Transition Metal Coordination Chemistry

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Lecture 1:

What's interesting about Transition Metal Coordination Chemistry?

Who's idea was it anyway?

Recommended books

M.J. Winter, d-block Chemistry, Oxford Chemistry Primers, OUP, 2001

M.S. Silberberg, Chemistry, 3rd Ed, Mc GrawHill, 2003 (chapter 23)

C.E. Housecroft, A.G. Sharpe, Inorganic Chemistry, 1st Ed, PrenticeHall, 2001

J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, 4th Ed., HarperCollins, 1993

Introduction Transition Elements Properties

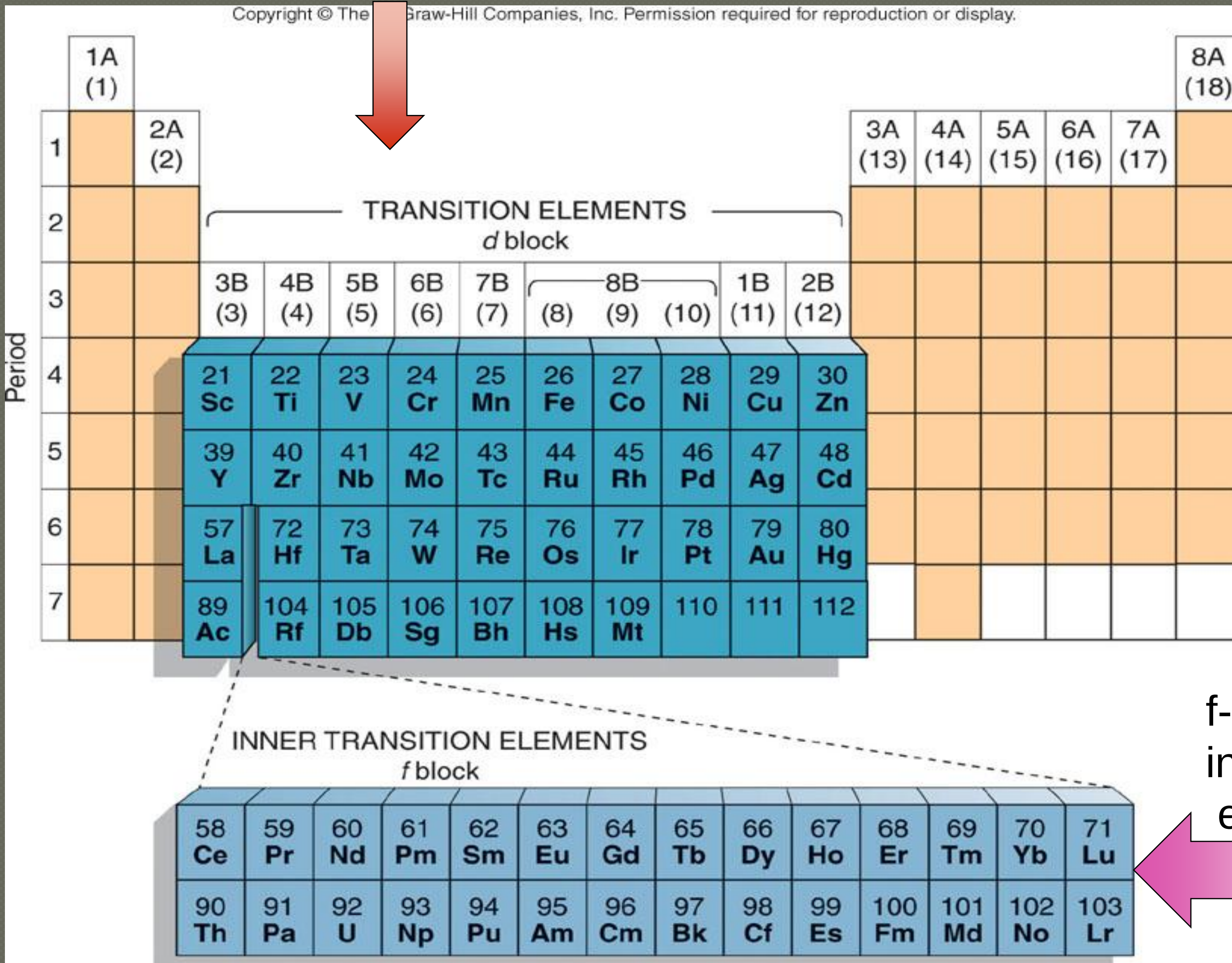
- **Periodic Table**
- **Electronic configuration**
- **Oxidation state**
- **Transition Elements Properties**
- **Coordination Theory.**
  - **- Chain theories.**
  - **- Werner theories.**

What is a transition metal?

“an element with valance d- or f-electrons”

