



## Comparative study of transition metals

Comparative Study of Transition Elements (Mount Kenya University)

## The d-block elements

s-block elements		d-block elements										p-block elements					
Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub						

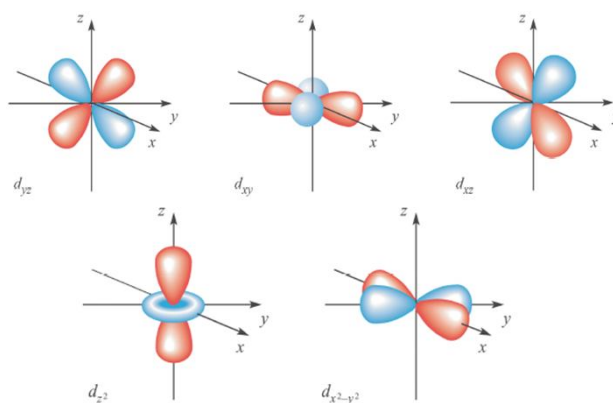
• d-block elements include Sc-Zn, Y-Cd, La(or Lu)-Hg.

H&S, Fig 1.13, p. 23

- Valence orbitals for d-block elements:  $ns, (n-1)d, np$
- Transition elements: atom has an incomplete d-subshell (d-orbitals still filling), OR atom gives rise to a cation with an incomplete d-subshell
- Why "transition" metals?

s-metals form ionic compounds; p-metals (Grps 13-16) show high degree of covalent bonding. The **transition** from mainly ionic to mainly covalent bonding occurs from Group 4 to 11.

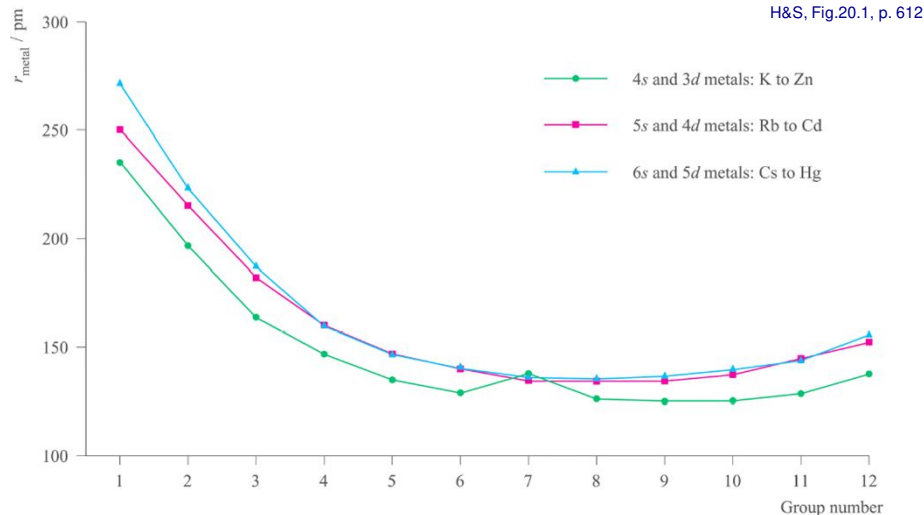
## Transition metal chemistry is d-orbitals/electrons



H&S, Fig 1.1, p. 15

- Properties of transition metal ions are very sensitive to the # of d-electrons *and* how they are arranged in the d-orbitals
- Knowledge of  $d^n$  is critical to understanding colours, magnetism, and reactions of TM ions.

## The d-block elements: trends in metallic radii



- d-block metals mostly much smaller than corresponding s-block metals
- within “triads”, 1st row d-block metals much smaller than 2nd or 3rd row metals
- “lanthanoid contraction”: 2nd and 3rd row radii very similar

## The d-block elements

- metallic solids: mostly the same structures we’ve already seen

H&S, Table 6.2, p. 153

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1814	1941	2183	2180	1519	1811	1768	1728	1358	693
378	470	514	397	283	418	428	430	338	130
164	147	135	129	137	126	125	125	128	137
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
1799	2128	2750	2896	2430	2607	2237	1828	1235	594
423	609	721	658	677	651	556	377	285	112
182	160	147	140	135	134	134	137	144	152
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
1193	2506	3290	3695	3459	3306	2719	2041	1337	234
423	619	782	850	774	787	669	566	368	61
188	159	147	141	137	135	136	139	144	155

♦ = hcp; ● = ccp (fcc); ● = bcc  
 ← Metal lattice type  
 ← Melting point (K)  
 ← Standard enthalpy of atomization (kJ mol<sup>-1</sup>)  
 ← Metallic radius for 12-coordinate atom (pm)

- coinage metals
- platinum group (Ru, Os, Rh, Ir, Pd, Pt)
- “triads”

- similarity of metallic radii leads to easy formation of alloys (H&S 6.7, pp.155-158)

Alloys: Intimate mixtures (or even compounds) of two or metals, or metals and non-metals, which changes the physical and chemical properties of them aterial

e.g. substitutional alloys

Atoms of “solute” metal occupy sites in the lattice of the “solvent” metal. E.g. sterling silver - 92.5% Ag, 7.5% Cu - both metals adopt ccp lattices and their  $r_{\text{metal}}$  are similar

e.g. interstitial alloys

Atoms of solute occupy Oh or Td interstitial holes in the lattice of the solvent. E.g. carbon steels (0.03 - 1.5% C). E.g. of both sub and interstit = stainless steels Mn, Ti, V, Co, W

## The d-block elements: variable oxidation states

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	0	0	0	0	0	0	0	[0]	[2]
3	2	2	2	2	2	2	2	1	
	3	3	3	3	3	3	3	2	
	4	4	4	4	4	4	4	3	
		5	5	5				[4]	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
			0	0	0	0	0	1	[2]
3	2	2	2	[2]	2	2	2	2	
	3	3	3	3	3	3	3	3	
	4	4	4	4	4	4	4		
		5	5	5	5	5			
			6	6	6	6			
				7	7				
				8	8				
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
			0	0	0	0	0	[0]	1
3	2	2	2	1	2	1	2	1	2
	3	3	3	3	3	3	3	[2]	
	4	4	4	4	4	4	4	3	
		5	5	5	5	5	5	5	
			6	6	6	6	6		
				7	7				
				8	8				

**-d block elements have many oxidation states available to them and therefore different colours, reactivities and coordination complexes**

**-due to size and general similarity across the T.M.  $\text{Fe}^{2+}$  and  $\text{Co}^{3+}$  have more in common than  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$**

H&S, Table 20.3, p. 618

### Electron configurations of the d-block elements and ions

- Aufbau principal dictates orbitals are filled in the order of lowest energy to highest. For the transition *element* valence orbitals, this is:  $ns < (n-1)d < np$

e.g. first row transition elements:  $\text{Ti}^{(0)} 4s^2 3d^2$ ;  $\text{Pd}^{(0)} 4s^2 3d^8$  (recall  $\text{Cr}^{(0)} 4s^1 3d^5$ )

- For higher oxidation states  $M^{n+}$ , however, the energies of  $(n-1)d$  orbitals tend to be lower in energy than the  $ns$  orbitals.

(Recall: orbital energies affected by principal quantum number ( $n$ ), effective nuclear charge experienced by electrons ( $Z_{\text{eff}}$ ) and  $e^-e^-$  repulsions as subshells are filled.) Removal of one or more electrons (oxidation) reduces overall  $e^-$  repulsion and lowers energy; this effect is most pronounced for d-orbital energies, relative to s or p. Consequence: loss of  $1e^-$  prompts reorganization of energy levels; remaining  $e^-$  "fall" into d-orbitals, which are now lower in energy. Effect even more pronounced for loss of  $2e^-$  to give  $M^{2+}$ .

- Transition metal *ions* (mostly) have no s-electrons, only d-electrons in their valence shell.

Can think of  $M^{2+}$  (and higher OS) as having lost the  $ns^2$  electrons "first" (most easily).

- Therefore we discuss the electron configurations of  $M^{n+}$  as " $d^n$ "

here " $n$ " is *not* the principal quantum number or the charge - it is the number of d-electrons in the valence shell of the T.M. ion.

E.g.  $\text{Ti}^{3+}$  has  $d^1$  configuration;  $\text{Cr}^{3+}$  is  $d^3$ ,  $\text{V}^{5+}$  is  $d^0$

## Electron configurations of the d-block ions: $d^n$

- Find  $d^n$  for any transition metal ion using by checking its group number in the periodic table:  $n = \text{group \#} - \text{charge on ion}$

E.g.  $\text{Ti}^{3+}$ :  
 Ti is in group 4  
 charge is +3  
 $n = 4 - (+3) = 1$   
 Therefore  $\text{Ti}^{3+}$  has  $d^1$  configuration

$\text{Ti}^{(0)}$  has  $4s^2 3d^2$ . Removing  $3e^-$  should give  $4s^1$  configuration, based on orbital filling order, but ionization causes the 3d orbitals to drop lower than 4s in energy, so the configuration becomes  $3d^1 4s^0$ , or  $d^1$ .

Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

## Electron configurations of the d-block ions: $d^n$

- Find  $d^n$  for any transition metal ion using by checking its group number in the periodic table:  $n = \text{group \#} - \text{charge on ion}$

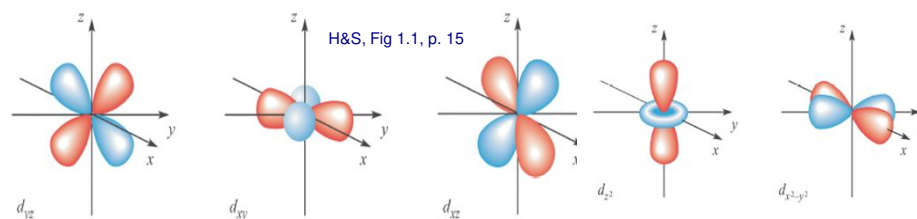
E.g.  $\text{Ti}^{3+}$ :  
 Ti is in group 4  
 charge is +3  
 $n = 4 - (+3) = 1$   
 Therefore  $\text{Ti}^{3+}$  has  $d^1$  configuration

$\text{Ti}^{(0)}$  has  $4s^2 3d^2$ . Removing  $3e^-$  should give  $4s^1$  configuration, based on orbital filling order, but ionization causes the 3d orbitals to drop lower than 4s in energy, so the configuration becomes  $3d^1 4s^0$ , or  $d^1$ .

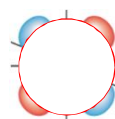
E.g.  $\text{Ni}^{2+}$ :  
 Ni is in group 10  
 charge is +2  
 $n = 10 - (+2) = 8$   
 Therefore  $\text{Ni}^{2+}$  has  $d^8$  configuration

Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12
21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

## Impact of the filling d-shell on properties of transition metal ions



Recall diffuseness of the d-orbitals: they penetrate the nucleus far less than s or p-orbitals. They stick out to the edges of the metal ion. The  $e^-$  in the d-shell are affected more by the surrounding electronic environment (i.e. solvent, ligands) than s or p electrons would be.



- Properties of transition metal ions are very sensitive to the # of d-electrons *and* how they are arranged in the d-orbitals

Likewise, the d-electrons themselves also influence significantly the metal ion's coordination environment.

- Knowledge of  $d^n$  is critical to understanding colours, magnetism, and reactions of TM ions.

