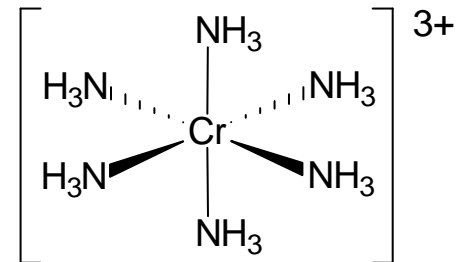


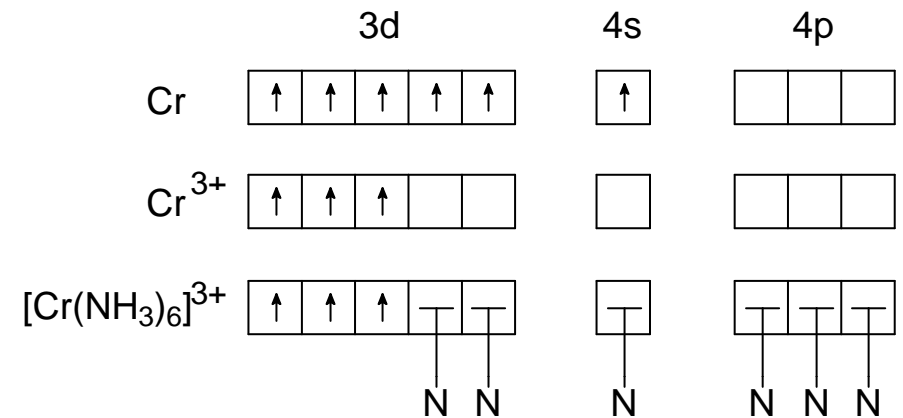
Die Bindung in Übergangsmetallkomplexen

Klassische Koordinationschemie (Alfred Wernersche)

- Valenzstruktur-Theorie (Valenzbindungstheorie)
- **Ligandenfeld-Theorie**
- Molekülorbital-Theorie

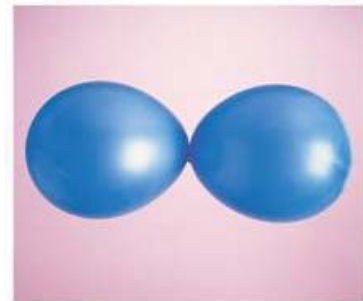


	II	d-Block										III
		3	4	5	6	7	8	9	10	11	12	
3	Mg											Al
4	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
5	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
6	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl
7	Ra	Lr	Unq									



d^2sp^3 Hybridisierung

Maximierung repulsiver Wechselwirkungen um das Metall



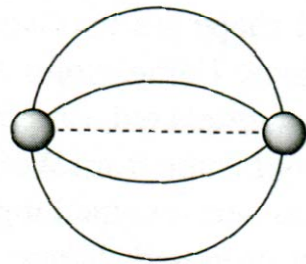
(a) Zwei Ballons nehmen eine lineare Anordnung ein.



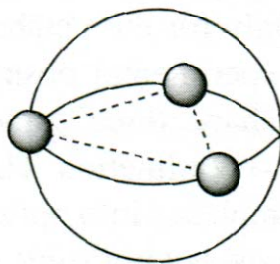
(b) Drei Ballons nehmen eine trigonal ebene Anordnung ein.



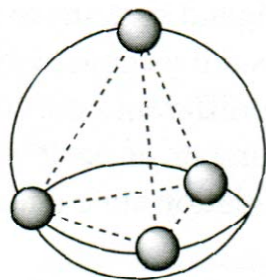
(c) Vier Ballons nehmen eine tetraedrische Anordnung ein.



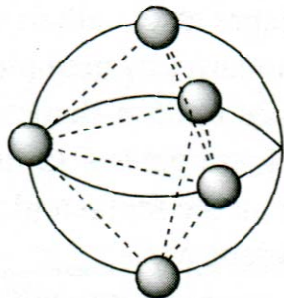
two point charges
linear



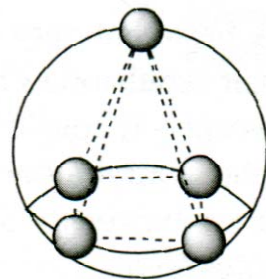
three point charges
trigonal planar



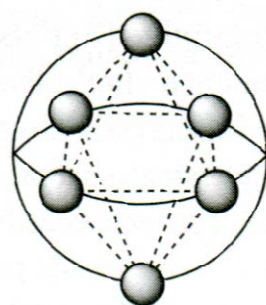
four point charges
tetrahedral



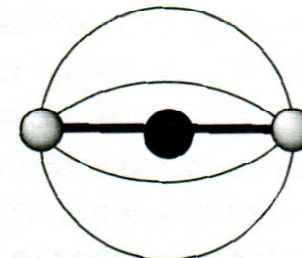
five point charges
trigonal bipyramidal



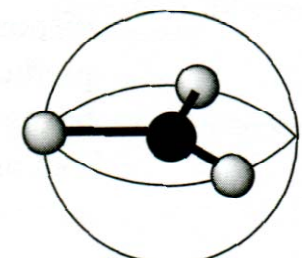
five point charges
square pyramidal



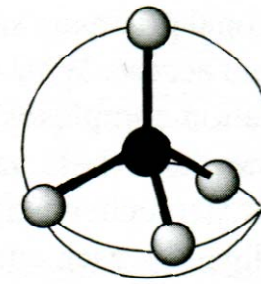
six point charges
octahedral



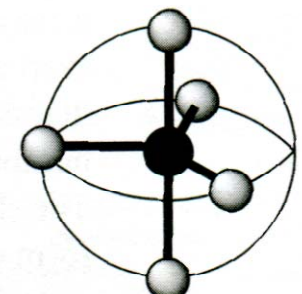
two-coordination
linear



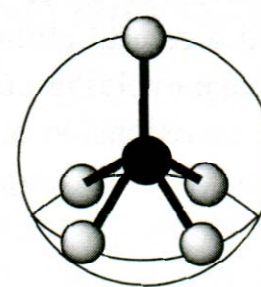
three-coordination
trigonal planar



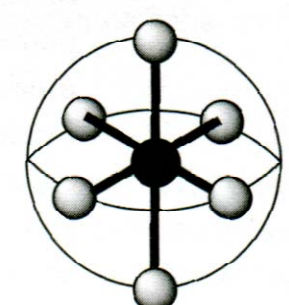
four-coordination
tetrahedral



five-coordination
trigonal bipyramidal



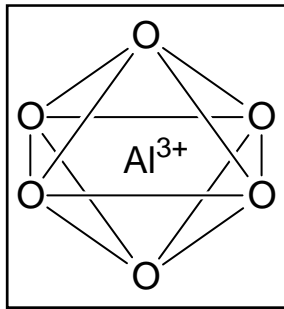
five-coordination
square pyramidal



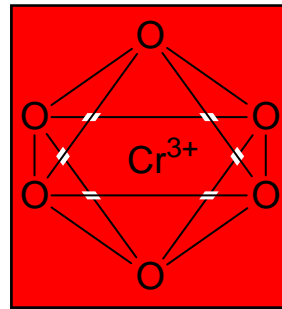
six-coordination
octahedral

Kristallfeld-Theorie

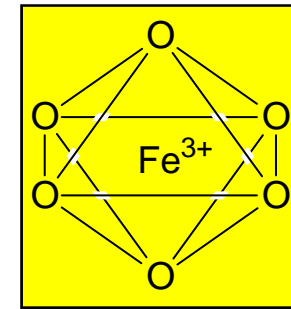
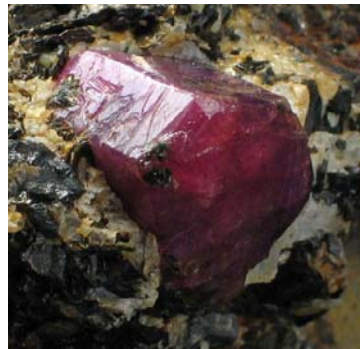
Kristallfeld-Theorie wurde zunächst entwickelt, um die Farbe von Feststoffen zu erklären.



