Advanced Transition Metal Chemistry – Periodic Table
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Lecture – 4
Introduction to Transition Elements

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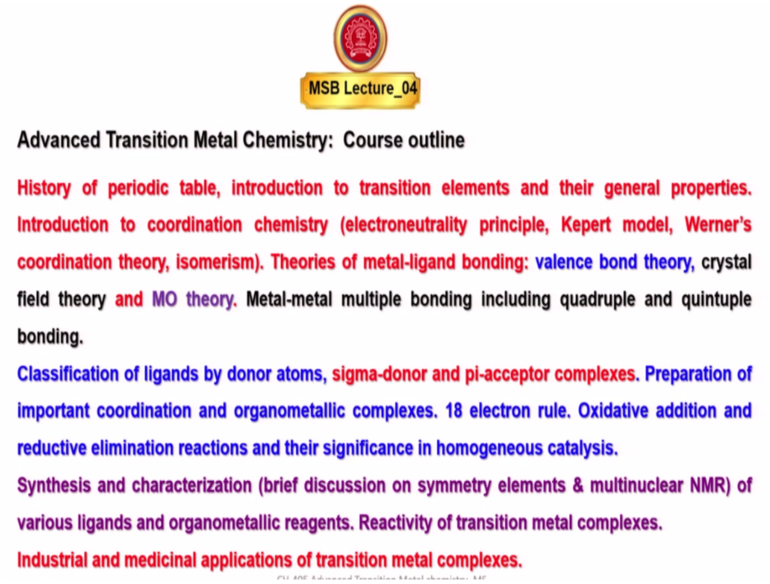

MSB Lecture_04

Advanced Transition Metal Chemistry: Course outline

History of periodic table, introduction to transition elements and their general properties. Introduction to coordination chemistry (electroneutrality principle, Kepert model, Werner's coordination theory, isomerism). Theories of metal-ligand bonding: valence bond theory, crystal field theory and MO theory. Metal-metal multiple bonding including quadruple and quintuple bonding.

Classification of ligands by donor atoms, sigma-donor and pi-acceptor complexes. Preparation of important coordination and organometallic complexes. 18 electron rule. Oxidative addition and reductive elimination reactions and their significance in homogeneous catalysis.

Synthesis and characterization (brief discussion on symmetry elements & multinuclear NMR) of various ligands and organometallic reagents. Reactivity of transition metal complexes.

Industrial and medicinal applications of transition metal complexes.

Once again, welcome to MSB lecture series on advanced transition metal chemistry. I am sure you are having a wonderful time in reading chemistry. Let me begin the lecture with an introduction to transition elements. Before I start about the introduction and discussing more about transition elements, let me give the course outline. And of course, I had already discussed the history of periodic table.

I am going to start soon introduction to transition elements and their general properties. Once that is done, I will begin with an introduction to coordination chemistry that includes the electroneutrality principle, Kepert model, Werner's coordination theory in detail and then isomerism. Once that is completed, I shall begin with theories of metal-ligand bonding that includes valence bond theory, crystal field theory and molecular orbital theory.

I would give more attention to crystal field theory to explain all possible geometries and their splitting and then I shall tell you about metal-metal multiple bonding including quadruple and quintuple bonding. And ligands are an important components of coordination chemistry. So, I shall do the classification of ligands by donor atoms. There are several ways to do the classification, but the most appropriate and the suitable method is to do the classification of ligands by donor atoms.

And then that can tell you about different types of ligands including sigma donor and pi acceptor and the corresponding complexes and preparation of important coordination and organometallic complexes also are included. And once that is done, I shall tell you more about Sidgwick rule and 18 electron rule and also effective atomic number. And later, I shall discuss two important reactions as far as the application of organometallic compounds; coordination compounds in homogeneous catalysis is concerned, that is oxidative addition and reductive elimination reactions, and also their significance in homogeneous catalysis. Once it is done, if time permits I shall tell you about synthesis and characterization of various ligands and organometallic reagents. And also, I shall tell you about the reactivity of transition metal complexes.

And if time permits, I shall briefly discuss about important symmetry and multinuclear NMR or interpretative NMR or interpretative molecular spectroscopy, in order to help you in understanding and characterizing organometallic compounds and coordination compounds. And at the end or in between I shall tell you about the application of transition metal complexes in industry and medicine. With this course outline, let me start the introduction.

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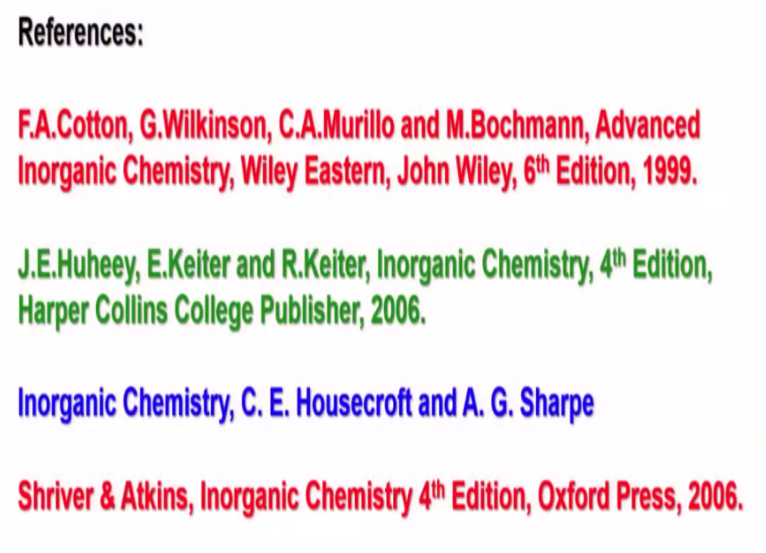

References:

F.A.Cotton, G.Wilkinson, C.A.Murillo and M.Bochmann, Advanced Inorganic Chemistry, Wiley Eastern, John Wiley, 6th Edition, 1999.

J.E.Huheey, E.Keiter and R.Keiter, Inorganic Chemistry, 4th Edition, Harper Collins College Publisher, 2006.

Inorganic Chemistry, C. E. Housecroft and A. G. Sharpe

Shriver & Atkins, Inorganic Chemistry 4th Edition, Oxford Press, 2006.

