Synthesis and characterization of inorganic complexes

Content:

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General synthesis methods

Prevalent characterization

Review some experiment

Laboratory

12 section advanced experiment

Interoperation of results

References:

Direct Synthesis Of Coordination and Organmetallic Compounds

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References:

Purification of laboratory Chemical 6th

By:

W. L. F. Armarego

Ch. L. L. Chai

:

Practical Skills in Chemistry

By:

J. R. Dean & et al

WERNER/JORGENSEN CONTROVERSY

Sophus Jorgensen

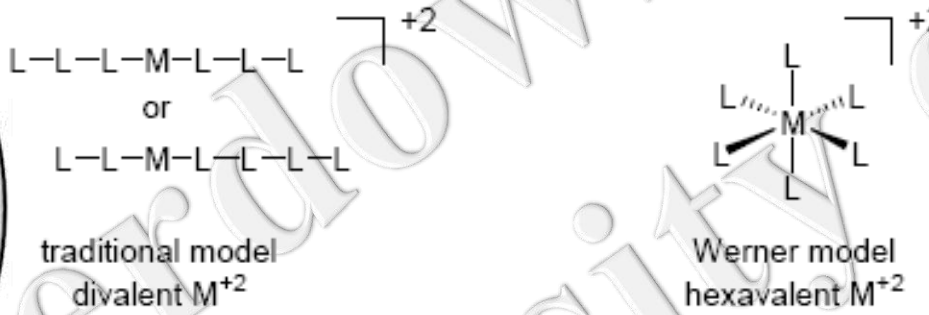

Figure 2. Opposing coordination models

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Alfred Werner

"Probably the greatest conceptual contribution to inorganic chemistry—comparable in both direct and indirect impact to the concept of the tetrahedral carbon atom in organic chemistry—is Alfred Werner's concept of coordination compounds and his general theory of how they behave." Albert Cotton

Compounds that contain metal complexes are called coordination compounds.

$CoCl_3$ and NH_3.

$[Co(NH_3)_6]Cl_3$ and $[CoCl(NH_3)_5]Cl_2$

Differing reactivity with $AgNO_3$.

Alfred Werner
1866-1919

THE METALS

Transition element

Elements with incomplete d shell

Mercury (Hg) is the only transition metal that is not a solid.

Form cations in beautifully coloured

Is Zn a transition metal?

THE TRANSITION METALS

(A) Position

First/ second/ third row TMs

- Size *decreases* down a group
- Lanthanide contraction (filling of f orbitals)

  Sizes of 2nd row and 3rd row TMs are similar (why)

Ion	Cr^{3+}	Mo^{3+}	Ru^{3+}	Ir^{3+}
Size/Å (CN = 6)	0.76	0.83	0.82	0.82

(B) Early/late Transition element

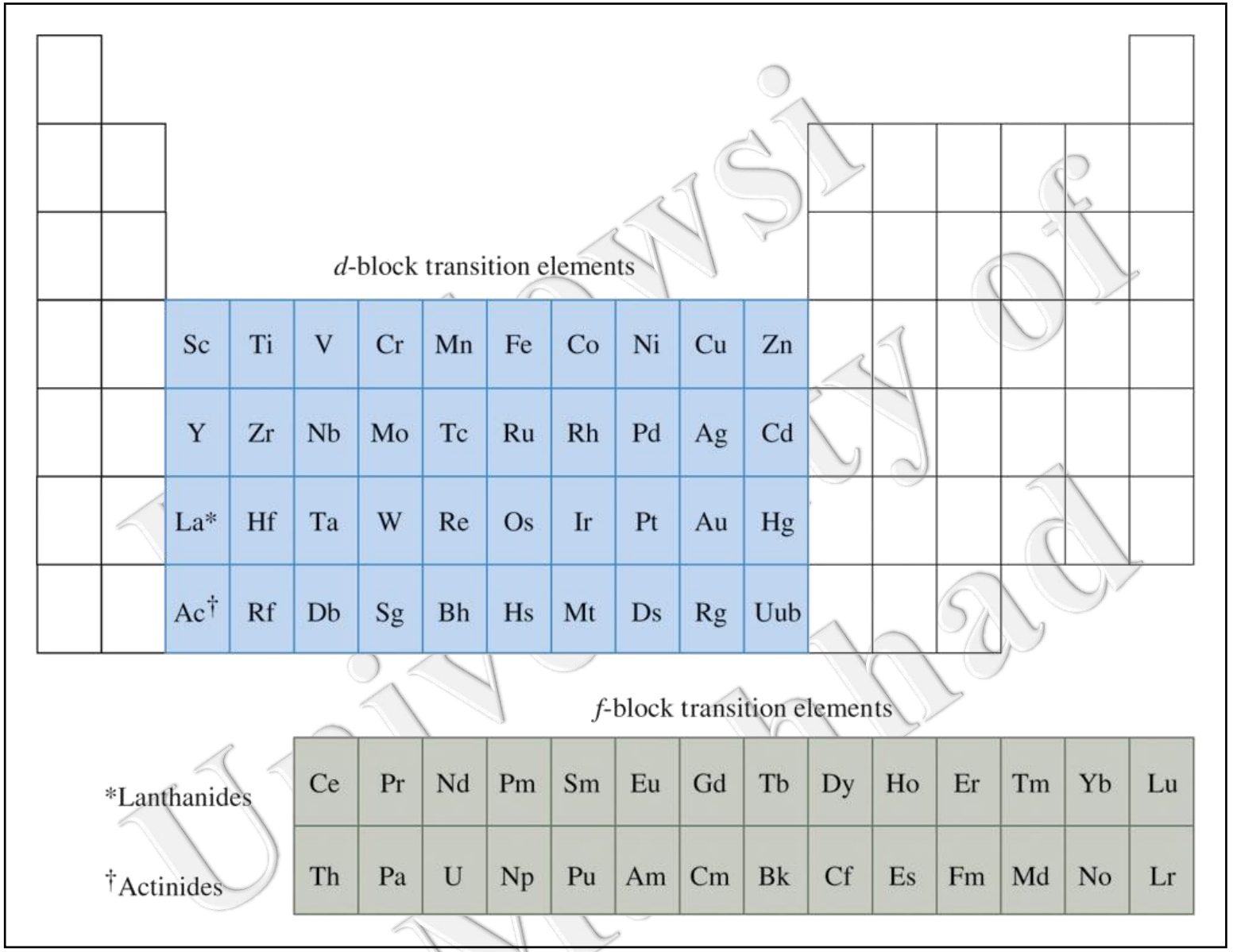
Early: on the LHS of the periodic table (e.g. Ti)

