CH432 Coordination Chemistry
คม432 เคมีโคออร์ดิเนชัน

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Course Outline (21.34%)

I) **Nomenclature of coordination compounds**

II) **Coordinate bond**

II)Structure and isomer of coordination compounds

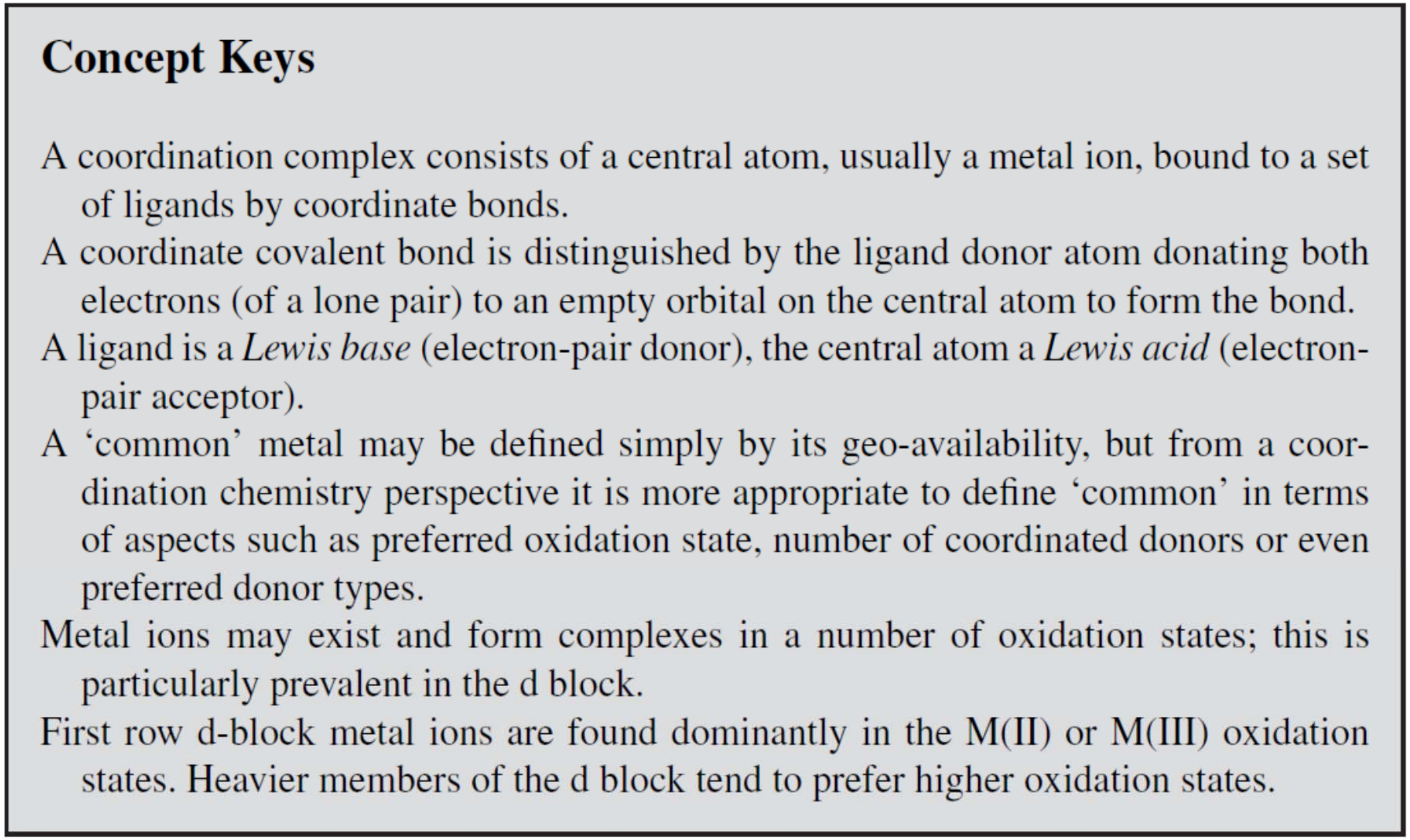
III)Preparation and reaction of coordination compounds

IV)Introduction of supramolecular chemistry and applications

References:

1. G.A. Lawrance, **Introduction to Coordination Chemistry**, John Wiley & Sons Ltd, 2010.
2. P.W. Atkins, T.L. Overton, J.P. Rourke, M.T. Weller, F.A. Armstrong, **Shriver and Atkins' Inorganic Chemistry**, 5th Edition, W. H. Freeman and Company New York, 2010.
3. G.L. Miessler, D.A. Tarr, **Inorganic Chemistry**, 3th Edition, Pearson Prentice Hall, 2004.
4. C.E. Housecroft, A.G. Sharpe, **Inorganic Chemistry**, 2nd Edition, Pearson Prentice Hall, 2005.
5. สุจิตรา ยังมี, **เคมีโคออร์ดิเนชัน**, 2549.

Coordination concept



Concept Keys

A coordination complex consists of a central atom, usually a metal ion, bound to a set of ligands by coordinate bonds.

A coordinate covalent bond is distinguished by the ligand donor atom donating both electrons (of a lone pair) to an empty orbital on the central atom to form the bond.

A ligand is a *Lewis base* (electron-pair donor), the central atom a *Lewis acid* (electron-pair acceptor).

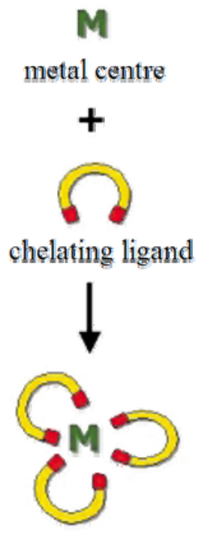
A ‘common’ metal may be defined simply by its geo-availability, but from a coordination chemistry perspective it is more appropriate to define ‘common’ in terms of aspects such as preferred oxidation state, number of coordinated donors or even preferred donor types.

Metal ions may exist and form complexes in a number of oxidation states; this is particularly prevalent in the d block.

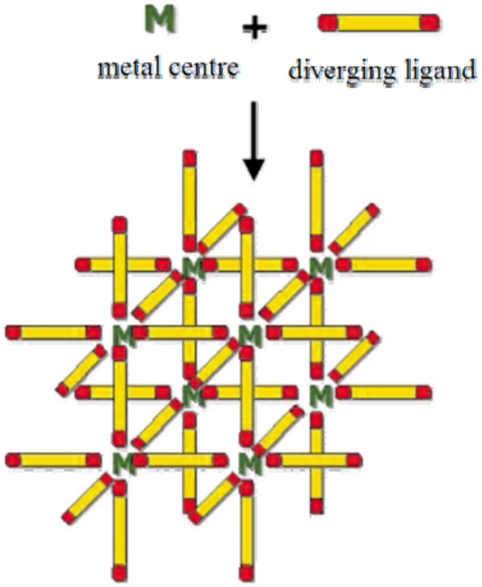
First row d-block metal ions are found dominantly in the M(II) or M(III) oxidation states. Heavier members of the d block tend to prefer higher oxidation states.

G.A. Lawrance, **Introduction to Coordination Chemistry**, John Wiley & Sons Ltd, 2010.

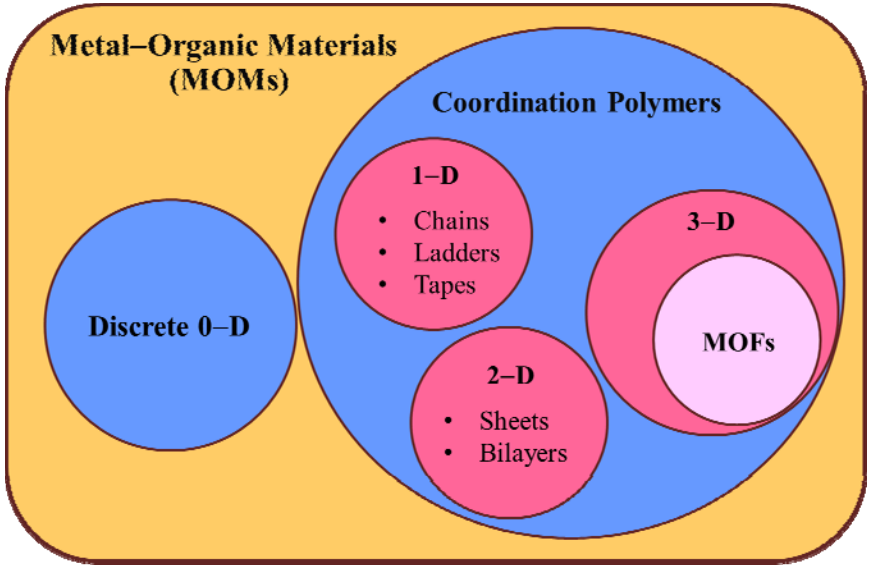
Metal–Organic Materials (MOMs)



coordination compound



coordination network



Metal–Organic Materials (MOMs)

Discrete 0–D

Coordination Polymers

1–D

- Chains
- Ladders
- Tapes

2–D

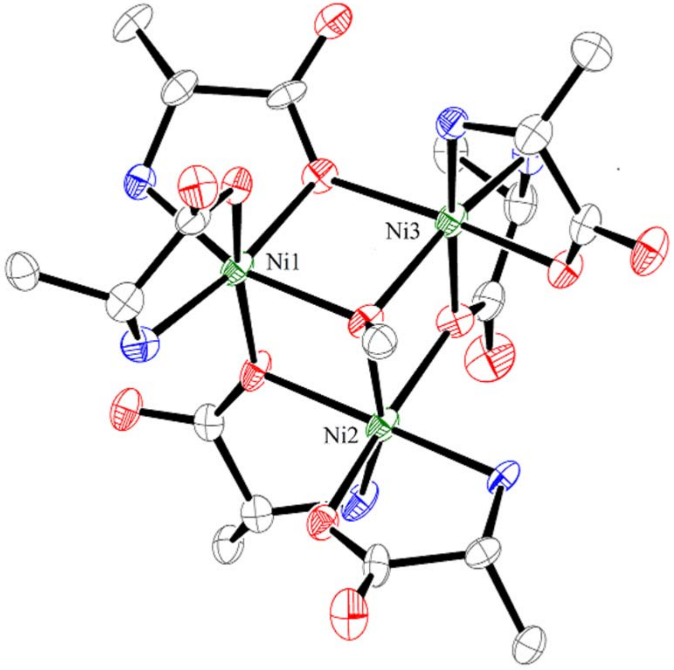
- Sheets
- Bilayers

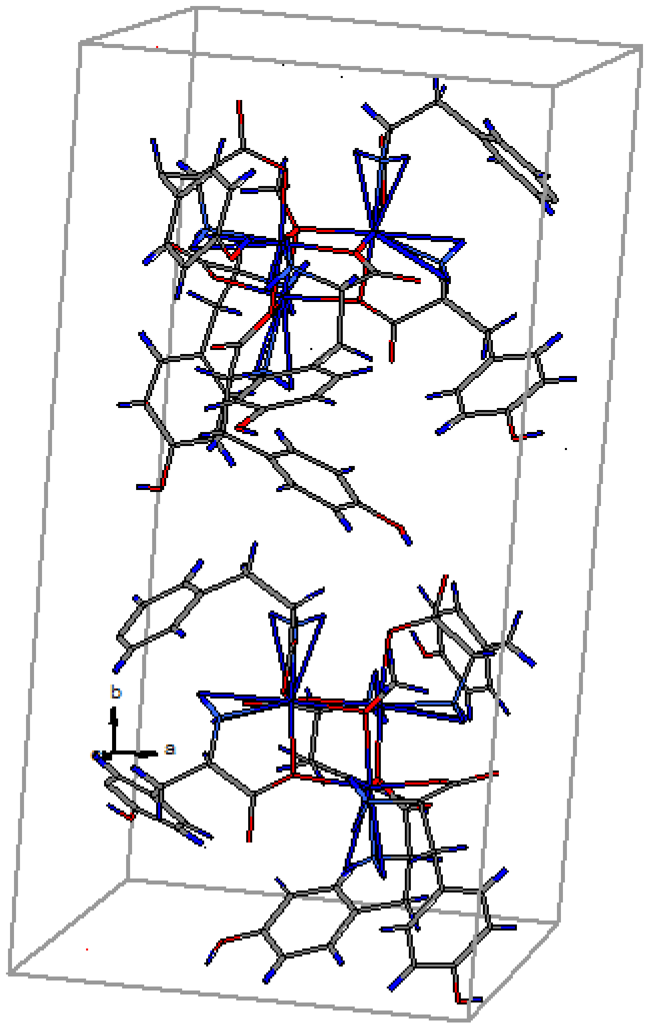
3–D

MOFs

Metal–Organic Materials (MOMs)

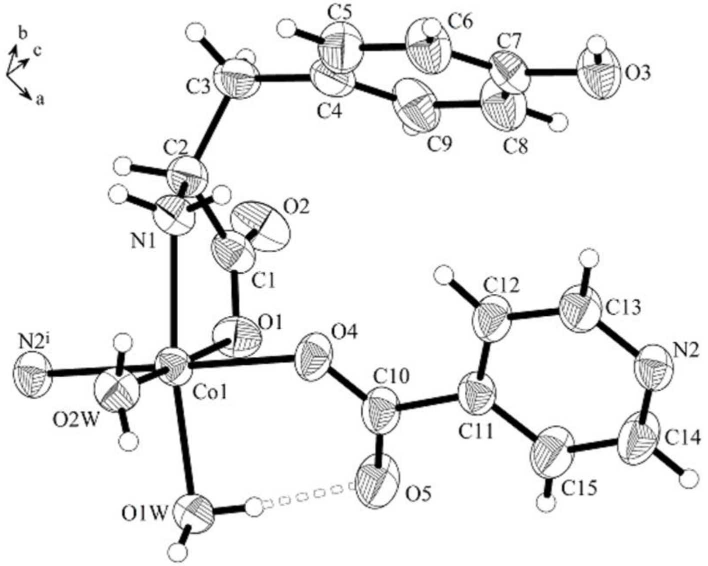
0–D

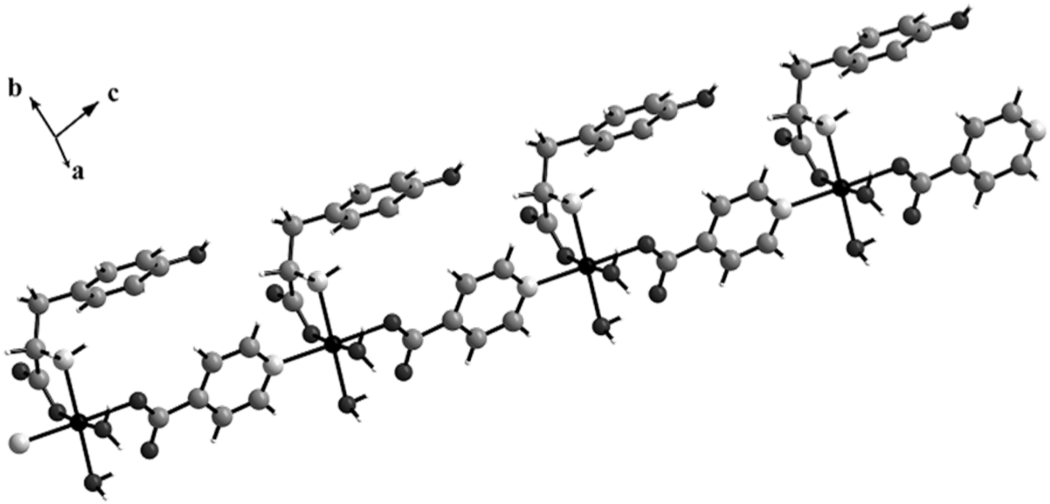




Metal–Organic Materials (MOMs)

1-D

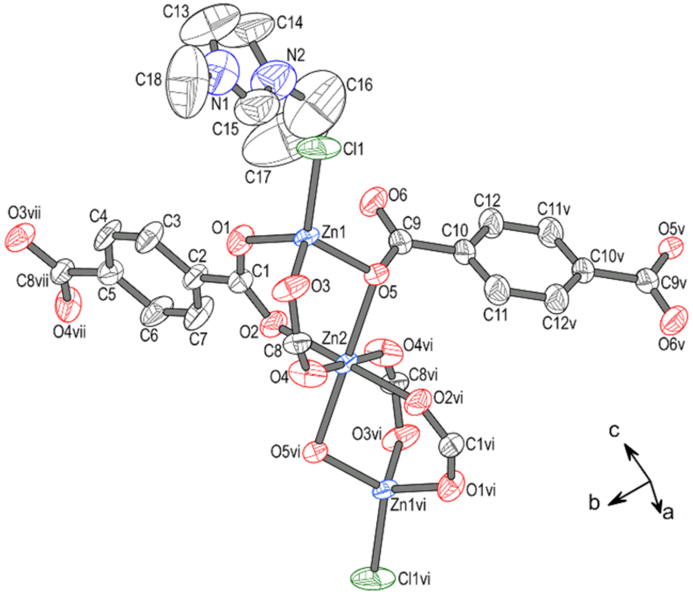


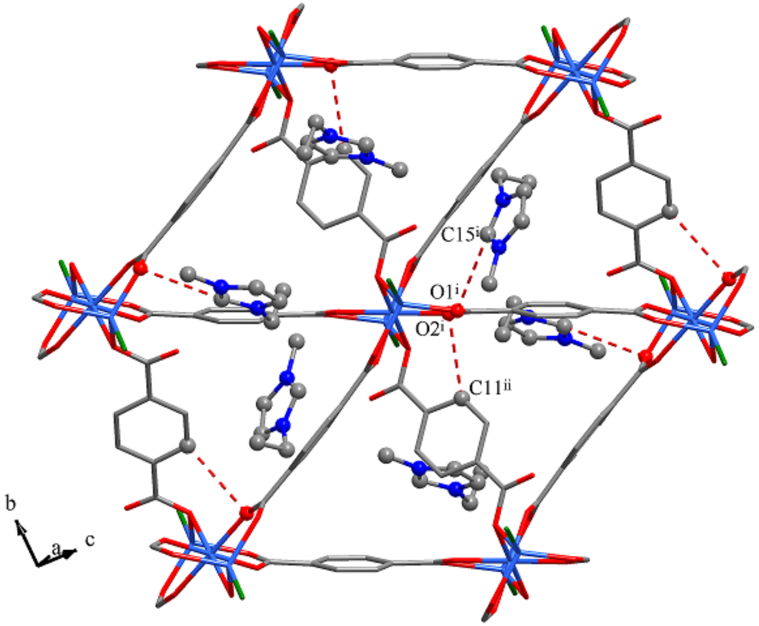


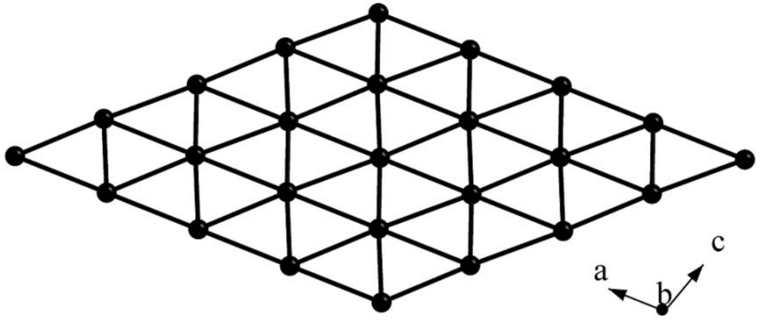
$Co(C_9H_{10}NO_3)(C_6H_4NO_2)(H_2O)_2$ (**II**)

Metal–Organic Materials (MOMs)

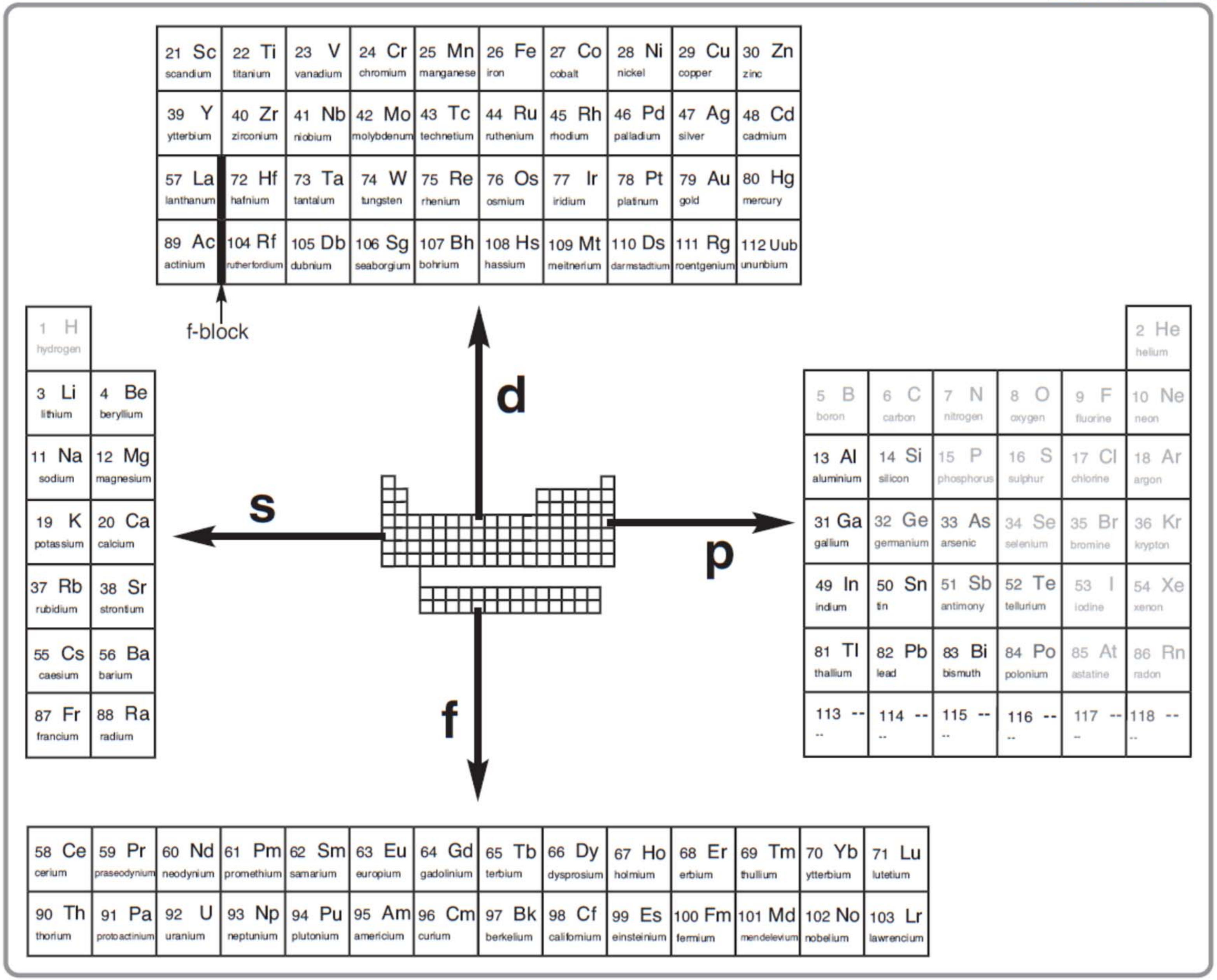
2-D







Metals



21 Sc scandium	22 Ti titanium	23 V vanadium	24 Cr chromium	25 Mn manganese	26 Fe iron	27 Co cobalt	28 Ni nickel	29 Cu copper	30 Zn zinc
39 Y ytterbium	40 Zr zirconium	41 Nb niobium	42 Mo molybdenum	43 Tc technetium	44 Ru ruthenium	45 Rh rhodium	46 Pd palladium	47 Ag silver	48 Cd cadmium
57 La lanthanum	72 Hf hafnium	73 Ta tantalum	74 W tungsten	75 Re rhenium	76 Os osmium	77 Ir iridium	78 Pt platinum	79 Au gold	80 Hg mercury
89 Ac actinium	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Uub ununbium

1 H hydrogen	
3 Li lithium	4 Be beryllium
11 Na sodium	12 Mg magnesium
19 K potassium	20 Ca calcium
37 Rb rubidium	38 Sr strontium
55 Cs caesium	56 Ba barium
87 Fr francium	88 Ra radium

					2 He helium
5 B boron	6 C carbon	7 N nitrogen	8 O oxygen	9 F fluorine	10 Ne neon
13 Al aluminium	14 Si silicon	15 P phosphorus	16 S sulphur	17 Cl chlorine	18 Ar argon
31 Ga gallium	32 Ge germanium	33 As arsenic	34 Se selenium	35 Br bromine	36 Kr krypton
49 In indium	50 Sn tin	51 Sb antimony	52 Te tellurium	53 I iodine	54 Xe xenon
81 Tl thallium	82 Pb lead	83 Bi bismuth	84 Po polonium	85 At astatine	86 Rn radon
113 -- --	114 -- --	115 -- --	116 -- --	117 -- --	118 -- --

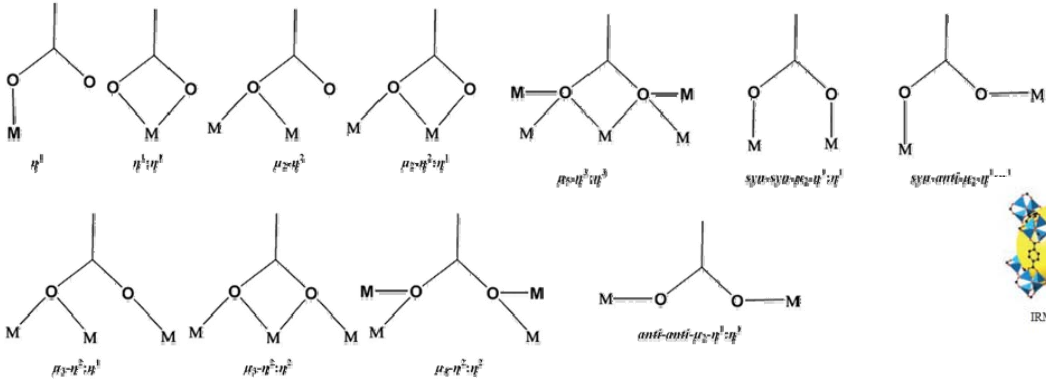
58 Ce cerium	59 Pr praseodynium	60 Nd neodynium	61 Pm promethium	62 Sm samarium	63 Eu europium	64 Gd gadolinium	65 Tb terbium	66 Dy dysprosium	67 Ho holmium	68 Er erbium	69 Tm thulium	70 Yb ytterbium	71 Lu lutetium
90 Th thorium	91 Pa protoactinium	92 U uranium	93 Np neptunium	94 Pu plutonium	95 Am americium	96 Cm curium	97 Bk berkelium	98 Cf californium	99 Es einsteinium	100 Fm fermium	101 Md mendelevium	102 No nobelium	103 Lr lawrencium

