

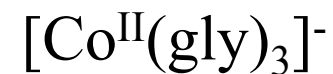
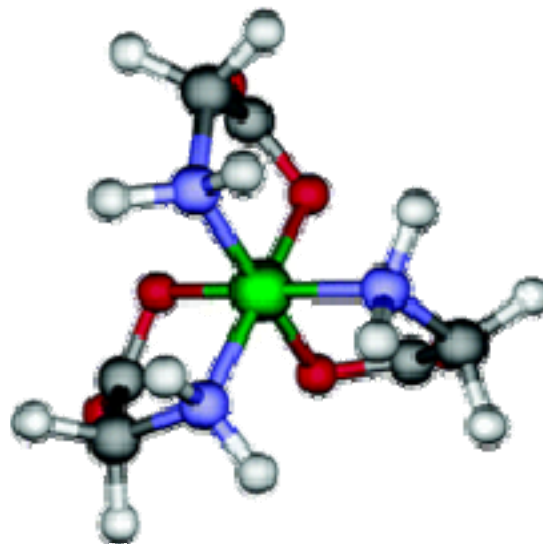
Koordinační chemie



Alfred Werner
(1866-1919)

NP za chemii 1913

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



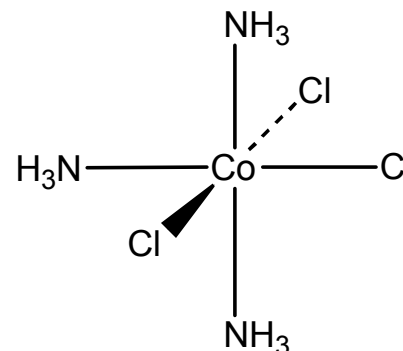
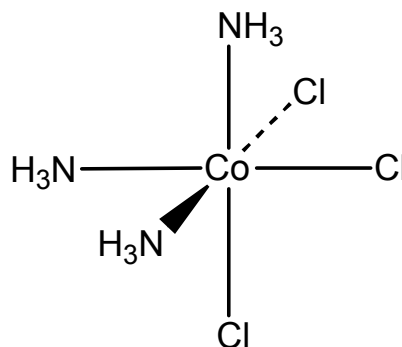
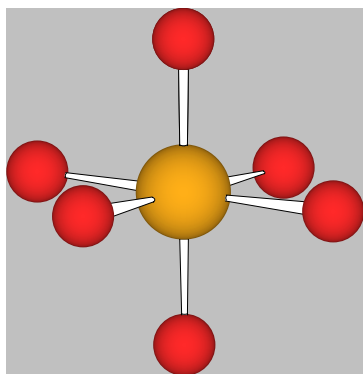
Koordinační sloučeniny

Experimentální výsledky nesouhlasí s dosavadní teorií

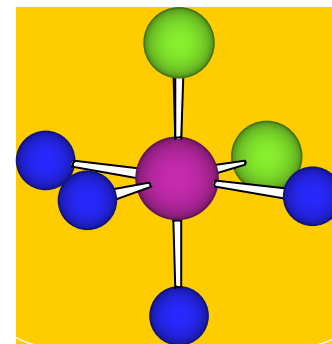
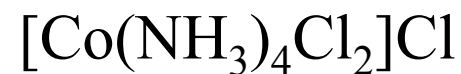
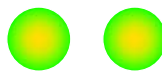
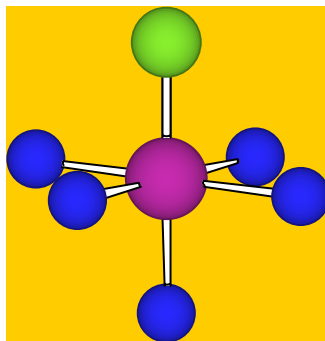
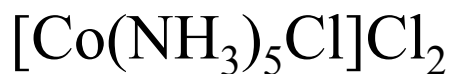
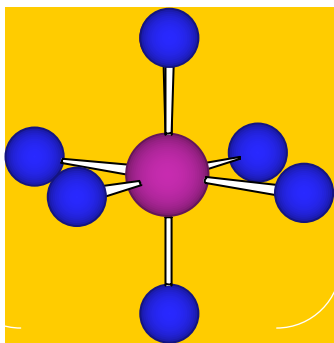
→ nová teorie (model)

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

Oktaedr



Koordinační sloučeniny



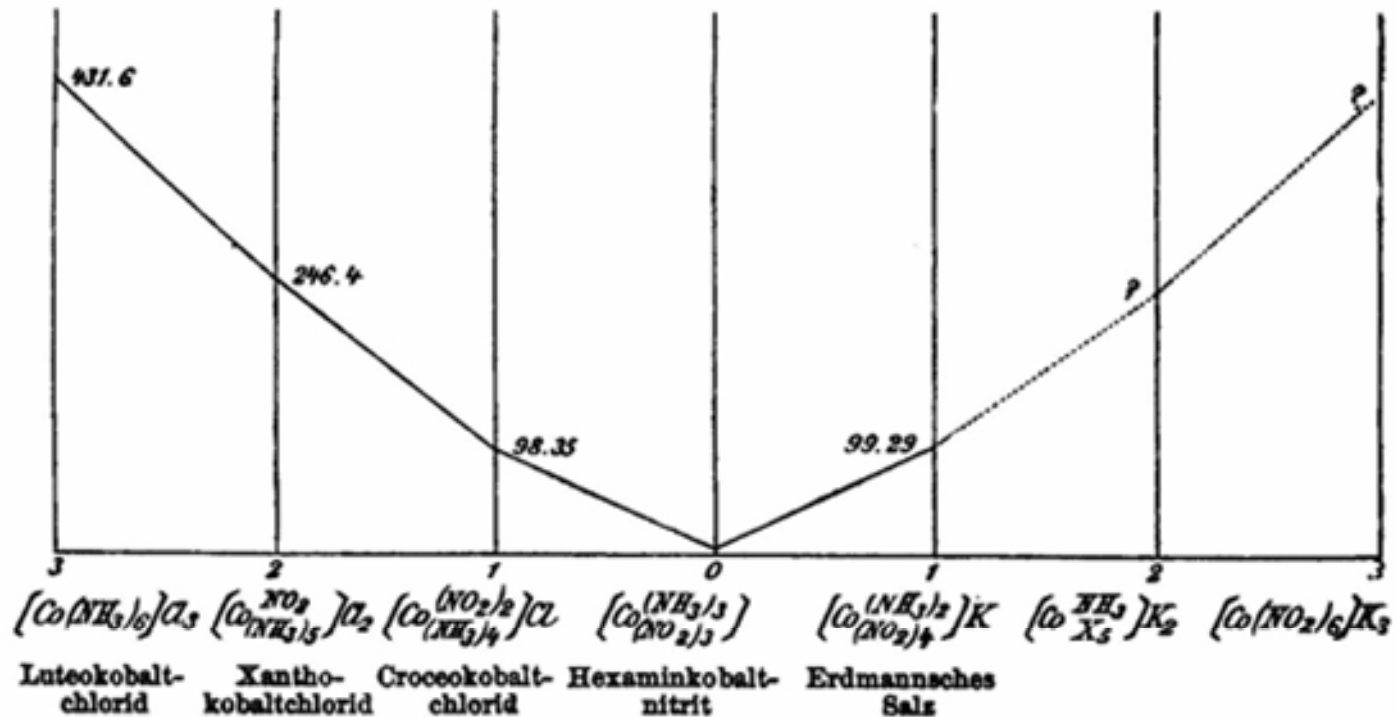
Kov v oxidačním stavu $n+$ (primární valence)

Komplex má koordinační číslo m (sekundární valence)

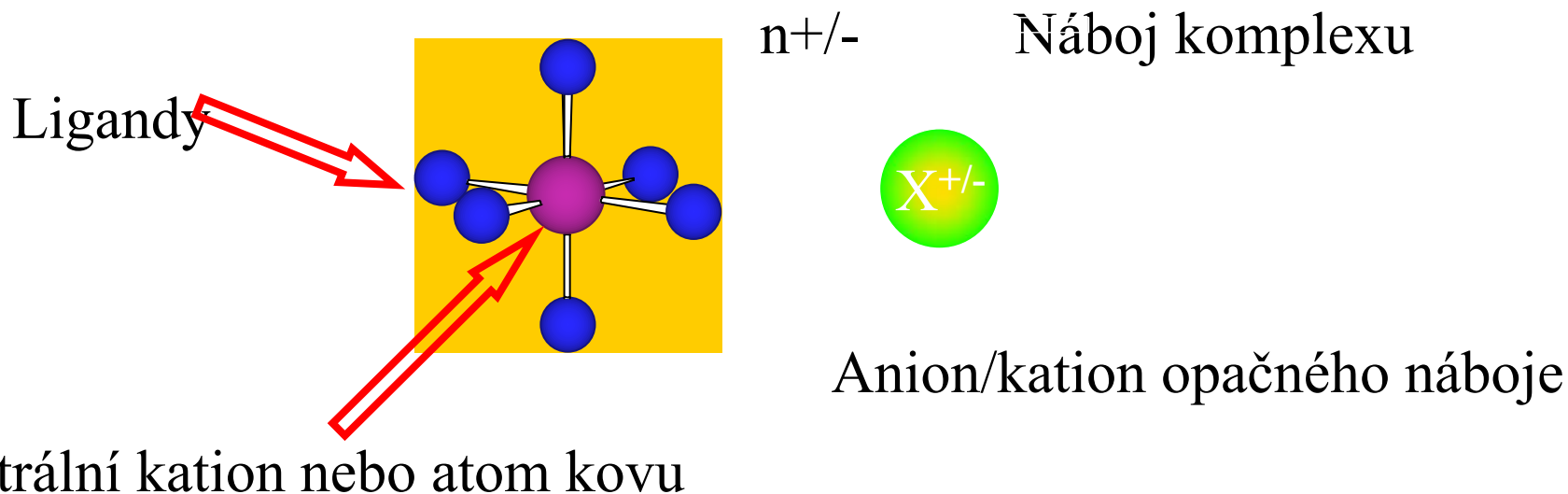
Ligandy vázány k centrálnímu atomu donor-akceptorovými vazbami

Koordinální sloučeniny

Elektrická vodivost roztoků komplexních sloučenin



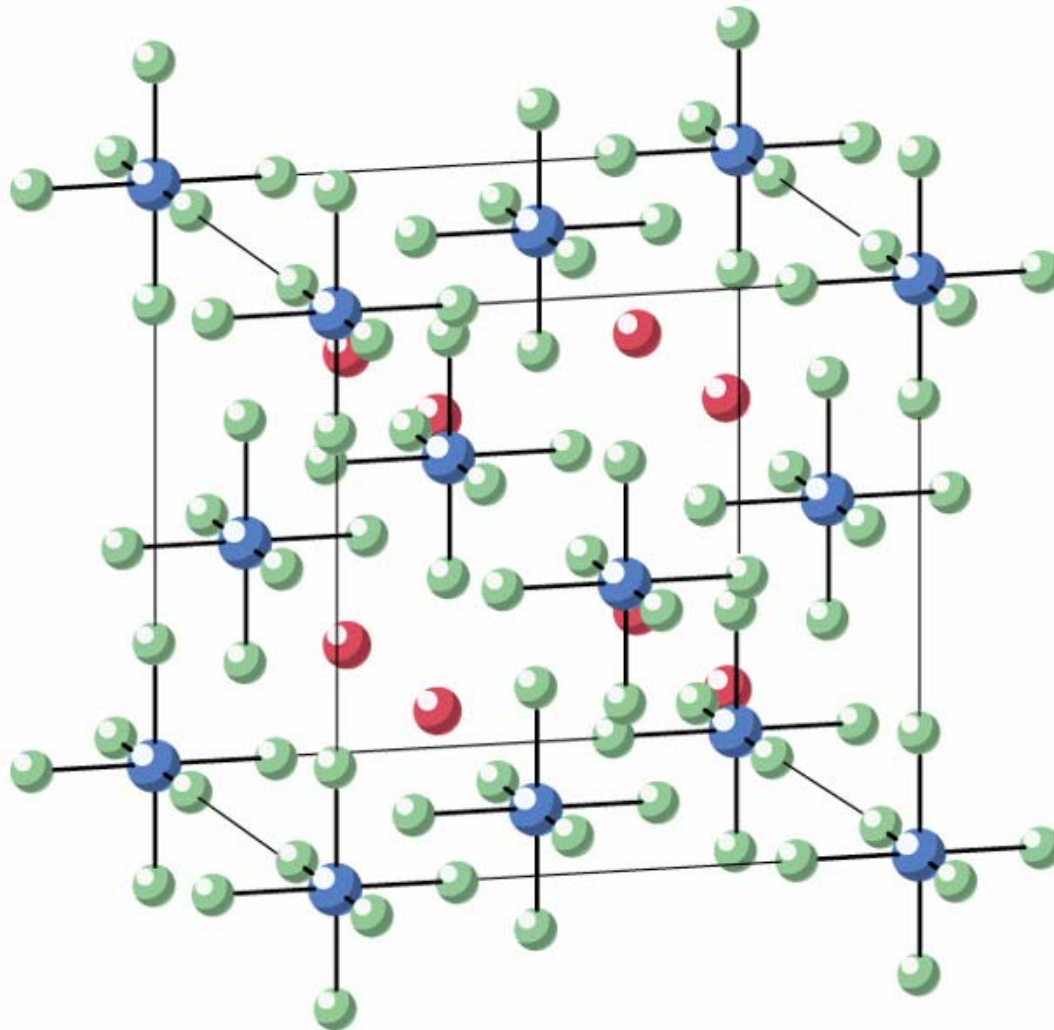
Koordinační sloučeniny



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

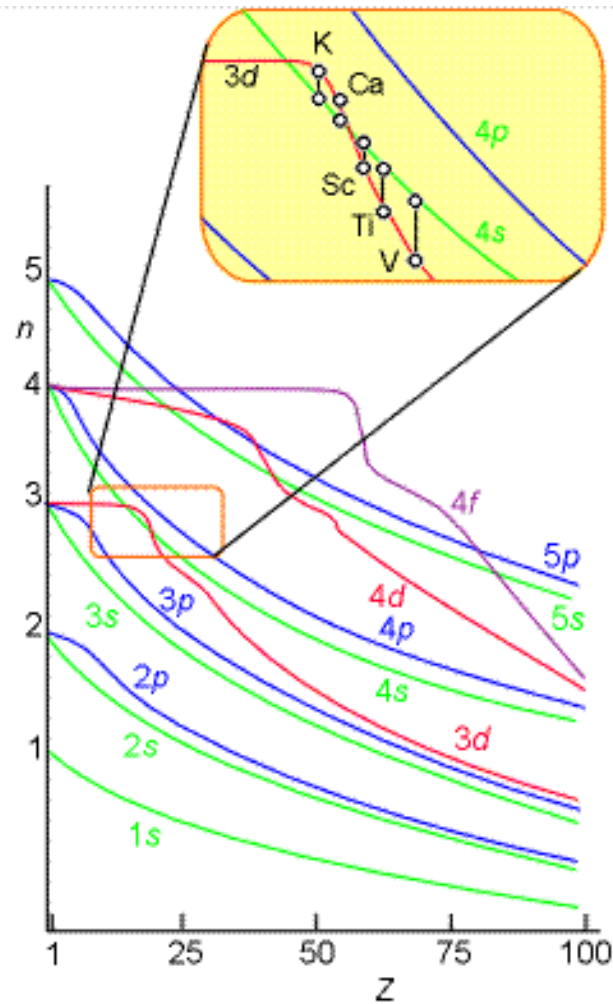
Počet ligandů = koordinační číslo

Koordinační sloučeniny v pevné fázi

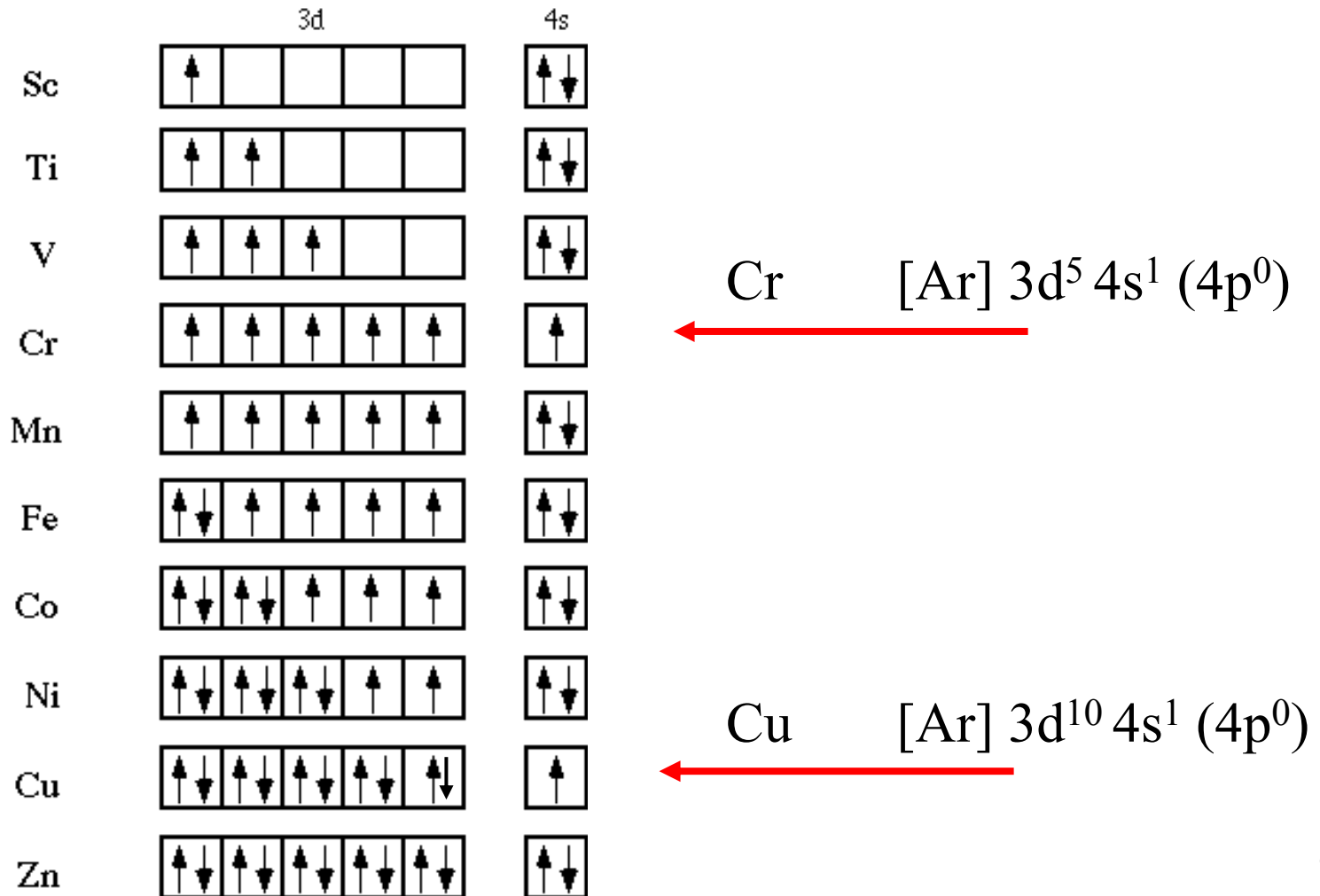


Změna pořadí energetických hladin

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



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)

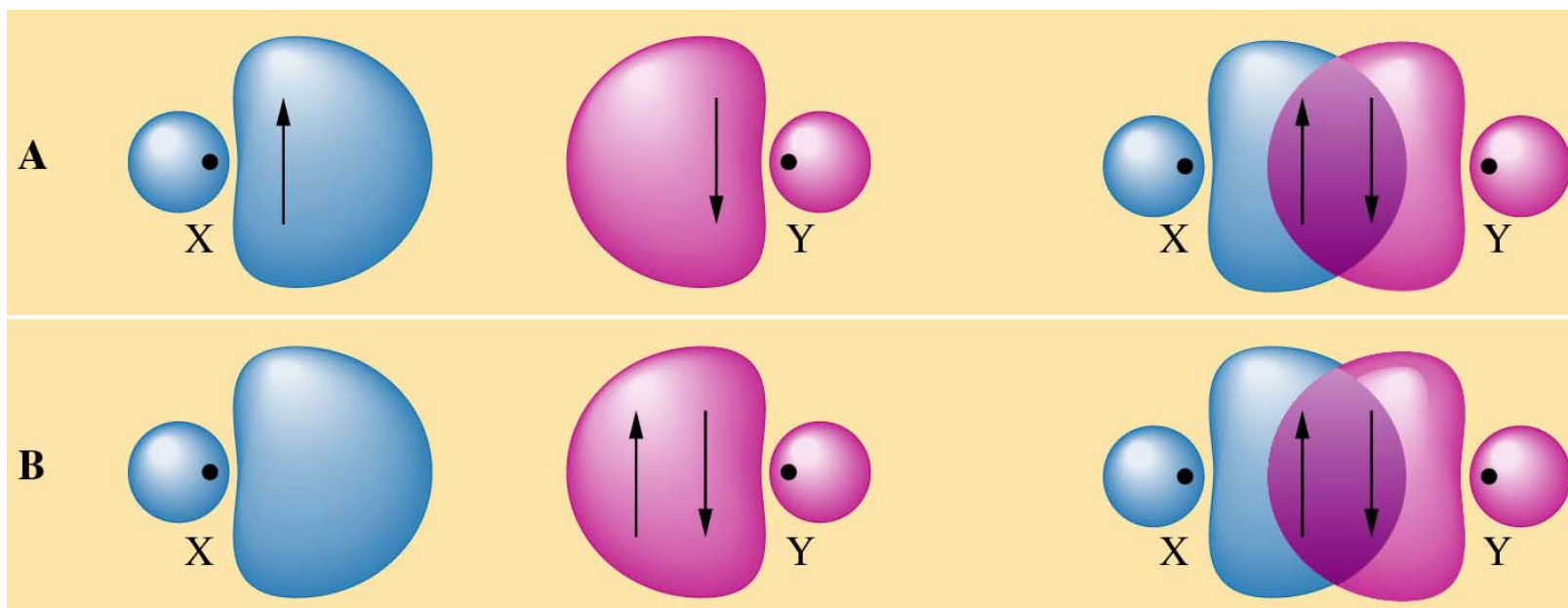
Period										
Fourth	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	631	658	650	652	717	759	758	737	745	906
Fifth	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	616	660	664	685	702	711	720	805	731	868
Sixth	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	538	680	761	770	760	840	880	870	890	1007

