

Advanced Inorganic Chemistry

Part 2: Coordination Chemistry

1. Introduction

- Coordination chemistry deals with (metallic) coordination compounds.
- **Coordination compounds** are neutral **complexes** (e.g. $\text{Ni}(\text{CO})_4$) or **ionic compounds** in which at least one of the ions is a **complex** (e.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$).
- In a complex, a central metal atom or ion is surrounded by a set of **ligands**.
All metals (can) form complexes.
- Ligands can be molecules (e.g. CO , NH_3) or ions (e.g. OH^- in $\text{Na}[\text{Al}(\text{OH})_4]$).
- Complexes are combinations of **Lewis acids** (the central metal atoms) with a number of **Lewis bases** (the ligands).
- The ligand atom forming the bond to the central atom is called the **donor atom**.
- The central metal atom or ion (the Lewis acid) is the **acceptor atom**.
- The number of donor atoms in the first coordination sphere of the central atom is the **coordination number** (with $2 \leq \text{cn} \leq 12$).
- The coordination number is governed by the **size** of the central atom or ion, the **steric interactions** between the ligands, and the **electronic interactions** between the central atoms or ions and the ligands → **electronic structure**.

1. Introduction

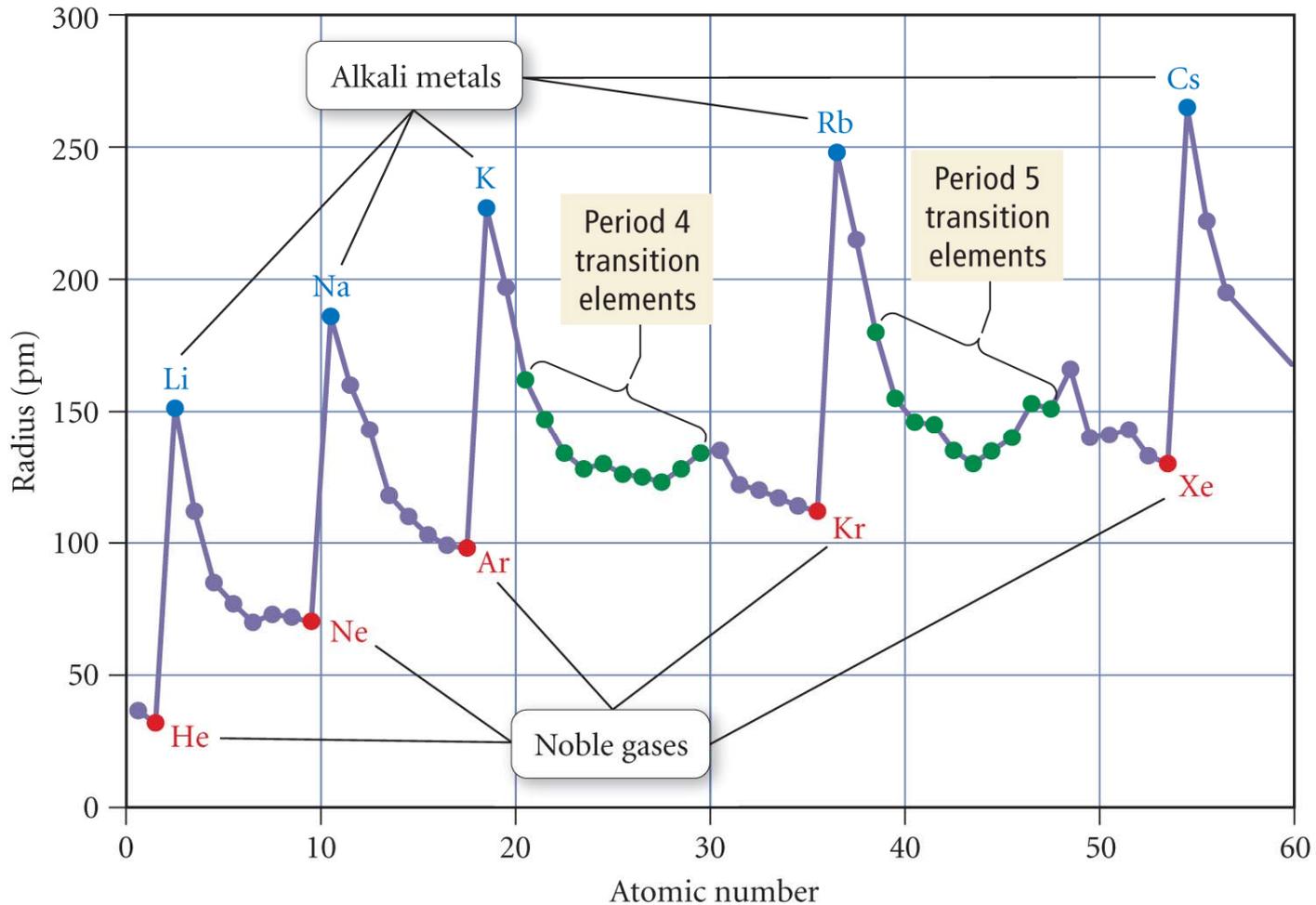
The most frequent oxidation states of transition metals

Ti IV	V III, IV, V	Cr III, VI	Mn II, IV, VII	Fe II, III	Co II, III	Ni II	Cu I, II
Zr IV	Nb V	Mo IV, VI	Tc –	Ru IV, VIII	Rh III	Pd II	Ag I
Hf IV	Ta V	W IV, VI	Re IV, VII	Os IV, VIII	Ir III, IV	Pt II, IV	Au I, III

s-Orbitale		f-Orbitale														d-Orbitale										p-Orbitale						
s ¹ s ²		f ¹ f ² f ³ f ⁴ f ⁵ f ⁶ f ⁷ f ⁸ f ⁹ f ¹⁰ f ¹¹ f ¹² f ¹³ f ¹⁴														d ² d ³ d ⁴ d ⁵ d ⁶ d ⁷ d ⁸ d ⁹ d ¹⁰										p ¹ p ² p ³ p ⁴ p ⁵ p ⁶						
1	1 H	2 He																														
2	3 Li	4 Be																														
3	11 Na	12 Mg																														
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	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	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	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	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Eka-Pt	111 Eka-Au	112 Eka-Hg	113 –	114 –	115 –	116 –	117 –	118 –
s-Block			f-Block														d-Block										p-Block					

1. Introduction

Atomic Radii



1. Introduction

Electronic configuration of the 3d transition elements

	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

Electronic configuration of the Lanthanides

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

1. Introduction

Principal features of the **geometrical structures** of metal complexes were found by the chemist **Alfred Werner** (Swiss, 1866-1919) with the help of optical and geometrical isomerism, reaction patterns, and conductivity measurements (hard compared to today with the possibility to use XRD, UV, IR etc.),

The colours (and magnetism) he could not explain.

Short definition:

Coordination compounds consist of neutral or ionic complexes in which a central atom or ion is bonded to more ligand atoms than expected with respect to its charge and position in the periodic table forming square-planar, tetrahedral, or octahedral surroundings.



Alfred Werner
1866 - 1919

2. Basic Nomenclature

Nomenclature of formulas and names follows the **IUPAC** rules.

Formulas:

Complexes are marked with parenthesis (square brackets []). The order is:

1. metal ion 2. charged ligands 3. neutral ligands (e.g. $[\text{Al}(\text{OH})(\text{H}_2\text{O})_5]\text{Cl}_2$)

Order of atoms is sometimes changed to show M-L bonds, like e.g. in $[\text{Fe}(\text{OH}_2)_6]^{2+}$.

Names:

1. First, ligands in alphabetic order are named, the add of “o” marks ionic ligands

Trivial names of ionic ligands are:

F ⁻	fluoro	OH ⁻	hydroxo	SCN ⁻	thiocyanato (rhodano)
Cl ⁻	chloro	O ₂ ²⁻	peroxo	CH ₃ O ⁻	methoxo
Br ⁻	bromo	S ²⁻	thio	CH ₃ S ⁻	methylthio
I ⁻	iodo	HS ⁻	mercapto	NO ₂ ⁻	nitro
O ²⁻	oxo	CN ⁻	cyano	NO ₃ ⁻	nitrato

Names of neutral ligands are:

H ₂ O	aqua	NH ₃	ammine
CO	carbonyl	NO	nitrosyle

2. Basic Nomenclature

Numbers of identical ligands are given in Greek as a prefix:

1	mono	4	tetra	7	hepta	10	deca
2	di	5	penta	8	octa	11	undeca
3	tri	6	hexa	9	nona	12	dodeca

Bridging ligands are marked with μ !

To avoid confusion, bis, tris, tetrakis as prefixes are used instead of di, tri, tetra etc.

$(\text{CH}_3)_2\text{NH}$ = dimethylamin is unambiguous, but: $((\text{CH}_3)\text{NH}_2)_2$ = two methylamin ligands =

bis(methylamin), not dimethylamin!

2. For anionic complexes, the suffix “ate” is added to the name of the central ion, sometimes with the Latin names like ferrate, aurate, plumbate, stannate for Fe, Au, Pb, Sn.
3. For anionic complexes, the name of the cation is named in front of the complex.
4. After the name, the oxidation state of the central ion is given in Roman numbers, but may be given also as Arabian numbers in parenthesis after the complex marking the charge of the complex.
5. First (in front of the name), a prefix which indicates the structure, like e.g. cis/trans, is given.

2. Basic Nomenclature

Examples



Potassiumtetrafluorooxochromate(III)



Sodiumtetrahydroxoaluminate(III)



Ammoniumhexachloroplumbate



Tetracarbonylnickel(0)



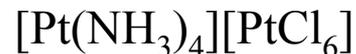
Pentaamminechlorocobalt(III)



Pentaaquahydroxyaluminate(III)chloride



Diamminetetrachloroplatinum(IV)



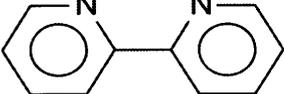
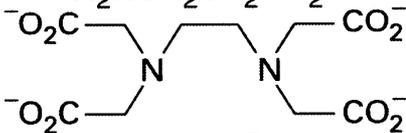
Tetraammineplatinum(0)hexachloroplatinate(VI)



Potassiumtetrachloroaurate(III)

2. Basic Nomenclature

Other examples, including chelating ligands, are:

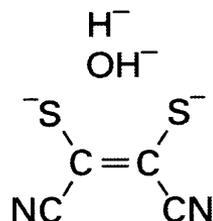
Name	Formula	Abbreviation	Classification
Acetylacetonato	$(\text{CH}_3\text{COCHCOCH}_3)^-$	acac	B(O)
Ammine	NH_3		M(N)
Aqua	OH_2		M(O)
2,2-Bipyridine		bpy	B(N)
Bromo	Br^-		M(Br)
Carbonato	CO_3^{2-}		M(O) or B(O)
Carbonyl	CO		M(C)
Chloro	Cl^-		M(Cl)
Cyano	CN^-		M(C)
Diethylenetriamine	$\text{NH}(\text{C}_2\text{H}_4\text{NH}_2)_2$	dien	T(N)
Ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	en	B(N)
Ethylenediaminetetraacetato		edta	S(N,O)
Glycinato	$\text{NH}_2\text{CH}_2\text{CO}_2^-$	gly	B(N,O)

*M: monodentate, B: bidentate, T: tridentate, Te: tetradentate, S: sexidentate. The letters in parentheses identify the donor atoms

2. Basic Nomenclature

Hydrido
Hydroxo

Maleonitriledithiolato



mnt

M
M(O)
B(S)

Nitrilotriacetato

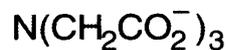
Nitro, nitrito-*N*

Oxo

Oxalato

Nitrito

Tetraazacyclotetradecane

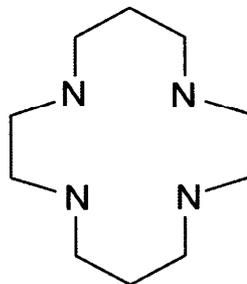


nta

ox

cyclam

Te(N,O)
M(N)
M
B(O)
M(O)
Te(N)



Thiocyanato

Isothiocyanato

2,2',2''-Triaminotriethylamine



trien

M(S)
M(N)
Te(N)

Complexes with identical/non-identical ligands are named homoleptic/heteroleptic.

3. *Geometry of Complexes and Coordination Polyhedra*

The main structural characteristics of complexes are their **coordination numbers** and **coordination polyhedra**. The number of coordinated atoms or ligands and the type of the coordination polyhedra depend on the size of the central atom or ion, the identity of the ligands and their steric interactions, and the electronic interactions between the central atom or ion and the ligands.

Coordination numbers can vary between 2 and 12. Those with 4, 5, and 6 are the most important coordination numbers.

Coordination number 2

(mainly in solution)



Complexes with coordination number 2 are rare. They are only formed by central atoms of the group 11, i.e. Cu^+ , Ag^+ and Au^+ (e.g. $[\text{AgCl}_2]^-$).

The complexes are linear. Bent geometries as they are found in three-atomic molecules like H_2O have never been found with complexes.

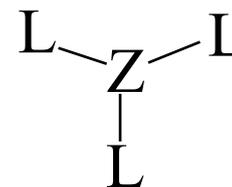
3. Geometry of Complexes and Coordination Polyhedra

Coordination number 3

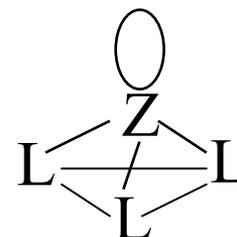
Complexes with coordination number 3 are seldom.

Examples are HgI_3^- , $[\text{Pt}(\text{P}\{\text{C}_6\text{H}_5\}_3)_3]$.

The complexes are **trigonal planar**, sometimes slightly deformed. There is no possibility for the formation of isomers in complexes of type $[\text{ZL}_2\text{L}']$ or $[\text{ZLL}'\text{L}'']$



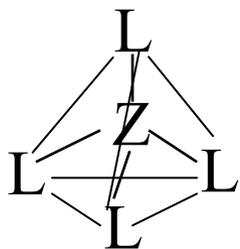
Due to a free electron pair, some complexes of cn 3 like NH_3 , OR_3^+ or SR_3^+ have the form of a **trigonal pyramid**. They are said to be pseudo- or ψ -tetrahedral as the free electron pair and the three ligands occupy the four corners of a tetrahedron.



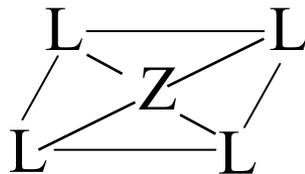
3. Geometry of Complexes and Coordination Polyhedra

Coordination number 4

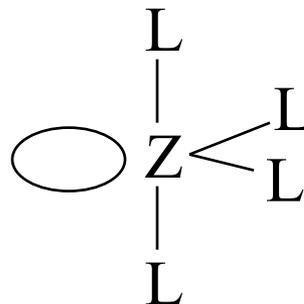
For the very common coordination number 4, four different structures are possible:



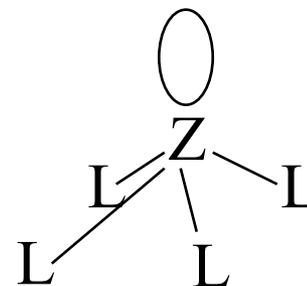
tetrahedral



square planar



bisdiphenoidal



tetragonal pyramidal

Examples:

tetrahedral: $[\text{Al}(\text{OH})_4]^-$, $[\text{Cd}(\text{CN})_4]^{2-}$, $[\text{BF}_4]^-$

square planar: $[\text{PtCl}_4]^{2-}$, $[\text{Ni}(\text{diacetyldioxim})_2]$, $[\text{AuF}_4]^-$

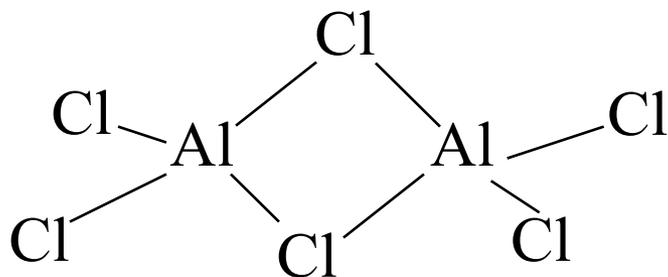
bisdiphenoidal: main group elements with a free electron pair like $[\text{AsF}_4]^-$, $[\text{SbCl}_4]^-$

The bisdiphenoid can become distorted towards a tetragonal pyramid when the electron pair needs more space.

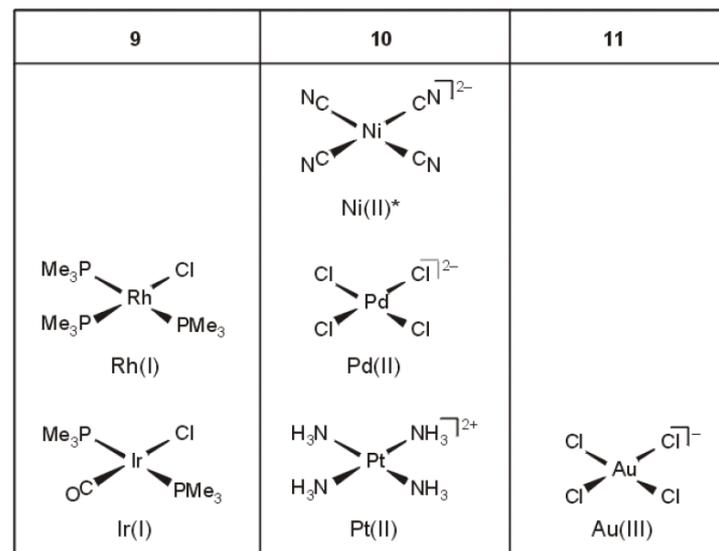
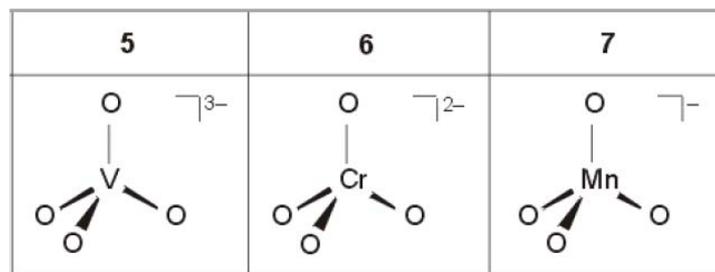
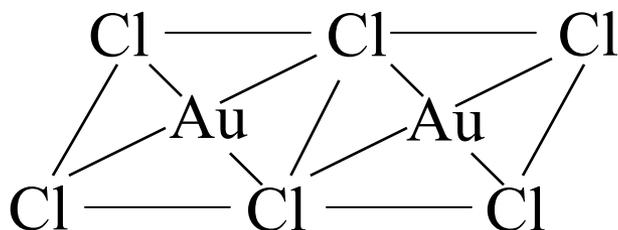
3. Geometry of Complexes and Coordination Polyhedra

Sometimes there is a cn of 4 although the formula suggests cn 3:

Gaseous AlCl_3 for instance is dimeric, i.e. is built from two tetrahedra sharing one edge so that two chloro ligands are bridging and four are end standing



In the case of $(\text{AuCl}_3)_2$, the central atoms are square planar coordinated by 4 chloro ligands with 2 of them in bridging positions.

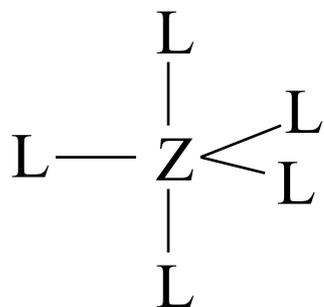


3. Geometry of Complexes and Coordination Polyhedra

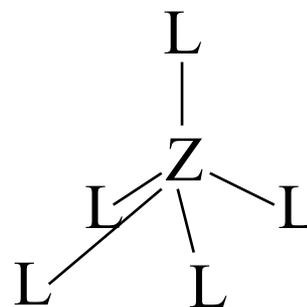
Coordination number 5

This coordination number is formed not as often than cn 4.

There are two different geometries possible:



trigonal bipyramid



tetragonal pyramid

Examples:

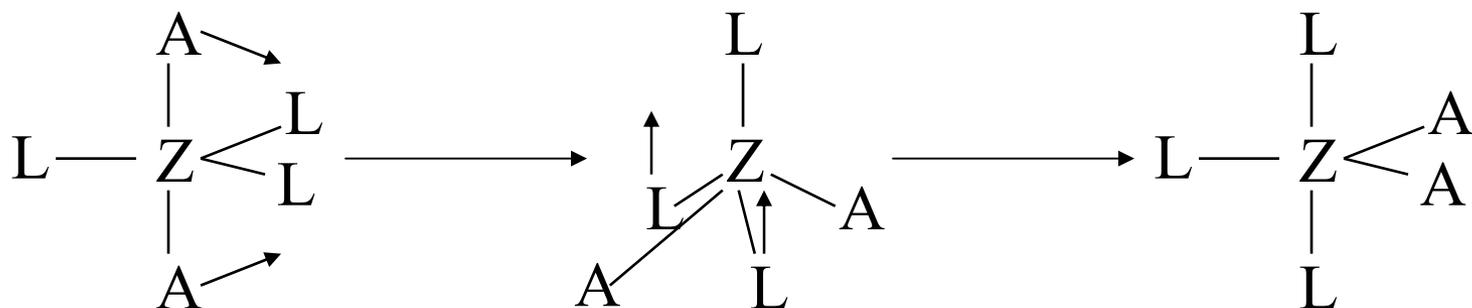
Trigonal bipyramid: $\text{Fe}(\text{CO})_5$, $[\text{SnCl}_5]^-$

Tetragonal pyramid: $[\text{VO}(\text{acetylacetonate})_2]$

In the trigonal bipyramidal coordination, one can distinguish between **equatorial** and **apical positions** of the ligands.

