

## **Lanthanides & Actinides**

**Lanthanides**(also called lanthanoids) are called first inner transition series or third transition and come immediately after lanthanum. They are classified as f- block elements along with the actinides. They are commonly called the rare earths. They are characterized by the filling up of the 4f energy levels which are not usually involved in bonding. These highly electropositive elements have a common oxidation state of +3 and generally resemble each other in their chemical and physical properties. They have a generic symbol “Ln”.

### **Discovery And Occurrence**

In 1794, Swedish chemist, Gadolin, discovered an oxide called yttria. Yttria was broken down to– yttria, erbia and terbia. Over the years, more separation was achieved, and more oxide discovered e.g. lutetia. The names were later obtained by changing the ending –a to -um.

Major sources of lanthanides are Monazite (sand-composed of phosphates of thorium(Th), cerium(Ce), neodymium(Nd) and lanthanum(La)); the phosphate portion of monazite contains small traces of other lanthanide ions and the only lanthanide that does not occur naturally is promethium(Pm), which is made artificially by nuclear reaction. Madagascar is a mixed fluorocarbonate  $M^{III}CO_3F$  where M is La or the lanthanide metals. It provides 20% total supply of lanthanides.

### **Lanthanide Contraction**

Each succeeding lanthanides differs from its immediate predecessor in having one or more electron in the 4f (though there are some exceptions) and an extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus. This leads to a gradual increase in the attraction of the nucleus to the electrons in the outermost shell as the nuclear charge increases, and a consequent contraction in the atomic radius. In lanthanide contraction, the ionic

radii of the lanthanides decrease progressively with increase atomic number from lanthanum ( $\text{La}^{+3}=0.115\text{nm}$ ) to Lutetium ( $\text{Lu}^{+3}=0.093\text{nm}$ ) . As the ionic radii contract along the lanthanide series, the ability to form complex ions increases and this is the basis of their separation on an ion exchange column.

### **Electronic Structure**

$_{57}\text{La}$  has one  $5d^1$  and two  $6s^2$  electrons; the next element cerium( $_{58}\text{Ce}$ ), however, while still retaining two  $6s^2$  electrons has two electrons in the  $4f^2$  orbital and none in the  $5d$  orbital. The atoms of the elements from cerium to lutetium have between 2 and 14 electrons in the  $4f$  orbital.

The filling up of the  $4f$  orbital is regular with one exception; Europium( $_{63}\text{Eu}$ ) has the outer electronic structure of  $[\text{Xe}]4f^75d^06s^2$  and the next element gadolinium( $_{64}\text{Gd}$ ) has an extra electron in the  $5d$  shell,  $[\text{Xe}]4f^75d^16s^2$  [when all seven  $4f$  shells are singly occupied, a degree of stability is conferred on the atom]. Ytterbium( $_{70}\text{Yb}$ ) has a full complement of  $4f$  electrons ( $[\text{Xe}]4f^{14}5d^06s^2$ ) and the extra electron in the lutetium( $_{71}\text{Lu}$ ) atom enters the  $5d$  shell ( $[\text{Xe}]4f^{14}5d^16s^2$ ). Only lanthanum, gadolinium and lutetium have single  $5d$  electrons. The other lanthanides do not have electrons on their  $5d$  orbitals.

**Table** Configurations and ionic radii for the lanthanoids.

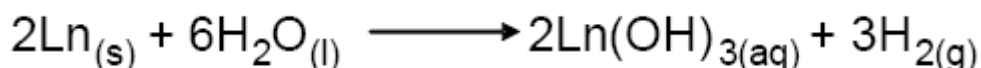
Element	Symbol	Electronic configurations*		M <sup>3+</sup> ionic radius/Å
		Atomic	M <sup>3+</sup>	
Lanthanum	La	$5d^1 6s^2$	–	1.061
Cerium	Ce	$4f^2 6s^2$	$4f^1$	1.034
Praesodymium	Pr	$4f^3 6s^2$	$4f^2$	1.013
Neodymium	Nd	$4f^4 6s^2$	$4f^3$	0.995
Promethium	Pm	$4f^5 6s^2$	$4f^4$	0.979
Samarium	Sm	$4f^6 6s^2$	$4f^5$	0.964
Europium	Eu	$4f^7 6s^2$	$4f^6$	0.950
Gadolinium	Gd	$4f^7 5d^1 6s^2$	$4f^7$	0.938
Terbium	Tb	$4f^9 6s^2$	$4f^8$	0.923
Dysprosium	Dy	$4f^{10} 6s^2$	$4f^9$	0.908
Holmium	Ho	$4f^{11} 6s^2$	$4f^{10}$	0.894
Erbium	Er	$4f^{12} 6s^2$	$4f^{11}$	0.881
Thulium	Tm	$4f^{13} 6s^2$	$4f^{12}$	0.869
Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{13}$	0.858
Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$	0.848

\*Outside of closed [Xe] shell.

### General Properties

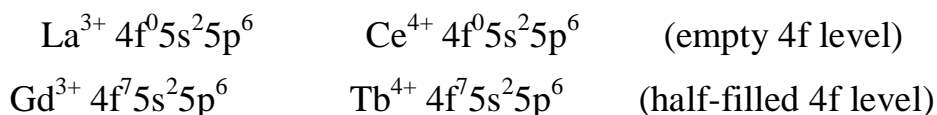
- 1) The metals are silvery white in colour.
- 2) They generally have high melting and boiling points and are very hard
- 3) They are good conductors of heat and electricity.
- 4) Many of the lanthanide ions form coloured ions
- 5) The lanthanides exhibit a principal oxidation state of +3 in which the M<sup>+3</sup> ion contains an outer shell containing 8 ( $5s^2 5p^6$ ) electrons and an underlying layer containing up to 14 4f electrons.
- 6) They exhibit paramagnetism because of the presence of unpaired electrons
- 7) They readily tarnish in air and burn to give oxides (all give trioxides except Ce which forms CeO<sub>2</sub>).

- 8) They also combine with the following non-metals –N, S, halogens, H.
- 9) The hydrides are non-stoichiometric but have a composition of  $MH_3$ . These hydrides liberate hydrogen from water.
- 10) The lanthanides also liberate hydrogen from water as does their hydrides and a vigorous evolution of same gas from dilute non-oxidizing acids.

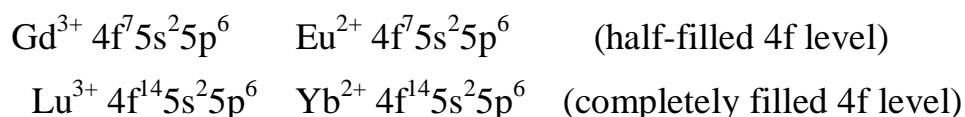


### Oxidation States

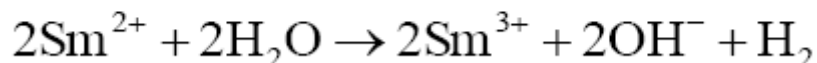
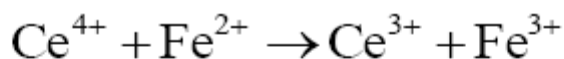
Lanthanides exhibits a principal oxidation state of +3 which contain an outer shell containing 8 electrons ( $5s^2 5p^6$ ) and an underlying layer containing up to 14 electrons. The +3 ions of La, Gd and Lu which contain respectively an empty, a half-filled, and a completely filled 4f level are especially stable. Ce can exhibit an oxidation state of +4 in which it has the same electronic structure with  $La^{+3}$  i.e. an empty 4f level-noble gas configuration). Also,  $Tb^{4+}$  (Terbium) exists which has the same electronic structure as  $Gd^{3+}$  i.e. a half-filled 4f level. An empty, a half-filled and a completely filled 4f shell confers some extra stability on a particular oxidation state.



