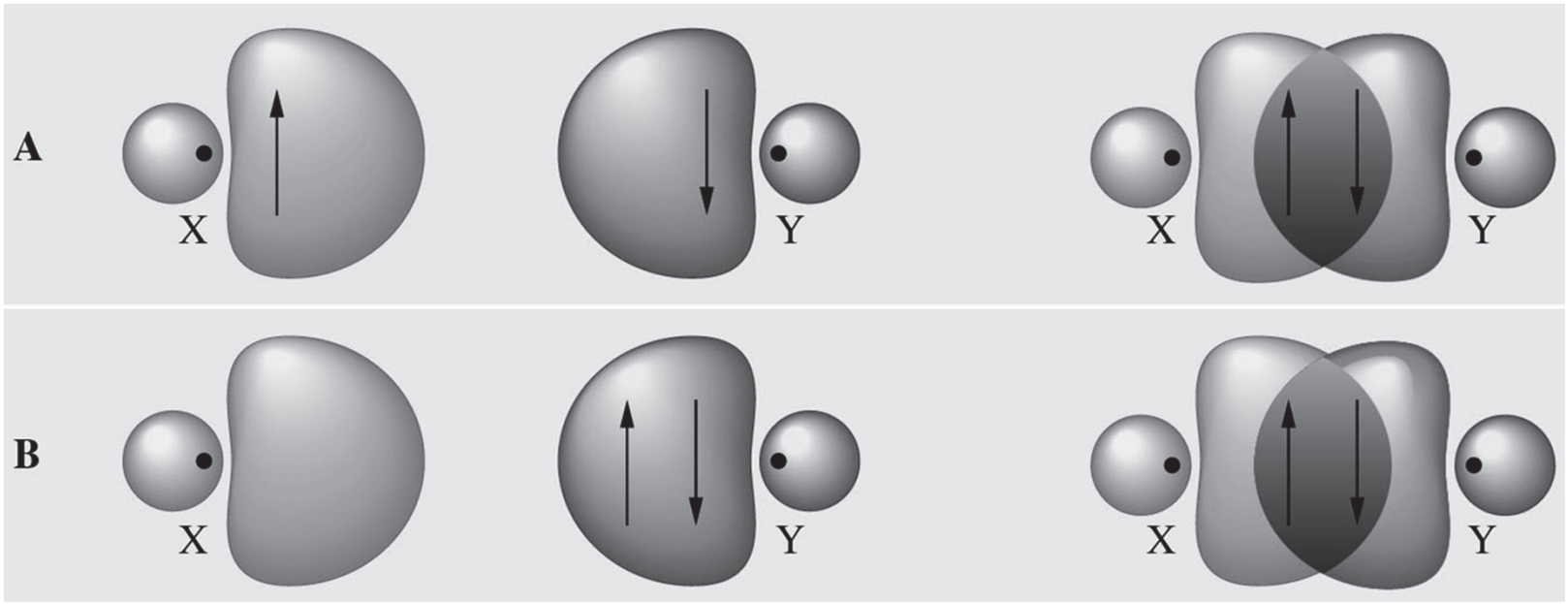
Donor-akceptorová vazba

donor-akceptorová vazba je ekvivalentní kovalentní vazbě



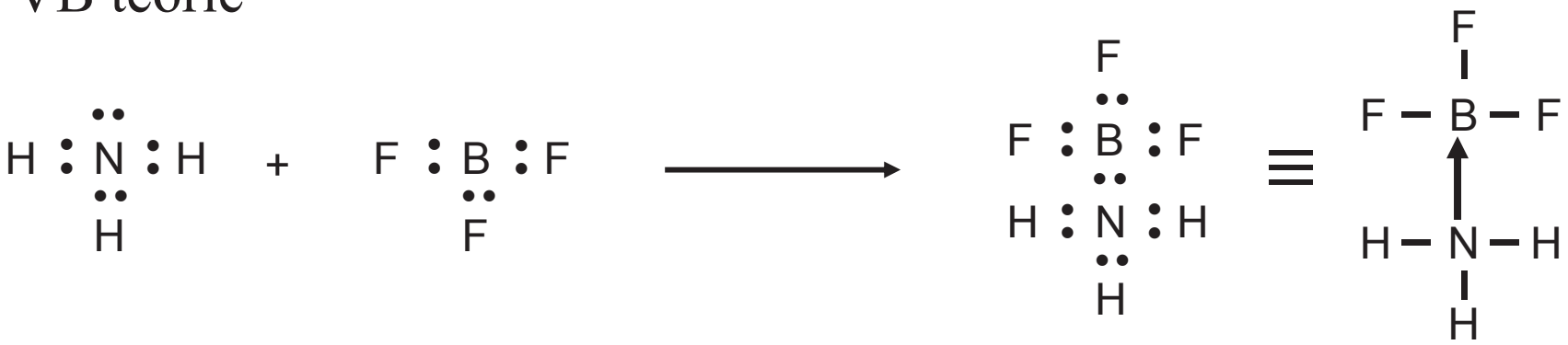
Akceptor
Volný orbital

Donor
Volný e pár

Kovalentní vazba

Donor-akceptorová vazba

VB teorie



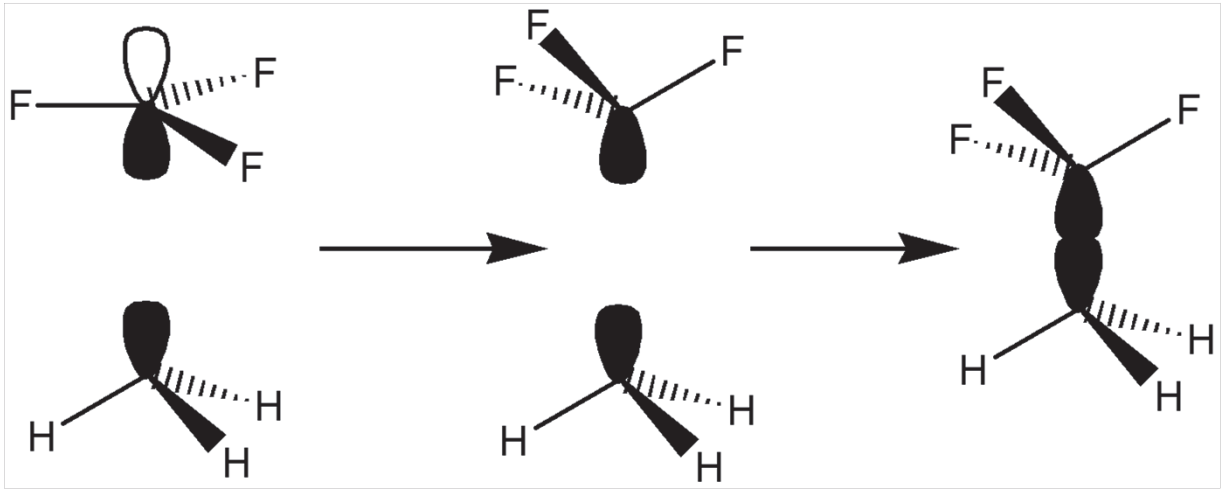
NH_3 + BF_3 ⟶ $H_3N \rightarrow BF_3$

⟶ Donor-akceptorová vazba