## More common ligands in transition metal complexes

Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Dimethylsulfoxide	DMSO	Monodentate	
Acetylacetonate ion	[acac] <sup>-</sup>	Bidentate	
Oxalate or ethanedioate ion	[ox] <sup>2-</sup>	Bidentate	
2,2'-Bipyridine	bpy or bipy	Bidentate	
1,10-Phenanthroline	phen	Bidentate	
1,4,7-Triazaheptane <sup>‡</sup>	dien	Tridentate	
1,4,7,10-Tetraazadecane <sup>‡</sup>	trien	Tetradentate	
N,N',N'',N'''-Ethylenediaminetetraacetate ion <sup>‡</sup>	[EDTA] <sup>4-</sup>	Hexadentate	See equation 7.75

<sup>‡</sup> The older names (still in use) for 1,2-ethanediamine, 1,4,7-triazaheptane and 1,4,7,10-tetraazadecane are ethylenediamine, diethylenetriamine, triethylenetetramine.

<sup>‡</sup> Although not systematic by the IUPAC rules, this is the commonly accepted name for this anion.

**Triphenylphosphine**

**monodentate**

**PPh<sub>3</sub>**

H&S, Table 7.7b,c, p. 204

## Some common ligands in transition metal complexes

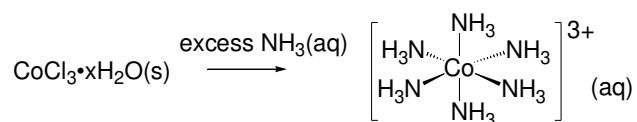
Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Water		Monodentate	
Ammonia		Monodentate	
Tetrahydrofuran	THF	Monodentate	
Pyridine	py	Monodentate	
1,2-Ethanediamine <sup>†</sup>	en	Bidentate	

<sup>†</sup> The older names (still in use) for 1,2-ethanediamine, 1,4,7-triazaheptane and 1,4,7,10-tetraazadecane are ethylenediamine, diethylenetriamine and triethylenetetramine. [H&S, Table 7.7a, p. 204](#)

Notice these are all neutral ligands. CO is another e.g. of a neutral monodentate L. Can also have anionic ligands: Cl<sup>-</sup>, halides, OH<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, CN<sup>-</sup>, SCN<sup>-</sup>

Bidentate en can bind to a central metal atom/ion with more than one donor atom. Is a *chelating* ligand, and gives *chelate* rings (e.g. 5-membered ring), which are characterized by the size of a *bite angle*.

## Coordination chemistry of the d-block elements



### Properties:

Octahedral complex

6 NH<sub>3</sub> in inner coordination sphere

3 Cl<sup>-</sup> in outer coordination sphere and H<sub>2</sub>O

Lewis acid: Co, Lewis Base: NH<sub>3</sub>

NH<sub>3</sub> is a ligand and monodentate

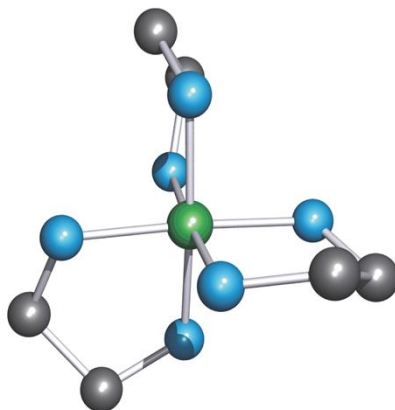
Diamagnetic, low spin, d<sup>6</sup>

If AgNO<sub>3</sub> was added 3 equivalents of AgCl would ppt.

Yellow complex, absorbs violet light

7.12

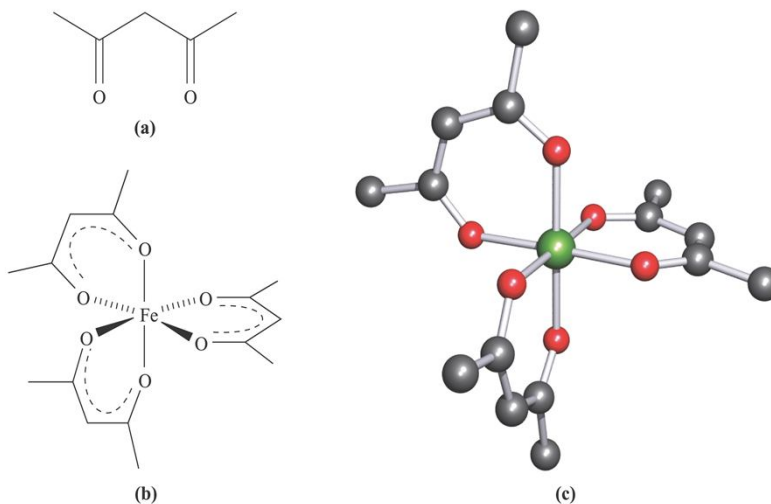
## Metal: ligand complex (bidentate ligand)



**Fig. 7.12** This modelled structure of a complex  $[M(en)_3]^{n+}$  illustrates that the ligand en coordinates to give a puckered chelate ring. Colour code: M, green; N, blue; C, grey.

Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008

7.10



**Fig. 7.10** (a) The structure of pentane-2, 4-dione (acetylacetone), Hacac; (b) Fe(III) forms an octahedral complex with  $[acac]^-$ ; (c) the structure of the coordination complex  $[Fe(acac)_3]$ , determined by X-ray diffraction [J. Iball *et al.* (1967) *Acta Crystallogr.*, vol. 23, p. 239]. Colour code: Fe, green; C, grey; O, red.

Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008

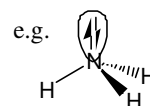


## Predicting structures of coordination complexes

- VSEPR works well for compounds of the s- and p-block elements

e.g.  $\text{NH}_3$

3 bonding pairs (N-H bonds)  
1 non bonding pair (lone pair)  
lone pair is stereochemically active  
 $\therefore$  tetrahedral electronic geometry  
 $\therefore$  trigonal pyramidal molecular geometry



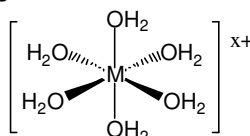
- VSEPR does not explain the d block metal complexes

e.g.  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

$d^8$

$[\text{V}(\text{H}_2\text{O})_6]^{3+}$

$d^2$



two M complexes have identical geometries, despite very different  $e^-$ -configurations!

- Metal complex structures are not *directly* affected by the number or presence of non-bonding electrons.

i.e. non-bonding electrons are **not** stereochemically active

## Predicting structures of coordination complexes

- For coordination complex geometries, use the “Kepert model”: ligands considered to repel each other as do point charges ( $e^-$  pairs) in VSEPR model.

This model predicts structure of complex based on coordination number (C.N.):

<u>Coordination Number</u>	<u>Geometry</u>
2	linear
3	trigonal planar (TP)
4	tetrahedral (Td) or square planar
5	trigonal bipyramidal (TBP) or square pyramidal (Sq. Py)
6	Octahedral (Oh)

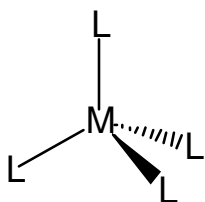
These geometries predominate, although real structures can be distorted:  
e.g. steric effects (very bulky ligands, restricted or stiff chelate rings) or electronic effects (issues of orbital filling/energies)

TABLE 9.3 Overview of molecular geometries

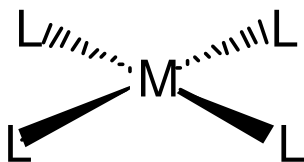
Electron Pairs	2	3	4	5	6
Electron Pair Geometry					
	Linear	Trigonal planar	Tetrahedral	Trigonal bipyramidal	Octahedral
Molecular Geometry: Zero Lone Pairs					
	Linear AB <sub>2</sub>	Trigonal planar AB <sub>3</sub>	Tetrahedral AB <sub>4</sub>	Trigonal bipyramidal AB <sub>5</sub>	Octahedral AB <sub>6</sub>
Molecular Geometry: One Lone Pair					
		Bent (V-shaped) AB <sub>2</sub>	Trigonal pyramidal AB <sub>3</sub>	Seesaw AB <sub>5</sub>	Square pyramidal AB <sub>6</sub>
Molecular Geometry: Two Lone Pairs					
			Bent (V-shaped) AB <sub>2</sub>	T-shaped AB <sub>5</sub>	Square planar AB <sub>4</sub>
Molecular Geometry: Three Lone Pairs					
				Linear AB <sub>2</sub>	

Copyright © 2007 Pearson Benjamin Cummings. All rights reserved.

Coordination number : 4

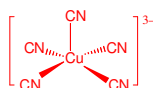
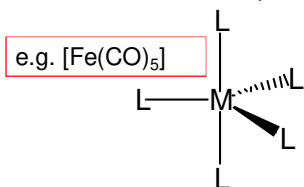


e.g.  $[\text{MnO}_4]^-$  ( $d^0$ )  $[\text{CoCl}_4]^{2-}$  ( $d^7$ )  
 $[\text{Ni}(\text{Br})_4]^{2-}$  ( $d^8$ )  $[\text{Ni}(\text{CO})_4]$  ( $d^{10}$ )



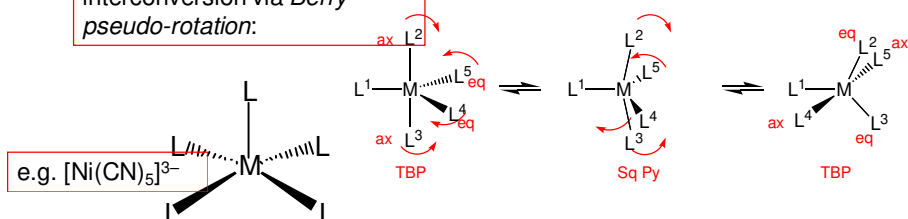
Square planar geometry less common but happens when planarity is important and when  $\pi$  bonding occurs.  
 also strongly favoured for  $d^8$  ions ( $\text{Ni}^{2+}$ ,  $\text{Rh}^+$ ,  $\text{Pt}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Au}^{3+}$ )  
 e.g.  $[\text{PdCl}_4]^{2-}$   $[\text{RhCl}(\text{PPh}_3)_3]$   
 $\text{trans-}[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$   
 Exceptions: some  $\text{Ni}^{2+}$  complexes are Td (see above)

Coordination number: 5  
(less common than 4 or 6)

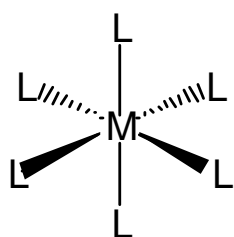


Very close in energies; facile interconversion via *Berry pseudo-rotation*:

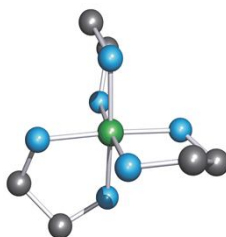
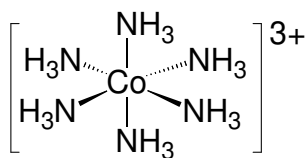
Exists as mixture of both TBP & SqPy



Coordination number: 6

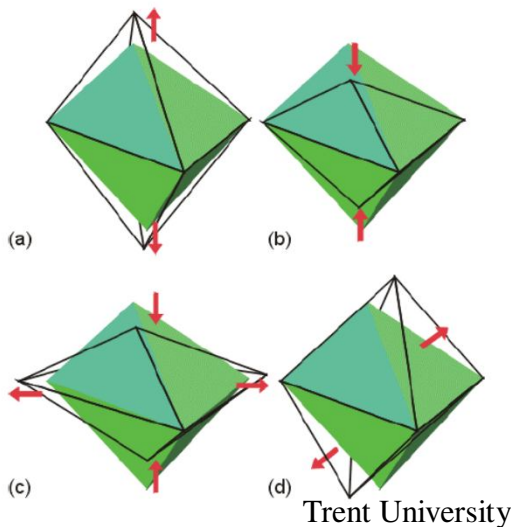


common coordination number  
found for  $d^0$  to  $d^9$  metals  
highly symmetrical in undistorted form