Also,  $Eu^{+2}$  is isoelectronic with  $Gd^{+3}$  i.e. half-filled 4f level and  $Yb^{+2}$  (Ytterbium) is isoelectronic with  $Lu^{+3}$



In addition, +2 and +4 states exist for elements that are close to these states. For example,  $Sm^{2+}$  and  $Tm^{2+}$  occur with  $f^6$  and  $f^{13}$  arrangements and  $Pr^{4+}$  and  $Nd^{4+}$  have  $f^1$  and  $f^2$  arrangements. The most stable oxidation state is  $Ln^{3+}$  and  $Ln^{2+}$  and  $Ln^{4+}$  are less stable.  $Ce^{4+}$  is strongly oxidizing and  $Sm^{2+}$  is strongly reducing:



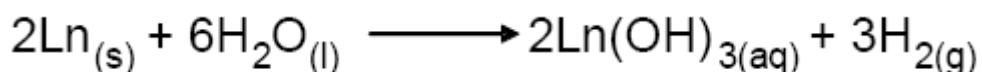
{Ce<sup>4+</sup> and Sm<sup>2+</sup> are converted to +3 state, showing that it is the most stable oxidation state}.

### **Chemical properties of the compounds of various (+3) oxidation state**

The trivalent state is characteristics of all the lanthanides. The standard potentials (E°) are all high and vary in a regular way over a small range (-2.48 to -2.26 volts) depending on the size. They are more reactive than aluminum (-1.66 volts) and slightly more than magnesium(-2.36volts).

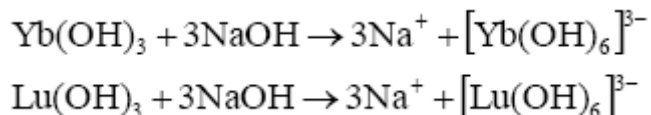
#### ***Hydroxides:***

Based on their reactivity, they react slowly with cold water, but more rapidly on heating to form the hydroxide.



The hydroxides which are definite compounds are precipitated as gelatinous precipitates by the addition of NH<sub>4</sub>OH to aqueous solutions. They can be obtained in the crystalline form by aging Ln<sub>2</sub>O<sub>3</sub> in strong alkali at high temperature and pressure. They are **ionic** and **basic**. They are less basic than Ca(OH)<sub>2</sub> but more basic than Al(OH)<sub>3</sub> which is amphoteric. The hydroxides are basic enough as to absorb CO<sub>2</sub> and form carbonates. The basicities of the hydroxides decreases with increasing atomic number as will be expected for decreasing ionic radii. Ce(OH)<sub>3</sub> is the most basic

while  $\text{Lu}(\text{OH})_3$  is the least basic. The decrease in basic properties can be seen by dissolving the hydroxides of the later members in hot concentrated sodium hydroxide which produces complexes.

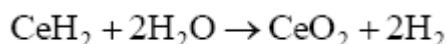


### ***Oxides:***

The metals readily tarnish in air and on heating in oxygen, they all give the oxides,  $\text{Ln}_2\text{O}_3$  which resembles Ca to Ba group Cerium alone forms  $\text{CeO}_2$ . They oxides are also ionic and basic and readily reacts with water to give the hydroxides. Yb and Lu form a protective oxide film which prevents the whole metal forming oxide unless heated to  $1000^\circ\text{C}$ .

### ***Hydrides:***

The hydrides are formed when the metal reacts with  $\text{H}_2$ . This requires heating up to  $300\text{-}400^\circ\text{C}$  to initiate the reaction. The products-dihydrides,  $(\text{LnH}_2)$  are solids: black, metallic and conduct electricity. This is because the Ln ion exists in the +3 and has  $2\text{H}^-$  ion and an electron which occupies a conduction band. Exceptions are Eu and Yb which form the divalent compounds;  $\text{EuH}_2$  and  $\text{YbH}_2$ . These are salt-like and contain  $\text{M}^{2+}$  and two  $\text{H}^-$ . Yb forms non-stoichiometric hydrides approximately  $\text{YbH}_{2.5}$ . The hydrides generally, liberate hydrogen from water, are stable to heat up to  $900^\circ\text{C}$  and react with  $\text{O}_2$  to form the oxide.



The dihydrides take up H when heated under pressure and all but Eu form salt like hydrides  $\text{LnH}_3$ (which has  $\text{Ln}^{3+}$  and three  $\text{H}^-$ .) since there are no delocalized electron, they do not show metallic conduction.

## Coordination Complexes:

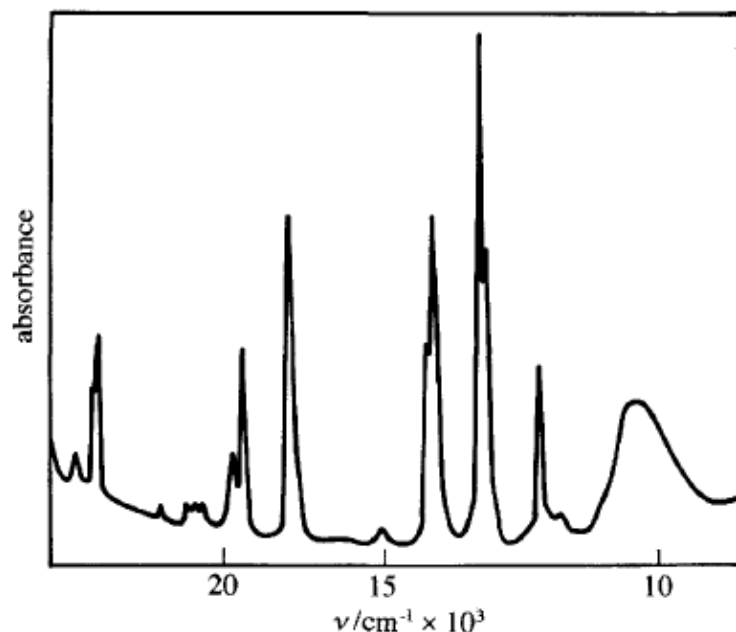
$\text{Ln}^{3+}$  forms complexes of high coordination numbers. The coordination numbers for  $[\text{Ln}(\text{OH}_2)_n]^{3+}$  in aqueous solution are up to 9 for the early lanthanoids and 8 for the later smaller members. The  $\text{Ln}^{3+}$  ions readily form complexes with  $\text{F}^-$  and  $\text{O}^-$  donor ligands eg with  $\text{H}_2\text{O}$ , EDTA,  $\beta$ -diketonate, citric acid, oxalic acid ligands. Partially fluorinated  $\beta$ -diketonate ligand  $\text{CF}_3\text{COCHCOCF}_3$  (Fod) produces complexes with  $\text{Ln}^{3+}$  that are volatile and soluble in organic solvents {because of their volatility, they are used as precursors for the synthesis of lanthanoid-containing superconductors by vapour deposition} Charged ligands have highest affinity for the smallest  $\text{Ln}^{3+}$  ion.

Examples of Metal complexes:

Coordination number	Complex	Shape
4	$[\text{Lu}(2,6\text{-dimethylphenyl})_4]^-$	Tetrahedral
6	$[\text{Ce}^{\text{IV}}\text{Cl}_6]^{2-}$	Octahedral
6	$[\text{Er}(\text{NCS})_6]$	Octahedral
7	$[\text{Y}(\text{acetylacetonate})_3\text{H}_2\text{O}]$	Mono-capped trigonal prism
8	$[\text{La}(\text{acetylacetonate})_3(\text{H}_2\text{O})_2]$	Square antiprism
8	$[\text{Ce}^{\text{IV}}(\text{acetylacetonate})_4]$	Square antiprism
8	$[\text{Eu}(\text{acetylacetonate})_3(\text{phenanthroline})]$	Square antiprism
8	$[\text{Ho}(\text{tropolonate})_4]^-$	Docecahedral
9	$[\text{Nd}(\text{H}_2\text{O})_9]^{3+}$	Tri-capped trigonal prism
9	$[\text{Sm}(\text{NH}_3)_9]^{3+}$	Tri-capped trigonal prism
10	$[\text{Ce}^{\text{IV}}(\text{CO}_3\text{-O, O'})_5]^{6-}$	
10	$[\text{Ce}^{\text{IV}}(\text{NO}_3)_4(\text{Ph}_3\text{PO})_2]$	(each nitrate ion is bidentate)
11	$[\text{La}(\text{OH}_2)_5(\text{NO}_3\text{-O, O'})_3]^{2-}$	
12	$[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]^{2-}$	Icosahedral (each nitrate ion is bidentate)
12	$[\text{La}(\text{NO}_3\text{-O, O'})_6]^{3-}$ , $[\text{La}(\text{OH}_2)_2(\text{NO}_3\text{-O, O'})_5]^{2-}$	

## **Optical properties and Spectra of Lanthanoid complexes**

Lanthanide ions are weakly coloured. The spectra of their complexes show much narrower bands because the *f* orbitals overlap only weakly with the ligand orbitals.



