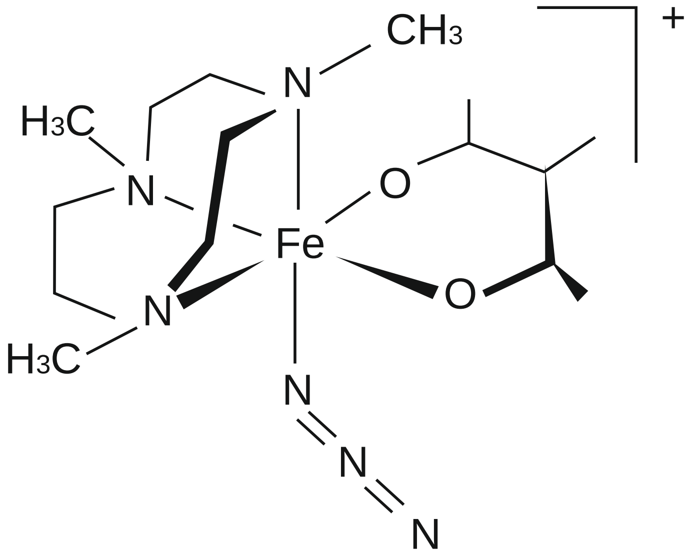
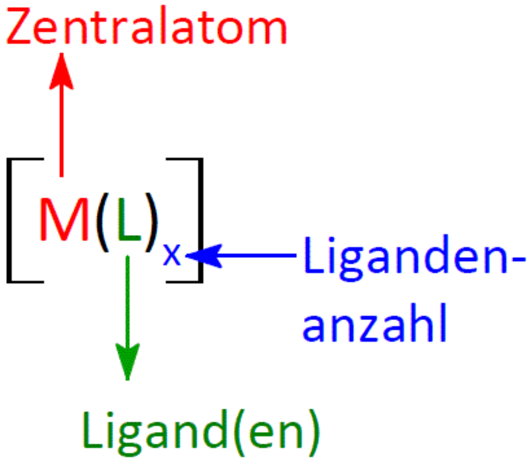
Coordination and Transition Metal Chemistry

Content

1. Classification of the Elements
2. d-Orbitals
3. Coordinative Bonding
4. Complexes
5. Nomenclature of Coordinative Compounds
6. Ligands
7. Stability of Complexes
8. Structures and Isomers
9. Concepts of Bonding
10. Chemistry of Transition Metals
11. Chemistry of Lanthanides





Zentralatom

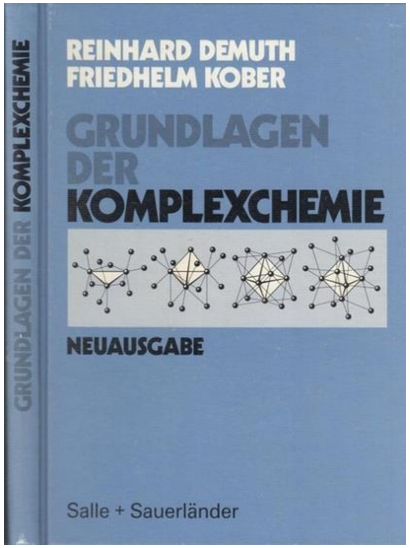
$[M(L)_x]$

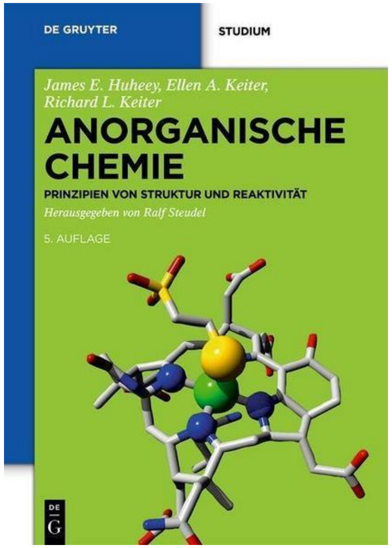
Liganden-
anzahl

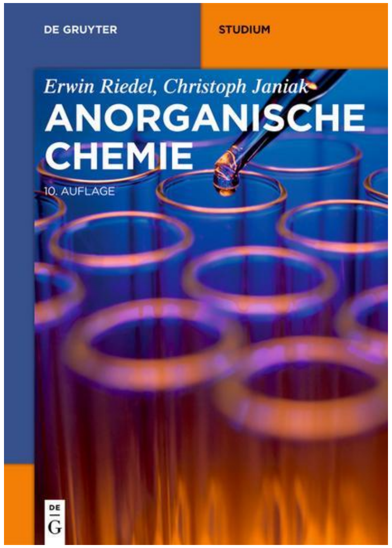
Ligand(en)

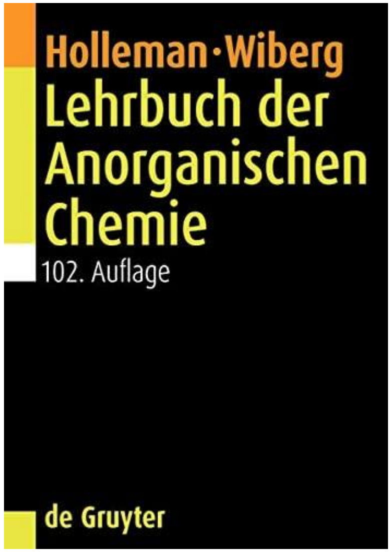
Literature

- R. Demuth, F. Kober, Grundlagen der Komplexchemie
  Salle + Sauerländer, 1979
- J.E. Huheey, E.A. Keiter, R. Keiter, Anorganische Chemie
  De Gruyter, 3. Auflage 2003
- A.F. Hollemann, N. Wiberg, Lehrbuch der anorganischen Chemie, De Gruyter, 102. Auflage 2007
- E. Riedel, C. Janiak, Anorganische Chemie
  De Gruyter, 10. Auflage 2022

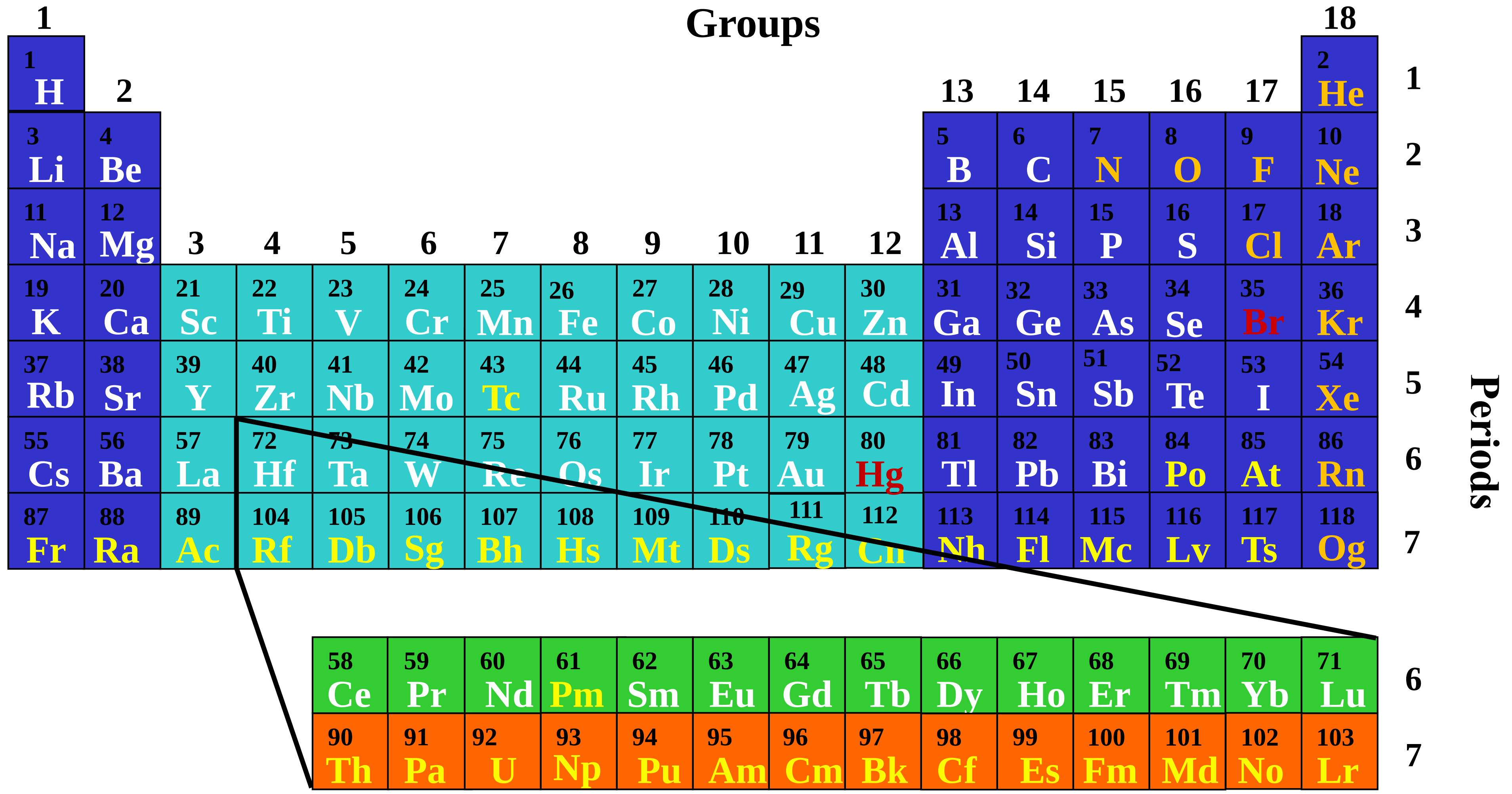








1. Classification of the Elements



Groups

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Period														
6	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Main group elements	s- and p-block elements	ns^xnp^y	n = 1-7, x = 1-2, y = 1-6
Subgroup elements (transitions metals)	d-block elements	nd^x	n = 3-5, x = 1-10
Lanthanids (rare earth metals)	4f-block elements	$4f^x$	x = 1-14
Actinids	5f-block elements	$5f^x$	x = 1-14

1. Classification of the Elements

Electron Configuration of the 3d-Transition Metals

$[\mathrm{Ar}]4s^2 3d^x$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

Electron Configuration of the 4d-Transition Metals

$[\mathrm{Kr}]5s^2 4d^x$

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
5s	2	2	1	1	1	1	1	0	1	2
4d	1	2	4	5	6	7	8	10	10	10

Electron Configuration of the 5d-Transition Metals

$[\mathrm{Xe}]4f^{14} 6s^2 5d^x$

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
6s	2	2	2	2	2	2	2	1	1	2
5d	1	2	3	4	5	6	7	9	10	10

⇒ More stable configuration due to lower energetic states of the d-orbitals

1. Classification of the Elements

Electron Configuration of the Lanthanides and their Cations

Metals

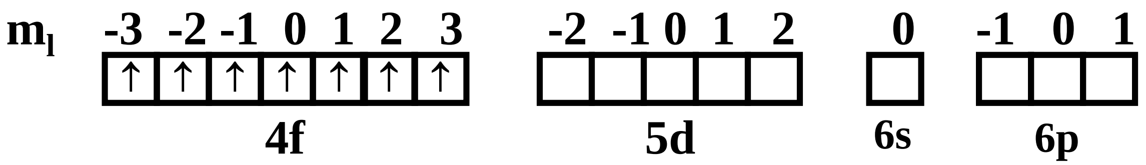
[Xe]	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14

Cations

[Xe]	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
	Ce^{4+}	Pr^{4+}	Nd^{4+}				Sm^{2+}	Eu^{2+}	Dy^{4+}					Tm^{2+}	Yb^{2+}
								Tb^{4+}							
4f	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

Examples

$Gd^{3+}/Eu^{2+}/Tb^{4+}$



Total spin $S = \Sigma s = 7/2$ → $2S+1 = 8$ → highly paramagnetic ions

1. Classification of the Elements

Particularities of Transition Metals

1. Variable oxidation states

The highest oxidation state corresponds to the group number and thus exhibit the electron configuration nd^0 with $n = 3, 4, 5$

2. Stability also in low oxidation states

In presence of certain ligands, i.e. π-acceptor ligandes e.g. CO, alkenes, and so on TM ions form stable complexes in low or even negative oxidation states. Carbonylates (anionic carbonyl complexes) can attain the oxidation state -4:

$[Mo^{-IV}(CO)_4]^{4-}$

NiO

Nd_2O_3

Ho_2O_3

Er_2O_3

3. Optical properties

Special electronic transitions

- **within partly occupied d- or f-orbitals**
- **between 4f and 5d orbitals of rare earth ions: Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{2+}, Eu^{2+}, Tm^{2+}, Yb^{2+}**
- **due to shift of electron density from the metal ion to ligands (MLCT), from ligands to the metal ion (LMCT) or between metal ions (MMCT)**

1. Classification of the Elements

Particularities of Transition Metals

4. Unpaired electrons: Energy technology, catalysis, luminescence, magnetism (see above)

Incomplete occupied d or f orbitals result in many energy levels with rather little energy spacing as well as high magnetic moments

- **Energy technol.: Accumulators, batteries, fuel & solar cells, superconductors, wind turbines**
- **Catalysis: Biochemistry (enzymes), technical catalysis, polymerisation & condensation**
- **Luminescence: displays, laser, light sources, optical marker, Scintillators**
- **Magnetism: Fe/Co magnets, REE magnets, NMR contrast agents, sensors**

5. Formation of complexes variable coordination number, geometry and reactivity

Basis of catalytical processes as well as transport processes: biology and technology

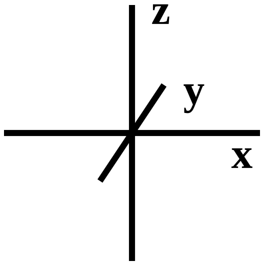
6. Peculiar physical properties of metals

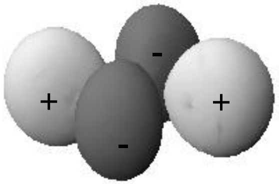
- **high electrical and thermal conductivity**
- **high melting and boling points, high density**
- **high ductility**
- **high resistance towards O_2, acids, and bases**

Iridium crucibles (T_m = 2465 ° C)

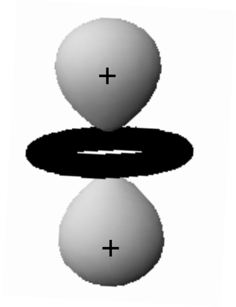
2. d-Orbitals

The five d-Orbitals Can Be Divided into two Groups: Three are located between the Axes of the Cartesian Coordinate System and two Actually onto them

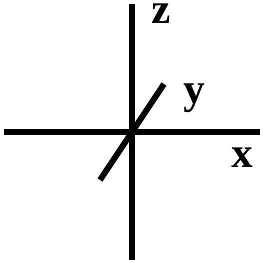


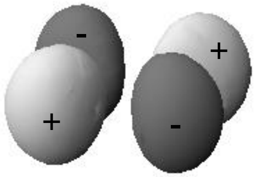


d_{x2-y2}

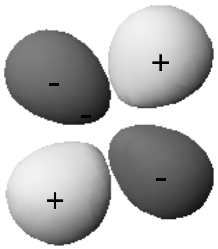


d_{z2}

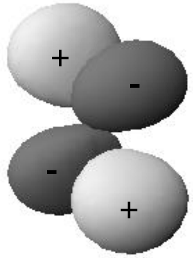




d_{xy}



d_{xz}



d_{yz}

The d-orbitals are accessible for the formation of chemical bonds

Octet rule → 18-electrons rule

3. Coordinative Bonding

Ionic Bonding

Formally speaking, all bonding electrons are transferred to the more electronegative bonding partner

$2\ Na + Cl_2 \rightarrow 2\ Na^+ + 2\ Cl^-$

Covalent Bonding

2-centres-$2e^-$: The bonding electrons are contributed by two bonding partners and are distributed evenly between them (typical covalent bond): H_2, F_2

3-centres-$2e^-$: The bonding electrons originate from two bonding partners but are distributed between three of them: H_3^+, B_2H_6

3-centres-$4e^-$: The four bonding electrons originate from two bonding partners partners but are distributed between three of them: HF_2^-, H-bridges

Coordinative (Dative) Bonding

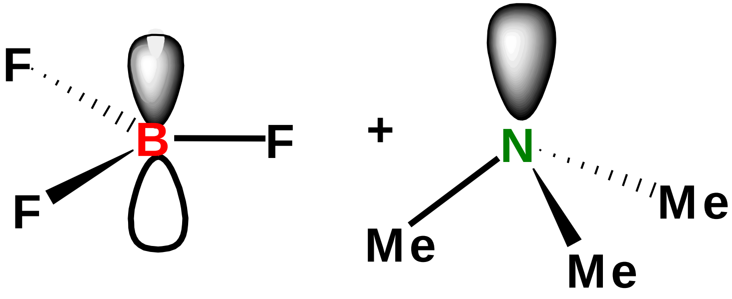
The bonding electrons are donated by a single bonding partner solely

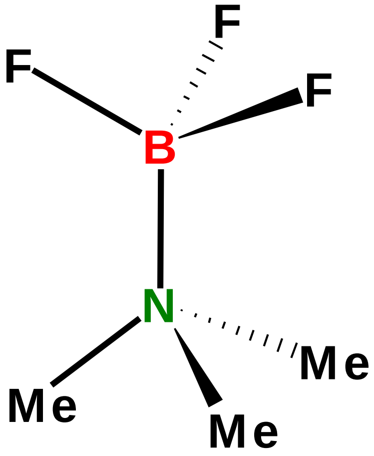
$Z + |L \rightarrow Z\text{-}L$

3. Coordinative Bonding

The Coordinative (Dative) Bond Is the Product of a Lewis Acid-Base Reaction

$BF_3 + NMe_3 \rightarrow [Me_3N\text{-}BF_3]$

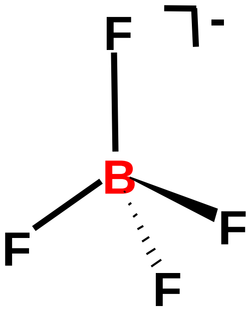




Lewis-acid
(acceptor)

Lewis-base
(donor)

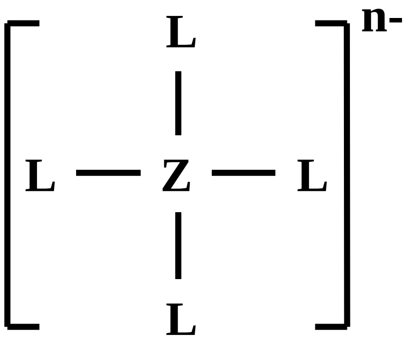
$BF_3 + F^- \rightarrow [BF_4]^-$



4. Complexes

Definition of Complexes

Complexes or coordination compounds are molecules or ions CL_n, wherein an either uncharged or charged central atom C is surrounded by a number - according to its coordination number - of either charged or uncharged mono- or polyatomic groups L



lat. complexus = embrace, lat. coordinare = associate

C = central atom = complex centre, coordination centre → acids

L = ligands, ligand shell, coordination sphere → bases

Alfred Werner (1866 - 1919)

All ligands of same kind	**homoleptic complexes**	$[Ni(CN)_4]^{2-}$
Different ligands	**heteroleptic complexes**	$[MoCl_4(O)_2]^{2-}$

4. Complexes

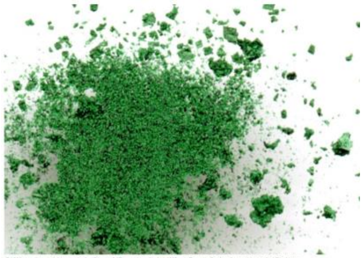
Studies of Alfred Werner (Nobel Prize 1913) on Cobalt Compounds

a) $CoCl_3{\cdot}6NH_3$	yellow	Luteo
b) $CoCl_3{\cdot}5NH_3$	red	Purpureo
c) $CoCl_3{\cdot}4NH_3$	green	Praseo
d) $CoCl_3{\cdot}4NH_3$	violet	Violeo

Gravimetrical determination of chloride with $AgNO_3$ gives

a)	3 AgCl	$[Co(NH_3)_6]^{3+} + 3\ Cl^-$	
b)	2 AgCl	$[Co(NH_3)_5Cl]^{2+} + 2\ Cl^-$	
c, d)	1 AgCl	$[Co(NH_3)_4Cl_2]^{+} + 1\ Cl^-$	2 isomers (cis and trans)

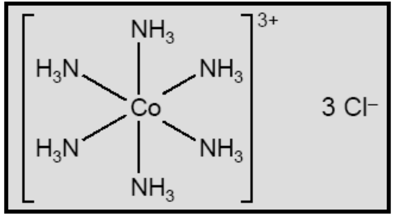
Zu "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. cis-[CoCl2(NH3)4]Cl.jpg



Zu "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. trans-[CoCl2(NH3)4]Cl.jpg

Werner's deductions:

- Co^{3+} is always 6-coordinate
- Ligands are arranged in octahedra

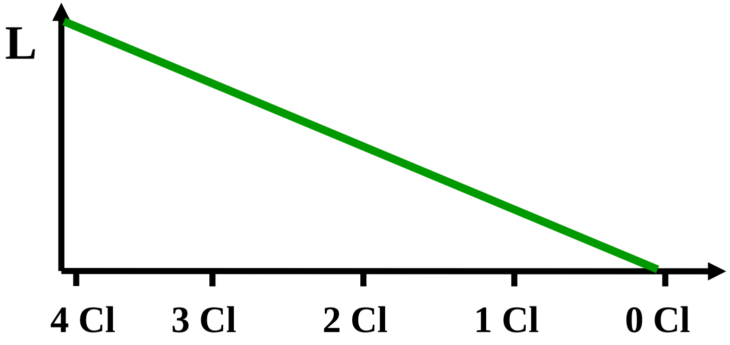


4. Complexes

Studies upon the Electrical Conductivity L During the Formation of Complexes

Complex	L [S·cm^2/mol]	Number of ions per formula unit	Number of Cl$^-$-ions per formula unit
$[Pt(NH_3)_6]Cl_4$	523	5	4
$[Pt(NH_3)_5Cl]Cl_3$	404	4	3
$[Pt(NH_3)_4Cl_2]Cl_2$	228	3	2
$[Pt(NH_3)_3Cl_3]Cl$	97	2	1
$[Pt(NH_3)_2Cl_4]$	0	0	0
$K[Pt(NH_3)Cl_5]$	108	2	0
$K_2[PtCl_6]$	256	3	0

- The electrical conductivity L of the aqueous solution of the complexes is defined by the amount of dissolved cations and anions per formula unit.
- Neutral complexes do not contribute to the electrical conductivity of a solution.



5. Nomenclature of Coordinative Compounds

Construction of a Complexes' Formula

Rule 1: The cation is always placed in front of the anion and complexes are enclosed between squared brackets, e.g. $K_4[Fe(CN)_6]$

Rule 2: The central atom is positioned at first position, e.g. $[Fe(CN)_6]^{4-}$, $[PF_6]^-$

Rule 3: Anionic ligands come first before neutral ligands

Rule 4: Alphabetical ordering within a class of ligands

Rule 5: Molecular ligands as well as abbreviations are written in brackets

Rule 6: Oxidation number as superscript behind the central atom, e.g. $[Fe^{II}(CN)_6]^{4-}$, $[Co^{III}(NO_2)_3(NH_3)_3]$, $[Co^{II}Cl_2(en)_2]$

5. Nomenclature of Coordinative Compounds

Deduction of the Name

Rule 1: Ligands in alphabetical order prior to the name of the central atom (last!) with di, tri, … as prefix for multiple ligands

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

Hexaamminecobalt(III)

Rule 2: Statement of:

a) oxidation number of central atom as Roman cipher in parentheses (e.g. II) or

b) charge of coordinating unit as Arabic cipher + charge (e.g. 3+)

behind the corresponding unit

$[PtCl_4]^{2-}$	$[Ni(CN)_5]^{3-}$
Tetrachloroplatinate(II)	Pentacyanonickelate(3-)

Anionic complexes end on ate!

Attention!	Cu: Cuprate	Fe: Ferrate	Pb: Plumbate	Hg: Mercurat
	Au: Aurate	Sn: Stannate	Ag: Argentate	Sb: Stibate

5. Nomenclature of Coordinative Compounds

Deduction of the Name

Rule 3: Anionic ligands which end in “-ide” are replaced with an ending “-o” (bromide→bromo), anions ending with “-ite” and "-ate” are replaced with endings “-ito” and “-ato”, respectively. Most neutral and formally cationic ligands carry their normal name.

There are a few exceptions to the naming of neutral ligands

Ammonia	NH_3	ammine
Carbon monoxide	CO	carbonyl
Water	H_2O	aqua (aquo)
Nitrogen monoxide	NO	nitrosyl
Oxygen	O_2	oxygenyl

6. Ligands

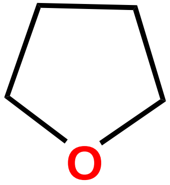
Regularly Used Ligands

Formel	*Ligandname*	*Formel*	*Ligandname*
F^-	**Fluoro**	**H_2**	**Diwasserstoff**
Cl^-	**Chloro**	**O_2**	**Disauerstoff**
O^{2-}	**Oxo, Oxido**	**H_2O**	**Aqua**
S^{2-}	**Sulfido, Thio**	**H_2S**	**Sulfan, Hydrogensulfid**
$(SH)^-$	**Hydrogensulfido**	**H_2S_2**	**Disulfan, Hydrogendisulfid**
$(SO_4)^{2-}$	**Sulfato**	**CO**	**Carbonyl**
$(C_2O_4)^{2-}$	**Oxalato, Ethandionato**	**CS**	**Thiocarbonyl**
N^{3-}	**Nitrido**	**N_2**	**Distickstoff**
P^{3-}	**Phosphido**	**NH_3**	**Ammin**
$(CN)^-$	**Cyano oder Cyanido**	**PH_3**	**Phosphan**
$(NCO)^-$	**Cyanato**	**P_4**	**Tetraphosphor**
$(NCS)^-$	**Thiocyanato**	**$(CH_3)_3N$**	**Trimethylamin**
$(NH_2)^-$	**Amido, Azanido**	**$(CH_3)_3P$**	**Trimethylphosphan**
$(NH)^{2-}$	**Imido, Azandiido**	**$HN{=}NH$**	**Diazen**
$(PH_2)^-$	**Phosphanido**	**$HP{=}PH$**	**Diphosphen**
N_3^-	**Azido**	**NO**	**Nitrosyl**
$(NO_3)^-$	**Nitrato**	**NS**	**Thionitrosyl**
$(NO_2)^-$	**Nitrito**	**N_2O**	**Distickstoffoxid**

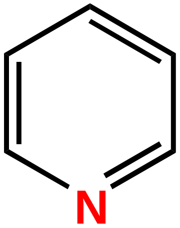
Dentallity of ligands = Number of atoms that bind to the central metal atom

6. Ligands

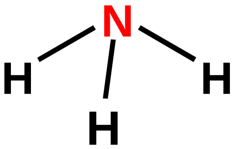
Monodentate Ligands



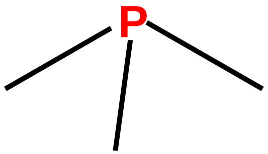
THF
Tetrahydrofurane



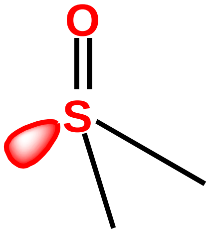
Pyridine



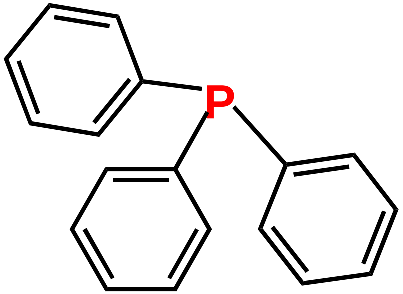
Ammine



Trimethylphosphane



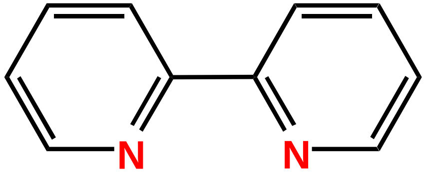
dmso
Dimethylsulphoxide



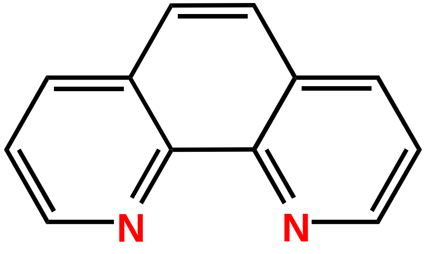
Triphenylphosphane

6. Ligands

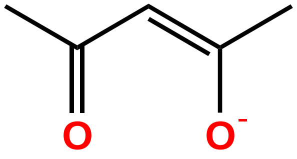
Bidentate Ligands



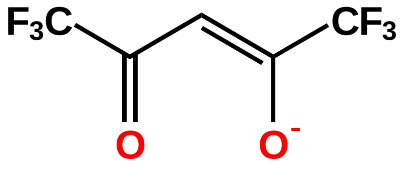
bpy
2,2´-Bipyridine



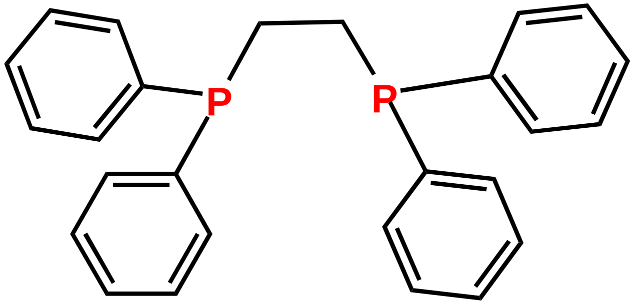
phen
1,10-Phenanthroline



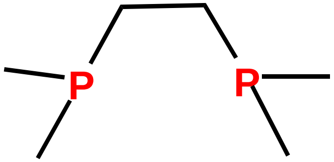
acac
Acetylacetonate



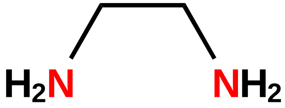
hfacac
Hexafluoroacetylacetonate



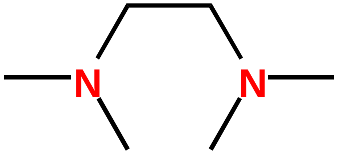
dppe
Diphenylphosphinoethane



dmpe
Dimethylphosphinoethane



en
Ethylene
diamine



tmeda
Tetramethylene
diamine

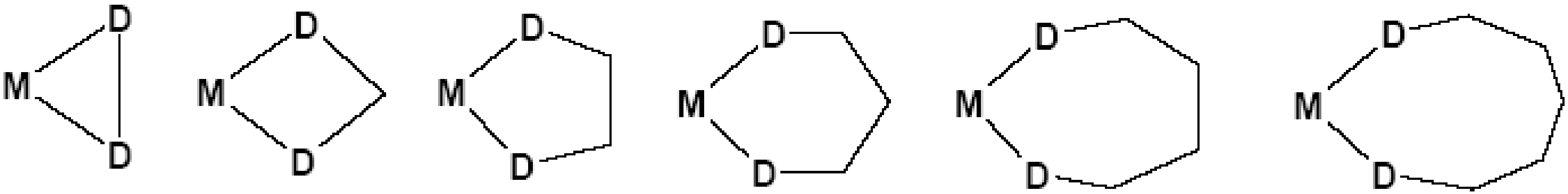
6. Ligands

Chelating Ligands

Bidentate ligands are also called chelating ligands (Greek: *chele* = claw).

Literally, the ligand grabs the metal “in it’s claws”. If thereby (chelating)rings with five or six members are created, the formation of such complexes is entropically favoured in comparison to the formation of a complex with only monodentate ligands and thus considerable more stable.

⇒ Chelating effect (entropic effect)



60° **90°** **108°** **120°** **Inner angle = $(N-2)180^\circ/N$**

ring tension

optimal ring size

(optimal stability)

declining chelating effect

6. Ligands

Chelating Ligands

The formation of complexes with chelating ligands results in more stable complexes compared to the formation with mono dentate ligands

$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \leftrightarrows [Ni(NH_3)_6]^{2+} + 6\ H_2O$ $K_K = 2.0 \cdot 10^9$

$[Ni(H_2O)_6]^{2+} + 3\ en \leftrightarrows [Ni(en)_3]^{2+} + 6\ H_2O$ $K_K = 3.8 \cdot 10^{17}$

Formation of $[Ni(NH_3)_6]^{2+}$-complexes ⇒ number of particles remains the same

Formation of $[Ni(en)_3]^{2+}$-complexes ⇒ number of particles increases ⇒ $\Delta S^0 > 0$

Formation of a complex with a chelating ligand leads to a increase in entropy!

ΔH is about equal for both cases

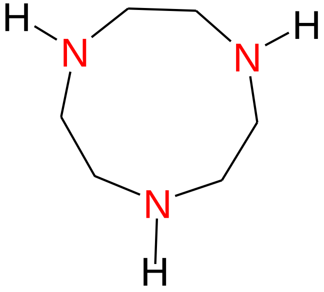
$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta G^\circ = -RT \cdot \ln K_K$ with K_K = complex formation constant

$(\Delta\Delta G^\circ = 0 - T\Delta\Delta S^\circ)$

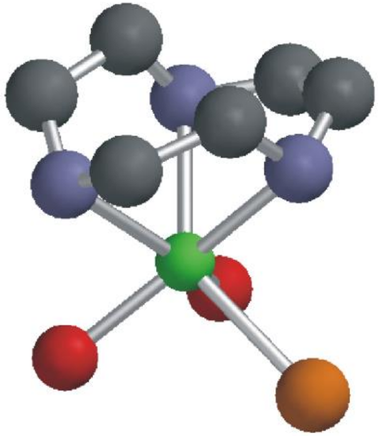
Formation of $[Ni(en)_3]^{2+}$ ⇒ more negative ΔG° ⇒ higher K_K

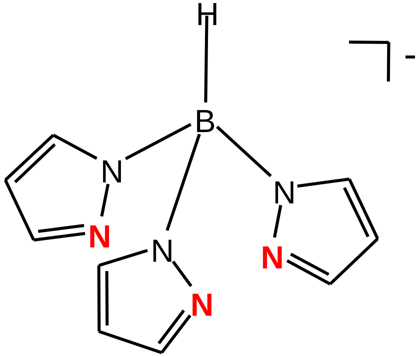
6. Ligands

Tridentate Ligands

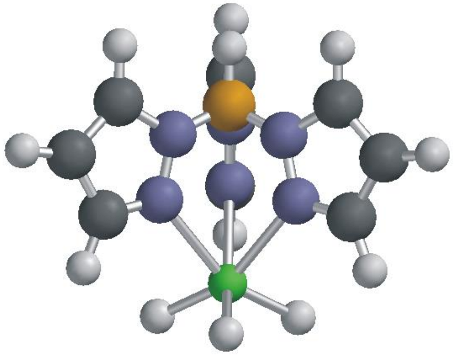


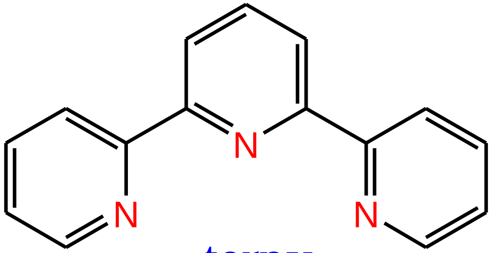
tacn
Triazacyclo*nonan*



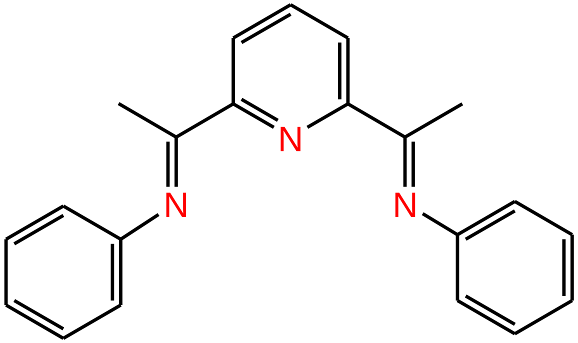


Tp
Trispyrazolylborate





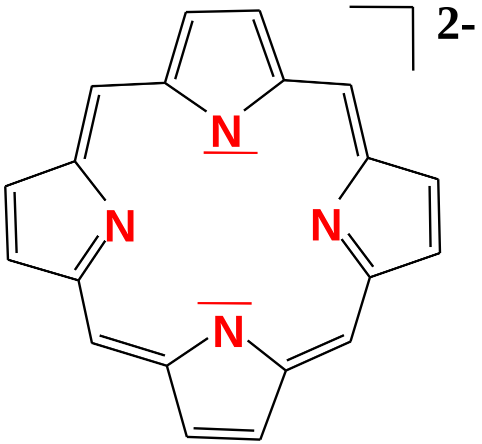
terpy
2,2´,2´´-Terpyridin



Diimin-Pyridin

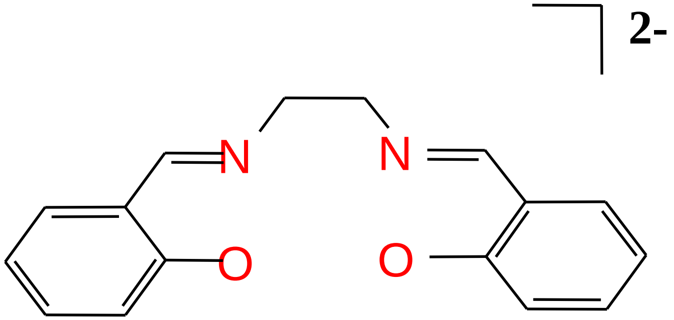
6. Ligands

Tetradentate Ligands



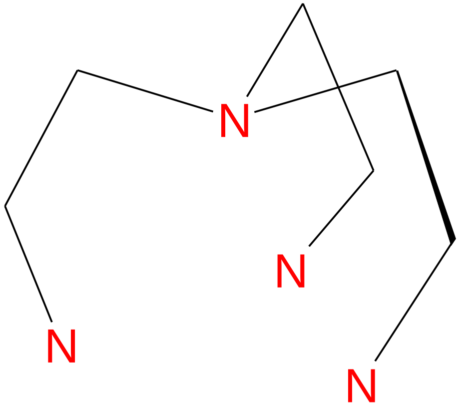
por

Porphyrine



salen

Bis(salicylidene)ethylenediamine

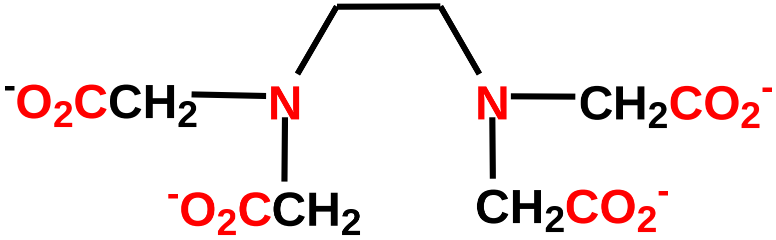


tren

Triethylenetetramine

6. Ligands

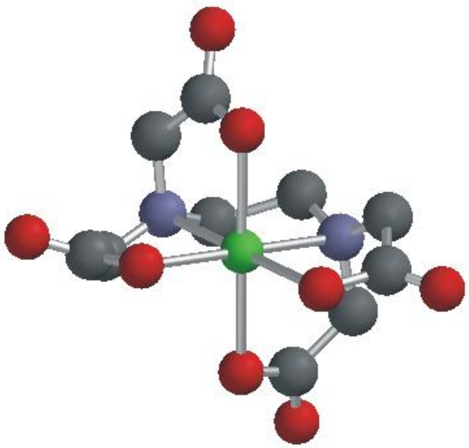
Hexadentate Ligands

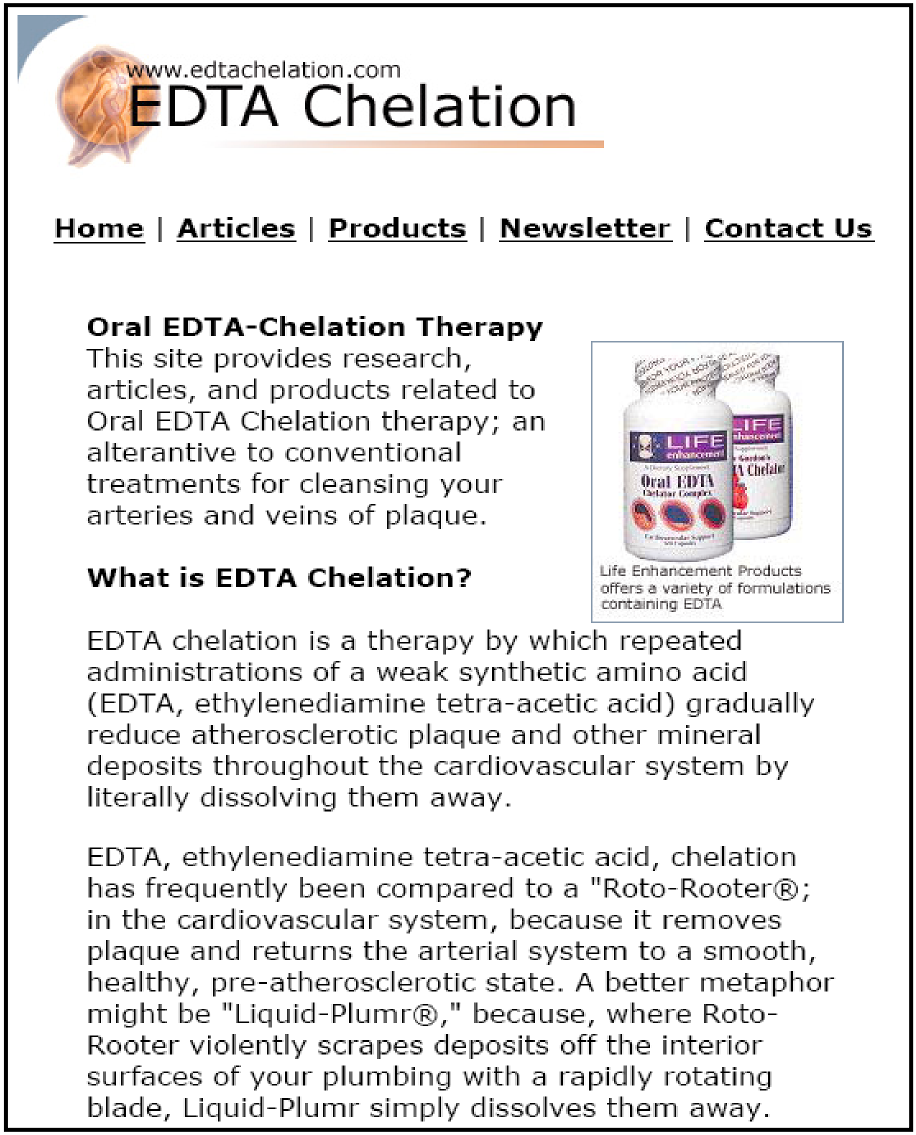


EDTA

Ethylenediaminetetraacetate

is an extraordinary good complexing agent





Oral EDTA-Chelation Therapy

This site provides research, articles, and products related to Oral EDTA Chelation therapy; an alterantive to conventional treatments for cleansing your arteries and veins of plaque.

Life Enhancement Products offers a variety of formulations containing EDTA

What is EDTA Chelation?

EDTA chelation is a therapy by which repeated administrations of a weak synthetic amino acid (EDTA, ethylenediamine tetra-acetic acid) gradually reduce atherosclerotic plaque and other mineral deposits throughout the cardiovascular system by literally dissolving them away.

EDTA, ethylenediamine tetra-acetic acid, chelation has frequently been compared to a "Roto-Rooter®; in the cardiovascular system, because it removes plaque and returns the arterial system to a smooth, healthy, pre-atherosclerotic state. A better metaphor might be "Liquid-Plumr®," because, where Roto-Rooter violently scrapes deposits off the interior surfaces of your plumbing with a rapidly rotating blade, Liquid-Plumr simply dissolves them away.

7. Stability of Complexes

Definition of Complex Stability

Complex equilibria in solution (cleavage of ligands)

$[ML_n] \leftrightarrows [ML_{n-1}] + L$ K_D with K_D = dissociation constant, n = coordination number

Normally, the formation of a complex proceeds step by step

$M + L \leftrightarrows [ML]$ K_1

$$\boxed{K_1 = \frac{c(ML)}{c(M) \cdot c(L)}}$$

$[ML] + L \leftrightarrows [ML_2]$ K_2

$[ML_2] + L \leftrightarrows [ML_3]$ K_3

$$\boxed{K_3 = \frac{c(ML_3)}{c(ML_2) \cdot c(L)}}$$

and so on

total constant of formation = K_B = $ß_n$

$[ML_{n-1}] + L \leftrightarrows [ML_n]$ K_n

$$\boxed{K_n = \frac{c(ML_n)}{c(ML_{n-1}) \cdot c(L)}} \Rightarrow \boxed{K_B = \beta_n = \prod_{i \ldots n} K_i = \frac{c(ML_n)}{c(M) \cdot c(L)^n}}$$

7. Stability of Complexes

Complex Stability Using $[Cd(CN)_4]^{2-}$ as a Example

Stepwise formation of the complex from Cd^{2+} and CN^-

$Cd^{2+} + CN^- \leftrightarrows [Cd(CN)]^+$ $K_1 = 10^{5.5}$

$[Cd(CN)]^+ + CN^- \leftrightarrows [Cd(CN)_2]^0$ $K_2 = 10^{5.2}$

$[Cd(CN)_2]^0 + CN^- \leftrightarrows [Cd(CN)_3]^-$ $K_3 = 10^{4.6}$

$[Cd(CN)_3]^- + CN^- \leftrightarrows [Cd(CN)_4]^{2-}$ $K_4 = 10^{3.5}$

$Cd^{2+} + 4\ CN^- \leftrightarrows [Cd(CN)_4]^{2-}$ $K_B\ (ß_4) = 10^{18.8}$

$\Rightarrow$ Often, the more ligands already bound to the metal centre, the lower the complex formation constant K_n gets!

