Coordination Numbers and Geometry

Lecture 2. CHEM1902 (C 10K) Coordination Chemistry The total number of points of attachment to the central element is termed the **coordination number** and this can vary from 2 to as many as 16, but is usually 6. In simple terms, the coordination number of a complex is influenced by the relative sizes of the metal ion and the ligands and by electronic factors, such as charge which is dependent on the electronic configuration of the metal ion. These competing effects are described by the term **ionic potential** which is defined as the charge to radius ratio.

Based on this, it can be seen that the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate.

Coordination Number 2

This arrangement is not very common for first row transition metal ion complexes and some of the best known examples are for Silver(I). In this case we have a low charge and an ion at the right hand side of the d-block indicating smaller size
For instance, a method often employed for the detection of chloride ions involves the formation of the linear diamminesilver(I) complex.
The first step is:

$$Ag^+ + Cl^- \rightarrow AgCl \text{ (white ppt)}$$

and to ensure that the precipitate is really the chloride salt, two further tests must be done:

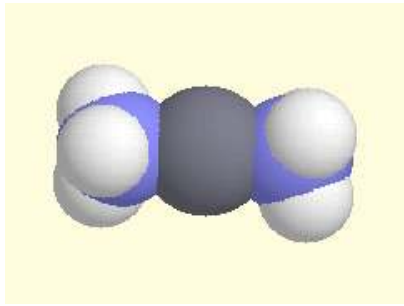
$$AgCl + 2\ NH_3 \rightarrow [Ag(NH_3)_2]^+$$

and

$$[Ag(NH_3)_2]^+ + HNO_3 \rightarrow AgCl \text{ (re-ppts)}$$

The reaction of a bidentate ligand such as 1,2-diaminoethane with Ag+ does not lead to chelated ring systems, but instead to linear two coordinate complexes. One reason for this is that bidentate ligands can NOT exist in *trans* arrangements that is they can NOT span 180 degrees.

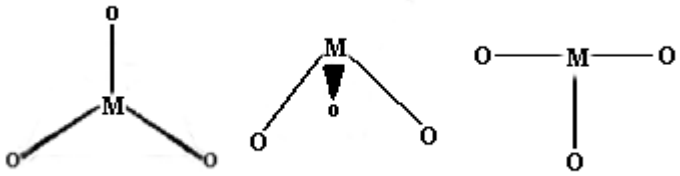
The linear $[Ag(NH_3)_2]^+$ ion



Although $[Ag(en)]ClO_4$ involves a normally bidentate ligand, in this case the structure is polymeric and the silver ion still retains a CN=2.

Coordination Number 3

Once again, this is not very common for first row transition metal ions. Examples with three different geometries have been identified:



Trigonal planar

Well known for main group species like CO_3^{2-} etc, this geometry has the four atoms in a plane with the bond angles between the ligands at 120 degrees.

Trigonal pyramid

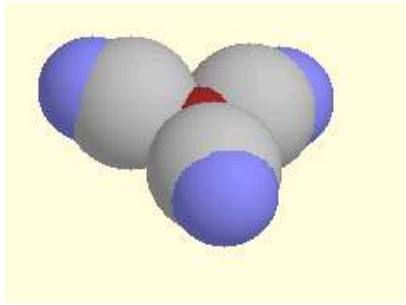
More common with main group ions.

T-shaped

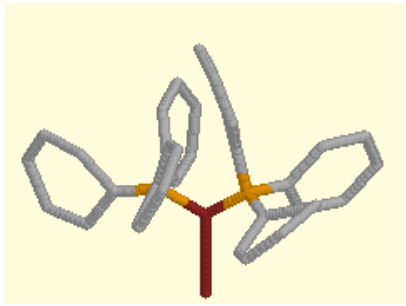
The first example of a T-shaped molecule was found in 1977.

Trigonal planar - D3h

$[Cu(CN)_3]^{2-}$



$[Cu(PPh_3)_2Br]$

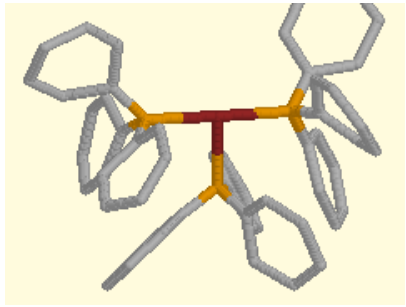


To help view more easily, the H atoms are turned off.

Trigonal pyramid

T-shaped

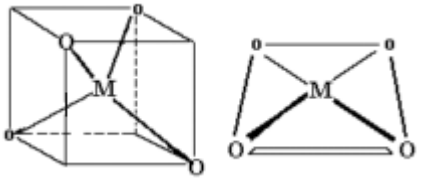
$[Rh(PPh_3)_3]^+$



To help view more easily, the H atoms are turned off.