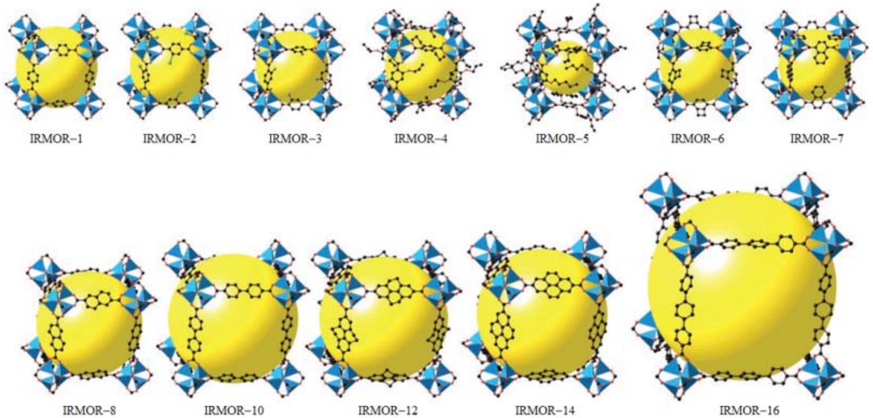
Organic ligands

Carboxylased-based *Flexibility* → **Rigid ligand**

"Displaying multiple coordination modes"

"provide more rigid structures and better structural prediction"

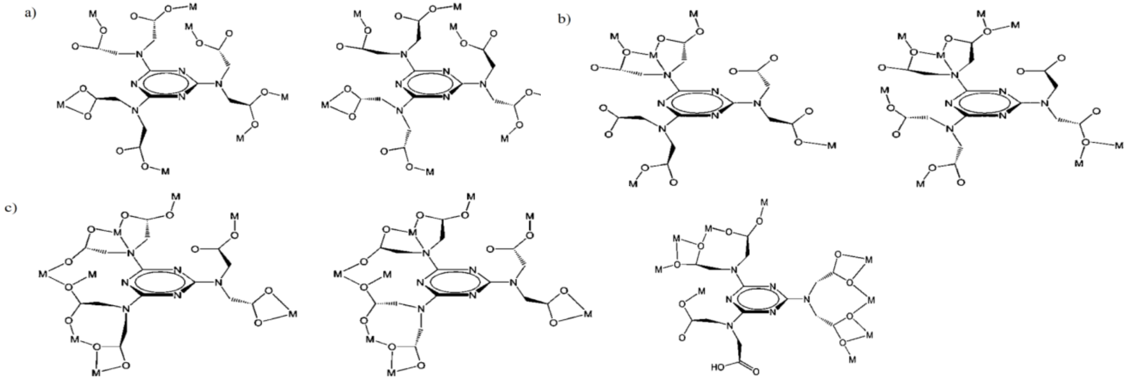




Flexibility ↓

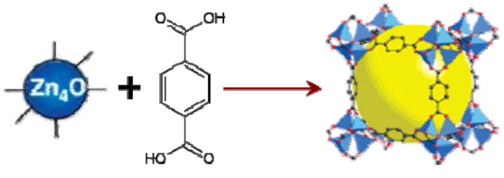
Flexible ligand

"offer a great variety of interesting structures and properties"



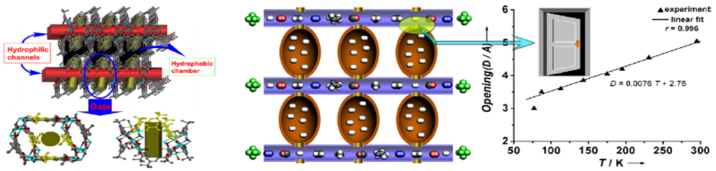
Applications of MOMs

- gas storage

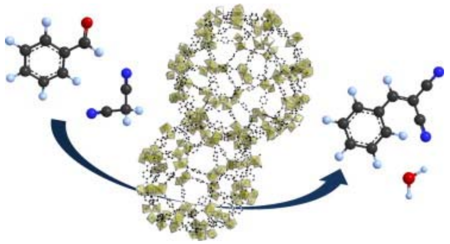


MOF-5, 2900 m^2/g

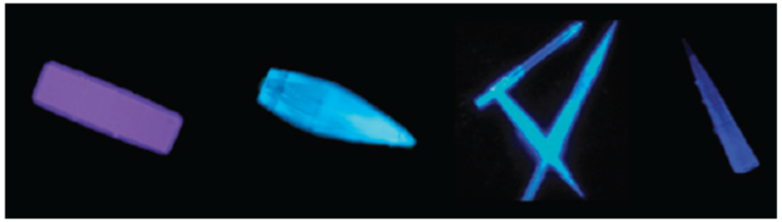
- selective gas adsorption

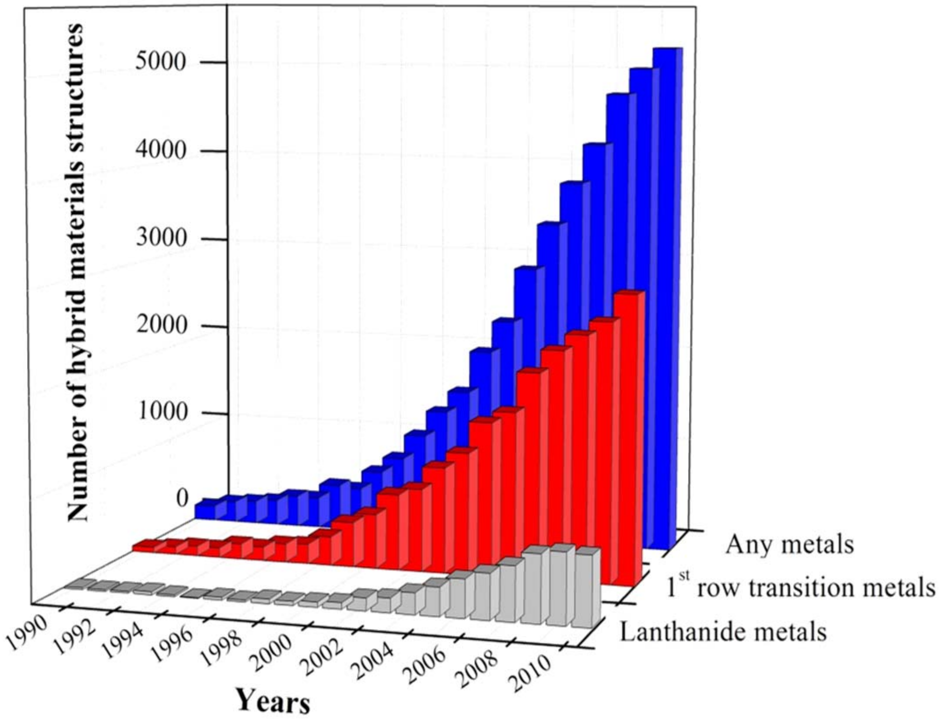


- catalysis



- luminescent materials





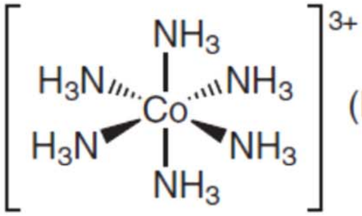
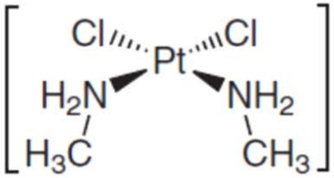
The outgrowth in numbers of MOMs reported in Cambridge Structure Database during 1990 to 2011

(B. Yotnoi, D.Phil Thesis, 2012.)

Chem. Soc. Rev., 38 (2009) 1213 ,Coord. Chem. Rev. 253 (2009) 3042., Micropor. Mesopor. Mate. 164 (2012) 38.

Nomenclature of coordination compounds

Terms of a structural drawing *(a written name or a formula)*

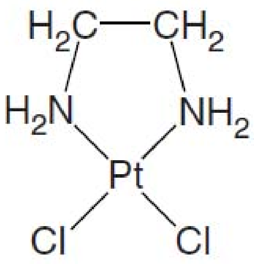
molecular drawing	*molecular formula*	*molecular name*
 $(NO_3^-)_3$	$[Co(NH_3)_6](NO_3)_3$	hexaamminecobalt(III) nitrate
	*cis*-$[PtCl_2(NH_2CH_3)_2]$	*cis*-dichlorobis(methanamine)platinum(II)

- Coordination compounds
- Coordination entity
- Coordination number
- Counter ion
- Central atom
- Oxidation state
- Ligands
- Coordination mode
- Chelation
- Bridging ligands

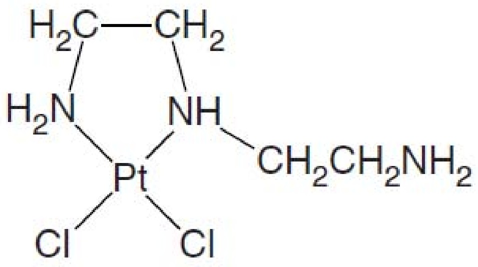
Chelation

“Denticity”

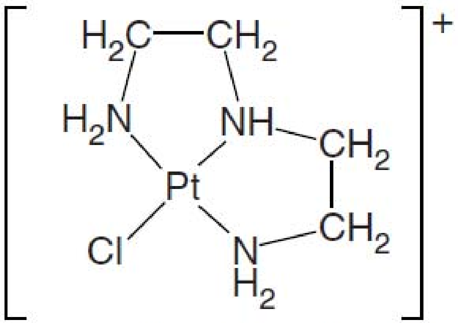
The number of donor atoms from a given ligand attached to the same central atom.



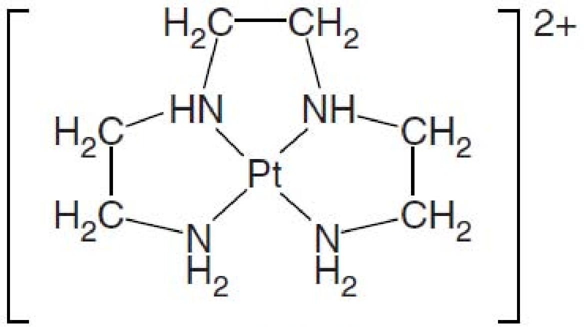
bidentate chelation



bidentate chelation



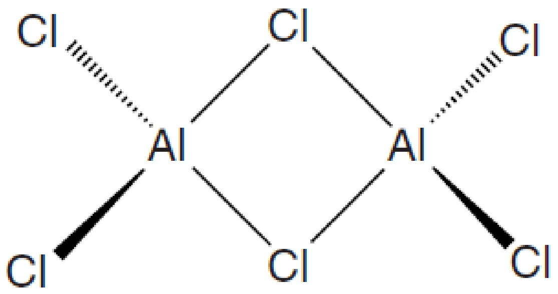
tridentate chelation



tetradentate chelation

Bridging ligands

If a potentially bidentate ligand, such as ethane–1,2–diamine, coordinates to two metal ions, it does not chelate but coordinates in a monodentate fashion to each metal ion, forming a connecting link or **bridge**. *e.g.* $[(H_3N)_5Co(\mu\text{–}NH_2CH_2CH_2NH_2)Co(NH_3)_5]^{6+}$

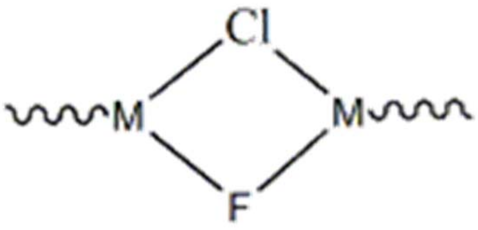


$[Al_2Cl_4(\mu\text{-}Cl)_2]$ or $[Cl_2Al(\mu\text{-}Cl)_2AlCl_2]$

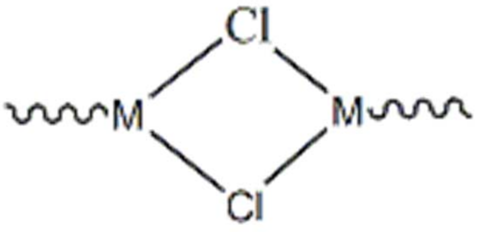
di-μ-chlorido-tetrachlorido-1κ^2*Cl*,2κ^2*Cl*-dialuminium

These ligands are identified by the Greek letter **mu (μ)** to indicate the ligand is bridging together with a *superscript n* to indicate the number of metal atoms to which the ligand is attached. ⇒ **“Polynuclear complexes”**

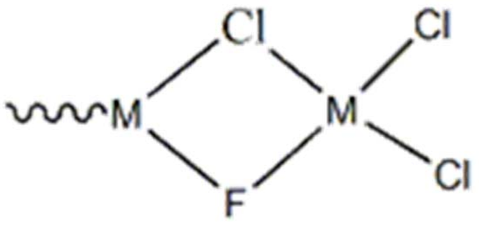
Bridging ligands



μ–chlorido–μ–fluorido



di–μ–chlorido

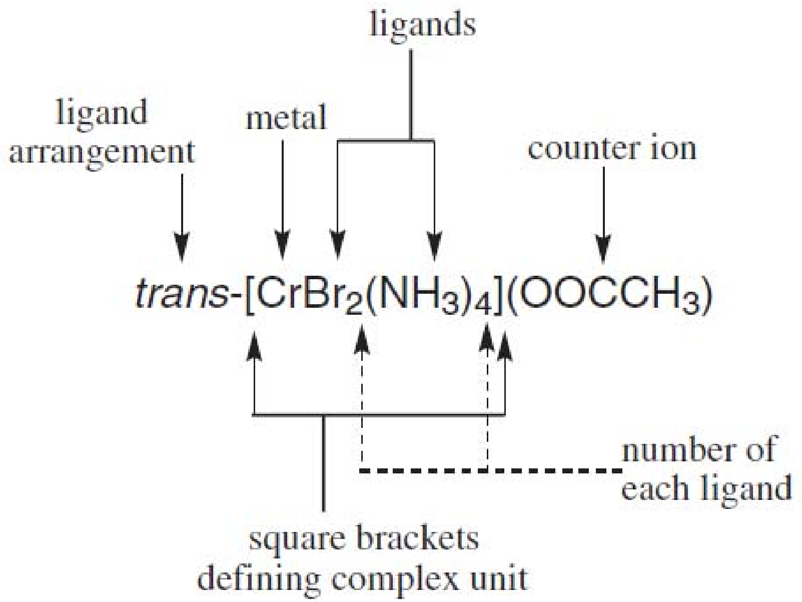


μ–chloridodichlorido–μ–fluorido

<u>Examples</u>

$[Fe_2(CN)_{10}(\mu\text{–}CN)]^{5-}$	μ–cyano–bis(pentacyanidoferrate(III))
$[Fe_2(CO)_6(\mu\text{–}CO)_3]$	tri–μ–carbonyl–bis(tricarbonyliron(0))
$[\{Co(NH_3)_4\}_2(\mu\text{–}Cl)(\mu\text{–}OH)]^{4+}$	μ–chlorido–μ–hydroxido–bis(tetraamminecobalt(III))

Nomenclature of coordination compounds



ligands

ligand arrangement

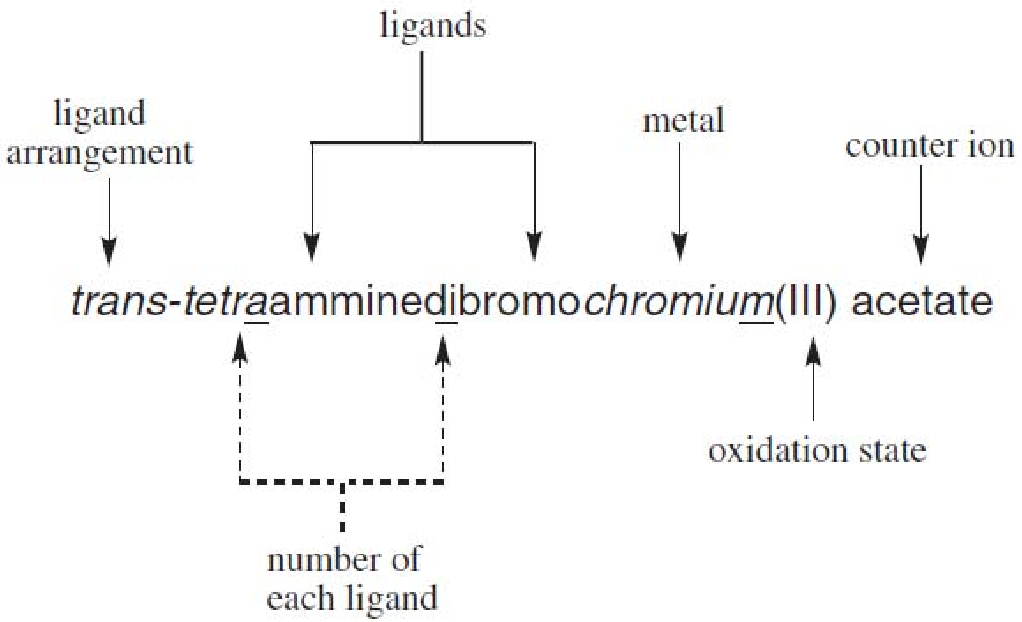
metal

counter ion

$\textit{trans}\text{-}[CrBr_2(NH_3)_4](OOCCH_3)$

number of each ligand

square brackets defining complex unit



ligands

ligand arrangement

metal

counter ion

trans-*tetra*amminedibromo*chromium*(III) acetate

oxidation state

number of each ligand

Nomenclature of coordination compounds

Simple Ligands

- **Neutral ligands** ⇒ usually unchanged

  e.g. $NH_2CH_2CH_2NH_2$ = Ethylenediamine (en)

  $C_{10}H_8N_2$ = 2,2'–bipyridine (pipy)

- **Common ligands**

H_2O	NH_3	CO	NO
aqua	ammine	carconyl	nitrosyl

- **Anionic ligands** ⇒ changed to always end in –o

Free anion	Coordinated anion	Free anion	Coordinated anion
Cl^-, chloride	chlorido	HO^-, hydroxide	hydroxido
O_2^-, superoxide	superoxido	CN^-, cyanide	cyanido
SCN^-, thiocyanate	thiocyanato	CO_3^{2-}, carbonate	carbonato
NO_3^-, nitrate	nitrato	NO_2^-, nitrite	nitrito
N_3^-, azide	azido	NH_2^-, amide	amido
ClO_4^-, perchlorate	perchlorato	SO_4^{2-}, sulfate	sulfato

Nomenclature of coordination compounds

Complexes

- **Neutral complexes** ⇒ have only a single 'word' name

  "no spaces are left between parts of the name that refer to the same coordination entity"

- **Ionic complexes** ⇒ are written as two 'words', with one word name for the cation and one word name for the anion.

  For all ionic complexes, invariably, the cation is named first, and the anion last.

- Ligands are arranged first, in alphabetical order, followed by the name of the metal ion. The oxidation number of the central metal atom is included at the end of the name, as a Roman numeral in parentheses.

- In anionic complexes the name of the metal is modified to an –ate ending (*e.g.* molybdenum to molybdate, or zinc to zincate)

Nomenclature of coordination compounds

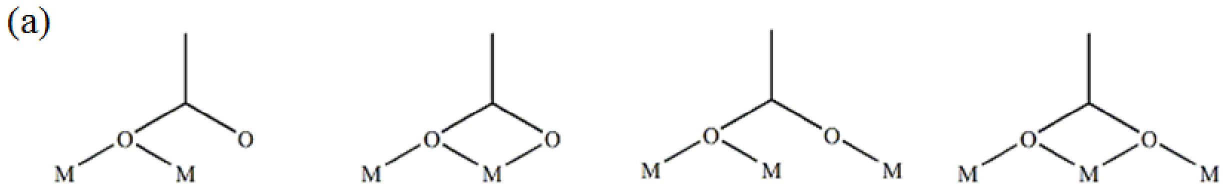
In writing the formula representation of a complex,

- The metal is written first at left after the opening square bracket.
- Ligands are listed in alphabetical order of the first letter of the formula or standard abbreviation that is used for each ligand

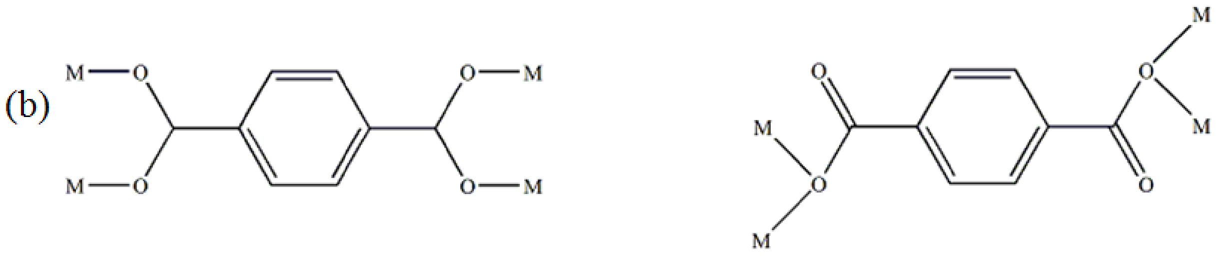
  (For example Cl before NH_3 before H_2O
  (en) before NH_3)
- Any bridging ligands in polynuclear complexes are listed after terminal ligands, and if more than one in increasing order of bridging multiplicity (i.e. number of bonds to metals).
- The formula is completed with a closing square bracket.
- If there are any counter–ions, their standard formulae are written before (cations) or after (anions) the complex formula.

μ-Notation

A Greek letter **μ (mu)** indicates the bridging bonding mode of ligands. The number of metal atoms connected by a bridging ligand is indicated by a right subscript, **μ_n**, where $n \geq 2$ (Fig. a). . The μ is placed before the ligand name and separated by a hyphen (Fig. b). . In the case of multiple bridging modes, μ_n is listed in descending order of complexity.



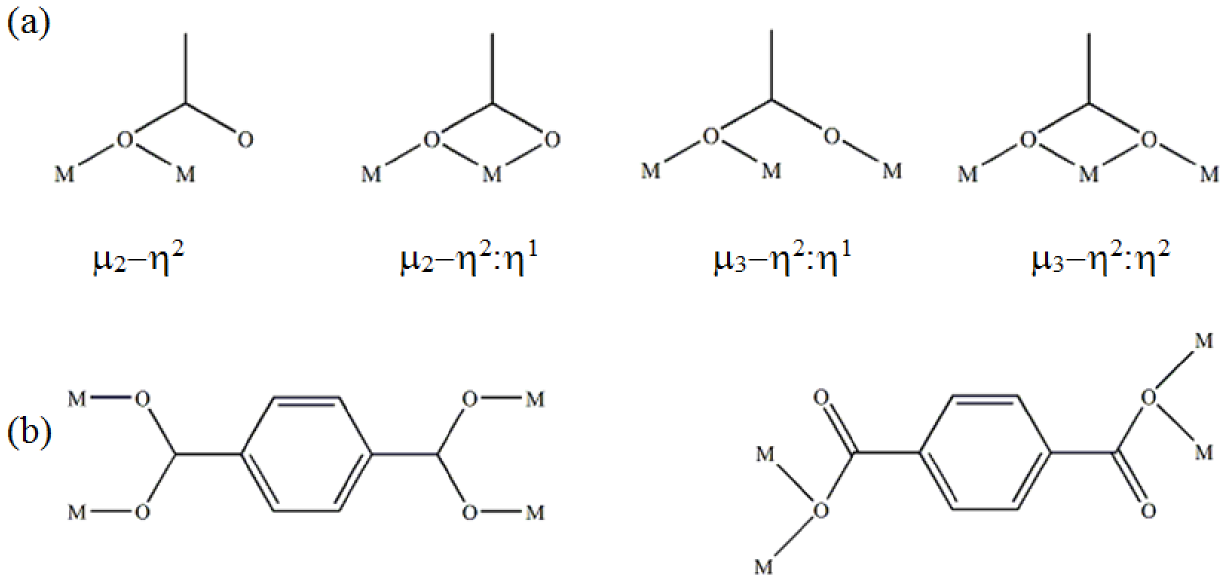
μ_2–η^2 μ_2–η^2:η^1 μ_3–η^2:η^1 μ_3–η^2:η^2



μ_4–η^4–1,4–benzenedicarboxylate

η–Notation

A Greek letter **η (eta)** is used to specify the hapticity of a ligand, which is the number of contiguous ligating atoms that are involved in bonding to one or more metals (Fig. a). The number of contiguous atoms in the ligand coordinated to the metal is indicated by a right superscript numeral.

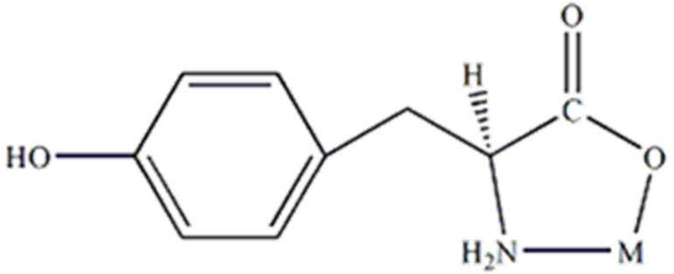


$\mu_2–\eta^2$ $\mu_2–\eta^2:\eta^1$ $\mu_3–\eta^2:\eta^1$ $\mu_3–\eta^2:\eta^2$

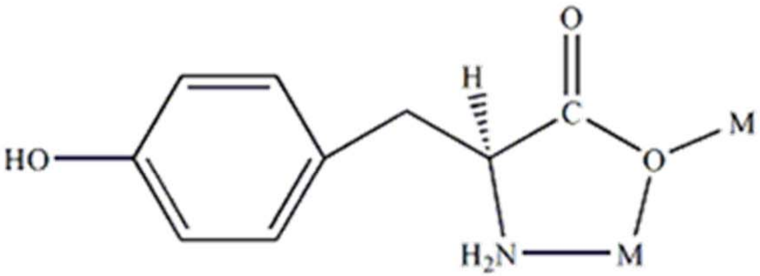
$\mu_4–\eta^4$–1,4–benzenedicarboxylate

κ–Notation

- A Greek letter **κ (kappa)** is used to indicate the attachment of the coordinating atoms of a polydentate ligand bonding to a metal center in the polynuclear complexes.
- A right superscript numeral is added to the symbol **κ** in order to indicate the number of identically bound ligating atoms in the flexidentate ligand.
- When a polydentate ligand contains several nonequivalent ligating atoms, each is indicated by its italicized element symbol preceded by **κ**.