<u>Explanations for this behaviour</u>

- Sterical hindrance
- Coulomb-effect hinders the addition of more charged ligands, such as CN^-
- Decrease in entropy, because the systems becomes more ordered, i.e. $\Delta S_r^0 < 0$

7. Stability of Complexes

Thermodynamic and Kinetic Complex Stability

Thermodynamic Stability is expressed by the complex formation constant K_B and ß, respectively. The higher this constant, the more stable the complex (unstable – stable)

Free reaction enthalpy $\Delta G_r^0 = -RT \cdot \ln K_B$

Example:

$$[Ni(H_2O)_6]^{2+} + 4\ CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ni(CN)_4]^{2-} + 6\ H_2O \qquad K_B \sim 10^{29}$$

The equilibrium is shifted almost completely on the right side, meaning the complex is thermodynamically stable. But still, the ligand exchange proceeds very fast, which means that the kinetic stability is poor (labile – inert)

Free activation enthalpy $\Delta G_r^{\neq}$

$$[Ni(CN)_4]^{2-} + 4\ {}^{14}CN^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ni({}^{14}CN)_4]^{2-} + 4\ CN^- \qquad \tau_{1/2} = 30\ s\ (fast)$$

7. Stability of Complexes

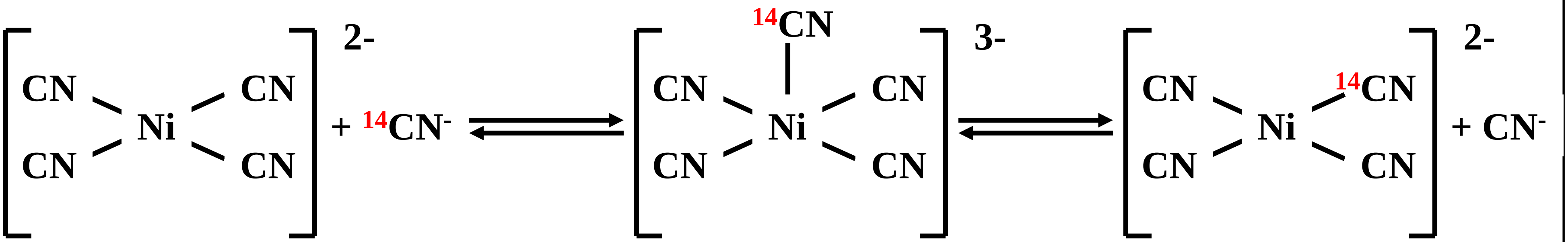
The Kinetic Complex Stability or the Reactivity of a Complex Is Determined by the Structure of the Complex and the Possible Reaction Pathway

Octahedral complexes

$$[CrCl_2(H_2O)_4]^+ + 2\,H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cr(H_2O)_6]^{3+} + 2\,Cl^-$$

⇒ Very slow ligand exchange, although the hexa aquachrom(III) complex is more stable

Square-planar complexes



⇒ Very fast ligand exchange, although there is no thermodynamic reason for it

7. Stability of Complexes

Dependence of Stability Constants of Metal Complexes

1. Central Atom

$Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$

⇒ Correlates with decreasing ionic radius of the cation or increasing ionic charge density, respectively

2. Ligands

- Chelating effect, macro cyclic effect
- Polarizability (hard - soft)

Hard and Soft Acids and Bases HSAB Concept (R.G. Pearson 1963)

- Metal atoms = acids (electron acceptors)
- Ligands = bases (electron donators)
- High stability: soft metal atoms – soft ligands
  hard metal atoms - hard ligands
- Low stability: soft metal atoms - hard ligands
  hard metal atoms – soft ligands

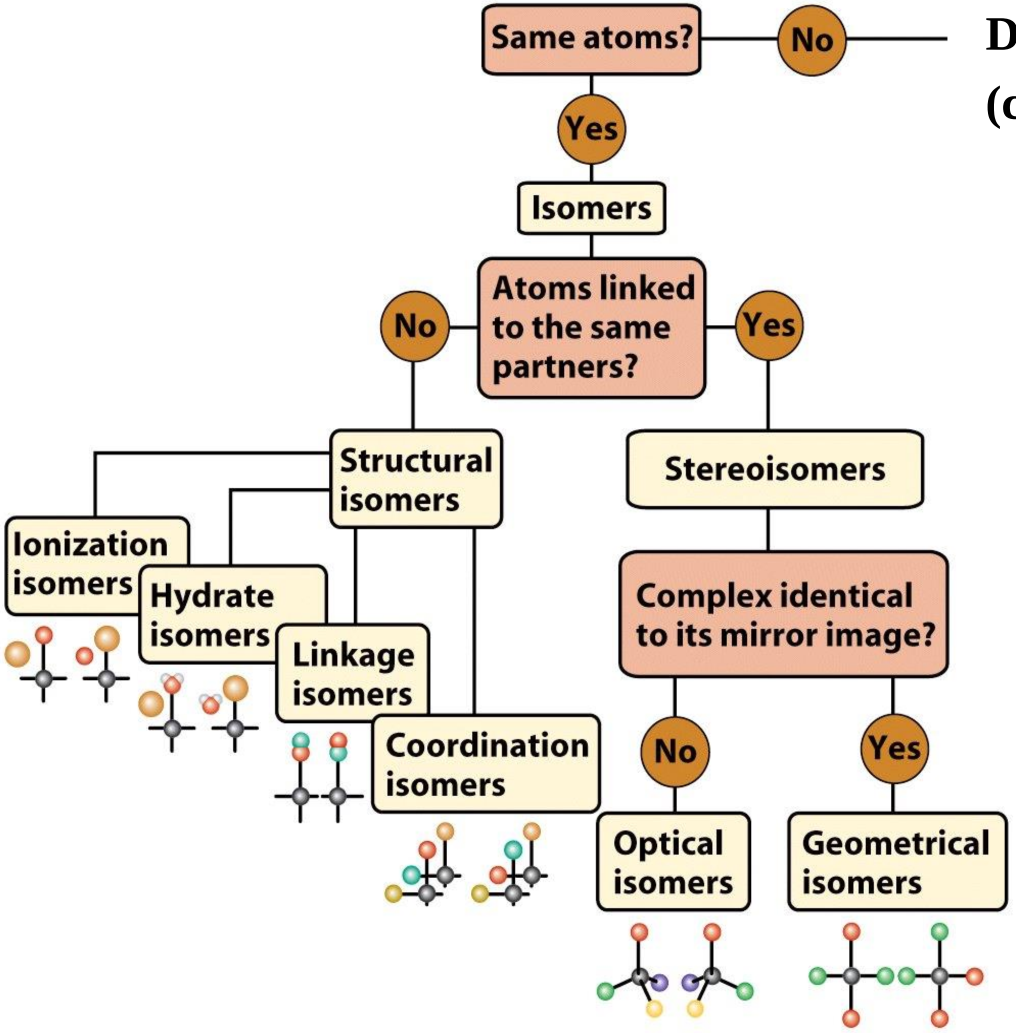
7. Stability of Complexes

HSAB Concept: Classification of Metal Atoms (Acids) and Ligands (Bases)

	Bases	Acids
Hard	NH_3, R-NH_2, N_2H_4, H_2O, OH^-, O^{2-}, R-OH, RO^-, R_2O, CO_3^{2-}, R-COO^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, ClO_4^-, F^-, Cl^- *Electron shell is hard to deform*	H^+, Li^+, Na^+, K^+, Ba^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ti^{4+}, Zr^{4+}, VO^{3+}, Cr^{3+}, Cr^{6+}, Mn^{2+}, Mn^{4+}, Mn^{7+}, Fe^{3+}, Co^{3+}, Al^{3+}, Ga^{3+}, In^{3+} *Strongly polarizing*
In between	N^{3-}, N_2, Ph-NH_2, NO_2^-, Br^- C_5H_5N, SO_3^{2-}	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Rh^{3+}, Ir^{3+}, Ru^{3+}, Sn^{2+}, Pb^{2+}
Soft	H^-, R^-, CN^-, CO, SCN^-, R_3P, R_2S, RS^-, $S_2O_3^-$, I^- *Electron shell is readily deformed*	Pd^{2+}, Pt^{2+}, Cu^+, Ag^+, Hg^+, Hg^{2+}, Tl^+, Me^0 *Weakly polarizing*

8. Structures and Isomers

Differentiation: Compounds vs. Isomers



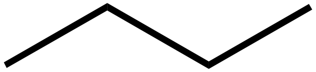
Different compositions (chemical formulae)

8. Structures and Isomers

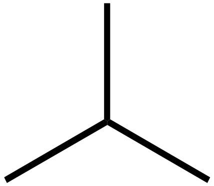
Isomers Are Compounds with the Same Molecular Formula but Different Spatial Arrangement of the Atoms

1. Structure or Constitutional Isomers

Connectivity of the atoms differs



Butane



2-Methylpropane (isobutane)

2. Stereoisomers

Identical connectivity but different spatial arrangement of the atoms

8. Structures and Isomers

1. Constitutional Isomerism

a) Ionisation isomerism

- Exists in complex salts where ligands and counter ions can interchange positions
- Example:

  $[Co(NH_3)_5(SO_4)]Br$ red compound

  $[Co(NH_3)_5Br]SO_4$ violet compound

b) Hydration isomerism

- Special case of ionisation isomerism whereby H_2O can either be a ligand or incorporated as water of crystallization
- Example:

  $[Cr(H_2O)_6]Cl_3$

  $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

  $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$

8. Structures and Isomers

1. Constitutional Isomerism

c) Coordination isomerism

- In salts where cations and anions consist of complexes, ligands can be interchanged between the cations and the anions
- Example:

$[Co(NH_3)_6]\ [Cr(CN)_6]$

$[Cr(NH_3)_6]\ [Co(CN)_6]$

d) Bond or salt isomerism

- Asymmetrical ligands that possess various linking positions, can be coordinated in multiple ways
- Examples:

$^{\ominus}|C\equiv N|$ **bonding via C-atom: cyano, via N-atom: isocyano**

$^{\ominus}\overline{\underline{|S}}-C\equiv N|$ **bonding via S-atom: thiocyanato, via N-atom: isothiocyanato**

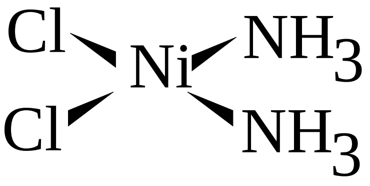
8. Structures and Isomers

2. Stereoisomerism

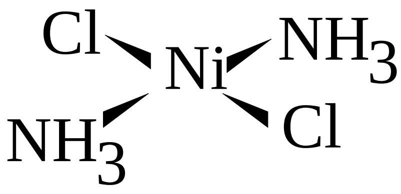
a) cis-trans isomerism

- Occurs in square-planar or octahedral complexes which comprise of two different ligands L and L‘ , so that the bonding angle L-Z-L can be 90° (cis) or 180° (trans)
- Square-planar complexes

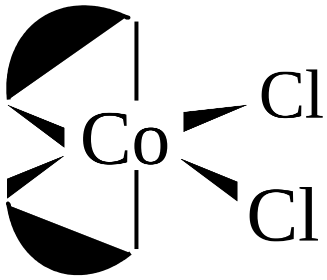
Octahedral complexes



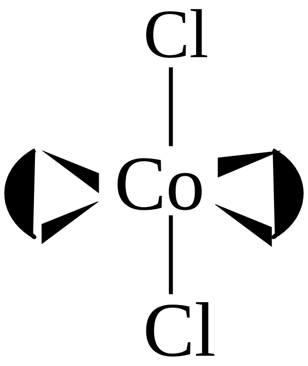
cis



trans



cis

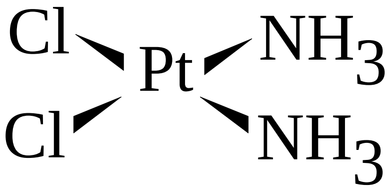


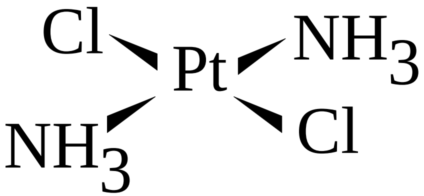
trans

Excursion: cis-Platinum

The Metal Complex cis-Platinum Is Cancerostatic

cis-diamminedichloroplatinum(II) (Peyrone's salt)





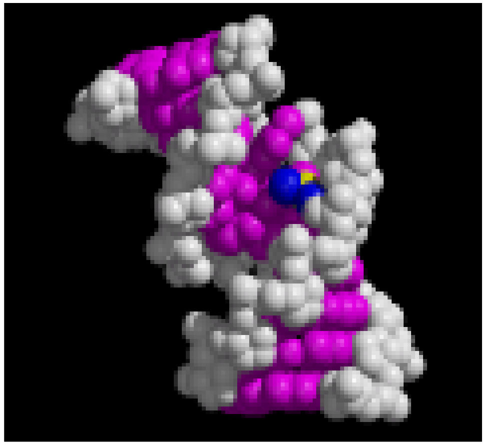
orange yellow

0.252 g/100 ml H_2O

bright yellow

0.037 g/100 ml H_2O

The square-planar cis-platinum disrupts the DNA structure of cancerous cells which leads to apoptosis of those cells



⇒ Chemotherapeutic for bronchial carcinoma and tumours within the genitourinary system

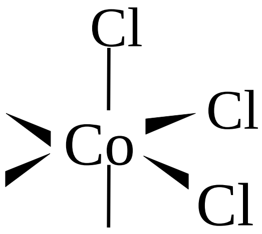
⇒ 95% success rate

8. Structures and Isomers

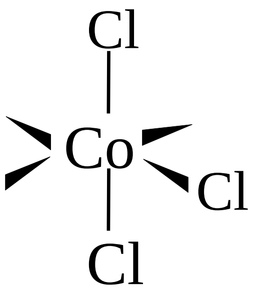
2. Stereoisomerism

b) fac-mer Isomerism

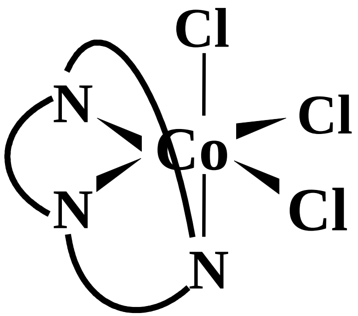
- If a octahedral complex consists of three identical ligands, two of them can be arranged in two different ways



fac(ial)



mer(idional)



Macroclic, tridentate ligands enforce a facial arrangement, e.g. 1,4,7-triazacyclononane

c) Optical isomerism

- Molecules or complexes which image and mirror image can not be superimposed, are called chiral
- The two isomers of chiral molecules are called enantiomers

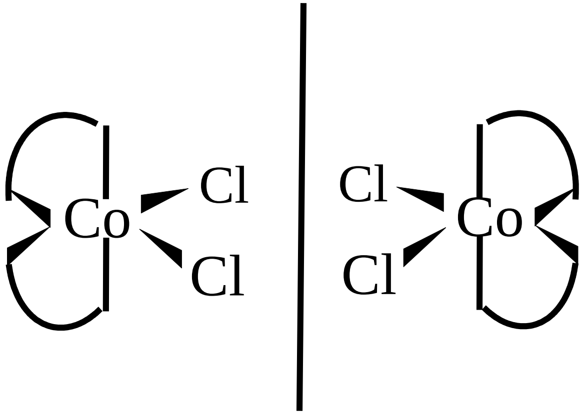
8. Structures and Isomers

2. Stereoisomerism

c) Optical isomerism explained, using the example of octahedral cobalt complexes

cis-isomers

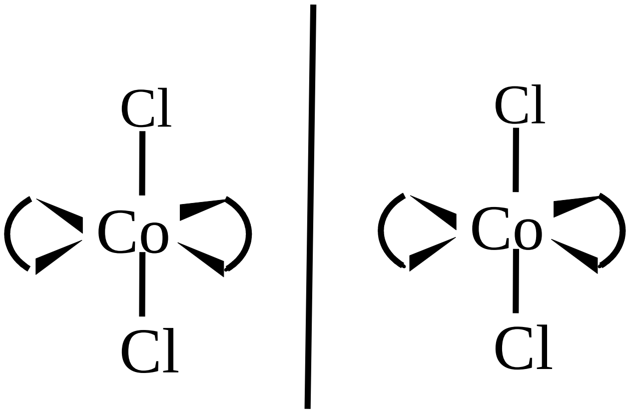
mirror plane



⇒ enantiomers

trans-isomers

mirror plane



⇒ identical

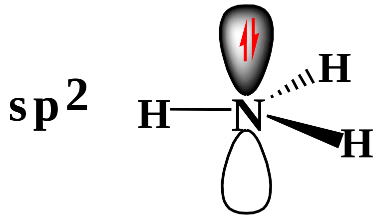
If a molecule exhibits inversion or mirror symmetry, it can not be chiral!

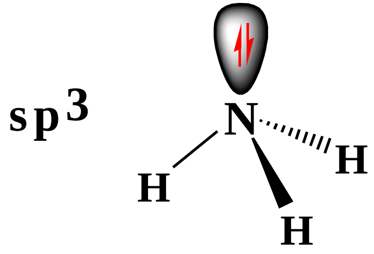
8. Structures and Isomers

Structures in Main Group Chemistry

Predictions by Valence Shell Electron Pair Repulsion (VSEPR) model!

Coordination number	Polyhedron
2	linear arrangement
3	equilateral triangle
4	tetrahedron
5	trigonal bipyramidal
6	octahedron
7	pentagonal bipyramidal
8	dodecahedron, hexahedron
9	triply capped prism
10	doubly trigonal-bipyramidal
12	Icosahedron





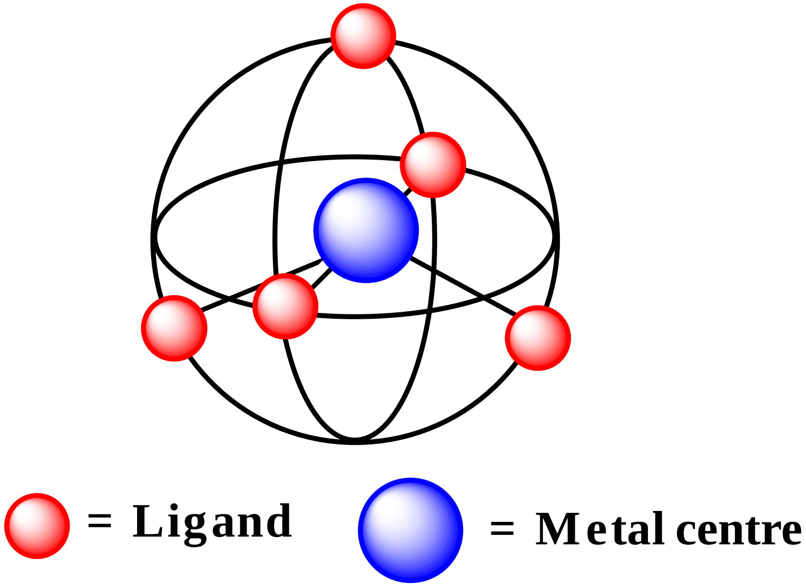
Free electron pairs show greater spatial demand than binding electron pairs

8. Structures and Isomers

Method of Kepert et al.

⇒ **The inter-ligand interaction is repulsive**

⇒ **The ligands are arranged on a sphere in such a way that repulsion between them is minimised**



(David L. Kepert, *Inorganic Stereochemistry*, Springer, Berlin 1982)

8. Structures and Isomers

Geometry of Complexes

Coordination number (CN)

- Number of bound ligand to the metal center
- Between 2 and 12
- Dependent on
  - Size of the central atom
  - Sterical interaction between ligands
  - Electronic interaction between ligands and metal center

Coordination polyhedra

- Geometrical structure formed by the ligands around the metal center
- Symmetry is determined by sterical and electronical demands

8. Structures and Isomers

Geometry of Complexes

Coordination number 2

- Only with bulky ligands or elements from group 11 (IB) and 12 (IIB)
- Preferably for metals with d^{10}-configuration
- Structure: linear or almost linear
- Examples:

$[Ag(NH_3)_2]^+$	$H_3N-Ag-NH_3$
$[CuCl_2]^-$	$Cl-Cu-Cl$
$[Hg(CN)_2]^-$	$N\equiv C-Hg-C\equiv N$
$[Au(CN)_2]^-$	$N\equiv C-Au-C\equiv N$

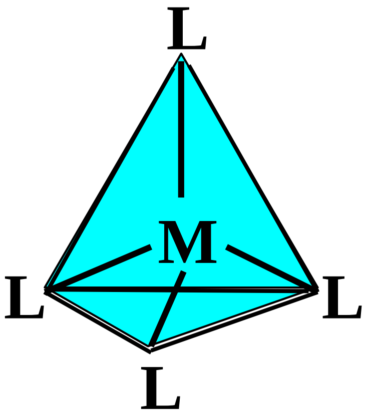
8. Structures and Isomers

Geometry of Complexes

Coordination number 4 (common)

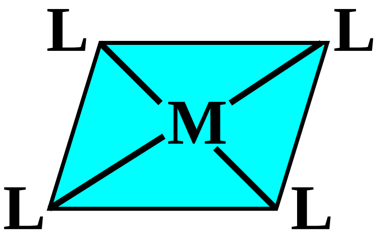
1. Tetrahedral coordination preferably for metals with d^7- or d^{10}-configuration

   Examples: $[Al(OH)_4]^-$, $[Cd(CN)_4]^{2-}$, $[BF_4]^-$



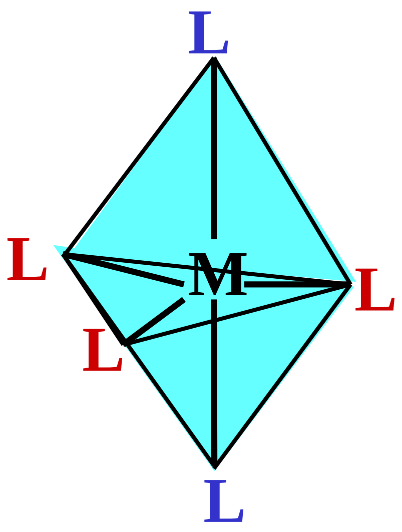
2. Square-planar coordination preferably for metals with d^8-configuration

   Example: $[PtCl_4]^{2-}$, $[Ni(dimethylglyoxim)_2]$, $[AuF_4]^-$



8. Structures and Isomers

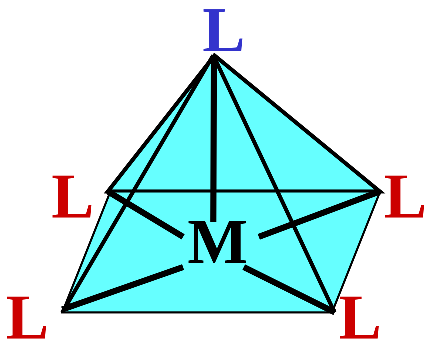
Geometry of Complexes



Coordination number 5 (rare)

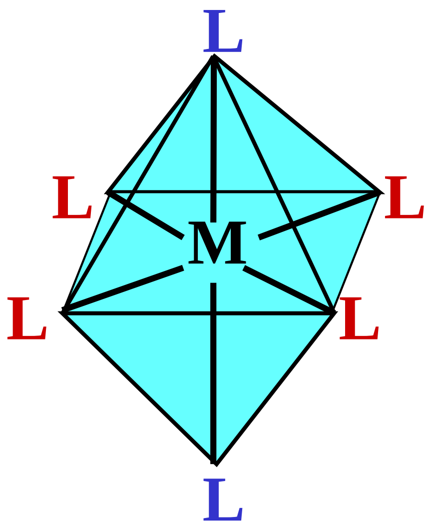
1. **Trigonal-bipyramidal coordination, equatorial and axial (apical) positions**
   Examples: Fe(CO)$_5$, [SnCl$_5$]$^-$

2. **Square-pyramidal coordination preferably for highly asymmetrical ligand sphere, e.g. oxo-ligands**
   Examples: [VO(acetylacetonate)$_2$]



8. Structures and Isomers

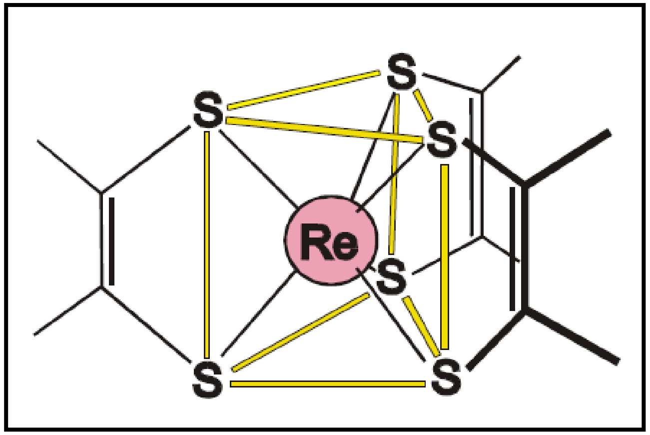
Geometry of Complexes



Coordination number 6 (most common)

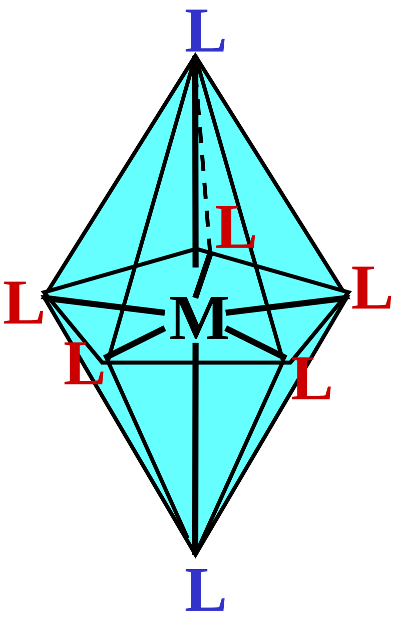
1. Octahedral coordination,
   equatorial and axial (apical) positions
   Examples: $[Cr(NH_3)_6]^{3+}$, $[Al(OH_2)_6]^{3+}$, $[Fe(CN)_6]^{3-}$

2. Trigonal-prismatic coordination,
   can be caused by sterical demand of
   the ligand sphere
   Examples: $[Re(S_2C_2Ph)_3]$, $[W(CH_3)_6]$



8. Structures and Isomers

Geometry of Complexes

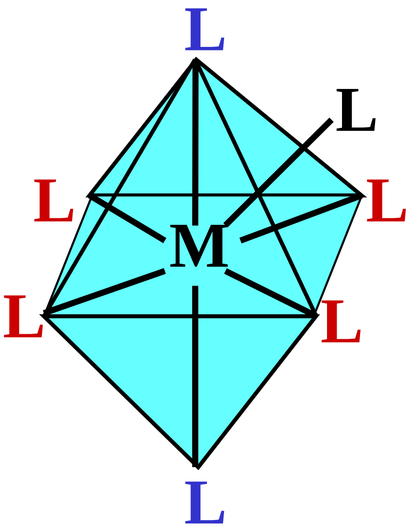


Coordination number 7

1. **Pentagonal-bipyramidal coordination**
   equatorial and axial (apical) positions
   Examples: IF_7, $[UO_2F_5]^{3-}$, $[HfF_7]^{3-}$

2. **Capped trigonal-prismatic coordination**
   Examples: $[TaF_7]^{3-}$

3. **Capped octahedral coordination**
   Examples: $[IF_6]^-$, $[NbOF_6]^{3-}$

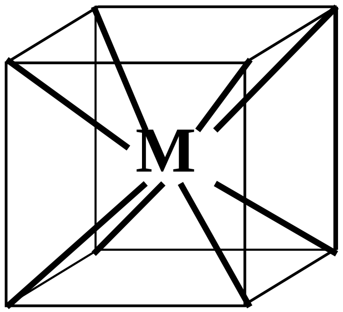


8. Structures and Isomers

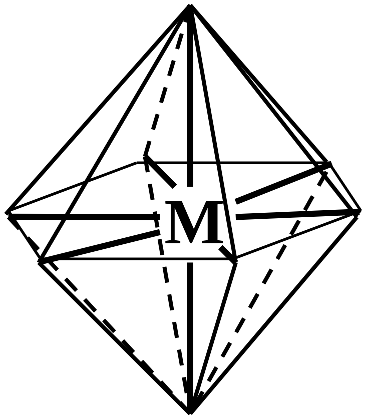
Geometry of Complexes

<u>Coordination number 8</u>

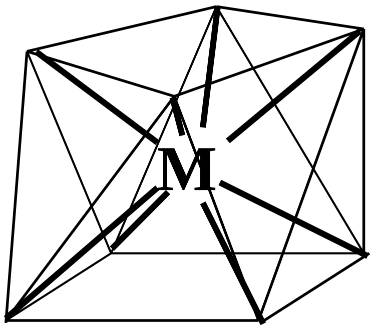
1. **Cubic coordination (rare)**
   Examples: $[UF_8]^{3-}$



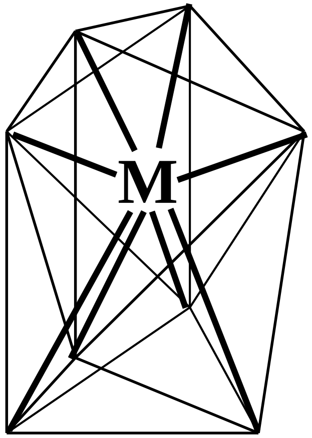
2. **Hexagonal-bipyramidal coordination**
   Examples: $[UO_2(acetylacetonate)_3]$



3. **Squared-antiprismatic coordination**
   Examples: $[TaF_8]^{3-}$, $[ReF_8]^{3-}$



4. **Dodecahedral coordination**
   Examples: $[Mo(CN)_8]^{4-}$, $[W(CN)_8]^{4-}$



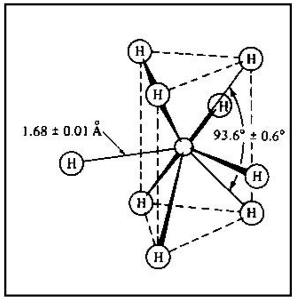
The difference in energy between the configurations becomes smaller with increasing coordination number

⇒ Fluctuations between different configurations

8. Structures and Isomers

Geometry of Complexes

CN	Structure type	Examples
2	linear	$[Ag(CN)_2]^-$
3	trigonal-planar, trig.-aplanar (trig.-pyramidal)	$[HgI_3]^-$
4	tetrahedral, square-planar	$[NiCl_4]^{2-}$, $[PtCl_4]^{2-}$
5	trigonal-bipyramidal, square-pyramidal	$[Fe(CO)_5]^0$
6	octahedral, trigonal-prismatic	$[Fe(OH_2)_6]^{2+}$
7	pentagonal-bipyramidal, capped trigonal-prismatic, capped octahedral	
8	cubic, hexagonal-bipyramidal, dodecahedral, squared-antiprismatic	
9	triply capped prismatic	$[Ln(H_2O)_9]^{3+}$, $[ReH_9]^{2-}$
10	doubly trigonal-bipyramidal	$(PPh_3Et)_2[Ce(NO_2)_5]$
12	icosahedral	$(NH_4)_2[Ce(NO_2)_6]$



8. Structures and Isomers

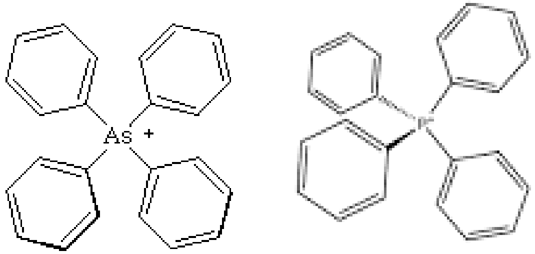
Geometry of Complexes

Realisation of low coordination numbers

- Metals in low oxidation states (π-backbonding) or small metal cations in high oxidation states
- Ligands with π-backbondung: Carbonyles, O^{2-}, N^{3-}
- Soft donor atoms (N, C, P, S)
- Large ligands
- Counter ions with low basicity, e.g. $CF_3SO_3^-$, BF_4^-, PF_6^-

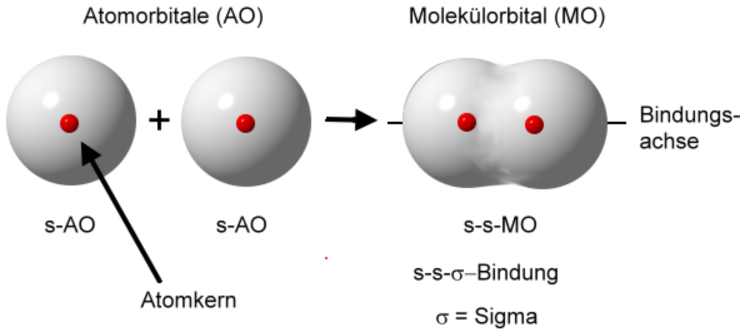
Realisation of high coordination numbers

- Metals in intermediate oxidation states
- Hard donor atoms (F, O, N, ...)
- Small ligands
- Large non-acidic cations, e.g. $[P(Ph_4)]^+$ or $[As(Ph_4)]^+$



9. Concepts of Bonding

Chemical Bonding in Complexes Can Be Described by Three Different Theories



- **Valence Bond (VB) theory**
- **Crystal Field or Ligand Field theory**
- **Molecular Orbital (MO) theory**

Valence (VB) Bond theory (Heitler and London 1927, Zeitschrift für Physik 44 (1927) 455)

Explanation of

- **geometry (most of the time)**
- **magnetic properties**
- **but not colour of transition metal complexes!**

In detail, the VB-model demands the following:

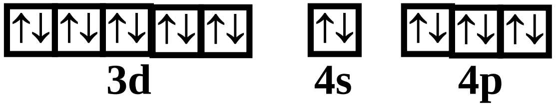
Covalent bonds are formed by the overlap of empty metal orbitals (acids) with occupied donor orbitals (bases), i.e. the ligands must possess one free pair of electrons.

9. Concepts of Bonding

Number of Valence Electrons

18-Valence Electrons (VE) rule

- **The 18-VE-rule (Nevil Sidgwick 1927) states that transition metal complexes are thermodynamically stable, if the metal atom disposes of 18 VE, and with that accomplishes the electronic configuration of the corresponding noble gas that follows in the periodic table**



- **Most, but not all, complexes follow the 18-VE-rule!**

- **The lower the oxidation state/atomic number of the metal atom, and the higher the π-acceptability of the ligands, the more likely it is that the 18-VE-rule is satisfied**
  ⇒ metal organic compounds (organometallic compounds)

The number of electrons of the metal atom is calculated by the addition of its number of valence electrons, for the respective oxidation number, and the number of bonding electrons donated by the ligands!

9. Concepts of Bonding

The 18-VE-Rule

Typical examples

$[Co(NO_2)_6]^{3-}$		$[PtCl_6]^{2-}$		$[Ag(NH_3)_4]^+$	
Co^{3+}	6 VE	Pt^{4+}	6 VE	Ag^+	10 VE
6 NO_2^-	12 VE	6 Cl^-	12 VE	4 NH_3	8 VE
	18 VE		18 VE		18 VE

Examples that violate the rule

$[Cr(NH_3)_6]^{3+}$		$[Ni(NH_3)_6]^{2+}$		$[CoCl_4]^{2-}$	
Cr^{3+}	3 VE	Ni^{2+}	8 VE	Co^{2+}	7 VE
NH_3	12 VE	6 NH_3	12 VE	4 Cl^-	8 VE
	15 VE		20 VE		15 VE

9. Concepts of Bonding

The 18-VE-Rule

Metal organic compounds obey the 18-VE-rule in most cases!

$[\mathrm{Cr(CO)_6}]$		$[\mathrm{Fe(CO)_5}]$		$[\mathrm{Ni(CO)_4}]$	
Cr	6 VE	Fe	8 VE	Ni	10 VE
6 CO	$\underline{\text{12 VE}}$	5 CO	$\underline{\text{10 VE}}$	4 CO	$\underline{\text{8 VE}}$
	18 VE		18 VE		18 VE

If the metal possess a odd number of electrons, dimers are formed readily or the complex can be reduced easily

$$[\mathrm{Mn}^{-I}(\mathrm{CO})_5]^- \xleftarrow{\text{reduction}} [\mathrm{Mn}^{0}(\mathrm{CO})_5] \xrightarrow{\text{dimerisation}} [\mathrm{Mn}_2^{0}(\mathrm{CO})_{10}]$$

Not existing!

$$[\mathrm{Co}^{-I}(\mathrm{CO})_4]^- \longleftarrow [\mathrm{Co}^{0}(\mathrm{CO})_4] \longrightarrow [\mathrm{Co}_2^{0}(\mathrm{CO})_8]$$

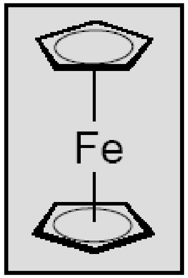
9. Concepts of Bonding

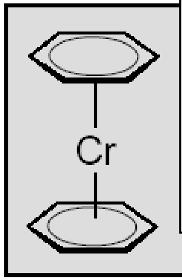
The 18-VE-Rule

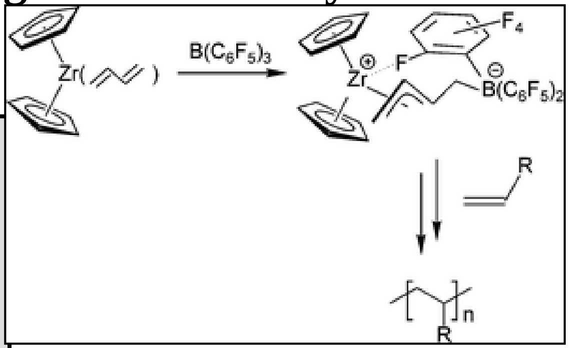
The carbonyl ligand (CO) is, as many others (CN^-, NH_3, OH^-, H_2O, olefins, ...), too,
A typical 2-electron donator

But a ligand can also donate more electrons:

Butadiene	4 → Ligand for polymerisation via Ziegler-Natta catalyst
Cyclopentadienyl radical	5
Benzene (benzol)	6



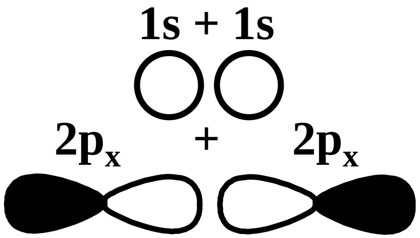




$[Fe(C_5H_5)_2]$		$[Mn(CO)_5C_2H_4]^+$		$[Cr(C_6H_6)_2]$	
Fe	8 VE	Mn^+	6 VE	Cr	6 VE
$2\ C_5H_5\cdot$	$\underline{\text{10 VE}}$	5 CO	10 VE	$2\ C_6H_6$	$\underline{\text{12 VE}}$
	18 VE	$1\ C_2H_4$	$\underline{\text{2 VE}}$		18 VE
			18 VE		

9. Concepts of Bonding

Valence Bond (VB) Theory („revisited“)



Assumptions

1. Interaction of atoms if they approach each other
2. Localised bonds due to overlap of suitable atom orbitals
3. Formation of molecule orbitals (mathematics: Linear Combination of Atomic Orbitals LCAOs)
4. Occupation of MOs by an electron pair, whereby the spin of both electrons must be antiparallel to each other (→ Pauli principle)
5. Enhancement of electron density between nuclei causes attraction fo the positively charged cores and the negative electron cloud
6. Bonding occurs if the overlapping atom orbitals exhibit suitable symmetry (→ +/+ or -/-)
7. Structure of formed molecules is governed by the geometry of the formed molecule orbitals

Experimentally determined molecule geometry is not always in line with the presence of pure s-, p- and d-atom orbitals ⇒ Hybridisation (model)

9. Concepts of Bonding

Valence Bond (VB) Theory

L. Pauling + J.C. Slater further developed the theory

⇒ **The spatial arrangement of the ligands is explained by the hybridisation of the orbitals, located at the central atom:**

Hybridisation	preferred coordination geometry
sp	linear
sp^2	trigonal-planar
sp^2d	squared-planar
sp^3	tetrahedral
sp^3d	trigonal-bipyramidal
sp^3d^2	octahedral
sp^3d^3	pentagonal-bipyramidal
sp^3d^4	cubic

LCAOs for sp^3-Hybridisation

$$\psi_1 = \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z})$$

$$\psi_2 = \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z})$$

$$\psi_3 = \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z})$$

$$\psi_4 = \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z})$$

- **Hybridisation is a mathematical tool and not the description of a physical reality!**
- **Solely atom orbitals with similar energy form hybrid orbitals**

9. Concepts of Bonding

Valence Bond (VB) Theory

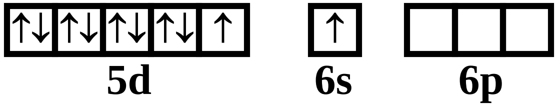
M + |L → M←L dative(coordinative) metal-ligand bonding

<u>Formally, the formation of a complex can be described by the following steps</u>

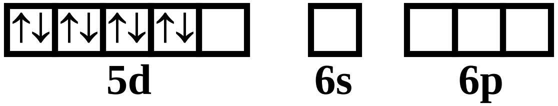
Course of action

Example: tetrachloroplatinate(II) $[\mathrm{Pt}^{II}\mathrm{Cl}_4]^{2-}$

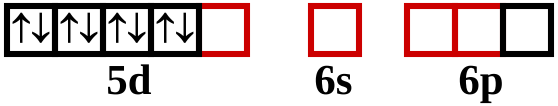
1. Electronic configuration of the metal atom?



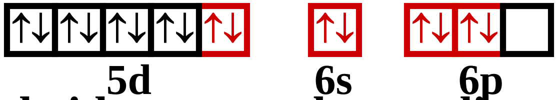
2. Formation of the corresponding metal cation by ionisation



3. Hybridisation of free metal orbitals



4. Formation of covalent σ-bonds by the overlap of empty metal hybrid orbitals with occupied ligand orbitals (free electron pairs)

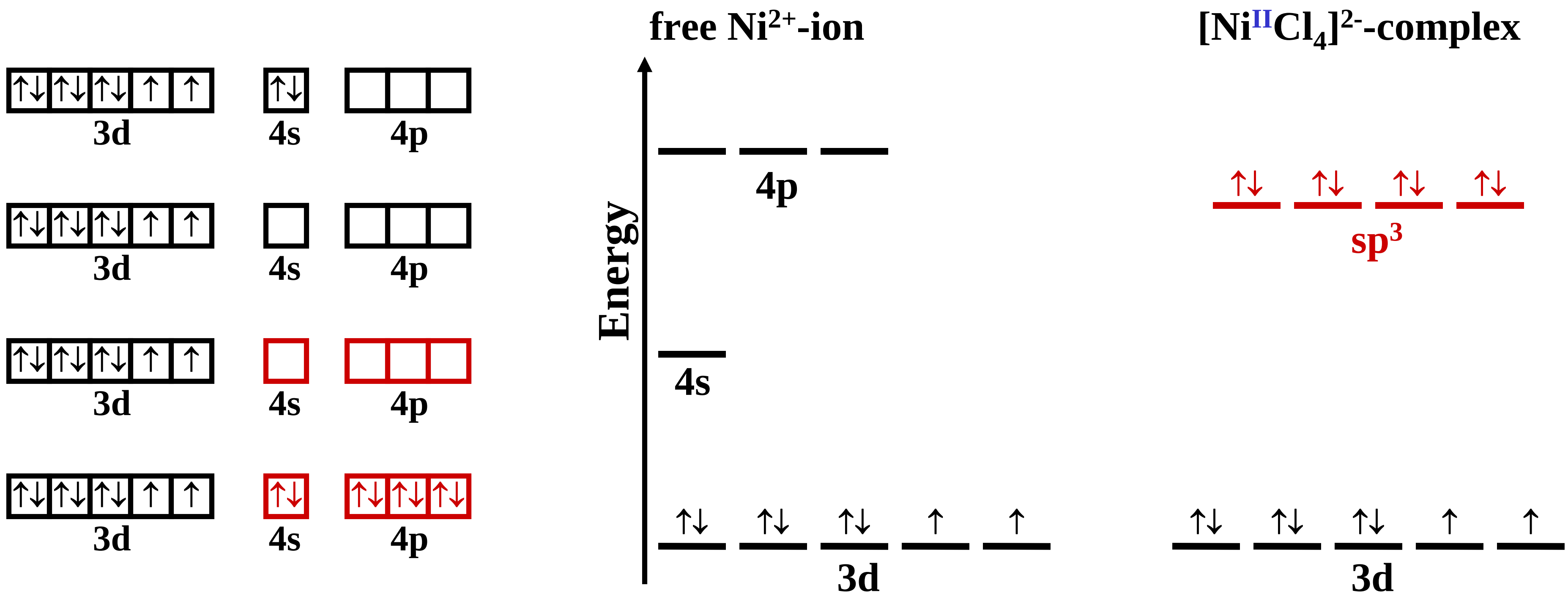


sp^2d-hybrid, square-planar, diamagnetic

9. Concepts of Bonding

Valence Bond (VB) Theory

Further example: Tetrachloronickelate(II) $[Ni^{II}Cl_4]^{2-}$



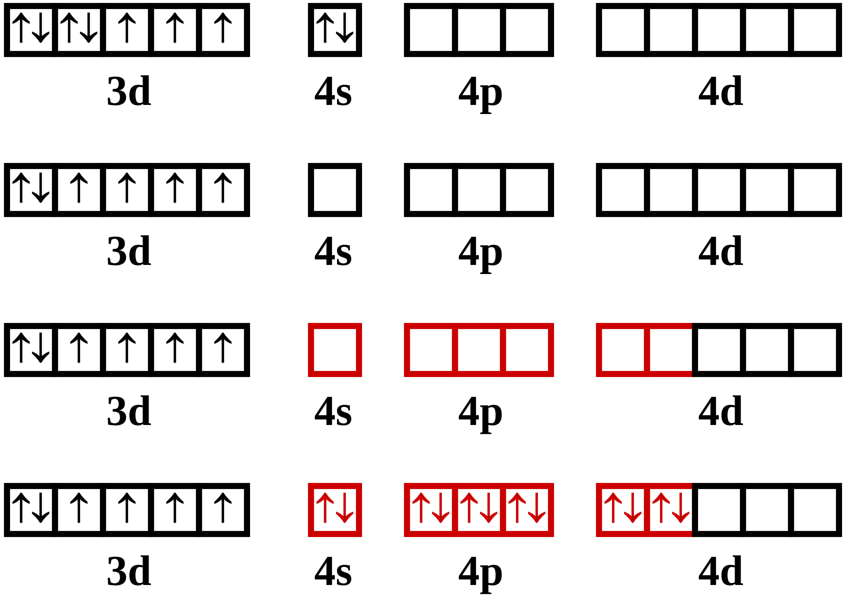
sp^3-hybrid, tetrahedral, paramagnetic (two unpaired electrons: $\mu_{calc.} = 2.83\ \mu_B$)

9. Concepts of Bonding

Valence Bond (VB) Theory

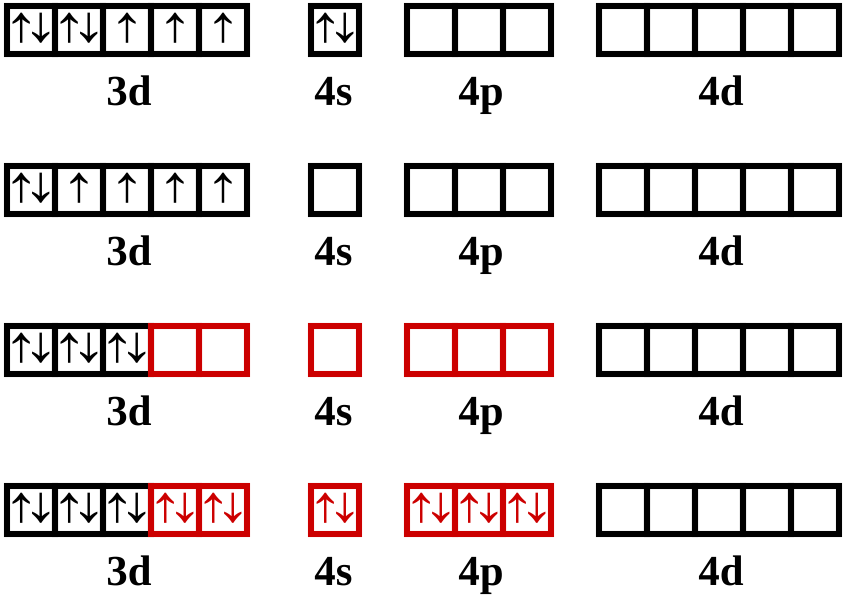
High and low spin complexes

High spin $[Co^{III}F_6]^{3-}$



sp³d²-hybrid, octahedral,
paramagnetic (4 unpaired electrons)
“magnetically normal“

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



sp³d²-hybrid, octahedral,
diamagnetic (no unpaired electrons)
“magnetically anomalous“

9. Concepts of Bonding

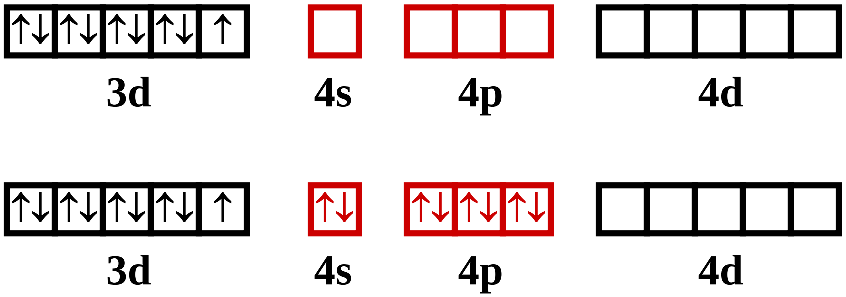
Shortcomings of Valence Bond (VB) Theory

No explanation for:

- Temperature dependence of magnetic moment
- Spectroscopic properties of complexes (colour)
- Properties of excited electronic states

Furthermore, VB theory often falls short predicting the structure of square-planar complexes

Example: $[Cu(NH_3)_4]^{2+}$ is square-planar, but according to VB theory the complex should exhibit tetrahedral coordination, due to the expected sp^3-hybridisation


Cu^{2+}-ion

$[Cu^{II}(NH_3)_4]^{2+}$

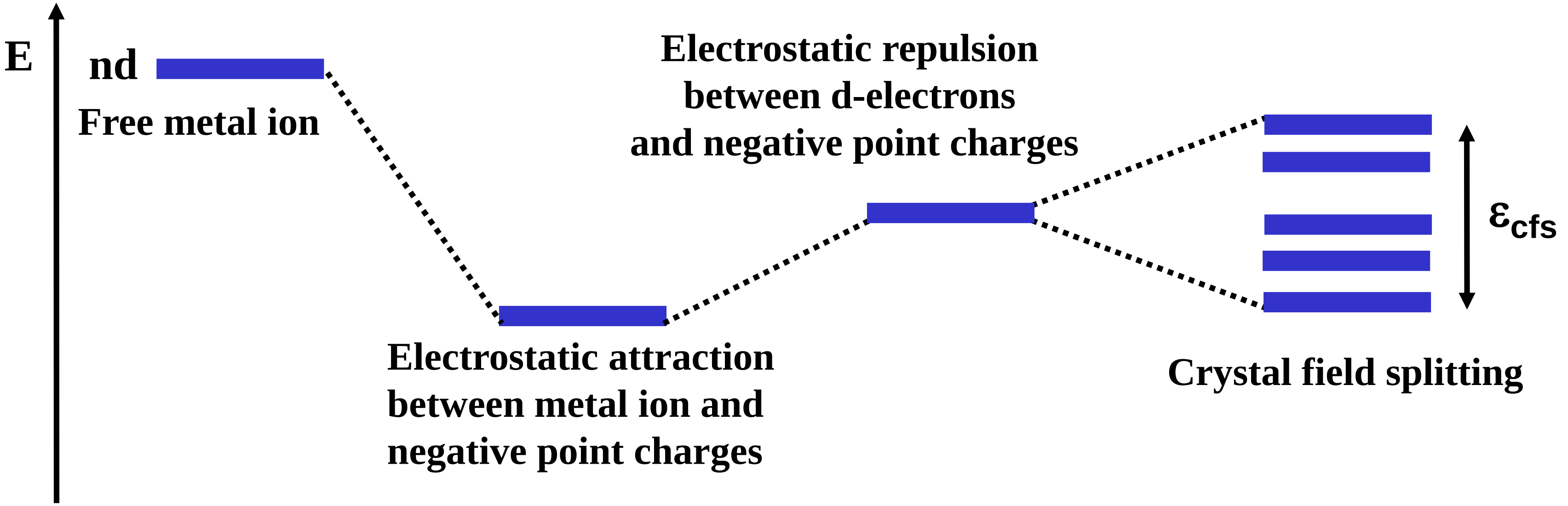
9. Concepts of Bonding

Crystal Field Theory

Assumptions

- The isolated metal atom possesses five degenerate d-orbitals
- The metal atom is situated in a chemical surrounding of electrical point charges
- Between the metal atom and the ligands only electrostatic interactions arise