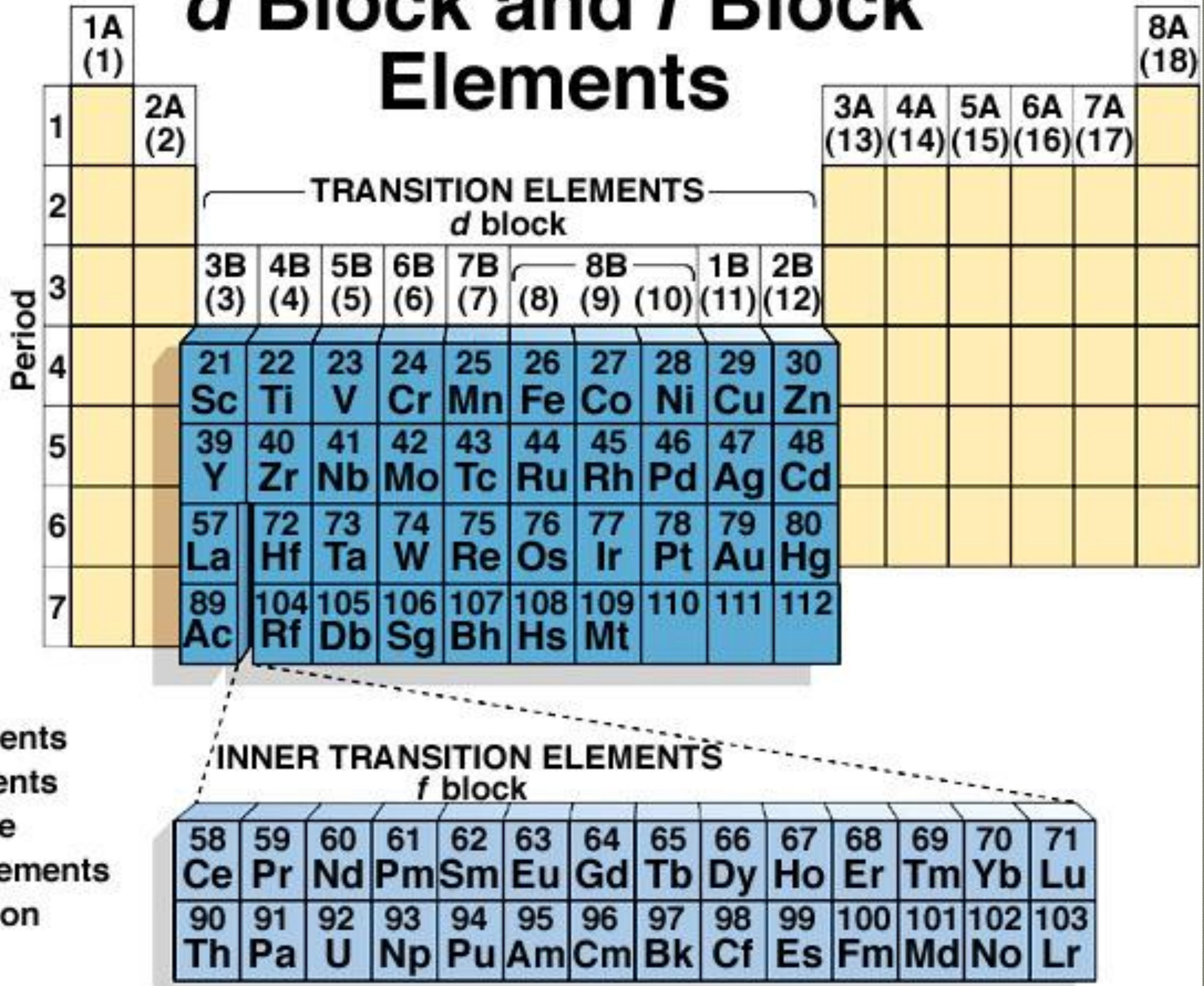
ie. a d-block or f-block metal

d-block: transition elements



f-block:
inner transition
elements

d Block and *f* Block Elements



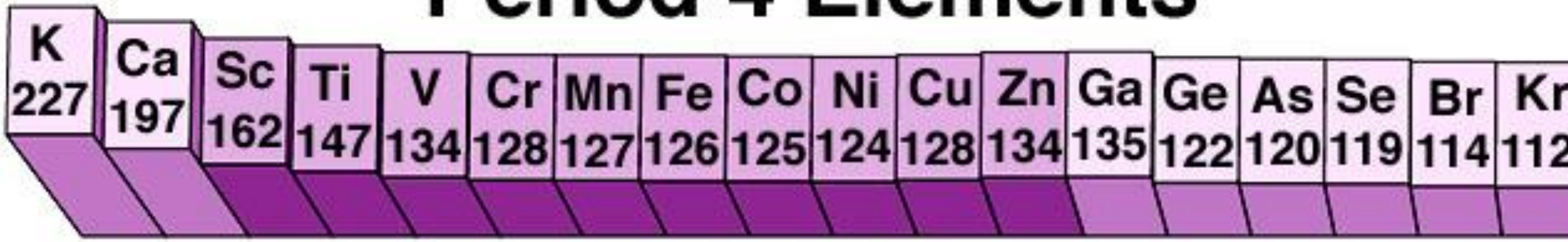
d block elements
f block elements
Periodic table
Transition elements
Inner transition elements

Transition Elements Properties

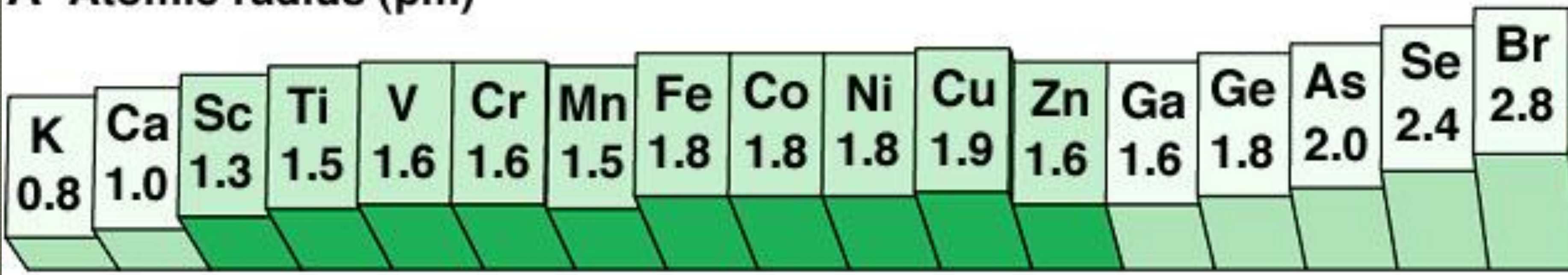
Properties:

- There are several common characteristic properties of transition elements:
- · They often form colored compounds.
- · They can have a variety of different oxidation states.
- · They are often good catalysts.
- · They are silvery-blue at room temperature (except copper and gold).
- · They are solids at room temperature (except mercury).
- · They form complexes.
- . Transition metals exhibit interesting magnetic (Bara magnetic properties)

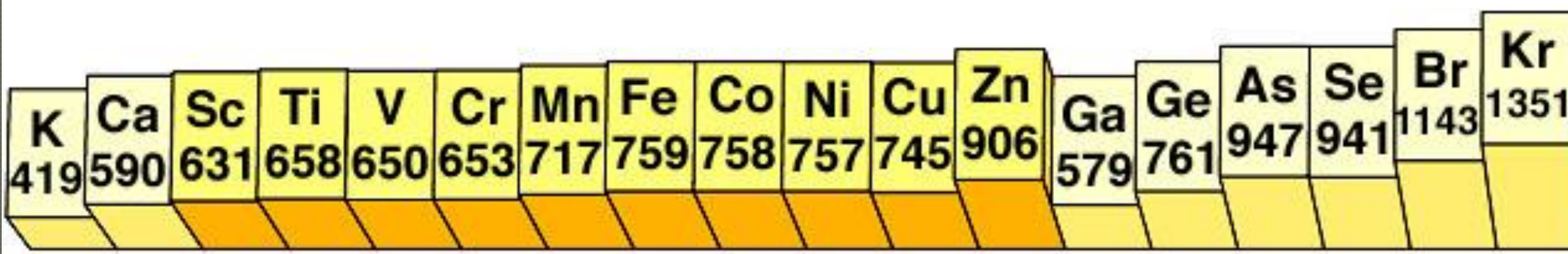
Horizontal Trends in Period 4 Elements



A Atomic radius (pm)