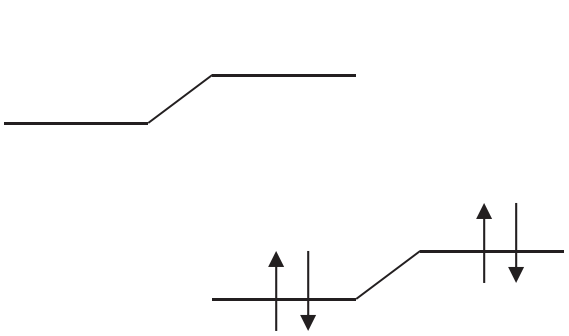
Donor-akceptorová vazba

NH_3 + BF_3 ⟶ $H_3N \rightarrow BF_3$

VB teorie



MO teorie

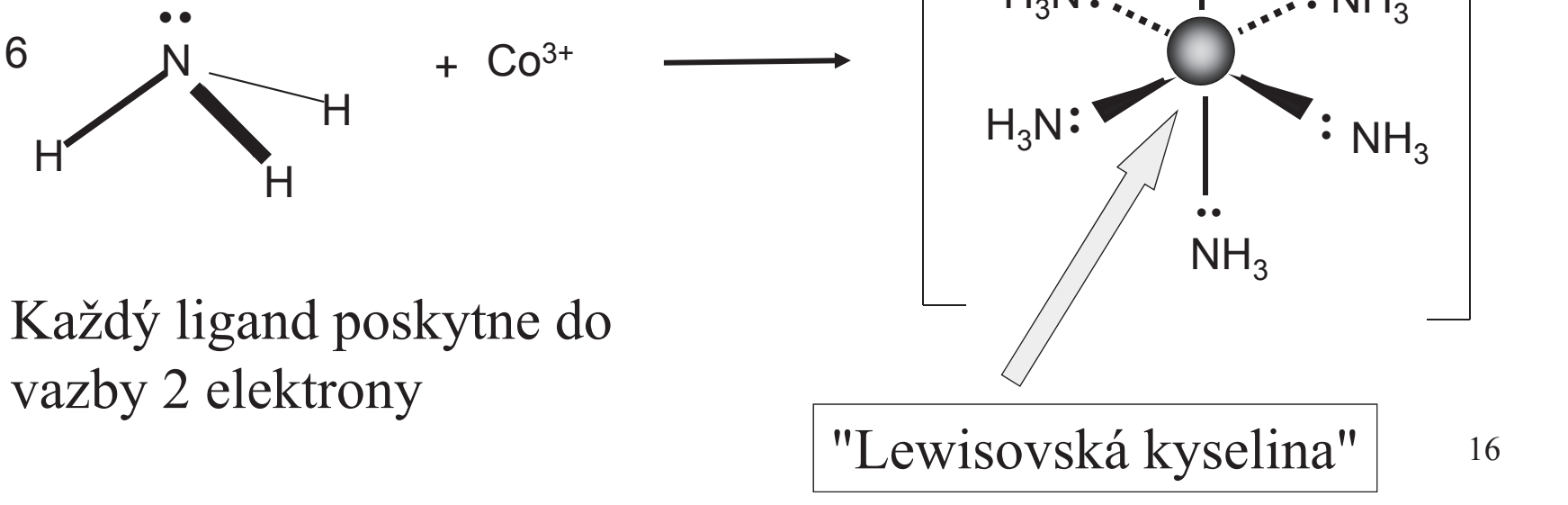


Donor-akceptorová vazba

VB teorie

"Lewisovská báze"

$[Co(NH_3)_6]^{3+}$

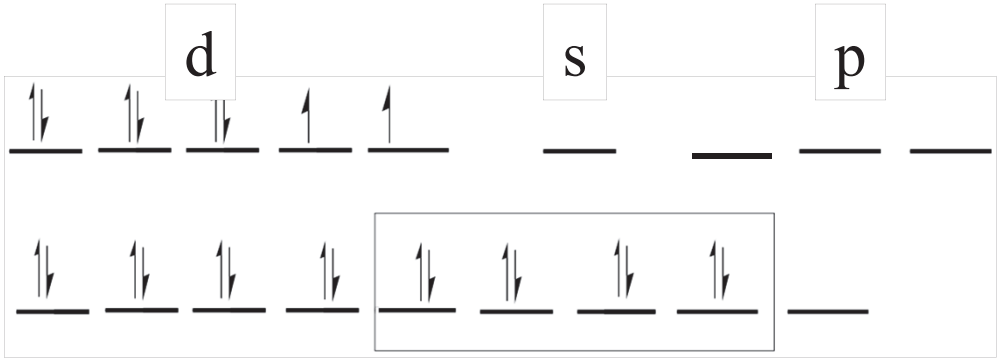


Každý ligand poskytne do vazby 2 elektrony

"Lewisovská kyselina"