Stepwise formation of a complex according to crystal field theory



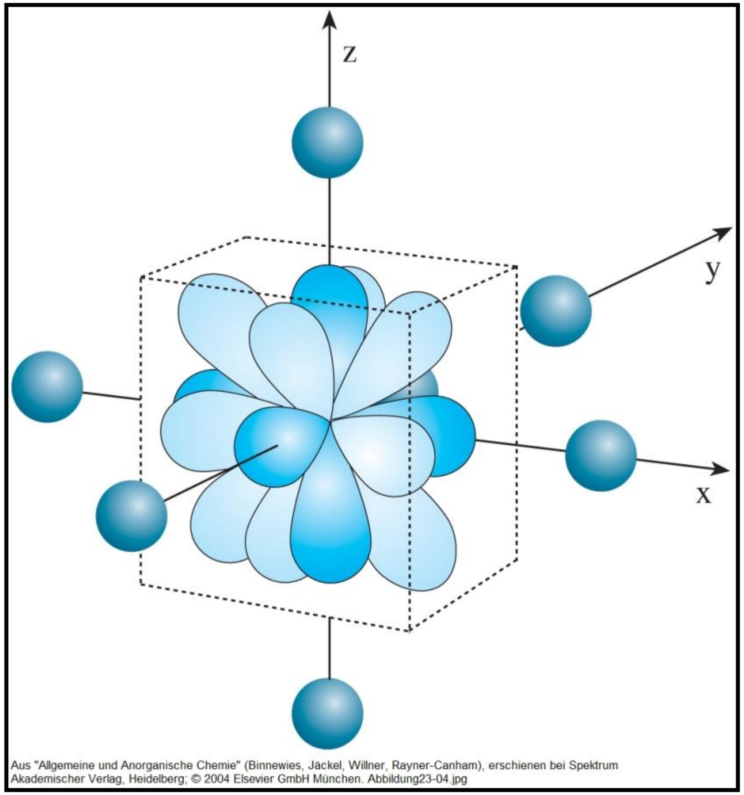
9. Concepts of Bonding

Crystal Field Theory

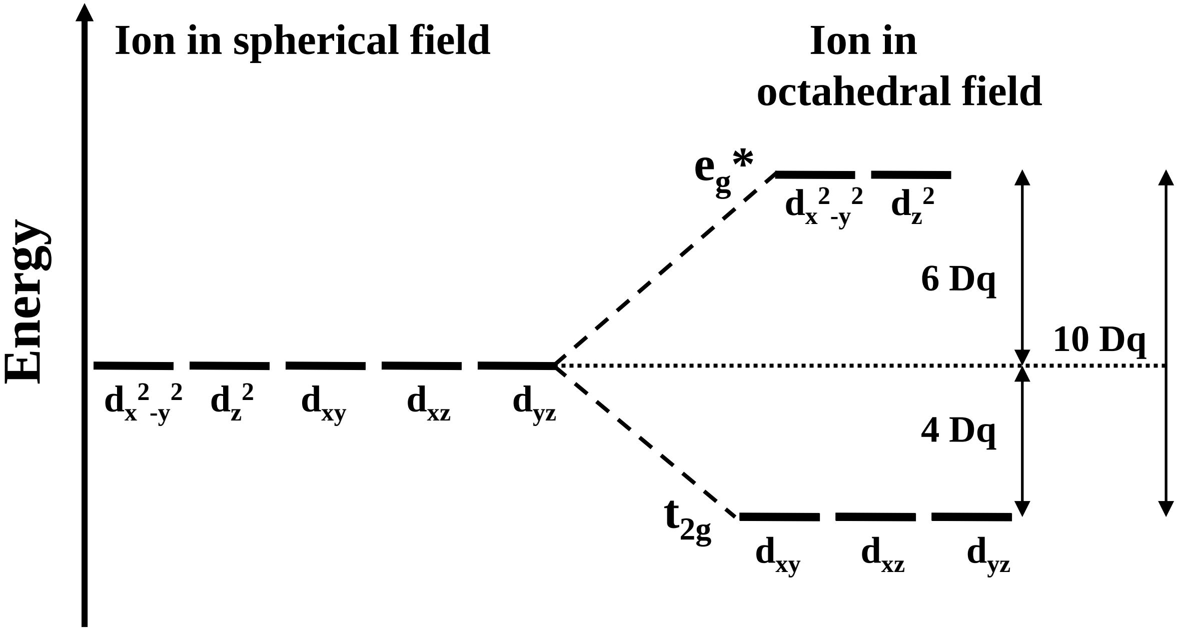
$$Dq = 1/6 \cdot [z \cdot e^2 \cdot \langle r^4 \rangle / 4\pi \cdot \varepsilon_0 \cdot a^5]$$

with
z = Formal charge of metal ion
e = Charge of electron = $1.602 \cdot 10^{-19}$ C
r = Distance d-electron from nucleus
a = Metal ligand distance

Octahedral crystal field (1 d-electron)



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-04.jpg



The energy gap between the t_{2g} and e_g*-orbitals is called – also for historical reasons – 10 Dq or Δ_O (10 Dq ~ 0.6 – 6.0 eV ~ 5000 - 50000 cm^{-1} ~ 200 - 2000 nm)

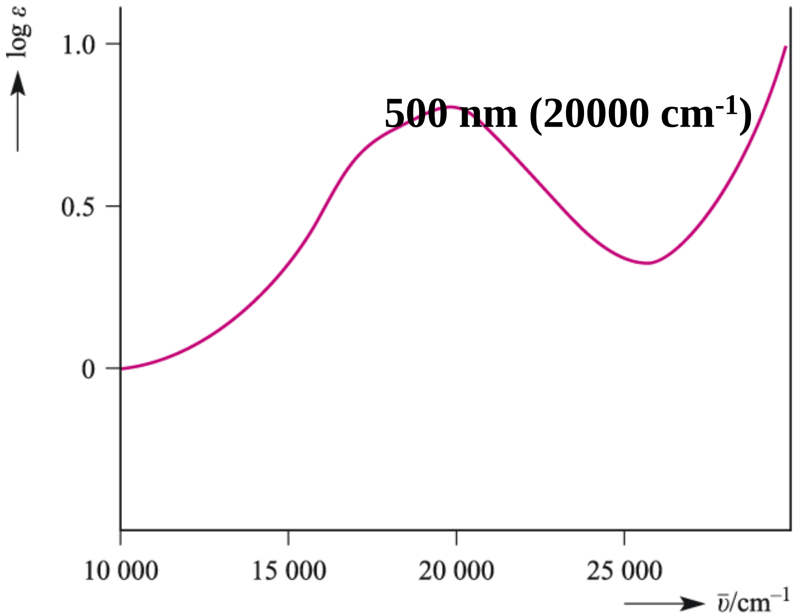
9. Concepts of Bonding

Crystal Field Theory

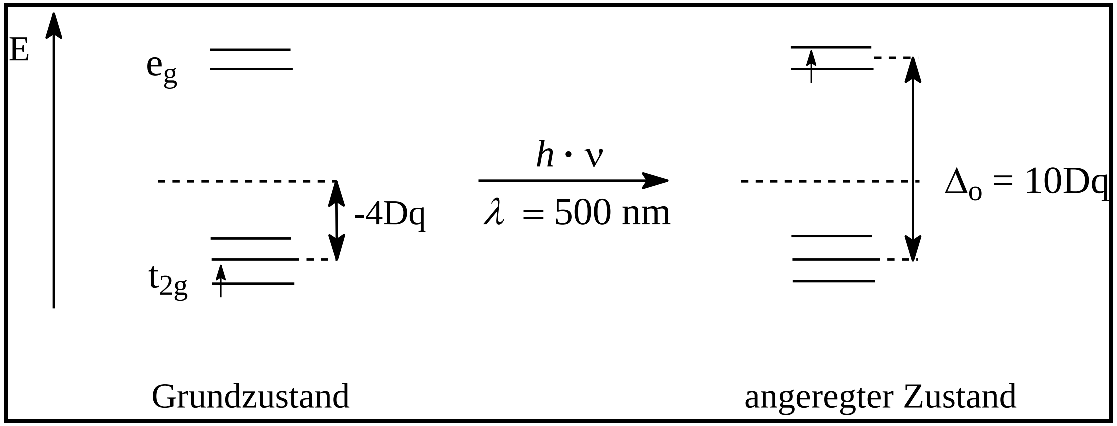
Octahedral crystal field (1 d-electron)

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

The complex is violet in colour, thus absorbing from around 500 nm on



Absorptions spectrum of the solution



$$\Delta_O = h{\cdot}c/\lambda$$

$$= 3.97{\cdot}10^{-19}\ \text{J/photon}\ (\text{x}\ N_A)$$

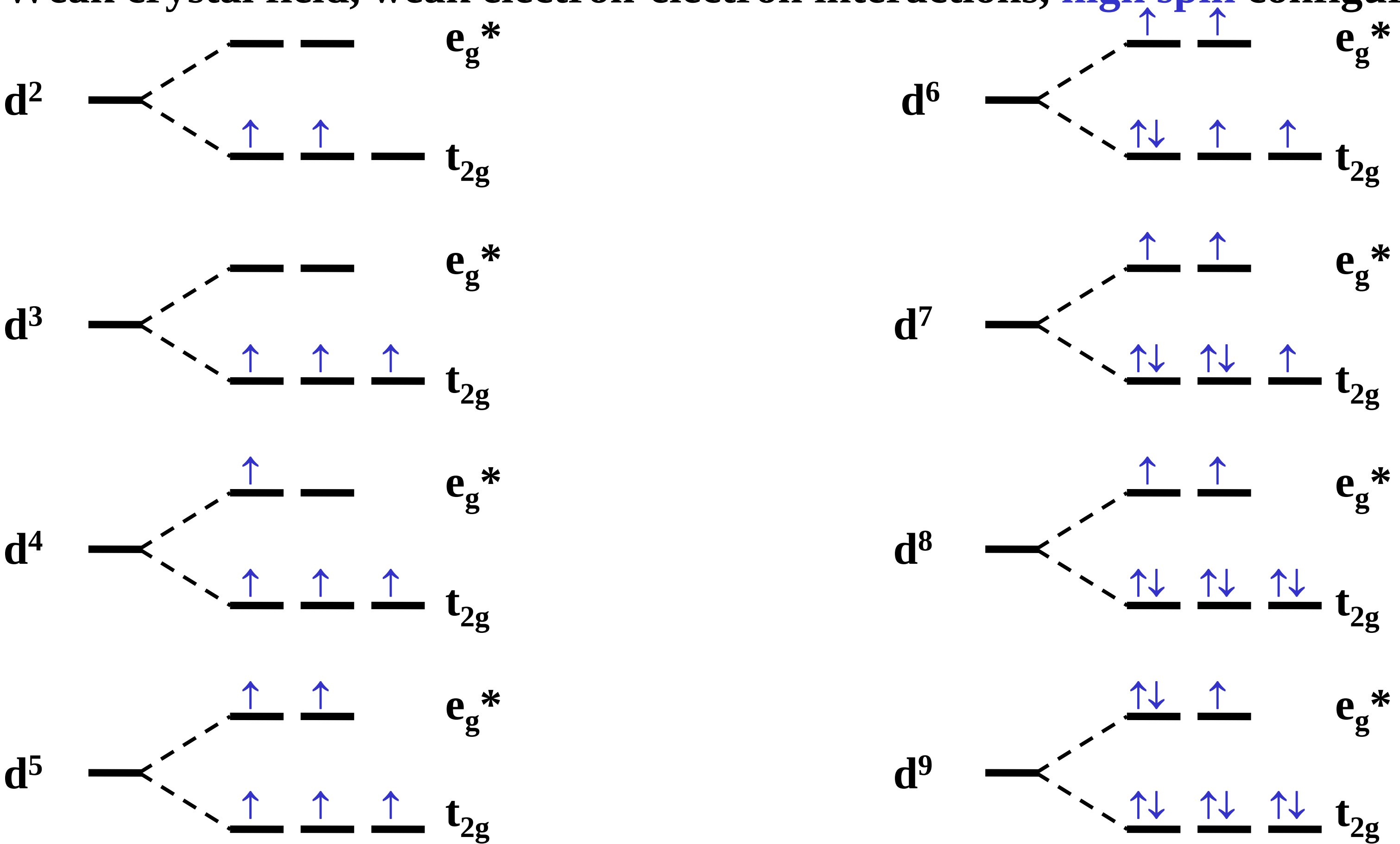
$$= 239\ \text{kJ/mol photons}$$

9. Concepts of Bonding

Crystal Field Theory

Octahedral crystal field (n d-electrons)

Weak crystal field, weak electron-electron interactions, high spin configuration

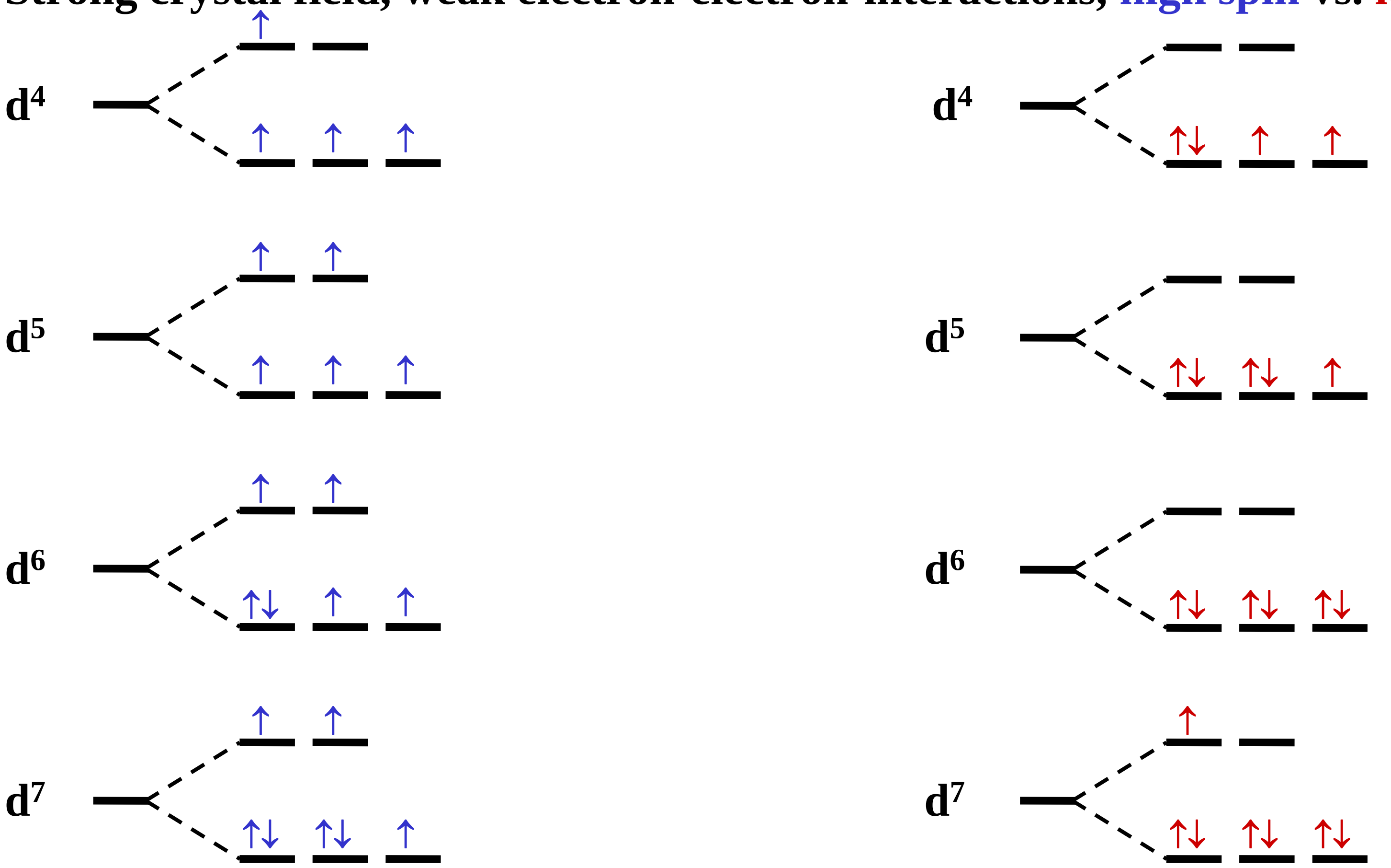


9. Concepts of Bonding

Crystal Field Theory

Octahedral crystal field (n d-electrons)

Strong crystal field, weak electron-electron-interactions, high spin vs. low spin



1 x spin pair energy

2 x spin pair energy

2 x spin pair energy

1 x spin pair energy

9. Concepts of Bonding

Crystal Field Theory

Crystal field stabilisation energy CFSE in octahedral crystal field

CFSE = $x(-4Dq_o) + y(+6Dq_o)$ + SPE

SPE = spin pair energy
x = number of electrons in t_{2g}
y = number of electrons in e_g*

d^n	CFSE high spin	CFSE low spin	ΔCFSE	Examples
0	$0\ Dq_o$	-	-	Sc^{3+}, Y^{3+}, Ln^{3+}, Ti^{4+}
1	$-4\ Dq_o$	-	-	Ti^{3+}
2	$-8\ Dq_o$	-	-	V^{3+}
3	$-12Dq_o$	-	-	Cr^{3+}, Mo^{3+}, W^{3+}
4	$-6\ Dq_o$	$-16\ Dq_o$+ 1 SPE	$-10\ Dq_o$ + 1 SPE	Mn^{2+}
5	$0\ Dq_o$	$-20\ Dq_o$ + 2 SPE	$-20\ Dq_o$ + 2 SPE	Mn^{2+}, Fe^{3+}, Ru^{3+}
6	$-4\ Dq_o$	$-24\ Dq_o$ + 2 SPE	$-20\ Dq_o$ + 2 SPE	Co^{3+}, Ru^{2+}, Ir^{3+}
7	$-8\ Dq_o$	$-18\ Dq_o$ + 1 SPE	$-10\ Dq_o$ + 1 SPE	Co^{2+}
8	$-12\ Dq_o$	-	-	Ni^{2+}
9	$-6\ Dq_o$	-	-	Cu^{2+}
10	$0\ Dq_o$	-	-	Cu^{+}, Zn^{2+}

Spin pairing occurs, if 10 Dq > SPE!

9. Concepts of Bonding

Crystal Field Theory

Crystal field splitting in octahedral crystal field

Consequences:

- **High spin complexes are less stable than low spin complexes**
- **Ions with d^3 (Cr^{3+}, Mo^{3+}, W^{3+}) or d^6 (Co^{3+}, Rh^{3+}, Ir^{3+}) low spin configuration form highly inert complexes**

Dimension of crystal field splitting

- **Atomic number of metal atom (position in periodic table)**

  With increasing atomic number, the core charge increases, resulting in a strengthened electrostatic field strength
- **Trend for 10 Dq:** $3d \xrightarrow{\sim +50\%} 4d \xrightarrow{\sim +25\%} 5d$

3d	4d	5d
$[Co(NH_3)_6]^{3+}$ 22870 cm^{-1}	$[Rh(NH_3)_6]^{3+}$ 34100 cm^{-1}	$[Ir(NH_3)_6]^{3+}$ 41200 cm^{-1}
$[Co(en)_3]^{3+}$ 23200 cm^{-1}	$[Rh(en)_3]^{3+}$ 34600 cm^{-1}	$[Ir(en)_3]^{3+}$ 41400 cm^{-1}

- **Oxidation states of the metal atom (ionic charge density)**

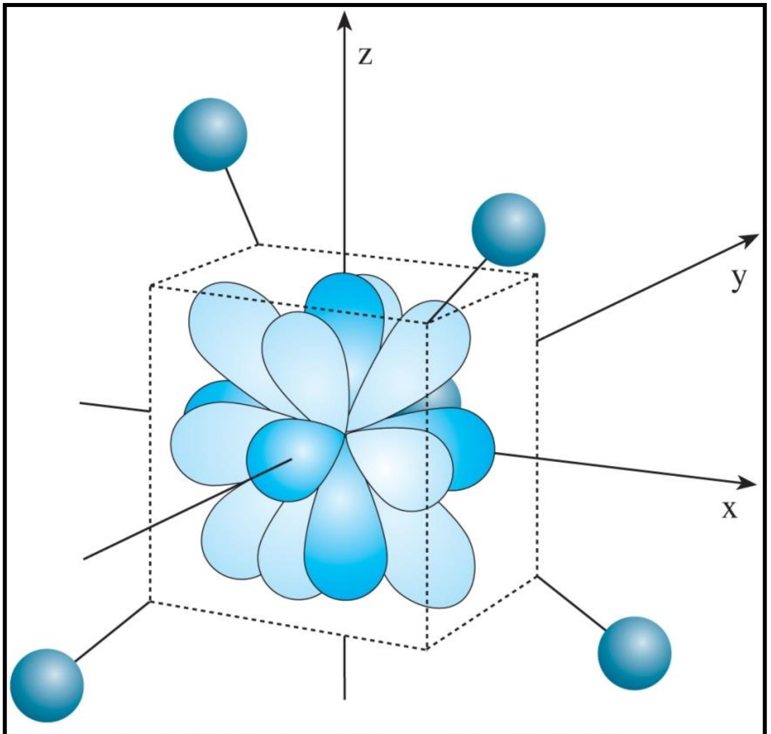
  Trend for 10 Dq: $M^{2+} < M^{3+} < M^{4+} \ldots$

⇒ Metals of the 4d- and 5d-series in high oxidation states form low spin complexes, only

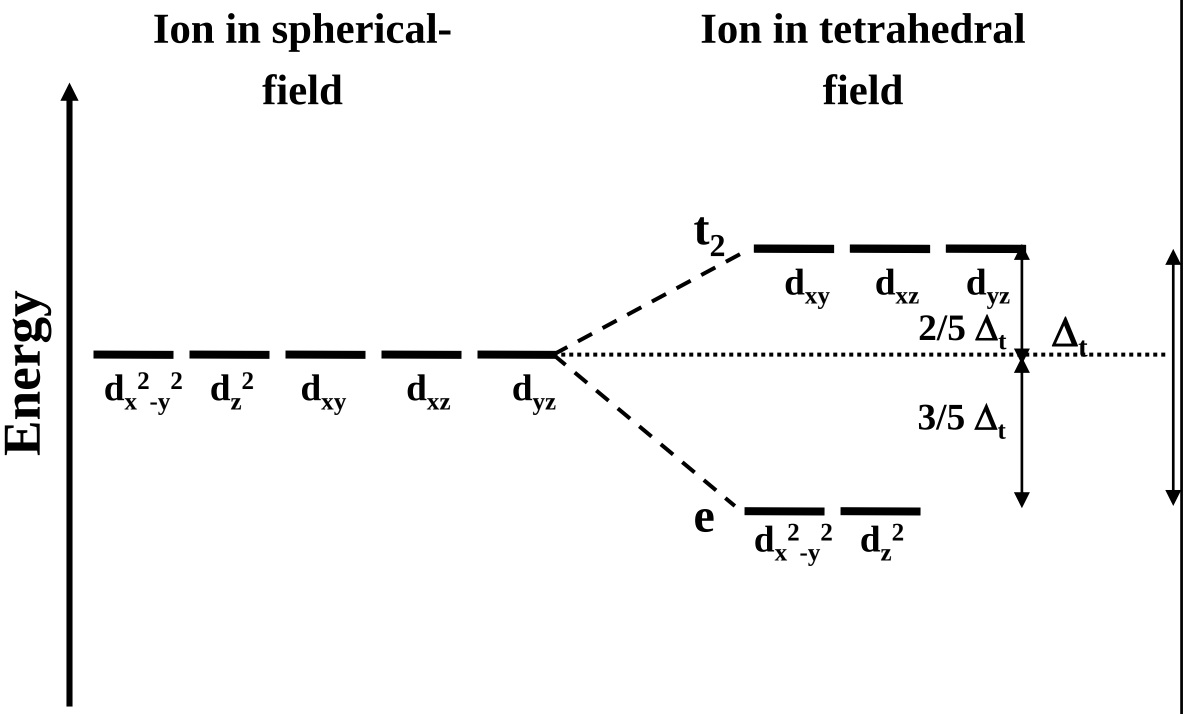
9. Concepts of Bonding

Crystal Field Theory

Tetrahedral crystal field (1 d-electron)



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-08.jpg



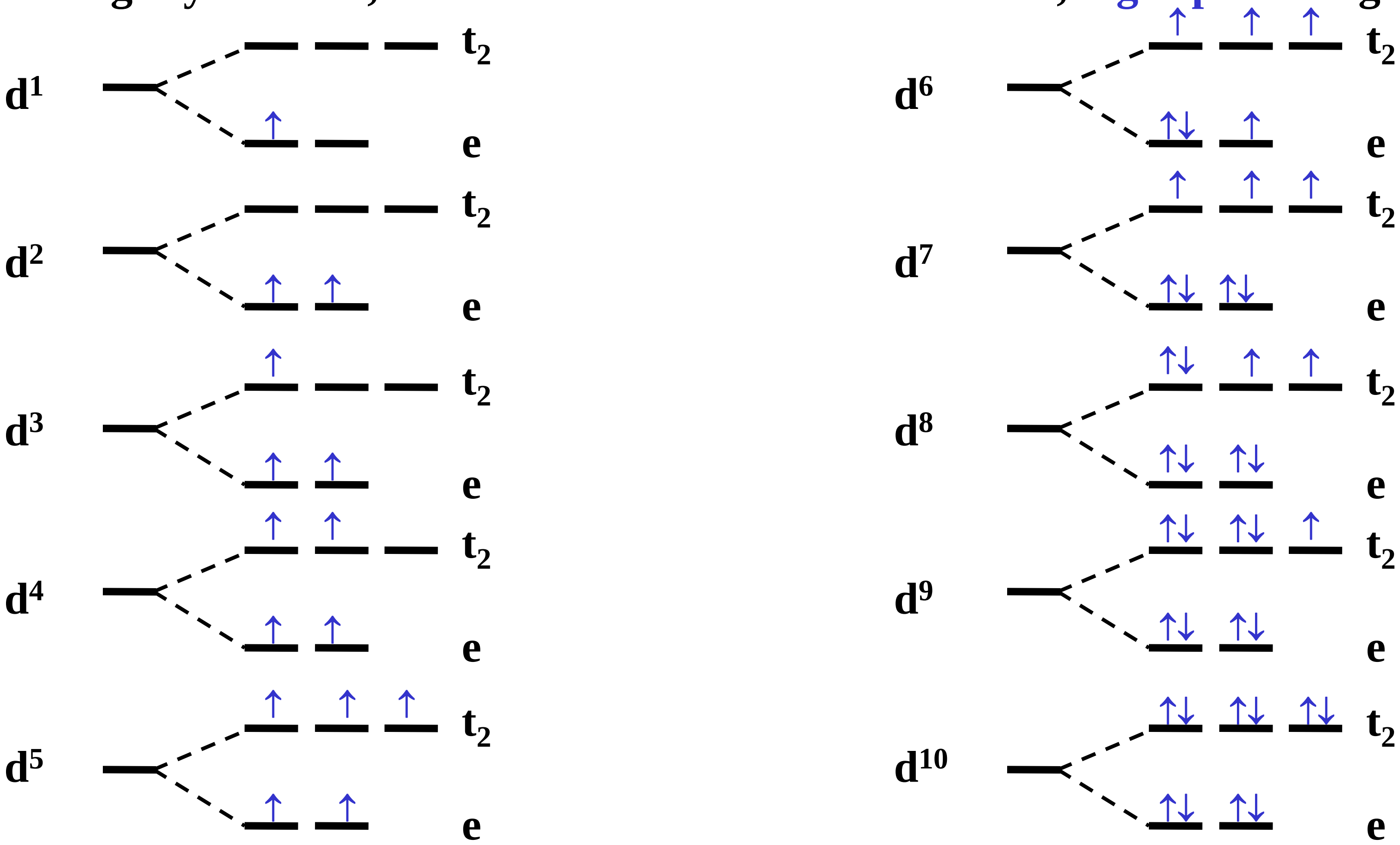
The energy gap between t_2- and e-orbitals, Δ_t, amounts to only 4/9 of Δ_o, since there are only four instead of six ligands which are furthermore not aligned along the axes of the d-orbitals

9. Concepts of Bonding

Crystal Field Theory

Tetrahedral crystal field (n d-electrons)

Strong crystal field, weak electron-electron interactions, high spin configuration



⇒ Low spin configurations would be possible for d^3 – d^6

9. Concepts of Bonding

Crystal Field Theory

Crystal field stabilisation energy in tetrahedral vs. octahedral crystal field

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

"site preference"

d^n	CFSE(tetrahedral)	CFSE(octahedral)	ΔKFSE(octah. – tetrah.)
1	$-2.67\ Dq_o$	$-4\ Dq_o$	$-1.33\ Dq_o$
2	$-5.33\ Dq_o$	$-8\ Dq_o$	$-2.67\ Dq_o$
3	$-3.55\ Dq_o$	$-12\ Dq_o$	$-8.45\ Dq_o$
4	$-1.78\ Dq_o$	$-6\ Dq_o$ (h.s.)	$-4.22\ Dq_o$
		$-16\ Dq_o$ + 1 SPE (l.s.)	$-14.22\ Dq_o$ + 1 SPE
5	$0\ Dq_o$	$0\ Dq_o$ (h.s.)	$0\ Dq_o$
		$-20\ Dq_o$ + 2 SPE (l.s.)	$-20\ Dq_o$ + 2 SPE
6	$-2.67\ Dq_o$	$-4\ Dq_o$ (h.s.)	$-1.33\ Dq_o$
		$-24\ Dq_o$ + 2 SPE (l.s.)	$-21.33\ Dq_o$+ 2 SPE
7	$-5.33\ Dq_o$	$-8\ Dq_o$ (h.s.)	$-2.67\ Dq_o$
		$-18\ Dq_o$ + 1 SPE (l.s.)	$-12.67\ Dq_o$ + 1 SPE
8	$-3.55\ Dq_o$	$-12\ Dq_o$	$-8.45\ Dq_o$
9	$-1.78\ Dq_o$	$-6\ Dq_o$	$-4.22\ Dq_o$
10	$0\ Dq_o$	$0\ Dq_o$	$0\ Dq_o$

9. Concepts of Bonding

Crystal Field Theory

Crystal field splitting in tetrahedral crystal field

Amounts to only 4/9 of the splitting in a octahedral crystal field!

- Solely high spin complexes
- Ions with a electronic configuration that gives rise to high CFSE, e.g. [Ar]d^3-, [Ar]d^5(low spin)- or [Ar]d^6(low spin)-configuration, prefer – if possible – octahedral coordination ⇒ ordinary spinel → inverse spinel

Tetrahedral coordination polyhedra are observed for:

- Sterically demanding ligands, such as chloro, bromo and iodo ligands
- Ligands forming multiple bonds to the metal centre, e.g. oxo and nitrido ligands

Remember: There is no electronic configuration, where the electronic stabilisation in a tetrahedron is higher than in a octahedron (site preference) ⇒ octahedral geometry favoured

Exception: d^5 (high spin) and d^{10}, since in these cases CFSE for octahedral and tetrahedral geometry equals zero

9. Concepts of Bonding

Spinels are Compounds of the Following Composition, AB_2O_4

The oxygen anions almost form a cubic close packing (cubic face centred). In the spinel $MgAl_2O_4$, 1/8 of all tetrahedral sites are occupied by Mg atoms (A^{II}), 1/2 of all octahedral sites are taken up by Al atoms (B^{III}) in such a way, that every O atom is coordinated by one Mg and three Al atoms in a distorted tetrahedral fashion

A^{II} = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn

B^{III} = Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Rh, Ni

Normal spinel structure

$[A^{II}]^{tetr.}[B^{III}]^{oct.}{}_2O_4$

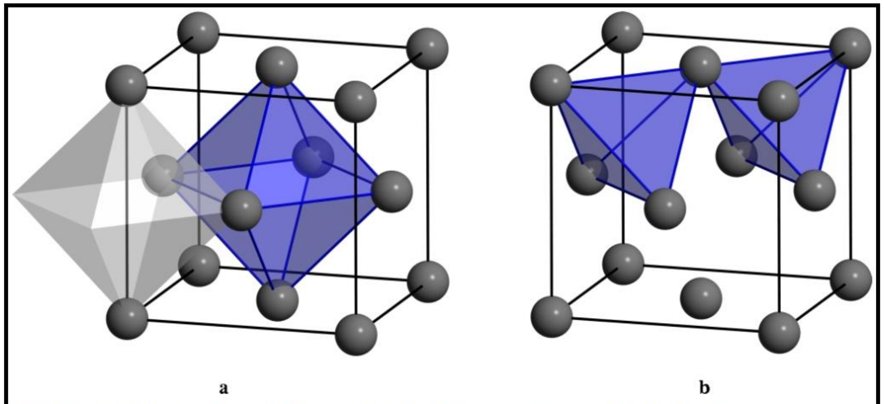
Examples: $MgAl_2O_4$, $MnMn_2O_4$ (Mn_3O_4), $FeAl_2O_4$
$CoCo_2O_4$ (Co_3O_4)

Inverse spinel structure

$[B^{III}]^{tetr.}[A^{II}]^{oct.}[B^{III}]^{oct.}O_4$

Examples: $CoFe_2O_4$, $FeFe_2O_4$ (Fe_3O_4), $NiFe_2O_4$

Octahedral and tetrahedral sites



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung04-11.jpg

9. Concepts of Bonding

Crystal Field Theory

The site preference determines the distribution of the transition metal cations in spinels

Mn_3O_4	Mn^{2+}	d^5 high spin	no site preference
	Mn^{3+}	d^4 high spin	site preference = -4.22 Dq
			⇒ preferably octahedral site $[\mathrm{B^{III}}]^{oct.}$

⇒ normal spinel $[\mathrm{Mn^{II}}]^{tetr.}[\mathrm{Mn^{III}}]^{oct.}{}_2O_4$

Fe_3O_4	Fe^{2+}	d^6 high spin	site preference = -1.33 Dq
			⇒ preferably octahedral site $[\mathrm{A^{II}}]^{oct.}$
	Fe^{3+}	d^5 high spin	no site preference

⇒ Inverse spinel $[\mathrm{Fe^{III}}]^{tetr.}[\mathrm{Fe^{II}}]^{oct.}[\mathrm{Fe^{III}}]^{oct.}O_4$, meaning all Fe^{2+}-ions occupy octahedral sites and force half of the Fe^{3+}-ions onto tetrahedral sites

9. Concepts of Bonding

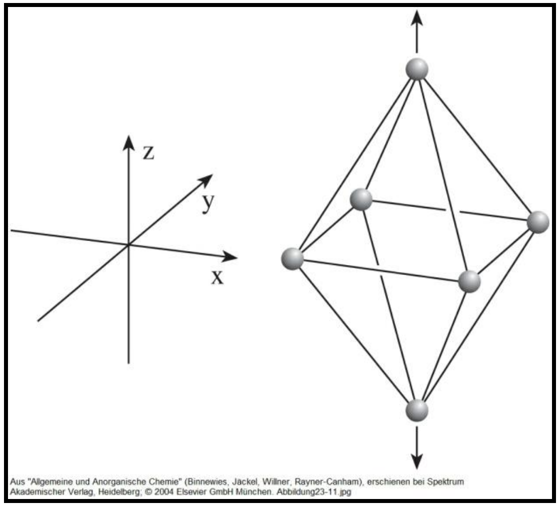
Crystal Field Theory

Tetragonally distorted octahedral crystal field

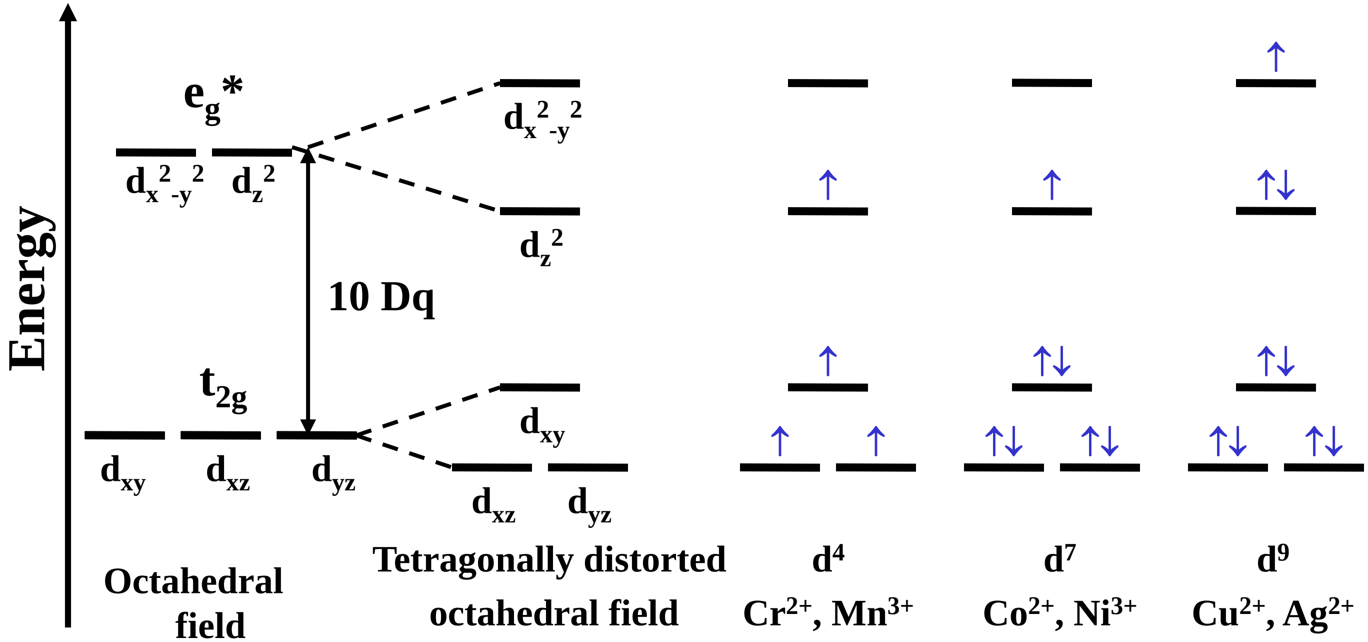
Jahn-Teller-Theorem (Hermann Arthur Jahn and Edward Teller 1937)

“Every non-linear molecule, which possesses a degenerate electronic state, is prone to distortion, lowering the symmetry und thus revoking electronic degeneration“

⇒ Large gain in energy for d^4(high spin), d^7(low spin) and d^9-configuration



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-11.jpg



Energy

e_g^*

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

10 Dq

t_{2g}

d_{xy} d_{xz} d_{yz}

Octahedral field

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

d_{z^2}

d_{xy}

d_{xz} d_{yz}

Tetragonally distorted octahedral field

d^4
Cr^{2+}, Mn^{3+}

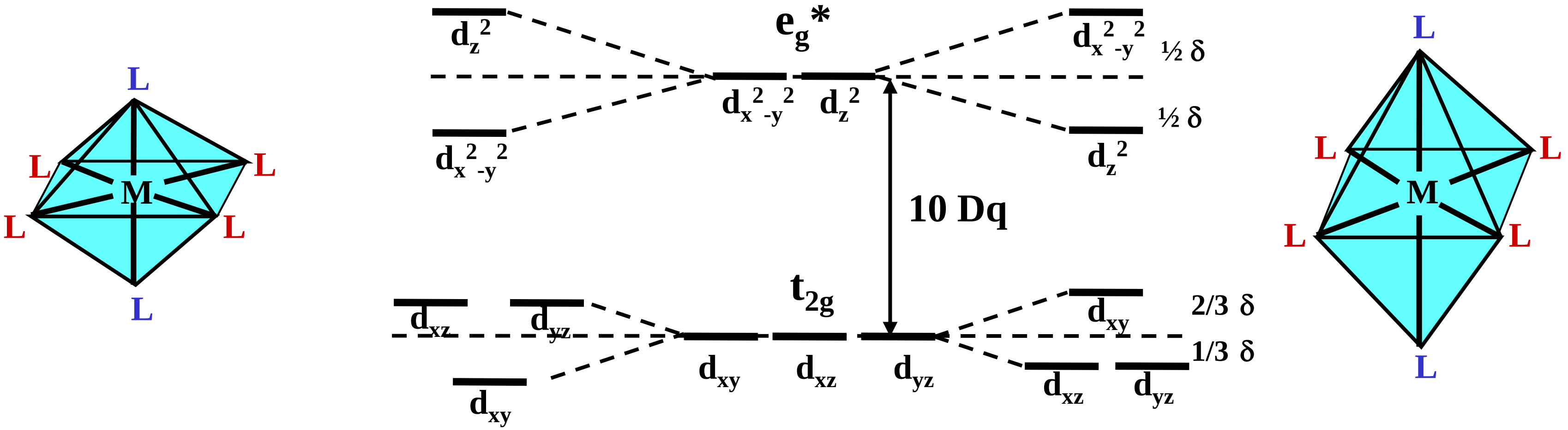
d^7
Co^{2+}, Ni^{3+}

d^9
Cu^{2+}, Ag^{2+}

9. Concepts of Bonding

Crystal Field Theory

Tetragonally distorted crystal field as a result of the Jahn-Teller effect

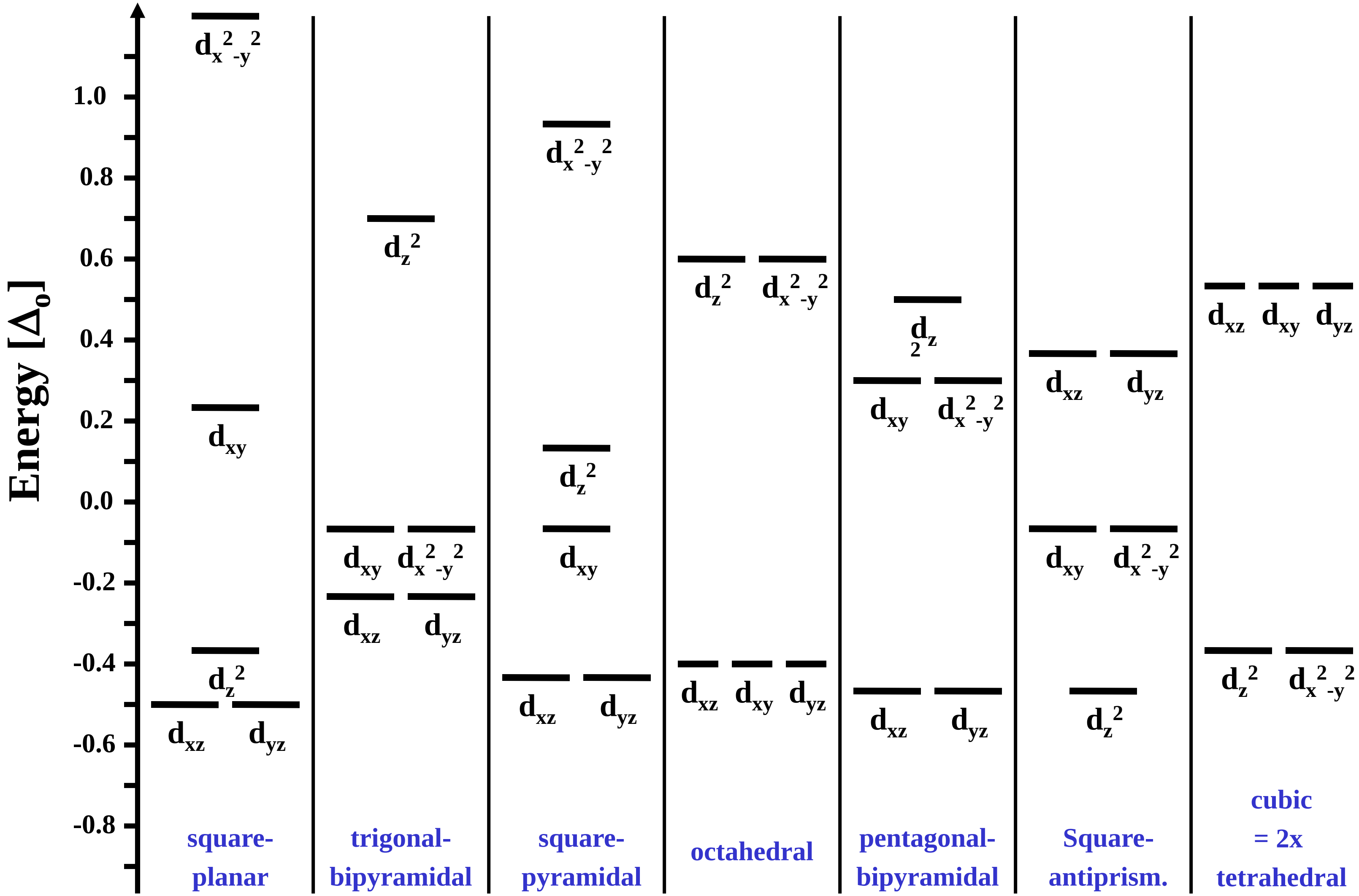


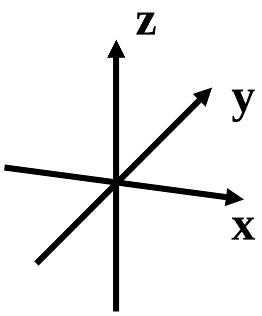
Electronic configuration	nd^1	nd^2	nd^3	nd^4	nd^5	nd^6	nd^7	nd^8	nd^9	nd^{10}
High spin J.T.	Weak	Weak	-	Strong	-	Weak	Weak	-	Strong	-
Low spin J.T.	Weak	Weak	-	Weak	Weak	-	Strong	-	Strong	-

9. Concepts of Bonding

Crystal Field Theory

Crystal field
splitting
in various
crystal field
symmetries





9. Concepts of Bonding

Crystal Field Theory – Applications and Implications

1. Magnetic properties ↔ electronic configuration

paramagnetic Fe(II)-compounds: (unpaired electrons)	high spin (magnetically normal)
diamagnetic Fe(II)-compounds: (no unpaired electrons)	low spin (magnetically anomalous)

2. Optical properties (absorption and luminescence spectra)

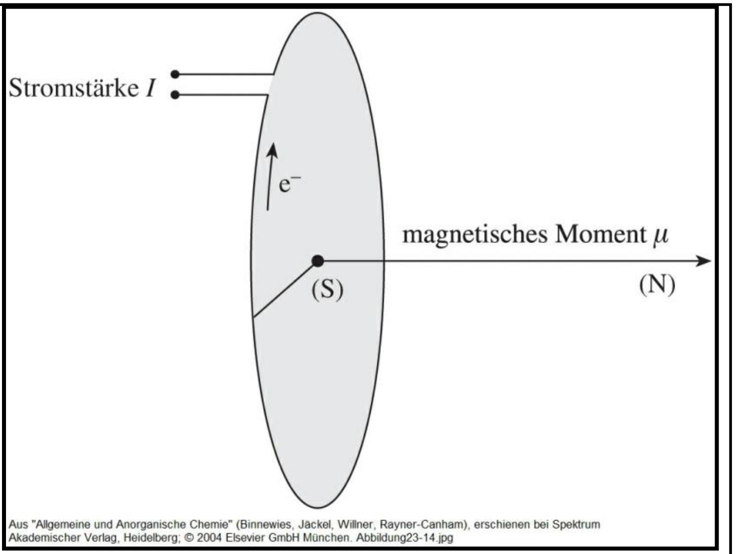
3. Ionic radii of transition metal cations

