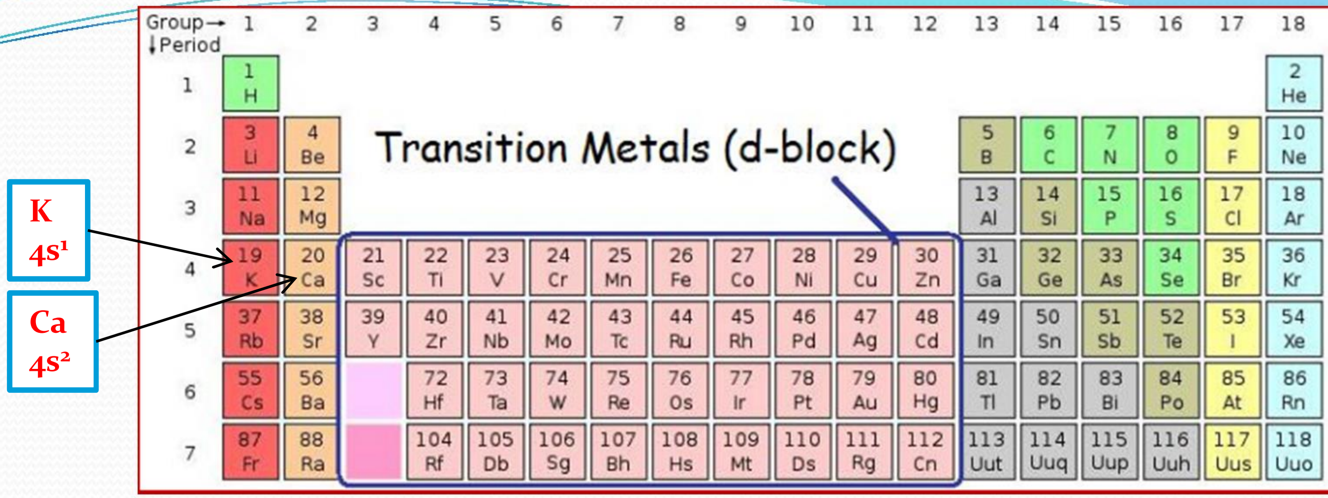
Transition Metals and d-Block Metal Chemistry



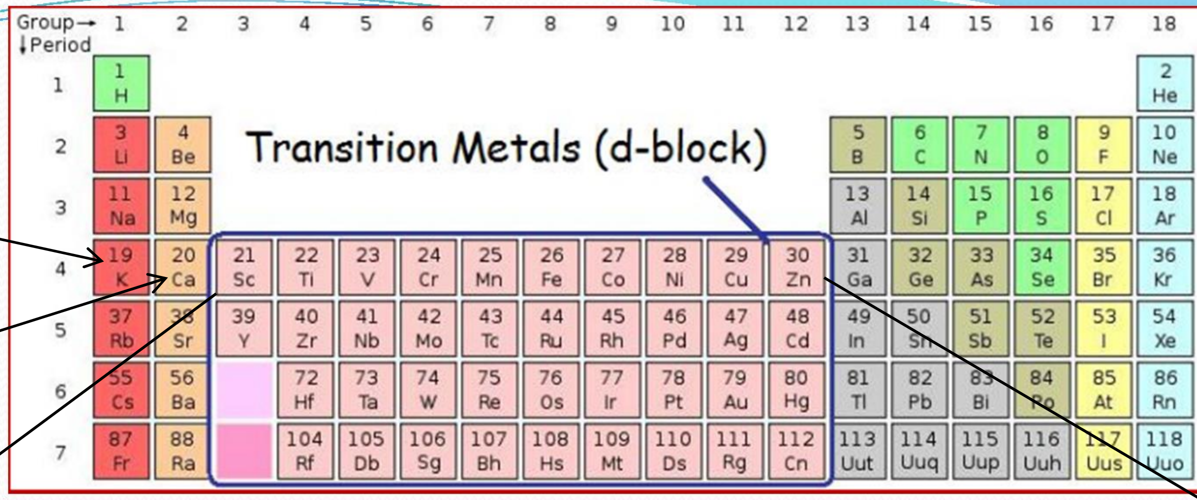
What are d-block metals?

The elements in groups 3–12 are defined as the so-called d-block metals.