																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



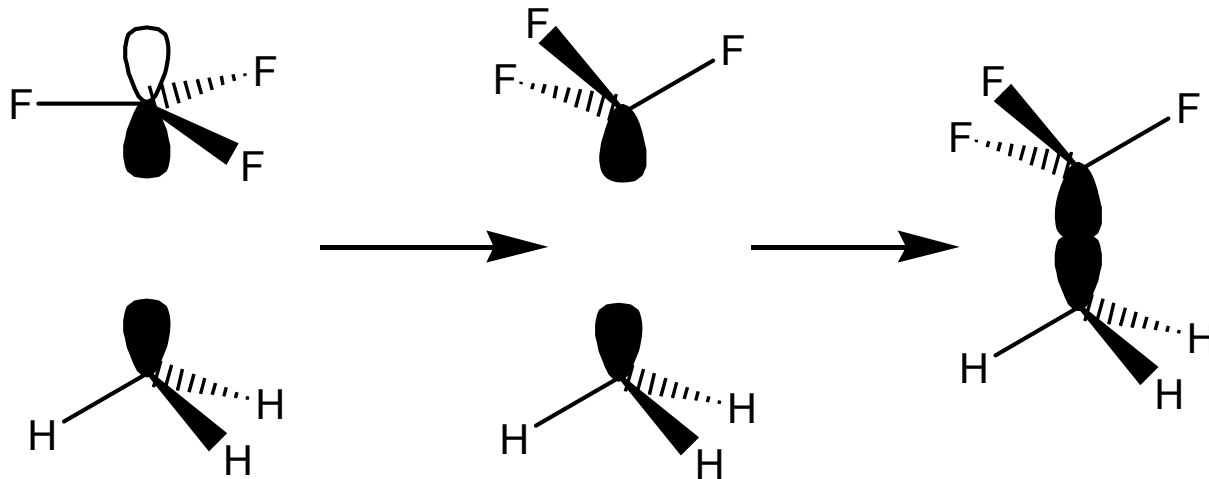
Akceptor
Volný orbital

Donor
Volný e pár

Kovalentní vazba

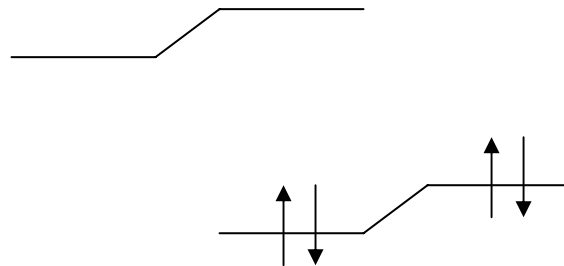
Donor-akceptorová vazba

VB teorie

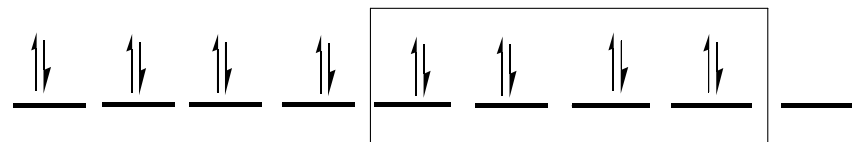


B

MO teorie

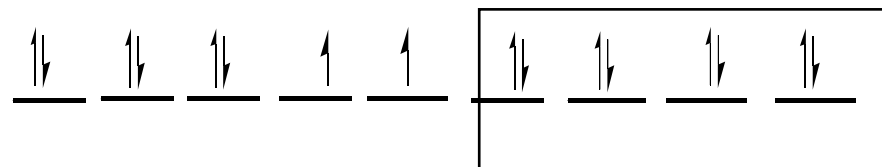


N



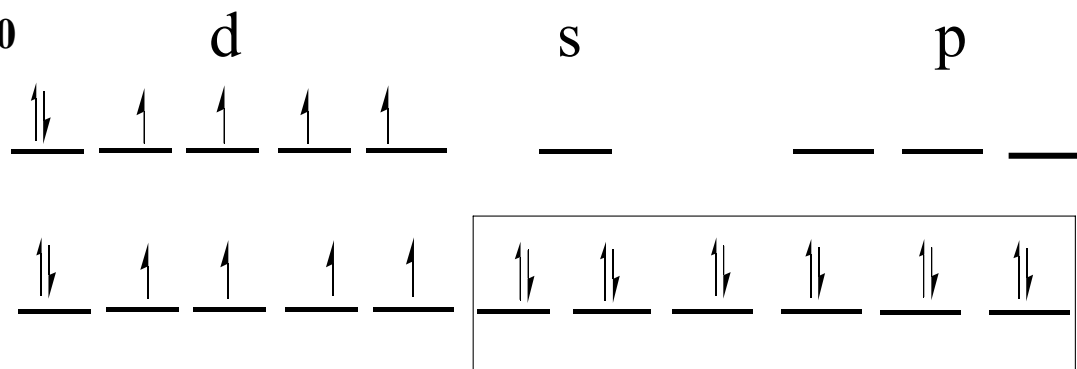
dsp² hybridní orbitály

elektrony z Cl⁻, čtvercový



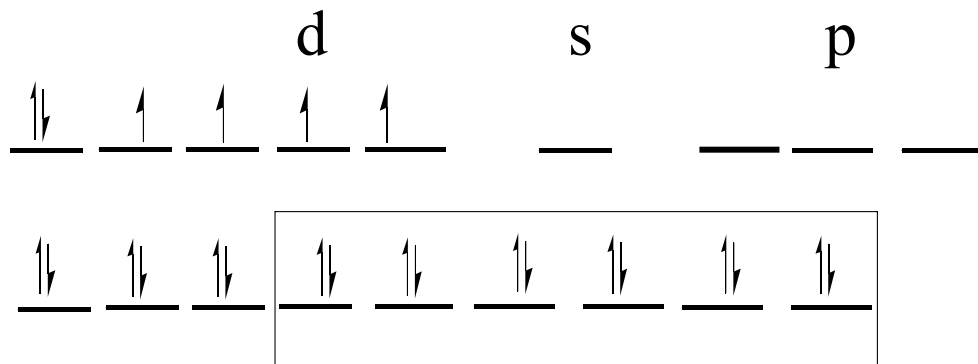
sp³ hybridní orbitály

elektrony z Cl⁻, tetraedrický



sp^3d^2 hybridní orbitaly

elektrony z F^- , oktaedrický

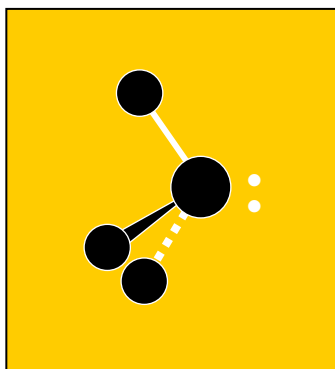


d^2sp^3 hybridní orbitaly

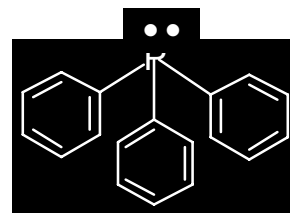
elektrony z NH_3 , oktaedrický

Monodentátní ligandy

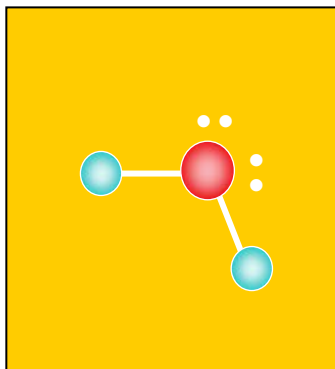
CO
oxid uhelnatý



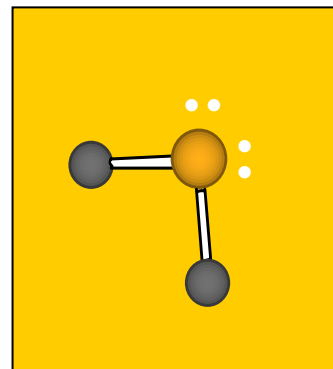
NH_3
amoniak



PPh_3
fosfan



H_2O
voda



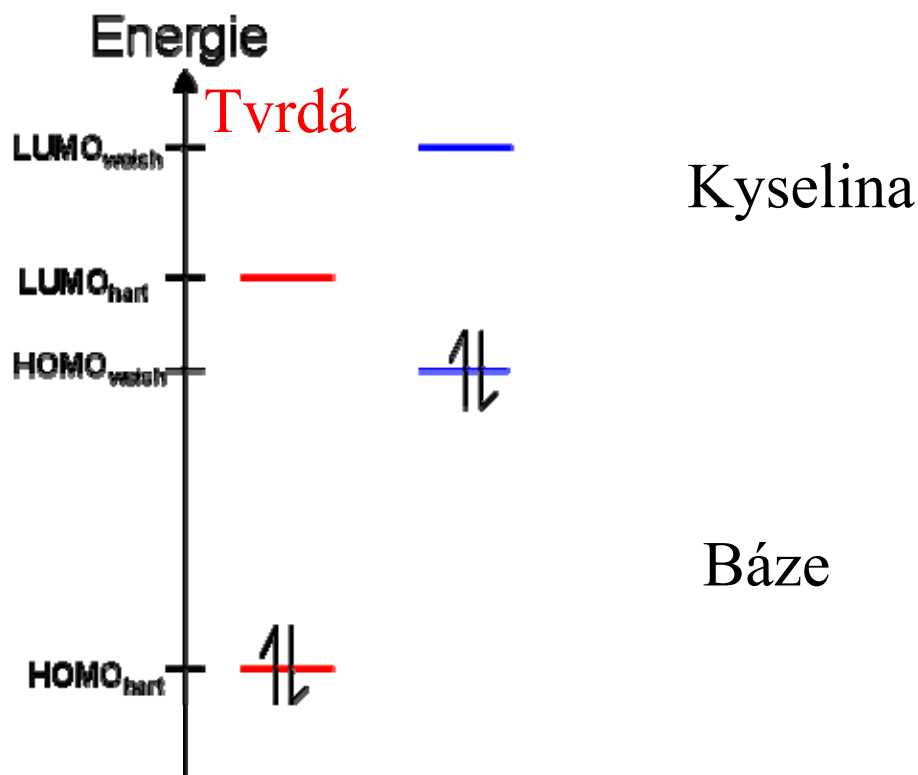
SR_2
thioether

HSAB = Teorie tvrdých a měkkých kyselin a bazí

R. Pearson 1963

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

Nízká oxidační čísla jsou stabilizována CO , CN^-



HSAB

Tvrdé donorní atomy

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

Malé donorní atomy

Silně elektronegativní

Málo polarizovatelné



Tvrdé kovy

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

Malé atomy (1. přech. řada)

Vysoký náboj

Měkké donorní atomy

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

Velké donorní atomy

Málo elektronegativní

Snadno polarizovatelné

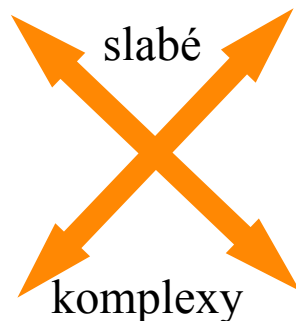


Měkké kovy

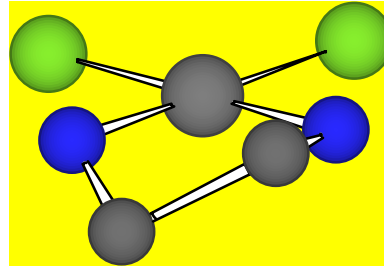
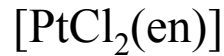
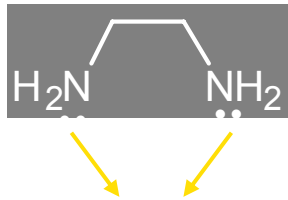
Ag(I) , Cu(I) , Hg(II) , Au(I)

Velké atomy (2. a 3. přech. řada)

Malý náboj

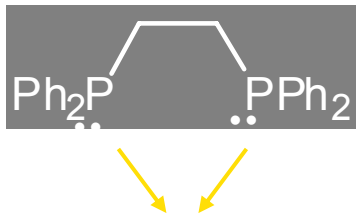


Neutrální bidentátní ligandy

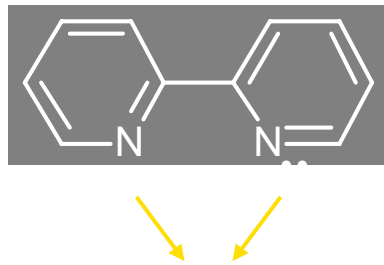


pětičlenný chelátový cyklus
čtvercově planární komplex

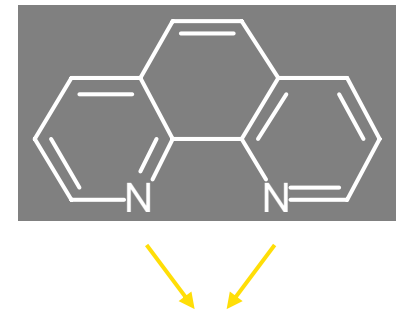
1,2-diaminoethan = ethylendiamin = en



1,2-difenylofosfinoethan
dppe



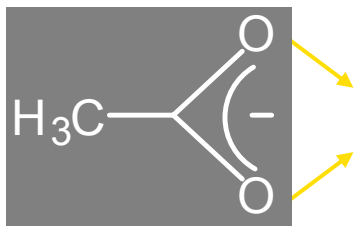
2,2'-bipyridin
bipy



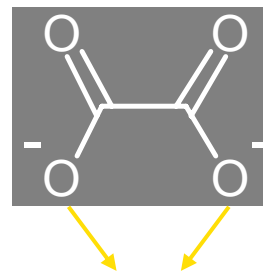
1,10-fenanthrolin
phen

Chelatace - ligandy jsou vázány velmi pevně k centrálnímu atomu

Aniontové bidentátní ligandy

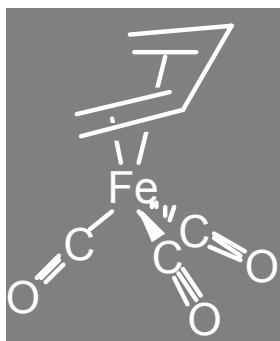


acetát = ac^-



oxalát = ox^{2-}

π -donorní bidentátní ligand

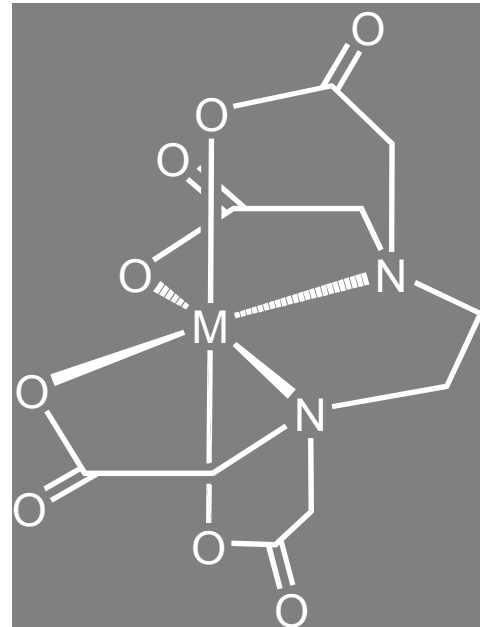
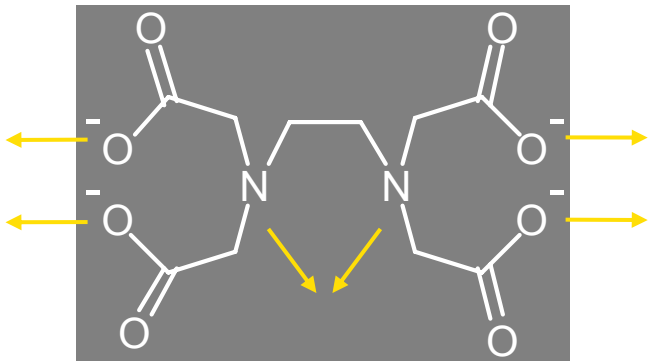


Multidentátní ligandy

tetraanion kyseliny ethylendiamintetraoctové

EDTA

Hexadentátní



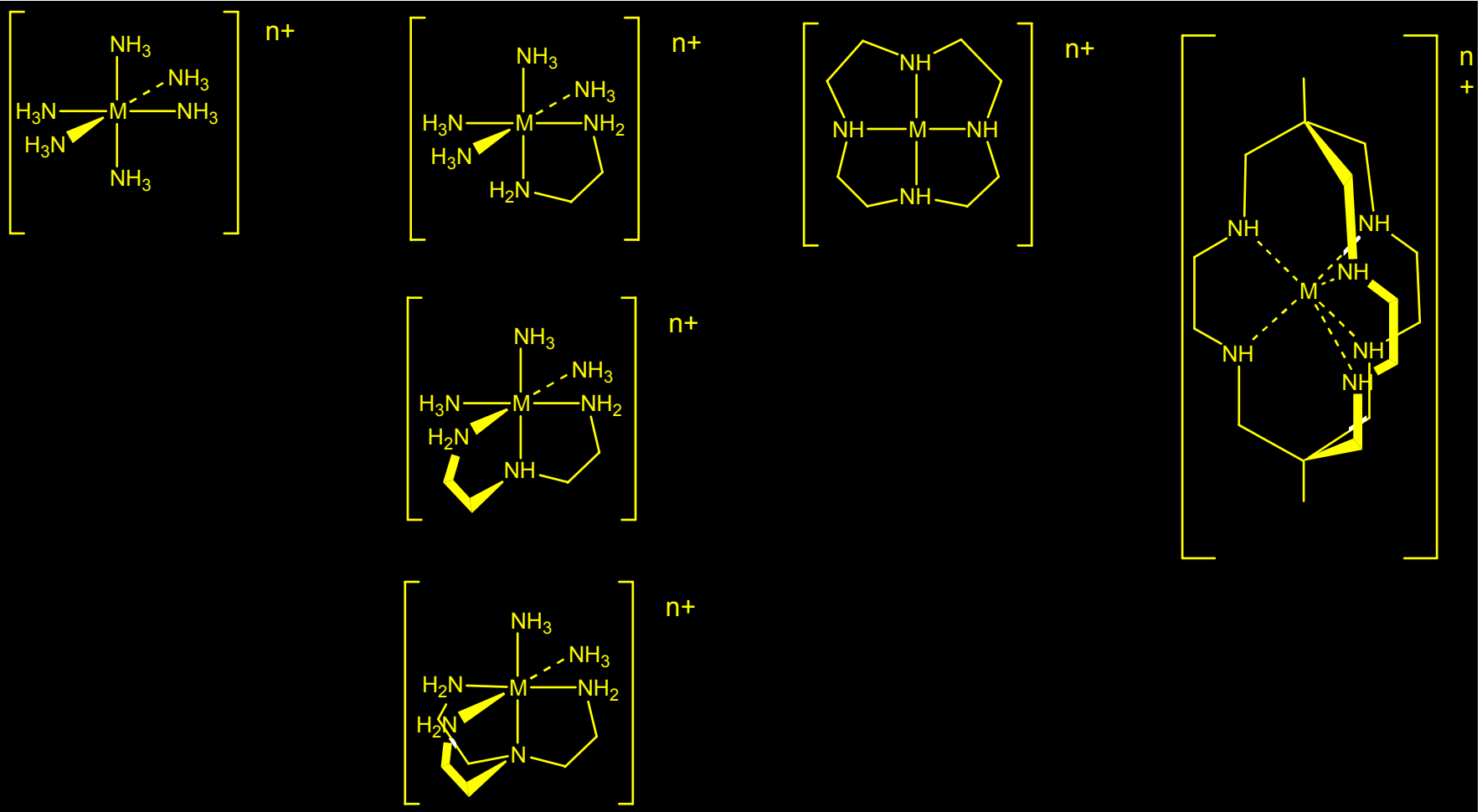
Topologie komplexů

komplexace

chelatace

makrocyclický efekt

kryptátový efekt



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-

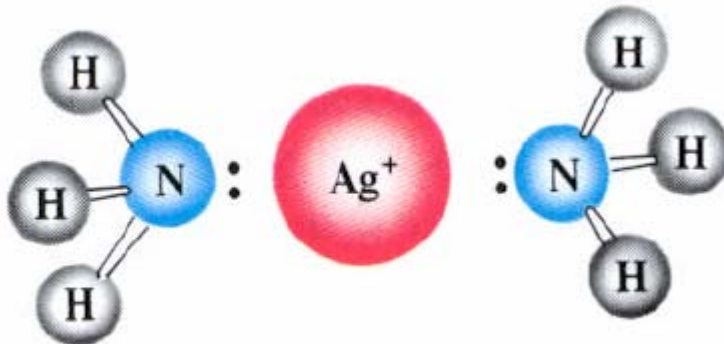
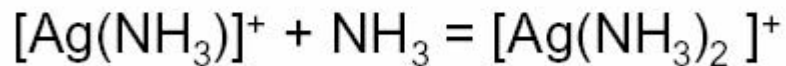
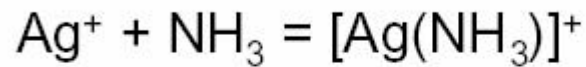
Názvosloví komplexních sloučenin

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

Stabilita komplexů

Konstanta stability komplexu = rovnovážná konstanta tvorby

Vysoká hodnota K
= stabilní komplex

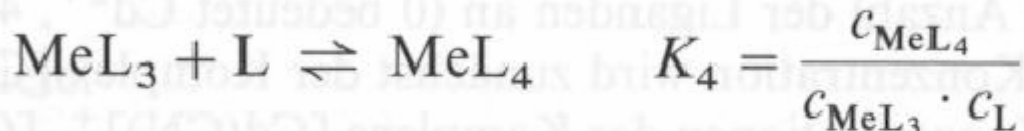
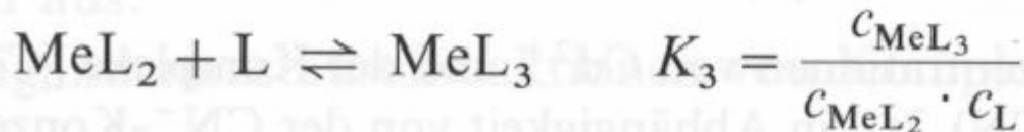
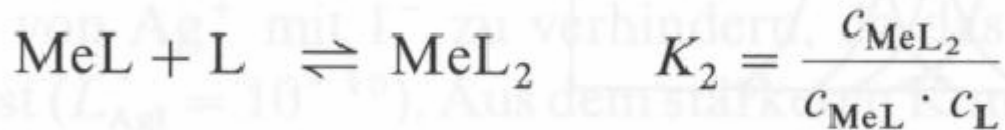
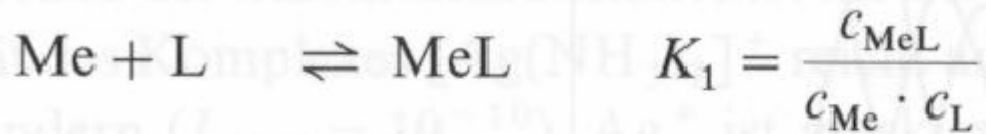


$$K_1 = \frac{[\text{AgNH}_3^+]}{[\text{Ag}^+][\text{NH}_3]}$$

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

Stabilita komplexů

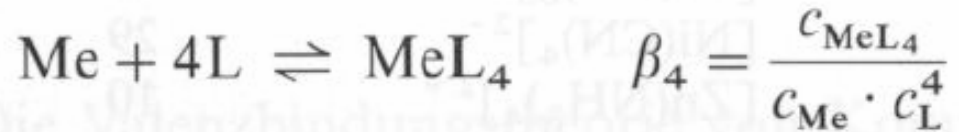
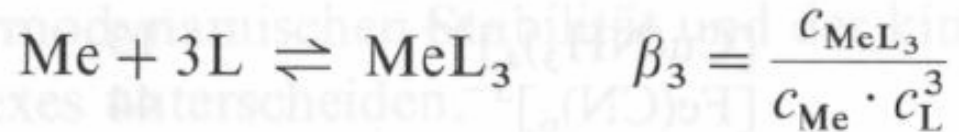
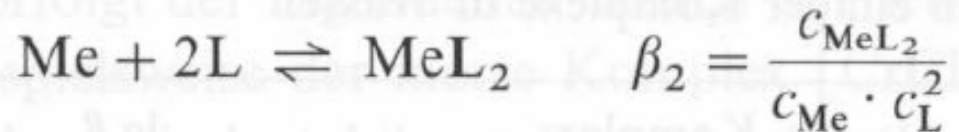
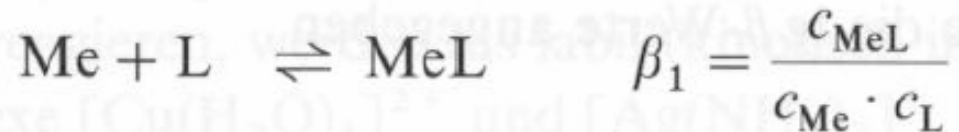
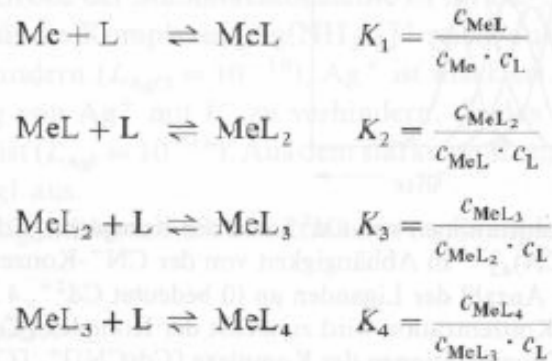
Konstanta stability komplexu ML_n



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

Stabilita komplexů

Celková konstanta stability komplexu



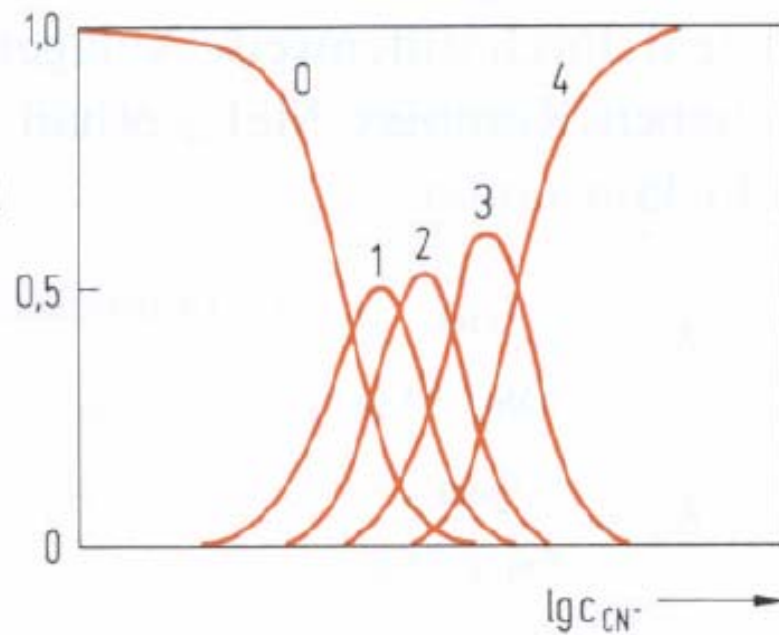
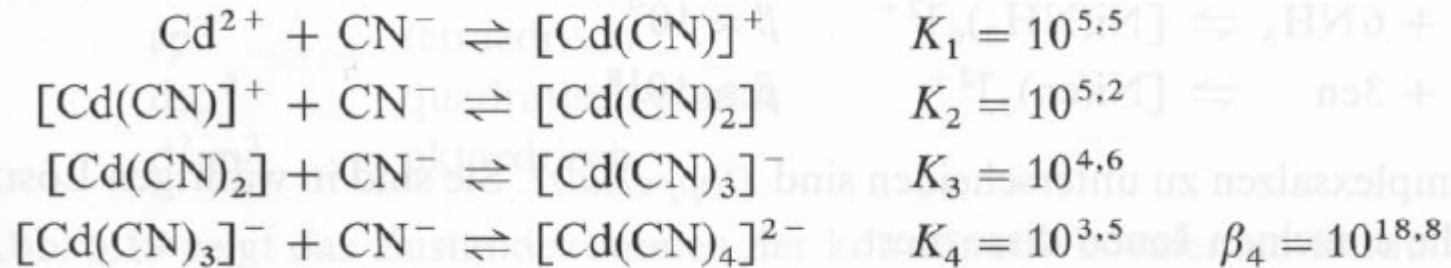
$$\beta_n = K_1 \cdot K_2 \dots K_n$$

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

Stabilita komplexů

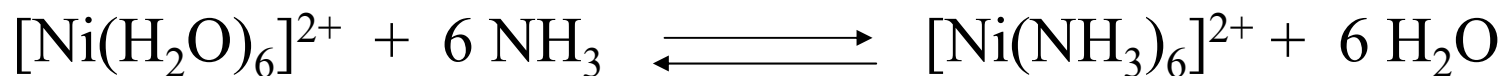
Komplex	$\lg \beta$	Komplex	$\lg \beta$
$[\text{Ag}(\text{NH}_3)_2]^+$	7	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	13
$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	13	$[\text{Fe}(\text{CN})_6]^{3-}$	44
$[\text{Ag}(\text{CN})_2]^-$	21	$[\text{Fe}(\text{CN})_6]^{4-}$	35
$[\text{Au}(\text{CN})_2]^-$	37	$[\text{Ni}(\text{CN})_4]^{2-}$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

Stabilita komplexů

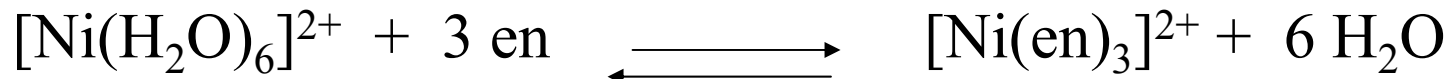


Chelátový efekt

$$\log K = 8.61$$



$$\log K = 18.28$$



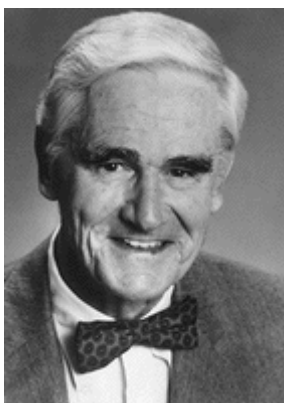
$$\Delta G = -RT \ln K = \Delta H - T\Delta S$$

ΔH stejná pro obě reakce (Ni-O \rightarrow Ni-N)

