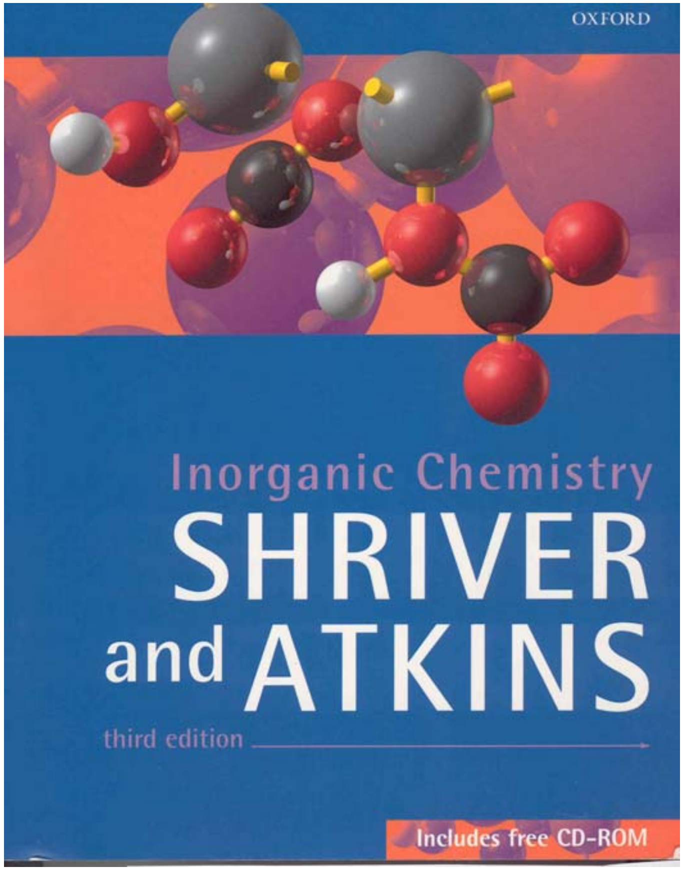
Coordination and Special Materials Chemistry

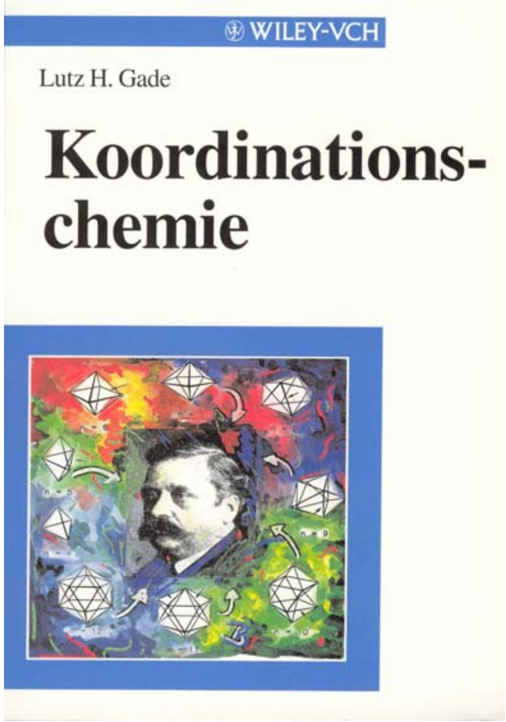
Elective I/II: WS 2005/6 (Lecture)

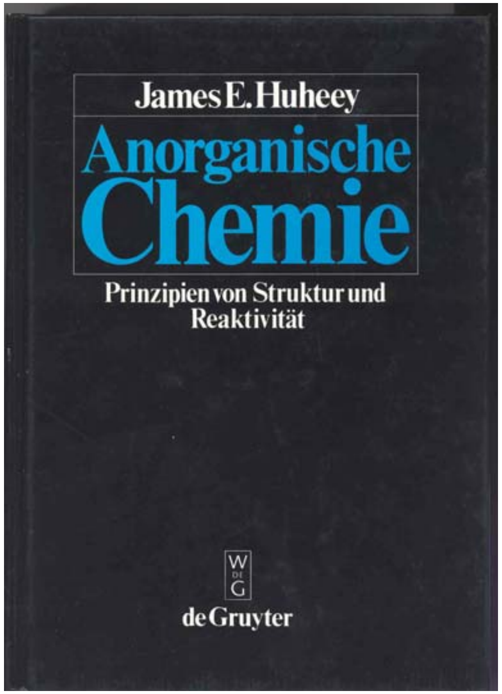
H.J. Deiseroth

Part 1

Coordination and special materials Chemistry
Recommended Textbooks



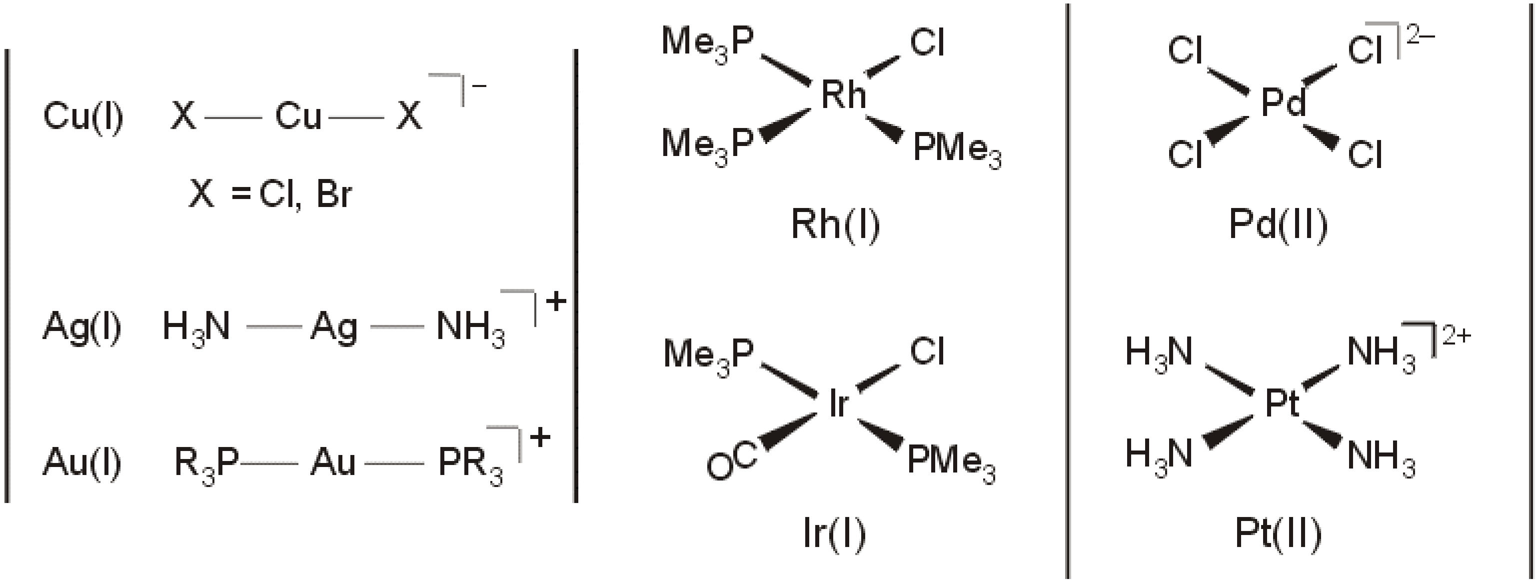


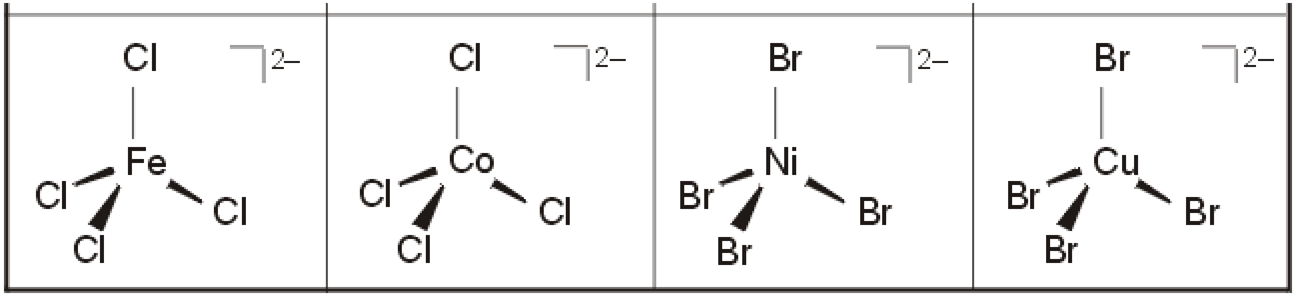


Coordination and special materials Chemistry

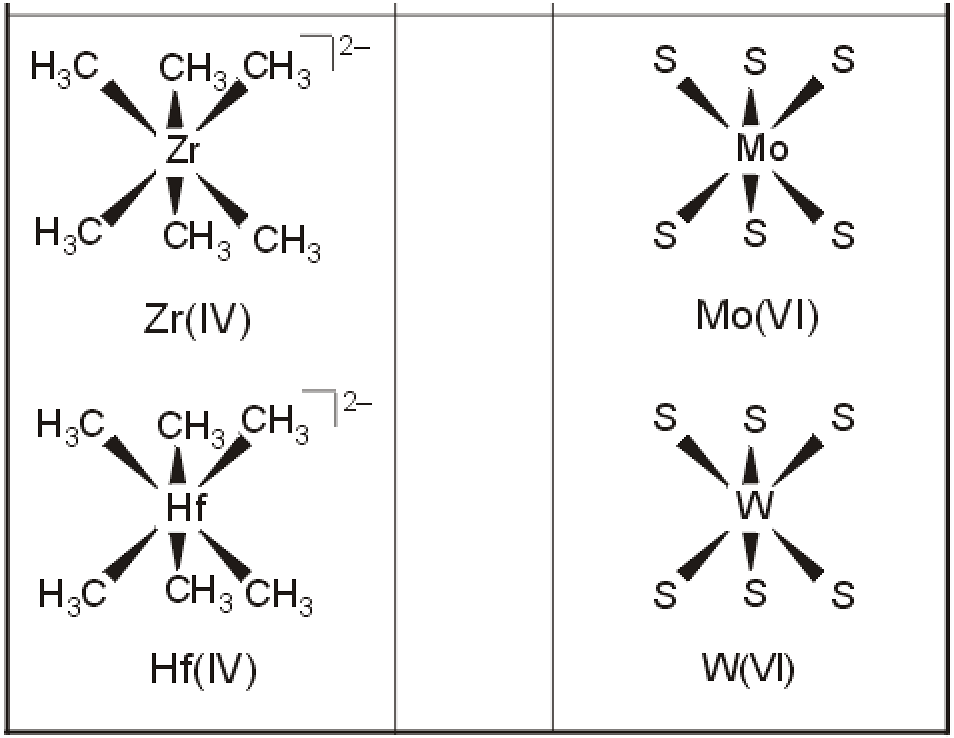
Coordination chemistry is the chemistry of compounds formed between metal ions and other neutral or negatively charged molecules

Examples





Coordination and special materials Chemistry



Important terms:

ligand, central atom, coordination number(CN), donor atom, acceptor atom.

complex compounds ⇔ **coordination compounds**.

Compounds having the same chemical formula but different structures are called **isomers**. Isomers with different geometic arrangements of ligands are called **geometric isomers** whereas isomers whose structures are mirror images of each other are called **optical isomers**. When a beam of polarized light passes optical isomers or their solutions, the plane of polarization rotates in different directions. The beam rotates to the left for one isomer, and right for its mirror image.

How did the study of coordination compounds start?

The coordination chemistry was pioneered by Nobel Prize winner Alfred Werner (1866-1919). He received the Nobel Prize in 1913 for his coordination theory of transition metal-amine complexes.

Werner studied the metal-amine complexes such as $[Co(NH_3)_6Cl_3]$ and recognized the existence of several forms of cobalt-ammonia chloride. These compounds have different color and other characteristics. The chemical formula has three chloride ions per mole, but the number of chloride ions that precipitate with Ag^+ ions per formula is not always three. He thought only **ionized chloride ions** will form a precipitate with silver ions. In the following table, the number below the **Ionized Cl-** is the number of ionized chloride ions per formula. To distinguish ionized chloride from the coordinated chloride, Werner formulated the **Complex formula** and explained structure of the cobalt complexes.

Proposed Structures of Cobalt Amonia Complexes from the Number of Ionized Chloride ions

$CoCl_3$ $6NH_3$: Yellow $[Co(NH_3)_6]Cl_3$
$CoCl_3$ $5NH_3$ Purple$[Co(NH3)_5Cl]Cl_2$
$CoCl_3$ $4NH_3$ Green *trans*-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3$ $4NH_3$ Violet *cis*-$[Co(NH_3)_4Cl_2]Cl$

The structures of the complexes were proposed based on a coordination sphere of 6. The 6 ligands can be ammonia molecules or chloride ions. Two different structures were proposed for the last two compounds, the *trans* compound has two chloride ions on opposite vertices of an octahedron, whereas the the two chloride ions are adjacent to each other in the *cis* compound. The *cis* and *trans* compounds are known as geometric isomers. Isomerism is a very common feature of coordination compounds and will be discussed in detail later.