Korund ($\alpha\text{-Al}_2\text{O}_3$)



Rubin ($\text{Al}_2\text{O}_3 \cdot x \text{Cr}_2\text{O}_3$)

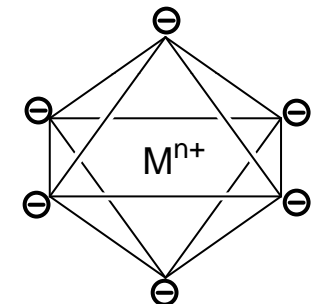


Topas ($\text{Al}_2\text{O}_3 \cdot x \text{Fe}_2\text{O}_3$)



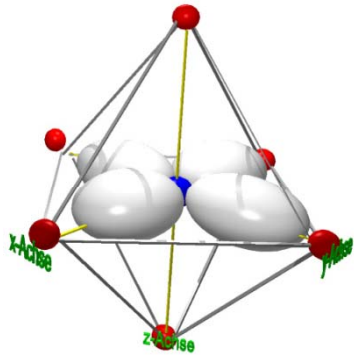
Rein elektrostatisches Modell:

- Liganden und Zentralatom als sich gegenseitig beeinflussende Punktladungen (keine kovalenten Anteile, keine Orbitalüberlappungen).
- Das elektrische Feld der Liganden beeinflusst die Orbitale des Zentralatoms - die Entartung der d-Orbitale wird aufgehoben.
- Nur Betrachtung der d-Orbitale - restliche Orbitale bilden gefüllte Schalen.

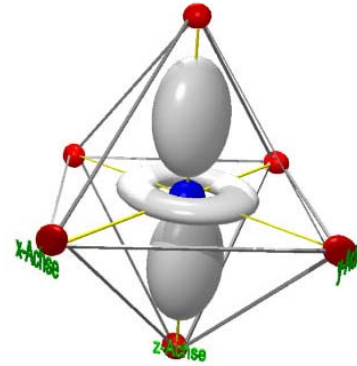


Oktaederfeld

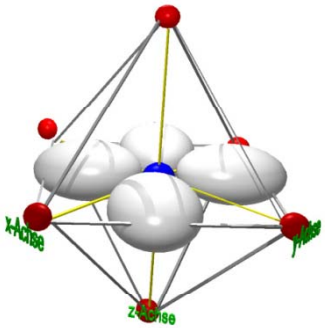
$d_{x^2-y^2}$



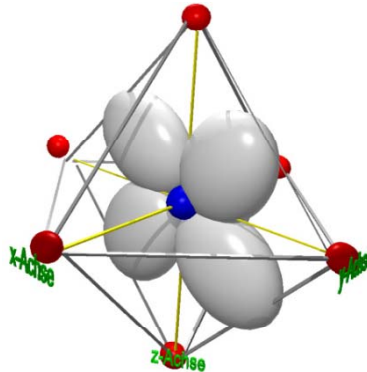
d_{z^2}



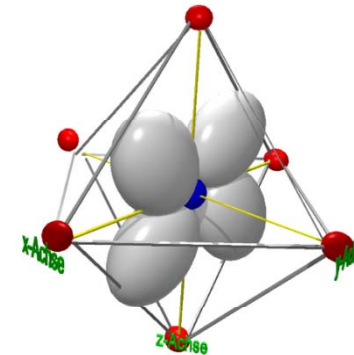
d_{xy}



d_{xz}



d_{yz}

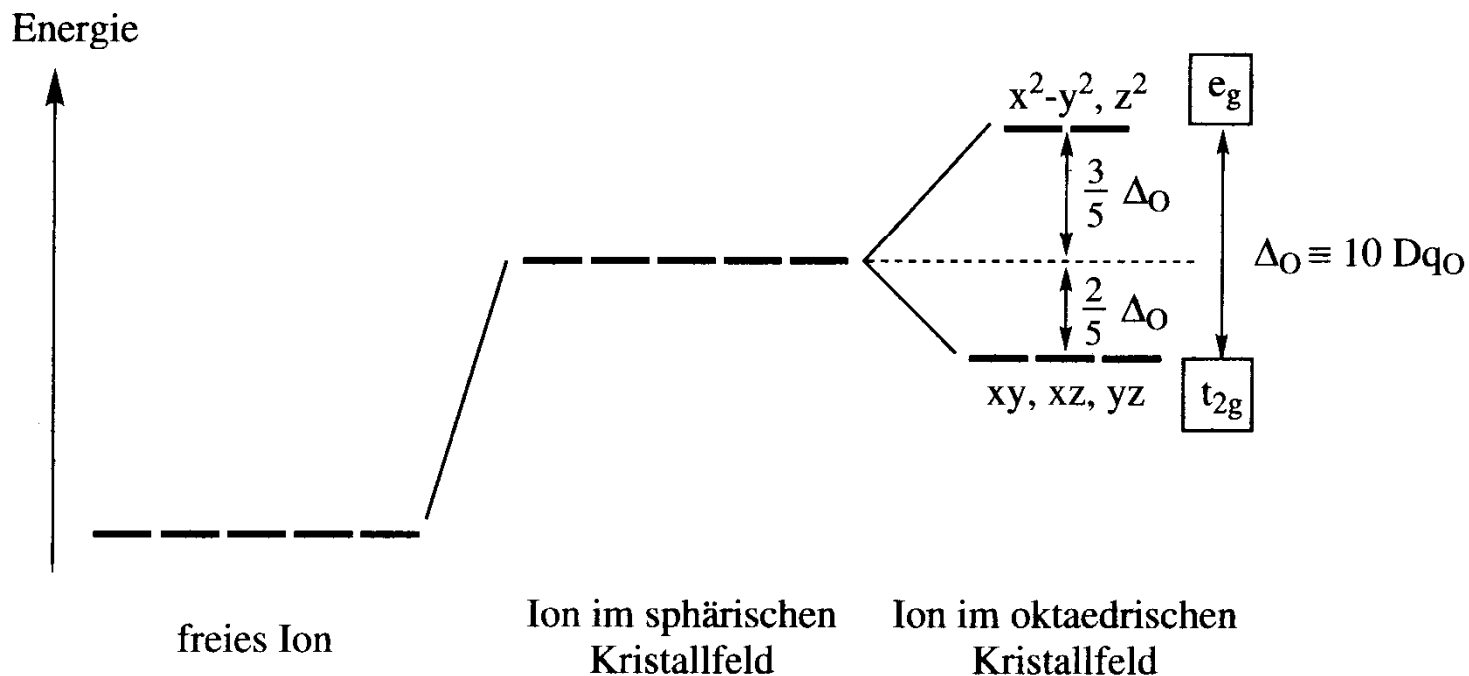


Annäherung der Liganden

an das freie Zentralion aus den Richtungen x , $-x$, y , $-y$, z , $-z$:

- $d_{x^2-y^2}$, d_{z^2} -AO's liegen auf den Achsen \rightarrow große elektrostatische Abstoßung.
- d_{xy} , d_{xz} , d_{yz} -AO's liegen zwischen den Achsen \rightarrow geringe elektrostatische Abstoßung.