Of course, the books I have referred in framing this course are given here. F. A. Cotton's 6th edition Advanced Inorganic Chemistry and of course Huheey's Inorganic Chemistry 4th edition. And another interesting and very important and informative book, Inorganic Chemistry by C. E. Housecroft and A. G. Sharpe and also I am using Inorganic Chemistry 4th edition by Shriver and Atkins.

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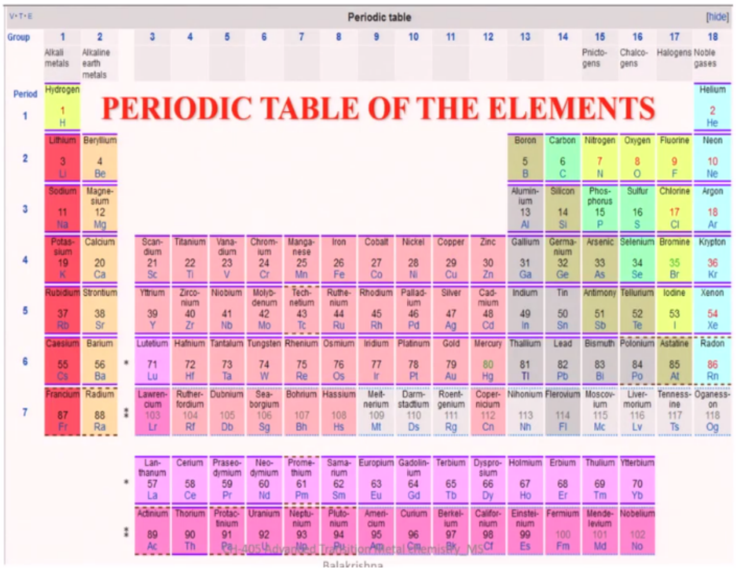

V·T·E Periodic table [hide]

PERIODIC TABLE OF THE ELEMENTS

Group	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	Alkali metals	Alkaline earth metals														Pnictogens	Chalcogens	Halogens	Noble gases
Period 1	Hydrogen 1 H																		Helium 2 He
2	Lithium 3 Li	Beryllium 4 Be												Boron 5 B	Carbon 6 C	Nitrogen 7 N	Oxygen 8 O	Fluorine 9 F	Neon 10 Ne
3	Sodium 11 Na	Magnesium 12 Mg												Aluminium 13 Al	Silicon 14 Si	Phosphorus 15 P	Sulfur 16 S	Chlorine 17 Cl	Argon 18 Ar
4	Potassium 19 K	Calcium 20 Ca		Scandium 21 Sc	Titanium 22 Ti	Vanadium 23 V	Chromium 24 Cr	Manganese 25 Mn	Iron 26 Fe	Cobalt 27 Co	Nickel 28 Ni	Copper 29 Cu	Zinc 30 Zn	Gallium 31 Ga	Germanium 32 Ge	Arsenic 33 As	Selenium 34 Se	Bromine 35 Br	Krypton 36 Kr
5	Rubidium 37 Rb	Strontium 38 Sr		Yttrium 39 Y	Zirconium 40 Zr	Niobium 41 Nb	Molybdenum 42 Mo	Technetium 43 Tc	Ruthenium 44 Ru	Rhodium 45 Rh	Palladium 46 Pd	Silver 47 Ag	Cadmium 48 Cd	Indium 49 In	Tin 50 Sn	Antimony 51 Sb	Tellurium 52 Te	Iodine 53 I	Xenon 54 Xe
6	Caesium 55 Cs	Barium 56 Ba	*	Lutetium 71 Lu	Hafnium 72 Hf	Tantalum 73 Ta	Tungsten 74 W	Rhenium 75 Re	Osmium 76 Os	Iridium 77 Ir	Platinum 78 Pt	Gold 79 Au	Mercury 80 Hg	Thallium 81 Tl	Lead 82 Pb	Bismuth 83 Bi	Polonium 84 Po	Astatine 85 At	Radon 86 Rn
7	Francium 87 Fr	Radium 88 Ra	**	Lawrencium 103 Lr	Rutherfordium 104 Rf	Dubnium 105 Db	Seaborgium 106 Sg	Bohrium 107 Bh	Hassium 108 Hs	Meitnerium 109 Mt	Darmstadtium 110 Ds	Roentgenium 111 Rg	Copernicium 112 Cn	Nihonium 113 Nh	Flerovium 114 Fl	Moscovium 115 Mc	Livermorium 116 Lv	Tennessine 117 Ts	Oganesson 118 Og
			*	Lanthanum 57 La	Cerium 58 Ce	Praseodymium 59 Pr	Neodymium 60 Nd	Promethium 61 Pm	Samarium 62 Sm	Europium 63 Eu	Gadolinium 64 Gd	Terbium 65 Tb	Dysprosium 66 Dy	Holmium 67 Ho	Erbium 68 Er	Thulium 69 Tm	Ytterbium 70 Yb		
			**	Actinium 89 Ac	Thorium 90 Th	Protactinium 91 Pa	Uranium 92 U	Neptunium 93 Np	Plutonium 94 Pu	Americium 95 Am	Curium 96 Cm	Berkelium 97 Bk	Californium 98 Cf	Einsteinium 99 Es	Fermium 100 Fm	Mendelevium 101 Md	Nobelium 102 No		

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And this periodic table is very important for a chemist and once we know the periodic trends and also the position of each element in the periodic table and how these properties are varying about, the chart to size ratio, and all those things, understanding chemistry of whether main group elements or transition elements, will be very easy and, give more emphasis for at least remembering 30 elements in the periodic table and writing their electronic configuration.