Basic Nomenclature: naming of coordination compounds

- The names of complexes **start** with the **ligands (in alphabetical order)**, the **anionic ones first** , followed by **neutral ligands**, the **central atom** and the **oxidation state (**Roman numerals).
- If the complex is negative, the name ends with "**ate**".
- names of anionic ligands end with **„o“ : chloro-**, **oxo-**, **fluoro-, cyano.**
- neutral ones **without** specific ending: (exception: H_2O: **aqua**, NH_3: **ammine**) C_5H_5N, **pyridine**, $NH_2CH_2CH_2NH_2$, **ethylenediamine**, $C_5H_4N-C_5H_4N$, **dipyridyl**, $P(C_6H_5)_3$: **triphenylphosphine**, CO: **carbonyl,** CS: **thiocarbonyl,**

$[Co(NH_3)_5Cl]Cl_2$: Chloro-penta-ammine-cobalt(III)chloride
$[Cr(H_2O)_4Cl_2]Cl$: Dichloro-tetra-aquo-chromium(III)chloride
$K[PtCl_3NH_3]$: Potassium-tri-chloro-ammine-platinate(II)
$PtCl_2(NH_3)_2$: Diammine-di-chloro-platinum(II)
$[Co(en)_3]Cl_3$: Tris(ethylenediamine)-cobalt(III)chloride
$Ni(PF_3)_4$: Tetrakis(phosphorus(III)fluoride)-nickel(0)

simple ligands: di- tri-, tetra-, penta-, hexa- ...
complex ligands: bis-, tris-, tetrakis- ...

Constitution and Coordination Number

The most important factors that determine the constitution and coordination number of a complex are:

- size of the central atom - steric interactions between ligands
- electronic interactions

Higher coordination numbers (CN‘s) are favoured:

- in complexes with atoms (and ions) of the **periods 5 and 6**
- on the **left of a row of the d-block** where atoms are relatively large and have a small number of d-electrons
- for central atoms with a high oxidation number and thus a mall number of remaining d-electrons (e.g. $[Mo(CN)_8]^{4-}$

The low coordination numbers two and three

CN = 2 is very common for complex ions and molecules of Cu(I), Au(I), Ag(I) and Hg(II)

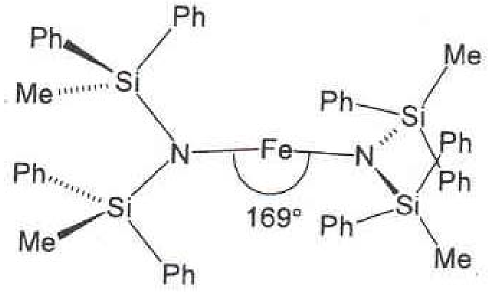
Cu(I) $[\mathrm{X{-}Cu{-}X}]^-$

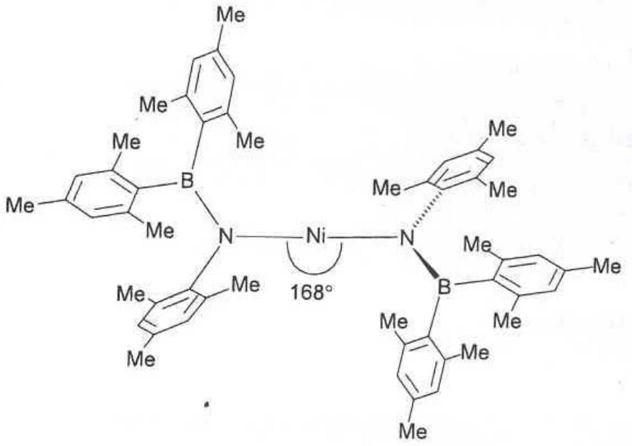
$\mathrm{X} = \mathrm{Cl, Br}$

Ag(I) $[\mathrm{H_3N{-}Ag{-}NH_3}]^+$

Au(I) $[\mathrm{R_3P{-}Au{-}PR_3}]^+$

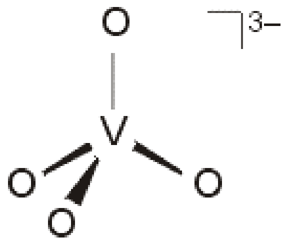
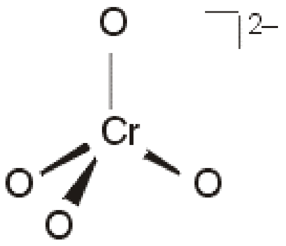
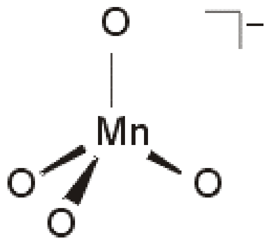
$\mathrm{H_3C{-}Hg{-}CH_3}$

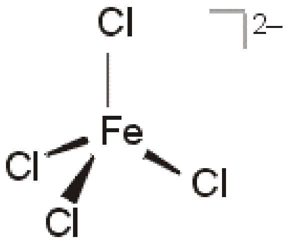
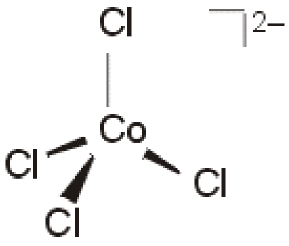
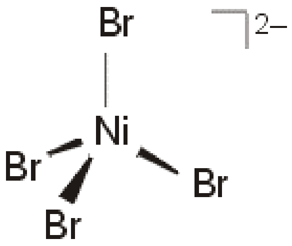
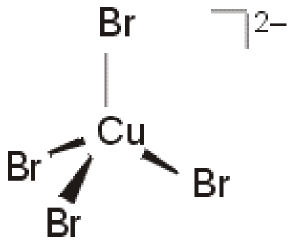




CN = 3 is very rare among normal coordinmation compounds of d-metals

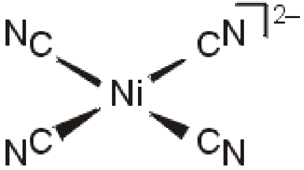
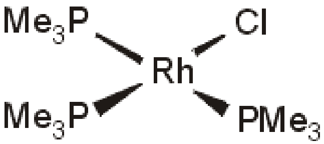
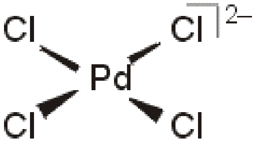
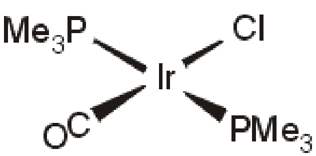
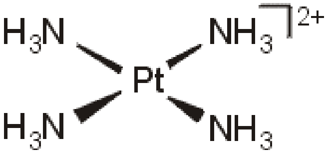
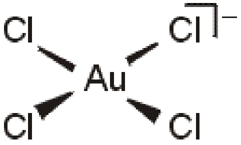
CN = 4: tetrahedral

5	6	7
		

8	9	10	11
			

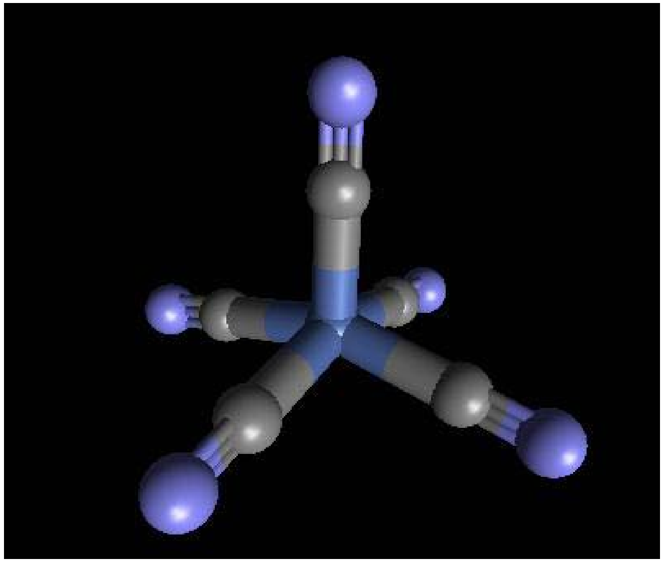
Summary chart 7.2 Tetrahedral complexes

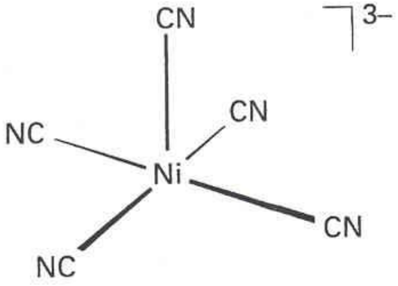
CN = 4: square planar

9	10	11
	 Ni(II)*	
 Rh(I)	 Pd(II)	
 Ir(I)	 Pt(II)	 Au(III)

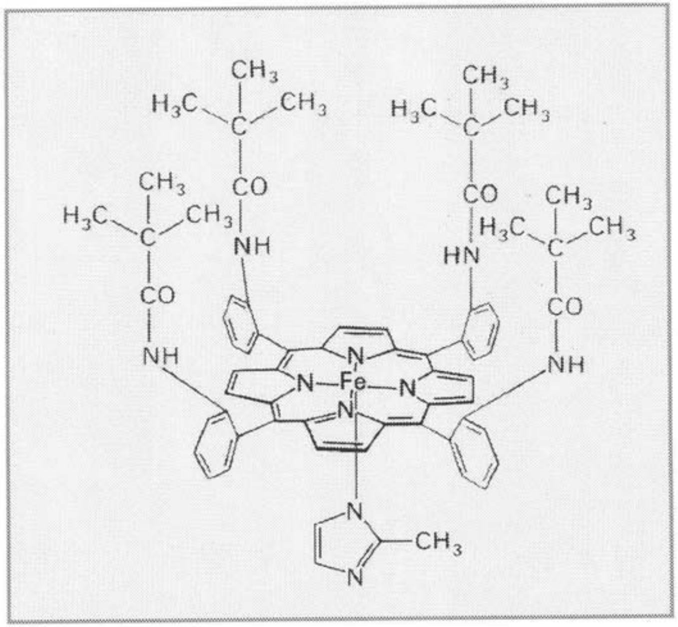
Preferred coordination of d^8 central atoms !!

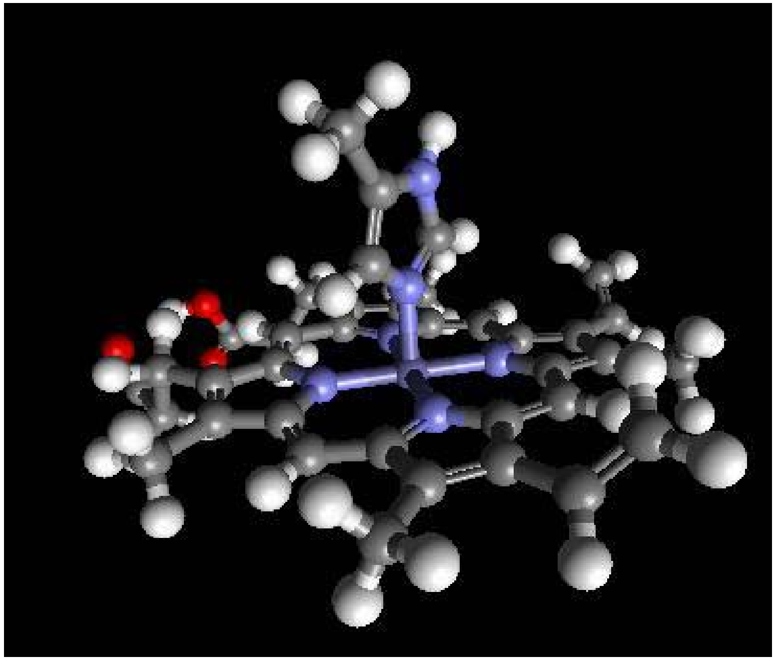
CN = 5: Square pyramidal (e.g. active center of myoglobin)



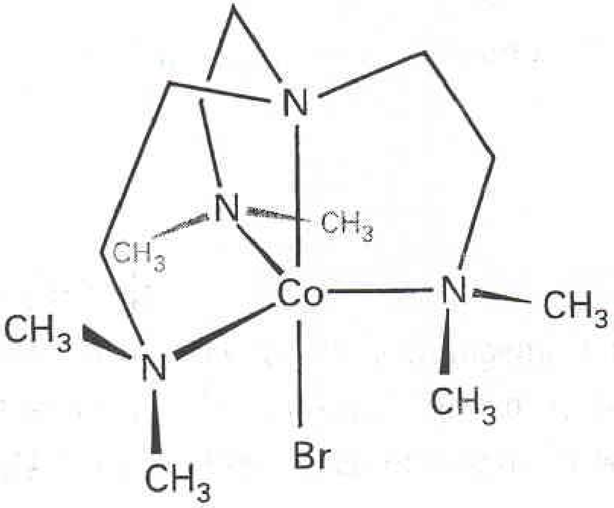


9a $[Ni(CN)_5]^{3-}$ (square-pyramidal conformation)