3. Geometry of Complexes and Coordination Polyhedra

Slight deformations of the trigonal bipyramid in the way indicated below, lead to the formation of a tetragonal pyramid.



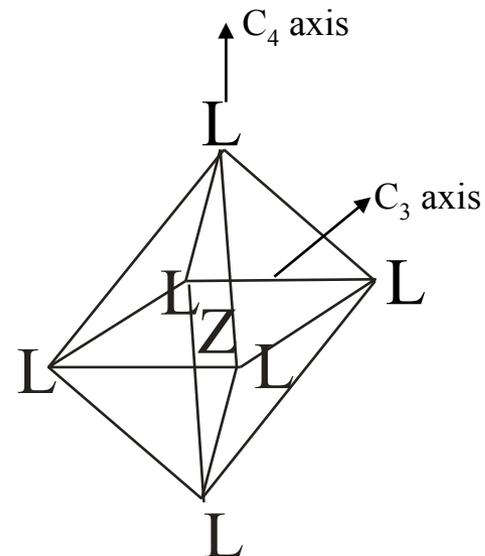
This can lead to an internal **exchange** of the apical and equatorial positions of the **ligands**.

3. Geometry of Complexes and Coordination Polyhedra

Coordination number 6

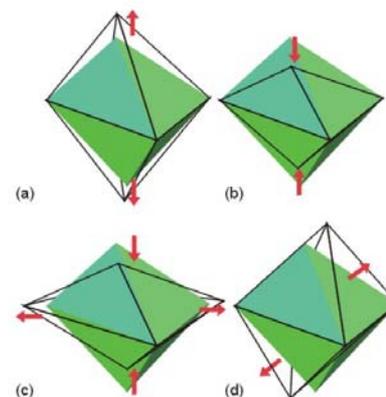
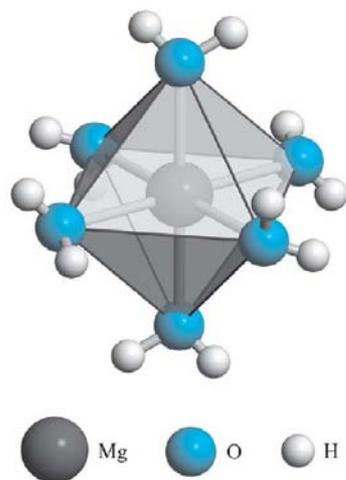
Of the possible coordination geometries (octahedral, trigonal prismatic, trigonal antiprismatic and hexagonal planar), only the octahedral, the trigonal prismatic (e.g. for Cd), and the antiprismatic coordination is observed in coordination compounds.

Frequently, the octahedra are not ideal, i.e. not all edges are equally long. This may be caused by an elongation or a compression along the 4 fold axis or by an elongation along the 3 fold axis Resulting in a trigonal antiprismatic polyhedron.



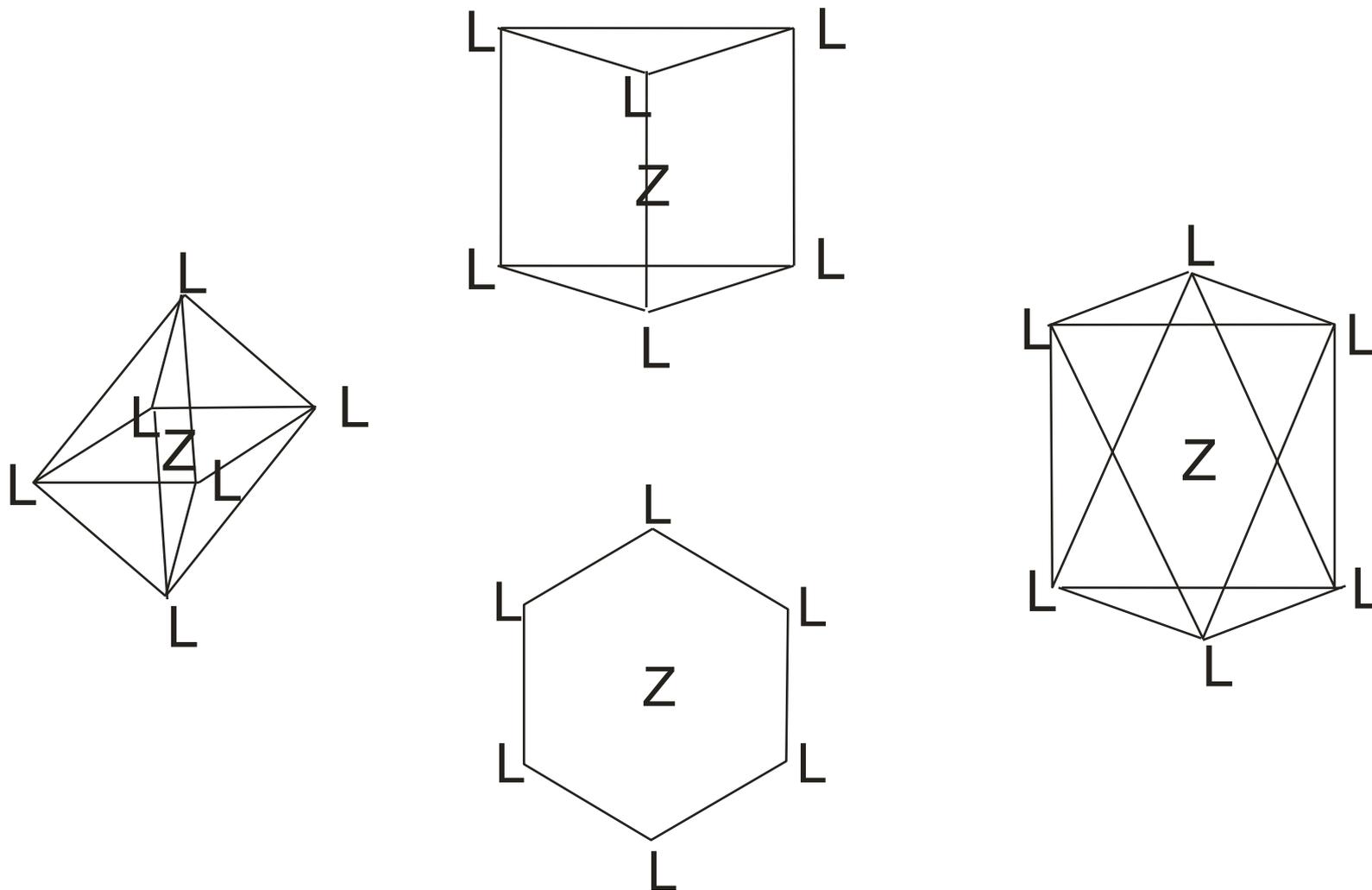
[Mg(H₂O)₆]²⁺

Types of distortions of octahedra



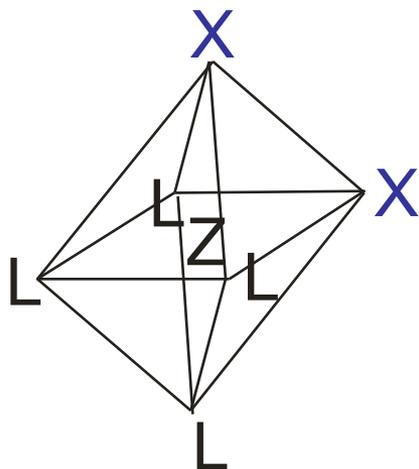
3. Geometry of Complexes and Coordination Polyhedra

Possible arrangements of 6 ligands L around a central atom Z (please name)

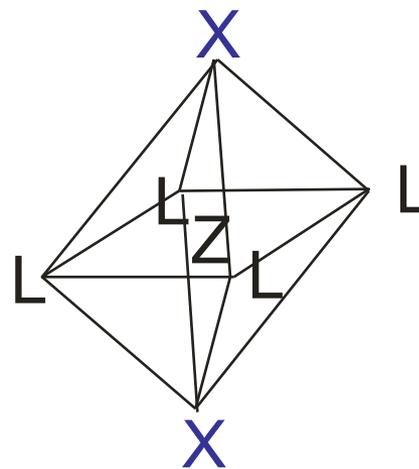


3. Geometry of Complexes and Coordination Polyhedra

In octahedral complexes of composition $[ZL_4X_2]$, two different arrangements of the ligands X are possible, leading to a **cis** or a **trans configuration**.



cis

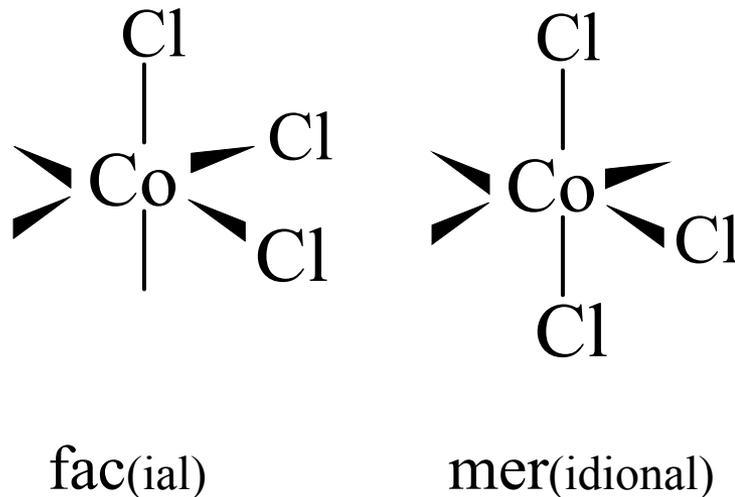


trans

Cis and trans configurations of octahedral $[ZL_4X_2]$ complexes

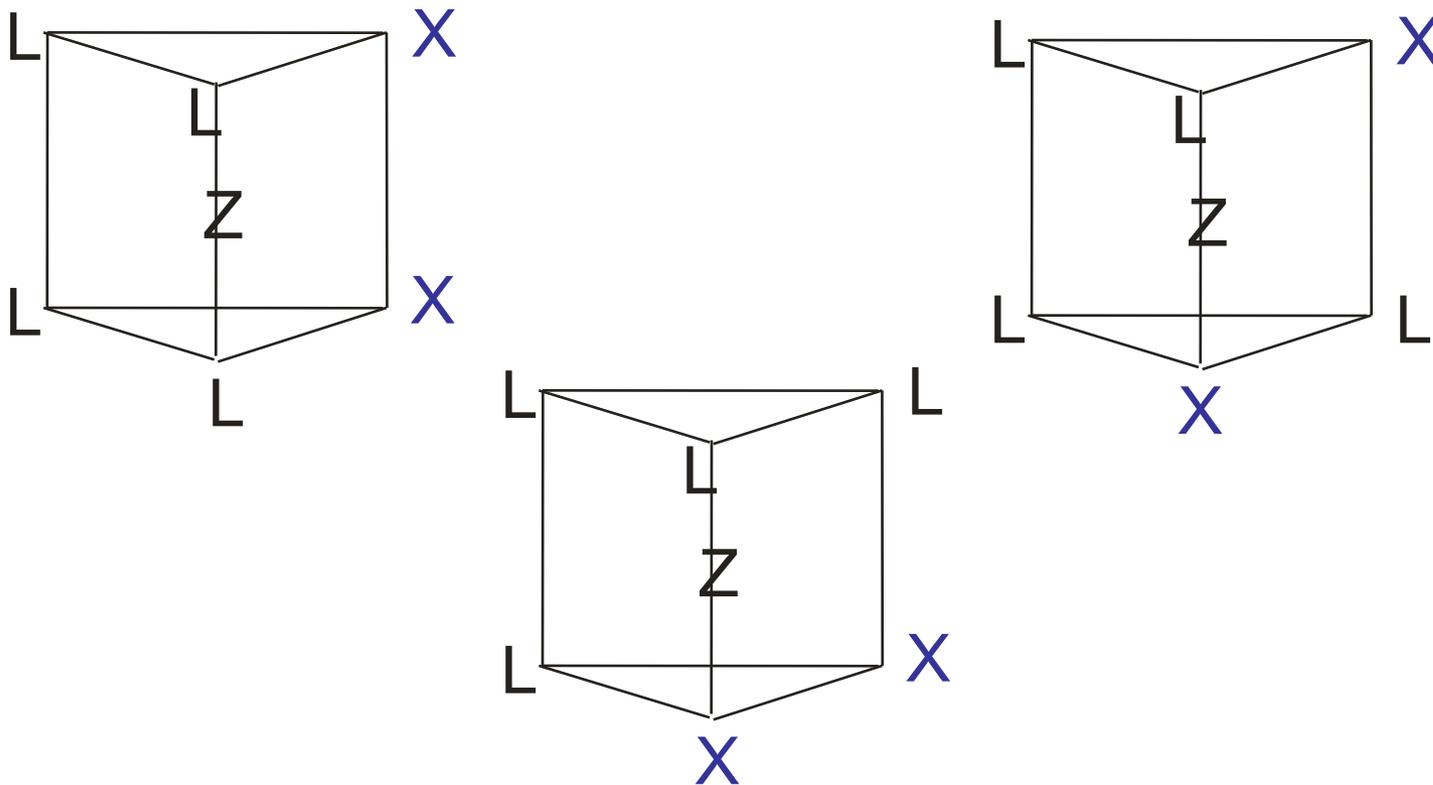
3. Geometry of Complexes and Coordination Polyhedra

In octahedral complexes of composition $[ZL_3X_3]$, identical ligands can be arranged in a manner that they all are in a cis position, i.e. arranged on an octahedral face (facial) or that two of them are in a trans position, i.e. three on a meridian (meridonal).



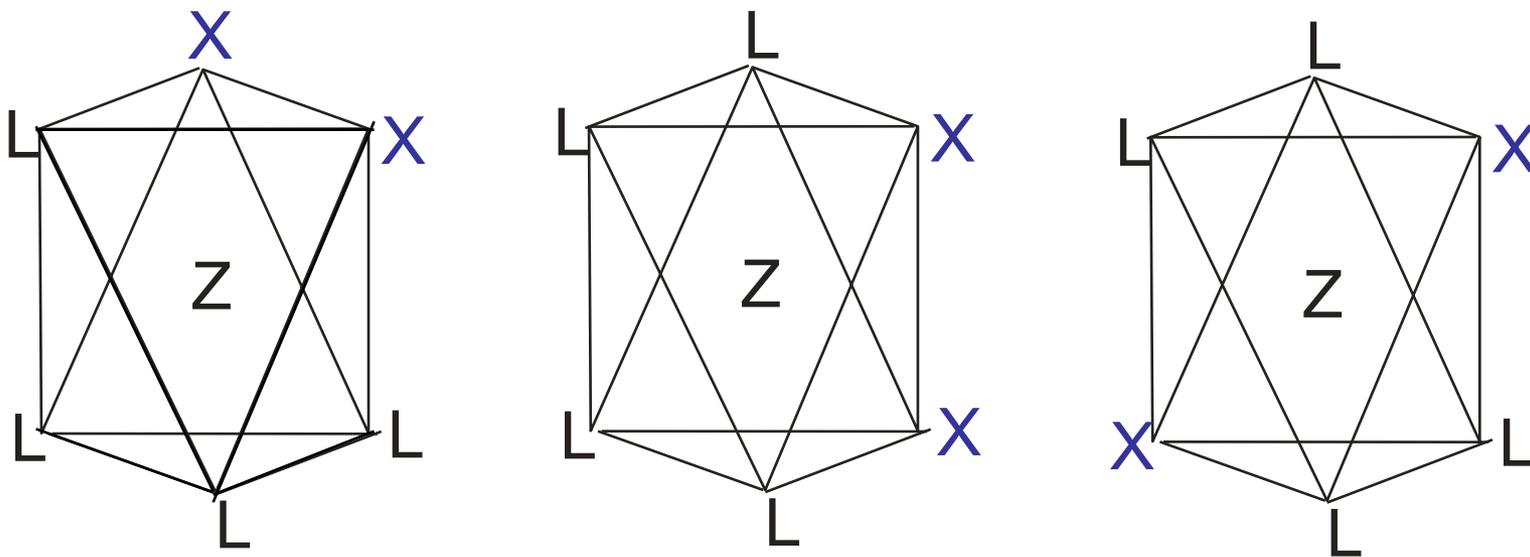
Fac(ial) and **mer(idional)** configurations of octahedral $[ZL_3X_3]$ complexes

3. Geometry of Complexes and Coordination Polyhedra



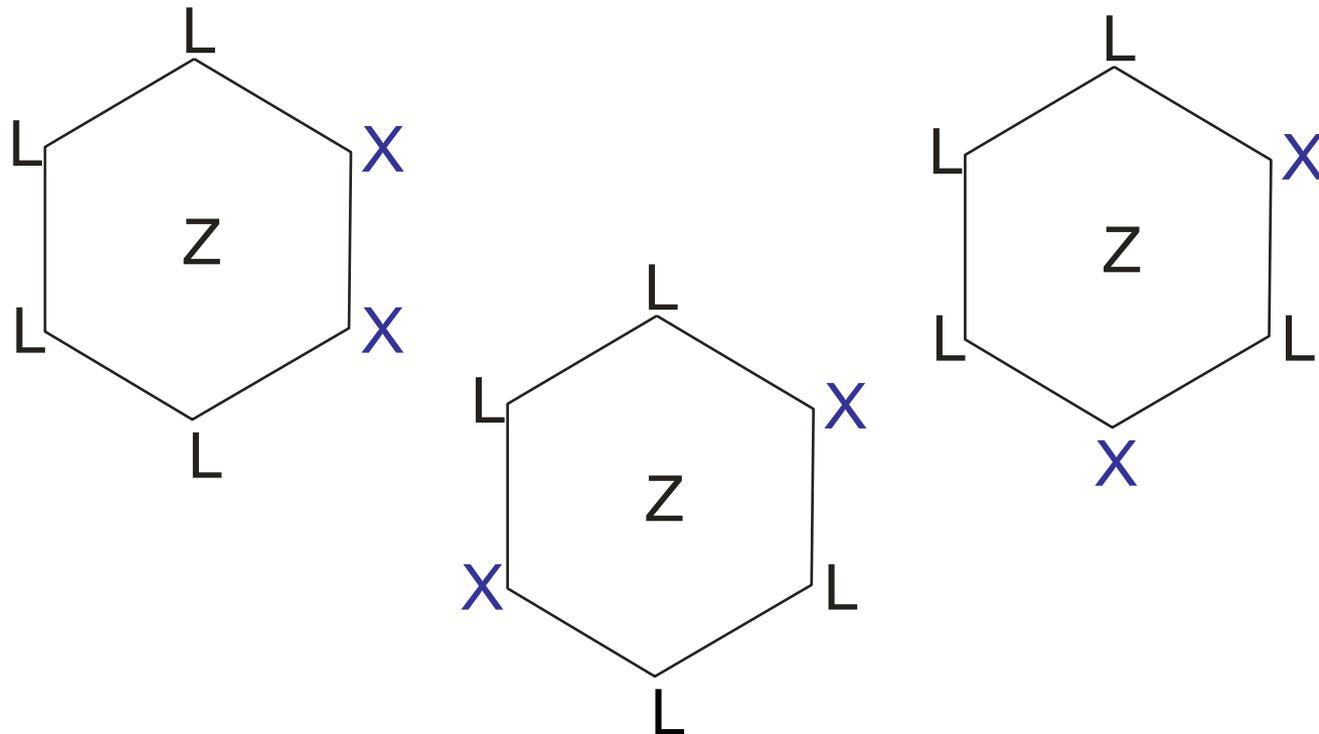
Possible arrangements of the ligands in a trigonal prismatic $[ZL_4X_2]$ complex with a trans and two cis configurations of the ligands X

3. Geometry of Complexes and Coordination Polyhedra



Possible arrangements of the ligands in a trigonal antiprismatic (octahedron elongated/compressed along C_3) complex of composition $[ZL_4X_2]$.