Orbitalaufspaltung im Oktaederfeld



$$E = h\nu = h \frac{c}{\lambda} = hc\tilde{\nu}$$

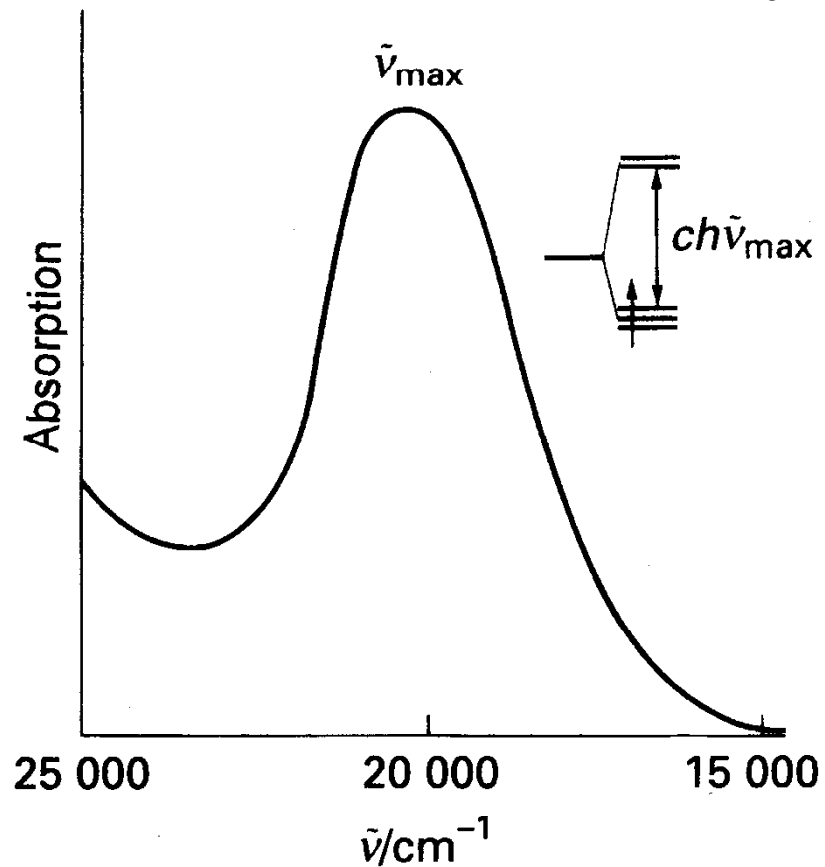
Die Oktaederfeldaufspaltung $\Delta_O = 10 Dq_O$ liegt in der Größenordnung von

$\Delta_O =$	84	-	480	kJ/mol
$\tilde{\nu} =$	7000	-	40000	cm^{-1}
$\lambda =$	1430	-	250	nm

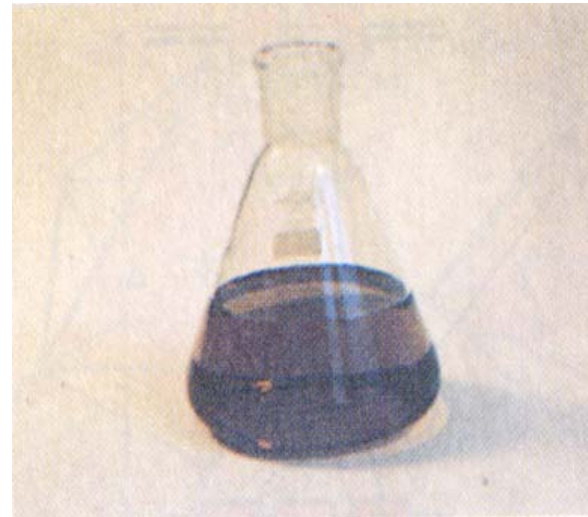
d¹-Elektronenkonfiguration

Bei d¹-Elektronenkonfigurationen ist die direkte Messung von $\Delta_O = 10 Dq$ möglich.

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



$$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu}$$



Übergang $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$

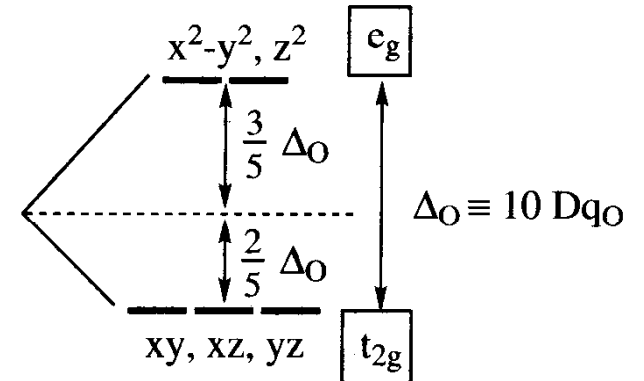
$\tilde{\nu}$	\approx	20000	cm^{-1}
λ	\approx	500	nm
Δ_O	\approx	240	kJ/mol

$[\text{ReF}_6]$: $\Delta_O \equiv 32500 \text{ cm}^{-1}$

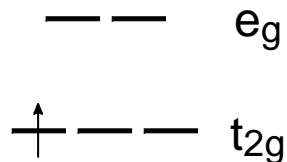
Elektronenbesetzung der Orbitale beim Oktaeder

Ligandenfeldstabilisierungsenergie (LFSE):

Energiegewinn gegenüber dem Ion im sphärischen Feld

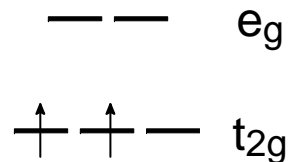


d¹ (Ti³⁺)



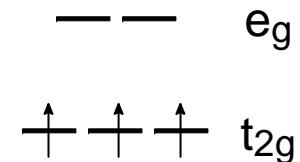
LFSE = $-0,4 \Delta_O = -4 Dq_O$

d² (V³⁺)



LFSE = $-8 Dq_O$

d³ (Cr³⁺)



LFSE = $-12 Dq_O$

1. Hundsche Regel: Regel der maximalen Multiplizität

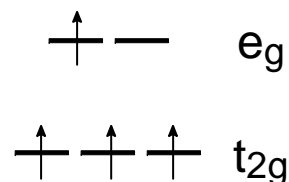
Elektronenbesetzung der Orbitale beim Oktaeder

Spinpaarungsenergie (P):

Energie, die aufgebracht werden muss, um zwei Elektronen in einem Orbital unterzubringen (1. Coulombsche Abstoßung; 2. Verlust an Austauschenergie).

d^4 (Cr^{2+})

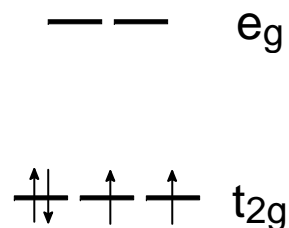
high-spin



$$\text{LFSE} = -6 Dq_0$$

$$\Delta_0 < P$$

low-spin

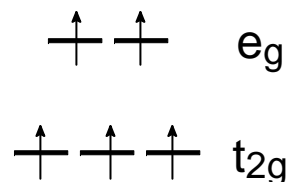


$$\text{LFSE} = -16 Dq + P$$

$$\Delta_0 > P$$

d^5 (Mn^{2+} , Fe^{3+})