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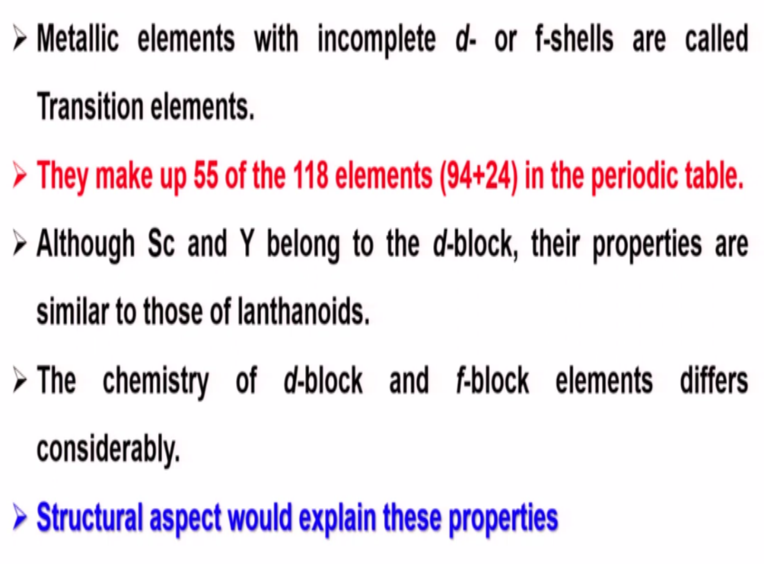

- Metallic elements with incomplete *d*- or f-shells are called Transition elements.
- They make up 55 of the 118 elements (94+24) in the periodic table.
- Although Sc and Y belong to the *d*-block, their properties are similar to those of lanthanoids.
- The chemistry of *d*-block and *f*-block elements differs considerably.
- Structural aspect would explain these properties

When we talk about the transition elements or metallic elements, they have incomplete d or f shells and if any metallic element that has an incomplete d or f shells, are called as transition elements. So, they make up 55 of the 118 elements. That means we have 94 natural elements and 24 manmade elements, out of which 3d, 4d, 5d series, we have 9 ~~electrons~~ elements each that means 27 and we have 4f and 5f, ~~we have~~ about 28 elements.

Together we have 55 elements that constitute transition elements. Although Scandium and Yttrium belong to the d-block, their properties are similar to those of lanthanoids. The chemistry of d-block and the f-block elements differ considerably. And of course, structural aspects would explain these properties in a very clear way. When we look into d-block, as I mentioned, we have three blocks 3d, 4d and 5d.

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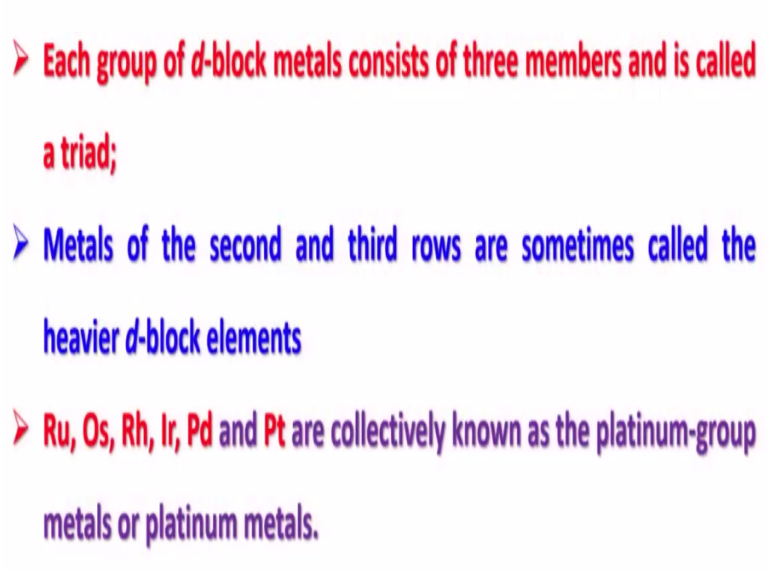

- Each group of *d*-block metals consists of three members and is called a triad;
- Metals of the second and third rows are sometimes called the heavier *d*-block elements
- Ru, Os, Rh, Ir, Pd and Pt are collectively known as the platinum-group metals or platinum metals.

Each group of d-block metals consists of three members and is called a triad. For example, if I consider chromium, molybdenum and tungsten or if I consider a nickel, palladium, platinum or copper, silver and gold or cobalt, rhodium, Iridium, in this fashion okay. So, each set is called a triad. Metals of the second and third row are sometimes called the heavier d-block elements. And if you see the chemistry of 3d elements, differ considerably from 4d and 5d series.

Whereas 4d and 5d have a lot of resemblance and they have almost very similar properties. And here ruthenium, osmium, rhodium, iridium, palladium and platinum are collectively known as platinum group metals or platinum metals. When you see some book stating platinum metal you should not get confused about only the platinum, the platinum metals refer to these 6 elements together that is ruthenium, osmium, rhodium, iridium, palladium and platinum.

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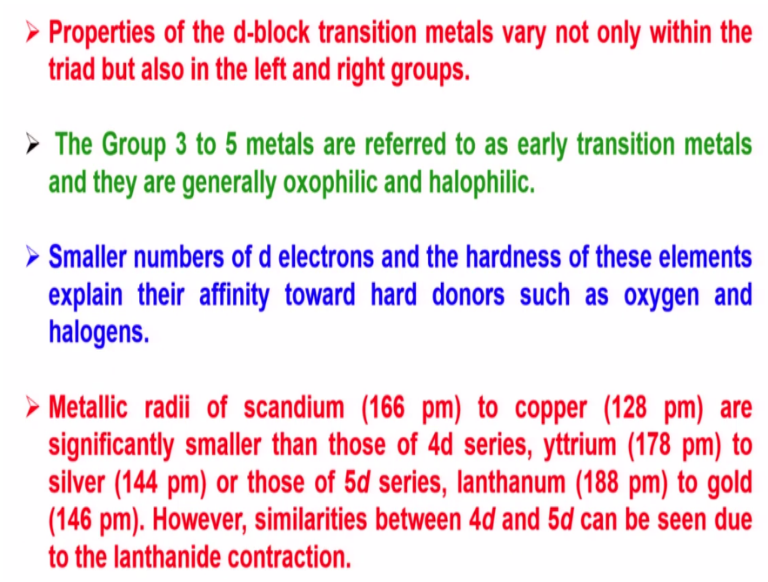

- Properties of the d-block transition metals vary not only within the triad but also in the left and right groups.
- The Group 3 to 5 metals are referred to as early transition metals and they are generally oxophilic and halophilic.
- Smaller numbers of d electrons and the hardness of these elements explain their affinity toward hard donors such as oxygen and halogens.
- Metallic radii of scandium (166 pm) to copper (128 pm) are significantly smaller than those of 4d series, yttrium (178 pm) to silver (144 pm) or those of 5*d* series, lanthanum (188 pm) to gold (146 pm). However, similarities between 4*d* and 5*d* can be seen due to the lanthanide contraction.