Pt^{2+} [Xe] $4f^{14}\,5d^8\,4s^0$

$PtCl_4^{2-}$

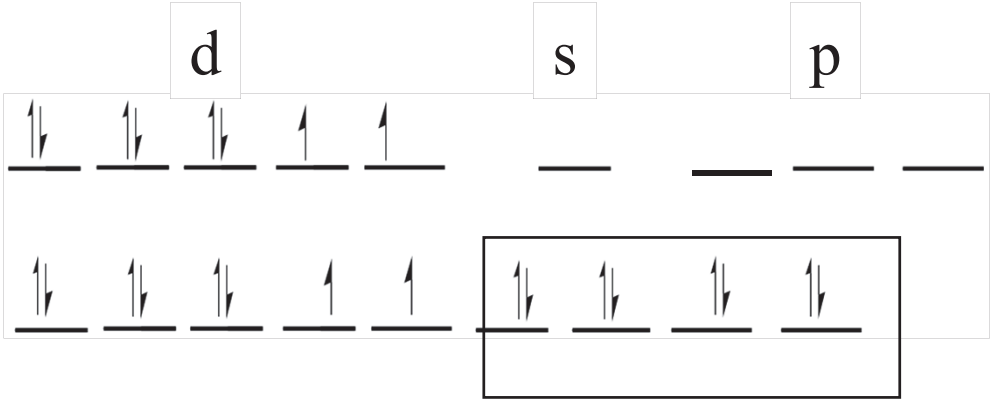


dsp^2 hybridní orbitaly

elektrony z Cl^-, čtvercový

Ni^{2+} [Ar] $3d^8 4s^0$

$NiCl_4^{2-}$

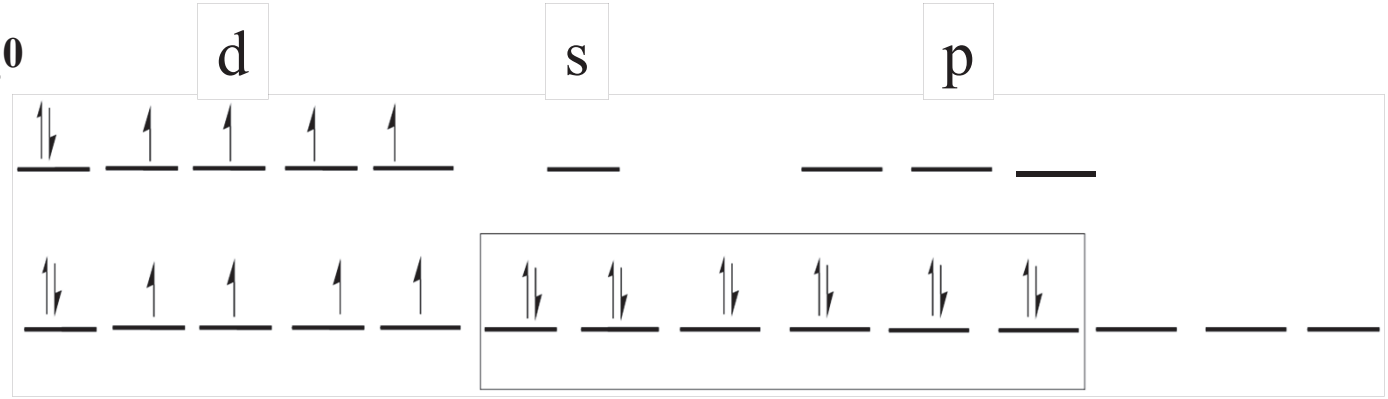


sp^3 hybridní orbitaly

elektrony z Cl^-, tetraedrický

Co^{3+} [Ar] $3d^6 4s^0$

CoF_6^{3-}

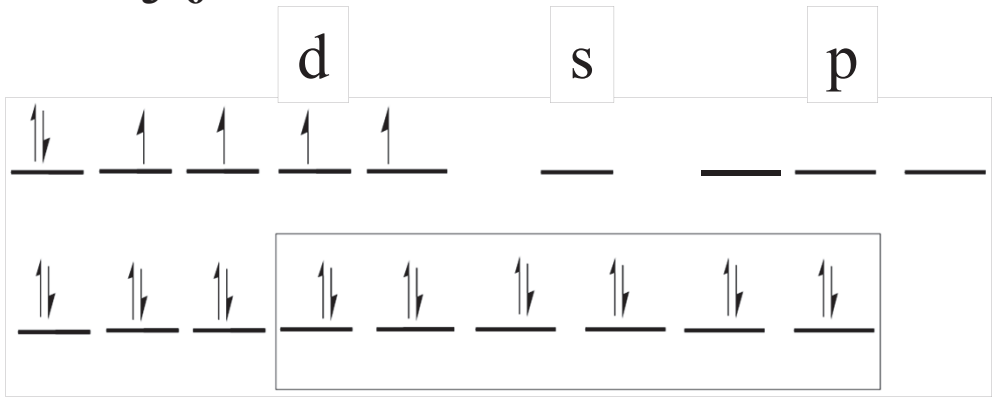


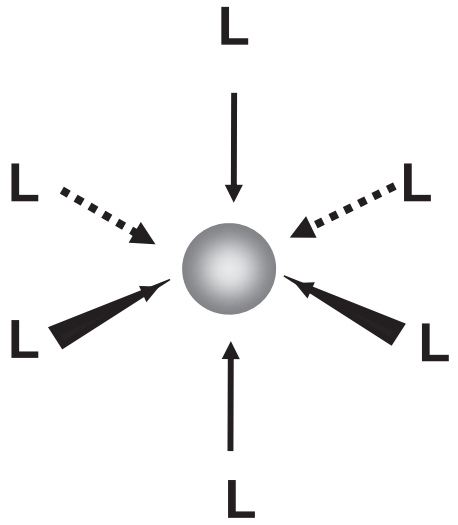
sp^3d^2 hybridní orbitaly

elektrony z F^-, oktaedrický

Co^{3+} [Ar] $3d^6 4s^0$

$Co(NH_3)_6^{3+}$





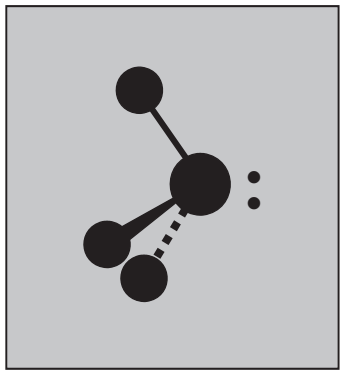
d^2sp^3 hybridní orbitaly