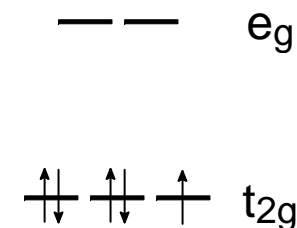
high-spin



$$\text{LFSE} = 0$$

$$\Delta_0 < P$$

low-spin



$$\text{LFSE} = -20 Dq + 2 P$$

$$\Delta_0 > P$$

Elektronenbesetzung der Orbitale beim Oktaeder

d^6 (Fe²⁺, Co³⁺)

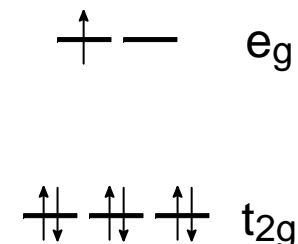
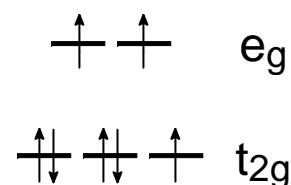
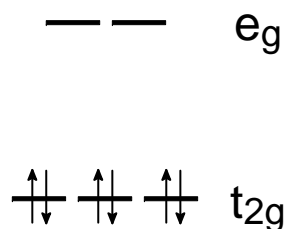
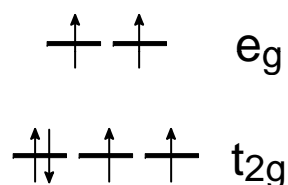
d^7 (Co²⁺)

high-spin

low-spin

high-spin

low-spin



LFSE = -4 Dq_o

LFSE = -24 Dq + 2 P

LFSE = -8 Dq_o

LFSE = -18 Dq + P

$\Delta_o < P$

$\Delta_o > P$

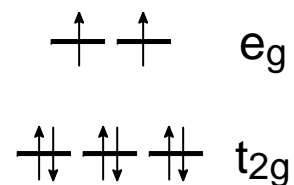
$\Delta_o < P$

$\Delta_o > P$

Für d⁴-, d⁵-, d⁶-, d⁷-Konfigurationen sind high- und low-spin-Anordnungen möglich.

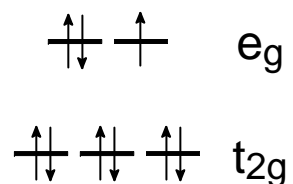
Elektronenbesetzung der Orbitale beim Oktaeder

d⁸ (Ni²⁺)



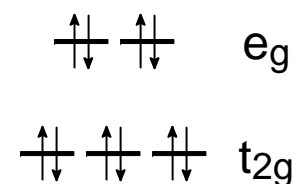
$$\text{LFSE} = -12 Dq_o$$

d⁹ (Cu²⁺)



$$\text{LFSE} = -6 Dq_o$$

d¹⁰ (Zn²⁺)



$$\text{LFSE} = 0 Dq_o$$

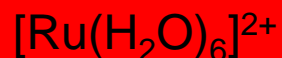
Für d¹-, d²-, d³- sowie für d⁸- d⁹-, d¹⁰-Konfigurationen kann keine Unterscheidung zwischen high- und low-spin Anordnung getroffen werden.

Für d⁴-, d⁵-, d⁶-, d⁷-Konfigurationen sind high- und low-spin-Anordnungen möglich.

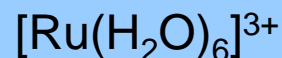
Faktoren, die Δ_o beeinflussen

1. Die Oxidationsstufe des Metallions

Δ_o nimmt mit steigender Oxidationsstufe des Metallions zu.



$$\Delta_o \equiv 19800 \text{ cm}^{-1}$$



$$\Delta_o \equiv 28600 \text{ cm}^{-1}$$



$$\Delta_o \equiv 15600 \text{ cm}^{-1}$$



$$\Delta_o \equiv 22000 \text{ cm}^{-1}$$

2. Die Art des Metallions

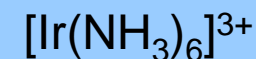
Δ_o nimmt innerhalb einer Gruppe von oben (3d-Elemente) nach unten (5d-Elemente) zu.
Konsequenz: 4d- und 5d-Elemente liegen immer (bis auf eine Handvoll Ausnahmen) in der low-spin-Konfiguration vor.



$$\Delta_o \equiv 22870 \text{ cm}^{-1}$$

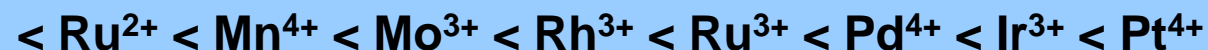


$$\Delta_o \equiv 34100 \text{ cm}^{-1}$$



$$\Delta_o \equiv 41200 \text{ cm}^{-1}$$

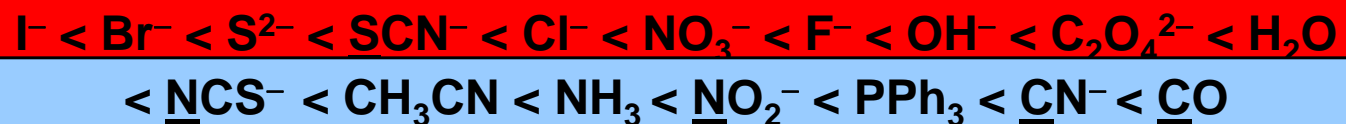
Irving-Williams Reihe



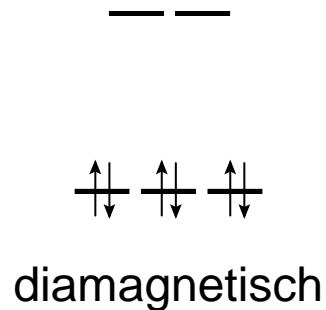
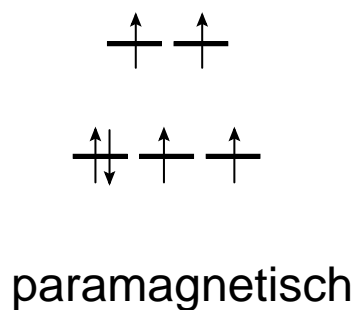
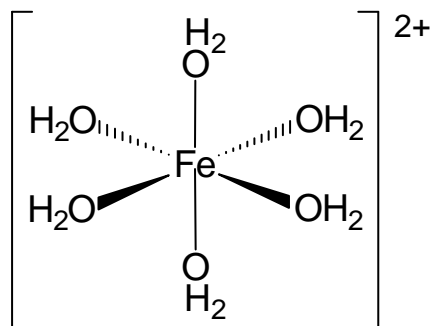
Faktoren, die Δ_o beeinflussen

3. Die Art der Liganden

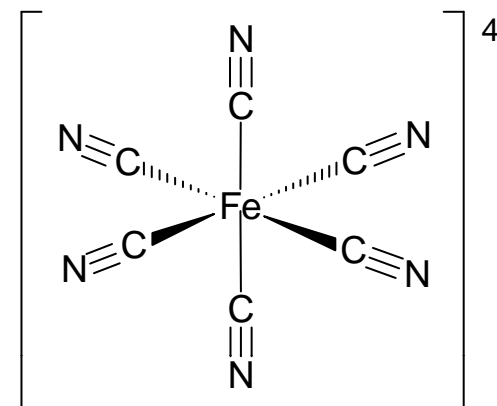
Spektrochemische Reihe: Messung von Δ_o (nicht mit nur einem Metall möglich)



