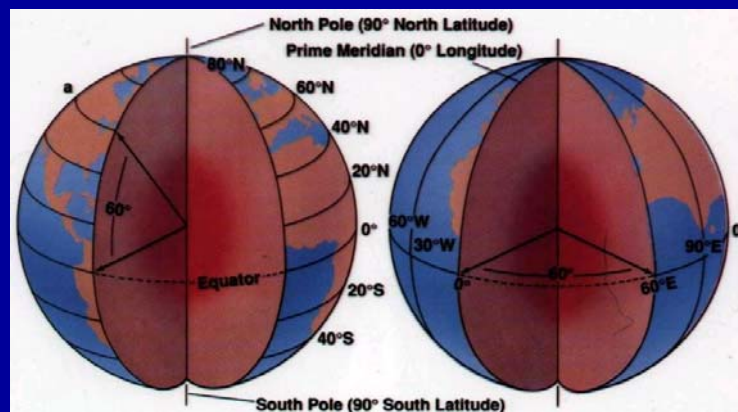
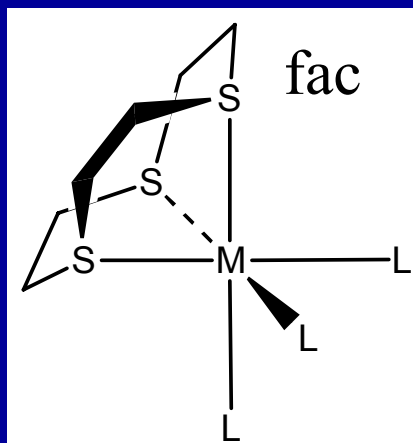
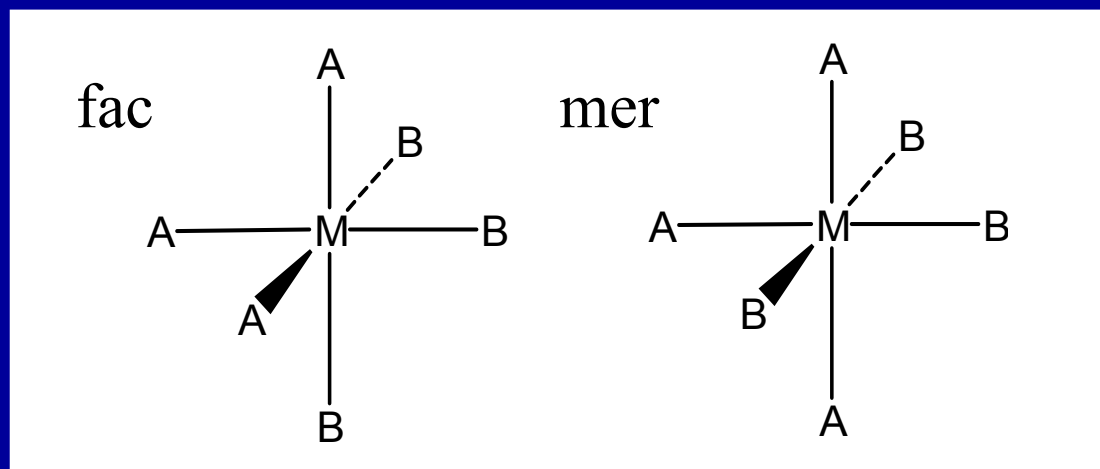
Prostorová (stereo) izomerie

Cisplatina = kancerostatikum



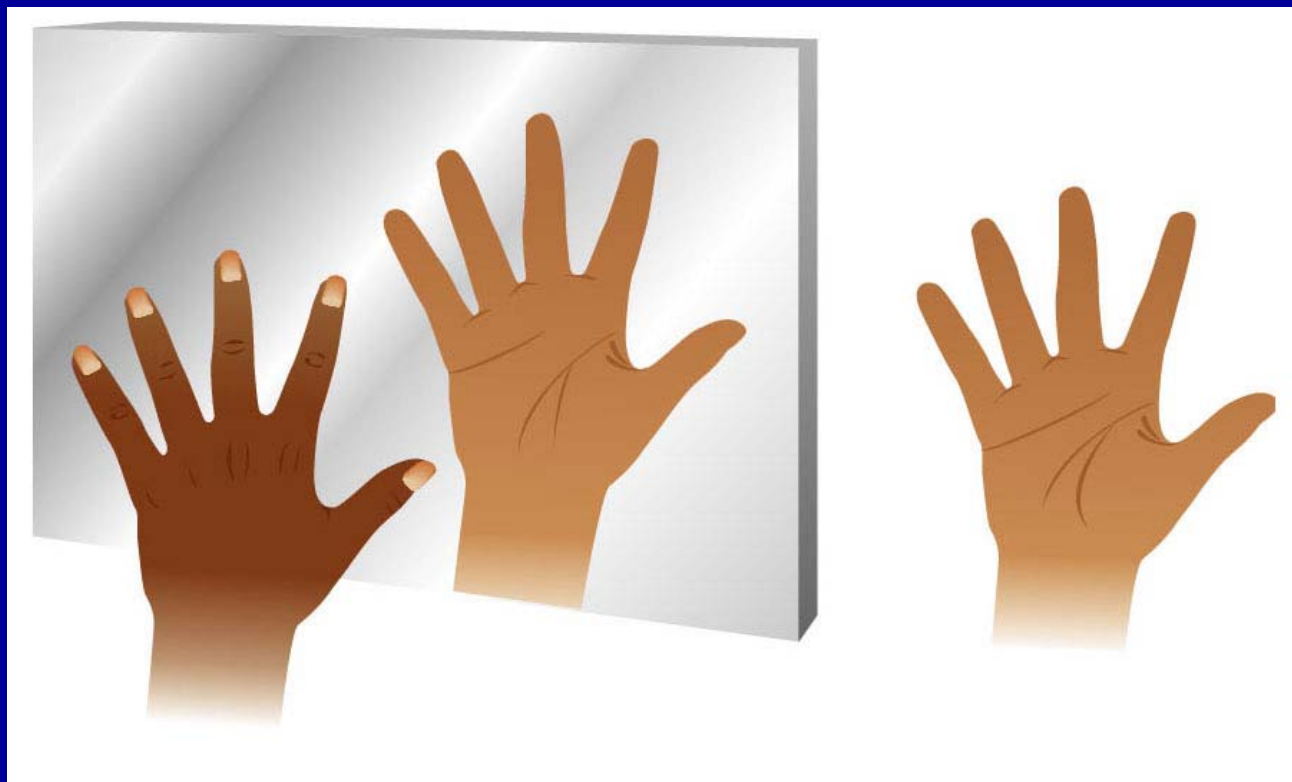
Prostorová (stereo) izomerie

Geometrická: mer-fac, diastereomery



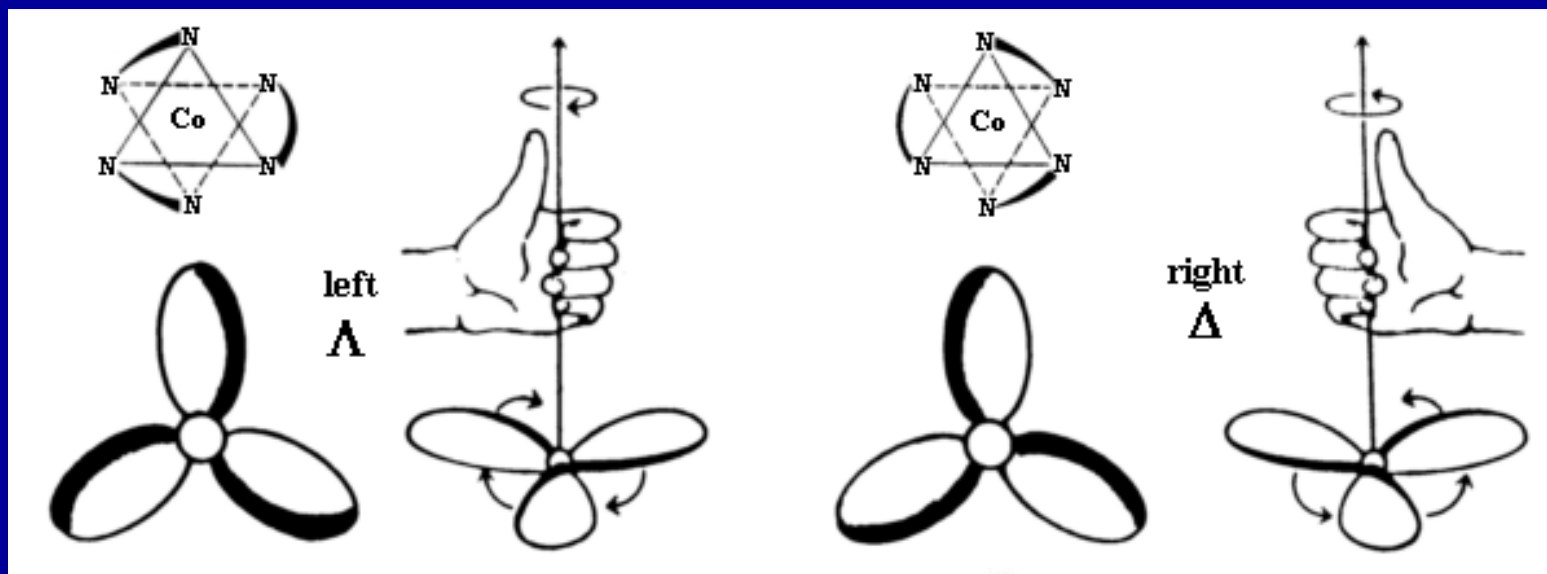
Prostorová (stereo) izomerie

Optická izomerie - chiralita - enantiomery



Prostorová (stereo) izomerie

Optická: enantiomery

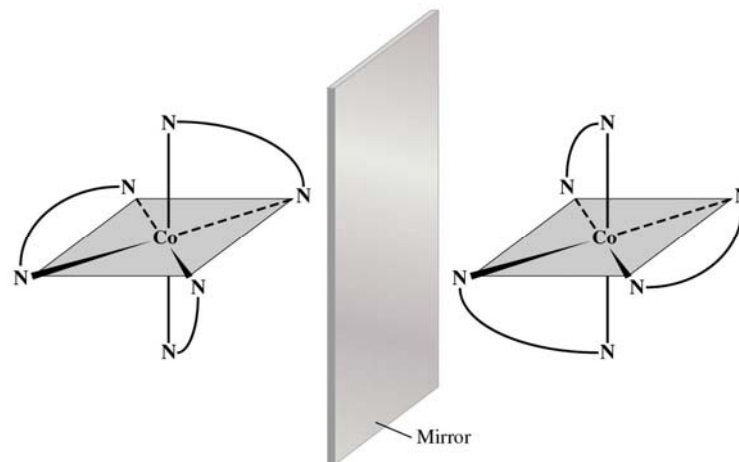


Chiralita

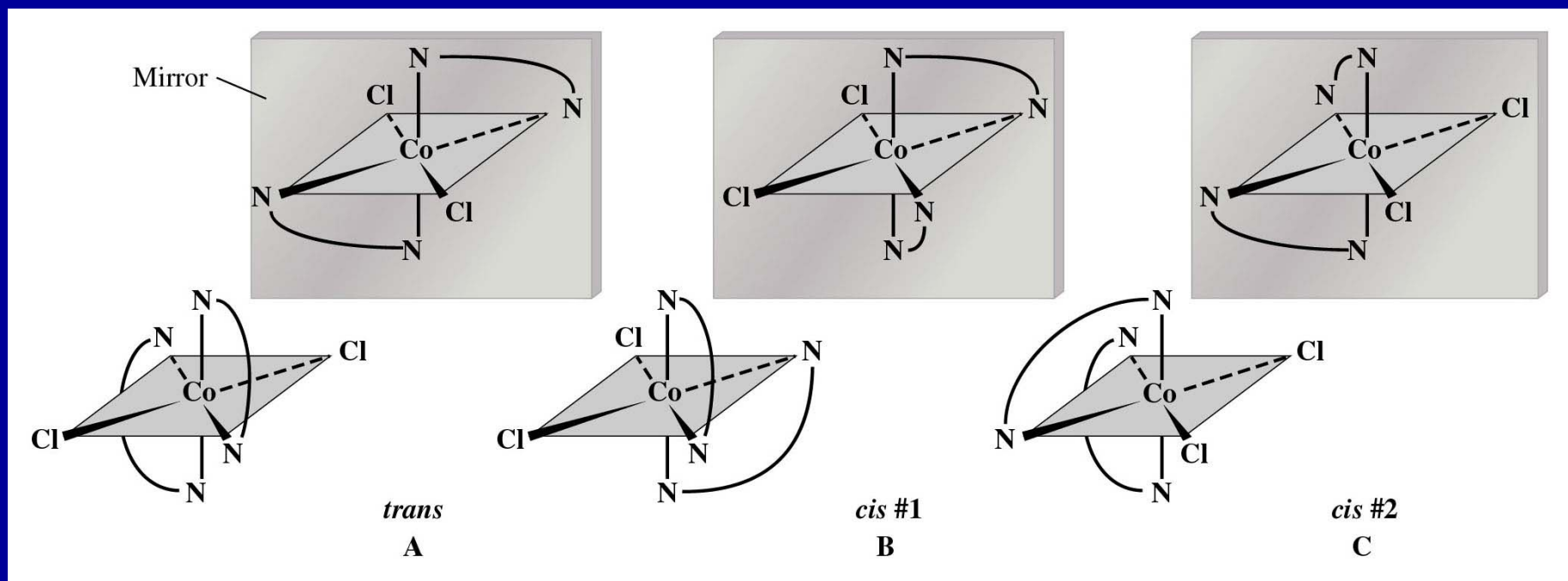
Molekula nemá S_n

S_1 = rovina symetrie

S_2 = střed symetrie



Prostorová (stereo) izomerie



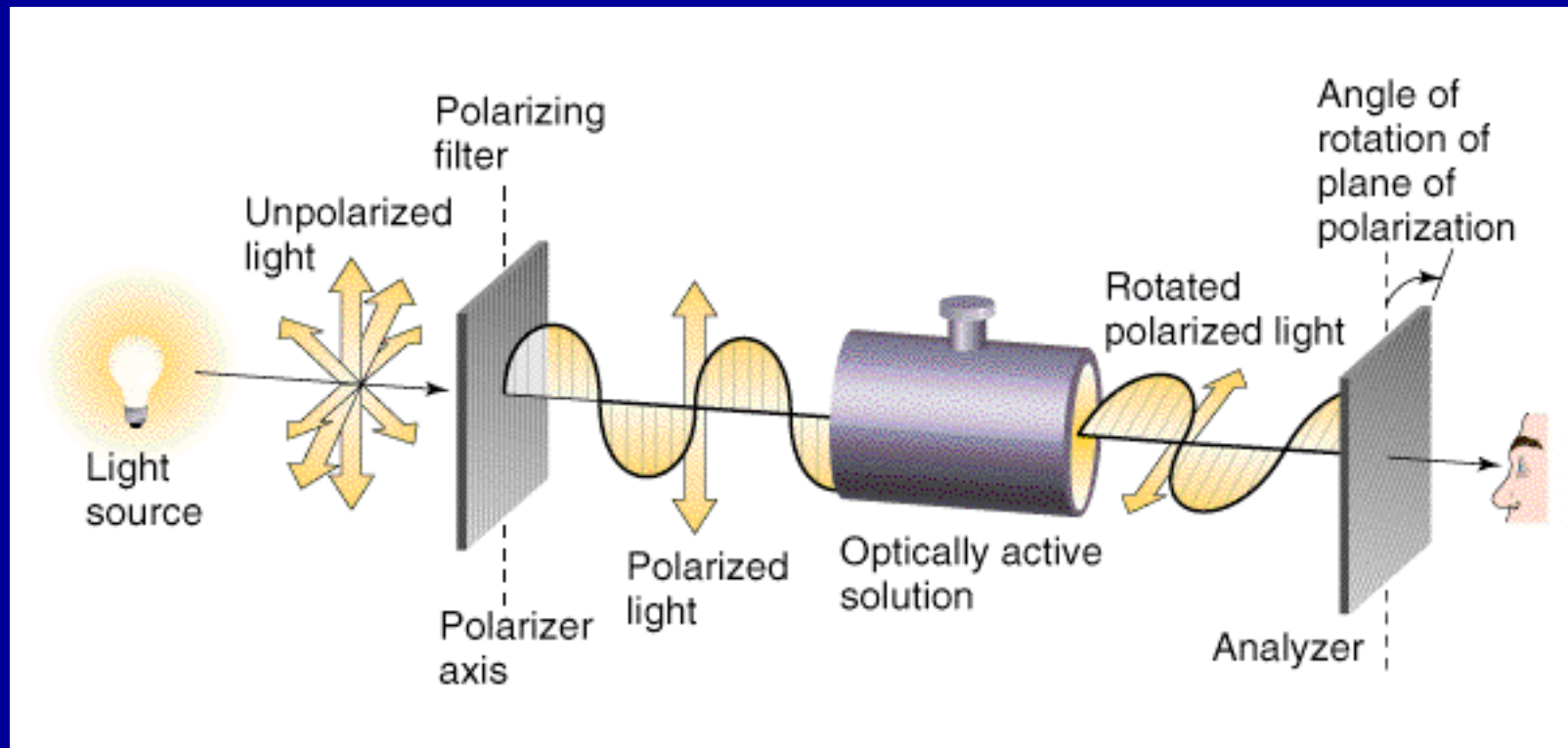
Optická rotace

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)