So, properties of the d-block transition metals vary not only within the triad as I had mentioned, but also in the left and right groups. The group 3 to 5 metals are referred to as early transition metals and they are generally oxophilic and halophilic. That means those having electronic configuration of d~~-~~^{1}, d^2~~d 2~~ and d^3~~d 3~~, they have up to 5 electrons in their valence shell, ~~.~~

c~~C~~onsidering 2s electrons~~.~~; T~~t~~hey are referred to as early transition elements or almost having up to d^5~~d 5~~ electrons are considered as early transition metals. And once we cross manganese and go further towards the right side of the periodic table, they are considered as later transition metals. So, smaller number of d-~~-~~electrons in the early metals and the hardness of these elements explain their affinity towards hard donors such as oxygen and halogens. That is the reason they are called oxophilic and halophilic.

And metallic radii of scandium to copper ~~that means~~ varies significantly starting from 166 picometre (pm) to 128 picometre and this is smaller than those of 4d series. For example, yttrium starts with 178 ~~picometre~~ pm to silver one 144 ~~picometre~~ pm and those of 5d series starts with lanthanum at 188 ~~picometre~~ pm to gold having 146 ~~picometre~~pm. So, however, similarities between 4d and 5d can be seen due to the lanthanide contraction.

I shall tell you more about lanthanide contraction later. And when you go down a group the atomic radius increases markedly from the first to the second series as an additional electron shell is added. However, the atoms of the second and third row elements tend to be very similar in size. Again, this is due to the lanthanide contraction, which occurs across the f-block. The *f*-block elements contract as an additional *f*-electron is added across a period and the core electrons are not really screening the outer valence electrons.

So, this contradiction offsets the addition of an extra electron shell between series 2 and 3. So this effect is most marked to the left of the *s*-block just following the lanthanide contraction. So after lanthanum, lanthanum of the scandium group and the atomic radii for zirconium and hafnium are almost identical and these elements are very hard to distinguish. I shall show you the plot, then it becomes very clear.

The effect has largely disappeared by the time we reach the copper group and although silver and gold have almost identical atomic radii, their chemistries are quite different. So, cadmium and mercury have very different atomic radii and quite different behaviours as well.

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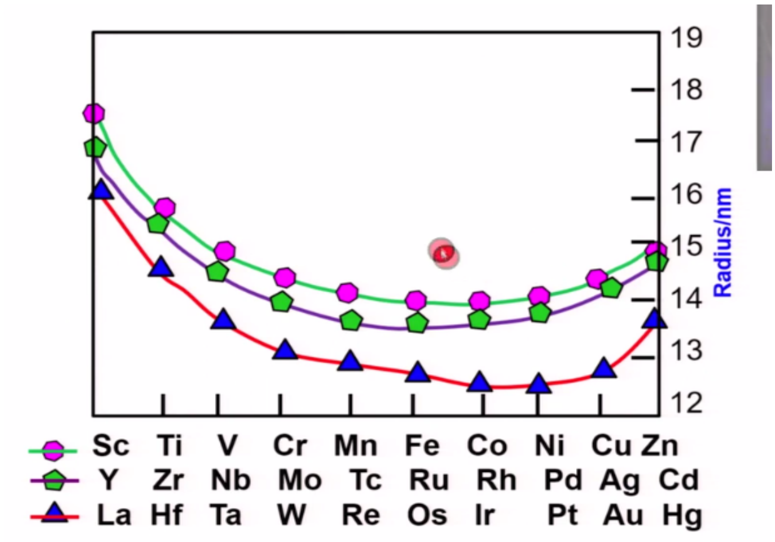

1/18/2022 Trends in atomic radii of transition elements

You can see the trends I had mentioned in atomic radii of transition elements. You can see the atomic radii is decreasing steadily until it hits manganese and iron and then slowly this increases and you know that as more and more electrons are added to the same shell what happens here, effective nuclear charge increases. As a result, valence electrons are pulled more towards the nucleus that resulting in the decrease of radii.

But on the other hand, once it is half-filled we have the maximum, after that one, when you add more and more electrons to the d shell like d^6~~d 6~~, d^7~~d 7~~, d^8~~d 8~~ what happens, you have to consider interelectron repulsion also. Because of interelectron repulsion, what happens, the size increases. So, the trends are clearly seen and the trends are very comparable among 3*d*, 4*d* and 5*d* series.

So, the first period of transition metals behave quite differently from the second and third period as I had already mentioned. The second and third elements in each transition group tend to behave very similarly to one another since their atoms are of similar size, whereas the first period have distinct behaviour. That means when you look into physical as well as chemical properties of 3d elements, they differ significantly compared to 4d and 5d series.

Whereas 4d and 5d have remarkable similarities between them. To understand the chemistry of the transition elements, one need to understand the effect that the d-~~-~~electrons have. Consider first, the very different shapes of the d-~~-~~orbitals. When we have to understand the coordination chemistry, ~~and~~ understanding of the shapes of various orbitals and their relative orientation are very important, I shall elaborate more when we go to the bonding concepts.

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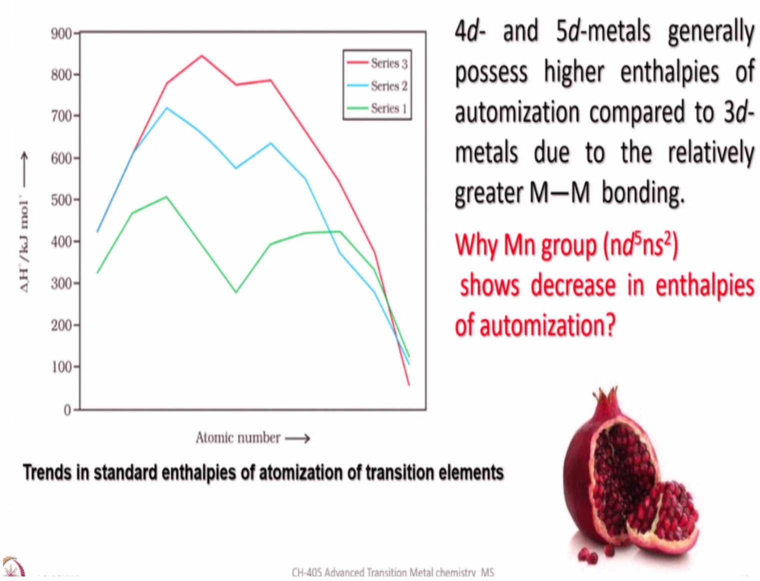

Trends in standard enthalpies of atomization of transition elements

4*d*- and 5*d*-metals generally possess higher enthalpies of automization compared to 3*d*-metals due to the relatively greater M—M bonding.