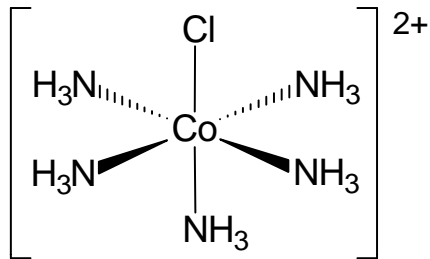
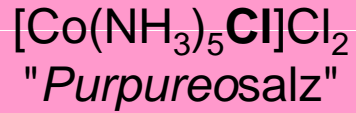
$FeSO_4 \cdot 7 H_2O$
"Eisenvitriol"



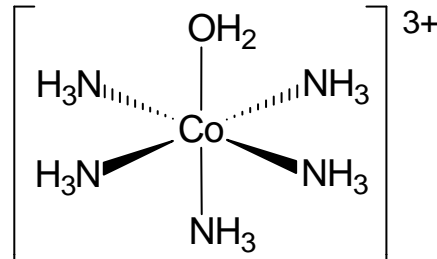
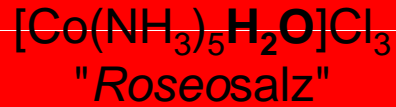
$K_4[Fe(CN)_6]$
"Gelbes Blutlaugensalz"



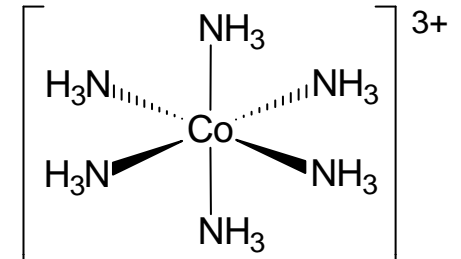
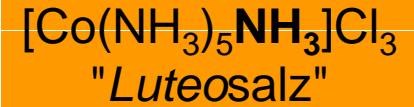
Cobaltamine