Transition Metals (d block elements)

K
$4s^1$

Ca
$4s^2$



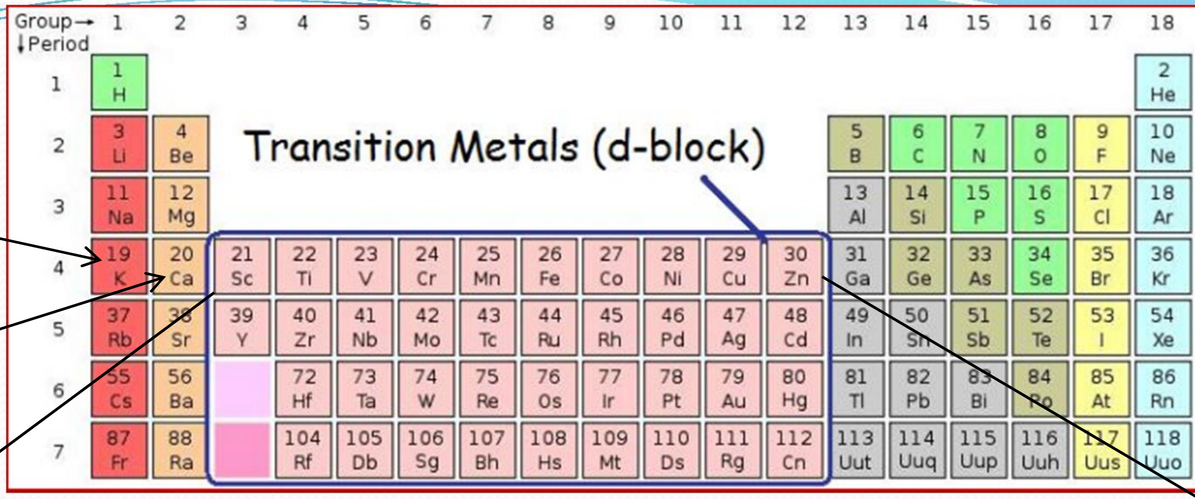
Across period →

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

Cr - $4s^13d^5$
- half filled more stable

Cu - $4s^13d^{10}$
- fully filled more stable

Transition Metals (d block elements)



K
$4s^1$

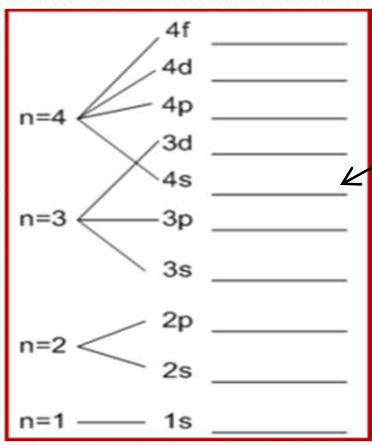
Ca
$4s^2$

Across period

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

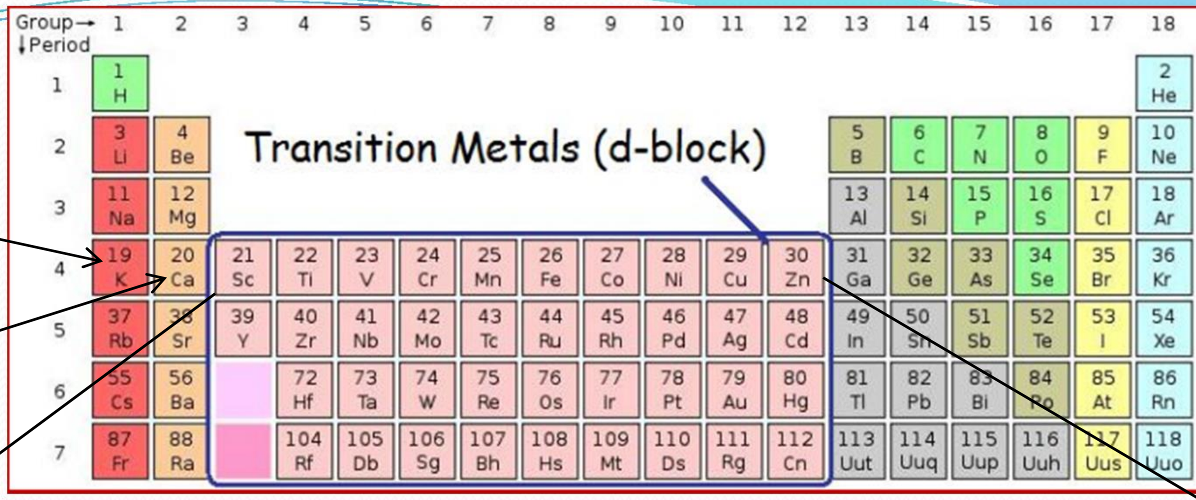
Cr - $4s^13d^5$
- half filled more stable