3. Geometry of Complexes and Coordination Polyhedra

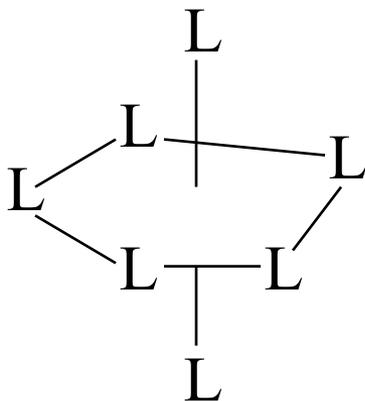


Possible arrangements of the ligands in a hexagonal planar $[ZL_4X_2]$ complex

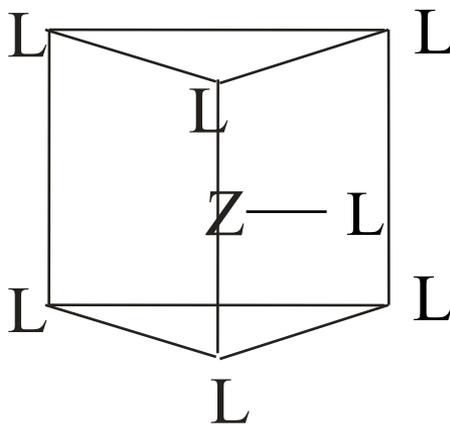
3. Geometry of Complexes and Coordination Polyhedra

Coordination number 7

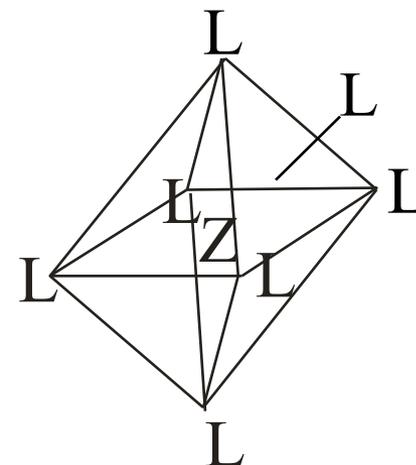
3 different co-ordination polyhedra exist for CN 7. The energetic difference between them is low. Sometimes the coordination polyhedron changes when the cation changes



pentagonal bipyramid



monocapped trigonal prism



monocapped octahedron

Examples:

pentagonal bipyramid: $[\text{UO}_2\text{F}_5]^{3-}$, $[\text{HfF}_7]^{3-}$

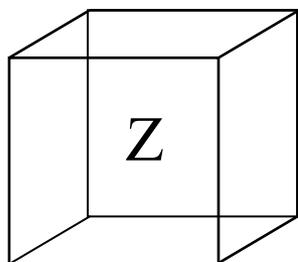
monocapped trigonal prism: $[\text{TaF}_7]^{3-}$

monocapped octahedron: $[\text{IF}_6]^-$, $[\text{NbOF}_6]^{3-}$

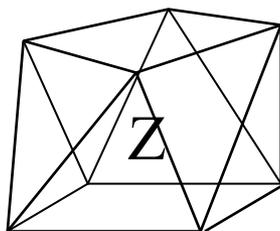
3. Geometry of Complexes and Coordination Polyhedra

7. Coordination number 8

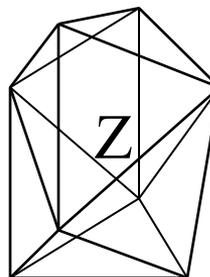
4 different coordination polyhedra exist for cn 8. The energetic differences between them are low. They become lower with increasing cn .



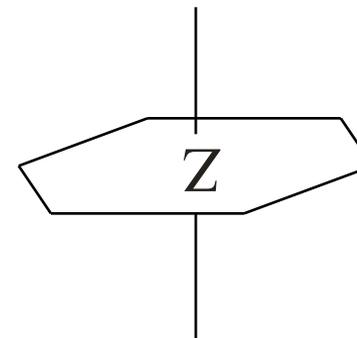
cube



square antiprism



dodecahedron



hexagonal bipyramid

Examples:

Cube: seldom, but $[\text{UF}_8]^{3-}$

Square antiprism: more stable than cube $[\text{TaF}_8]^{3-}$, $[\text{ReF}_8]^{3-}$

Dodecahedron: $[\text{Mo}(\text{CN})_8]^{4-}$, $[\text{W}(\text{CN})_8]^{4-}$

Hexagonal bipyramid: $[\text{UO}_2(\text{acetylacetonate})_3]^-$

4. *Isomerism and Chirality*

Isomerism in coordination compounds

Isomers (equal in parts) are molecules having the same molecular formula, but different constitution, configuration, or conformation, i.e. having different arrangement of the atoms in space. The structures of isomers are not superimposable.

Isomers have different physical and/or chemical properties.

There are two main groups of isomers:

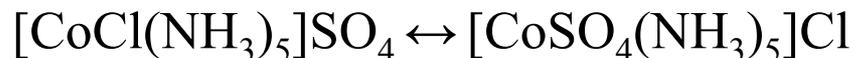
- **Structural isomers** have different constitution, i.e. they contain the same number and kind of atoms, but differ in their connectivity and bond structure, respectively.
- **Stereoisomers** have the same constitution but different configuration or conformation, i.e. they contain the same number and kind of atoms with the same connectivity between them, but differ in the spatial arrangement of the atoms.

In complex chemistry, additionally the terms ligand, linkage, ionization, hydrate, coordination, and optical isomerism are used.

4. Isomerism and Chirality – Structural Isomers

- Ionization isomerism

Complex salts which show ionization isomerism are composed in such a way that a ligand and a counter ion change their places, e.g.



- Solvate or hydrate isomerism

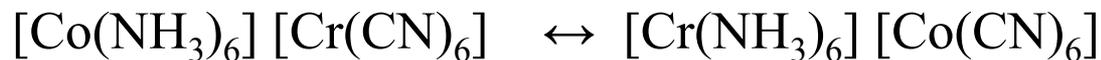
Is a special case of ionization isomerism. Here solvate or water molecules are present as ligands or as solvent or water of crystallization, e.g.



4. Isomerism and Chirality – Structural Isomers

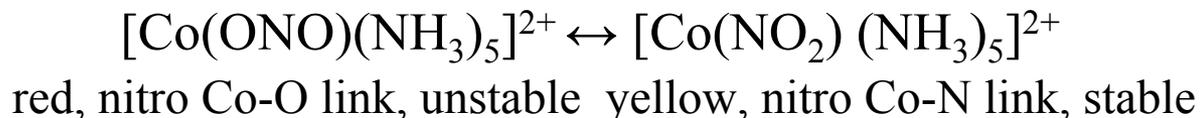
- Coordination isomerism

If in a complex salt both anion and cation are complexes, there can be an exchange of all the ligands between cation and anion, e.g.



- Linkage isomerism I

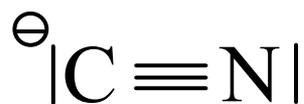
If a ligand contains more than one atom with a free electron pair, the ligand may be bonded to the central atom via different atoms, e.g.



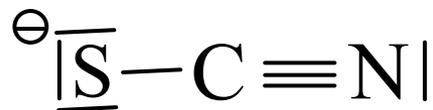
4. Isomerism and Chirality – Structural Isomers

- Linkage isomerism II

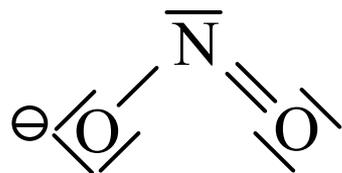
If a ligand contains more than one atom with a free electron pair, the ligand may be bonded to the central atom via different atoms, e.g.



bonding via C → cyano-
bonding via N → isocyano-



bonding via S → thiocyanato-
bonding via N → isothiocyanato-



bonding via N → nitro-
bonding via O → nitrito-

4. Isomerism and Chirality - Stereoisomers

Stereoisomers can be divided in two groups:

- **Enantiomers**, i.e. stereoisomers where different isomers are non-superimposable mirror-images of each other and
- **Diastereoisomers**, i.e. all stereoisomers that are not enantiomers. Diastereomers are again subdivided into *cis-trans isomers*, which have restricted rotation within the molecule (typically they containing a double bond) and *conformational isomers (conformers)*, which can rotate about one or more single bonds within the molecule.

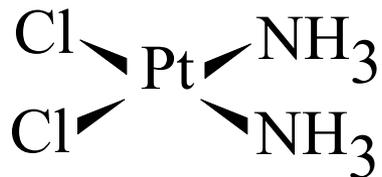
4. Isomerism and Chirality (Stereoisomers)

Diastereoisomers I

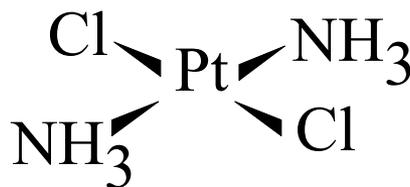
- cis - trans isomerism

If e.g. a square planar or an octahedral complex contains two ligands of the same type, they can be arranged so that the angle L - Z - L is 90° (cis) or 180° (trans).

square planar

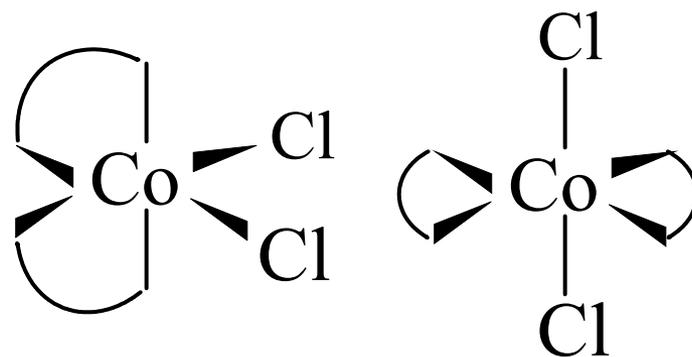


cis



trans

octahedral



cis

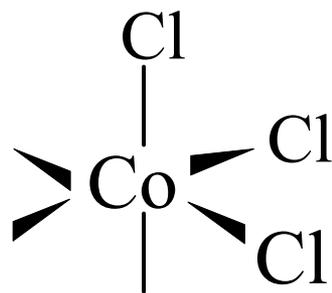
trans

4. Isomerism and Chirality (Stereoisomers)

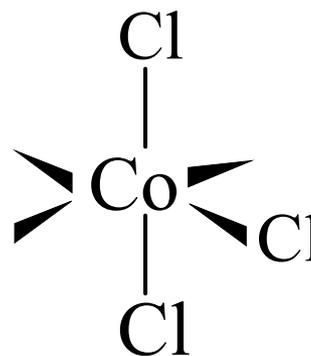
Diastereoisomers II

- fac - mer isomerism

If an octahedral complex contains three ligands of the same type they can be arranged such that they all are in a cis position, i.e. they occupy the corners of an octahedral face (\rightarrow **facial**) or that two of them are in a trans position, i.e. they are positioned on a meridian (\rightarrow **meridional**).



fac(ial)

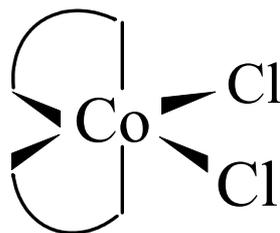


mer(idional)

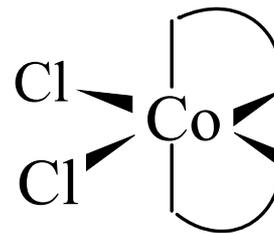
4. Isomerism and Chirality (Stereoisomers)

Enantiomers

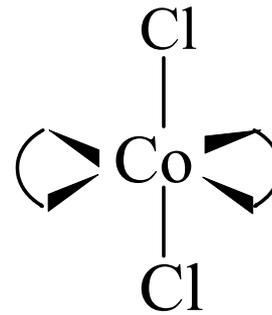
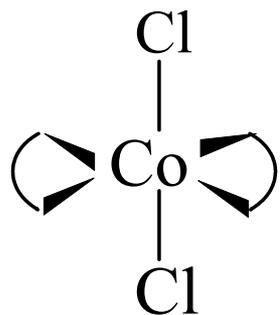
Stereoisomers where different isomers are non-superimposable mirror-images of each other are said to be *chiral*. The two mirror images are so called enantiomers.



mirror plane



mirror plane



The corresponding trans complex is not an enantiomer, because the mirror images are superimposable, i.e. they are *achiral*.

4. Isomerism and Chirality (Stereoisomers)

If a molecule or complex is either

asymmetric, i.e. has no symmetry at all (its symmetry is C_1), or
dissymmetric, i.e. has no center of inversion or a mirror plane or other S_n^* ,
it is called **chiral**.

Due to the chirality it has a non-superimposable mirror image.

* S_n are improper rotation axes, S_1 is identical to a mirror plane, S_2 is identical to a center of inversion

4. Isomerism and Chirality (Stereoisomers)

Optical isomerism

- If the lifetimes of the two enantiomers of a chiral molecule are long enough to be separable they are called **optical isomers**.
- Pure enantiomers are optically active, they rotate the plane of polarized light in different directions.
This is the only difference in the physical properties of the two enantiomers.

5. Bonding in Complexes

Useful ideas, models, and theories to explain the nature of the bond between the central ion and its ligands in transition metal complexes are:

Shared-electron pair theory of Lewis (1902), first applied to complex compounds by N.V. Sidgewick (1927), assuming that complexes are stable if the sum of the shared valence electrons of the metal and the ligands reach noble gas configuration.

Very simple and thus treated in this lecture.

Valence-bond (VB) model of W. Heitler and F. London (1927), first applied to complex compounds by L. Pauling (1939), assuming that the ligands form coordinative or dative valence bonds to the metal ion or atom and that atomic orbitals of the metal mix to form hybrid orbitals with a specific geometry and symmetry.

5. Bonding in Complexes

Further ideas, models, and theories to explain the nature of the bond between the central ion and its ligands in transition metal complexes are:

Crystal field theory (CFT) of H. Bethe , J.H. van Vleck , and L. Orgel (1929-35), treats the ligands as point charges or dipoles and describes how they influence the splitting of the d-orbitals of the central ion or atom, but does not take into account the overlap of ligand and metal atom orbitals.

Ligand field theory (LFT), developed between 1930 and 1950 a.a. by J.H. van Vleck, F.E. Ilse and H. Hartmann can be considered as an CFT extension such that all levels of covalent interactions are incorporated into the model. Useful and simple method. Treated in this lecture.

MO theory of [F. Hund](#) and [R. Mulliken](#) (1927) is the best to explain the bonding in complex compounds with respect to their physical and chemical properties, but one must know the energies of the relevant orbitals.

5. Bonding in Complexes (18-electron rule)

Shared-electron pair theory of Lewis, octet or 18-electron rule

The formation of a complex is described as an **acid-base reaction**. The bond electrons of the ligands (normally 2) are transferred to the metal ion or atom and bonds of type $M \leftarrow L$ are formed.

The sum of the valence electrons of the central atom (Lewis acid) and those donated from the ligands (Lewis base), the *effective electron number* should be equal to the number of electrons of the following noble gas.

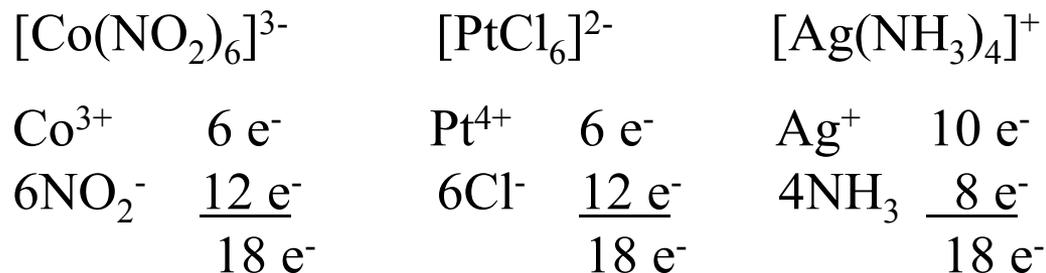
Procedure: add the numbers of valence electrons of the metal ion and the numbers of electrons donated by the ligands.

18 electron rule based on the **octet theory of Lewis** this is the first attempt to account for the bonding in complexes.

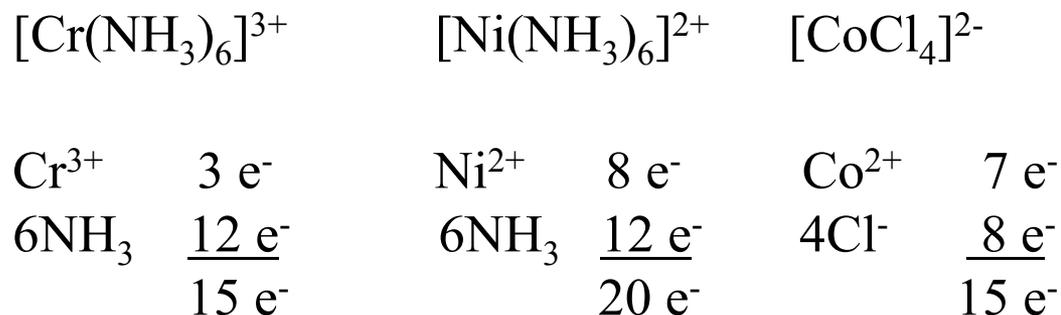


5. Bonding in Complexes (18-electron rule)

Examples:



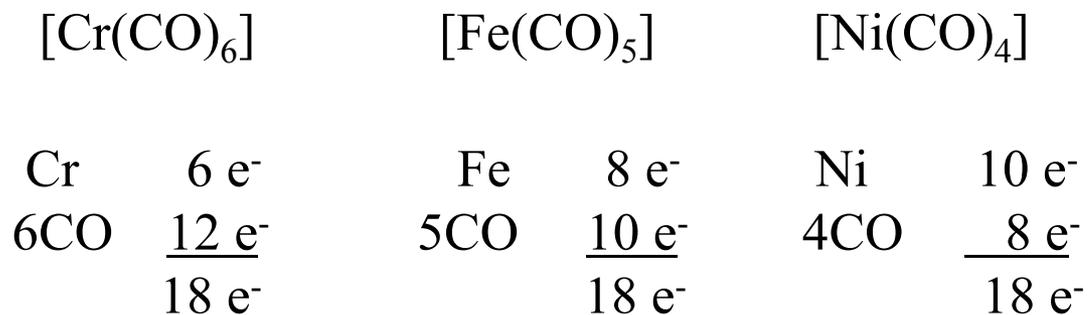
Many complexes do not obey the 18 electron rule, but are stable, e.g.:



18 electron rule is valid only for inner orbital complexes

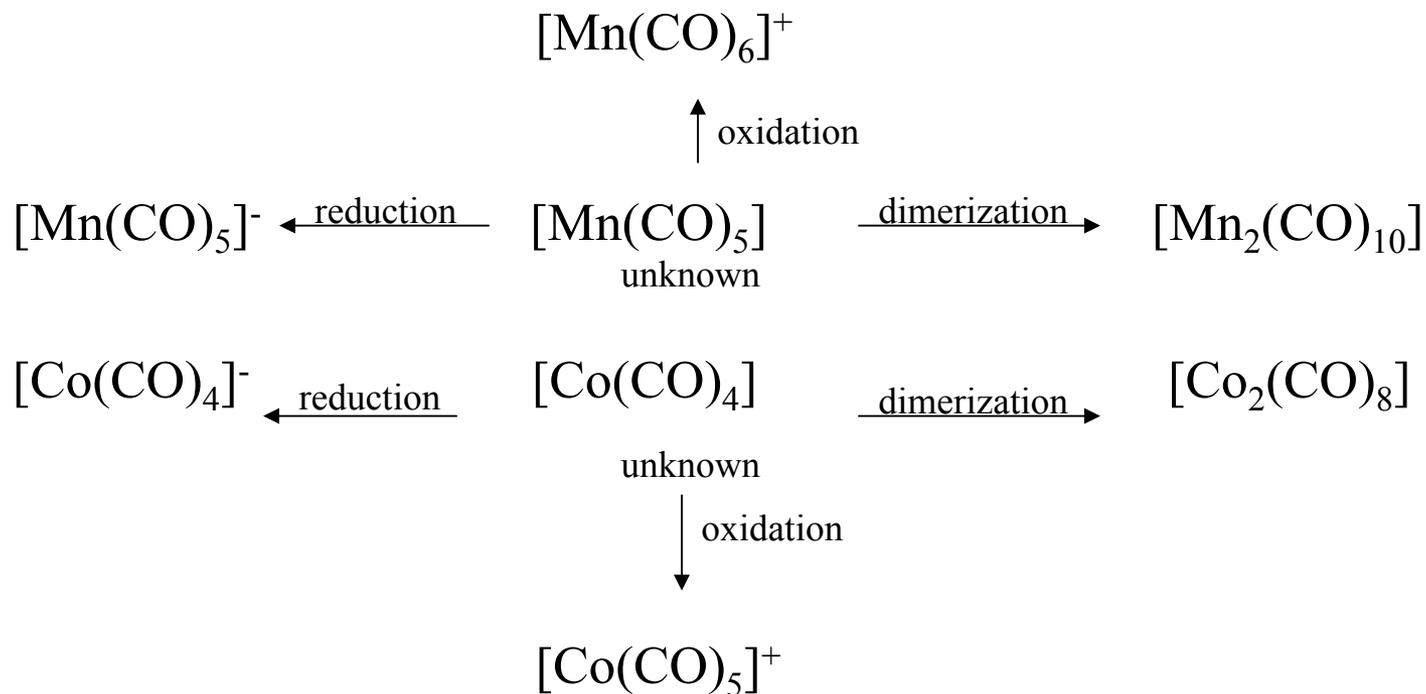
5. Bonding in Complexes (18-electron rule)

The 18 electron rule is useful for organometallic compounds and carbonyl complexes, which obey this rule in most cases, e.g.:



5. Bonding in Complexes (18-electron rule)

Carbonyl complexes with odd numbers of electrons form dimers or are reduced or oxidized



5. Bonding in Complexes (18-electron rule)

Similarly the formation of olefin complexes and metallocenes may be explained by the 18 electron rule:

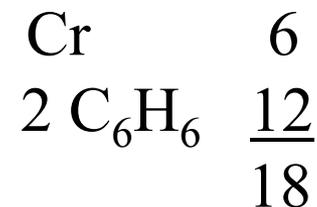
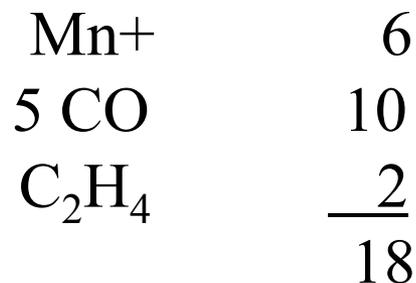
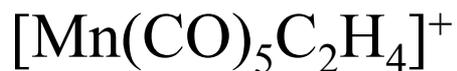
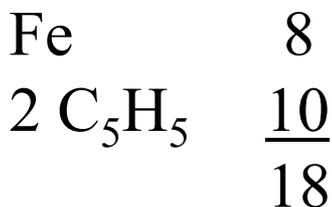
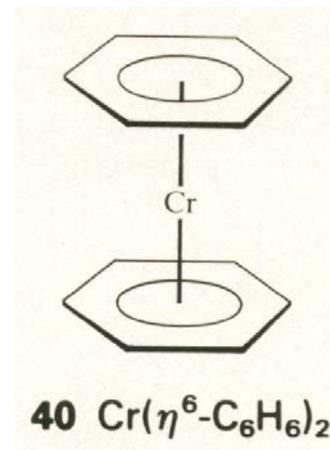
Olefines donate 2 electrons /double bond

ethylene 2

butadiene 4

benzene 6

cyclopentadienyl radical 5



5. Bonding in Complexes (*Crystal/ligand field theory*)

We have seen that the ligands of a transition metal complex are a Lewis bases being able to donate each a pair of electrons to form a covalent bond, and that the metal is a Lewis acid with an empty orbital that can accept a pair of electrons from each of the ligands to form a covalent bond. This bond is sometimes called a **coordinate covalent bond** or a **dative covalent bond** to indicate that both electrons in the bond come from the ligand.