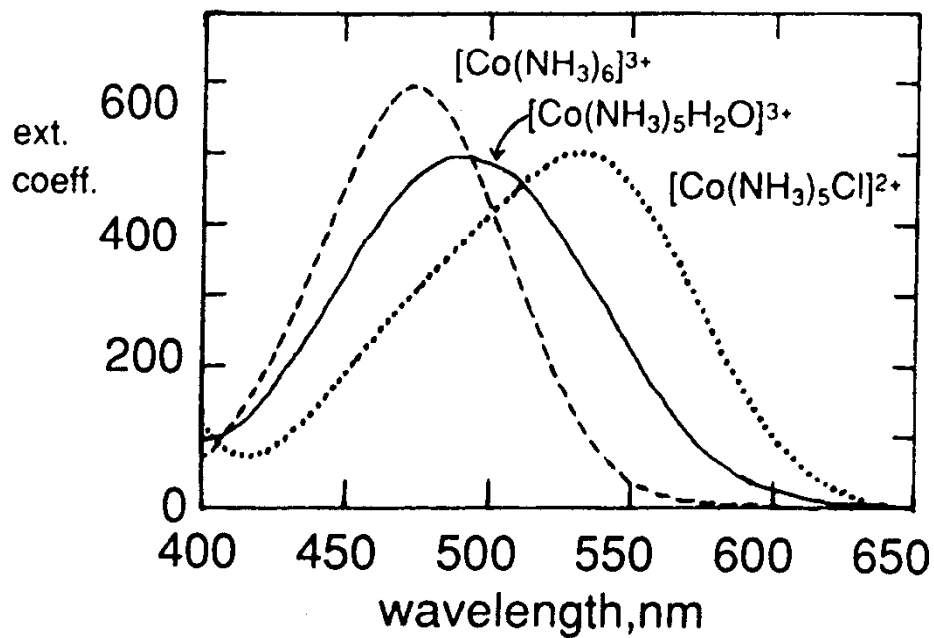
$$\lambda_{\text{max}} = 530$$



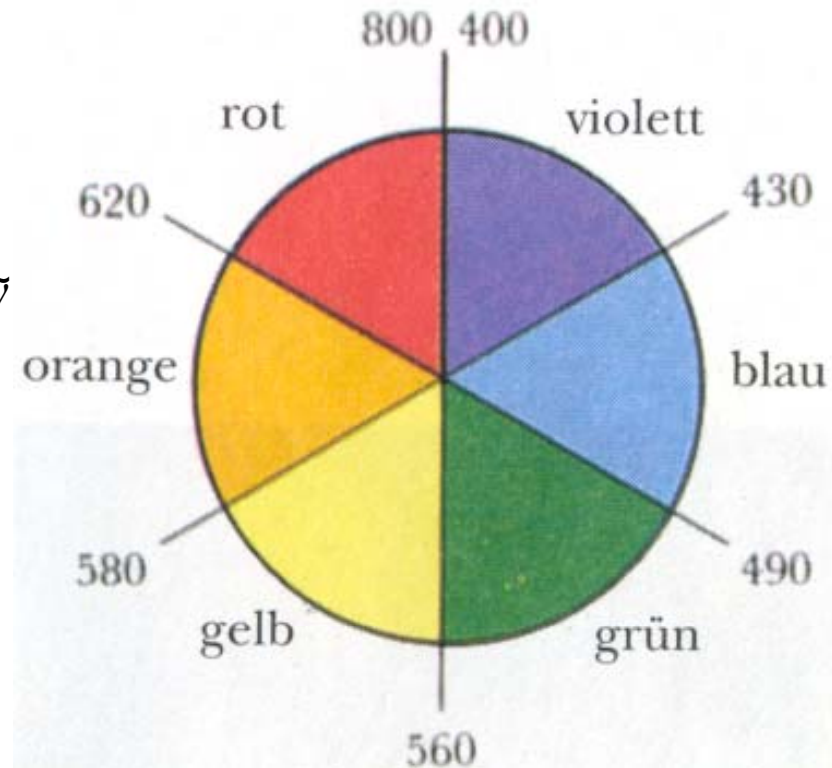
$$\lambda_{\text{max}} = 495$$



$$\lambda_{\text{max}} = 457$$



$$E = h \frac{c}{\lambda} = hc\bar{\nu}$$



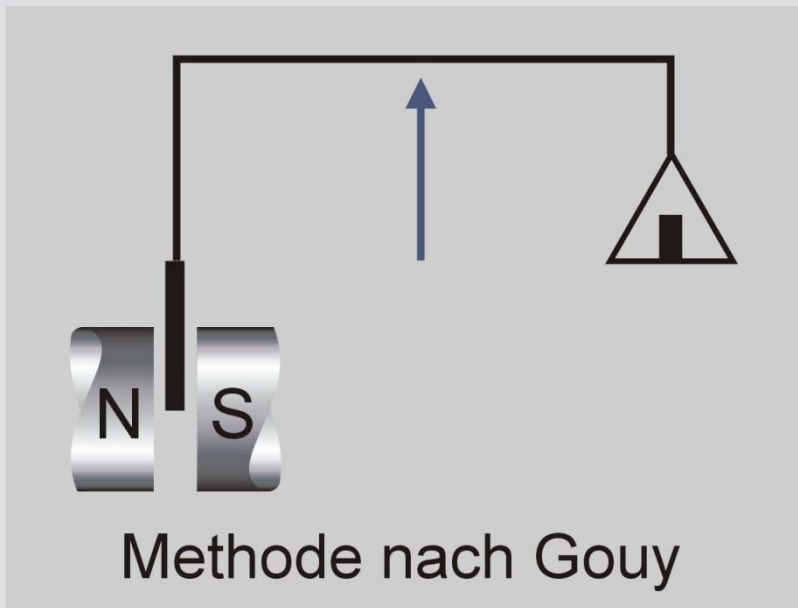
Bestimmung des magnetischen Momentes



Messung magnetischer Eigenschaften

Diamagnetische Stoffe

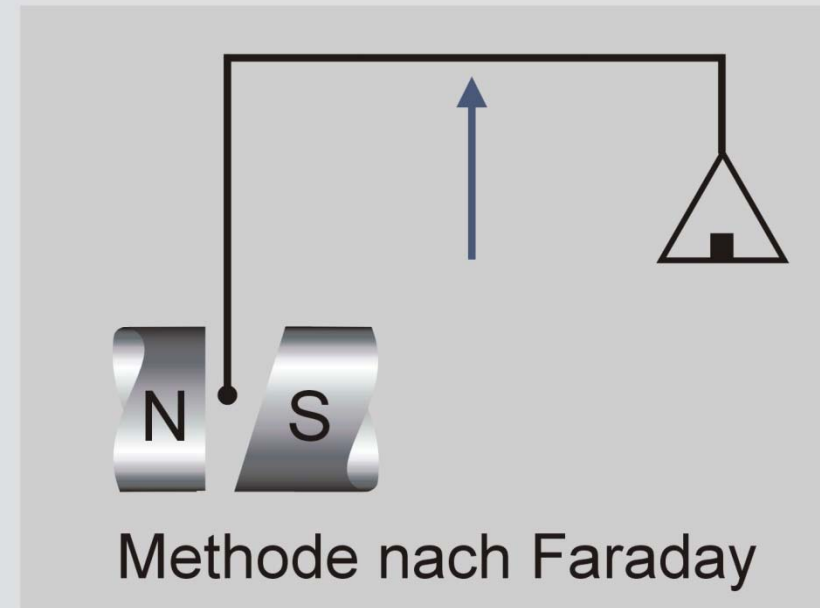
- ❖ erfahren Abstoßung
- ❖ werden scheinbar leichter