CN = 5: trigonal bipyramidal



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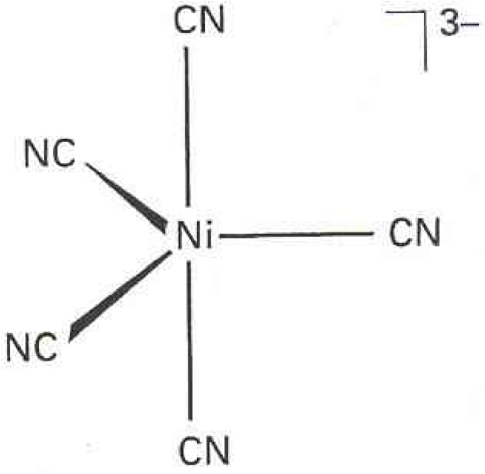
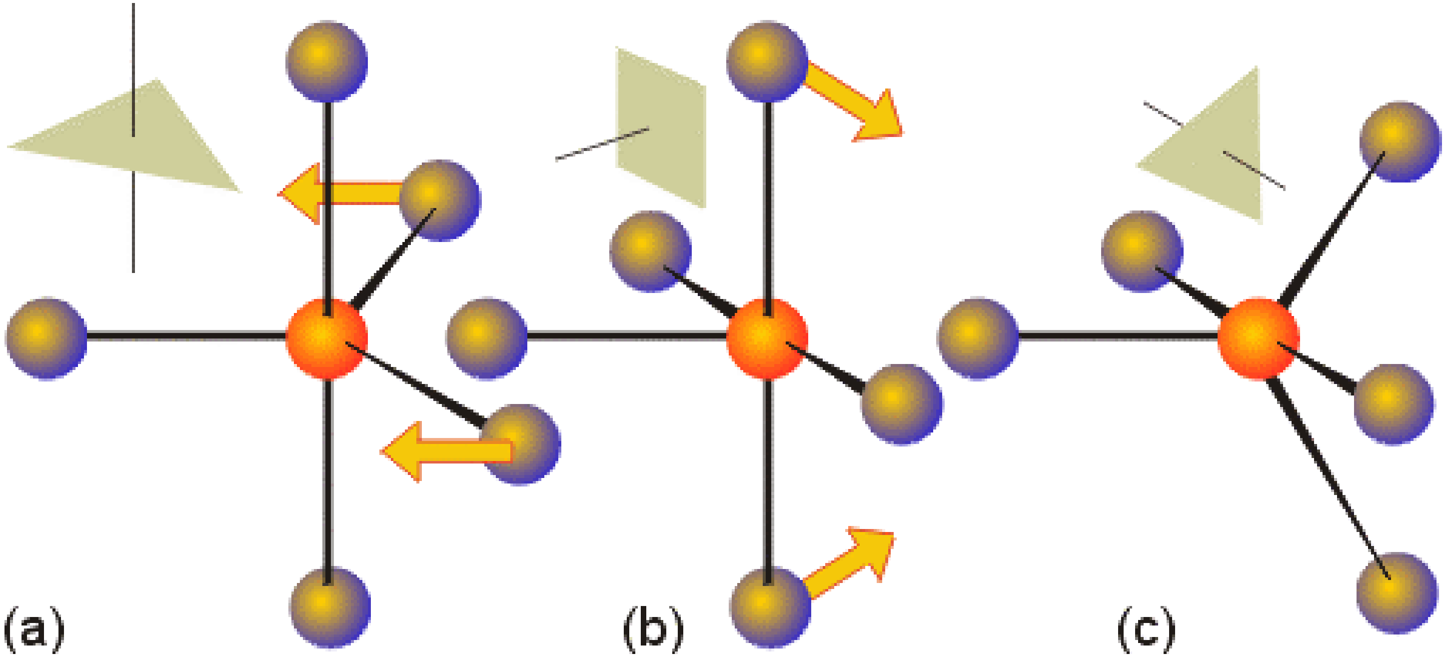


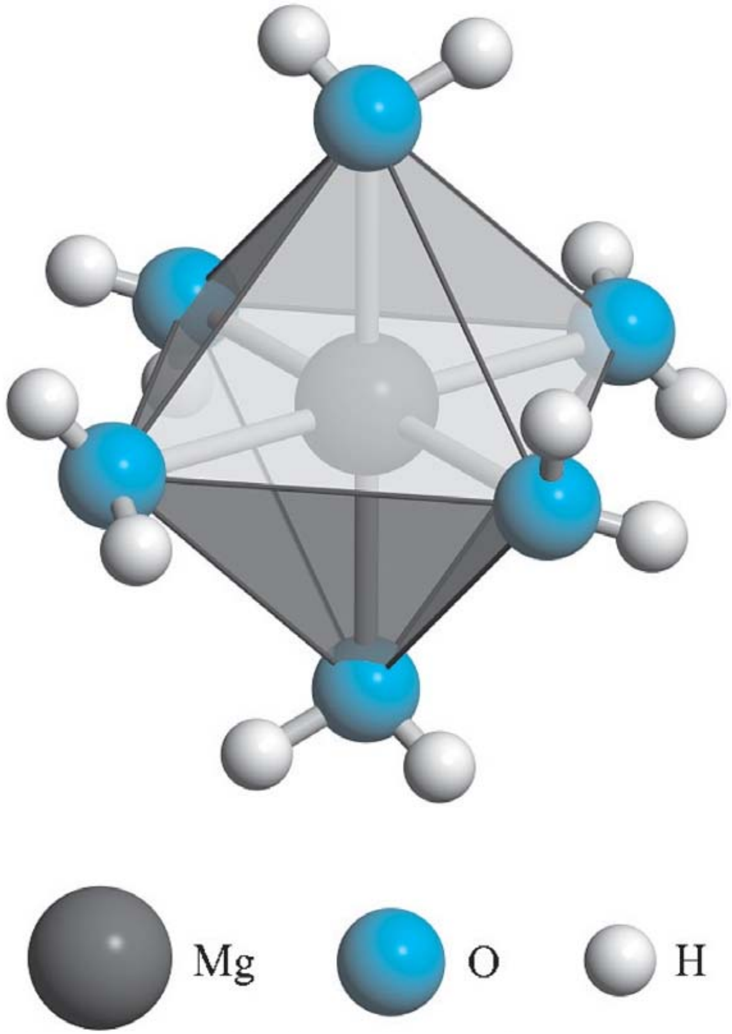
9b $[Ni(CN)_5]^{3-}$ (trigonal-bipyramidal conformation)

CN = 5: Pseudorotation

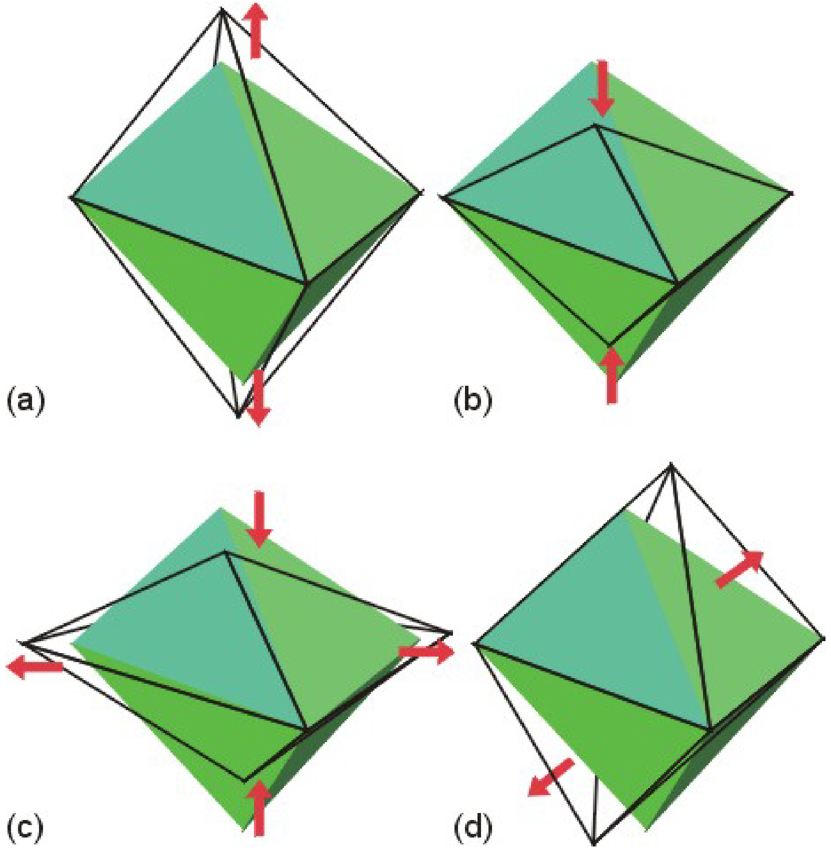


CN = 6: octahedral

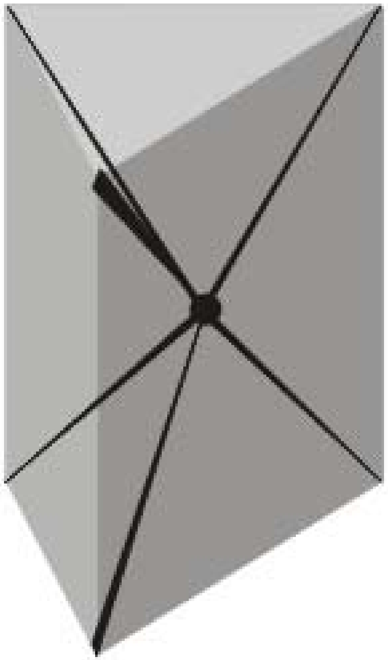
$[Mg(H_2O)_6]^{2+}$



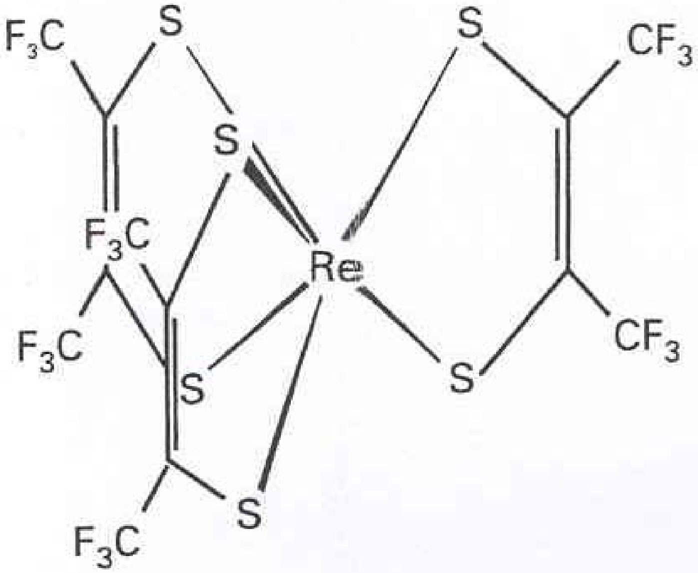
Types of distortions of octahedra



CN = 6: trigonal prismatic



11 Trigonal-prismatic complex, D_{3h}



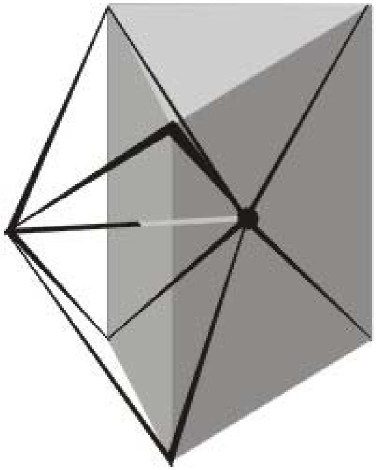
CN > 6

- rare with 3d elements but more common with 4d and 5d metals

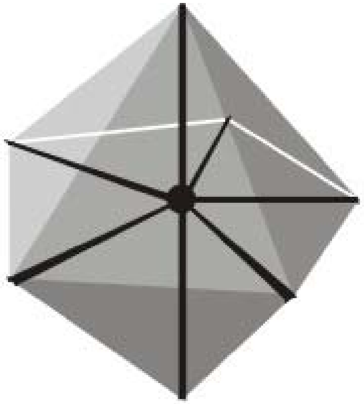
CN = 7: (mono-)capped octahedron, capped trigonal prism, pentagonal bipyramid

e.g. $[ZrF_7]^{3-}$, $[ReOCl_6]^{2-}$, $[UO_2(OH_2)_5]^{2+}$ ...