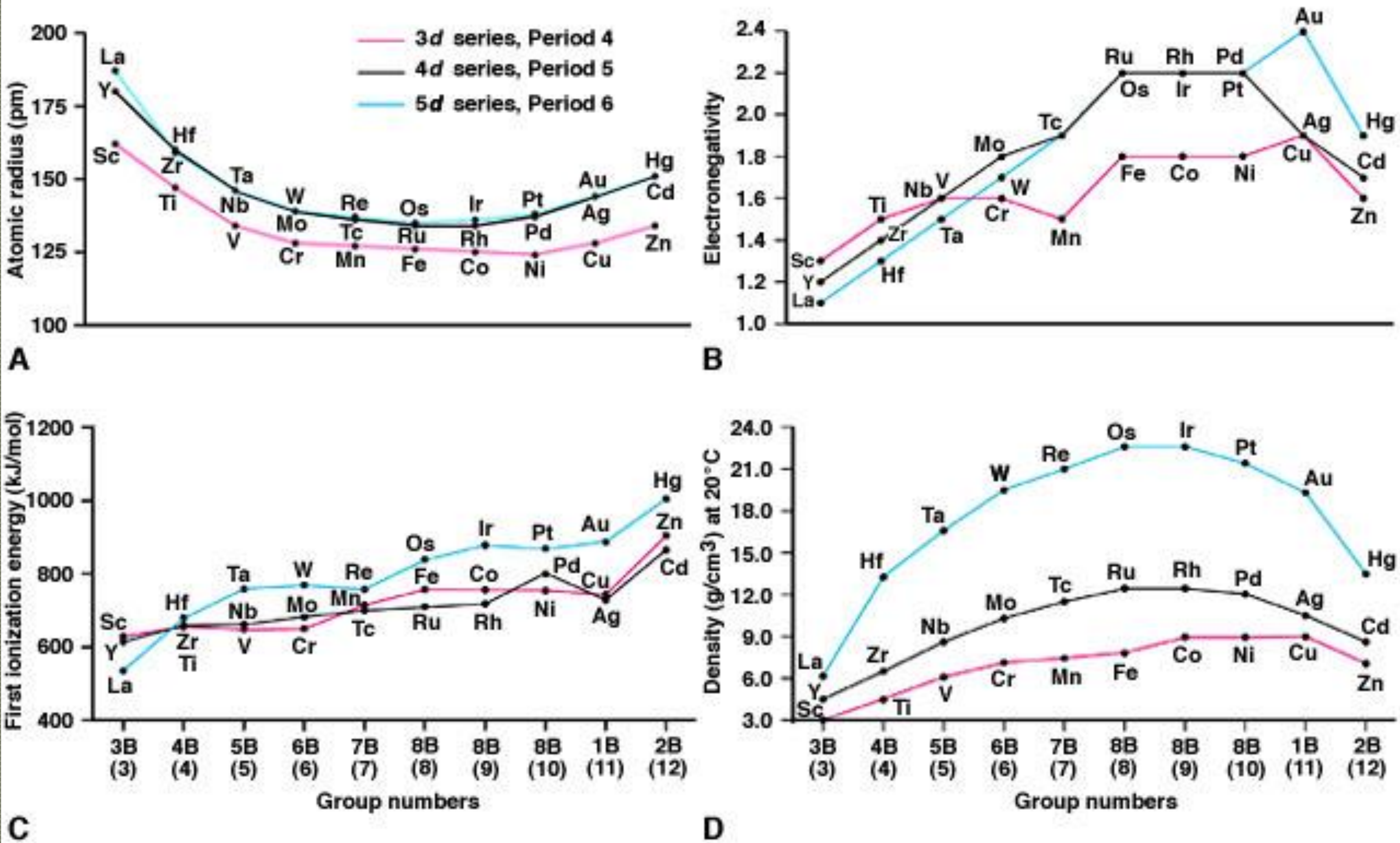


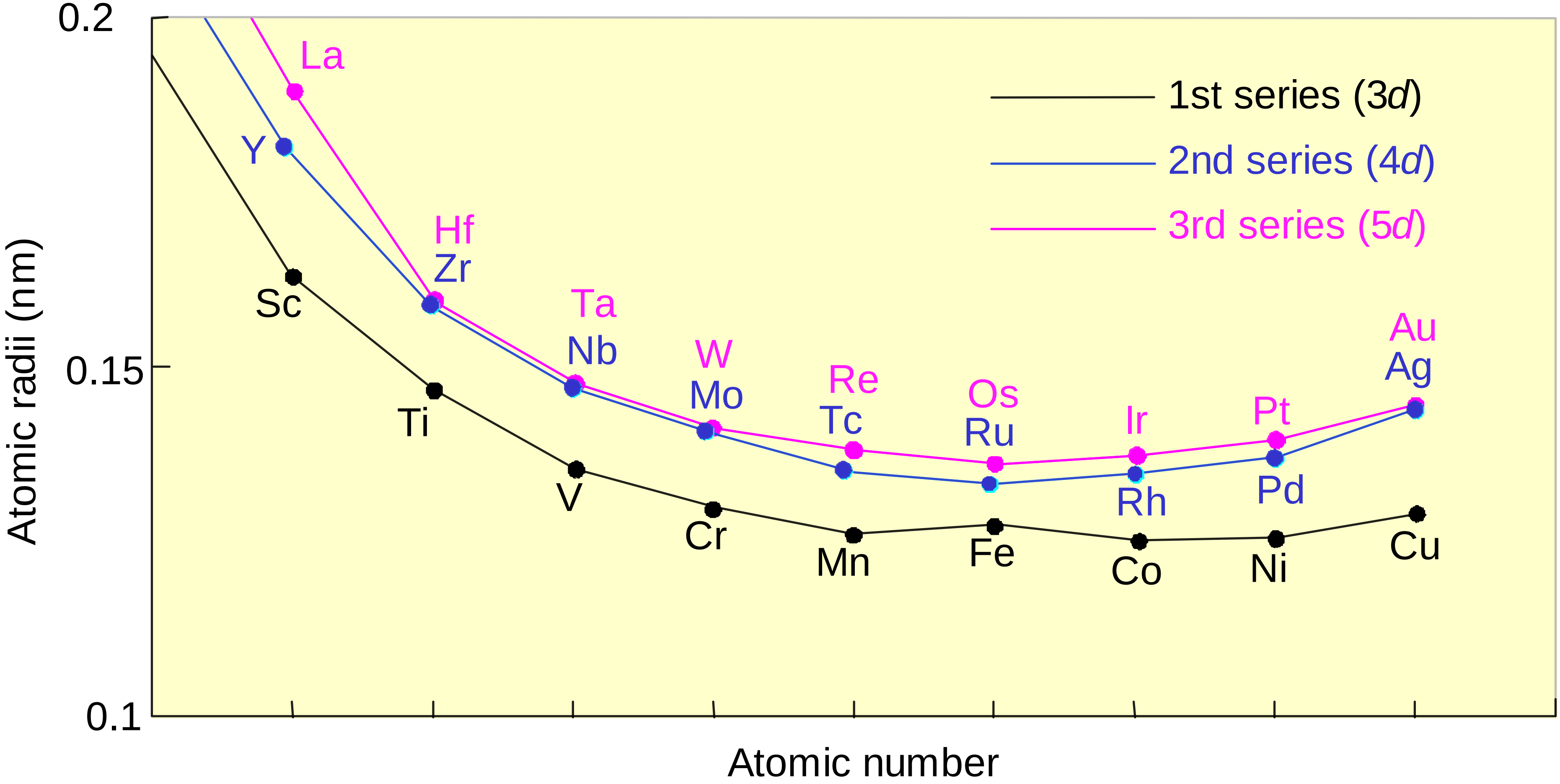
B Electronegativity



C First ionization energy (kJ/mol)

Vertical Trends within the Transition Elements





0.2
0.15
0.1
Atomic radii (nm)
Atomic number
1st series (3d)
2nd series (4d)
3rd series (5d)
La
Y
Sc
Hf
Zr
Ti
Ta
Nb
V
W
Mo
Cr
Re
Tc
Mn
Os
Ru
Fe
Ir
Rh
Co
Pt
Pd
Ni
Au
Ag
Cu

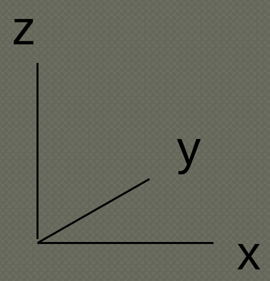
Electronic configuration of the 3d transition elements

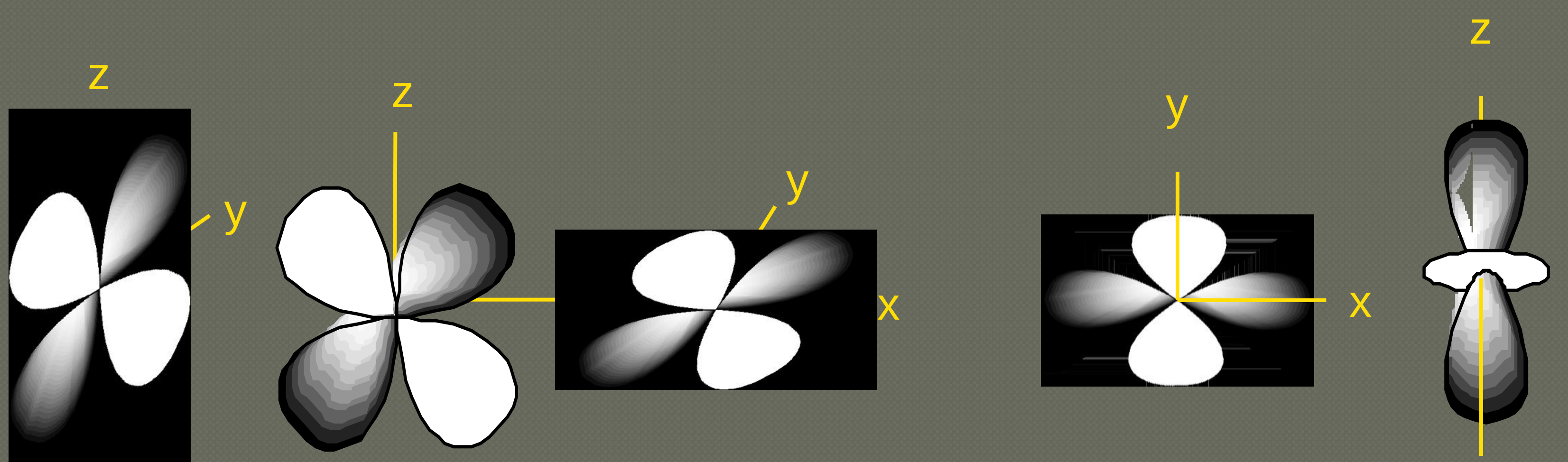
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
4s	2	2	2	1	2	2	2	2	1	2
3d	1	2	3	5	5	6	7	8	10	10