4. Hydration enthalpies of transition metal cations

5. Lattice energy of transition metal salts

9. Concepts of Bonding

Crystal Field Theory



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-14.jpg

To 1. Magnetic properties

The base unit of the magnetic momentum is called

Bohr's magneton, and equals the magnetic momentum, induced by a single electron on a circular path - with Bohr's radius (53 pm) - around a proton

$$\boxed{\mu_B = \frac{e \cdot \hbar}{2 \cdot m_e}}$$

Every moving electrical charge induces a magnetic field with the magnetic momentum µ (exp.: electrical current in a wire)

For elements of the first row of transition metals with n unpaired electrons, the following approximate correlation can be stated:

$$\boxed{\mu_{ber} = \sqrt{n(n+2)} \cdot \mu_B}$$

"Spin only value", i.e. only spin angular momentum and no orbital momentum

$$\boxed{\mu_{ber} = 2\sqrt{S(S+1)} \cdot \mu_B}$$

Total spin S = Σs with s = ½ and S = n/2

9. Concepts of Bonding

Crystal Field Theory

To 1. Magnetic properties

The calculated spin-only values are in good agreement with experimental data

⇒ For this reason it is possible to deduce the number of unpaired electrons in 3d-complexes directly from magnetic measurements

3d-Ion	Electronic configuration	n	$\mu_{calc.}$ [μ_B] *high spin*	$\mu_{exp.}$ [μ_B]
Ti^{3+}	$[Ar]3d^1$	1	1.73	1.7 – 1.8
V^{3+}, Cr^{4+}, Mn^{5+}	$[Ar]3d^2$	2	2.83	2.7 – 2.9
V^{2+}, Cr^{3+}, Mn^{4+}	$[Ar]3d^3$	3	3.87	3.7 – 3.9
Cr^{2+}, Mn^{3+}	$[Ar]3d^4$	4	4.90	4.8 – 4.9
Mn^{2+}, Fe^{3+}	$[Ar]3d^5$	5	5.92	5.7 – 6.0
Fe^{2+}, Co^{3+}	$[Ar]3d^6$	4	4.90	5.0 – 5.6
Co^{2+}, Ni^{3+}	$[Ar]3d^7$	3	3.87	4.3 – 5.2
Ni^{2+}	$[Ar]3d^8$	2	2.83	2.9 – 3.9
Cu^{2+}	$[Ar]3d^9$	1	1.73	1.9 – 2.1
Cu^{+}, Zn^{2+}	$[Ar]3d^{10}$	0	0	0

9. Concepts of Bonding

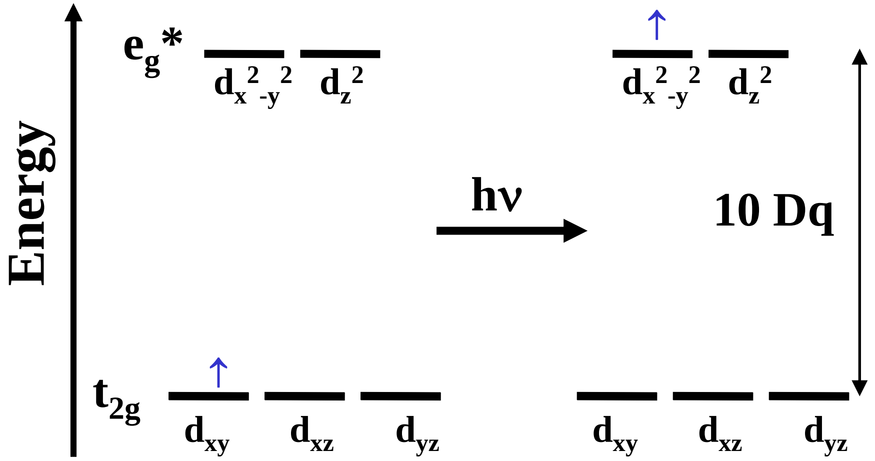
Crystal Field Theory

To 2. Optical properties

Electronic transitions between d-orbitals (d-d-transitions) often lead to absorption bands situated in the visible spectral range

Example: octahedral Ti^{3+}-complexes

Complex	10 Dq [kJ/mol]	10 Dq [nm]
$[Ti(H_2O)_6]^{3+}$	239	500
$[TiF_6]^{3-}$	203	630
$[TiCl_6]^{3-}$	160	770



CFSE: $CO > CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > NO_3^- > Cl^- > SCN^- > S^{2-} > Br^- > I^-$

(10 Dq) *strong field* *weak field*

⇒ Spectrochemical series

- Arranges ligands relative to the strength of the resulting crystal field splitting
- The sequence can not be explained by crystal field theory (point charges)

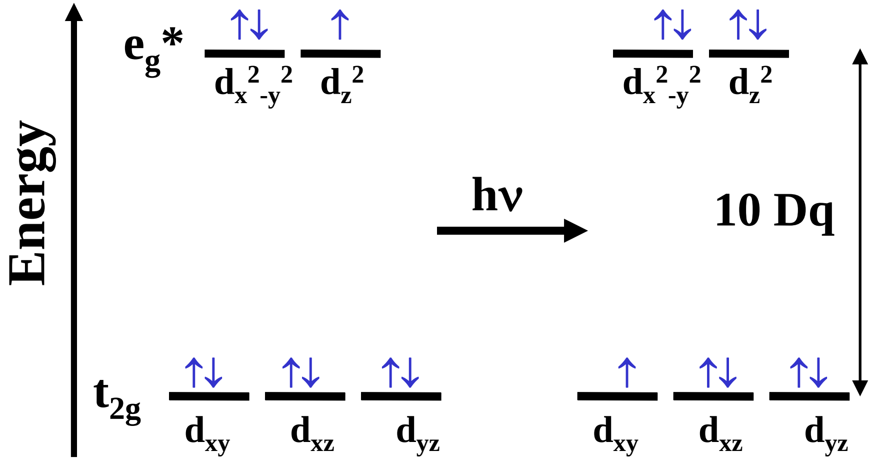
9. Concepts of Bonding

Crystal Field Theory

To 2. Optical properties

Example: octahedral Cu^{2+}-complexes (d^9)

Complex	10 Dq	Colour
$[Cu(H_2O)_6]^{2+}$	800 nm	colourless
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	670 nm	pale blue
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	600 nm	blue



**Comparably simple situations – one absorption band – can also be found for octahedral complexes with d^4 high spin or d^6 high spin configurations at the metal centres.
For the electronic configurations $d^2 – d^8$, the situation becomes more complex, due to interactions between the electrons (electron-electron-correlation)**

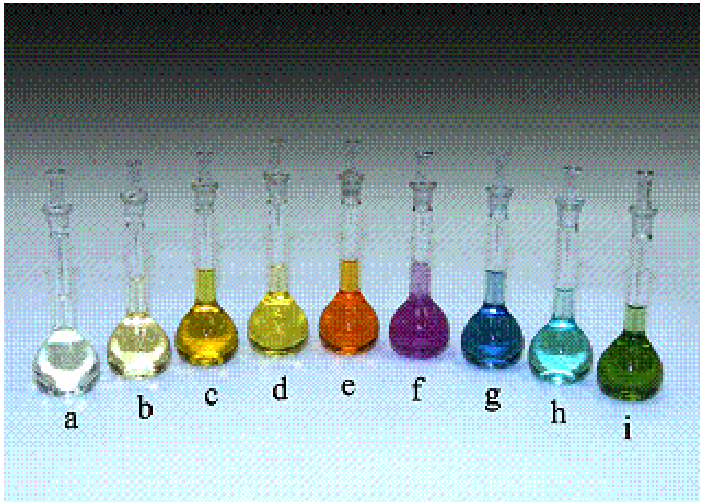
9. Concepts of Bonding

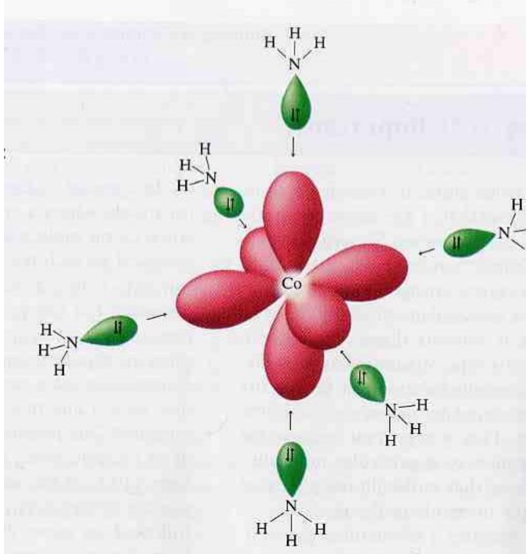
Crystal Field Theory

To 2. Optical properties

Example: Octahedral Co^{3+}-complexes (d^6 low spin)

#	Complex	10 Dq	Colour	Absorption
a	$[Co(CN)_6]^{3-}$	↑	colourless	UV
b	$[Co(NO_2)_6]^{3-}$		pale yellow	violet
c	$[Co(phen)_3]^{3+}$		yellow	blue
d	$[Co(en)_3]^{3+}$		deep yellow	cyan-blue
e	$[Co(NH_3)_6]^{3+}$		orange	cyan
f	$[Co(gly)_3]^{3+}$		violet	green
g	$[Co(H_2O)_6]^{3+}$		blue	yellow
h	$[Co(ox)_3]^{3-}$		cyan	orange
i	$[Co(CO_3)_3]^{3-}$		green	red (+ blue)





9. Concepts of Bonding

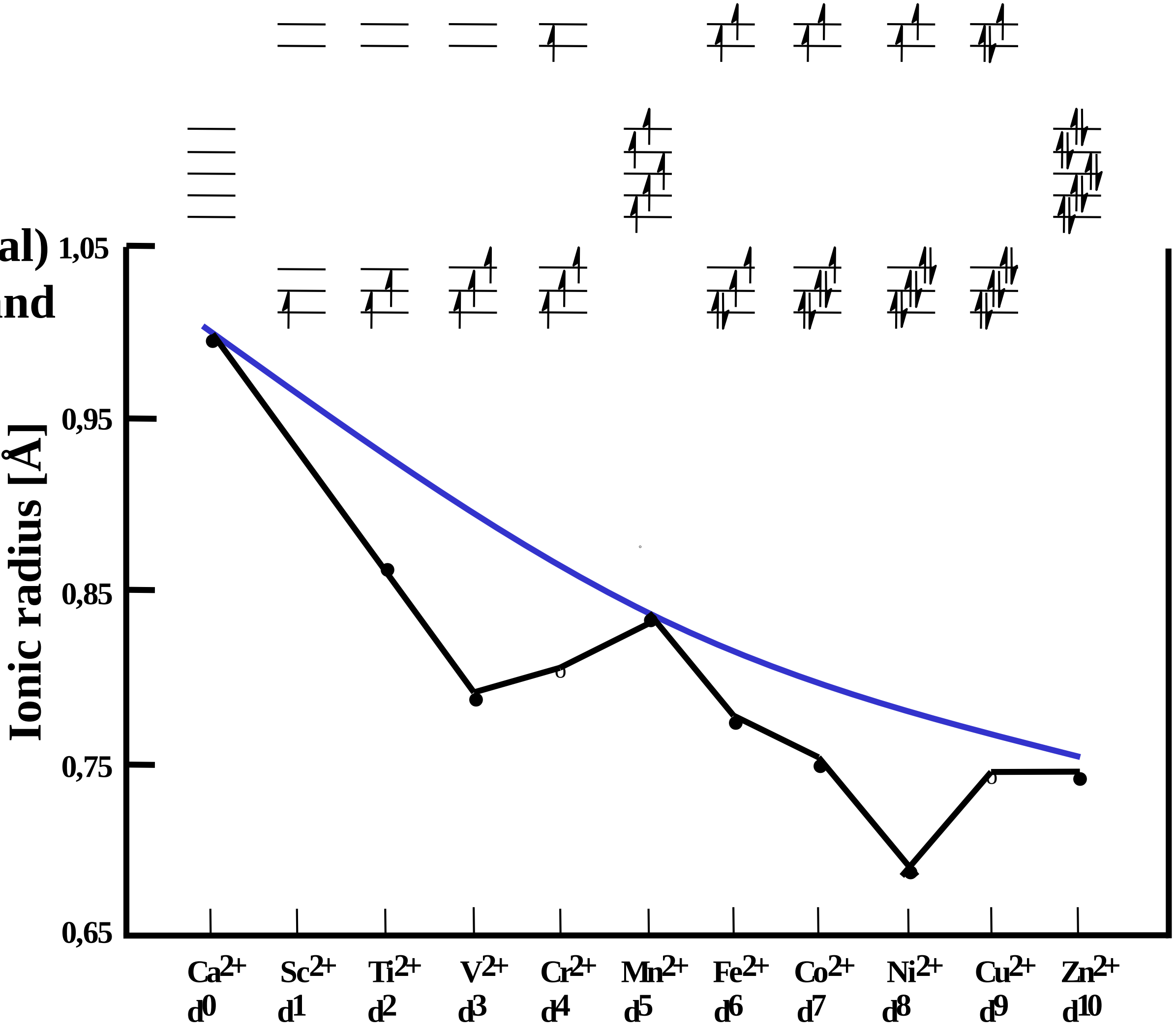
Crystal Field Theory

To 3. Ionic radii

A plot of the ionic radii of divalent 3d-ions in the oxides MO (M = metal) in octahedral ligand coordination and high spin state does not show a steady linear decrease (blue graph)!

⇒ Electronic configurations with unoccupied orbitals, which are directed to the ligands (d_{z^2}, $d_{x^2-y^2}$), result in small ionic radii

⇒ V^{2+}, Ni^{2+}



9. Concepts of Bonding

Crystal Field Theory

<u>To 4. Hydration enthalpy</u>

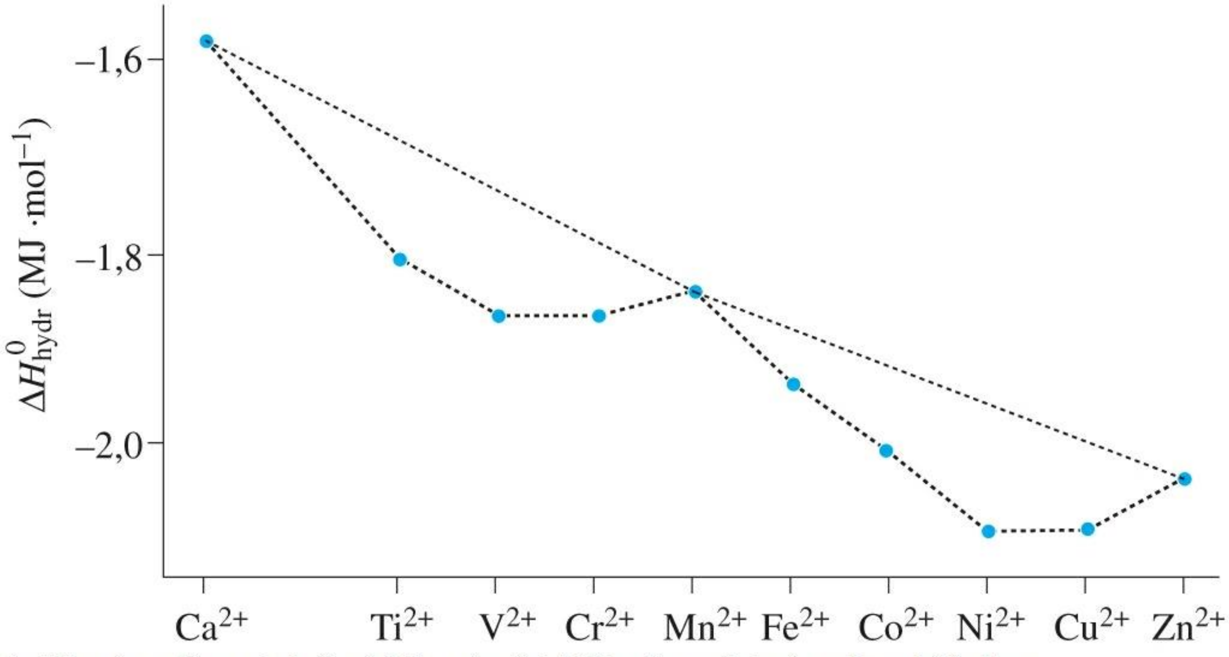
During the reaction:

$$M^{n+}(g) + 6\ H_2O(l) \rightarrow [M(H_2O)_6]^{n+}(aq)$$

energy is set free by the electrostatic forces between the metal, M, and the ligand, water

Small cations provide high hydration enthalpies

Therefore, the trend for hydration enthalpies corresponds with the one for the ionic radii



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-17.jpg

9. Concepts of Bonding

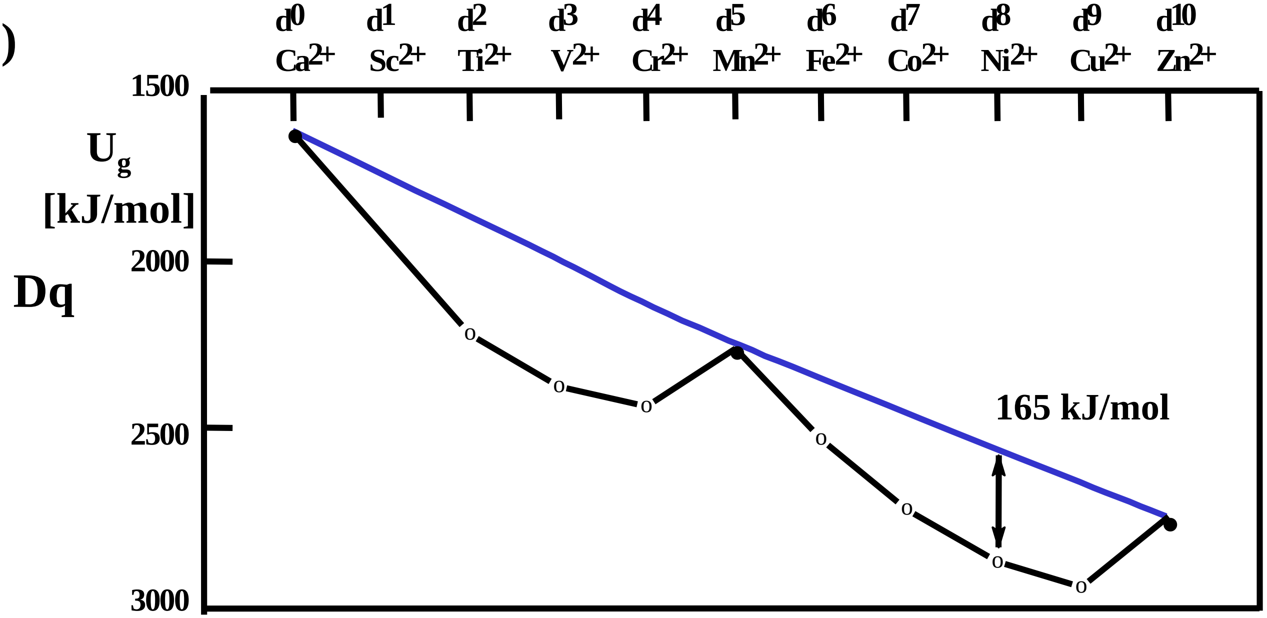
Crystal Field Theory

To 5. Lattice energy of transition metal salts

$M^{n+}(g) + n/2\ O^{2-}(g) \rightarrow MO_{n/2}(s)$

Through the deviation between measured and calculated values for U_g, the parameter 10 Dq (crystal field splitting) can be calculated

Lattice energies for difluorides of the 3d-metals



$Ni^{2+}\ [Ar]d^8 \Rightarrow t_{2g}^{6}\ e_g^{*2}$

Crystal field stabilisation energy CFSE = -12 Dq

$U_g(\text{exp.}) - U_g(\text{calc.}) = 165\ \text{kJ/mol} = 13600\ \text{cm}^{-1} = 12\ \text{Dq}$

$10\ \text{Dq} = 11330\ \text{cm}^{-1}$

9. Concepts of Bonding

Ligand Field Theory

Disadvantages of crystal field theory: There is a number of spectroscopic phenomena that the concept of electrostatic point charges can not explain: Electron Paramagnetic Resonance (EPR) spectra, ordering of spectrochemical series

⇒ It is necessary to account for the covalence of the metal-ligand bond

Effects of covalent interactions

- **Delocalisation of electron density from metal d-orbitals towards ligands (nephelauxetic effect)**
- **Reduction of inter-electronic repulsion at the metal centre**
- **Shift of electron density towards ligands, possibly leading to weakening of intra-ligand bonds (back-bonding-effect)**

⇒ Change of electronic, magnetic, and spectroscopic properties

9. Concepts of Bonding

Ligand Field Theory

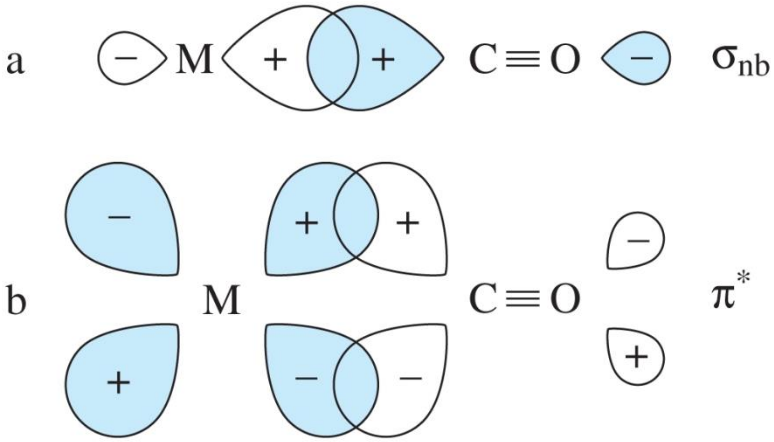
Back-bonding to ligands

- Typically for metalcarbonyls and -nitrosyls
- Metal experiences formally low oxidation states, coinciding with high electron density that is reduced by a withdrawal of charge towards the ligands

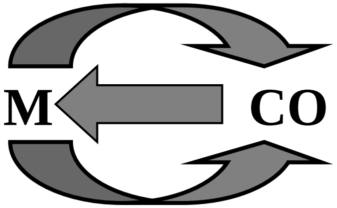
Example: $M(CO)_6$ "metalcarbonyl" $M-C\equiv O|$ ↔ $M=C=O$

a) σ-donor-bond

b) π-acceptor-bond



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung23-29.jpg



"synergetic effect"

9. Concepts of Bonding

Ligand Field Theory

Explanation for the sequence of ligands within the spectrochemical series

$CO > CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > NO_3^- > Cl^- > SCN^- > S^{2-} > Br^- > I^-$

strong ligands	weak ligands
π-back-bonding	no π-back-bonding

The spectrochemical series does not correlate with the charge of the ligands, but with the ability of the ligands to delocalise electron density from the metal atom and thus intensifying the positive charge density or effective field strength at the metal atom.

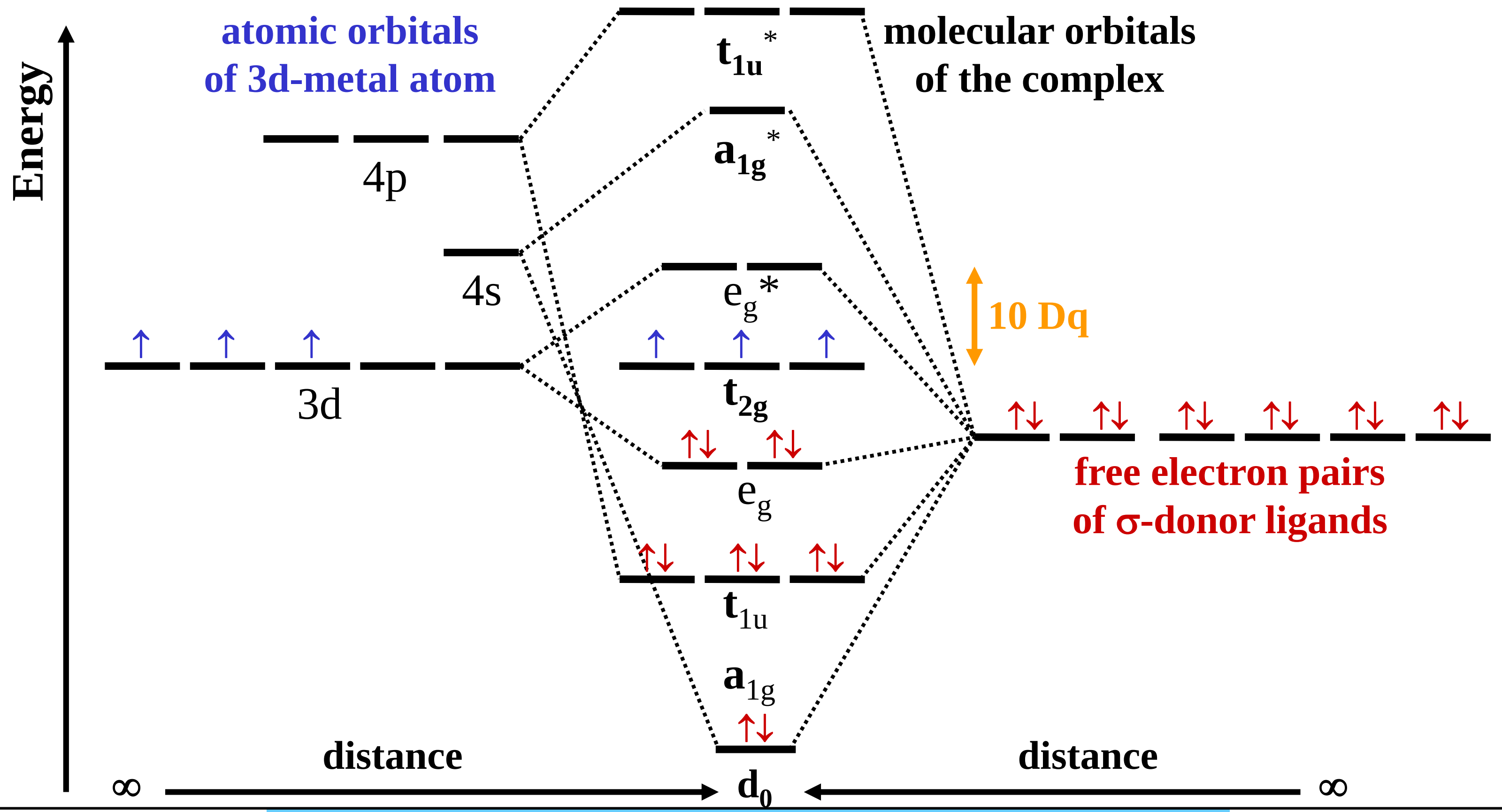
π-acceptor ligands: (back-bonding)	stabilise metals in low oxidation states ⇒ CO, NO
π-donor ligands: (multiple metal-ligand-bonds)	stabilise metals in high oxidation states ⇒ O^{2-}, N^{3-}

9. Concepts of Bonding

Molecular Orbital (MO) Theory

⇒ **Overlap of metal and ligand orbitals leads to the formation of molecular orbitals**

⇒ **Example: octahedral complex consisting of 6 σ-donor ligands and 3d-metal atom**



9. Concepts of Bonding

Molecular Orbital (MO) Theory

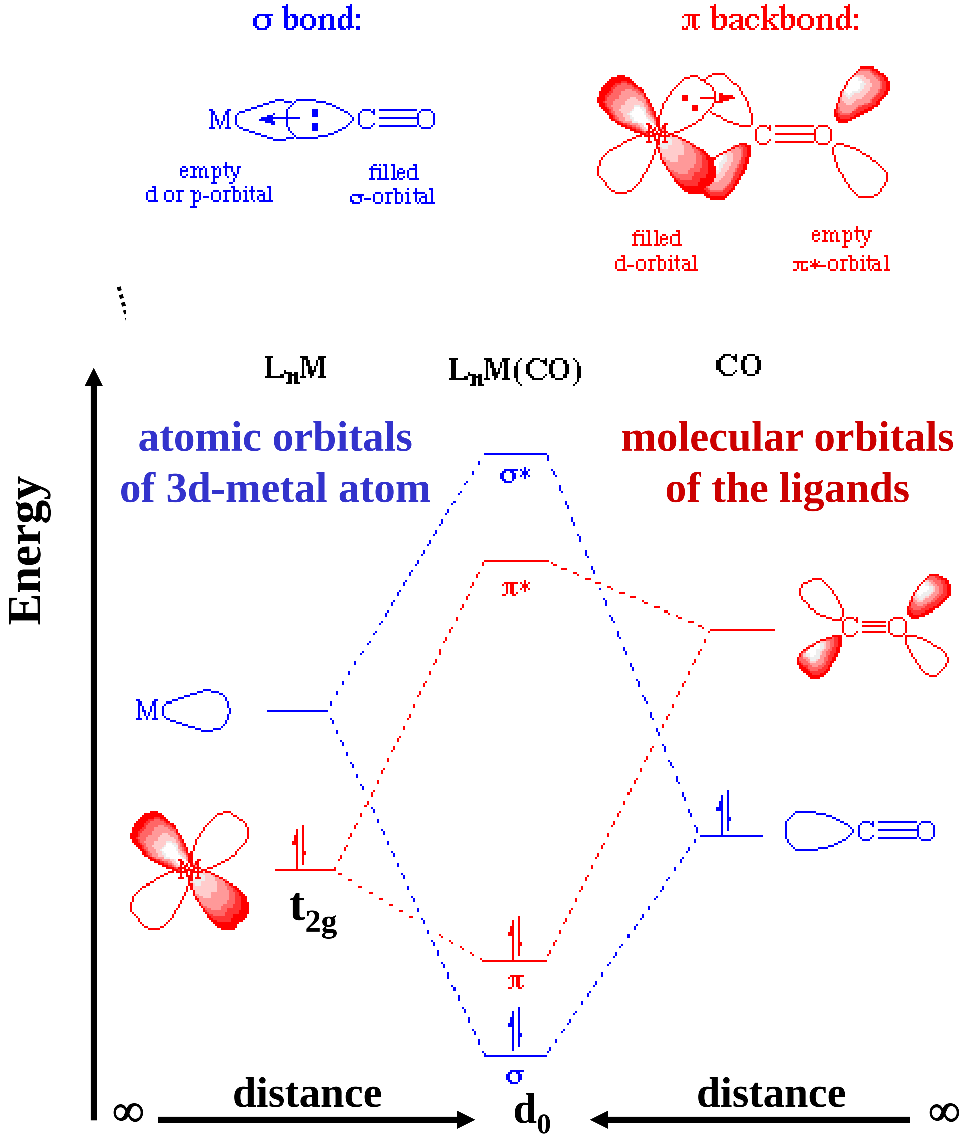
Consequences of π-back-bonding

- **Strengthening of metal-ligand bond**
- **Increase of crystal field splitting by lowering the energy of t_{2g}-orbitals**
- **Weakening of intra-ligand bonds by transfer of electronic density into anti-bonding ligand orbitals**

  ⇒ Decrease of vibrational frequencies

  ⇒ Increased reactivity of the ligands (activation)

  ⇒ Catalytic and enzymatic reactions



9. Concepts of Bonding

Molecular Orbital (MO) Theory

Explanation for the sequence of ligands within the spectrochemical series

$CO > CN^- > NO_2^- > en > NH_3 > H_2O > OH^- > F^- > NO_3^- > Cl^- > SCN^- > S^{2-} > Br^- > I^-$

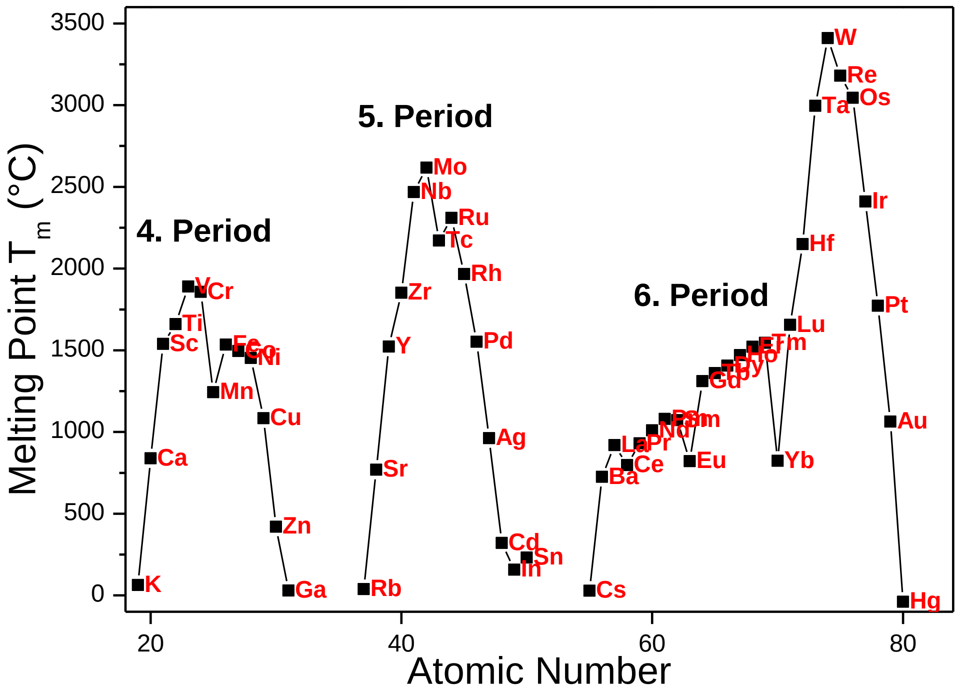
strong ligands		weak ligands
unoccupied π*-orbitals	no suitable p-orbitals	occupied p-orbitals
π-acceptor ligands	exclusively σ-donor ligands	π-donor ligands

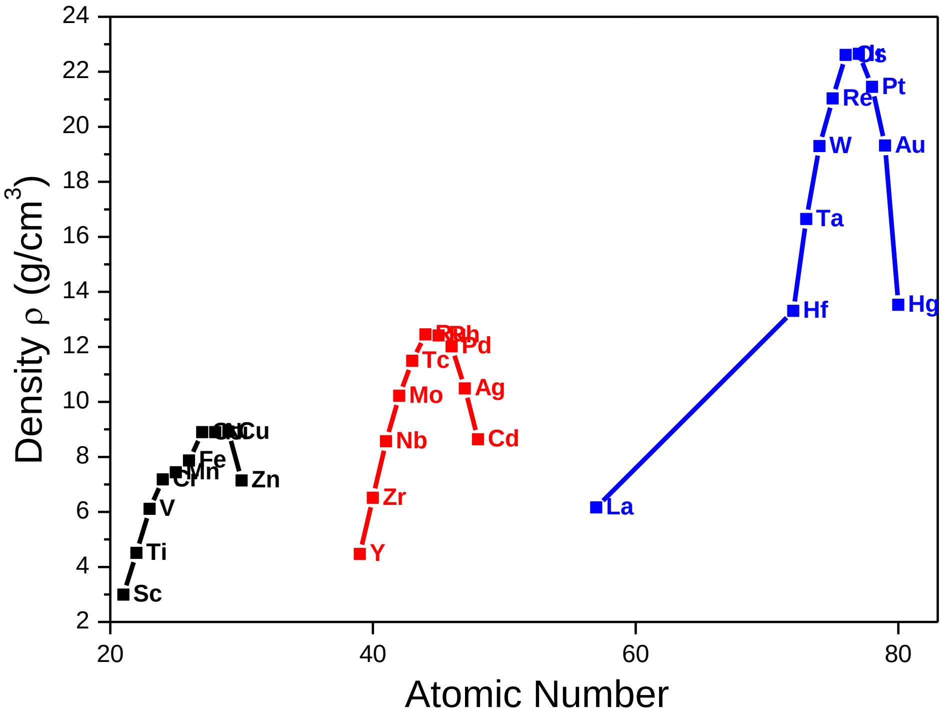
Type of ligand	Effect upon metal-ligand-bond	Crystal field splitting
π-acceptor	highly stabilising	high
σ-donor	stabilising	intermediate
π-donor	destabilising	small

10. Chemistry of Transition Metals

Physical Properties

Transition metals experience high melting/boiling points, along with high/highest densities





Numerous transition metals are highly relevant as materials or catalysts

(→ chemicals records: http://www.fh-muenster.de/FB1/Juestel/ScienceFun.shtm)

10. Chemistry of Transition Metals

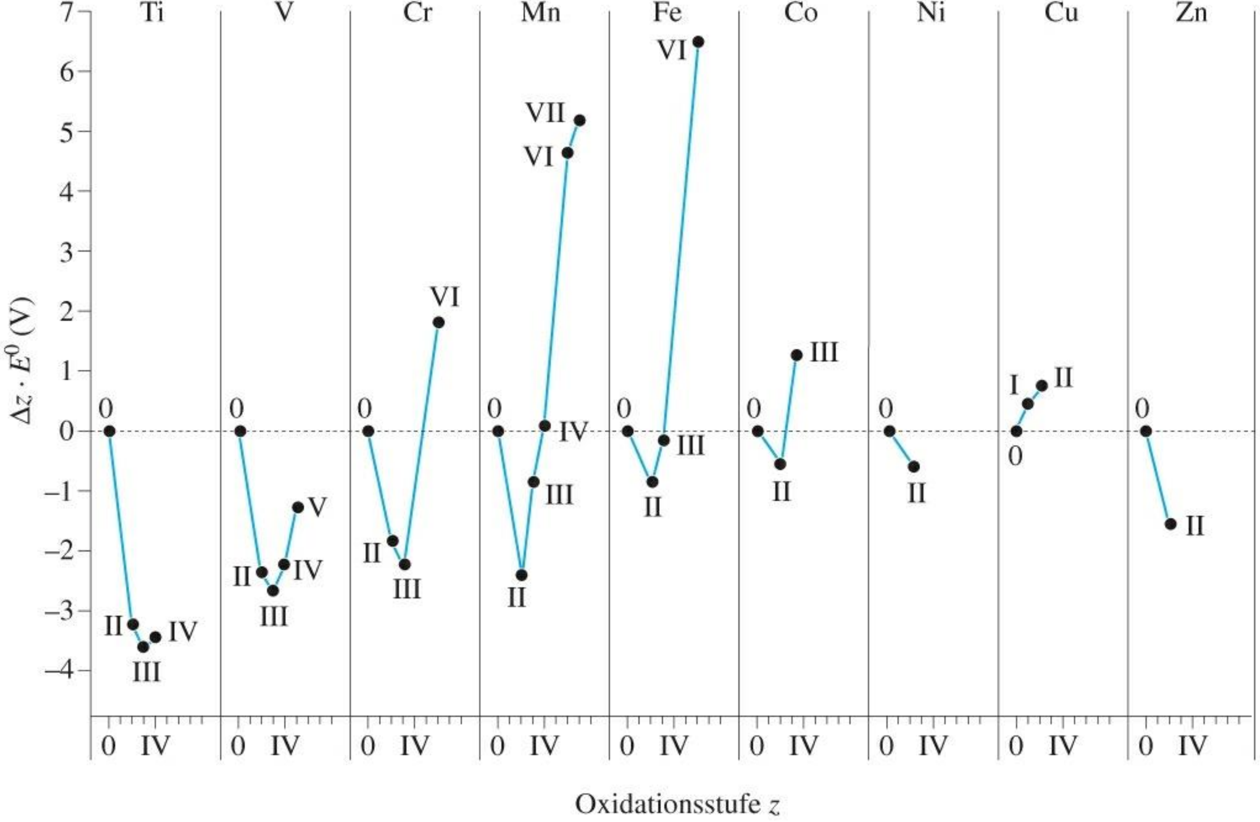
Oxidation States

3d-Elements	**Sc** +3	**Ti** +2, +3, +4	**V** +2, +3, +4, +5	**Cr** +2, +3, +6	**Mn** +2, +3 +4, +7	**Fe** +2, +3	**Co** +2, +3	**Ni** +2	**Cu** +1, +2	**Zn** +2
4d-Elements	**Y** +3	**Zr** +4	**Nb** +5	**Mo** +4, +6	**Tc*** +7	**Ru** +2, +3, +4	**Rh** +3	**Pd** +2	**Ag** +1, +2	**Cd** +2
5d-Elements	**La** +3	**Hf** +4	**Ta** +5	**W** +4, +6	**Re** +4, +7	**Os** +4, +8	**Ir** +3, +4	**Pt** +2, +4	**Au** +1, +3	**Hg** +1, +2

- **All TM, with a sufficient abundance in the earth's crust and relatively stable low oxidation states, are accessible for biological/biochemical processes, and are thus of great importance as trace elements**
- **Highest oxidation states (Mn^{VII}, Os^{VIII}) are only possible with π-donor ligands (O^{2-}, N^{3-}) ⇒ $[MnO_4]^-$, OsO_4, $[OsO_3N]^-$, whereas MnF_7 and OsF_8 are not known, while MnF_4 is a strong oxidising agent**

10. Chemistry of Transition Metals

Oxidation States (Frost-Diagram of 3d-Metals in Acidic Solution)



- Metallic titanium is a potent reductive agent
- Mn^{VI}, Mn^{VII} and Fe^{VI} are strong oxidising agents
- Most stable oxidation states: $Ti^{III/IV}$, V^{III}, Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{0}, Zn^{II}
  $\Rightarrow$ Copper is a noble metal, i.e. $E^0 > 0.0$ V

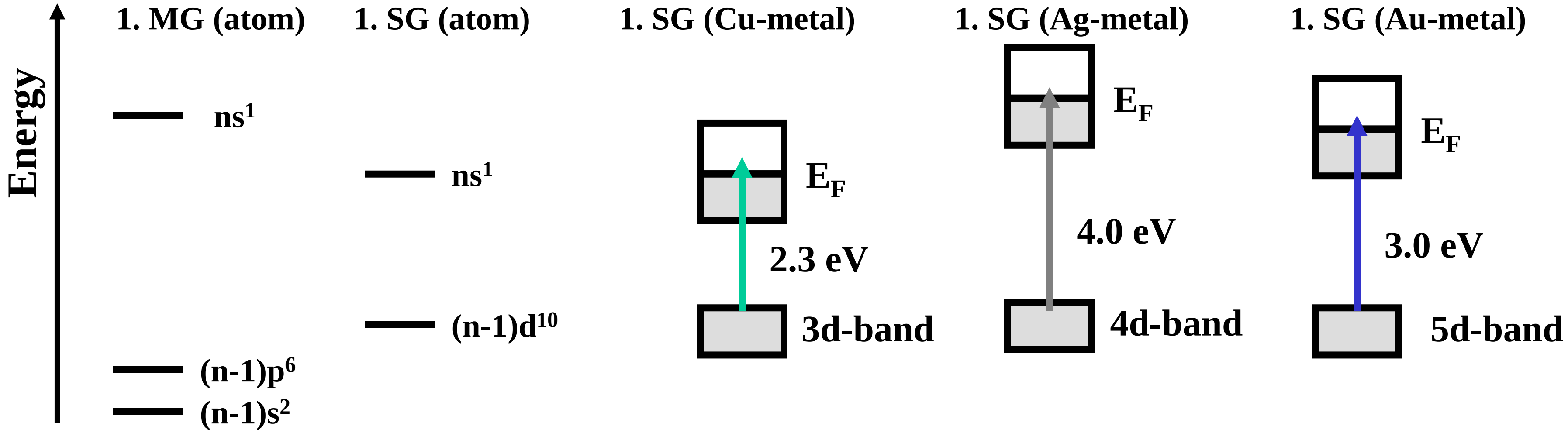
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

⇒ 1. Subgroup or group 11 $(n\text{-}1)d^{10}ns^1$ with n = 4, 5, 6

Properties of the elements:

- Melting points at about 1000° C (readily form alloys and are easy to be refound)
- High electric conductivity (Ag > Cu > Au)
- ns^1-electron is more tightly bound than in alkaline metals, due to the higher core charge
- Copper and gold are, together with Cs, the only coloured metals ⇒ absorption in visible range of the spectrum



10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

⇒ Metals of the copper group and their respective alloys “coined” the development of the first advanced civilisations (Au: 5000 BC, Ag: ca. 3500 BC, Copper Age: ca. 5000 BC, Bronze Age: ca. 3000 BC)

Alloys of technical importance

Brass rolls

Name	Main component	Alloying addition
Brass	Cu	Zn
Bronze	Cu	Sn
Cupronickel	Cu	Ni
Nickel silver	Cu	Ni, Zn
Billion	Cu	Ag
White gold	Au	Pd, Ni
Red gold	Au	Cu

(→ presentations)

Bronze statue

White gold ring

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Occurrence

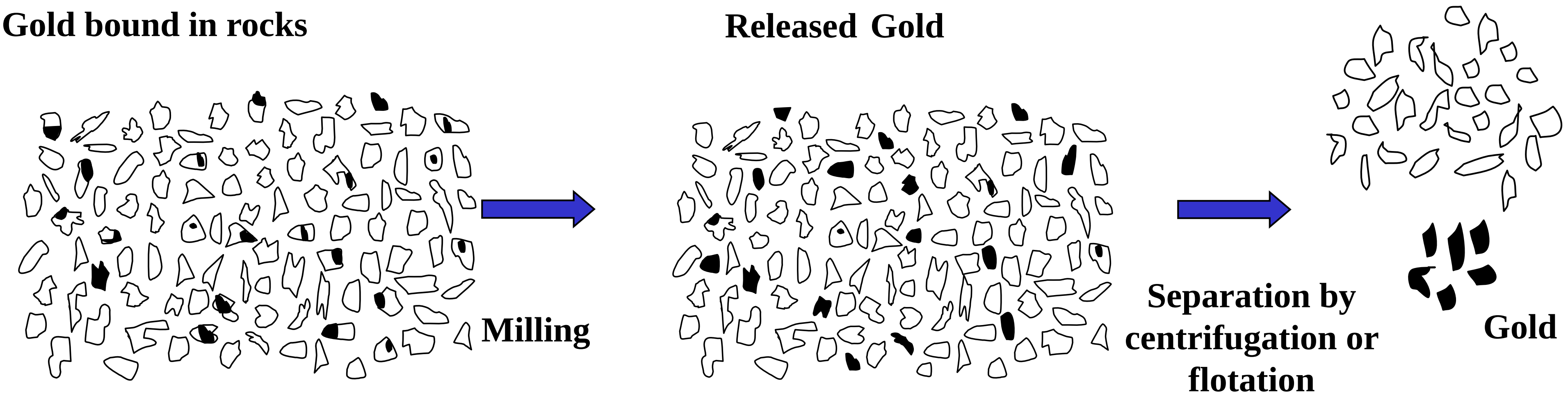
Copper (aes cyprium, cuprum)	Cu_2S	Copper shine
Cyprus	$CuFeS_2$	Chalcopyrite
	$Cu(OH)_2 \cdot CuCO_3$	Malachite
	Cu	Dignified
Silver (argos, argentum)	Ag_2S	Silver glance
shiny, white	Ag	Sterling
Gold (aurum)	Au	Dignified
shiny, blank	(E175)	Gold leaf

Fabrication

- Cu and Ag by calcination of sulphide ores, e.g. Cu_2S or Ag_2S
  $2\ Cu_2S + 3\ O_2 \rightarrow 2\ Cu_2O + 2\ SO_2$
  $2\ Cu_2O + Cu_2S \rightarrow 6\ Cu + SO_2$
- Au (and partially Ag, too) by cyaniding (→ presentations)

10. Chemistry of Transition Metals

Excursion: Gold mining



Gold bound in rocks

Milling

Released Gold

Separation by centrifugation or flotation

Minerals (Quartz)

Gold

Chemical	Formula	pH-value	Formed Au complex
Thio urea	$(NH_2)_2C{=}S$	1-4	$[Au(NH_2CSNH_2)_2]^+$
Bromide	Br^-	1-7	$[AuBr_4]^-$
Iodide	I^-	1-5	$[AuI_2]^-$
Thiocyanate	SCN^-	1-3	$[Au(SCN)_4]^-$
Thiosulphate	$S_2O_3^{2-}$	8-11	$[Au(S_2O_3)_2]^{3-}$
Chlor compounds	Cl^-, OCl^-, Cl_2, ClO_3^-	1-4	$[AuCl_4]^-$

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Oxidation States

Coinage metal	Oxidation state	E^0_{M/M^+} [V]	1. IE [kJ/mol]	soluble in
Cu	+1, +2, +3	0.52	745.3	HNO_3
Ag	+1, +2, +3	0.80	730.8	HNO_3
Au	+1, +3	1.68	889.9	HNO_3/HCl (1:3)

Cu^+ and Au^+ tend to disproportionate in aqueous solution

$2\ Cu^+ \rightarrow Cu^0 + Cu^{2+}$ Hydration enthalpy of Cu^{2+}: -2100 kJ/mol, Cu^+: -590 kJ/mol

Ag^+ is stable 2. Ionisation energy: $Ag^+ > Au^+ > Cu^+$

$3\ Au^+ \rightarrow 2\ Au^0 + Au^{3+}$ High CFSE for square-planar Au^{3+}($[Xe]4f^{14}5d^8$)-ions

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Stereo chemistry

⇒ Strong influence of oxidation state

+I (d^{10}): Cu^+, Ag^+, Au^+ favour CN 2 ⇒ linear coordination ⇒ $[H_3N\rightarrow Ag\leftarrow NH_3]^+$

Tetrahedral coordination of Cu^+ in $[Cu(py)_4]^+$ and $[Cu(CN)_4]^{3-}$

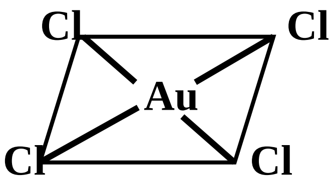
⇒ sp^3-hybridisation (CFSE = 0)

Due to the high energy gap between s- and p-orbitals, Ag^+ and Au^+ generally form no tetrahedral complexes!