Crystal field theory (CFT) treats the ligands as point charges or dipoles and describes how they influence the splitting of the d-orbitals of the central ion or atom, but does not take into account the overlap of ligand and metal atom orbitals.

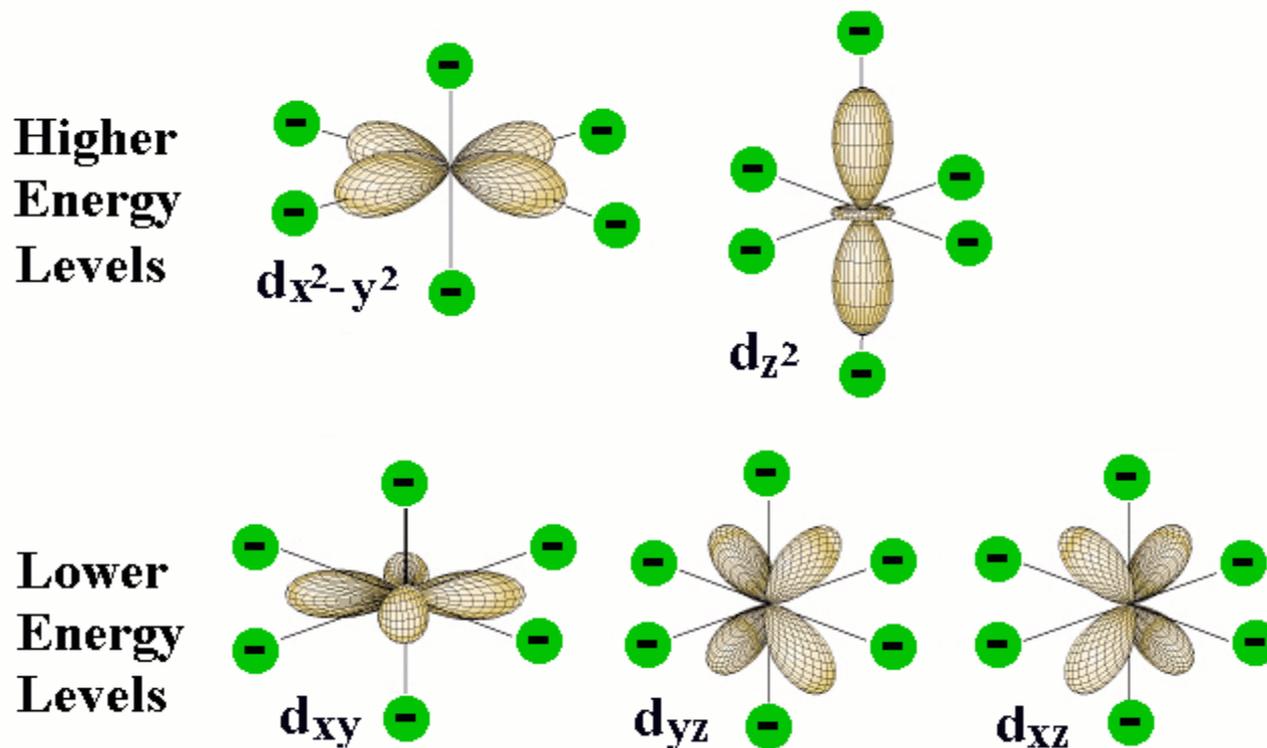
Ligand field theory (LFT) can be considered as an *CFT* extension such that all levels of covalent interactions between the transition metal and the ligands are incorporated into the model mainly on an *molecular orbital (MO)* level.

5. Bonding in Complexes (Crystal/ligand field theory)

For both theories, the knowledge of the shape, structure, and energy of the d-orbitals of the metal ions or atoms and their behavior under the influence of the ligands during the formation of the complex is important, i.e.:

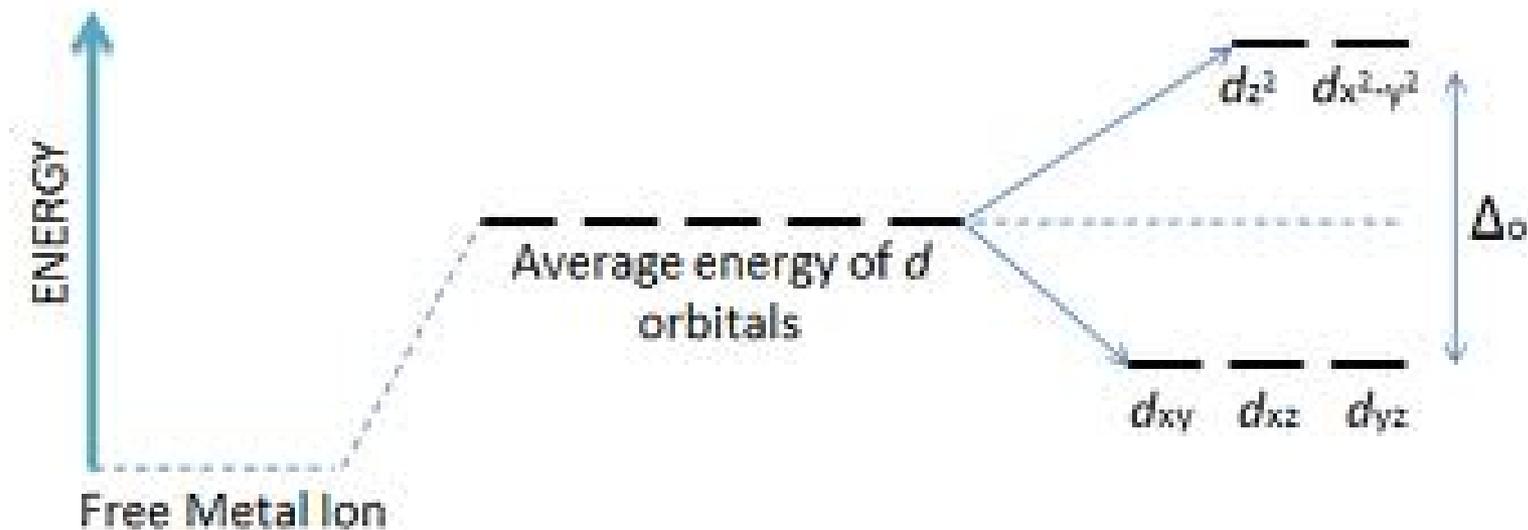
- The energies of the d-orbitals of the free metal or ion is lowered under the formation of the complex due to electrostatic interactions. This energy is the main part of the formation energy of the complex and the corresponding energy level is called the „free ion or metal“ energy level.
- This energy level, i.e. the energy of the d-orbitals of the central ions or metals is enlarged due to the repulsion forces between the orbitals of the ion or metal and the ligands and the repulsion forces between the ligands under the formation of degenerate d-orbitals if the crystal or ligand field is spherical.
- The degenerate d-orbitals of the spherical complex split under the influence of the geometry and symmetry of the real crystal or ligand field. The energy split of the d-orbitals is named Δ_0 .

5. Bonding in Complexes (Crystal/ligand field theory)



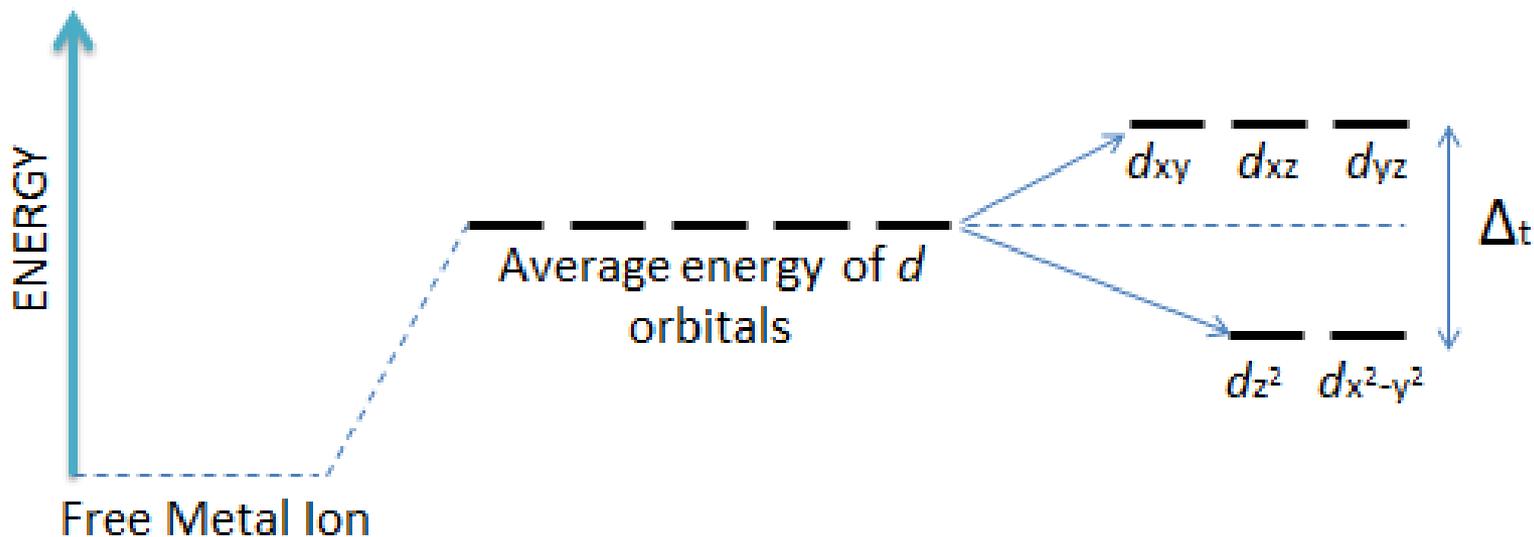
Energy change of d-orbitals under the influence of the ligands
(after <http://www.chem1.com/acad/webtext/chembond/cb09.html>)

5. Bonding in Complexes (Crystal/ligand field theory)



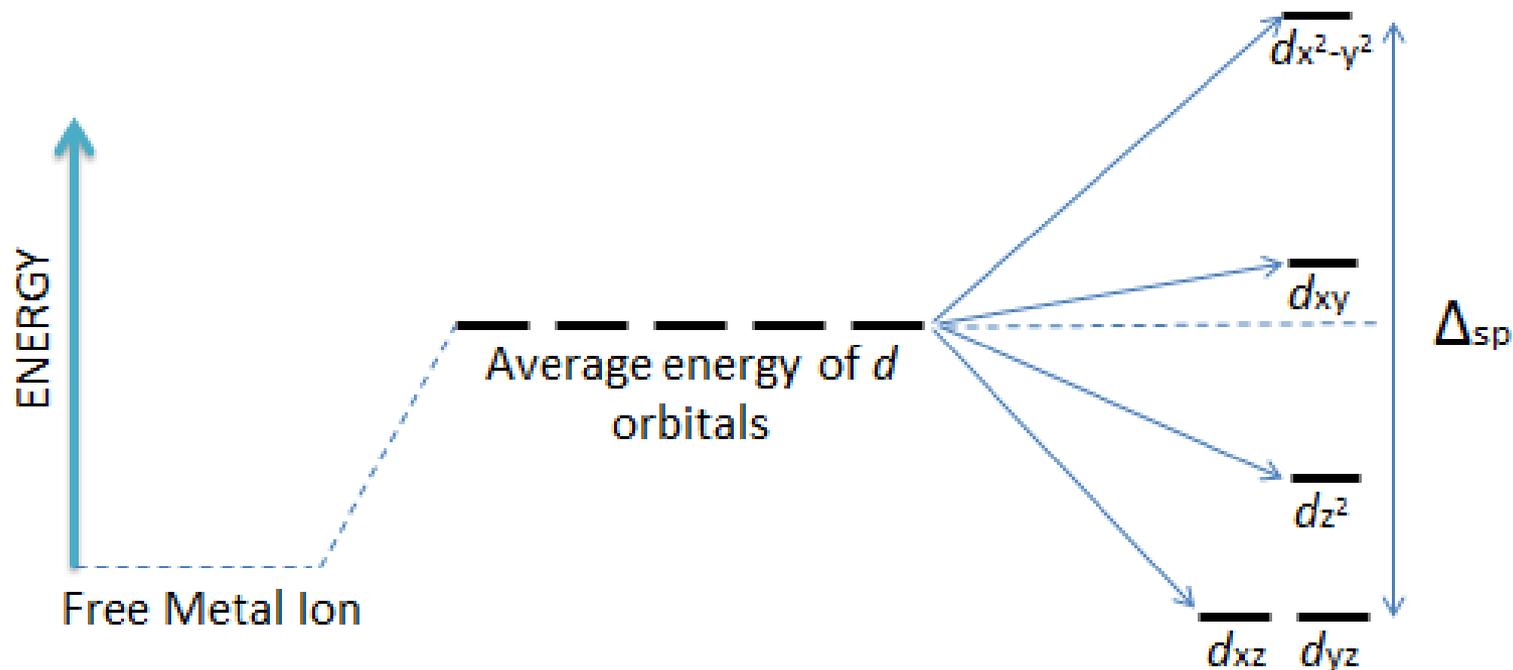
Energy split of d-orbitals under the influence of an octahedral crystal/ligand field
(after <http://chemwiki.ucdavis.edu>)

5. Bonding in Complexes (Crystal/ligand field theory)



Energy split of d-orbitals under the influence of an tetrahedral crystal/ligand field
(after <http://chemwiki.ucdavis.edu>)

5. Bonding in Complexes (Crystal/ligand field theory)

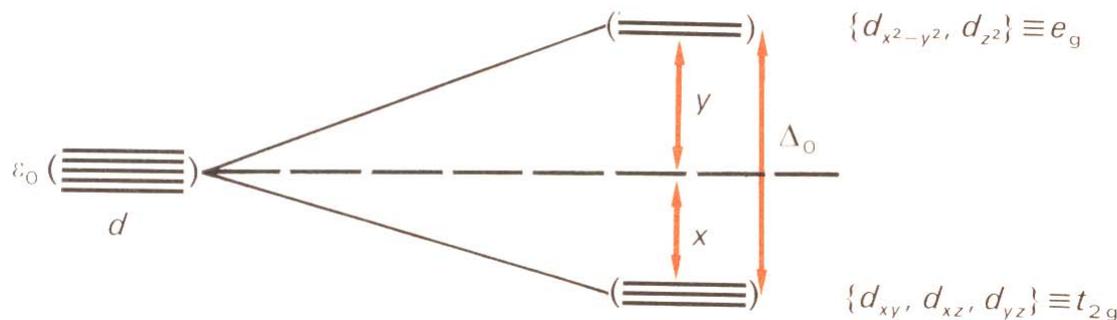
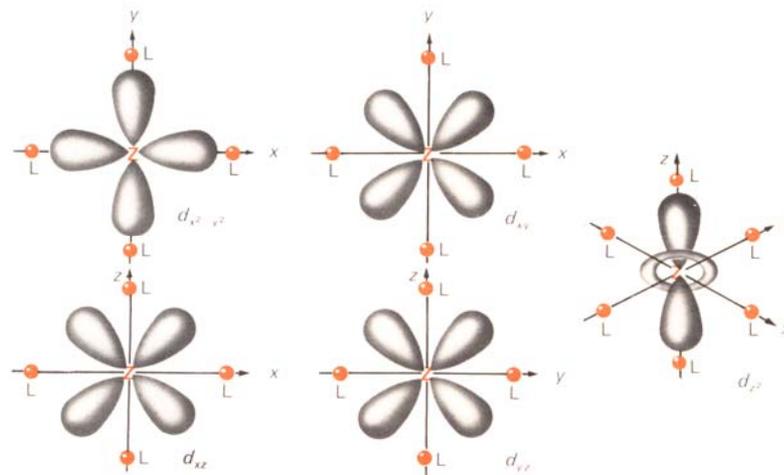
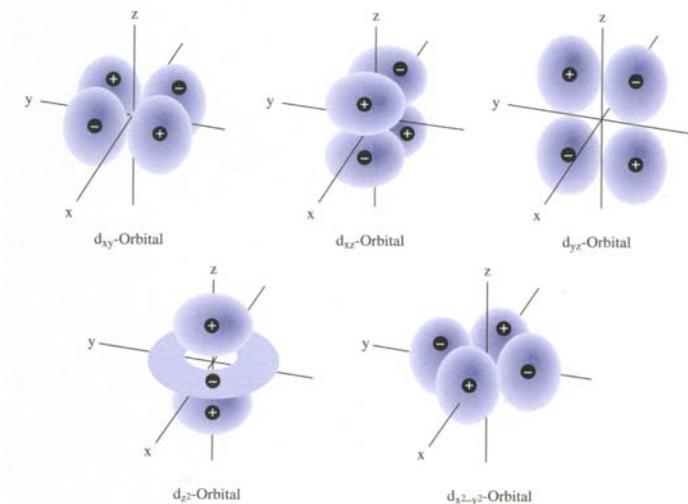


Energy split of d-orbitals under the influence of an square planar crystal/ligand field
(after <http://chemwiki.ucdavis.edu>)

5. Bonding in Complexes (Crystal/ligand field theory)

Shape of d orbitals

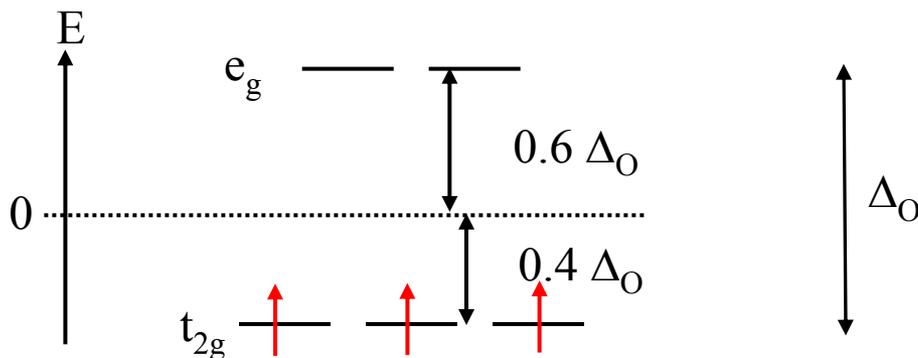
Position of ligands relative to the d orbitals



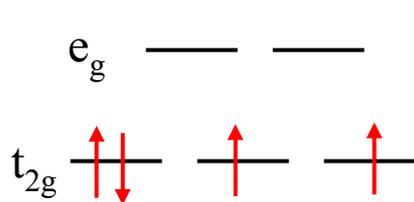
Splitting of d orbitals in an octahedral field of ligands into t_{2g} and e_g orbitals

5. Bonding in Complexes (Crystal/ligand field theory)

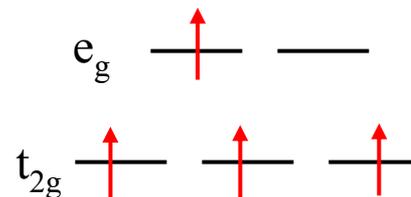
Agreement: The energy of the t_{2g} and e_g states are relative to an average value ($\equiv 0$)



For d^4 to d^7 two different possibilities of orbital occupation:



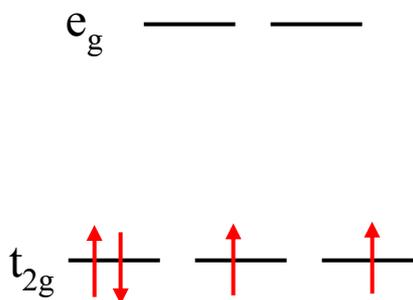
Low-spin (LS) complexes



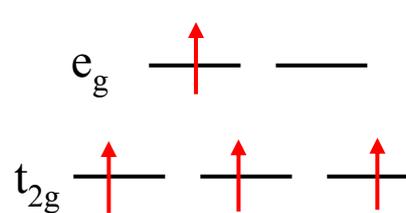
High-spin (HS) complexes

5. Bonding in Complexes (Crystal/ligand field theory)

Whether a complex is LS or HS depends on the amount of the splitting Δ_O :



Large Δ_O :
 \Rightarrow Large splitting
 \Rightarrow LS



small Δ_O :
 \Rightarrow small splitting
 \Rightarrow HS

5. Bonding in Complexes (Crystal/ligand field theory)

To understand the general trends for the amount of Δ some empirical rows are established:

1. Ligands: Δ_O increases from I⁻ to CO (from the bottom right to the top left of the PT) by
I⁻ < Br⁻ < S²⁻ < **SCN⁻** < Cl⁻ < NO₃⁻ < F⁻ < OH⁻ < ox²⁻ < H₂O < **NCS⁻** < CH₃CN < NH₃ < en <
bipy < phen < **NO₂⁻** < PPh₃ < **CN⁻** < **CO** (bold letters show the bonding atoms)

⇒ the **spectrochemical row** (only σ or additional π bonding)

2. Metal Ions:

: Δ_O increases with increasing oxidation state.