## Distortions from Octahedral Geometry

- Compression or elongation of opposite vertices leads to tetragonal distortion (a) and (b)
- Also rhombic (c) and trigonal distortions (d)



Structures can be studied by their distortions from octahedral

## Unusually low or high coordination numbers

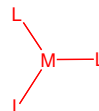
•  $CN \leq 3$  are unusual. Metal “prefers” to be surrounded by a minimum of 4L. Linear (CN 2) or trigonal planar (CN 3) complexes mainly observed for:

(i)  $d^{10}$  atoms or ions such as  $Cu^+$ ,  $Ag^+$ ,  $Au^+$ ,  $Hg^{2+}$

e.g.  $[Cl-Cu-Cl]^-$   $[H_3N-Ag-NH_3]^+$   $[Ph_3P-Au-Cl]$   $[Cu(CN)_3]^{2-}$   $[Pt(PPh_3)_3]$

(ii) Other  $d^n$ , with very bulky ligands

e.g.  $[Y\{N(SiMe_3)_2\}_3]$  -this is the bis(trimethylsilyl)amide ligand, a bulky version of  $NH_2^-$  (draw this)

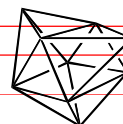


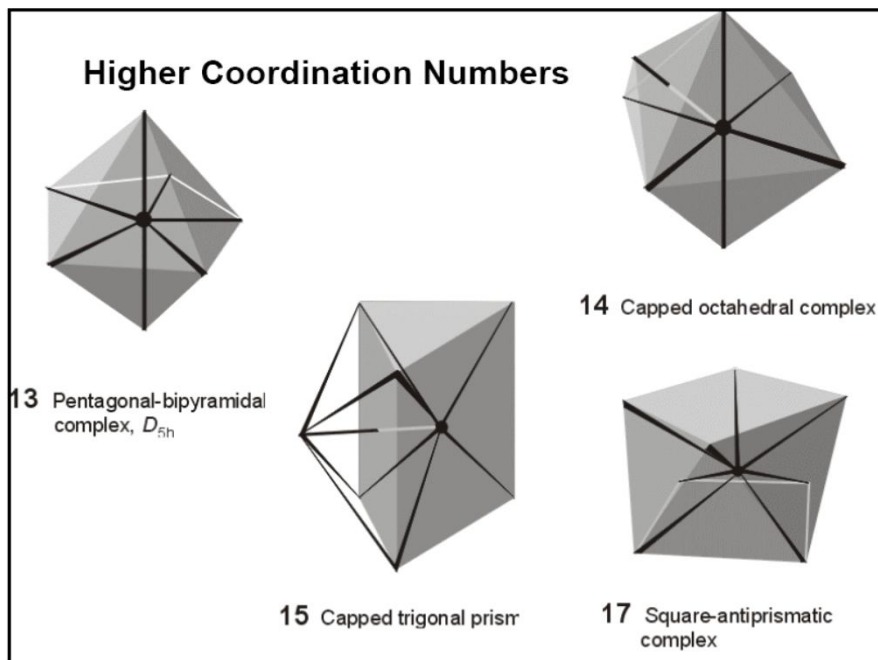
•  $CN \geq 7$  are seen for “early” metal ions and those with very large  $r_{catino}$ . These complexes have more possible geometries (e.g. pentagonal or hexagonal bipyramids, monocapped octahedrons, tricapped trigonal prisms).

e.g. C.N. =7  $[NbF_7]^{3-}$   $[V(CN)_7]^{4-}$

e.g. C.N. =8  $Na_3[TaF_8]$   $[Y(H_2O)_8]^{3+}$

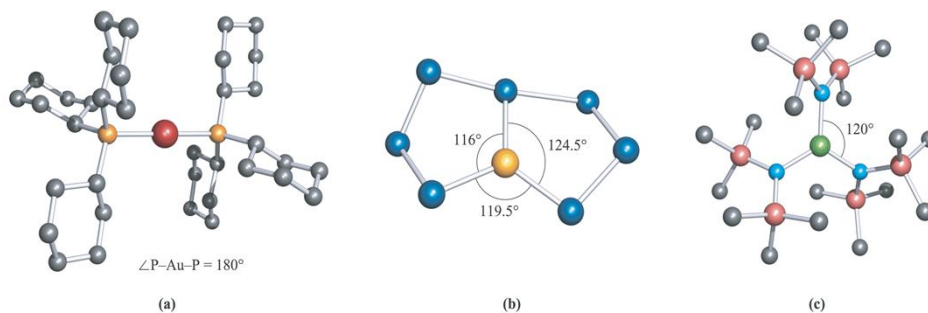
e.g. C.N. =9  $[ReH_9]^{2-}$





Not to memorise

#### 20.4

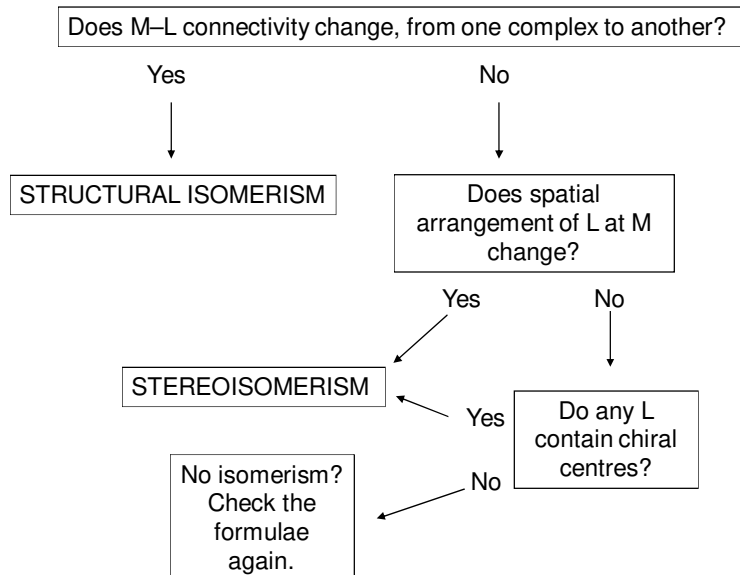


**Fig. 20.4** Examples of 2- and 3-coordinate structures (X-ray diffraction data): (a)  $[\text{Au}\{\text{P}(\text{cyclo-C}_6\text{H}_{11})_3\}_2]^+$  in the chloride salt [J.A. Muir *et al.* (1985) *Acta Crystallogr., Sect. C*, vol. 41, p. 1174], (b)  $[\text{AgTe}_7]^{3-}$  in the salt  $[\text{Et}_4\text{N}][\text{Ph}_4\text{P}]_2[\text{AgTe}_7]$  [J.M. McConnachie *et al.* (1993) *Inorg. Chem.*, vol. 32, p. 3201] and (c)  $[\text{Fe}\{\text{N}(\text{SiMe}_3)_2\}_3]$  [M.B. Hursthouse *et al.* (1972) *J. Chem. Soc., Dalton Trans.*, p. 2100]. Hydrogen atoms are omitted for clarity. Colour code: Au, red; Ag, yellow; Fe, green; C, grey; P, orange; Te, dark blue; Si, pink; N, light blue.

Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008

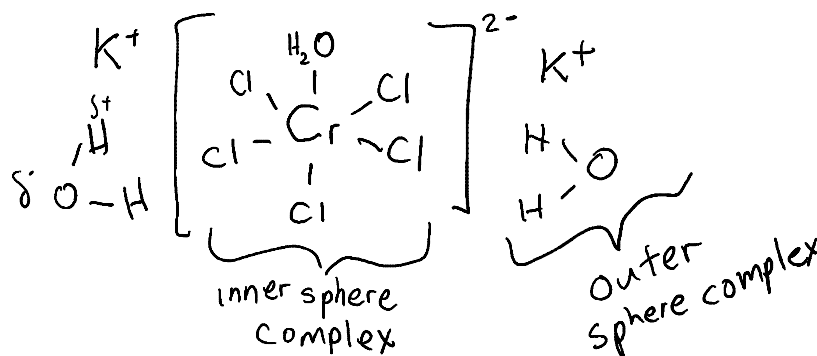
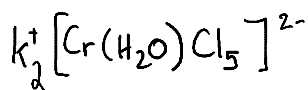
## Isomerism flowchart for coordination complexes

- For two or more compounds having the same formula:

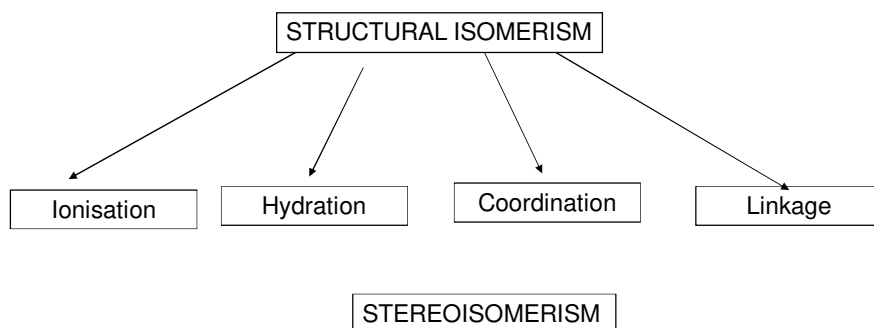


## Inner versus Outer Coordination Sphere

- Inner sphere complex** is the species formed only by the ligands directly attached to the central metal ion (primary coordination sphere)
- Outer sphere complex** is the same species expanded to include subsequent layers which interact at a distance
  - Counter ions through coulombic attraction
  - Solvent molecules orientated by dipole-dipole (can be induced) interactions



## Isomerism of coordination complexes



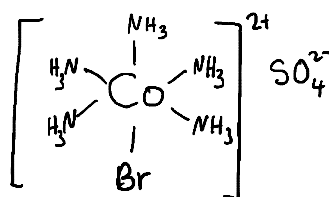
### Structural isomerism : ionization isomers

**1) Ionization isomers:** represent an exchange of different anions between inner & outer coordination spheres

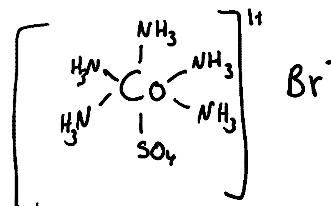
e.g.  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{SO}_4)$

vs

$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$



$(\text{Co}^{3+}, d^6)$



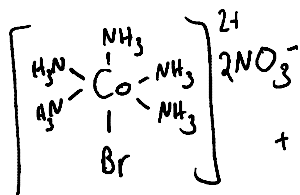
~distinguish  
by wet  
chemistry...

e.g.

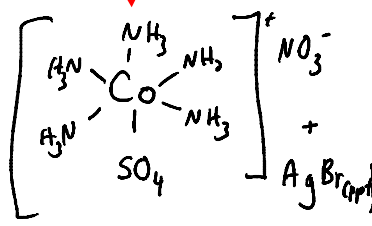
$\text{Pb}(\text{NO}_3)_2$  or  $\text{Ba}(\text{NO}_3)_2$

e.g.

$\text{AgNO}_3$



+  $\text{PbSO}_4(\text{ppt})$   
or  
 $\text{BaSO}_4(\text{ppt})$



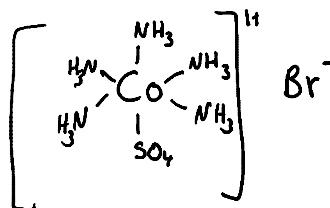
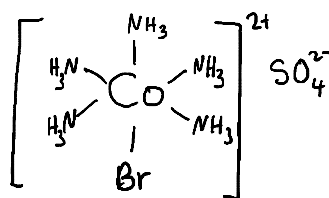
## Structural isomerism : ionization isomers

Note that ppt reactions ONLY affect the anions in the outer sphere.