L–*p*–tyrosinato–$\kappa^{2}N,O$



μ_2–*L*–*p*–tyrosinato–$\kappa^{3}N,O:O$

Comparison of the eta and kappa conventions

- The eta convention is applied in cases where contiguous donor atoms within a given ligand are involved in bonding to a central atom

  (It is used only when there is more than one ligating atom)

- The kappa convention is used to specify bonding from isolated donor atoms to one or more central atoms.

- In cases where two or more identical ligands (or parts of a polydentate ligand) are bound to a central atom, a superscript is used on k to indicate the number of donor atom–to–central atom bonds.

Locators

- Structural features of molecules associated with stereochemistry and isomerism are indicated by prefixes attached to the name, and italicized, and separated from the rest of the name by a hyphen.

- Typical of this type are the geometry indicators *cis*–, *trans*–, and *fac*–, *mer*–.

- Examples

cis–$[PtCl_2(py)_2]$	cis–dichloridobis(pyridine)platinum(II)
mer–$[IrH_3\{P(C_6H_5)_3\}_3]$	mer–trihydridotris(triphenylphosphane)iridium(III)

Metal–metal bonding

- Metal–metal bonding may be indicated in names by placing italicized atomic symbols of the appropriate central atoms, separated by an 'em' dash and enclosed in parentheses, after the list of central atom names and before the ionic charge.

  $[Br_4ReReBr_4]^{2-}$ bis(tetrabromidorhenate)(*Re*—*Re*)(2–)

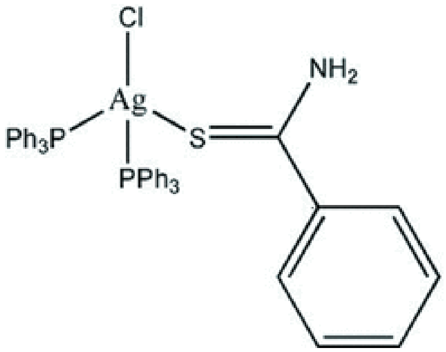
  $[Mn_2(CO)_{10}]$ bis(pentacarbonylmanganese)(*Mn*—*Mn*)

- The central atom element symbols are placed in the same order as the central atoms appear in the name

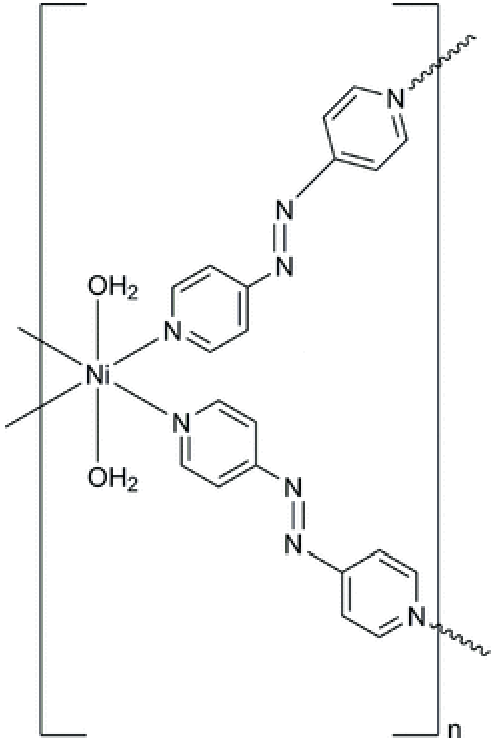
  $[CoCu_2Sn(CH_3)(\mu\text{-}C_2H_3O_2)_2(C_5H_5)]$

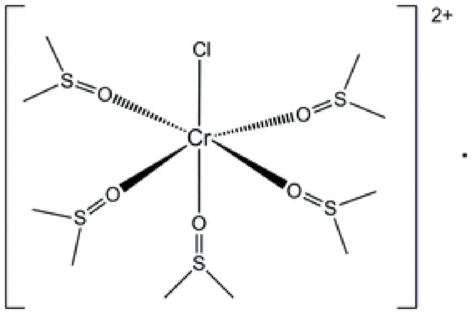
  bis–(μ–acetato)cyclopentadienylmethylcobaltdicoppertin

Examples

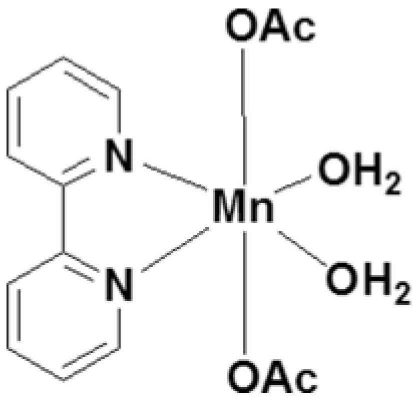


(benzenecarbothioamide–κS)chloridobis(triphenylphosphane–κP)silver(I)





chloridopentakis(dimethyl sulfoxide–κO)chromium(III)



bis(acetato–κO)diaqua(2,2'–bipyridine–$\kappa^2 N,N'$)manganese(II)

poly[[trans–diaquabis[μ–*trans*–4,4'–(diazenediyl)dipyridine]nickel(II)]

Examples: Symmetrical dinuclear entities

$[Re_2Br_8]^{2-}$	bis(tetrabromidorhenate)(Re — Re)(2–)
$[Mn_2(CO)_{10}]$	bis(pentacarbonylmanganese)(Mn — Mn)
$[\{Cr(NH_3)_5\}_2(\mu\text{–}OH)]^{5+}$	μ–hydroxido–bis(pentaamminechromium)(5+)
$[\{PtCl(PPh_3)\}_2(\mu\text{–}Cl)_2]$	di–μ–chlorido–bis[chlorido(triphenylphosphane)platinum]
$[\{Fe(NO)_2\}_2(\mu\text{–}PPh_2)_2]$	bis(μ–diphenylphosphanido)bis(dinitrosyliron)
$[\{Cu(py)\}_2(\mu\text{–}O_2CMe)_4]$	tetrakis(μ–acetato–**κ**O: **κ**O’)bis[(pyridine)copper(II)]

Examples: Unsymmetrical dinuclear entities

$[ClHgIr(CO)Cl_2(PPh_3)_2]$

carbonyl-1κ*C*-trichlorido-1κ^2*Cl*,2κ*Cl*-bis(triphenylphosphane-1κ*P*)iridiummercury(*Ir*—*Hg*)

$[(H_3N)_5\overset{1}{Cr}(\mu\text{-}OH)\overset{2}{Cr}(NH_2Me)(NH_3)_4]^{5+}$

nonaammine-1κ^5*N*,2κ^4*N*-μ-hydroxido-(methanamine-2κ*N*)dichromium(5+)

$[(H_3N)_3\overset{1}{Co}(\mu\text{-}NO_2)(\mu\text{-}OH)_2\overset{2}{Co}(NH_3)_2(py)]^{3+}$

pentaammine-1κ^3*N*, 2κ^2*N*-di-μ-hydroxido-μ-nitrito-1κ*N*:2κ*O*-(pyridine-2κ*N*)dicobalt(3+)

$[(bpy)(H_2O)\overset{1}{Cu}(\mu\text{-}OH)_2\overset{2}{Cu}(bpy)(SO_4)]$

aqua-1κ*O*-(2,2′-bipyridine-1κ^2*N*,*N*′)(2,2′-bipyridine-2κ^2*N*,*N*′)-di-μ-hydroxido-(sulfato-2κ*O*)dicopper(II)

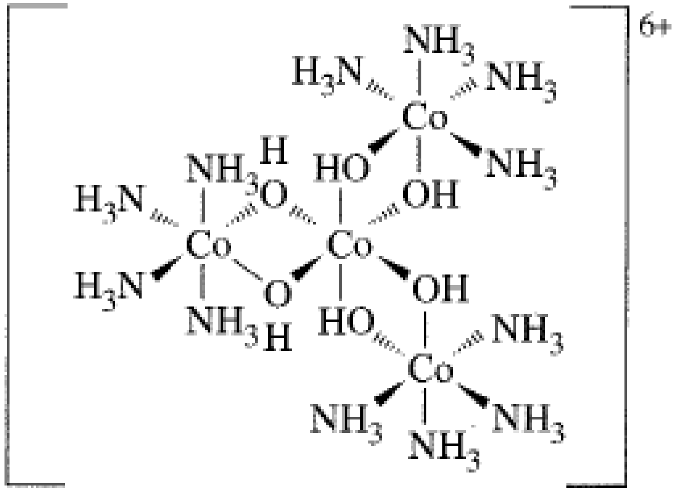
$[\{Co(NH_3)_3\}_2(\mu\text{-}NO_2)(\mu\text{-}OH)_2]^{3+}$

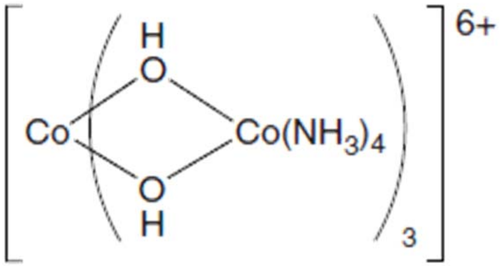
di-μ-hydroxido-μ-nitrito-κ*N*:κ*O*-bis(triamminecobalt)(3+)

Examples: Polynuclear complexes

$[Be_4(\mu_4\text{-}O)(\mu\text{-}O_2CMe)_6]$
hexakis(μ-acetato-κO:$\kappa O'$)-μ_4-oxido-*tetrahedro*-tetraberyllium

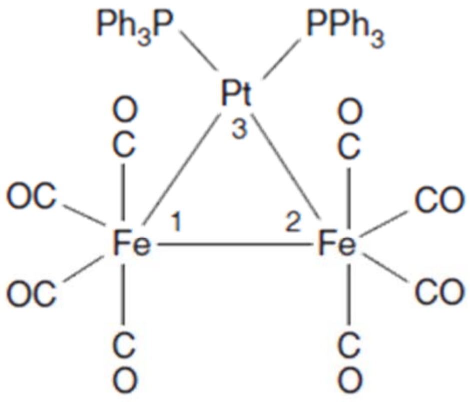
$[Os_3(CO)_{12}]$
dodecacarbonyl-1$\kappa^4 C$,2$\kappa^4 C$,3$\kappa^4 C$-*triangulo*-triosmium(3 Os—Os)





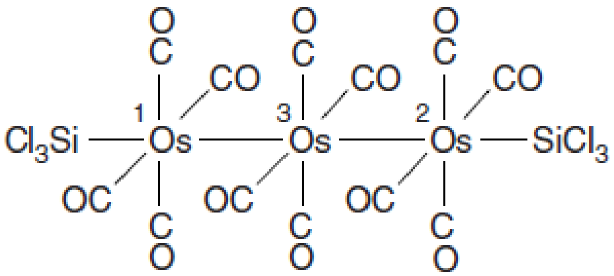
$[Co\{(\mu\text{-}OH)_2Co(NH_3)_4\}_3]^{6+}$
dodecaammine-1$\kappa^4 N$,2$\kappa^4 N$,3$\kappa^4 N$-hexa-μ-hydroxido-1:4$\kappa^4 O$;2:4$\kappa^4 O$;3:4$\kappa^4 O$-tetracobalt(6+)

Examples: Polynuclear complexes



octacarbonyl-1κ^4*C*,2κ^4*C*-bis(triphenylphosphane-3κ*P*)-*triangulo*-diironplatinum(*Fe*—*Fe*)(2 *Fe*—*Pt*)

[Os$_3$(CO)$_{12}$(SiCl$_3$)$_2$]



dodecacarbonyl-1κ^4*C*,2κ^4*C*,3κ^4*C*-bis(trichlorosilyl)-1κ*Si*,2κ*Si*-triosmium(*Os*^{1}—*Os*^{3})(*Os*^{2}—*Os*^{3})

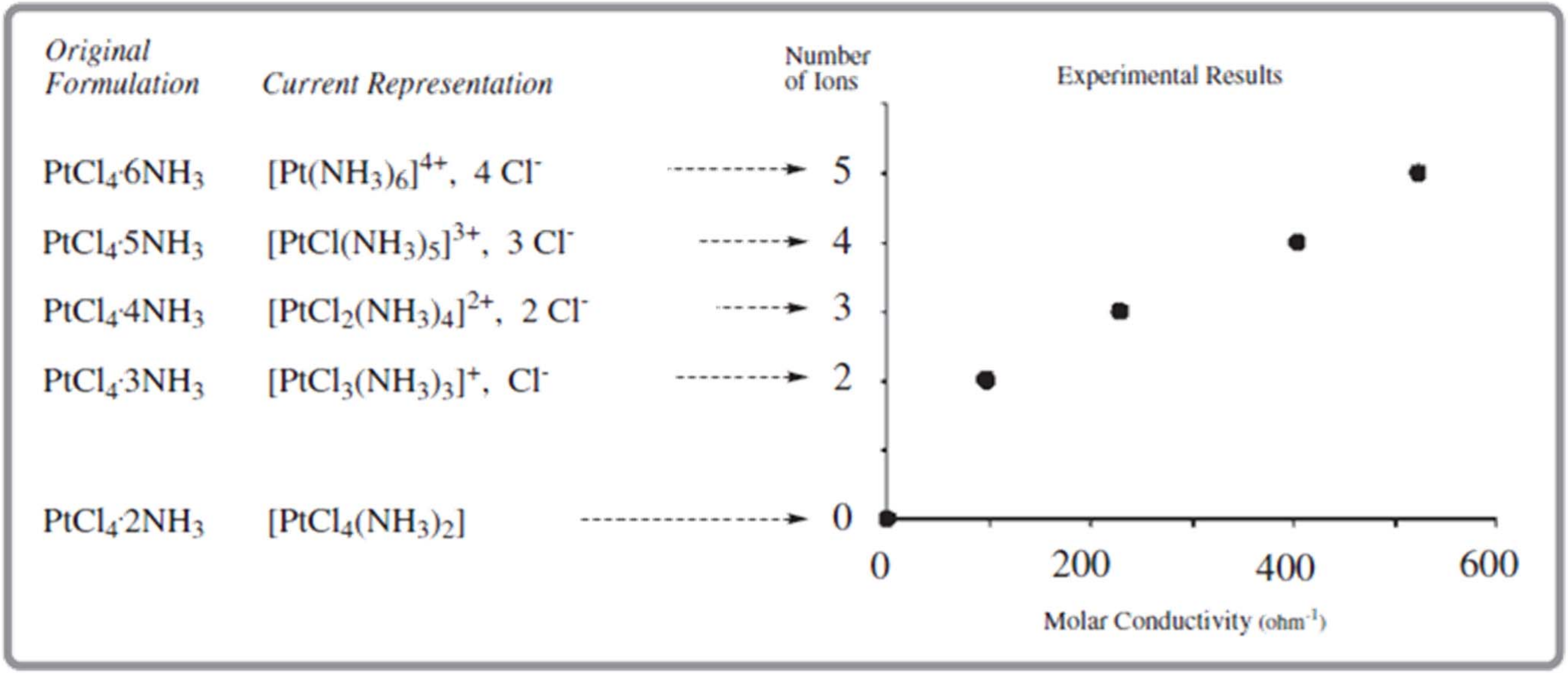
The foundation of coordination chemistry

$CoCl_3 \cdot 6NH_3$ ⇒ Tassaert complex

(regdish–brown malogany)

Molecule	Conductivity	Amount of silver halide precipitated upon addition of silver ion
$CoCl_3 \cdot 6NH_3$	High	3
$CoCl_3 \cdot 5NH_3$	Medium	2
$CoCl_3 \cdot 4NH_3$	Low	1
$IrCl_3 \cdot 3NH_3$	No	0

The foundation of coordination chemistry

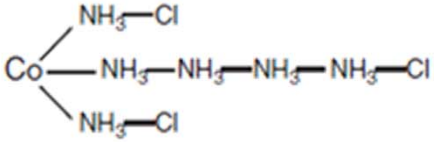
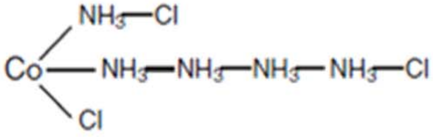
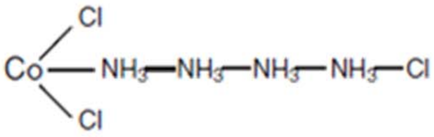
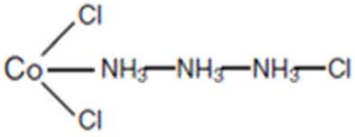


Original Formulation	*Current Representation*	Number of Ions
$PtCl_4{\cdot}6NH_3$	$[Pt(NH_3)_6]^{4+}$, 4 Cl^-	5
$PtCl_4{\cdot}5NH_3$	$[PtCl(NH_3)_5]^{3+}$, 3 Cl^-	4
$PtCl_4{\cdot}4NH_3$	$[PtCl_2(NH_3)_4]^{2+}$, 2 Cl^-	3
$PtCl_4{\cdot}3NH_3$	$[PtCl_3(NH_3)_3]^{+}$, Cl^-	2
$PtCl_4{\cdot}2NH_3$	$[PtCl_4(NH_3)_2]$	0

Identifying ionic composition from molar conductivity experiments for a series of platinum(IV) complexes of ammonia and chloride ion.

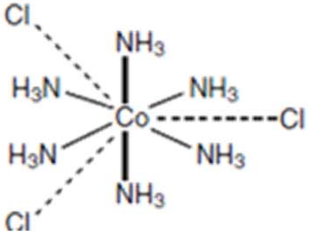
The foundation of coordination chemistry

Jørgensen's chain theory

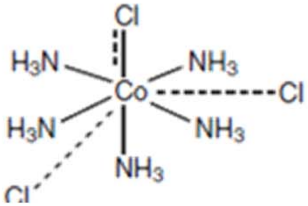





Werner's theory

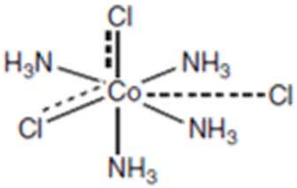
$[Co(NH_3)_6]Cl_3$



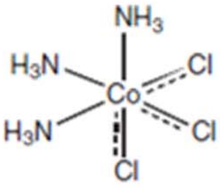
$[CoCl(NH_3)_5]Cl_2$



$[CoCl_2(NH_3)_4]Cl$



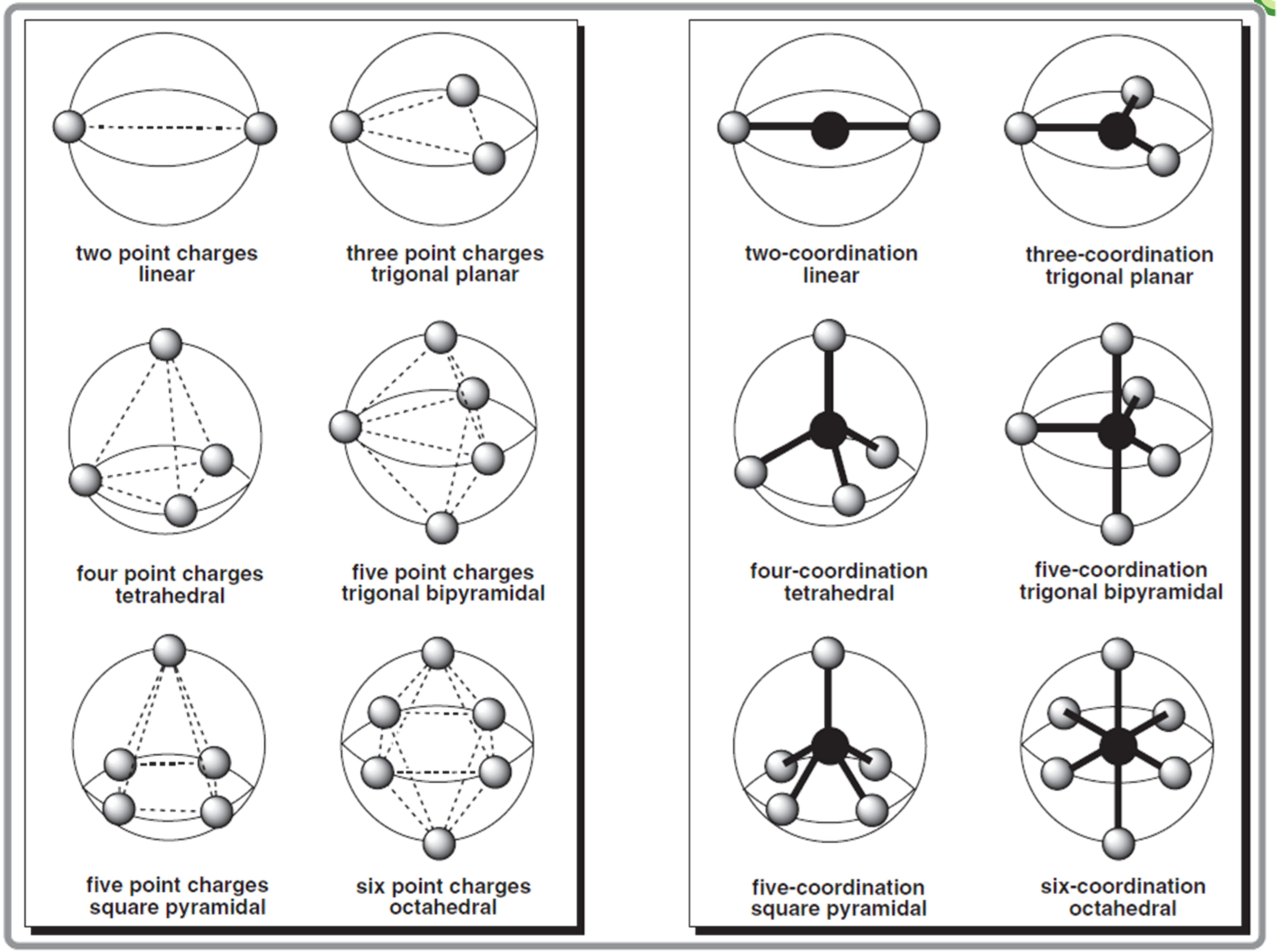
$[CoCl_3(NH_3)_3]$



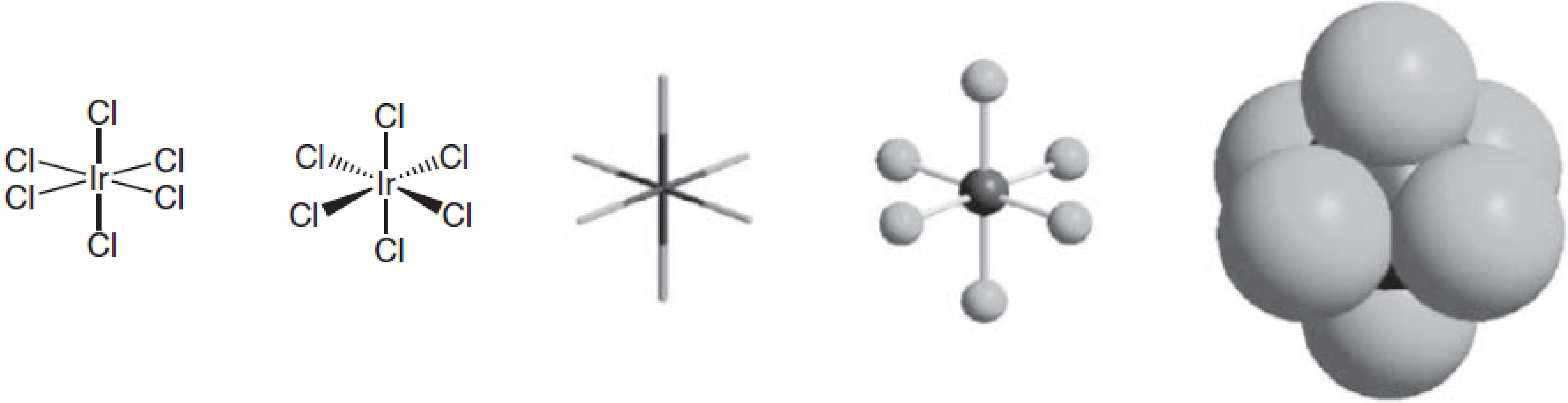
"Birth of modern coordination chemistry"

- **Primary valence** (corresponds to oxidation state)
- **Secondary valence** (coordination number)

The foundation of coordination chemistry



The foundation of coordination chemistry



basic drawing

drawing with perspective

stick model

ball and stick model

space-filling model

Various ways in which metal complexes can be represented, illustrated for the simple octahedral complex ion $[IrCl_6]^{2-}$

The Nature of Bonding in Metal Complexes

- The metals of the d block characteristically exist in stable oxidation states for which the *n*d subshell has only partial occupancy by electrons.
- The chemical and physical properties characteristic of the transition elements are determined by the partly filled *n*d subshells
- In the simple atomic model of the first-row d-block elements, the set of closely-spaced levels involving 4s, 4p and 3d orbitals can be considered as the valence orbitals.
- This provides the luxury of nine orbitals (1 s, 3 p and 5 d), giving rise to what is called the nine-orbital (or 18-electron) rule that attempts to explain metal–donor coordination numbers of up to nine.

Effective atomic number rule (EAV rule)

- Number represents the total number of electrons surrounding the nucleus of a metal atom in a metal complex.
- For the EAN rule, the metal atom tends to surround itself with sufficient ligands that the resulting effective atomic number is numerically equal to the atomic number of the noble-gas element found in the same period in which the metal is situated.

  [18 (Argon, Ar), 36 (Krypton, Kr), 54 (Xenon, Xe) and 86 (Radon, Rn)]
- The EAN rule is often referred to as the "18-electron rule" since, if one counts only valence electrons.