Δ_O increases inside a group from top to bottom ⇒



Prediction: left positioned metals + left positioned ligands ⇒ weak field complexes (high spin)

right positioned metals + right positioned ligands ⇒ strong field complexes (low spin)

Halides, H₂O + 3d ions ⇒ weak field complexes, NH₃ mostly, CN⁻ always strong field complexes!

5. Bonding in Complexes (Crystal/ligand field theory)

Ligand field splitting Δ_O in ML_6 complexes

	Ions	Ligands				
		Cl^-	H_2O	NH_3	en	CN^-
d^3	Cr^{3+}	13.7	17.4	21.5	21.9	26.6
d^5	Mn^{2+}	7.5	8.5		10.1	30
d^5	Fe^{3+}	11.0	14.3			(35)
d^6	Fe^{2+}		10.4			(32.8)
	Co^{3+}		(20.7)	(22.9)	(23.2)	(34.8)
	Rh^{3+}	(20.4)	(27.0)	(34.0)	(34.6)	(45.5)
d^8	Ni^{2+}	7.5	8.5	10.8	11.5	

Energies in units of 1000 cm^{-1} , numbers in parenthesis are values for low spin complexes

Please note that $1\text{ eV} = 8.065,5\text{ cm}^{-1}$ and $10.000\text{ cm}^{-1} = 1,24\text{ eV}$

5. Bonding in Complexes (Crystal/ligand field theory)

for a $t_{2g}^x e_g^y$ configuration: $LFSE = (x \cdot 0.4 - y \cdot 0.6) \Delta_O$

Table : Ligand field stabilisation energies (LFSE)

d ⁿ	example	octahedron				tetrahedron	
		strong field		weak field			
		N	LFSE	N	LFSE	N	LFSE
d ⁰	Ca ²⁺ , Sc ³⁺	0	0	0	0	0	0
d ¹	Ti ³⁺	1	0.4	1	0.4	1	0.6
d ²	V ³⁺	2	0.8	2	0.8	2	1.2
d ³	Cr ³⁺ , V ²⁺	3	1.2	3	1.2	3	0.8
d ⁴	Cr ²⁺ , Mn ³⁺	2	1.6	4	0.6	4	0.4
d ⁵	Mn ²⁺ , Fe ³⁺	1	2.0	5	0	5	0
d ⁶	Fe ²⁺ , Co ³⁺	0	2.4	4	0.4	4	0.6
d ⁷	Co ²⁺	1	1.8*	3	0.8*	3	1.2
d ⁸	Ni ²⁺	2	1.2*	2	1.2*	2	0.8
d ⁹	Cu ²⁺	1	0.6*	1	0.6*	1	0.4
d ¹⁰	Cu ⁺ , Zn ²⁺	0	0	0	0	0	0

N: number of unpaired electrons

LSFE in units of Δ_O or Δ_T ; $\Delta_T \approx 0.45 \Delta_O$

* undistorted

5. Bonding in Complexes (Colors)

Colors of some gems

Ruby: $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ (Korund) red

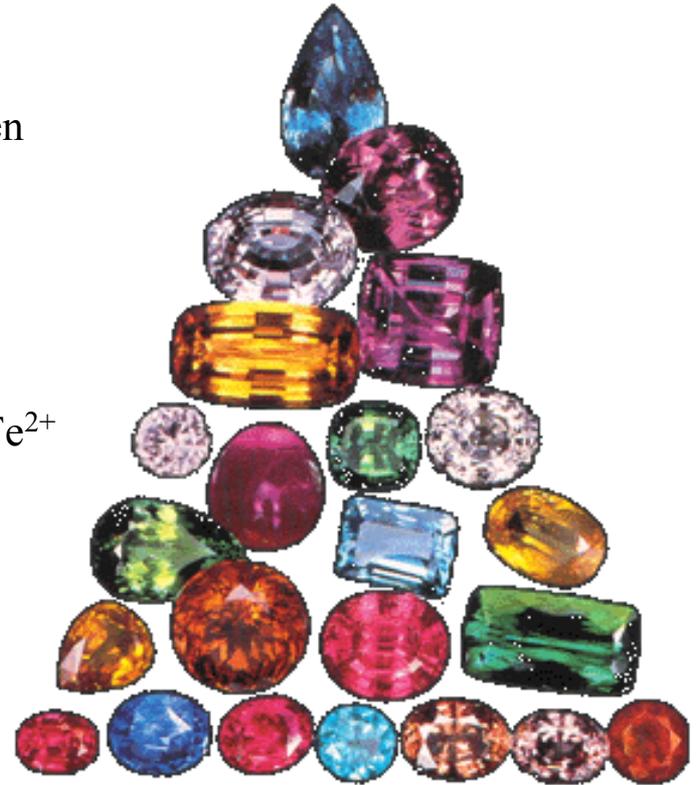
Emerald (Smaragd): $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18}):\text{Cr}^{3+}$ (Beryll) green

Amethyst: $\text{SiO}_2:\text{Fe}^{4+}$ (*charge transfer* = CT) violet

Sapphire: $\text{Al}_2\text{O}_3:\text{Fe}^{2+}, \text{Ti}^{4+}$ (CT) light blue

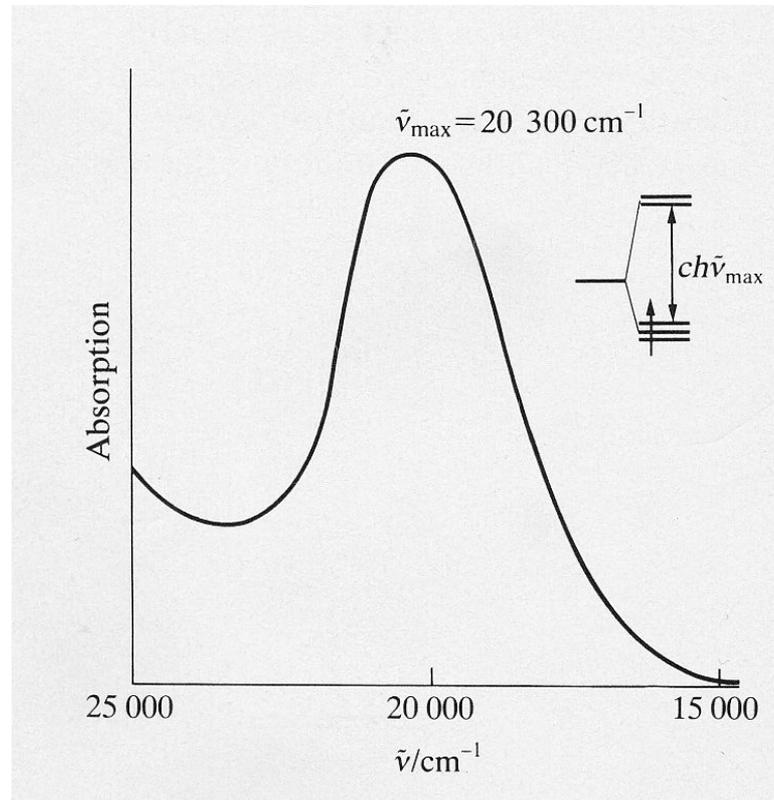
Aquamarine: $\text{Be}_3\text{Al}_2(\text{Si}_6\text{O}_{18}):\text{Fe}^{2+}, \text{Fe}^{3+}$ (CT between Fe^{2+}

and Fe^{3+} = *intervalence charge transfer*) dark blue



5. Bonding in Complexes (Colors)

Colors of coordination compounds: Optical Spectroscopy



Optical absorption spectrum of the d¹ complex [Ti(OH₂)₆]³⁺

($20.300\text{ cm}^{-1} = 2,517\text{ eV}$ 493 nm (blue-green → purple) for the transition e_g ← t_{2g})

5. Bonding in Complexes (Colors)

Ligand field splitting Δ_O in ML_6 complexes

	Ions	Ligands				
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d^8	Ni^{2+}	7.5	8.5	10.8	11.5	

Energies in units of 1000 cm^{-1} , numbers in parenthesis are values for low spin complexes

The ligand field splitting Δ_O : corresponds to the color of the respective complex
(Please note that $1\text{ eV} = 8.065,5\text{ cm}^{-1}$ and $10.000\text{ cm}^{-1} = 1,24\text{ eV}$)

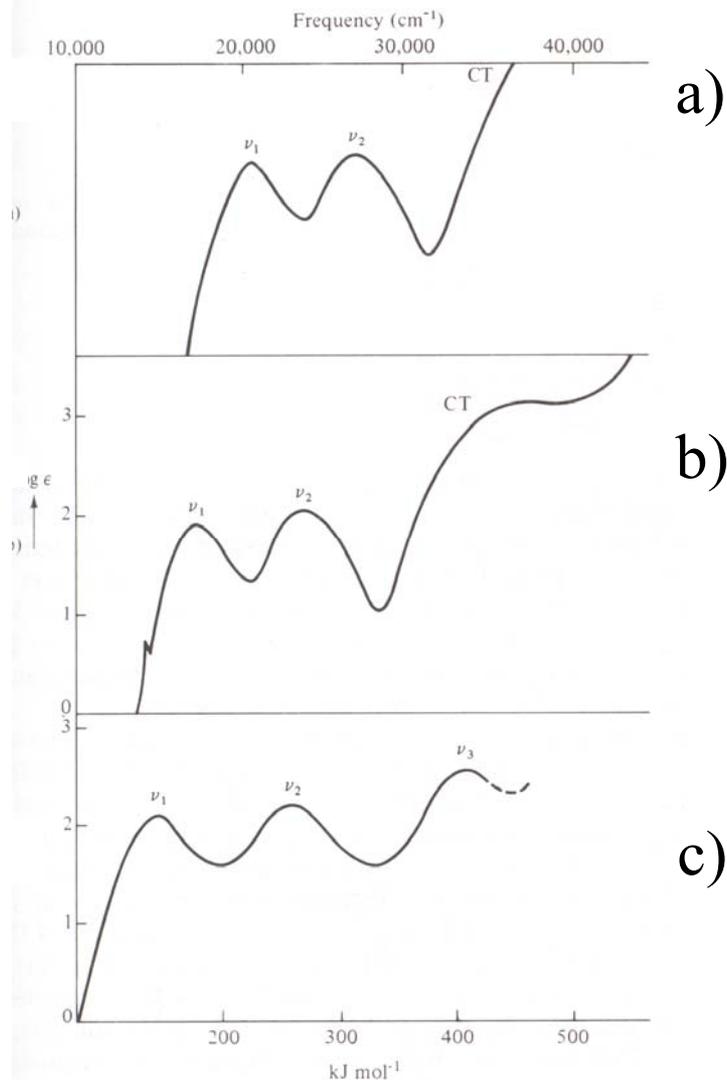
5. Bonding in Complexes (Colors)

Optical Spectroscopy

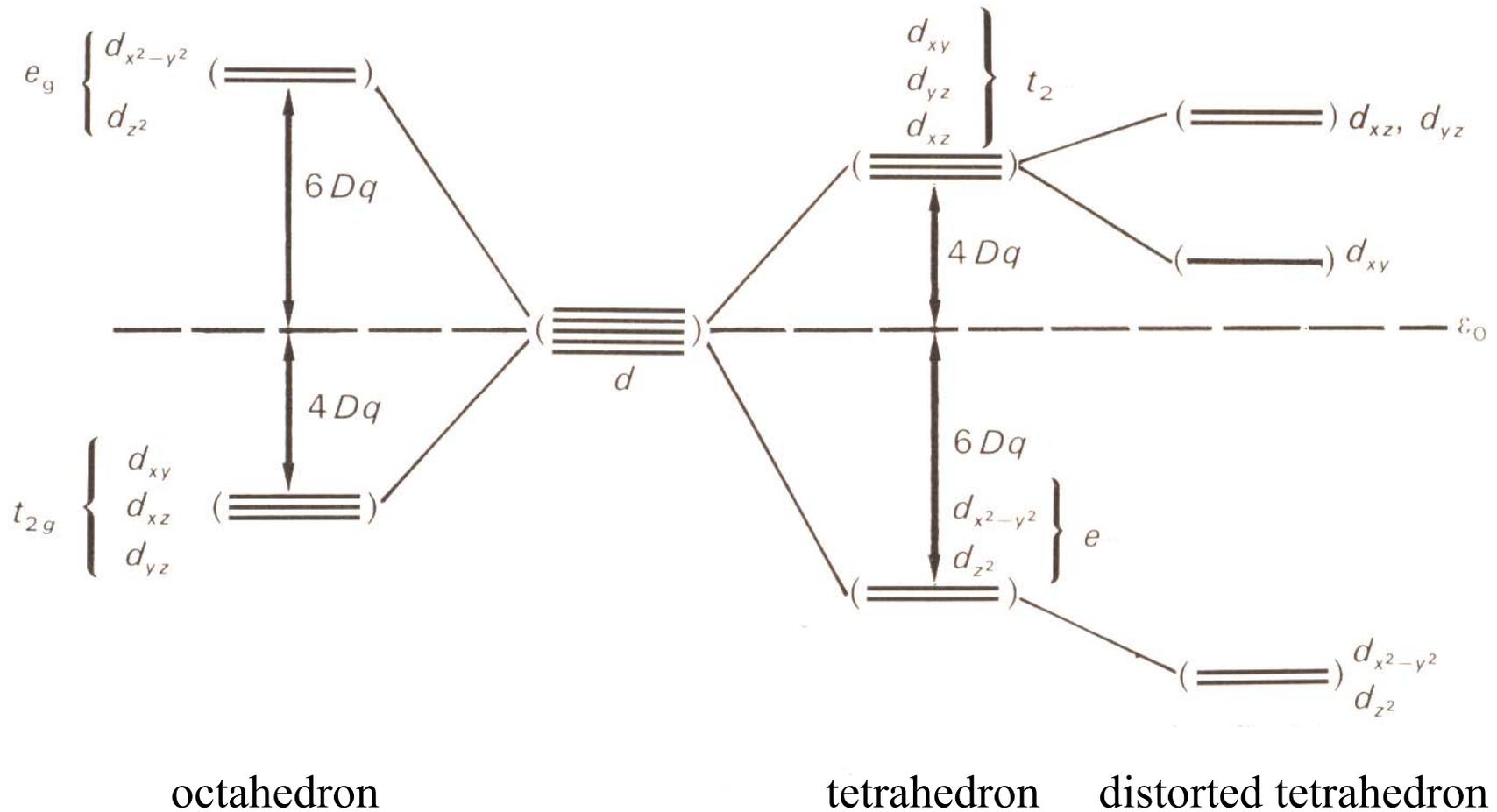
UV/VIS absorption spectra of three chromium(III) complexes:



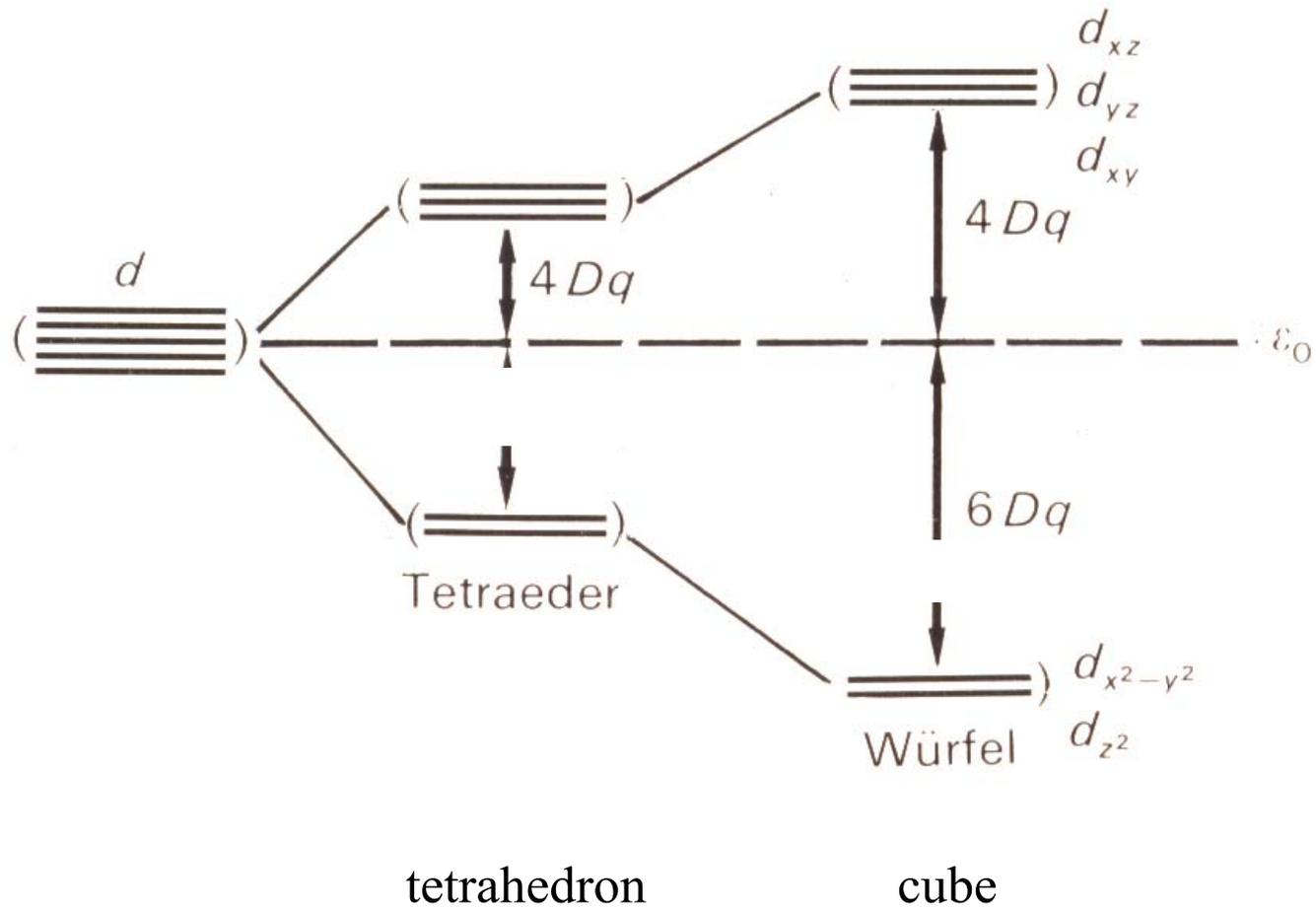
Look for the shift of the two absorption peaks ν_1 and ν_2 to lower frequencies.