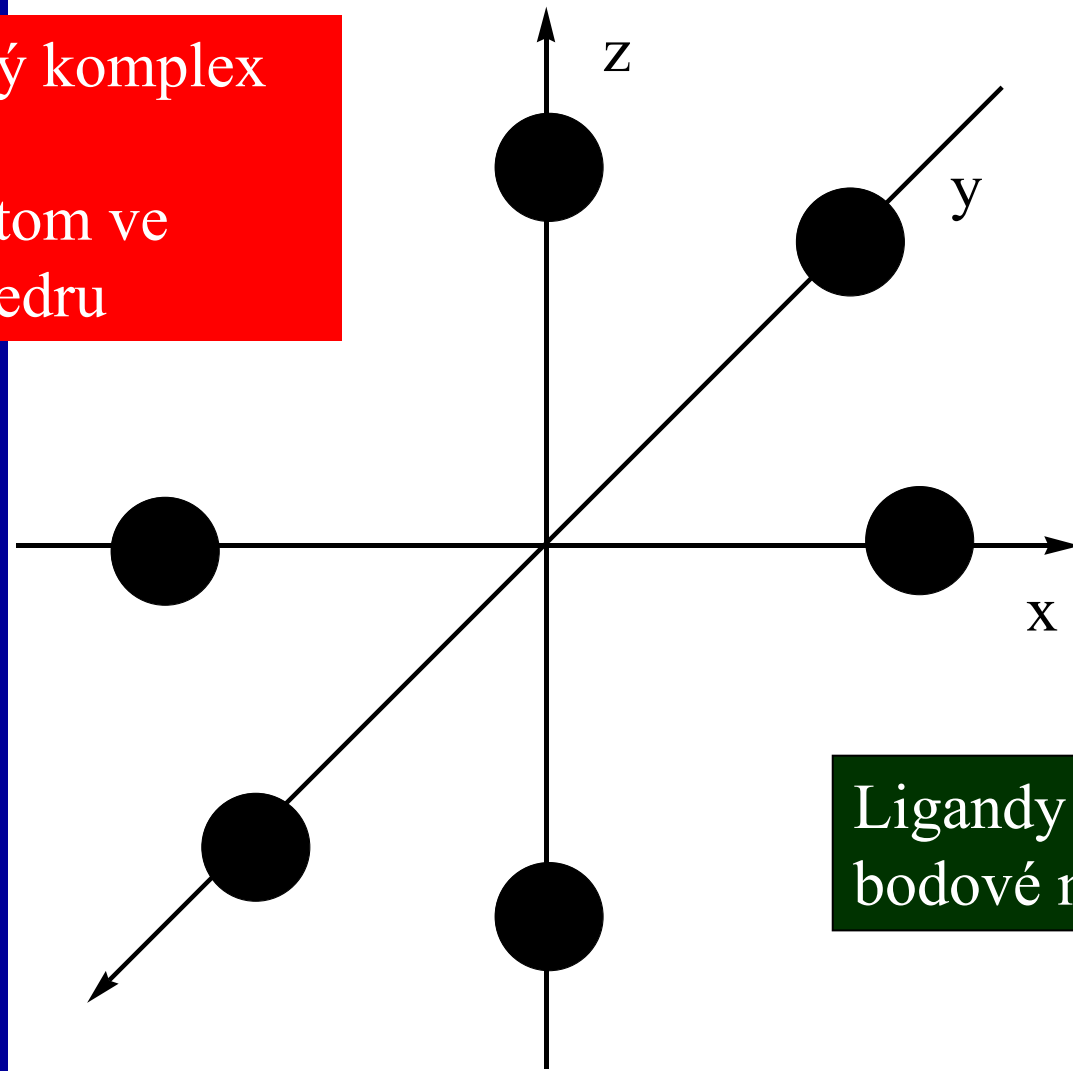
1935, modifikace J. H. Van Vleck Podíl kovalence

4) MO

Teorie ligandového pole

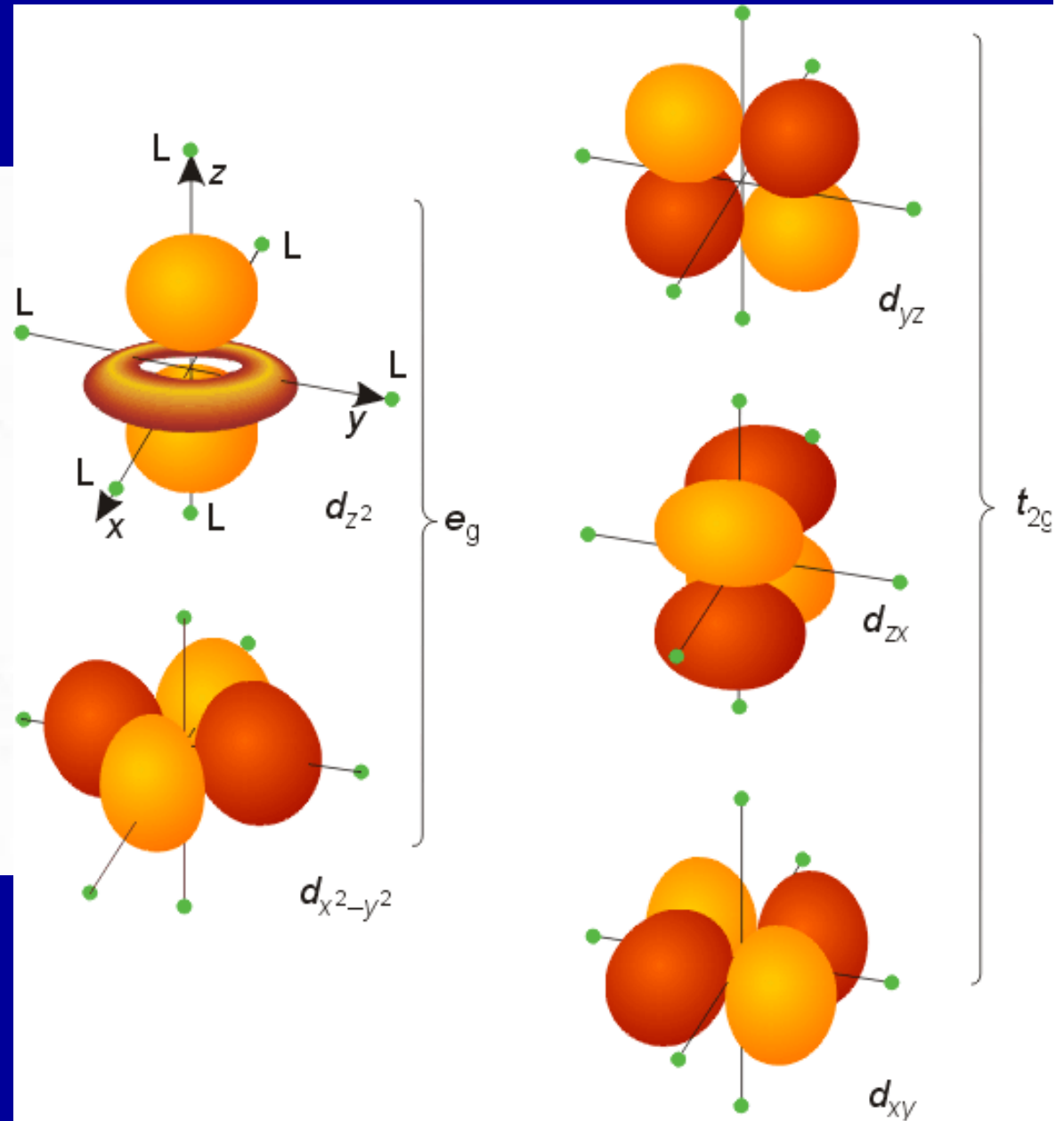
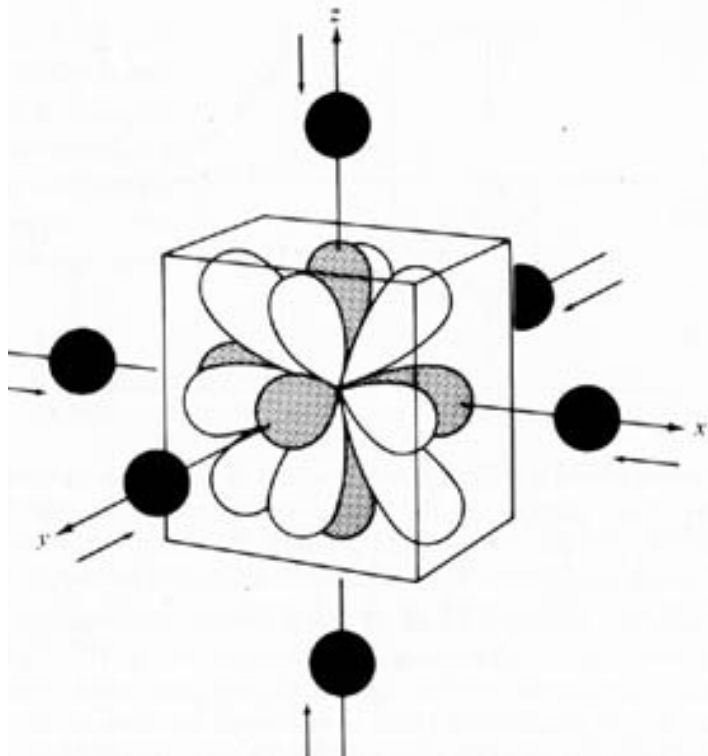
Oktaedrický komplex

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

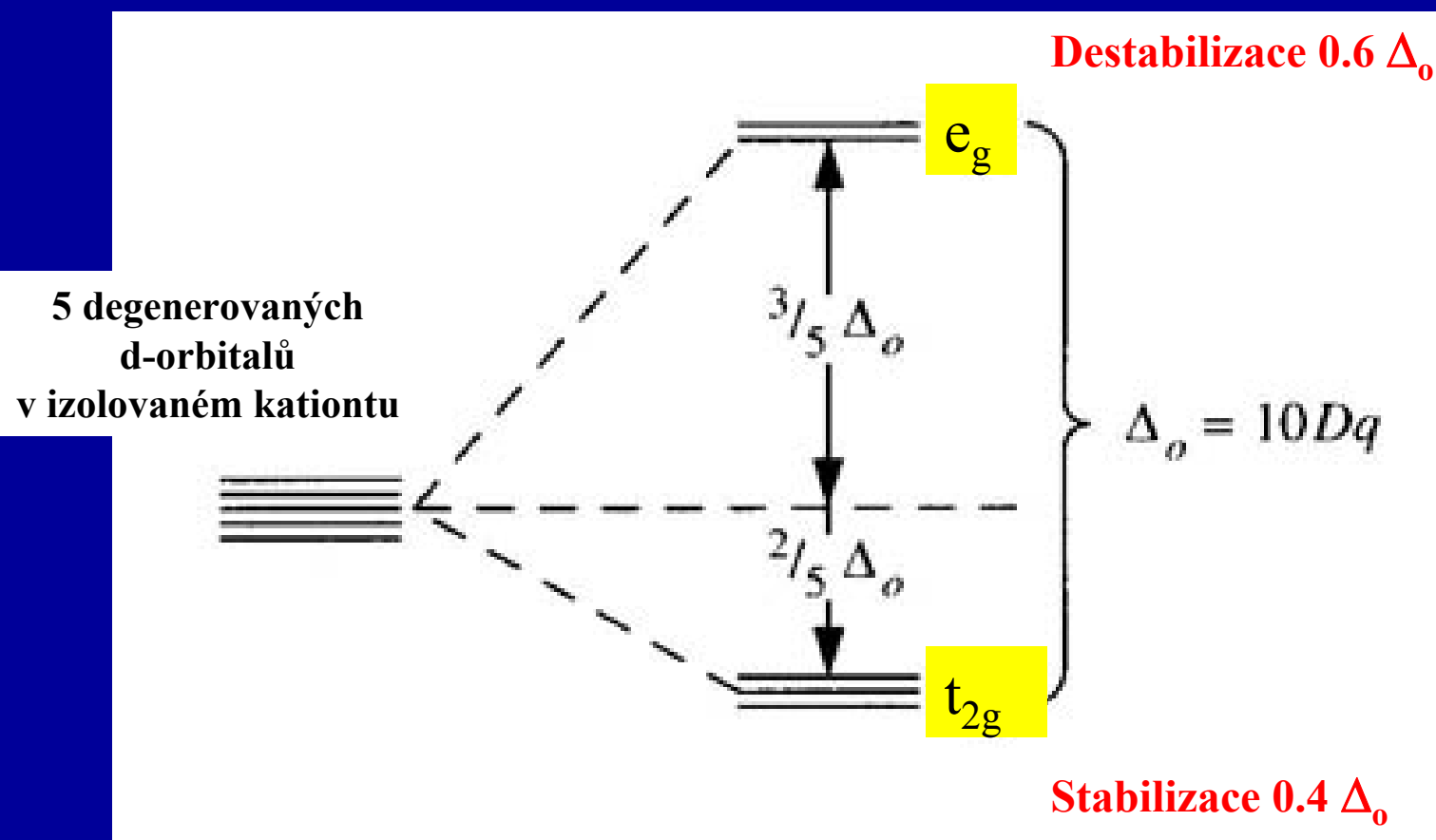
Energy ↑

Energy of
attraction of
point charges

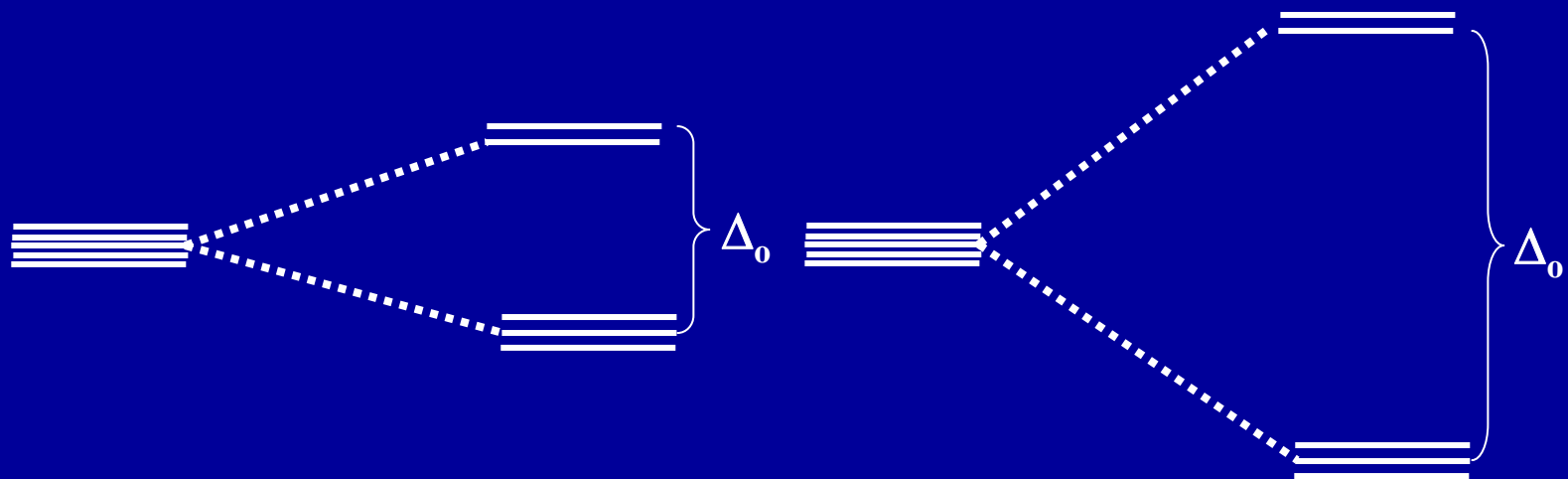
d_{z^2} $d_{x^2-y^2}$
 d_{xy} d_{yz} d_{xz}

↑ 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

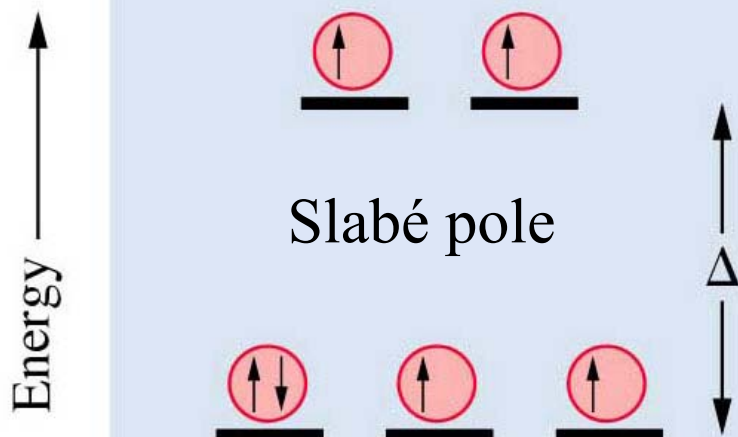
Silné pole

$\Delta_o > P$ (párovací energie)

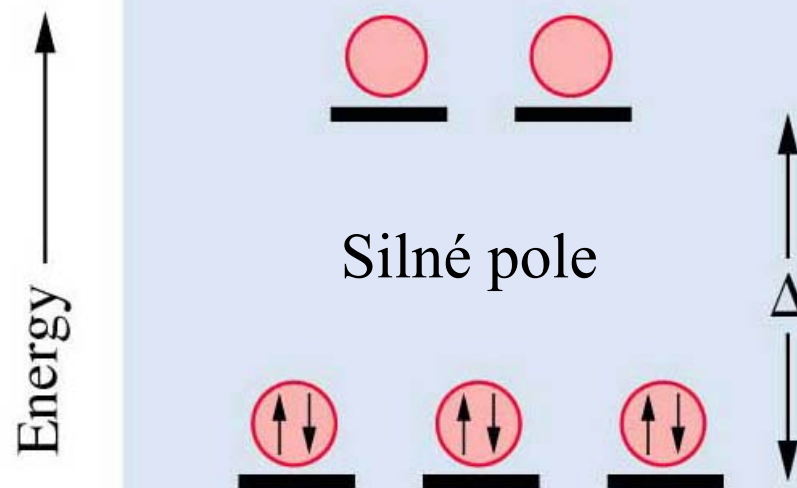
Nížkospinové komplexy

Stabilizační energie ligandového pole, CFSE

Vysokospinové komplexy



Nízkospinové komplexy



Δ_o roste

Slabé pole

Silné pole

		e	CFSE		e	CFSE
d ¹	t _{2g} ¹	1	0.4 Δ _o	t _{2g} ¹	1	0.4 Δ _o
d ²	t _{2g} ²	2	0.8 Δ _o	t _{2g} ²	2	0.8 Δ _o
d ³	t _{2g} ³	3	1.2 Δ _o	t _{2g} ³	3	1.2 Δ _o
d ⁴	t _{2g} ³ e _g ¹	4	0.6 Δ _o	t _{2g} ⁴	2	1.6 Δ _o
d ⁵	t _{2g} ³ e _g ²	5	0.0 Δ _o	t _{2g} ⁵	1	2.0 Δ _o
d ⁶	t _{2g} ⁴ e _g ²	4	0.4 Δ _o	t _{2g} ⁶	0	2.4 Δ _o
d ⁷	t _{2g} ⁵ e _g ²	3	0.8 Δ _o	t _{2g} ⁶ e _g ¹	1	1.8 Δ _o
d ⁸	t _{2g} ⁶ e _g ²	2	1.2 Δ _o	t _{2g} ⁶ e _g ²	2	1.2 Δ _o