Cu - $4s^13d^{10}$
- fully filled more stable



Transition metal have partially filled 3d orbitals
- *3d and 4s electrons can be lost easily*
- *electrons filled from 4s level first then 3d level*

Transition Metals (d block elements)



K $4s^1$

Ca $4s^2$

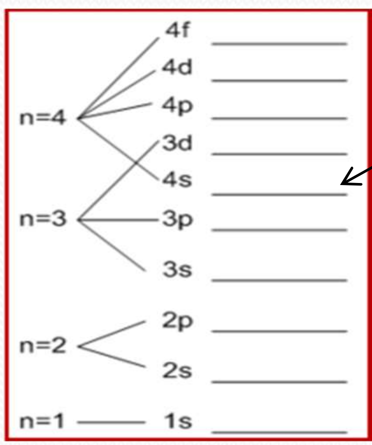
Across period

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

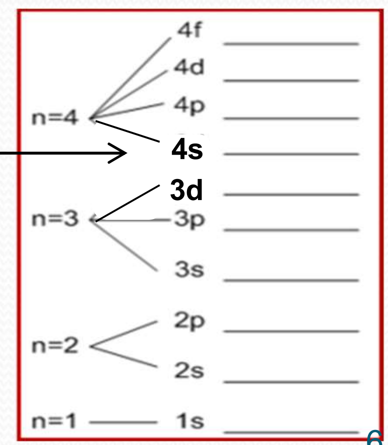
Cr - $4s^1 3d^5$
- half filled more stable

Cu - $4s^1 3d^{10}$
- fully filled more stable

Transition metal have partially filled 3d orbitals
- *3d and 4s electrons can be lost easily*
- *electrons filled from 4s level first then 3d level*
- *electrons lost from 4s level first then 3d level*

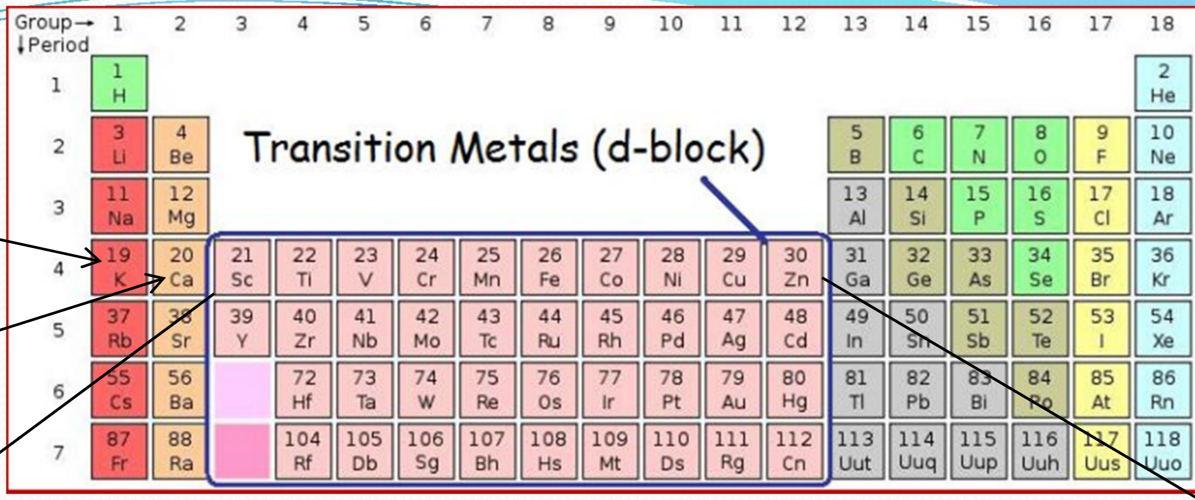


Filling electrons- 4s level lower, filled first



Losing electrons- 4s higher, lose first

Transition Metals (d block elements)



