

Introduction to the d-block elements.

21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39
39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4
71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6

Electronic configurations:

One of the most important aspects of d-block chemistry is to work out the electronic configuration of the metal ion in its complex, i.e. how many d-electrons it has, whether it is d^6 , d^9 , d^{10} etc. The first step is to work out the formal oxidation state, and then the number of d-electrons is the number of electrons left in its valence shell. This is because in the ion the d sub-shell is lower in energy than the preceding s sub-shell, i.e. the 3d sub-shell is lower in energy than the 4s sub-shell in the first row d-block cations.

Thus: $[\text{Fe}(\text{CN})_6]^{4-}$ is Fe(II). It is a $8 - 2 = d^6$ metal ion:

total valence electrons for Fe(0) oxidation state of Fe(II)

	1	2	3	4	5	6	7	8	
	19	20	21	22	23	24	25	26	
4s sub-shell →	K	Ca	Sc	Ti	V	Cr	Mn	Fe	← 3d sub-shell
	39.10	40.08	44.96	47.87	50.94	52.00	54.94	55.85	

Electronic configurations:

Some other examples:

$[\text{Rh}(\text{NH}_3)_6]^{2+}$: it contains Rh(II). $9-2 = d^7$

1	2	3	4	5	6	7	8	9
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9

$[\text{Fe}(\text{CO})_5]$: it contains Fe(0): $8-0 = d^8$

1	2	3	4	5	6	7	8
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85

Electronic configurations:

Some other examples:

$[\text{Cr}(\text{NH}_3)_6]^{3+}$: it contains Cr(III). $6-3 = d^3$

1	2	3	4	5	6
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00

$[\text{Zn}(\text{CN})_4]^{2-}$: it contains Zn(II): $12-2 = d^{10}$

1	2	3	4	5	6	7	8	9	10	11	12
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39

Characteristic properties:

1) Color: The complexes of the d-block metal ions are usually colored, except, very often, those of d^0 and d^{10} metal ions. The colors are due to:

a) electronic transitions of d-electrons within the d sub-shell. These are known as $d \rightarrow d$ transitions. d^0 and d^{10} metal ions do not show these transitions.

b) electronic transitions from the metal ion to the ligand ($M \rightarrow L$ transitions) or ligand to the metal ion ($L \rightarrow M$ transitions), which are known as charge-transfer transitions, and these can occur for d^0 to d^{10} metal ions.

c) The ligands themselves may be colored, and this color may contribute to the color of the complex.

Characteristic properties:

2) Paramagnetism: When there are unpaired electrons in the d sub-shell, these will lead to paramagnetism. Thus, in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ the three d electrons (it is d^3) are unpaired. Thus, like the O_2 molecule which is paramagnetic, Cr(III) is paramagnetic. A d^{10} metal ion (e.g. Zn(II)) has a filled d sub-shell, and a d^0 metal ion (e.g. Ti(IV)) has no d-electrons, so neither of these can be paramagnetic.

3) Variable oxidation states: Most d-block metal ions display variable oxidation states. Thus, for example, Mn displays oxidation states from Mn(-III) (in $[\text{Mn}(\text{CO})(\text{NO})_3]$) through Mn(0) (in $[\text{Mn}_2(\text{CO})_{10}]$) to Mn(VII) (in $[\text{MnO}_4]^-$). The known oxidation states for first-row d-block ions are as follows (excluding very low oxidation states as found only in organometallic compounds):

Oxidation states of first-row d-block ions:

The most stable oxidation states are in **red**, rarer oxidation states **pale blue**:

3	4	5	6	7	8	9	10	11	12
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
		1	1	1	1	1	1	1	
	2	2	2	2	2	2	2	2	2
3	3	3	3	3	3	3	3	3	
	4	4	4	4	4	4	4	4	
		5	5	5	5				
			6	6	6				
				7					