Why Mn group (nd^5ns^2) shows decrease in enthalpies of automization?

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Another interesting feature can be seen here. So, trends in standard enthalpies of atomization of transition elements is given here. And if you see here, ~~a~~ steadily, as more and more electrons are added to the *d*-~~-~~orbital, enthalpy is increasing. And once it comes to a half-filled electronic configuration, it dips and then rises again and falls considerably. That means enthalpy of atomization is steadily increasing and then it decreases.

One should explain this one, by looking into the electronic configuration and to what extent metal-metal bonding is playing the role, but the interesting thing is why it drops in case of manganese group having electronic configuration of nd^5~~d 5~~(~~-~~n+1)s~~-~~^{2}. That means it shows a decrease in enthalpy of atomization. The reason is very simple, here we have d^5s^2~~d 5s 2~~ electronic configuration.

And when you have d^5s^2 ~~d 5s 2~~electronic configuration because they are half-~~-~~filled and they are stable and they are pulled towards nucleus more readily and they have very minimum interelectronic repulsion. As a result, electrons dislodging from their position is difficult, as a result metallic bonding will be little weaker compared to others and hence the enthalpy of atomization decreases here in this case.

And if you are surprised to know what is atomization, it is almost like you can see pomegranate, picking one grain at a time and separating them is like enthalpy of atomization. Now, they are all put together in the lattice, if you start taking out that is very nicely comparable to the enthalpy of atomization. And this decrease in enthalpy of atomization for manganese group is also reflected in the melting point.

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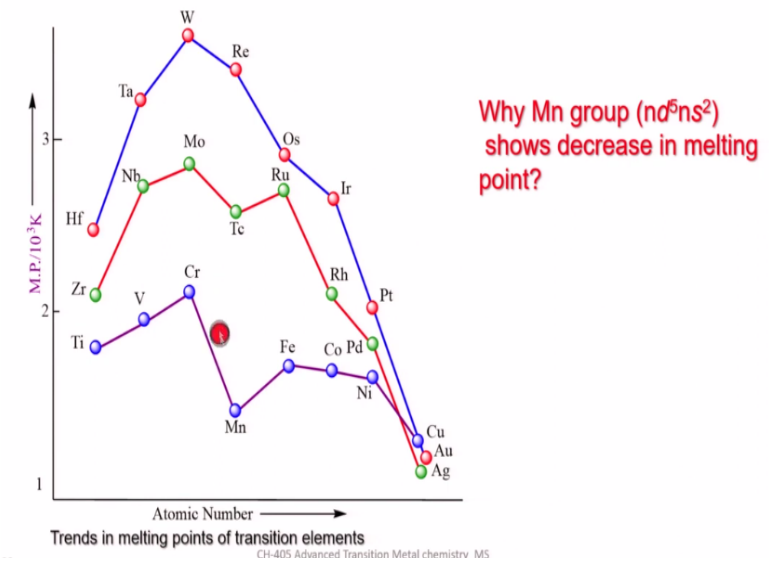

Why Mn group (nd^5ns^2) shows decrease in melting point?

Trends in melting points of transition elements

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So, let me show you here why Mn group shows a decrease in melting point? That means as I mentioned here the enthalpy of atomization also drops, as a result what happens? Taking out these atoms or separating these items will be very easy and hence melting point also drops in these cases having d^5s^2~~nd 5 ns 2~~ electronic configuration. So, in the absence of bridging ligands, the formation of metal-metal bonds is difficult for these early transition elements.

The reason is very simple, they do not have sufficient unutilized electrons in their d orbitals and bridging ligands such as halides, amides, alkoxides and aryloxides have available lone pairs that can be donated to the metal ions. Metal is in high valence state and the empty orbitals are there and coordination number is small. As a result, they have all ingredients to expand its coordination number and to accommodate more electrons in their empty orbitals.

As a result what happens? If the ligands with sufficient lone pairs are available, they readily use them as bridging ligands. Organometallic compounds of these metals are known strongly to activate CH bonds in hydrocarbons. The reason is they are electron deficient compounds and they have vacant d-orbitals. They readily undergo beta-hydride elimination due to which they are more reactive and thermally unstable.

For example, if you take tetramethyl titanium that is stable up to –40 ~~degrees centigrade~~°C. And then if you consider tetraethyl titanium that is stable up to –60 °C~~degrees centigrade~~. Above –60 °C ~~degrees centigrade~~ that readily decomposes because ethyl group has beta-hydrogen, so beta-hydrogen elimination readily happens and that compound decomposes. That means if I ask you a question about the stability of tetramethyl titanium and tetraethyl titanium, without any hesitation you can say tetramethyl titanium is more stable compared to tetraethyl titanium.

Because in case of methyl you do not have beta-~~a~~hydrogen, and however both are thermally unstable. Late transition metals are soft and have high affinity towards sulfur or selenium. That is the reason if you look into late transition elements including group 12, they exist in nature in the form of sulphide ore, for example cinnabar, PbS, zinc sulphide, etc.

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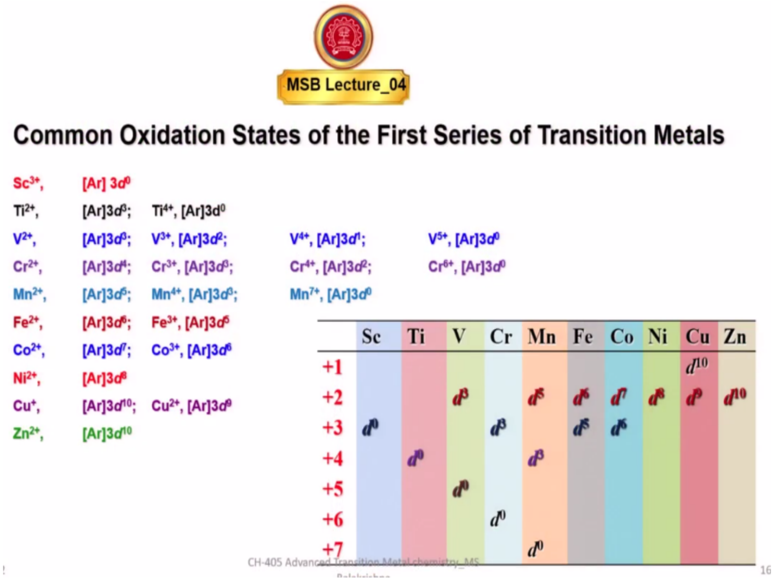
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Common Oxidation States of the First Series of Transition Metals