K $4s^1$

Ca $4s^2$

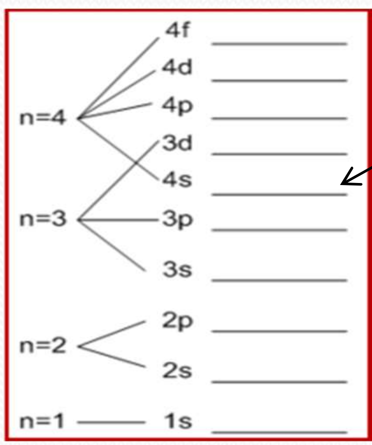
Across period

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

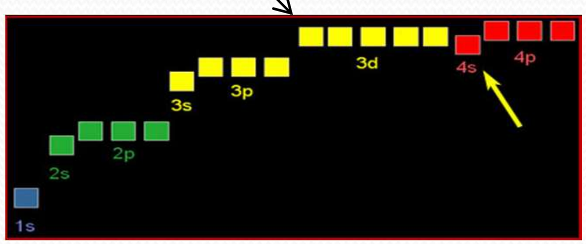
Cr - $4s^13d^5$
- half filled more stable

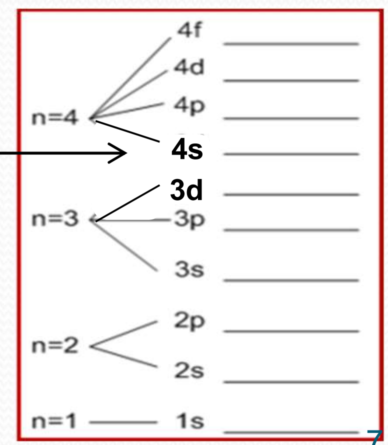
Cu - $4s^13d^{10}$
- fully filled more stable

Transition metal have partially filled 3d orbitals
- *3d and 4s electrons can be lost easily*
- *electrons filled from 4s level first then 3d level*
- *electrons lost from 4s level first then 3d level*
- *3d and 4s energy level close together (similar in energy)*



Filling electrons- 4s level lower, filled first





Losing electrons- 4s higher, lose first

Transition Metals (d block elements)

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

Lose Electrons ↓ Ions formation

Ti^{2+}	V^{2+}	Cr^{3+}	Mn^{4+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$4s^0 3d^2$	$4s^0 3d^3$	$4s^0 3d^3$	$4s^0 3d^3$	$4s^0 3d^6$	$4s^0 3d^7$	$4s^0 3d^8$	$4s^0 3d^9$

Incomplete filled d orbitals

Transition metal : d block elements with half/partially filled d orbitals/sublevels in one or more of its oxidation states → therefore, the group 12 metals zinc (Zn), cadmium (Cd) and mercury (Hg) are not typically classified as transition metals

Transition Metals (d block elements)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

Lose Electrons | Ions formation

Ti^{2+}	V^{2+}	Cr^{3+}	Mn^{4+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$4s^03d^2$	$4s^03d^3$	$4s^0 3d^3$	$4s^0 3d^3$	$4s^03d^6$	$4s^03d^7$	$4s^03d^8$	$4s^03d^9$

Incomplete filled d orbitals

Sc^{3+}
$4s^o3d^o$

Zn^{2+}
$4s^o3d^{10}$

Sc not transition elements.

- *Sc → Sc^{3+} - (empty d orbital)*
  $4s^23d^1$ → $4s^o3d^o$

Zn not transition elements.

- *Zn → Zn^{2+} - (fully filled d orbital)*
  $4s^23d^{10}$ → $4s^o3d^{10}$

Transition Metals (d block elements)

Transition Metals

- *d block elements with half/partially filled d orbitals/sublevels in one or more of its oxidation states*

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

Lose Electrons | Ions formation

Ti^{2+}	V^{2+}	Cr^{3+}	Mn^{4+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
$4s^0 3d^2$	$4s^0 3d^3$	$4s^0 3d^3$	$4s^0 3d^3$	$4s^0 3d^6$	$4s^0 3d^7$	$4s^0 3d^8$	$4s^0 3d^9$