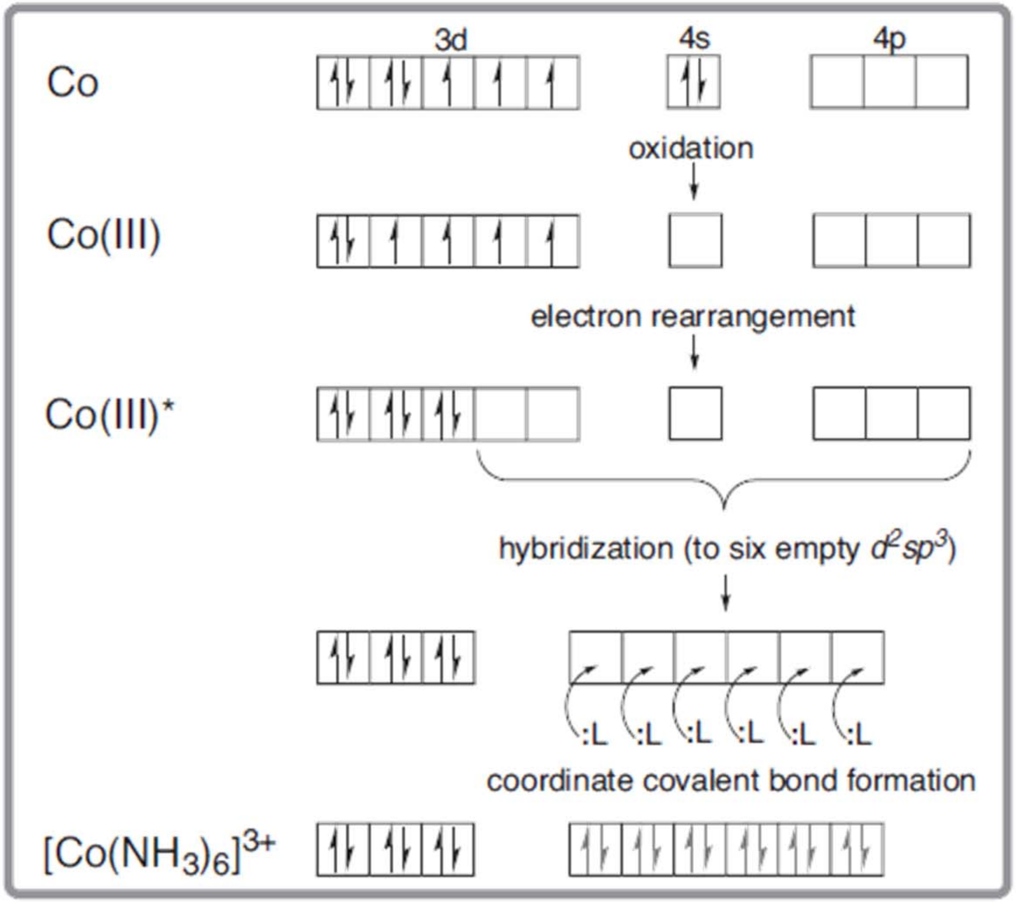
$Cr(CO)_6$	18-electron rule	EAN rule
	$Cr = 6\ e^-$	$Cr = 24\ e^-$
	$6\ CO = 12\ e^-$	$6\ CO = 12\ e^-$
	$Cr(CO)_6 = 18\ e^-$	$Cr(CO)_6 = 36\ e^-$

Effective atomic number rule (EAN rule)

Complexes	e^- of M^{n+}	e^- from ligand	EAN
$[Co(NH_3)_6]^{3+}$	27 – 3 = 24	6 × 2 = 12	36 (Kr)
$[Pt(NH_3)_6]^{4+}$	78 – 4 = 74	6 × 2 = 12	86 (Rn)
$[Fe(CN)_6]^{4-}$	26 – 2 = 24	6 × 2 = 12	36
$[Fe(CO)_5]$	26	5 × 2 = 10	36
$[Cr(CO)_6]$	24	6 × 2 = 12	36
$[Ni(CO)_4]$	28	4 × 2 = 8	36
$[Ni(NH_3)_6]^{2+}$	26	6 × 2 = 12	38
$[Ni(CN)_4]^{2-}$	26	4 × 2 = 8	34
$[Cr(NH_3)_6]^{3+}$	21	6 × 2 = 12	33

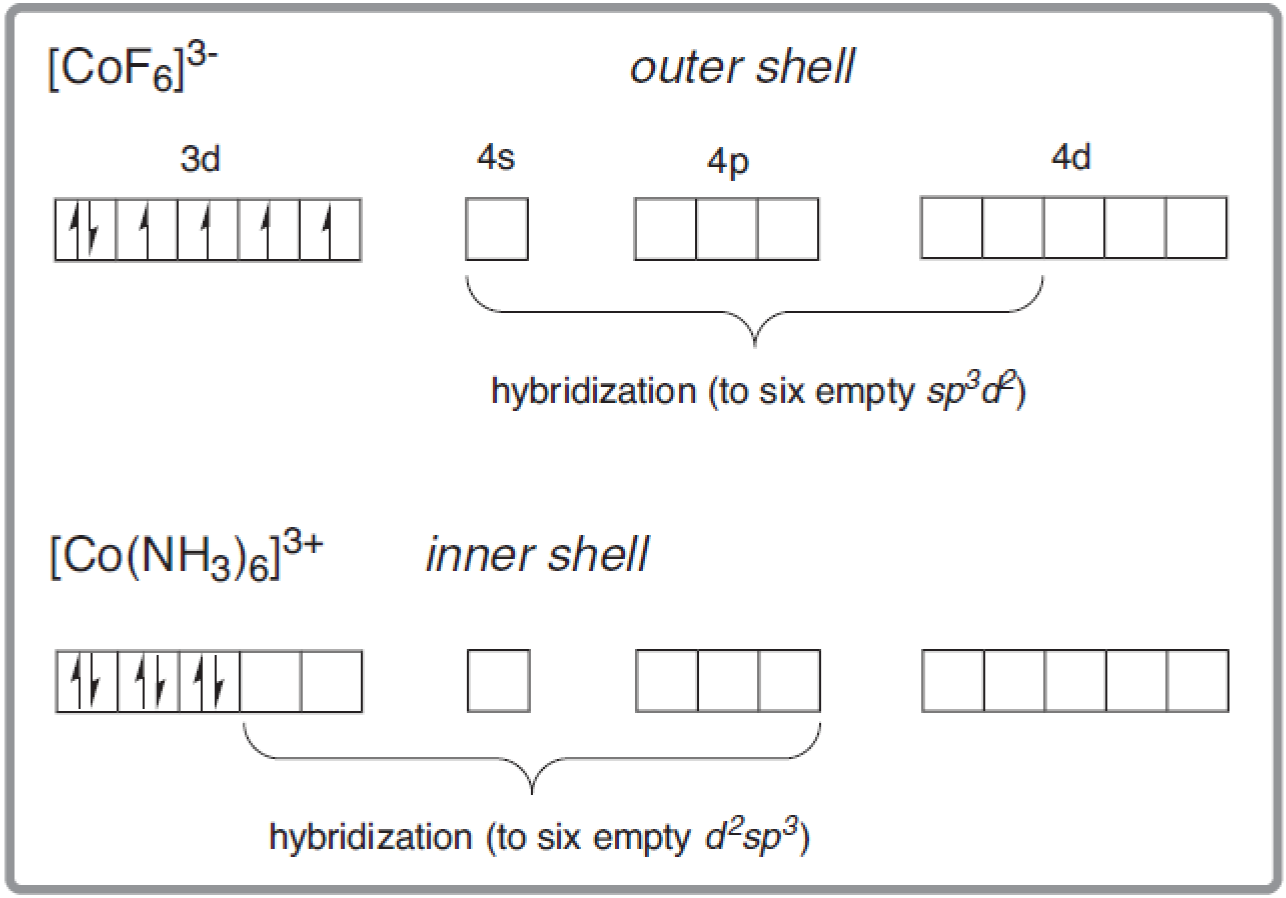
Valence Bond Theory (VBT)

"Describes bonding in terms of hybrid orbitals and electron pairs"



A simple valence bond description of bonding for the $[Co(NH_3)_6]^{3+}$ complex ion.

Valence Bond Theory (VBT)



4s–4p–4d

“outer orbital complexes”

“high–spin complexes”

⇧

Magnetic properties

⇩

3d–4s–4p

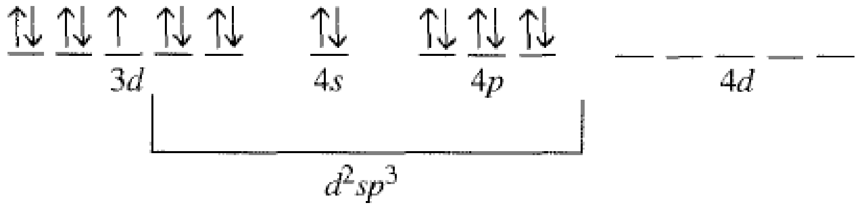
“inner orbital complexes”

“low–spin complexes”

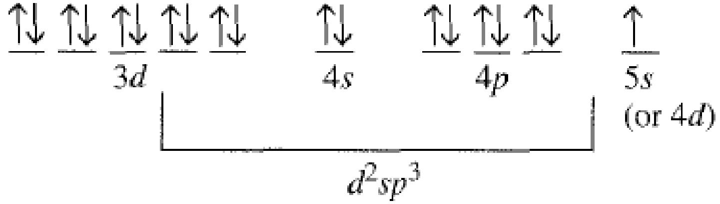
The extended valence bond description of *inner shell* and *outer shell* bonding for octahedral cobalt(III) complexes, required as a result of different *d*-electron arrangements on the metal. The six empty hybridized orbitals can in each case accommodate six bonding lone pairs from six ligand donor atoms.

Valence Bond Theory (VBT)

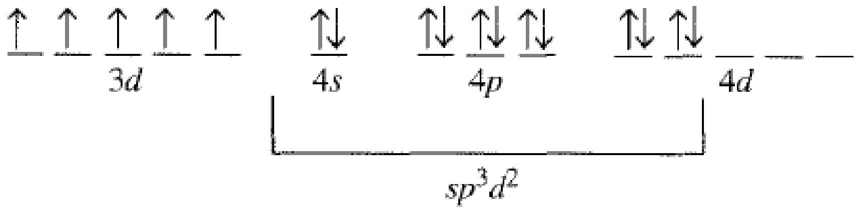
For a d^5 metal ion:
Inner orbital



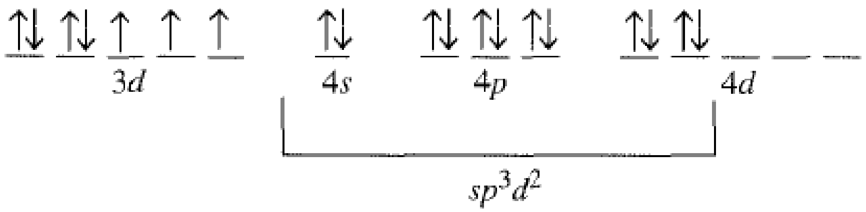
For a d^7 metal ion:
Inner orbital



For a d^5 metal ion:
Outer orbital

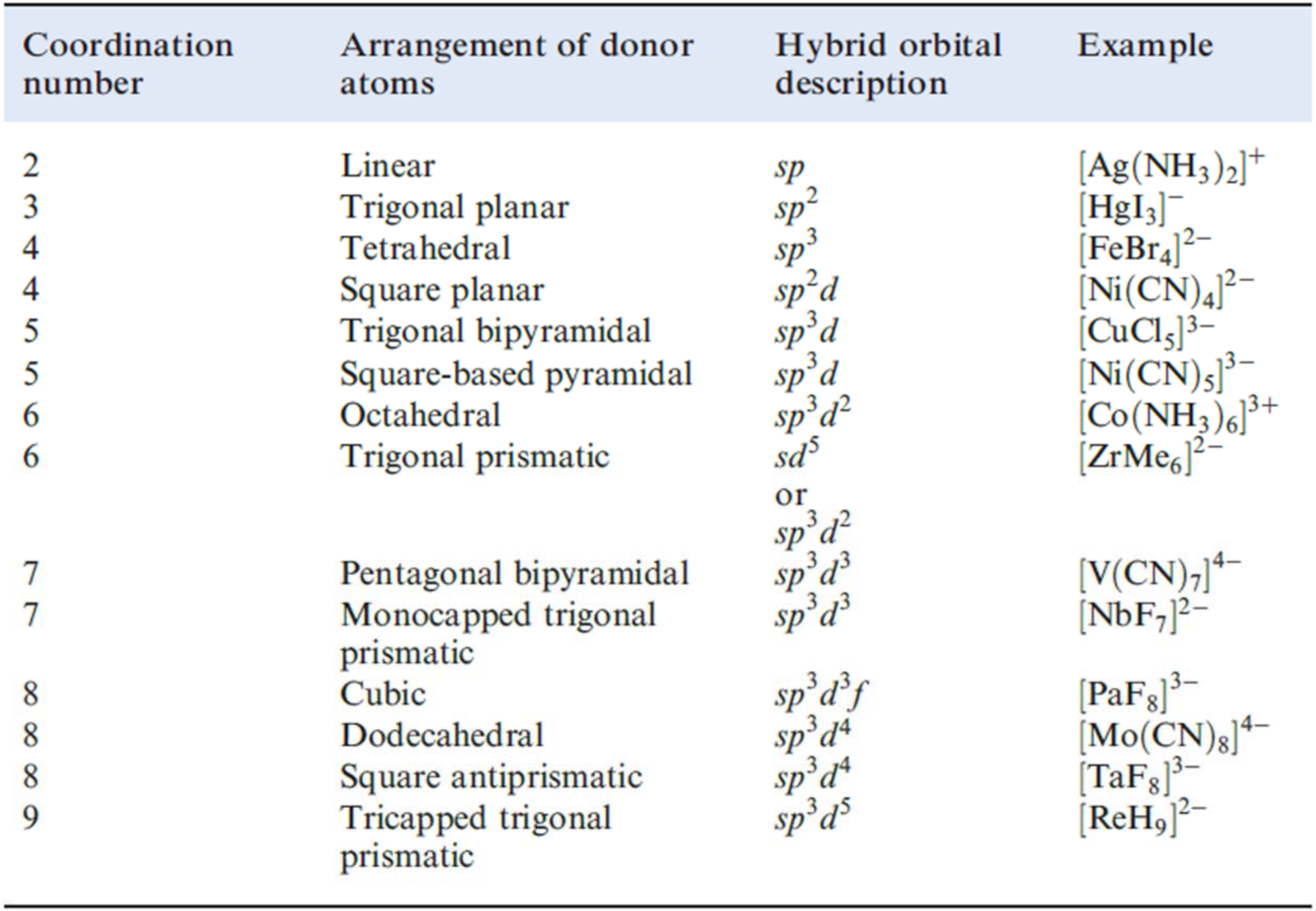


For a d^7 metal ion:
Outer orbital



Inner and Outer Orbital Complexes. In each case, ligand electrons fill the d^2sp^3 bonding orbitals. The remaining orbitals contain the electrons from the metal.

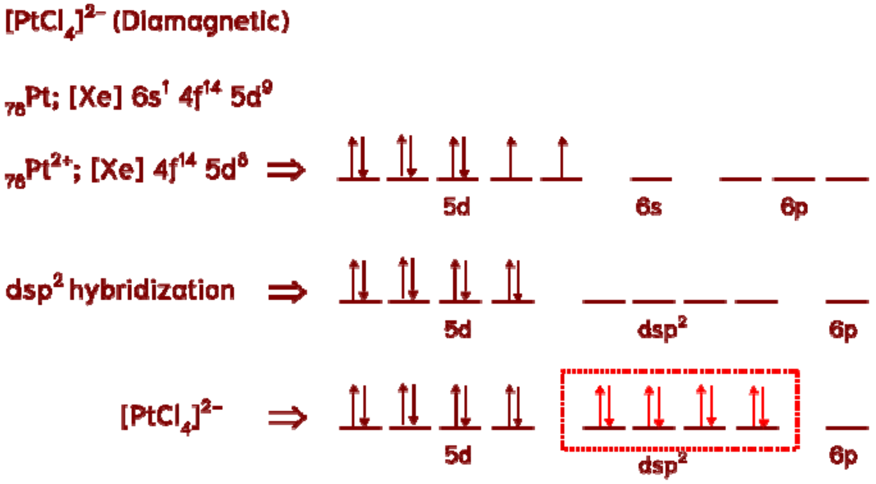
Valence Bond Theory (VBT)



Coordination number	Arrangement of donor atoms	Hybrid orbital description	Example
2	Linear	sp	$[Ag(NH_3)_2]^+$
3	Trigonal planar	sp^2	$[HgI_3]^-$
4	Tetrahedral	sp^3	$[FeBr_4]^{2-}$
4	Square planar	sp^2d	$[Ni(CN)_4]^{2-}$
5	Trigonal bipyramidal	sp^3d	$[CuCl_5]^{3-}$
5	Square-based pyramidal	sp^3d	$[Ni(CN)_5]^{3-}$
6	Octahedral	sp^3d^2	$[Co(NH_3)_6]^{3+}$
6	Trigonal prismatic	sd^5 or sp^3d^2	$[ZrMe_6]^{2-}$
7	Pentagonal bipyramidal	sp^3d^3	$[V(CN)_7]^{4-}$
7	Monocapped trigonal prismatic	sp^3d^3	$[NbF_7]^{2-}$
8	Cubic	sp^3d^3f	$[PaF_8]^{3-}$
8	Dodecahedral	sp^3d^4	$[Mo(CN)_8]^{4-}$
8	Square antiprismatic	sp^3d^4	$[TaF_8]^{3-}$
9	Tricapped trigonal prismatic	sp^3d^5	$[ReH_9]^{2-}$

Hybridization schemes for the σ–bonding frameworks of different geometrical configurations of ligand donor atoms

Valence Bond Theory (VBT)



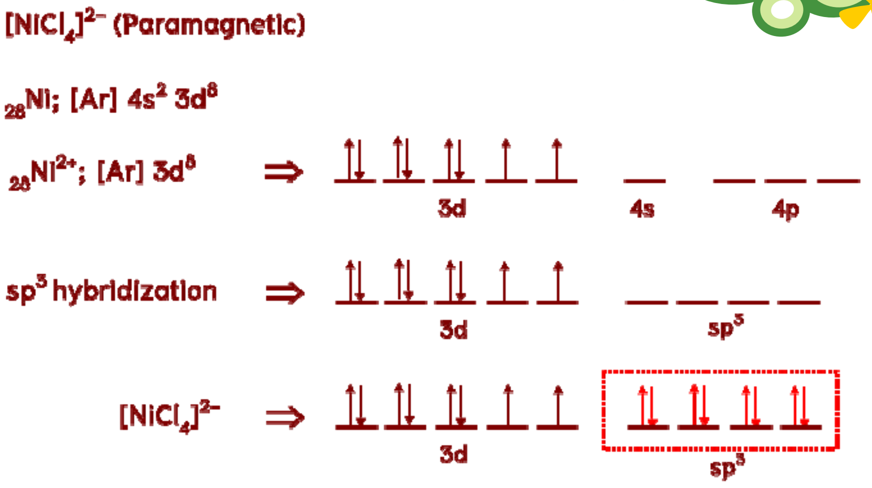
$[PtCl_4]^{2-}$ (Diamagnetic)

$_{78}Pt$; $[Xe]\ 6s^1\ 4f^{14}\ 5d^9$

$_{78}Pt^{2+}$; $[Xe]\ 4f^{14}\ 5d^8$ ⇒

dsp² hybridization ⇒

$[PtCl_4]^{2-}$ ⇒



$[NiCl_4]^{2-}$ (Paramagnetic)

$_{28}Ni$; $[Ar]\ 4s^2\ 3d^8$

$_{28}Ni^{2+}$; $[Ar]\ 3d^8$ ⇒

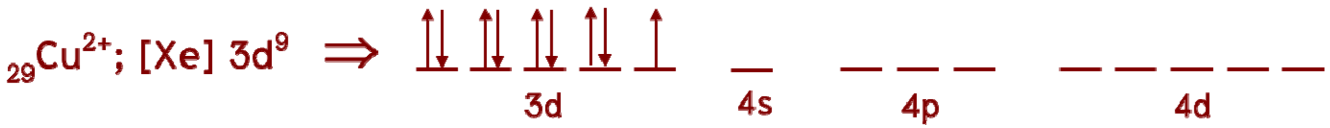
sp³ hybridization ⇒

$[NiCl_4]^{2-}$ ⇒

$[PtCl_4]^{2-}$ (Diamagnetic) ⇒ dsp² hybridization ⇒ Square planar

$[NiCl_4]^{2-}$ (Paramagnetic) ⇒ sp³ hybridization ⇒ Tetrahedral

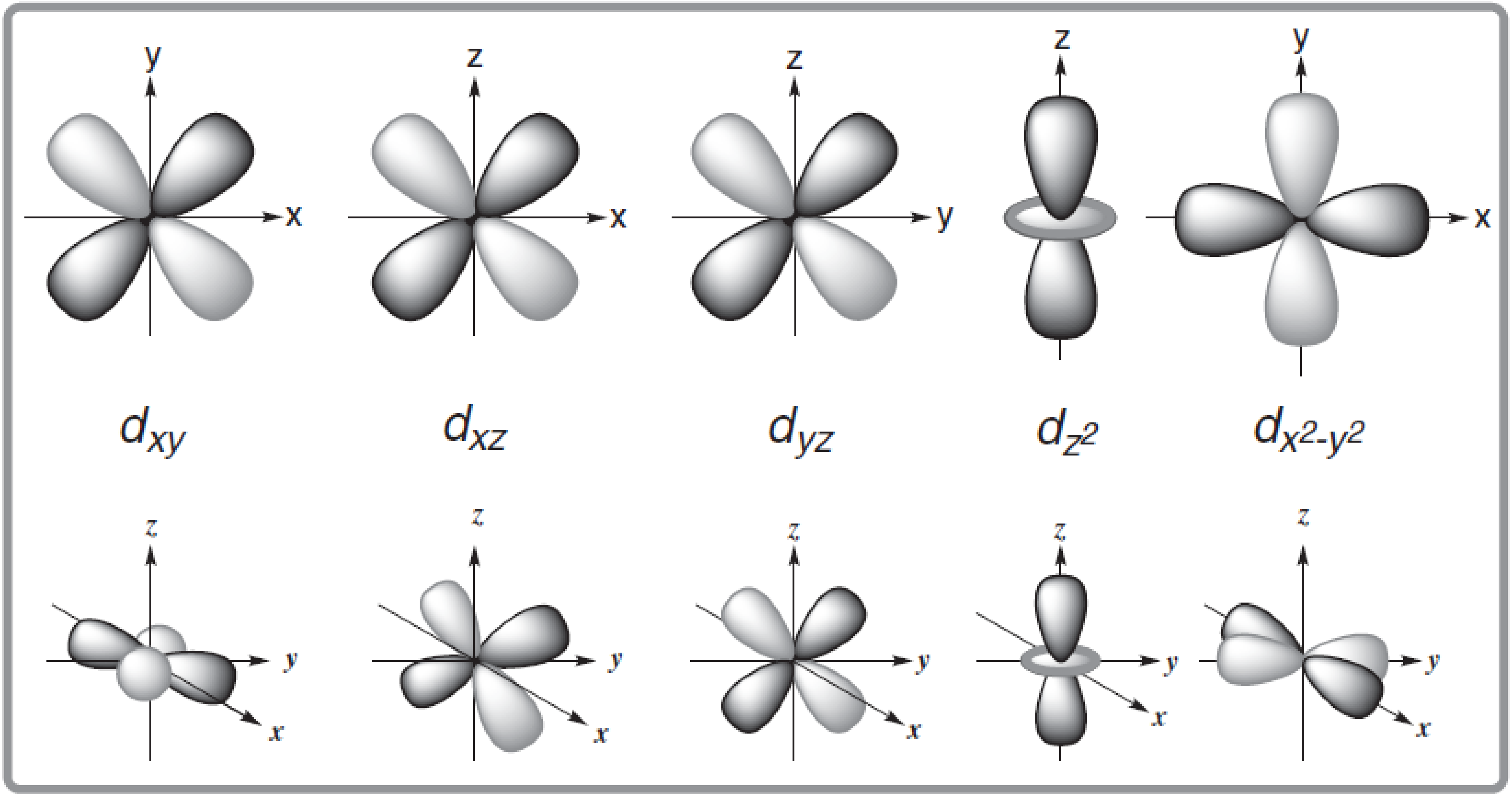
$[Cu(NH_3)_4]^{2+}$ (Paramagnetic) ⇒ ???