**Figure .** Absorption spectrum of an aqueous solution of  $\text{Nd}^{3+}$  ions.

The 4*f* orbitals are deeply embedded inside the atom and well shielded by 5*s* and 5*p* electrons. The *f* electrons are practically unaffected by complex formation; hence colour remains almost constant for a particular ion regardless of the ligands (see Table below). The bands due to *f-f* transition are sharp compared to the broad bands for *d-d* transition. Absorption bands due to 4*f*-5*d* transitions are broad and are affected by ligand environment.

All lanthanoid ions (except  $\text{La}^{3+}$  (*f*<sup>0</sup>) and  $\text{Lu}^{3+}$  (*f*<sup>14</sup>) show luminescence  $\text{Eu}^{3+}$  (*f*<sup>6</sup>) and  $\text{Tb}^{3+}$  (*f*<sup>8</sup>) showing particularly strong emissions. This has been attributed to the large number of excited states that exist which decays to the ground state with either emission of energy (fluorescence) or non-radiative pathways. The origin of this is *f-f* transition. The luminescence of lanthanoid complexes is the reason they are used as phosphors on TV screens and fluorescent lighting.



**The Colours Of Some Aqueous Lanthanides**

Ions	No of 4f e`s	Colour	Ions	No of 4f e`s	Colour	Ions	No of 4f e`s	Colour	Isoelectronic Ln <sup>3+</sup>
La <sup>3+</sup>	4f <sup>0</sup>	Colourless	Lu <sup>3+</sup>	4f <sup>14</sup>	Colourless	Ce <sup>4+</sup>	4f <sup>0</sup>	Orange-red	La <sup>3+</sup> Colourless
Ce <sup>3+</sup>	4f <sup>1</sup>	Colourless	Yb <sup>3+</sup>	4f <sup>13</sup>	Colourless	Sm <sup>2+</sup>	4f <sup>6</sup>	Yellow	Eu <sup>3+</sup> Pale pink
Pr <sup>3+</sup>	4f <sup>2</sup>	Green	Tm <sup>3+</sup>	4f <sup>12</sup>	Green	Eu <sup>2+</sup>	4f <sup>7</sup>	Pale greenish yellow	Gd <sup>3+</sup> Colourless
Nd <sup>3+</sup>	4f <sup>3</sup>	Lilac	Er <sup>3+</sup>	4f <sup>11</sup>	Lilac	Yb <sup>2+</sup>	4f <sup>14</sup>	Colourless	Lu <sup>3+</sup> Colourless
Pm <sup>3+</sup>	4f <sup>4</sup>	pink	Ho <sup>3+</sup>	4f <sup>10</sup>	Pink				
Sm <sup>3+</sup>	4f <sup>5</sup>	Yellow	Dy <sup>3+</sup>	4f <sup>9</sup>	Yellow				
Eu <sup>3+</sup>	4f <sup>6</sup>	Pale pink	Tb <sup>3+</sup>	4f <sup>8</sup>	Pale pink				
Gd <sup>3+</sup>	4f <sup>7</sup>	Colourless							

\*Elements with (n) f electrons often have similar colour to those with (14-n)f electrons.

## Magnetic properties

**Key point:** *The magnetic moments of lanthanoid compounds arise from both spin and orbital contributions.*

The magnetic moment  $\mu$  of many d-metal ions can be calculated by using the spin-only approximation because the strong ligand field quenches the orbital contribution. For the lanthanoids, where the spin-orbital coupling is strong, the orbital angular momentum contributes to the magnetic moment, and the ions behave like almost free atoms. Therefore, the magnetic moment must be expressed in terms of the total angular momentum quantum number  $J$ :

$$\mu = g_J \{J(J+1)\}^{1/2} \mu_B$$

where the Landé  $g$ -factor is

$$g_J = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

and  $\mu_B$  is the Bohr magneton. Theoretical values of the magnetic moment of the ground states of the Ln<sup>3+</sup> ions are summarized in Table below in general these values agree well with experimental data.

■ **A brief illustration.** As we have seen, the ground state term symbol for  $\text{Pr}^{3+} (f^2)$  is  $^3\text{H}_4$  with  $L = 5$ ,  $S = 1$ , and  $J = 4$ . It follows that

$$g_J = 1 + \frac{1(1+1) - 5(5+1) + 4(4+1)}{2 \times 4(4+1)} = 1 + \frac{2 - 30 + 20}{40} = \frac{4}{5}$$

Therefore

$$\mu = g_J \{J(J+1)\}^{1/2} \mu_B = \frac{4}{5} \{4(4+1)\}^{1/2} \mu_B = 3.58 \mu_B \quad \blacksquare$$

Electron configurations, colours, and magnetic moments (at 298 K) of the  $\text{Ln}^{3+}$  ions

Element	Configuration	Colour in aqueous solution	Ground state	Magnetic moment	
				Theory $\mu / \mu_B$	Observed <sup>§</sup> $\mu / \mu_B$
Lanthanum	$[\text{Xe}]$	Colourless	$^1\text{S}_0$	0	0
Cerium	$[\text{Xe}]f^1$	Colourless	$^2\text{F}_{5/2}$	2.54	2.46
Praseodymium	$[\text{Xe}]f^2$	Green-yellow	$^3\text{H}_4$	3.58	3.47–3.61
Neodymium	$[\text{Xe}]f^3$	Violet	$^4\text{I}_{9/2}$	3.68	3.44–3.65
Promethium	$[\text{Xe}]f^4$	—	$^5\text{I}_4$	2.83	—
Samarium	$[\text{Xe}]f^5$	Yellow	$^6\text{H}_{5/2}$	0.84 (1.55–1.65) <sup>¶</sup>	1.54–1.65
Europium	$[\text{Xe}]f^6$	Pink	$^7\text{F}_0$	0 (3.40–3.51) <sup>¶</sup>	3.32–3.54
Gadolinium	$[\text{Xe}]f^7$	Colourless	$^8\text{S}_{7/2}$	7.94	7.9–8.0
Terbium	$[\text{Xe}]f^8$	Pink	$^7\text{F}_6$	9.72	9.69–9.81
Dysprosium	$[\text{Xe}]f^9$	Yellow-green	$^6\text{H}_{15/2}$	10.63	10.0–10.6
Holmium	$[\text{Xe}]f^{10}$	Yellow	$^5\text{I}_8$	10.60	10.4–10.7
Erbium	$[\text{Xe}]f^{11}$	Lilac	$^4\text{I}_{15/2}$	9.59	9.4–9.5
Thulium	$[\text{Xe}]f^{12}$	Green	$^3\text{H}_6$	7.57	7.0–7.5
Ytterbium	$[\text{Xe}]f^{13}$	Colourless	$^2\text{F}_{7/2}$	4.54	4.0–4.5
Lutetium	$[\text{Xe}]f^{14}$	Colourless	$^1\text{S}_0$	0	0

<sup>¶</sup> The values in parentheses include expected contribution from terms other than the ground state.  
<sup>§</sup> From compounds such as  $\text{Ln}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$  and  $\text{Ln}(\text{Cp})_2$ .

## **Applications of Lanthanides**

1. Use as catalysts: Lanthanide catalysts have been repeatedly recommended for use in numerous organic reactions, including the hydrogenation of ketones to form secondary alcohols, the hydrogenation of olefins to form alkanes, the dehydrogenation of alcohols and butanes, and the formation of polyesters.
2. Use in the glasses industry: Cerium oxide has been found to be a more rapid polishing agent for glass than rouge, and are used in the polishing of lenses for cameras, binoculars, and eyeglasses, as well as in polishing mirrors and television faceplates.
3. Use in the metallurgical industry: Small amounts of misch metal and cerium have long been added to other metals or alloys to remove their nonmetallic impurities. Misch metal added to cast iron makes a more malleable nodular iron. Added to some steels, it makes them less brittle.
4. Use in the television industry: It has been found that if a small amount of europium oxide ( $\text{Eu}_2\text{O}_3$ ) is added to yttrium oxide ( $\text{Y}_2\text{O}_3$ ), it gives a brilliant-red phosphor.
5. Other applications: Another significant industrial application of rare earths is in the manufacture of strong permanent magnets. Alloys of cobalt with rare earths, such as cobalt–samarium, produce permanent magnets that are far superior to most of the varieties now on the market.