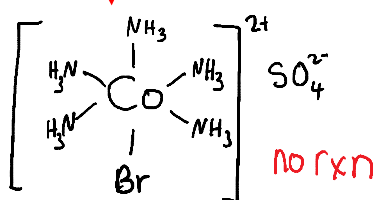
e.g.  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{SO}_4)$

vs

$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$

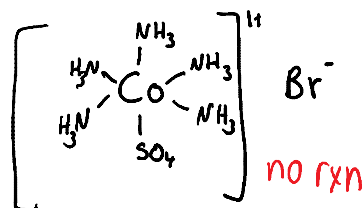


e.g.  
 $\text{AgNO}_3$



e.g.

$\text{Pb}(\text{NO}_3)_2$  or  $\text{Ba}(\text{NO}_3)_2$



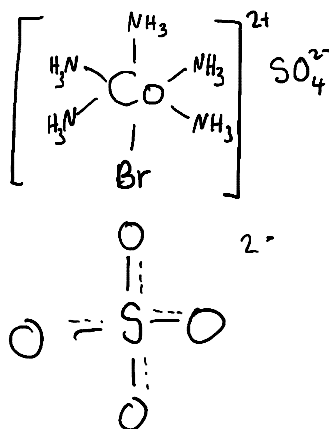
## Structural isomerism : ionization isomers

Can distinguish by IR spectroscopy

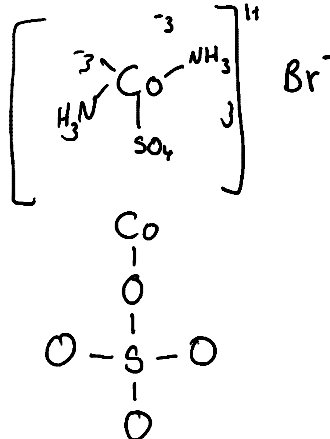
e.g.  $[\text{Co}(\text{NH}_3)_5\text{Br}](\text{SO}_4)$

vs

$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$



"free"  $\text{SO}_4^{2-}(\text{aq})$   
One  $\nu_{\text{sulphate}}$  stretch



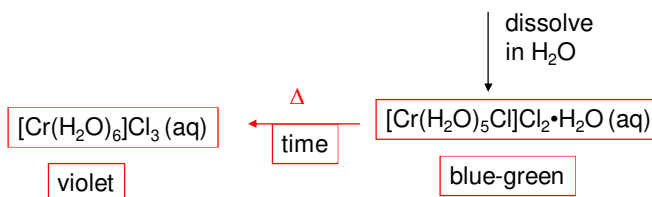
"bound"  $\text{SO}_4^{2-}$  ligand: lower symmetry  
three  $\nu_{\text{sulphate}}$  stretches



## Structural isomerism : hydration isomers

**2) Hydration isomers:** represent an exchange of  $\text{H}_2\text{O}$  and an anion between inner & outer coordination spheres

e.g. green crystals of chromium trichloride hydrate have formula  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$



How to tell these apart?

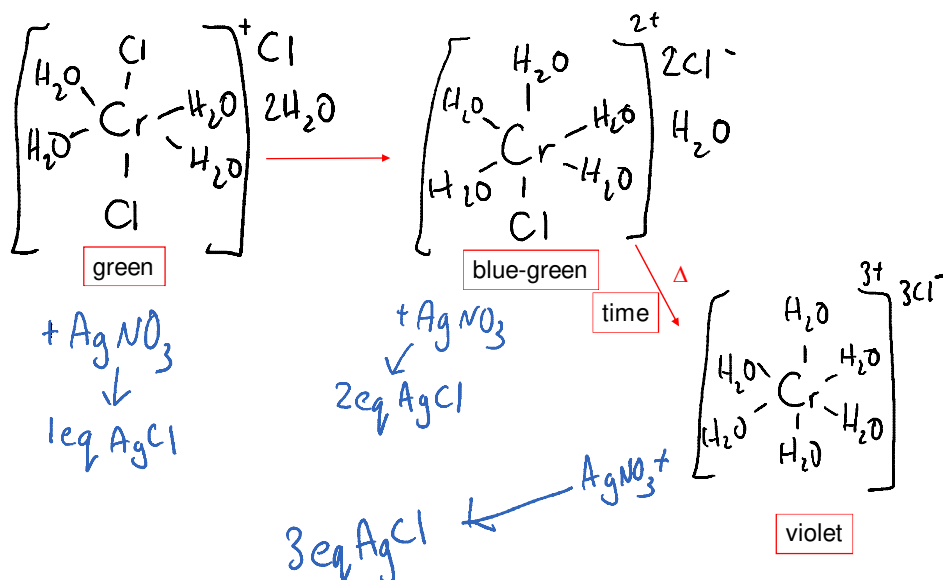
1) UV (diff colours)

2) quantitatively (wet chem)

e.g. ppt  $\text{Cl}^-$  ions with  $\text{Ag}^+$ , weigh ppt to find out # of equivalents of  $\text{Cl}^-$  that were in the outer coordination sphere

## Structural isomerism : hydration isomers

• Hydration isomers: represent an exchange of  $\text{H}_2\text{O}$  and an anion between inner & outer coordination spheres, can tell apart by UV and wet chemistry



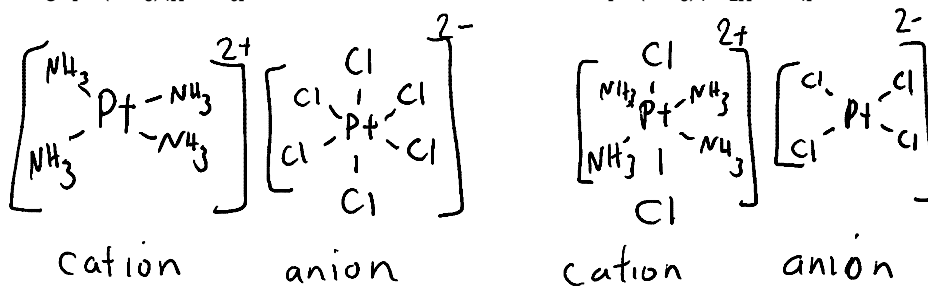
### Structural isomerism : coordination isomers

**3) Coordination isomers:** special case for salts in which both anion and cation are complex ions - represents exchange of ligands between the two metal centres

e.g.  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_6]$

vs

$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2][\text{PtCl}_4]$



Pt ox state    2+  
                   $d^8$

                  4+  
                   $d^6$

                  4+  
                   $d^6$

                  2+  
                   $d^8$

e.g.  $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$

vs

$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

### Structural isomerism : linkage isomers

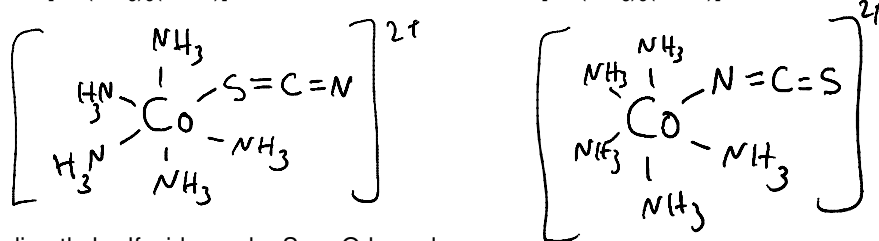
**4) Linkage isomers:** can be seen for ligands with two or more potential donor atoms

e.g. thiocyanate  $[\text{S}=\text{C}=\text{N}]^-$

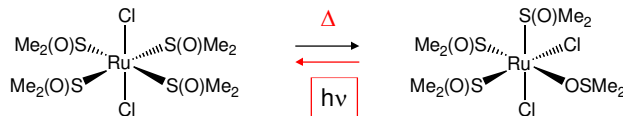
$[\text{Co}(\text{NH}_3)_5(\text{SCN})]^{2+}$

vs

$[\text{Co}(\text{NH}_3)_5(\text{NCS})]^{2+}$



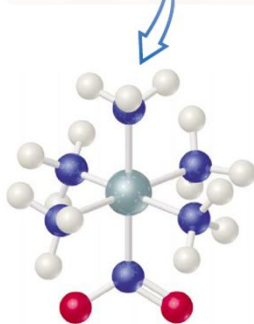
e.g. dimethyl sulfoxide can be S- or O-bound



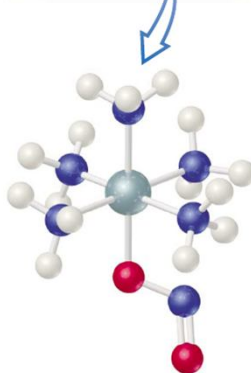
H&S, Eqn 20.11, p.629

## Linkage isomerism in coordination complexes

e.g.  $\text{NO}_2$  can be N- (nitro) or O- (nitrito) bound



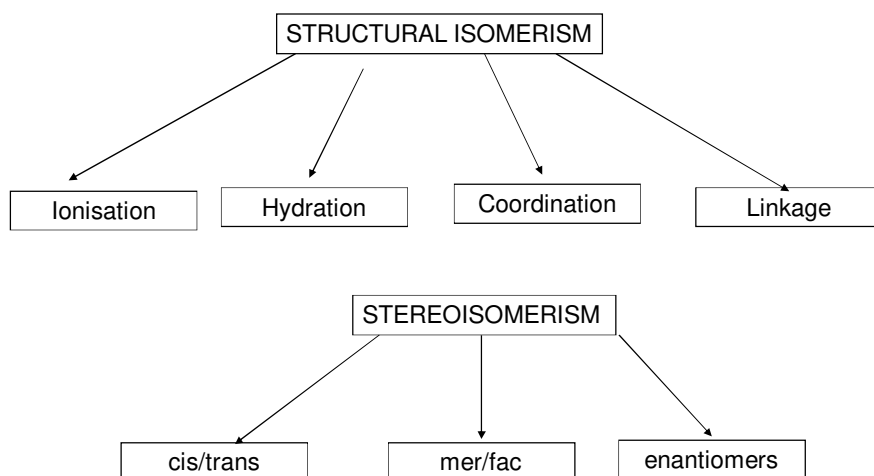
Nitro isomer



Nitrito isomer

Brown et al, Fig.24.18, p.1027

## Isomerism of coordination complexes

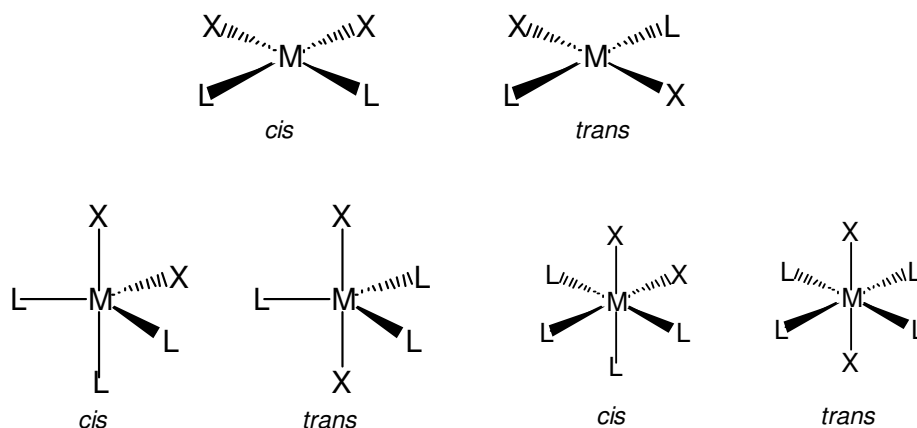


## Stereoisomerism in coordination complexes H&S 20.8

- Complexes with the same formula, for which L-to-M connectivity remains the same, but spatial arrangement of ligands is different.