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

e = počet nepárových elektronů

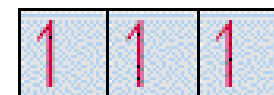
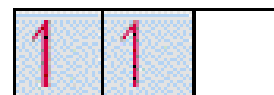
Rozštěpení d-hladin v O_h poli

Obsazení energetických hladin elektrony:

Výstavbový princip

Hundovo pravidlo

Pauliho princip



Rozštěpení d-hladin v O_h poli

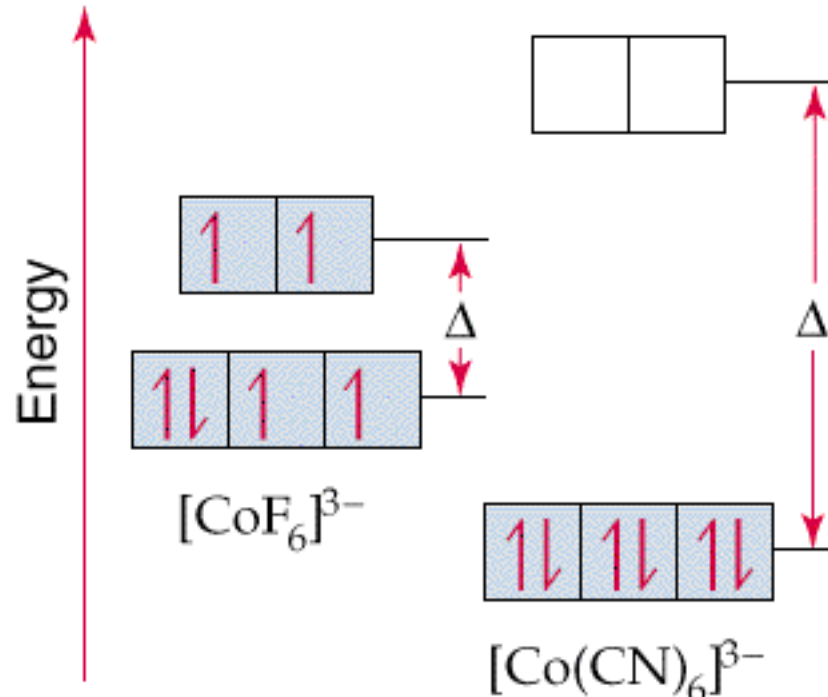
Vysokospinový komplex

Nízkospinový komplex

Slabé pole

Malé štěpení

Slabý ligand



Silné pole

Velké štěpení

Silný ligand

Stabilizační energie ligandového pole

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

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

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

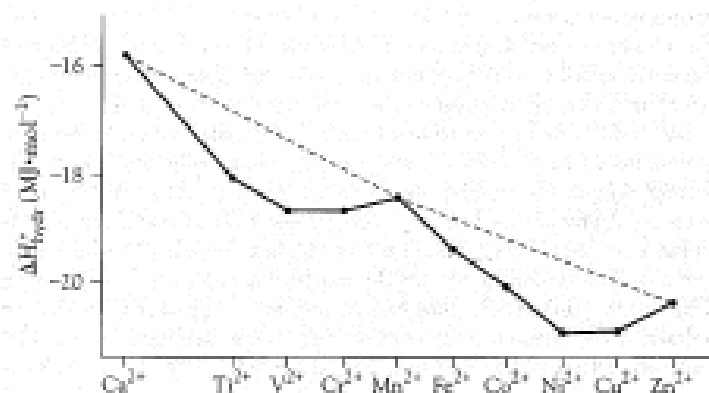


Table 18.3 Crystal field stabilization energies (CFSE) for the dipositive, high spin ions of various Period 4 metals

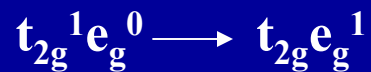
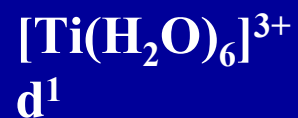
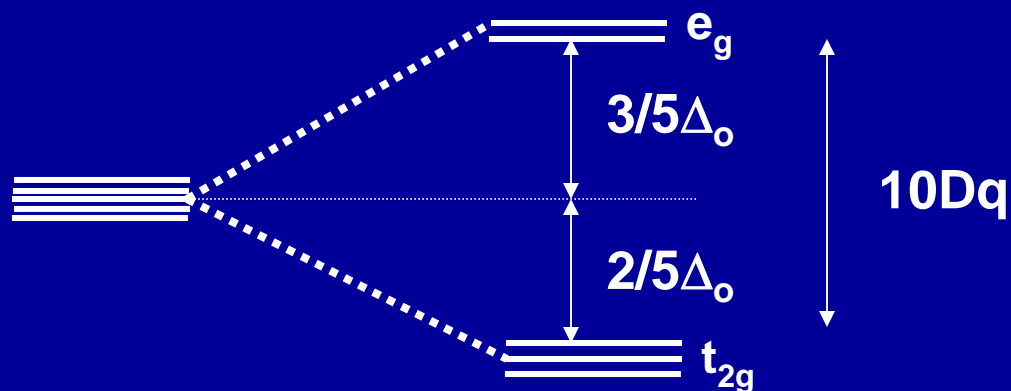
Ion	Configuration	CFSE
Ca ²⁺	d ⁰	-0.0 Δ_{oct}
—	d ¹	-0.4 Δ_{oct}
Ti ²⁺	d ²	-0.8 Δ_{oct}
V ²⁺	d ³	-1.2 Δ_{oct}
Cr ²⁺	d ⁴	-0.6 Δ_{oct}
Mn ²⁺	d ⁵	-0.0 Δ_{oct}
Fe ²⁺	d ⁶	-0.4 Δ_{oct}
Co ²⁺	d ⁷	-0.8 Δ_{oct}
Ni ²⁺	d ⁸	-1.2 Δ_{oct}
Cu ²⁺	d ⁹	-0.6 Δ_{oct}
Zn ²⁺	d ¹⁰	-0.0 Δ_{oct}

d^0

d^5

d^{10}

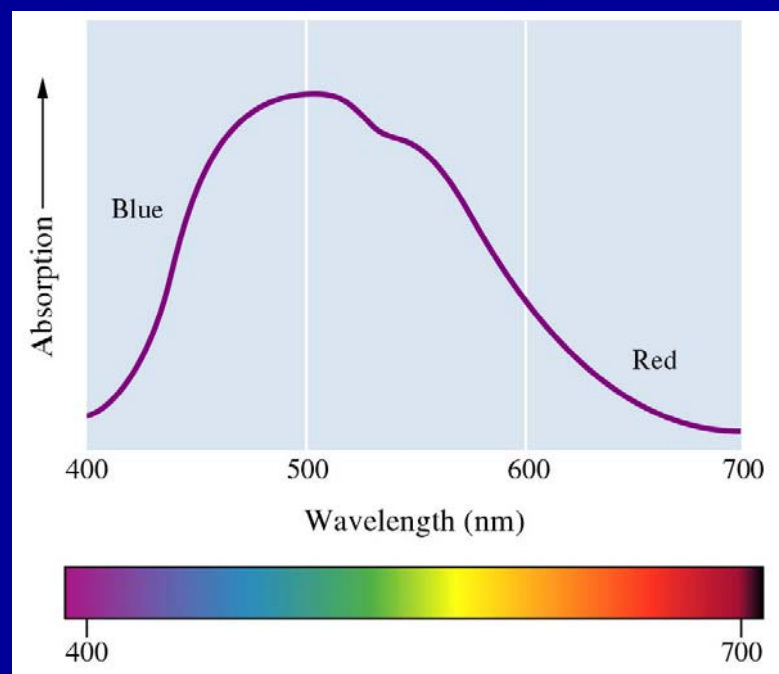
Rozštěpení d-hladin v O_h poli



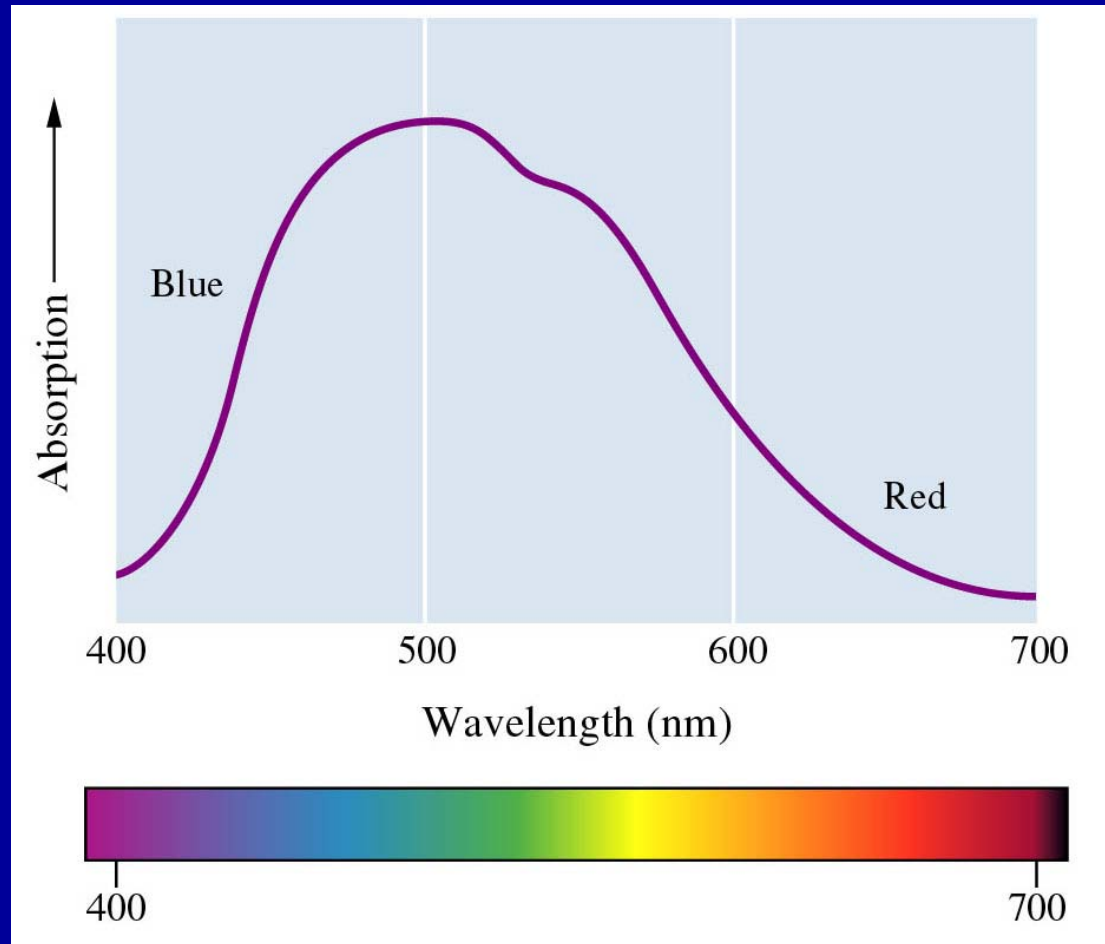
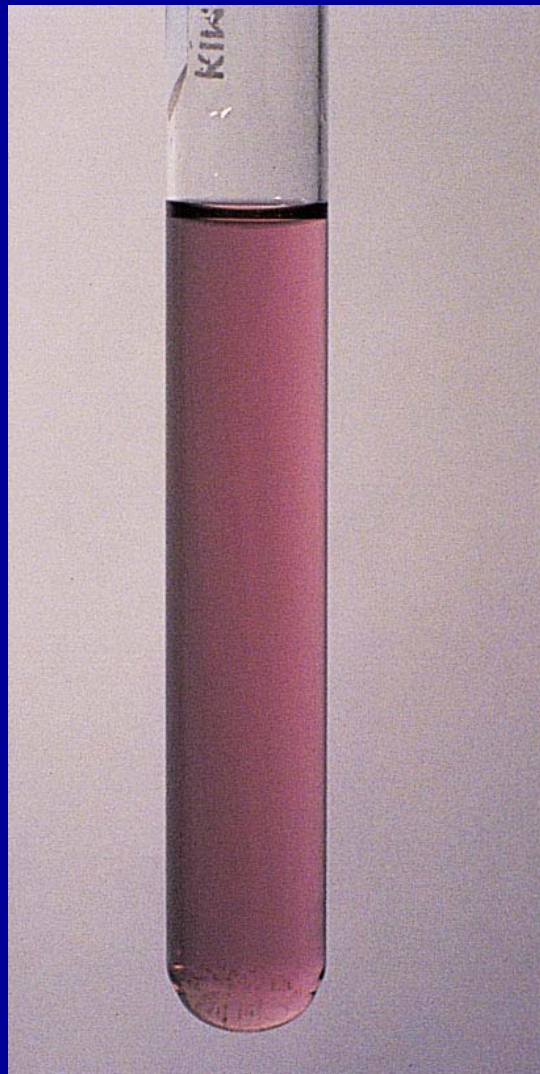
růžový

243 kJ mol^{-1}

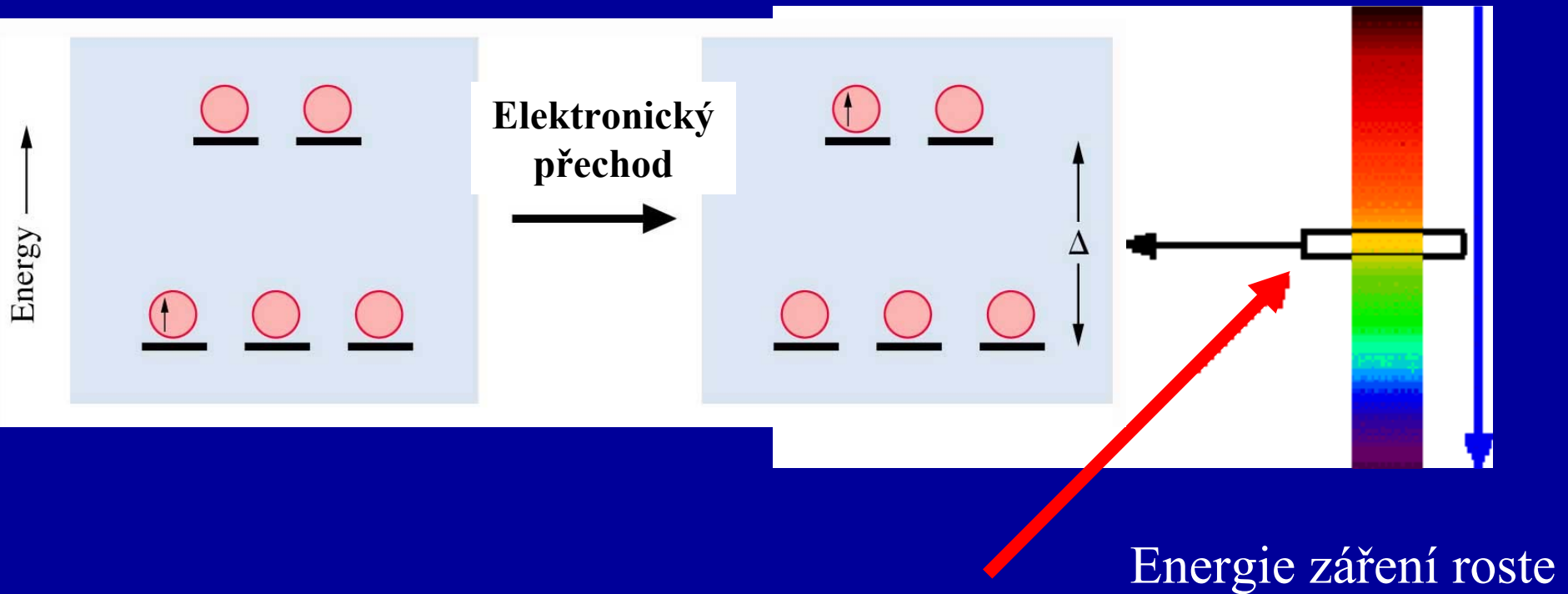
(Δ_o)