## **Actinide Series**

The group also known as Heavier elements or inner series transition elements following actinium element contains metal. Actinides series elements of which uranium( U, elt 92) and plutonium( Pu, elt 94) are best known are built up by completion of the 5f orbitals.

## **Arrangement of the Actinides series elements in periodic table**

They are found at the final row of the periodic table followed by filling of the 6p orbital.

Atomic no	Element	Symbol	Oxidation states
89	Actinium	Ac	III
90	Thorium	Th	(III), IV
91	Protactinium	Pa	(III), IV, V
92	Uranium	U	III,IV,V VI
93	Neptunium	Np	III,IV,V,VI,VII
94	Plutonium	Pu	III,IV,V,VI,VII
95	Americium	Am	II,III,(IV),VI
96	Curium	Cm	III,(IV)
97	Berkelium	Bk	III,IV
98	Californium	Cf	(II),III,IV
99	Einsteinium	Es	(II),III
100	Fermium	Fm	(II),III
101	Mandeleevium	Md	(II),III
102	Nobelium	No	II,III
103	Lawrencium	Lr	III

## **Occurrence and Preparation of The Elements**

With the exception of Th and U( natural) the actinoids are man made, synthesized by artificial radioactivity i.e by bombardment with slow moving neutron.

## **General Properties**

1) The elements are all metals with fairly high melting points though the values are considerably lower than for the transition elements.

- 2) The sizes of the ions decreases regularly along the series because of the poor screening of the nuclear charge by the f- orbital results in an actinide contraction similar to the lanthanide contraction.
- 3) The actinides are much more dense.
- 4) They are reactive metals like La and the lanthanons.

### **Compounds of Actinides Series**

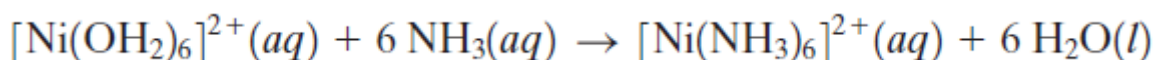
Th shows +2, +3, +4 oxidation state. +4 is the most stable and the  $\text{Th}^{4+}$  ion is known both in the solid and in solution with basic character.  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  is the best known salt, and it is very soluble in water.

## Synthesis of Coordination Compounds

There are many different routes of synthesizing coordination compounds, the two most common being ligand replacement and oxidation-reduction.

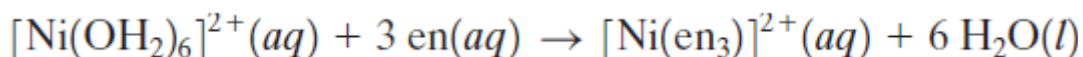
### **1-Ligand Replacement Reactions**

Many transition metal complexes are synthesized in aqueous solution by displacement of the water ligands. For example, we can produce the hexaamminenickel(II) ion by adding an excess of aqueous ammonia to a solution of the hexaaquanickel(II) ion:



Ammonia, which is higher than water in the spectrochemical series, readily replaces the water ligands. In other words, the nickel-ammonia bond is stronger than the nickel-water bond, and the process is exothermic. Hence, the reaction is enthalpy driven.

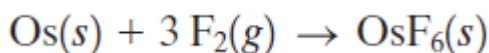
If we are dealing with a chelating ligand, we find that the equilibrium is driven strongly to the right by entropy factors as well. This situation can be illustrated by the formation of the tris(1,2-diaminoethane)nickel(II) ion from the hexaaquanickel(II) ion:



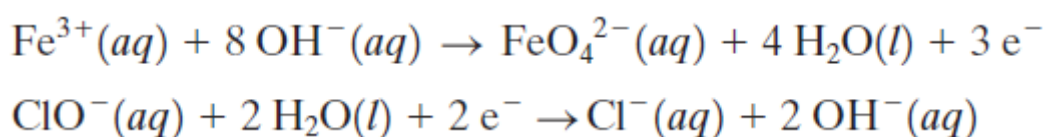
In this case, we have a similar enthalpy increase, but there is also a major entropy increase because the total number of ions and molecules has increased from four to seven. It is the entropy factor that results in such strong complex formation by chelating ligands, behavior that is known as the **chelate effect**.

## 2-Oxidation-Reduction Reactions

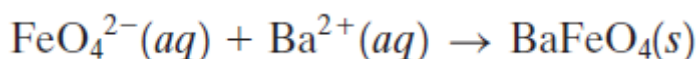
Redox reactions are particularly important as a means of synthesizing compounds in “abnormal” oxidation states. High-oxidation-state fluorides can be synthesized by simple combination reactions, for example:



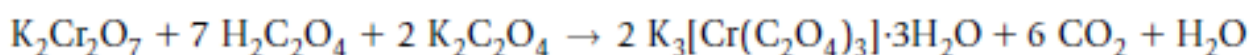
Other high-oxidation-state compounds and polyatomic ions can be produced using oxidizing agents. For example, the red-purple ferrate(VI) ion,  $\text{FeO}_4^{2-}$ , can be prepared using the hypochlorite ion in basic solution:



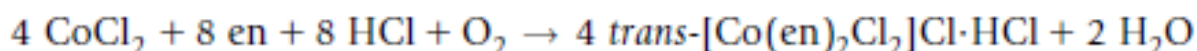
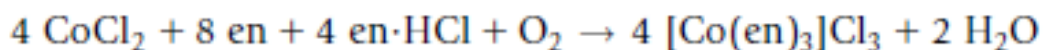
The ion can then be precipitated as the barium salt:



Oxalic acid is a reducing agent, but it also serves as a source of the oxalate ion, which is a good chelating agent. An interesting reaction of this type involves the reduction of dichromate by oxalic acid as shown by the following equation:



In other reactions, the metal may be oxidized as the complex is formed. Numerous complexes of Co(III) have been prepared by the oxidation of solutions containing Co(II). This technique is particularly useful in the case of cobalt because  $\text{Co}^{3+}$  is a strong oxidizing agent that reacts with water if it is not stabilized by complexation. In the following reactions, en is ethylenediamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  :

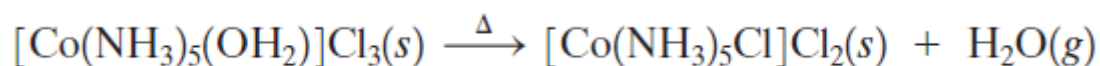


Heating the product of the second reaction yields *trans* - $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  by the loss of HCl. Dissolving *trans* - $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  in water and evaporating the solution by

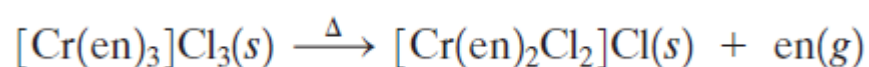
heating results in the formation of *cis* -  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  as the result of an isomerization reaction.

### 3-Partial Decomposition Reactions

In a few cases, the identity of the coordinating ligands can be changed by gentle heating and vaporization of the more volatile ligand. An example in cobalt(III) chemistry is



and an example from chromium(III) chemistry is





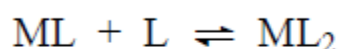
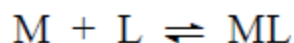
## Reaction mechanisms of coordination complexes

There are two factors effect on the reaction mechanisms, which are **thermodynamic** and **kinetic** factors. The two are intimately interrelated in the detailed mechanisms of inorganic reactions in solutions.

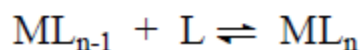
### Thermodynamic factors

#### *Formation constants*

Most metal complexes readily reach some form of equilibrium in reaction in solution, depending on the nature of the ligands attached to the metal, and the ligand concentration in the surrounding solution. This is expressed quantitatively by formation constants of the form:



Etc.



$$K_1 = [ML]/[M][L]$$

$$K_2 = [ML_2]/[ML][L]$$

$$K_n = [ML_n]/[ML_{n-1}][L]$$

These stepwise constants are the ones to consider when seeking to understand the relationships between structure and reactivity.