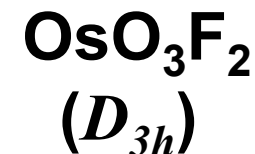
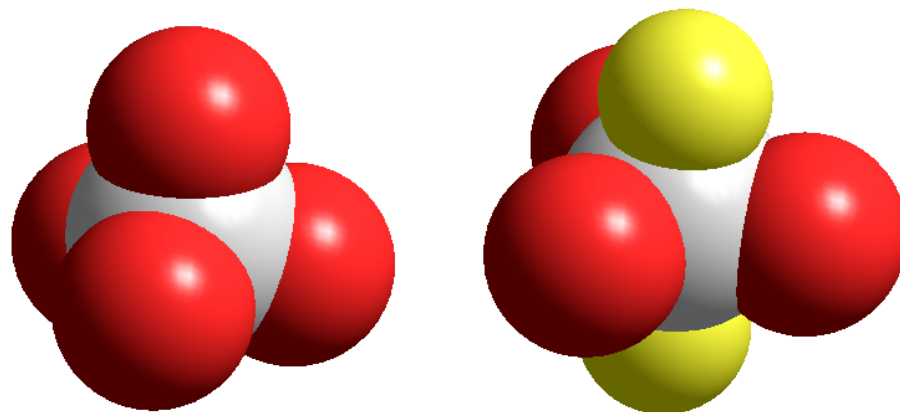
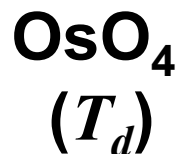
These achieve the group oxidation state

Maximum at Mn(VII)

The higher oxidation states become progressively less stable as the divalent state becomes dominant

The heavier d-block elements:

The patterns of stable oxidation states for the heavier d-block elements resemble those for the first row of d-block elements, except that higher oxidation states become more stable. Thus, for example, with the Fe-group, Fe(III) is the highest common oxidation state for Fe, and oxidation states such as Fe(IV) through Fe(VI) are achieved only with great difficulty, and Fe cannot achieve the group oxidation state of Fe(VIII). In contrast, both Ru and Os can achieve the M(VIII) oxidation state in the oxides RuO_4 and OsO_4 , with OsO_4 being the more stable. Os(VIII) also exists in compounds such as $[\text{OsO}_3\text{F}_2]$.



Oxidation states of the Ni, Pd, and Pt group:

As mentioned above, Ni(II) is the most common oxidation state for Ni, with Ni(III) and Ni(IV) being much less stable. In contrast, although Pd(II) and Pt(II) are the more stable oxidation states for these elements, it becomes much easier to achieve the M(IV) state as one moves down the group. Thus Pd(IV), and even more so Pt(IV), are quite stable, showing the ability of heavier d-block elements to achieve higher oxidation states. An important example of Pt(IV) is in the orange complex $(\text{NH}_4)_2[\text{PtCl}_6]$. It is also possible to achieve the Pt(VI) oxidation state in compounds such as $[\text{PtF}_6]$. Other examples of M(VI) fluoro complexes of heavier d-block elements are IrF_6 , OsF_6 , ReF_6 , and WF_6 . By contrast, CrF_6 is thought to exist, but is too unstable to characterize properly.

Characteristic properties:

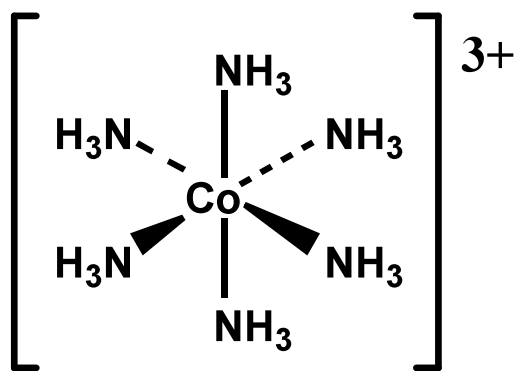
4) Complex-formation: The d-block metal ions form a wide variety of complexes, of generally high stability, with ligands such as EDTA or F^- , Cl^- , and OH^- , or ethylene diamine (en), as well as many others, much as was the case for the main group metal cations. Many of the d-block metal ions are powerful Lewis acids, as can be seen by comparison with some main group element cations:

<u>metal ion:</u>	<u>Al^{3+}</u>	<u>Co^{3+}</u>	<u>Mg^{2+}</u>	<u>Zn^{2+}</u>
ionic radius (Å):	0.54	0.55	0.74	0.74
$\log K_1(\text{EDTA})$:	16.4	41.4	8.8	16.5
$\log K_1(OH^-)$:	8.5	13.5	2.6	5.0