Sc^{3+}
$4s^0 3d^0$

Zn^{2+}
$4s^0 3d^{10}$

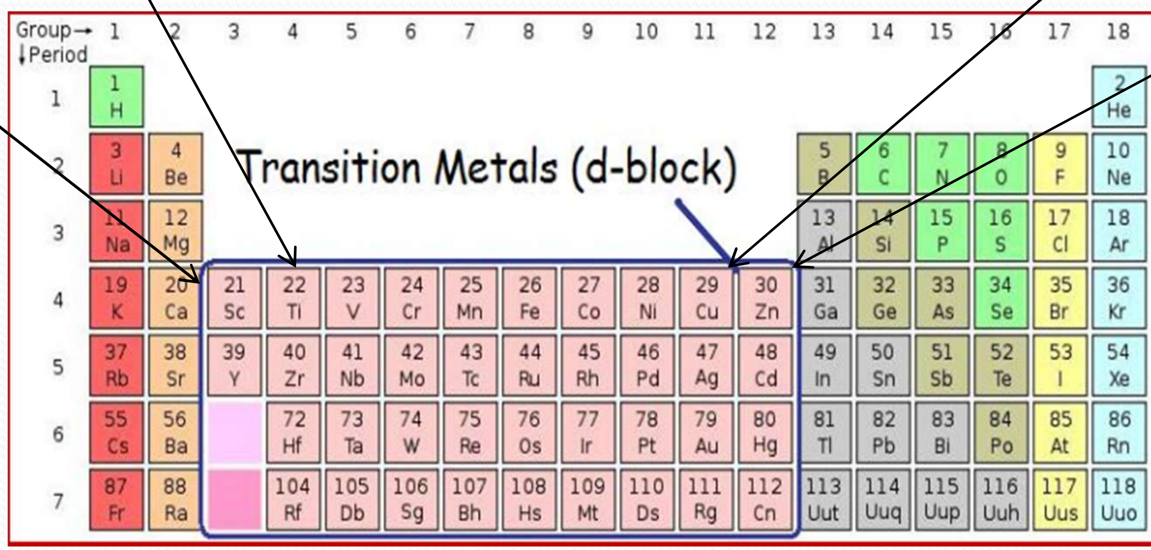
Incomplete filled d orbitals

Sc not transition elements.

- *Sc → Sc^{3+} - (empty d orbital)*
  $4s^2 3d^1$ → $4s^0 3d^0$

Zn not transition elements.

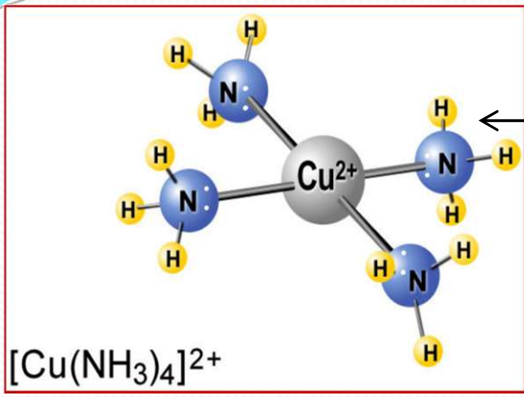
- *Zn → Zn^{2+} - (fully filled d orbital)*
  $4s^2 3d^{10}$ → $4s^0 3d^{10}$



Transition Metals (d block elements)

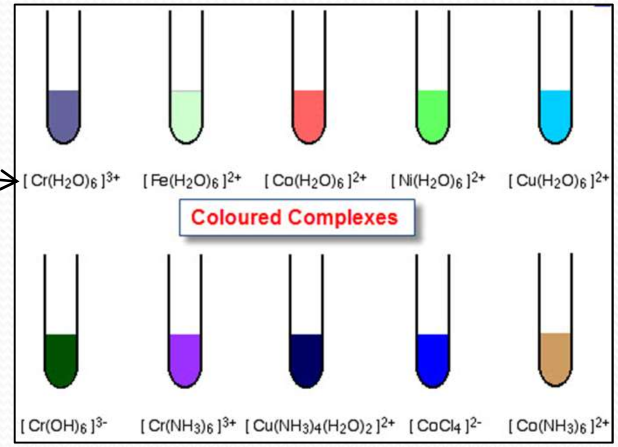
Properties of Transition metals
- Formation of complex ions
- Formation coloured complexes
- Variable oxidation states
- Catalytic activity