~ These *stereoisomers* will have different physical and spectroscopic properties

- cis* (same side) and *trans* (opposite side) isomers

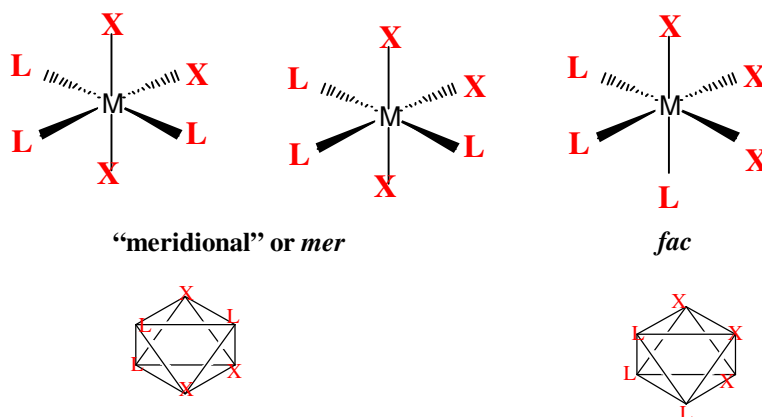


## Stereoisomerism in coordination complexes H&S 20.8

- Complexes with the same formula, for which L-to-M connectivity remains the same, but spatial arrangement of ligands is different.

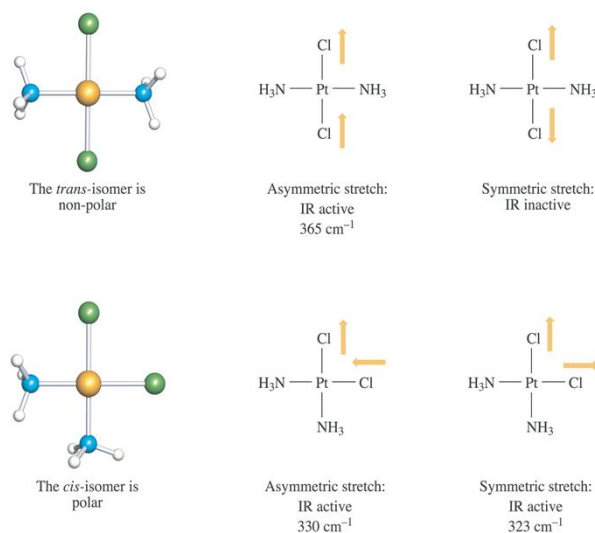
~ These *stereoisomers* will have different physical and spectroscopic properties

- facial (*fac*) and meridional (*mer*) isomers of octahedral complexes  $ML_3X_3$



## Stereoisomerism in coordination complexes

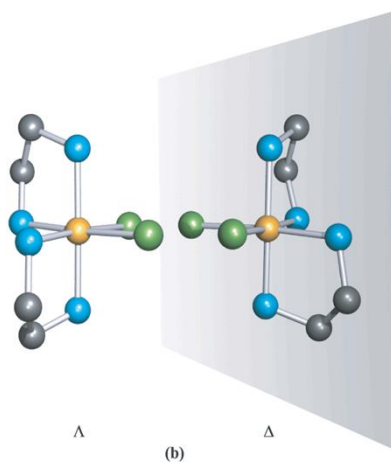
20.14



**Fig. 20.12** The *trans*- and *cis*-isomers of the square planar complex  $[\text{PtCl}_2(\text{NH}_3)_2]$  can be distinguished by IR spectroscopy. The selection rule for an IR active vibration is that it must lead to a *change in molecular dipole moment*.

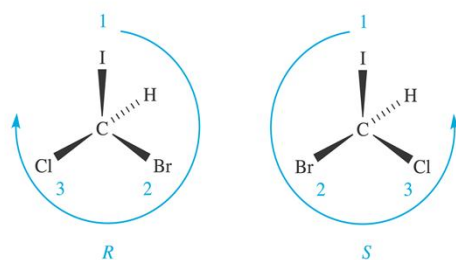
20.16

## Stereoisomerism in coordination complexes

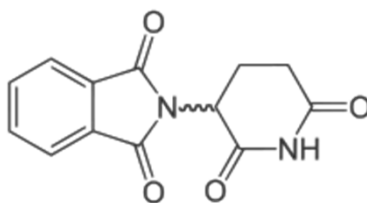


**Fig. 20.13b** The complexes (b) *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$  are chiral. The enantiomers are nonsuperposable mirror images of one another. Hydrogen atoms are omitted from the diagrams for clarity. Colour code: Cr, green; Co, yellow; Cl, green; N, blue; O, red; C, grey. (Continued)

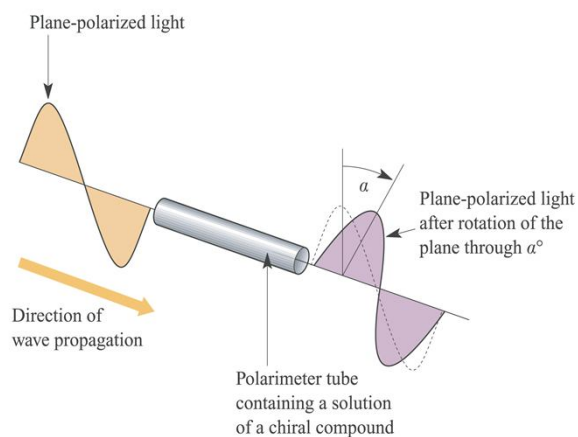
Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008

**Box 20.3a** Definitions and notation for chiral complexes.

Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008



## Stereoisomerism in coordination complexes



**Fig. 20.14** One enantiomer of a chiral compound rotates the plane of linearly polarized light through a characteristic angle,  $\alpha^\circ$ ; the instrument used to measure this rotation is called a polarimeter. The direction indicated (a clockwise rotation as you view the light as it emerges from the polarimeter) is designated as  $+\alpha^\circ$ . The other enantiomer of the same compound rotates the plane of polarized light through an angle  $-\alpha^\circ$ .

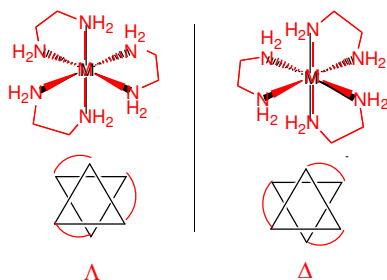
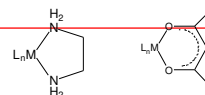
Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008

Stereoisomerism in coordination complexes (cont'd) M&S 20.8

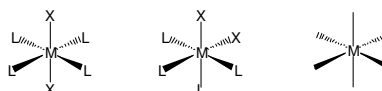
- Can also have *optical isomers* of *chiral* complexes.

- These *enantiomers* are non-superimposable mirror images, with identical physical and spectroscopic properties

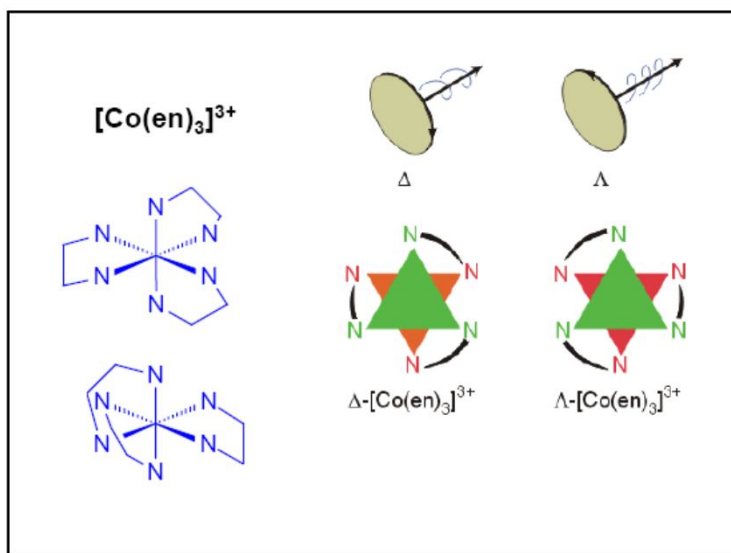
- relevant for Oh complexes containing bidentate ligands  
e.g. tris(chelate) complexes



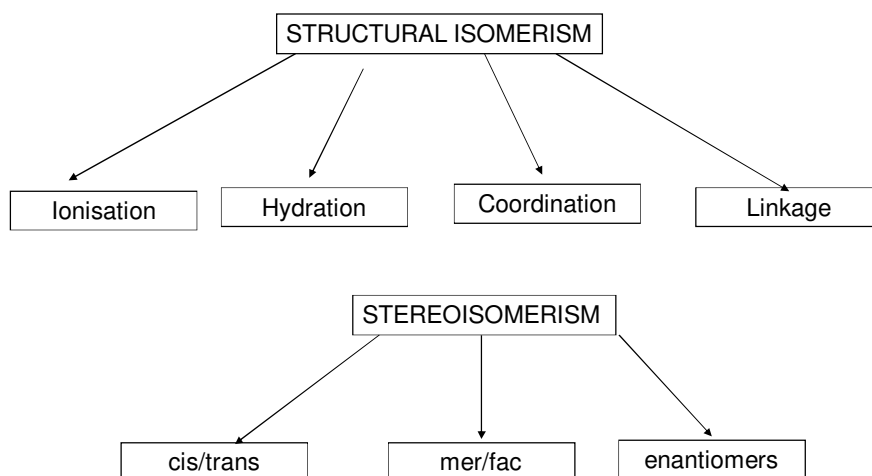
e.g. *cisoid* bis(chelate) complexes



materials capable of rotating plane-polarized light



## Isomerism of coordination complexes

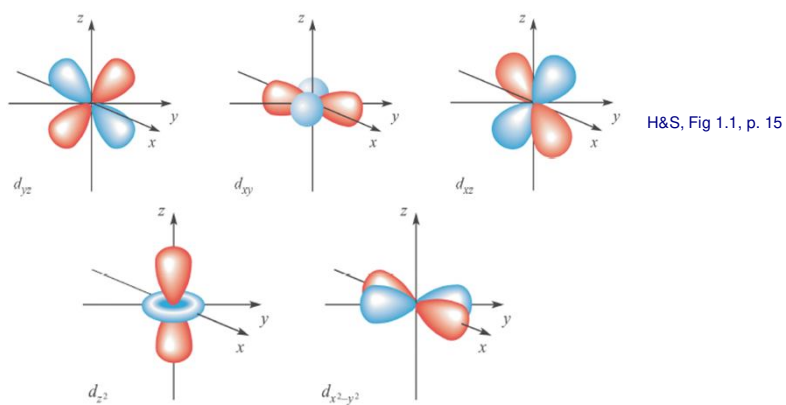




## Crystal Field Theory and Molecular Orbital Diagrams in $ML_n$ complexes.

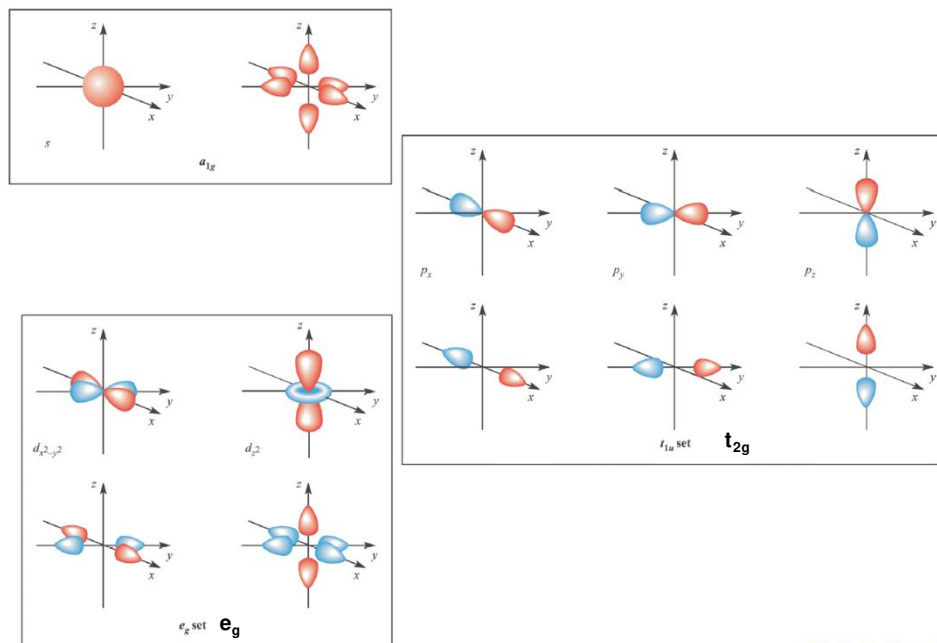


Transition metal chemistry is d-orbitals/electrons



- Properties of transition metal ions are very sensitive to the # of d-electrons *and* how they are arranged in the d-orbitals
- Knowledge of  $d^n$  is critical to understanding colours, magnetism, and reactions of TM ions.