$_{29}Cu^{2+}$; $[Xe]\ 3d^9$ ⇒

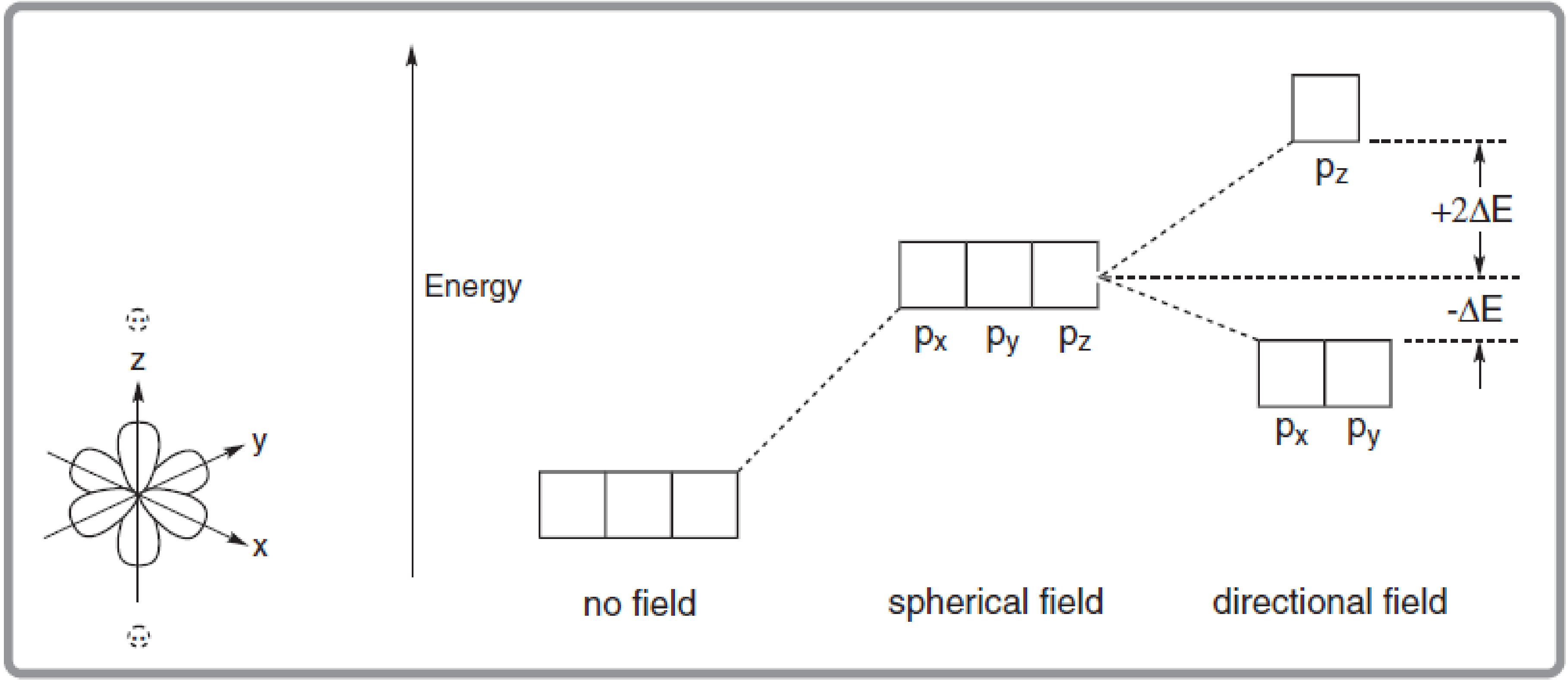
“Can not explain electronic spectrum and magnetic properties of complexes”

Crystal Field Theory (CFT)



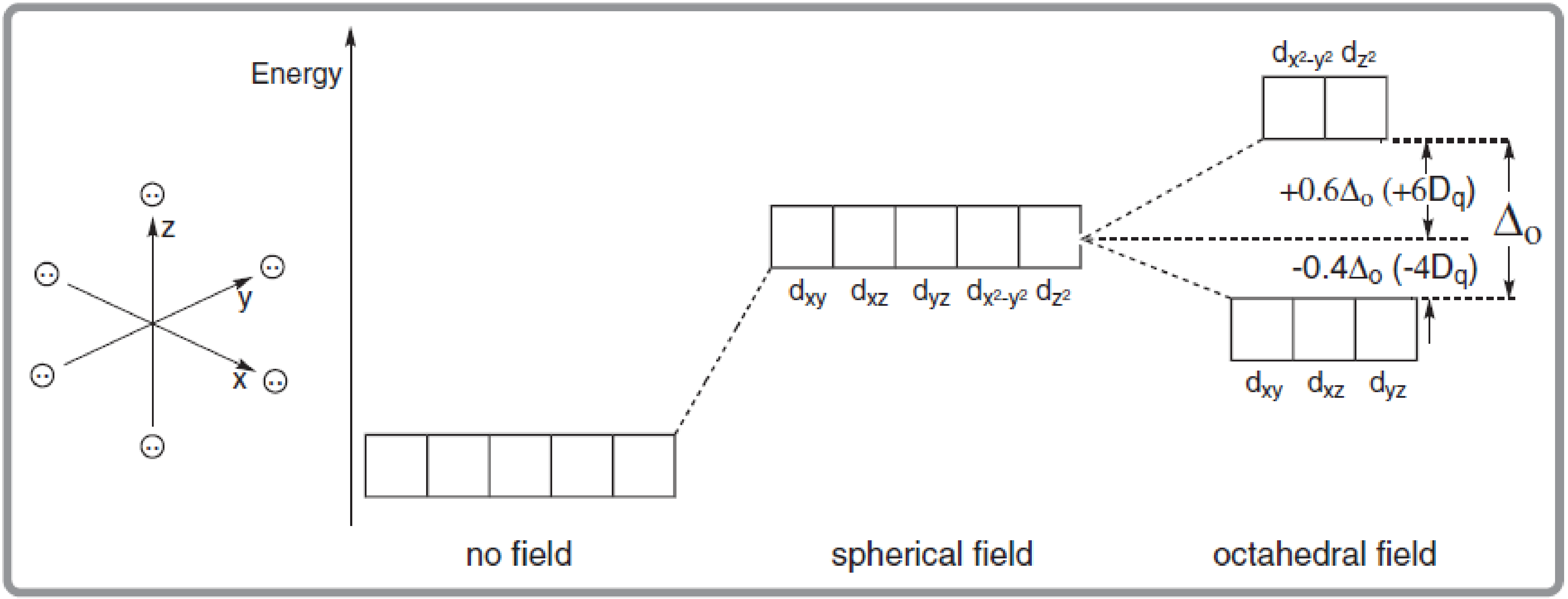
The five d orbitals of d-block elements, each represented in two different views.

Crystal Field Theory (CFT)



The concept of crystal field influences applied for purely illustrative purposes to a set of p orbitals. The directional field here results from imposing a specific interaction along the *z* axis alone.

Crystal Field Theory (CFT)



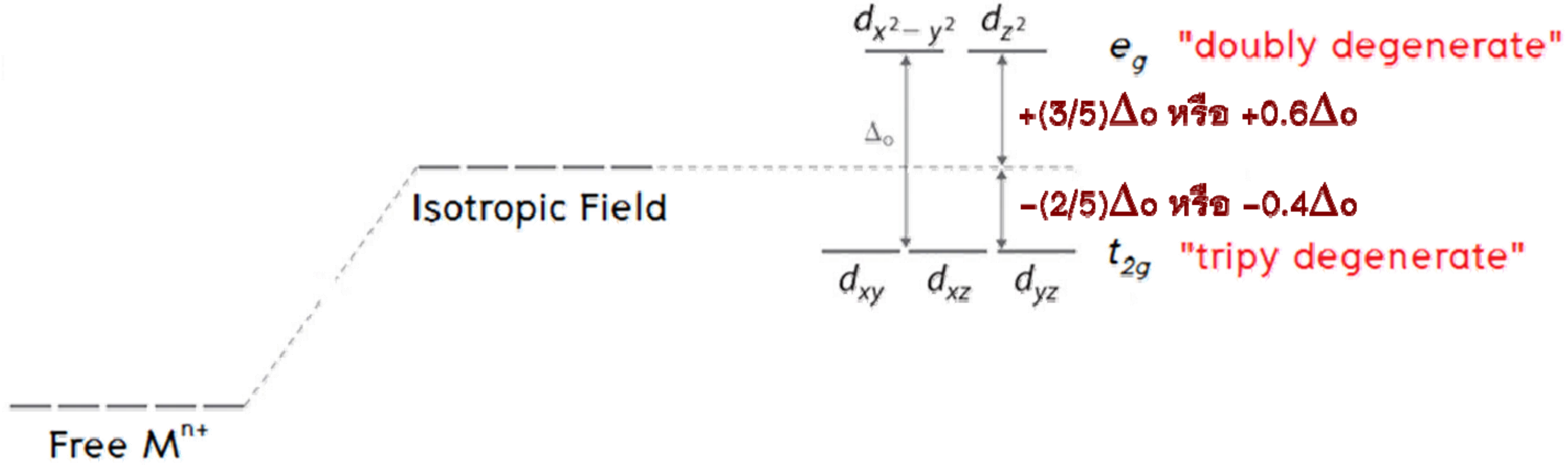
Crystal field influences for a set of d orbitals in an octahedral field.

Δ_o = Crystal Field Stabilization Energy (CFSE) = 10Dq

(o: octahedral; Dq: quantize difference = $Ze^2r^4/6d^5$)

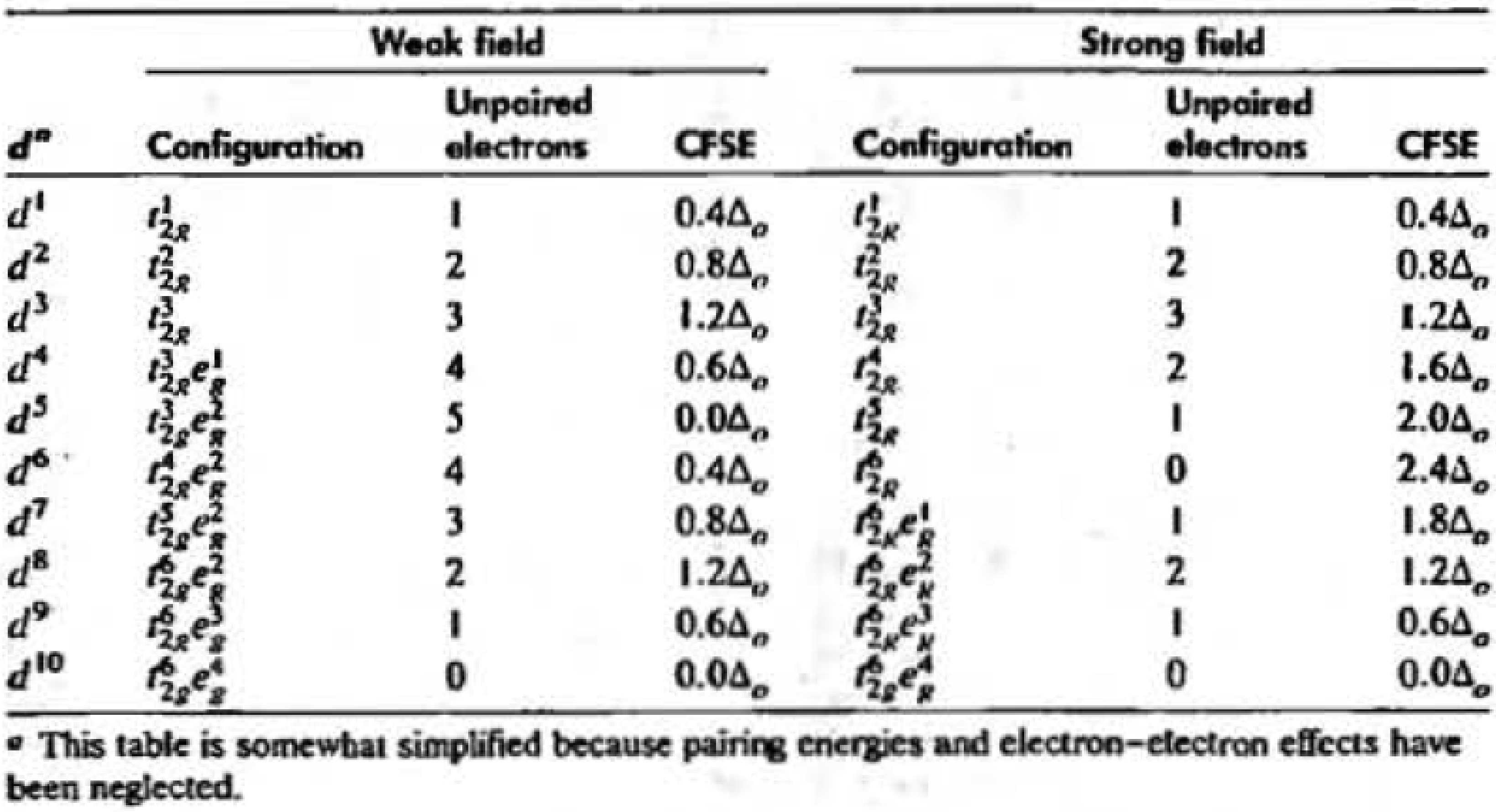
Crystal Field Theory (CFT)

$O_h(m3m)$	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$	*s*–orbital
A_{2g}	1	1	–1	–1	1	1	–1	1	1	–1		
E_g	2	–1	0	0	2	2	0	–1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$	*d*–orbital
T_{1g}	3	0	–1	1	–1	3	1	0	–1	–1		
T_{2g}	3	0	1	–1	–1	3	–1	0	–1	1	(xy, yz, zx)	
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1		
A_{2u}	1	1	–1	–1	1	–1	1	–1	–1	1		
E_u	2	–1	0	0	2	–2	0	1	–2	0		
T_{1u}	3	0	–1	1	–1	–3	–1	0	1	1	(x, y, z)	*p*–orbital
T_{2u}	3	0	1	–1	–1	–3	1	0	1	–1		



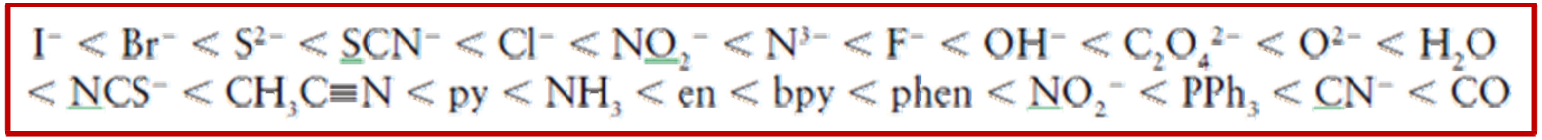
Crystal Field Theory (CFT)

Crystal field effects for weak and strong octahedral fields



	Weak field			Strong field		
d^n	Configuration	Unpaired electrons	CFSE	Configuration	Unpaired electrons	CFSE
d^1	t_{2g}^1	1	$0.4\Delta_o$	t_{2g}^1	1	$0.4\Delta_o$
d^2	t_{2g}^2	2	$0.8\Delta_o$	t_{2g}^2	2	$0.8\Delta_o$
d^3	t_{2g}^3	3	$1.2\Delta_o$	t_{2g}^3	3	$1.2\Delta_o$
d^4	$t_{2g}^3e_g^1$	4	$0.6\Delta_o$	t_{2g}^4	2	$1.6\Delta_o$
d^5	$t_{2g}^3e_g^2$	5	$0.0\Delta_o$	t_{2g}^5	1	$2.0\Delta_o$
d^6	$t_{2g}^4e_g^2$	4	$0.4\Delta_o$	t_{2g}^6	0	$2.4\Delta_o$
d^7	$t_{2g}^5e_g^2$	3	$0.8\Delta_o$	$t_{2g}^6e_g^1$	1	$1.8\Delta_o$
d^8	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$	$t_{2g}^6e_g^2$	2	$1.2\Delta_o$
d^9	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$	$t_{2g}^6e_g^3$	1	$0.6\Delta_o$
d^{10}	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$	$t_{2g}^6e_g^4$	0	$0.0\Delta_o$

[a] This table is somewhat simplified because pairing energies and electron–electron effects have been neglected.



$I^- < Br^- < S^{2-} < \underline{S}CN^- < Cl^- < N\underline{O}_2^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O$
$< \underline{N}CS^- < CH_3C{\equiv}N < py < NH_3 < en < bpy < phen < \underline{N}O_2^- < PPh_3 < \underline{C}N^- < CO$

Weak-field

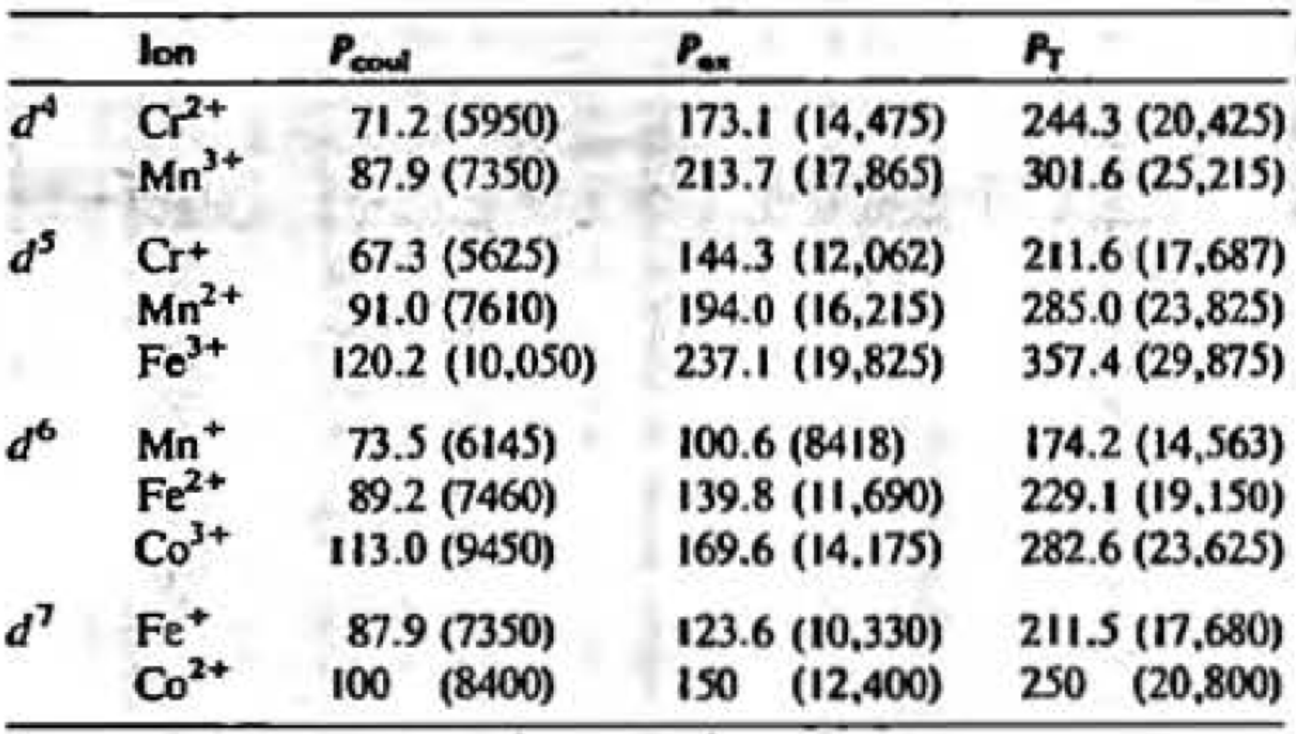
(High-spin)

Strong-field

(Low-spin)

Crystal Field Theory (CFT)

Pairing energies (kJ/mol) for some 3d metal



	Ion	P_{coul}	P_{ex}	P_T
d^4	Cr^{2+}	71.2 (5950)	173.1 (14,475)	244.3 (20,425)
	Mn^{3+}	87.9 (7350)	213.7 (17,865)	301.6 (25,215)
d^5	Cr^+	67.3 (5625)	144.3 (12,062)	211.6 (17,687)
	Mn^{2+}	91.0 (7610)	194.0 (16,215)	285.0 (23,825)
	Fe^{3+}	120.2 (10,050)	237.1 (19,825)	357.4 (29,875)
d^6	Mn^+	73.5 (6145)	100.6 (8418)	174.2 (14,563)
	Fe^{2+}	89.2 (7460)	139.8 (11,690)	229.1 (19,150)
	Co^{3+}	113.0 (9450)	169.6 (14,175)	282.6 (23,625)
d^7	Fe^+	87.9 (7350)	123.6 (10,330)	211.5 (17,680)
	Co^{2+}	100 (8400)	150 (12,400)	250 (20,800)

Pairing Energy

$P_{coulombic}$ (Coulombic repulsion energy)

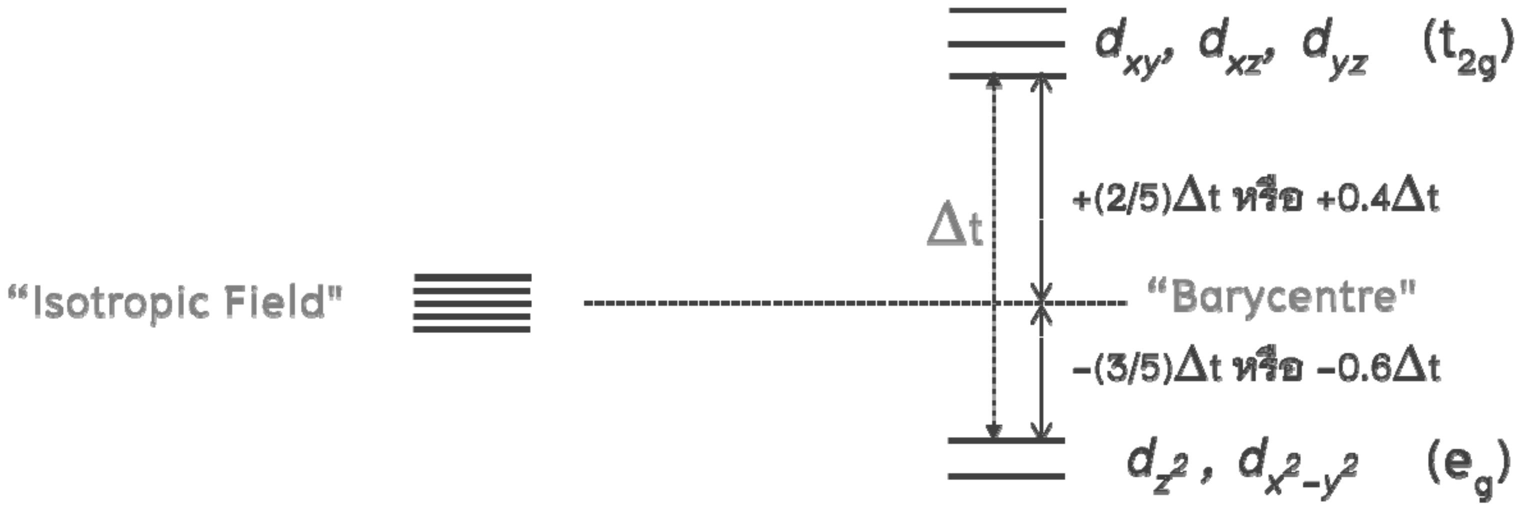
(decrease on increasing M size: 3d>4d>5d)

$P_{exchange}$ (Exchange energy)

(increase with number of aligned electron; maximum at d^5)

Crystal Field Theory (CFT)

Tetrahedral Field

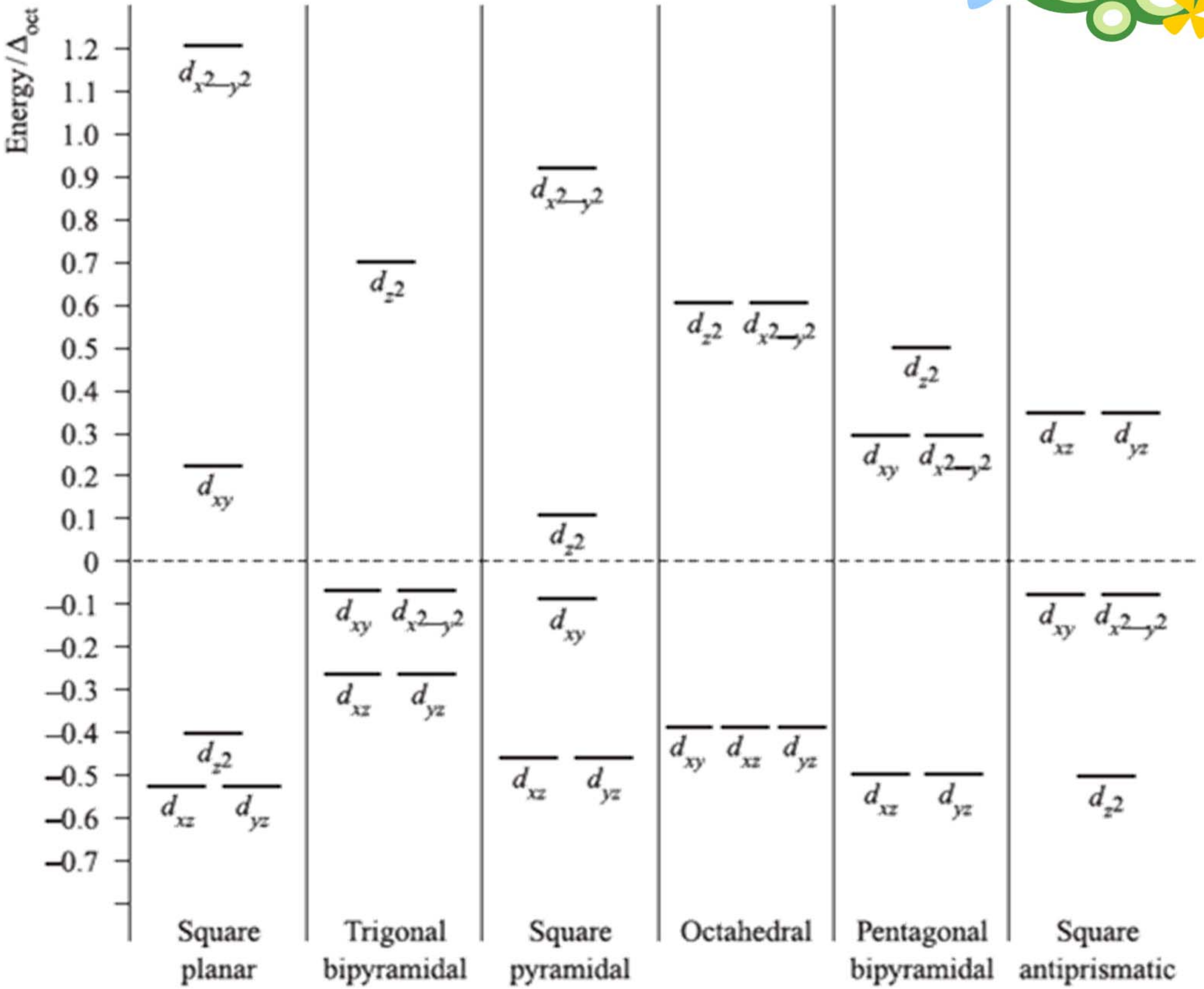


Δt = Crystal Field Splitting Energy (CFSE) = $\frac{4}{9}\Delta o$

"High spin"

Crystal Field & Ligand Field Theories (CFT & LFT)

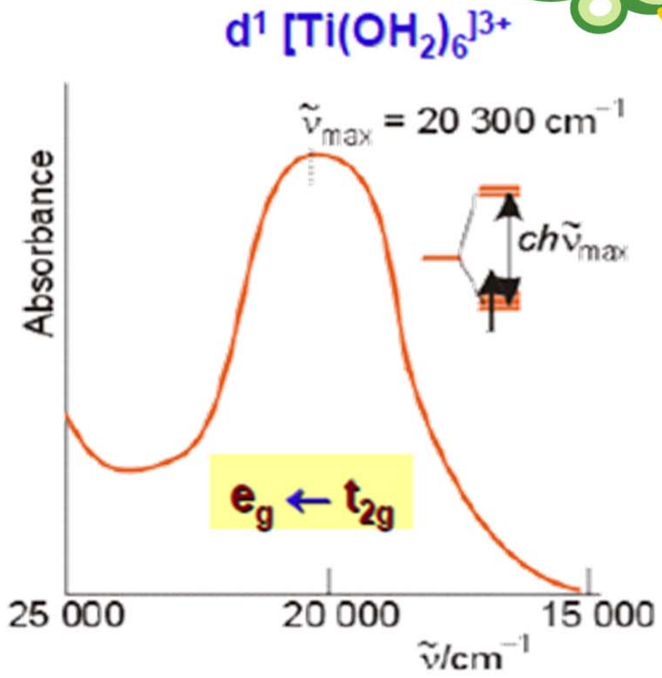
"Different shape arrangement of point charges will lead to a different characteristic outcome"

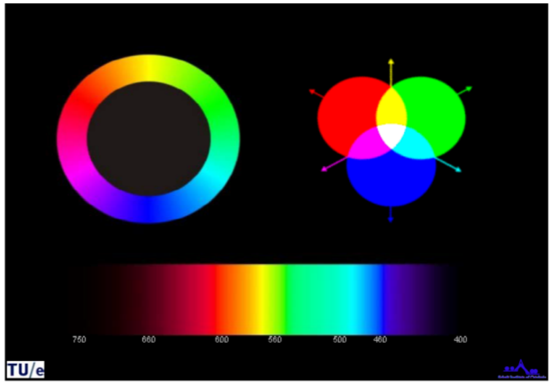


Crystal field splitting diagrams for some common fields

Color of transition metal complexes

- Light is absorbed by the complex
- Electron is excited into a higher level
- Δ_o is the energy gap between e_g and t_{2g} orbitals





Visible Light and Complementary Colors

Wavelength Range (nm)	*Wave Numbers (cm⁻¹)*	*Color*	*Complementary Color*
<400	>25,000	Ultraviolet	
400–450	22,000–25,000	Violet	Yellow
450–490	20,000–22,000	Blue	Orange
490–550	18,000–20,000	Green	Red
550–580	17,000–18,000	Yellow	Violet
580–650	15,000–17,000	Orange	Blue
650–700	14,000–15,000	Red	Green
>700	<14,000	Infrared	

Spectrochemical Series

- The ligand field splitting Δ_o is strongly dependent on the nature of the ligand.