Sc^{3+}, [Ar] $3d^0$
Ti^{2+}, [Ar]$3d^2$; Ti^{4+}, [Ar]$3d^0$
V^{2+}, [Ar]$3d^3$; V^{3+}, [Ar]$3d^2$; V^{4+}, [Ar]$3d^1$; V^{5+}, [Ar]$3d^0$
Cr^{2+}, [Ar]$3d^4$; Cr^{3+}, [Ar]$3d^3$; Cr^{4+}, [Ar]$3d^2$; Cr^{6+}, [Ar]$3d^0$
Mn^{2+}, [Ar]$3d^5$; Mn^{4+}, [Ar]$3d^3$; Mn^{7+}, [Ar]$3d^0$
Fe^{2+}, [Ar]$3d^6$; Fe^{3+}, [Ar]$3d^5$
Co^{2+}, [Ar]$3d^7$; Co^{3+}, [Ar]$3d^6$
Ni^{2+}, [Ar]$3d^8$
Cu^{+}, [Ar]$3d^{10}$; Cu^{2+}, [Ar]$3d^9$
Zn^{2+}, [Ar]$3d^{10}$

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+1									d^{10}	
+2			d^3		d^5	d^6	d^7	d^8	d^9	d^{10}
+3	d^0			d^3		d^5	d^6			
+4		d^0			d^3					
+5			d^0							
+6				d^0						
+7					d^0					

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So, let us look into the common oxidation states of the first series of transition elements. You can see scandium group, the common oxidation state is +3. In case of titanium, we have d^2s^2 ~~d 2s 2~~, so group oxidation is +4. And also we come across +3 and +2 and they are a little unstable. In case of vanadium, we come across +2, +3 as well as +5 oxidation states. And in case of manganese, we can see all possible oxidation states and up to seven.

And in case of iron, we will see +2 and +3 are the most common ones. In case of cobalt also +2 and +3 are common. In case of nickel, we see nickel ~~-~~2+ and in some cases nickel 4+ ~~And~~ , and copper shows +1 and +2 states and zinc shows +2 oxidation state.

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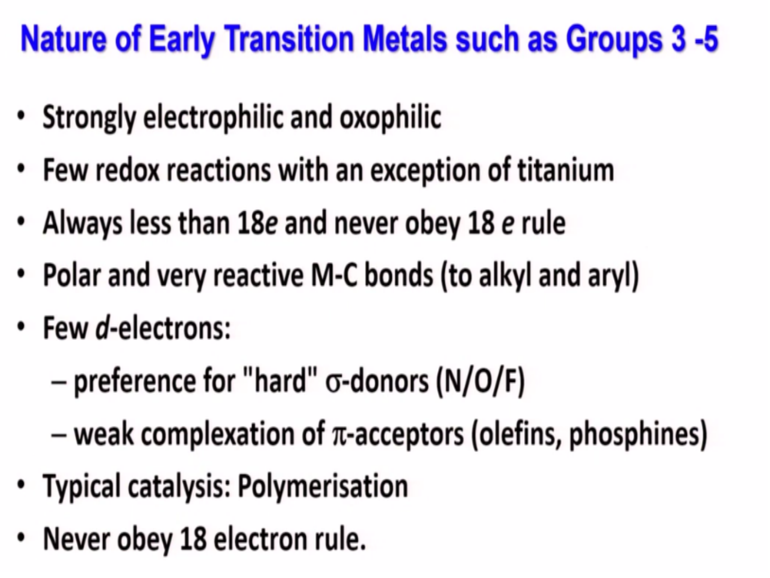
Nature of Early Transition Metals such as Groups 3 -5

- Strongly electrophilic and oxophilic
- Few redox reactions with an exception of titanium
- Always less than 18*e* and never obey 18 *e* rule
- Polar and very reactive M-C bonds (to alkyl and aryl)
- Few *d*-electrons:
  - preference for "hard" σ-donors (N/O/F)
  - weak complexation of π-acceptors (olefins, phosphines)
- Typical catalysis: Polymerisation
- Never obey 18 electron rule.

Let us look into the nature of early transition elements, so that has an implication on their properties. So, these elements are strongly electrophilic and oxophilic and few redox reactions with an exception of titanium. Always less than 18 electrons will be there in their valence shell and hence they can never obey 18 electron rule. I shall tell you more about why some elements can never obey 18 electron rule, when I will be discussing in more detail, this effective atomic number.

And early transition elements are polar and very reactive. They have polar and very reactive M-C bonds whether it is alkyl or aryl, and few d-electrons are there, as a result they are hard sigma donors, hard acids and also they prefer hard sigma donors such as nitrogen, oxygen or fluorine. ~~And t~~They form weak complexation with pi-acceptor ligands such as olefins and phosphines.

Unless phosphines are strong sigma donors, early metals reluctantly form bonds with phosphines and a typical catalytic process they promote is polymerization. And one should remember always even with coordination number 6 and having octahedral geometry, they can never obey 18 electron rule.

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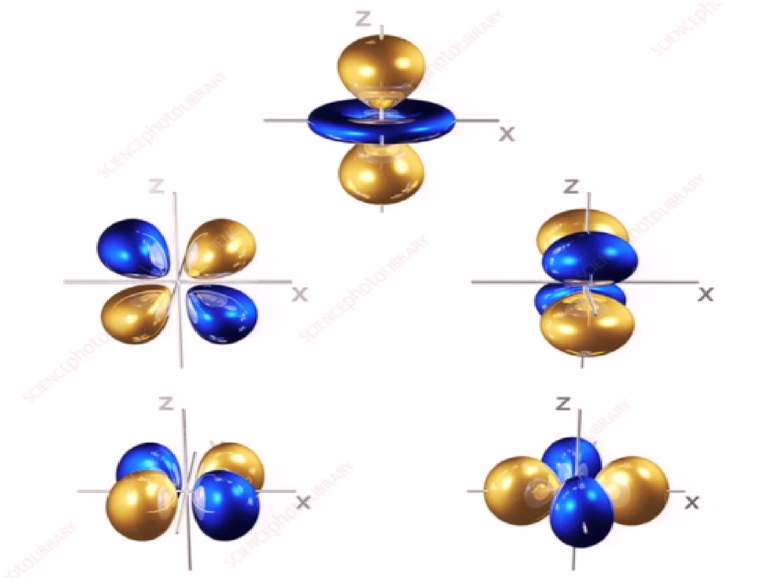

And just I have shown you d-orbitals and their shapes here and of course we have d_{z^2} ~~square~~, d_{xz}, d_{yz} and $d_{x^2-y^2}$ ~~square~~ and d_{yz}. Let us look into the ligands.