Coordination Number 4

Two different geometries are possible. The tetrahedron is the more common while the square planar is found almost exclusively with metal ions having a d^8 electronic configuration.



Tetrahedral

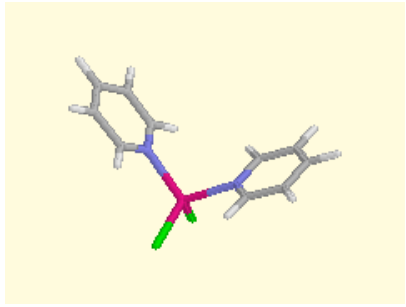
The chemistry of molecules centred around a tetrahedral C atom is covered in organic courses. To be politically correct, please change all occurrences of C to Co. There are large numbers of tetrahedral Cobalt (II) complexes known.

Square Planar

This is fairly rare and is included only because some extremely

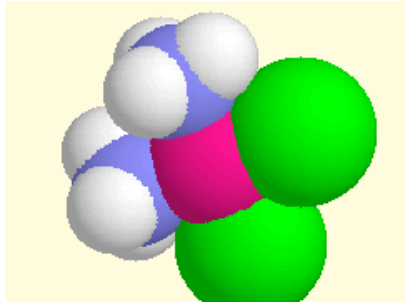
Tetrahedral

$Copyr_2Cl_2$



Square Planar

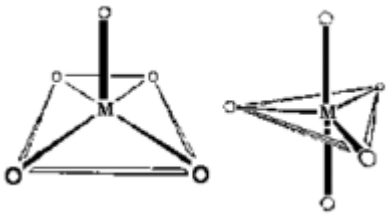
cisplatin - $cis\text{-}Pt(NH_3)_2Cl_2$



important molecules exist with this shape.

The *cis*- isomer is a powerful anti-cancer drug whereas the *trans*- is inactive.

Coordination Number 5



Square pyramid

Trigonal Bipyramid

The structure of $[Cr(en)_3][Ni(CN)_5]$ 1.5 H_2O was reported in 1968 to be a remarkable example of a complex exhibiting both types of geometry in the same crystal.

The reaction of cyanide ion with Ni^{2+} proceeds via several steps:

$$Ni^{2+} + 2\ CN^- \rightarrow Ni(CN)_2$$

$$Ni(CN)_2 + 2\ CN^- \rightarrow [Ni(CN)_4]^{2-}$$

orange-red

$$\log(\beta 4) = 30.1$$

$$[Ni(CN)_4]^{2-} + CN^- \rightarrow [Ni(CN)_5]^{3-}$$

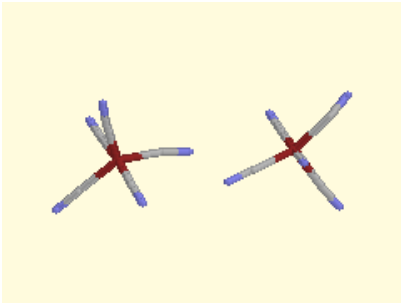
deep red

Oxovanadium salts (Vanadyl, VO^{2+}) often show square pyramidal geometry, for example, $VO(acac)_2$. Note that the Vanadium(IV) can be considered coordinatively unsaturated and addition of pyridine leads to

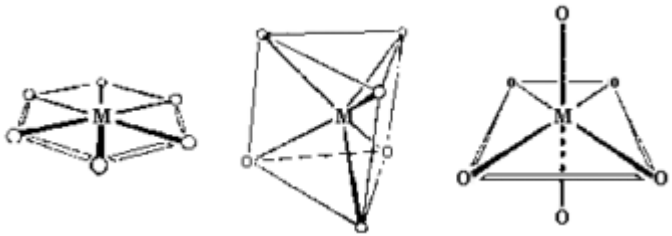
Square pyramid

Trigonal Bipyramid

$[Ni(CN)_5]^{3-}$



the formation of an octahedral complex.



Hexagonal planar

Unknown for first row transition metal ions, although the arrangement of six groups in a plane is found in some higher coordination number geometries.