Formation complex ions



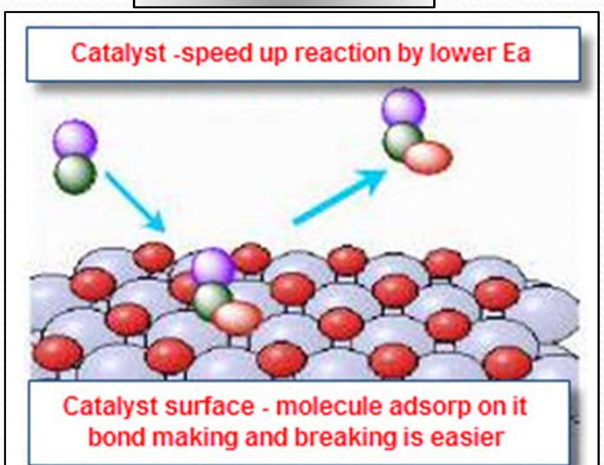
http://www.dlt.ncssm.edu/tiger/chem8.htm

Formation coloured complexes



http://www.chemguide.co.uk/inorganic/transition/features.html

Catalytic activity



Sci-Media/Images/Catalytic-converter-catalyst

Variable Oxidation states

Variable oxidation state

			+7				
		+6	+6	+6			
	+5	+5	+5	+5	+5		
+4	+4	+4	**+4**	+4	+4	+4	
+3	**+3**	**+3**	+3	**+3**	**+3**	+3	+3
+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**
							+1
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
[Ar] $3d^2 4s^2$	[Ar] $3d^3 4s^2$	[Ar] $3d^5 4s^1$	[Ar] $3d^5 4s^2$	[Ar] $3d^6 4s^2$	[Ar] $3d^7 4s^2$	[Ar] $3d^8 4s^2$	[Ar] $3d^{10} 4s^1$

http://elementalolympics.wordpress.com/2011/02/28/variable-oxidation-states-and-catalysts/

Transition Metals (d block elements) – Variable Oxidation States

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

Oxidation state +2 more common on right (Co → Zn)
- *Harder to lose electron as Nuclear charge of Co - Zn is getting higher (NC ↑)*

Oxidation state +3 more common on left (Sc → Fe)
- *Easier to lose electron as Nuclear charge of Sc – Fe is lower (NC ↓)*

Oxidation state for Mn is highest +7

Higher oxidation state exist when elements bond to oxygen – oxides/oxyanions

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
+7					$(MnO_4)^-$						oxides oxyanion
+6				Cr_2O_7	$(MnO_4)^{2-}$						
+5			V_2O_5								
+4		$TiCl_4$	$(VO_2)^{2+}$		$MnCl_4$						chlorides
+3	$ScCl_3$	$TiCl_3$	VCl_3	$CrCl_3$	$MnCl_3$	$FeCl_3$					
+2				$CrCl_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$	$NiCl_2$	$CuCl_2$	$ZnCl_2$	

				+7					
			+6	+6					
		+5							
	+4			+4					
+3	+3	+3	+3	+3	+3				
			+2	+2	+2	+2	+2	+2	+2

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

Transition Metals (d block elements) – Variable Oxidation States

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

Oxidation state +2 more common on right (Co → Zn)
- *Harder to lose electron as Nuclear charge of Co - Zn is getting higher (NC ↑)*

Oxidation state +3 more common on left (Sc → Fe)
- *Easier to lose electron as Nuclear charge of Sc – Fe is lower (NC ↓)*

Oxidation state for Mn is highest +7

Higher oxidation state exist when elements bond to oxygen – oxides/oxyanions

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
+7					$(MnO_4)^-$						oxides oxyanion
+6				Cr_2O_7	$(MnO_4)^{2-}$						
+5			V_2O_5								
+4		$TiCl_4$	$(VO_2)^{2+}$		$MnCl_4$						
+3	$ScCl_3$	$TiCl_3$	VCl_3	$CrCl_3$	$MnCl_3$	$FeCl_3$					chlorides
+2				$CrCl_2$	$MnCl_2$	$FeCl_2$	$CoCl_2$	$NiCl_2$	$CuCl_2$	$ZnCl_2$	

Oxidation number increases

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

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

← +3 oxidation state more common

+2 oxidation state more common →

Transition Metal Complexes

Ligands

- Neutral molecules or ions that have lone pair of electrons that can be used to form bond to metal
- Lewis base = electron pair donor