ΔS vysoká pro chelataci, vzniká více částic

Cheláty, makrocykly, kryptáty

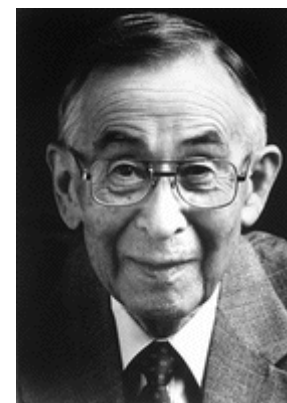
Nobelova cena za chemii 1987



Donald J. Cram



Jean-Marie Lehn

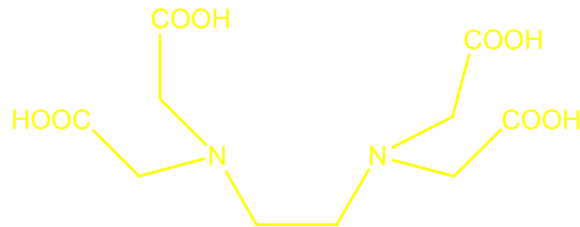


Charles J. Pedersen

Cheláty, makrocykly, kryptáty

EDTA

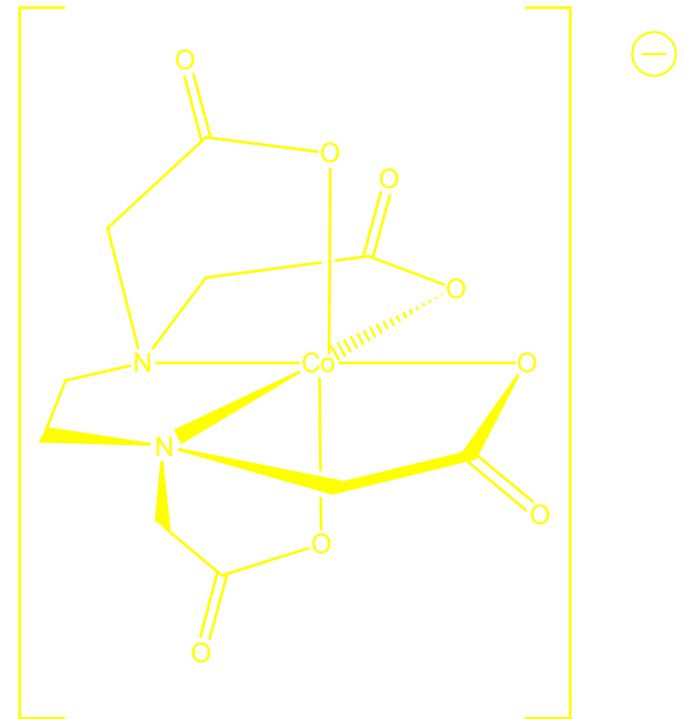
kyselina ethylendiamintetraoctová



Chelatační terapie Pb otravy

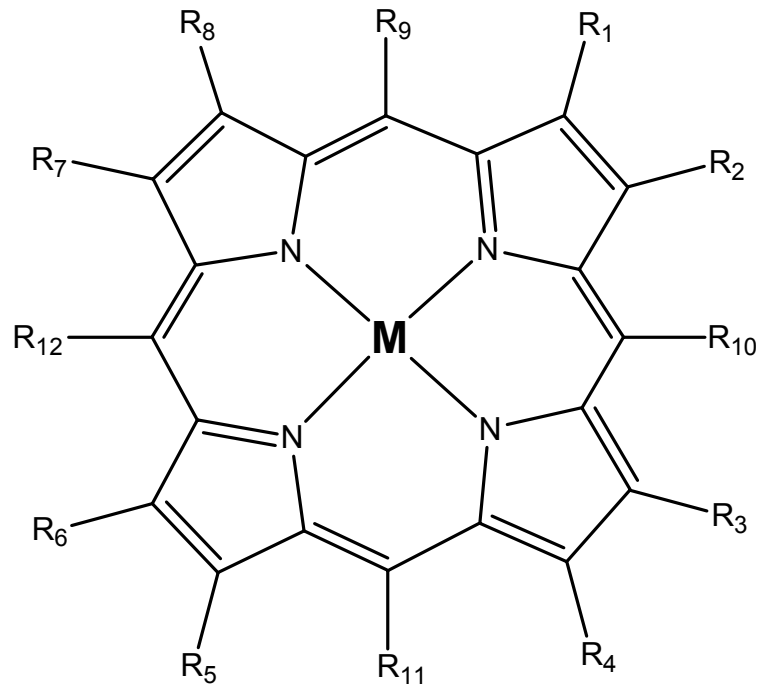
Chelatometrie

Rozpouští CaCO_3

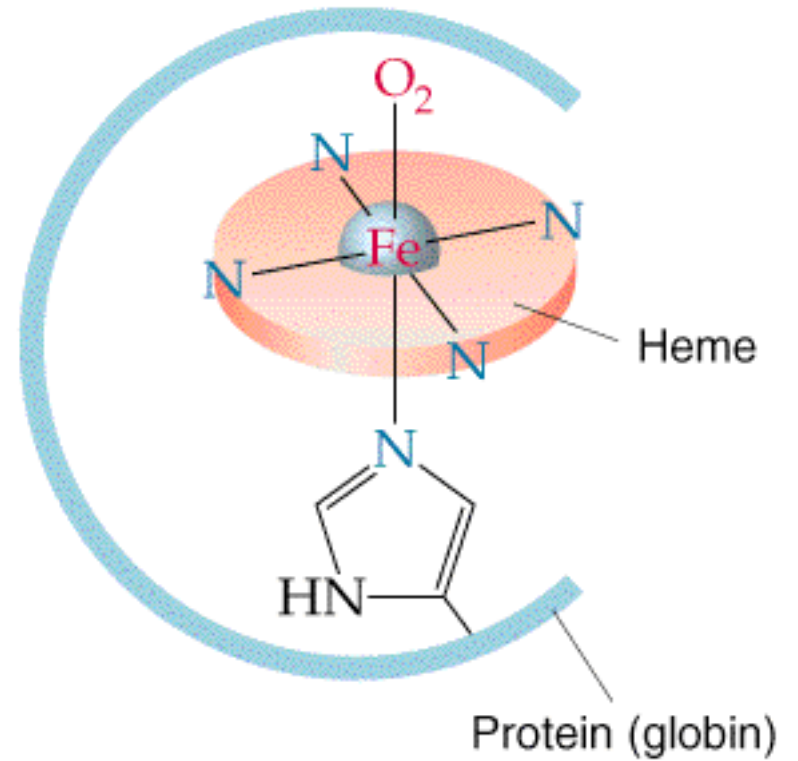
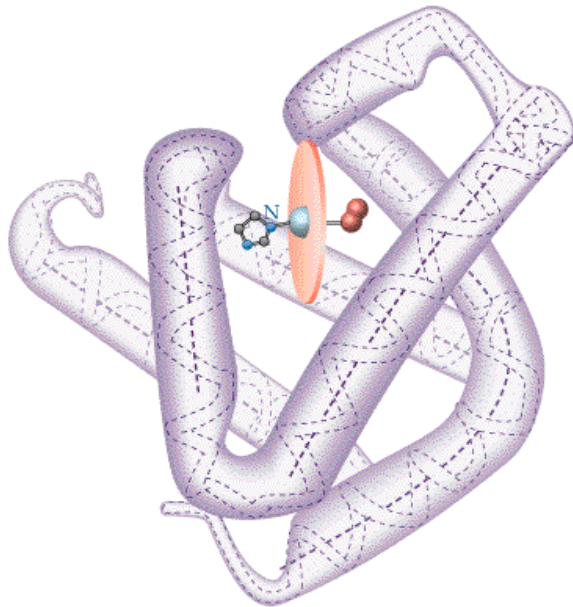
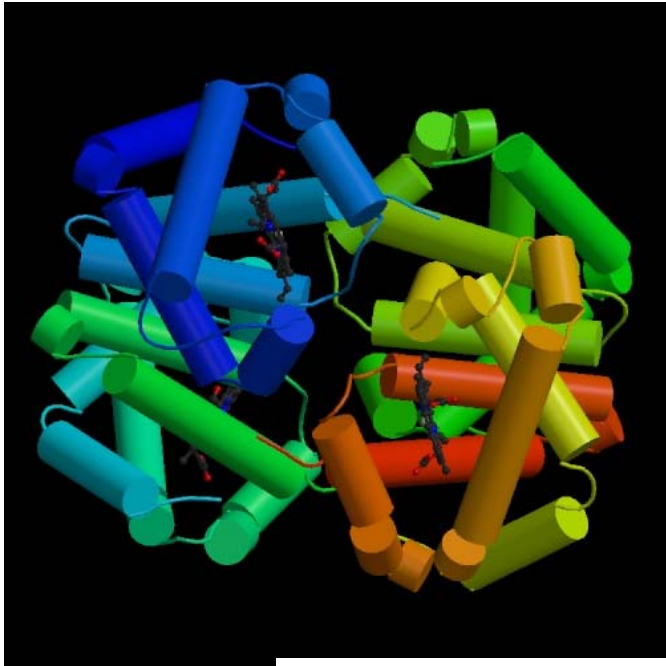


Cheláty, makrocykly, kryptáty

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

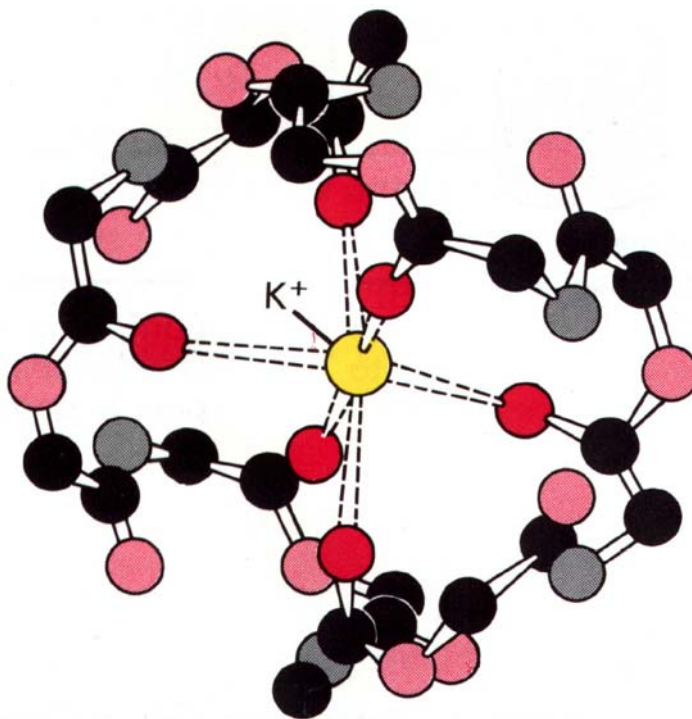


Hemoglobin



Cheláty, makrocycly, kryptáty

Valinomycin

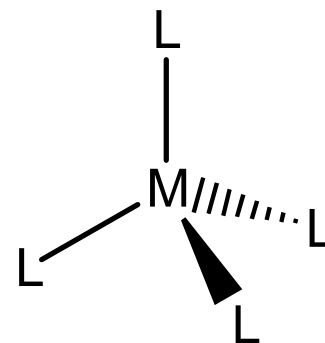
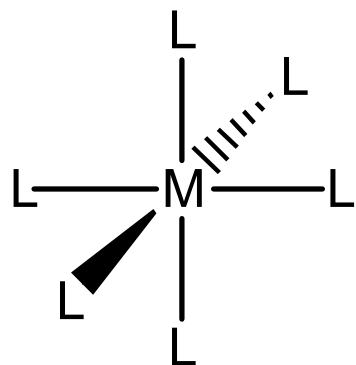


Tvary molekul a iontů

Prvky hlavních skupin >>>> VSEPR

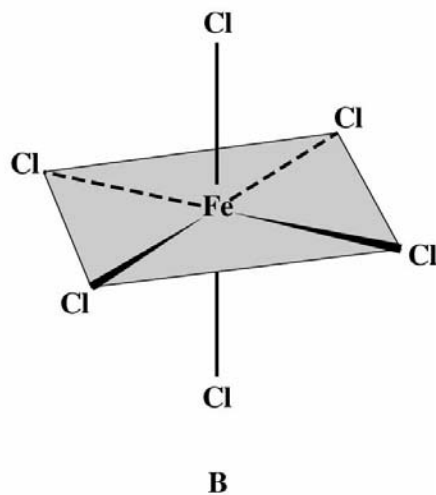
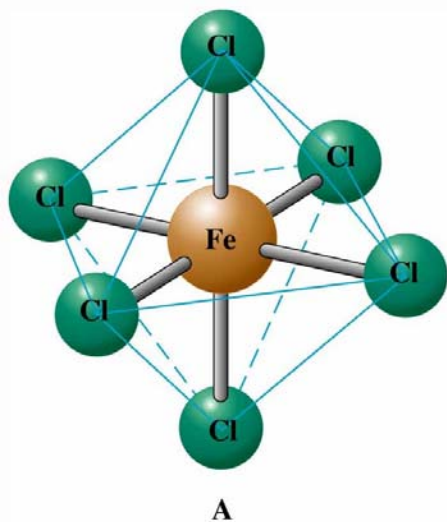
Přechodné prvky >>>>>>>>> Teorie ligandového pole

Nejdůležitější tvary komplexních částic



Oktaedrické komplexy O_h

Tetraedrické komplexy T_d



Nejdůležitější tvary komplexních částic

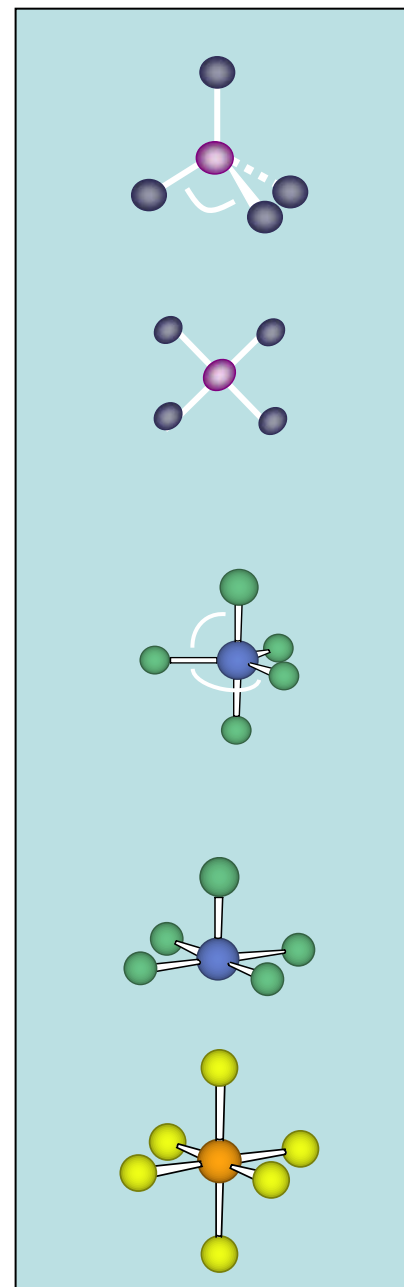
Tetraedrický $109^{\circ} 28'$ C.N. 4

Čtvercově planární 90° 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

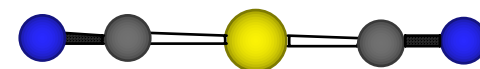
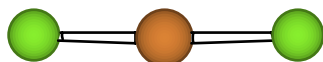
Koordinační číslo 2

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

lineární

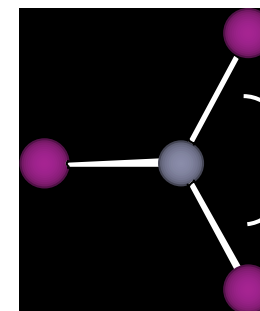
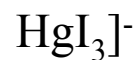
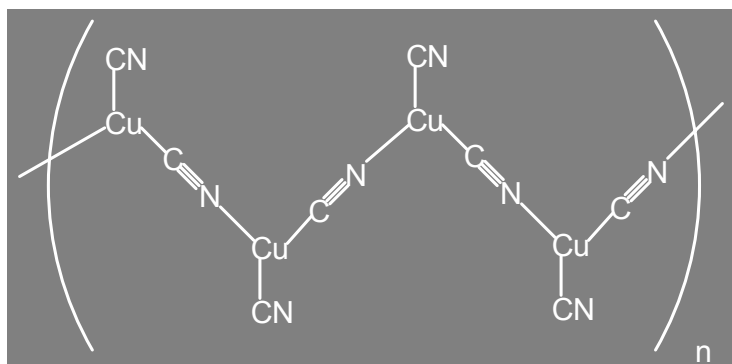


180°



Koordinační číslo 3

trigonálně planární

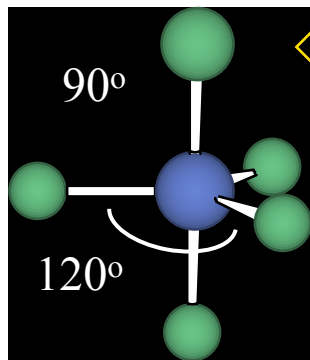


120°

Nejdůležitější tvary komplexních částic

Koordinační číslo 5

Trigonálně bipyramidální

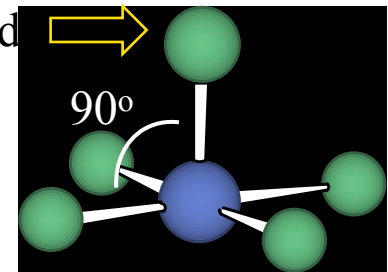


axiální ligandy

ekvatoriální ligandy

Čtvercově pyramidální

apikální ligand



bazální ligandy

Tyto dvě struktury mají velmi podobnou energii

Izomerie komplexních sloučenin

Konstituční (strukturní) izomerie

Vazebná

Koordinační

Ionizační

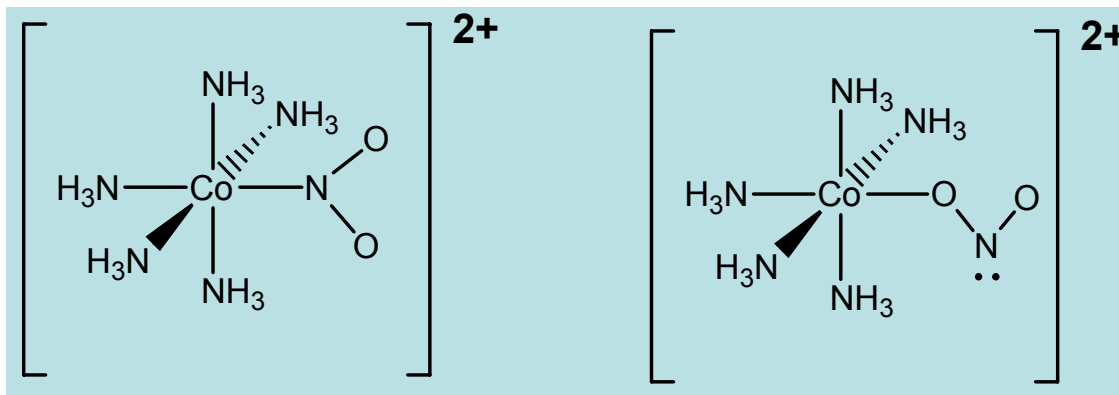
Prostorová (stereo) izomerie

Geometrická

Optická

Konstituční (strukturní) izomerie

Vazebná: SCN^- , NO_2^- , OCN^-

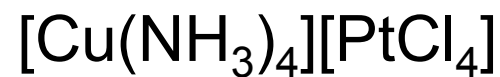
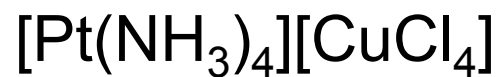


nitro-

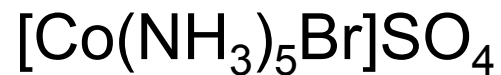
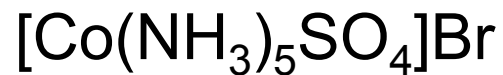
nitrito-

Konstituční (strukturní) izomerie

Koordinační:

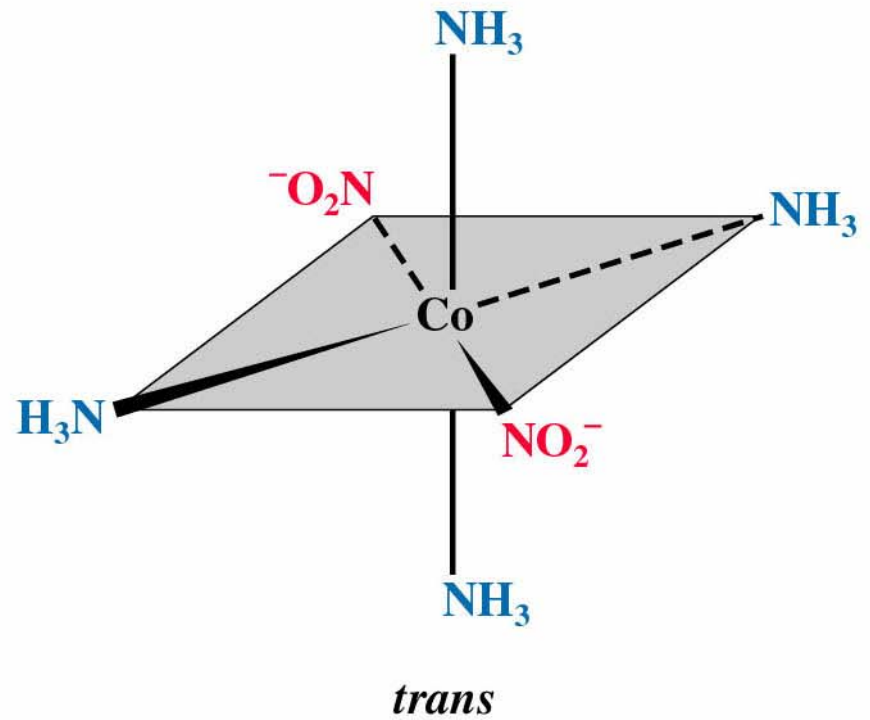
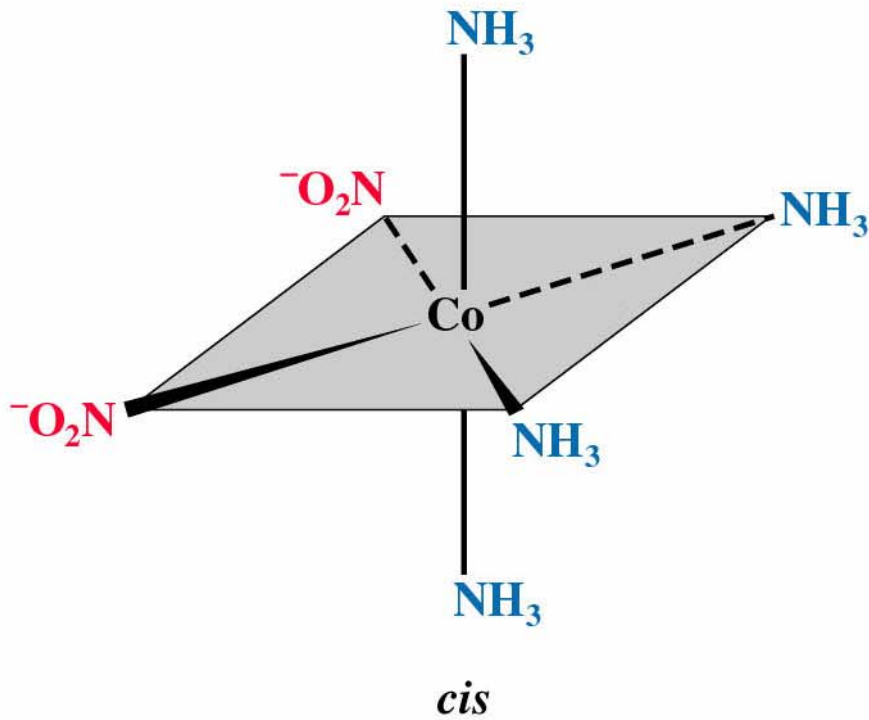


Ionizační:

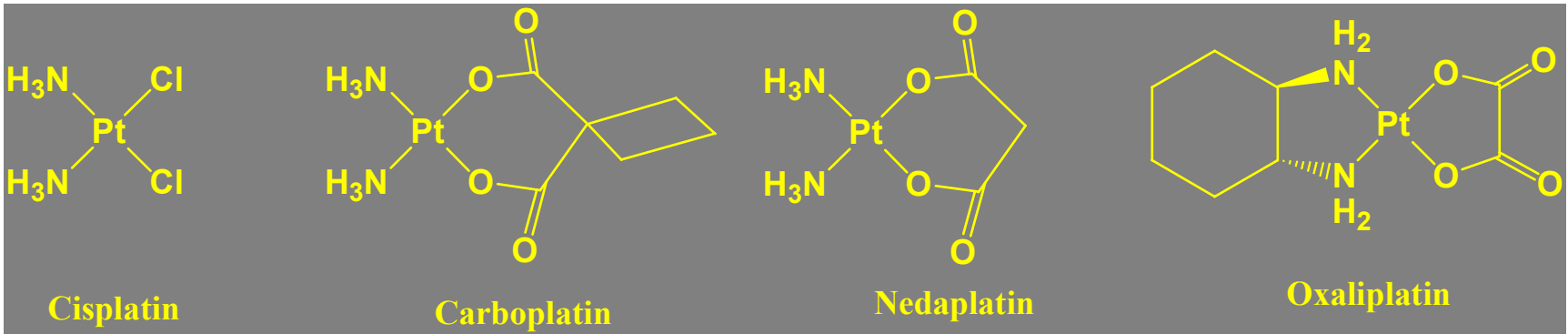


Prostorová (stereo) izomerie

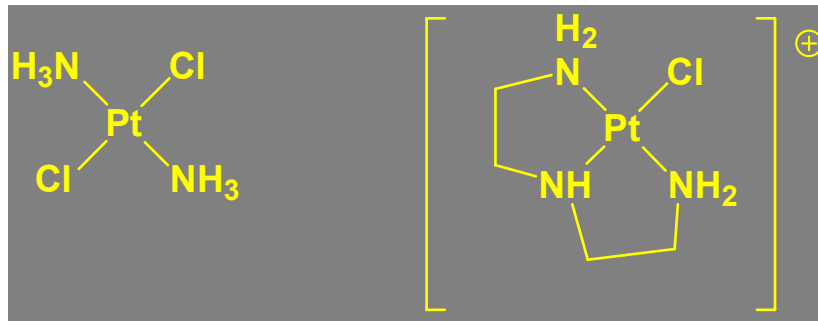
Geometrická: cis-trans, diastereomery



Protinádorové léky

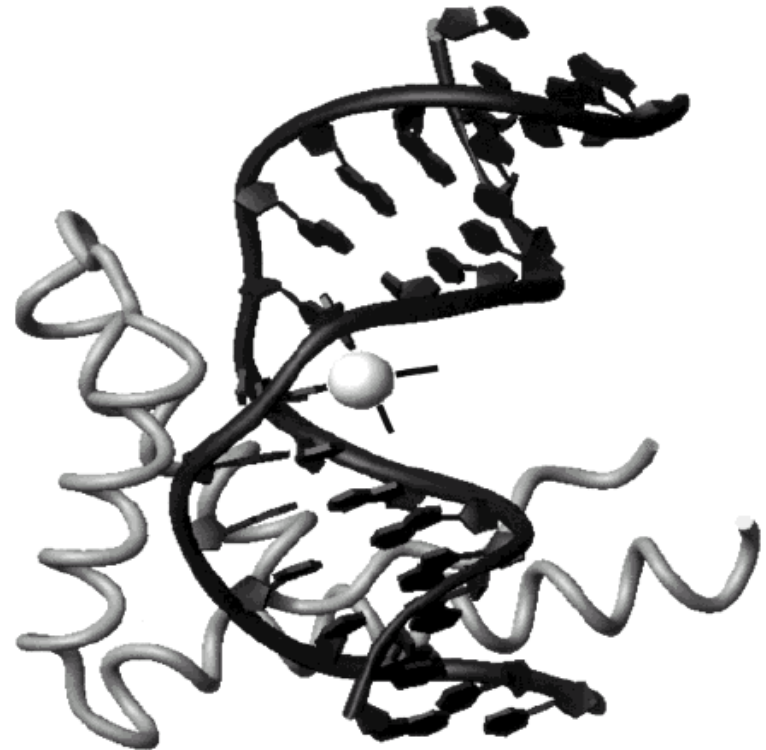
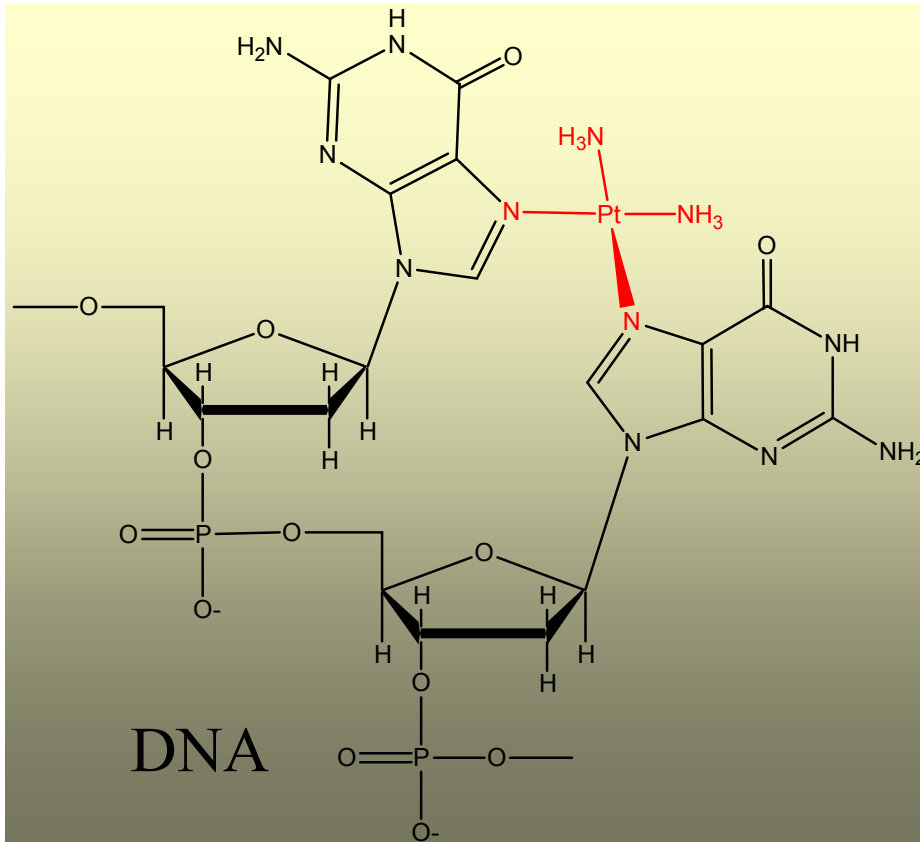


Neaktivní látky



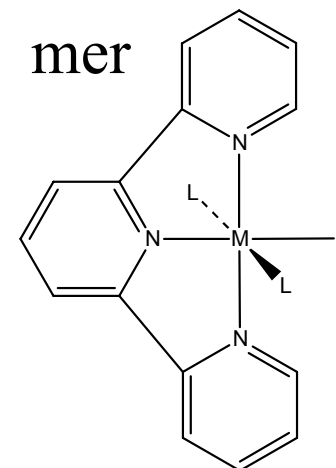
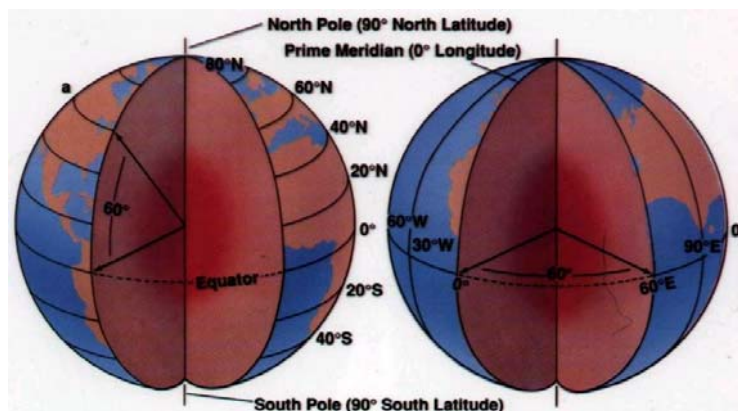
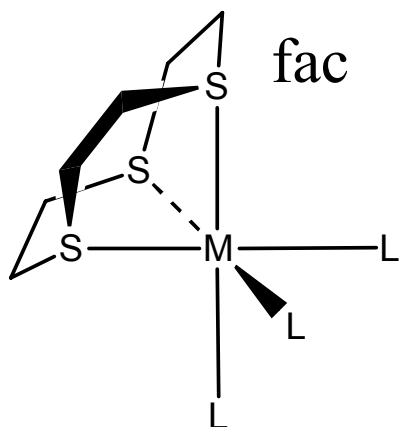
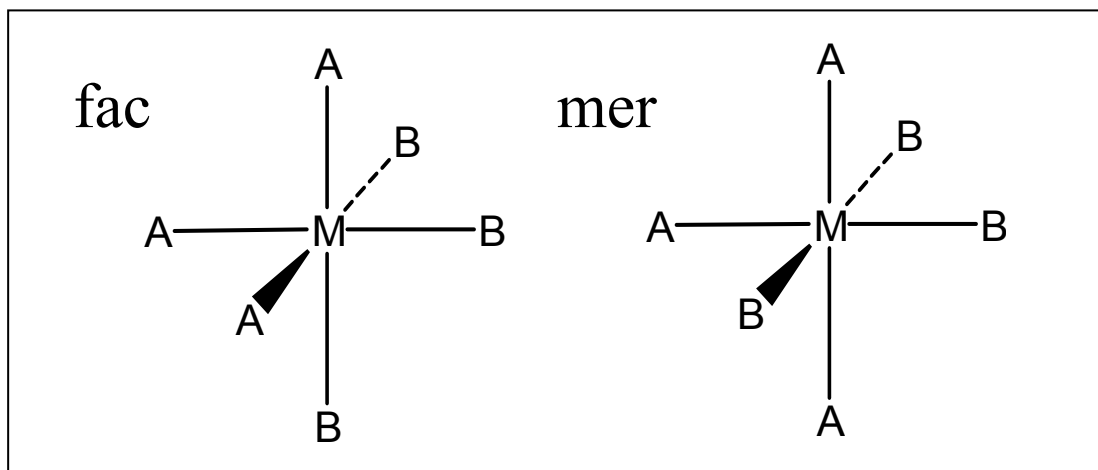
Prostorová (stereo) izomerie

Cisplatina = kancerostatikum



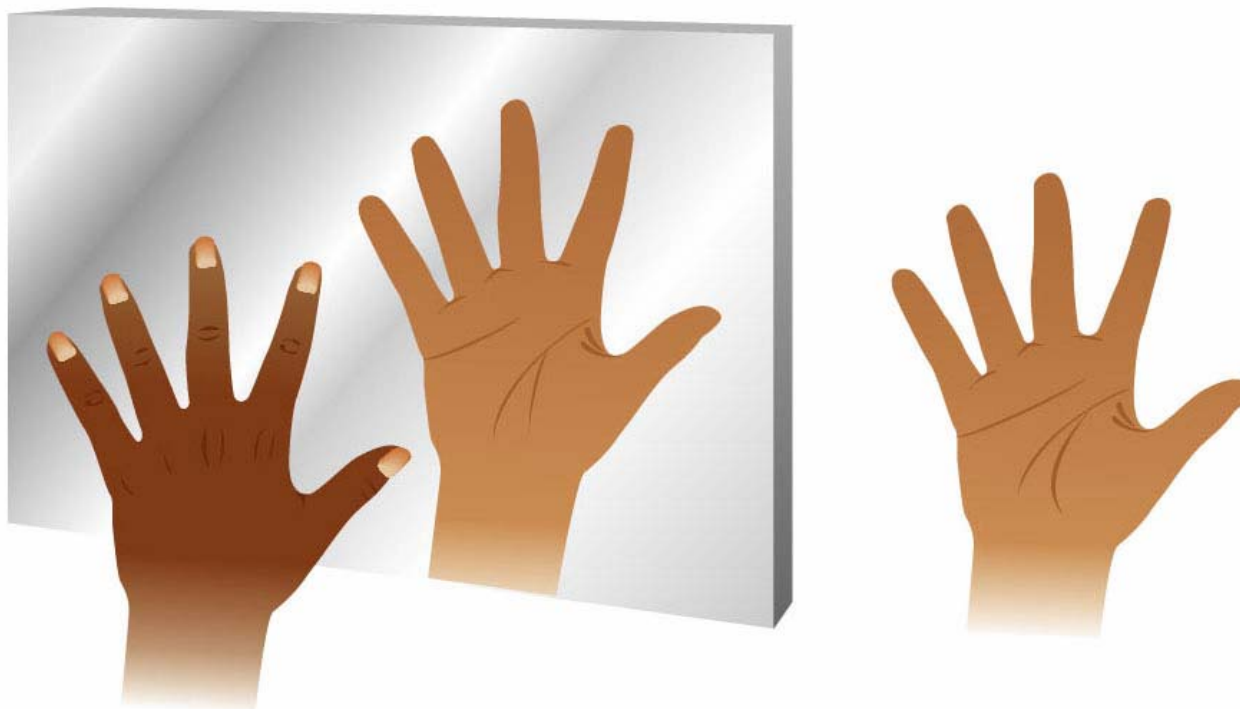
Prostorová (stereo) izomerie

Geometrická: mer-fac, diastereomery



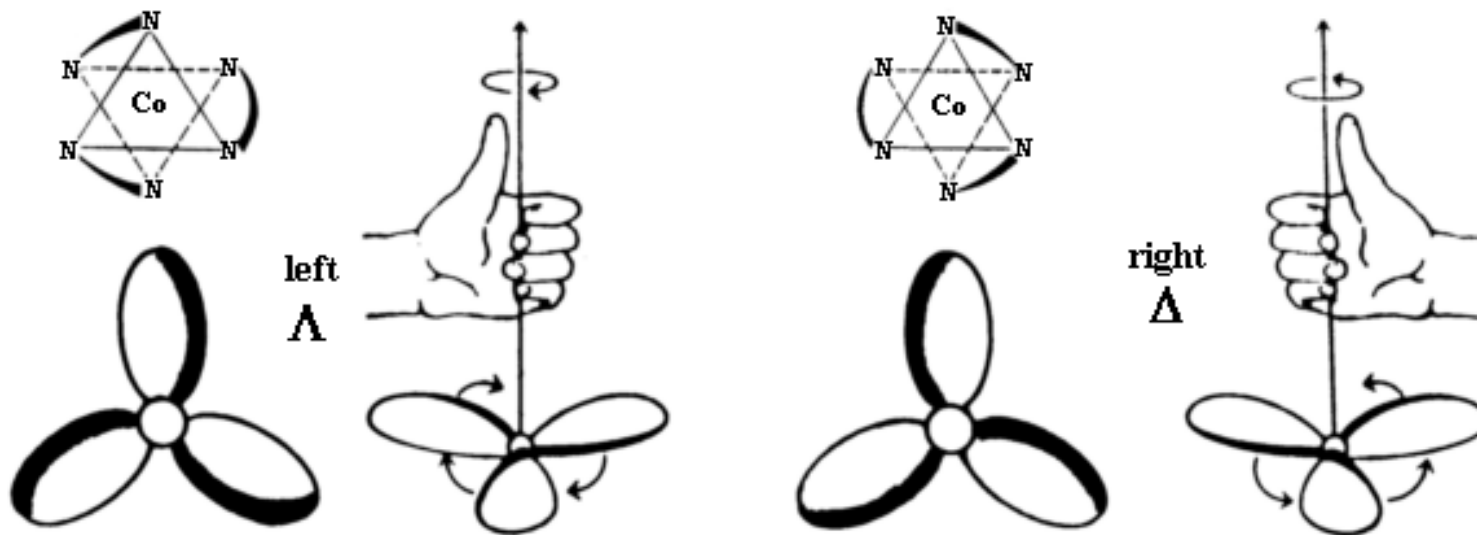
Prostorová (stereo) izomerie

Optická: enantiomery

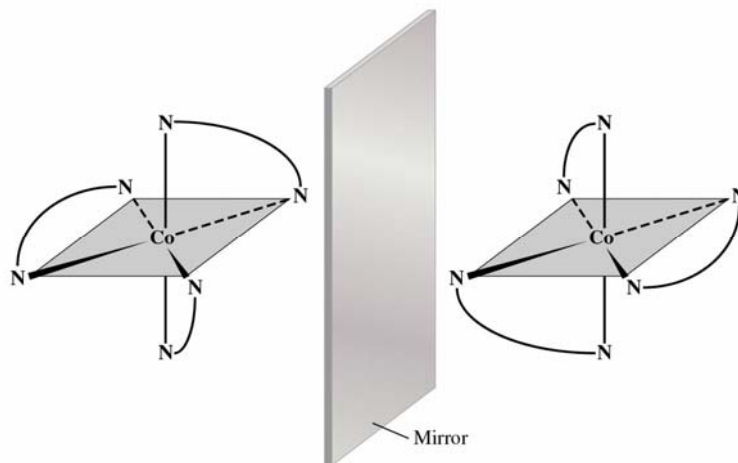


Prostorová (stereo) izomerie

Optická: enantiomery



Nemá S_n



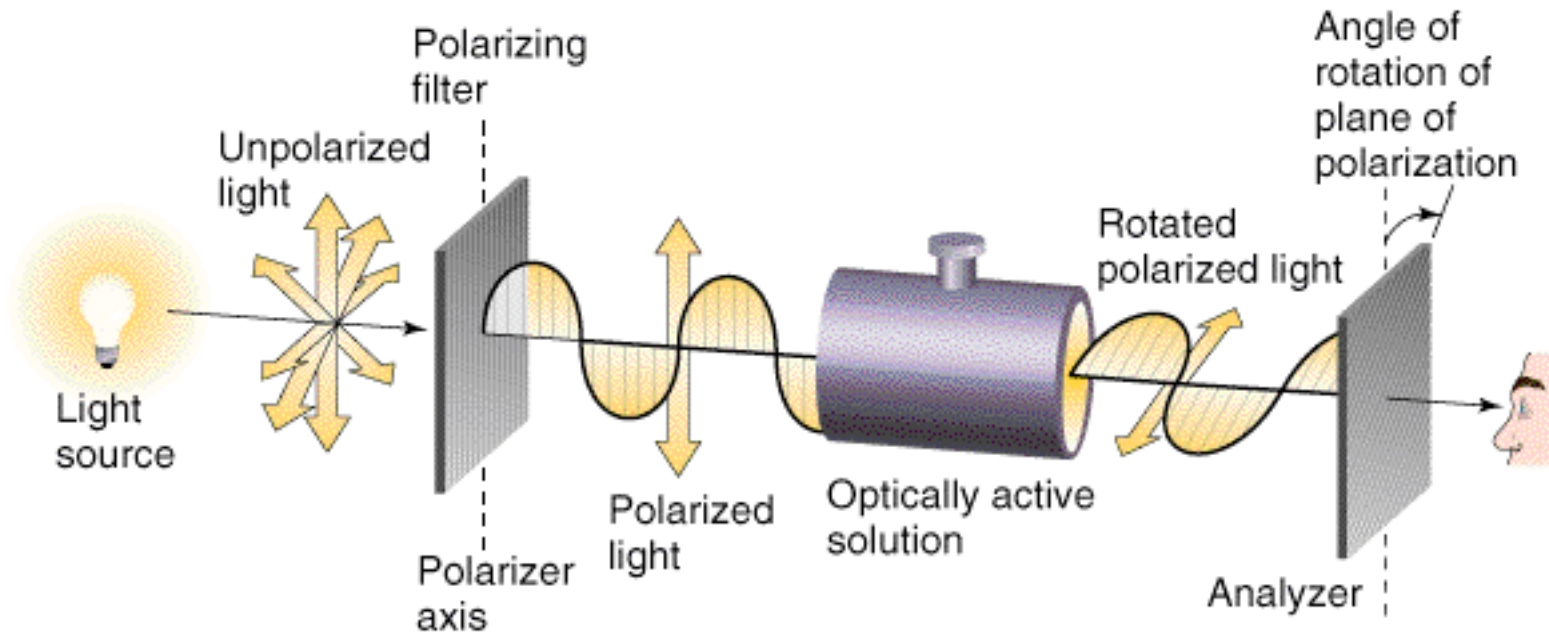
Optická rotace

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

Polarizované světlo – filtrem vybrán jen jeden

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)

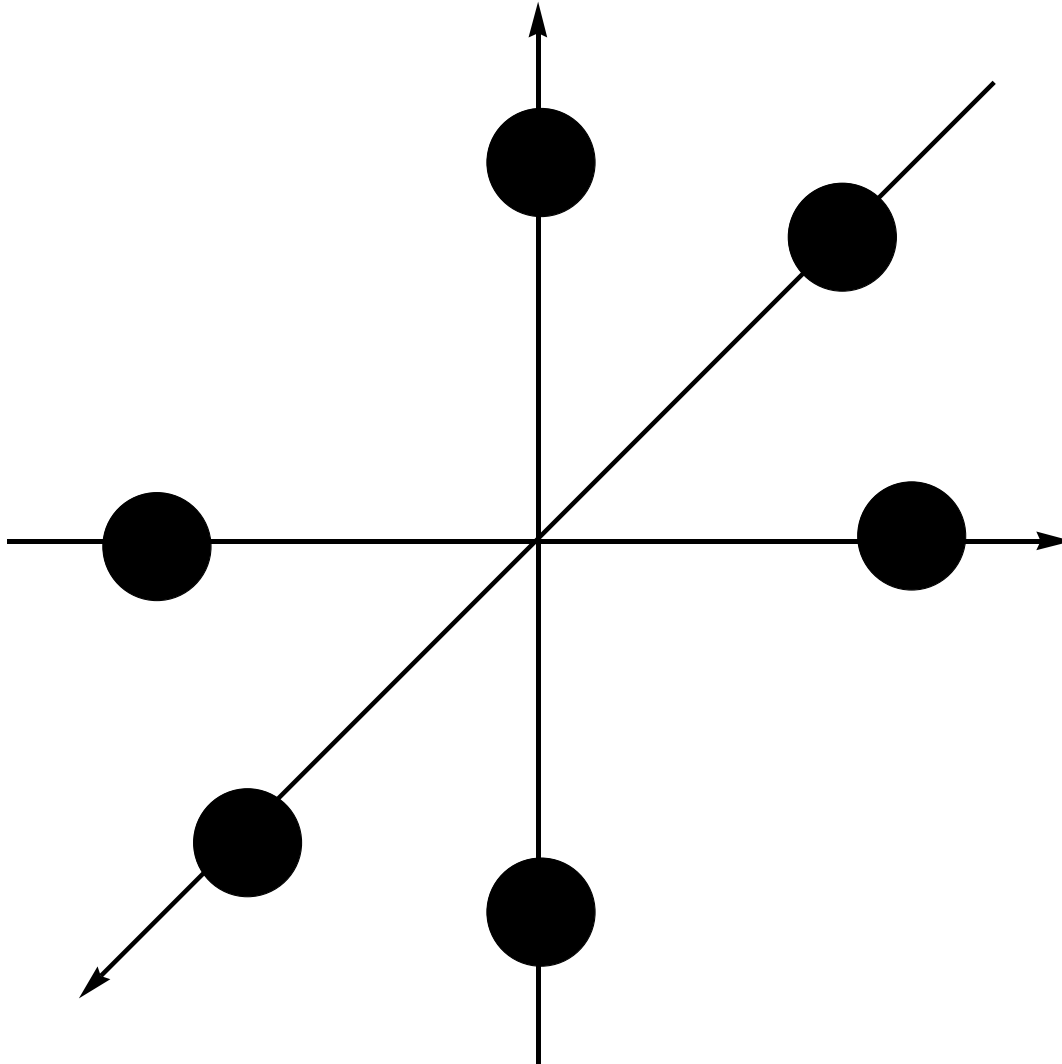
1929, Hans Bethe Čistě elektrostatické interakce mezi ligandy a kovem

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

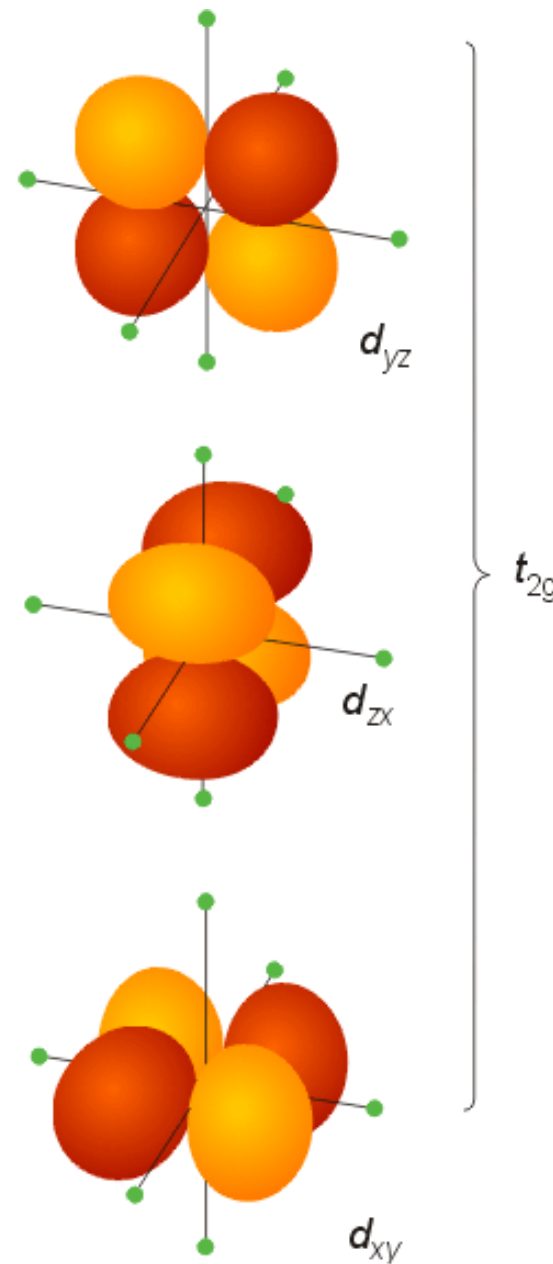
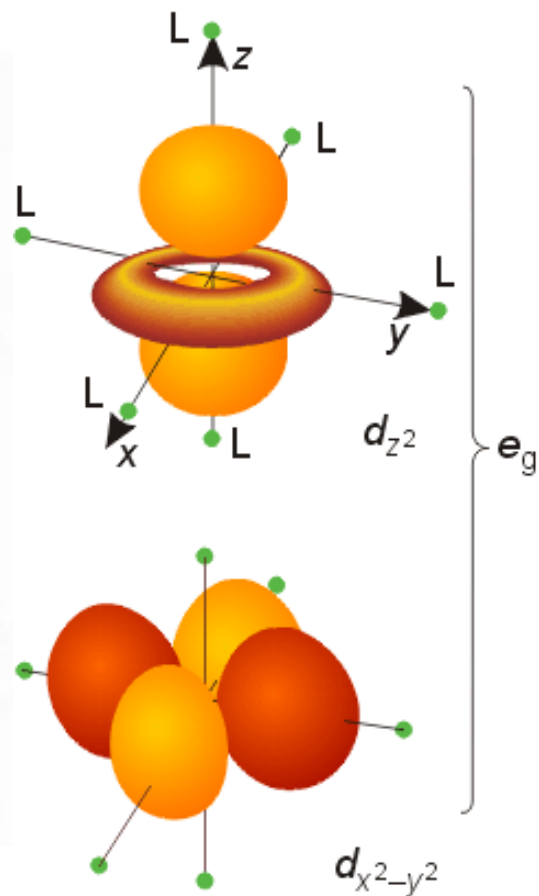
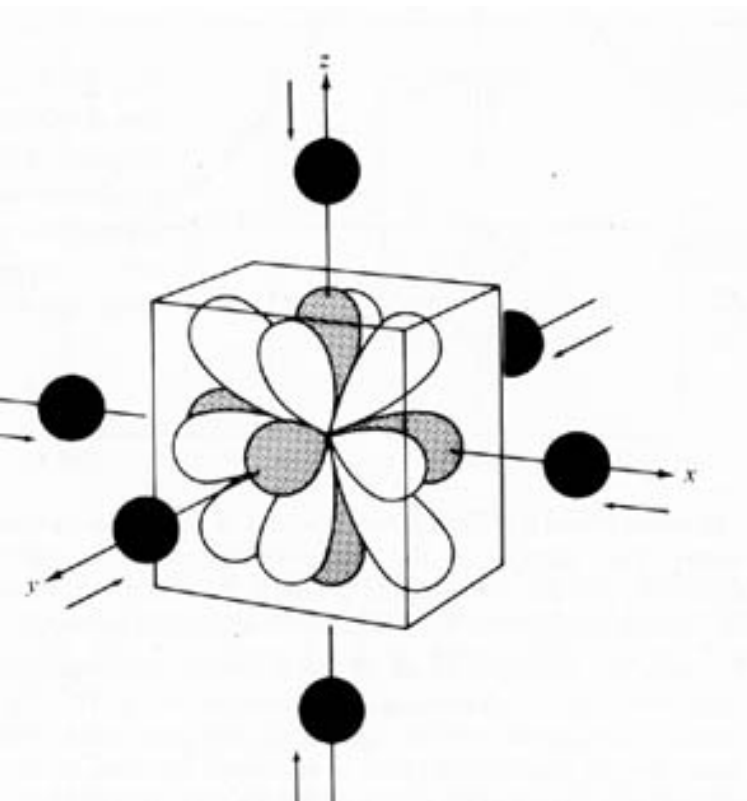
1935, modifikace J. H. Van Vleck Podíl kovalence