14 Capped octahedral complex

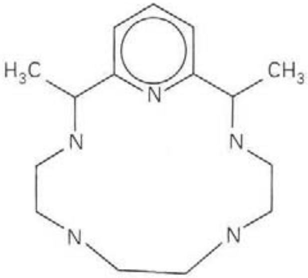


15 Capped trigonal prism



13 Pentagonal-bipyramidal complex, D_{5h}

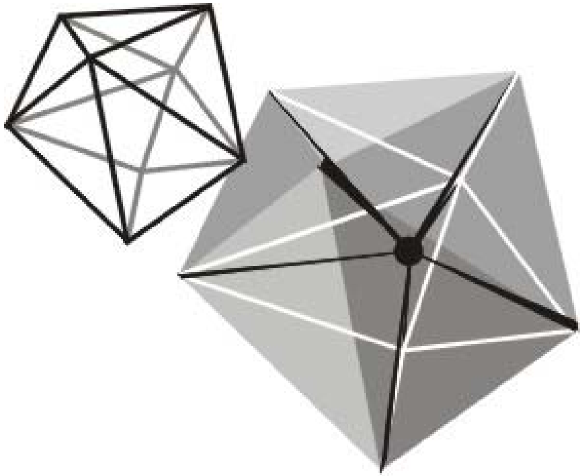
CN 7 is favoured by specific „ligand design“:



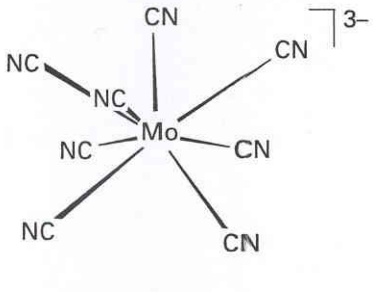
CN > 6

CN = 8: square antiprism („archimedian“ antiprism), trigonal dodecahedron, (cube)

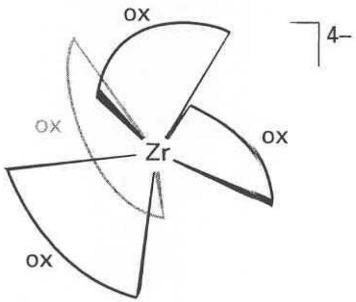
17 Square-antiprismatic complex



18 Dodecahedral complex



19 $[Mo(CN)_8]^{3-}$

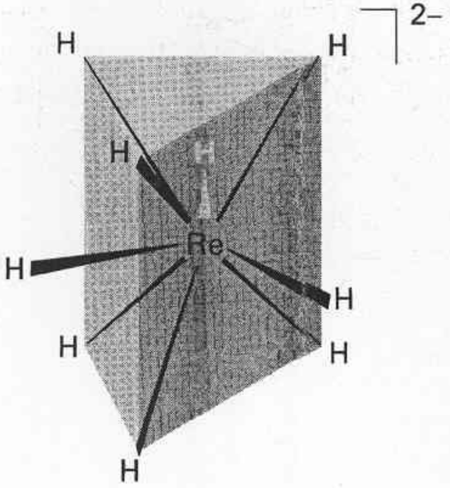


20 $[Zr(ox)_4]^{4-}$

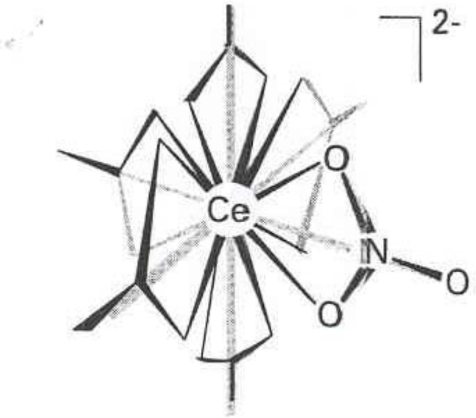
CN > 6

CN = 9: common with Re (e.g. $[ReH_9]^{2-}$) and f-block elements (e.g. $[Nd(OH_2)_9]^{3+}$)

CN > 9: important only for complexes with heavy metal central atoms
(e.g. f-elements)

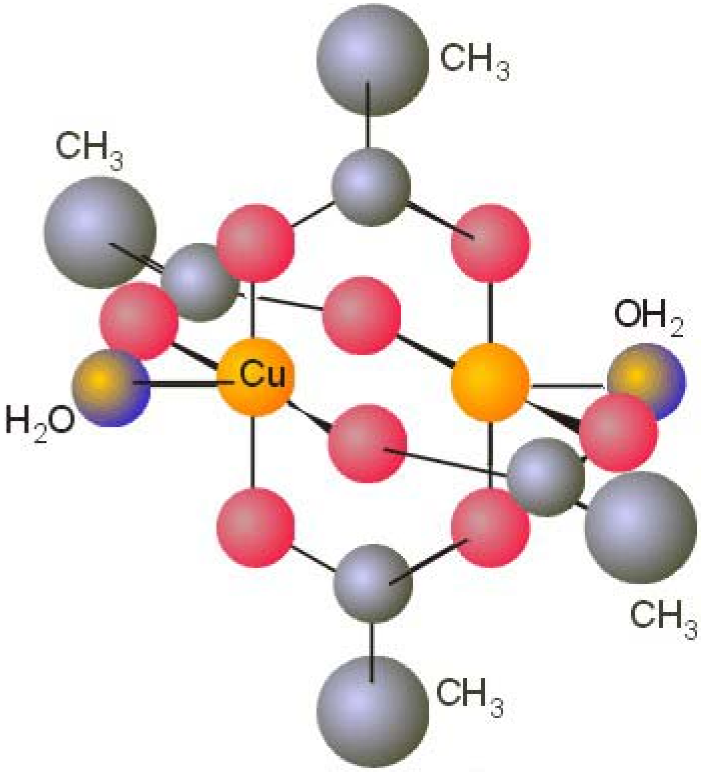


21 $[ReH_9]^{2-}$, D_{3h}

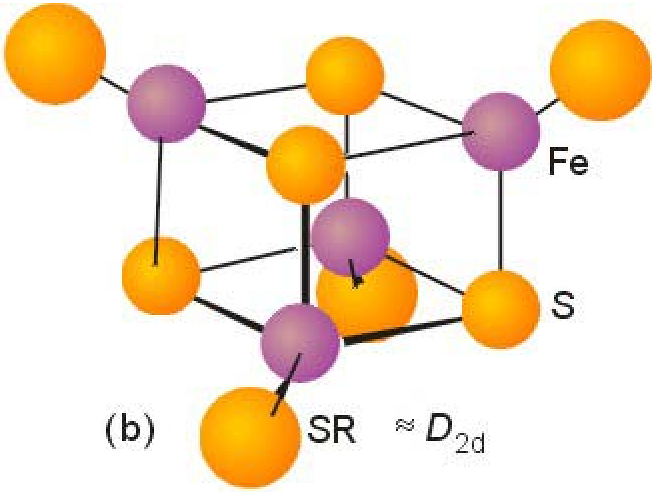


22 $[Ce(NO_3)_6]^{2-}$

Polymetallic coordination compounds with and without covalent metal-metal bonds

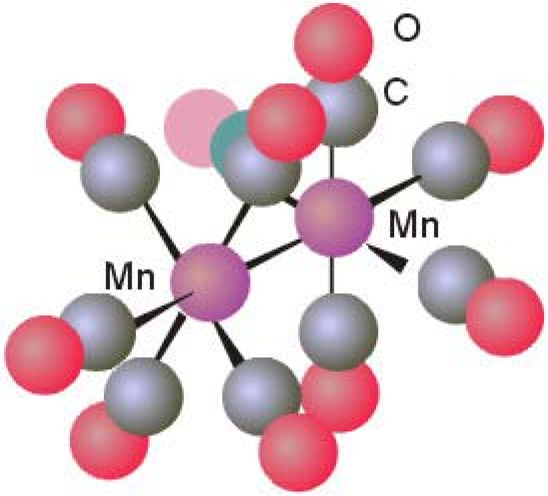


(a) $\approx D_{4h}$



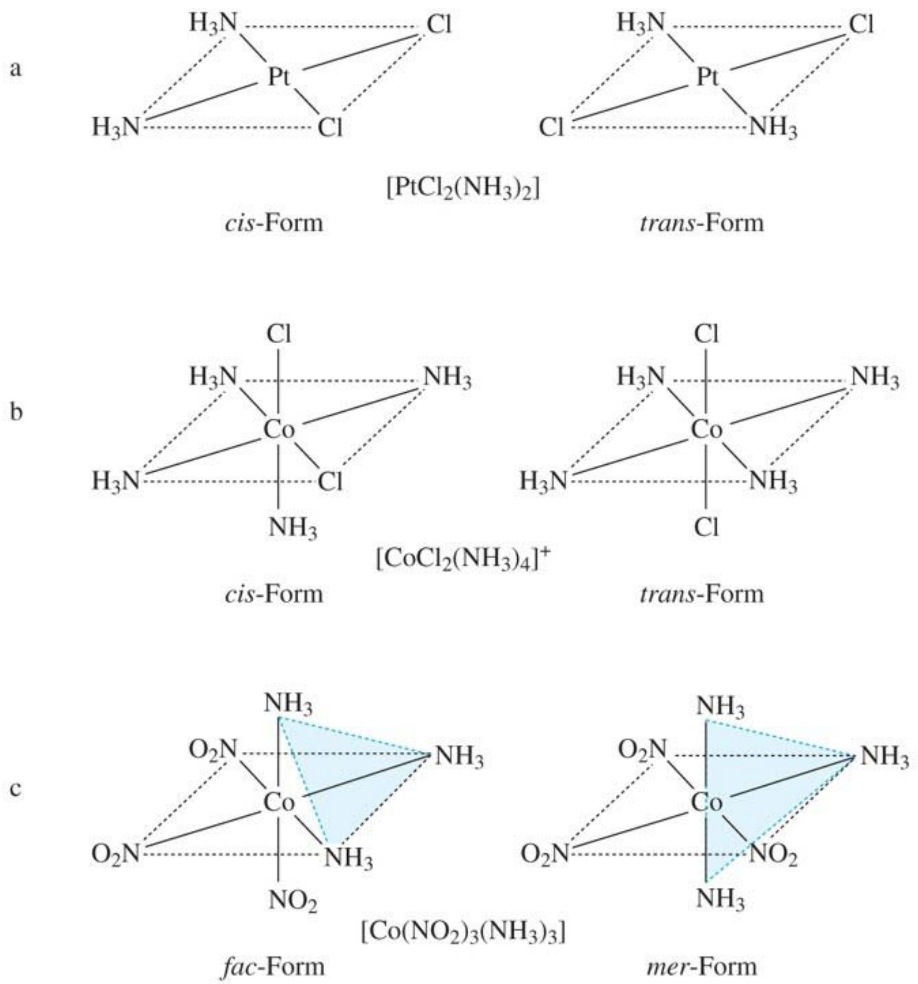
(b) $\approx D_{2d}$

(c) $D_{\infty h}$



(d)

Isomerism



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung12-05.jpg

mer: meridional
fac: facial

Isomerism and Chirality

- A **chiral** molecule is not superimposable on its own mirror image
- Chiral molecules show **optical isomerism** (rotation of the plane of polarized light)
- Two mirror-image isomers form an **enantiomeric pair** (**“racemate”**)
- **Diastereomers** are molecules with **more** than **one** center of chirality (e.g. organic sugar molecules)

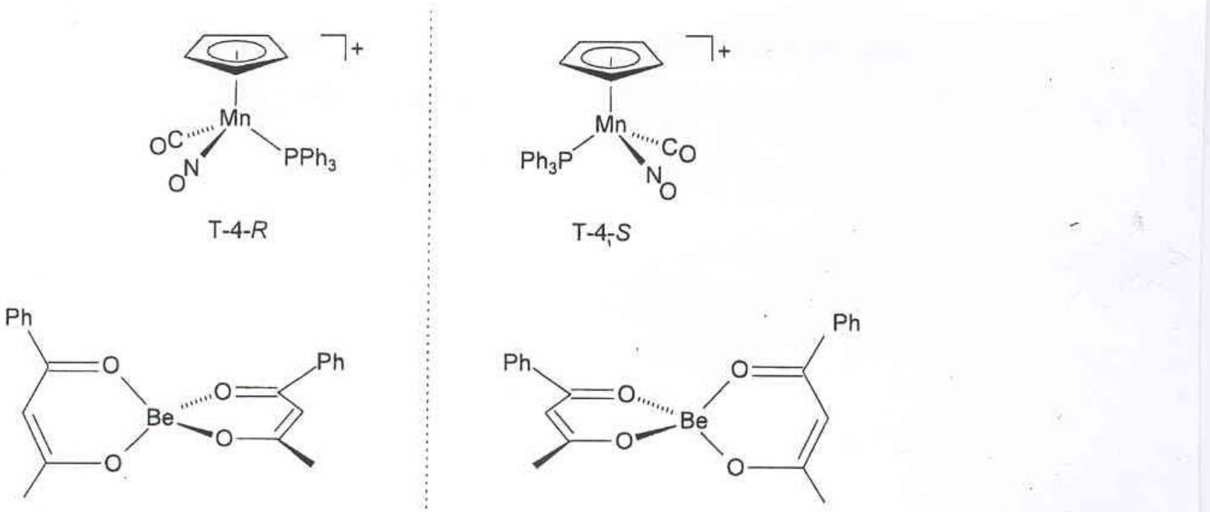
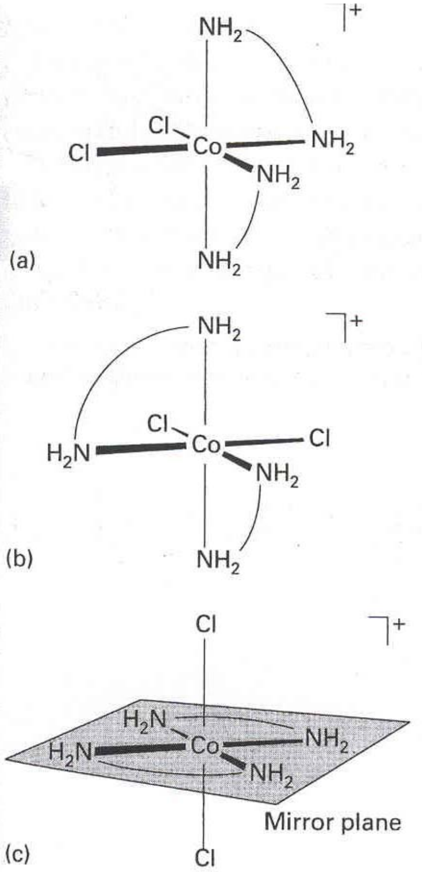
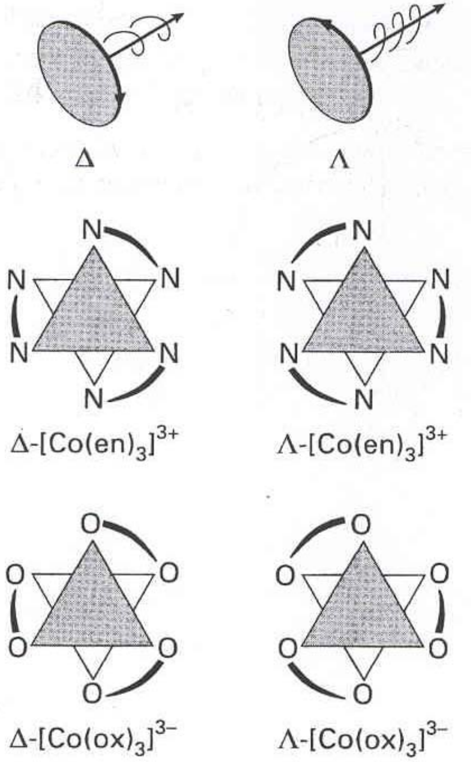


Abb. 10.5. Enantiomerenpaare der chiralen Komplexe $[Mn(Cp)CO(NO)(PPh_3)]^+$ und $[Be(benzoylacetonat)_2]$.