When we want to calculate the concentration of the final product (the complex  $ML_n$ ) we use the **overall formation constant**,  $\beta_n$ :



$$\beta_n = [ML_n]/[M][L]^n$$

As may be verified by multiplying together the individual stepwise constants, the overall formation constant is the product of the stepwise constants:

$$\beta_n = k_{f1} \cdot k_{f2} \cdot k_{f3} \cdot \dots \cdot k_{fn}$$

The inverse of each  $K_f$ , the **dissociation constant**,  $K_d$ , is also sometimes useful, and is often preferred when we are interested in the concentration of ligand that is required to give a certain concentration of complex:

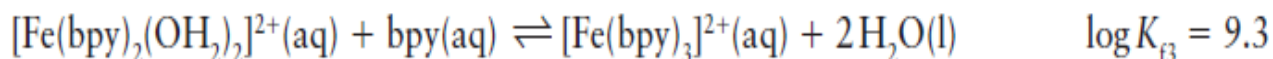
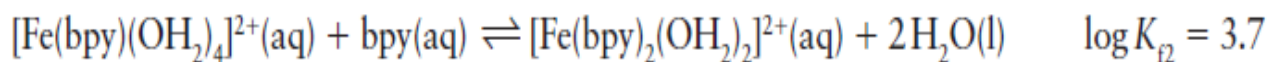
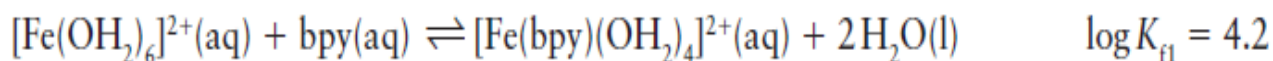


### ***Trends in successive formation constants***

Normally, we will see for a series of stepwise constants the numerical order:

$$K_1 > K_2 > K_3 > \dots > K_n$$

As a reaction proceeds, fewer ligands are available in solution to coordinate, so this order is further enhanced. However, sometimes one of the higher-order constants is found to be significantly greater than an earlier one. This usually means that some significant structural change has occurred, such as the transition from high-spin to low-spin configurations. This occurs, for example in the three step:



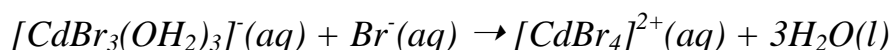
The constant for three step is much greater than for the first two ligand-attachment reactions, accompanying the change from high spin  $d^6$  to low-spin  $d^6$ .

Another example is the conversion of  $\text{Cd}^{2+}$  to  $[\text{CdBr}_4]^{2-}$ , involving the change from octahedral to tetrahedral geometry as in following example.

**Example:** The successive formation constants for complexes of cadmium with  $\text{Br}^-$  are  $K_{f1} = 36.3$ ,  $K_{f2} = 3.47$ ,  $K_{f3} = 1.15$ ,  $K_{f4} = 2.34$ . Suggest an explanation of why  $K_{f4} > K_{f3}$ .

**Answer:** The anomaly suggests a structural change, so we need to consider what it might be. Aqua complexes are usually six-coordinate whereas halogeno complexes of  $\text{M}^{2+}$  ions are commonly tetrahedral.

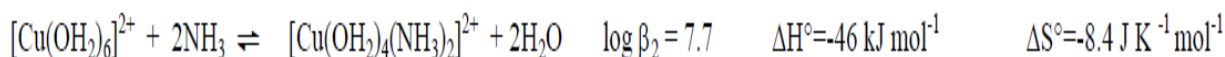
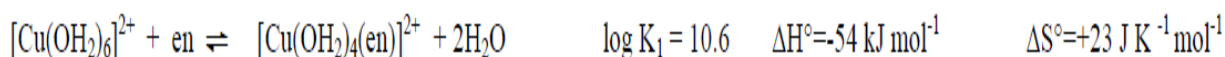
The reaction of the complex with three  $\text{Br}^-$  groups to add the fourth is



This step is favoured by the release of three  $\text{H}_2\text{O}$  molecules from the relatively restricted coordination sphere environment. The result is an increase in  $K_f$ .

### ***Chelate effect***

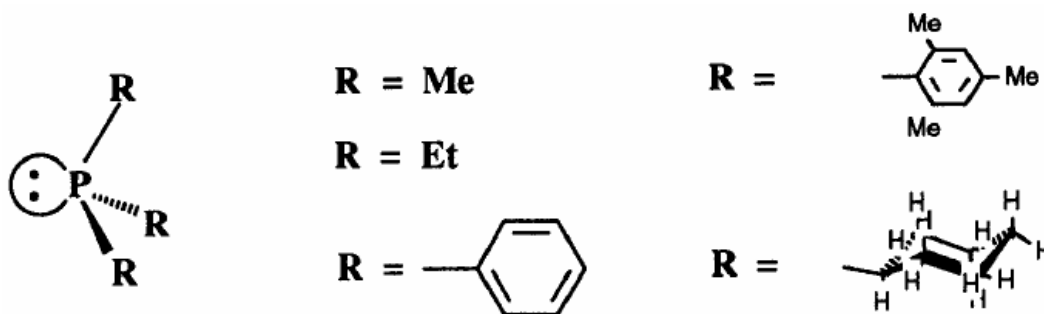
Consider the following equilibria:



Although essentially the same copper-nitrogen bonds are formed in the two complexes, the formation of the **en** complex is distinctly favoured. Note in particular that the first reaction involves an increase in entropy. This is because two water molecules are released into solution when one en coordinates. The preference of chelate coordination is called the **chelate effect** and, as derived, is an entropic effect.

### ***Steric factors***

If a ligand carries bulky side groups, the strength of the metal-ligand bond may be compromised by repulsive effects. For example, much has been made of the substituent effects in phosphine ligands of the type:

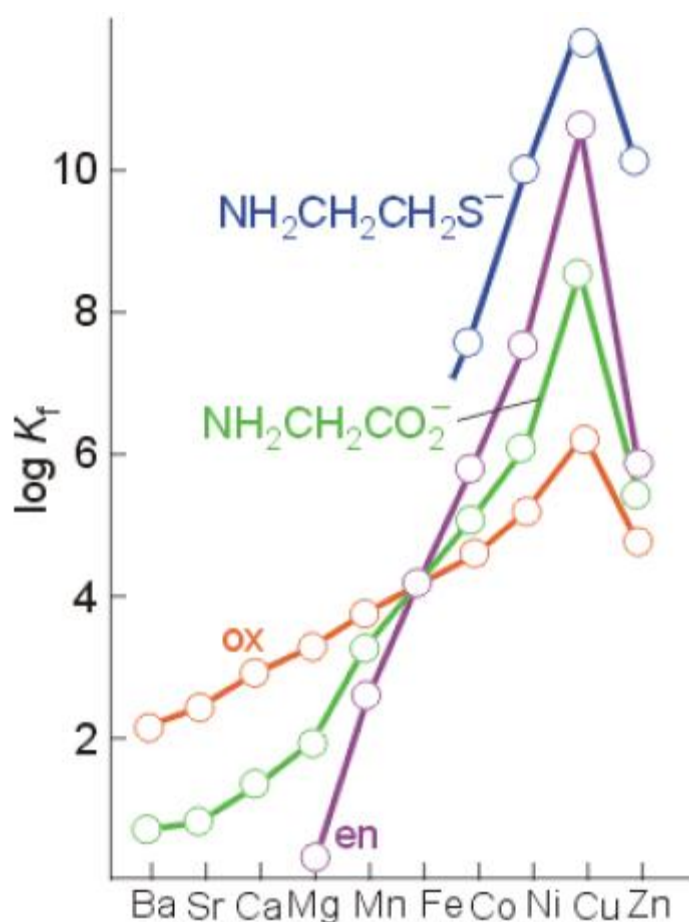


The larger mesityl or cyclohexyl groups cause significant steric interaction with other ligands, weakening the metal-ligand bonds.

### ***Hardness and softness***

Pearson classified Acids and Bases as a Hard and Soft Acids and Bases (**HSAB**), which relates the strength of bonding interactions to matching the polarizability of the components of the bond. Hard metals, i.e., those with high charge and small size, form strong complexes with hard ligands bonded via oxygen and fluorine. Soft metals such as Pt and Au form strong complexes with polarizable ligands like phosphines and sulfur ligands.