elektrony z NH_3, oktaedrický

Monodentátní ligandy

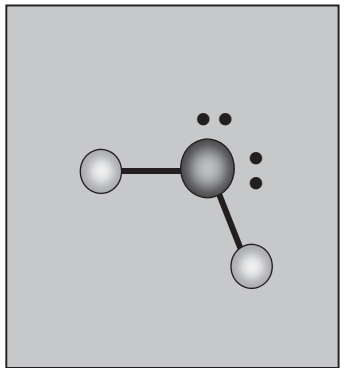
CO
oxid uhelnatý

$Ni(CO)_4$, $Fe(CO)_5$, $Mo(CO)_6$

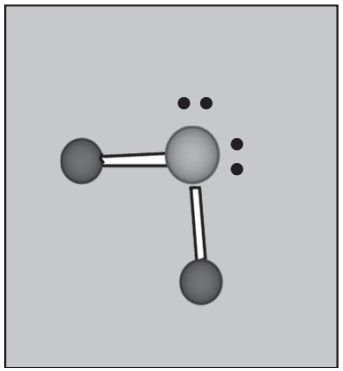


NH_3
amoniak

PPh_3
fosfan



H_2O
voda

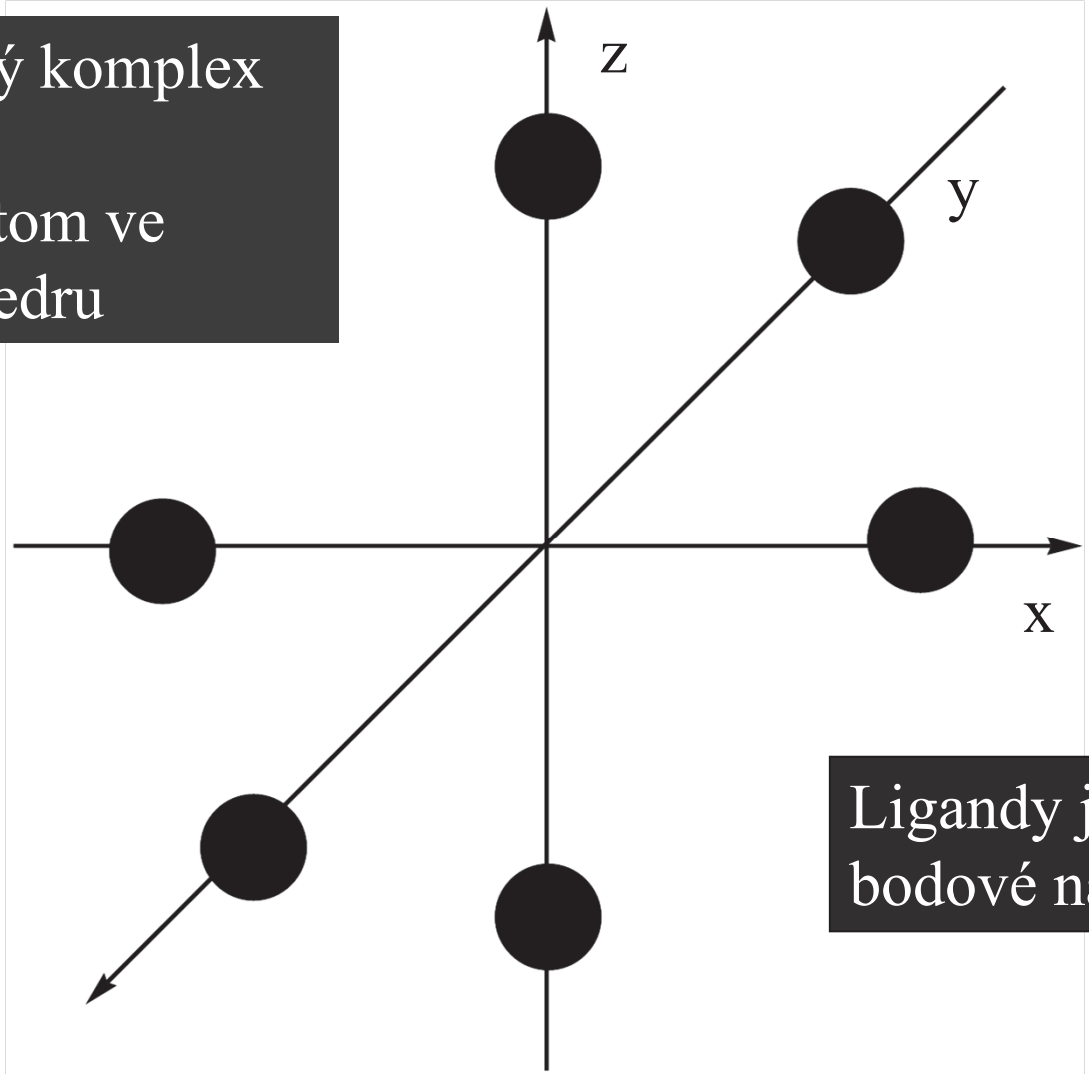


SR_2
thioether

Teorie ligandového pole

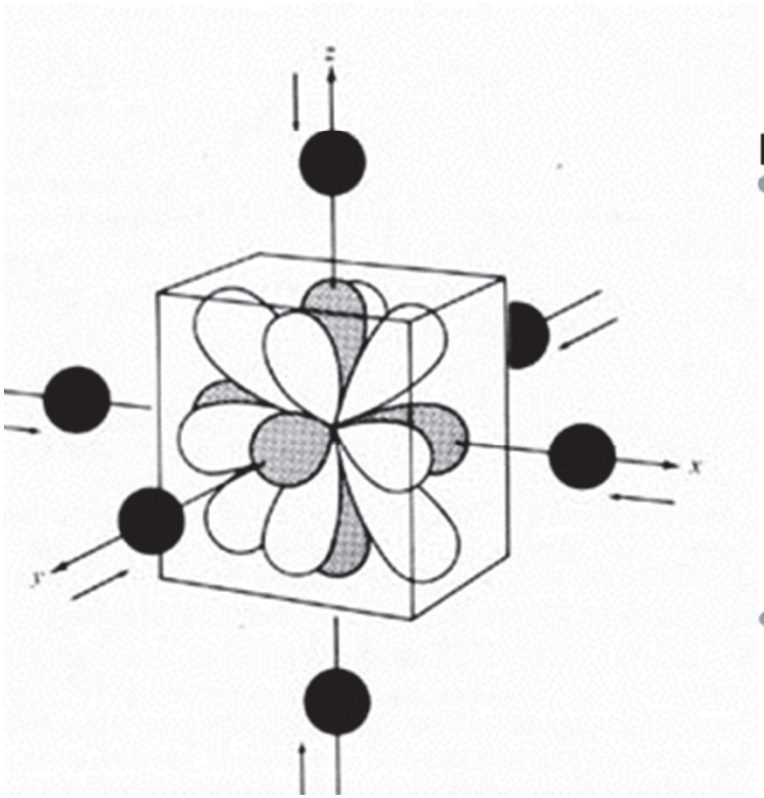
Oktaedrický komplex

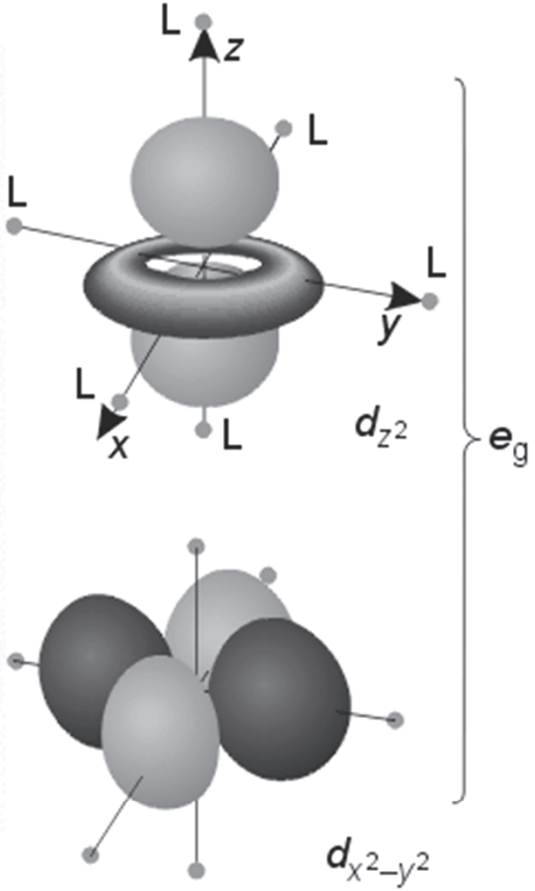
Centrální atom ve středu oktaedru

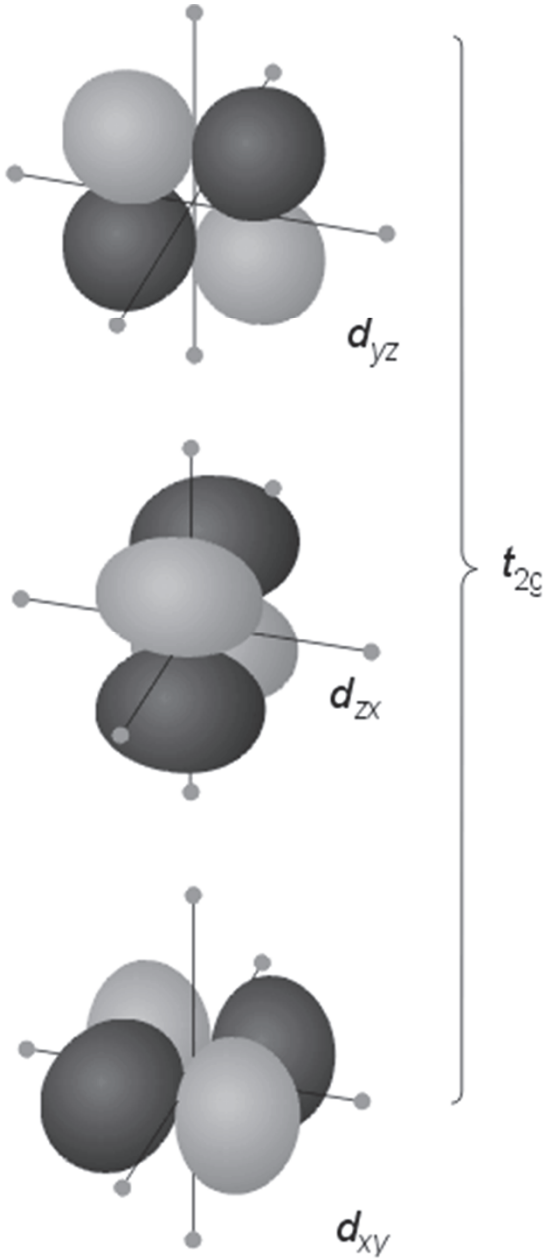


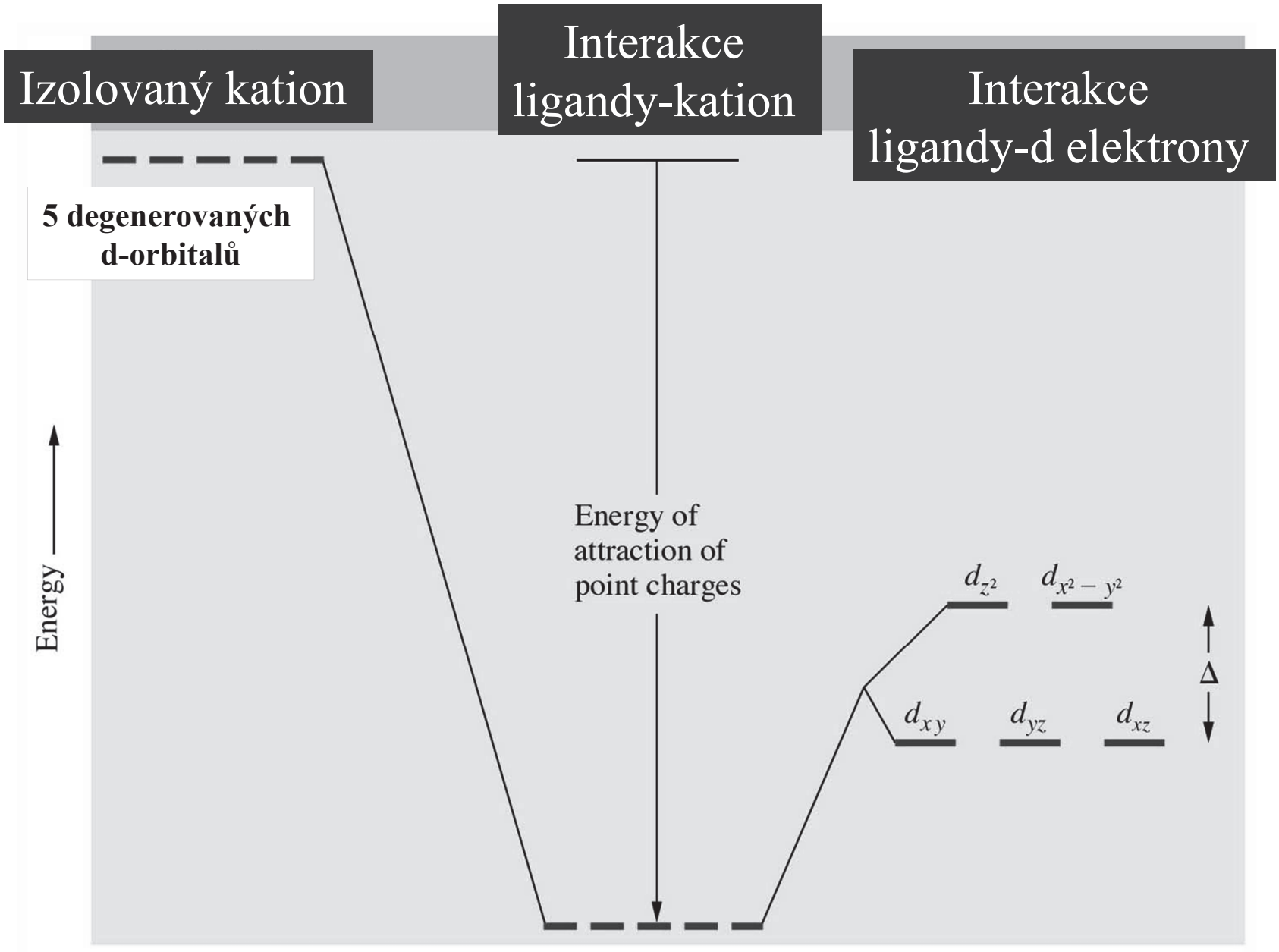
Ligandy jako záporné bodové náboje