4) MO

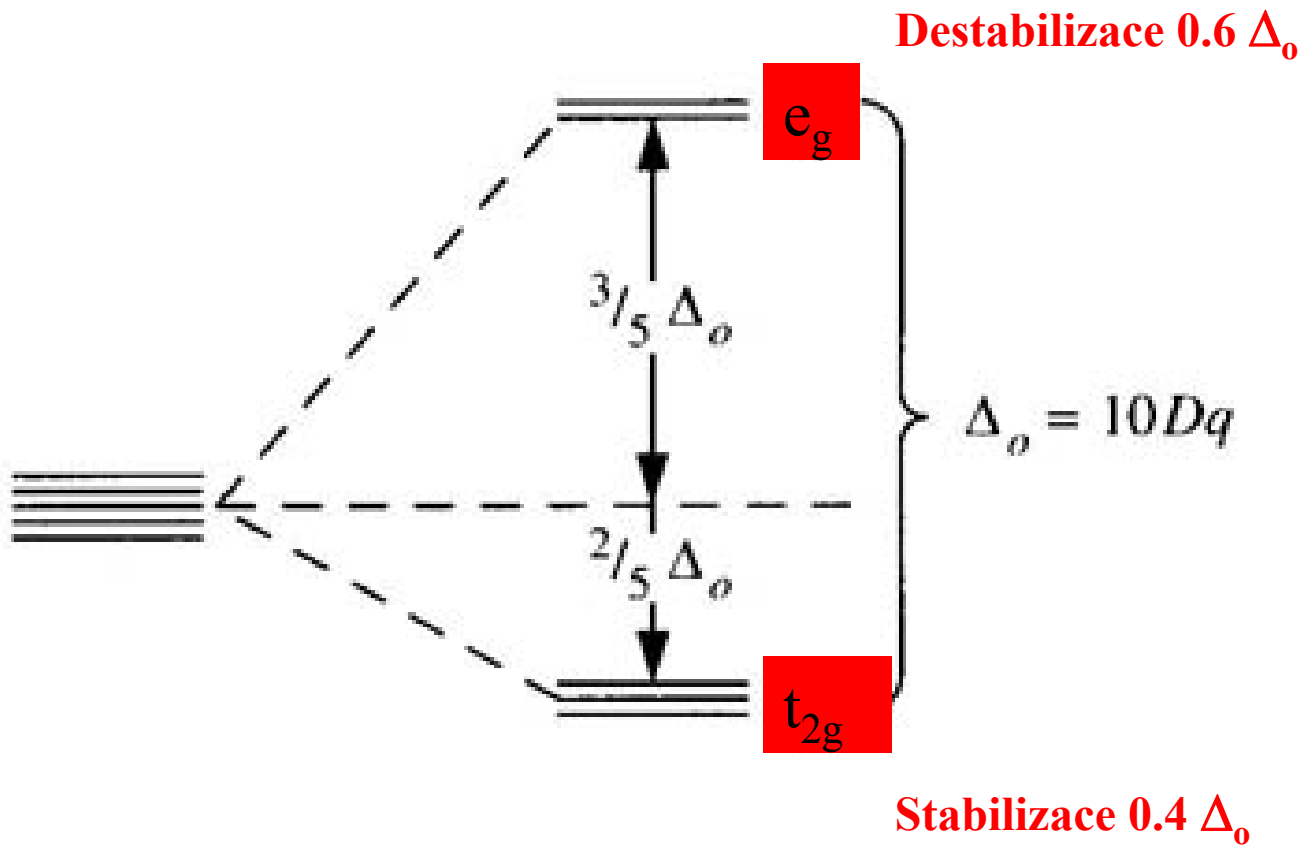
Teorie ligandového pole



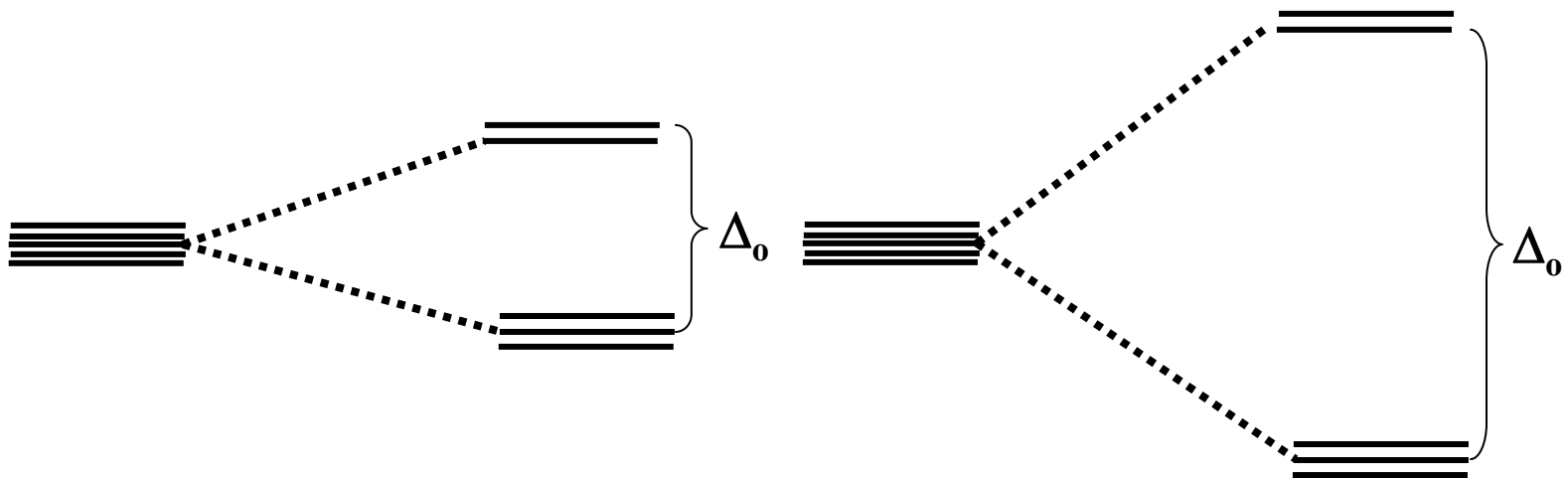
d-orbitals v oktaedrickém poli ligandů



Rozštěpení d-hladin v O_h poli



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



Slabé pole

$\Delta_o < P$ (párovací energie)

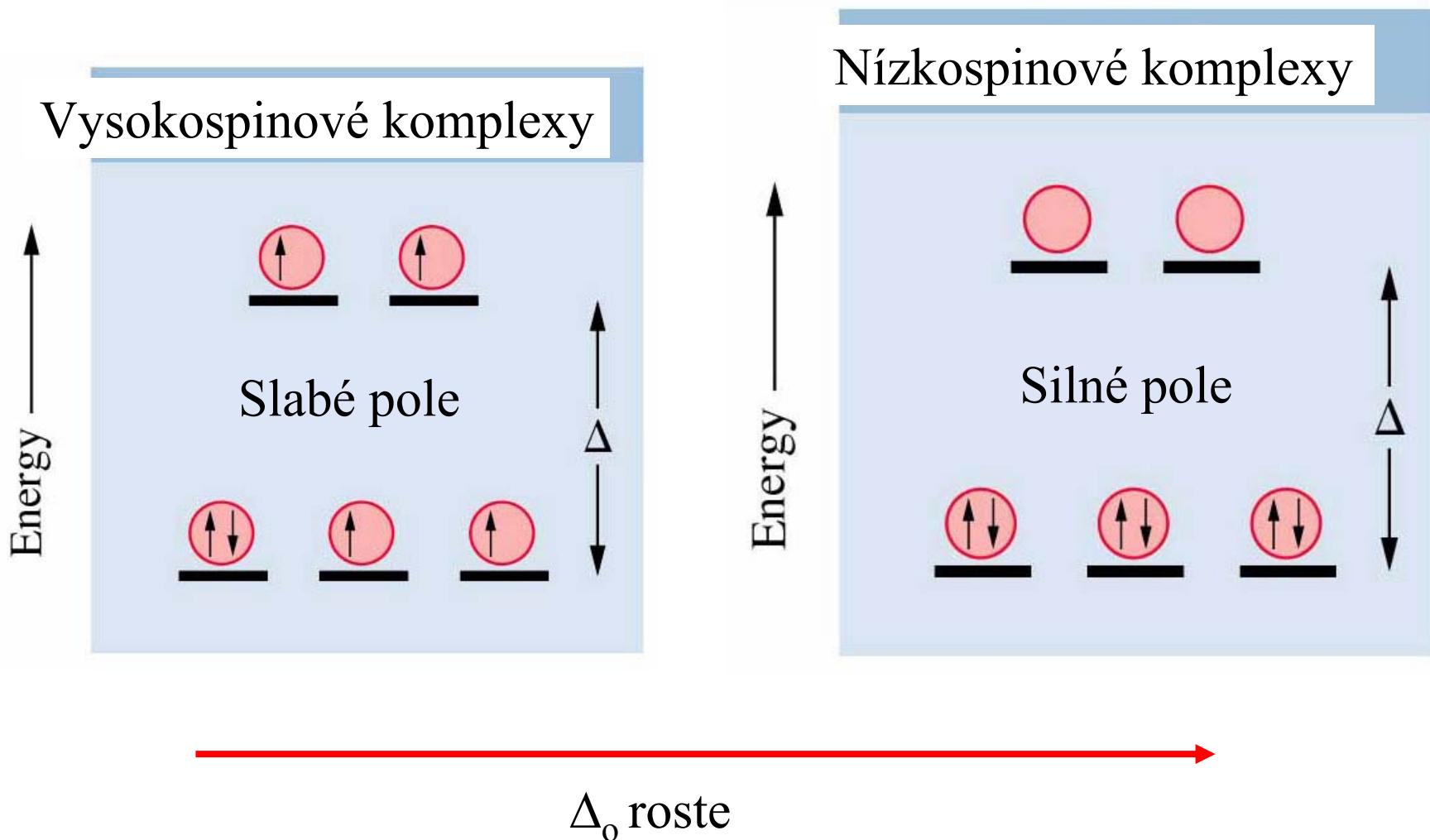
Vysokospinové komplexy

Silné pole

$\Delta_o > P$ (párovací energie)

Nížkospinové komplexy

Stabilizační energie ligandového pole



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

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

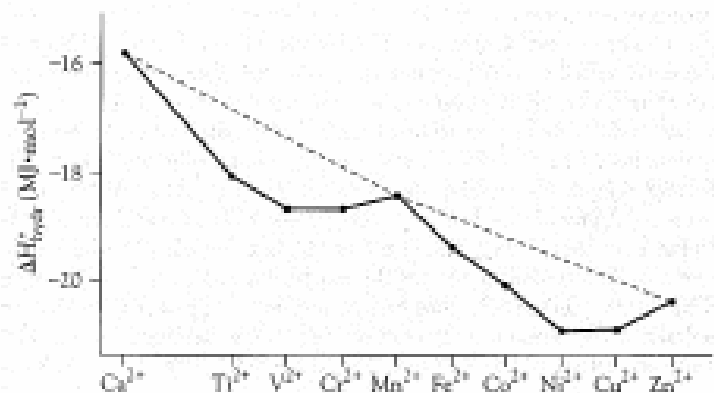
e = počet nepárových elektronů

Stabilizační energie ligandového pole

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

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

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



d^0

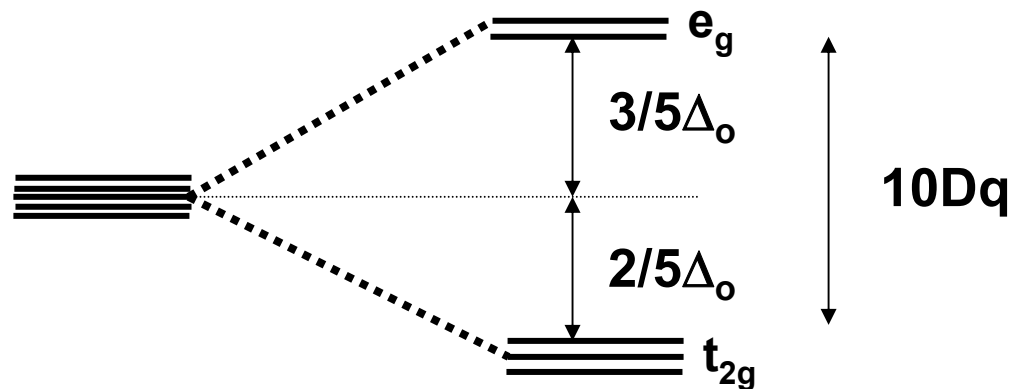
d^5

d^{10}

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

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

Rozštěpení d-hladin v O_h poli

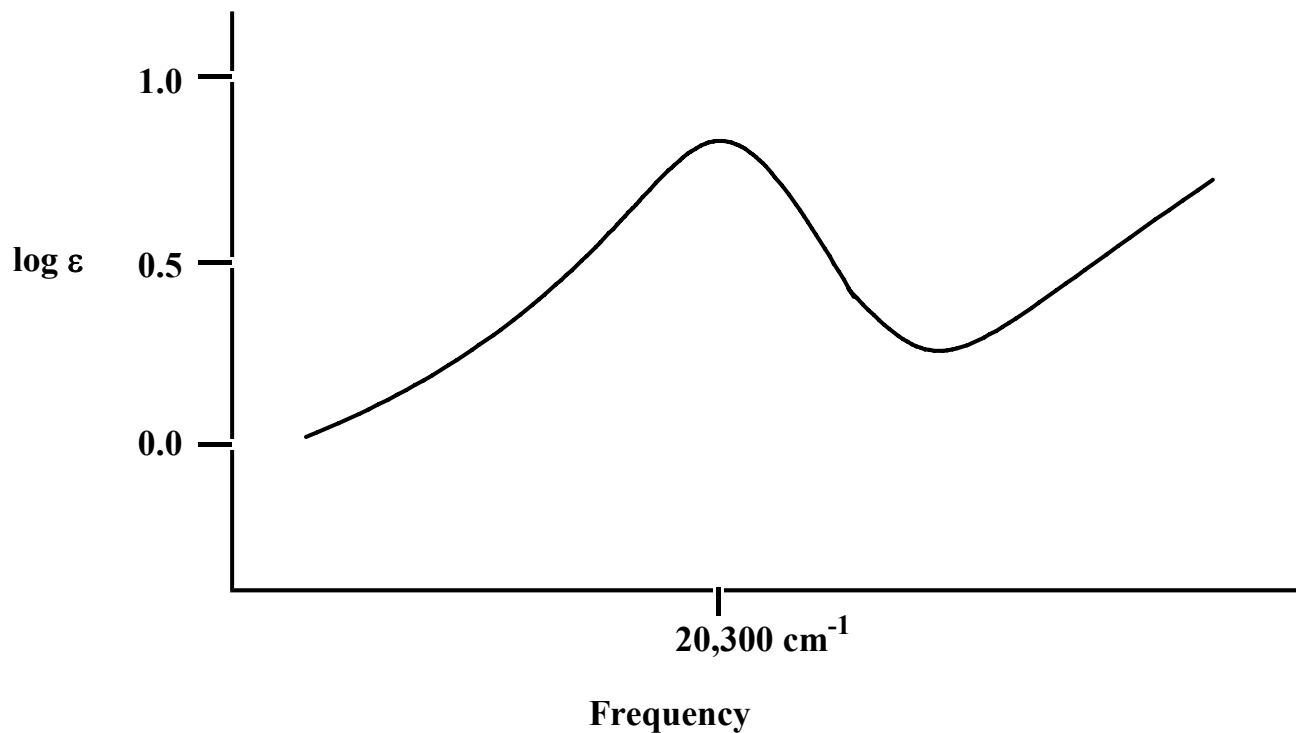


$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
 d^1

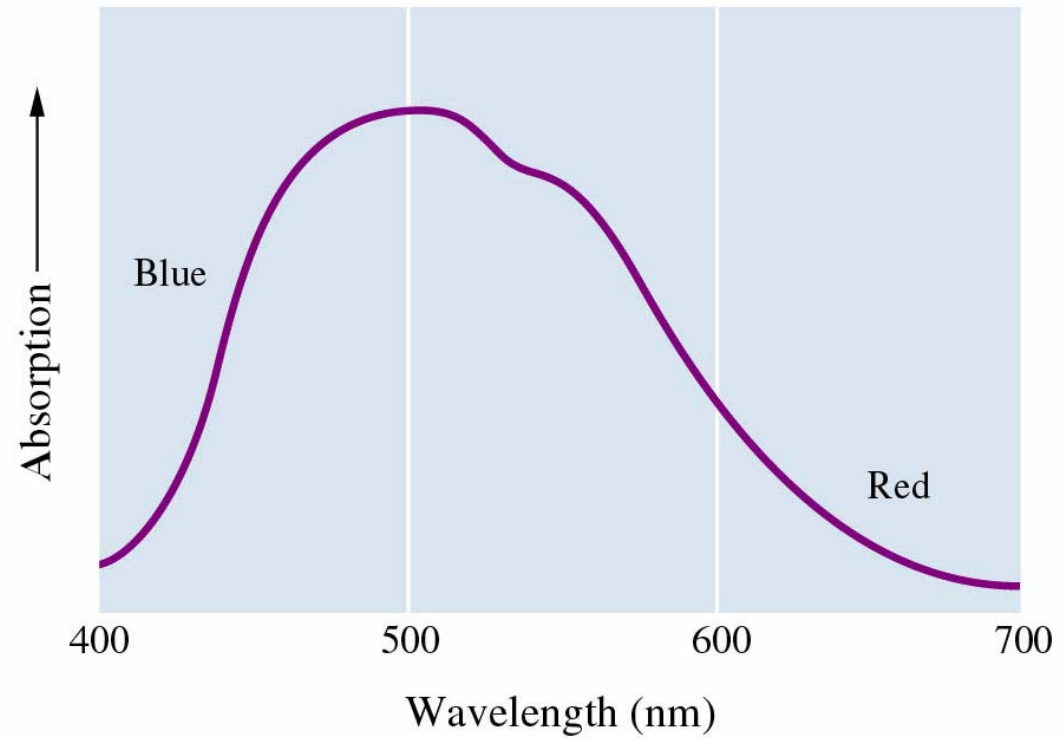
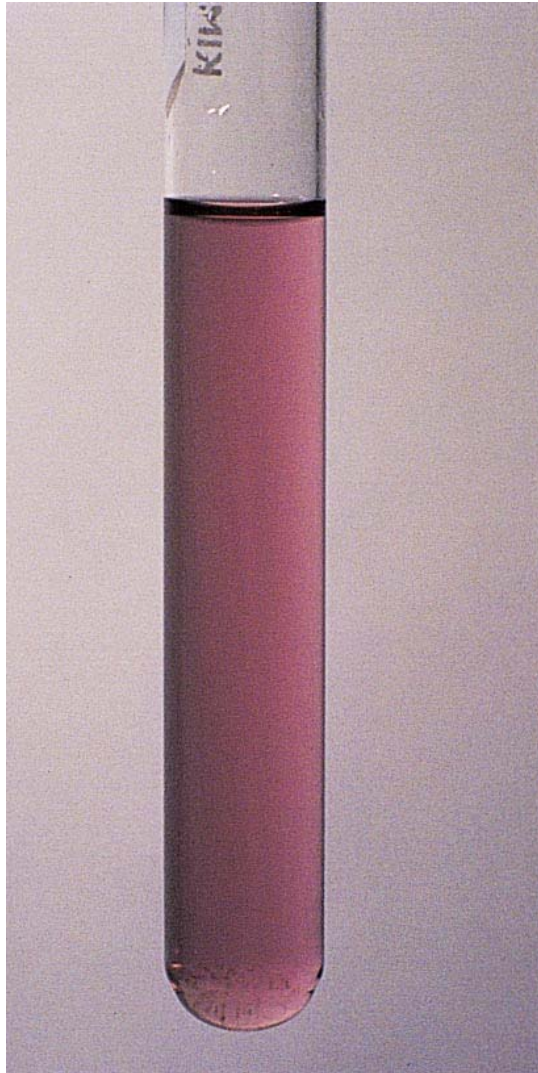
$t_{2g}^1 e_g^0 \longrightarrow t_{2g} e_g^1$

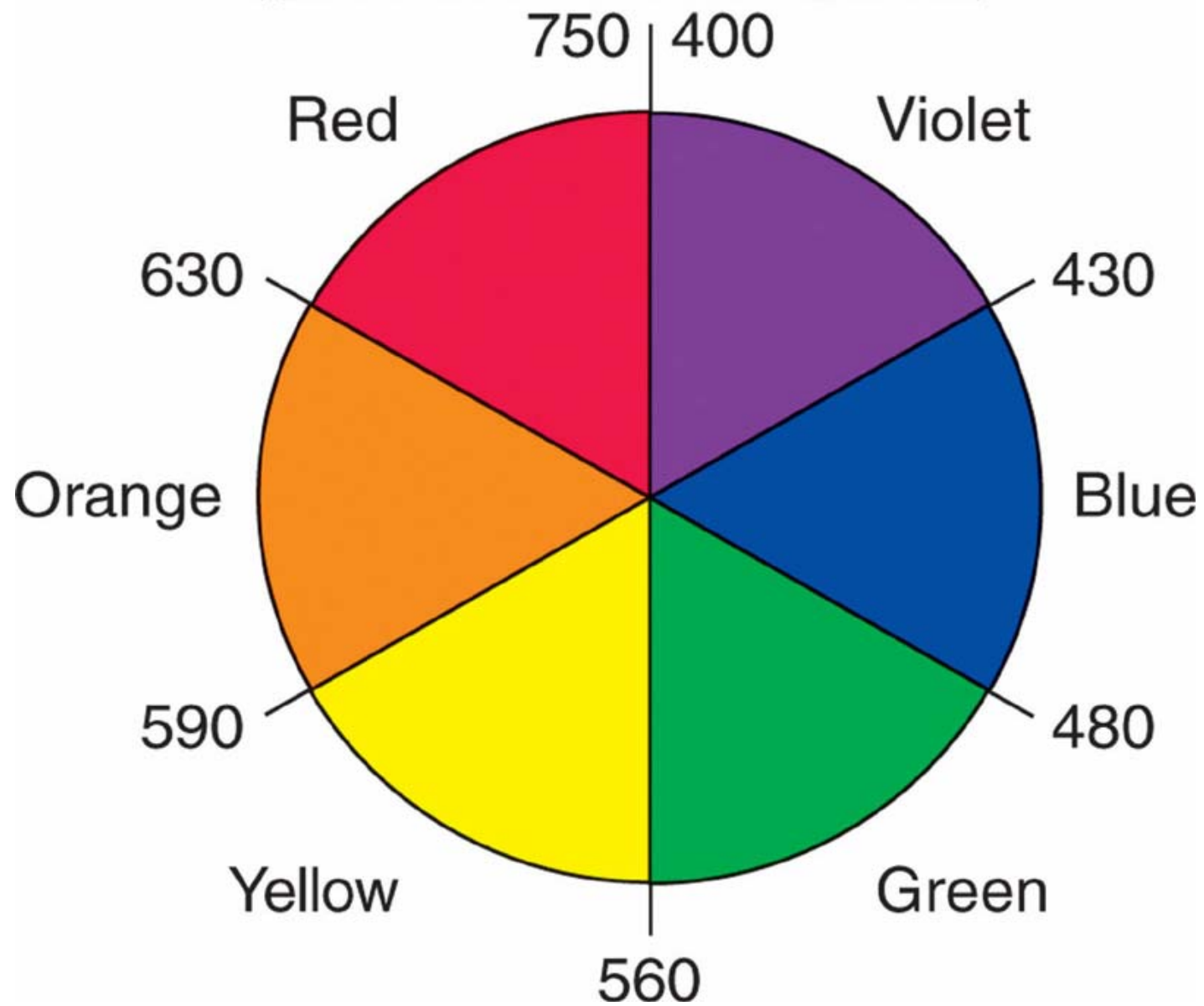
růžový

243 kJ mol^{-1}
 (Δ_o)