																		Most often seen as Lewis bases							
																		Borderline bases		Hard bases					
																		C 2.55		N 3.04		O 3.44		F 3.98	
Hard acids																		Hard acids							
																		Borderline acids							
																		(+2)							
																		Cu(+1) 2.0							
																		Zn 1.65							
																		Cd 1.69							
																		In(+3) 1.78(+1)		Sn(+4) 1.96(+2)		Sb 2.05			



## Kinetic factors

### *Inert and labile complexes*

Henry Taube, Nobel laureate and Canadian born, suggested in 1952 the inert/labile classification of metal complexes with respect to their kinetic stability.

**Labile** refers to complexes with  $t_{1/2} < 1$  min for a 0.1 M solution at RT

**Inert** refers to complexes with  $t_{1/2} > 1$  min for a 0.1 M solution at RT

Good examples to illustrate this are:

$[\text{Co}(\text{NH}_3)_6]^{3+}$  which is unstable to acid hydrolysis with  $\log K_f = 30$  in 6M acid. Yet it is an inert complex, the reaction taking several days at RT.

$[\text{Ni}(\text{CN})_4]^{2-}$  is thermodynamically stable, but kinetically labile. This can be proven by putting labeled  $\text{CN}^-$  in solution, whereby the label gets statistically incorporated into the complex, and this happens very quickly.

The reaction mechanisms of labile complexes must be studied with specialized methods, e.g., stopped-flow kinetics, laser photolysis, etc.

### ***Ligand-field rationale for inert and labile complexes***

A few general trends are observed to predict lability of complexes:

1. All complexes of s-block ions except the smallest ( $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$ ) are very labile.
2. Across the 3d series, complexes of d-block M(II) ions are moderately labile, with distorted Cu(II) complexes among the most labile. However,  $d^6$  complexes with strong-field ligands are an exception. Complexes of M(III) ions are less labile.
3. Complexes of low oxidation state  $d^{10}$  ions ( $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Hg}^{2+}$ ) are highly labile.
4. Strong-field  $d^3$  and  $d^6$  octahedral complexes of the 3d series are generally inert, all others are generally labile.
5. In the 3d series, the least labile M(II) and M(III) ions are those with greatest LFSE.
6. Inertness is quite common among the complexes of the 4d and 5d series, which reflects the high LFSE.
7. The M(III) ions of the f-block are all very labile.

Using Taube's rule-of-thumb for labile and inert complexes, it is possible to correlate the two groups with the ground-state  $d^n$  configuration of the metals (see Table below). Inert complexes are those with half-full or more  $t_{2g}$  levels and empty  $e_g$  levels. Filling the  $e_g$  levels weakens the M-L bonds since these are anti-bonding. But filling the  $t_{2g}$  orbitals has no effect on bonding. Instead, filling this level with electrons makes the approach of an incoming ligand unfavourable due to electron repulsion. Therefore, these complexes are inert. Clearly, changes from inert to labile

can depend on the ligand-field strength of the original ligands. For example: low-spin  $d^6$  versus high-spin  $d^6$ .

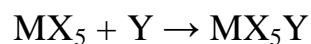
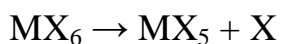
$d$ Electronic Configuration ( $O_h$ Symmetry)	Example of Metal Ion	Typical Octahedral Complex	Taube Classification	Approximate $t_{1/2}$ (s)
$d^0(t_{2g})^0$	Ti(IV)	$[\text{TiCl}_6]^{2-}$	Labile	—
$d^1(t_{2g})^1$	Ti(III)	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	Labile	—
$d^2(t_{2g})^2$	V(III)	$[\text{V}(\text{phen})_3]^{3+}$	Labile	—
$d^3(t_{2g})^3$	V(II)	$[\text{V}(\text{H}_2\text{O})_6]^{2+}$	Inert	$7 \times 10^{-5}$
$d^4(t_{2g})^3(e_g)^1$	Cr(II)	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$	Labile	$3 \times 10^{-9}$
$d^4(t_{2g})^4$	Cr(II)	$[\text{Cr}(\text{CN})_6]^{4-}$	Inert	Very large
$d^5(t_{2g})^3(e_g)^2$	Mn(II)	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	Labile	$1 \times 10^{-7}$
$d^5(t_{2g})^5$	Mn(II)	$[\text{Mn}(\text{CN})_6]^{4-}$	Inert	Very large
$d^6(t_{2g})^4(e_g)^2$	Fe(II)	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$	Labile	$7 \times 10^{-7}$
$d^6(t_{2g})^6$	Fe(II)	$[\text{Fe}(\text{CN})_6]^{4-}$	Inert	Very large
$d^7(t_{2g})^6(e_g)^1$	Co(II)	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	Labile	$1 \times 10^{-6}$
$d^8(t_{2g})^6(e_g)^2$	Ni(II)	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	Labile	$4 \times 10^{-5}$
$d^9(t_{2g})^6(e_g)^3$	Cu(II)	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$	Labile <sup>a</sup>	$2 \times 10^{-9}$
$d^{10}(t_{2g})^6(e_g)^4$	Ga(III)	$[\text{Ga}(\text{H}_2\text{O})_6]^{3+}$	Labile	$< 7 \times 10^{-5}$

### Nucleophilicity

Lewis bases are nucleophiles, while Lewis acids are electrophiles. As we discussed above, the Lewis-base strength gives us information about equilibrium constants and is a thermodynamic parameter. The nucleophilicity of a ligand is the kinetic counterpart, which provides us with information about the rate of a reaction.

### Dissociative (D) and associative (A) mechanisms

First we will discuss the **Dissociative Mechanism**, in which the transition state involves complete dissociation of one of the usually six ligands.



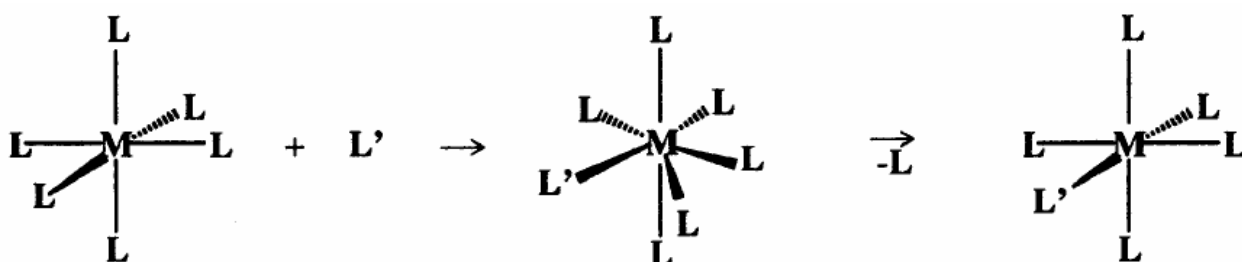


Here, the transition state is the five coordinate complex  $\text{MX}_5$ . The structure of this species may be trigonal bipyramidal or square planar:



Of course, as a transition state, it exists only for a very short time.

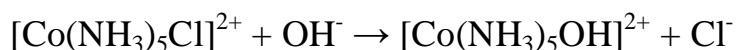
In the **Associative Mechanism (A)** the incoming ligand attacks the metal complex to form a hepta-coordinate transition state, from which the other ligand is displaced to reform a hexa-coordinate species.



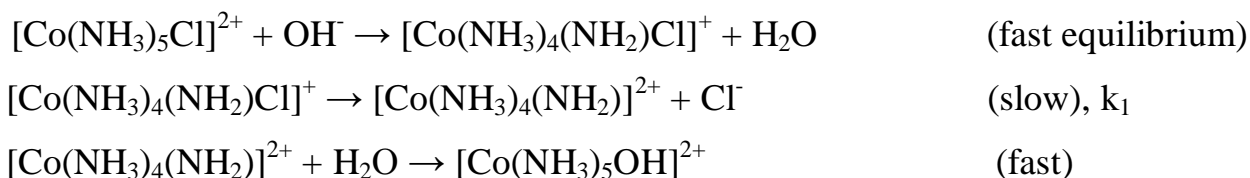
The transition state has evenly constructed bonds for all the ligands, allowing for differences in chemical structure for different atom types. For a square-planar complexes, an associative mechanism will lead to a penta-coordinate transition state.