Late: on the RHS of the periodic table (e.g. Pt)

Usually, for metal complexes

- **Early TM : high metal oxidation state, e.g. Ti(IV), V(V) (high valent);**
- **hard metal ions (binds to hard ligands)**

- **Late TM : low metal oxidation state, e.g. Pt(II), Au(I) (low valent);**
- **soft metal ions (binds to soft ligands)**



Metal Oxidation states

Variable

Up to +8 in Os & Ru

Re has widest range: -3 $\Rightarrow$ +7 !

Werner's Coordination Theory

primary valence => ion charge

secondary valence => coordination number

inner sphere => ligands bonded directly to metal ion

outer sphere => next sheath of ions or molecules

Coordination compounds:

* Combination of two or more atoms, ions, or molecules where a bond is formed by sharing a pair of electrons originally associated with only one of the compounds.

•Co-ordination complexes are compounds in which several ligands are co-ordinated to a transition metal cation.

Coordination compounds:

-Ion containing central metal ion bound to one or more **ligands**

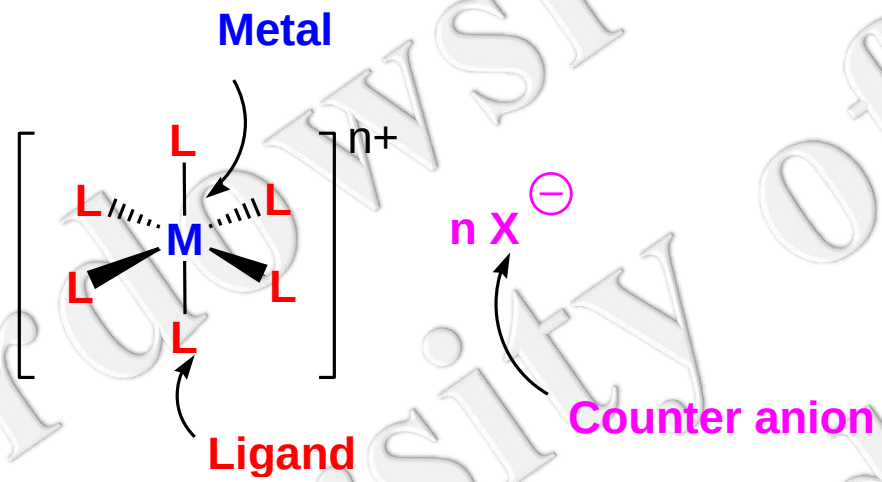
Lewis base (or e^- donor) that forms bond w/metal

When complex ion combines w/counter-ions (non-ligands) they yield a neutral compound

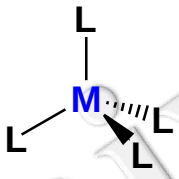
Coordination compounds:

Some co-ordination complexes and complex salts contain extra water molecules which were trapped during crystallization. These complexes are also **hydrates**.

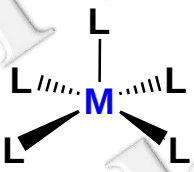
Coordination compounds (metal complexes)



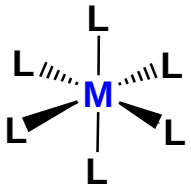
Common geometry



Tetrahedral

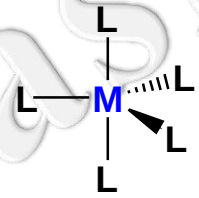


Square pyramidal



Octahedral

Square planar



Trigonal bipyramidal

LIGANDS

(A) Charge (formal charge)

Neutral (e.g. :CO, :PR_3, :NH_3)

Anionic (e.g. Cl^-, O^{2-}, CH_3^-)

Cationic (rare!) (e.g. NO^+, $C_7H_7^+$)

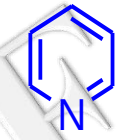
(B) Hard/Soft properties

Hard : period 1 donor (NH_3, $\underline{O}H_2$)

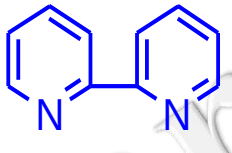
Soft : carbon (CO, CH_3^-, $CH_2{=}CH_2$) & period 2 donors ($\underline{P}R_3$, $\underline{S}R_2$)

No. of donor atom

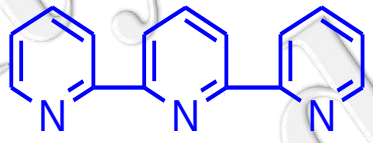
unidentate	bidentate	tridentate
NH_3 ammonia or ammine	$NH_2CH_2CH_2NH_2$ ethylenediamine (en)	$NH(CH_2NH_2)_2$ diethylenetriamine (dien)



pyridine
py



2,2'-bipyridine
bipy



2,2':6',6''-terpyridine
terpy

Metal complexes with polydentate (chelating) ligands are more stable than those with unidentate analogues.

Chelate effect