- ❖ homogenes Magnetfeld
- ❖ große Probenmengen

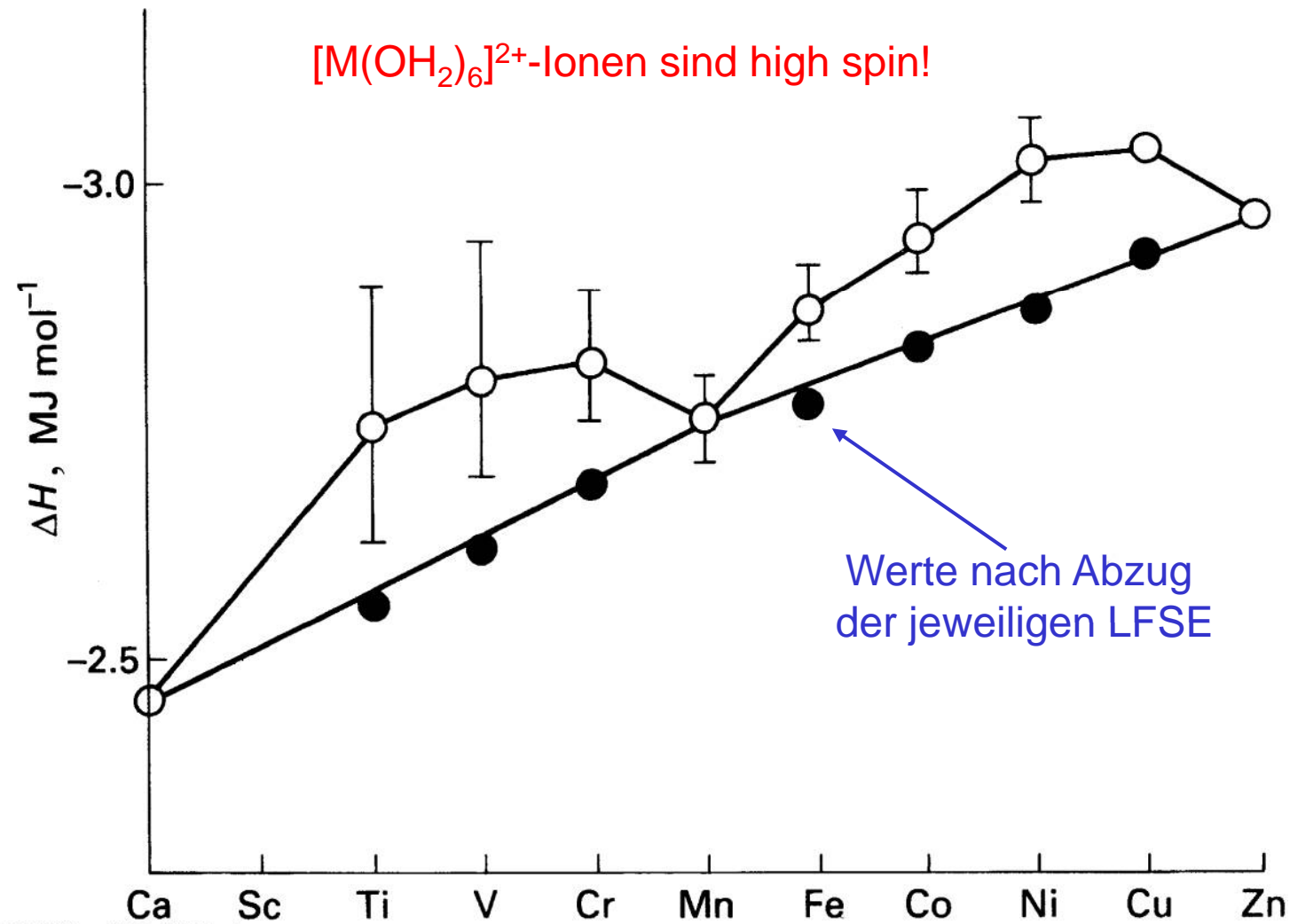
Paramagnetische Stoffe

- ❖ erfahren Anziehung
- ❖ werden scheinbar schwerer

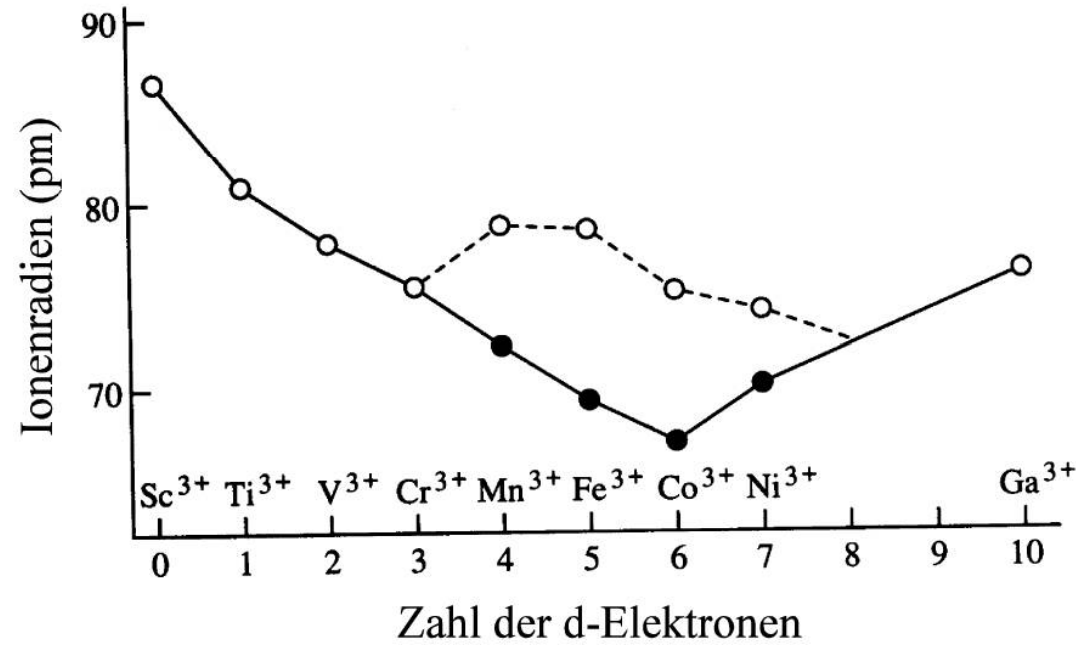
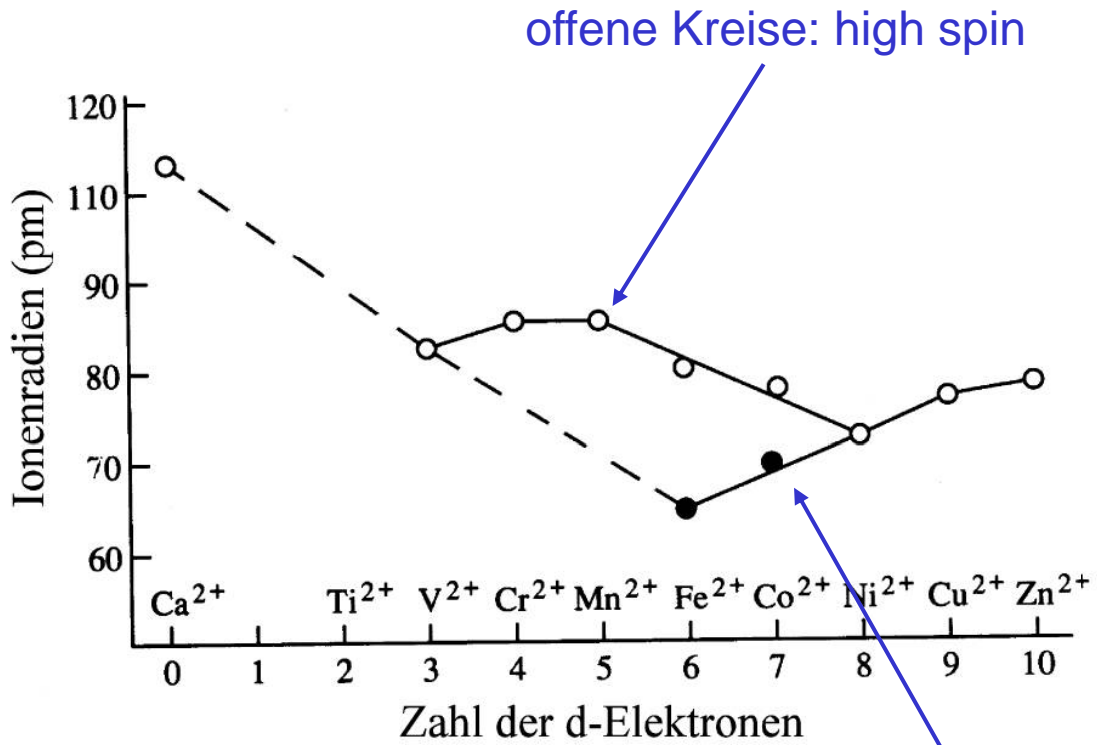


- ❖ inhomogenes Magnetfeld
- ❖ kleine Probenmengen

Gang der Hydratationsenthalpien der M^{2+} -Ionen

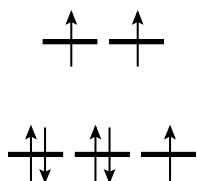
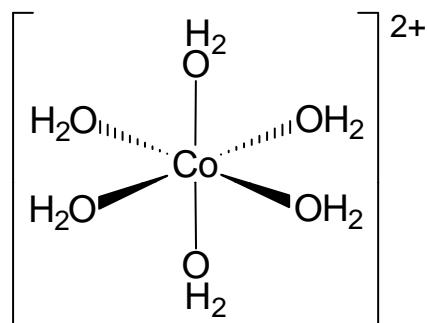
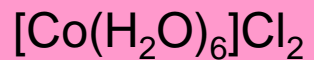


Radien zwei- und dreiwertiger 3d-Ionen

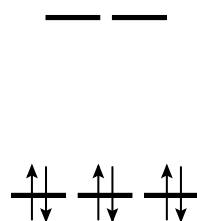
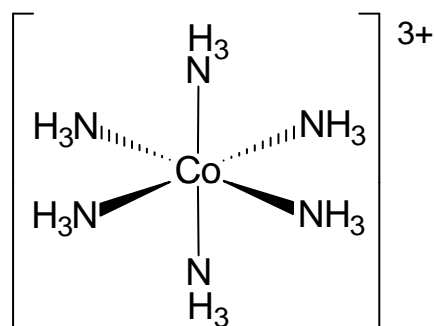
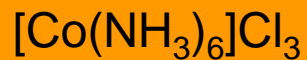


gefüllte Kreise: low spin

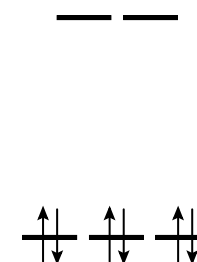
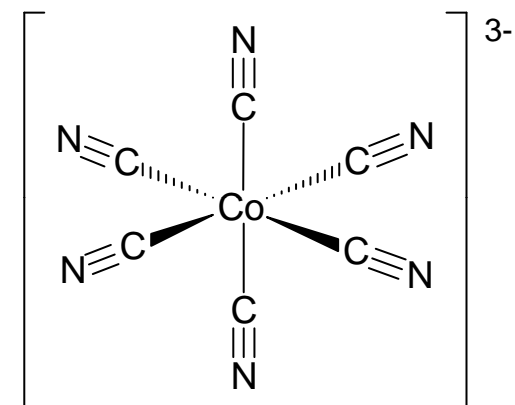
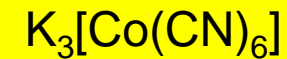
Beeinflussung der Redoxpotentiale