+II (d^9): Favoured coordination geometry for Cu^{2+}-complexes is a distorted octahedron → $[Cu(NH_3)_4(H_2O)_2]^{2+}$, $[Cu(H_2O)_6]^{2+}$ and square-planar → $[CuCl_2(H_2O)_2]^0$

⇒ Jahn-Teller-Effect

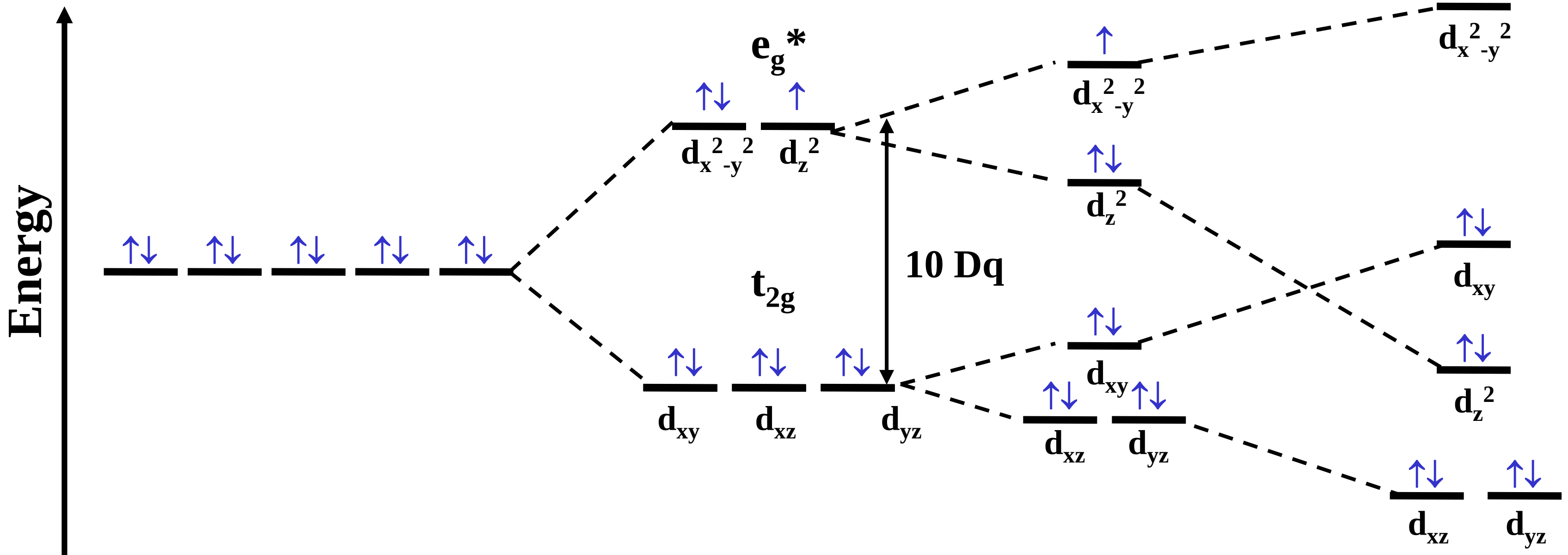
+III (d^8): Au^{3+} is usually coordinated in a square-planar fashion → $[AuCl_4]^-$



10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Stereochemistry and crystal field splitting



Spherical field
d^{10} (Cu^+, Ag^+, Au^+)

Octahedral field
d^9 (Cu^{2+}, Ag^{2+})

Tetragonally distorted
octahedral field by
Jahn-Teller-effect

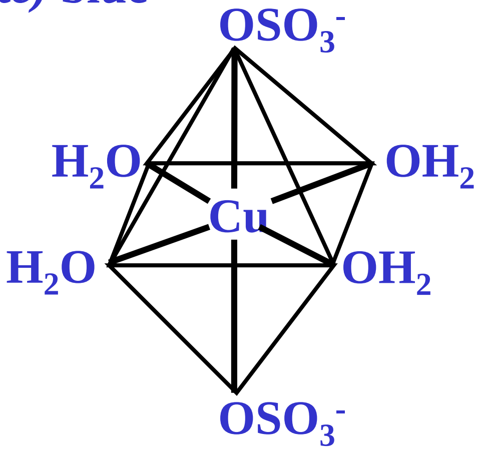
Square-
planar field

Maximal stabilisation
for d^9 (Cu^{2+}, Ag^{2+}) ions

Maximal stabilisation
for d^8 (Au^{3+}) ions

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)



Cu(II)-compounds

$CuSO_4 \cdot 5\ H_2O$ or $[Cu(H_2O)_4]SO_4 \cdot H_2O$ (copper*(II)-sulphate-pentahydrate)* blue

Synthesis

$$2\ Cu + O_2 + 2\ H_2SO_4 \rightarrow 2\ CuSO_4 + 2\ H_2O$$

Dehydration

$$CuSO_4 \cdot 5H_2O \xrightarrow[130\,^\circ C]{} CuSO_4 \cdot H_2O \xrightarrow[250\,^\circ C]{} CuSO_4$$

(blue) **(white)**

White (dry) copper sulphate readily takes up H_2O becoming blue in the process
⇒ detection of small amounts of H_2O, e.g. in ethanol

Copper sulphate behaves as an acid, when dissolved in water (cation acid)

$$CuSO_4 \cdot 5\ H_2O(s) + H_2O \rightarrow [Cu(H_2O)_6]^{2+}(aq) + SO_4^{2-}(aq)$$

$$[Cu(H_2O)_6]^{2+} + H_2O \leftrightarrows [Cu(OH)(H_2O)_5]^+ + H_3O^+$$

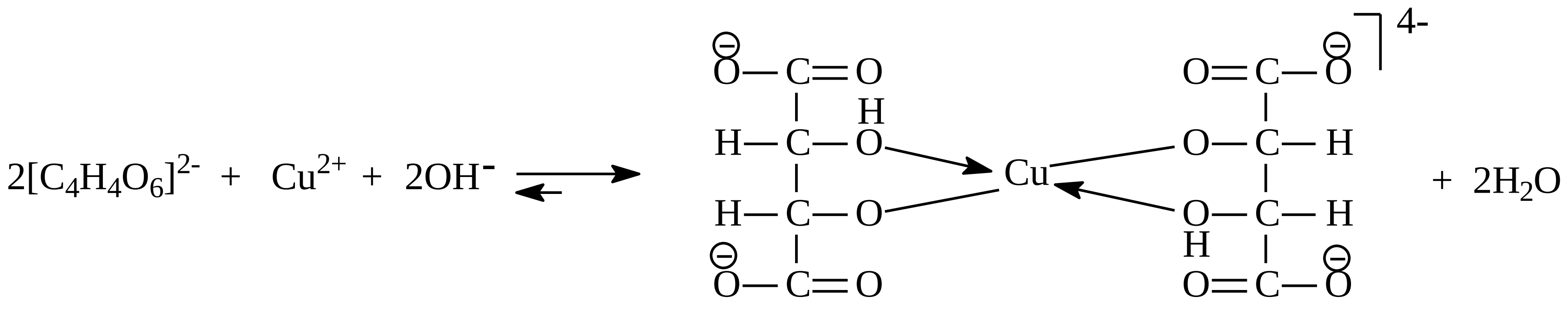
⇒ pH of a 0.1 molar solution ~ 3

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Cu(II)-compounds

Bis(tartrato)cuprate(II)-complex (Fehling's solution 1850)



löslicher tiefblauer Cu(II)-Komplex

In presence of reducing agents and elevated temperatures, reduction to poorly soluble Cu_2O takes place, which than precipitates as brick red (in the beginning yellow) powder

Fehling's test: detection of reducing agents (aldehydes and sugars, such as D-Glucose)
⇒ analysis of urine (diabetes)

$$\mathbf{R\text{-}CH{=}O + 2\ Cu^{2+} + H_2O \rightarrow R\text{-}COOH + Cu_2O\downarrow + 2\ H^+}$$

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Cu(I)-compounds

In water readily soluble Cu(I)-compounds disproportionate:

$Cu_2SO_4(s) \rightarrow Cu^{2+}(aq) + SO_4^{2-}(aq) + Cu(s)$ **high hydration enthalpy for Cu^{2+}**

Remember: Ions disproportionate, if the redox potential for the reduction to the next lower oxidation state is more positive than the redox potential for the oxidation to the next higher oxidation state

Reduced form	⇆	Oxidised form	+ e^-	Standard potential E^0 [V]
Cu	⇆	Cu^+	+ e^-	+0.52
Cu^+	⇆	Cu^{2+}	+ e^-	+0.15

$Cu^+ + Cu^+ \leftrightarrows Cu + Cu^{2+}$ $\Delta E = E^0_{Cu/Cu+} - E^0_{Cu+/Cu2+} = +0.52\ V - 0.15\ V = +0.37\ V$

Poorly soluble Cu(I)-compounds (Cu_2O, CuI, CuCN, Cu_2S) are stable in aqueous solution and do not disproportionate

⇒ Impact of solubility upon redox potentials

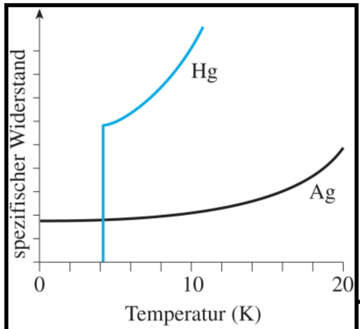
Excursion: Superconductor

Superconductors Are Materials which Specific Electrical Resistance Diminish to About Zero, Below a Certain Transition Temperature (T_c)

⇒ **Virtually lossless electrical power transmission possible**

⇒ **Application in superconducting magnetic coils**

⇒ **(N)MR-devices, magnetometer, particle accelerator**

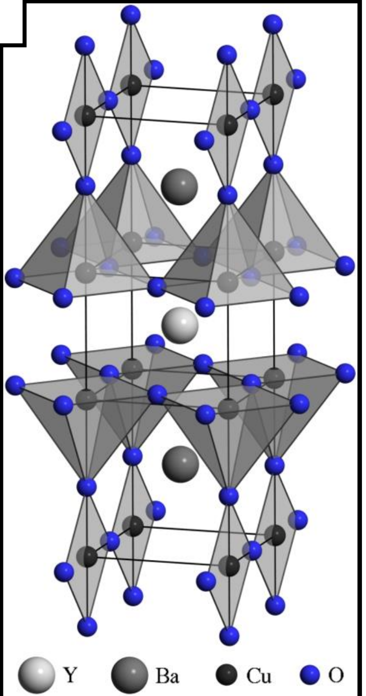


Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-42.jpg

History of superconductor research

Year	Material	T_c [K]	
1911	Hg	4.2	*H.K. Onnes*
1972	Nb_3Ge	23.3	
1986	$La_{1.8}Ba_{0.2}CuO_4$	35	*J.G. Bednorz, K.A. Müller*
1987	$YBa_2Cu_3O_{7-x}$	93	
1988	$Bi_2Sr_2Ca_{n-1}Cu_nO_x$	125	> 77 K = $T_b(N_2)$
1993	$HgBa_2CuO_{4+x}$	155	⇒ liquid nitrogen as cooling agent

High-temperature superconductors ⇒ mixed-valent Cu(II)/Cu(III)-ceramics



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-43.jpg

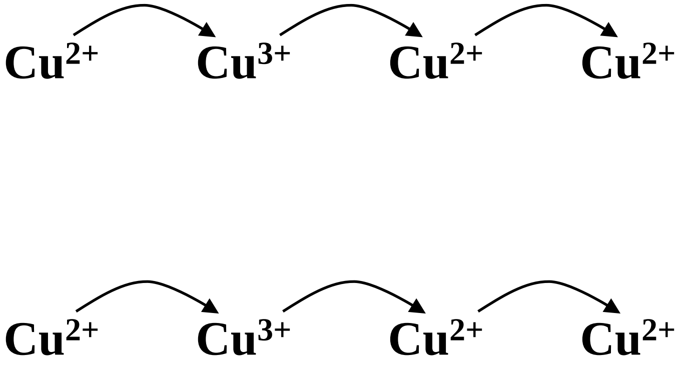
10. Chemistry of Transition Metals

$YBa_2Cu_3O_{7-x}$ – Electronic properties

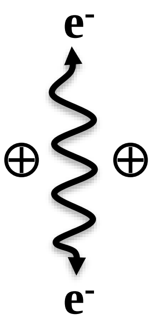
Dependence on Oxygen content

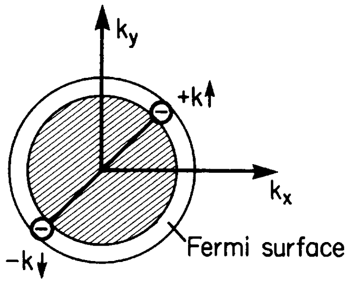
•	$YBa_2Cu_3O_{6.5}$	100% Cu^{2+}	[Ar]$3d^9$, paramagnetic, distorted octahedr. (J.T.-Effect)
•	$YBa_2Cu_3O_7$	66,7% Cu^{2+}	[Ar]$3d^9$, paramagnetic, distorted octahedr. (J.T.-Effect)
		33,3% Cu^{3+}	[Ar]$3d^8$, diamagnetic, quadratic-planar

Layer structure enables 2D-conductivity


Cu^{2+} Cu^{3+} Cu^{2+} Cu^{2+}

Cu^{2+} Cu^{3+} Cu^{2+} Cu^{2+}





Coppling of electrons
by virtual phonons
to form Cooper-Pairs (Bosons)

Cu^{2+}(distorted octahedral) ↔ Cu^{3+} (quadratic-planar) ⇒ Oscillations (J.-T.-Polarons)

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Ag(I)-compounds

- Most Ag(I) salts (Ag_2CO_3, Ag_3PO_4 and AgX with X = Cl, Br, I, SCN, OCN, N_3) are poorly soluble

  ⇒ high covalence, high lattice energies and low hydration enthalpies
- $3\ Ag + 4\ HNO_3 \rightarrow NO + 2\ H_2O + AgNO_3$ (soluble in water) ⇒ application as precursor for other silver salts and as Höllenstein

Ag(I)-halides

AgX	Covalence	Solubility	Colour	Sensitivity to light
AgCl	↓	↑	white	↓
AgBr			yellowish-white	
AgI			yellow	

⇒ photosensitive pigments

Excursion: The Photographic Process

B/W as well as Colour Photography Require a Photosensitive Layer that Can Be Brought upon a Substrate as a Thin Layer (Film)

1. Fabrication

$AgNO_3(aq) + KX(aq) \rightarrow AgX\downarrow(s) + KNO_3(aq)$ with X = Br^-, 3-5 mol-% I^-

(+ sensitizers)

AgBr and AgI are yellow and absorb only in the blue region of the spectrum.

The sensitizers absorb in the green, yellow and red region of the spectrum and transfer the energy into the conduction band of AgBr, so that all spectral colours trigger the reaction

Colloidally dispersed AgX, means finely distributed AgX (grain), upon transparent substrate (silver bromide gelatine)

⇒ potentially too insensitive to light

⇒ maturation with thiosulphate, $S_2O_3^{2-}$ and NH_3

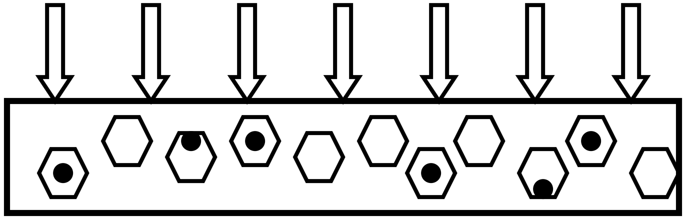
⇒ Formation of seed crystals, e.g. Ag_2S

⇒ considerable spike in photosensitivity

“seeds on nanometer scale“

Excursion: The Photographic Process

B/W and Colour Photography are Based on the Photo Induced Reduction of AgBr Crystallites



2. Exposure

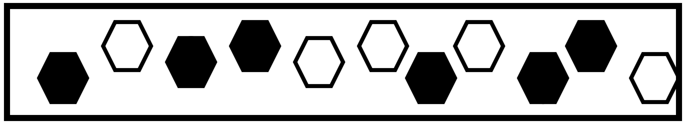
n AgBr(s) $\xrightarrow{h\nu}$ Ag$_n$ + n Br (bound by gelatine)

Silver seeds → latent picture seed (10 – 100 Ag atoms)

latens (lat.) = concealed, hidden

3. Development

2 AgX + hydroquinone + 2 OH$^-$ → Ag + 2 X$^-$ + quinone + 2 H$_2$O



Conversion of the latent picture to the actual visible picture by complete reduction of AgBr grains (~ 10^{12} Ag atoms)

4. Fixation

AgX + 2 S$_2$O$_3^{2-}$ → [Ag(S$_2$O$_3$)$_2$]$^{3-}$ + X$^-$

Removal of non-exposed AgX through treatment with fixing salt, Na$_2$S$_2$O$_3$

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Au(I)-compounds

- Halides: $AuX + X^- [AuX_2]^-$ (linear)
- Importance of cyaniding (→ presentations)

  $4\ Au + 2\ H_2O + O_2 + 8\ KCN \rightarrow 4\ K[Au(CN)_2] + 4\ KOH$

  (gold ore) (dicyanoaurate(I)-complex)

  $2\ [Au(CN)_2] + Zn \rightarrow [Zn(CN)_4]^{2-} + 2\ Au$

  (dust) (raw gold)

- The colourless Au^+-ion shows disproportionation in solution:

Reduced form	$\leftrightarrows$	Oxidised form	$+ e^-$	Standard potential E^0 [V]
2 Au	$\leftrightarrows$	$2\ Au^+$	$+ 2e^-$	+1.69
Au^+	$\leftrightarrows$	Au^{3+}	$+ 2e^-$	+1.40

$2\ Au^+ + Au^+ \leftrightarrows 2\ Au + Au^{3+}$

$\Delta E = E^0_{Au/Au+} - E^0_{Au+/Au3+} = +1.69\ V - 1.40\ V = +0.29\ V$

10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Au(III)-compounds

$Au + 3\ H_3O^+ + 4\ Cl^- + HNO_3 \rightarrow [AuCl_4]^- + NO + 5\ H_2O$

Evaporation leads to tetrachloro auric acid $H[AuCl_4]\cdot 3H_2O$

$\Rightarrow$ gold salt: $Na[AuCl_4]\cdot 2H_2O$

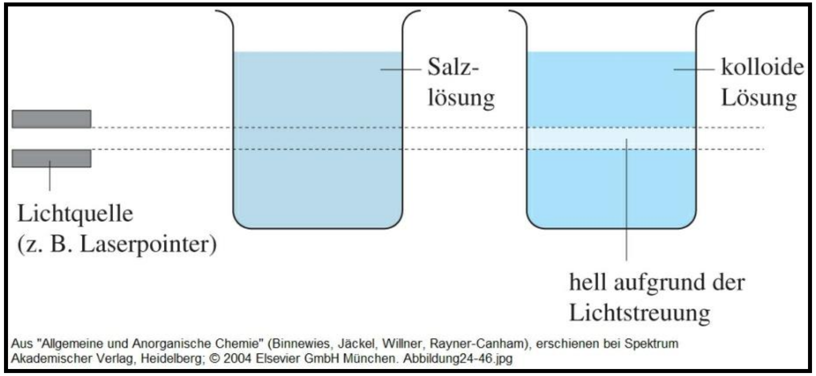
Gold cluster and colloidal gold

$2\ Na[AuCl_4]\cdot 2H_2O + 3\ SnCl_2 + 2\ H_2O \rightarrow 2\ NaCl + 12\ HCl + 3\ SnO_2$ + colloidal Au

(Cassius' gold purple)

$Au^{3+} + 3\ e^- \rightarrow Au \rightarrow Au_{13} \rightarrow Au_{55}$ (cluster) $\rightarrow Au_n$ (with $n = 10^3 – 10^9$, colloids 1 – 100 nm)

Colloids can be detected by the Tyndall-effect (light scattering)



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-46.jpg

10. Chemistry of Transition Metals

Zinc Group

⇒ 2. subgroup or group 12 $(n-1)d^{10}ns^2$ with n = 4, 5, 6

The elements possess a relatively noble character, du to their full outer electron shell, which becomes particularly apparent for Hg

Properties of the elements

Element	T_m[°C]	Oxidation state	$r(M^{2+})$ [pm]	E° (M/M^{2+}) [V]	
Zn	419	+II	74	-0.76	(non-precious)
Cd	321	+II	97	-0.40	(non-precious)
Hg	-39	+I, +II	110	+0.85	(precious)

⇒ Hg is the only metal liquid at room temperature, exhibiting a vapour pressure of $2.6 \cdot 10^{-3}$ mbar at that temperature

Alloy

Brass	Zn + Cu		
Amalgams	Hg + Na and Hg + Zn	dental filling	amalgam lamps
	Hg + Ag/Cu/Sn	reducing agent at the lab	

10. Chemistry of Transition Metals

Zinc Group

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

Occurrence

Zink (zinc spar)	ZnS	sphalerite
	$ZnCO_3$	zinc spar
Cadmium (Greek: kadmeia)	CdS	greenocite
Mineral name	$CdCO_3$	otavite
Mercury (Greek: hydrargyrum)	HgS	zinnober
(Germanic: queck, quick)	$Hg[Sb_4S_7]$	levingstonite

(Latin: mercurium)
Water silver, mobile, Mercury
(Arabic: alzaybiq, الزئبق) → alkimiya

Preparation by calcination

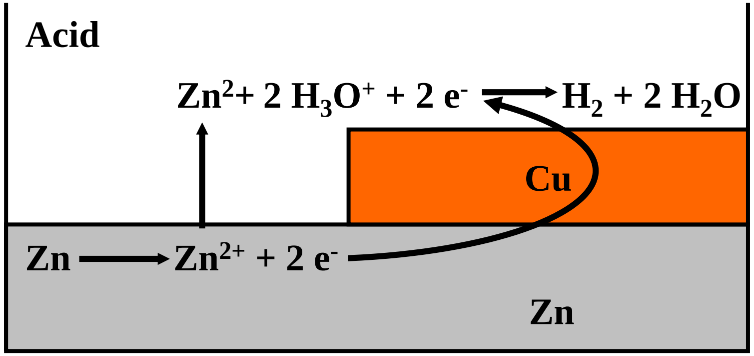
- Zn/Cd: $2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$
  $ZnO + CO \rightarrow Zn + CO_2$
- Hg: $HgS + O_2 \rightarrow Hg + SO_2$

10. Chemistry of Transition Metals

Zinc Group

Reactions and applications of Zinc

- Soluble in acids and bases (amphoteric character of $Zn(OH)_2$) under development of H_2:
  $Zn + 2\,H^+ \rightarrow Zn^{2+} + H_2\uparrow$
  $Zn + 2\,OH^- + 2\,H_2O \rightarrow [Zn(OH)_4]^{2-} + H_2\uparrow$
- Highly pure Zinc (99.999%) is not attacked any more (H_2-overvoltage 0.7 V, kinetic inhibition of the discharge of H_3O^+ ions upon the Zinc surface)
  Therefore: Zn + dil. $HCl \rightarrow$ very weak development of H_2
  But: $Zn + Cu^{2+}$ + dil. $HCl \rightarrow$ violent development of H_2
  Explanation: $Zn + Cu^{2+} \rightarrow Cu + Zn^{2+} \Rightarrow$ Copper precipitates upon the Zinc $\Rightarrow$ zinc surface is occupied by Cu $\Rightarrow$ local elements are formed



Metals more precious than Zinc catalyse the solvation of Zn, which is why corrosion inhibition by galvanization works

Redox pair	E^0 [V]
Zn/Zn^{2+}	-0.76
Fe/Fe^{2+}	-0.41

10. Chemistry of Transition Metals

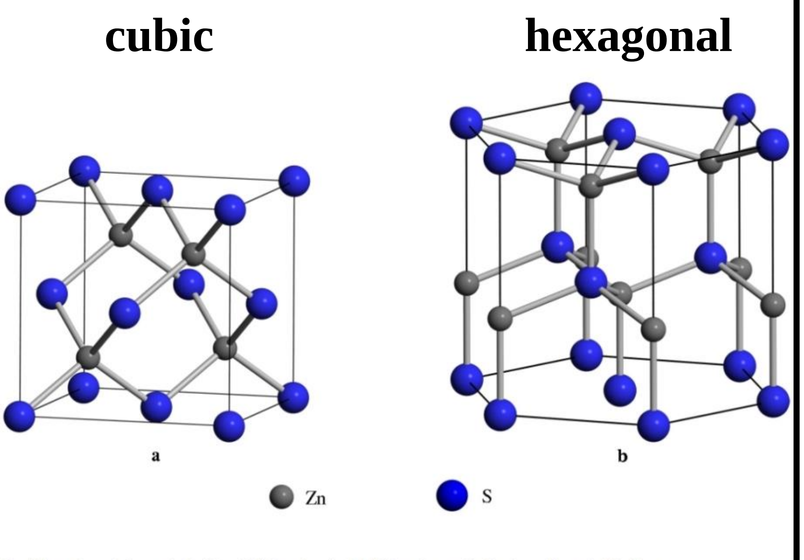
Zinc Group

Zinc(II)-compounds

- Zinc sulphate heptahydrate “zinc vitriol“
  $ZnSO_4 \cdot 7H_2O = [Zn(H_2O)_6] \cdot H_2O$
- Zinc oxide “zinc white“: pigment with wurtzite-like structure
  $ZnO \rightarrow ZnO{:}Zn$ (yellow) ⇒ Upon heating, anion defects occur
  $ZnO + Co_2O_3 \rightarrow ZnCo_2O_4$ (Rinmans’ green) ⇒ normal spinel
- Zink sulphide: dimorphous white pigment ⇒ zinc blende (sphalerite) ⇌ wurtzite
  Zinc blende: cubic close packing of anions
  Wurtzite: hexagonal close packing of anions
  Doping results in a variety of phosphors:

ZnS:Ag	450 nm
ZnS:Cu,Al,Au	530 nm
ZnS:Mn	580 nm

⇒ application in RGB cathode ray tubes
and electroluminescence screens



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung04-13.jpg

10. Chemistry of Transition Metals

Zinc Group

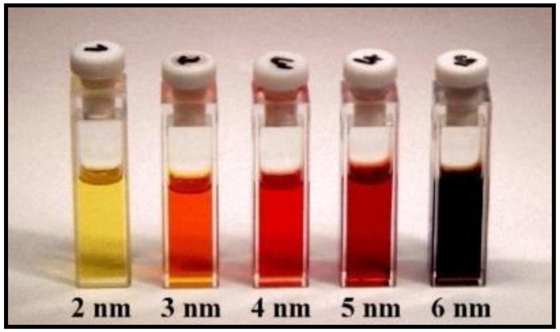
Reactions and applications of Cadmium

- $Cd(OH)_2$ in contrary to $Zn(OH)_2$ is not amphoteric!

$$\begin{tikzcd}
Cd^{2+} + 2\,OH^- \arrow[r] & Cd(OH)_2\downarrow \arrow[r, "OH^-"'] \arrow[d, "NH_3"] & \text{no reaction} \\
 & {[Cd(NH_3)_6]^{2+} + 2\,OH^-} &
\end{tikzcd}$$

- Cd^{2+} can be detected next to Cu^{2+} ⇒

$$\begin{tikzcd}
Cu^{2+}/Cd^{2+} \arrow[d, "+\,NH_3"'] \\
{[Cu(NH_3)_4]^{2+} + [Cd(NH_3)_6]^{2+}} \arrow[d, "+\,CN^-"', "\text{(discolouration)}"] \\
{[Cu(CN)_4]^{3-} + \frac{1}{2}(CN)_2\uparrow + [Cd(CN)_4]^{2-}} \arrow[d, "+\,S^{2-}"'] \\
CdS\downarrow \text{ yellow}
\end{tikzcd}$$



- Cadmium sulphide, CdS, and Cadmium selenide, CdSe, are used as pigments and quantum dots

10. Chemistry of Transition Metals

Zinc Group

Redox chemistry of mercury

- Hg forms Hg^+ and, as Hg^{2+}, salts

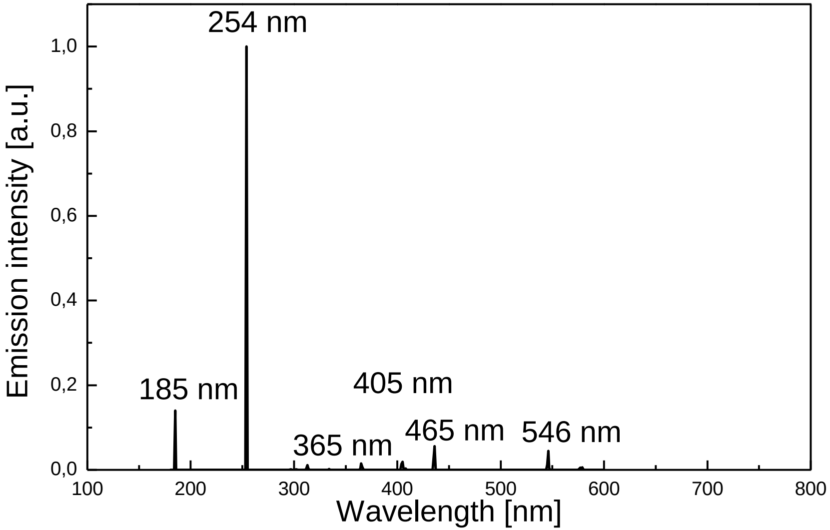
  $2\ Hg \leftrightarrows Hg_2^{2+} + 2\ e^-$ $E^0 = +0.79\ V$

  $Hg_2^{2+} \leftrightarrows 2\ Hg^{2+} + 2\ e^-$ $E^0 = +0.91\ V$

  $Hg \leftrightarrows Hg^{2+} + 2\ e^-$ $E^0 = +0.85\ V$
- Hg^+-salts contain dimeric Hg_2^{2+} (metal-metal bonds!)
- Hg_2^{2+} does not disproportionate, but reagents that drastically reduce the concentration of $Hg2^{2+}$ (precipitation agents (OH^-, S^{2-}) or complexing agents (CN^-)) lead to disproportionation

Application of Hg in:

- Hg-low pressure discharge lamps (1 – 5 mg)
  - Fluorescent tubes, compact fluorescent lamps
- Hg-high pressure discharge lamps (> 10 mg)
  - Street lighting, projector, head lights
- Thermo- and barometer
- Hg-switch
- Amalgams



10. Chemistry of Transition Metals

Zinc Group

Mercury(I)-compounds

- **$Hg_2(NO_3)_2$ is soluble**

- **Halides: Hg_2X_2 (with X = Cl, Br, I) are poorly soluble**

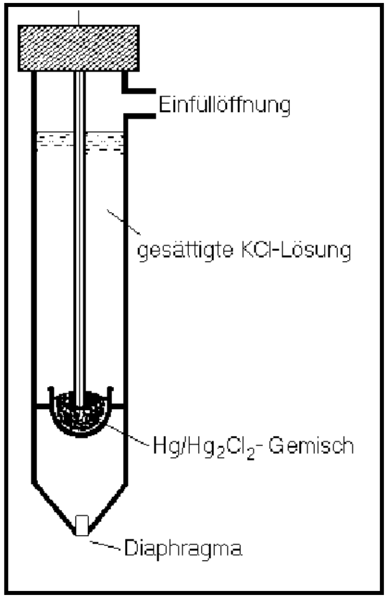
$$Hg_2(NO_3)_2 \xrightarrow{\text{dil. } HNO_3} [H_2O\text{-}Hg\text{-}Hg\text{-}OH_2]^{2+} \xrightarrow{\text{2 NaCl}} Hg_2Cl_2\downarrow \text{ (white)}$$

Mercury(I)-nitrate Diaquamercury(I)-complex Mercury(1)-chloride

- **Mercury(I)-chloride is also called calomel (deep black), since a black colour arises upon treatment with NH_3**

$$\underset{}{Hg_2Cl_2} + 2\,NH_3 \rightarrow \underset{\text{(white)}}{[HgNH_2]Cl} + \underset{\text{(black)}}{Hg\downarrow} + NH_4^+ + Cl^-$$

- **The calomel electrode ($Hg/Hg_2Cl_2/Cl^-$) is a regularly used reference electrode in electrochemistry**



10. Chemistry of Transition Metals

Zinc Group

Mercury(II)-compounds

- Hg(II)-salts are highly covalent und thus poorly soluble
- Only HgF_2 and $Hg(NO_3)_2$ are built iogenicly
- $Hg + O_2 \rightarrow HgO$ (red)
- $Hg^{2+} + 2\ OH^- \rightarrow H_2O + HgO$ (yellow) ⇒ smaller particles
- $HgCl_2$ (sublimate) is white, melts at 280 °C and and boils at 303 °C!
  ⇒ molecular lattice consists of linear Cl-Hg-Cl molecules
- HgI_2 is dimorphous: α-HgI_2(red) ⇆ ß-HgI_2(yellow) at T = 127 °C
  It reacts with excess I^- to the tetraiodomercurate anion:
  $HgI_2 + 2\ I^- \rightarrow [HgI_4]^{2-}$
- Nessler's reagent: solution of K_2HgI_4 in potash lye
  for the detection of ammonia: $2\ K_2HgI_4 + NH_3 \rightarrow [Hg_2N]I + 4\ KI + 3\ HI$
  (orange to brown)
- $[HgI_4]^{2-} + 2\ Ag^+ \rightarrow \underset{\text{(yellow)}}{Ag_2[HgI_4]\downarrow} \overset{35\ °C}{\leftrightarrows} \underset{\text{(orange-red)}}{Ag_2[HgI_4]}$
- $[HgI_4]^{2-} + 2\ Cu^+ \rightarrow \underset{\text{(red)}}{Cu_2[HgI_4]\downarrow} \overset{70\ °C}{\leftrightarrows} \underset{\text{(black)}}{Cu_2[HgI_4]}$ ⇒ thermochromism

10. Chemistry of Transition Metals

Titanium Group

4. Sub group / group 4 (n-1)d^2ns^2 with n = 4, 5, 6

Those elements are highly reactive and do react with N_2 and H_2 at elevated temperatures

Properties of the elements

Element	Density [g/cm^3]	T_m[° C]	T_b [° C]	Oxidation state	r(M^{4+}) [pm]
Ti	4.54	1670	~3350	+II, +III, +IV	61
Zr	6.51	1850	~4400	+IV	72
Hf	13.31	2230	~4700	+IV	71

Zr and Hf resemble one another in terms of chemistry, which is why they are often associated with one another

Ti-alloys (DIN 17851): Light metals → $\rho < 5$ g/cm^3

Ti + Fe, C, N, O

Ti + Al, V, Mn, Mo, Pd, Cu, Zr, Sn

⇒ Aviation industry, ship building, chemical plant construction, engines, implants….

WILEY-VCH

Titan und Titanlegierungen

Herausgegeben von Manfred Peters und Christoph Leyens

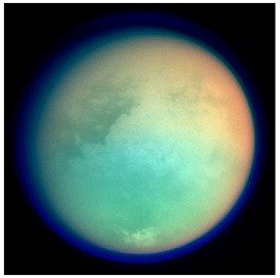
DGM

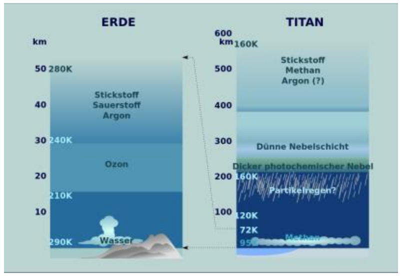
10. Chemistry of Transition Metals

The Titanium Group

Occurrence

Titanium (Titans)	TiO_2	Rutile
Gods/giants in Greek myth.		Anatase
		Brookite
	$FeTiO_3$	Ilmenite
	$CaTiO_3$	Perovskite
	$CaTiO[SiO_4]$	Titanite





Zirconium (name of mineral)	ZrO_2(monoclinic)	Baddeleyite
Named after the mineral zircon	ZrO_2(tetragonal)	> 1100 ° C
	ZrO_2(cubic)	> 2350 ° C
	$ZrSiO_4$	Zircon

Hafnium (Hafnia) always a companion in Zr-minerals

Copenhagen

(lat.: Hafnia)

10. Chemistry of Transition Metals

The Titanium Group

Synthesis

Lab synthesis: $TiO_2 + 2\ CaH_2 \rightarrow Ti + 2\ H_2 + 2\ CaO$

Kroll process: $TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2$

- Titanium is separated from the blend of Titanium, Magnesium dichloride, and Magnesium residues by high temperature vacuum sintering
- Magnesium dichloride is cleaved into Mg and Cl_2 by electrolysis
- The resulting material is brittle and porous → Titanium sponge

Arkel-de Boer process: $TiI_4 \overset{1200\,°C}{\underset{600\,°C}{\leftrightarrows}} Ti + 2\ I_2$ (hot W-wire) ⇒ Highly purified Titanium

Zirconium Zr and Hafnium Hf

More or less analogue to Titanium

10. Chemistry of Transition Metals

The Titanium Group

Titan(IV) compounds

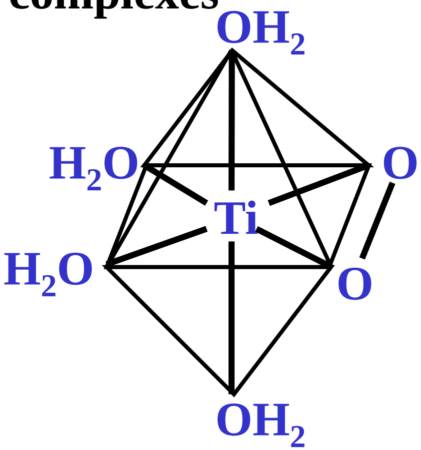
- [Ar] configuration ⇒ most stable oxidation state, colourless
- Ti^{4+} is small and highly charged ⇒ strongly polarising (high ionic charge density)

  $Ti^{4+} + 6\ H_2O \rightarrow 2\ H^+ + [Ti(OH)_2(OH_2)_4]^{2+}$ “cation base“

  In aqueous solution, there are thus no Ti^{4+} cations but aqua hydroxo complexes that can be verified by the reaction with H_2O_2:

  $[Ti(OH)_2(OH_2)_4]^{2+} + H_2O_2 \rightarrow [Ti(O_2)(OH_2)_4]^{2+} + 2\ H_2O$

  (orange-yellow)



- Treatment of TiO_2 with HNO_3 or H_2SO_4 yields double salts

  $TiO_2 + H_2SO_4 \rightarrow TiO(SO_4) + H_2O$

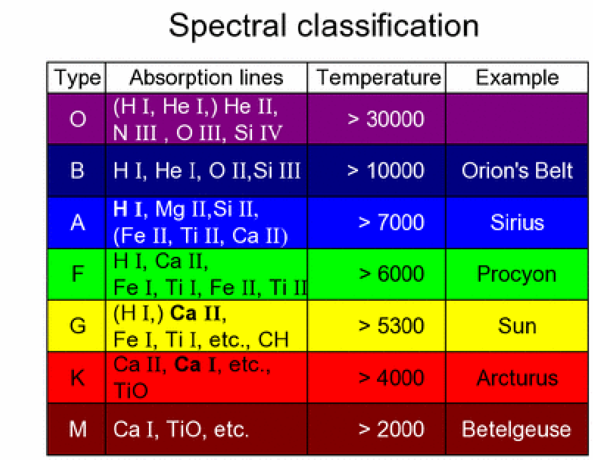
  $TiO_2 + 2\ HNO_3 \rightarrow TiO(NO_3)_2 + H_2O$

  that contain polymeric Ti-O-Ti-O-Ti zig-zag chains
- However, the reaction of Ti^{4+}-containing solutions with oxalates yield tetramers

  $4\ [Ti(OH)_2(OH_2)_4]^{2+} + 8\ C_2O_4^{2-} \rightarrow [Ti_4O_4(C_2O_4)_8]^{8-}$

10. Chemistry of Transition Metals

The Oxide Ion O^{2-} as Ligand

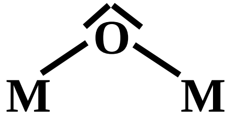


Spectral classification

Type	Absorption lines	Temperature	Example
O	(H I, He I,) He II, N III , O III, Si IV	> 30000	
B	H I, He I, O II,Si III	> 10000	Orion's Belt
A	**H I**, Mg II,Si II, (Fe II, Ti II, Ca II)	> 7000	Sirius
F	H I, Ca II, Fe I, Ti I, Fe II, Ti II	> 6000	Procyon
G	(H I,) **Ca II**, Fe I, Ti I, etc., CH	> 5300	Sun
K	Ca II, **Ca I**, etc., TiO	> 4000	Arcturus
M	Ca I, TiO, etc.	> 2000	Betelgeuse

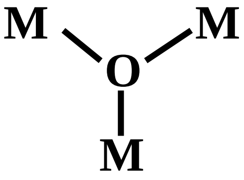
1. **Terminal oxo groups** **M=O**
   Vanadyl cation **$[V{=}O]^+$**
   Permanganate anion **$[MnO_4]^-$**

2. **μ_2-oxo-groups** **M – O – M** **or**

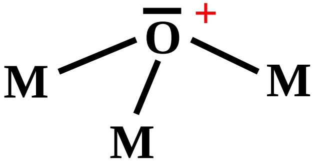


   $[L_2Fe_2(catecholate)_2(\mu_2\text{-}O)]$ with L = 1,4,7-trimethyl-1,4,7-triazacyclononane
   $[Cr_2O_6(\mu_2\text{-}O)]^{2-}$

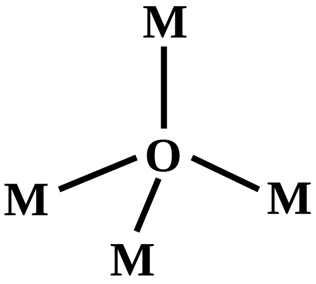
3. **μ_3-oxo-groups**
   $[Mn_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6]^+$
   $[Hg_3Cl_3(\mu_3\text{-}O)]^+$



or

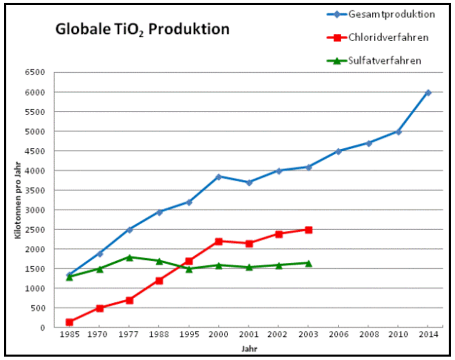


4. **μ_4-oxo-groups**
   $[Be_4(\mu_4\text{-}O)(\mu\text{-}CH_3COO)_6]$
   $[Be_4(\mu_4\text{-}O)(\mu\text{-}NO_3)_6]$



10. Chemistry of Transition Metals

The Titanium Group



Titanium dioxide TiO_2

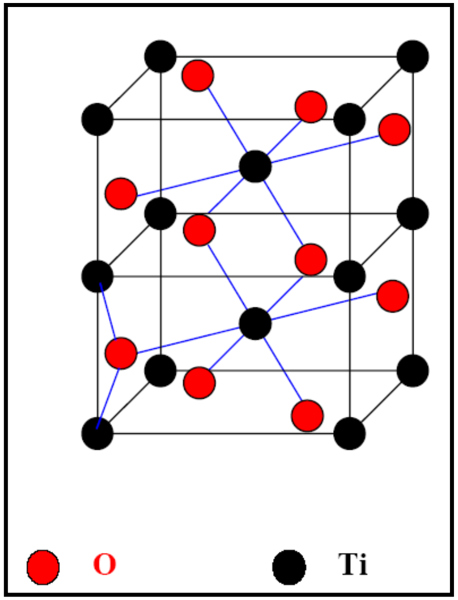
Synthesis → see presentations

Structure

- **Ti is coordinated octahedrally by O**
- **3 modifications: rutile, brookite, anatase**

⇒ Different connectivity of TiO_2-octahedra

Rutile-structure



Properties

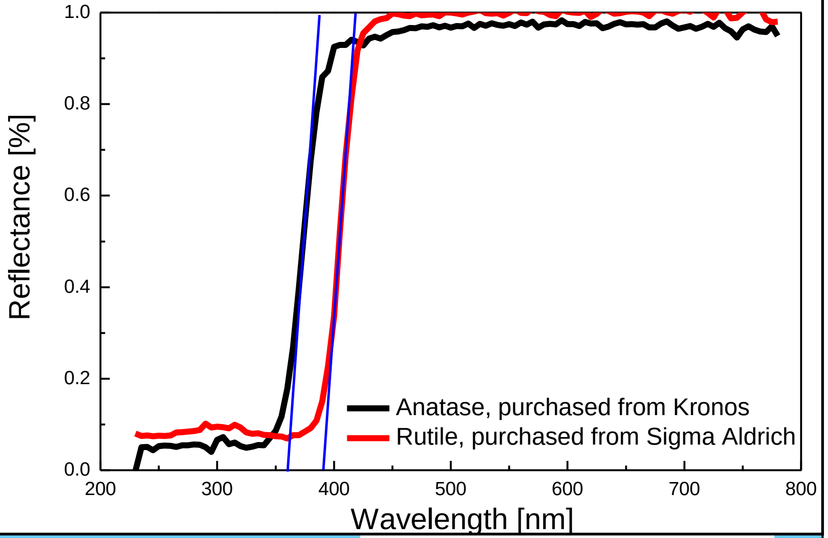
- **Photocatalytic activity**

$$TiO_2 + h\nu \rightarrow TiO_2^*(e^- + h^+)$$

$$TiO_2^*(e^- + h^+) + A + D \rightarrow TiO_2 + A^- + D^+$$

- **High refractive index:**

Modification	E_g [eV]	E_g [nm]	n
Anatase	3.5	360	2.55
Rutile	3.2	390	2.79



10. Chemistry of Transition Metals

The Titanium Group

Photocatalytic water treatment with TiO_2 (Anatas)

Excitation by absorption of UV-A/B radiation

$TiO_2 + h\nu \rightarrow TiO_2^*(e^- + h^+)$

Acceptor A:

$e^- + M^{n+} \rightarrow M^{(n-1)+}$

$O_2 + e^- \rightarrow O_2^-$

$O_2 + 2\,e^- + 2\,H^+ \rightarrow H_2O_2$

$H_2O_2 + H^+ + e^- \rightarrow {\cdot}OH + H_2O$

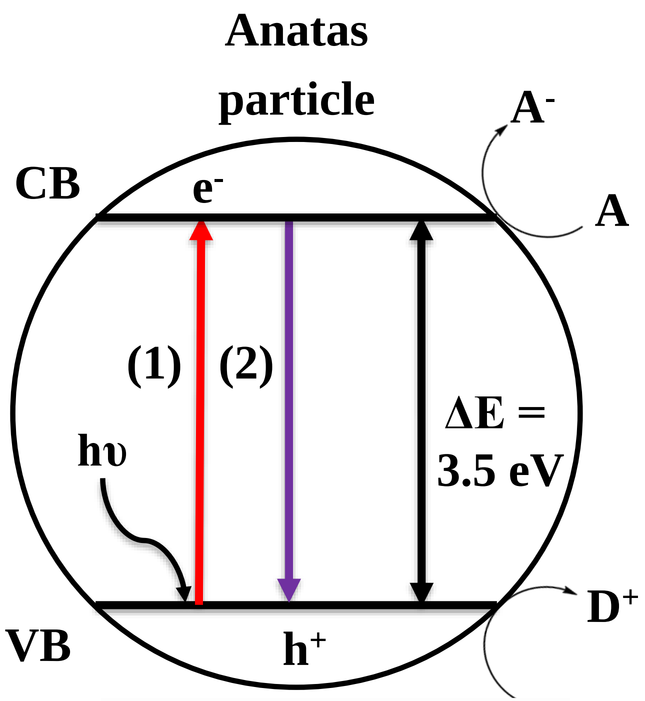
Donor D:

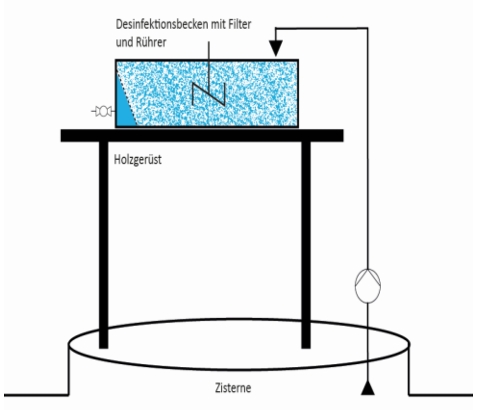
$h^+ + H_2O \rightarrow {\cdot}OH + H^+$

$h^+ + OH^- \rightarrow {\cdot}OH$

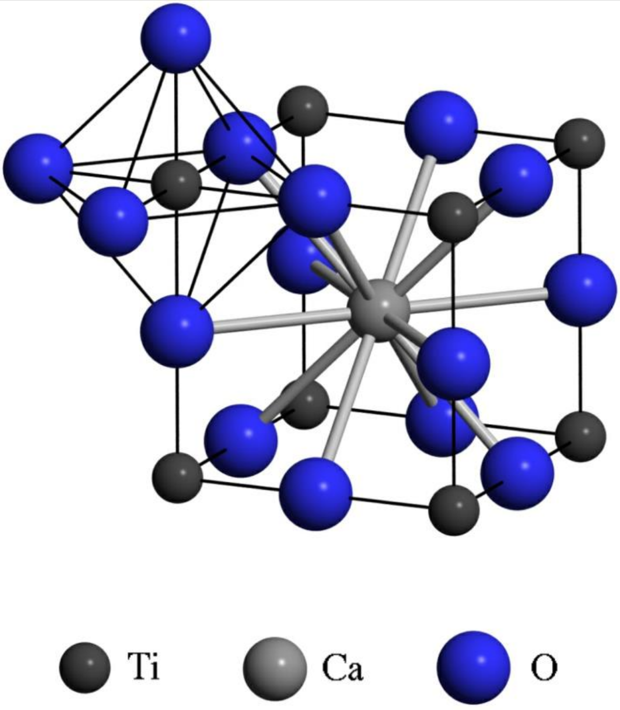
${\cdot}OH + R_{(ads)} \rightarrow {\cdot}R_{(ads)} + H_2O \rightarrow HO\text{-}R_{(ads)} \rightarrow \rightarrow \rightarrow CO_2 + H_2O$

Improved Material: $Bi_4Ti_3O_{12}$ (BTO), due to smaller band gap, i.e. ~ 3,0 eV which means that blue light is absorbed





Excursion: Ferroelectrics and Perowskites



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-09.jpg

Perowskites ABX_3

⇒ $CaTiO_3$, $SrTiO_3$, $BaTiO_3$, $PbTiO_3$, KIO_3, $LaCoO_3$, ...