Electronic configuration of the Lanthanides

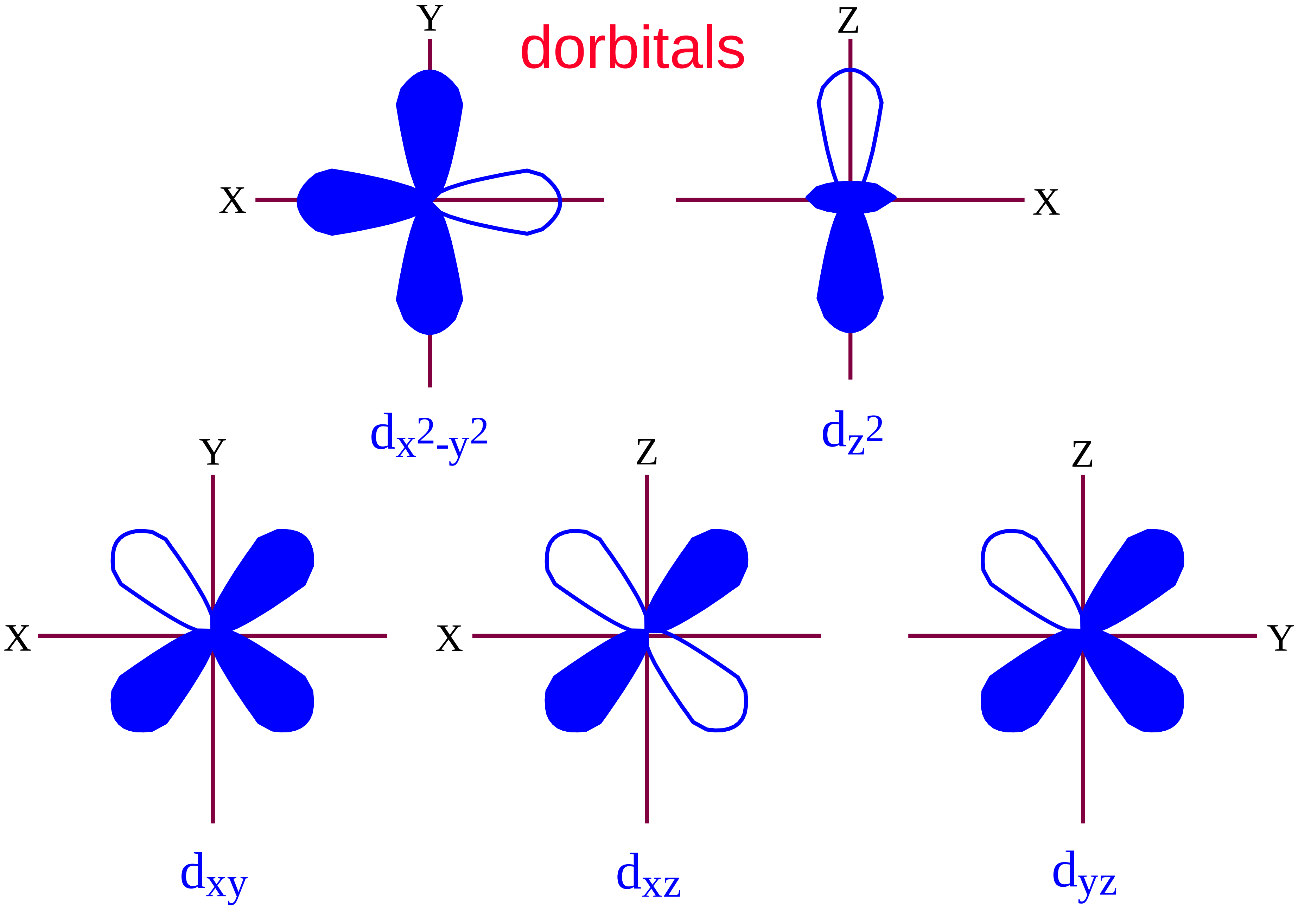
	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf
6s	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
5d	1	1	0	0	0	0	0	1	0	0	0	0	0	0	1	2
4f	0	1	3	4	5	6	7	7	9	10	11	12	13	14	14	14

Shapes of d-orbitals





yz xz xy x^2-y^2 z^2


dorbitals
Y
X
dx2-y2
Z
X
dz2
Y
X
dxy
Z
X
dxz
Z
Y
dyz

Orbital Occupancy

Table 23.1 Orbital Occupancy of the Period 4 Transition Metals

Element	4s	3d	4p	Unpaired Electrons
Sc	↑↓	↑ - - - -	- - -	1
Ti	↑↓	↑ ↑ - - -	- - -	2
V	↑↓	↑ ↑ ↑ - -	- - -	3
Cr	↑	↑ ↑ ↑ ↑ ↑	- - -	6
Mn	↑↓	↑ ↑ ↑ ↑ ↑	- - -	5
Fe	↑↓	↑↓ ↑ ↑ ↑ ↑	- - -	4
Co	↑↓	↑↓ ↑↓ ↑ ↑ ↑	- - -	3
Ni	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑	- - -	2
Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	- - -	1
Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	- - -	0

Electronic Configurations

Element	Configuration
Sc	$[Ar]3d^1 4s^2$
Ti	$[Ar]3d^2 4s^2$
V	$[Ar]3d^3 4s^2$
Cr	$[Ar]3d^5 4s^1$
Mn	$[Ar]3d^5 4s^2$

$$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$$

Electronic Configurations

Element	Configuration
Fe	[Ar] $3d^6 4s^2$
Co	[Ar] $3d^7 4s^2$
Ni	[Ar] $3d^8 4s^2$
Cu	

[Ar]$3d^{10}4s^1$

Zn

[Ar]$3d^{10}4s^2$

$$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$$

Multiple Oxidation States

Oxidation States and *d*-Orbital Occupancy

Table 23.2 Oxidation States and *d*-Orbital Occupancy of the Period 4 Transition Metals*

Oxidation State	3B (3) Sc	4B (4) Ti	5B (5) V	6B (6) Cr	7B (7) Mn	8B (8) Fe	8B (9) Co	8B (10) Ni	1B (11) Cu	2B (12) Zn
0	0 (d^1)	0 (d^2)	0 (d^3)	0 (d^5)	0 (d^5)	0 (d^6)	0 (d^7)	0 (d^8)	0 (d^{10})	0 (d^{10})
+1			+1 (d^3)	+1 (d^5)	+1 (d^5)		+1 (d^7)	+1 (d^8)	+1 (d^{10})	
+2		+2 (d^2)	+2 (d^3)	+2 (d^4)	+2 (d^5)	+2 (d^6)	+2 (d^7)	+2 (d^8)	+2 (d^9)	+2 (d^{10})
+3	+3 (d^0)	+3 (d^1)	+3 (d^2)	+3 (d^3)	+3 (d^4)	+3 (d^5)	+3 (d^6)	+3 (d^7)	+3 (d^8)	
+4		+4 (d^0)	+4 (d^1)	+4 (d^2)	+4 (d^3)	+4 (d^4)	+4 (d^5)	+4 (d^6)		
+5			+5 (d^0)	+5 (d^1)	+5 (d^2)		+5 (d^4)			
+6				+6 (d^0)	+6 (d^1)	+6 (d^2)				
+7					+7 (d^0)					

*Most important in color.

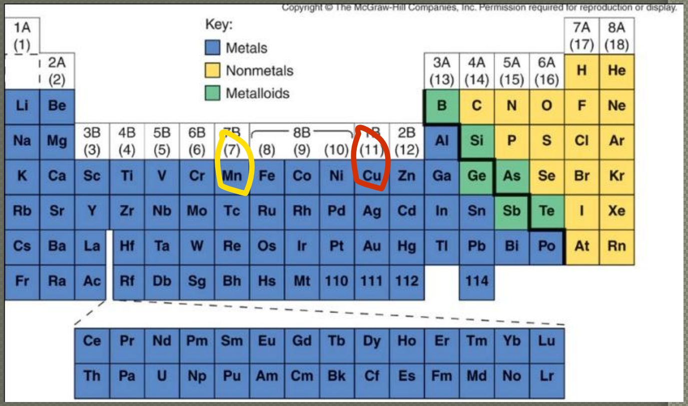
Oxidation States of Transition Elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4		+4		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

loss of ns e^-s

loss of ns and (n-1)d e^-s

Working out numbers of d-electrons from oxidation states:



1st: how many electrons are there in the shell?