d-orbitaly v oktaedrickém poli ligandů



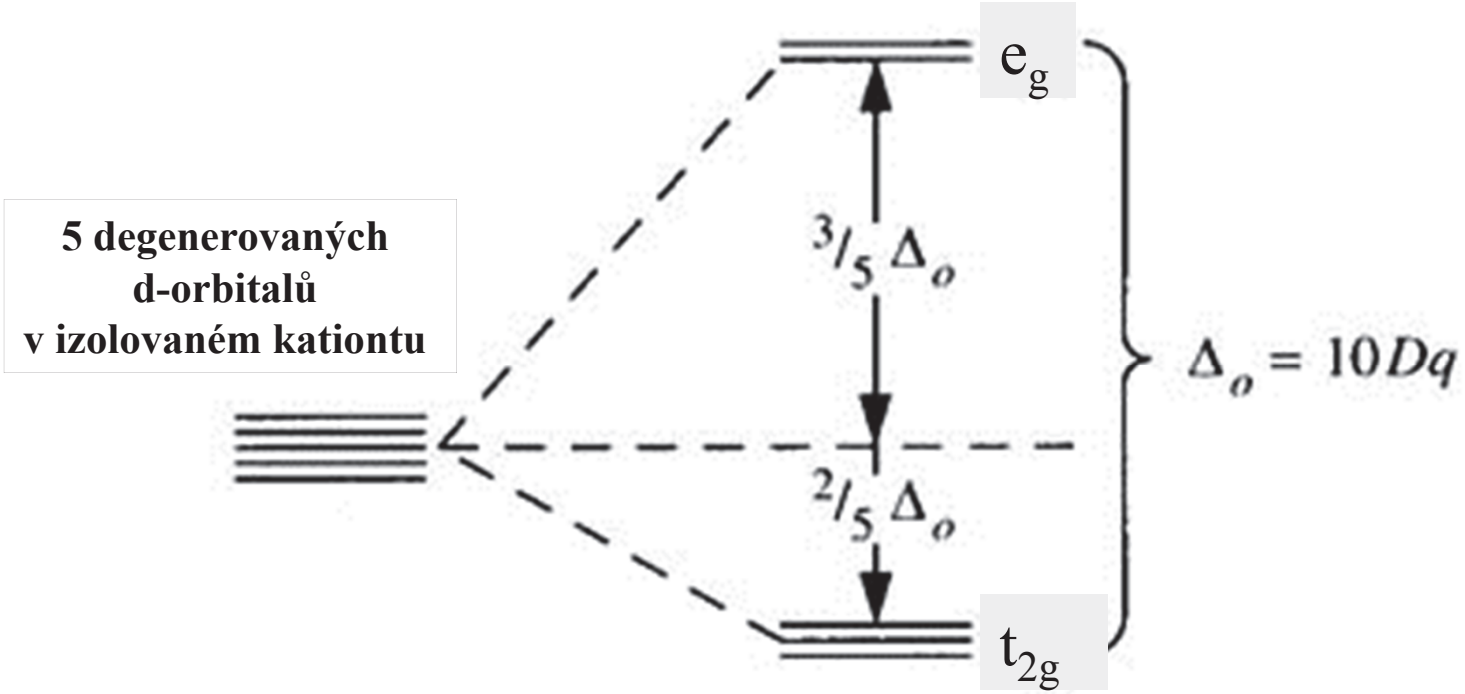





Izolovaný kation
Interakce ligandy-kation
Interakce ligandy-d elektrony
5 degenerovaných d-orbitalů
Energy
Energy of attraction of point charges
d_{z^2}
$d_{x^2-y^2}$
d_{xy}
d_{yz}
d_{xz}
Δ

Rozštěpení d-hladin v O_h poli

Destabilizace 0.6 Δ_o

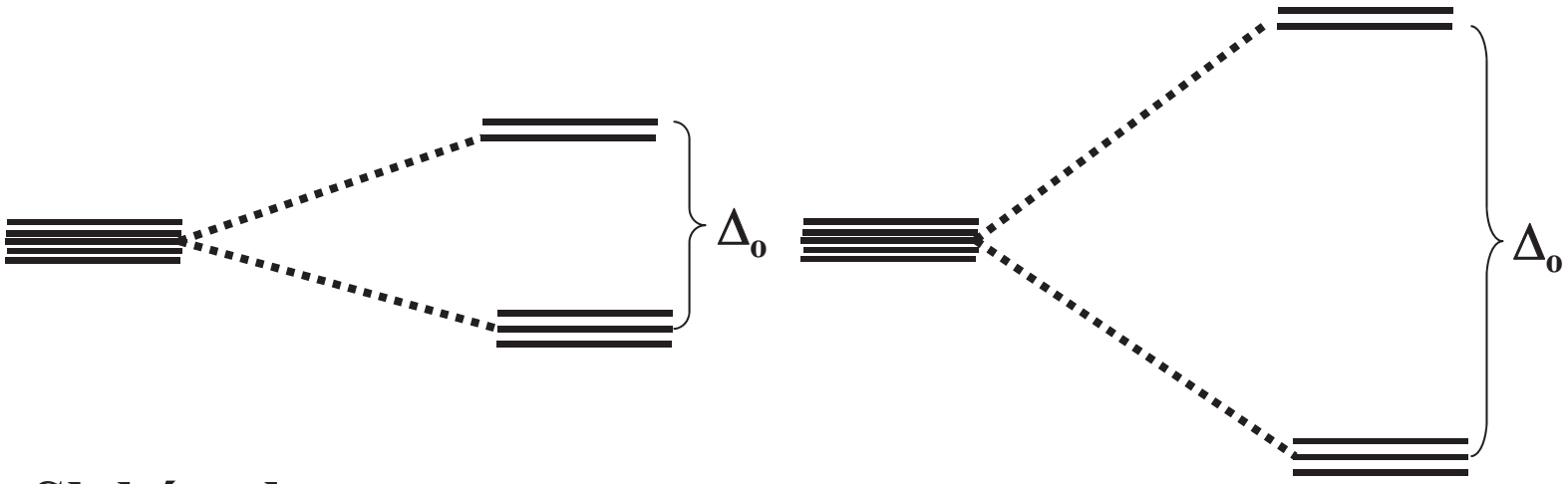


5 degenerovaných d-orbitalů v izolovaném kationtu

Stabilizace 0.4 Δ_o

Stabilizační energie ligandového pole

(CFSE = Crystal Field Stabilization Energy)



Slabé pole

$\Delta_o < P$ (párovací energie)