- Cubic primitive unit cell
  i.e. $\alpha = ß = \gamma = 90°$, $a = b = c$
- Corner connected TiO_6 octahedra
- Me^+, Me^{2+}, Me^{3+} occupy twelvefold coordinate voids

Ferroelectrics

⇒ Possess areas (domains) in the crystal which are uniformly polarised in one spatial dimension

- These domains exhibit a permanent dipole moment
- Throughout the whole crystal, the differently polarized domains are distributed statistically ⇒ compensation dipole moments
- When introduced to an electrical field, the dipole moments are going to align themselves
  ⇒ The orientation partly persists even after the cut-off of the electrical field (storage effect)

⇒ Ferroelectricity (cooperative phenomenon)

- $BaTiO_3$ is particularly ferroelectric ($\varepsilon \sim 1000$) ⇒ application in capacitors

10. Chemistry of Transition Metals

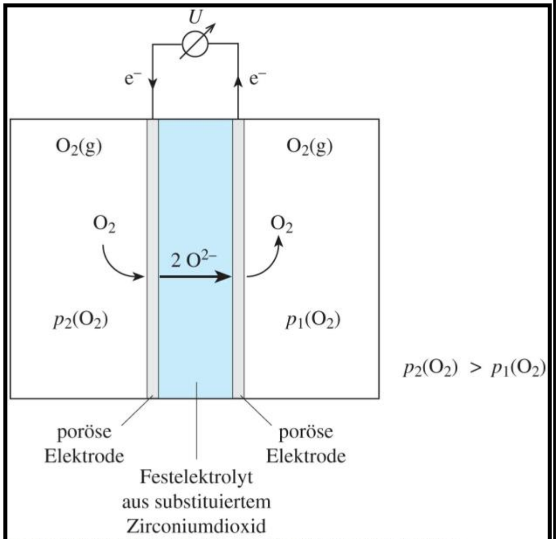
The Titanium Group

Zirconium- and Hafnium-compounds

- In compounds, Zr and Hf are mostly tetravalent
- ZrO_2 and HfO_2 possess high melting points and are poorly soluble (only in H_2SO_4):
  $ZrO_2 + 2\ H_2SO_4 \rightarrow Zr(SO_4)_2 + 2\ H_2O$
- ZrX_4 and HfX_4 with X = F, Cl, Br, I known
- $ZrX_4 + H_2O \rightarrow ZrOCl_2{\cdot}8\ H_2O$ (tetramer: $[Zr_4(OH)_8(H_2O)_{16}]^{8+}\ 8Cl^{-}{\cdot}12H_2O$)

Application of Zirconium and Hafnium

• ZrO_2/CaO, MgO	fire-resistant tools (crucibles, furnaces)
• ZrO_2/Y_2O_3	λ-probe (→ presentations)
	fuel cell
	Nernst-stick: IR-radiation source
• $La_2Hf_2O_7$:Ce	Scintillators
• $Lu_4Hf_3O_{12}$	Scintillators (ρ = 9,04 g/cm³)



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-11.jpg

10. Chemistry of Transition Metals

The Vanadium Group

5. Sub group or group 5 ⇒ 5 valence electrons

Vanadium [Ar]$3d^3 4s^2$	Niobium [Kr]$4d^4 5s^1$	Tantalum [Xe]$4f^{14} 5d^3 6s^2$

Properties of the elements

Element	Density [g/cm³]	T_m[° C]	T_b [° C]	Oxidation state	$r(M^{5+})$ [pm]
V	6.11	1910	3407	+II, +III, +IV, +V	54
Nb	8.58	2477	4744	(+III, +IV), +V	64
Ta	16.65	3017	5458	(+III, +IV), +V	64

Stability of the oxidation state +V strongly increases from V to Ta!

Alloys

• Vanadium steel	Fe + V (up to 0.5%)	tool steel
• Ferro-Niobium	Nb + Fe (28 – 33.5%)	steel construction
• Tantalum-Niobium-steel	Ta + Fe	rocket engines
• Tantalumcarbide	Ta + C	cutting tool

10. Chemistry of Transition Metals

The Vanadium Group

Occurrence

Vanadium (Vanadis)	VS_4	**Patronite**
Byname of Nordic goddess Freya	$Pb_5(VO_4)_3$	**Vanadinite**
Niobium (Niobe)	$(Fe,Mn)(Nb,Ta)_2O_6$	**Columbite**
Daughter of Tantalus		
Tantalum (Tantalus)	$(Fe,Mn)(Nb,Ta)_2O_6$	**Tantalite**
Greek saga figure		

Vanadinit, Mibladen/Marokko, Foto und Copyright: T. Seilnacht

Vanadium synthesis and purification

$4\ VS_4 + 2\ Na_2CO_3 + 21\ O_2 \rightarrow 4\ NaVO_3 + 16\ SO_2 + 2\ CO_2$

$NaVO_3 + H_2O \rightarrow$ polyvanadates + NaOH

Heating of polyvanadates upon 700° C $\rightarrow V_2O_5$

$V_2O_5 + 5\ Ca \rightarrow 2\ V + 5\ CaO$

Arkel-de Boer process

$2\ V + 5\ I_2 \leftrightarrows 2\ VI_5 \Rightarrow$ high purity Vanadium

10. Chemistry of Transition Metals

The Vanadium Group

Properties and reactions of Vanadium

- **Four stable oxidation states**

⇒ Versatile redox chemistry:

$[(H_2O)_4V(O)_2]^+ + e^- + 2\,H^+ \leftrightarrows [(H_2O)_5V{=}O]^{2+}$ $E^0 = +1.0\ V$ **by SO_2**

(cis, colourless) ***(deep blue)***

$[(H_2O)_5V{=}O]^{2+} + e^- + 2\,H^+ \leftrightarrows [V(H_2O)_6]^{3+}$ $E^0 = +0.36\ V$ **by Zn**

(deep blue) ***(grey green)***

$[V(H_2O)_6]^{3+} + e^- \leftrightarrows [V(H_2O)_6]^{2+}$ $E^0 = -0.26\ V$ **by Zn under Ar**

(grey green) ***(violet)***

- **VO_4^{3-} in aqueous solution:**

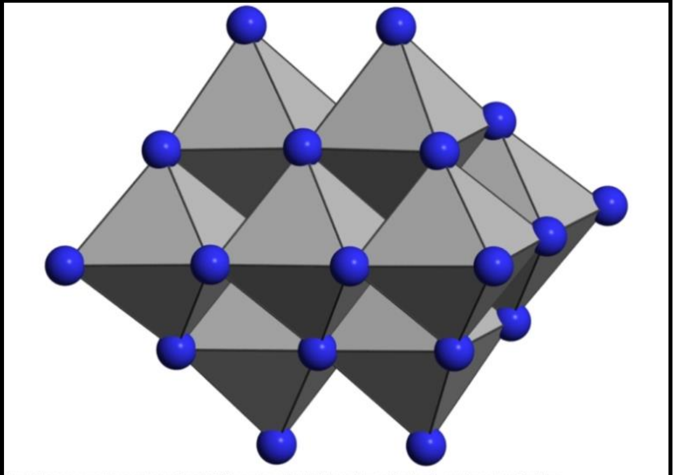
pH > 13 VO_4^{3-}

pH 6 – 13 $2\,HVO_4^{2-} \leftrightarrows V_2O_7^{4-} + H_2O$

$3\,H_2VO_4^- \leftrightarrows V_3O_9^{3-} + 3\,H_2O$

$4\,H_2VO_4^- \leftrightarrows V_4O_{12}^{4-} + 4\,H_2O$

pH 2 – 6 **formation of $V_6O_{16}^{2-}$ and $V_{10}O_{28}^{6-}$-anions**



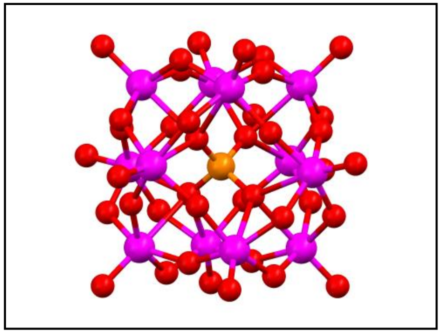
Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-12.jpg

10. Chemistry of Transition Metals

The Vanadium Group

Isopoly acids

- Oxo acids of transition metals that contain only on kind of metal
- Formation through condensation of metal anions
- Built up by corner or edge connected metal-oxo-polyhedra



Examples: $[V_{10}O_{28}]^{6-}$, $[Cr_2O_7]^{2-}$, $[Mo_7O_{24}]^{6-}$, $[H_2W_{12}O_{42}]^{10-}$

Heteropoly acids

- Isopoly acids where the central atom is an hetero atom
- They form through intercalation of hetero atoms in tetrahedra and octahedra voids
- The hetero atom can be a non-metal or a transition metal

Class	X:M	Hetero Group	Example
$[X^{n+}M_{12}O_{40}]^{(8-n)-}$ “α-Keggin-structures“	1:12	XO_4	$[PMo_{12}O_{40}]^{3-}$
$[X^{n+}M_6O_{24}]^{(12-n)-}$	1:6	XO_6	$[IW_6O_{24}]^{5-}$

with M = V, Cr, Mo, W and X = B, P, Si, I

10. Chemistry of Transition Metals

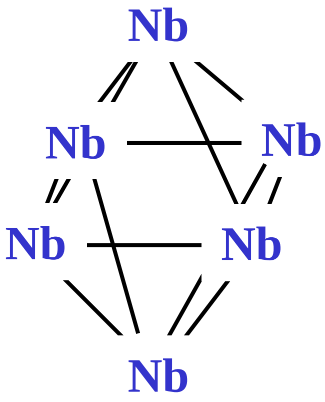
The Vanadium Group

Properties and reactions of Niobium and Tantalum

- The oxidation state +V is most stable
- In low oxidation states, preferably clusters are formed

$14\ NbCl_5 + 16\ Nb + 20\ NaCl \rightarrow 5\ Na_4[Nb_6Cl_{18}]$ (12 h at 850 ° C)

“octahedral Nb_6 Cluster“



Definition of the term Cluster

Higher molecular aggregates of transition metal compounds, where the metal centres are linked by M-M-bonds

M-M

M=M

M≡M

In rare cases also quadruple bonds between the transition metals can be observed

10. Chemistry of Transition Metals

The Vanadium Group

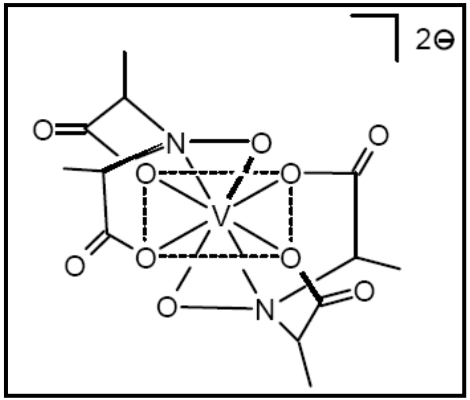
Biological aspects

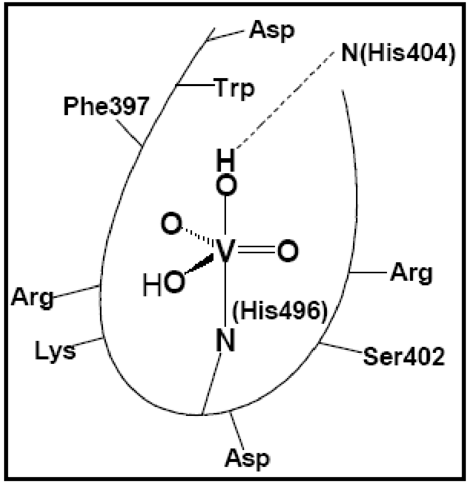
- **Amavadin**
  In fungus amanita muscaria (fly agaric)

- **Tunicates ("coat animals") use vanadocytes for their oxygen transportation, that contain Vanadium ions instead of Iron(II)-ions**
- **Peroxidases, in their active form, contain Vanadium(V)-ions in trigonal-bipyramidal coordination**

- **Nitrogenases**
  Some variations contain Mo-V-clusters

- **Insulin mimetics**





10. Chemistry of Transition Metals

The Chromium Group

6. Sub group or group 6 ⇒ 6 valence electrons

Chromium [Ar]$3d^5 4s^1$ Molybdenum [Kr]$4d^5 5s^1$ Tungsten [Xe]$4f^{14} 5d^4 6s^2$

⇒ An half-filled d-shell is reached by a change in electron configuration for Cr and Mo

Properties of the elements

Element	Density [g/cm^3]	T_m[° C]	T_b [° C]	Oxidation state	r(M^{6+}) [pm]
Cr	7.18	1903	2640	+II, +III, +VI	44
Mo	10.22	2620	4825	+IV, +VI	59
W	19.3	3410	5700	+IV, +VI	60

Lower oxidation states are accessible via π-acceptor ligands, e.g. Chromium-hexacarbonyl [$Cr(CO)_6$]

$M-C\equiv O \leftrightarrow M=C=O$ σ-donor- and π-back bonding

10. Chemistry of Transition Metals

The Chromium Group

Occurrence

Chromium (Chromos)	$FeCr_2O_4$	Chromiumironstone
Byname of Nordic goddess Freya	$PbCr_2O_4$	Crocoisite
Molybdenum (Molybdos)	MoS_2	Molybdenum glitter
Lead	$PbMoO_4$	Wulfenite
Tungsten (lat.: lupi spume)	$(Mn,Fe)WO_4$	Wolframite
Wolf-foam, wolf-cream	$CaWO_4$	Scheelit

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

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

Scheelit shows

Blue luminescence

Synthesis

Chromium through thermite process

$Cr_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Cr$

Ferrochromium (Chromium-iron-steel) by reduction with coke

$FeCr_2O_4 + 4\ C \rightarrow Fe + 2\ Cr + 4\ CO$

Molybdenum/Tungsten by reduction of the oxides with hydrogen

$MO_3 + 3\ H_2 \rightarrow M + 3\ H_2O$

10. Chemistry of Transition Metals

The Chromium Group

Properties and reactions of Chromium

Oxidation state +II

- $Cr + 2\,HCl \rightarrow Cr^{2+} + 2\,Cl^{-} + H_2$
- $CrCl_2$ is stable in H_2O under the exclusion of air ⇒ Formation of $[Cr(H_2O)_6]^{2+}$ (sky blue)
- Cr^{2+} is a strong reduction agent: $Cr^{2+} \rightarrow Cr^{3+} + e^{-}$ $E^0 = -0.41\ V$
- Cr^{2+}-complexes are kinetically unstable and exhibit Jahn-Teller distortion

Oxidation state +III

- Cr^{3+} exists in aqueous solution as hexaaquochromium(III)-ion which reacts acidic
  $[Cr(H_2O)_6]^{3+} + H_2O \leftrightarrows [Cr(H_2O)_5(OH)]^{2+} + H_3O^{+}$ $pK_S = 4.0$
- Chromium(III)-chloride in aqueous solution is transformed into its hydration isomers
  $[CrCl_3(H_2O)_3]^{0} \cdot 3H_2O \leftrightarrows [CrCl_2(H_2O)_4]^{+} + 2\,H_2O + Cl^{-} \leftrightarrows [CrCl(H_2O)_5]^{2+} + H_2O + 2\,Cl^{-}$
  (dark green) *(dark green)* *(light blue green)*
  $\leftrightarrows [Cr(H_2O)_6]^{3+} + 3\,Cl^{-}$ ⇒ slow ligand exchange, because Cr^{3+} is kinetically inert
  (violet)
- Cr^{3+} is stable in acidic and neutral conditions, but is easily oxidised in basic surroundings
  $2\,Cr^{3+} + 7\,H_2O \rightarrow Cr_2O_7^{2-} + 6\,e^{-}$ $E^0 = +1.33\ V$ at pH = 0
  $2\,Cr(OH)_3 + 5\,OH^{-} \rightarrow CrO_4^{2-} + 4\,H_2O + 3\,e^{-}$ $E^0 = +0.13\ V$ at pH = 14

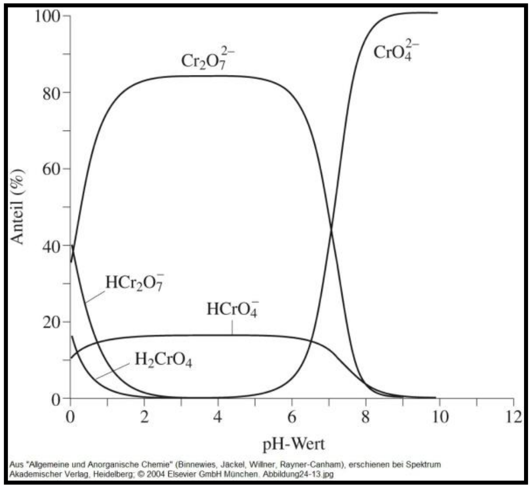
10. Chemistry of Transition Metals

The Chromium Group

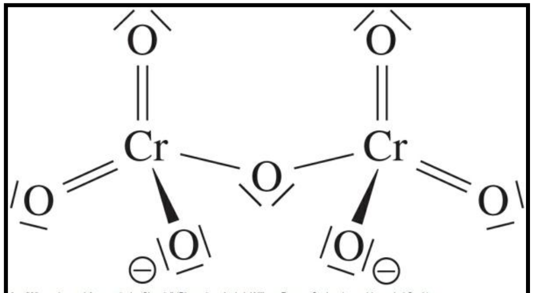
Properties and reactions of Chromium

Oxidation state +VI

- **Forms from oxidising melts of Cr^{3+}-salts:**
  $2\ Cr_2O_3 + 4\ Na_2CO_3 + 3\ O_2 \rightarrow 4\ Na_2CrO_4 + 4\ CO_2$
  $Cr_2O_3 + 2\ Na_2CO_3 + 3\ KNO_3 \rightarrow 2\ Na_2CrO_4 + 3\ KNO_2 + 2\ CO_2$
- **Chromate-dichromate-equilibrium:**
  $Cr_2O_7^{2-} + H_2O \leftrightarrows 2\ HCrO_4^- \leftrightarrows 2\ CrO_4^{2-} + 2\ H^+$
  (orange red) (yellow)
- **Chromic acid, H_2CrO_4, can be drained to the anhydride:**
  $H_2CrO_4 + H_2SO_4$ (conc.) $\rightarrow CrO_3 + H_3O+ + HSO_4^-$
  (red)
- **Chromate oxidises primary alcohols to aldehydes:**
- **$2\ CrO_4^{2-} + 3\ CH_3CH_2OH + 10\ H^+ \rightarrow 2\ Cr^{3+} + 3\ CH_3CHO + 8\ H_2O$**
- **Heating of dichromate with alkali metal chlorides in sulphuric acid yields chromyl chloride:**
  $K_2Cr_2O_7 + 4\ KCl + 3\ H_2SO_4 \rightarrow 2\ CrO_2Cl_2 + 3\ K_2SO_4 + 3\ H_2O$
  (deep red oil)

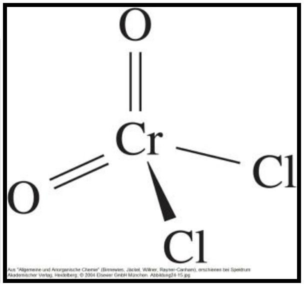


Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-13.jpg



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-14.jpg

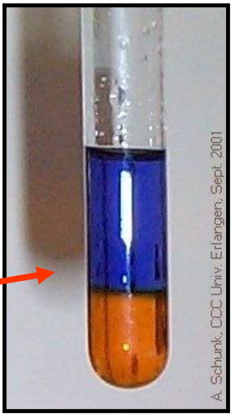
$K_2Cr_2O_7$



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-15.jpg

10. Chemistry of Transition Metals

The Chromium Group


A. Schunk, CCC Univ. Erlangen, Sept. 2001

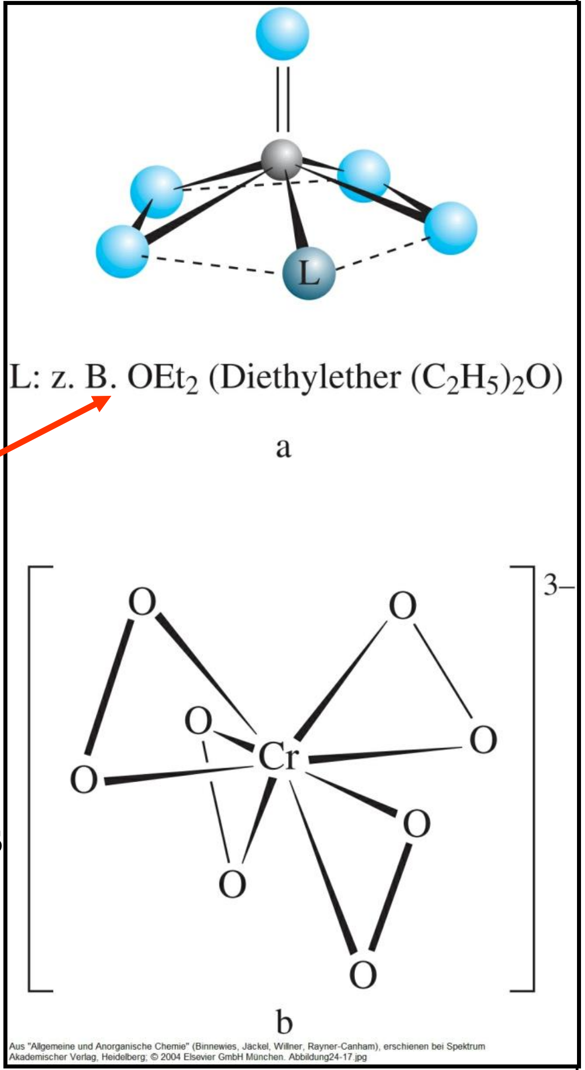
Properties and reactions of chromium

Oxidation state +VI

- **Treatment of chromate solutions with H_2O_2 yields Chromium(VI)-peroxide:**
  $HCrO_4^- + 2\ H_2O_2 + H_3O^+ \leftrightarrows CrO(O_2)_2 + 4\ H_2O$
  (deep blue)
- **The unstable Cr(VI)-peroxide can be stabilised by the formation of an adduct with diethylether or pyridine**
  $CrO(O_2)_2 + Et_2O \rightarrow [CrO(O_2)_2(Et_2O)]$
  (pentagonal-pyramidal)

Oxidation state +V

- **Known are: Li_3CrO_4, Na_3CrO_4 and CrF_5**
- **Reaction of H_2O_2 with alkaline alkali metal chromate solutions results in peroxochromate(V) M_3CrO_8**
  $[Cr(O_2)_4]^{3-} + 2\ H_3O^+ \leftrightarrows [CrO(O_2)_2(OH)]^- + 1.5\ H_2O_2 + H_2O$
  (red brown, dodecahedral) (blue violet)



L: z. B. OEt_2 (Diethylether $(C_2H_5)_2O$)

a

b

Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-17.jpg

10. Chemistry of Transition Metals

The Chromium Group

$CrCl_3·6H_2O$

Cr_2O_3

Solubility of Chromium compounds

	readily soluble	poorly soluble
+II	$CrCl_2$	
+III	$CrCl_3·6H_2O$ (complex salts)	$Cr(OH)_3$, Cr_2O_3, $CrCl_3$ (layered grid)
+VI	Na_2CrO_4, $K_2Cr_2O_7$	

Poorly soluble Chromium(III)-salts can be transformed into more readily soluble compounds by oxidation or reduction:

$CrCl_3 + e^-$ ⇆ $CrCl_2$ + Cl-

$[Cr(H_2O)_6]^{3+} + e^-$ ⇆ $[Cr(H_2O)_6]^{2+}$

d^3 kinetically stable → d^4 kinetically labile

Similar is true for poorly soluble Iron(III)- and Manganese(IV)-compounds:

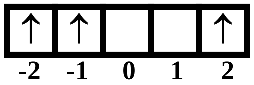
⇒ Of importance for the assimilation of Fe (Fe_2O_3) and Mn (MnO_2) from soil

Trick: Addition of M^{2+}-salts to poorly soluble M^{3+}-salts increases the solubility through the transfer of electrons on the crystal surfaces

10. Chemistry of Transition Metals

The Chromium Group

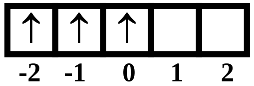
Optical spectra of Chromium(III)-compounds



3d

$S = \Sigma s = 3/2$

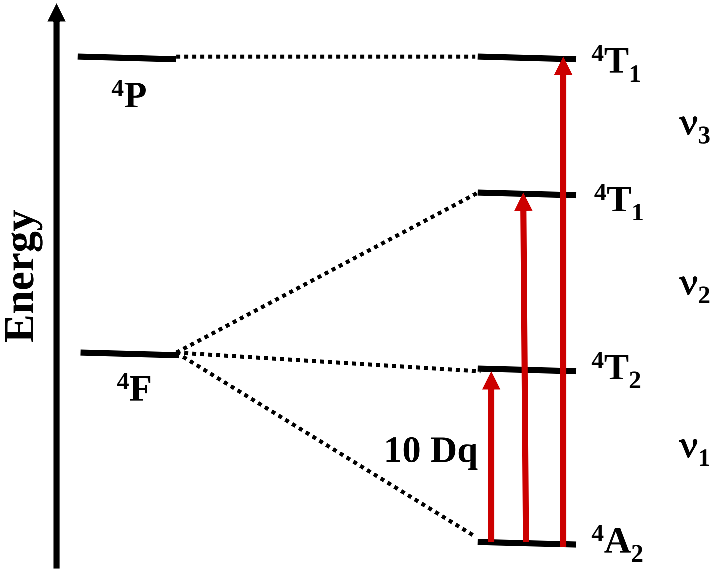
$L = |\Sigma l| = 1$



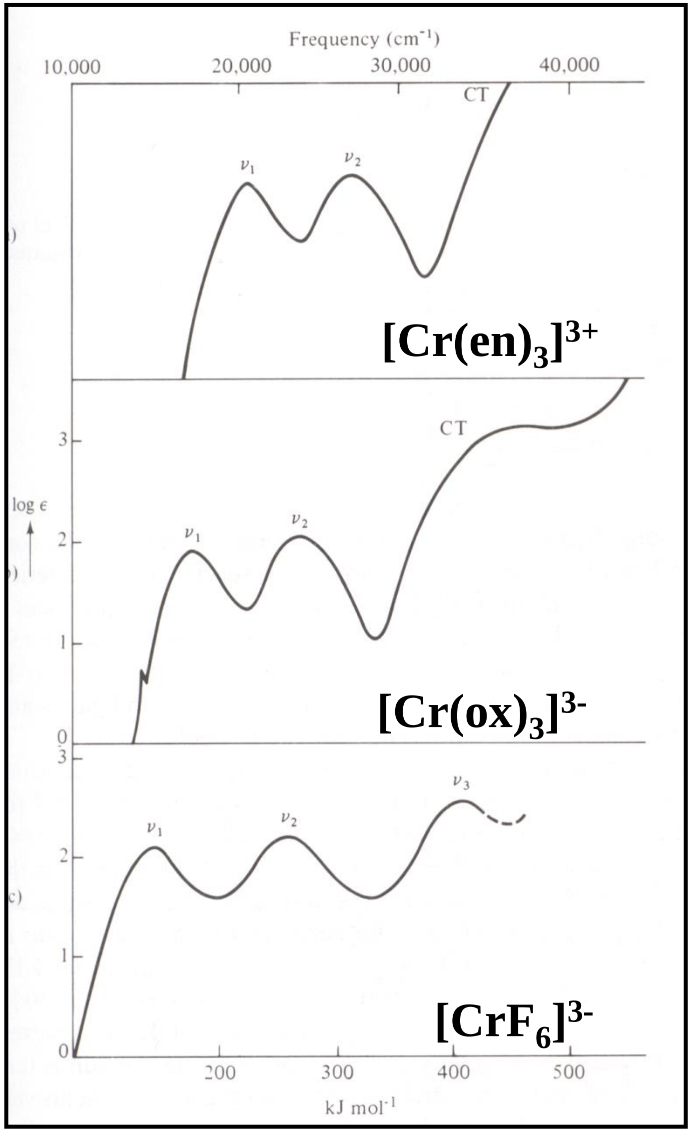
3d

$S = \Sigma s = 3/2$

$L = |\Sigma l| = 3$



Complex	10 Dq [cm^{-1}]	
$[Cr(CN)_6]^{3-}$	26700	
$[Cr(en)_3]^{3+}$	21900	en = ethylenediamine $C_2H_8N_2$
$[Cr(acac)_3]$	17800	acac = acetylacetonate $C_5H_7O_2^-$
$[Cr(ox)_3]^{3-}$	17500	ox = oxalate $C_2O_4^{2-}$
$[CrF_6]^{3-}$	14900	

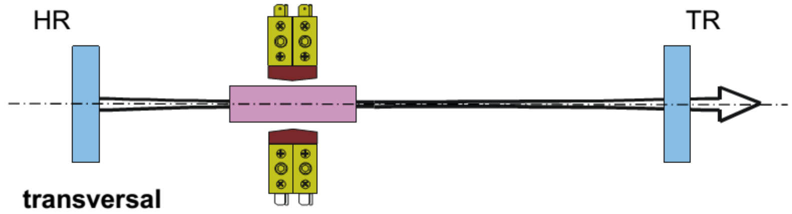


10. Chemistry of Transition Metals

The Chromium Group

Optical spectra of with Cr(III) doped solid state materials (e.g. oxides)

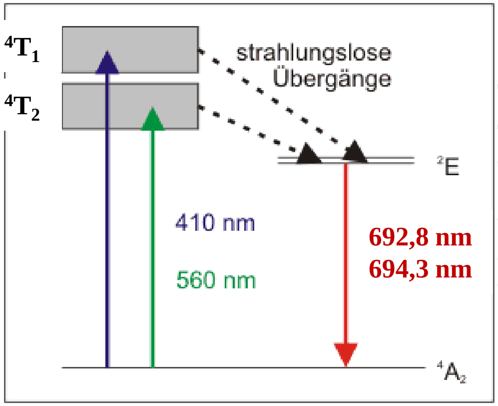
- **Al_2O_3:Cr (693 nm) ⇒ ruby ~ 0.1% Cr^{3+} ⇒ ruby solid state laser**
- **$Y_3Al_5O_{12}$:Cr (688 nm)**
- **$LiAlO_2$:Cr (690 nm)**
- **$BaMgAl_{10}O_{17}$:Cr (695 nm)**
- **$Lu_3Al_5O_{12}$:Cr (704 nm)**
- **$Y_3Ga_5O_{12}$:Cr (730 nm)**
- **$LaAlO_3$:Cr (735 nm)**
- **$Gd_3Ga_5O_{12}$:Cr (745 nm)**

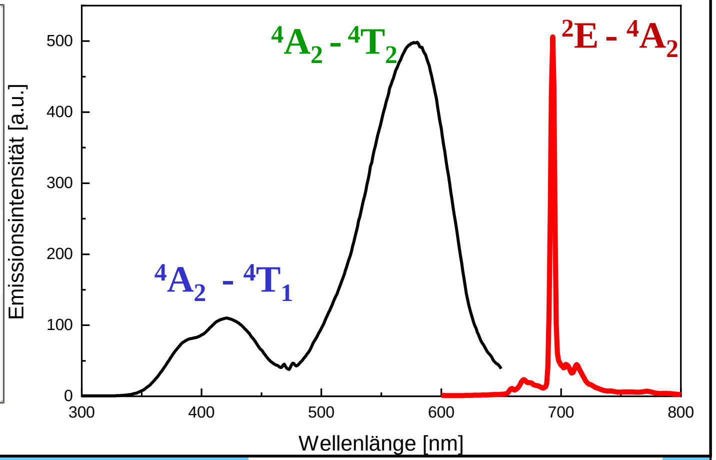


Influence of the crystal field on the exact position of the 3d-3d emission lines

- **weak for lines**
- **strong for bands**

Laser scheme, excitation and emission spectra of Al_2O_3:Cr (ruby)

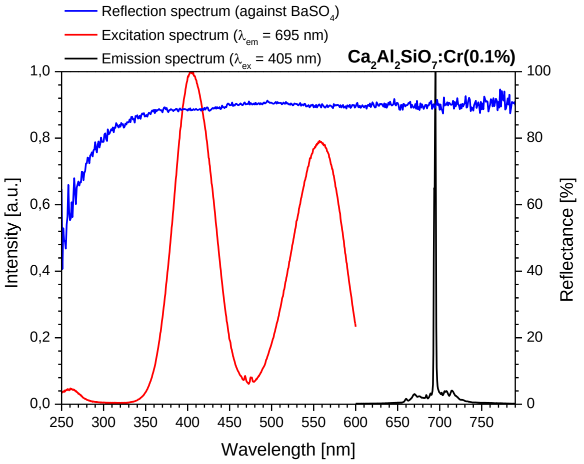




10. Chemistry of Transition Metals

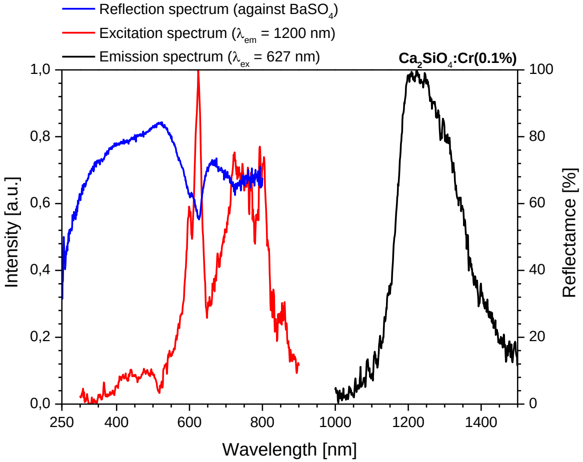
The Chromium Group

Optical spectra of Cr^{3+} doped solid state compounds (oxides)



Optical marker for inorganic phases in cement

$CaO-SiO_2$	$CaO-Al_2O_3$	$CaO-Al_2O_3-SiO_2$
Ca_3SiO_5	$Ca_3Al_2O_6$	$Ca_3Al_2Si_3O_{12}$
Ca_2SiO_4	$CaAl_2O_4$	$Ca_2Al_2SiO_7$
$Ca_3Si_2O_7$	$CaAl_4O_7$	$CaAl_2SiO_6$
$CaSiO_3$	$CaAl_{12}O_{19}$	$CaAl_2Si_2O_8$
$CaSi_2O_5$	$Ca_{12}Al_{14}O_{33}$	$Ca_3Al_6Si_2O_{16}$



Tracing alkalinity by luminescence

• Cr^{3+}	$Ca_2Al_2SiO_7$	red
• Cr^{4+}	Ca_2SiO_4	NIR
• Cr^{6+}	$CaAl_2O_4$	none

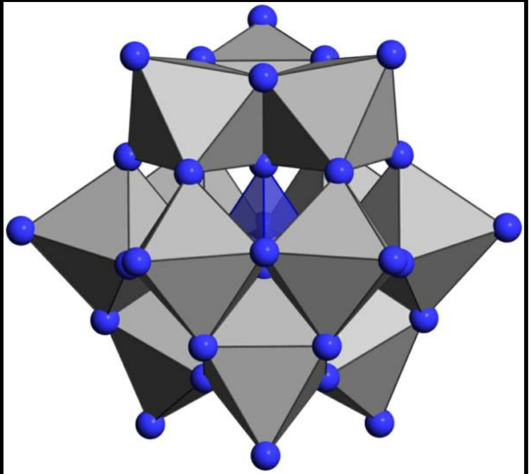
10. Chemistry of Transition Metals

The Chromium Group

Properties and reactions of Molybdenum and Tungsten

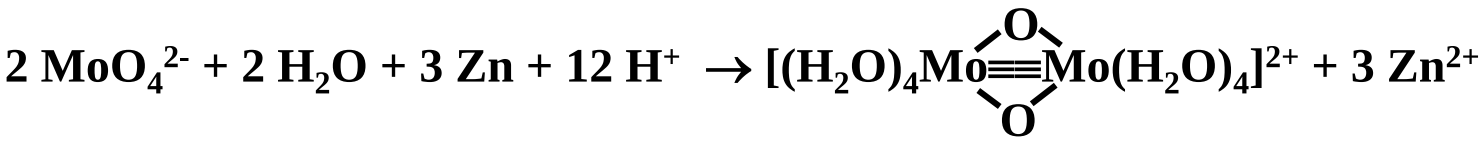
- MoO_3 and WO_3 are insoluble in water and acids, but soluble in alkaline lyes:
  $MoO_3 + 2\ OH^- \rightarrow MoO_4^{2-} + H_2O$
- At pH 6 and below isopoly anions are formed:
  $7\ MoO_4^{2-} + 8\ H^+ \rightarrow Mo_7O_{24}^{6-} + 4\ H_2O$
  $8\ MoO_4^{2-} + 12\ H^+ \rightarrow Mo_8O_{26}^{4-} + 6\ H_2O$
  $36\ MoO_4^{2-} + 64\ H^+ \rightarrow Mo_{36}O_{112}^{8-} + 32\ H_2O$

- Isopoly anions can incorporate hetero atoms:
  $12\ MoO_4^{2-} + HPO_4^{2-} + 23\ H^+ \rightarrow [PMo_{12}O_{40}]^{3-} + 12\ H_2O$
  (yellow) ⇒ detection of phosphate



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-21.jpg

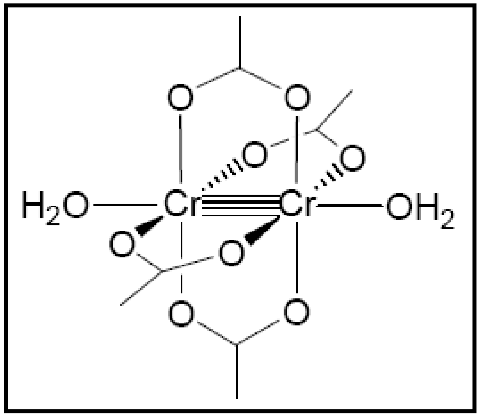
- Reduction of sodiumpolytungstate with H_2 yields
  Tungstic bronzes Na_nWO_3 $(0 < n < 1)$
- Reduction of MoO_4^{2-} with Zn/Hg ⇒ diamagnetic Mo^{3+}-complex:



$$2\ MoO_4^{2-} + 2\ H_2O + 3\ Zn + 12\ H^+ \rightarrow [(H_2O)_4Mo(\mu\text{-}O)_2{\equiv}Mo(H_2O)_4]^{2+} + 3\ Zn^{2+}$$

10. Chemistry of Transition Metals

The Chromium Group



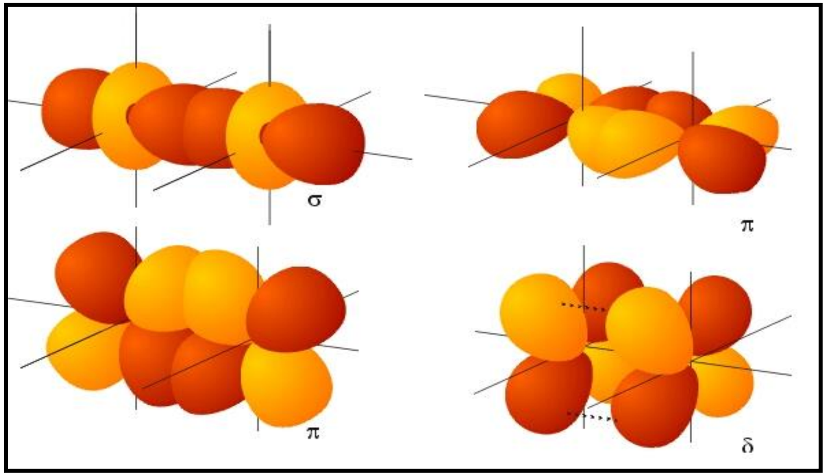
Metal-metal-bonds

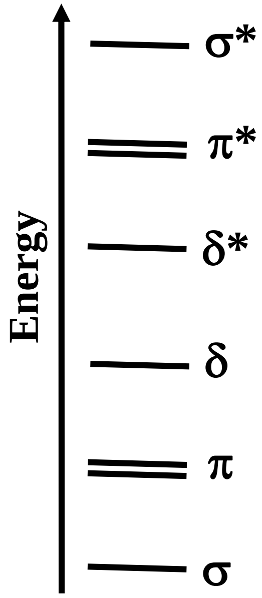
- Chromium(II)-acetate contains one Cr-Cr-quadruple bond
  $2\ [Cr(OH_2)_6]^{2+} + 4\ CH_3COO^- \rightarrow [Cr_2(H_2O)_2(\mu\text{-}OOCCH_3)_4] + 10\ H_2O$
- Molybdenum(II)-acetate also contains one Mo-Mo-quadruple bond
  $2\ [Mo(CO)_6]^0 + 4\ CH_3COOH \rightarrow [Mo_2(\mu\text{-}OOCCH_3)_4] + 12\ CO + 4\ H^+ + 4\ e^-$

σ-bonds 0 nodal plane
($s + s$, $p_z + p_z$, $d_{z^2} + d_{z^2}$)

π-bonds 1 nodal plane
($p_x + p_x$, $p_y + p_y$, $d_{xz} + d_{xz}$, $d_{yz} + d_{yz}$)

δ-bonds 2 nodal plane
($d_{xy} + d_{xy}$)





Cr(I) also forms Cr-Cr-quintuple bonds, e.g. in [PhCrCrPh]

10. Chemistry of Transition Metals

The Chromium Group

Biological aspects

Chromium

- Chromium(VI) acts carcinogenic, because it can oxidise OH-groups of the DNA
- Chromium(III) regulates the blood sugar level, together with insulin and glucagon

Molybdenum

- Only element of 2nd transition metal series of biological significance!
- In the form of molybdate MoO_4^{2-} soluble und thus readily available from sea water
- Biochemically relevant oxidation states: IV, V, VI ⇒ electron transfer reactions
- Coordination by O-, S-, and N-ligands
- Enzymes: nitrogenases, nitrate reductases, aldehyde oxidases

Tungsten

- Only element of 3rd transition metal series of biological relevance!
- Metalloenzymes in hypothermal archaebacteria are stable up to 110 ° C, due to strong metal-ligand interactions, stabilising the enzyme

10. Chemistry of Transition Metals

The Manganese Group

7. Sub group or group 7 ⇒ 7 valence electrons

Manganese [Ar]$3d^5 4s^2$ Technetium [Kr]$4d^5 5s^2$ Rhenium [Xe]$4f^{14} 5d^5 6s^2$

- Manganese is one of the most abundant heavy metals, second only to Iron
- $^{99}Tc^* \rightarrow {}^{99}Tc + \gamma$: $\tau_{1/2} = 6$ h $^{99}Tc \rightarrow {}^{99}Ru + ß^-$: $\tau_{1/2} = 2.1 \cdot 10^{-5}$ a

Properties of the elements

Element	Density [g/cm³]	T_m[° C]	T_b [° C]	Oxidation state	r(M^{7+}) [pm]
Mn	7.44	1247	2030	+II, +III, +IV, +VI, +VII	46
Tc	11.49	2250	4700	+IV, +V, +VII	56
Re	21.03	3180	5870	+IV, + V, + VI, +VII	53

Alloys

Ferromanganese	Mn(> 70%) + Fe + C	
Silicomanganese	Mn(65%) + Si(15-20%) + C	
Manganin	Cu(84%), Cu(12%), Ni(4%)	precision resistors
Manganese steel	Fe + Mn(10-18%)	railway tracka, armour plates

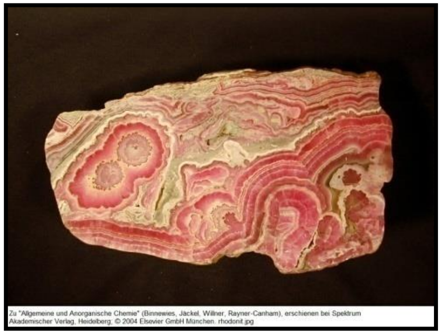
10. Chemistry of Transition Metals

The Manganese Group

Occurrence

Manganese (Greek: manganizein) ***cleaning: discolours ferrous glass***	MnO_2	**Pyrolustie (manganese ore)**
	$MnO(OH)$	**Manganite**
	Mn_3O_4	**Hausmannite**
	$MnSiO_4$	**Rhodonite**
Technetium (Grek: technetos) ***artificial***	**Traces in uranium ores**	
Rhenium (Rhineland) ***Home to the discoverer Ida Tacke***	**Companion in molybdenum ores (MoS_2)**	

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



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

Production of Manganese

1. **From Manganese ores with silicomanganese**

   $2\ MnO + Si \rightarrow 2\ Mn + SiO_2$

2. **Electrolysis of Manganese sulphate solutions**

   $2\ MnSO_4 + 2\ H_2O \rightarrow 2\ Mn + 2\ H_2SO_4 + O_2\uparrow$

10. Chemistry of Transition Metals

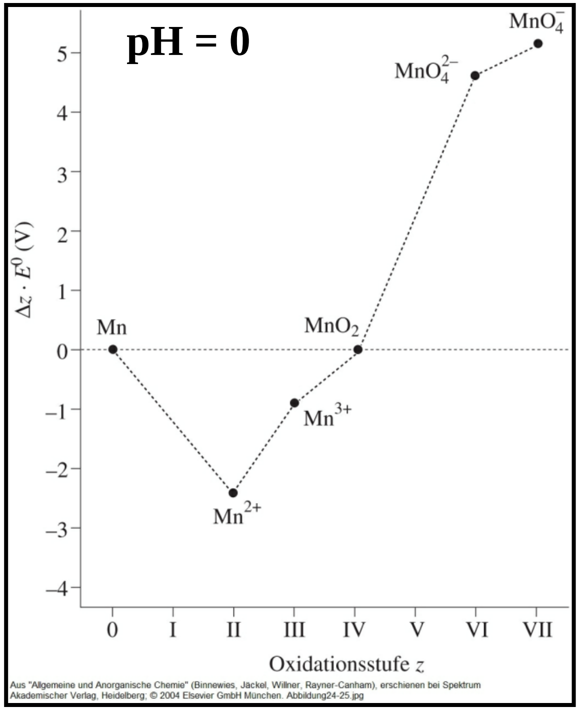
The Manganese Group

Oxidation states of Manganese

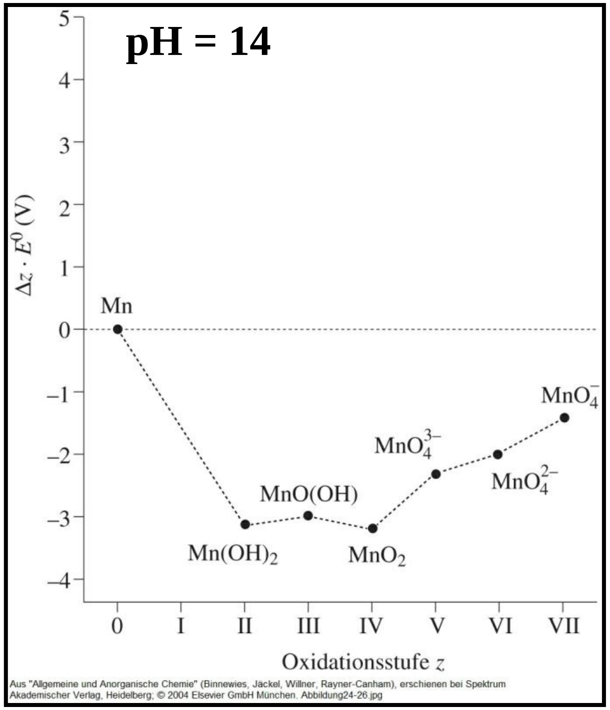
- **Manganese is relatively ignoble: Mn $\leftrightarrows$ $Mn^{2+} + 2\ e^-$ E° = -1.19 V**
- **In acidic solution Mn^{2+} is the most stable oxidation state**
- **In alkaline solution Mn^{4+} is the most stable species but also Mn^{2+} and Mn^{3+} experience high stability**