- count along the periodic table

e.g. Mn = 7 electrons   Cu = 11 electrons

2nd: how many electrons are lost?

- oxidation state

e.g. Mn(VII) = 7 electrons lost   Cu(II) = 2 electrons lost

3rd: how many electrons left over?

- subtract

e.g. Mn(VII) = 7 - 7 = no d-electrons, d^0 Cu(II) = 11 - 2 = 9 d-electrons = d^9

Rule: The electrons in the s-orbital are the first to be lost

Hence the only valance electrons available in a transition metal ion are d-electrons

Oxidation States of Manganese

Table 23.5 Some Oxidation States of Manganese

Oxidation state*	**Mn(II)**	Mn(III)	**Mn(IV)**	Mn(VI)	**Mn(VII)**
Example	Mn^{2+}	Mn_2O_3	MnO_2	MnO_4^{2-}	Mno_4^-
Ion configuration	d^5	d^4	d^3	d^1	d^0
Oxide acidity	BASIC				ACIDIC

*Most common states in boldface.

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Fe^{2+}

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Fe^{2+}

$$Fe - 2e^{-} \rightarrow Fe^{2+}$$

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Fe^{2+}

$$Fe - 2e^{-} \rightarrow Fe^{2+}$$

$[Ar]3d^6 4s^2$

valence ns e^{-}'s removed first

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Fe^{2+}

$$Fe - 2e^{-} \rightarrow Fe^{2+}$$

$[Ar]3d^6 4s^2$ $\qquad$ $[Ar]3d^6$

valence ns e^{-}'s removed first

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Co^{3+}

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Co^{3+}

$$Co - 3e^{-} \rightarrow Co^{3+}$$

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Co^{3+}

$$Co - 3e^{-} \rightarrow Co^{3+}$$

$[Ar]3d^{7}4s^{2}$

valence ns e^{-}'s removed first, then n-1 d e^{-}'s

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Co^{3+}

$$Co - 3e^{-} \rightarrow Co^{3+}$$

$[Ar]3d^7 4s^2$ $[Ar]3d^6$

valence ns e^-'s removed first, then n-1 d e^-'s

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Mn^{4+}

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Mn^{4+}

$$Mn - 4e^{-} \rightarrow Mn^{4+}$$

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Mn^{4+}

$$Mn - 4e^{-} \rightarrow Mn^{4+}$$

$[Ar]3d^{5}4s^{2}$

valence ns e^{-}'s removed first, then n-1 d e^{-}'s

Electronic Configurations of Transition Metal Ions

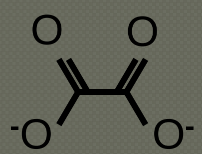
- Electronic configuration of Mn^{4+}

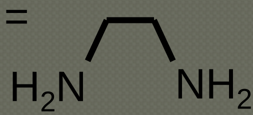
$$Mn - 4e^{-} \rightarrow Mn^{4+}$$

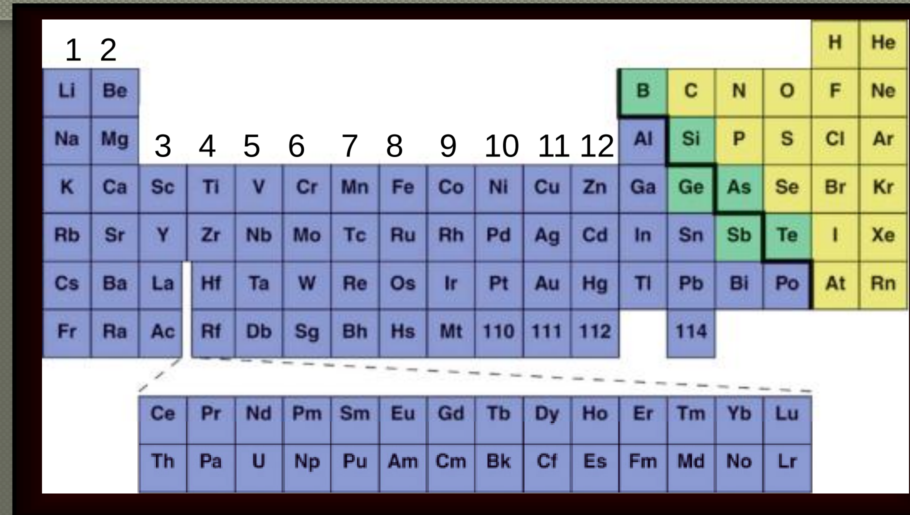
$[Ar]3d^5 4s^2$ $[Ar]3d^3$

valence ns e^-'s removed first, then n-1 d e^-'s

How many d-electrons has the metal?

ox = 

en = 



complex	O.S. of L	O.S. of M	no. d electrons
$[Cr_2O_7]^{2-}$	-2	+6	d^0
$[MnO_4]^-$	-2	+7	d^0
$[Ag(NH_3)_2]^+$	0	+1	d^{10}
$[Ti(H_2O)_6]^{3+}$	0	+3	d^1
$[Co(en)_3]^{3+}$	0	+3	d^6
$[PtCl_2(NH_3)_2]$	-1, 0	+2	d^8
$[V(CN)_6]^{4-}$	-1	+2	d^2
$[Fe(ox)_3]^{3-}$	-2	+3	d^5

biological activity

colour

magnetic behaviour

geometry

What's interesting about Transition Metal Complexes??

coordination number

medical applications

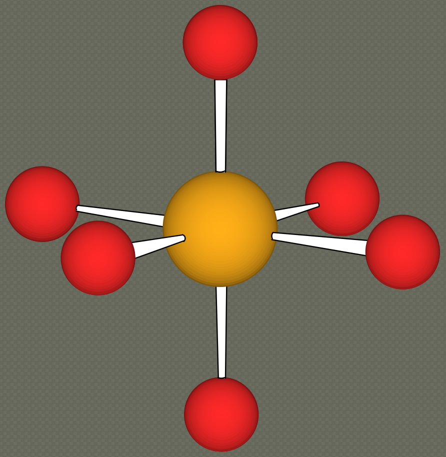
oxidation states

Colour of transition metal complexes

Ruby

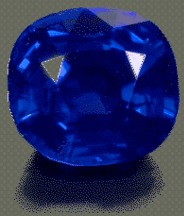
Corundum

Al_2O_3 with Cr^{3+} impurities



octahedral metal centre

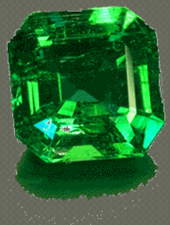
coordination number 6



Sapphire

Corundum

Al_2O_3 with Fe^{2+} and Ti^{4+} impurities



Emerald

Beryl

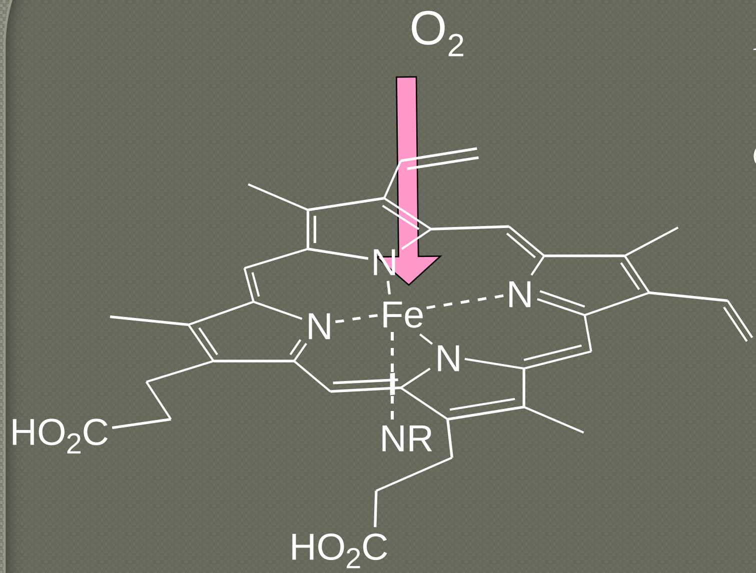
$AlSiO_3$ containing Be with Cr^{3+} impurities