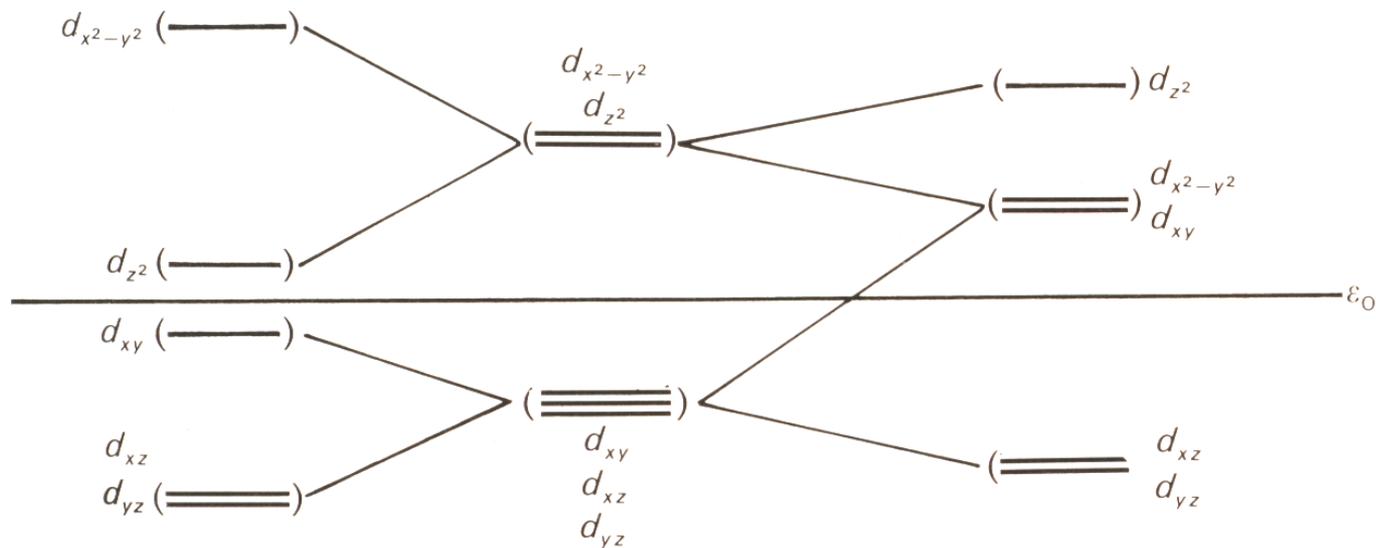
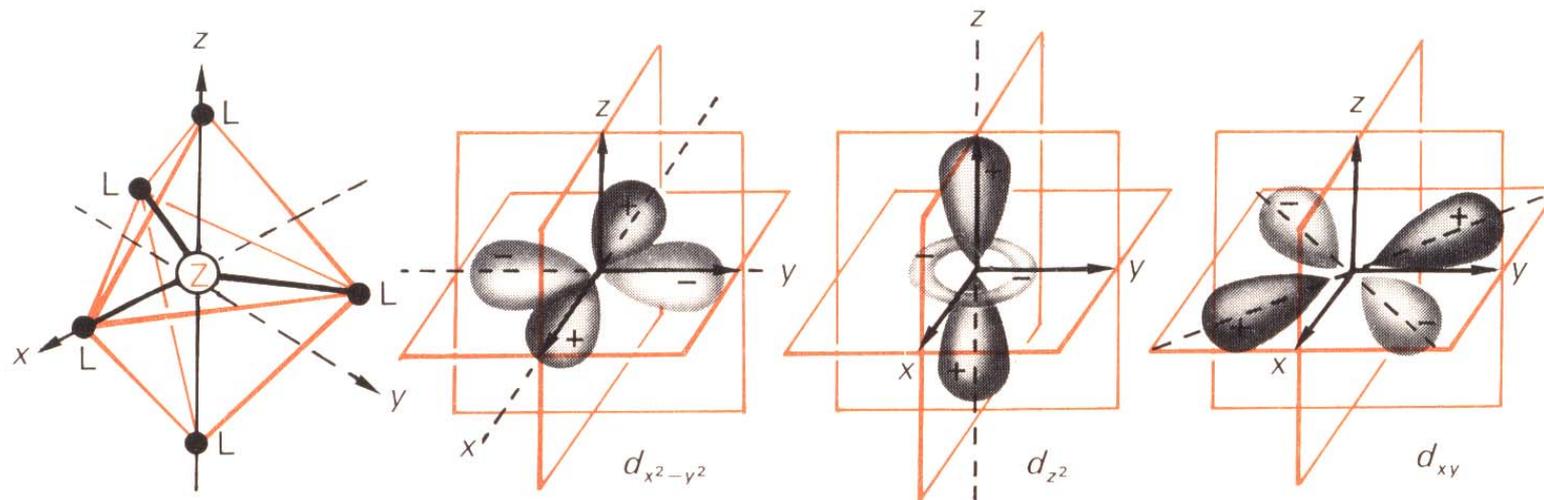
5. Bonding in Complexes (Symmetry splitting)



5. Bonding in Complexes (Symmetry splitting)



5. Bonding in Complexes (Symmetry splitting)



tetragonal pyramid

trigonal bipyramid

5. Bonding in Complexes (Symmetry splitting)

Octahedral, tetragonal and square planar complexes

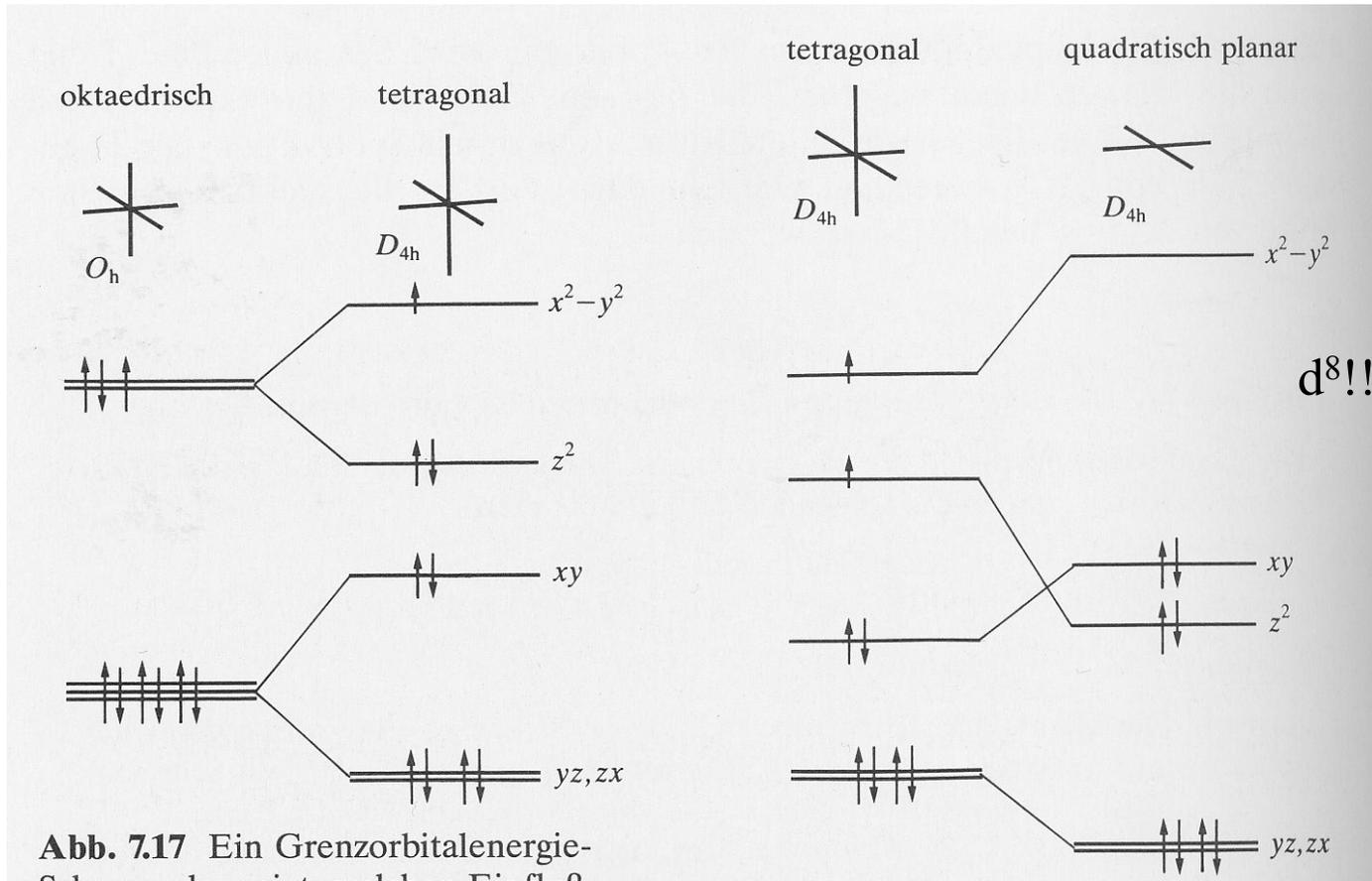


Abb. 7.17 Ein Grenzorbinalenergie-Schema, das zeigt, welchen Einfluss

octahedron

square bipyramid

square

5. Bonding in Complexes (*Jahn-Teller splitting*)

Non linear molecules which are in a degenerate electronic state tend to lower their symmetry to remove the degenerate state and thereby lower their energy.

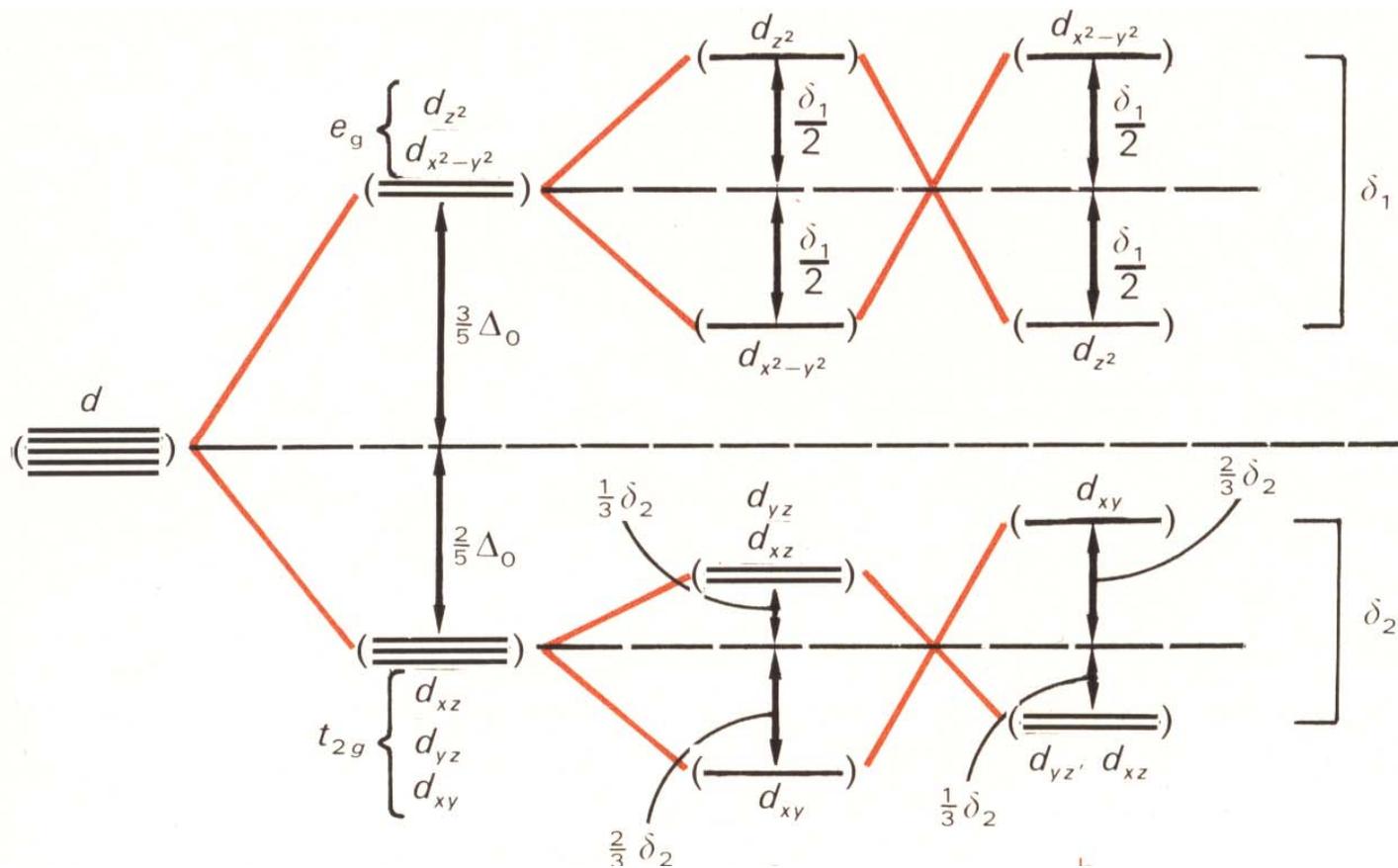
Examples: $\text{Cr}^{2+} d^4$ high spin $t_{2g}^3 e_g^1$

$\text{Co}^{2+} d^7$ low spin $t_{2g}^6 e_g^1$

$\text{Cu}^{2+} d^9$ $t_{2g}^6 e_g^3$

Distortion of the octahedron will cause a splitting of the e_g as well as the t_{2g} orbitals thus leading to a lower total energy.

5. Bonding in Complexes (Jahn-Teller splitting)



compressed elongated
 octahedron (along the z-axis)

6. Reactions (stability, reactivity) of complexes

Please remember that:

A chemical reaction has *kinetic* and *thermodynamic* aspects.

The quantity related to *kinetics* is the *reaction rate constant* k ; this constant is associated with the *activation energy* E_A required for the reaction to move forward.

The *thermodynamic* quantity is the *energy difference* resulting from the *free energy* (ΔG) given off during a chemical reaction.

While *kinetics* can tell us about the *rates of reactions* and how *fast equilibrium is reached*, they don't tell us anything about equilibrium conditions once the reaction equilibrates.

In the same measure, *thermodynamics* only gives us information regarding the *equilibrium conditions of products* (\rightarrow *equilibrium constants*) after the reaction takes place, but does not tell us the rate or velocity of reaction.

6. Reactions (stability, reactivity) of complexes

This leads to the expressions *thermodynamic stability* and *kinetic stability*.

Figures combined with *thermodynamic stability* are

equilibrium (formation, stability, dissociation) constants K for the reactions



leading to *stable* = **strong** (great K) or *unstable* = **weak** (small K) complexes.

Figures combined with *kinetic stability* are

reaction velocity v , *reaction rate constants* k , *life time* τ etc.

leading to **labile** complexes (those with great k , reacting quickly)

and so called **inert** or **nonlabile** complexes (small k , reacting slowly).

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions (thermodynamic and kinetic)

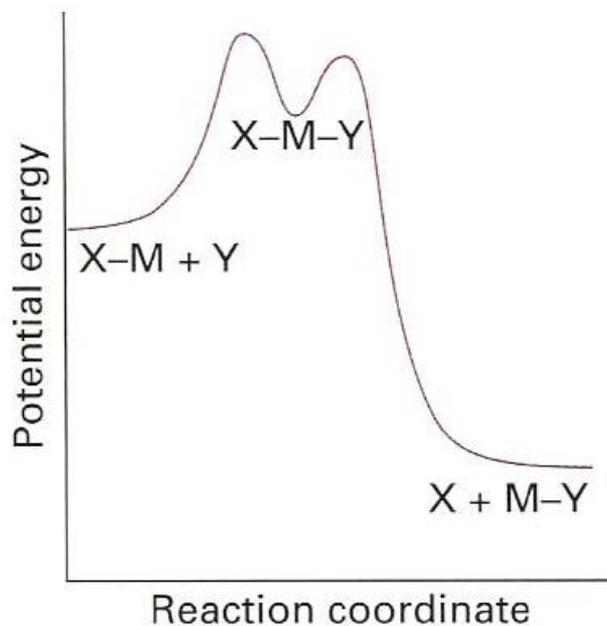


Fig. 20.4 The typical form of the reaction profile of a reaction with an associative mechanism.

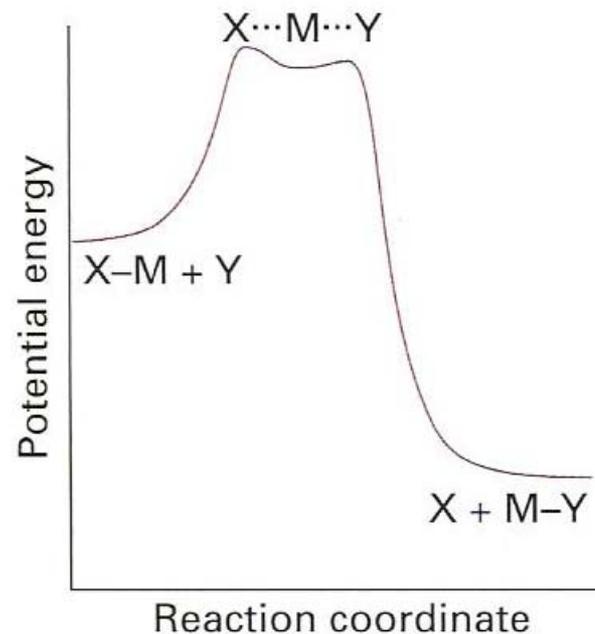


Fig. 20.5 The typical form of the reaction profile of a reaction with an interchange mechanism.

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions (thermodynamic)

Formation constants for the reaction $[M(H_2O)_n]^{m+} + L \rightleftharpoons [M(L)(OH_2)_{n-1}]^{m+} + H_2O$

Ion	Ligand	K_f	$\log K_f$	Ion	Ligand	K_f	$\log K_f$
Mg ²⁺	NH ₃	1.7	0.23	Pd ²⁺	Cl ⁻	1.25×10^5	6.1
Ca ²⁺	NH ₃	0.64	-0.2	Na ⁺	SCN ⁻	1.2×10^4	4.08
Ni ²⁺	NH ₃	525	2.72	Cr ³⁺	SCN ⁻	1.2×10^3	3.08
Cu ⁺	NH ₃	8.50×10^5	5.93	Fe ³⁺	SCN ⁻	234	2.37
Cu ²⁺	NH ₃	2.0×10^4	4.31	Co ²⁺	SCN ⁻	11.5	1.06
Hg ²⁺	NH ₃	6.3×10^8	8.8	Fe ²⁺	pyridine	5.13	0.71
Rb ⁺	Cl ⁻	0.17	-0.77	Zn ²⁺	pyridine	8.91	0.95
Mg ²⁺	Cl ⁻	4.17	0.62	Cu ²⁺	pyridine	331	2.52
Cr ³⁺	Cl ⁻	7.24	0.86	Ag ⁺	pyridine	93	1.97
Co ²⁺	Cl ⁻	4.90	0.69				

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions (thermodynamic, stability)

Table 20.2 Formation constants of Ni(II) amines, $[\text{Ni}(\text{NH}_3)_n(\text{OH}_2)_{6-n}]^{2+}$

n	K_f	$\log K_f$	K_n/K_{n-1} Experimental	Statistical*
1	525	2.72		
2	148	2.17	0.28	0.42
3	45.7	1.66	0.31	0.53
4	13.2	1.12	0.29	0.56
5	4.7	0.63	0.35	0.53
6	1.1	0.03	0.2	0.42

* Based on ratios of numbers of ligands available for replacement, with the reaction enthalpy assumed constant.

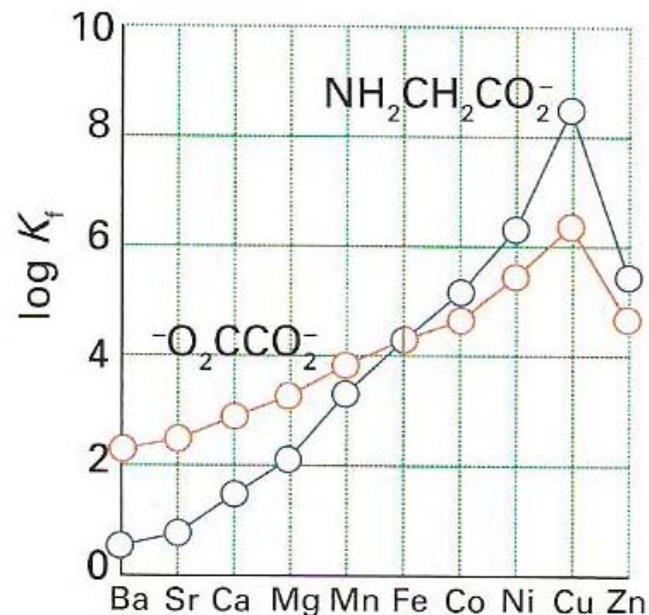
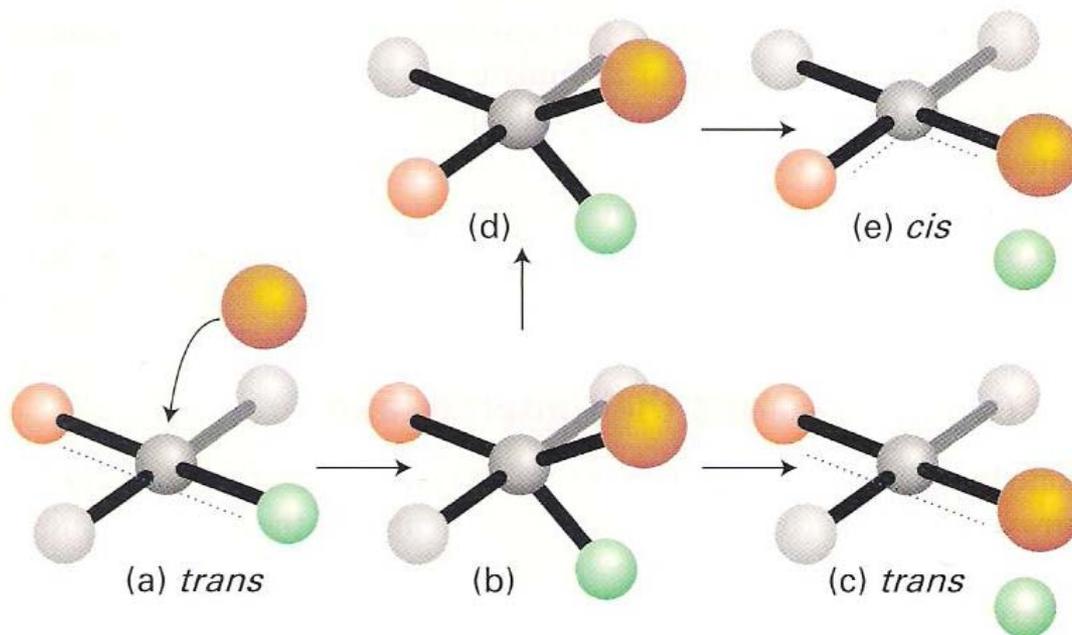


Fig. 20.1 The variation of formation constants for the M^{2+} ions of the Irving–Williams series.

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions (kinetic, stereochemistry)



Stereochemistry of substitution in a square planar complex

- normal path (a-b-c, fast), resulting in retention

- long-living intermediate (a-b-d-e, slow), resulting in pseudorotation to isomer e

6. Reactions (stability, reactivity) of complexes

Internal exchange reactions



Fig. 20.15 The exchange of axial and equatorial ligands by a twist through a square-pyramidal conformation of the complex.