Isomerism and Chirality

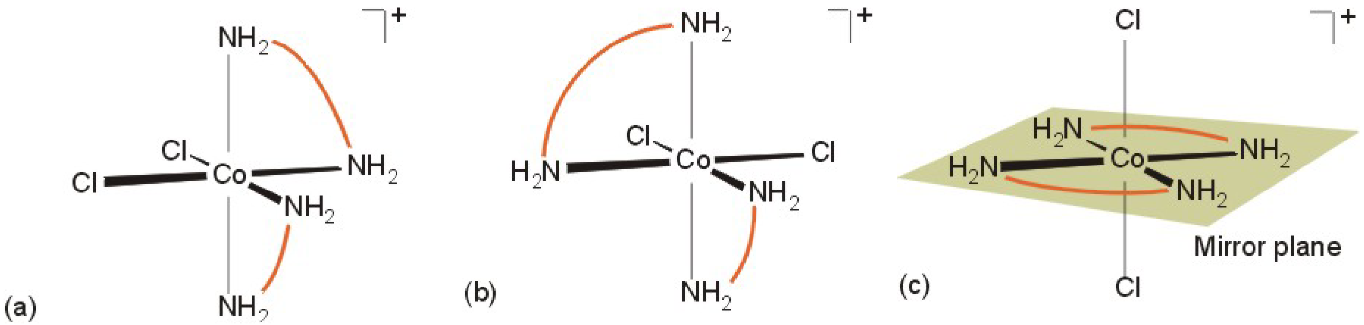


7.6 (a) and (b) Enantiomers of *cis*-$[CoCl_2(en)_2]$ and (c) the achiral *trans* isomer. The curves represent the CH_2CH_2 bridges in the en ligands. The mirror plane for testing whether there is an S_1 axis is also shown.



7.7 Absolute configurations of $[M(L—L)_3]$ complexes; Δ is a right-hand screw and Λ is a left-hand screw, as is indicated in the diagrams at the top of the figure by the direction that a screw would turn when being driven in the direction shown.

Isomerism and Chirality



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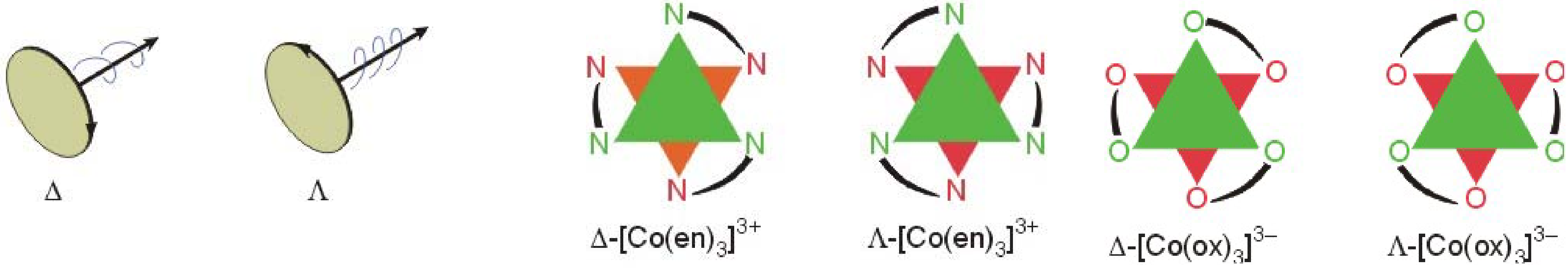


Δ-$[Co(en)_3]^{3+}$ Λ-$[Co(en)_3]^{3+}$ Δ-$[Co(ox)_3]^{3-}$ Λ-$[Co(ox)_3]^{3-}$

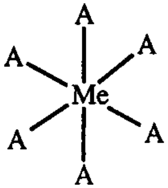
7.7 Absolute configurations of $[M(L{-}L)_3]$ complexes; Δ is a right-hand screw and Λ is a left-hand screw, as is indicated in the diagrams at the top of the figure by the direction that a screw would turn when being driven in the direction shown.

Isomerism and Chirality: Separation of enantiomers (racemates)

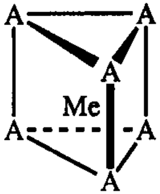
Optical activity is the **only** physical property that is **different** for the respective molecules of an enentiomeric pair. Diastereomeric molecules, however, show a variety of differences in their physical properties (e.g. solubilty, melting and decomposition behaviour, reactivity). Thus separation of enantiomers starts with the **reaction of the racemate (A, A‘) with another chiral molecule (B)**. The reaction products are diastereomers with **different** physical properties (e.g. solubility, reactivity) suitable for a separation. Subsequently the separated diastereomers can be treated again to form back the chiral starting molecules now separated from each other.

$$\begin{tikzcd}
(A\ A') + B \arrow[r] & AB \arrow[d, "-B"] & + & A'B \arrow[d] \\
 & A & + & A'
\end{tikzcd}$$

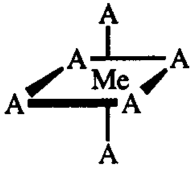
Isomerism and Chirality: yes or no ?



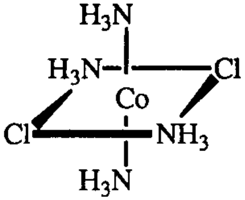
1
planar



2
prismatic



3
octahedral



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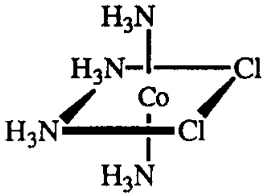

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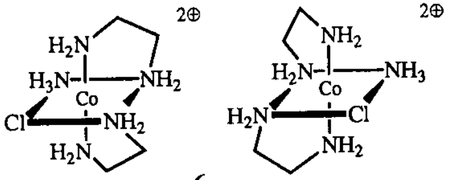

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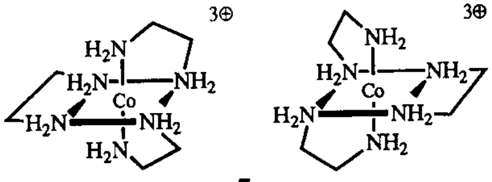

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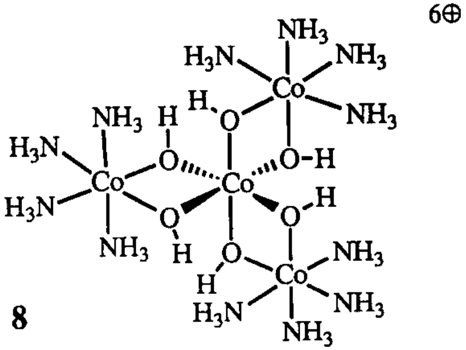
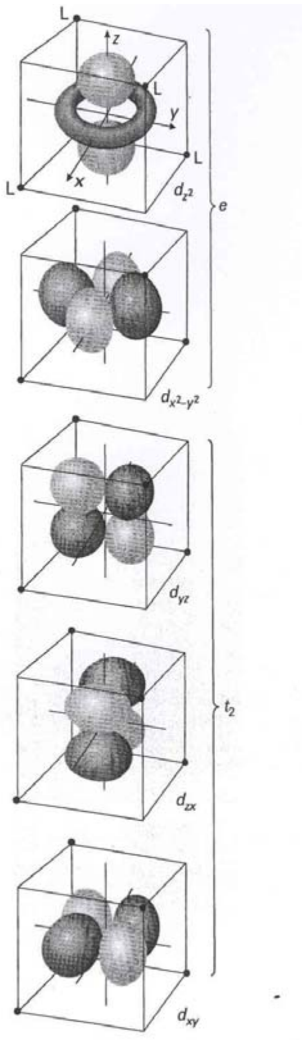


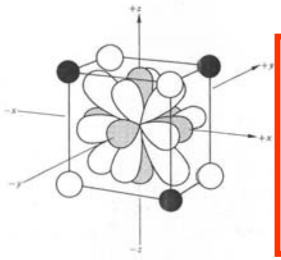
8

The resolution of these racemates was beautifully in accord with the octahedral geometry of the complexes, but the impact these results had in the chemical community was enhanced by the fact that,at this time, there were still some who clung to the half mystical belief that optical activity was somehow a special property associated with life and the asymmetric carbon atom. Any lingering doubts were completely dispelled by Werner in 1914 with the resolution of the 'inorganic' tetranuclear cobalt complex **8** into its two enantiomeric forms. A successor wrote of Werner:

Basic Crystal Field Theory: tetrahedral and octahedral field

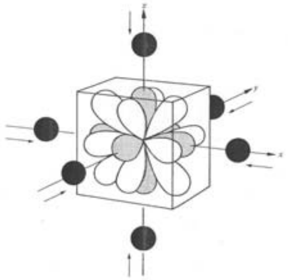


7.13 The effect of a tetrahedral crystal field on a set of *d* orbitals is to split them into two sets; the *e* pair (which point less directly at the ligands) lie lower in energy than the t_2 triplet.

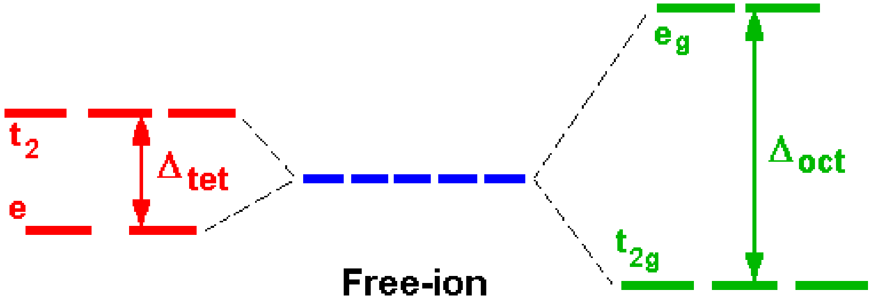


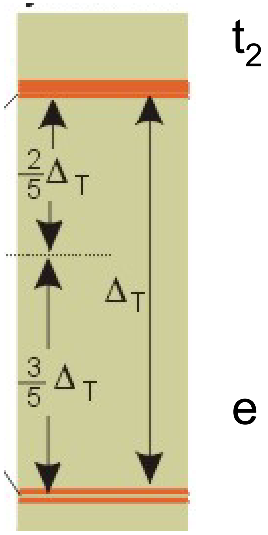
Tetrahedral

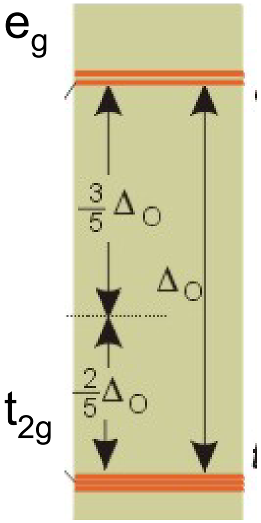
All atoms/molecules are treated as electrical point charges