Frost-diagram

of manganese in acidic (right) and alkaline (left) solution



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-25.jpg



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-26.jpg

10. Chemistry of Transition Metals

The Manganese Group

Oxidation state +II ([Ar]3d^5)

- **Compared to other divalent TM ions, Mn^{2+} is relatively stable and no reducing agent in acidic solution:**

			E^0 [V] at pH 0
Mn^{2+} (d^5)	⇆	Mn^{3+}(d^4) + e^-	1.5
Fe^{2+} (d^6)	⇆	Fe^{3+}(d^5) + e^-	0.75
Cr^{2+} (d^4)	⇆	Cr^{3+}(d^3) + e^-	-0.41

- **Manganese(II)-salts and –solutions are just weakly coloured, since absorption in the visible range of the spectrum is due to spin-forbidden d-d-transitions (d^5, high-spin), only**

$MnSO_4\cdot 7H_2O$	Manganese(II)-sulphate-heptahydrate	rose
$MnCl_2\cdot 4H_2O$	Manganes(II)-chloride-tetrahydrate	rose
$[Mn(H_2O)_6]^{2+}$	Hexaaquamanganese(II)-ion	light rose

- **Strongly coloured low-spin complexes are formed solely with very strong ligands**
  $[Mn(CN)_6]^{4-}$
  $[Mn(CN)_5(NO)]^{3-}$

10. Chemistry of Transition Metals

The Manganese Group

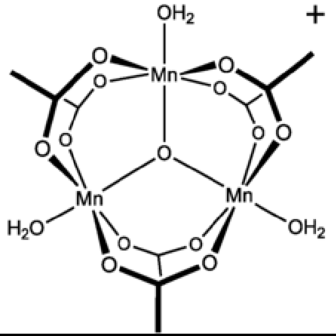
Oxidation state +III ([Ar]3d^4)

- **Dissolution of braunite, Mn_2O_3, in concentrated H_2SO_4**
  $Mn_2O_3 + 6\ H^+ + 9\ H_2O \rightleftarrows 2\ [Mn(H_2O)_6]^{3+}$
  yields a solution of garnet red hexaaquamanganese(III)-ions

- **Manganese(III)-ions tend to disproportionate**
  $2\ Mn^{3+} + 2\ H_2O \rightleftarrows Mn^{2+} + MnO_2 + 4\ H^+$
  if no reductive agent is present

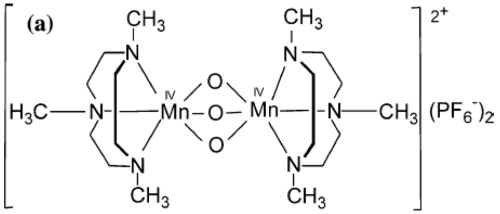
- **The stable deep red Manganese(III)-acetate is formed upon treatment of Manganese(II)acetate with permanganate in glacial acetic acid:**
  $3\ KMnO_4 + 12\ Mn(OAc)_2 + 11\ HOAc + 3\ H^+ \rightarrow 5\ [Mn_3O(OAc)_6]OAc\downarrow + 7\ H_2O + 3\ K^+$

  (HOAc = CH_3-COOH)



10. Chemistry of Transition Metals

The Manganese Group



Oxidation state +IV ([Ar]3d³)

$MnO_2 \cdot H_2O = MnO(OH)_2$ is a strong oxidising agent in acidic solution

pH = 0 $Mn^{2+} + 2\ H_2O \leftrightarrows MnO_2 + 4\ H^+ + 2\ e^-$ E° = +1.28 V

$MnO_2 + 4\ HCl \rightarrow MnCl_2 + Cl_2\uparrow + 2\ H_2O$

⇒ preparation of chlorine at laboratory scale

pH = 14 $2\ OH^- + Mn(OH)_2 \leftrightarrows MnO_2 + 2\ H_2O + 2\ e^-$ E° = -0.05 V

$4\ OH^- \leftrightarrows O_2 + 2\ H_2O + 4\ e^-$ E° = +0.40 V

⇒ O_2 oxidises Manganese(II)-hydroxide to $MnO_2 \cdot H_2O$

Oxidation state +VII ([Ar]3d⁰)

The violet permanganate ion, MnO_4^-, is a very strong oxidising agent in acidic solution

pH = 0 $MnO_4^- + 8\ H_3O^+ + 5\ e^- \leftrightarrows Mn^{2+} + 12\ H_2O$ E° = +1.51 V

pH = 5 E° = +1.04 V

pH = 7 E° = +0.85 V

$$\boxed{E = E^0 + \frac{0.059}{5}\lg\frac{[MnO_4^-][H_3O]^8}{[Mn^{2+}]}}$$

Permanganate can be synthesised by the oxidation of Mn^{2+} with PbO_2 in acidic surroundings

$2\ Mn^{2+} + 5\ PbO_2 + 4\ H^+ \leftrightarrows 2\ MnO_4^- + 5\ Pb^{2+} + 2\ H_2O$

10. Chemistry of Transition Metals

The Manganese Group

Oxidation state +VII ([Ar]$3d^0$)

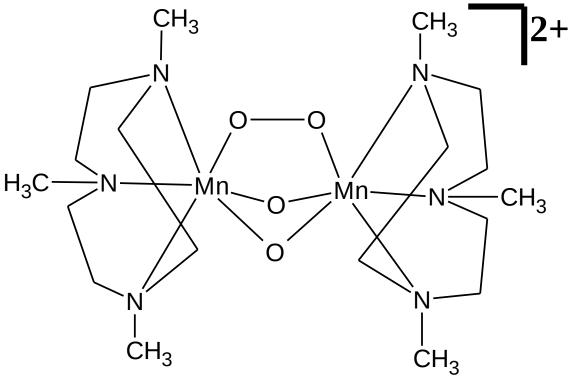
- Permanganate can be dehydrated to manganese heptoxide, using sulphuric acid:
  $KMnO_4 + H_2SO_4 \rightarrow 2\ Mn_2O_7 + K_2SO_4 + H_2O$
- Mn_2O_7 is highly oxidising: $2\ Mn_2O_7 \rightarrow 4\ MnO_2 + 3\ O_2$ “lightning under water“

Redox chemistry and colours of Manganese

Mn	$\underset{+2e^-}{\overset{-2e^-}{\leftrightarrows}}$	Mn^{2+}	$\underset{+e^-}{\overset{-e^-}{\leftrightarrows}}$	Mn^{3+}	$\underset{+e^-}{\overset{-e^-}{\leftrightarrows}}$	MnO_4^{4-}	$\underset{+e^-}{\overset{-e^-}{\leftrightarrows}}$	MnO_4^{3-}	$\underset{+e^-}{\overset{-e^-}{\leftrightarrows}}$	MnO_4^{2-}	$\underset{+e^-}{\overset{-e^-}{\leftrightarrows}}$	MnO_4^-
grey		rose		red		brown		blue		green		violet

Redox enzymes and photosystem II

Model complex for Mn-species, that cleaves O_2 during photosynthesis



⇒ Manganese complexes

10. Chemistry of Transition Metals

The Manganese Group

Rhenium compounds

Oxides and oxychlorides

- Re_2O_7, ReO_3, Re_2O_5, ReO_2,
- $ReOCl_4$, $ReOCl_3$

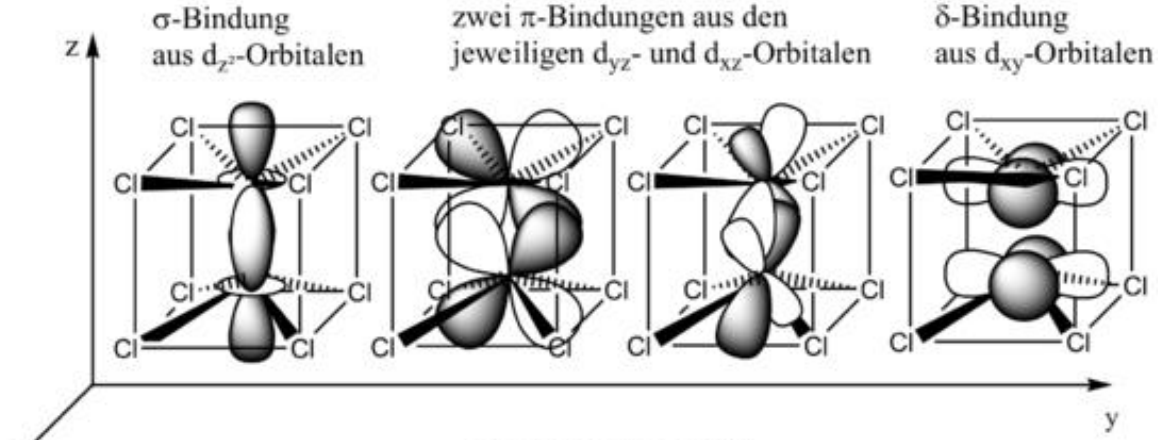
Halides

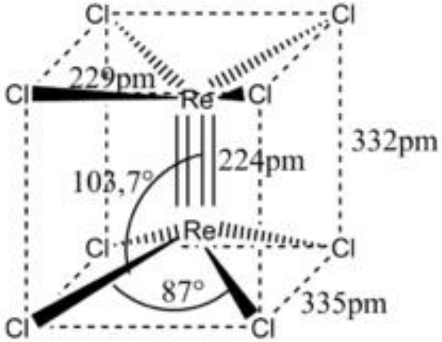
- $ReCl_6$, $ReCl_5$, $ReCl_4$, $ReCl_3$
- $[Re^{III}_2Cl_8]^{2-}$ with quadruple bond
- $Cp_2Re^{I}_2$ with bond order 4-6!

Re(I) complexes

- $[Xe]4f^{14}5d^6$ l.s. → large CFSE = -24 Dq_o
- $[Re(phenanthroimidazol)(CO)_3Br]$ for OLEDs?

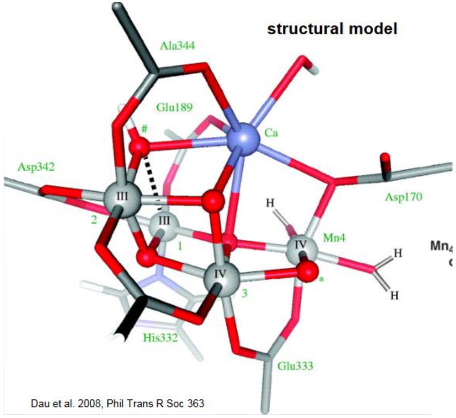
Lit.: Optical Materials 47 (2015) 173





10. Chemistry of Transition Metals

The Manganese Group



Dau et al. 2008, Phil Trans R Soc 363

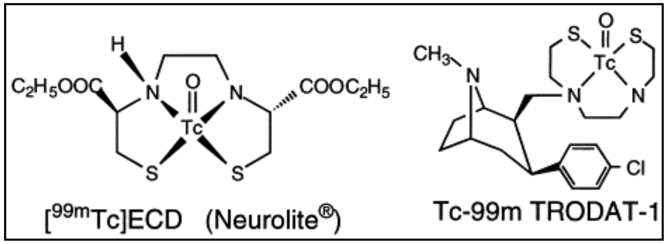
Biological aspects

Manganese

- Manganese is the key element in the photo reaction of photosynthesis, viz. it is responsible for the cleavage of water in the oxygen-releasing cluster:
  $Mn^{III}_4 \leftrightarrows Mn^{III}_3Mn^{IV} \leftrightarrows Mn^{III}_2Mn^{IV}_2 \leftrightarrows Mn^{III}Mn^{IV}_3 \leftrightarrows Mn^{IV}_4$
  $Mn^{IV}_4 + 2\ H_2O \rightarrow Mn^{III}_4 + 4\ H^+ + O_2$
  $2\ H_2O \rightarrow 4\ H^+ + 4\ e^- + O_2\uparrow$
  (→ presentations)

- Arginase: nitrogen-containing metabolite → synthesis of urea $H_2N\text{-}CO\text{-}NH_2$

- Superoxide dismutase: cleavage of the superoxide radical O_2^-
  $4\ O_2^- + 4\ H^+ \rightarrow 3\ O_2 + 2\ H_2O$
  Mn, besides Zn, Cu, Fe, and Se, is a cofactor for enzymes, acting as antioxidants



[^{99m}Tc]ECD (Neurolite®)   Tc-99m TRODAT-1

Technetium and Rhenium are of no biological importance, but ^{99m}Tc-complexes als ß-Strahler in der „Single Photon Emission Computer Tomographie (SPECT)“ verwendet

10. Chemistry of Transition Metals

The Iron Group

8. Sub group or group 8, 9 and 10 ⇒ 8, 9 or 10 valence electrons

Iron	**Cobalt**	**Nickel**	**⇒ Iron group**	***ignoble***
Ruthenium	**Rhodium**	**Palladium**	**⇒ light platinum metals**	***noble***
Osmium	**Iridium**	**Platinum**	**⇒ heavier platinum metals**	***noble***

- **Iron, Cobalt, and Nickel experience similar densities, boiling points, melting points, and are all ferromagnetic**
- **Osmium (22.59 g/cm^3) and Iridium (22.56 g/cm^3) are the two elements with the highest density!**

Properties of the elements of the Iron group

Element	Iron	Cobalt	Nickel
Density [g/cm^3]	7.87	8.90	8.90
T_m[° C]	1536	1499	1455
T_b [° C]	2860	2900	2880
Oxidation state	+II, +III	+II, +III	+II, +III
r(M^{2+}) [pm]	78(h.s.), 61(l.s.)	74(h.s.), 65(l.s.)	69
r(M^{3+}) [pm]	64(h.s.), 55(l.s.)	61(h.s.), 54(l.s.)	60(h.s.), 56(l.s.)

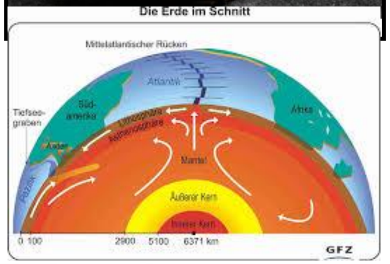
10. Chemistry of Transition Metals

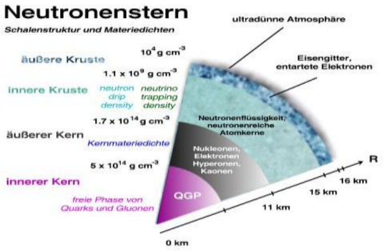
The Iron Group

Occurrence

Iron (Latin.: ferrum)	Fe_3O_4	**Magnetite**
Ghotic: isarn	Fe_2O_3	**Haematite**
	$Fe_2O_3 \cdot xH_2O$	**Brown Iron ore**
	$FeCO_3$	**Siderite**
	FeS_2	**Pyrite**
Cobalt (Goblin)	Co_3S_4	**Cobalt gravel**
Berggeist	CoAsS	**Cobalt glare**
Nickel (Nickel)	(Fe,Ni)S	**Iron Nickel gravel**
Berggeist	NiAs	**Niccolite**


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


Die Erde im Schnitt


Neutronenstern
Schalenstruktur und Materiedichten

Production

Iron and steel → presentation

Cobalt → calcination → CoO → $CoSO_4$ → electrolysis → Co

Nickel → calcination → NiO → $NiSO_4$ → electrolysis → Ni + 4 CO $\rightleftharpoons$ $Ni(CO)_4(g)$

10. Chemistry of Transition Metals

The Iron Group

Blast-Furnace-Process

“Continuous process“

1000 – 1500 t of Iron as well as slurry per day

Iron: Fe + C, P, Si, Mn, S

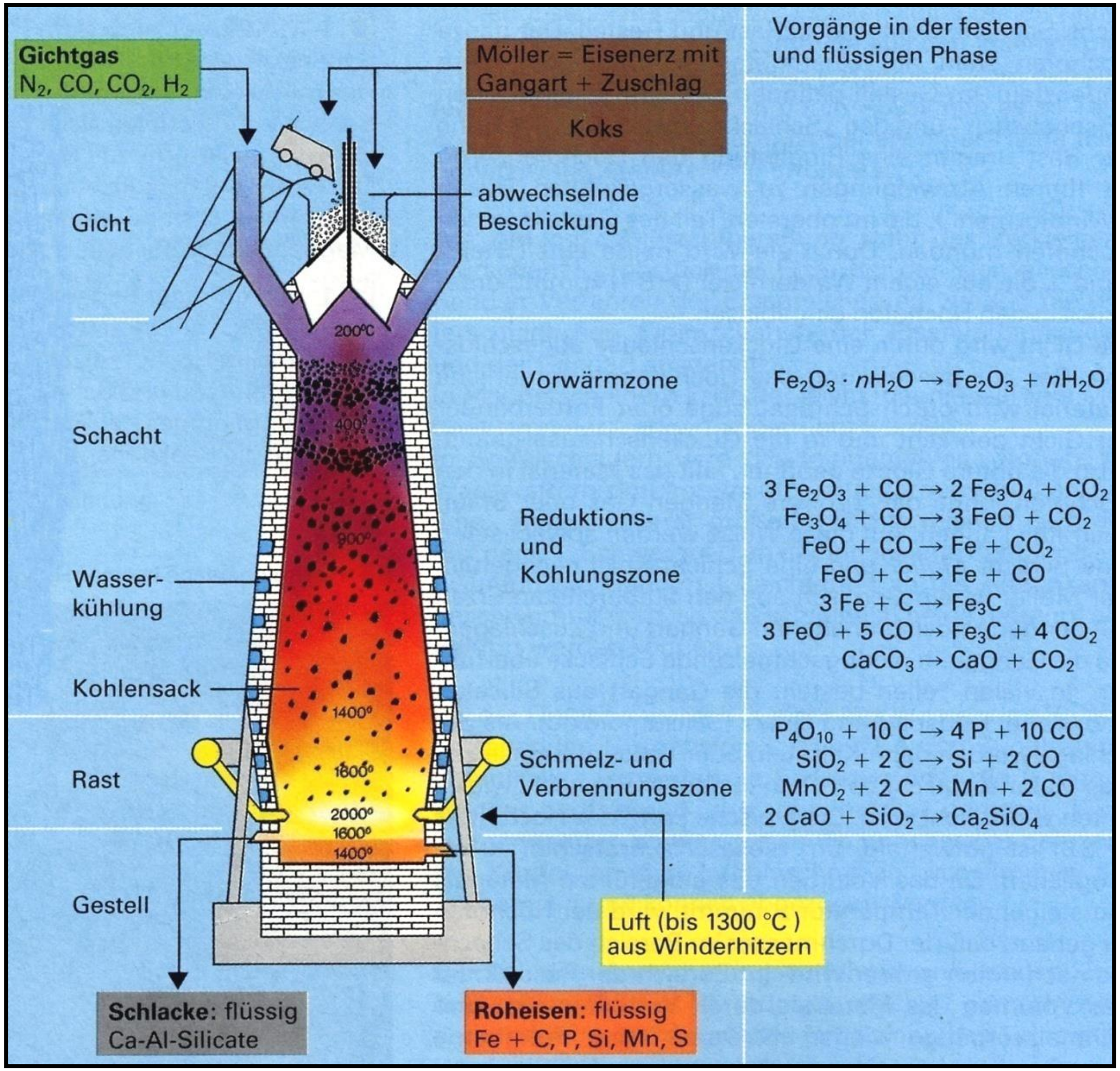
Slurry: Ca-Al-silicates

Reduction with CO

$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow$ “FeO” $\rightarrow Fe$

Boudouard-equilibrium

$C + CO_2 \leftrightarrows 2\,CO$



$Fe_2O_3 \cdot nH_2O \rightarrow Fe_2O_3 + nH_2O$

$3\,Fe_2O_3 + CO \rightarrow 2\,Fe_3O_4 + CO_2$
$Fe_3O_4 + CO \rightarrow 3\,FeO + CO_2$
$FeO + CO \rightarrow Fe + CO_2$
$FeO + C \rightarrow Fe + CO$
$3\,Fe + C \rightarrow Fe_3C$
$3\,FeO + 5\,CO \rightarrow Fe_3C + 4\,CO_2$
$CaCO_3 \rightarrow CaO + CO_2$

$P_4O_{10} + 10\,C \rightarrow 4\,P + 10\,CO$
$SiO_2 + 2\,C \rightarrow Si + 2\,CO$
$MnO_2 + 2\,C \rightarrow Mn + 2\,CO$
$2\,CaO + SiO_2 \rightarrow Ca_2SiO_4$

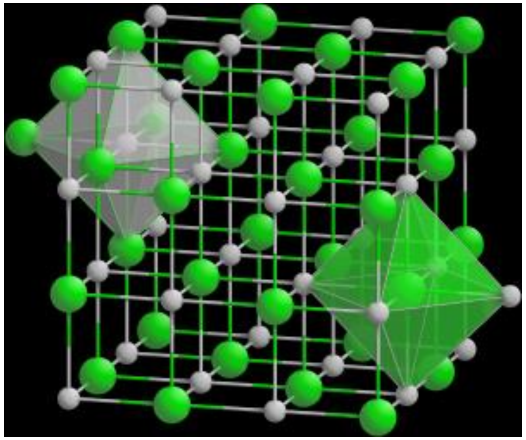
10. Chemistry of Transition Metals

The Iron Group

Non-stoichiometric compounds

Iron(II)-oxide does not exist as FeO but Fe_xO ($x = 0.833 < 0.957$)

Explanation



FeO crystallises in a NaCl-like structure, where part of the Fe-ions exhibit the trivalent oxidation state

⇒ Charge compensation

1. By cation vacancies (Schottky-defects)
2. By additional oxide anions on interstitials (Frenkel-defects)

Metals with a tendency for a change of valence form non-stoichiometric compounds

• MnO	Mn_xO	($x = 0.848 < 1.000$)
• CoO	Co_xO	($x = 0.988 < 1.000$)
• NiO	Ni_xO	($x = 0.999 < 1.000$)
• Ce_2O_3	CeO_x	($x = 1.50 < 1.52$)
• TiO_2	TiO_x	($x = 1.998 < 2.000$)

10. Chemistry of Transition Metals

The Iron Group

Iron(II) and Iron(III) compounds

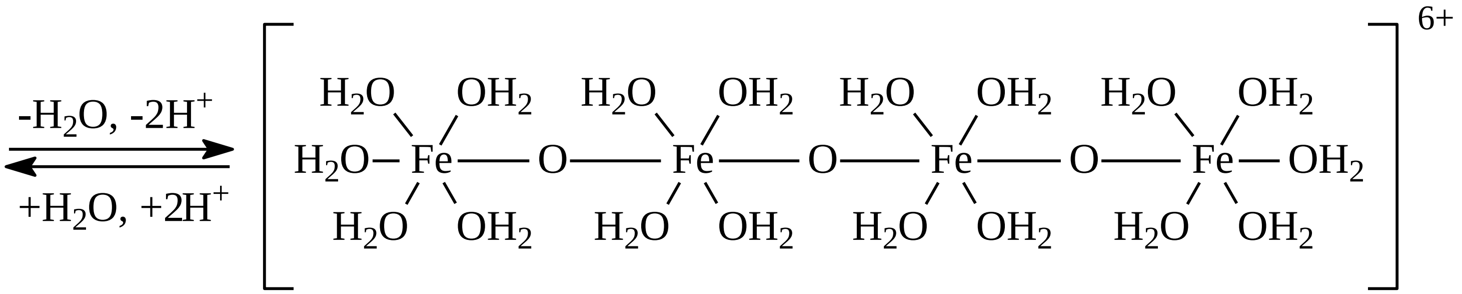
Acid-base chemistry

$[Fe^{II}(H_2O)_6]^{2+} + H_2O \leftrightarrows [FeOH(H_2O)_5]^{+} + H_3O^{+}$ $K = 10^{-7}$ pH of a 0.1 M solution ~ 4

$[Fe^{III}(H_2O)_6]^{3+} + H_2O \leftrightarrows [FeOH(H_2O)_5]^{2+} + H_3O^{+}$ $K = 10^{-7}$ pH of a 0.1 M solution ~ 2

$4\ [FeOH(H_2O)_5]^{2+} \rightarrow 2\ [(H_2O)_5Fe\text{-}O\text{-}Fe(H_2O)_5]^{4+} + 2\ H_2O$

(yellow brown)



$\rightarrow Fe_2O_3{\cdot}nH_2O$

rotbraun

Iron(II)-hydroxide

$Fe^{2+} + 2\ OH^{-} \leftrightarrows Fe(OH)_2$ $K_L = c(Fe^{3+}) \cdot c^2(OH^-) = 2{\cdot}10^{-15}\ mol^3/l^3$

Iron(III)-hydroxide

$Fe^{3+} + 3\ OH^{-} \leftrightarrows Fe(OH)_3$ $K_L = c(Fe^{3+}) \cdot c^3(OH^-) = 5{\cdot}10^{-38}\ mol^4/l^4$

10. Chemistry of Transition Metals

The Iron Group

Iron(II) and Iron(III) compounds

Redox chemistry

Redox reaction	E^0 [V] for pH = 0
$Fe \leftrightarrows Fe^{2+} + 2\,e^-$	-0.41
$Fe \leftrightarrows Fe^{3+} + 3\,e^-$	-0.036
$Fe^{2+} \leftrightarrows Fe^{3+} + e^-$	+0.77

⇒ **Strongly depends on pH, since the hydroxides are insoluble in neutral and alkaline environment**

Using the solubility products of $Fe(OH)_3$ and $Fe(OH)_2$, the redox potential can be calculated by means of the Nernst equation:

$$E(Fe^{2+}/Fe^{3+}) = E^0(Fe^{2+}/Fe^{3+}) + 0.059/n \cdot \lg(c(Fe^{3+})/c(Fe^{2+}))$$

$$\Rightarrow E(Fe^{2+}/Fe^{3+}) = +0.77\ V + 0.059 \cdot \lg(5 \cdot 10^{-38}/2 \cdot 10^{-15})\ V = -0.56\ V \quad \text{for } c(OH^-) = 1\ mol/l\ (pH\ 14)$$

Due to the considerable difference in the solubility products of $Fe(OH)_3$ and $Fe(OH)_2$, the system Fe^{2+}/Fe^{3+} becomes a strong reducing agent in alkaline milieu!

10. Chemistry of Transition Metals

The Iron Group

Iron(II) and Iron(III) compounds

Complex chemistry

- **Mainly octahedral and high-spin with the exception of CN$^-$-, phen- or bipy-ligands**

- **Stability of the oxidation states depends on the electronic properties of the ligands**

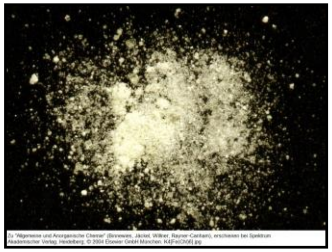
$[Fe(CN)_6]^{4-} \leftrightarrows [Fe(CN)_6]^{3-} + e^-$	$E^0 = +0.36\ V$	l.s.	negative charge!
$[Fe(H_2O)_6]^{2+} \leftrightarrows [Fe(H_2O)_6]^{3+} + e^-$	$E^0 = +0.77\ V$	h.s.	
$[Fe(bpy)_3]^{2+} \leftrightarrows [Fe(bpy)_3]^{3+} + e^-$	$E^0 = +0.96\ V$	l.s.	
$[Fe(phen)_3]^{2+} \leftrightarrows [Fe(phen)_3]^{3+} + e^-$	$E^0 = +1.12\ V$	l.s.	for pH = 0

- **Fe(III)-ions ⇒ high affinity to Oxygen-donor ligands**
  $[Fe(PO_4)_3]^{6-}$, $[Fe(C_2O_4)_3]^{3-}$
  Fe(II)-ions ⇒ high affinity to Nitrogen-donor ligands
  $[Fe(NH_3)_6]^{2+}$, $[Fe(en)_3]^{2+}$

- **$K_4[Fe(CN)_6]$ Potassiumhexacyanoferrate(II) yellow prussiate of potash**
  $K_3[Fe(CN)_6]$ Potassiumhexacyanoferrate(III) red prussiate of potash
  Name: Formerly obtained through heating of blood (Fe-, C-, and N-containing) with K_2CO_3 and subsequent leaching of the resulting salts with water

10. Chemistry of Transition Metals

The Iron Group



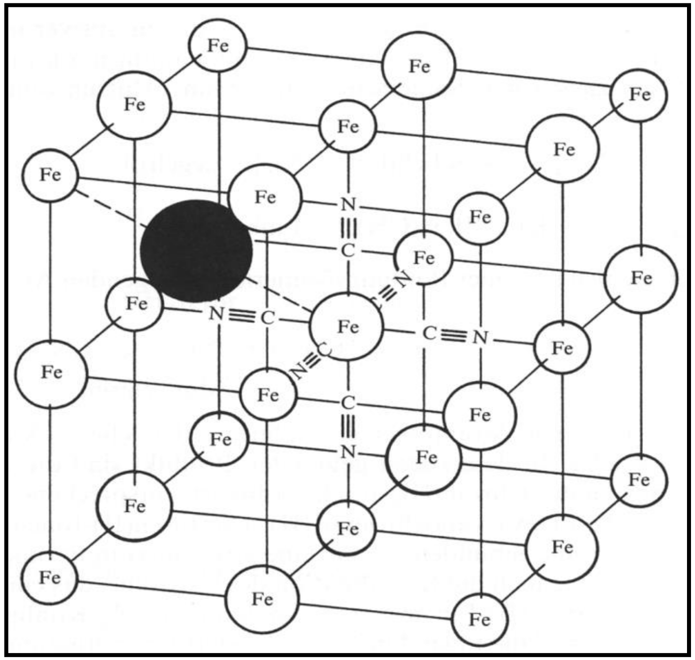
Iron(II) and Iron(III) compounds

Detection reaction

1. Fe^{3+} + yellow prussiate of potash → Prussian blue
   Fe^{2+} + red prussiate of potash → Prussian blue

Prussian blue = $Fe_4[Fe(CN)_6]_3 \cdot 14H_2O$

Structural motif $(NC)_5Fe\text{-}C{\equiv}N\text{-}Fe(NC)_5$



⇒ Charge-transfer complex (inter-valence band)

2. $[Fe(H_2O)_6]^{3+}$ + SCN^- → blood red complexes

$[Fe(SCN)(H_2O)_5]^{2+}$

$[Fe(SCN)_2(H_2O)_4]^+$

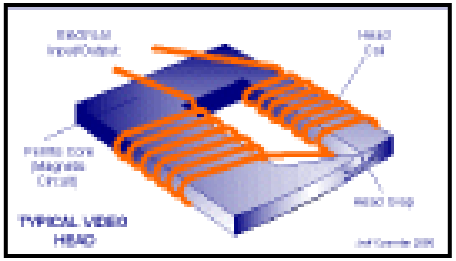
$[Fe(SCN)_3(H_2O)_3]^0 \rightarrow Fe(SCN)_3\downarrow + 3\ H_2O$

3. $[Fe(H_2O)_6]^{2+} + NO \rightarrow [Fe(H_2O)_5NO]^{2+} + H_2O$
   (Ring proof)

   NO, NO^+ oder NO^-?

10. Chemistry of Transition Metals

The Iron Group



Ferrites

Magneto ceramic materials

⇒ Binary and ternary iron oxides

Soft ferrites

- **Are easily and efficiently magnetised by an external magnetic field**
- **Magnets in writing and reading heads in audio and video recorders, hard drives etc.**
- **Electrical isolators, ferrimagnetic compounds with low saturation magnetisation in combination with low anisotropy in terms of the crystal structure**
- **MFe_2O_4 (spinels) with M = $Zn^{2+,}$ Mn^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}**
- **Typical composition: Fe-Mn-Zn-oxide with 70% Fe, 25% Mn, and 5% Zn**

Hard ferrites

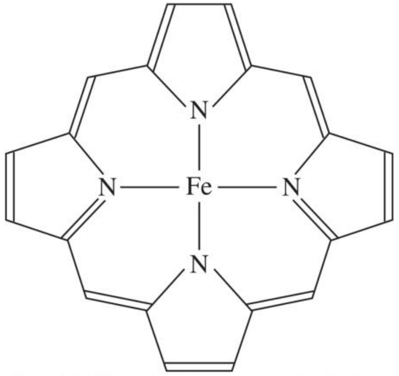
- **Maintain their magnetic properties after the initial magnetisation**
- **Permanent magnets in electric motors, speaker, generators, etc.**
- **$MFe_{12}O_{19}$ with M = Sr^{2+}, Ba^{2+}**

10. Chemistry of Transition Metals

The Iron Group

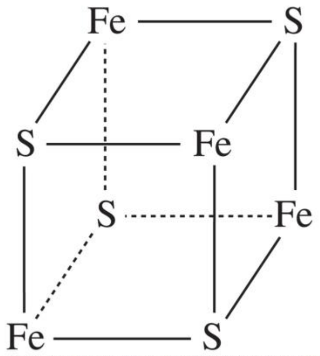
Bioinorganic chemistry of Iron

Iron takes part in the transportation of Oxygen and in a number electron transfer reactions



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-31.jpg

Haem-proteins (Iron-porphyrin-complexes)		E^0 [V]
Haemoglobin	O_2 transport	0.17
Myoglobin	O_2 storage	0.05
Cytochromes (a,b,c)	Electron transfer	0.04 – 0.40
Oxygenases	Oxygenation	
Oxidases	O_2 reduction to O_2^-, O_2^{2-}, O^{2-}	
Peroxidases	Oxidation with H_2O_2	
Katalases	H_2O_2 disproportionation to H_2O and O_2	



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-32.jpg

Non-Haem-proteins (Iron-Sulphur-cluster)		E^0 [V]
Rubridoxines	Electron transfer	-0.06
Ferredoxines	Electron transfer	-0.42
Nitrogenases	N_2 reduction to NH_3	
Transferrrines	Transport of Iron	
Ferritines	Storage of Iron	

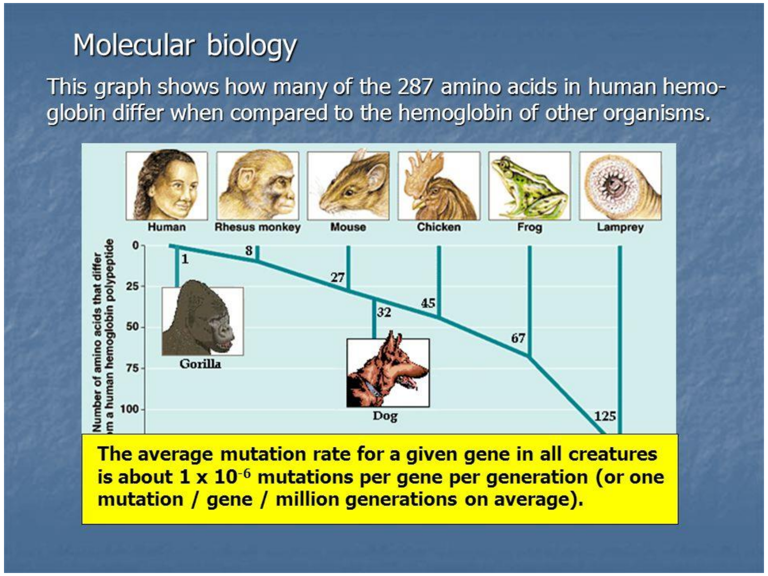
10. Chemistry of Transition Metals

The Iron Group

Bioinorganic chemistry of Iron

The adult human accommodates 4 g of Fe, 75% thereof being bound by erythrocytes in haemoglobin

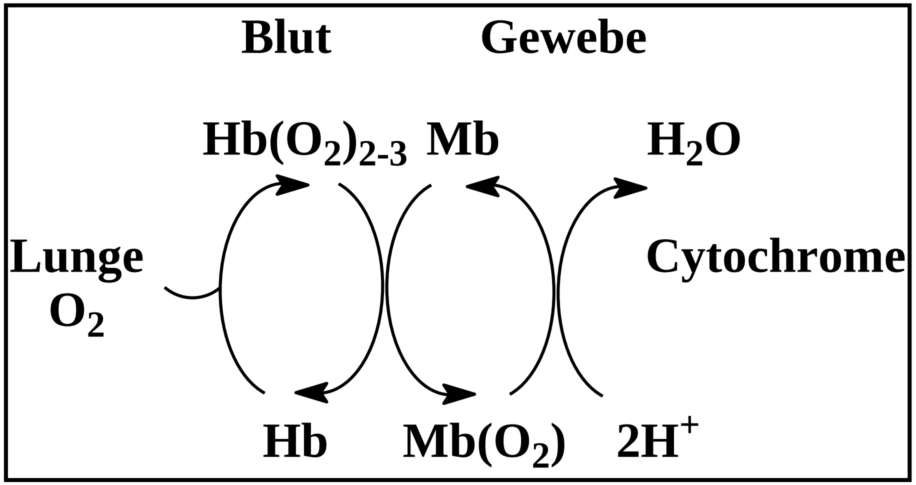
Oxygen transportation chain → respiratory chain



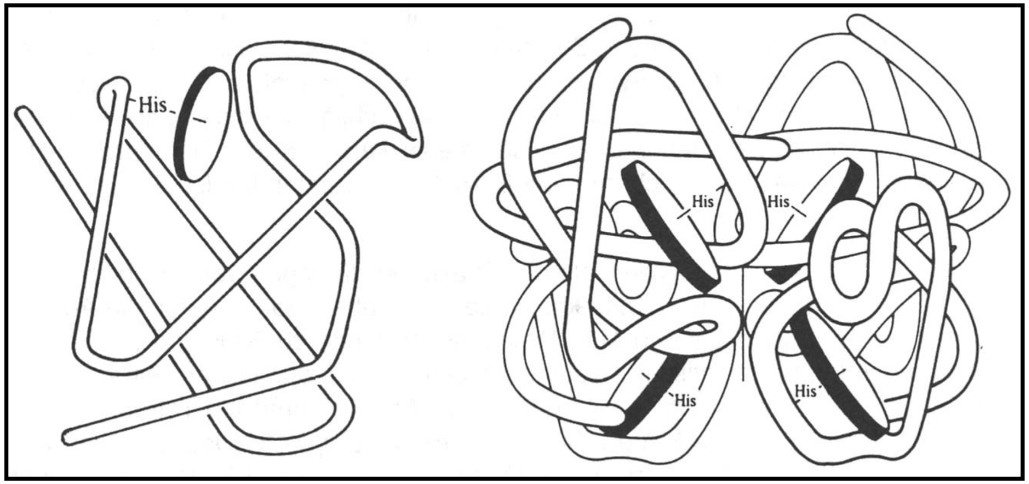
Molecular biology

This graph shows how many of the 287 amino acids in human hemoglobin differ when compared to the hemoglobin of other organisms.

The average mutation rate for a given gene in all creatures is about 1 x 10^{-6} mutations per gene per generation (or one mutation / gene / million generations on average).



Structure of myoglobin (Mb) & haemoglobin (Hb)



10. Chemistry of Transition Metals

The Iron Group

Function and structure of heme

Oxyhaemoglobin

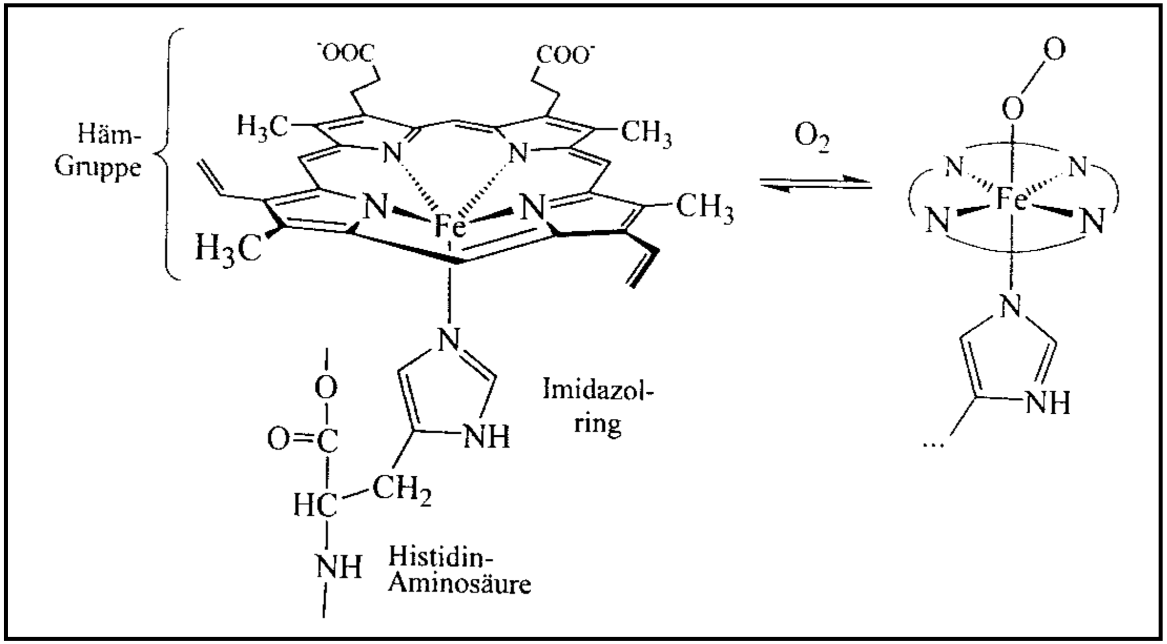
Fe^{2+}, $[Ar]3d^6$ l.s., diamagnetic

r = 75 pm ⇒ in-plane structure

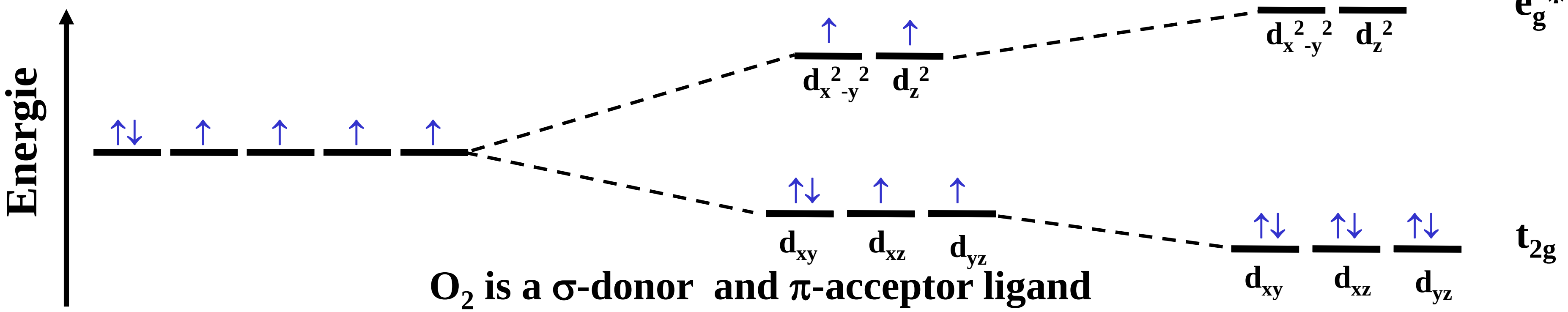
Deoxyhaemoglobin

Fe^{2+}, $[Ar]3d^6$ h.s., paramagnetic

r = 92 pm ⇒ out-of-plane structure



Free Fe^{2+} **Fe^{2+} in deoxyhaemoglobin** **Fe^{2+} in oxyhaemoglobin**



O_2 is a σ-donor and π-acceptor ligand

10. Chemistry of Transition Metals

The Iron Group

Cobalt(II) and Cobalt(III) compounds

Redox chemistry

Redox reaction	E^0 [V] for pH = 0
$Co \leftrightarrows Co^{2+} + 2\,e^-$	-0.28
$Co \leftrightarrows Co^{3+} + 3\,e^-$	+0.41
$Co^{2+} \leftrightarrows Co^{3+} + e^-$	+1.82

$[Co(H_2O)_6]^{2+} \leftrightarrows [Co(H_2O)_6]^{3+} + e^-$

rose ($3d^7$) blue ($3d^6$)

⇒ In contrary to Iron, divalent Cobalt is the most stable oxidation state in water

⇒ The ligands strongly influence the electrode potentials

$[Co(NH_3)_6]^{2+} \leftrightarrows [Co(NH_3)_6]^{3+} + e^-$ $E^0 = +0.10$ V

$[Co(CN)_5]^{3-} + CN^- \leftrightarrows [Co(CN)_6]^{3-} + e^-$ $E^0 = -0.83$ V

⇒ The high ligand field stabilisation energies stabilise Co(III)-complexes, and most octahedral Co(II)-complexes are unstable against oxidation by air, which can be traced back to their redox potentials

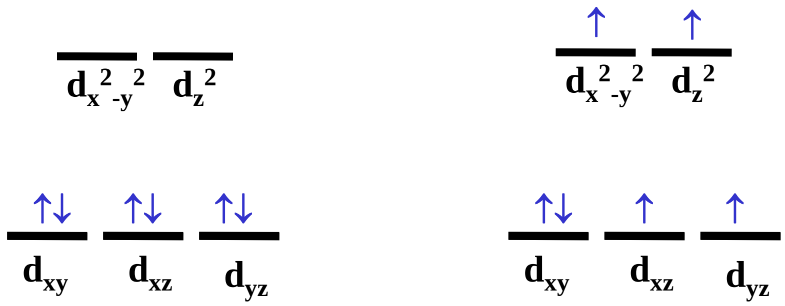
10. Chemistry of Transition Metals

The Iron Group

Cobalt(II) and Cobalt(III) compounds

Complex chemistry

- Co^{3+} (isoelectronic to Fe^{2+}) normally forms octahedral low-spin complexes, because then, high ligand field stabilisation energies (LFSE) can be reached:



LFSE $-24\ Dq_o + 2\ SPE$ $-4\ Dq_o$

- Low-spin Co(III)-complexes are kinetically inert, because antibonding e_g^*-orbitals are unoccupied
- Cobalt(III) forms a great number of stable complexes with Chromium(III), which can easily be separated into geometrical and optical isomers, due to their high kinetic stabillity

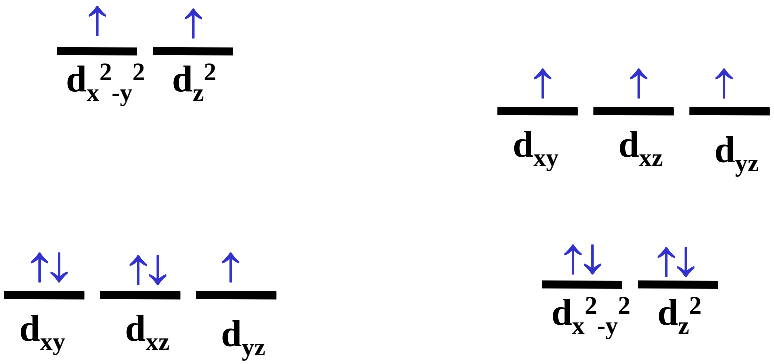
10. Chemistry of Transition Metals

The Iron Group

Cobalt(II) and Cobalt(III) compounds

Complex chemistry

- Co^{2+} ($3d^7$) are high-spin complexes and exhibit octahedral or tetrahedral coordination



LFSE $-8\ Dq_o$ $-8\ Dq_t = -5.33\ Dq_o$ ⇒ relative small difference

- Tetrahedral complexes are formed with monodental ligands, such as Cl^-, Br^-, SCN^-, OH^-
- Octahedral Co(II)-complexes are generally rose to red, while tetrahedral Co(II)-complexes are blue
- $[Co(H_2O)_6]^{2+} + 4\ Cl^- \rightarrow [CoCl_4]^{2-} + 6\ H_2O$

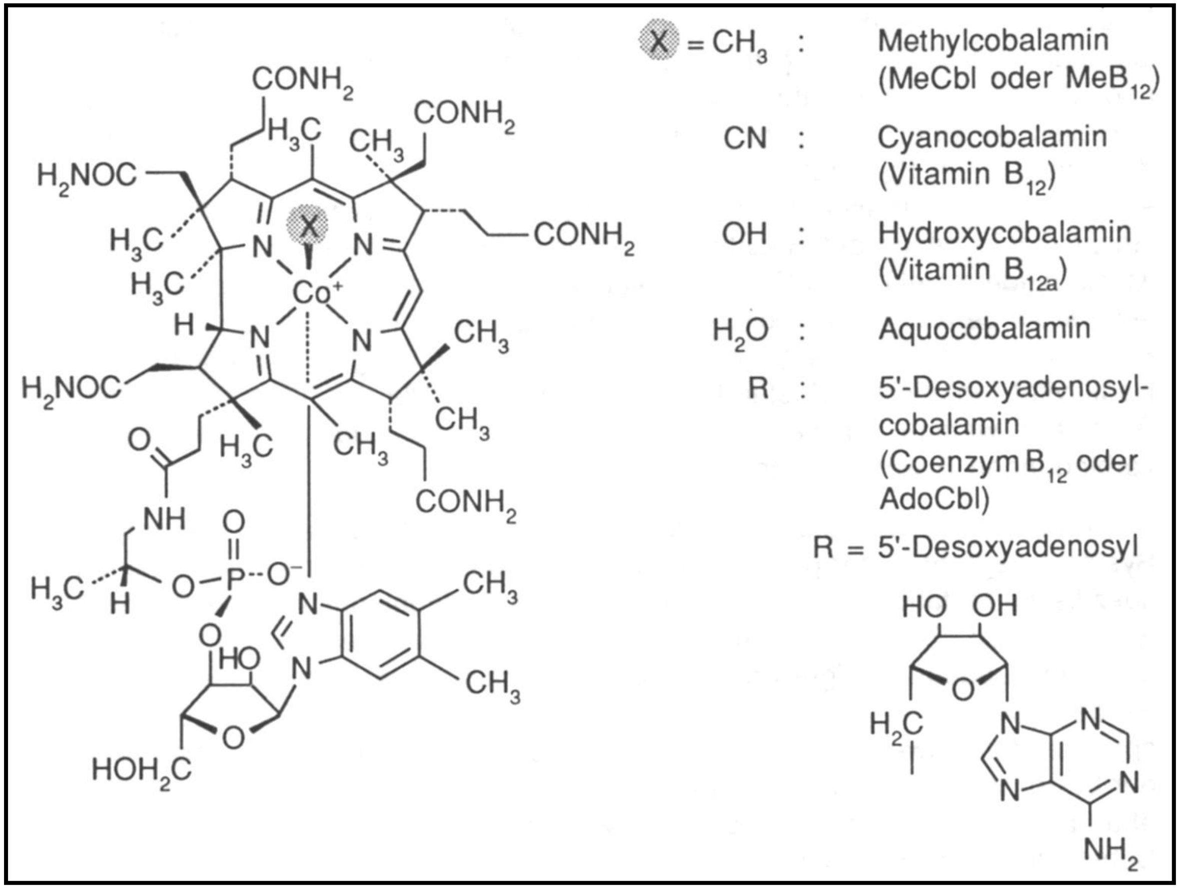
  (rose) (blue)

10. Chemistry of Transition Metals

The Iron Group

Bioinorganic chemistry of Cobalt

The adult human accommodates about 2.5 mg Cobalt, primarily bound in cobalamin (vitamin B_{12})



Alkylcobalamins participate in redox reactions, alkylations, and rearrangements.