### Symmetry matching of metal orbitals with ligand group orbitals



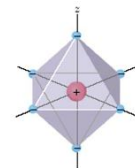
H&S, Fig21.12, p.649

### Crystal Field Theory

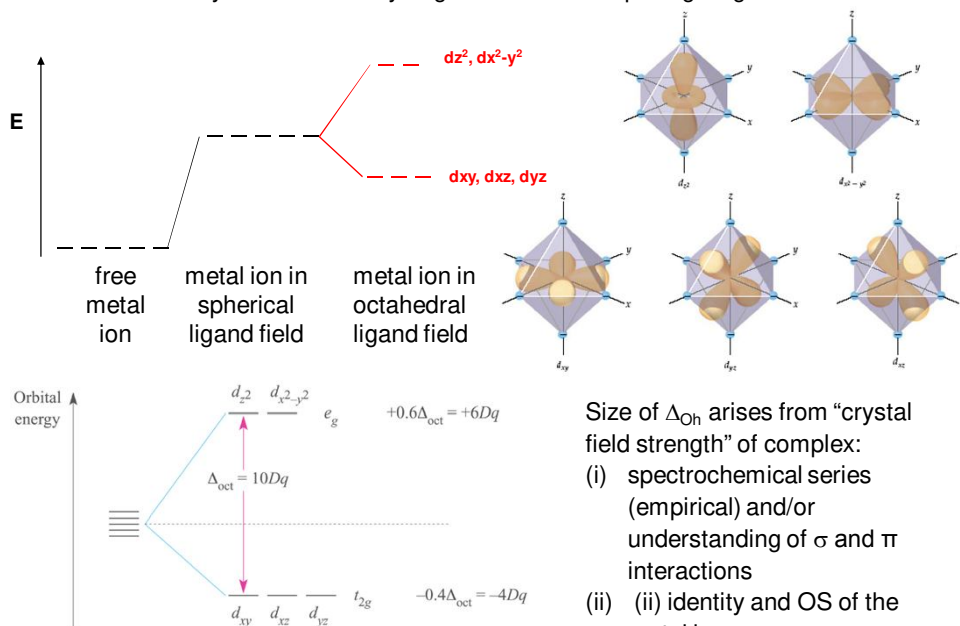
- *Crystal Field Theory* (CFT) provides a simple model for M-L interactions in coordination complexes, making it easier (than constructing a whole MO diagram) to predict the relative energies of the d-orbitals in these complexes. H&S 21.3, p.640
- CFT is an electrostatic model, which is pretty unrealistic, but it works really well for predicting the d-orbital splitting for a variety of complex geometries.
- Examines relative energies of the d-orbitals when  $M^+$  is placed in an "electric field" created by ligand (donor) electrons. Each L is considered as a "negative point charge".

Two features:

- (i) electrostatic *attraction* between  $M^+$  and L (holds complex together)
- (ii) electrostatic *repulsion* between electrons in d-orbitals and L point charges (destabilizes d-electrons - they are raised in energy - differently, depending on how directly the orbitals "point at" the ligands)



### Crystal Field Theory to generate an Oct splitting diagram

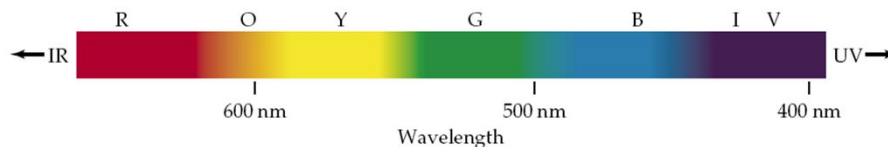


### Colours of transition metal complexes

- Colour arises from the absorption of light in the visible region of the spectrum. The colour (or energy) of the light absorbed represents the energy required to promote electrons from filled (or partially filled) orbitals to empty (or partially empty) orbitals.

H&S, Table 20.2, p.615

Colour of light absorbed	Approximate wavelength ranges / nm	Corresponding wavenumbers (approximate values) / $\text{cm}^{-1}$	Colour of light transmitted i.e. complementary colour of the absorbed light	In a 'colour wheel' representation, <sup>†</sup> complementary colours are in opposite sectors
Red	700–620	14 300–16 100	Green	
Orange	620–580	16 100–17 200	Blue	
Yellow	580–560	17 200–17 900	Violet	
Green	560–490	17 900–20 400	Red	
Blue	490–430	20 400–23 250	Orange	
Violet	430–380	23 250–26 300	Yellow	



Which solution is  $\text{Ni}(\text{NH}_3)_6^{3+}$  and which is  $\text{Ni}(\text{H}_2\text{O})_6^{3+}$ ?



Which solution is  $\text{Ni}(\text{NH}_3)_6^{3+}$  and which is  $\text{Ni}(\text{H}_2\text{O})_6^{3+}$ ?

N is less electronegative than O

∴  $\text{NH}_3$  is a stronger Lewis base than  $\text{H}_2\text{O}$  and will more readily donate its lone pair

∴ The M-L sigma bond for  $\text{Ni-NH}_3$  is stronger than  $\text{Ni-H}_2\text{O}$

∴ The  $\Delta_{\text{oct}}$  for  $\text{Ni}(\text{NH}_3)_6^{3+}$  is greater than  $\text{Ni}(\text{H}_2\text{O})_6^{3+}$

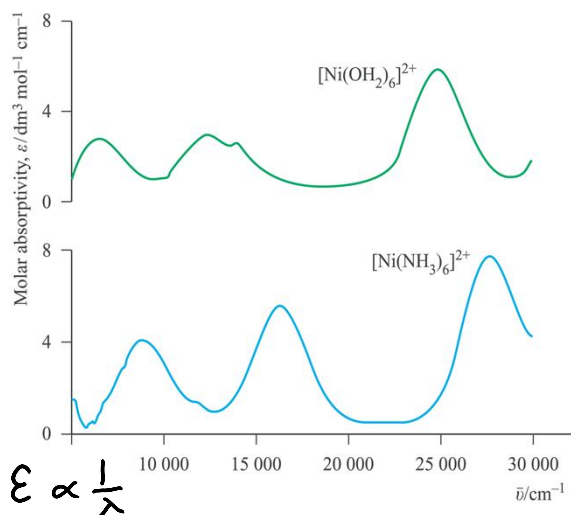
∴ Higher energy light will be absorbed by  $\text{Ni}(\text{NH}_3)_6^{3+}$  than by  $\text{Ni}(\text{H}_2\text{O})_6^{3+}$

• The green solutions will absorb red light and the violet solution will absorb yellow light.

• Yellow light is higher energy than red light.

Therefore the violet solution is  $\text{Ni}(\text{NH}_3)_6^{3+}$  and the green solution is  $\text{Ni}(\text{H}_2\text{O})_6^{3+}$

21.23



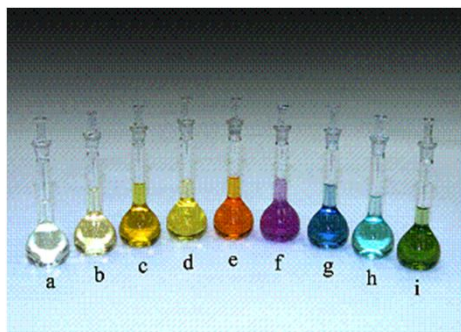
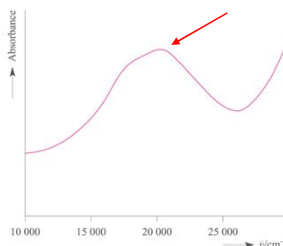
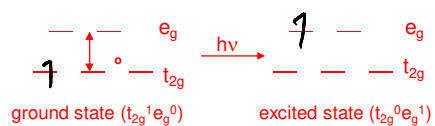
**Fig. 21.21** Electronic spectra of  $[\text{Ni}(\text{OH}_2)_6]^{2+}$  ( $0.101 \text{ mol dm}^{-3}$ ) and  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  ( $0.315 \text{ mol dm}^{-3}$ ) in aqueous  $\text{NH}_3$  solution) showing three absorption bands. Values of the molar absorptivity,  $\epsilon$ , are related to absorbance by the Beer–Lambert law (equation 21.12). [This figure is based on data provided by Christian Reber; see: M. Triest, G. Bussière, H. Bélisle and C. Reber (2000) *J. Chem. Ed.*, vol. 77, p. 670]

Housecroft and Sharpe, *Inorganic Chemistry*, 3rd Edition © Pearson Education Limited 2008

### Physical relevance of d-orbital splitting diagrams

- Colours of transition metal complexes: use electronic spectroscopy to measure  $\Delta_{\text{oct}}$

Simplest example: octahedral  $d^1$  complex

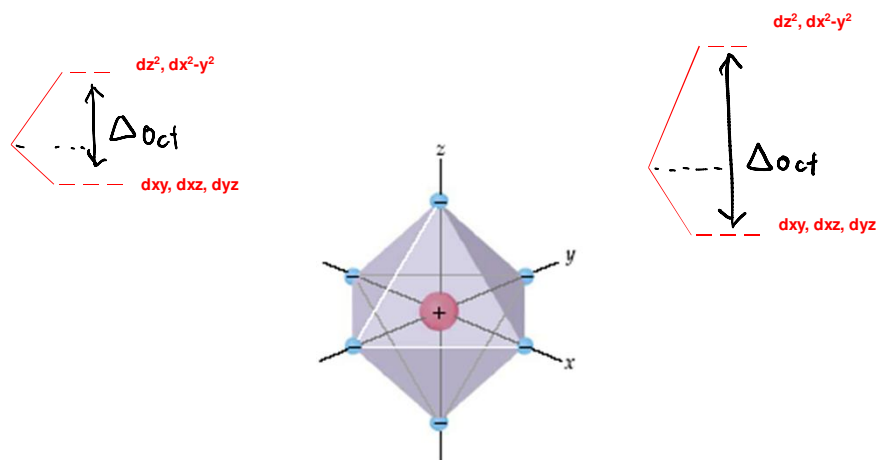


### The spectrochemical series & how to generate splitting diagrams

- Electronic spectroscopy studies of the complexes of many common ligands has allowed them to be ranked in terms of their overall effect on the size of  $\Delta_{\text{oh}}$ :



weak field ligands  $\longrightarrow$  increasing  $\Delta_{\text{oct}}$   $\longrightarrow$  strong field ligands



(a)  $\text{CN}^-$ , (b)  $\text{NO}_2^-$ , (c) phen, (d) en, (e)  $\text{NH}_3$ , (f) gly, (g)  $\text{H}_2\text{O}$ , (h)  $\text{ox}^{2-}$ , (i)  $\text{CO}_3^{2-}$ .