Metal

- Lewis Acid = electron pair acceptor
- Can accept more than one Ligand (Lewis base)

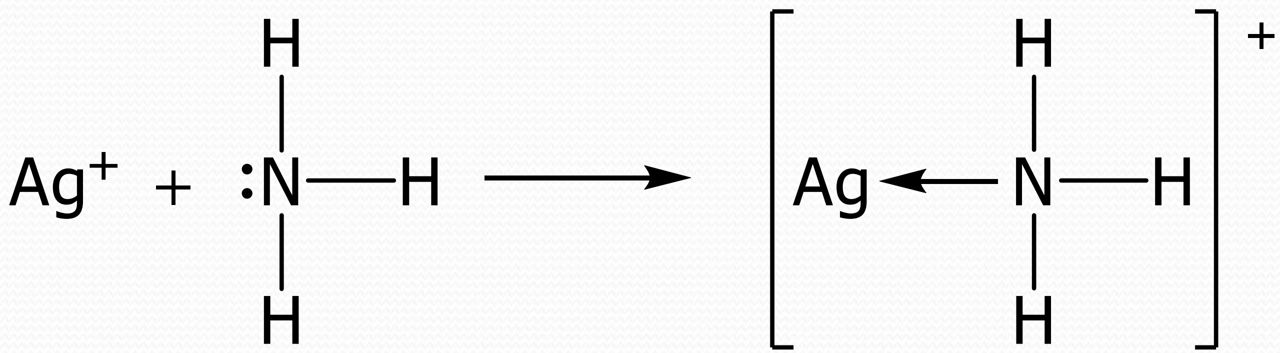
M—L bond

- Coordinate ***covalent*** bond
- Lewis acid base adduct formation

Transition Metal Complexes

Coordinate Covalent Bond

- Both electrons in shared pair come from same atom



Coordination Complexes

- Central metal atom surrounded by set of ligands
  - Complex ion: $[Co(NH_3)_6]^{3+}$, $[PtCl_4]^{2-}$

Transition Metals (d block elements) – Formation Complex Ions

Transition Metal ion + Ligands = Complex Ions

Transition Metal ion

- High charged density metal ion, partially filled 3d orbital
- Attract ligand (neutral, anion with lone pair electron)
- Form coordinate covalent bond – lone pair from ligands

Ligands

- Neutral/anion species that donate lone pair/non bonding electron pair to metal ion (complexing agents)
- Lewis base, lone pair donor – dative bond with metal ion
- Coordination number – number of ligands around central ion

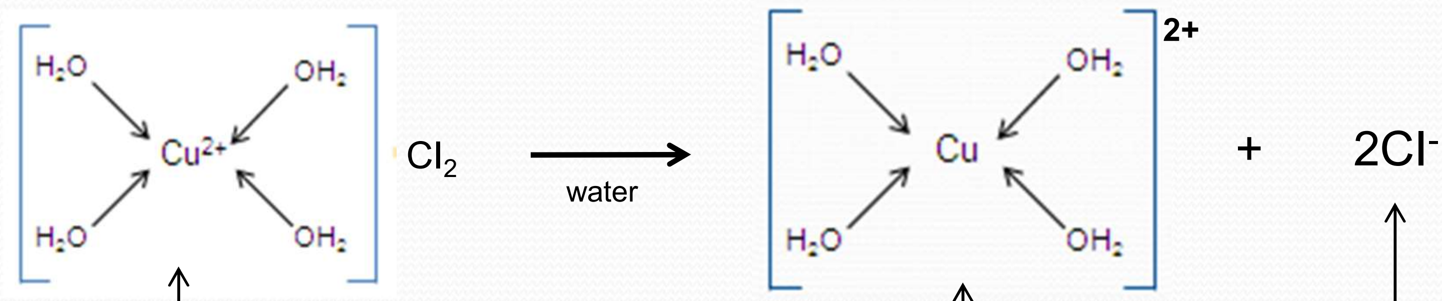
$$[Cu(H_2O)_4]Cl_2 \longrightarrow [Cu(H_2O)_4]^{2+} + 2Cl^-$$

Transition Metal ion + Ligands = Complex Ions

Transition Metal ion
- High charged density metal ion, partially filled 3d orbital
- Attract ligand (neutral, anion with lone pair electron)
- Form coordinate covalent bond – lone pair from ligands