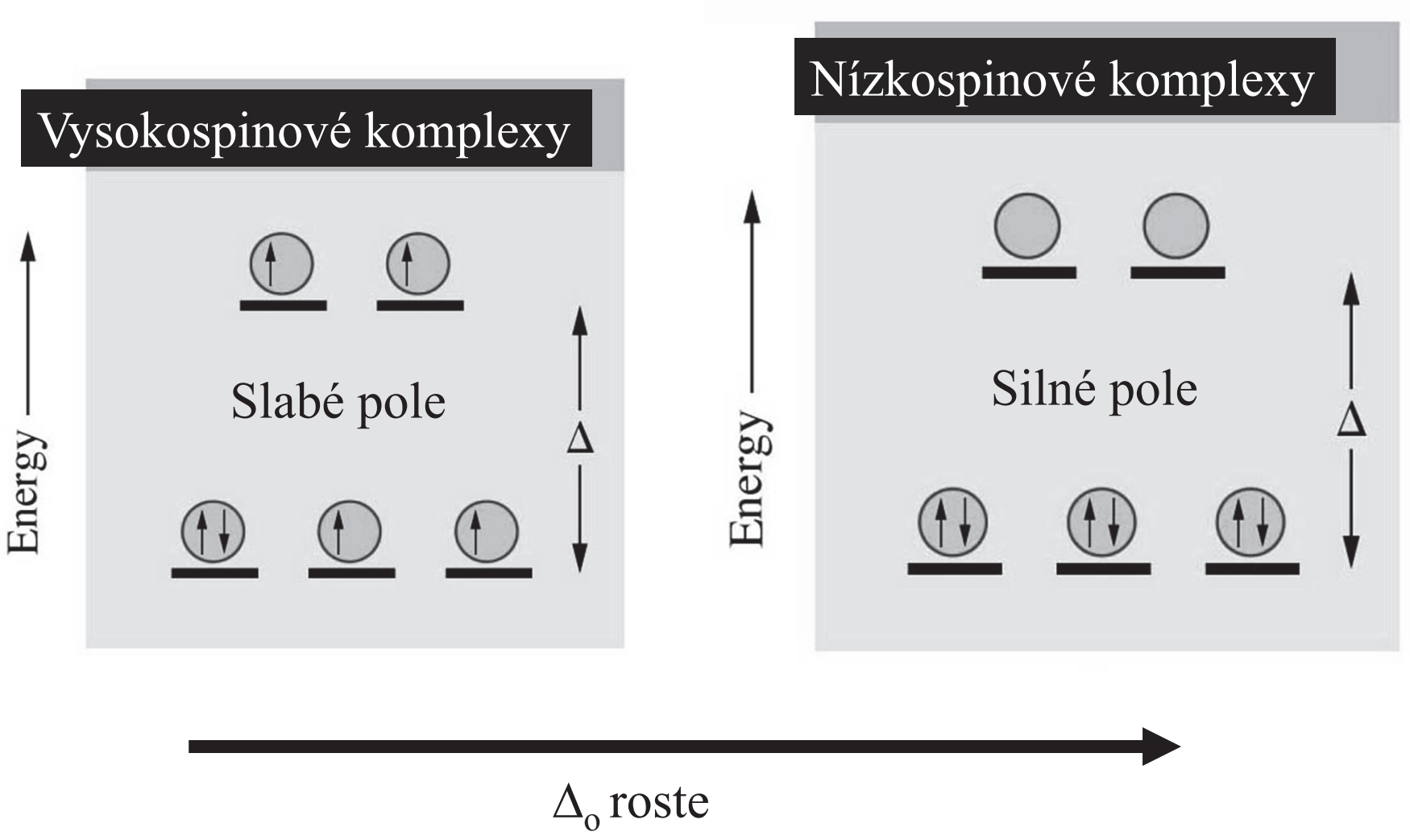
Vysokospinové komplexy

Silné pole

$\Delta_o > P$ (párovací energie)

Nízkospinové komplexy

Stabilizační energie ligandového pole, CFSE



	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

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

e = počet nepárových elektronů

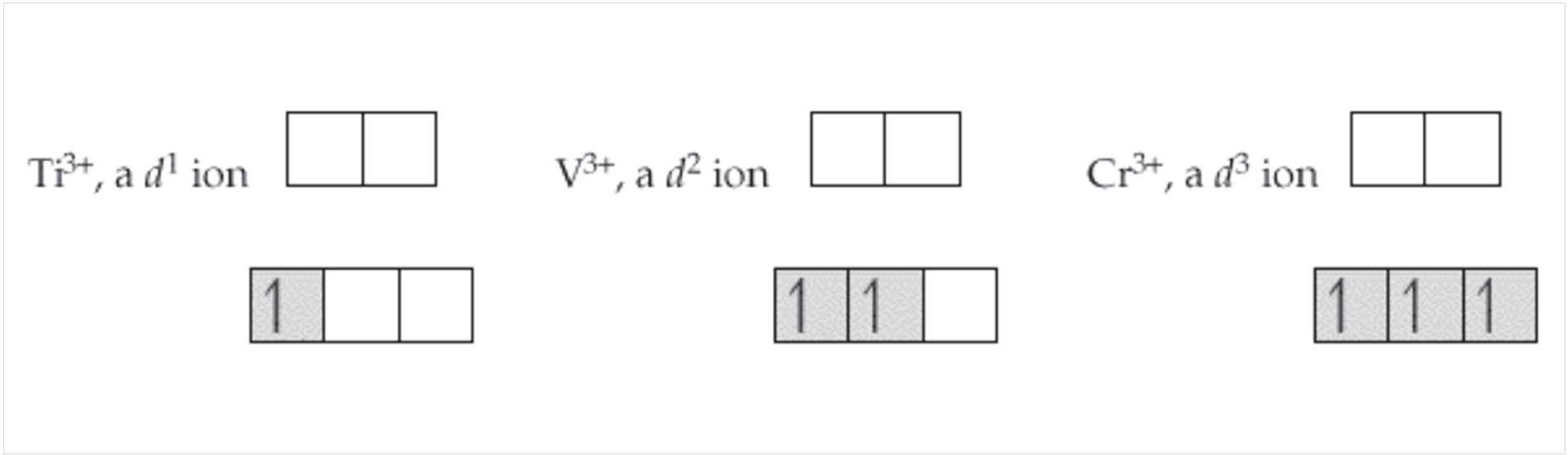
Rozštěpení d-hladin v O_h poli

Obsazení energetických hladin elektrony:

Výstavbový princip

Hundovo pravidlo

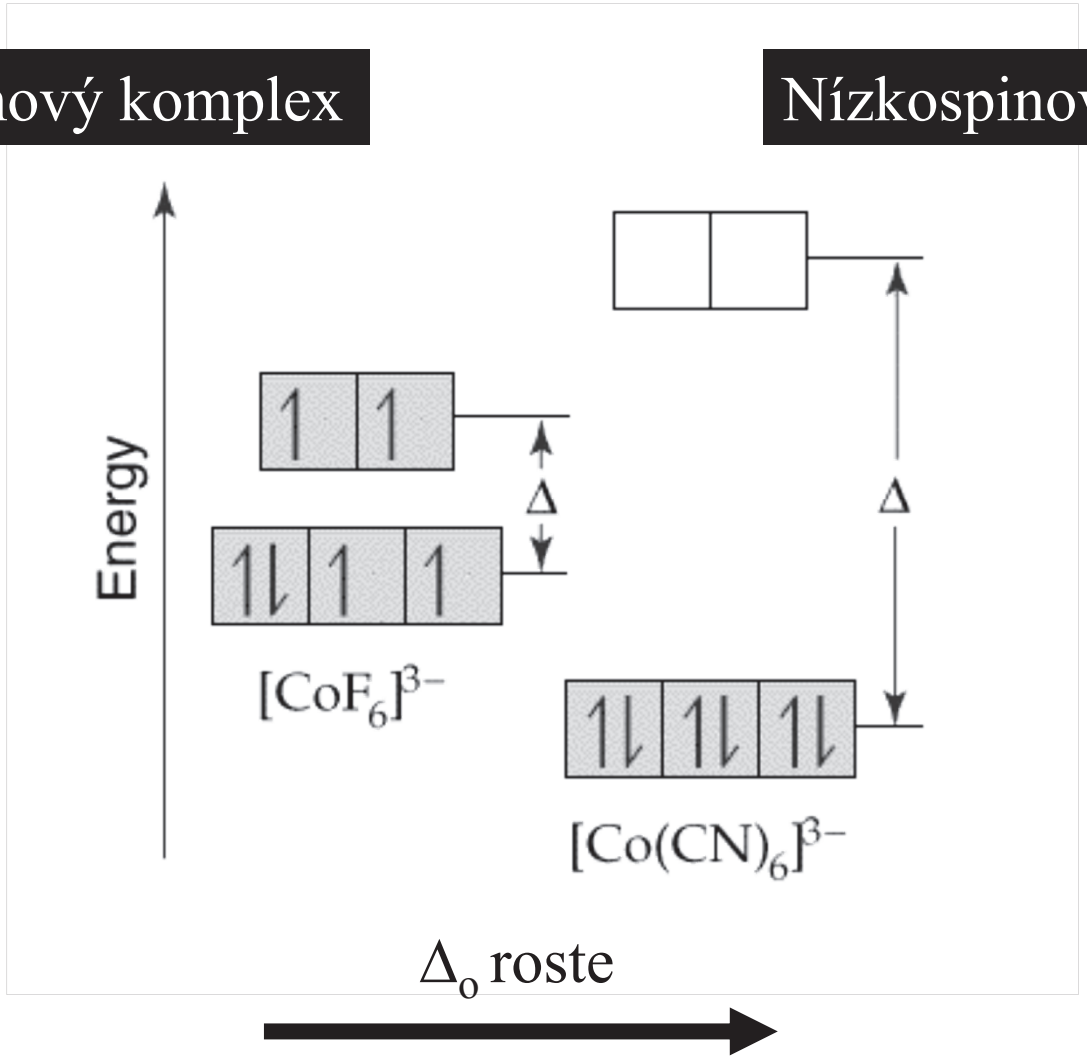
Pauliho princip



Rozštěpení d-hladin v O_h poli

Vysokospinový komplex

Nízkospinový komplex



Slabé pole

Malé štěpení

Silné pole

Velké štěpení

Slabý ligand

Silný ligand

Stabilizační energie ligandového pole

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

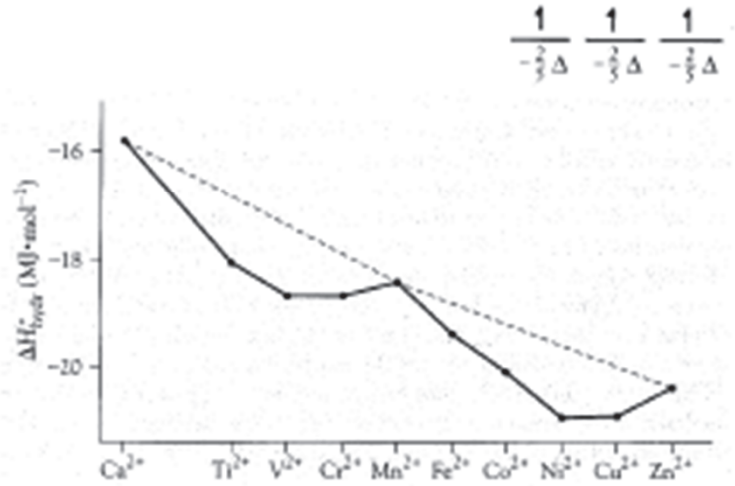
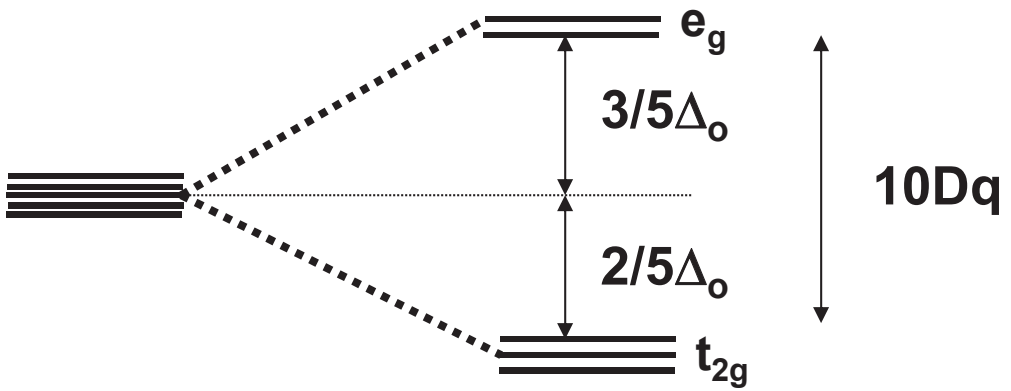


Table 18.3 Crystal field stabilization energies (CFSE) for the dipositive, high spin ions of various Period 4 metals

Ion	Configuration	CFSE
Ca^{2+}	d^0	$-0.0\,\Delta_{oct}$
—	d^5	$-0.4\,\Delta_{oct}$
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}	$-0.0\,\Delta_{oct}$

d^0 d^5 d^{10}

Rozštěpení d-hladin v O_h poli

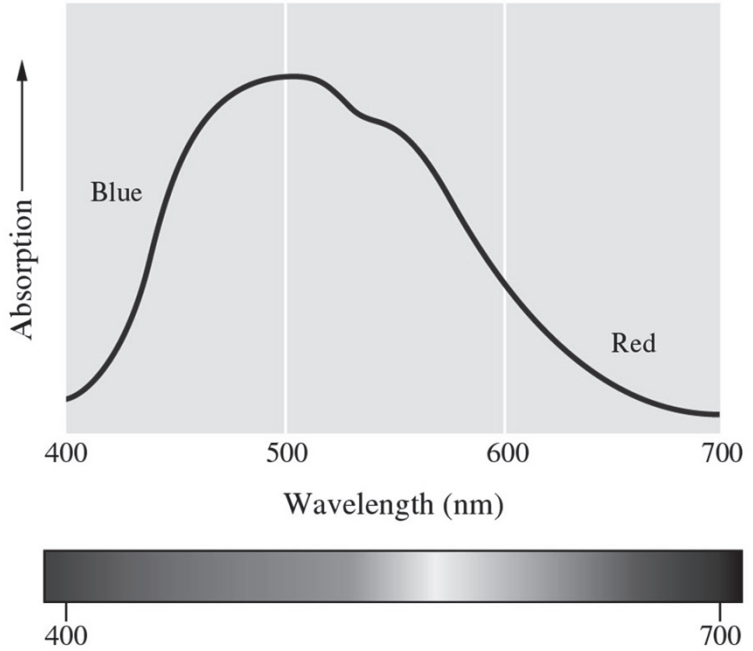


$[Ti(H_2O)_6]^{3+}$
d^1

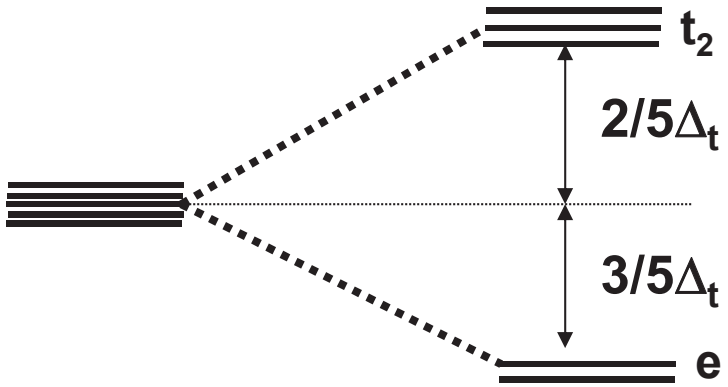
$t_{2g}^1 e_g^0 \longrightarrow t_{2g} e_g^1$

růžový

243 kJ mol^{-1} (Δ_o)