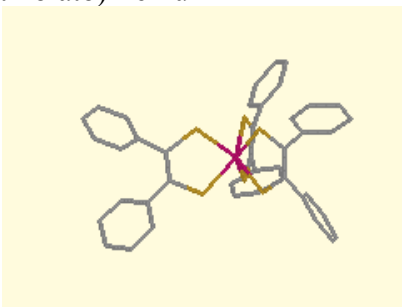
Trigonal prism

Coordination Number 6

Hexagonal planar

Trigonal prism

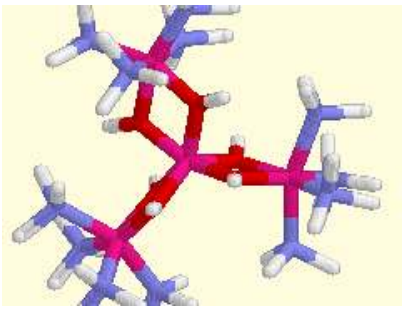
tris(cis-1,2-diphenylethene-1,2-dithiolato)rhenium



The ReS6 geometry is perfectly trigonal prismatic.

Octahedral (Oh)

Hexol



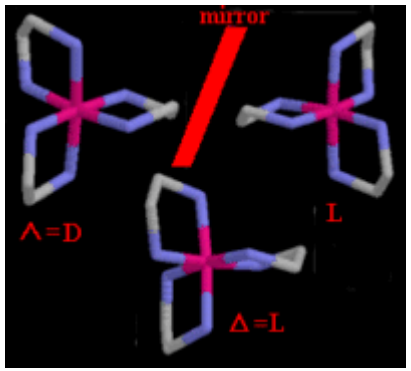
The first 'truly' inorganic complex to be resolved into its optical

Most trigonal prismatic compounds have three bidentate ligands such as dithiolates or oxalates and few are known for first row transition metal ions.

Octahedral

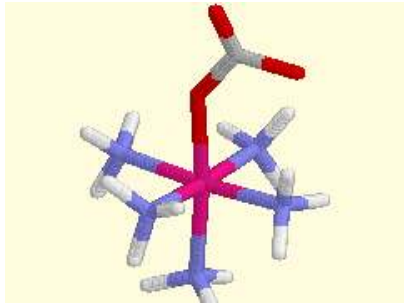
The most common geometry found for first row transition metal ions, including all aqua ions.
In some cases distortions are observed and these can sometimes be explained in terms of the Jahn-Teller Theorem.

isomers.
$[Co(en)_3]Cl_3$



The classic example of optical isomerism in octahedral coordination complexes (H atoms not shown).
D isomer
L isomer

$[Co(NH_3)_5CO_3]^+$



Capped octahedron (C3v)

$K_3[NbOF_6]$

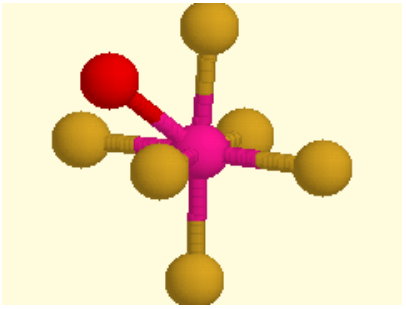
Coordination Number 7

Three geometries are possible:
Not very common for 1st row complexes and the energy difference between the structures seems small and distortions occur so that prediction of the closest "idealised" shape is generally difficult.

Capped octahedron (C3v)

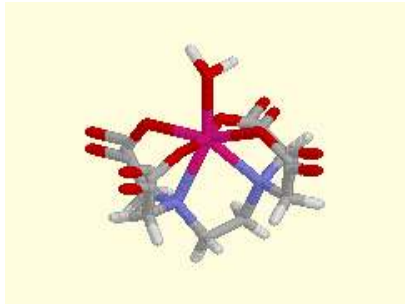
Capped trigonal prism (C2v)

Pentagonal Bipyramid (D5h)



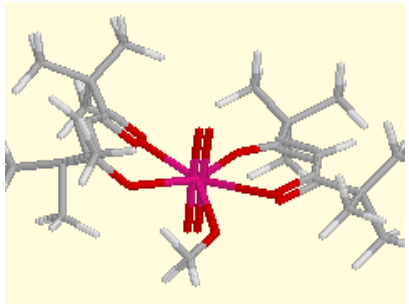
Capped trigonal prism (C2v)