### Ligand Substitution in Hexa-coordinate complexes

The rate of reaction for an A mechanism can usually be correlated to the nucleophilicity of the incoming ligand, which is similar in order to the spectrochemical series. Significant deviations from such an order usually indicate a more-complex-than-expected mechanism. A clear example is the hydrolysis of the chloropentammine cobalt(III) ion. The kinetics seems to be second order:



However, the rate of reaction is far greater than expected for the hydroxide ion with its relatively low nucleophilicity. An alternate mechanism has been proposed which highlights the strong Brønsted acidity of hydroxide, but its weak nucleophilicity:



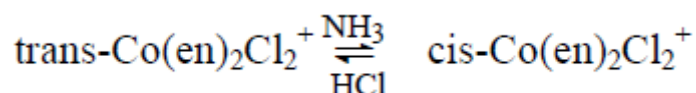
This reaction is actually D in step 2:

$$\text{Rate} = k_1 [\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$$

But the equilibrium concentration of this intermediate depends on  $[\text{OH}^-]$ , hence the apparent rate law is:

$$\text{Rate} = k_1' [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{OH}^-]$$

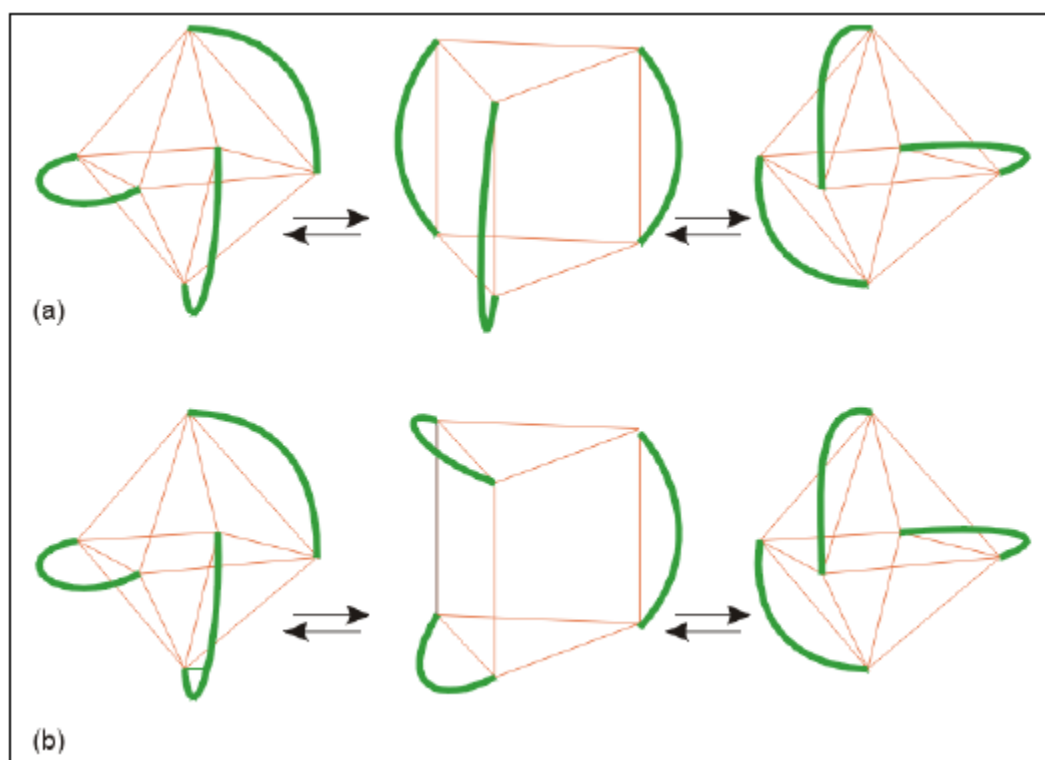
As a second example of substitution reactions of hexa-coordinate species, we look at the isomerization reaction:



This apparently occurs via a D mechanism, i.e., by dissociation of  $\text{Cl}^-$  to give a penta-coordinate intermediate. Re-attachment of the chloride then forms the other isomer. It is not immediately obvious how the pH would affect the preference of the chloride to either go trans to another chloride (acidic solution), or trans to the alkylamine (basic solution). What is clear is that a trigonal bipyramidal intermediate is involved, rather than a square pyramidal one, since only the former will lead to an isomerized complex. Protonation of the en ligand may also be involved in the pH control over this reaction.

As a final example, consider the racemization reactions of metal tris(chelate) complexes. For example,  $[\text{Ni}(\text{en})_3]^{2+}$ , which can be isolated in optically pure form,

and which readily racemizes in solution. The mechanisms of racemization are still under investigation. They are of two basic types: an intramolecular twist and ligand-dissociation mechanisms. For the above complex, an internal twist is commonly proposed. Two possible paths are the **Bailar twist** (Fig. (a)) and the **Ray-Dutt twist** (Fig. (b)). In a dissociation mechanisms, one arm of the ligand comes off, a trigonal bipyramidal intermediate forms, and the chelate re-attaches from a different type.



## Ligand Substitution in square-planar complexes

### *The observed rate law*

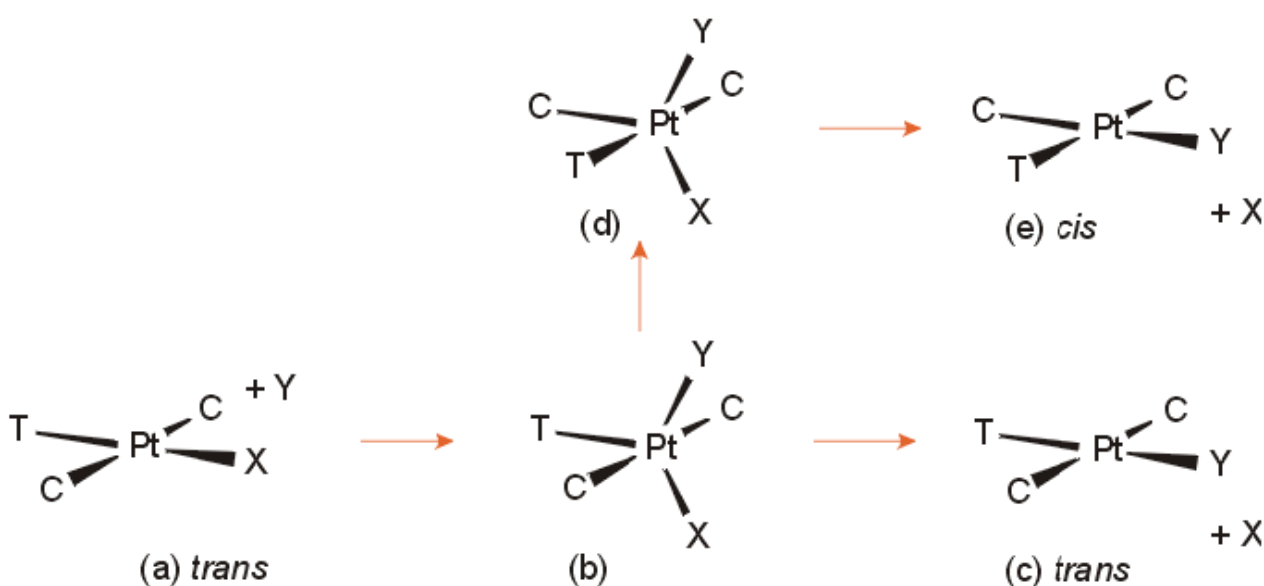
From many studies of substitution reactions at square-planar centres has come the general rate law:

$$\text{Rate} = (k_1 + k_2[L'])[ML_4]$$

Therefore, it appears that both, a **D** and an **A** mechanism are operating. However, this is in fact not the case. The apparent **D** mechanism, i.e.,  $k_1$  path, actually involves

solvent displacing L, and then in a fast step, L' replacing coordinated solvent. Thus the D mechanism is more important in solvents like MeOH than in CCl<sub>4</sub>.

For the complete mechanism, with the microsteps, refer to your textbook. The process is fundamentally A, whereas octahedral complexes are believed to undergo D type reactions in most cases. This is due to the fact that the square-planar molecule is coordinatively unsaturated. Whether the intermediate is trigonal bipyramidal or square pyramidal is not clear. Apparently there is not much energetic difference between the two.