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^-$
$< CH_3CN < py < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO$

- Δ_o is the larger, the more π–electrons the ligand has.
- Δ_o is small in the presence of many lone–pairs.

$$\underset{\text{(light blue)}}{Cu^{2+}(aq)} \xrightarrow[\text{shift}]{\text{hypochromic}} \underset{\text{(deep blue)}}{[Cu(NH_3)_4(H_2O)_2]^{2+}}$$

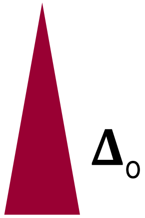
- Δ_o is relatively constant within a row of transition metals

  e.g. for M^{2+} (3d series), $\Delta_o \approx$ 7800 – 12000 cm^{-1}
  (Mn^{2+}) (Cr^{2+})

Spectrochemical Series

- Δ_o increases down a group 3d – 4d – 5d each by *ca.* 30%

$[Fe(CN)_6]^{4-}$	yellow
$[Ru(CN)_6]^{4-}$	pale color
$[Os(CN)_6]^{4-}$	colorless, (UV)



- Δ_o increases with increasing oxidation number

e.g. 3d series M^{2+} $\Delta_o \approx 10{,}000\ cm^{-1}$ $[Fe(CN)_6]^{4-}$ yellow

M^{3+} $\Delta_o \approx 20{,}000\ cm^{-1}$ $[Co(CN)_6]^{4-}$ colorless (UV)

- Spectrochemical series of metal ions.

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+}$

$< Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$

Magnetic momentum

- Compounds that tend to move out of a magnetic field are called "diamagnetic"
- Compounds that tend to move into a magnetic field are called "paramagnetic"
- Spin-only paramagnetism of d-metal complexes.

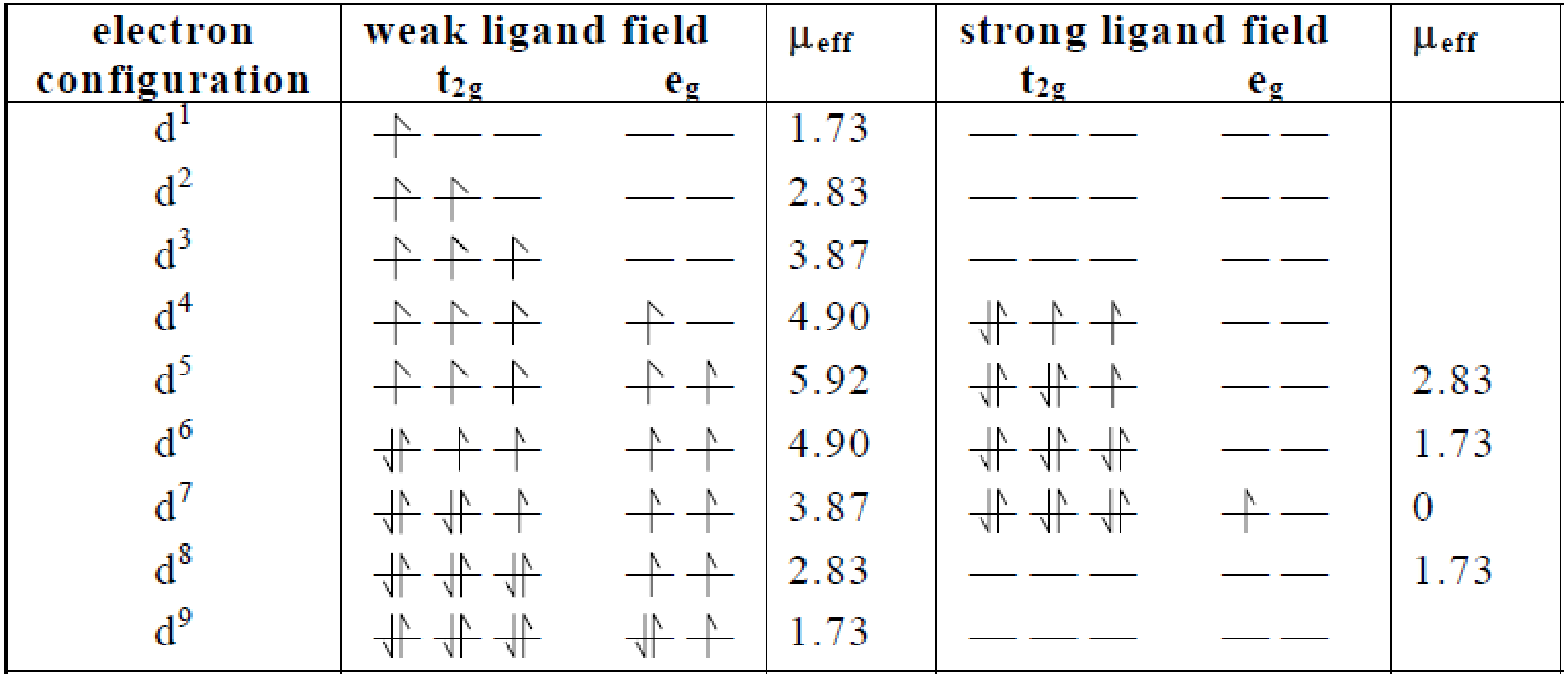
$$\mu = 2\,\mu_B \sqrt{s(s+1)}$$

μ_B : Bohr magneton

$$\mu_B = \frac{e\hbar}{2m_e} = 9.274\ 10^{-24}\ \mathrm{JT}^{-1}$$

For $s = ½$: $\mu = \mu_B \sqrt{n(n+2)}$; with n = number of unpaired e^-

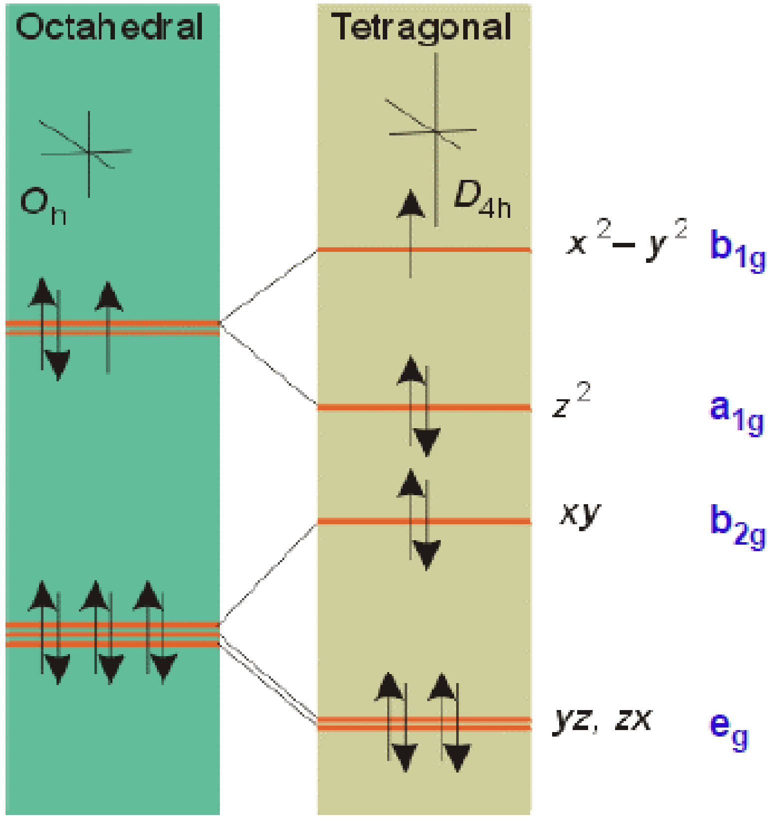
Magnetic momentum of octahedral complexes



electron configuration	weak ligand field		μ_{eff}	strong ligand field		μ_{eff}
	t_{2g}	e_g		t_{2g}	e_g	
d^1	↑ — —	— —	1.73	— — —	— —	
d^2	↑ ↑ —	— —	2.83	— — —	— —	
d^3	↑ ↑ ↑	— —	3.87	— — —	— —	
d^4	↑ ↑ ↑	↑ —	4.90	↑↓ ↑ ↑	— —	
d^5	↑ ↑ ↑	↑ ↑	5.92	↑↓ ↑↓ ↑	— —	2.83
d^6	↑↓ ↑ ↑	↑ ↑	4.90	↑↓ ↑↓ ↑↓	— —	1.73
d^7	↑↓ ↑↓ ↑	↑ ↑	3.87	↑↓ ↑↓ ↑↓	↑ —	0
d^8	↑↓ ↑↓ ↑↓	↑ ↑	2.83	— — —	— —	1.73
d^9	↑↓ ↑↓ ↑↓	↑↓ ↑	1.73	— — —	— —	

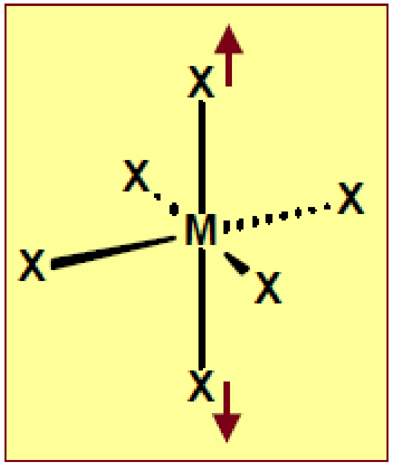
"Magnetic measurements can be used to determine the number of unpaired spins in a complex and thus to identify ground state configuration"

Tetragonal Distortion



- typical for d^7, d^8 and d^9

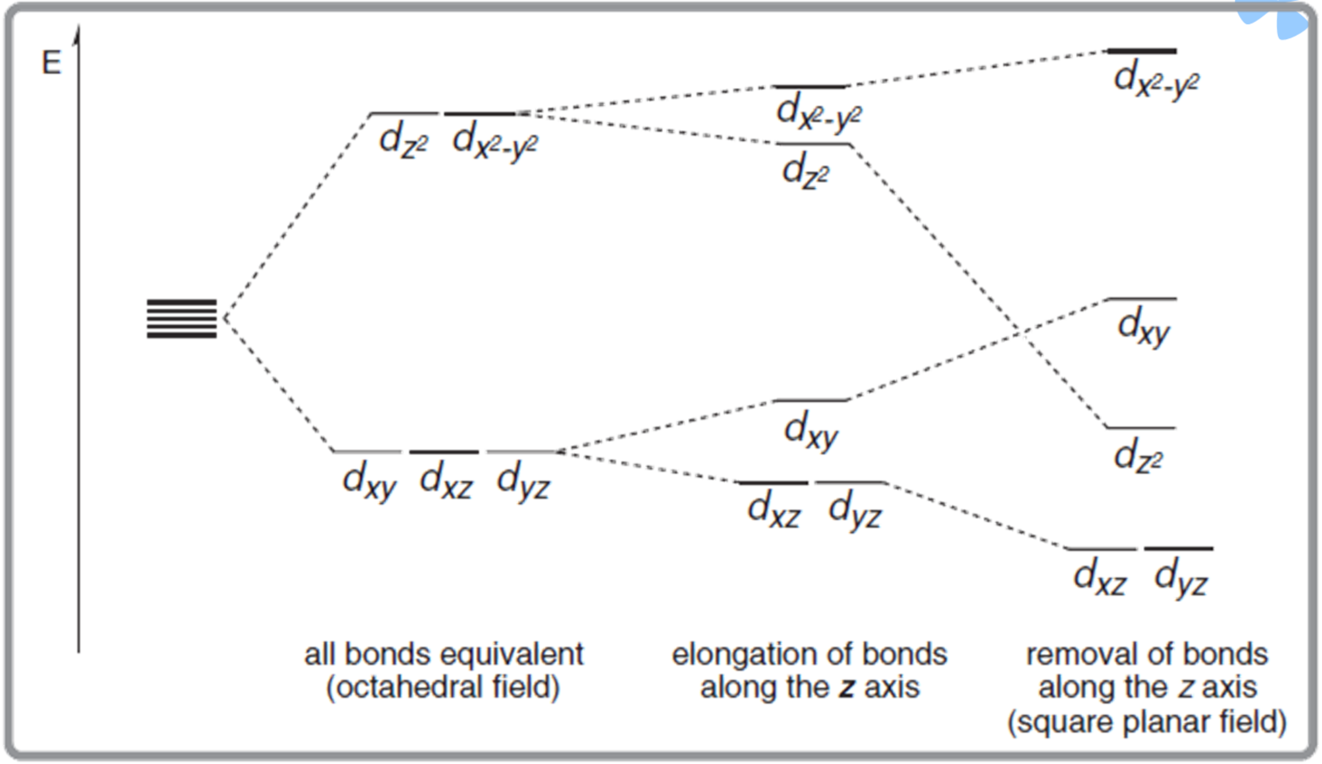
  Cu^{II} is a typical example



“Jahn–Teller Effect”

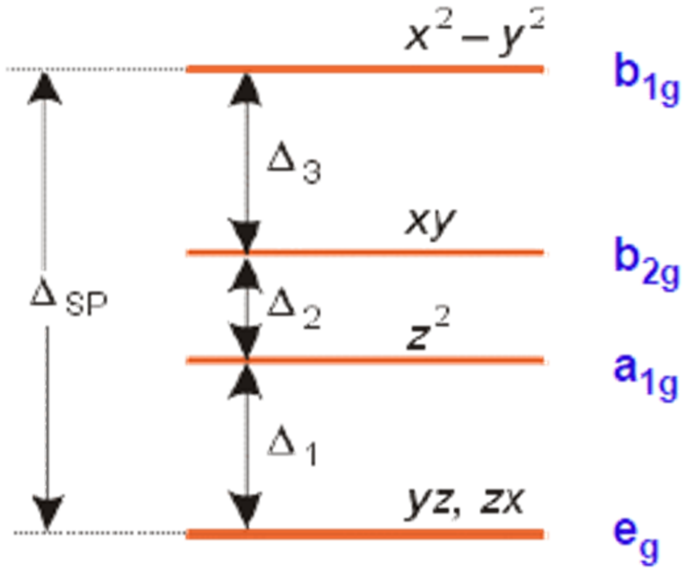
If the ground state of a nonlinear complex is orbitally degenerate, the complex will distort in order to lower energy by removing the degeneracy

Tetragonal Distortion



- Square planar complexes can be seen as the extreme case of a Jahn–Teller effect
- Typical examples are $4d^8$ and $5d^8$ complexes *e.g.* Rh^{I}, Ir^{I}, Pt^{II}, Pd^{II}, Au^{III}
- In $3d^8$ with halide (X^-) are tetrahedral (small splitting) $[NiX_4]^{2-}$ but : $[Ni(CN)_4]^{2-}$ is square planar

Square planar ligand field



$\boxed{\Delta_{SP} = 1.3\ \Delta_O}$

D_{4h} (4/mmm)	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	$h = 16$	
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(zx, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

Molecular Orbital Theory (MOT)

- CFT is not good enough!!! The bonding is not purely ionic.

Observation: Less d electron repulsion in complex than in free ion

Explanation: More space for d electron to delocalize when forming bond,

More distance between d electron in orbitals

(molecular orbital)

NEPHELAUXETIC EFFECT

- Ligand Filed Theory (LFT): Application of MO theory with focus on metal orbitals, better understanding of Δ_0.

Molecular Orbital Theory (MOT)

"The bonding originates from sharing of electron pair on the ligand between the ligand and the metal; the bond is predominantly covalent. *(coordinate covalent bond)*"

9 AOs for M + m AOs for L → (9+m) Mos

[ns + np + (n–1)d] (bonding & antibonding)

The building-up principle is used in conjunction with a MO energy diagram constructed by noting the symmetries of the d orbitals and linear combinations of ligand orbitals.

Molecular Orbital Theory (MOT)

MO formation in octahedral complex (O_h)

Two steps process:

1. Linear combinations of ligand orbital to form Ligand Group Orbitals (LGOs)
2. Formation of complex MO by the overlapping of LGOs with metal d orbitals along the Cartesian axis

Symmetry and Positive Sign compatibility

s orbital – a_{1g}

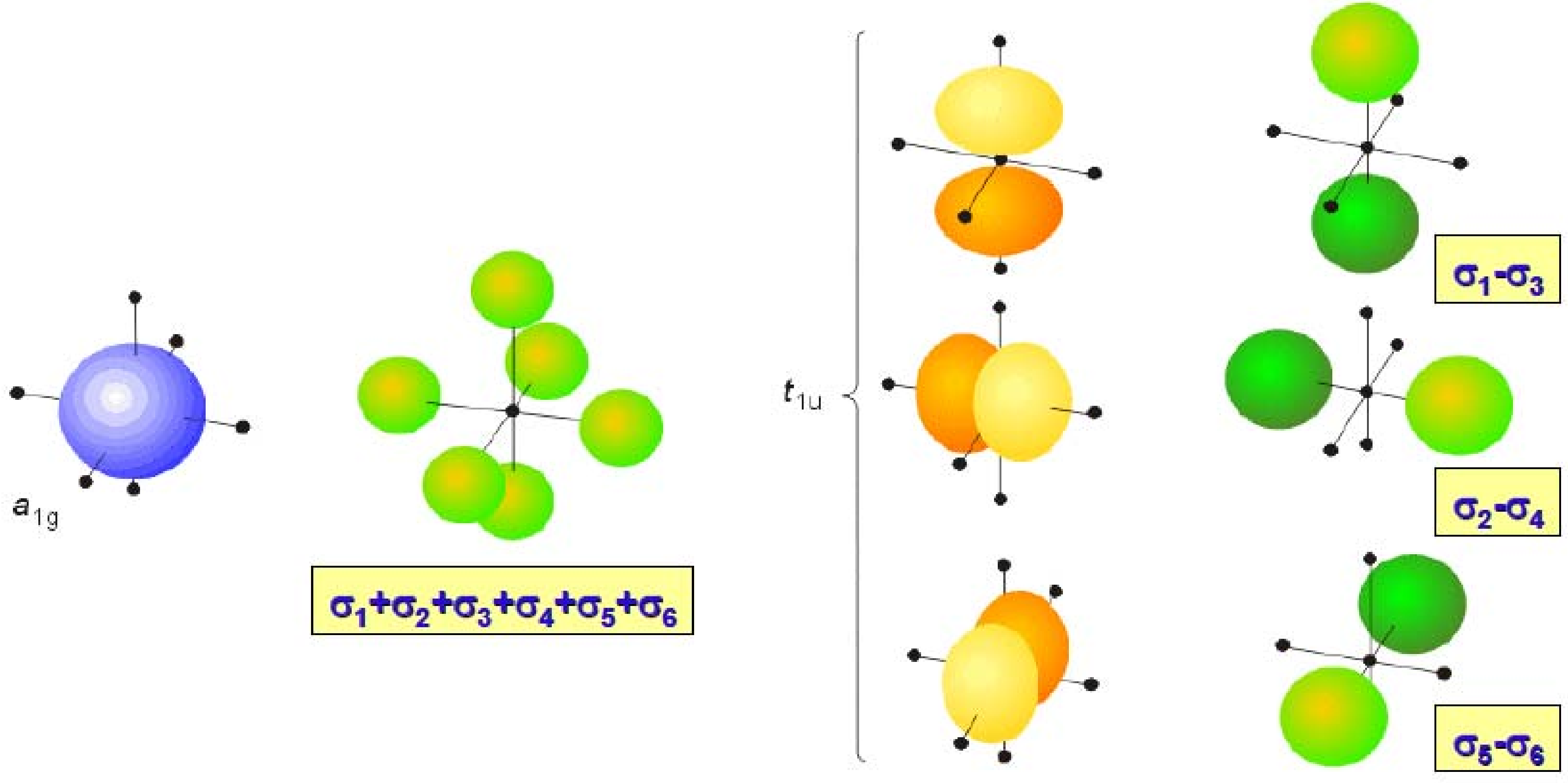
p orbital – t_{1u}

d orbital – e_g

– t_{2g}

Molecular Orbital Theory (MOT)

Six linear combinations of ligand **σ**–orbitals



$\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6$

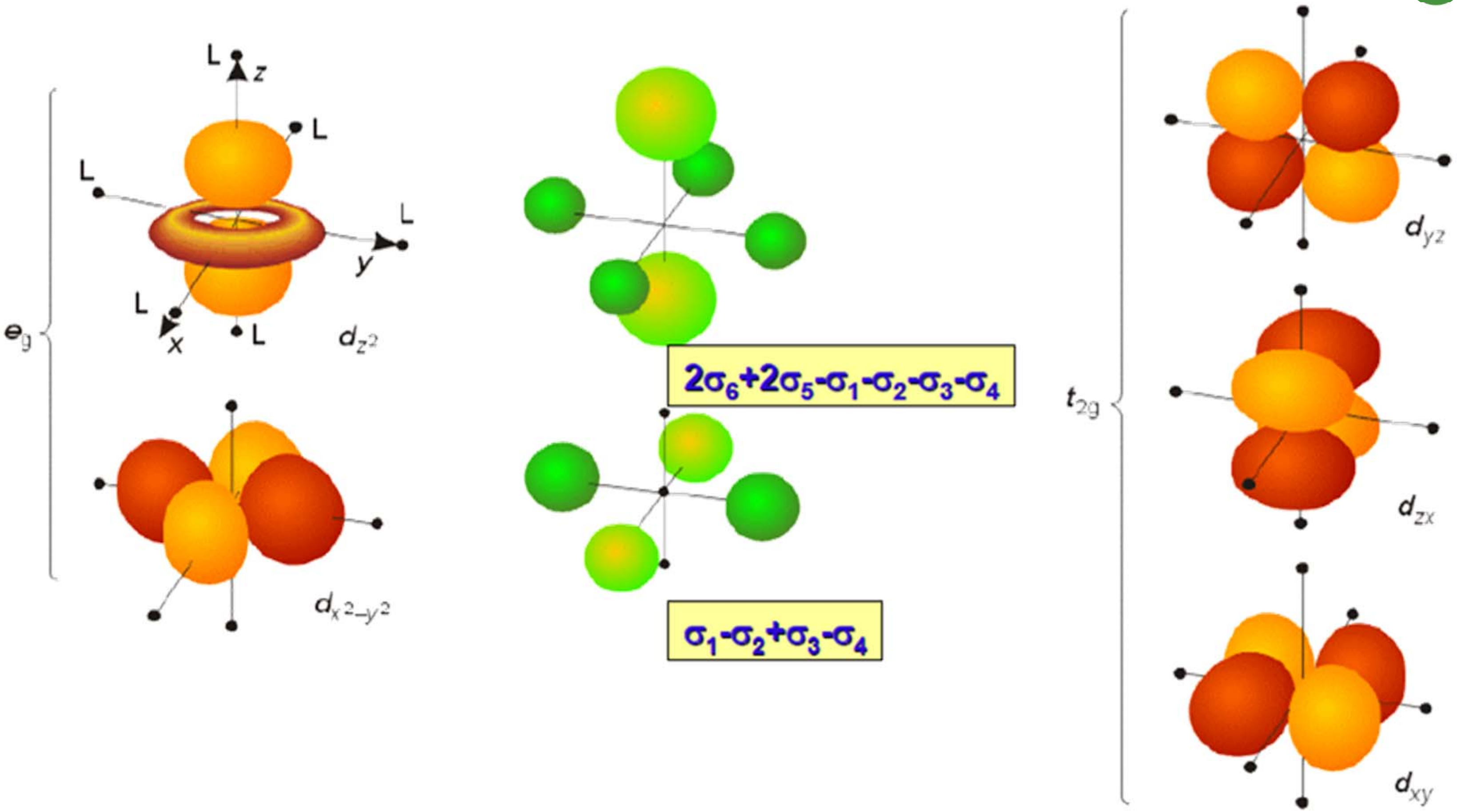
$\sigma_1-\sigma_3$

$\sigma_2-\sigma_4$

$\sigma_5-\sigma_6$

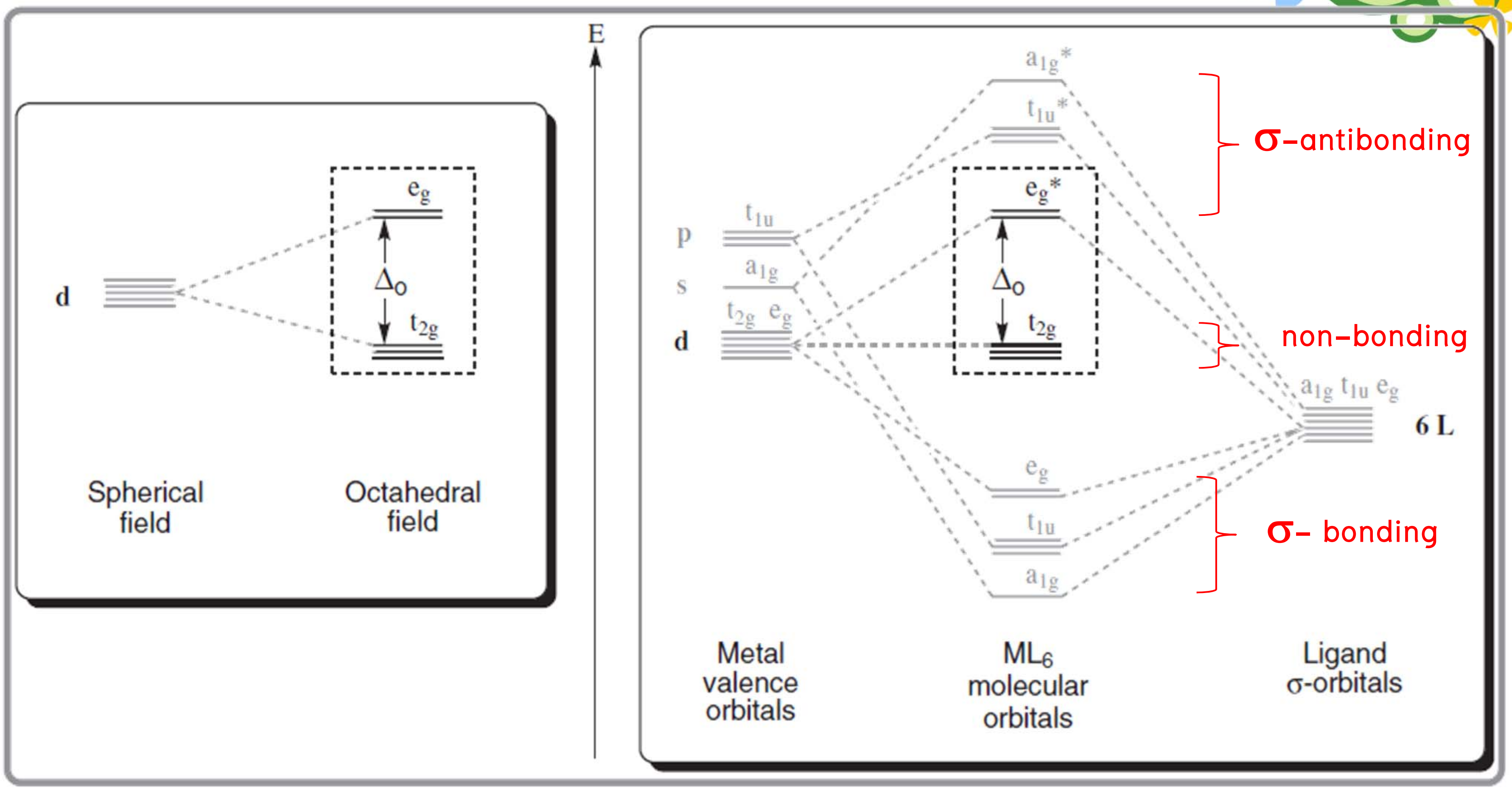
Symmetry labels

Molecular Orbital Theory (MOT)