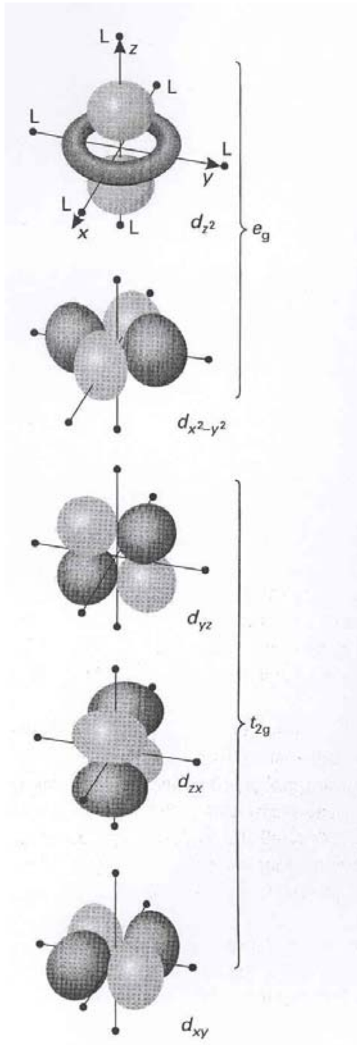


Octahedral





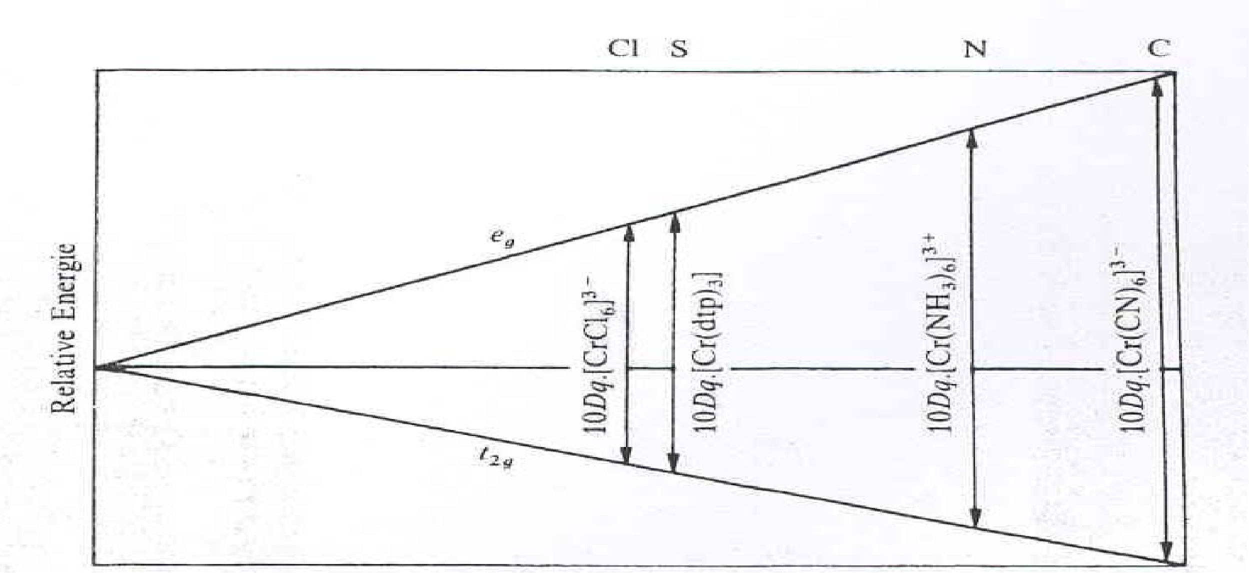




7.8 The orientation of the five *d* orbitals with respect to the ligands of an octahedral complex.

Basic Crystal Field Theory: splitting of energy levels

The influence of **different ligands** on the **size** of Δ = 10Dq



Increasing strength of the ligand field →

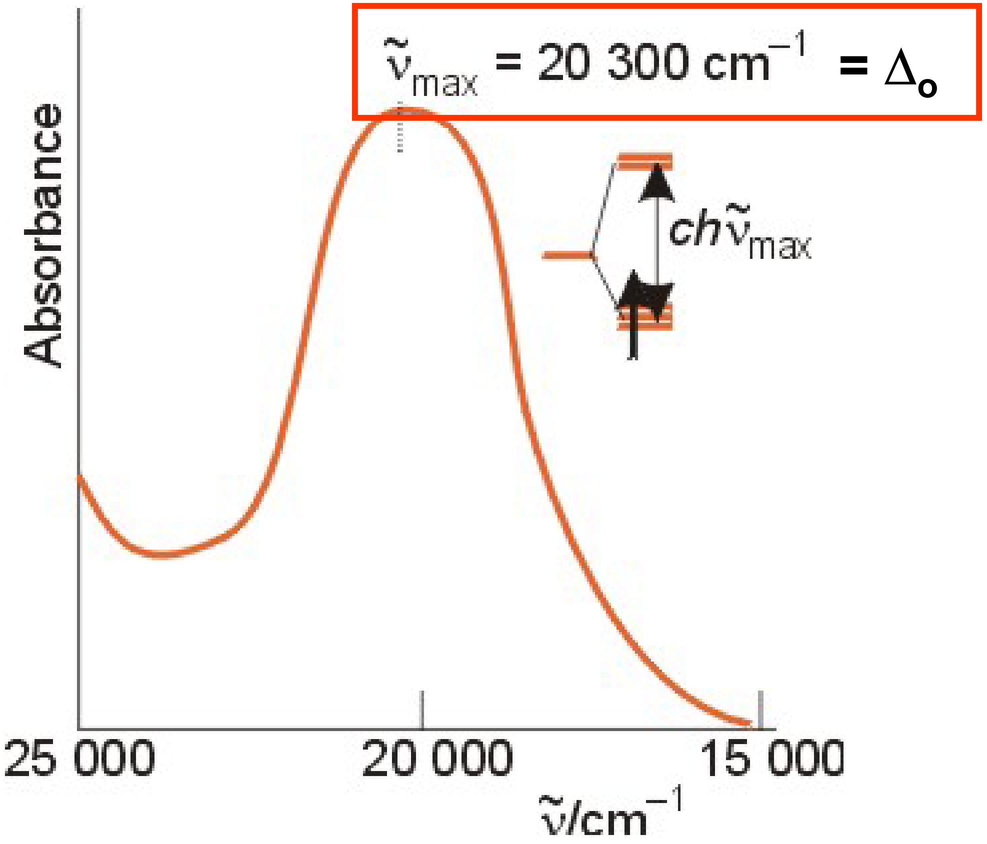
$I^- < S^{2-} < Cl^- < NO_3^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^- < CO$

The strength of the ligand field varies with:

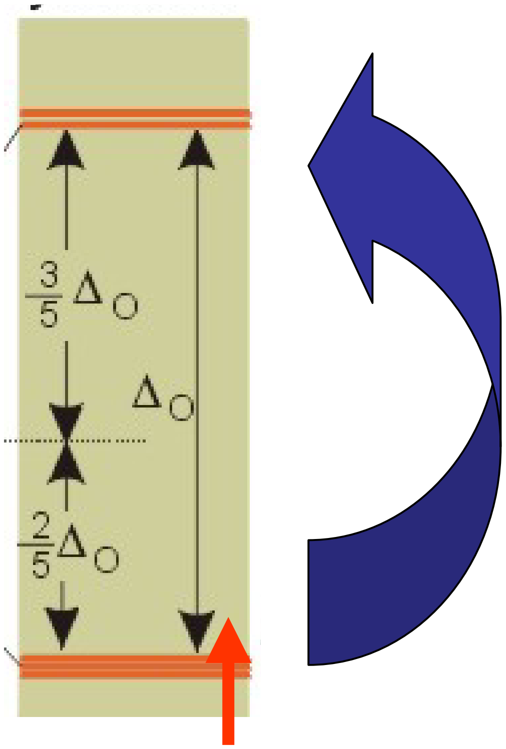
a) the **size and chemical properties** of the ligand (**no** simple relation !)

b) the **oxidation number of the central atom** (the higher the oxidation number the stronger the ligand field)

Basic Crystal Field Theory: optical spectrum and ligand field



$\tilde{\nu}_{max} = 20\ 300\ cm^{-1} = \Delta_o$

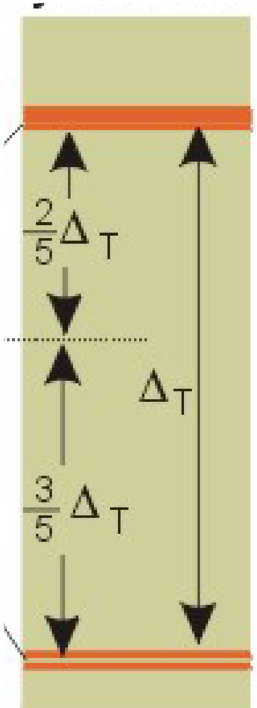


$[Ti(H_2O)_6]^{3+}$
Ti^{3+}: $(Ar)d^1$

Basic Crystal Field Theory: Ligand field stabilization energies (LFSE)

LFSE: Energetic stabilization **relative** to a field with **spherical** symmetry

Tetrahedral



Tetrahedral case:

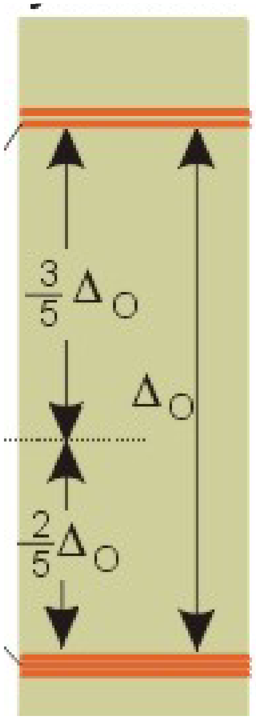
$$LFSE = (-0.6 \times x + 0.4 \times y) \times \Delta_T$$

Octahedral case:

$$LFSE = ((-0.4 \times x + 0.6 \times y) \times \Delta_O$$

x, y: number of unpaired electrons in the respective electronic states

Octahedral



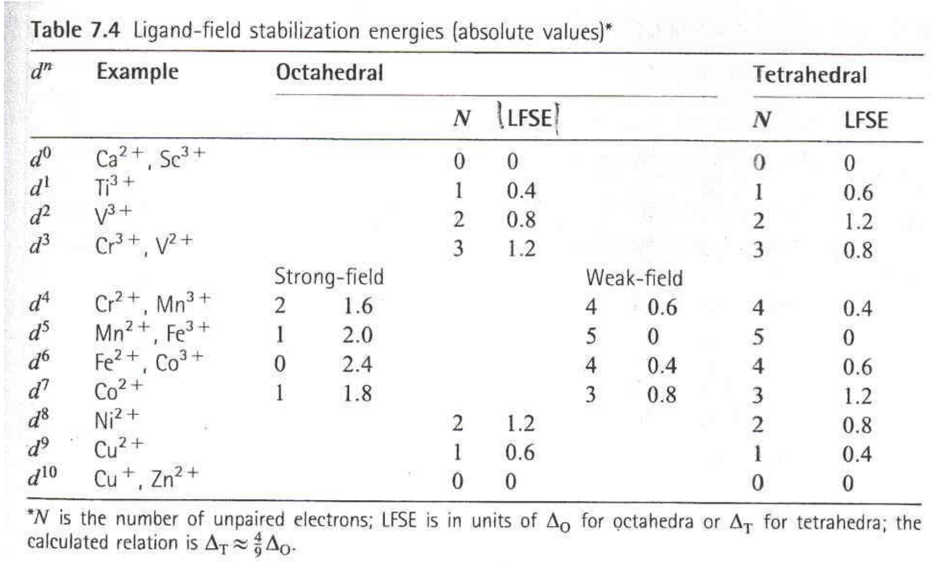


Table 7.4 Ligand-field stabilization energies (absolute values)*

d^n	Example	Octahedral						Tetrahedral	
				N	|LFSE|			*N*	LFSE
d^0	Ca^{2+}, Sc^{3+}			0	0			0	0
d^1	Ti^{3+}			1	0.4			1	0.6
d^2	V^{3+}			2	0.8			2	1.2
d^3	Cr^{3+}, V^{2+}			3	1.2			3	0.8
		Strong-field				Weak-field			
d^4	Cr^{2+}, Mn^{3+}	2	1.6			4	0.6	4	0.4
d^5	Mn^{2+}, Fe^{3+}	1	2.0			5	0	5	0
d^6	Fe^{2+}, Co^{3+}	0	2.4			4	0.4	4	0.6
d^7	Co^{2+}	1	1.8			3	0.8	3	1.2
d^8	Ni^{2+}			2	1.2			2	0.8
d^9	Cu^{2+}			1	0.6			1	0.4
d^{10}	Cu^{+}, Zn^{2+}			0	0			0	0

*N is the number of unpaired electrons; LFSE is in units of Δ_O for octahedra or Δ_T for tetrahedra; the calculated relation is $\Delta_T \approx \frac{4}{9}\Delta_O$.