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions (kinetic)

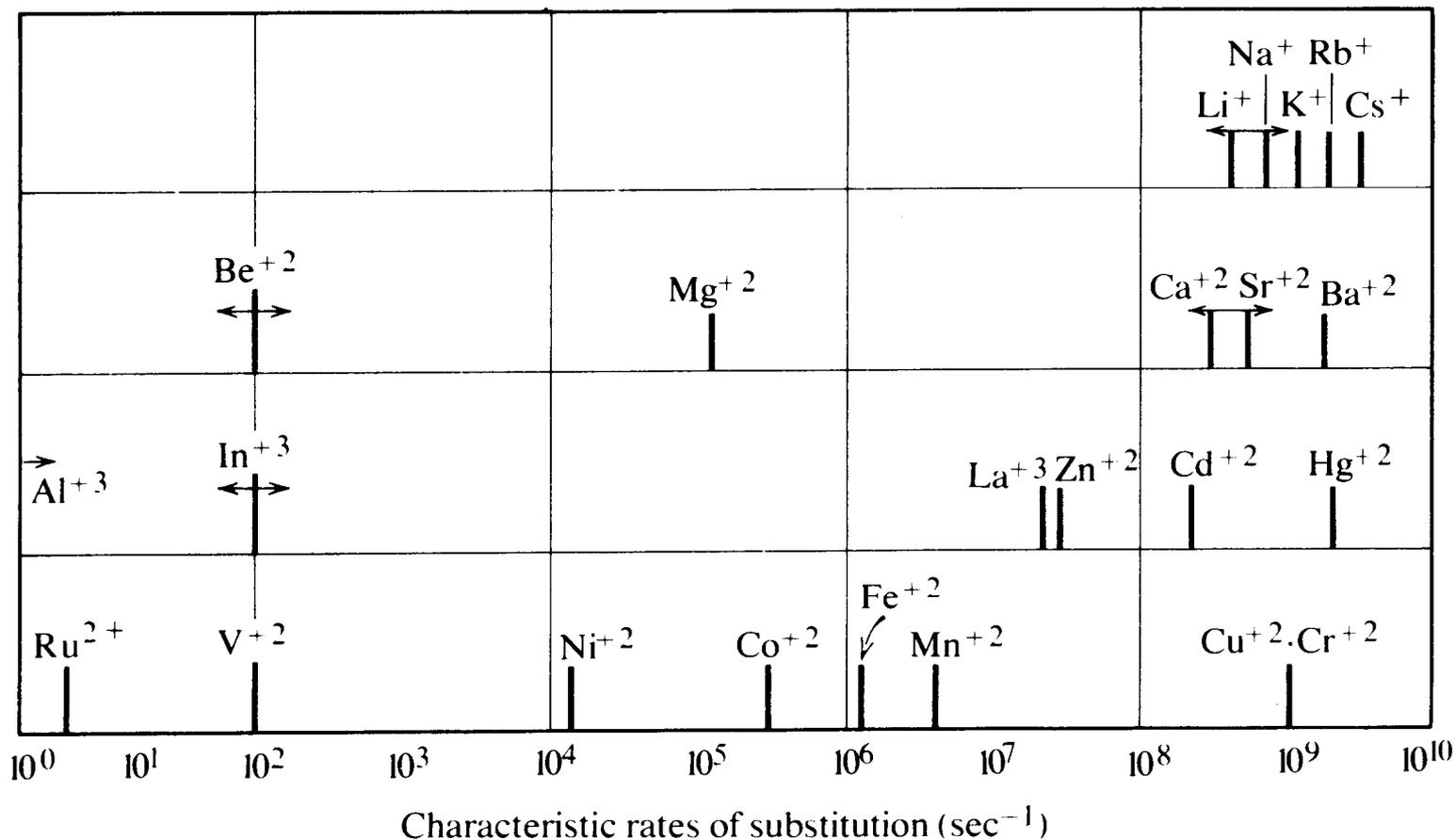


Figure 9.2 Exchange rates for metal aqua complexes. (From M. Eigen, *Pure Appl. Chem.* 1963, 6, 105.)

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions: Classification of metal ions

Classification of metal ions according to their exchange rate of ligands

- Class I** Very fast (diffusion-controlled) exchange of water occurs; $k \geq 10^8 \text{ sec}^{-1}$. The ions in this class are those of the alkali metals and alkaline earths (except for Be^{2+} and Mg^{2+}), Group IIB (except for Zn^{2+}), Cr^{2+} , and Cu^{2+} .
- Class II** Exchange-rate constants are between 10^4 and 10^8 sec^{-1} . The divalent first-row transition metal ions (except for V^{2+} , Cr^{2+} , and Cu^{2+}), as well as Mg^{2+} and the trivalent lanthanide ions, are members of this class.
- Class III** Exchange-rate constants are between 1 and 10^4 sec^{-1} . This class includes Be^{2+} , V^{2+} , Al^{3+} , Ga^{3+} , and several trivalent first-row transition metal ions.
- Class IV** Ions in this class are inert in Taube's sense; their rate constants for exchange fall between 10^{-6} and 10^{-3} sec^{-1} . Members of the set are Cr^{3+} , Co^{3+} , Rh^{3+} , Ir^{3+} and Pt^{2+} .

6. Reactions (stability, reactivity) of complexes

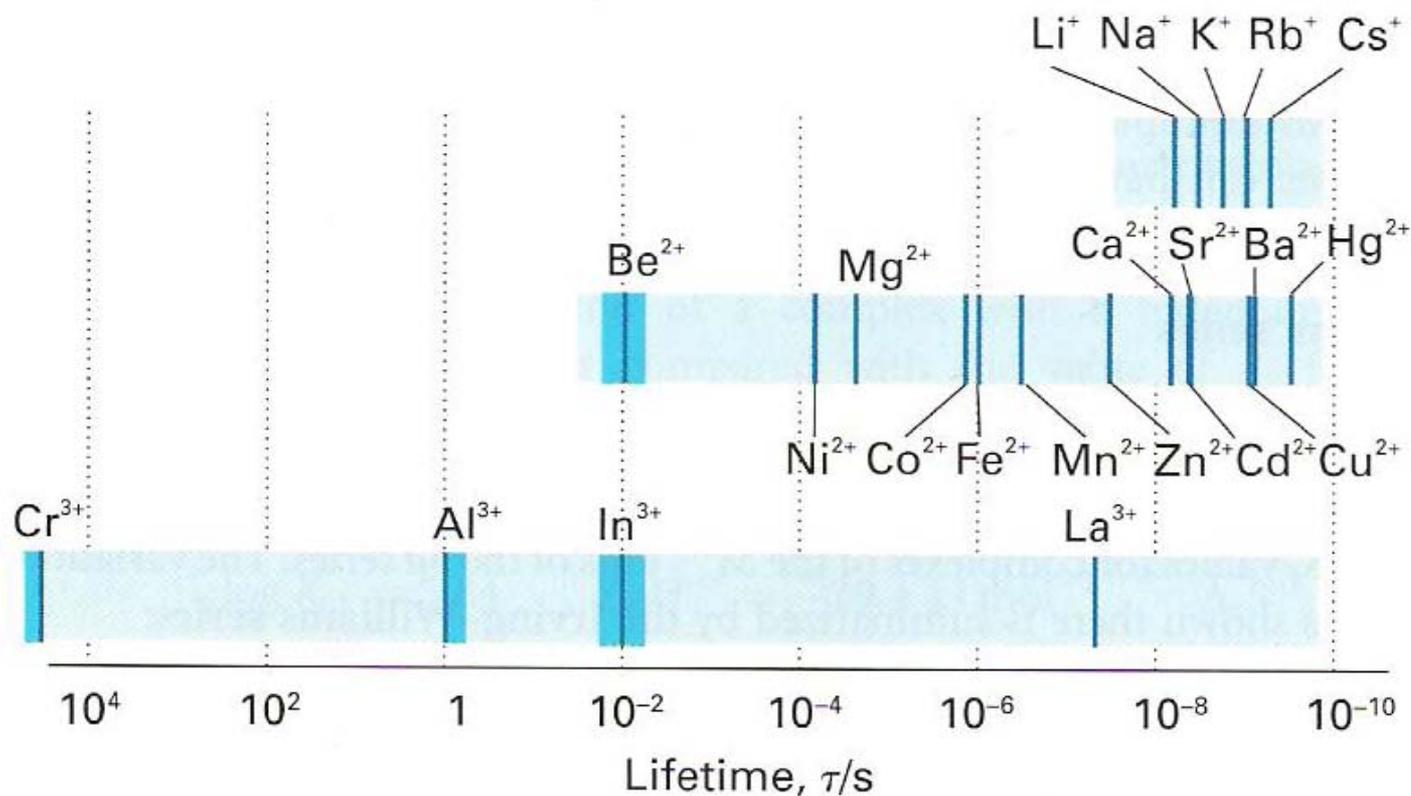
Ligand substitution reactions (kinetic)

Some further generalizations are as follows:

- 1 All complexes of s -block ions except the smallest (Be^{2+} and Mg^{2+}) are very labile.
- 2 Complexes of the M(III) ions of the f -block are all very labile.
- 3 Complexes of the d^{10} ions (Zn^{2+} , Cd^{2+} , and Hg^{2+}) are normally very labile.
- 4 Across the $3d$ series, complexes of d -block M(II) ions are generally moderately labile, with distorted Cu(II) complexes among the most labile.
- 5 Complexes of M(III) ions are distinctly less labile than M(II) ions.
- 6 d -Metal complexes with d^3 and low-spin d^6 configurations (for example Cr(III) , Fe(II) , and Co(III)) are generally nonlabile as they have large LFSEs. Chelate complexes with the same configuration, such as $[\text{Fe(phen)}_3]^{2+}$, are particularly inert.
- 7 Nonlability is common among the complexes of the $4d$ and $5d$ series, which reflects the high LFSE and strength of the metal–ligand bonding.

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions (kinetic)



Characteristic lifetimes for exchange of water molecules in aqua complexes

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions (kinetic)

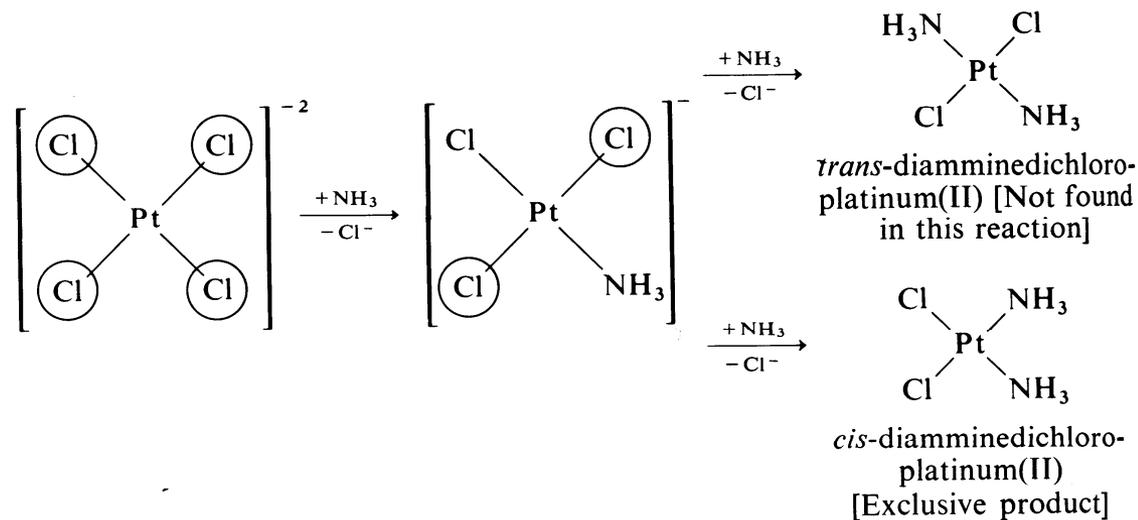
Table 20.3 Representative timescales of chemical and physical processes

Timescale*	Process	Example
10^8 s	Ligand exchange (inert complex)	$[\text{Cr}(\text{OH}_2)_6]^{3+} - \text{H}_2\text{O}$ (c. 32 years)
60 s	Ligand exchange (nonlabile complex)	$[\text{V}(\text{OH}_2)_6]^{3+} - \text{H}_2\text{O}$ (50 s)
1 ms	Ligand exchange (labile complex)	$[\text{Pt}(\text{OH}_2)_4]^{2+} - \text{H}_2\text{O}$ (0.4 ms)
1 μs	Intervalence charge transfer	$(\text{H}_3\text{N})_5\text{Ru}^{\text{II}} - \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{N} - \text{Ru}^{\text{III}}(\text{NH}_3)_5$ (0.5 μs)
1 ns	Ligand exchange (labile complex)	$[\text{Ni}(\text{OH}_2)_5(\text{py})]^{2+} - \text{H}_2\text{O}$ (1 ns)
10 ps	Ligand association	$\text{Cr}(\text{CO})_5 + \text{THF}$ (10 ps)
1 ps	Rotation time in liquid	CH_3CN (1 ps)
1 fs	Molecular vibration	Sn—Cl stretch (300 fs)

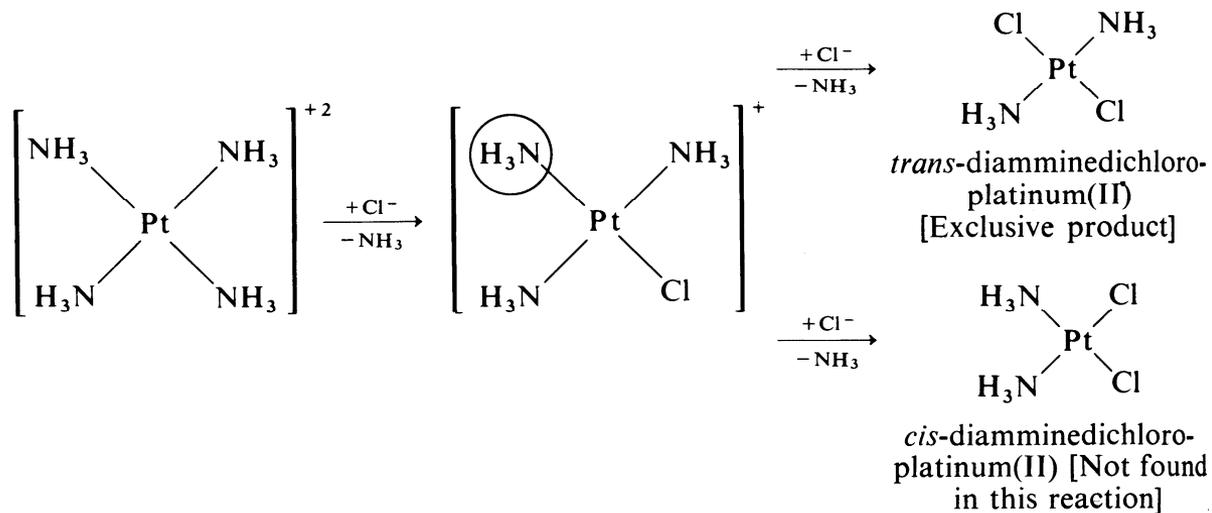
* Approximate time at room temperature.

6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions: Trans directing ligands



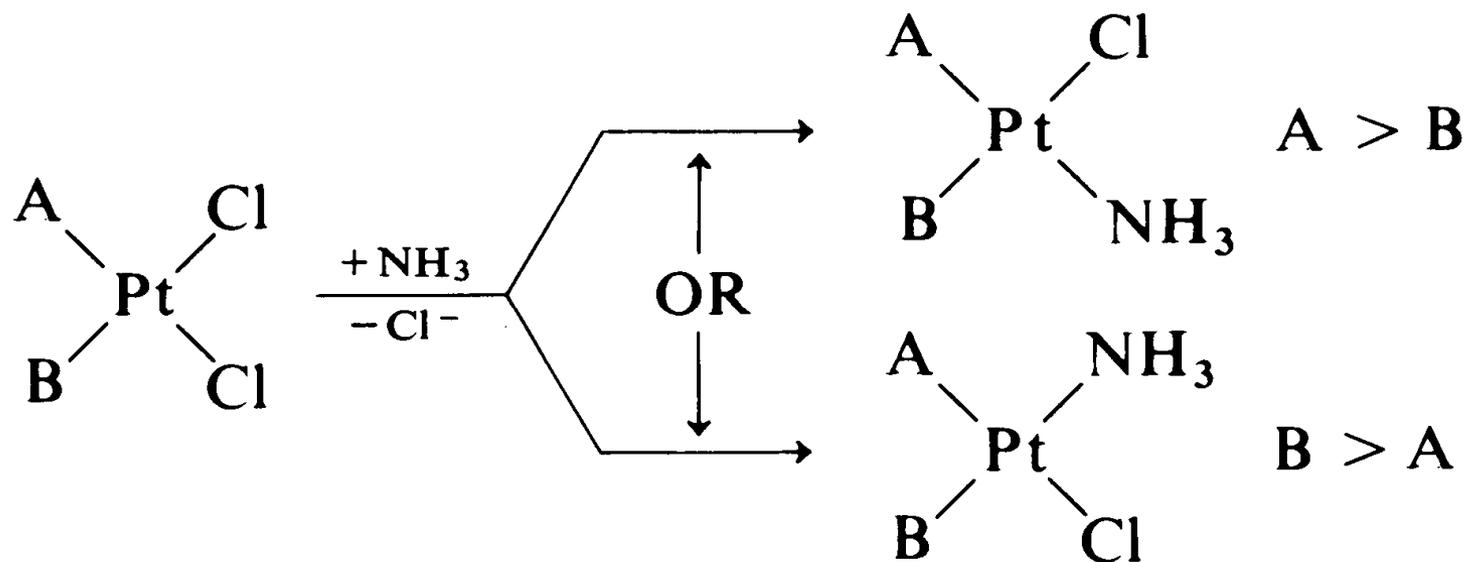
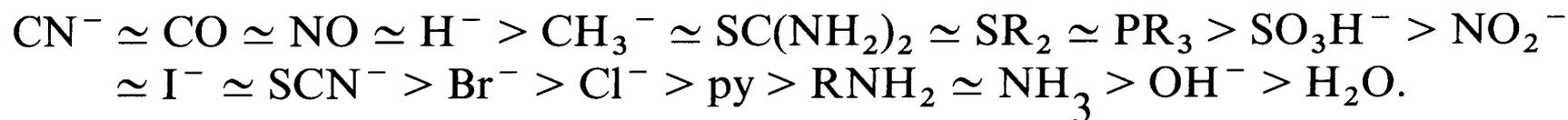
(11.3)



6. Reactions (stability, reactivity) of complexes

Ligand substitution reactions: Trans directing ligands

Series of trans-directing ligands



7. Metal Organic Compounds

Table 21.2 Typical ligands and their electron counts

(a) Neutral-ligand method

Ligand	Formula	Designation*	Electrons donated
Carbonyl	CO	L	2
Phosphine	PR ₃	L	2
Hydride	H	X	1
Dihydrogen	H ₂	L	2
η^1 -Alkyl, -alkenyl, -alkynyl, and -aryl groups	R	X	1
η^2 -Alkene	CH ₂ =CH ₂	L	2
η^2 -Alkyne	RCCR	L	2
Dinitrogen	N ₂	L	2
Butadiene	CH ₂ =CH—CH=CH ₂	L ₂	4
Benzene	C ₆ H ₆	L ₃	6
η^3 -Allyl	CH ₂ CHCH ₂	LX	3
η^5 -Cyclopentadienyl	C ₅ H ₅	L ₂ X	5

* Ligands are defined as **L type** if they are neutral two-electron donors (such as CO, PMe₃), and **X type** if, when they are considered to be neutral, they are one-electron radical donors (such as halogen atoms, H, CH₃).

7. Metal Organic Compounds

(b) Donor-pair method*

Ligand	Formula	Electrons donated
Carbonyl	CO	2
Phosphine	PR ₃	2
Hydride	H ⁻	2
Dihydrogen	H ₂	2
η^1 -Alkyl, -alkenyl, -alkynyl, and -aryl groups	R ⁻	2
η^2 -Alkene	CH ₂ =CH ₂	2
η^2 -Alkyne	RCCR	2
Dinitrogen	N ₂	2
Butadiene	CH ₂ =CH-CH=CH ₂	4
Benzene	C ₆ H ₆	6
η^3 -Allyl	CH ₂ CHCH ₂ ⁻	4
η^5 -Cyclopentadienyl	C ₅ H ₅ ⁻	6

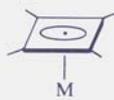
* We use this method throughout this book.

7. Metal Organic Compounds

Hapticity η of a ligand: number of atoms which are bonded to a metal ion!

Numbers of electrons and hapticity of some metal organic ligands

Tabelle 16.1 Einige organische Liganden.

Verfügbare Elektronen	Haptizität	Ligand	Metall-Ligand-Struktur
1	η^1	Methyl, Alkyl $\cdot\text{CH}_3, \cdot\text{CH}_2\text{R}$	$\text{M}-\text{CH}_3$
2	η^1	Alkylden (Carben)	$\text{M}=\text{C} \begin{matrix} \text{R} \\ \text{R} \end{matrix}$
2	η^2	Alken $\text{H}_2\text{C}=\text{CH}_2$	$\begin{matrix} >\text{C}=\text{C}< \\ \\ \text{M} \end{matrix}$
3	η^3	π -Allyl C_3H_5	$\begin{matrix} \\ \text{C}=\text{C}=\text{C} \\ \\ \text{M} \end{matrix}$
3	η^1	Alkylden (Carbin) $\text{C}-\text{R}$	$\text{M}\equiv\text{C}-\text{R}$
4	η^4	1,3-Butadien C_4H_6	
4	η^4	Cyclobutadien C_4H_4	
5	η^5 η^3 η^1	Cyclopentadienyl C_5H_5 (Cp)	
6	η^6	Benzol C_6H_6	
6	η^7	Tropylium C_7H_7^+	
6	η^6	Cycloheptatrien C_7H_8	
8 [†] (6) (4)	η^8 η^6 η^4	Cyclooctatetraen C_8H_8 (cot)	

* Für neutrale Liganden.