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Ligands

Compounds of metal ions coordinated by ligands are referred to as metal complexes.

Most ligands are neutral or anionic substances but cationic ones, such as the tropylium cation, are also known.

Neutral ligands, such as ammonia, NH_3, or carbon monoxide, CO, are independently stable molecules in their free states, whereas anionic ligands such as: Cl^- or $C_5H_5^-$, are stabilized only when they are coordinated to central metals.

Ligands are very important components of coordination compounds and organometallic compounds. Compounds of metal ions coordinated by ligands are referred to as metal complexes. So, that means in order to call a complex it should have a metal ion or neutral metal coordinated by ligands. And most ~~against~~ ligands are neutral or anionic substances;~~,~~ they can be ions or atoms or a group or a molecule.

But cationic ones are also known, for example nitrosyl cation or tropylium cation. Neutral ligands such as ammonia, carbon monoxide are independently stable molecules in their free states, whereas anionic ligands such as chloride or cyclopentadienyl are stabilized only when they are coordinated to central metals. So, I am going to show you the representative ligands. Common ligands ~~are~~ or those with complicated chemical formula or long names are expressed in abbreviated forms.

If we have to use routinely ligands having very lengthy name, then probably it is ideal to abbreviate and use the abbreviation but somewhere in the beginning we have to give the expansion and details about that ligand. So those ligands with one donor atom are called monodentate ligands and those with more than one donor atom are referred as bidentate, tridentate, tetradentate or polydentate ligands. For example: bi, tri, tetra, etc.

If both the donor atoms are bonded to the same metal, such ligands are called chelate ligands. The number of atoms bonded to a central metal is the coordination number that is secondary valency.

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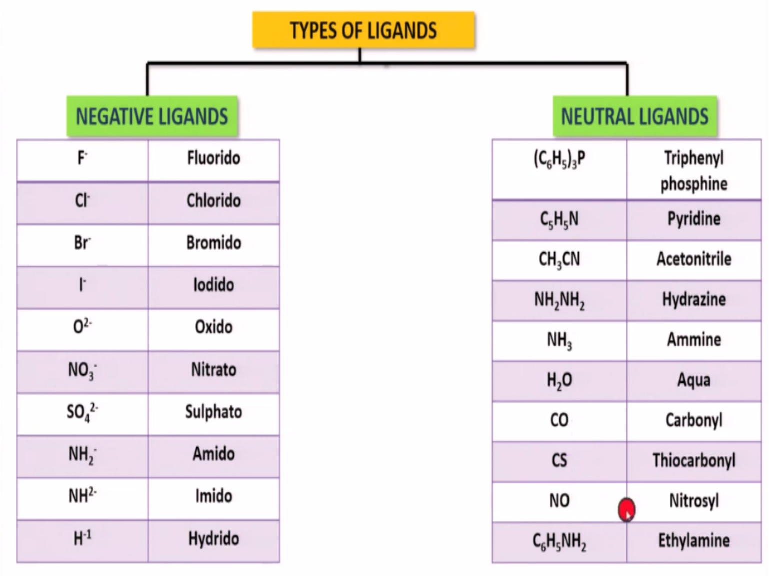

TYPES OF LIGANDS

NEGATIVE LIGANDS

F^-	Fluorido
Cl^-	Chlorido
Br^-	Bromido
I^-	Iodido
O^{2-}	Oxido
NO_3^-	Nitrato
SO_4^{2-}	Sulphato
NH_2^-	Amido
NH^{2-}	Imido
H^{-1}	Hydrido

NEUTRAL LIGANDS

$(C_6H_5)_3P$	Triphenyl phosphine
C_5H_5N	Pyridine
CH_3CN	Acetonitrile
NH_2NH_2	Hydrazine
NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
CS	Thiocarbonyl
NO	Nitrosyl
$C_6H_5NH_2$	Ethylamine

So, I have listed here the types of ligands. Of course negative ligands or anionic ligands are shown here, fluoride, chloride, bromide, iodide, oxide, nitrato, sulphato, amido, imido and hydrido. And here I have displayed neutral ligands. This is triphenyl phosphine and pyridine, acetonitrile, hydrazine, ammine. Ammonia is also called as ammine. Water called as aqua. Carbonyl, CS thiocarbonyl, again CS does not have an independent existence, but it can be generated *in situ* and can be used similar to carbon monoxide and nitrosyl and ethylamine.

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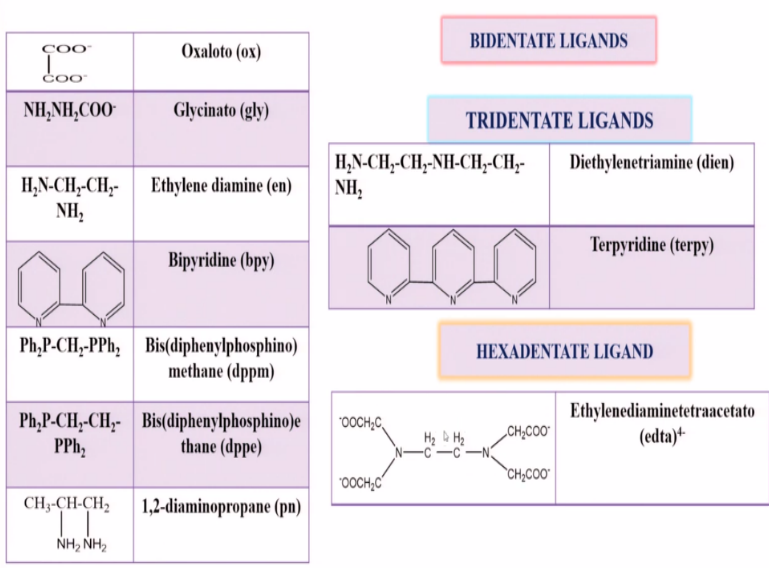