*The Chemical Educator*, Vol. 10, No. 2, Published on Web 02/03/2005,  
10.1333/s00897040867a, © 2005 *The Chemical Educator*

## The spectrochemical series

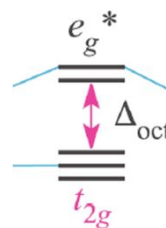
Amount of splitting  $\Delta_{\text{oct}}$  is due to the strength of the M-L  $\sigma$  bond

- Stronger Lewis Base ligands (ie  $\text{H}_2\text{O}$  vs  $\text{NH}_3$  vs  $\text{PPh}_3$  gives greater splitting (better able to donate their electron pair)
- Effect of  $\pi$  back donation
  - Ligands with filled p orbitals cannot receive electron density from the metal center through  $\pi$  back donation and therefore have a weaker  $\sigma$  bond
  - Ligands with empty p orbitals can receive electron density from the metal center through  $\pi$  back donation and therefore have a stronger  $\sigma$  bond

## Molecular Orbital Bonding in Coordination Complexes

Bonding between Ligands and Metal Complexes can be of three types

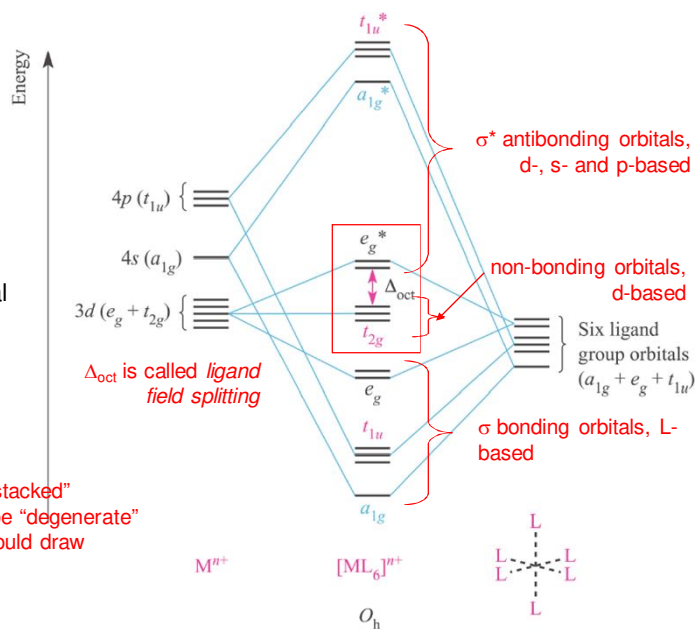
- a) Sigma bonds only
- b) Sigma plus pi donation from ligand (less  $\Delta_{\text{oct}}$  splitting)
- c) Sigma plus pi donation to ligand (greater  $\Delta_{\text{oct}}$  splitting)



## Molecular Orbital Bonding in coordination complexes (sigma bonding)

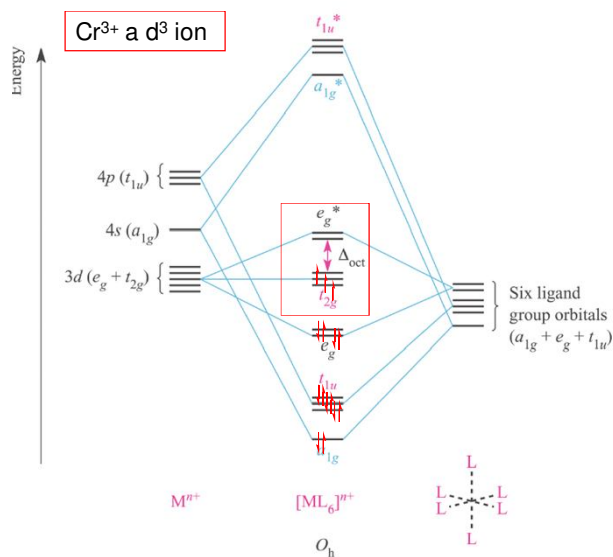
- An approximate MO diagram for the bonding in a six-coordinate,  $O_h$ , first-row transition metal complex, in which six identical ligands participate in sigma bonding with the metal ion.

Note: these clusters of "stacked" orbitals are intended to be "degenerate" within each stack. I.e. could draw frontier MOs like this:



## Molecular Orbital Bonding in coordination complexes (sigma bonding)

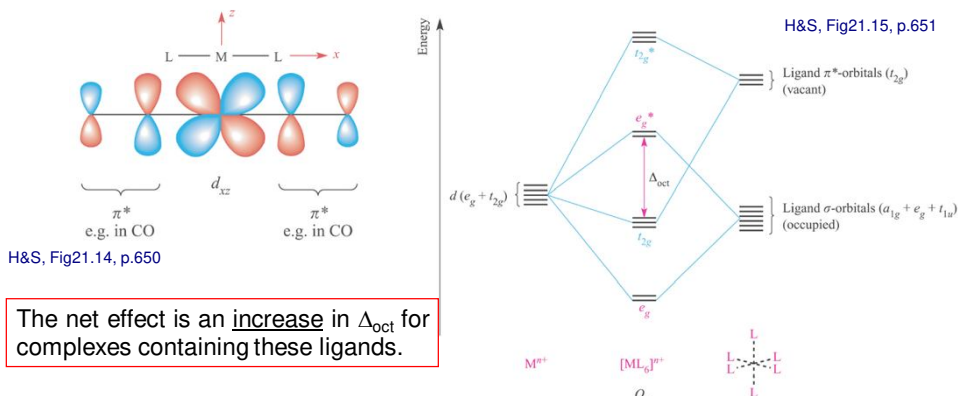
- With the approximate MO diagram in hand, fill with valence electrons for an  $O_h$ , first-row transition metal complex, such as  $[Cr(NH_3)_6]^{3+}$ , in which six identical ligands participate in  $\sigma$ -bonding with the metal ion.



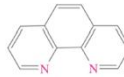
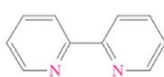


### Molecular Orbital Bonding in $ML_6$ complexes (sigma bonding and $\pi$ -donation to ligand)

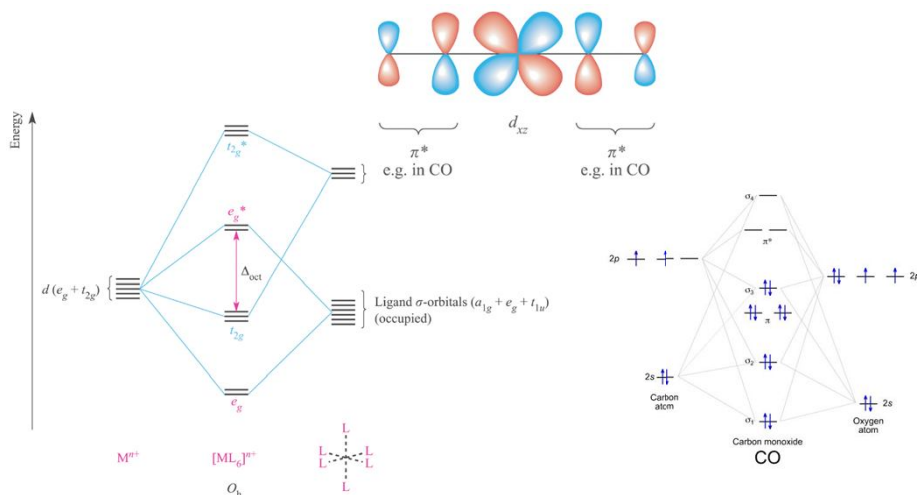
Ligands that are capable of  $\pi$ -acceptance from filled (or partially filled) metal d-orbitals ( $\pi$ -backbonding) also have additional effects on the d-orbital splitting in their metal complexes.



Other  $\pi$ -acceptor ligands include  $CN^-$  and, unlike their amine congeners, phosphines,  $PR_3$ . Finally, bipy and phen, because of their  $\pi$ -conjugated structures, also have "accessible, empty  $\pi^*$  orbitals, which make them " $\pi$ -acidic" relative to saturated N-donors like en and dien.



### Molecular Orbital Bonding in $ML_6$ complexes (sigma bonding and $\pi$ -donation to ligand)

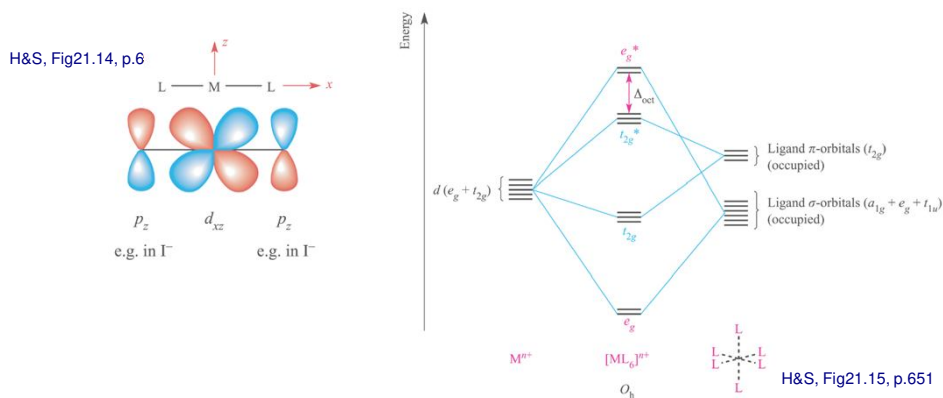


### Molecular Orbital Bonding in $ML_6$ complexes (sigma bonding and $\pi$ -donation from ligand)

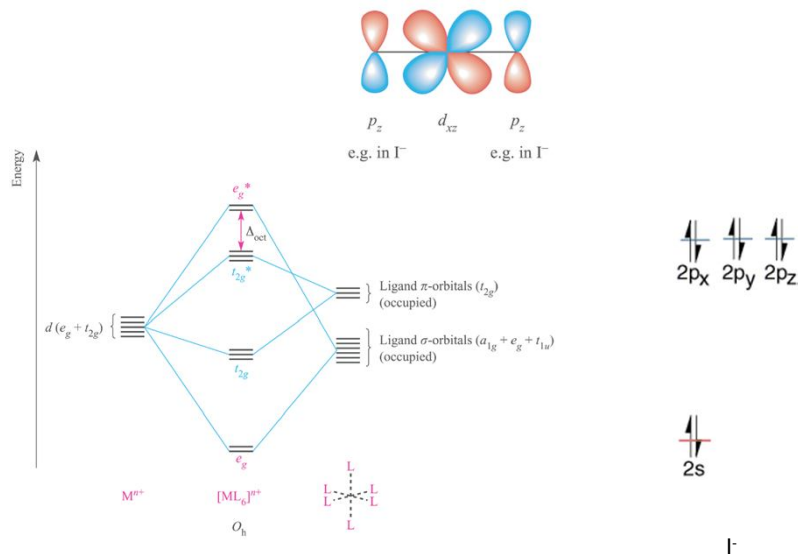
- Ligands that, in addition to  $\sigma$ -donation, are capable of  $\pi$ -donation to empty (or partially-filled) metal d-orbitals, have additional effects on the d-orbital splitting in their metal complexes (eg, halides).

The net effect is a decrease in  $\Delta_{O_h}$  for complexes containing these ligands.

$\pi$ -donor ligands can help stabilize metals in high OS.