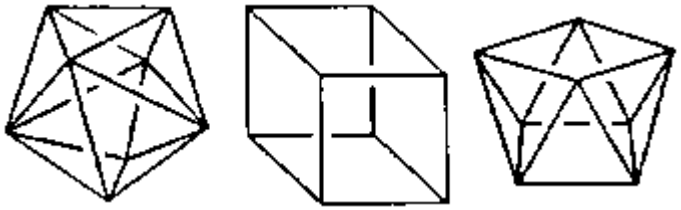
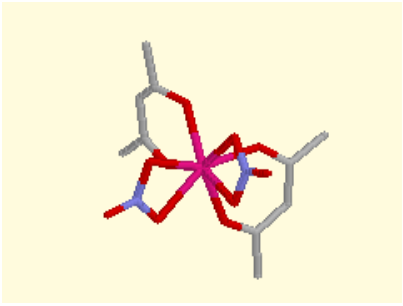
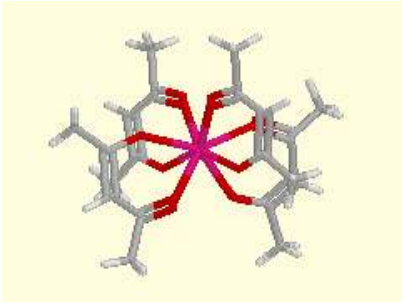
[V(III)(Hedta)(H_2O)]H_2O

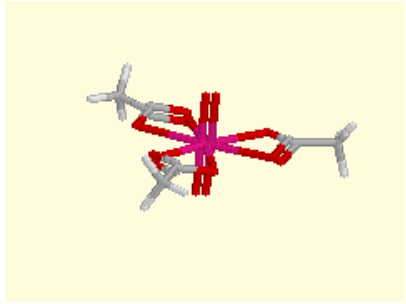
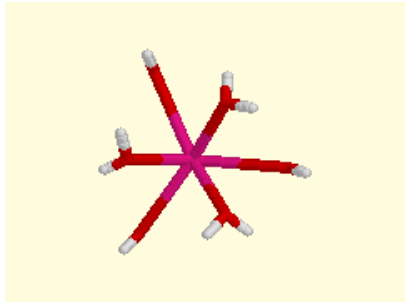


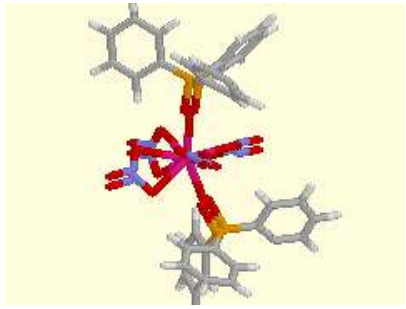
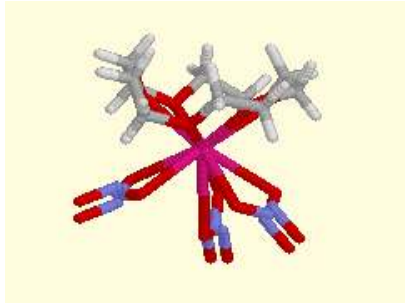
Pentagonal Bipyramid (D5h)

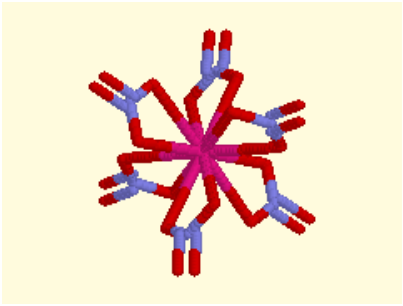
bis-(tert-butylacac)$_2$(DMSO)di-oxoUranium



	The UO7 geometry fits a pentagonal bipyramid.
Coordination Number 8  **Dodecahedron (D2d)** **Cube (Oh)** **Square antiprism (D4d)** **Hexagonal bipyramid (D6h)**	**Dodecahedron (D2d)** $Zr(acac)_2(NO_3)_2$  $[Zr(C_2O_4)_4]^{4-}$ is reported to have this shape as well. **Cube (Oh)** **Square antiprism (D4d)** $U(acac)_4$  **Hexagonal bipyramid (D6h)**

	$UO_2(OAc)_3$ 
Coordination Number 9 **Three-face centred trigonal prism (D3h)**	**Three-face centred trigonal prism (D3h)** Hydrated salts of the lanthanide elements eg $Eu(H_2O)_9]^{3+}$ 
Coordination Number 10 **Bicapped square antiprism (D4d)**	**Bicapped square antiprism (D4d)** Tetrakis(nitrato-O,O')-bis (triphenylphosphine oxide) cerium (IV)

	 Another example is [$Ce(NO_3)_5]^{2-}$
Coordination Number 11 **All-faced capped trigonal prism (D3h)**	**All-faced capped trigonal prism (D3h)** This is not a common stereochemistry. In aqua-(12-crown-4)-tris(nitrato-O,O')-cerium(III) (12-crown-4) solvate and (15-crown-5)-tris (nitrato-O,O')-cerium(III) the Cerium ion is 11 coordinate. 
	cuboctahedron (Oh) Ceric ammonium nitrate -$(NH_4)_2Ce(NO_3)_6$

Coordination Number 12 **cuboctahedron (Oh)**	

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