Ligands
- Neutral/anion species that donate lone pair/non bonding electron pair to metal ion (complexing agents)
- Lewis base, lone pair donor – dative bond with metal ion
- Coordination number – number of ligands around central ion

$$[Cu(H_2O)_4]Cl_2 \longrightarrow [Cu(H_2O)_4]^{2+} + 2Cl^-$$



Complex ion – $[Cu(H_2O)_4]CI_2$ also written as $CuCI_2$

Complex ion
- 4 water ligands attached
- 4 dative bonds
- Coordination number = 4

Anion
Counter ion

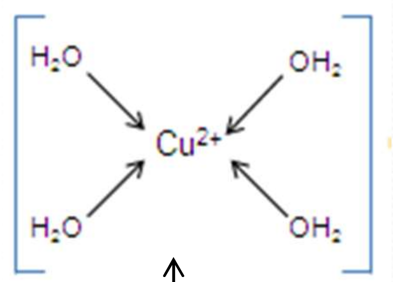
Coordination complexes: chemical structures that consist of a metal ion and the surrounding molecules or anions called the ligands.
Coordination compounds: are neutral compounds that contain a coordination complex.
Coordination number: maximum number of ligands can be accommodated by the metal ion, and is a property of the metal and its associated ligand.

Transition Metal ion + Ligands = Complex Ions

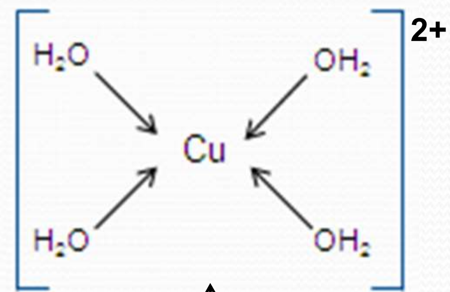
Transition Metal ion
- High charged density metal ion, partially filled 3d orbital
- Attract ligand (neutral, anion with lone pair electron)
- Form coordinate covalent bond – lone pair from ligands

Ligands
- Neutral/anion species that donate lone pair/non bonding electron pair to metal ion (complexing agents)
- Lewis base, lone pair donor – dative bond with metal ion
- Coordination number – number of ligands around central ion

$$[Cu(H_2O)_4]Cl_2 \longrightarrow [Cu(H_2O)_4]^{2+} + 2Cl^-$$



Cl_2 —water→

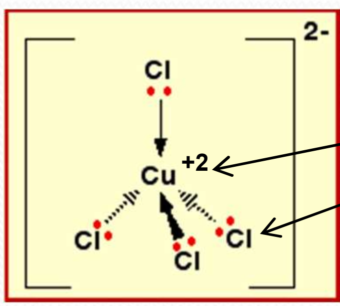


+ $2Cl^-$

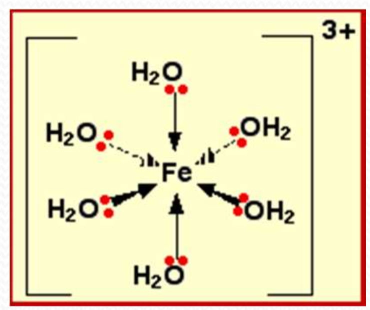
Complex ion – $[Cu(H_2O)_4]Cl_2$ also written as $CuCl_2$
Oxidation number +2

Complex ion
- 4 water ligands attached
- 4 dative bonds
- Coordination number = 4

Anion
Counter ion



Drawing complex ion
- *Overall charged on complex ion*
- *Metal ion in the center (+ve charged)*
- *Ligands attached*
- *Dative bonds from ligands*



Common Ligands

1. Monodentate M ←:L

- 1 donor atom
- 1 lone pair
- 1 bond to metal

Anions

F^-, Cl^-, Br^-, I^-, O^{2-}, S^{2-}, NO_2^-, C^-, OH^-, SCN^-, $S_2O_3^{2-}$

Molecules

H_2O, NH_3, CO

Common Ligands

2. Chelate or Polydentate Ligands

- Have two or more atoms on one molecule with lone pairs
  - Each of which can simultaneously form 2 e^- bonds to M^{n+}
  - Usually 5 or 6-membered rings with *M*
    - Sometimes form 4-membered rings
  - Must be nonlinear molecules