- No combination of ligand **σ**–orbitals has the symmetry of the metal t_{2g}–orbitals ⟹ Metal t_{2g}–orbitals do not participate in **σ**–bonding

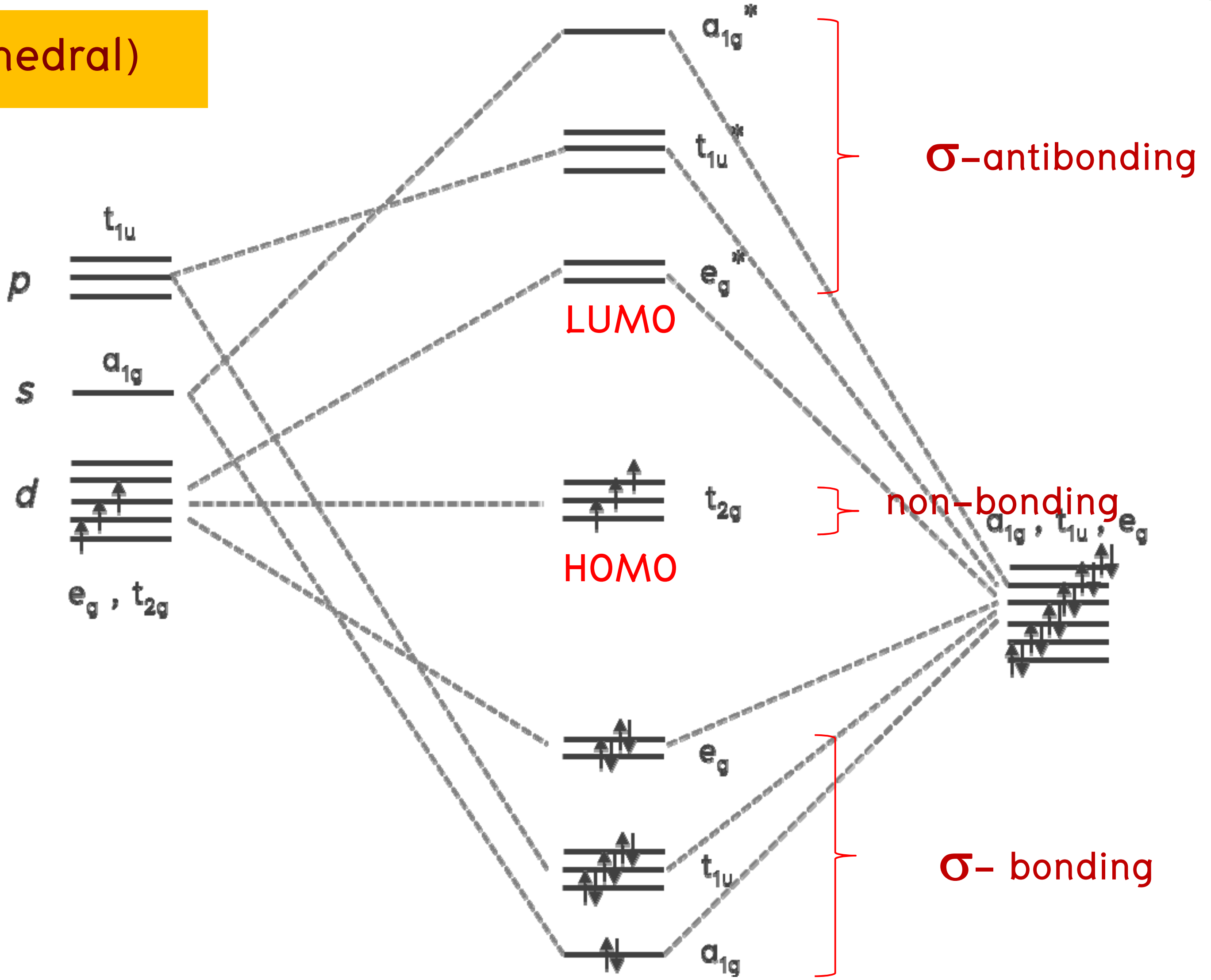
Molecular Orbital Theory (MOT)



Comparison of CFT (ionic) and LFT (molecular orbital) development of the d-orbital splitting diagram for octahedral systems. Both reduce to the equivalent consideration of insertion and location of metal d electrons in two degenerate sets of orbitals separated by a relatively small energy gap (Δ_o).

MOT : Octahedral complex (O_h)

d^3 (octahedral)



σ–antibonding

LUMO

non–bonding

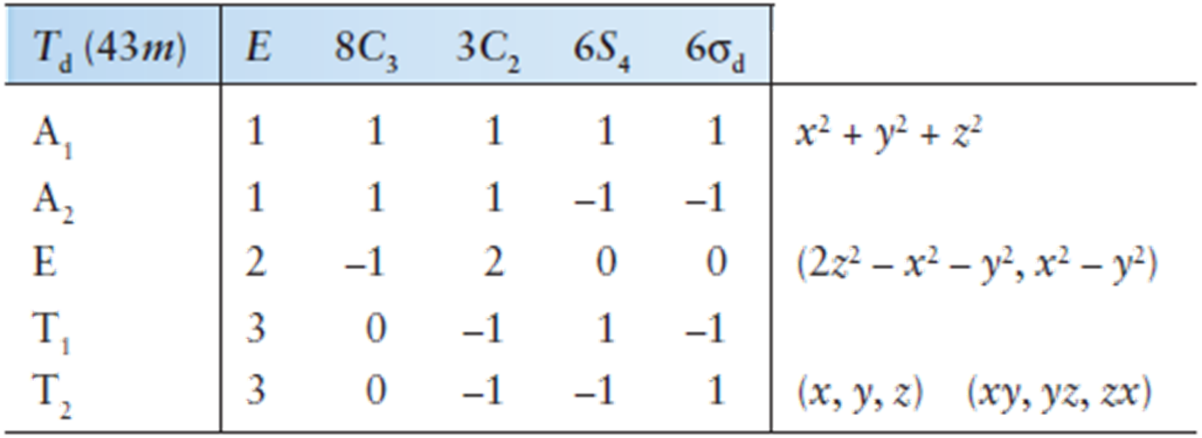
HOMO

σ– bonding

CFSE = 3(–0.4)Δo = –1.2Δo

MOT : Tetrahedral complex (T_d)

MO formation in tetrahedral complex (T_d)



T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	–1	–1	
E	2	–1	2	0	0	$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	–1	1	–1	
T_2	3	0	–1	–1	1	(x, y, z) (xy, yz, zx)

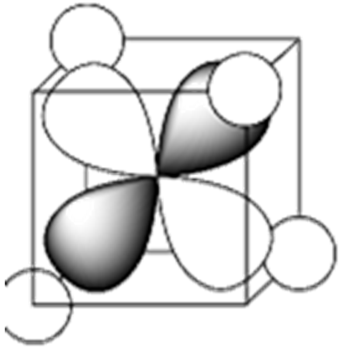
<u>Symmetry</u>

s orbital – a_1

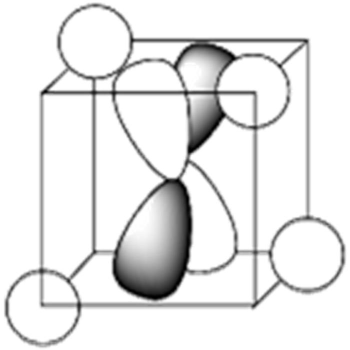
p orbital – t_2

d orbital – e

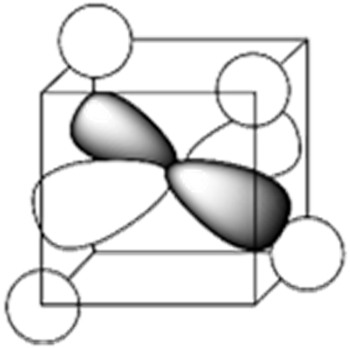
– t_2



d_{yz}



d_{xz}

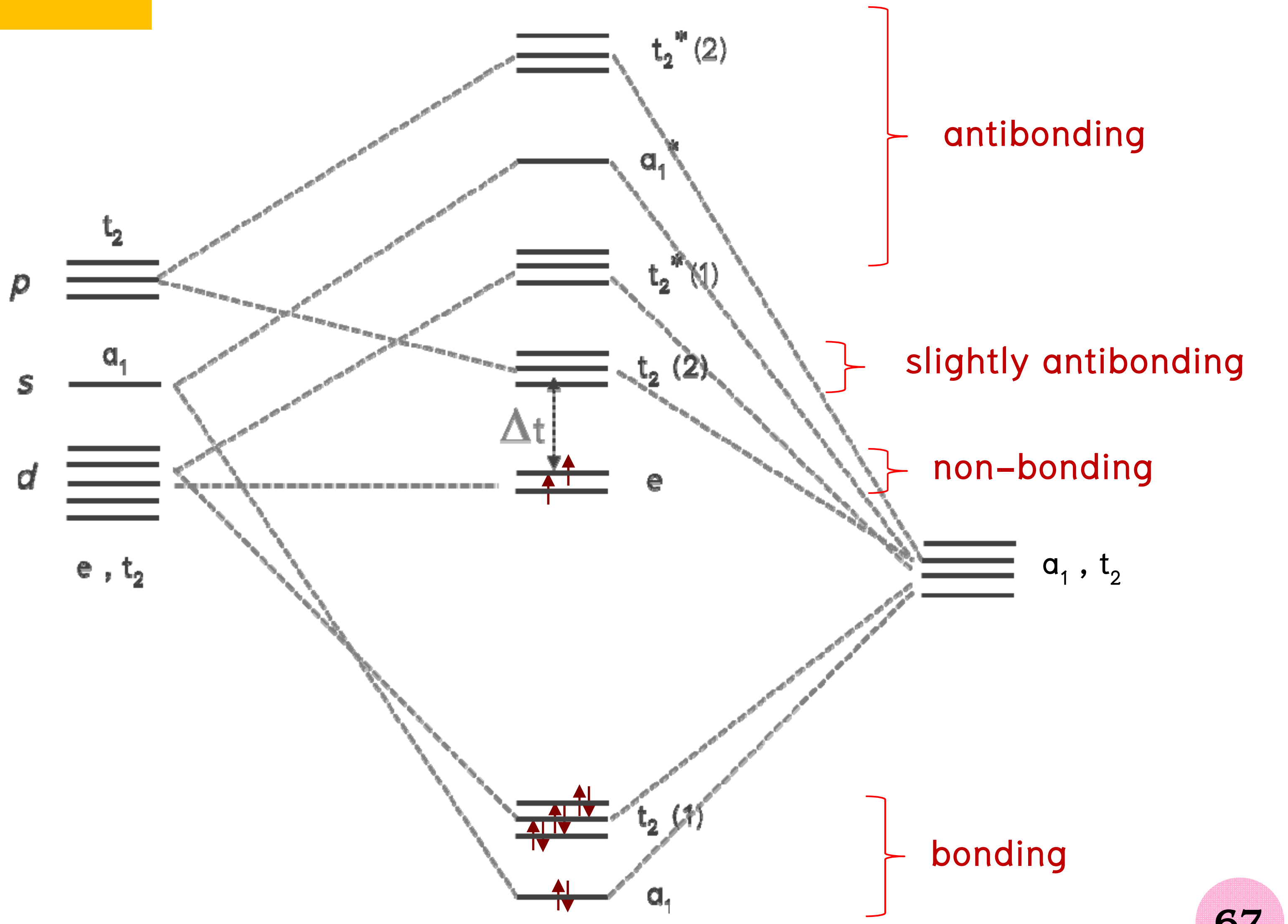


d_{xy}

LGOs: a_1, t_2

MOT : Tetrahedral complex (T_d)

d^2 (tetrahedral)



MOT : Square planar complex (D_{4h})

Symmetry

s orbital – a_{1g}

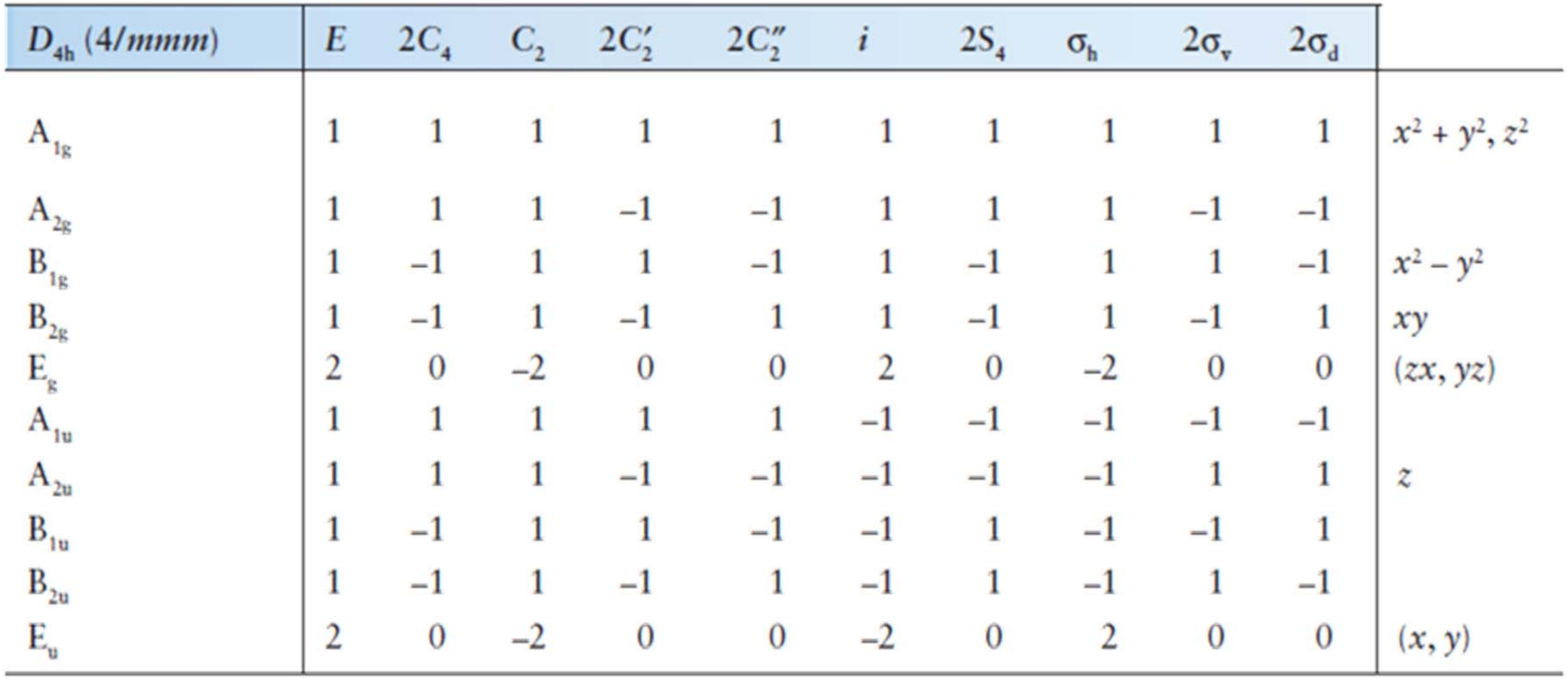
p orbital – a_{2u} (p_z), e_u (p_x , p_y)

d orbital – e_g (d_{xz}, d_{yz})

– a_{1g} (d_{z^2}) , B_{2g} (d_{xy})

– b_{1g} ($d_{x^2-y^2}$) , B_{2g} (d_{xy})

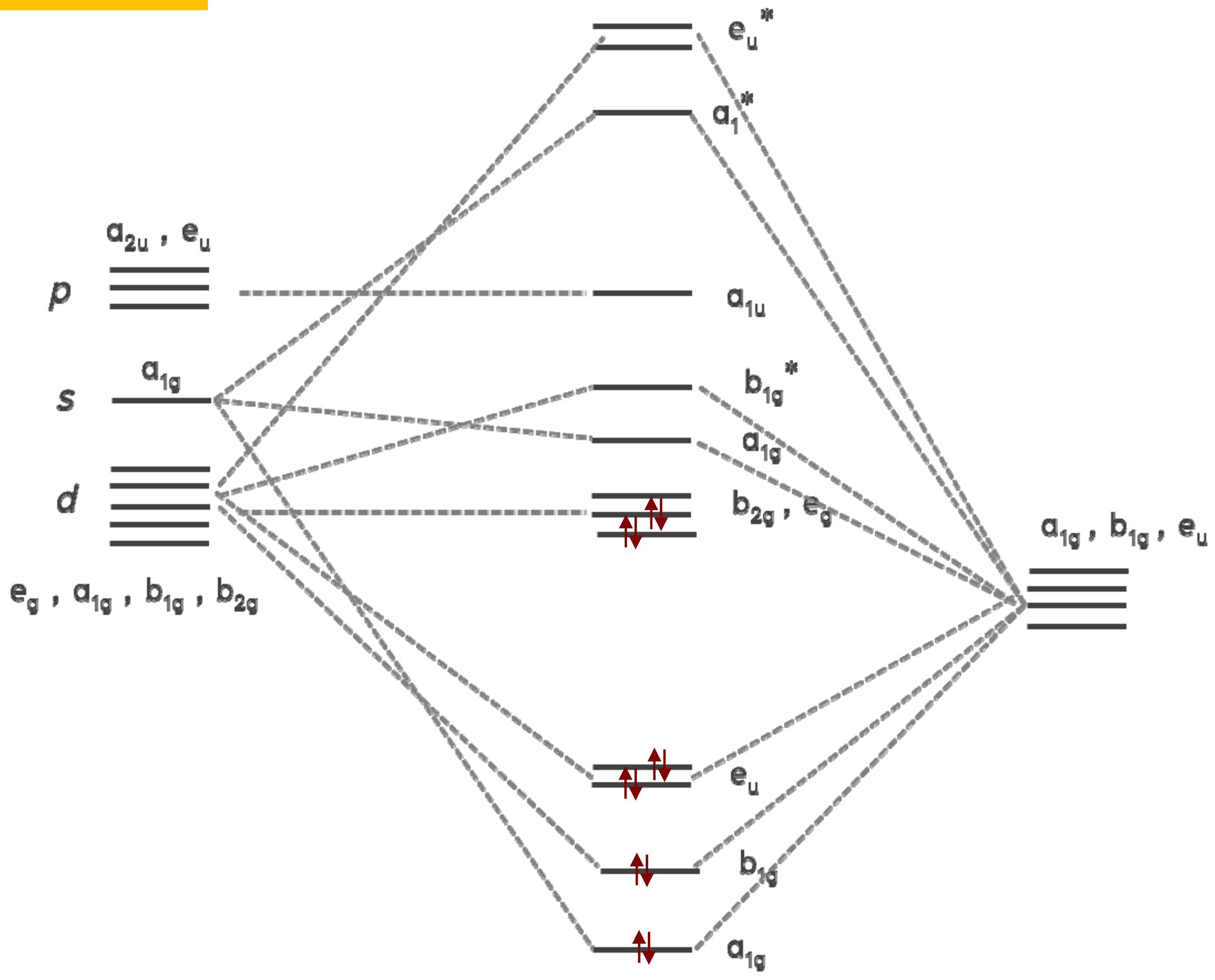
LGOs: a_{1g} , b_{1g} , e_u



D_{4h} (4/*mmm*)	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	x^2+y^2, z^2
A_{2g}	1	1	1	–1	–1	1	1	1	–1	–1	
B_{1g}	1	–1	1	1	–1	1	–1	1	1	–1	x^2-y^2
B_{2g}	1	–1	1	–1	1	1	–1	1	–1	1	xy
E_g	2	0	–2	0	0	2	0	–2	0	0	(zx, yz)
A_{1u}	1	1	1	1	1	–1	–1	–1	–1	–1	
A_{2u}	1	1	1	–1	–1	–1	–1	–1	1	1	z
B_{1u}	1	–1	1	1	–1	–1	1	–1	–1	1	
B_{2u}	1	–1	1	–1	1	–1	1	–1	1	–1	
E_u	2	0	–2	0	0	–2	0	2	0	0	(x, y)

MOT : Square planar complex (D_{4h})

d^8 (square planar)

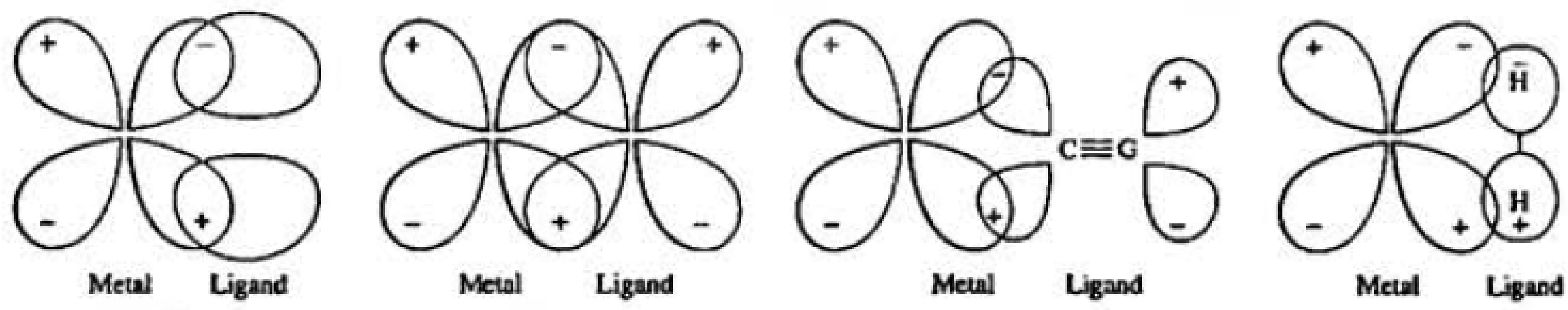


MOT : Formation of π bonding

LGOs orbital possible for π bonding : t_{1u}, t_{2u}, t_{1g}, t_{2g}

Metal d and p orbital possible for π bonding : t_{1u} (p_x, p_y, p_z), t_{2g} (d_{xy}, d_{yz}, d_{xz})

Four types of π bonding formation



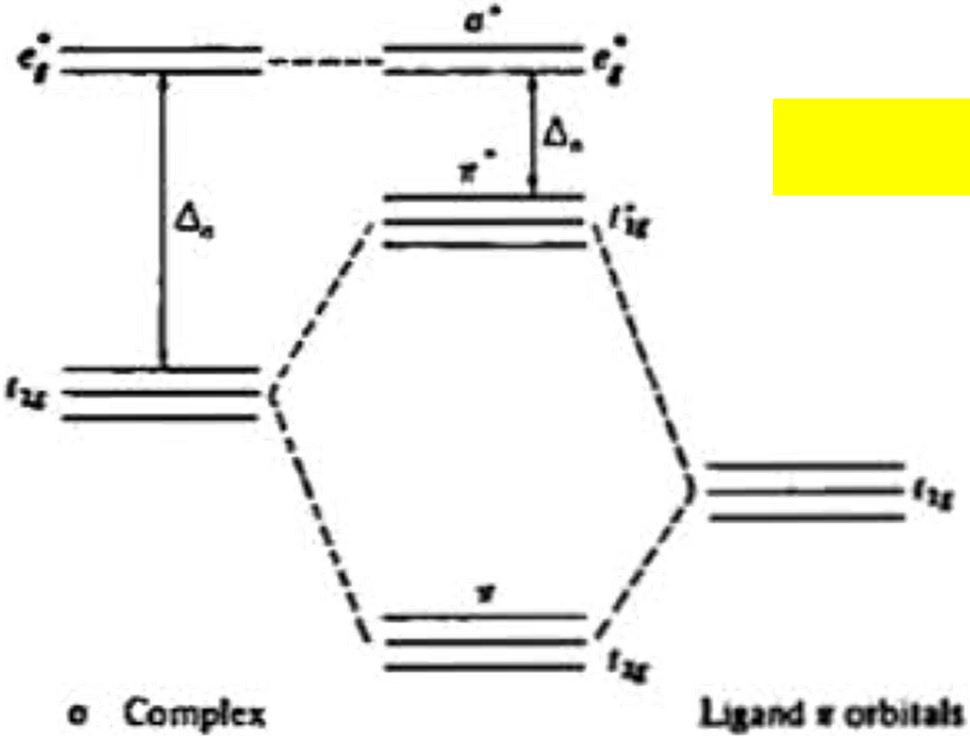
Bond type	Ligand
d_π–d_π	RO^-, RS^-, O^{2-}, F^-, Cl^-, Br^-, I^-, $R2N^-$
d_π–p_π	R_3P, R_3As, R_2S
d_π–π^*	CO, RNC, pyridine, CN^-, N_2, NO^{2-}, en
d_π–σ^*	H2, R_3P, alkane