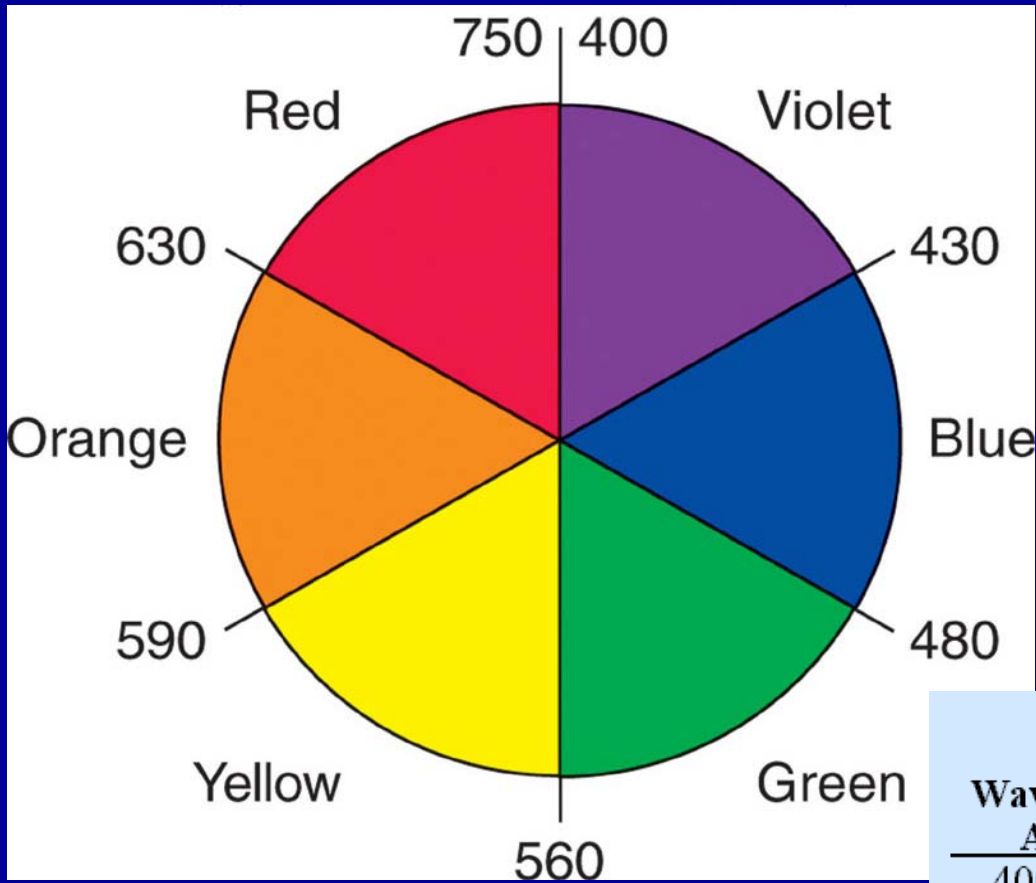
UV-vis absorpční spektrum $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



Elektronické přechody



Tato energie je právě dostatečná pro excitaci elektronu



Absorbované světlo



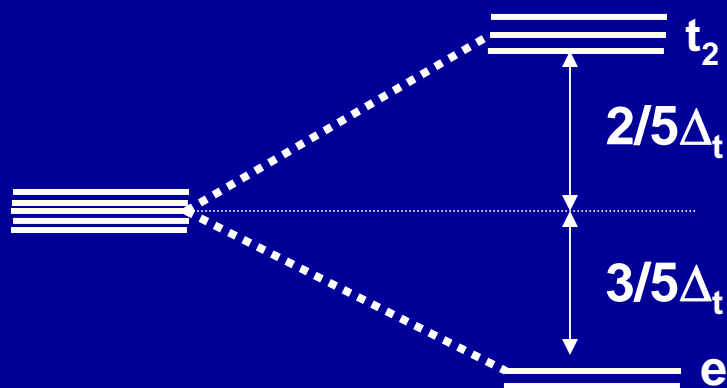
Prošlé světlo



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



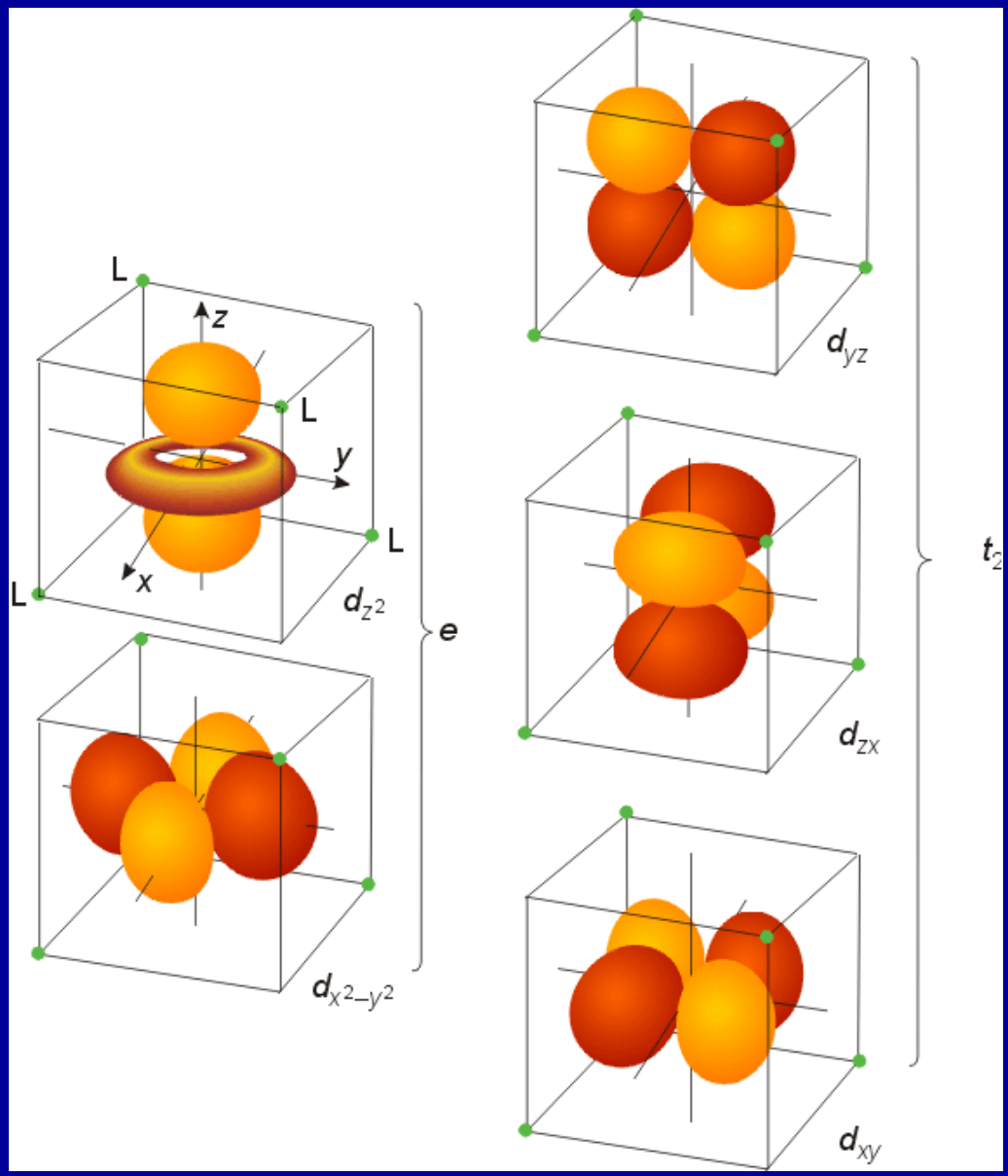
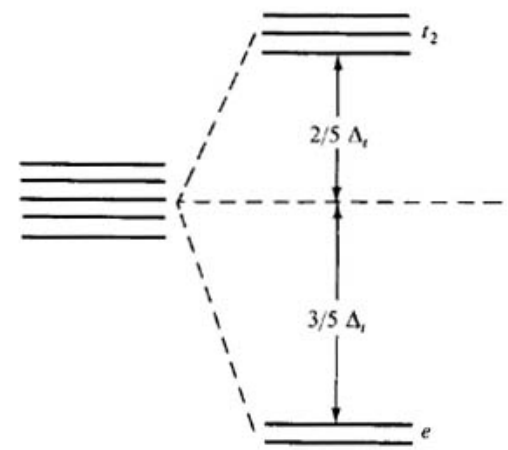
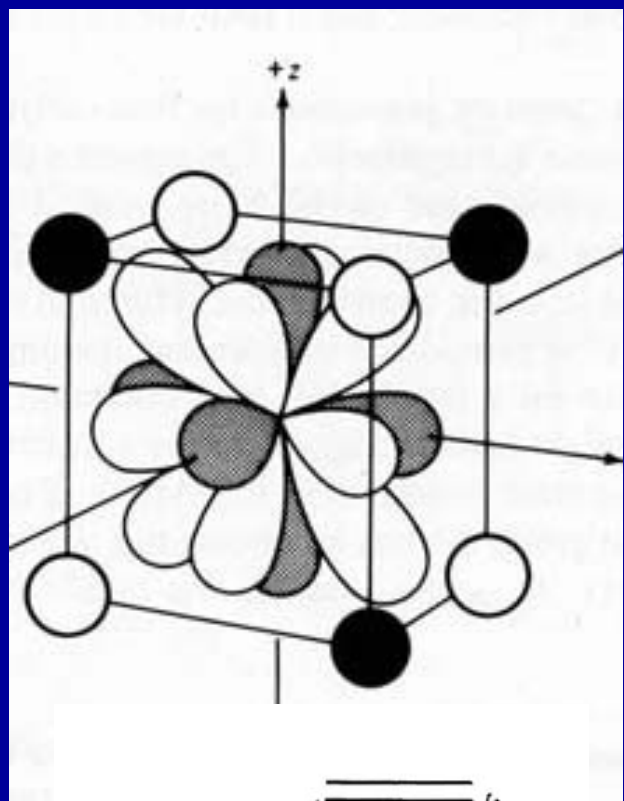
Rozštěpení d-hladin v T_d poli



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

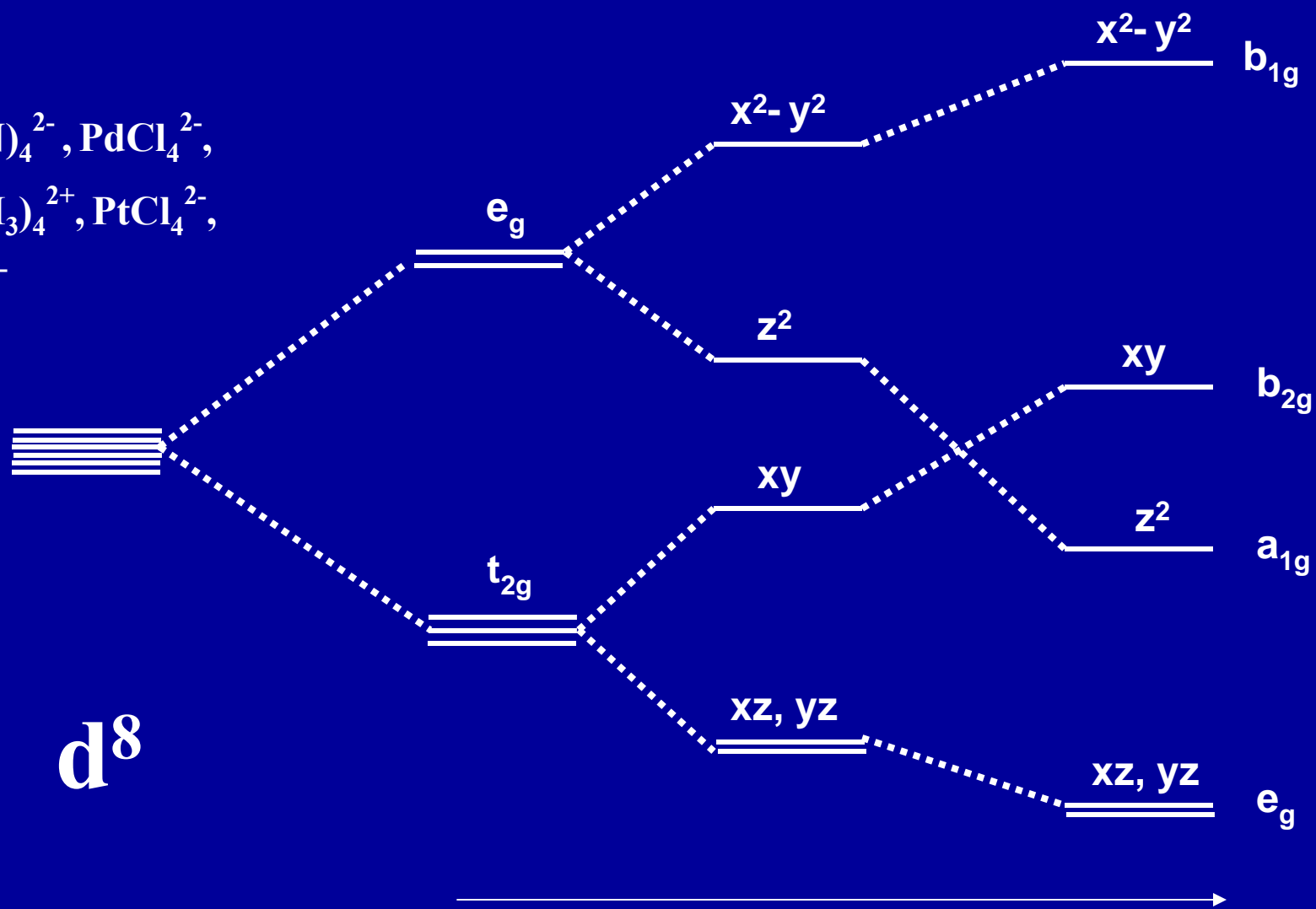
T_d komplexy jsou vždy vysokospinové
žádný d-orbital nemíří přímo k ligandům (jako u
 O_h) slabší interakce

d-orbitaly v tetraedrickém poli ligandů



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

$\text{Ni}(\text{CN})_4^{2-}$, PdCl_4^{2-} ,
 $\text{Pt}(\text{NH}_3)_4^{2+}$, PtCl_4^{2-} ,
 AuCl_4^-



Odtržení ligandů v ose z

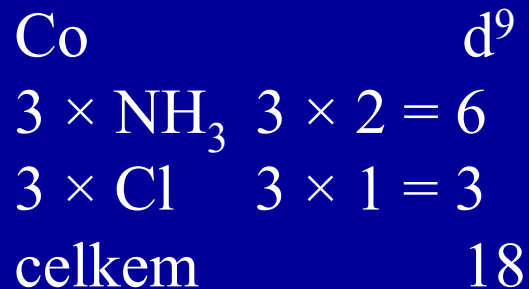
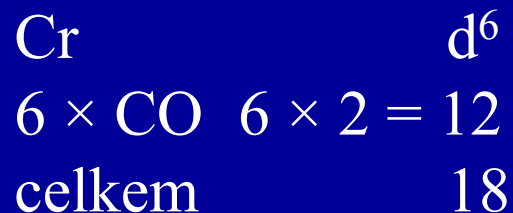
18-ti elektronové pravidlo

Počet d-elektronů neutrálního kovu

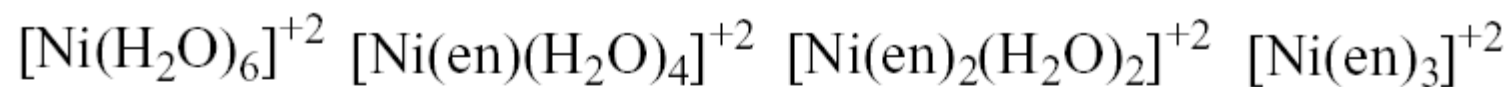
+ 2 e neutrální ligandy

+ 1 e aniontové ligandy

součet 18 pro stabilní komplexy



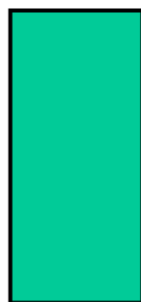
Vliv ligandů na vlastnosti komplexů



green



green/blue



blue

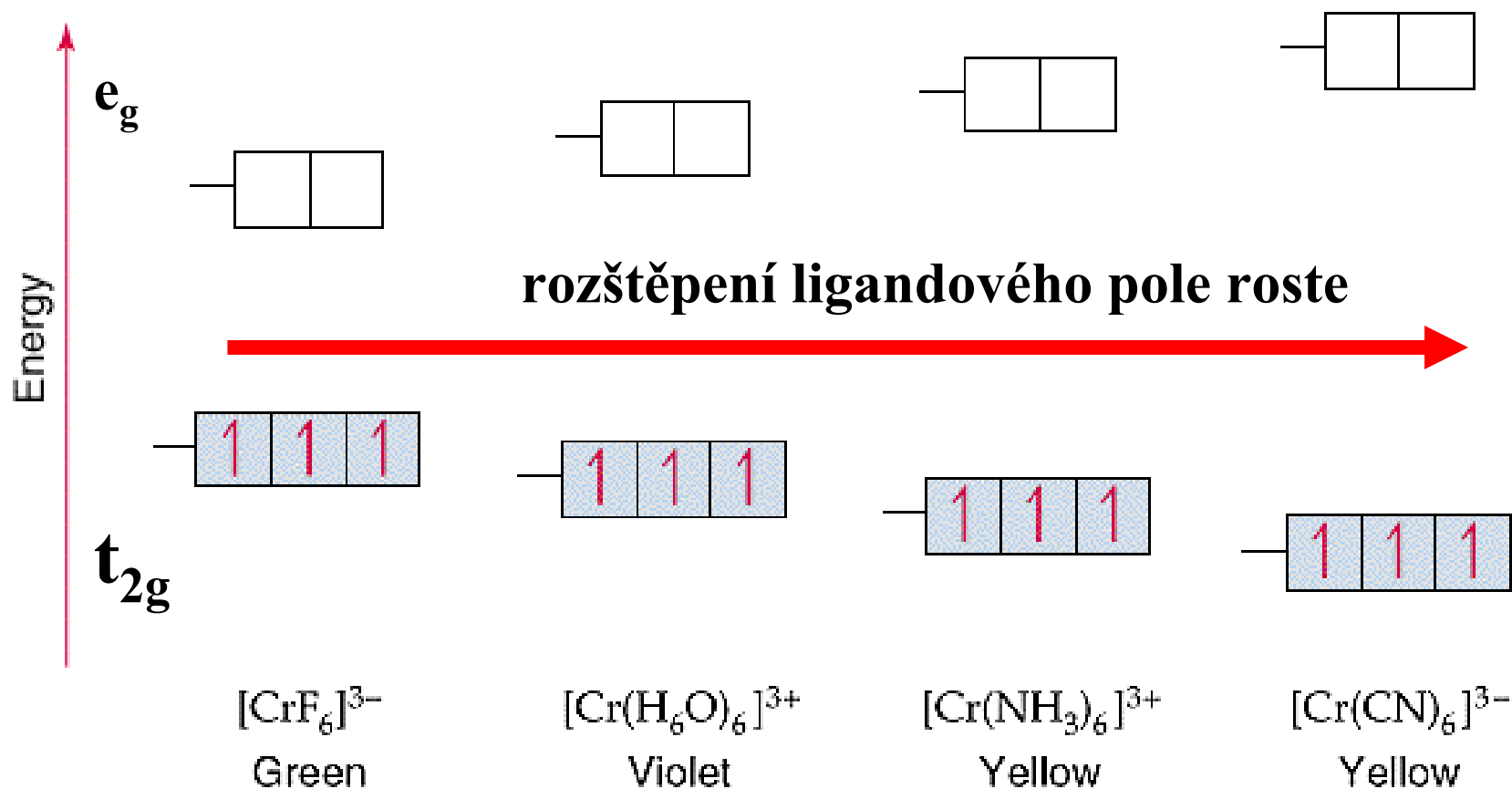


purple



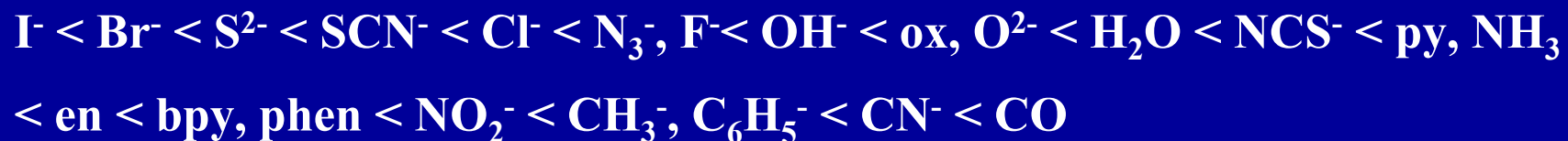
en = ethylendiammin

Vliv ligandů na vlastnosti komplexů



Faktory ovlivňující velikost rozštěpení ligandového pole

Spektrochemická řada ligandů:



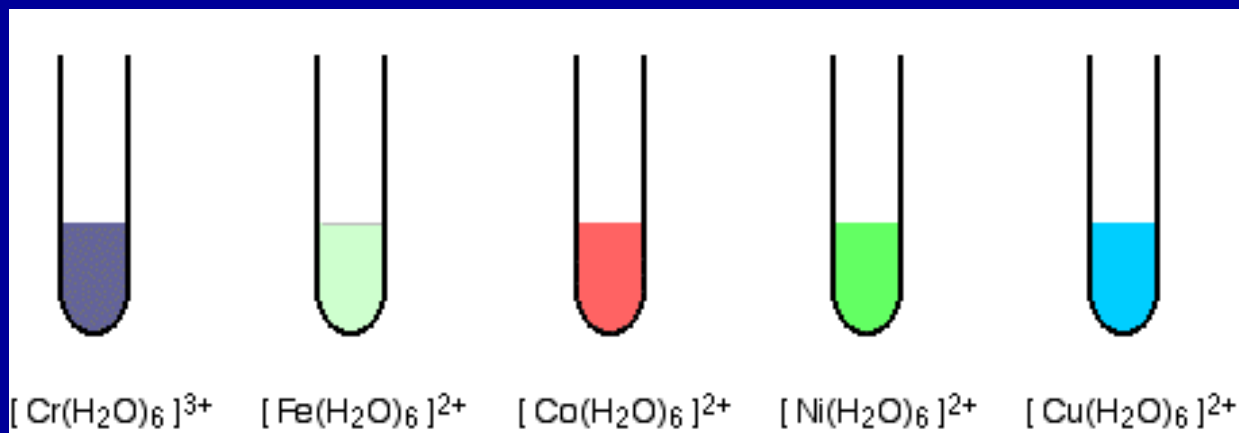
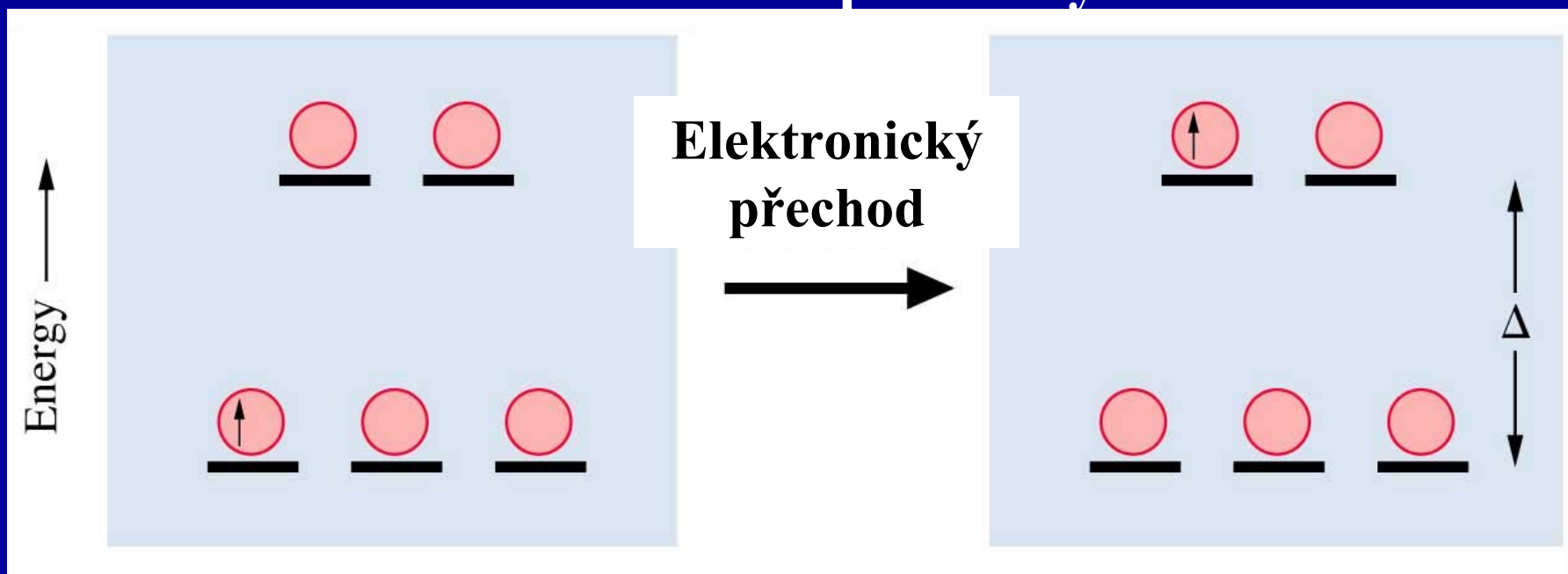
Centrální atom:

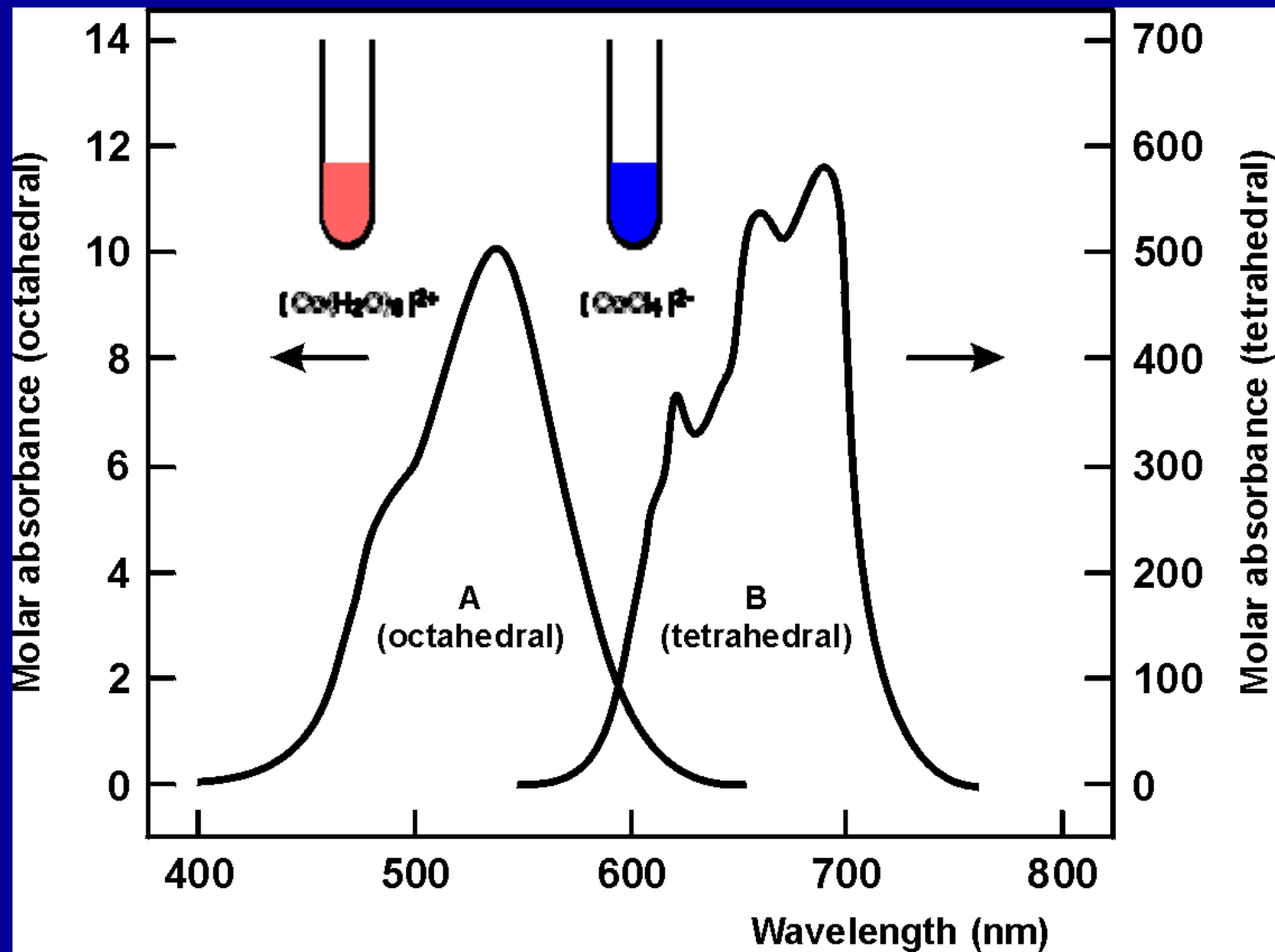


Typ koordinace $4/9 \Delta_o = \Delta_t$

Síla a délka vazby M-L

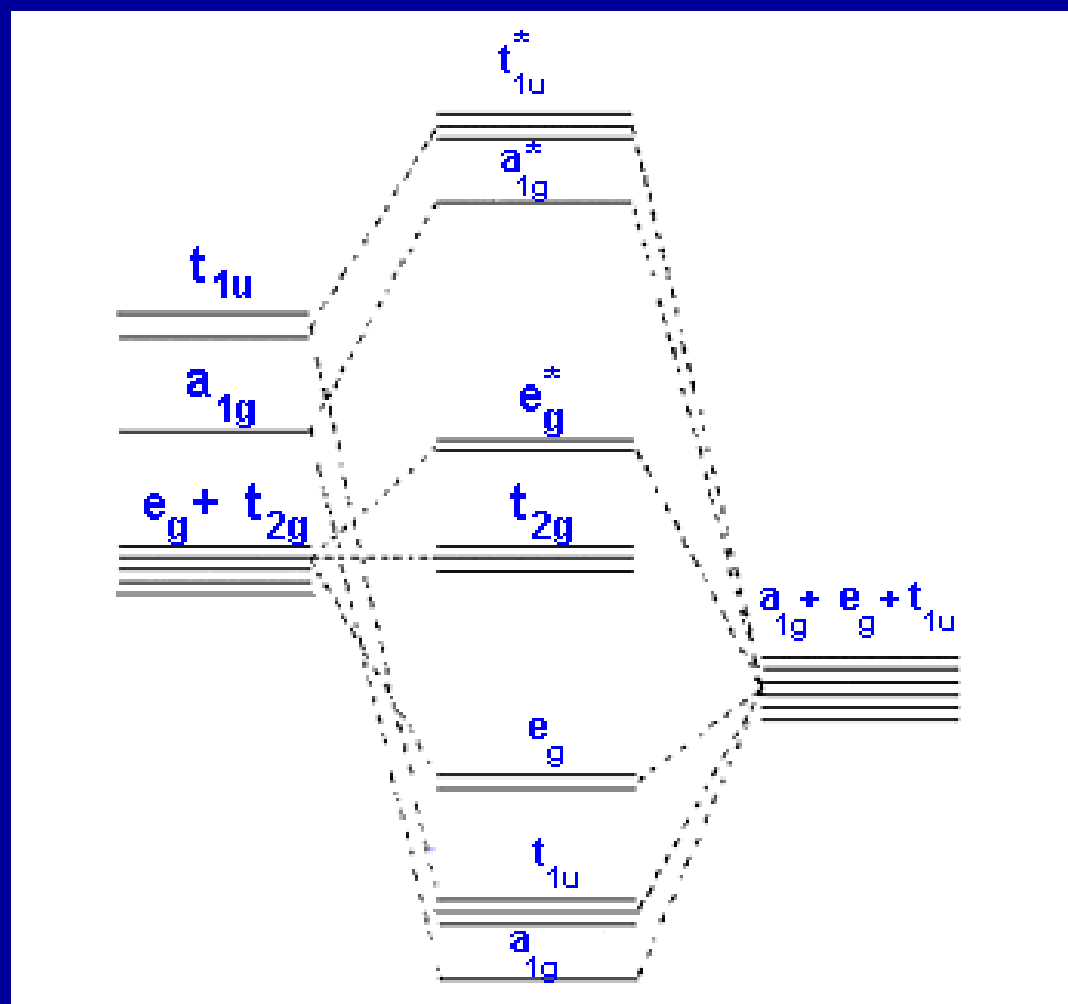
Elektronické přechody





Popis vazby v komplexech pomocí MO

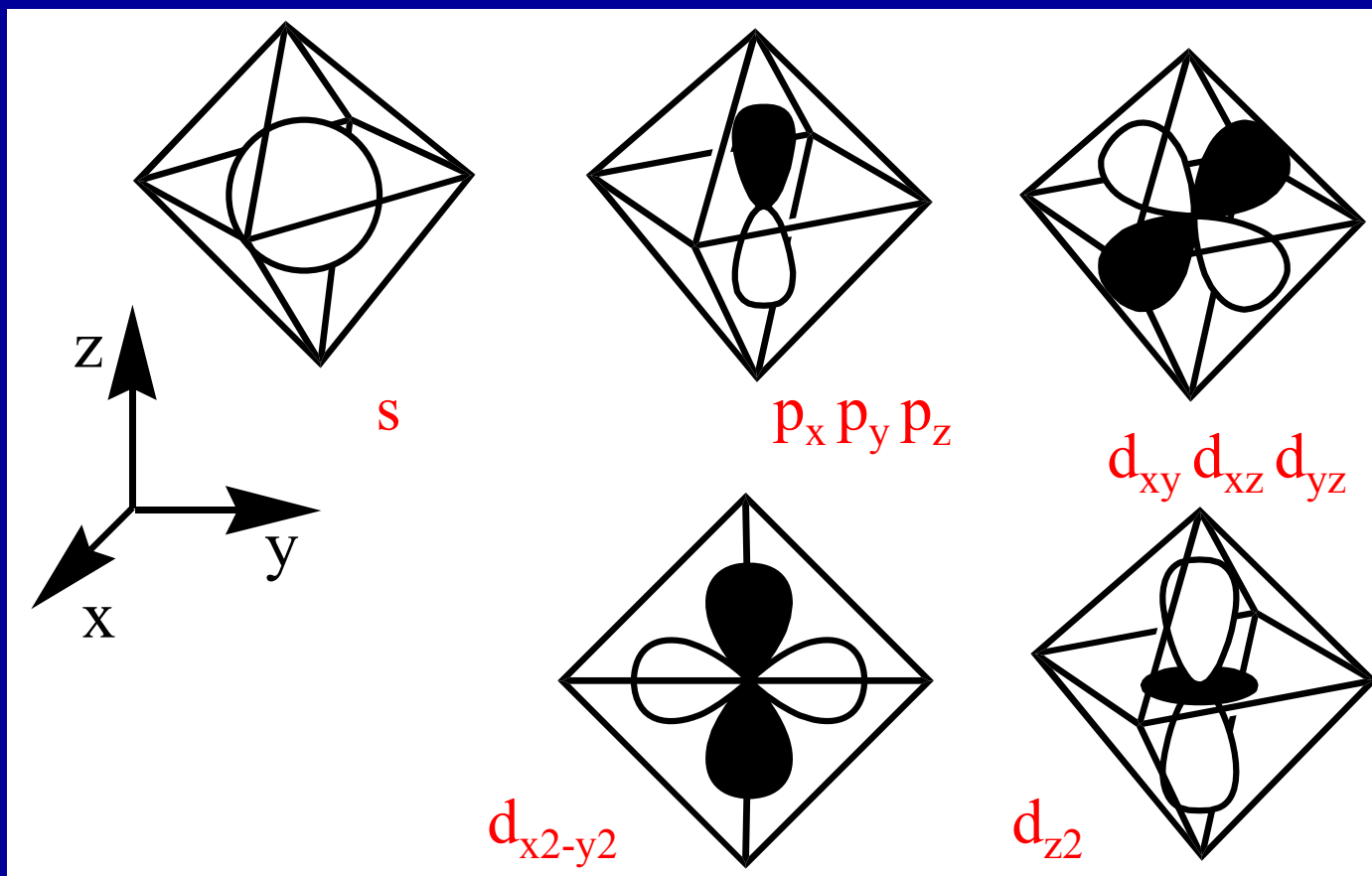
3 x np
 1x ns
 5x (n-1) d
 Orbitaly kovu