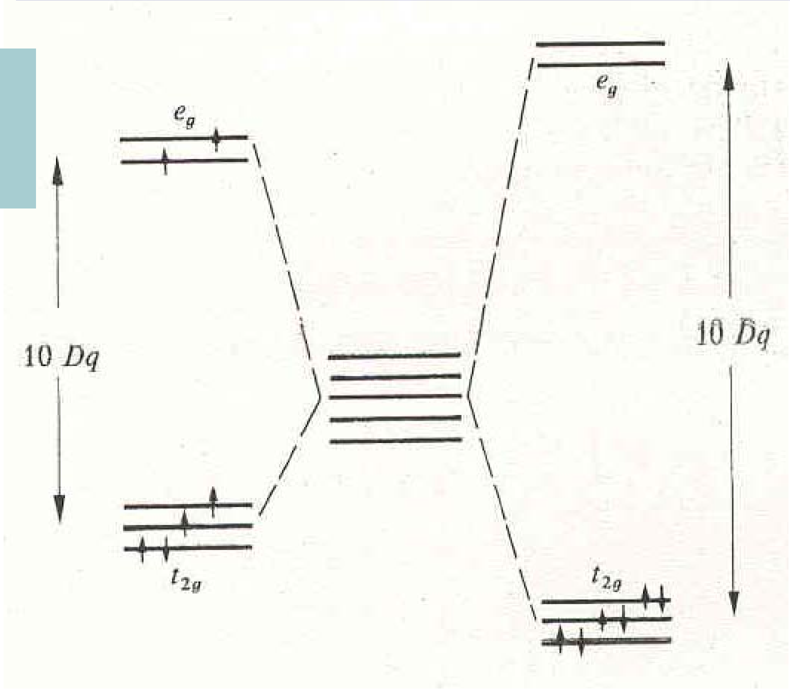
Basic Crystal Field Theory: Weak Field – Strong Field

Spin **pairing energy** versus **ligand field splitting**

octahedral complex

weak field **strong field**

d^6 high spin
(paramagnetism)

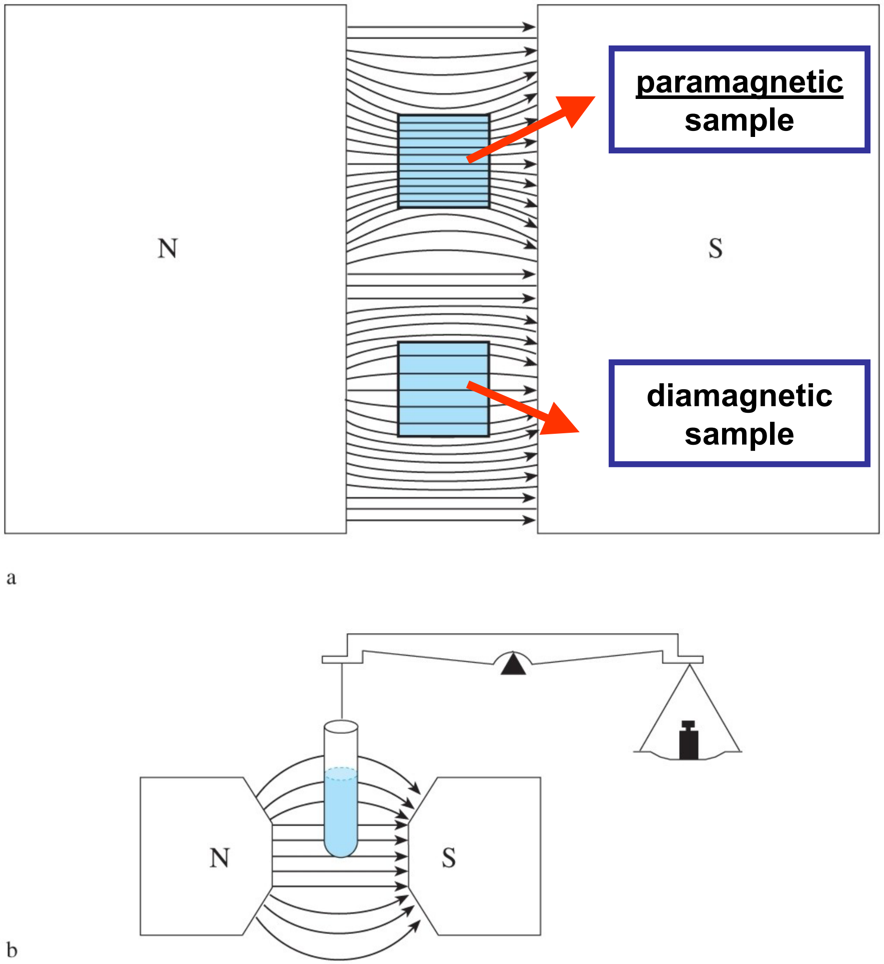


d^6 low spin
(diamagnetism)

high spin: maximum number of unpaired electrons
low spin: minimum number of unpaired electrons

→ measurement of magnetic moment

Magnetism of coordination compounds



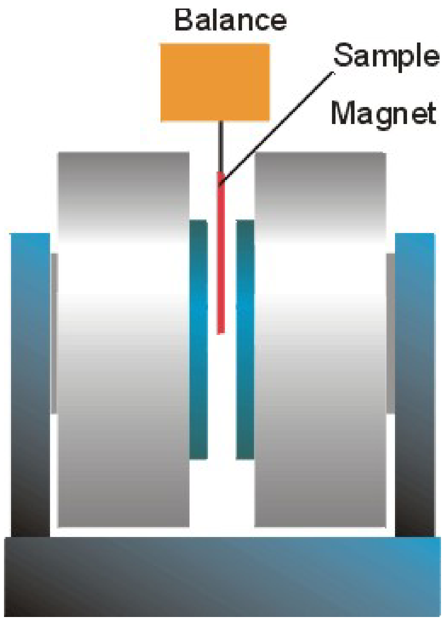
paramagnetic sample

diamagnetic sample

Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-13.jpg

central atom with **unpaired valence electrons** ⇒ **paramagnetism**

central atom with **paired valence electrons only** ⇒ **diamagnetism**

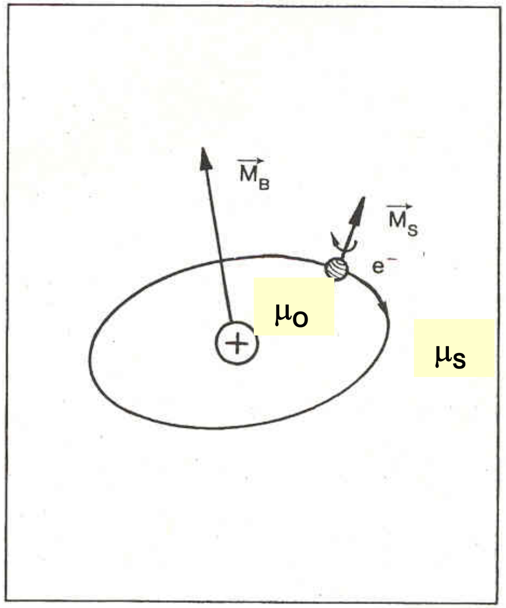


Magnetism of coordination compounds: magnetic (dipole) moments

In general there are **two components** of the resulting magnetic moment of an atom (ion):

⇒ **orbital angular momentum (μ_O)** ⇒ **spin momentum (μ_S)**

- In most coordination compounds with **3d elements** as central atoms (but **not** 4d and 5d !!) the orbital angular momentum can be neglected (technical term: “quenched”).
- typical for 3d complexes with **one** central atom: **spin only magnetism (μ_S)**



Definition of μ_S:

$$\mu_S = \mu_B \times 2 \times (S(S+1))^{1/2}$$

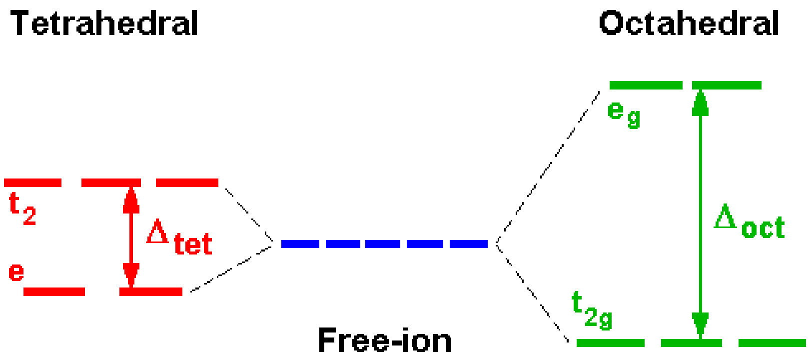
$\mu_B = 9{,}27 \times 10^{-24}$ Am^2 (Bohr magneton,
smallest quantity of a magnetic moment)

S = ½n (Total spin quantum number)
n: number of <u>unpaired electrons</u>

n	1	2	3	4	5
μ_S	1,73	2,83	3,87	4,90	5,91

Special aspects of the electronic structure of complexes with CN 4

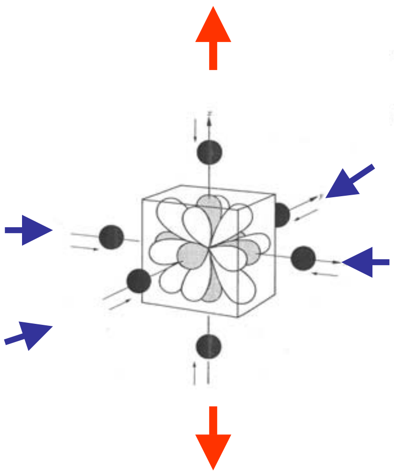
1. Tetrahedral coordination

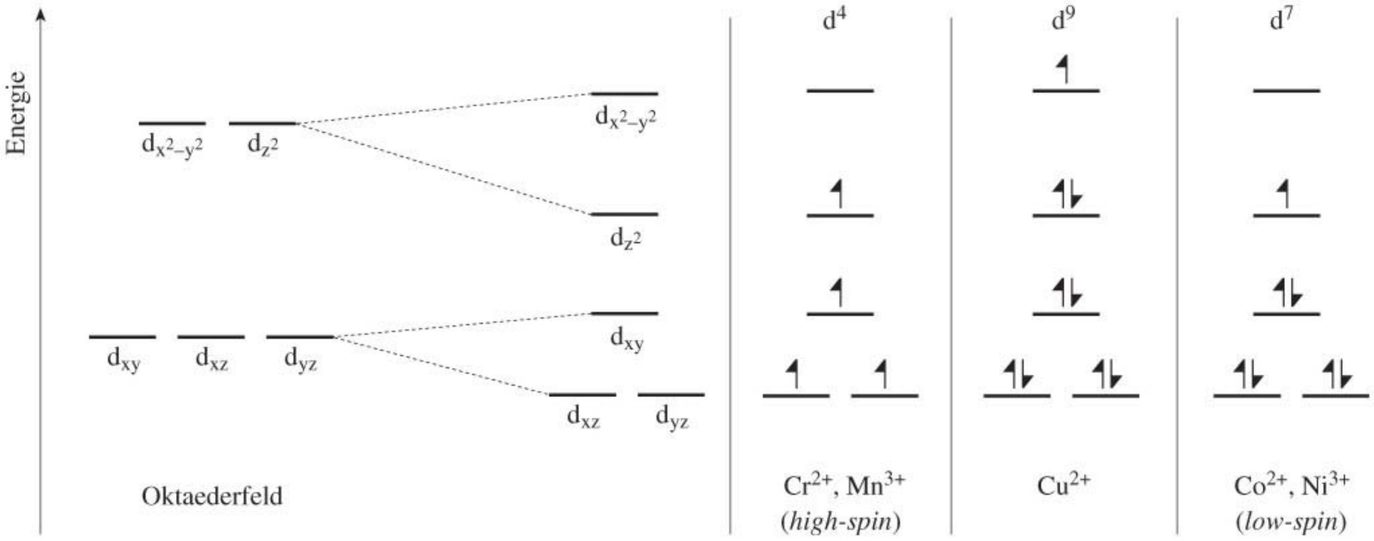


- **inverse splitting (compared to octahedral case**

- **only the weak field case is of importance (⇒ high spin magnetism)**

2. Tetragonal and square planar coordination ⇒ (**Jahn-Teller-effect)**





Ligand-field theory

Crystal field theory has problems to explain why the ligand field splitting for some uncharged molecules (e.g. CO) is unusually large and is moderate for others (e.g. NH_3).