Transiton Metal Trace Elements in Humans

Table 23.A Some Transition Metal Trace Elements in Humans

Element	Biomolecule Containing Element	Function of Biomolecule
Vanadium	Protein (?)	Redox couple in fat metabolism (?)
Chromium	Glucose tolerance factor	Glucose utilization
Manganese	Isocitrate dehydrogenase	Cell respiration
Iron	Hemoglobin and myoglobin Cytochrome *c* Catalase	Oxygen transport Cell respiration; ATP formation Decomposition of H_2O_2
Cobalt	Cobalamin (vitamin B_{12})	Development of red blood cells
Copper	Ceruloplasmin Cytochrome oxidase	Hemoglobin synthesis Cell respiration; ATP formation
Zinc	Carbonic anhydrase Carboxypeptidase A Alcohol dehydrogenase	Elimination of CO_2 Protein digestion Metabolism of ethanol

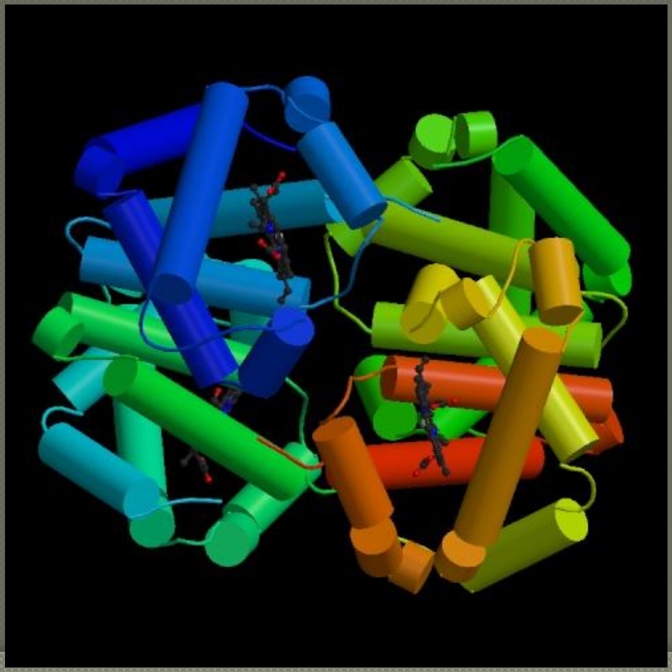
Haemoglobin

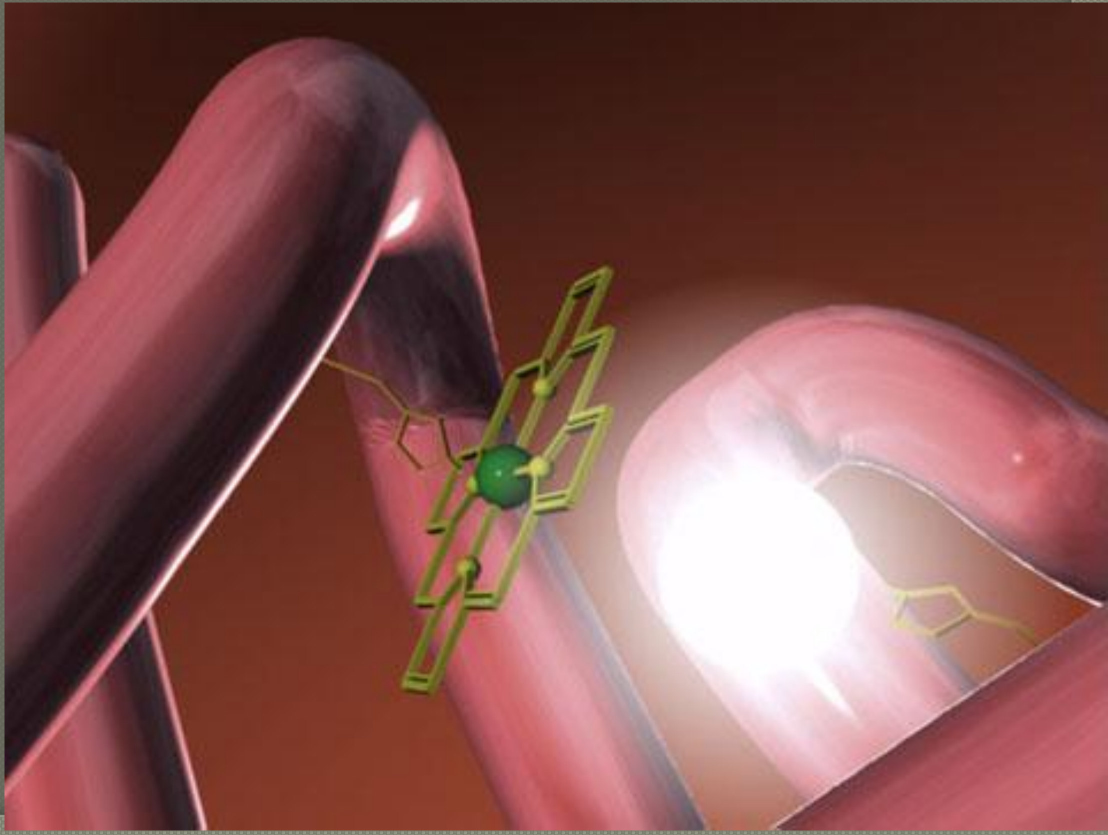


Oxygen carrier in blood Porphyrin-Fe

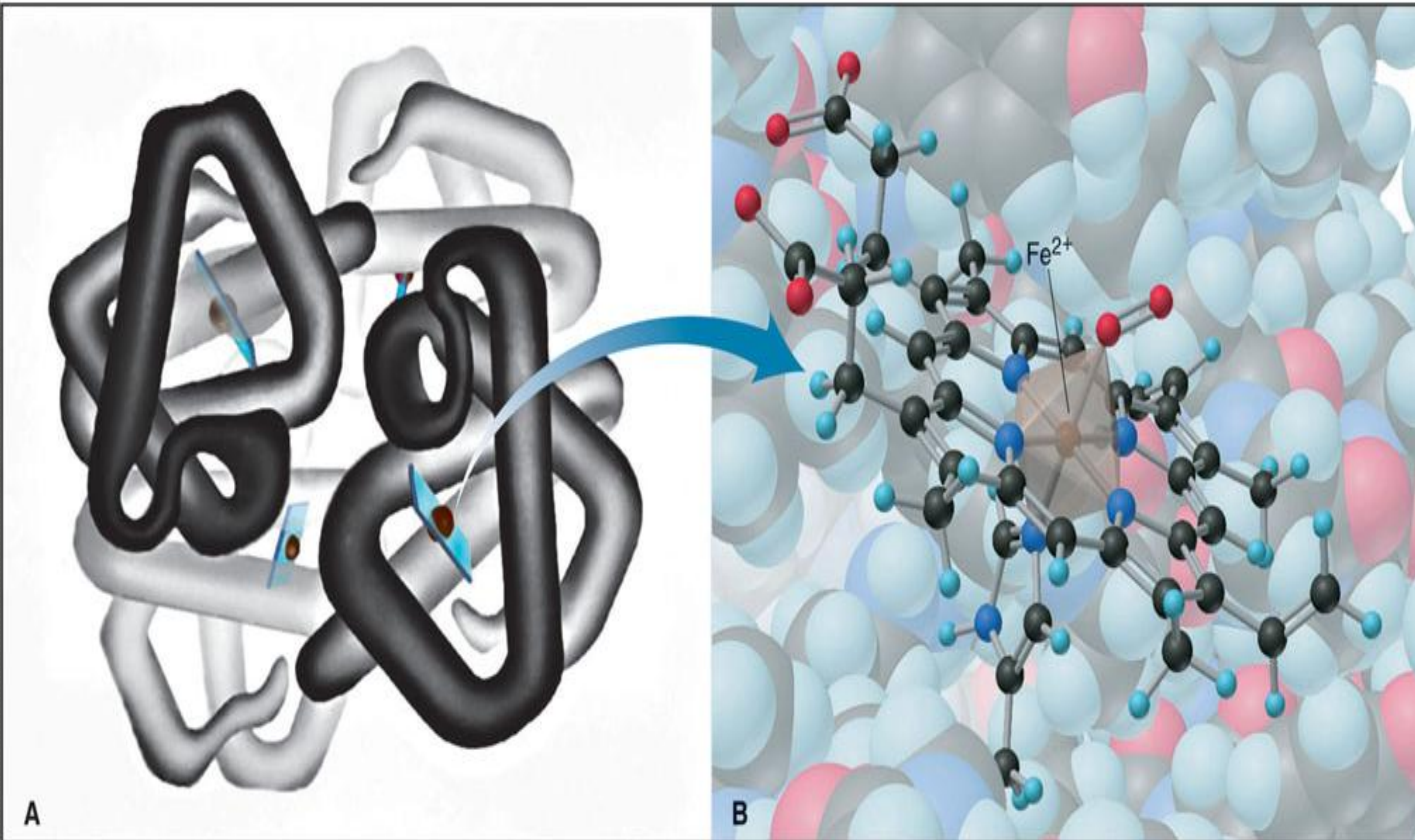
transition metal complex Fe(II) ion is

octahedrally coordinated Coordination number 6



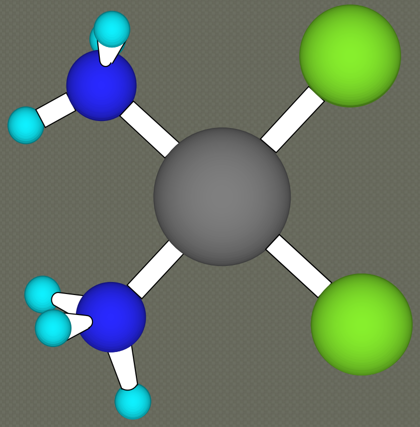


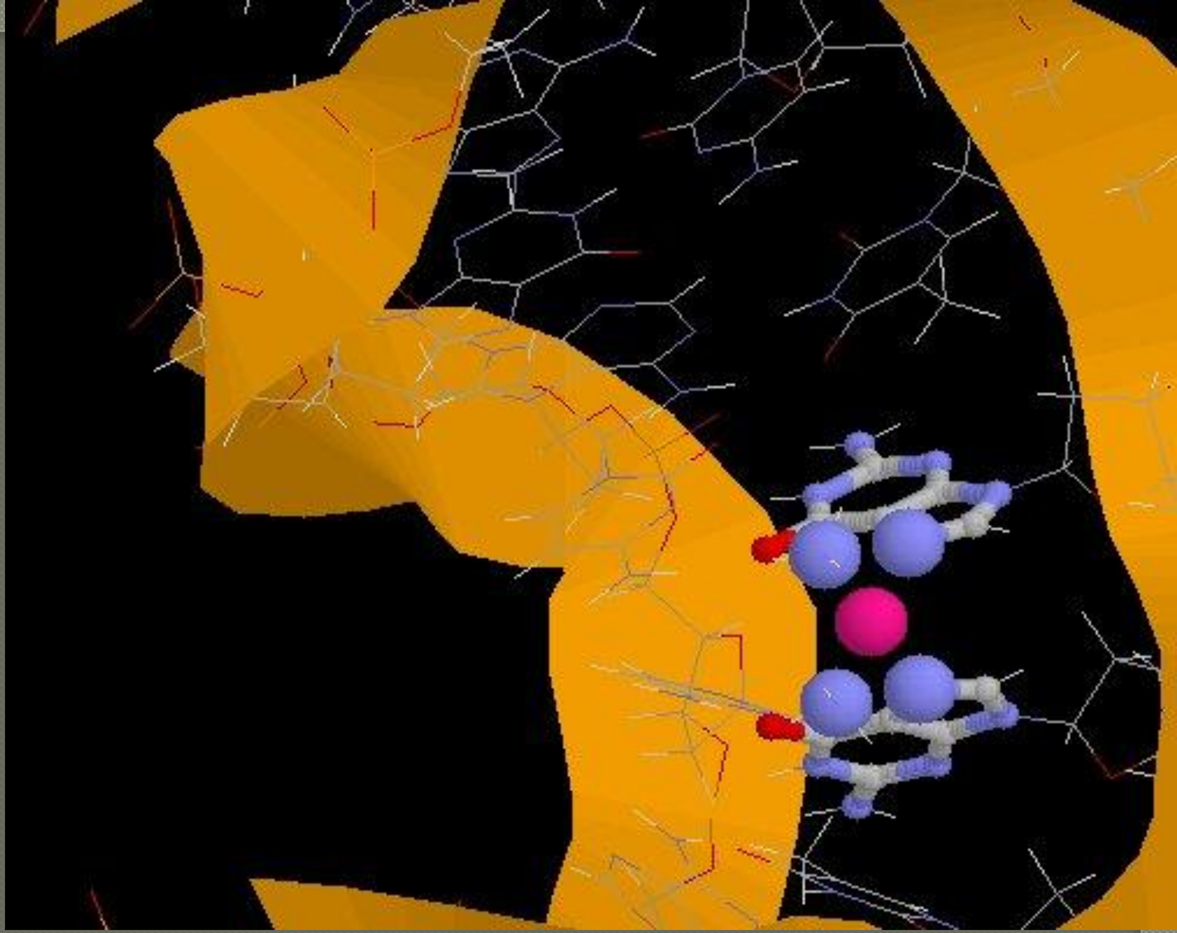
Hemoglobin & Oxyhemoglobin



Cisplatin

$[PtCl_2(NH_3)_2]$





square planar Pt(II)

coordination number 4

cis-isomer

the first of a series of platinum coordination complex-based anti-cancer drugs

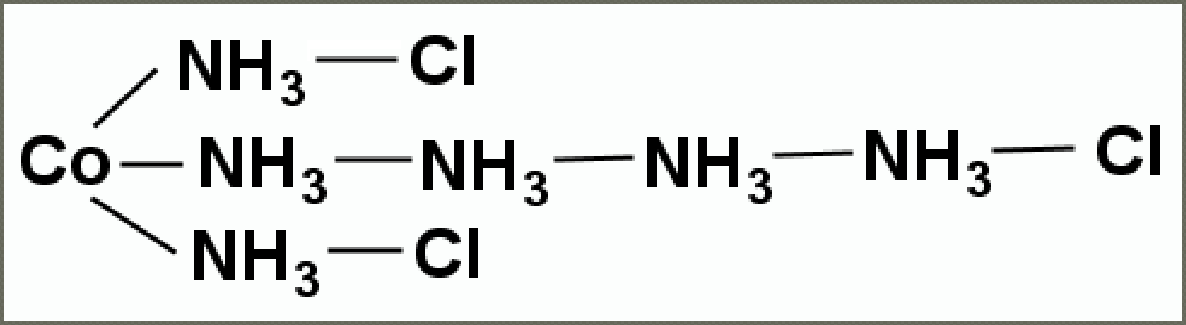
(Platinol-AQ)

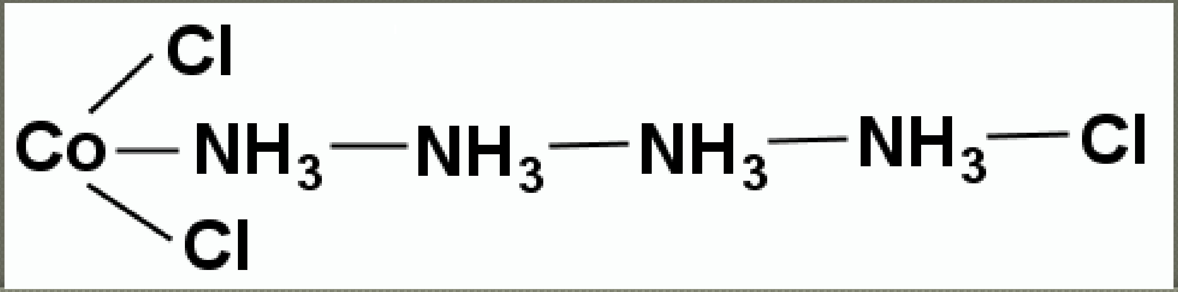
Chain Theories (Blomstrand – Jorgensen)