BIDENTATE LIGANDS

COO^-–COO^-	Oxaloto (ox)
$NH_2NH_2COO^-$	Glycinato (gly)
$H_2N-CH_2-CH_2-NH_2$	Ethylene diamine (en)
	Bipyridine (bpy)
$Ph_2P-CH_2-PPh_2$	Bis(diphenylphosphino) methane (dppm)
$Ph_2P-CH_2-CH_2-PPh_2$	Bis(diphenylphosphino)ethane (dppe)
$CH_3-CH(NH_2)-CH_2(NH_2)$	1,2-diaminopropane (pn)

TRIDENTATE LIGANDS

$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$	Diethylenetriamine (dien)
	Terpyridine (terpy)

HEXADENTATE LIGAND

	Ethylenediaminetetraacetato $(edta)^{4-}$

Apart from these, we also have several other ligands like oxala~~o~~to, bidentate ligand or it can be one tetradentate ligand because of other two C~~ double bond~~=O ~~oxygen atoms~~ and glycinato and ethylene diamine, bipyridine. Again bipyridine, we have 2,2-~~dash~~bipyridine, 4,4~~ dash~~-bipyridine and this is bisdiphenylphosphino methane and this is 1,2-

bisdiphenylphosphino ~~-~~ethane. The correct name should be 1,~~-~~2-~~-~~bisdiphenylphosphino ethane because 1,~~-~~1-~~-~~bisdiphenylphosphino ethane is also there.

~~And ~~1,~~-~~2-~~-~~diaminopropane. ~~And w~~When we look into tridentate ligands, we have diethylenetriamine or we also have terpyridine and also we have a hexadentate ligand called ~~edta~~EDTA, ethylenediaminetetraacetic acid.

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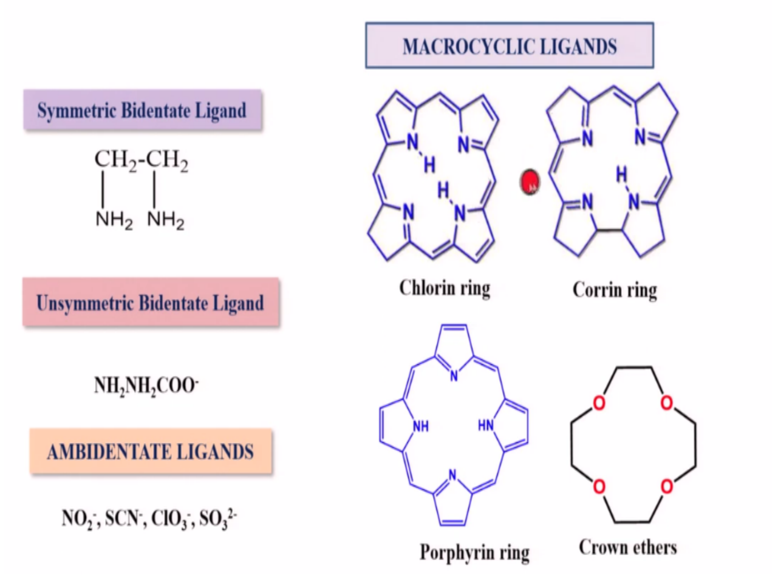

MACROCYCLIC LIGANDS

Symmetric Bidentate Ligand

CH_2-CH_2 / NH_2 NH_2

Unsymmetric Bidentate Ligand

$NH_2NH_2COO^-$

AMBIDENTATE LIGANDS

NO_2^-, SCN^-, ClO_3^-, SO_3^{2-}

Chlorin ring

Corrin ring

Porphyrin ring

Crown ethers

So, this is a symmetric bidentate ligand ethylenediamine, whereas this one having an amino and carboxylate groups is unsymmetrical bidentate ligand, and these are all ambidentate ligands where we have two different types of donor atoms ~~are there ~~and they can also exhibit linkage isomerism. And when you look into macrocyclic ligands, they are the important ~~macrocyclic ~~nitrogen macrocytic ligands, a chlorine ring, ~~Corrine ~~corrine ring, porphyrin ring and crown ethers.

So, valence shell electrons, in particular d electron configuration controls the structure and spectral and magnetic properties as well as the reactivity of complexes. That means knowing the valence shell electronic configuration of d~~-~~elements is very important. The theory of electronic structure is very important to understand the properties and reactivity and also the application in various aspects.

The nature of the metal ligand bond can be understood by analysing the molecular orbital diagram. Molecular orbital diagram can give a clearer picture of relative energies due to the interaction between the metal atomic orbitals and the ligand orbitals. Bonding, nonbonding and antibonding molecular orbitals assist in understanding the properties and reactivity of metal complexes.

Again, I will be spending a considerable amount of time in explaining the bonding concepts and also give you more emphasis for crystal field theory and molecular orbital theory to make you familiar with these bonding concepts, so that speculating their properties and reactivity would be much simpler.

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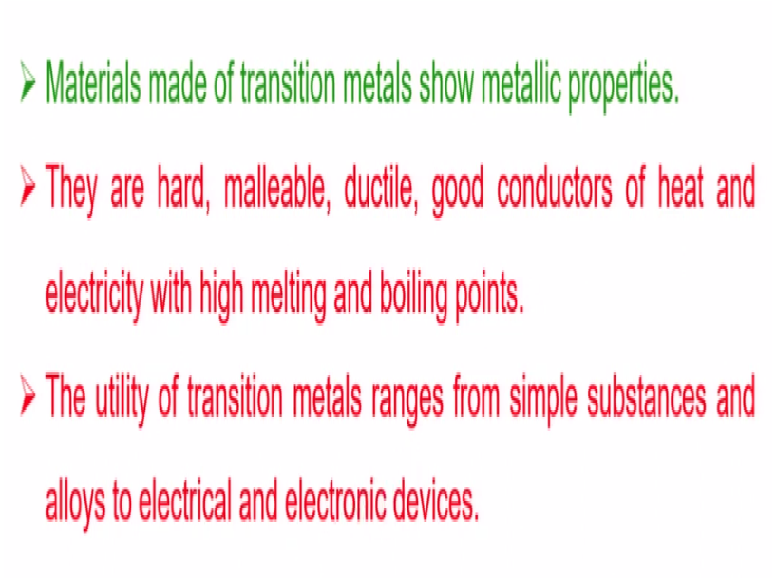

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Physical properties

Of course, this explains malleability of metals. Let me stop at this juncture and focus more about physical properties and other important properties related to transition elements in my next class. Until then, have a good time. Thank you.