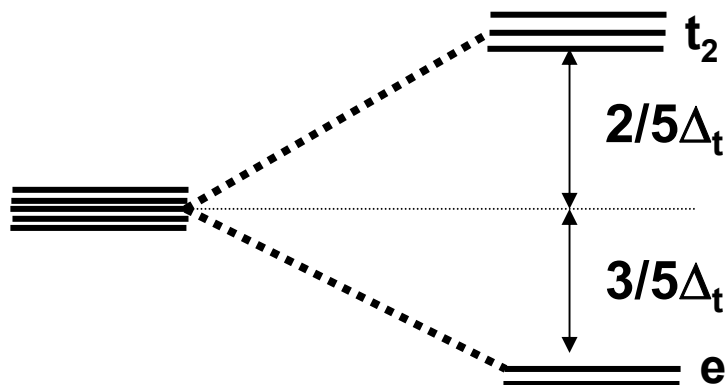


UV-vis spektrum $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$





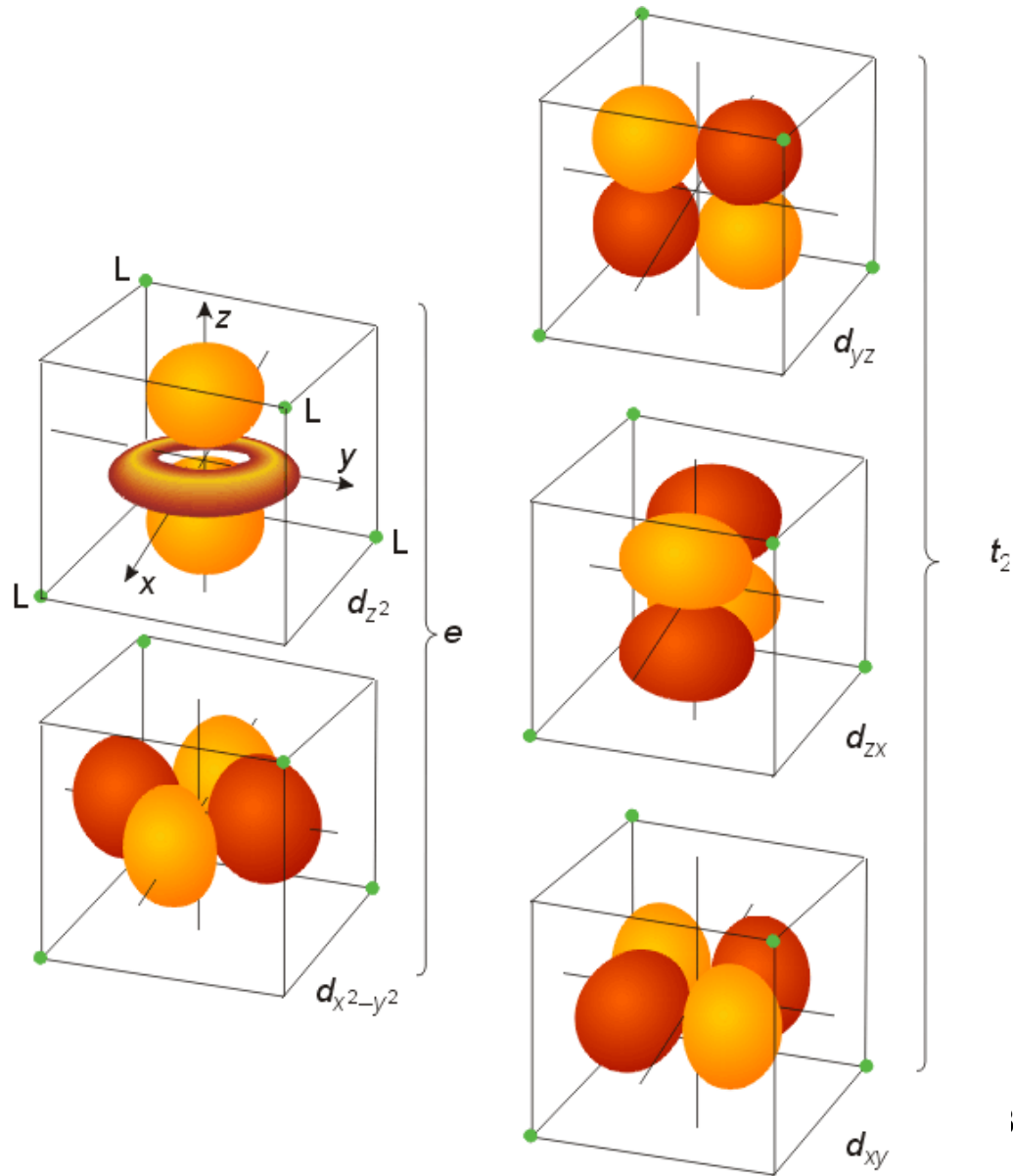
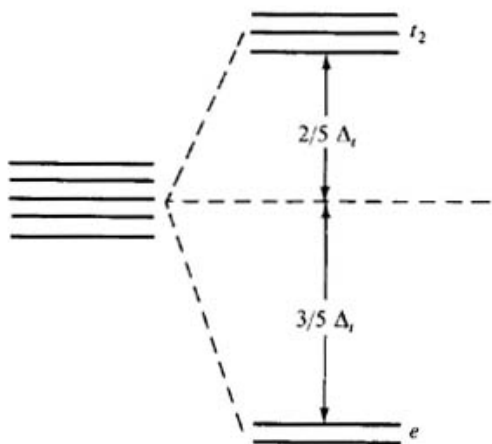
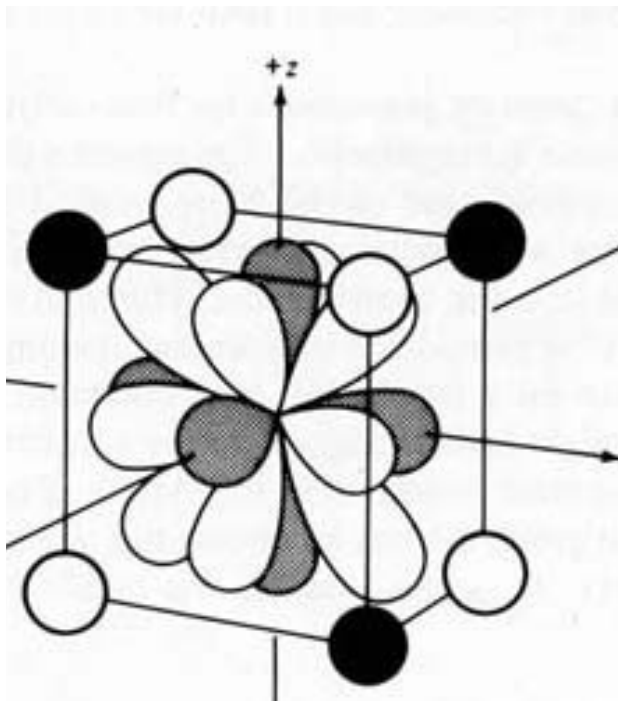
Rozštěpení d-hladin v T_d poli



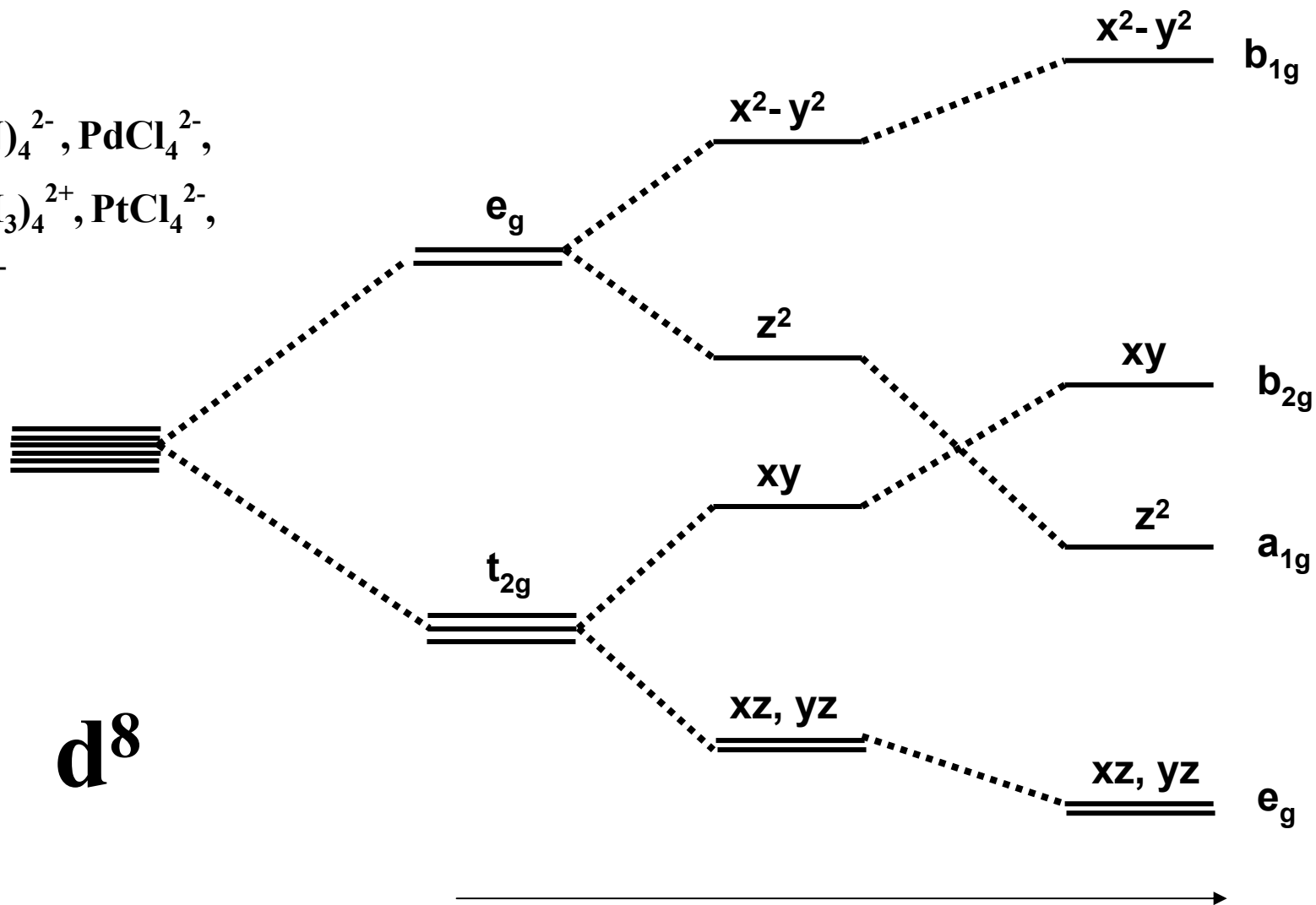
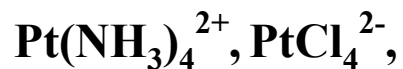
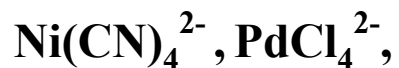
$$\Delta_t = 4/9 \Delta_o$$

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

d-orbitals v tetraedrickém poli ligandů



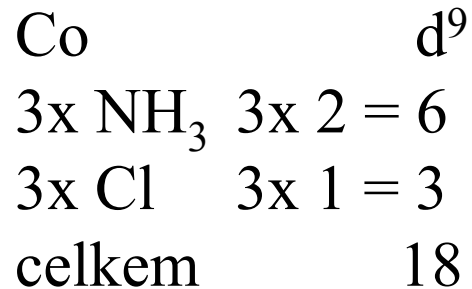
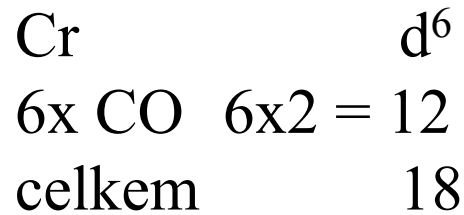
Rozštěpení d-hladin v čtvercovém poli (d^8)



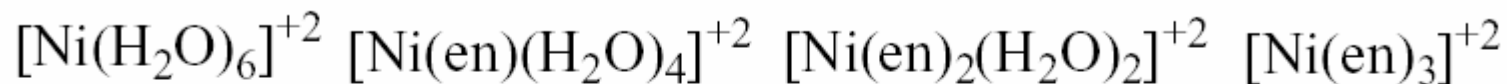
d^8

Odtržení ligandů v ose z

18-ti elektronové pravidlo



Vliv ligandů na vlastnosti komplexů



green



green/blue



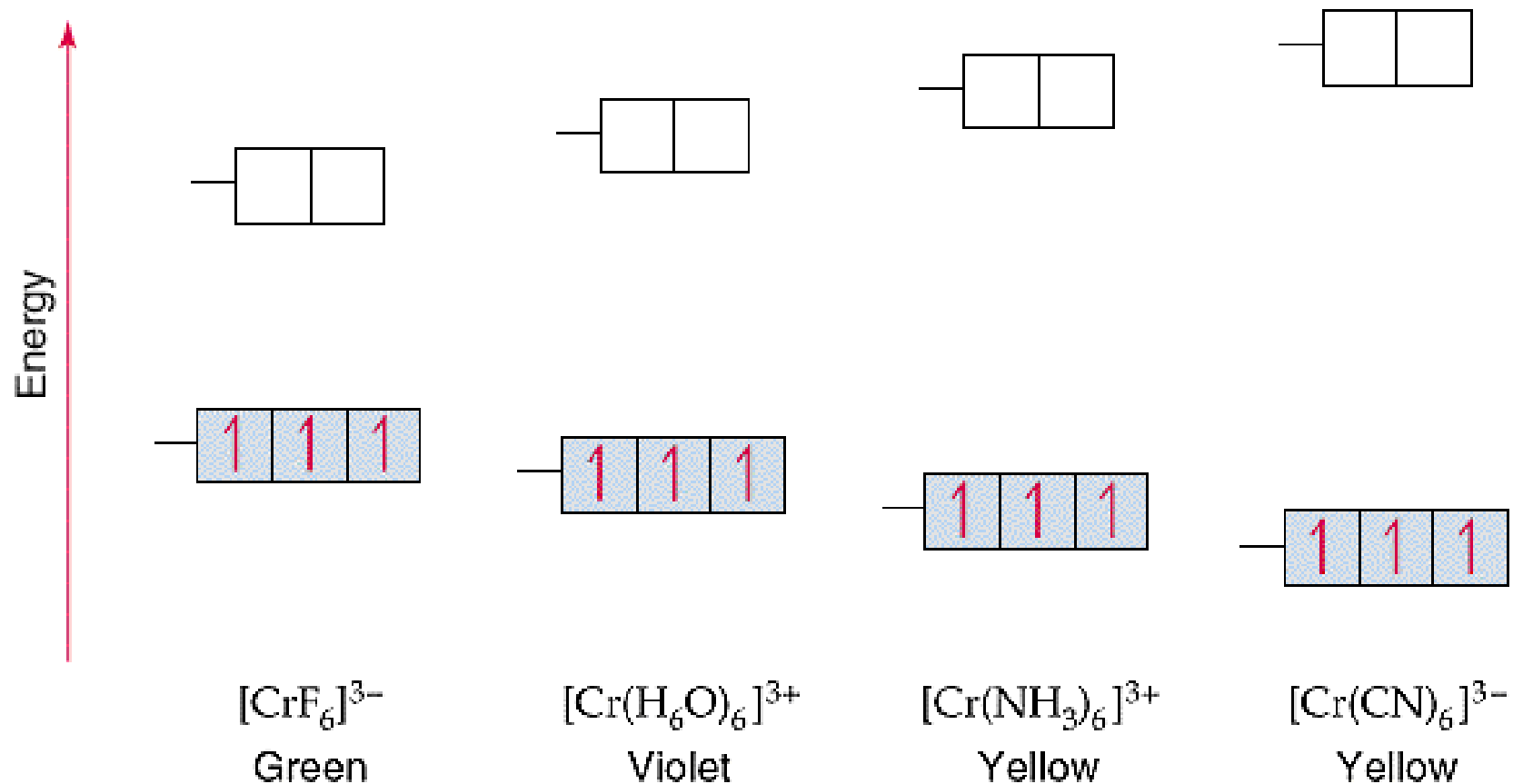
blue



purple

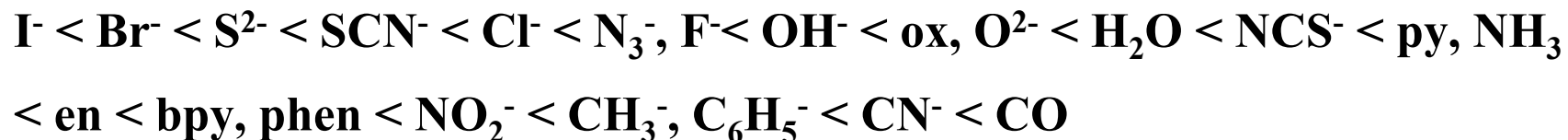


Vliv ligandů na vlastnosti komplexů

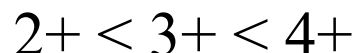


Faktory ovlivňující velikost rozštěpení ligandového pole

Spektrochemická řada ligandů:



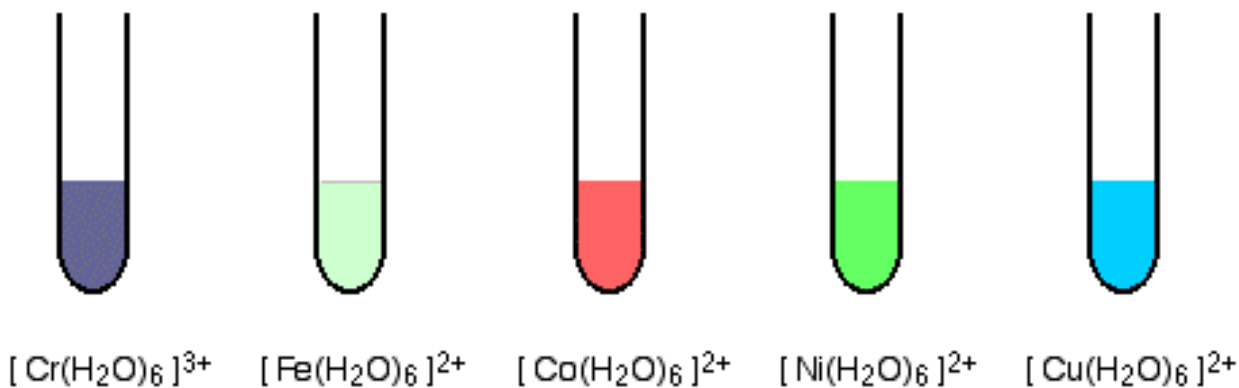
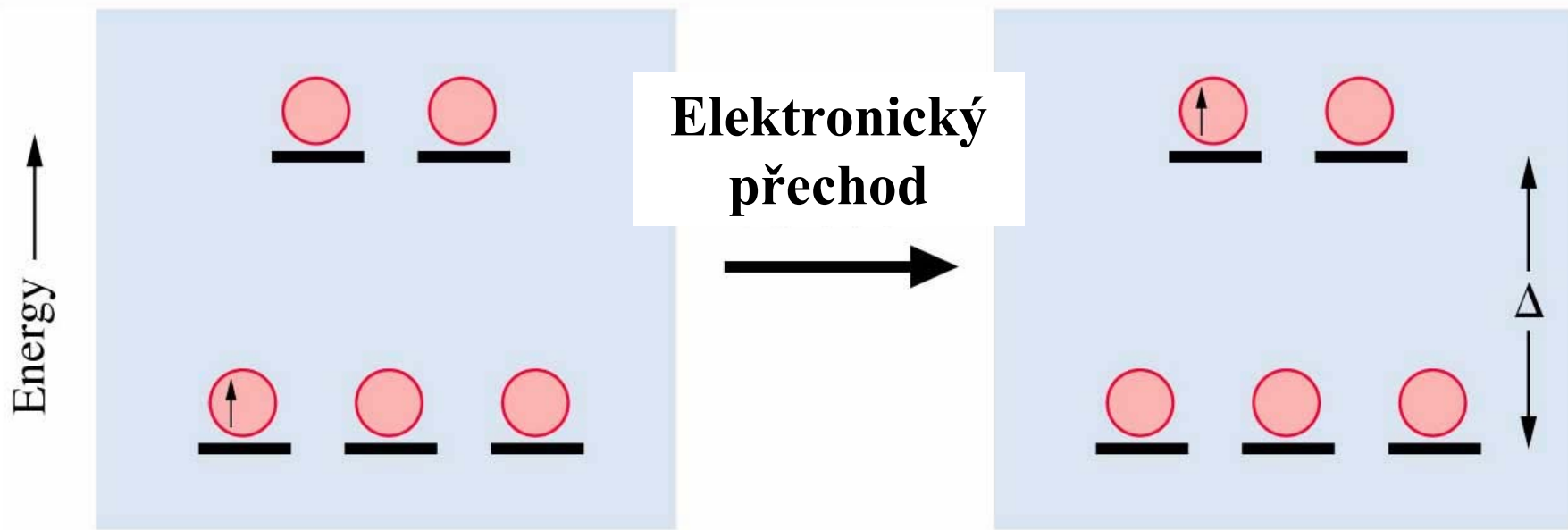
Centrální atom:



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

Síla a délka vazby M-L

Elektronické přechody



**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**)

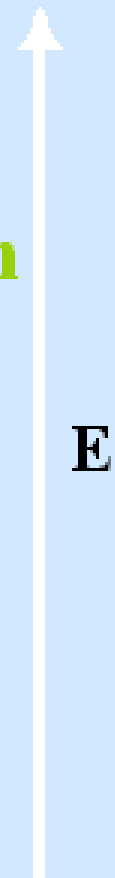
blue

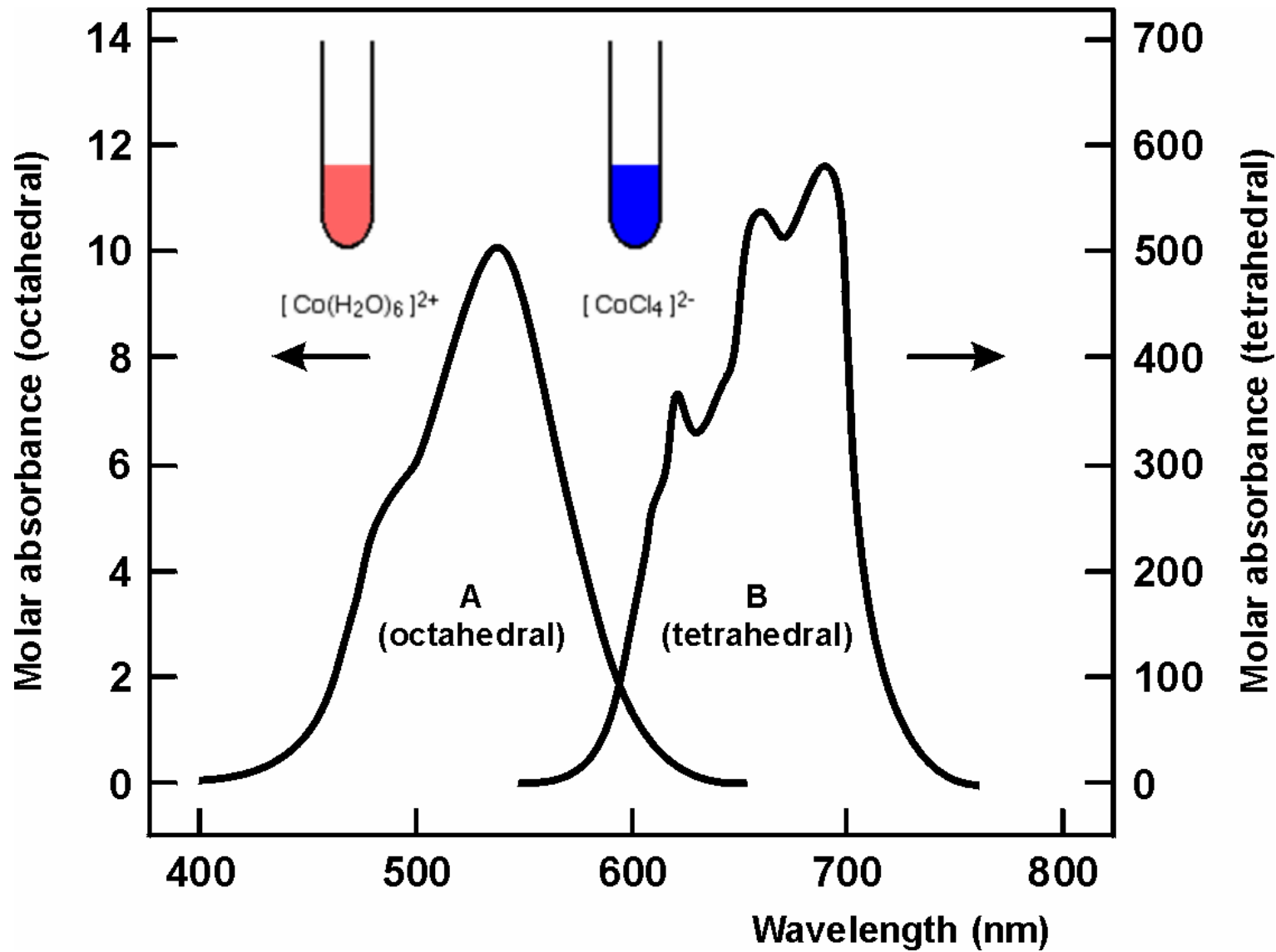
650 nm (**red**)

blue-green

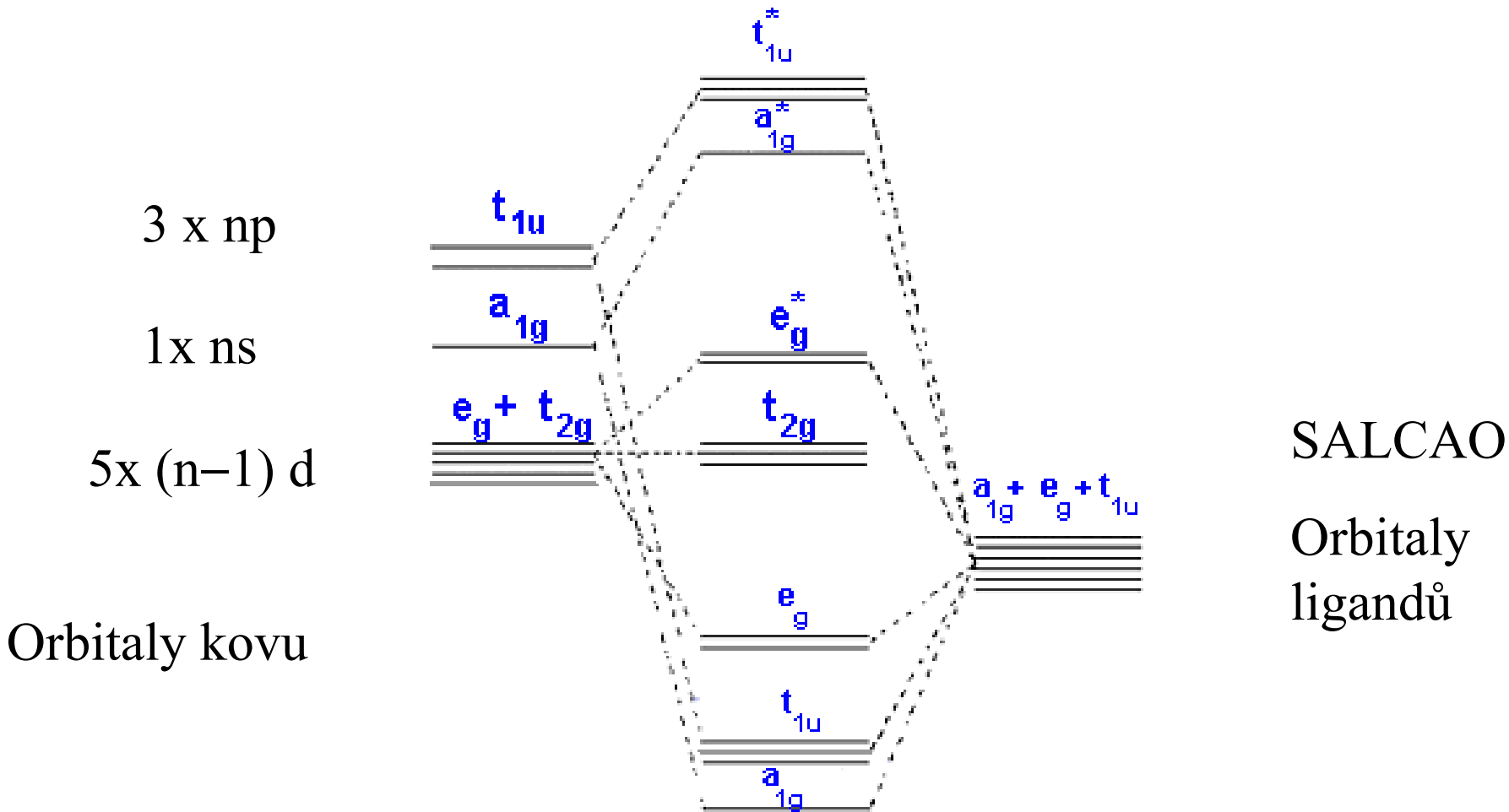
720 nm (**purple**)