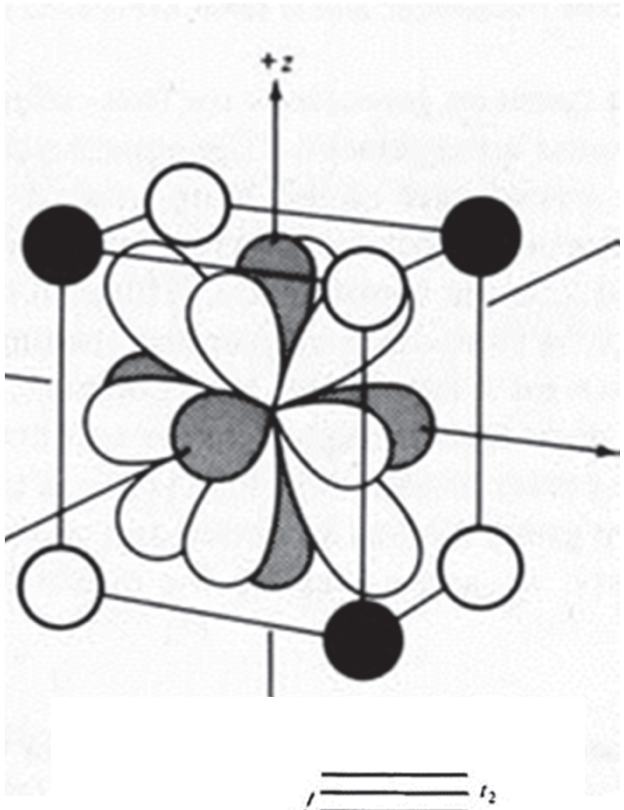
Rozštěpení d-hladin v T_d poli

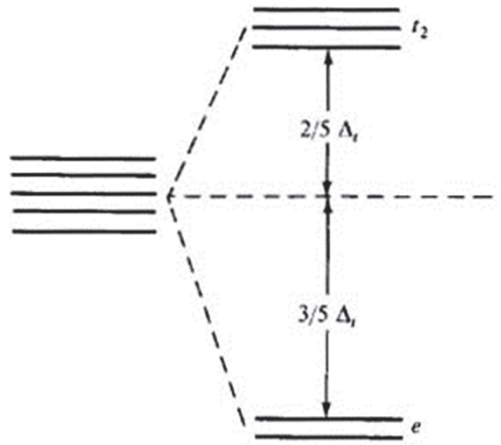


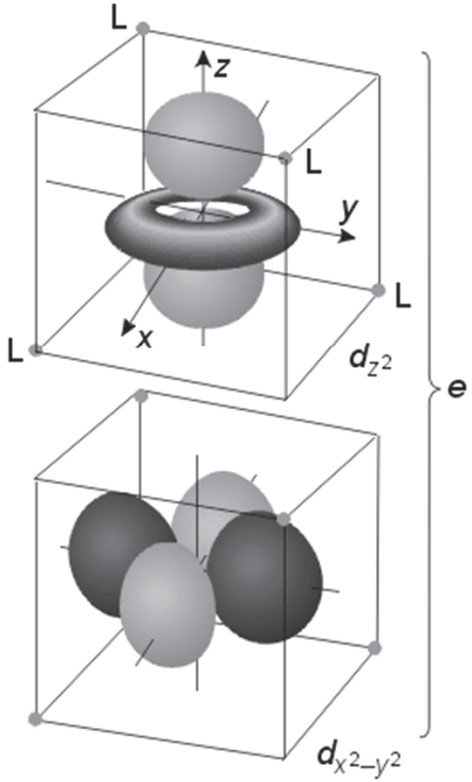
$\Delta_t = 4/9\ \Delta_o$

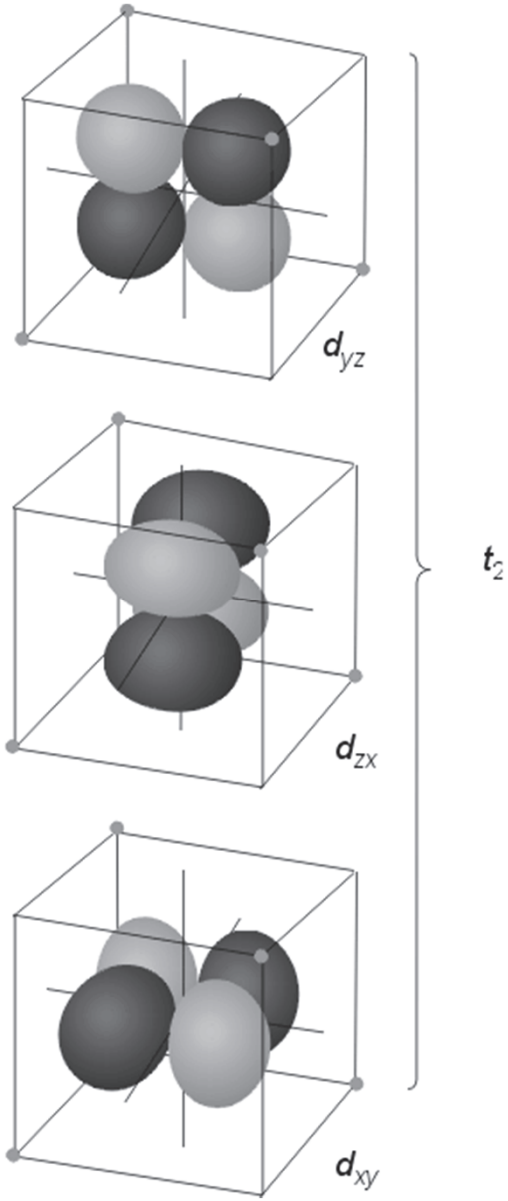
T_d komplexy jsou vždy vysokospinové
žádný d-orbital nemíří přímo k ligandům (jako u O_h)
slabší interakce

d-orbitaly v tetraedrickém poli ligandů

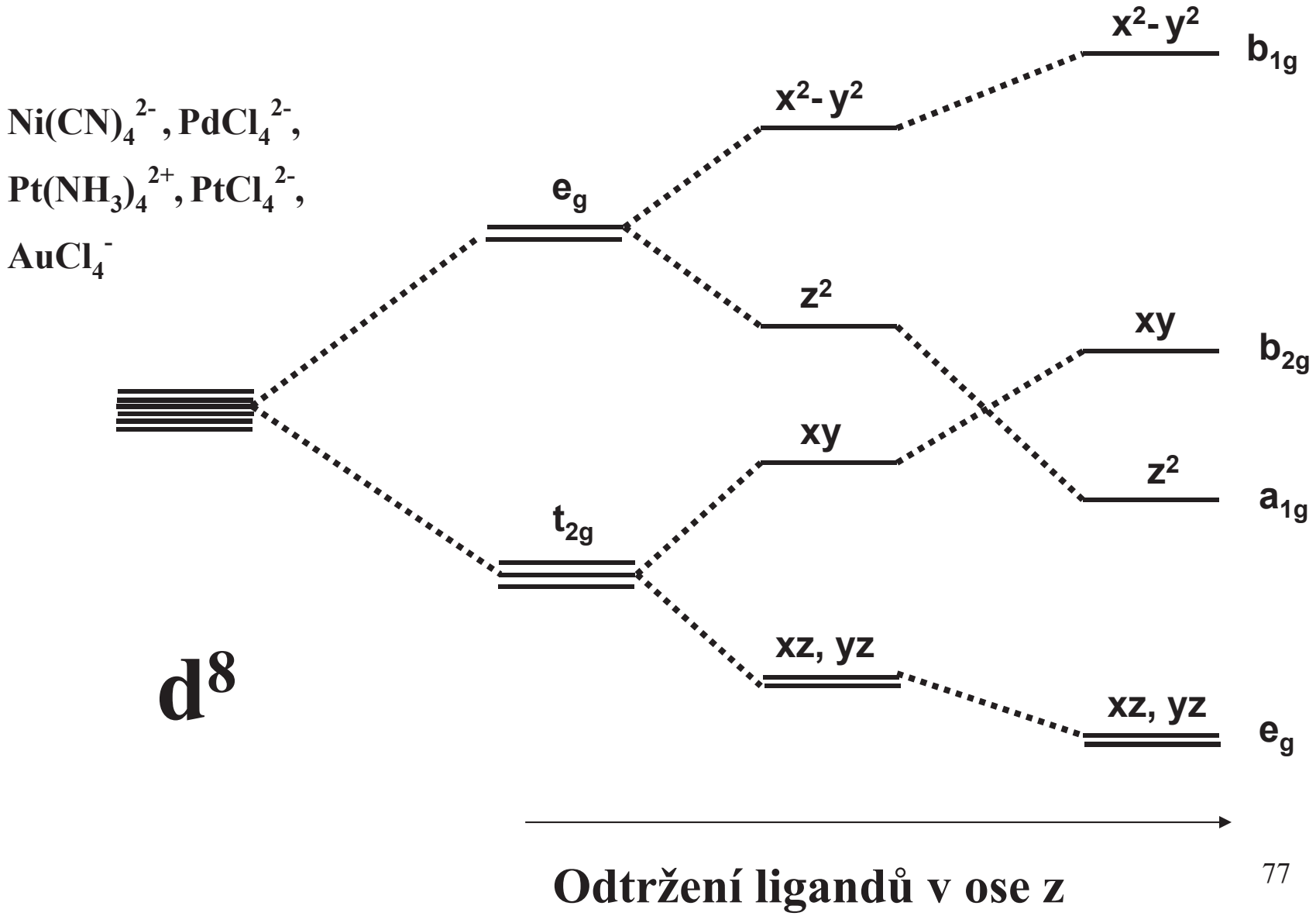








Rozštěpení d-hladin v čtvercovém poli (d^8)



18-ti elektronové pravidlo

Počet d-elektronů neutrálního kovu
+ 2 e neutrální ligandy
+ 1 e aniontové ligandy součet 18 pro stabilní komplexy

$Cr(CO)_6$	Cr	d^6
	$6 \times CO$	$6 \times 2 = 12$
	celkem	18

$[Co(NH_3)_3Cl_3]$	Co	d^9
	$3 \times NH_3$	$3 \times 2 = 6$
	$3 \times Cl$	$3 \times 1 = 3$
	celkem	18

Vliv ligandů na vlastnosti komplexů

$[Ni(H_2O)_6]^{+2}$	$[Ni(en)(H_2O)_4]^{+2}$	$[Ni(en)_2(H_2O)_2]^{+2}$	$[Ni(en)_3]^{+2}$
green	**green/blue**	**blue**	**purple**

en = ethylendiammin

Vliv ligandů na vlastnosti komplexů