Part of one-electron reductions or oxidations can be Co^{III}-, Co^{II}- and Co^{I}-species

Methylations (even of Hg^{2+}):

$Hg^{2+} \rightarrow HgCH_3^+ \rightarrow Hg(CH_3)_2$
(formation of methyl mercury)

10. Chemistry of Transition Metals

The Iron Group

Nickel(II) compounds

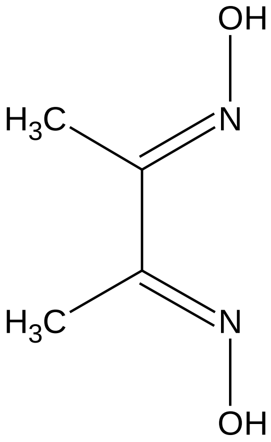
Hydrolysis

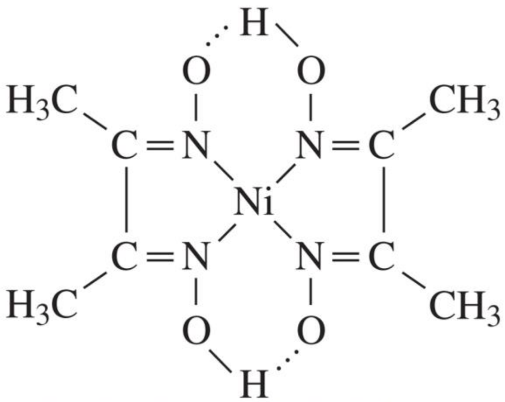
$Ni^{2+} + 2\ OH^- \rightarrow Ni(OH)_2\downarrow$ (green gel) $K_L = 2\cdot10^{-16}$ mol²/l²

Complexes

$Ni(OH)_2(s) + 6\ NH_3(aq) \rightarrow [Ni(NH_3)_6]^{2+}(aq) + 2\ OH^-(aq)$

$Ni^{2+}(aq) + 2\ H_2dmg(aq) \rightarrow [Ni(Hdmg)_2](s) + 2\ H^+(aq)$





Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung24-34b.jpg

Dimethylglyoxime (H_2dmg) **Bis(dimethylglyoximato)nickel(II)**

10. Chemistry of Transition Metals

The Iron Group

Nickel(II) compounds

Absorption spectra (octahedral complexes)

Electron configuration of Ni^{2+} [Ar]$3d^8$

Ground state ↑↓ ↑↓ ↑↓ ↑ ↑

1. excited state ↑↓ ↑↓ ↑ ↑ ↑↓

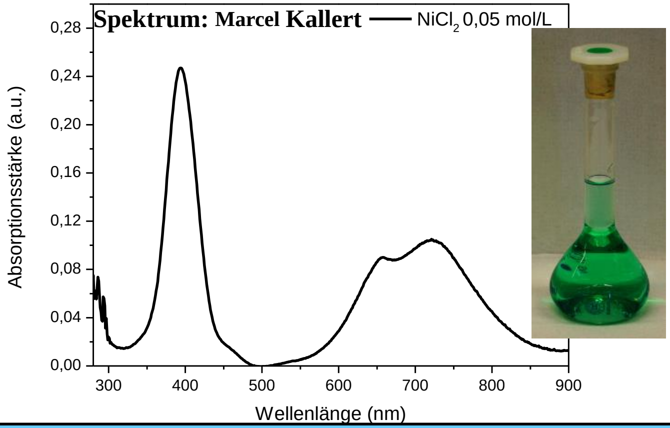
Free ion $S = \Sigma s = 1, L = |\Sigma l| = 3\ (F) \rightarrow {}^3F$

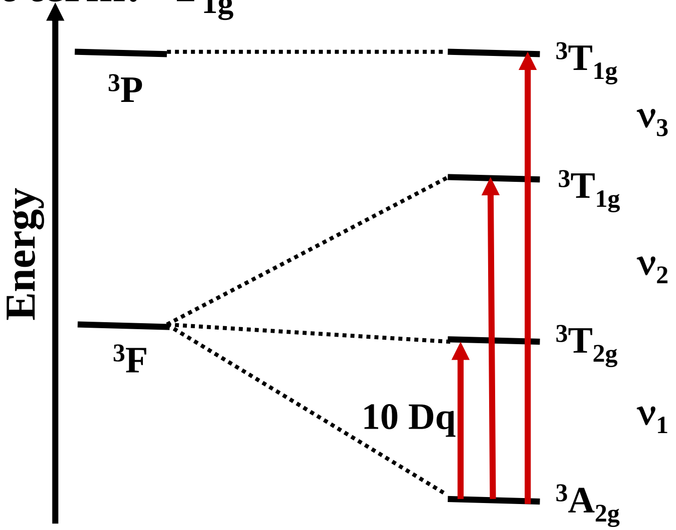
$S = \Sigma s = 1, L = |\Sigma l| = 1\ (P) \rightarrow {}^3P$

Coordinated ion split terms: ${}^3A_{2g}, {}^3T_{2g}, {}^3T_{1g}$

Split term: ${}^3T_{1g}$

$NiCl_2 \cdot 6H_2O(s) \rightarrow [Ni(H_2O)_6]^{2+}(aq) + 2\,Cl^-(aq)$



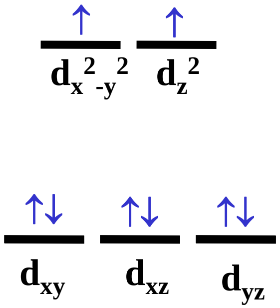
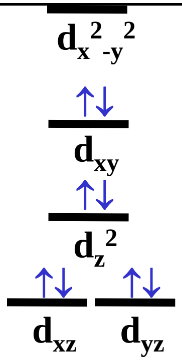
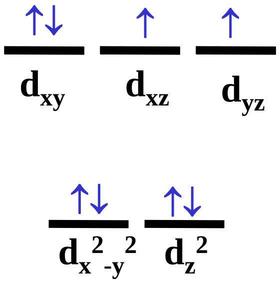


10. Chemistry of Transition Metals

The Iron Group

Nickel(II) compounds

Typical for Nickel(II) are octahedral, square-planar and tetrahedral complexes

Octahedral	Square-planar	Tetrahedral
H_2O NH_3 Ethylenediamine	Strong ligands, e.g. CN^- or ligands which force a square-planar arrangement, such as Hdmg	Cl^- Br^- I^-
Green, blue to violet paramagnetic	Yellow, red diamagnetic	Blue paramagnetic
		

10. Chemistry of Transition Metals

The Iron Group

Bioinorganic chemistry of Nickel(II)

a) Ureases: catalyse the decomposition of urea

$O{=}C(NH_2)_2 + H_2O \rightarrow NH_3 + O{=}C(OH)NH_2 \rightarrow NH_3 + CO_2$

(carbamidic acid is unstable!)

b) Hydrogenases

$2\,H^+ + 2\,e^- \leftrightarrows H_2$

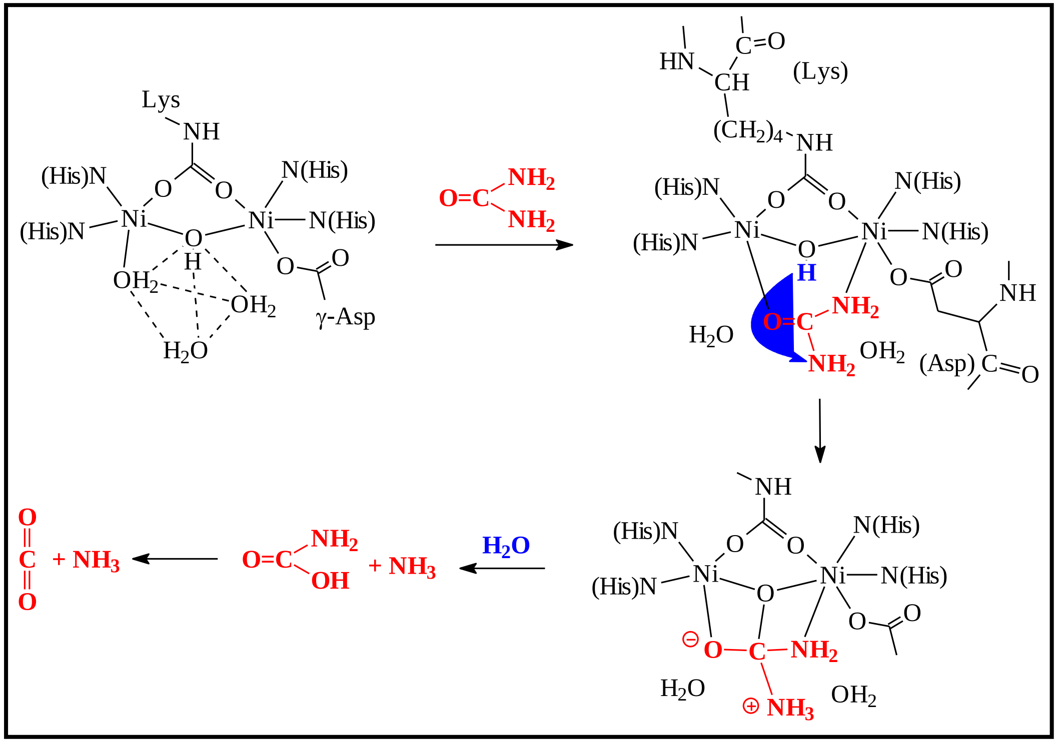
$CO_2 + H_2 \leftrightarrows CO + H_2O$

c) Acetyl-CoA-synthetases

HS-CoA + CO + Methyl-cobalamin

→ $MeC(O)S\text{-}CoA + H^+ + cobalamin^-$ (acetyl-CoA)

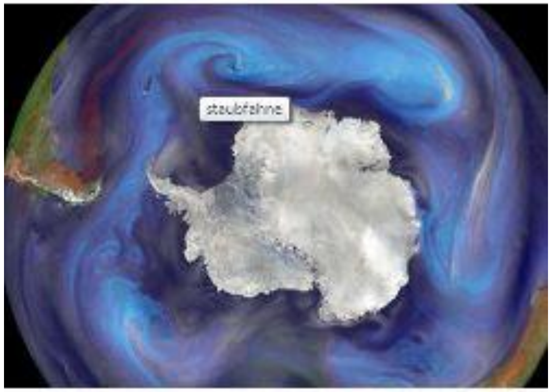
⇒ Acetyl-CoA = educt for acetylations in biochemistry



10. Chemistry of Transition Metals

The Iron-Platinum Group: Summary

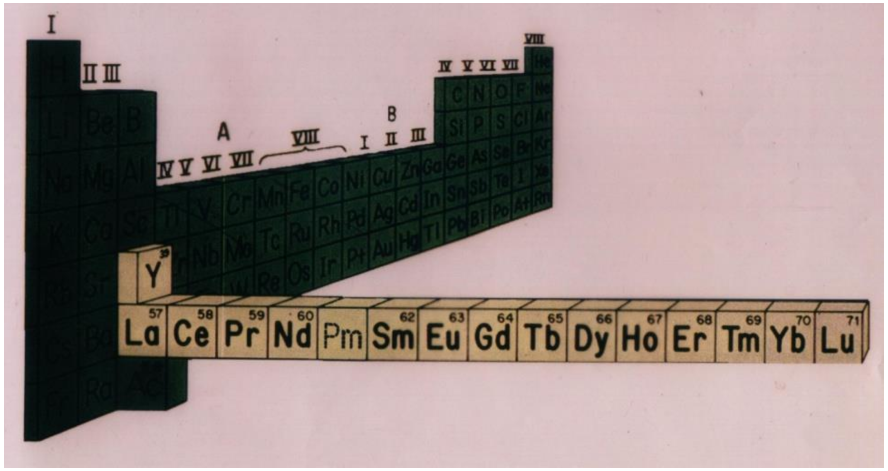
- **Fe, Co, and Ni are the only metals, which are ferromagnetic at room temperature**
- **These metals and their compounds, respectively are essential in biochemistry, mechanical and electrical engineering**
- **Fe fertilises marine phytoplankton and is thus a CO_2 sink with a strong impact on global climate → induced ice ages**
- **The nobel metals Ru, Rh, Pd and Pt as well as their oxides play an important role in heterogeneous catalysis**



Iron group	Cobalt group	Nickel group
„FeO“ antiferromagnetic Fe_3O_4 ferrimagnetic γ-Fe_2O_3 ferromagnetic α-Fe_2O_3 antiferromagnetic	CoO antiferromagnetic Co_3O_4 antiferromagnetic Co_2O_3 CoO_2	NiO antiferromagnetic Ni_2O_3 NiO_2
RuO_2 RuO_4	Rh_2O_3 RhO_2	PdO PdO_2
OsO_2 OsO_4	Ir_2O_3 IrO_2	PtO PtO_2

11. Chemistry of Lanthanides

Occurence and Production



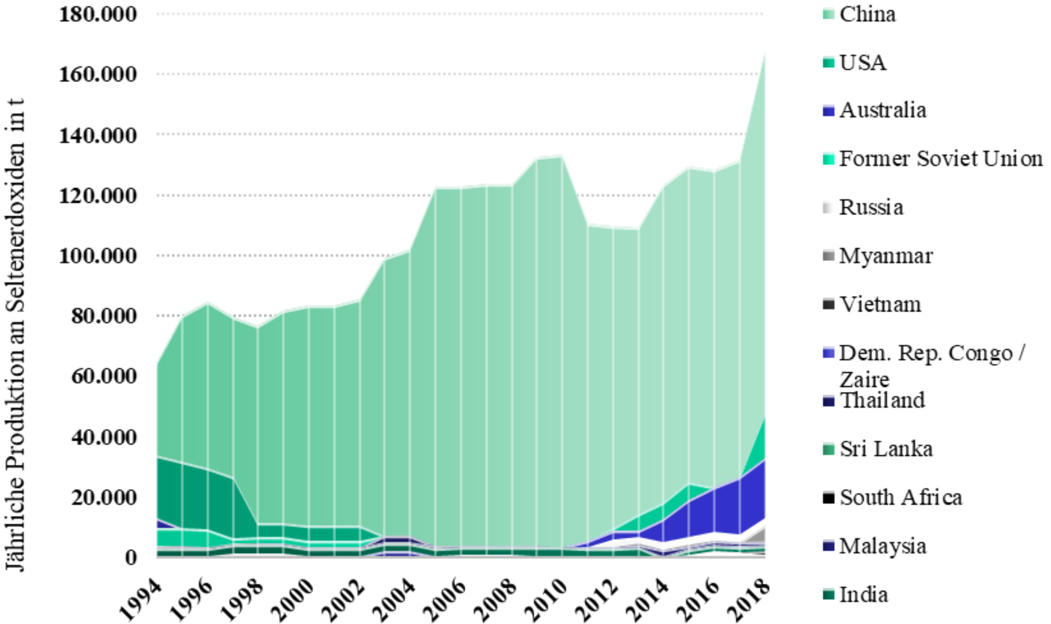
About 200 minerals known. Important are

• **Allanite**	$(Ce,Ca,Y)_2(Al,Fe)_3(SiO_4)_3(OH)$
• **Bastnaesite**	$(La,Ce\ Ln)(OH,F)CO_3$
• **Euxenite**	$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$
• **Fergusonite**	$YNbO_4$
• **Kolbeckite**	$ScPO_4{\cdot}2H_2O$
• **Loparite**	$(Ln,Na,Ca)_2(Ti,Nb)_2O_6$
• **Monazite**	$(La,Ce,Th,Ln)PO_4$
• **Xenotime**	$(Y,Ln)PO_4$

Annual production ~ 160.000 t
reserves ~ 120.000.000 t

China dominates REE world market!

Prices 2022:
About 15 (Sm) to 2500 (Tb) \$/kg Ln_2O_3



Lit.: R. Pöttgen, T. Jüstel, C. Strassert, Rare Earth Chemistry, DeGruyter 2020

11. Chemistry of Lanthanides

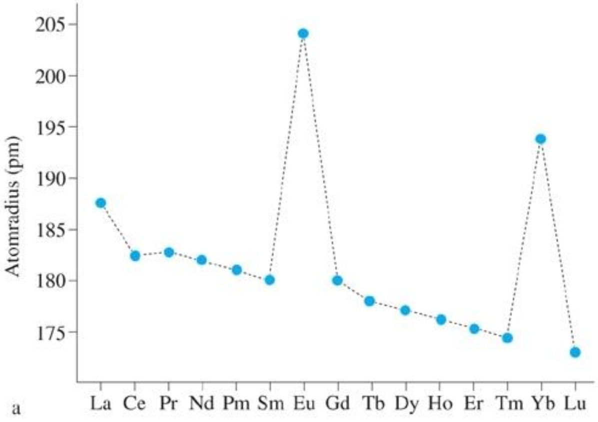
Physical properties

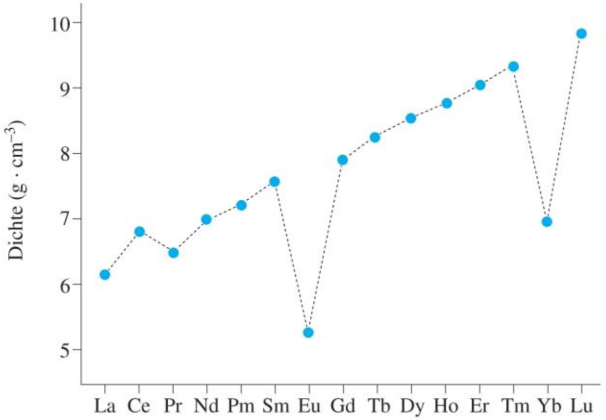
- The elements have high density (5-10 g/cm^3) and thus belong to the heavy metals
- Atom and ion radii decline within the series: Lanthanide contraction
- Dichte sowie Schmelz- und Siedepunkte nehmen mit ansteigender Ordnungszahl zu
- Metals and some alloys are ferromagnetic:

- Gd, Tb and Dy
- $Nd_2Fe_{14}B$ and $Pr_2Fe_{14}B$
- $SmCo_5$ and Sm_2Co_{17}

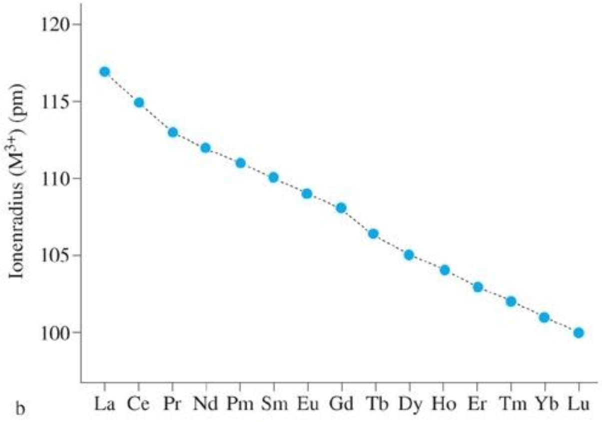
- Eu and Yb show strong deviation of their physical properties, since these atoms are rather large

Samples of the Rare Earth Metals (Fotograph by Julia Exeler)

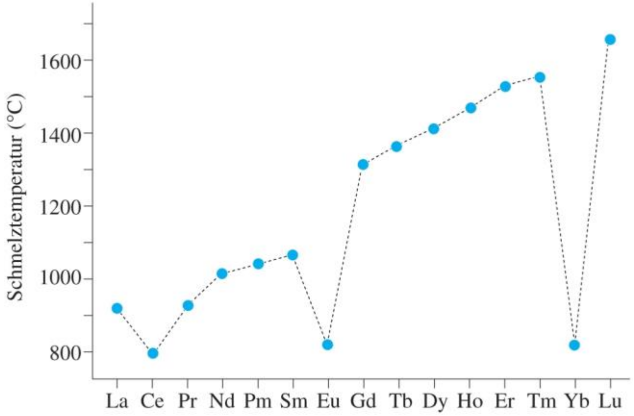




Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung25-04.jpg



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung25-03.jpg



Aus "Allgemeine und Anorganische Chemie" (Binnewies, Jäckel, Willner, Rayner-Canham), erschienen bei Spektrum Akademischer Verlag, Heidelberg; © 2004 Elsevier GmbH München. Abbildung25-05.jpg

11. Chemistry of Lanthanides

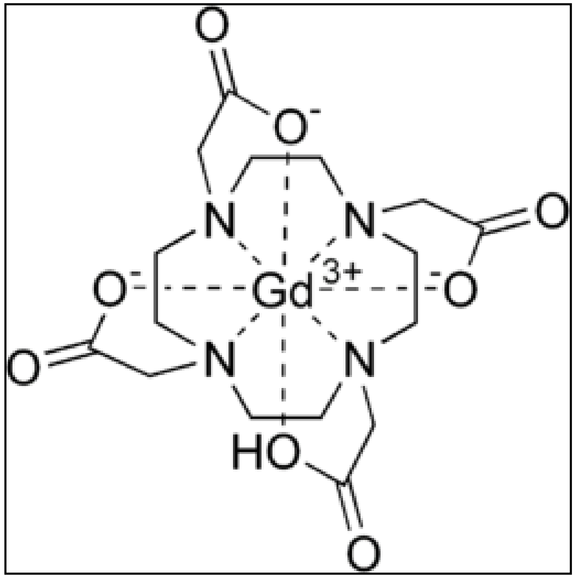
Chemical properties

- The metals are strong reducing agents, they react with air and water to form hydroxides
- Some alloys are the most strong magnetic materials
- The alkalinity and coordination number declines with chemical atomic number
- Stable oxidation states are +3, +2, +4, while weakly coloured ions are observed
- CFSE ~ 0 → lable complexes → macrocyclic and chelating ligands required
- Cations form in solution aqua complexes as for instance:
  $Nd(BrO_3)_3 \cdot 9H_2O = [Nd(H_2O)_9](BrO_3)_3$

$[Eu(ttfa)_3(phen)]$: Red emitting optical marker

$[Gd(DOTA)]^{2-}$: MRT contrast agent

with DOTA = 1,4,7,10-Tetraazacyclododecantetraacetate



- Ce^{4+}, Tb^{4+} and Pr^{4+} are (very) strong oxidizer
  $Ce^{4+} + e^- \leftrightarrows Ce^{3+}$ $E^0 = +1,61$ V (→ Cerimetry)
  $Tb^{4+} + e^- \leftrightarrows Tb^{3+}$ $E^0 = +3,1$ V
  $Pr^{4+} + e^- \leftrightarrows Pr^{3+}$ $E^0 = +3,2$ V

- Eu^{2+}, Sm^{2+}, Yb^{2+} and Tm^{2+} are strong reducing agents
  $Eu^{2+} \leftrightarrows Eu^{3+} + e^-$ $E^0 = -0,35$ V
  $Yb^{2+} \leftrightarrows Yb^{3+} + e^-$ $E^0 = -1,05$ V
  $Sm^{2+} \leftrightarrows Sm^{3+} + e^-$ $E^0 = -1,55$ V
  $Tm^{2+} \leftrightarrows Tm^{3+} + e^-$ $E^0 = -2,3$ V

11. Chemistry of Lanthanides

Chemical properties – Divalent cations

- Ln^{2+} ions show ionic radii comparable to the heavy alkaline earth metal cations

Sm^{2+}	122 pm	Ba^{2+}	135 pm
Eu^{2+}	117 pm	Sr^{2+}	118 pm
Tm^{2+}	103 pm	Ca^{2+}	100 pm
Yb^{2+}	102 pm		

  Therefore, the ion charge density, alkalinity and the chemical behaviour of the lanthanides is similar to the alkaline earth cations

- Isotypic solid state compounds

– EuF_2	SrF_2
– $EuSO_4$	$SrSO_4$
– YbF_2	CaF_2
– YbI_2	CaI_2

- Sulphates are hardly soluble, hydroxides are well soluble!

- Stability against oxidation: $Eu^{2+} > Yb^{2+} > Sm^{2+} > Tm^{2+}$ (instable in aqueous solution)

11. Chemistry of Lanthanides

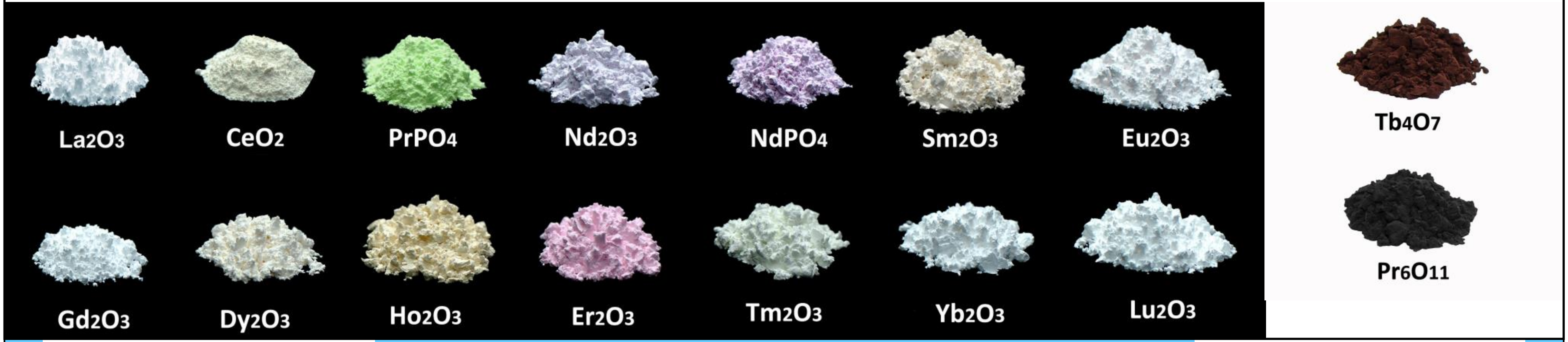
Optical properties

Cations : Incompletely filled 4f orbitals → $4f^n$-$4f^n$ as well as 4f5d and CT transitions

[Xe]	La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}
	Ce^{4+}	Pr^{4+}	Nd^{4+}				Sm^{2+}	Eu^{2+}	Dy^{4+}					Tm^{2+}	Yb^{2+}
								Tb^{4+}							
$4f^n$ n =	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Terms	$^1S_0$	$^2F_{5/2}$	$^3H_4$	$^4I_{9/2}$	$^5I_4$	$^6H_{5/2}$	$^7F_0$	$^8S_{7/2}$	$^7F_6$	$^6H_{15/2}$	$^5I_8$	$^4H_{15/2}$	$^3H_6$	$^2F_{7/2}$	$^1S_0$

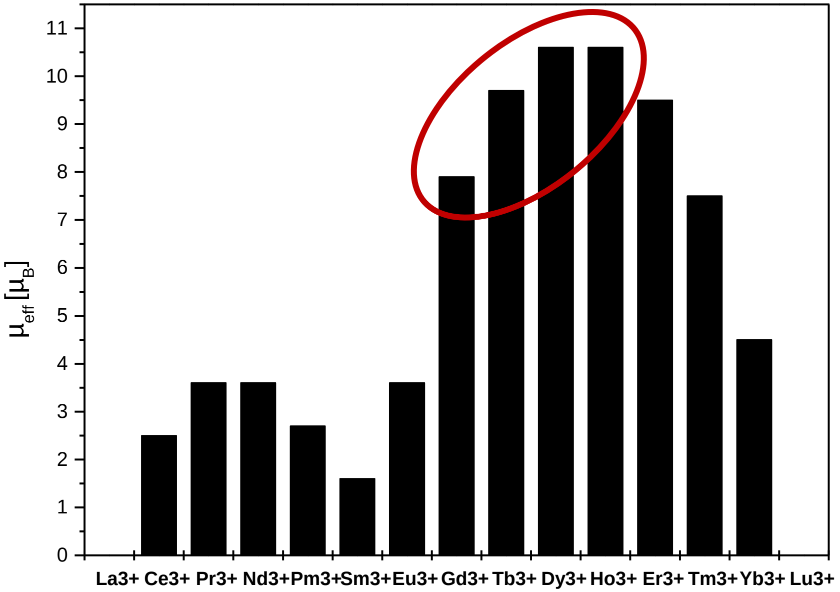
4f5d transitions Ce^{3+}, Pr^{3+}, Nd^{3+}, Tb^{3+}

MMCT transitions Some mixed-valence oxides and coordination compounds



11. Chemistry of Lanthanides

Magnetic properties



As cations strongly paramagnetic

- Gd^{3+} ⇒ magnetic contrast agents
- Tb^{3+} ⇒ Faraday rotators, e.g. KTb_3F_{10}
- Dy^{3+}/Ho^{3+} ⇒ Highest magnetic moment of all element cations ~ 10.6 μ_B
- For comparison: Fe^{3+}/Mn^{2+} $\mu_{eff} = 5.9\ \mu_B$

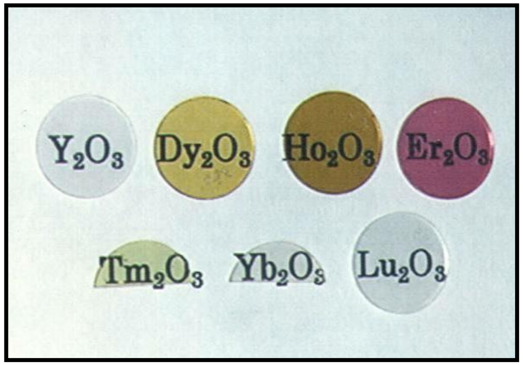
As component of ferromagnetic materials (solid state compounds)

- Garnets	$Y_3Fe_5O_{12}$ „YIG“ and $Gd_3Fe_5O_{12}$ „GdIG“
- Perovskites	$LnMO_3$ (with Ln = Gd, Tb and M = Mn, Fe, Co)
- Layered perovskites	Ba_2LnMO_6 (with Ln = Pr-Lu and M = Nb, Ta, Sb, Bi) Ln_2MIrO_6 (with Ln = La, Pr, Nd, Sm-Gd and M = Mg, Ni)

11. Chemistry of Lanthanides

Application areas of trivalent Ln ions

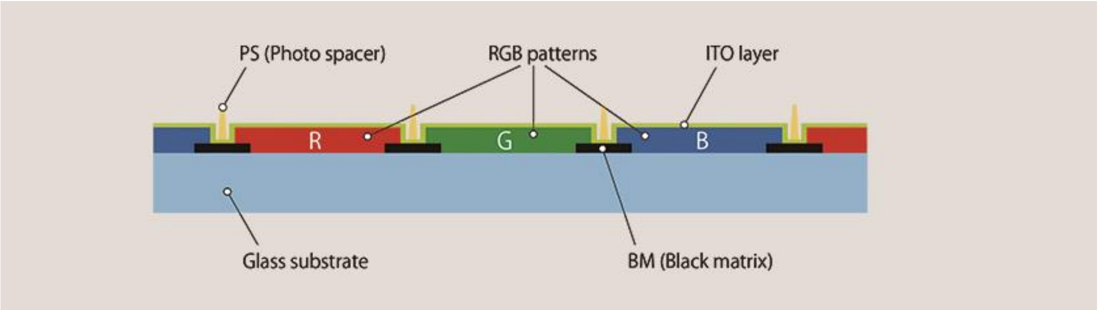
Y^{3+}	Super and ion conductors, alloys, laser gain media, luminescent materials
La^{3+}	High refractive glasses for lenses
Ce^{3+}	Scintillators, UV-Emitter, UV filter, luminecent materials, catalysts
Pr^{3+}	UV emitter, scintillators
Nd^{3+}	Laser gain media, coloured glasses
Sm^{3+}	Storage phosphors, afterglow pigments
Eu^{3+}	Bio marker, luminecent material, light sources, displays
Gd^{3+}	UV emitter, MRT and NMR contrast agents, UV-B emitter
Tb^{3+}	Faraday rotators, bio marker, light sources, displays, luminecent materials
Dy^{3+}	Laser gain media, optical thermometry
Ho^{3+}	Laser gain media
Er^{3+}	Laser gain media, NIR amplifier
Tm^{3+}	Laser gain media
Yb^{3+}	Laser gain media
Lu^{3+}	Scintillators, luminecent materials



11. Chemistry of Lanthanides

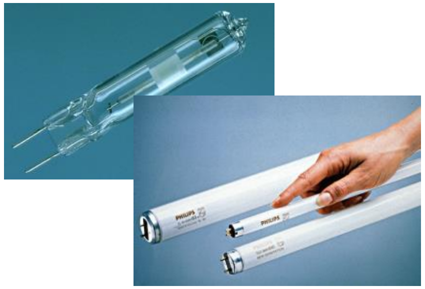
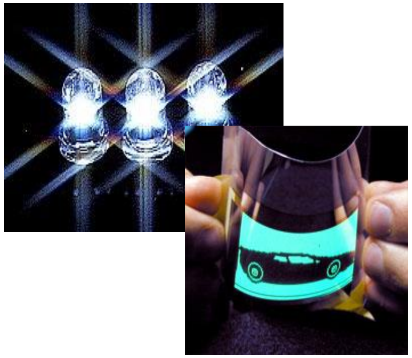
Application areas – Optical materials

La	La_2O_3	High refractive glasses for lenses e.g. in cameras and telescopes
Ce	Ce_2O_3/CeO_2	UV filter in light sources
Pr	Pr_2O_3/PrO_2	Colour filter in safety goggles
Nd	Nd_2O_3	Colour filter in lamp and display glass



11. Chemistry of Lanthanides

Application areas – Lighting technology

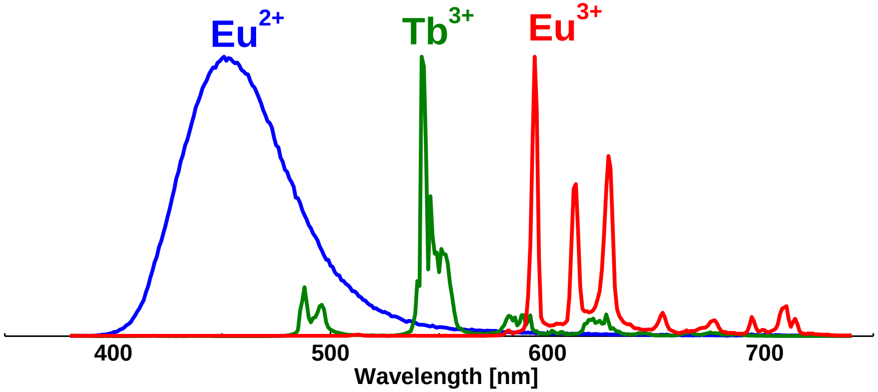
before 1870	since 1870	since 1930	since 1990
Chemical Oxidation	**Thermal Radiation**	**Low and high pressure discharges**	**Electroluminescence**
Mantles for gas lamps 99% ThO_2, 1% CeO_2	Incandescent and halogen light bulbs	Na and Hg vapour lamps, metal halide discharge lamps	Inorganic LEDs, OLEDs and PLEDs
			
Flint stones with mixed metal oxides 30% Fe, 70% La-Sm	Glass additives La_2O_3 / Ce_2O_3	Electrodes: Sc^{3+}, Y^{3+} Gas fillings DyI_3, HoI_3, TmI_3 Phosphors	Ceramic lenses Y, La, Gd, Lu Phosphors

11. Chemistry of Lanthanides

Application areas – Luminescence

Eu^{3+} ”Euro stars”

Eu^{2+} “Afterglow stars”

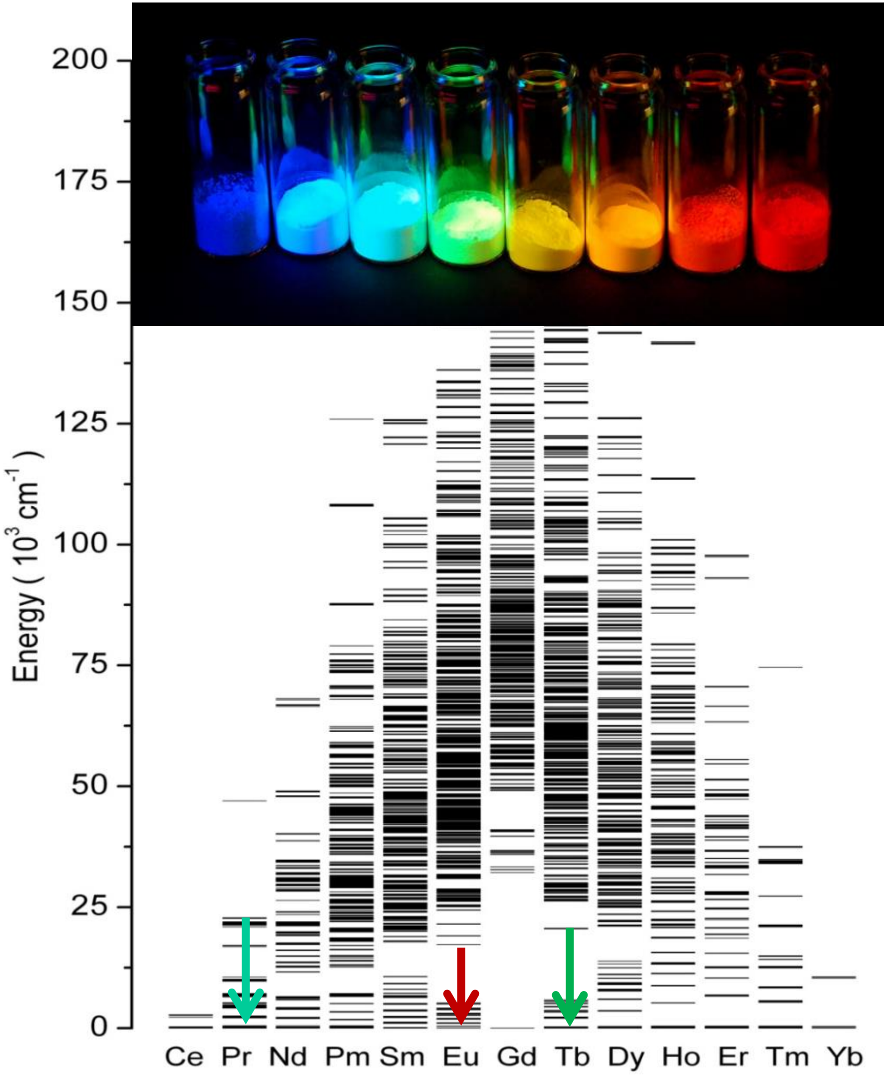


Rare earth ions

⇒ Many energy levels (N)

and optical transitions

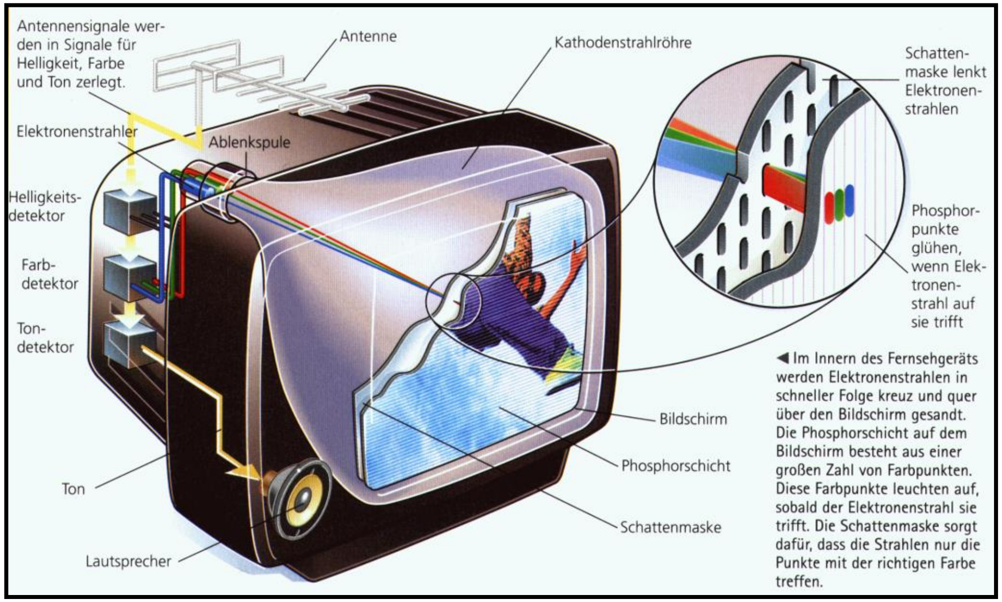
$$\boxed{N = \frac{(2o)!}{e!(2o-e)!}}$$



Eu^{3+} / Tb^{3+}: 3003 Energy levels!

11. Chemistry of Lanthanides

Application areas – Display technology



◀ Im Innern des Fernsehgeräts werden Elektronenstrahlen in schneller Folge kreuz und quer über den Bildschirm gesandt. Die Phosphorschicht auf dem Bildschirm besteht aus einer großen Zahl von Farbpunkten. Diese Farbpunkte leuchten auf, sobald der Elektronenstrahl sie trifft. Die Schattenmaske sorgt dafür, dass die Strahlen nur die Punkte mit der richtigen Farbe treffen.

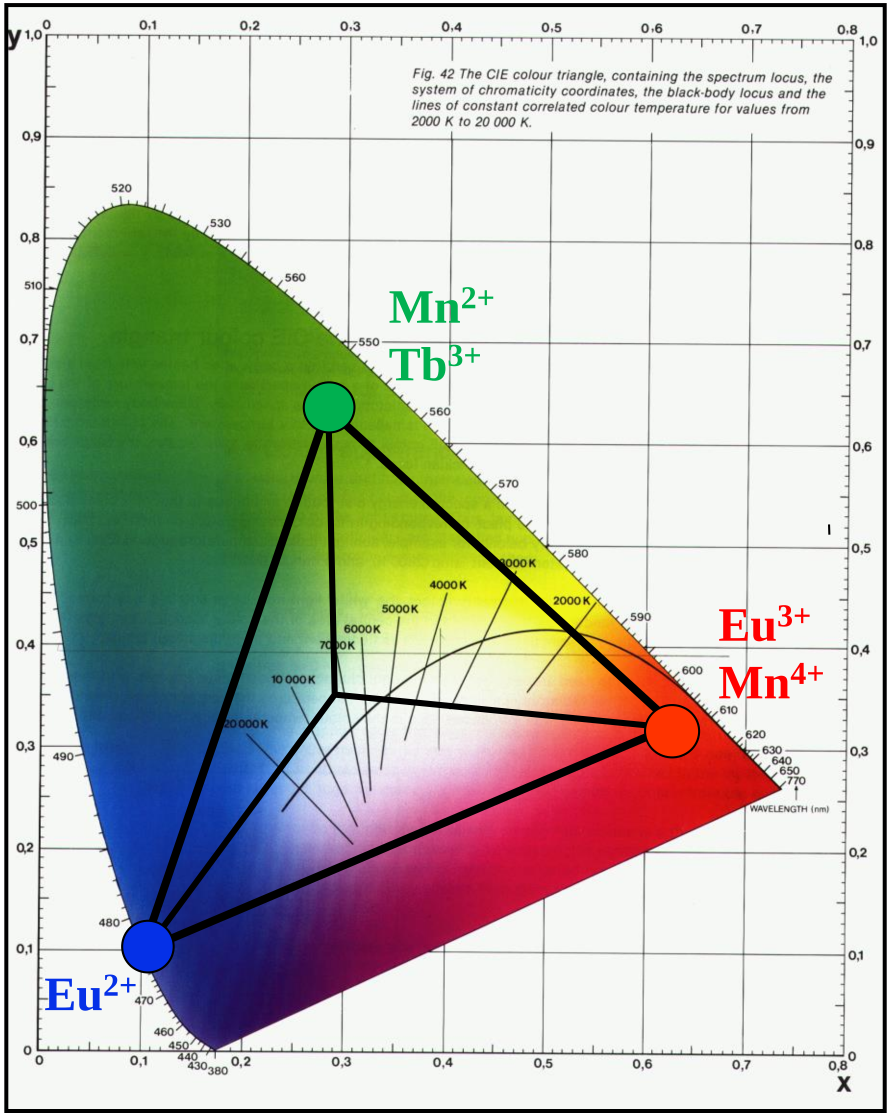


Fig. 42 The CIE colour triangle, containing the spectrum locus, the system of chromaticity coordinates, the black-body locus and the lines of constant correlated colour temperature for values from 2000 K to 20 000 K.

Cathode ray tubes

- $YVO_4:Eu^{3+}$
- $Y_2O_2S:Eu^{3+}$

Plasma displays

- $BaMgAl_{10}O_{17}:Eu^{2+}$
- $(Y,Gd)BO_3:Tb^{3+}$, $BaMgAl_{10}O_{17}:Eu^{2+}Mn^{2+}$
- $(Y,Gd)BO_3:Eu^{3+}$

11. Chemistry of Lanthanides

Application areas – Electrical engineering

Hard magnets	Super conductors	Ion conductors	Thermistors
Engines, generators, loudspeaker, microphones, telephones, head-phones, hearing aids magnetic couplers, sensors, suspension railways, lifting devices	NMR Devices Particle accelerators Fusion reactors SQUIDs	Fuel cells Lambda probes Sensors	Temperature sensors Inrush current limiter Voltage stabilizers
$Nd_2Fe_{14}B$ $SmCo_5$ Sm_2Co_{17}	$(La.Ba)_2CuO_4$ $YBa_2Cu_3O_7$	CeO_2:Ln Ln = La, Sm, Gd, Yb $La_2Mo_2O_9$ $LaCoO_3$:Sr $LaGaO_3$:Ba ZrO_2:Y	Sm_2O_3-Tb_2O_3