green

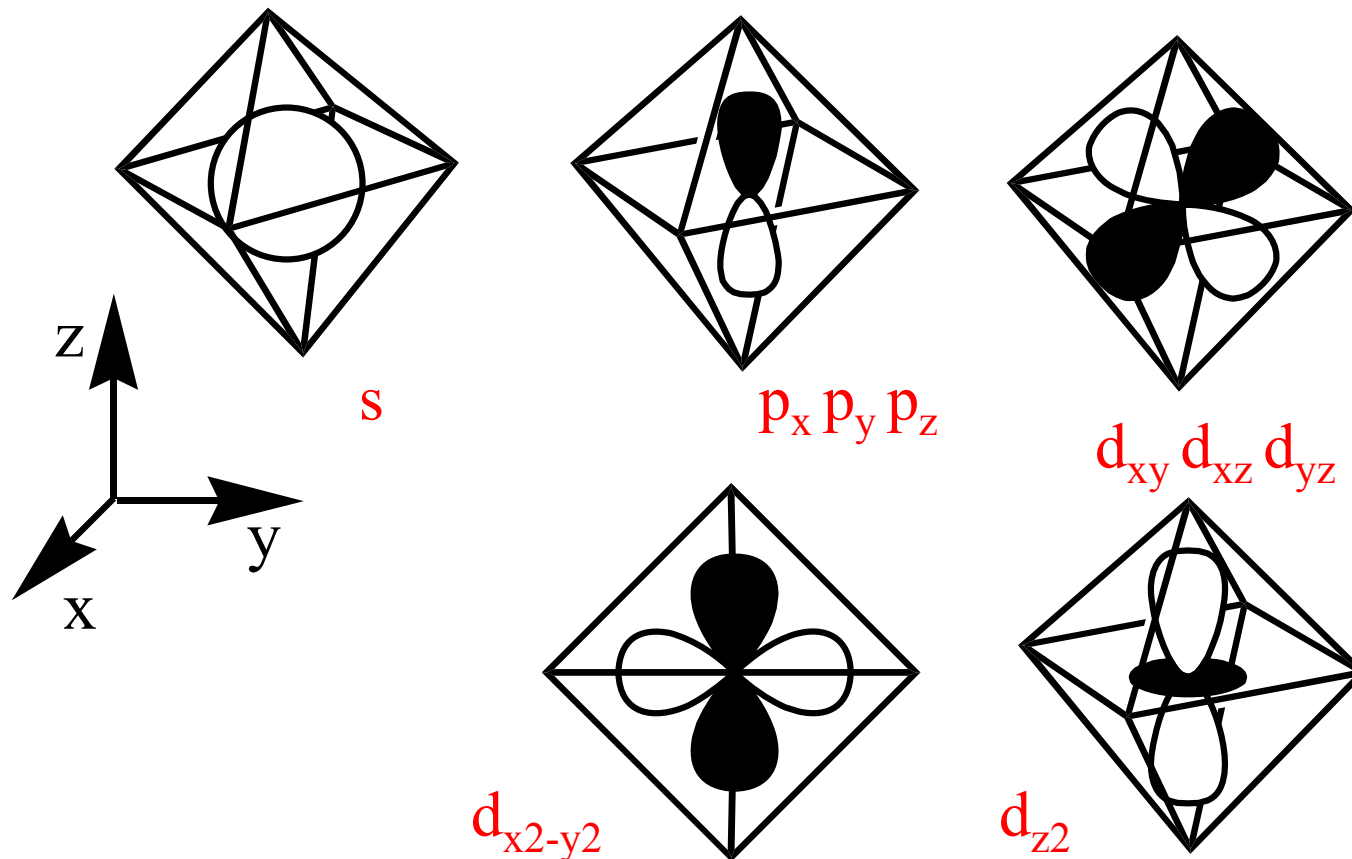


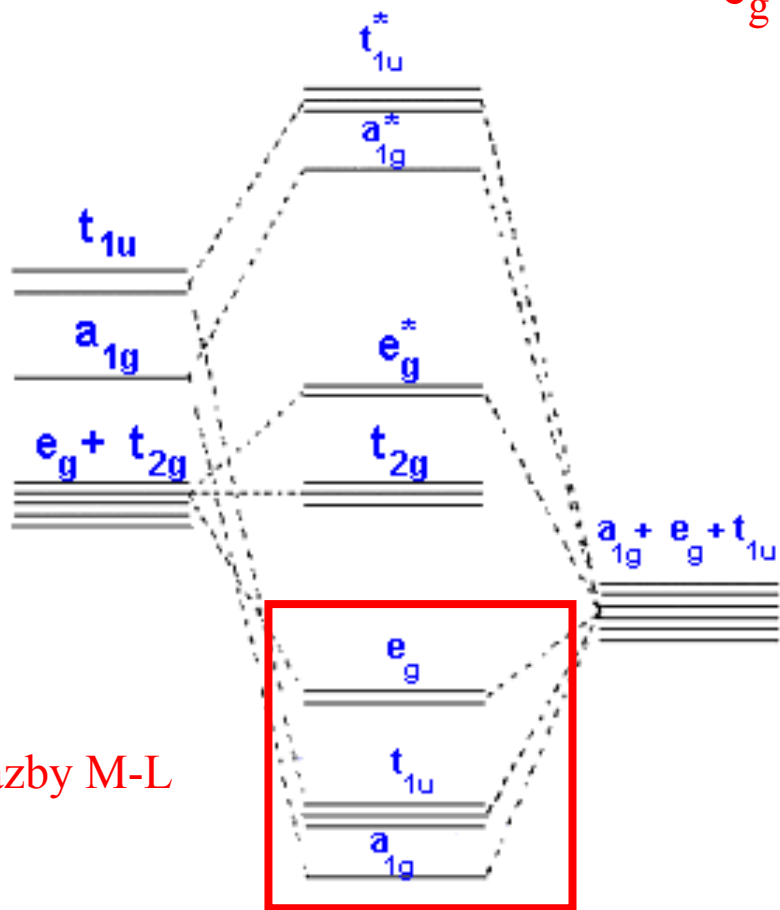
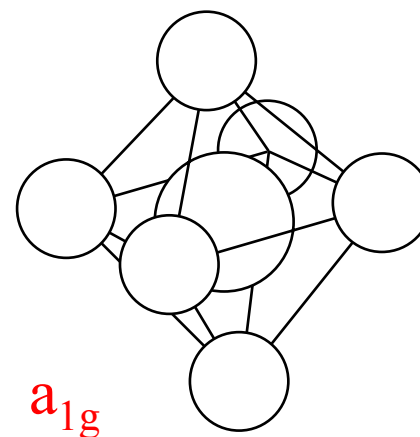
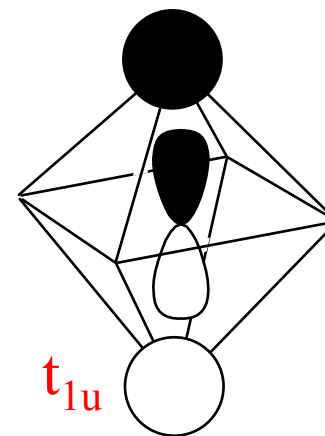
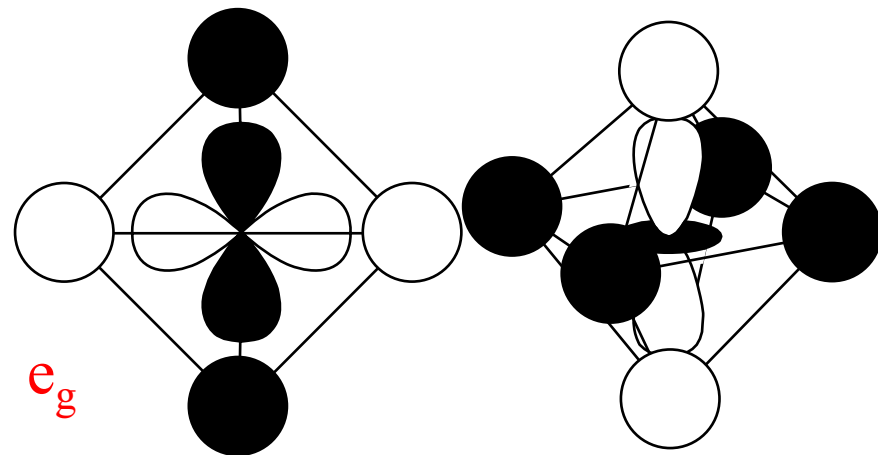


Popis vazby v komplexech pomocí MO



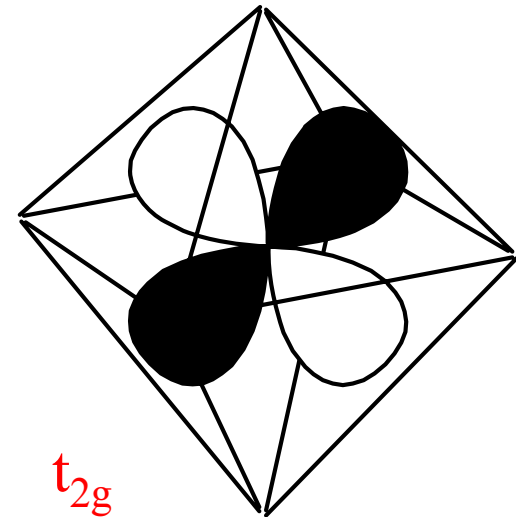
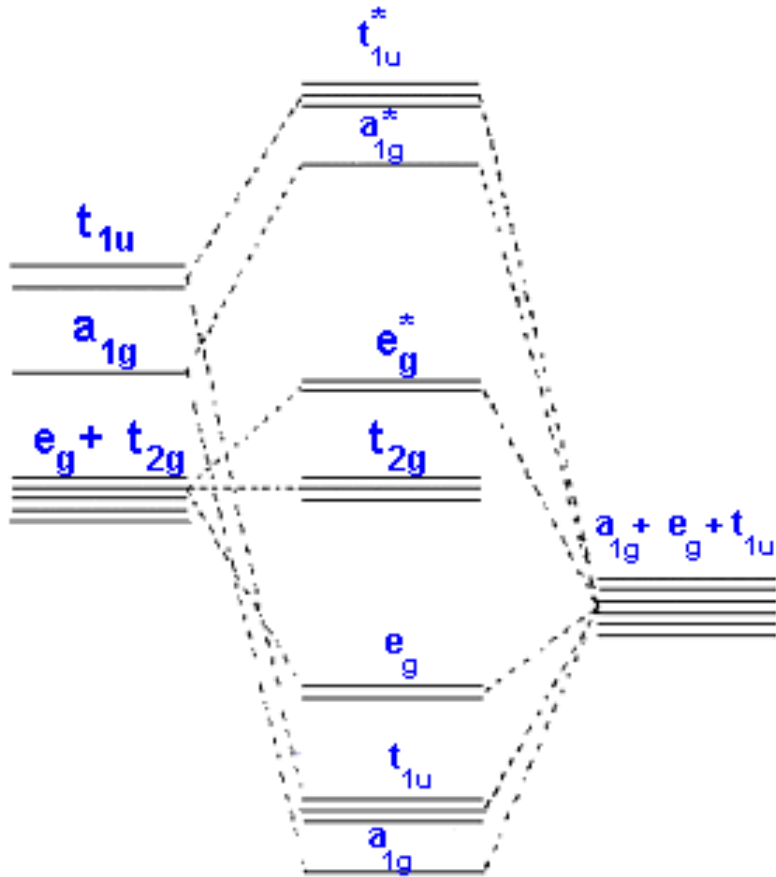
Valenční orbitály kovu



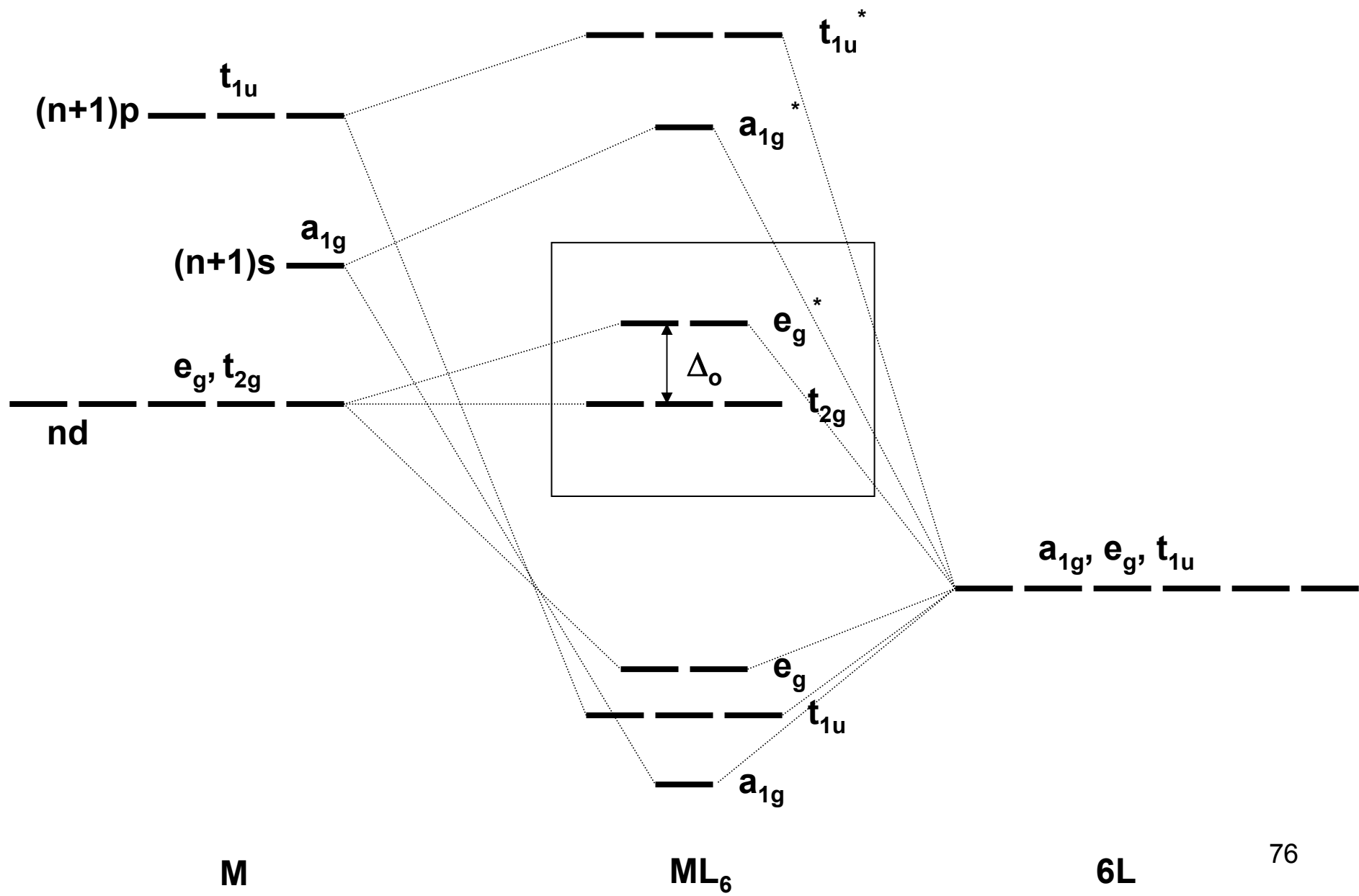


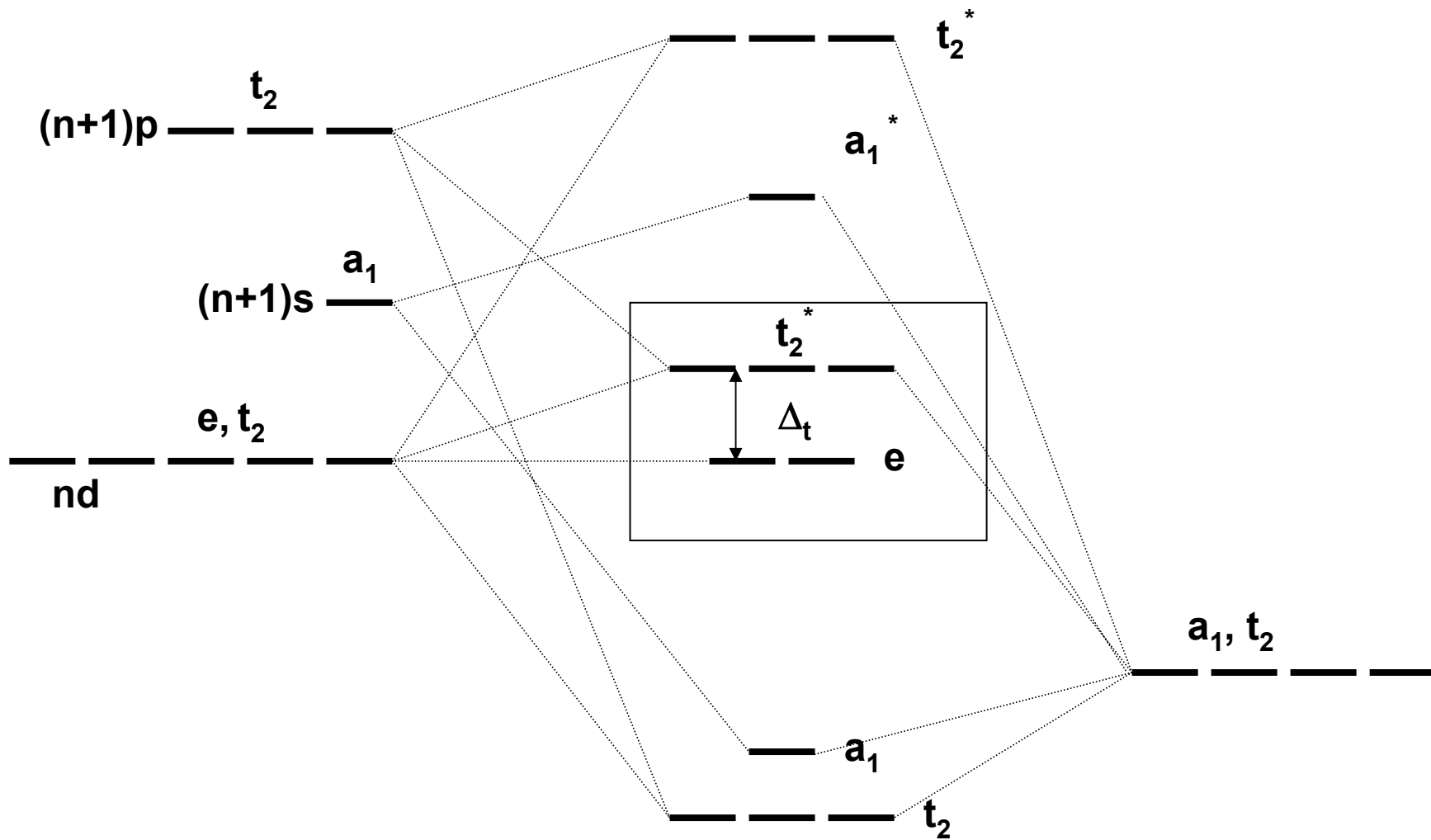
Sigma vazby M-L

Nevazebné d-orbitály



Neexistuje žádná vhodná kombinace AO ligandů

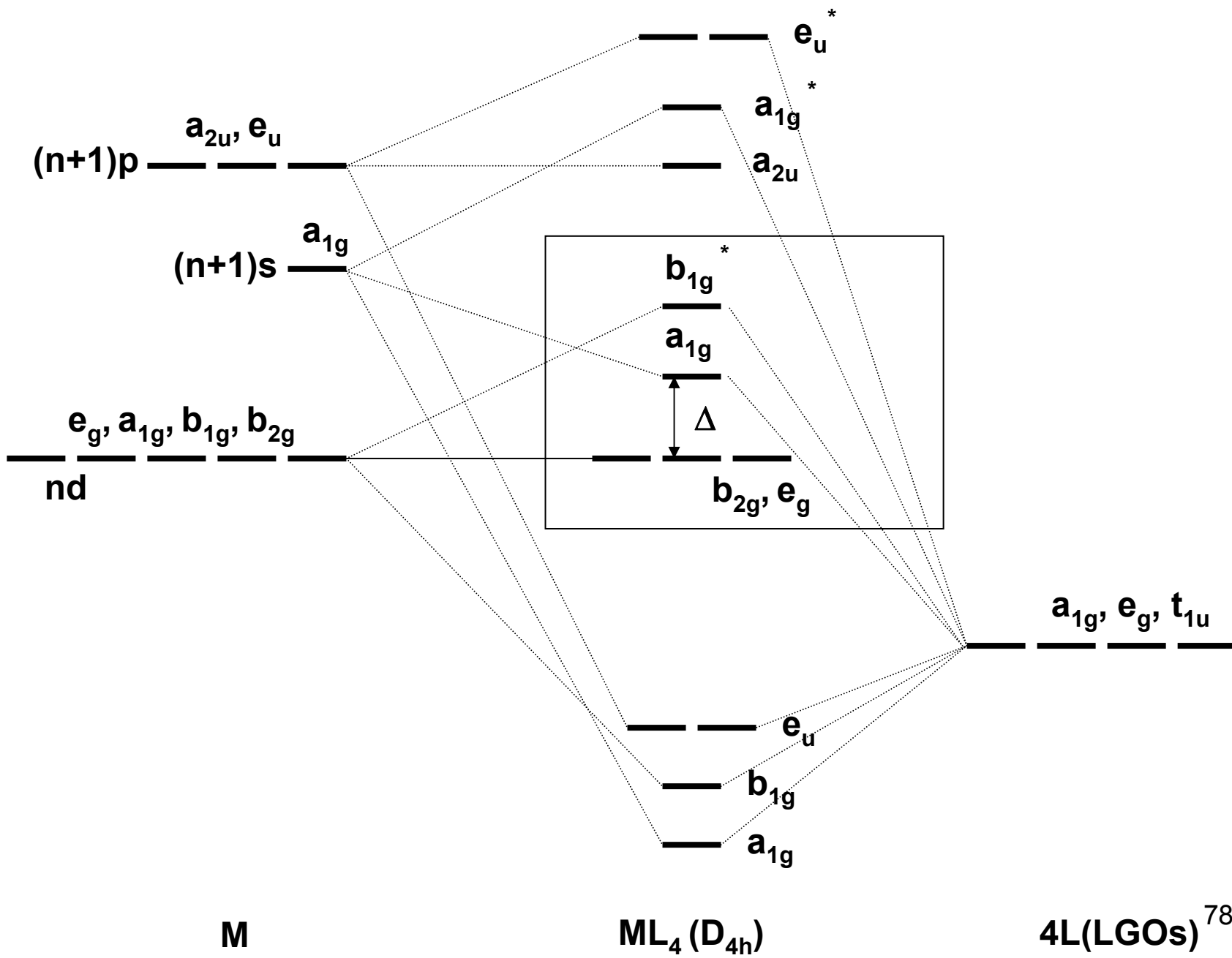




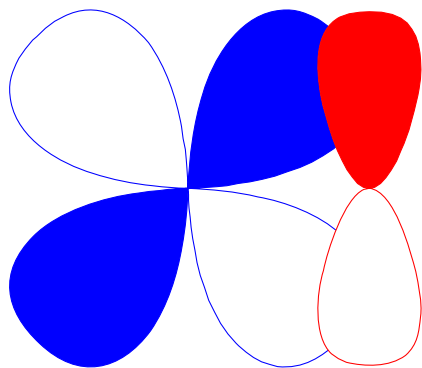
M

ML₄

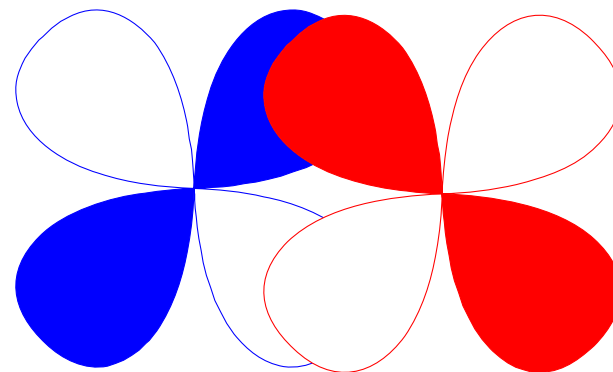
4L(LGOs)



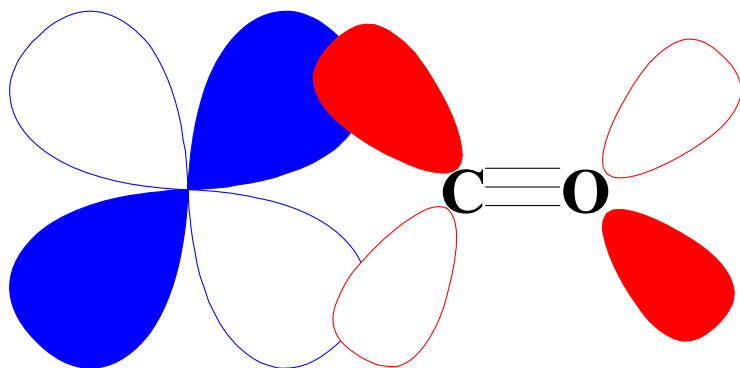
MO při π -vazbě



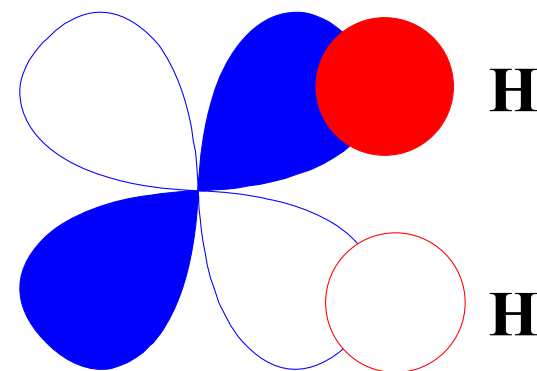
$p\pi-d\pi$ RO^- , RS^- , O^{2-} , F^- , Cl^- , Br^- , I^- , R_2N^-