Blomstrand then Jorgensen proposed chain structures

Only three atoms directly bonded to Co, directly bonded Cl atoms have stronger bonds than those bonded to N. Nitrogen atoms form

chains like C and have valence of five e.g. $CoCl_3.6NH_3$ with three available chlorides

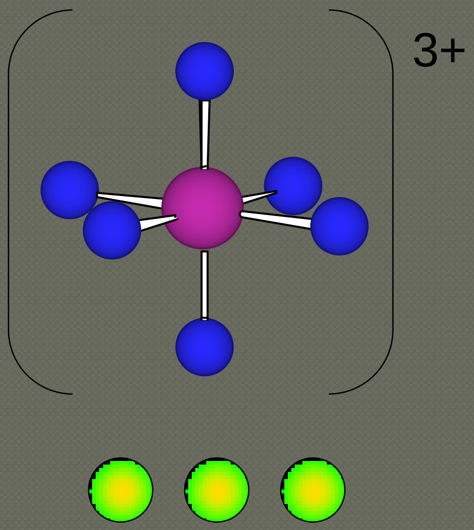


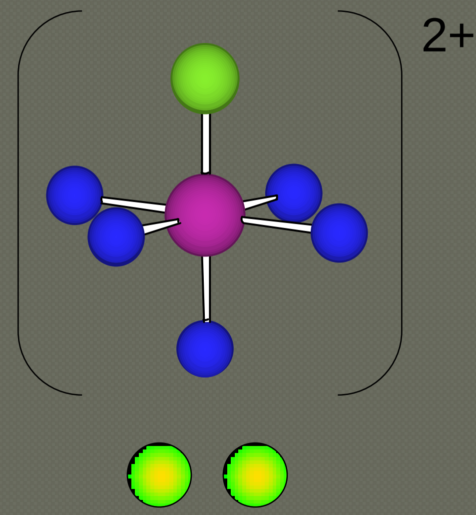


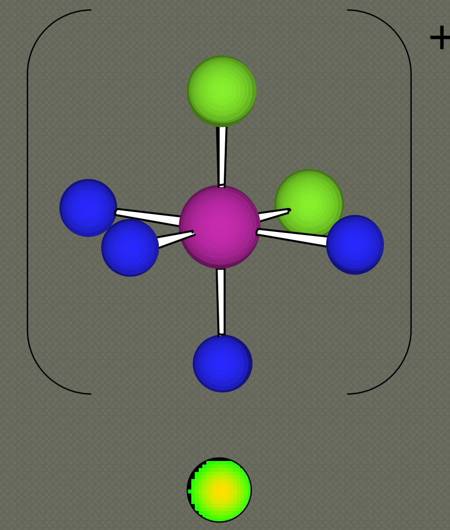
Alfred Werner – Nobel Prizewinner 1913

$CoCl_3 . 6NH_3$	yellow	xs Ag^+	3 moles AgCl
$CoCl_3 . 5NH_3$	purple	xs Ag^+	2 moles AgCl
$CoCl_3 . 4NH_3$	green	xs Ag^+	1 mole AgCl
$CoCl_3 . 3NH_3$		xs Ag^+	0 moles AgCl

$[Co(NH_3)_6]Cl_3$ $[Co(NH_3)_5Cl]Cl_2$ $[Co(NH_3)_4Cl_2]Cl$



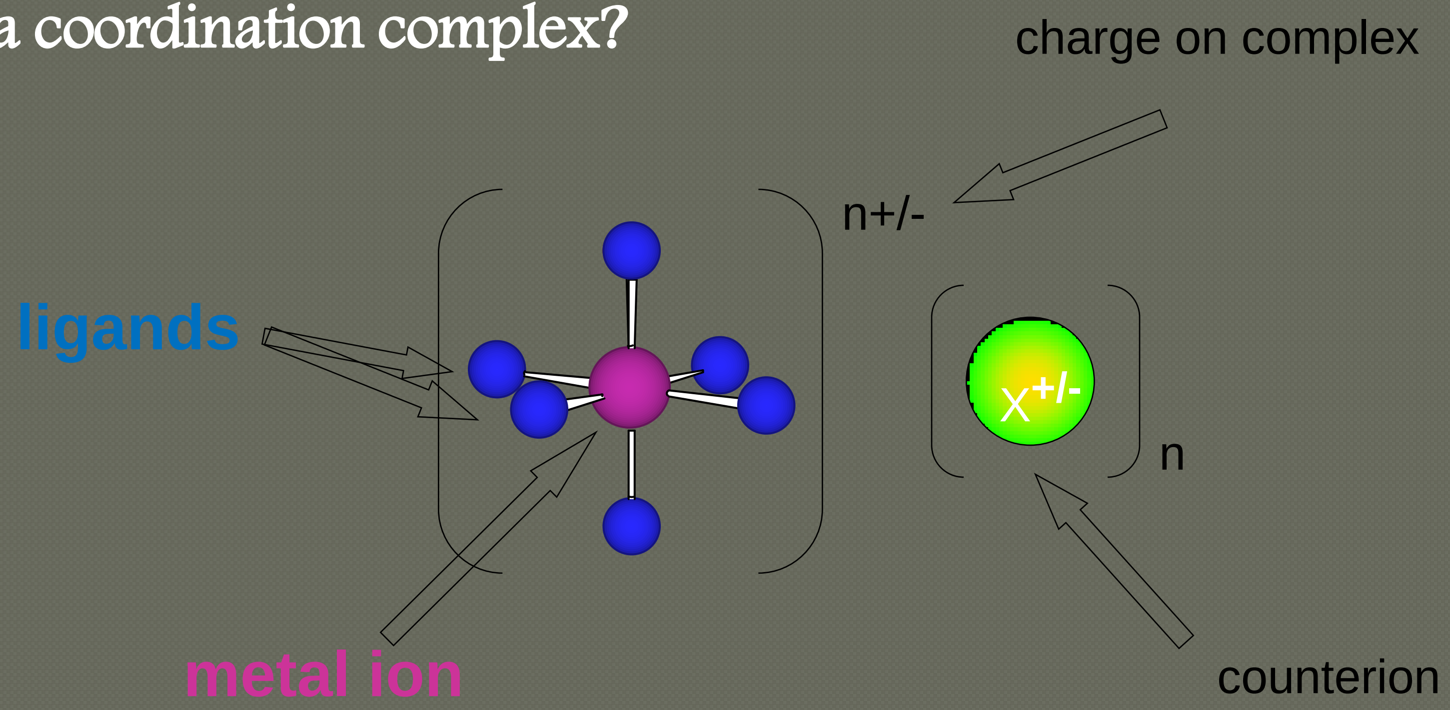




Werner's conclusions

1. The metal is in a particular oxidation state (primary valancy)
2. The complex has a fixed coordination number (secondary valancy)
3. The ligands are bound to the metal *via* a bond which resembles a covalent bond

What is a coordination complex?



Central metal ion or atom surrounded by a set of ligands

The ligand donates two electrons to the d-orbitals around the metal forming a

dative or coordinate bond

Alfred Werner and Coordination Compounds

Table 23.10 Some Coordination Compounds of Cobalt Studied by Werner

Traditional Formula	Werner's Data*: Total Ions	Werner's Data*: Free Cl^-	Modern Formula	Charge of Complex Ion
$CoCl_3 \cdot 6NH_3$	4	3	$[Co(NH_3)_6]Cl_3$	3+
$CoCl_3 \cdot 5NH_3$	3	2	$[Co(NH_3)_5Cl]Cl_2$	2+
$CoCl_3 \cdot 4NH_3$	2	1	$[Co(NH_3)_4Cl_2]Cl$	1+
$CoCl_3 \cdot 3NH_3$	0	0	$[Co(NH_3)_3Cl_3]$	—

*Moles per mole of compound.

The End