$$E^\circ(\text{Co}^{2+}/\text{Co}^{3+}) = 1,83 \text{ V}$$

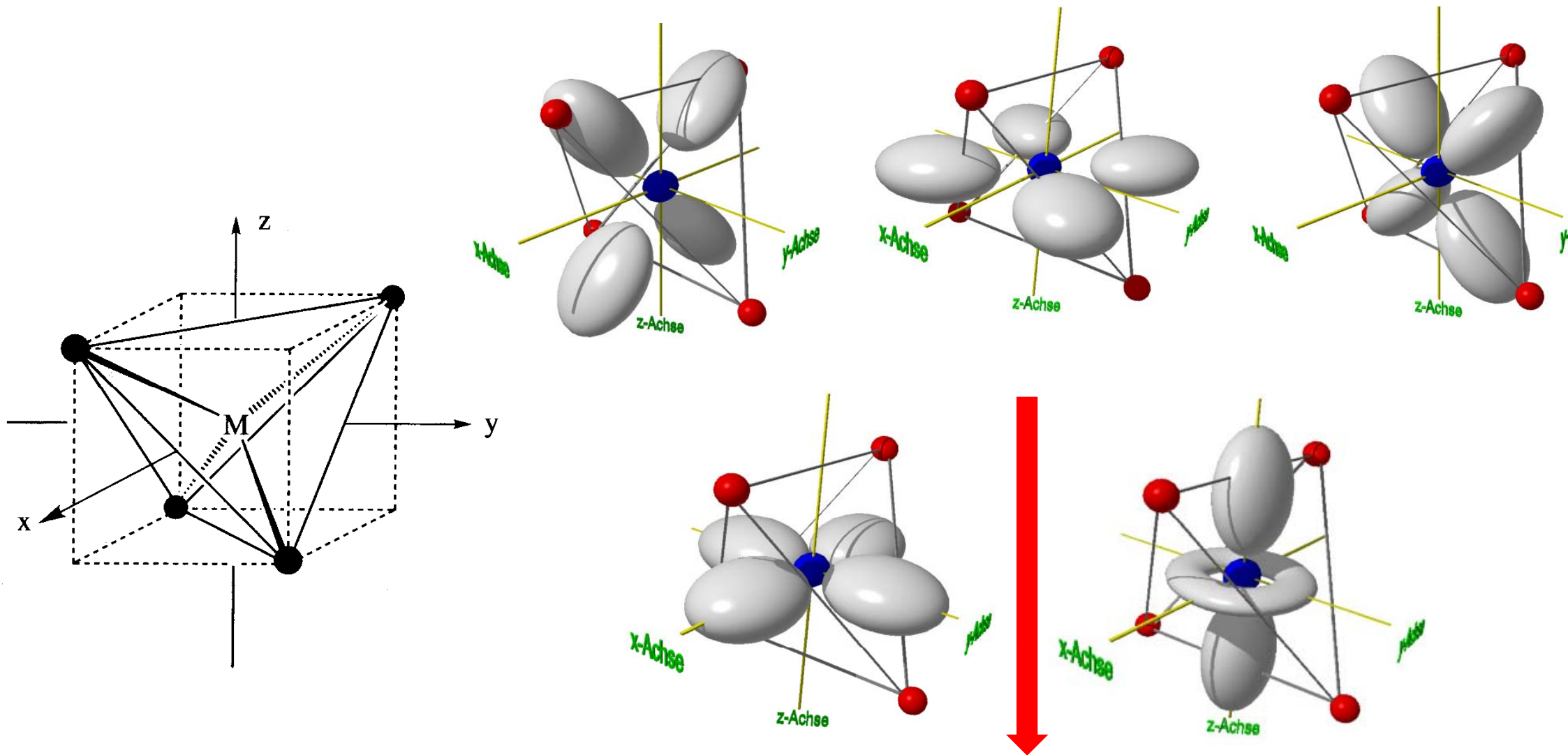


$$E^\circ(\text{Co}^{2+}/\text{Co}^{3+}) = 0,108 \text{ V}$$



$$E^\circ(\text{Co}^{2+}/\text{Co}^{3+}) = -0,83 \text{ V}$$

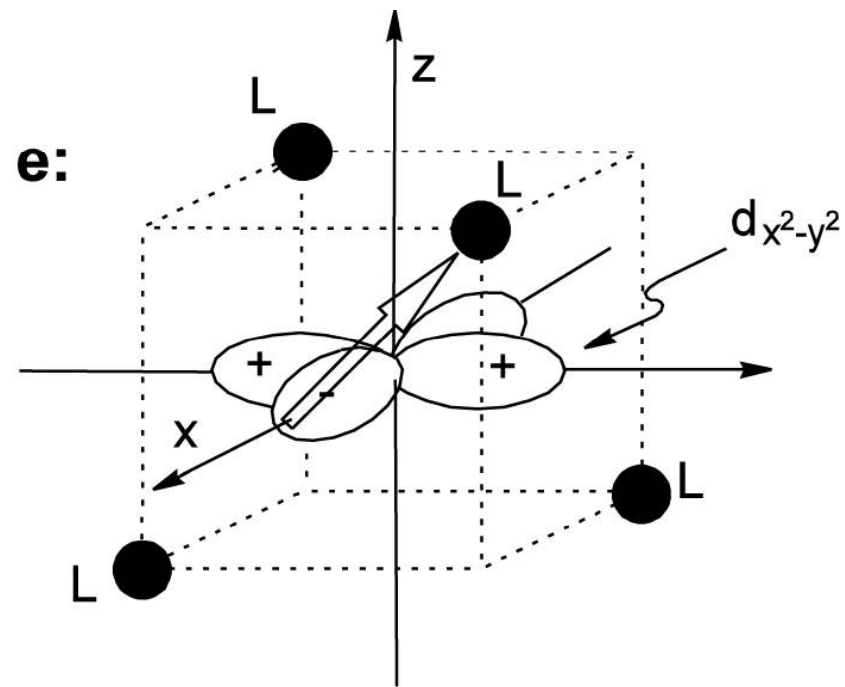
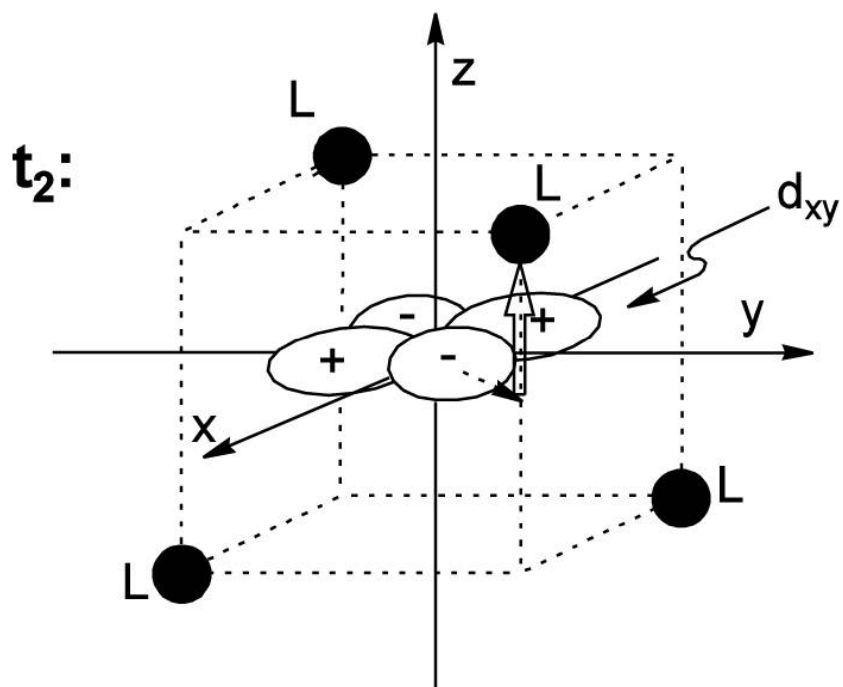
Tetraederfeld



**Stellung der Atome falsch:
Sie gehören in die Quadranten nicht auf die Achsen!**

Tetraederfeld

So lässt sich die unterschiedliche Nähe der Liganden zu den t_2 - und e-Orbitalen zu veranschaulichen:



$$\Delta_T = \frac{4}{9} \Delta_O$$