Two types of π ligand

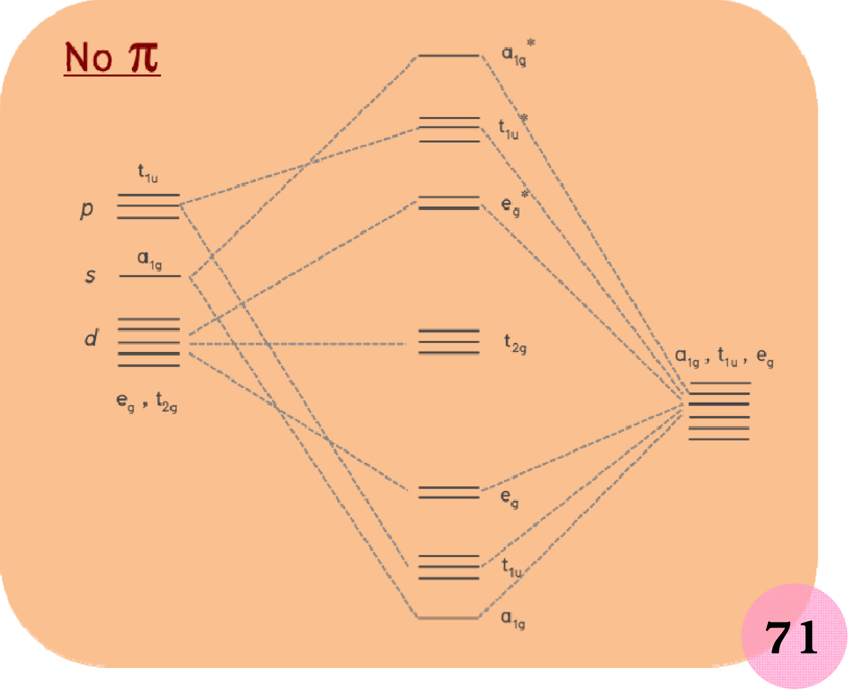
1. π donor or π base
2. π acceptor π acid

MOT : π donor ligands (π base)

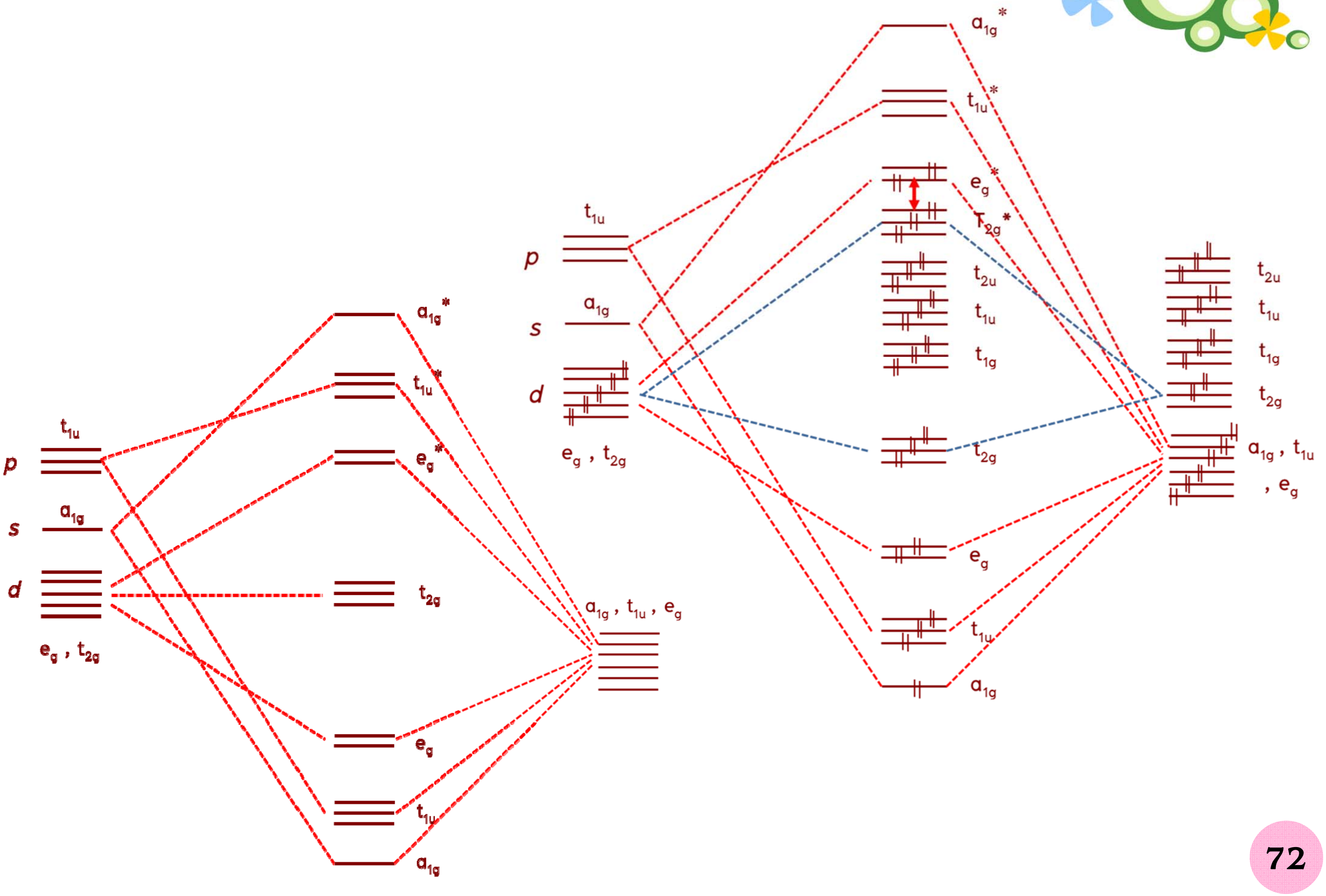
Filled p orbitals *e.g.* F^-, Cl^- (weak filed ligand)



π donor decrease Δ_o

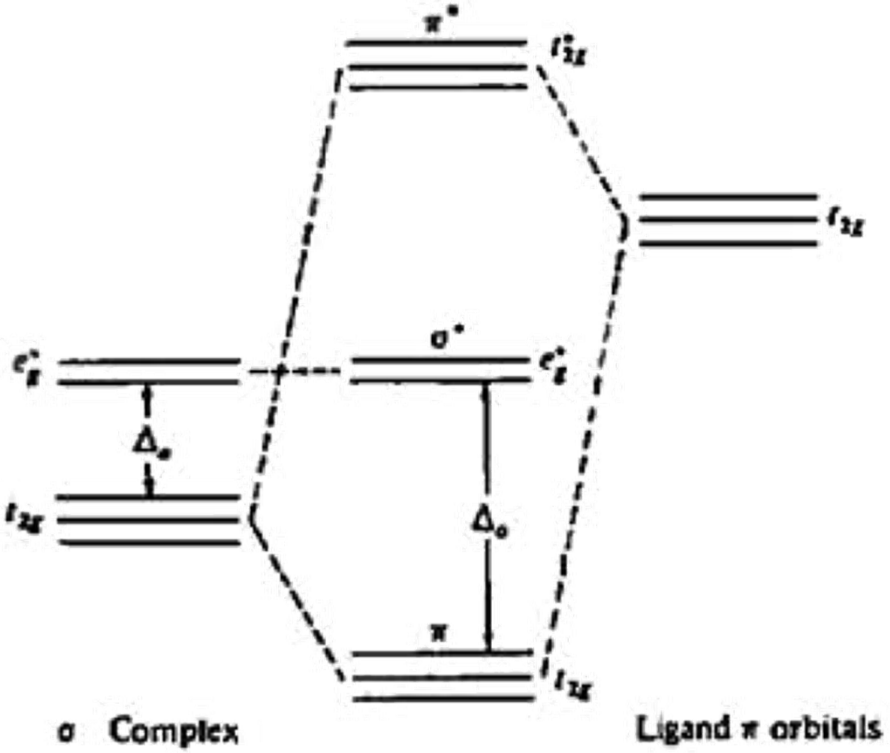


MOT : π donor ligands (π base)



MOT : π acceptor ligands (π acid)

Unoccupied p orbitals *e.g.* CO, PR_3 (strong filed ligand)



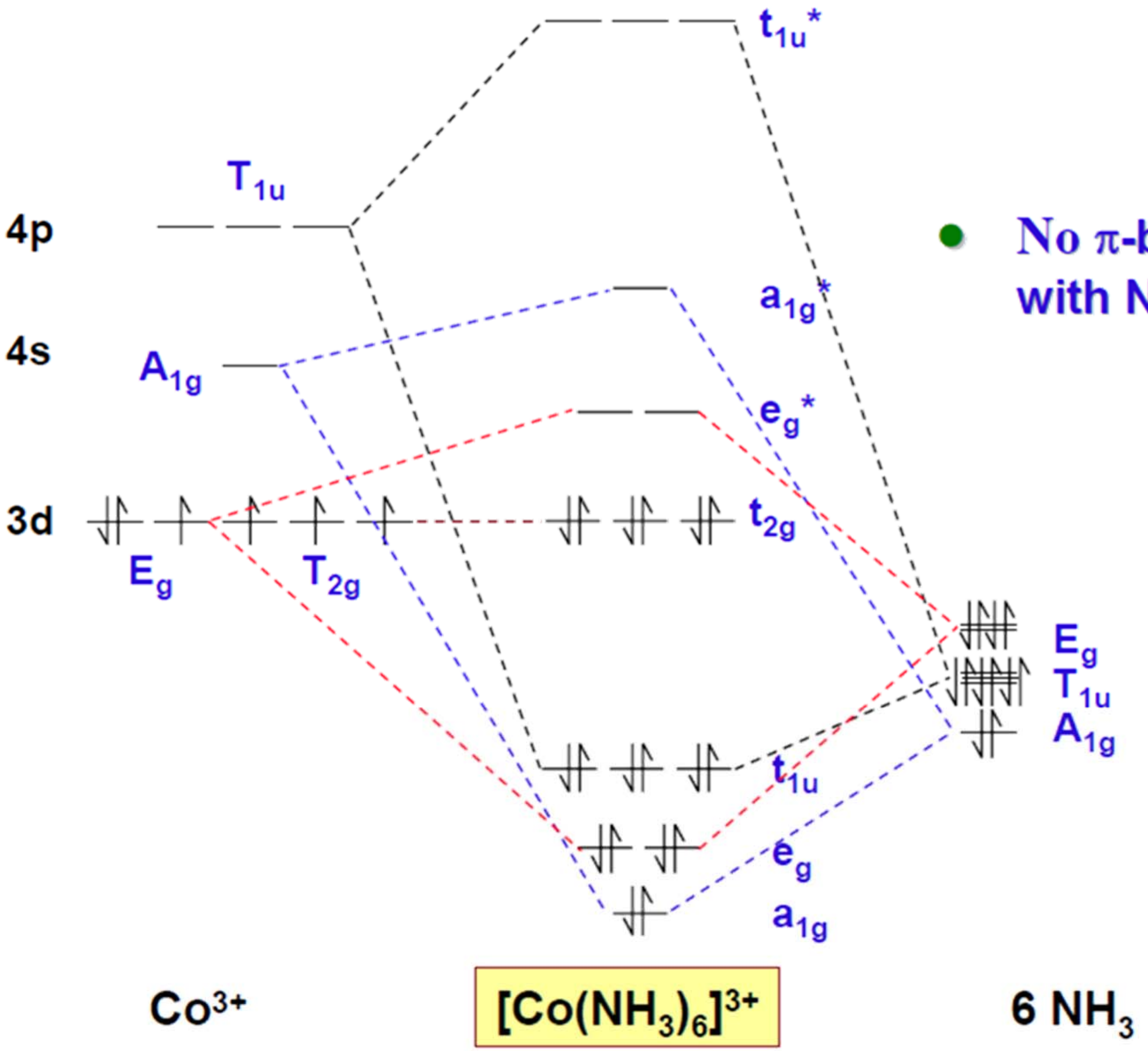
π acceptor increase Δ_o

increasing Δ_o →

$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < PR_3 < CO \cong PF_3$

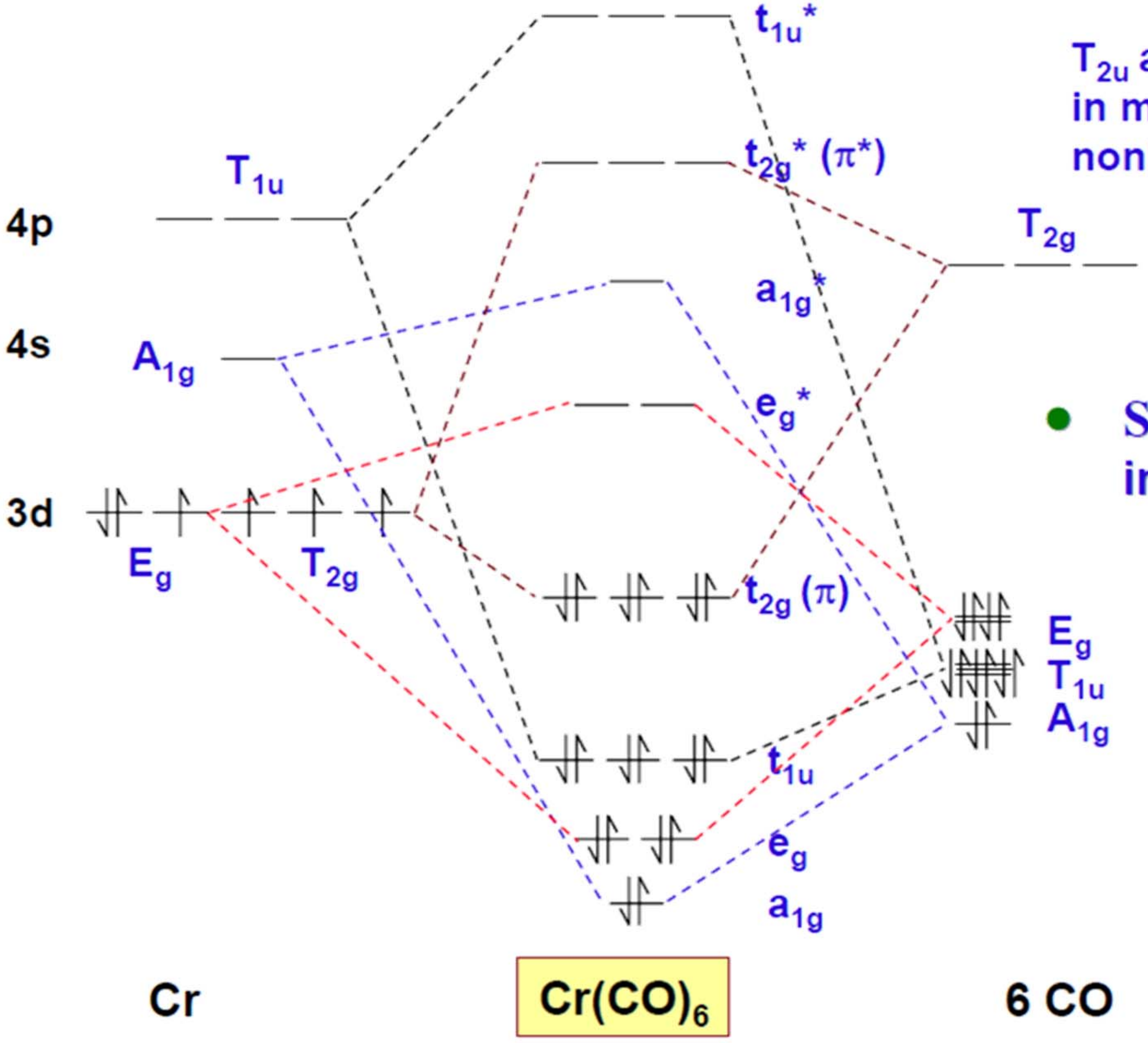
π-donor < weak π-donor < no π-effects < π-acceptor

MOT : π acceptor ligands (π acid)



- No π-bonding interaction with NH_3

MOT : π acceptor ligands (π acid)



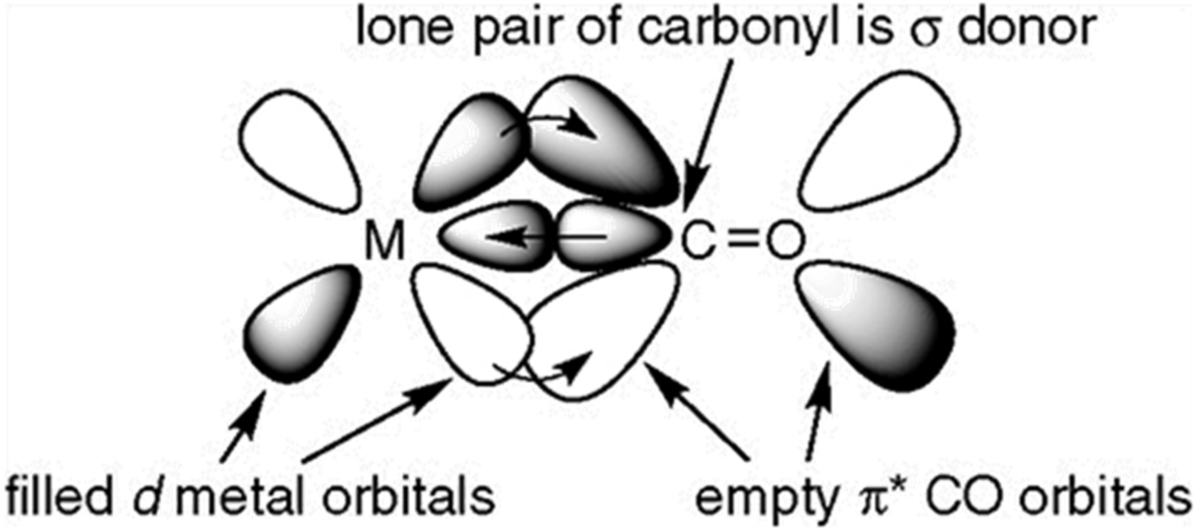
T_{2u} and T_{1g} have no match in metal orbitals, they are nonbonding

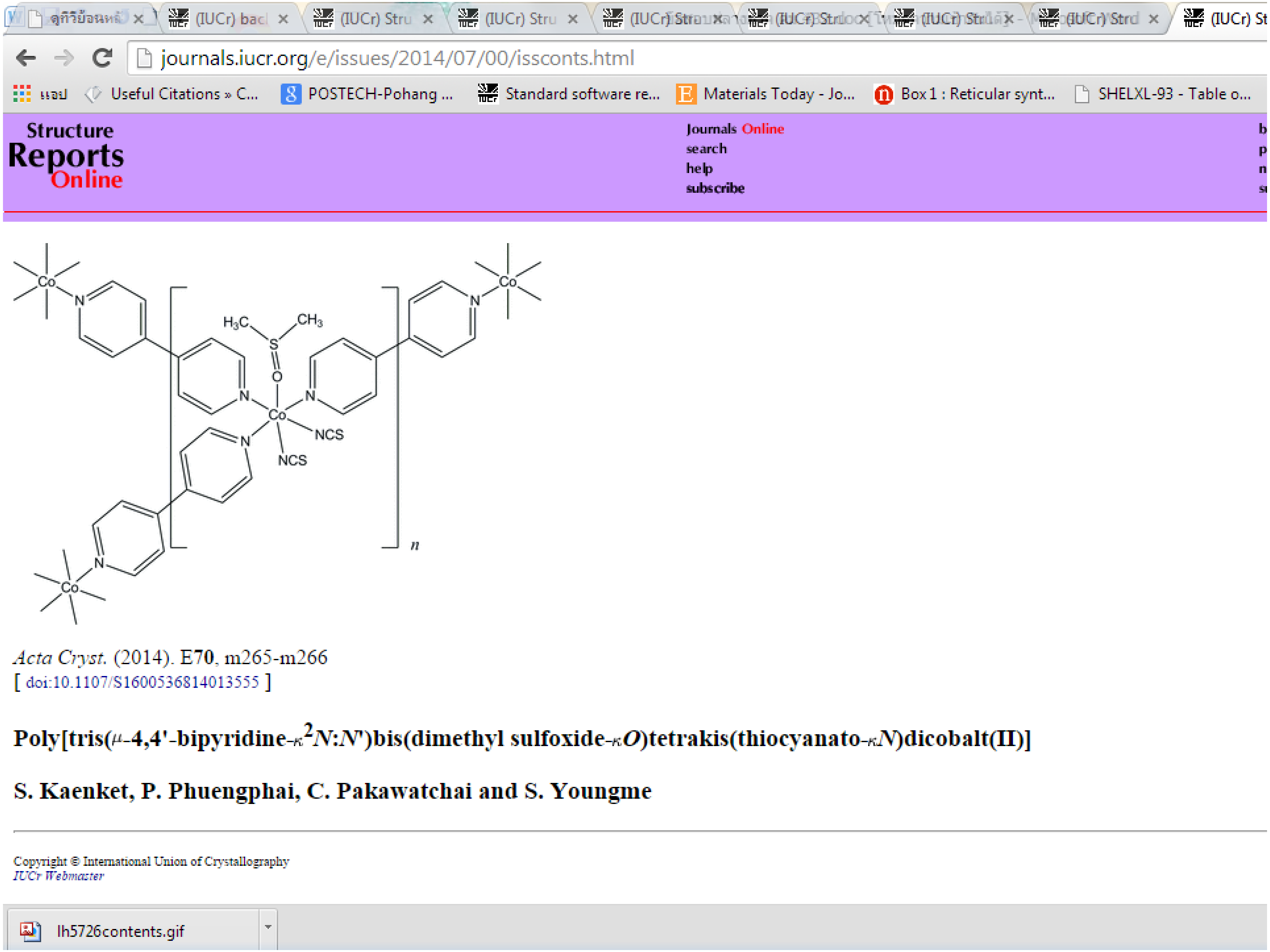
- Strong π-bonding interaction with CO

MOT : π acceptor ligands (π acid)

Electroneutrality principle and Synergic bonding

Electroneutrality principle: The central metal ion in a complex should be more or less neutral in charge – ligand are more electronegative, p back donation from metal to ligand compensating, yet enforcing, s donation from the ligand to the metal *(Synergic bonding)* and hence weakening intra-ligand bonding.





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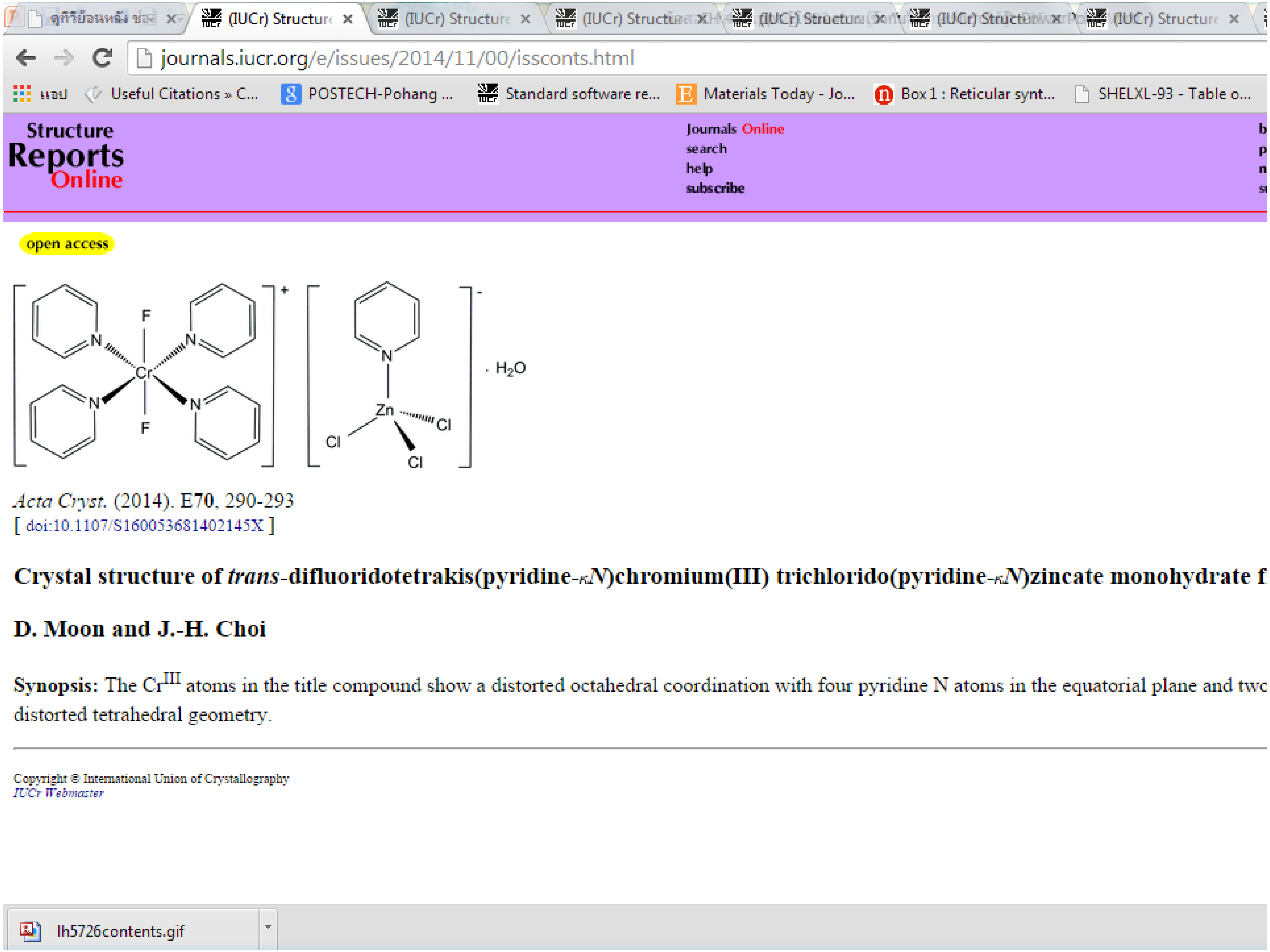
Poly[tris(μ-4,4'-bipyridine-κ^2*N*:*N*')bis(dimethyl sulfoxide-κ*O*)tetrakis(thiocyanato-κ*N*)dicobalt(II)]

S. Kaenket, P. Phuengphai, C. Pakawatchai and S. Youngme



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Crystal structure of *trans*-difluoridotetrakis(pyridine-κ*N*)chromium(III) trichlorido(pyridine-κ*N*)zincate monohydrate f

D. Moon and J.-H. Choi

Synopsis: The Cr^{III} atoms in the title compound show a distorted octahedral coordination with four pyridine N atoms in the equatorial plane and tw
distorted tetrahedral geometry.