† Wie verschiedene andere Polyen-Liganden in dieser Liste kann der cot-Ligand nur über einen Teil der verfügbaren Elektronenpaare koordinieren. Eine veränderliche Haptizität ist bei cot häufig.

7. *Metal Organic Compounds (Metal Carbonyls)*

Homoleptic (all ligands identical) carbonyls are known for most of the d-elements, except for Sc, Y, Cu, Ag, Au.

Homoleptic carbonyls of Pd and Pt are not very stable and exist only at low temperatures!

Carbonyls are used as starting materials for other metal organic compounds and for catalysis!

CO is a weak donor to the metal ion and builds a σ bond via C.

Metal electrons are delocalized due to interactions with LUMO ,

CO acts as a Lewis π acid \Rightarrow “ π back donation”,

thus CO is a very strong ligand.

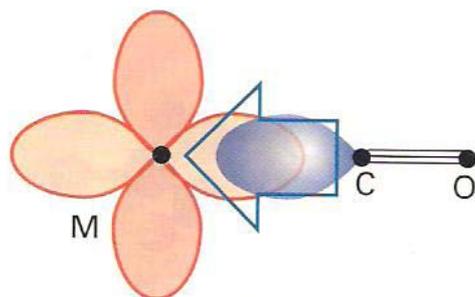
7. Metal Organic Compounds (Metal Carbonyls)

Table 21.5 Formulas and electron count for some 3d-series carbonyls

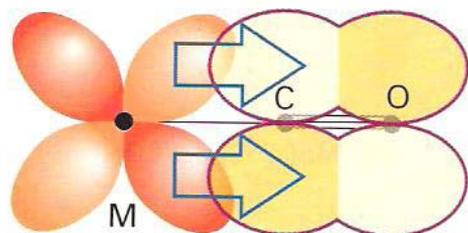
Group	Formula	Valence electrons	Structure
6	$\text{Cr}(\text{CO})_6$	Cr 6(CO) <hr/> 12 18	
7	$\text{Mn}_2(\text{CO})_{10}$	Mn 5(CO) M—M <hr/> 1 18	
8	$\text{Fe}(\text{CO})_5$	Fe 5(CO) <hr/> 10 18	
9	$\text{Co}_2(\text{CO})_8$	Co 4(CO) M—M <hr/> 1 18	
8	$\text{Ni}(\text{CO})_4$	Ni 4(CO) <hr/> 8 18	

7. Metal Organic Compounds (Metal Carbonyls)

Bonding in carbonyles: The 3σ orbital of CO serves as a very weak donor and the π^* orbitals act as acceptors.



15



16

The lone pair on C acts as a σ Lewis base (15) and the empty CO antibonding orbital as a Lewis π acid (16) \Rightarrow “ π -back donation”, CO is a very strong ligand!

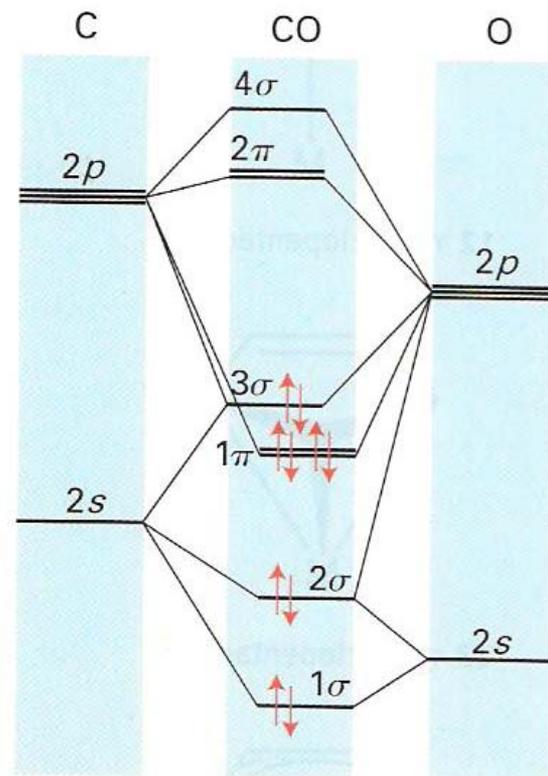


Fig. 21.3 The molecular orbital scheme for CO shows that the HOMO has σ symmetry and is essentially a lobe that projects away from the C atom. The LUM has π symmetry.

7. Metal Organic Compounds (Metal Carbonyls)

Metal Carbonyls

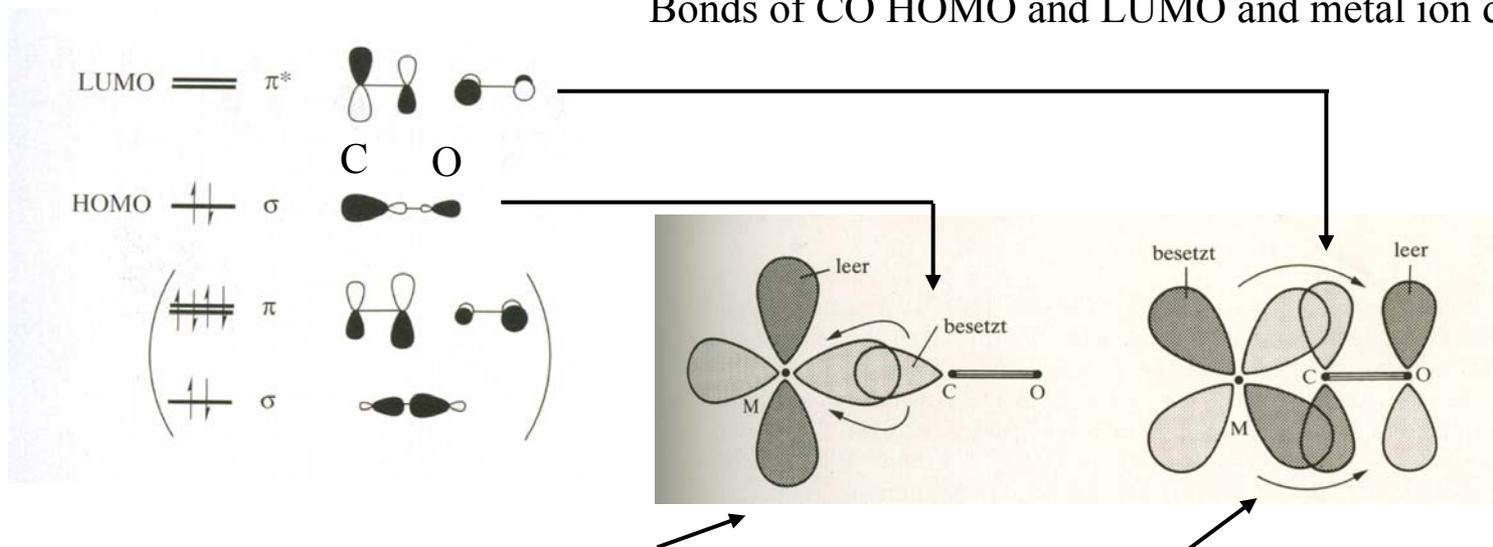
Homoleptic carbonyls are known for most of the d-elements, except for Sc, Y, Cu, Ag, Au

Homoleptic carbonyls of Pd and Pt are not very stable and exist only at low temperatures!

Carbonyls are used as starting materials for other metal organic compounds and for catalysis!

MO diagram of CO

Bonds of CO HOMO and LUMO and metal ion d orbitals



CO is a weak donor to metal ion and builds a σ bond

Metal electrons are delocalized due to interactions with LUMO, CO acts as π acid

\Rightarrow “ π -back donation”, CO is a very strong ligand!

7. Metal Organic Compounds (Metal Carbonyls)

CO can bond to one, two and three metal ions! Differences are observable in vibrational frequencies:
(the longer the bond the lower the frequencies)

Occupation of the π^* orbital (LUMO) due to π -back donation!

freies CO

$\tilde{\nu}_{\text{CO}} / \text{cm}^{-1}$

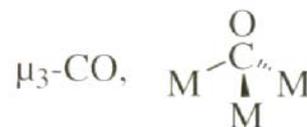
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terminales M-CO

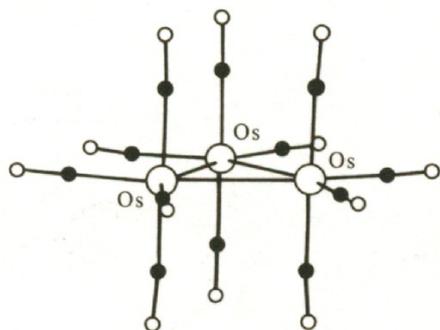
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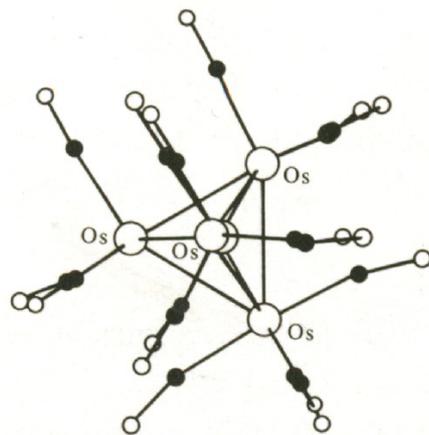
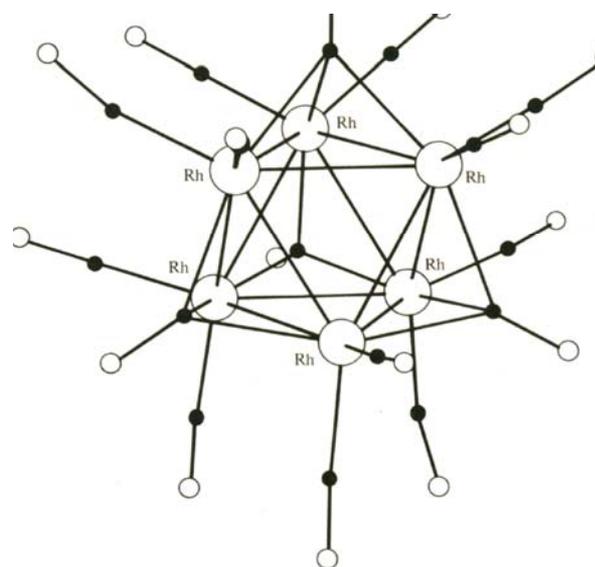
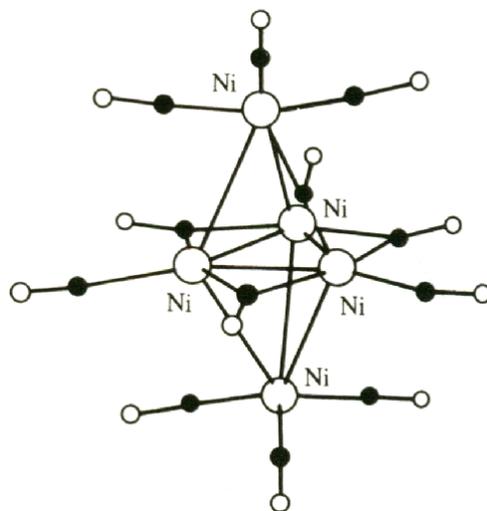
1750 - 1850



1620 - 1730



(b)



(d)

7. Metal Organic Compounds

Properties: Fe- and Ni-carbonyl are liquids at RT, other simple carbonyls are solids. Vapor pressures are high: at RT 47 kPa for Ni(CO)₄ and 12 kPa for Hexacarbonyltungsten. Additionally, all carbonyls, especially Ni(CO)₄ are toxic, so synthesis and handling has to be done very carefully!!! All carbonyls are nonpolar, so they are soluble in hydrocarbons.

Mononuclear carbonyls are weakly coloured. The intensity of colour increases with the number of metal ions (due to electronic transitions which are mainly located at the metal ions).

Pentacarbonyliron(0): light yellow liquid, Ennecarbonyldiiron(0) Fe₂(CO)₉: golden yellow solid, Dodecarbonyltriiron(0): dark green in solution, black in solid state.

Cyclic Polyene Complexes

Most important ligand: cyclopentadienyl (Cp). Metallocene: polyhapto-systems with cyclobutadien, cyclopentadien, aromates and cot (= cyclooctatetraene). A complex with a metal ion between two planar polyhapto rings is called "Sandwich Complex"! If the metal ion is not bonded to all C-atoms the ring is not planar.

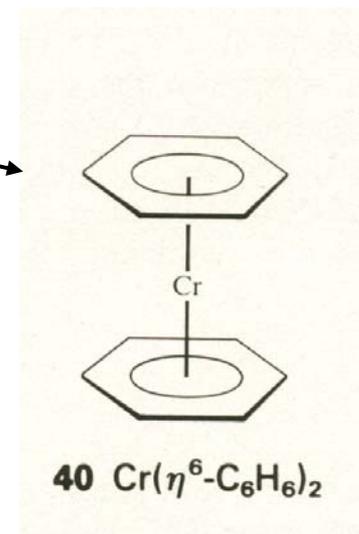
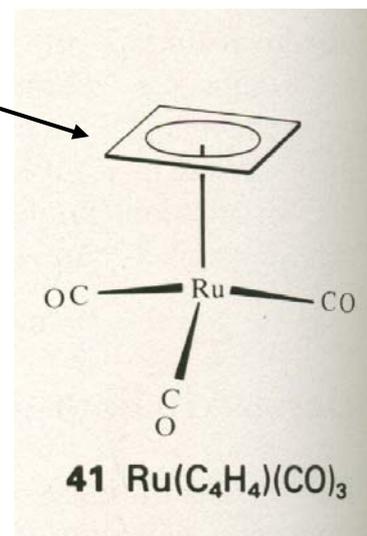
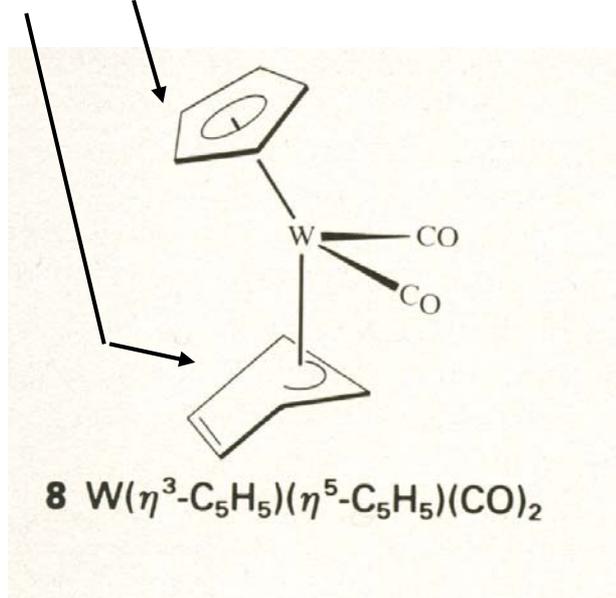
7. Metal Organic Compounds

Some examples: Ferrocene, Bisbenzenechrom (0)

Uranocene

Cyclobutadien is not stable as free molecule!

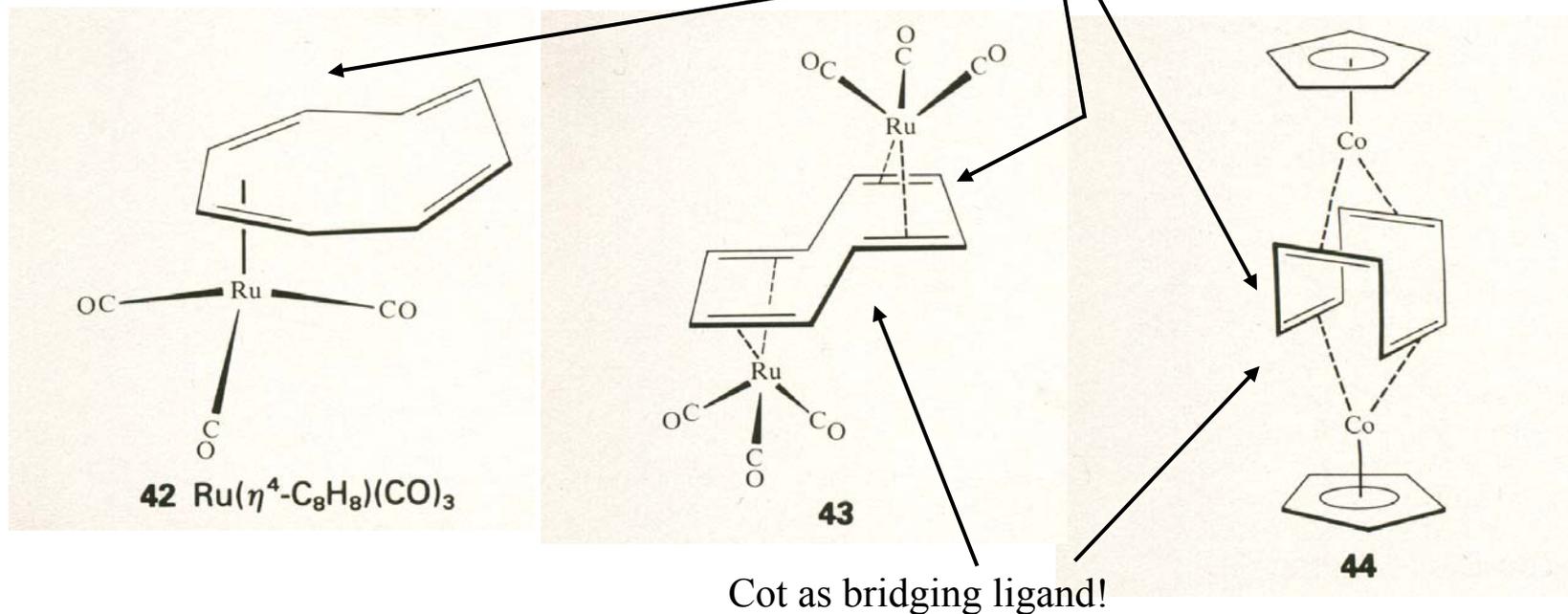
Cp can act as a η^1 , η^3 , or η^5 ligand.



Benzene (40) and the derivatives acts in general as a η^6 ligand.

7. Metal Organic Compounds

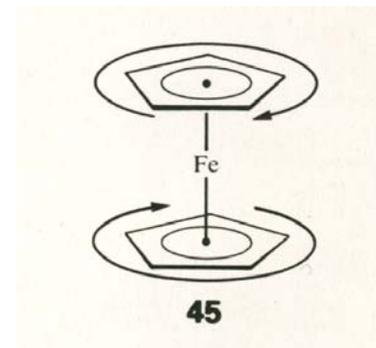
Cyclooctatetraene (cot) show different bond arrangements (η^2 , η^4 , η^6 , or η^8 ligand).



If cot act as a η^8 planar ligand it can be taken as $(\text{C}_8\text{H}_8)^{2-}$.

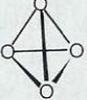
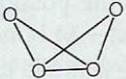
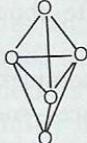
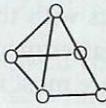
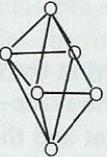
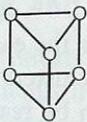
Fluctuation of complexes with cyclic ligands

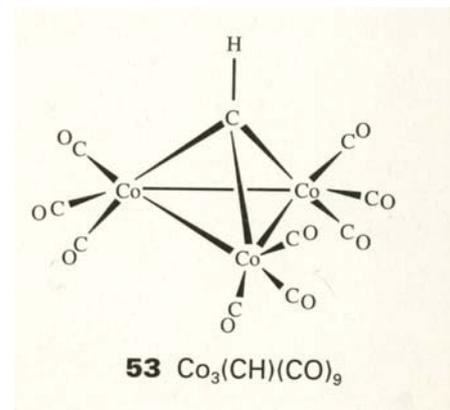
In gas phase the eclipsed form of ferrocene is about 4 KJ/mol more stable than the staggered one. But there is a rapid opposing rotation at room temperature (inner rotation).



Determination of the form of the metal frame: Wade-Mingos-Lauher rules!

Table 21.9 Correlation of cluster valence electron (CVE) count and structure

Number of metal atoms	Structure of metal framework	CVE count	Example
1	Single metal 	18	Ni(CO) ₄ (2)
2	Linear 	34	Mn ₂ (CO) ₁₀
3	Closed triangle 	48	[Co ₃ (CH)(CO) ₉] (78)
4	Tetrahedron 	60	Co ₄ (CO) ₁₂ (76)
	Butterfly 	62	[Fe ₄ (CO) ₁₂ C] ²⁻
	Square 	64	Os ₄ (CO) ₁₆
5	Trigonal bipyramid 	72	Os ₅ (CO) ₁₆
	Square pyramid 	74	Fe ₅ C(CO) ₁₅
6	Octahedron 	86	Ru ₆ C(CO) ₁₇
	Trigonal prism 	90	[Rh ₆ C(CO) ₁₅] ²⁻



Structure of Fe₅C(CO)₁₅
(C is an **interstitial** atom)