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

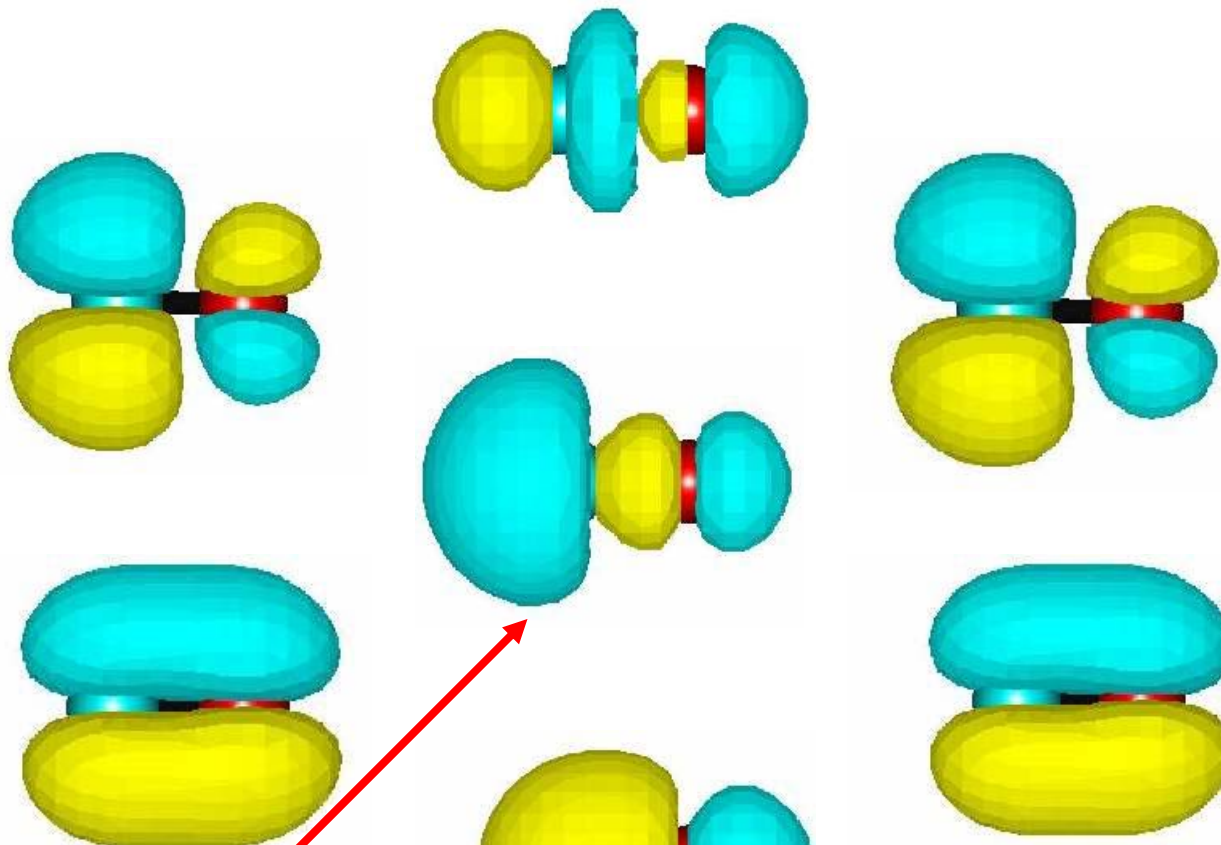


$d\pi-\pi^*$ CO , RNC , pyridin, CN^- , N_2 , NO_2^- , ethylen

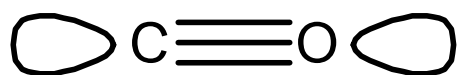


$d\pi-\sigma^*$ H_2 , R_3P , alkany

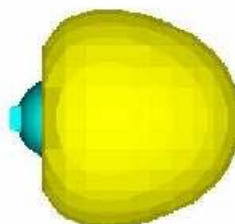
LUMO

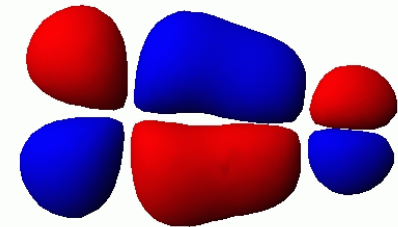
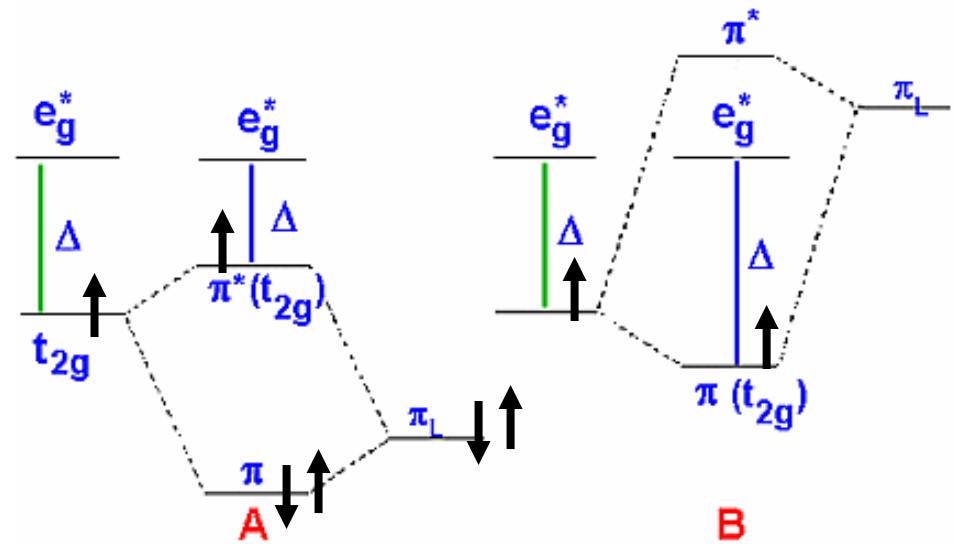
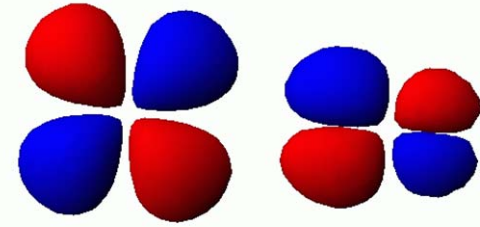
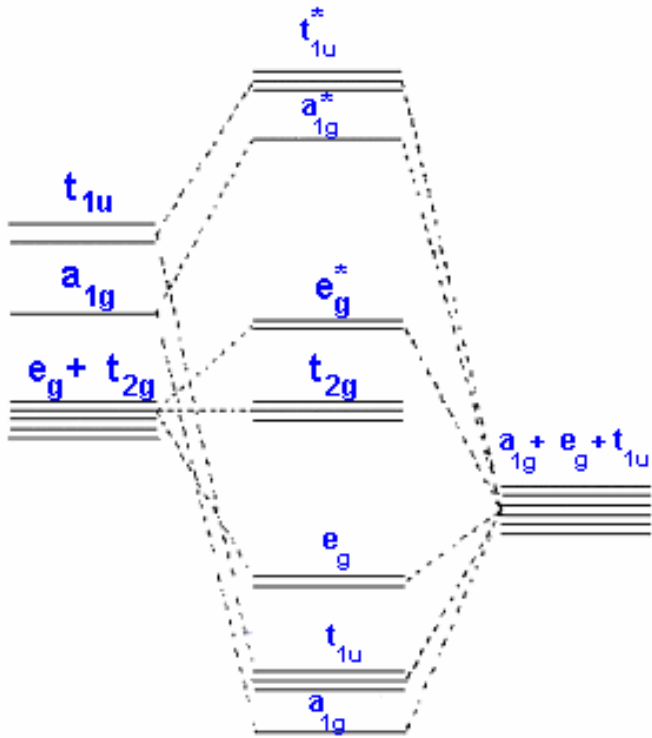


Volný e pár na C
HOMO

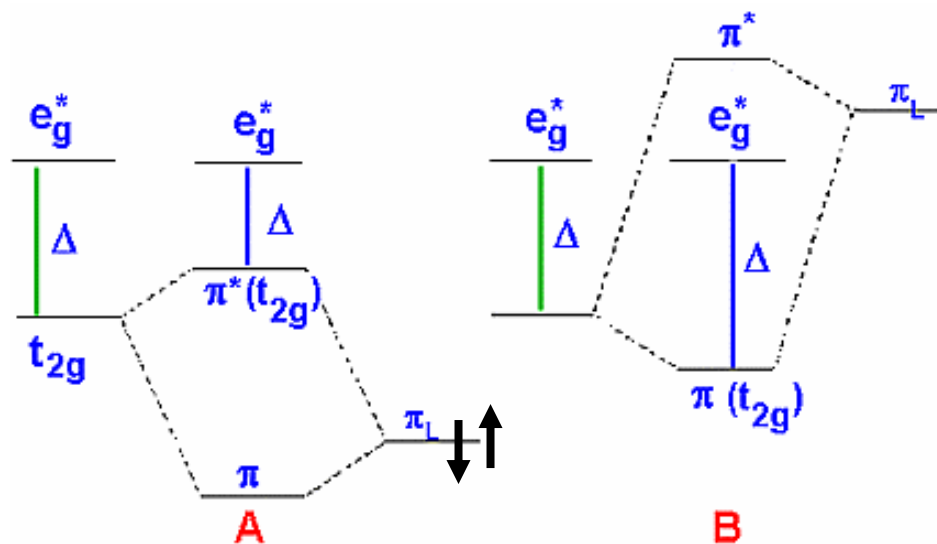


Volný e pár na O





Ligandy s pi orbitaly



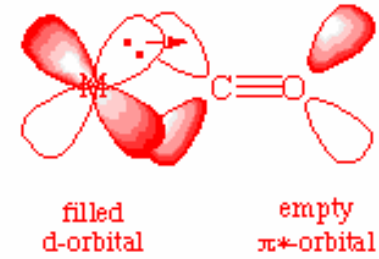
Pi baze

Pi kyselina

σ bond:



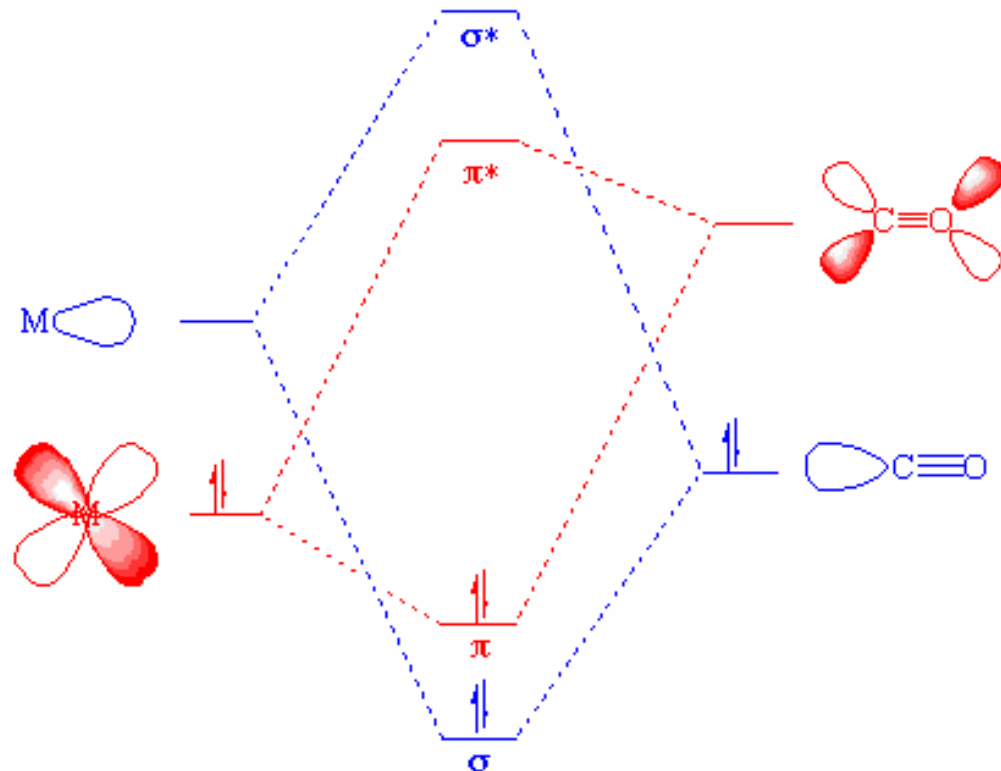
π backbond:



L_M

$L_M(\text{CO})$

CO



Zpětná pi donace
 $M \rightarrow \text{CO}$

Sigma donace
 $M \leftarrow \text{CO}$

Jahn-Tellerova distorze

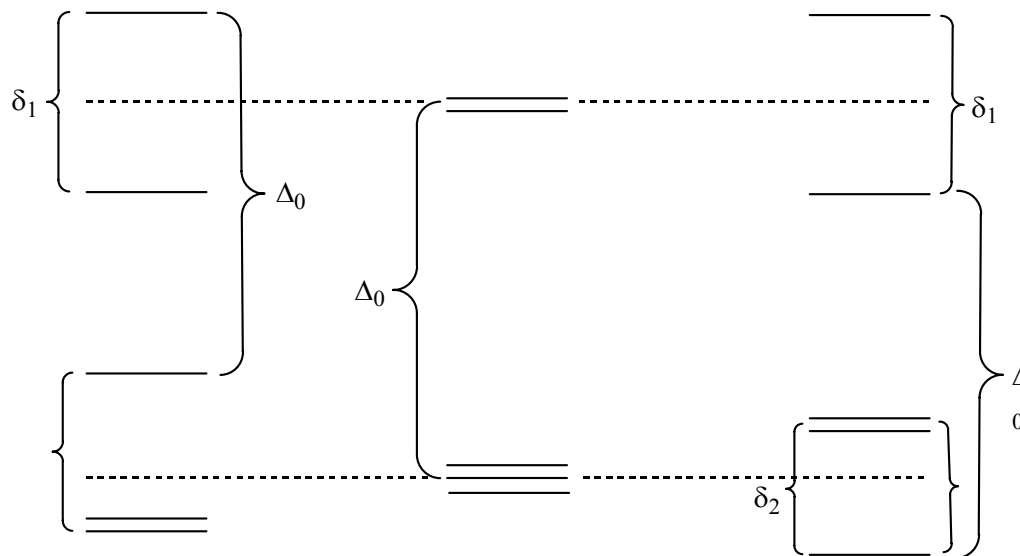
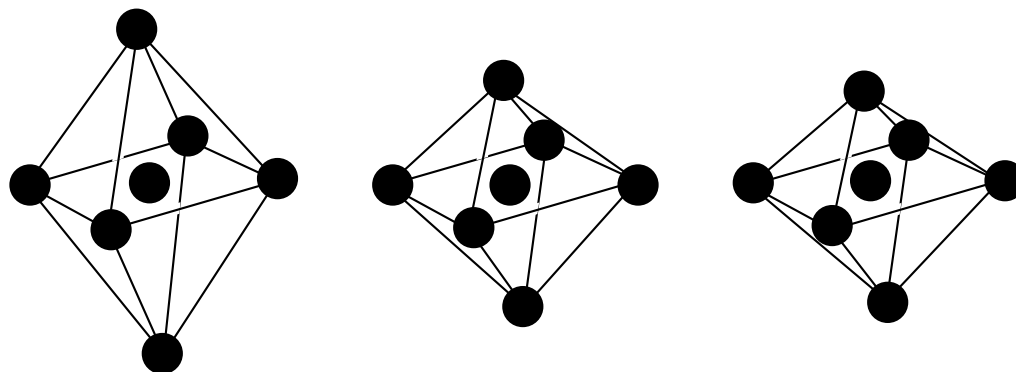
Degenerované hladiny

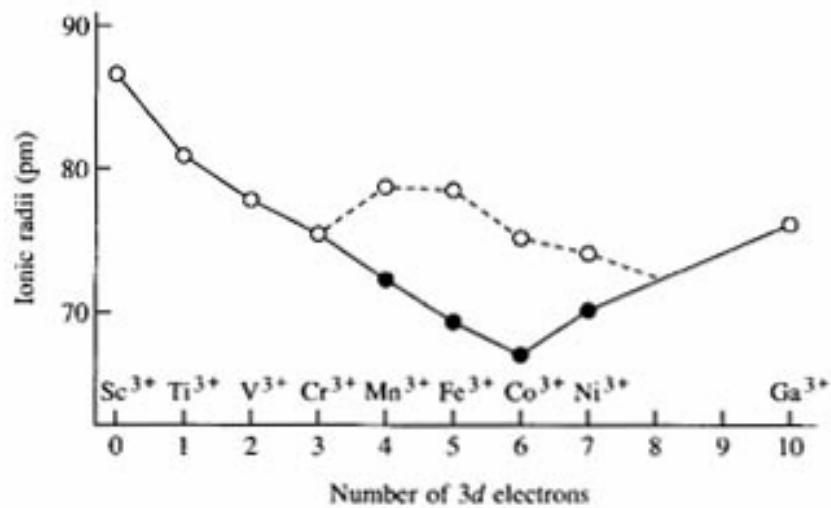
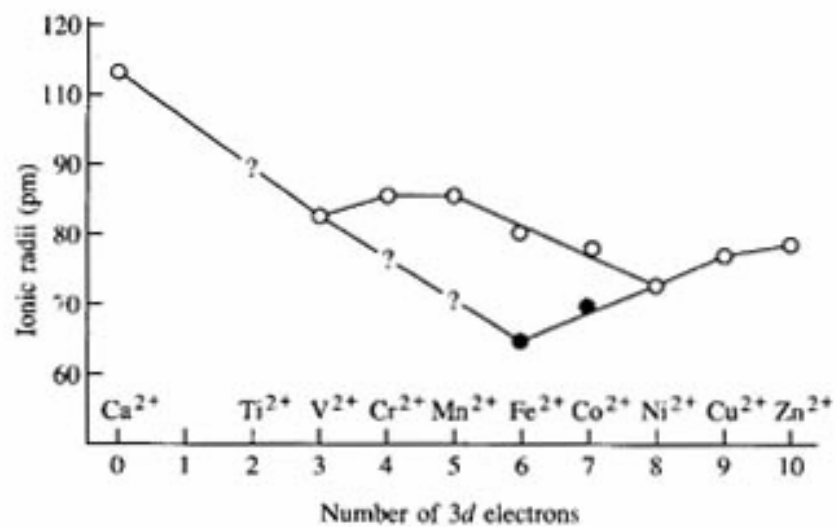
Částečně obsazené

Nelineární molekuly

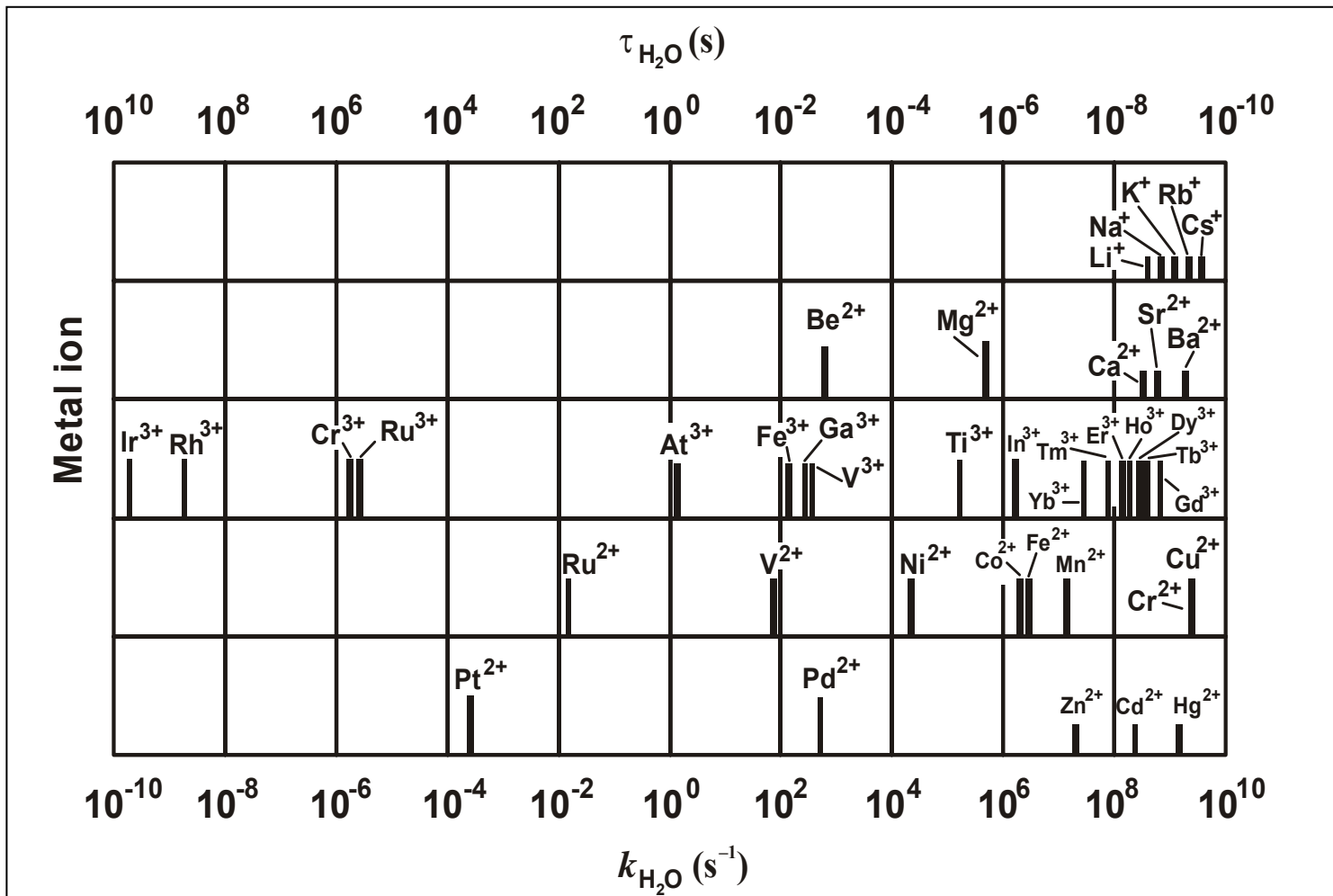
Degenerace se odstraní

deformací





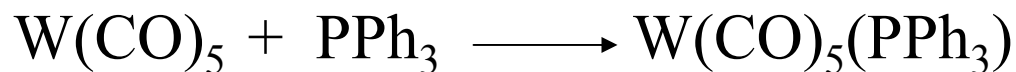
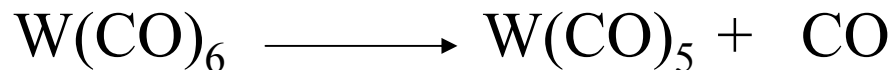
Kinetika



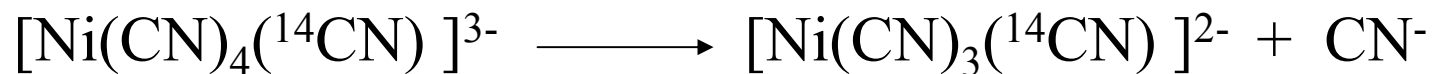
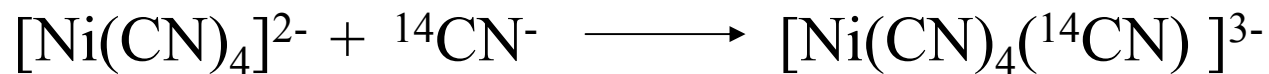
Mechanismy reakcí

Mechanismus

Disociativní (D)



Asociativní (A)



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

Trans-Influence (thermodynamic effect)

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

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

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

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

Trans-Effect (kinetic effect)

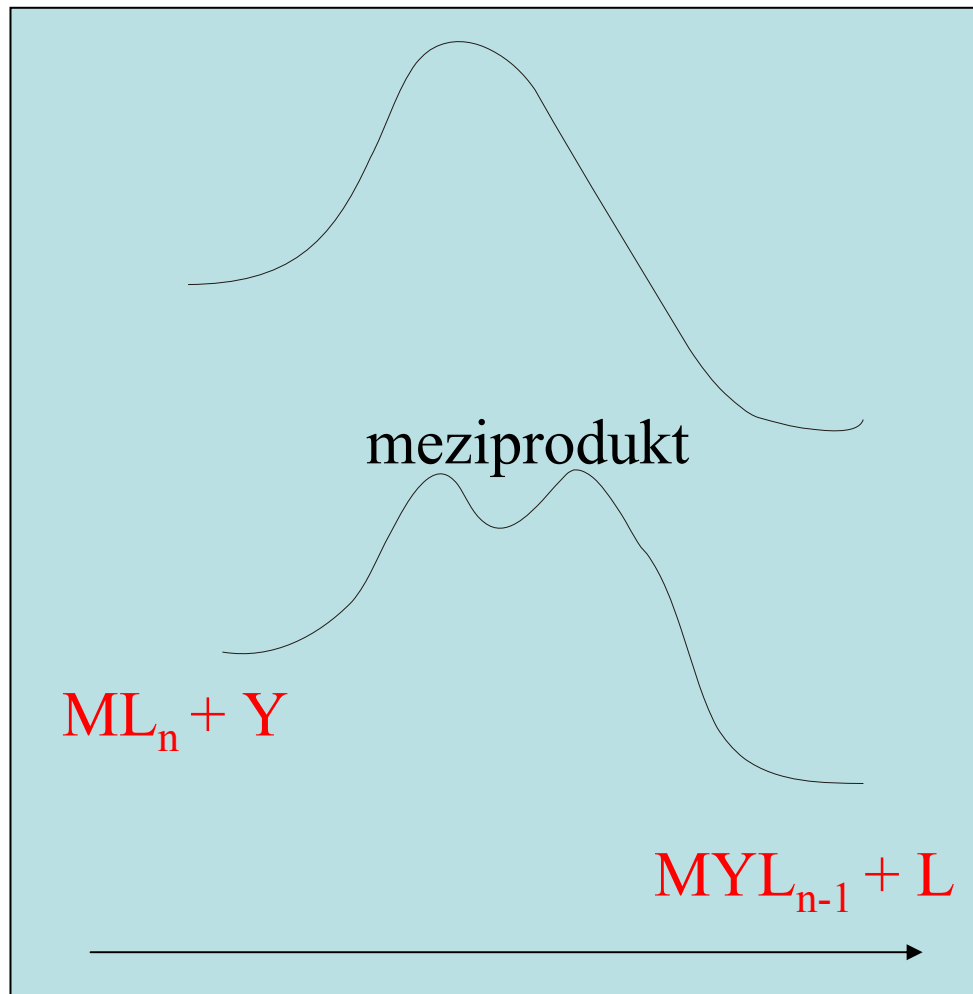
extent to which a ligand effects the rate of exchange of the ligand *trans* to itself

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

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

Mechanismy reakcí

Výměnný (I)



Magnetické vlastnosti komplexů

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

Magnetická susceptibilita

M = magnetizace

H = intenzita mg pole

Molární magnetická susceptibilita

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

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

Magnetický moment

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

Magnetické vlastnosti komplexů

Curie-Temperatur

Neél-Temperatur