### Molecular Orbital Bonding in $ML_6$ complexes (sigma bonding and $\pi$ -donation from ligand)



# Rules to determine the degree of d-orbital splitting

H&S 21.1

1) For a given  $M^{n+}$  ion, varying L gives predictable *trends* in  $\Delta_{Oh}$

p.637

$I^- < Br^- < [NCS]^- < Cl^- < F^- < [OH]^- < [ox]^{2-} \sim H_2O < [NCS]^- < py < NH_3 < en < bpy < phen < PPh_3 < [CN]^- \sim CO$



2) For a given  $ML_n$  with M in different OS: higher OS gives larger  $\Delta_{Oh}$  (Higher charge, better Lewis acid)



3) For a given  $[ML_n]^{x+}$  for metals in a single triad: heavier M gives larger  $\Delta_o$

4) (A *non-trend*) The trend in  $\Delta_o$  across the transition series is completely irregular. (For a given  $ML_n$  with M in the same OS.)

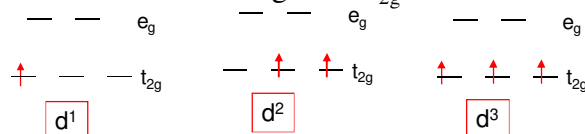
## Physical relevance of d-orbital splitting (spectroscopy)

Complex	$\Delta / \text{cm}^{-1}$	Complex	$\Delta / \text{cm}^{-1}$
$[TiF_6]^{3-}$	17 000	$[Fe(ox)_3]^{3-}$	14 100
$[Ti(OH_2)_6]^{3+}$	20 300	$[Fe(CN)_6]^{3-}$	35 000
$[V(OH_2)_6]^{3+}$	17 850	$[Fe(CN)_6]^{4-}$	33 800
$[V(OH_2)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(NH_3)_6]^{3+}$	22 900
$[Cr(OH_2)_6]^{3+}$	17 400	$[Co(NH_3)_6]^{2+}$	10 200
$[Cr(OH_2)_6]^{2+}$	14 100	$[Co(en)_3]^{3+}$	24 000
$[Cr(NH_3)_6]^{3+}$	21 600	$[Co(OH_2)_6]^{3+}$	18 200
$[Cr(CN)_6]^{3-}$	26 600	$[Co(OH_2)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(OH_2)_6]^{2+}$	8 500
$[Fe(OH_2)_6]^{3+}$	13 700	$[Ni(NH_3)_6]^{2+}$	10 800
$[Fe(OH_2)_6]^{2+}$	9 400	$[Ni(en)_3]^{2+}$	11 500

## Physical relevance of d-orbital splitting diagrams (spin and magnetism)

- High spin complexes have the maximum number of unpaired electrons; low spin complexes have the minimum number of unpaired electrons.

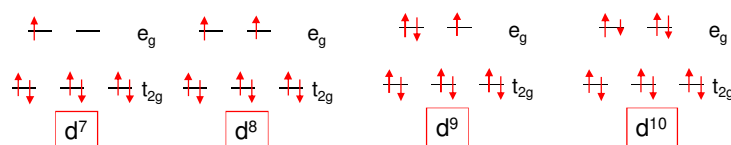
$d^1 \rightarrow d^3$  all electrons go into  $t_{2g}$  orbital



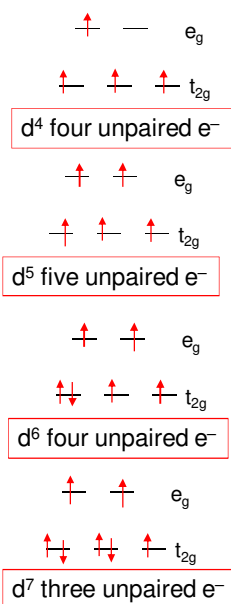
$d^4 \rightarrow d^6$  low spin or high spin

The total number of unpaired electrons for these  $O_{oct}$  complexes depends on the size of the energy gap,  $\Delta_{oct}$  relative to the energy cost of pairing electrons, "P" (recall Hund's rule).

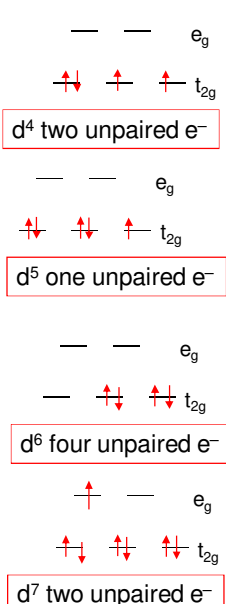
$d^7 \rightarrow d^{10}$  electrons must go into  $t_{2g}$  orbital and  $e_g$  orbitals



### "high spin"



### "low spin"



- Oct complexes of  $d^4$ ,  $d^5$ ,  $d^6$ , or  $d^7$  configurations can be "high spin" or "low spin"

- High spin complexes have the maximum number of unpaired electrons; low spin complexes have the minimum number of unpaired electrons.

- The total number of unpaired electrons for these Oh complexes depends on the size of the energy gap,  $\Delta$ , relative to the energy cost of pairing electrons, "P".

If  $\Delta_{oct} < P$ , the complex will be high spin

If  $\Delta_{oct} > P$ , the complex will be low spin

## Physical relevance of d-orbital splitting diagrams (spin and magnetism)

e.g.  $\text{Co}^{3+}$  is  $d^6$   
 $\text{F}^-$  is a weak field ligand  
 $\text{CN}^-$  is a strong field ligand  
 The  $\Delta_{\text{oct}}$  will be greater  $\text{Co}(\text{CN})_6^{3-}$  than for  $\text{CoF}_6^{3-}$

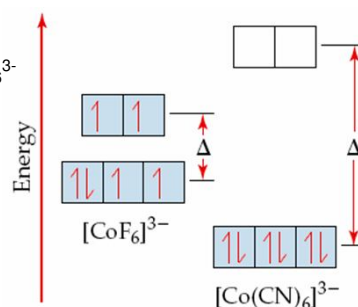
### Recall:

If  $\Delta_{\text{oct}} < P$ , the complex will be high spin

If  $\Delta_{\text{oct}} > P$ , the complex will be low spin

For  $\text{Co}(\text{CN})_6^{3-}$  the  $\Delta_{\text{oct}} > P$  and the complex is low spin

For  $\text{CoF}_6^{3-}$   $\Delta_{\text{oct}} < P$  and the complex will be high spin



- For many 1st row TM complexes, their magnetic moment,  $\mu_{\text{eff}}$ , can be *estimated* simply from the number of unpaired  $e^-$ ,  $n$ :  

$$\text{Est. } \mu = [4(n+2)]^{1/2} = [24]^{1/2} = 4.90\mu_B \text{ (vs 0)}$$

$$\mu_{\text{eff}}(\text{spin-only}) = [n(n+2)]^{1/2} \quad n = \text{number of unpaired electrons}$$

## Physical relevance of d-orbital splitting diagrams (spin and magnetism)

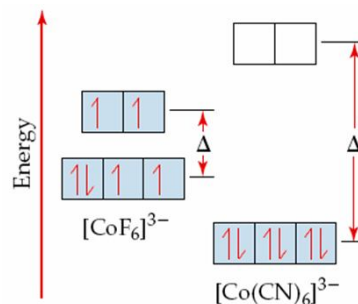
- For many 1st row TM complexes, their magnetic moment,  $\mu_{\text{eff}}$ , can be *estimated* simply from the number of unpaired  $e^-$ ,  $n$ :

$$\mu_{\text{eff}}(\text{spin-only}) = [n(n+2)]^{1/2}$$

$n = \text{number of unpaired electrons}$

$$\begin{aligned} \text{Est. } \mu_{\text{eff}} \text{ of } \text{Co}(\text{CN})_6^{3-} &= [4(4+2)]^{1/2} \\ &= [24]^{1/2} = 4.90\mu_B \end{aligned}$$

$$\begin{aligned} \text{Est. } \mu_{\text{eff}} \text{ of } \text{CoF}_6^{3-} &= [0(0+2)]^{1/2} \\ &= [0]^{1/2} = 0\mu_B \end{aligned}$$



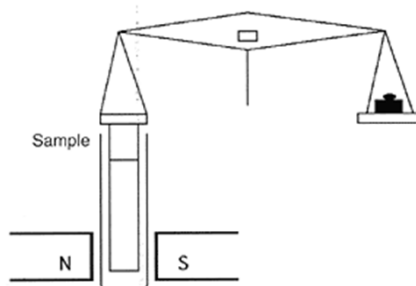
## Paramagnetism in 1st row transition metals

- We can *measure* the extent of the interaction of the unpaired electrons by weighing the complex in and out of a magnetic field. The weight difference is used to calculate  $\mu_{\text{eff}}$ .

- Compounds with unpaired  $e^-$  exhibit *paramagnetism*. Paramagnetic materials are attracted into a magnetic field.

The extent to which they are pulled into the field is given by their “magnetic moment”,  $\mu_{\text{eff}}$  (units  $\mu_B$ , Bohr magnetons)

Gouy balance:



## Paramagnetism in 1st row transition metals

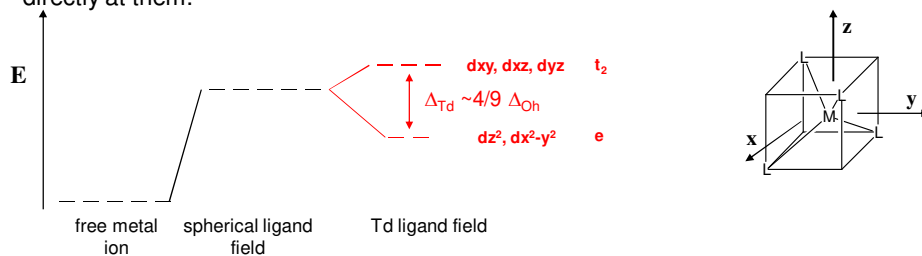
H&S 21.9  
pp.670-672

Metal ion	$d^n$ configuration	$S$	$\mu_{\text{eff}}(\text{spin-only}) / \mu_B$	Observed values of $\mu_{\text{eff}} / \mu_B$
$\text{Sc}^{3+}, \text{Ti}^{4+}$	$d^0$	0	0	0
$\text{Ti}^{3+}$	$d^1$	$\frac{1}{2}$	1.73	1.7–1.8
$\text{V}^{3+}$	$d^2$	1	2.83	2.8–3.1
$\text{V}^{2+}, \text{Cr}^{3+}$	$d^3$	$\frac{3}{2}$	3.87	3.7–3.9
$\text{Cr}^{2+}, \text{Mn}^{3+}$	$d^4$	2	4.90	4.8–4.9
$\text{Mn}^{2+}, \text{Fe}^{3+}$	$d^5$	$\frac{5}{2}$	5.92	5.7–6.0
$\text{Fe}^{2+}, \text{Co}^{3+}$	$d^6$	2	4.90	5.0–5.6
$\text{Co}^{2+}$	$d^7$	$\frac{3}{2}$	3.87	4.3–5.2
$\text{Ni}^{2+}$	$d^8$	1	2.83	2.9–3.9
$\text{Cu}^{2+}$	$d^9$	$\frac{1}{2}$	1.73	1.9–2.1
$\text{Zn}^{2+}$	$d^{10}$	0	0	0

H&S, Table 21.11, p.672

### Using CFT to generate Td & Sq Pl splitting diagrams

- In tetrahedral complexes, there are fewer ligands and none of the d-orbitals “point” directly at them.



- Tetrahedral complexes are always high spin, because  $\Delta_{Td}$  is so small relative to  $\Delta_{Oh}$  and most pairing energies, P.

### Using CFT to generate Td & Sq Pl splitting diagrams

- Square planar complexes are of lower symmetry than  $Oh$  or Td complexes, so there is a further loss of degeneracy of the d-orbitals.