### Nucleophilicity

In an A mechanism, the rate of reaction should depend on the nucleophilicity. This is indeed the case, and for Pt(II), by far the most studied d<sup>8</sup> transition metal cation, the order is found to be:

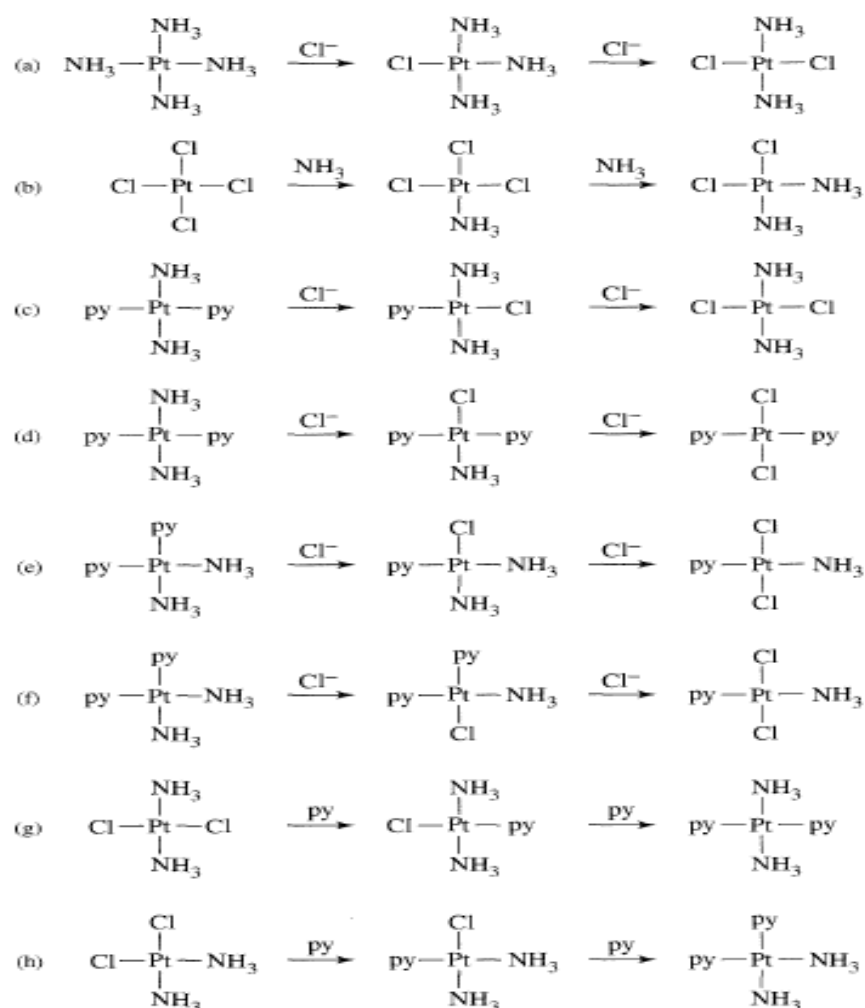


A related factor is the leaving ability of the displaced ligand. This is just the reverse of the nucleophilicity order: ligands which are good nucleophiles are poor leaving groups and vice versa.



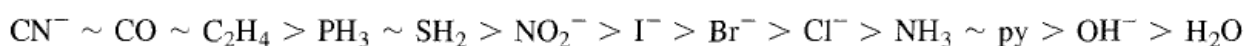
## *Trans effect*

In 1926, Chernyaev introduced the concept of the trans effect in platinum chemistry. The Trans Effect In reactions of square-planar Pt(II) compounds, ligands trans to chloride are more easily replaced than those trans to ligands such as ammonia; chloride is said to have a stronger trans effect than ammonia. When coupled with the fact that chloride itself is more easily replaced than ammonia, this trans effect allows the formation of isomeric



Stereochemistry and the *trans* Effect in Pt(II) Reactions. Charges have been omitted for clarity. In (a) through (f), the first substitution can be at any position, with the second controlled by the *trans* effect. In (g) and (h), both substitutions are controlled by the lability of chloride.

Pt compounds, as shown in the reactions of Figure above. In reaction (a), after the first ammonia is replaced, the second replacement is trans to the first  $\text{Cl}^-$ . In reaction (b), the second replacement is trans to  $\text{Cl}^-$  (replacement of ammonia in the second reaction is possible, but then the reactant and product are identical). The first steps in reactions (c) through (f) are the possible replacements, with nearly equal probabilities for replacement of ammonia or pyridine in any position. The second steps of (c) ' through (f) depend on the trans effect of  $\text{Cl}^-$ . Both steps of (g) and (h) depend on the ' : greater lability of chloride. By using reactions such as these, it is possible to prepare specific isomers with different ligands. Chernyaev and coworkers did much of this, preparing a wide variety of compounds and establishing the order of trans effect ligands:

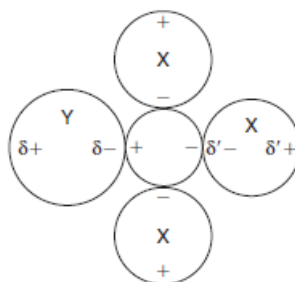


## Explanations Of The *Trans* Effect

### 1-polarization model

One of the approaches to explaining the *trans* effect in a square planar complex is known as the polarization model. The underlying principle in this approach is that the metal ion and the ligands undergo mutual polarization that results in some small charge separation even in spherical ions and ligands.

Suppose a complex has the composition  $\text{MX}_3\text{Y}$  and that Y is more polarizable than X. This situation is shown in Figure below .

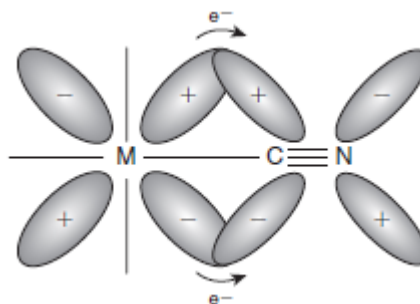


A square planar complex  $\text{MX}_3\text{Y}$  in which the ligands are polarizable.

Because Y is more polarizable than X, the charges separated in the ligands will be different. Based on the polarizabilities,  $|\delta|$  is greater than  $|\delta'|$ . This causes the charge distribution in the metal to be such that the more positive side will be directed toward Y and the slightly positive (or at least more negative) side toward X. This has the effect of making X less tightly bound and easier to remove. Thus, the ease with which X is replaced should increase as the polarizability of Y increases. In general, this trend is observed with the *trans* effect of the halides varying in the order  $\text{I}^-$  greater than  $\text{Br}^-$  greater than  $\text{Cl}^-$ . Because the metal is also polarized somewhat, the observed *trans* effect for  $d^8$  ions varies as  $\text{Pt}^{2+} > \text{Pd}^{2+} > \text{Ni}^{2+}$ .

## 2- $\pi$ bonding effects

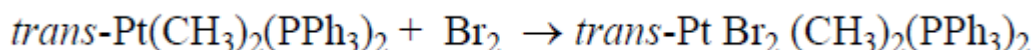
Another explanation for the origin of the *trans* effect lies in the ability of the metal and ligand to form  $\pi$  bonds. The ability of a ligand to accept back donation is dependent on it having empty orbitals of suitable symmetry to match the  $d$  orbitals on the metal. Ligands such as CO,  $\text{C}_2\text{H}_4$ , and  $\text{CN}^-$  have such (antibonding) orbitals. Bonding to cyanide ion can be shown as



## Oxidative Addition and Reductive Elimination

These are the only redox reactions we will discuss. They are a very important reaction types for the topic of organometallic chemistry and in catalysis. They are as closely related to ligand substitutions as to redox reactions. It also involves square-planar molecules.

In a square-planar 16-electron  $d^8$  metal complex, these orbitals are filled up to the  $a_{1g}$  level. This is a mildly antibonding orbital with primarily metal  $dz^2$  axial lone-pair character. In an oxidative addition, the metal lone-pair orbital donates an electron pair to an incoming ligand, whereby the metal is “oxidized” and the ligand attaches to the metal, hence oxidative addition. For example:



There are at least three mechanisms for oxidative additions to occur:

1. Concerted mechanism: e.g.  $\text{H}_2$  or  $\text{O}_2$  addition to Vaska's complex, leading to a cis product.
2. Nucleophilic attack of a metal complex on a polar molecule: e.g., reaction of  $[\text{Pd}(\text{PPh}_3)_4]$  with  $\text{CH}_3\text{Br}$ , leading to a trans complex.
3. Radical mechanism: a reactive radical attaches to the lone-pair orbital, followed by another radical either cis or trans: e.g., reaction of  $\text{XeF}_2$  with Vaska's complex.