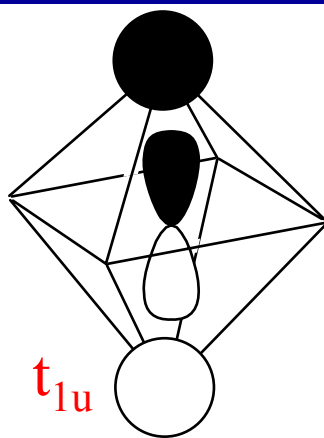
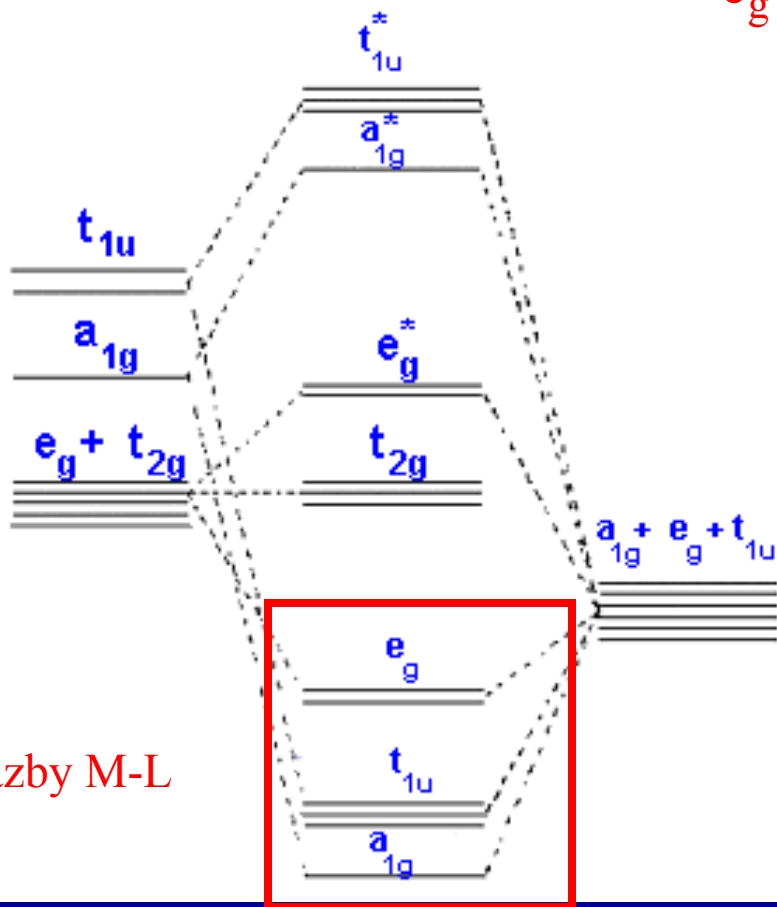
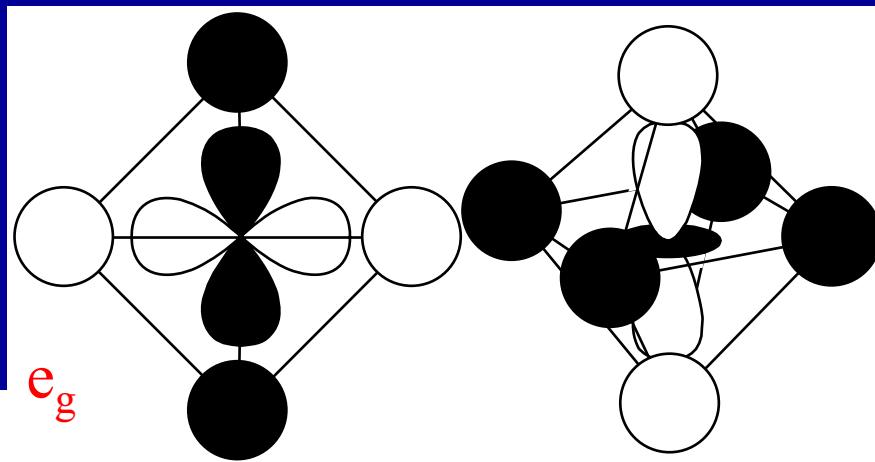


SALCAO

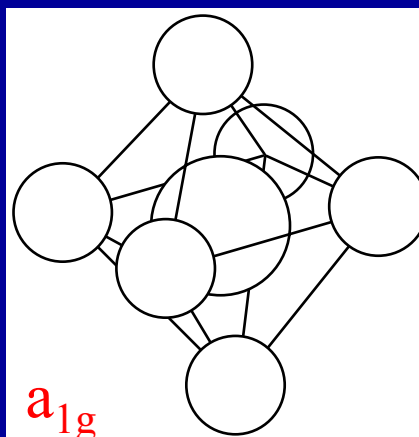
Orbitaly
 ligandů

Valenční orbitály kovu



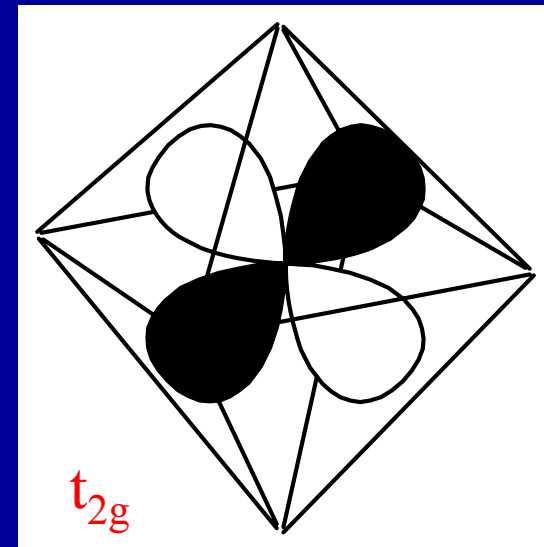
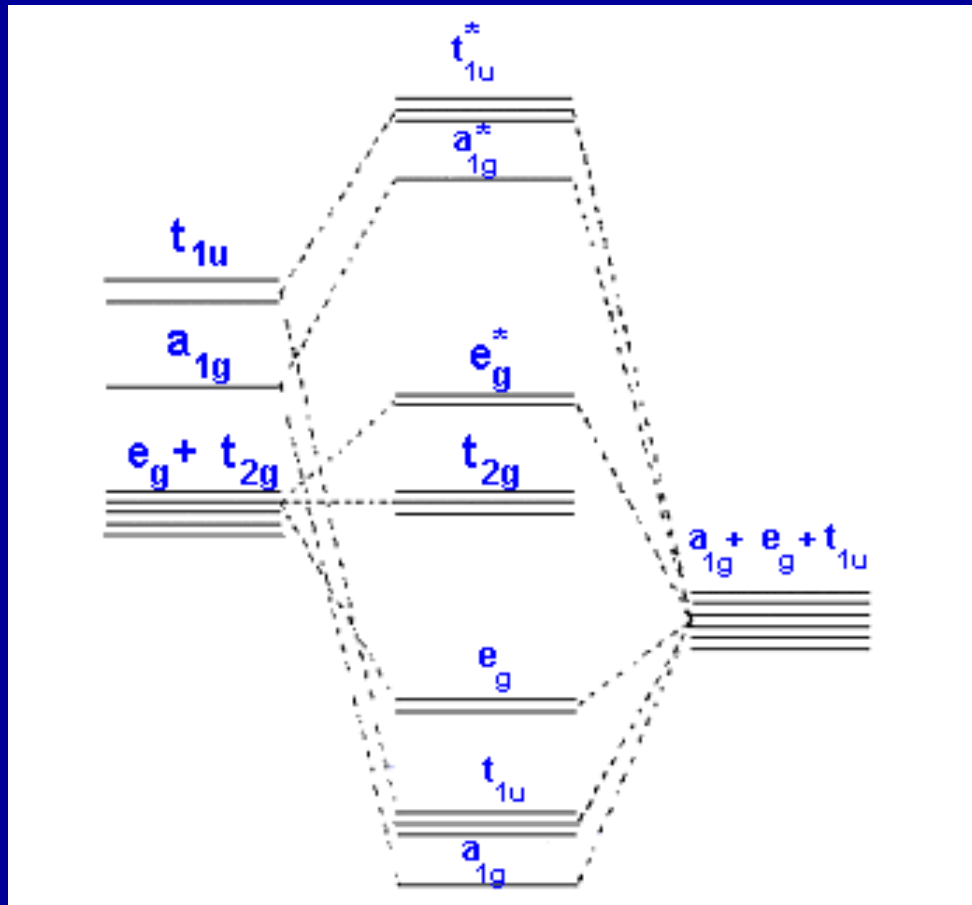


3 x np

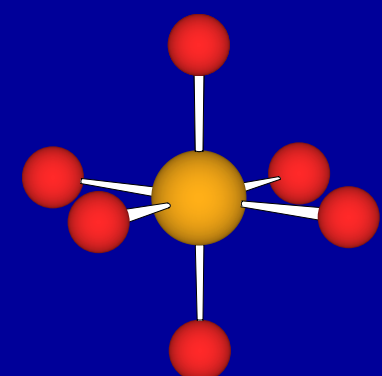
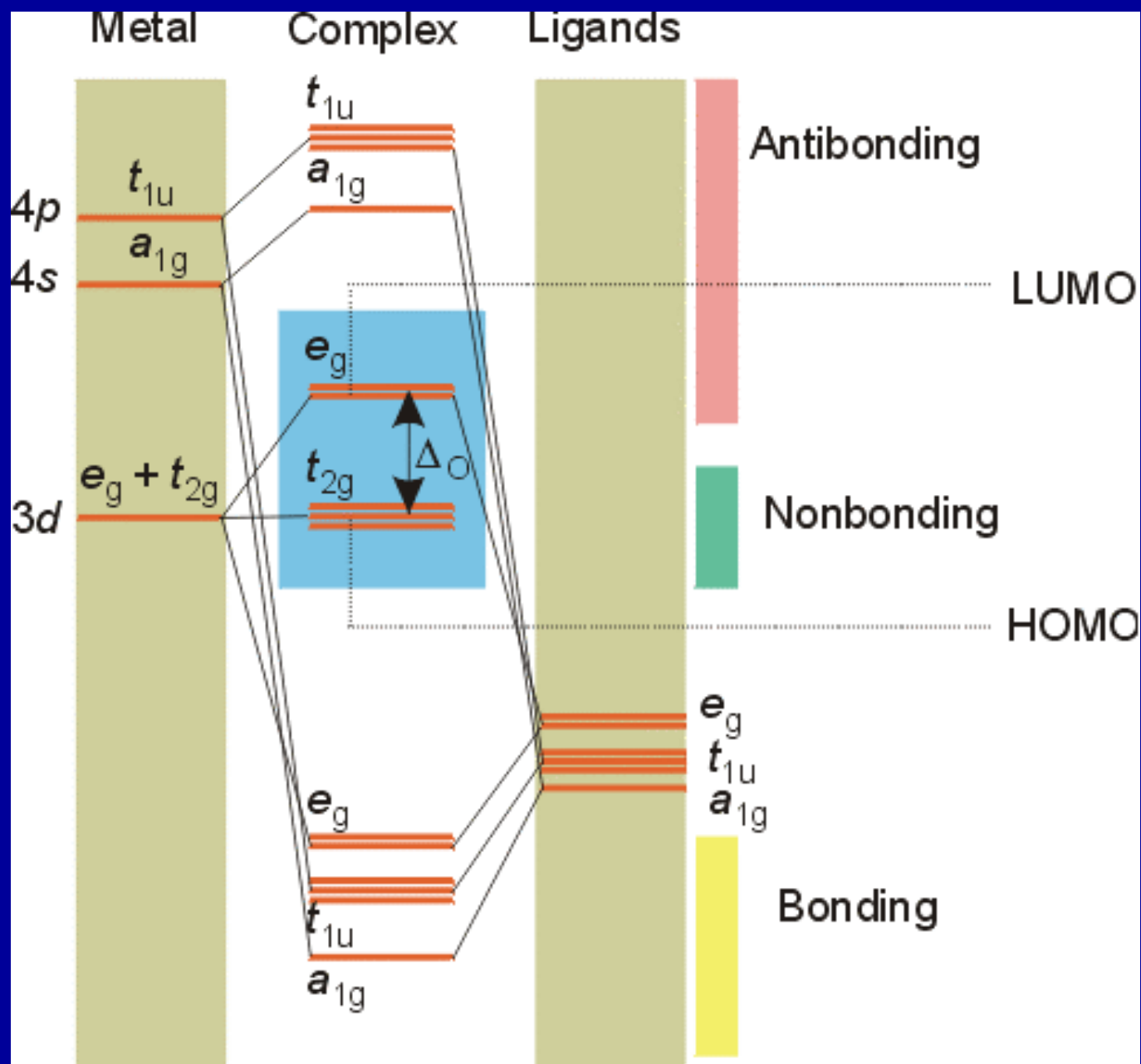


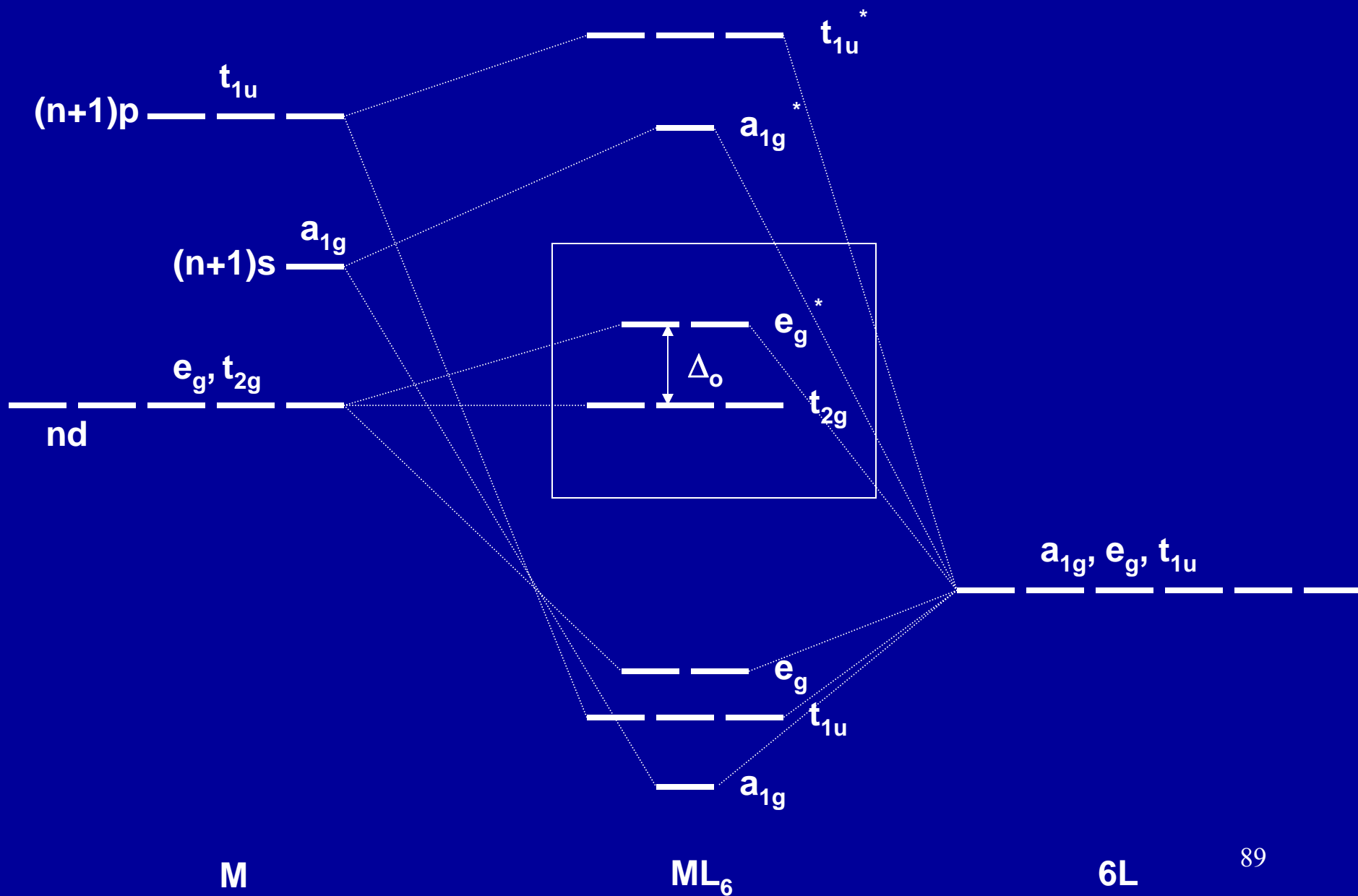
Sigma vazby M-L

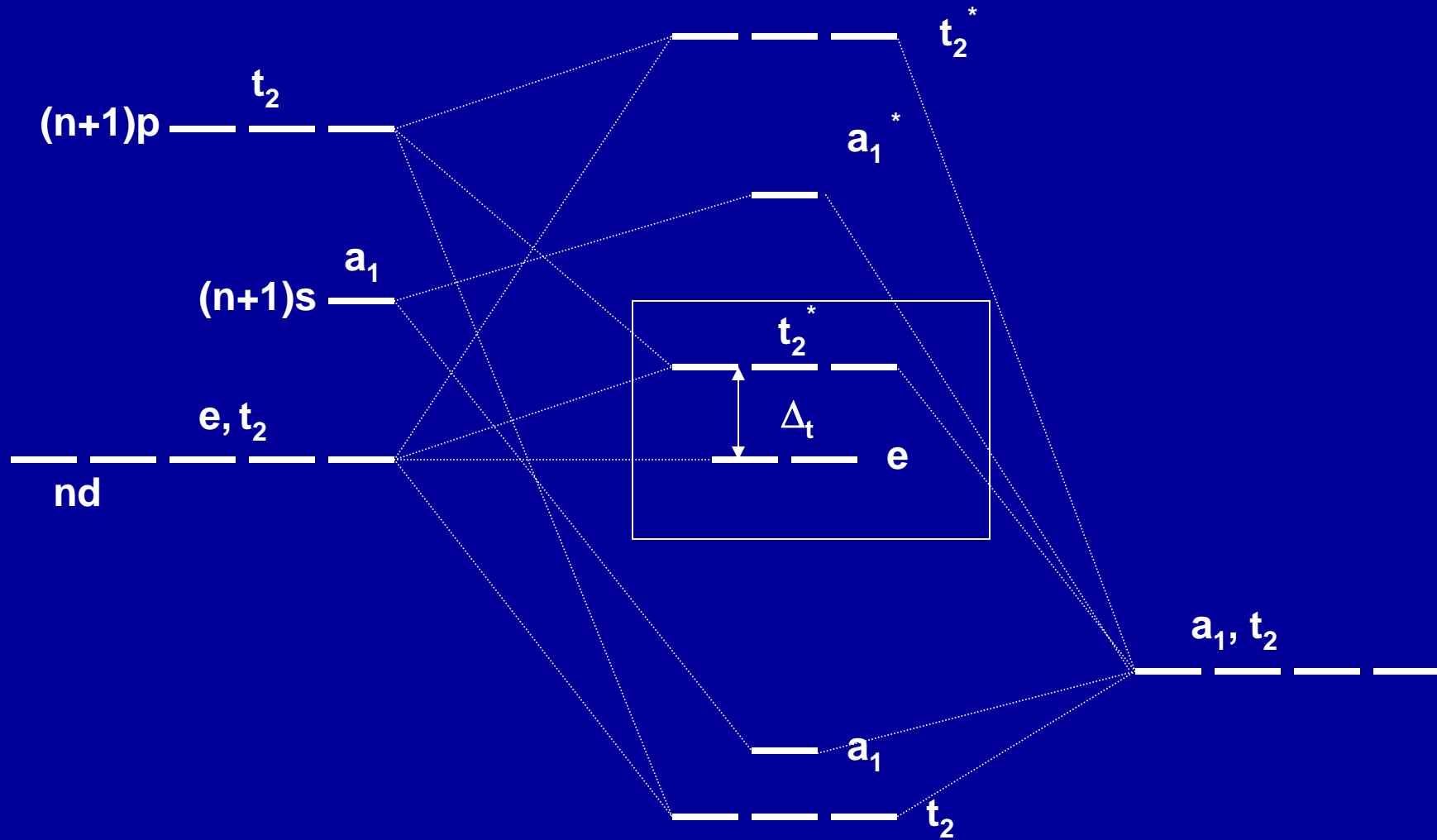
Nevazebné d-orbitaly



Neexistuje žádná vhodná kombinace AO ligandů (pro sigma vazbu)