⇒ solution: the interaction between ligands and central atom has to be discussed in terms of **atomic and molecular** orbitals and **not only** in terms of **point charges** (as in crystal field theory)

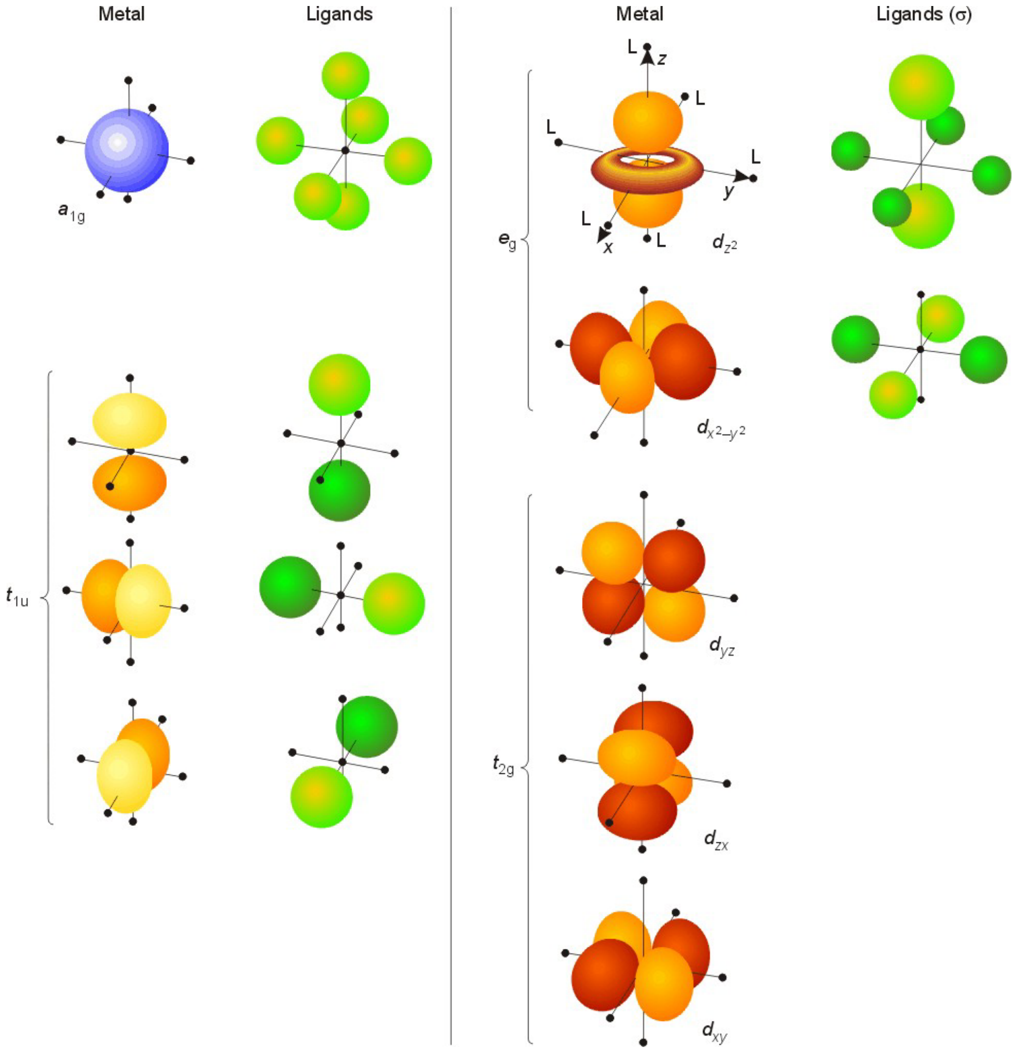
⇒ e.g. for **octahedral** symmetry, **σ-bonding** only

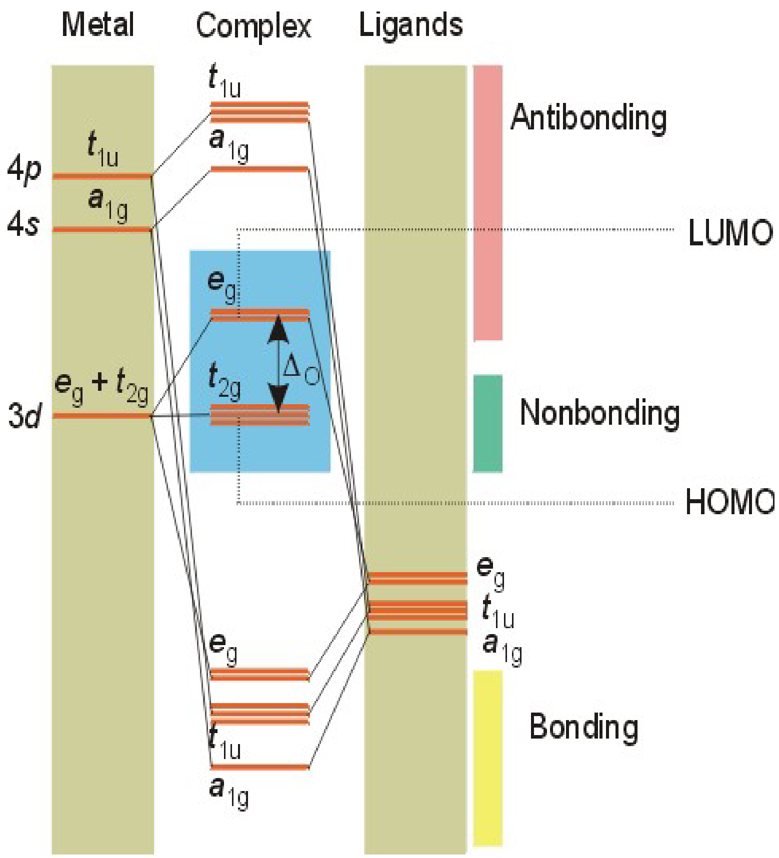
1. Analyze the symmetry properties of **groups** of atomic orbitals (**separate** for ligands and central atoms) ⇒ **symmetry adapted** orbitals

2. **Overlap** atomic orbitals of **similar** symmetry to form molecular orbitals (necessary: basic knowledge in **group theory** and basic **MO-theory**)

Central atom (3d-element) orbital	**symmetry label**	**Degeneracy**
s	a_{1g}	1
p_x, p_y, p_z	t_{1u}	3
d_{xy}, d_{xz}, d_{yz}	t_{2g}	3
$d_{x^2-y^2}$, d_{z^2}	e_g	2

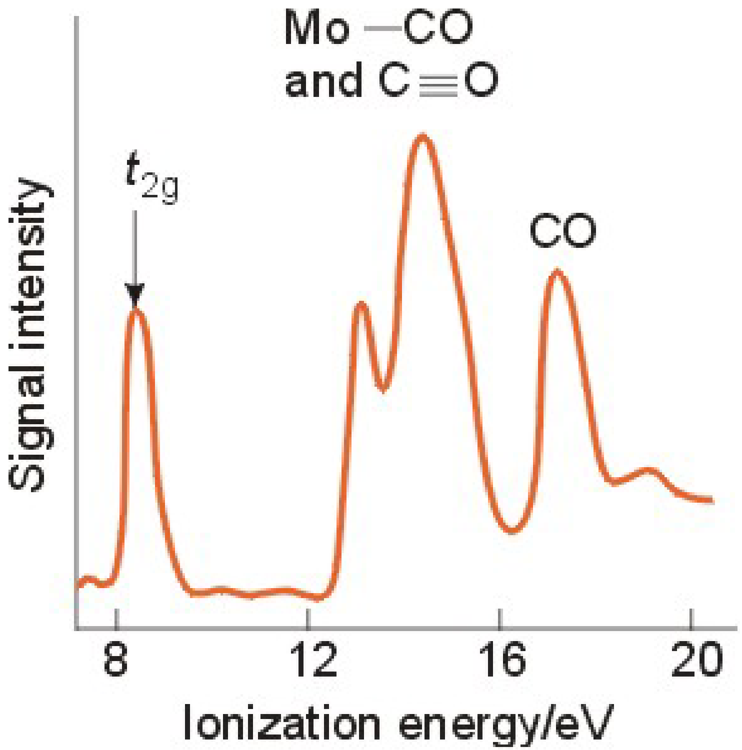
Ligand-field theory: symmetry-adapted groups of orbitals: σ-bonding



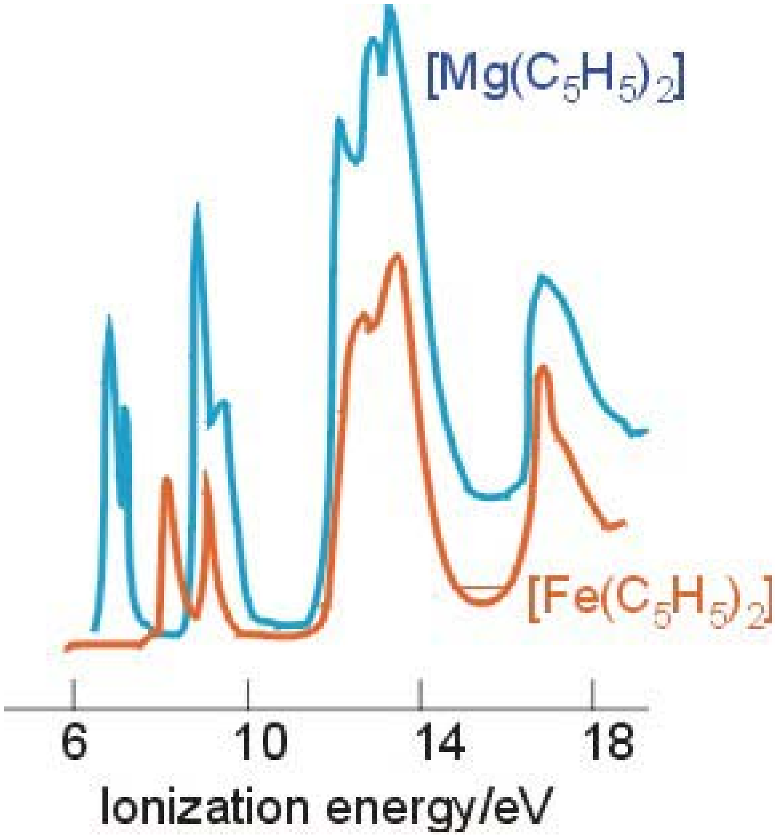


Ligand-field theory: Electronic Structure, PE-spectrum

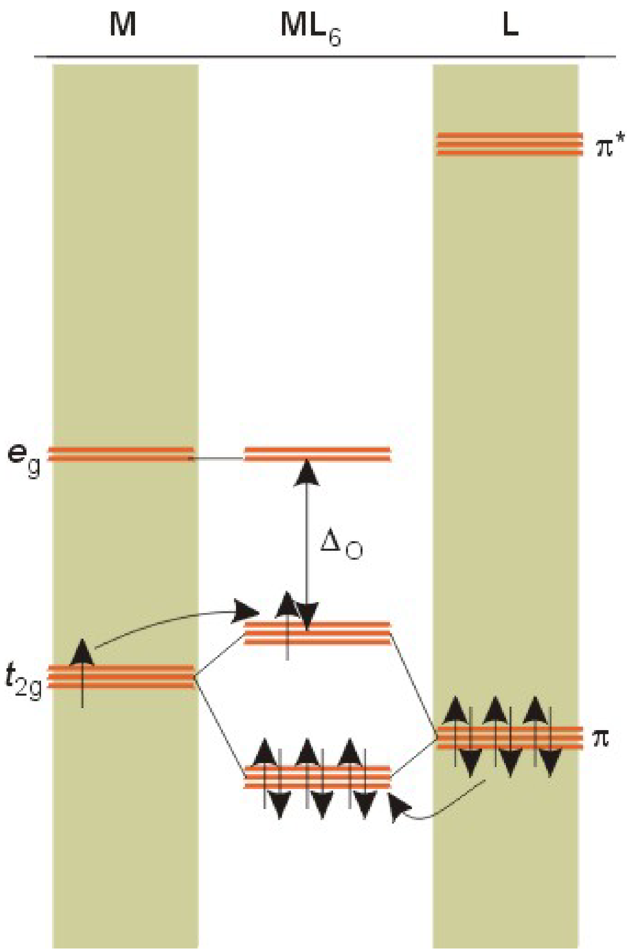
Exploring the electronic structure of a complex molecule by Photoelectron-Spectroscopy (PES):



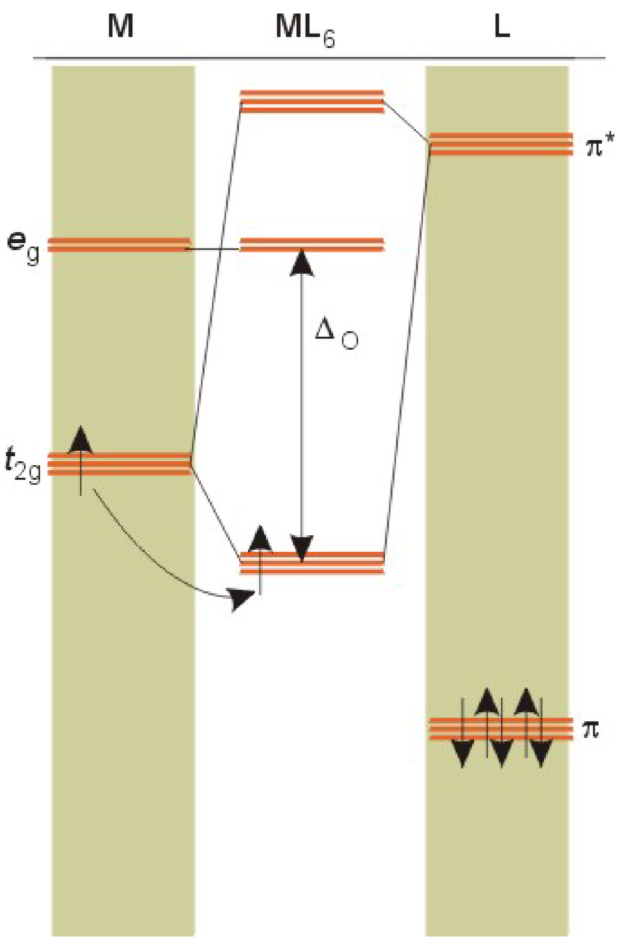
$Mo(CO)_6$



Ligand-field theory: π-bonding



π -donor ligand: completely filled low-energy **π-orbitals:** Δ Is reduced



π -acceptor ligand: incompletely filled low-energy **π-orbitals** Δ Is increased

Coordination Chemistry

Copy some basic informations from the blackboard during lecture:

- applications of the „law of mass action“ for complex molecules:

  formation and **dissociation** constants of complex molecules

- the **chelate** effect

- **lability** and **inertness** of complex molecules