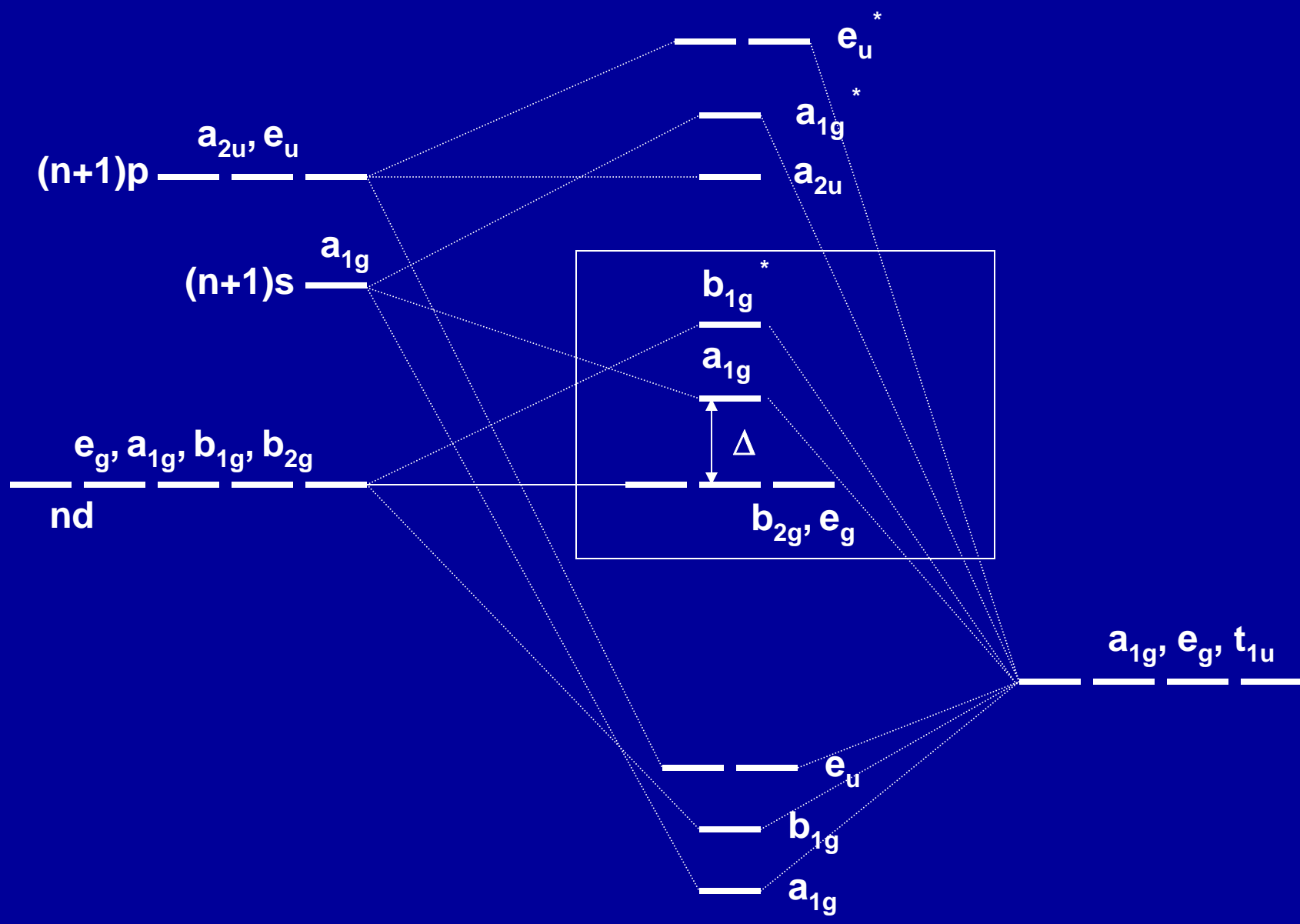




M

ML₄

4L(LGOs)₉₀

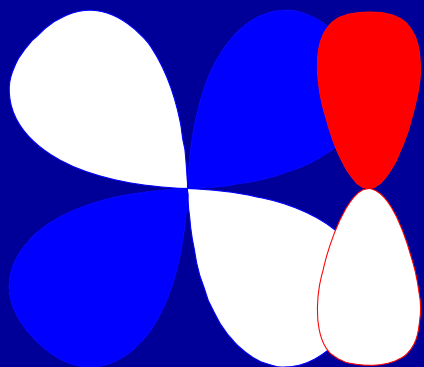


M

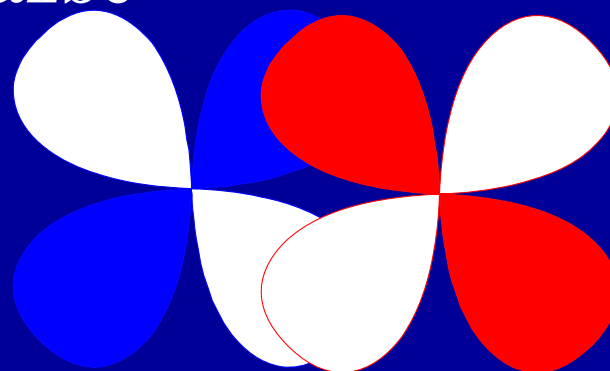
$ML_4 (D_{4h})$

$4L(LGOS)^{91}$

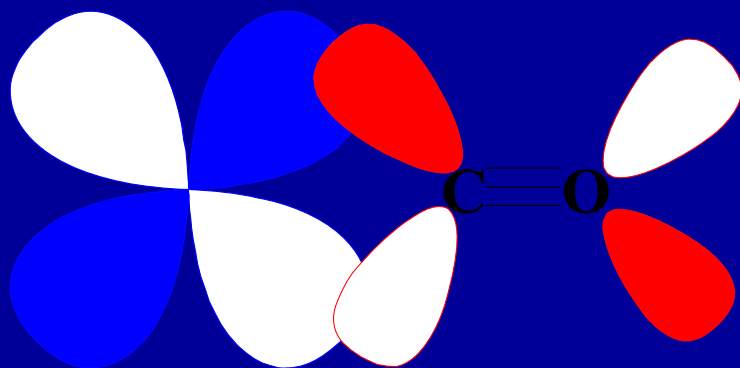
MO při π -vazbě



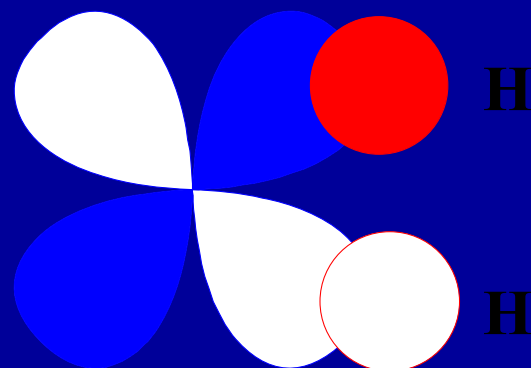
$p\pi-d\pi$ $RO^-, RS^-, O^{2-}, F^-, Cl^-, Br^-, I^-, R_2N^-$



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

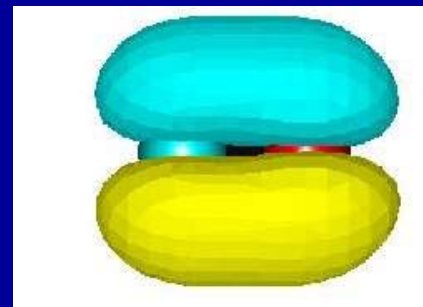
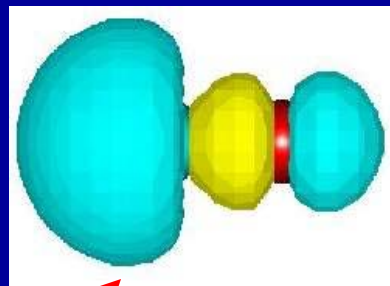
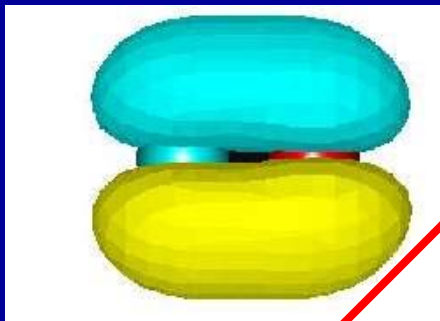
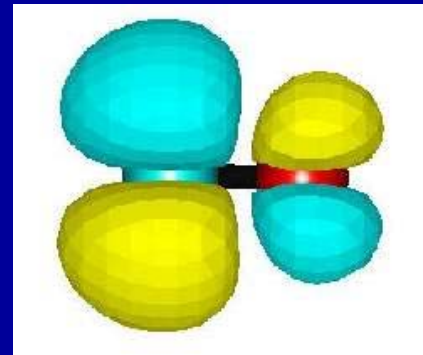
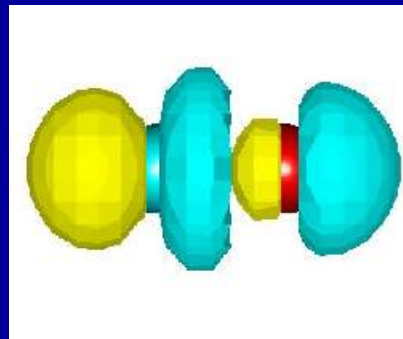
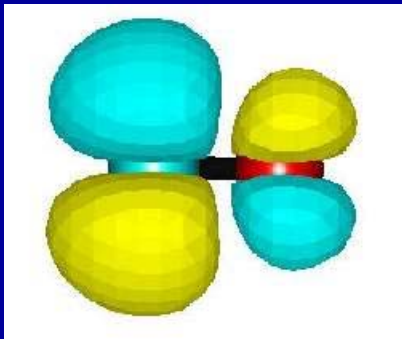


$d\pi-\pi^*$ $CO, RNC, \text{pyridin}, CN^-, N_2, NO_2^-, \text{ethylen}$



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

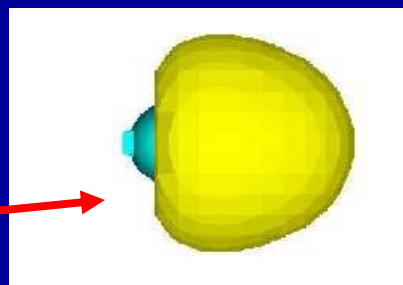
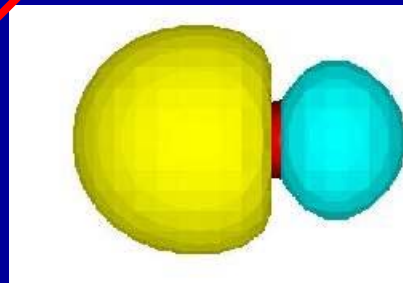
LUMO

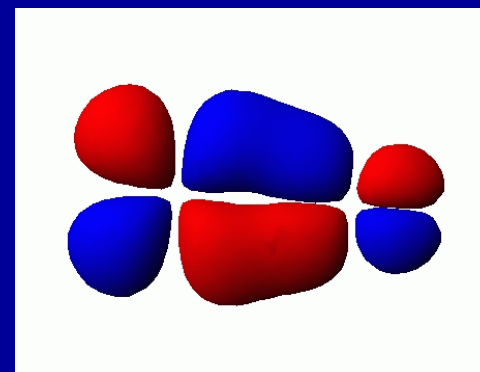
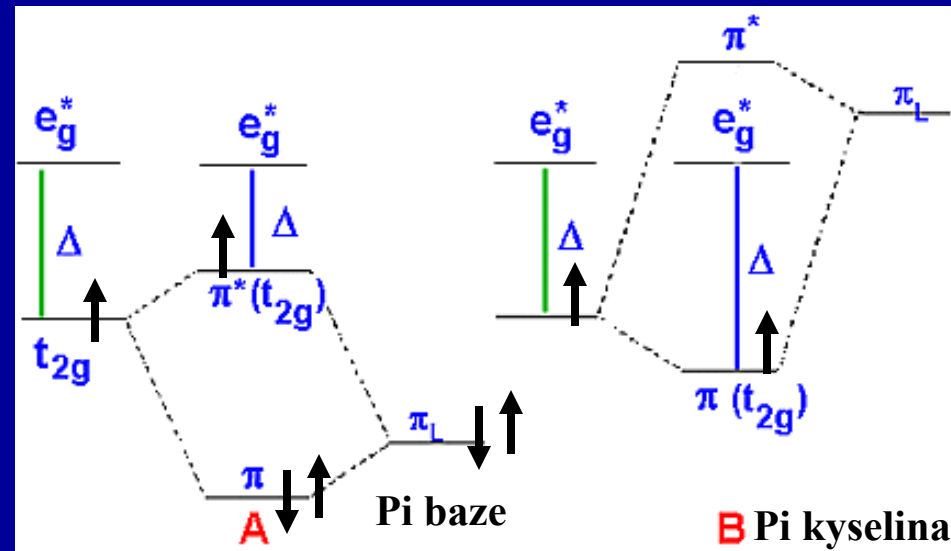
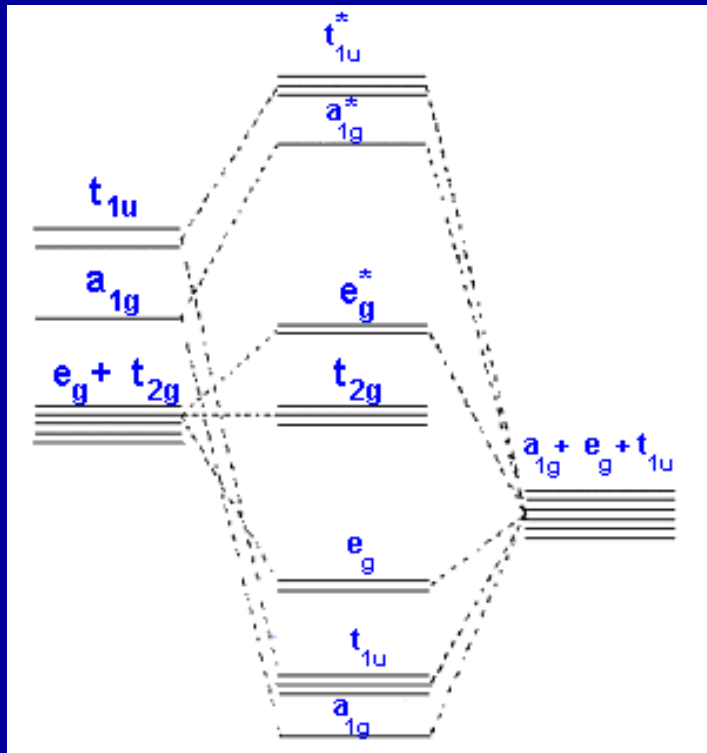
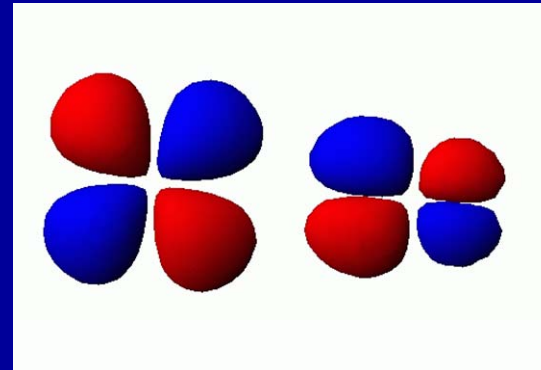


Volný e pár na C
HOMO

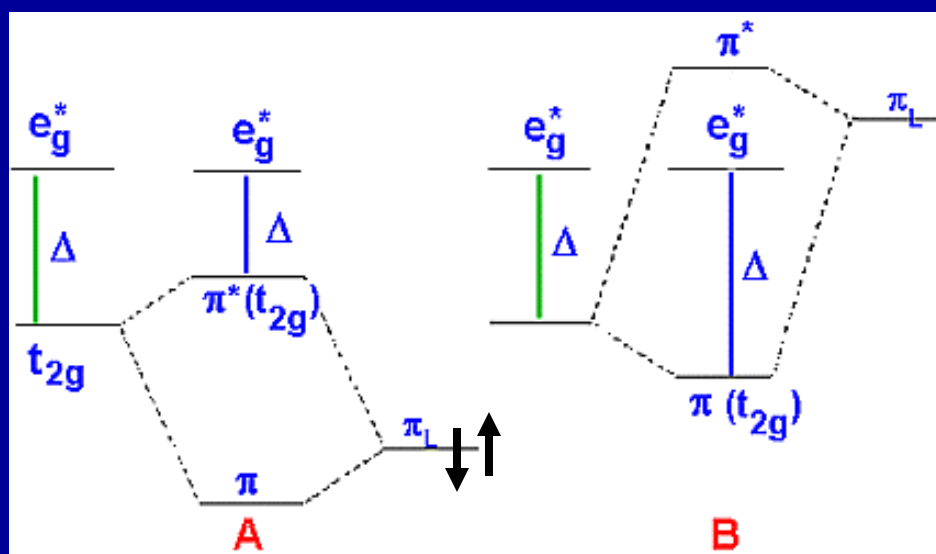


Volný e pár na O





Ligandy s pi orbitaly



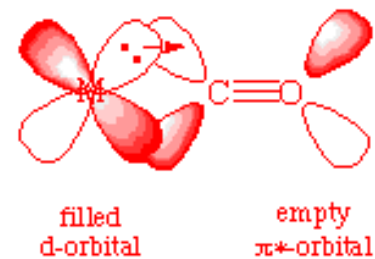
Pi baze

Pi kyselina

σ bond:



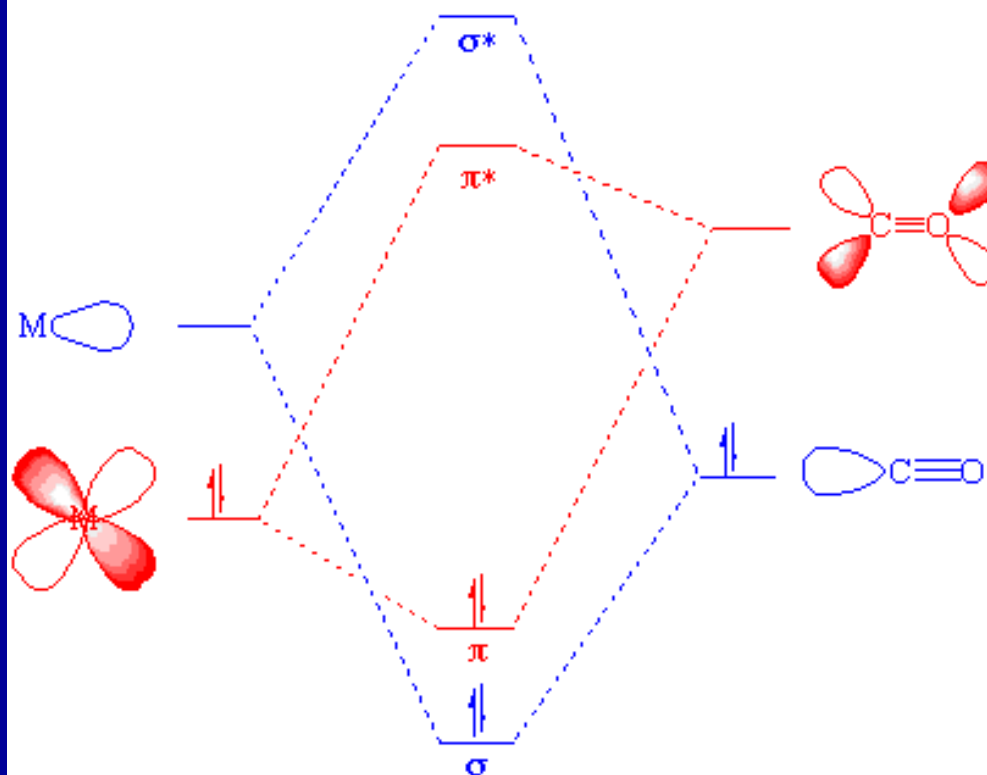
π backbond:



$L_{\pi}M$

$L_{\pi}M(CO)$

CO



Zpětná pi donace

$M \rightarrow CO$

Sigma donace

$M \leftarrow CO$

Jahn-Tellerova distorze

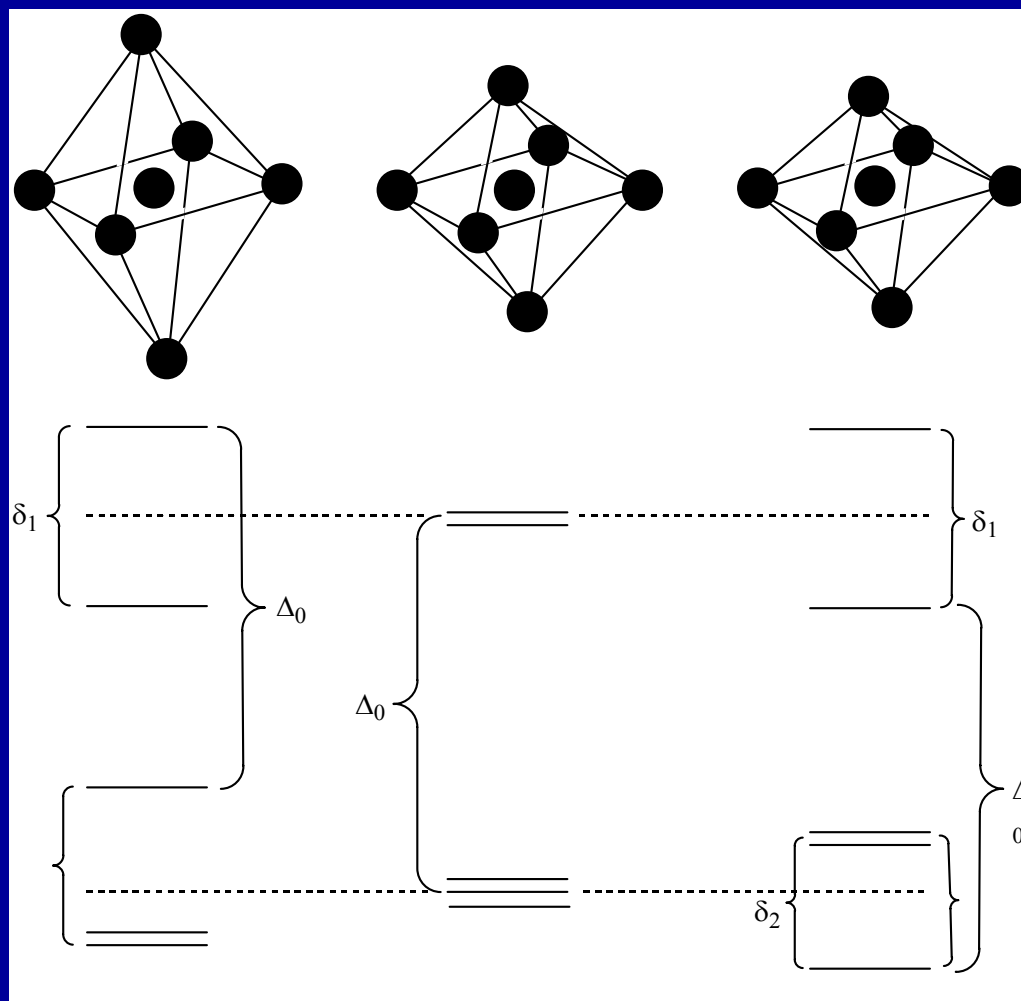
Degenerované hladiny

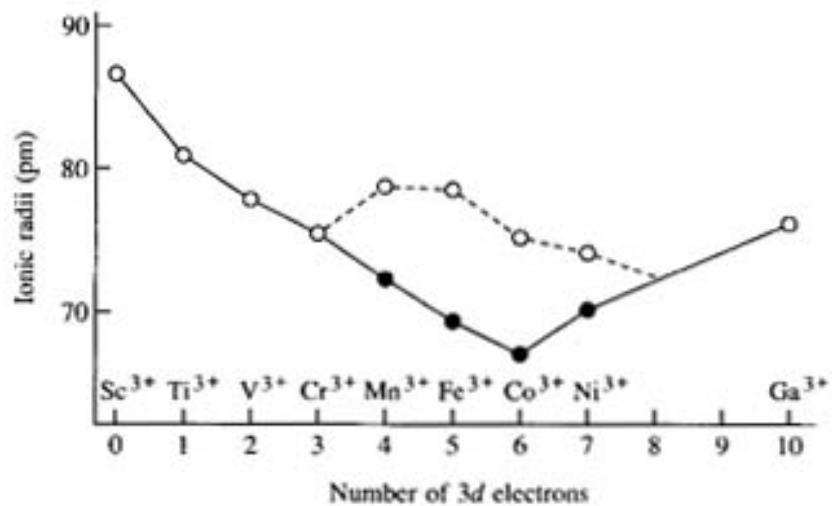
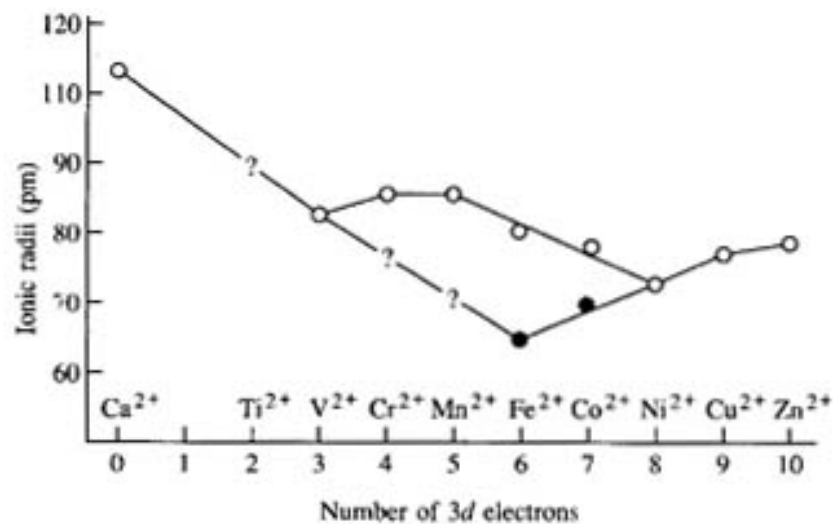
Částečně obsazené

Nelineární molekuly

Degenerace se odstraní

deformací

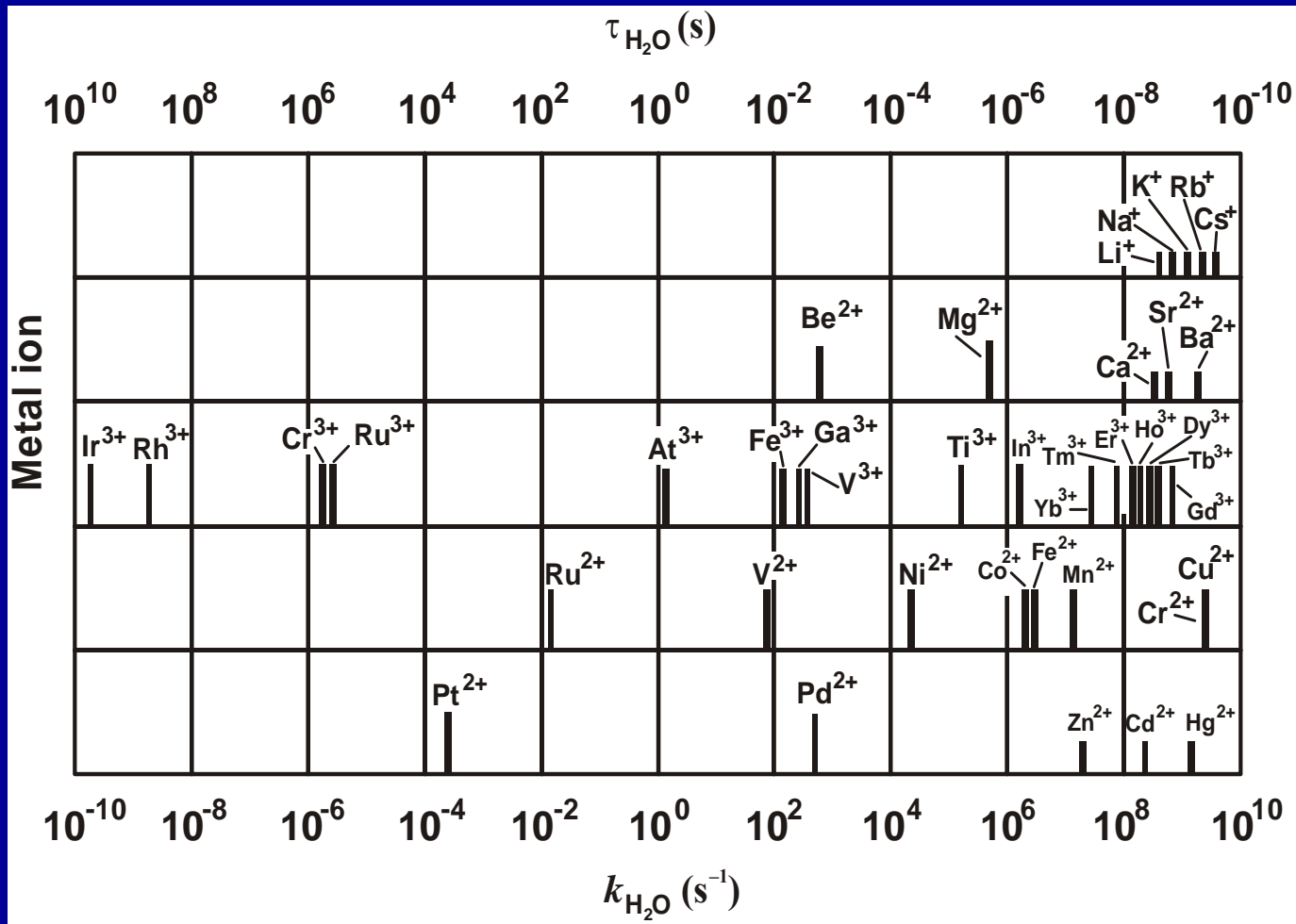




Kinetika



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)

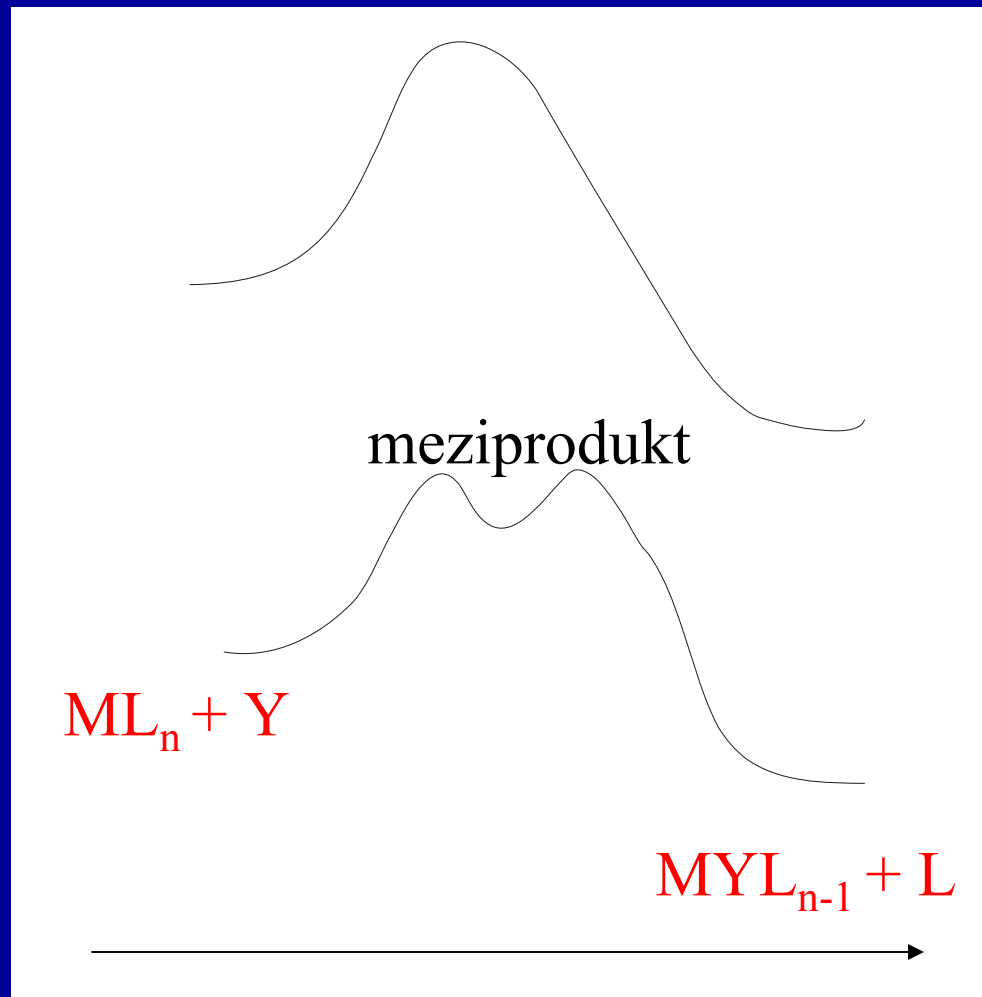
extent to which a ligand effects the rate of exchange of the ligand *trans* to itself

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