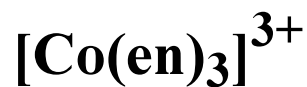
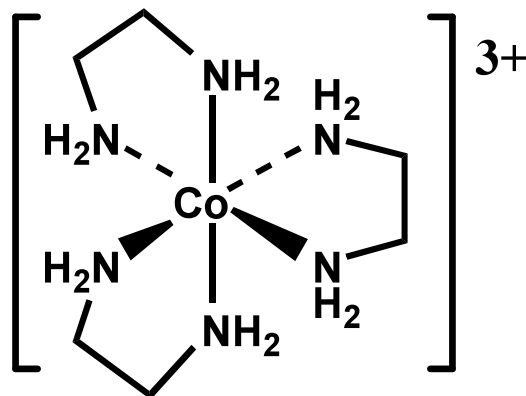
Coordination numbers:

The coordination geometry of the d-block elements tends to be mainly of three types. The most common is octahedral 6-coordinate, followed by square planar, which is limited to particular electronic configurations such as d^8 and d^9 . Tetrahedral geometry is less common, and also restricted largely to certain electronic configurations. For the main group metal ions, coordination numbers tend to be controlled by size and also charge, whereas for d-block metal ions, covalent orbital overlap becomes very important. Thus, knowing the electronic configuration of a d-block metal ion is an important part of predicting its coordination geometry. Thus, Co(III) , when it is low-spin d^6 is virtually always octahedral 6-coordinate. The meaning of 'low-spin', which is an aspect of the electronic configuration, will be dealt with later. Some examples of coordination geometries are:

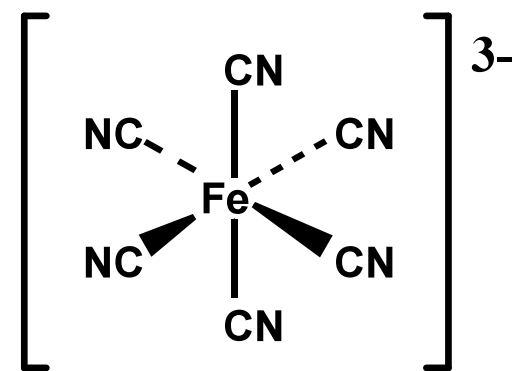
Coordination geometries:



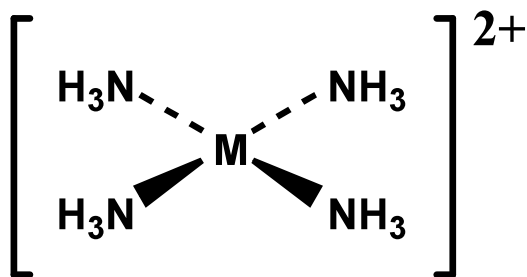
octahedral



octahedral

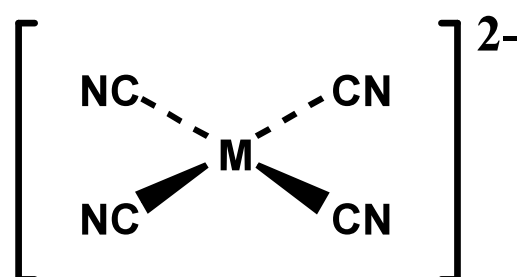


octahedral



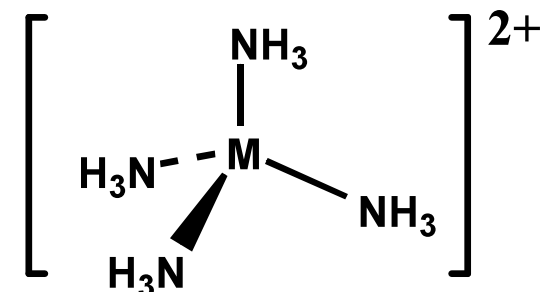
square planar

M = Cu(II), Pd(II)



square planar

M = Ni(II), Pd(II)

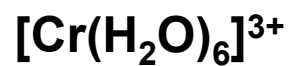
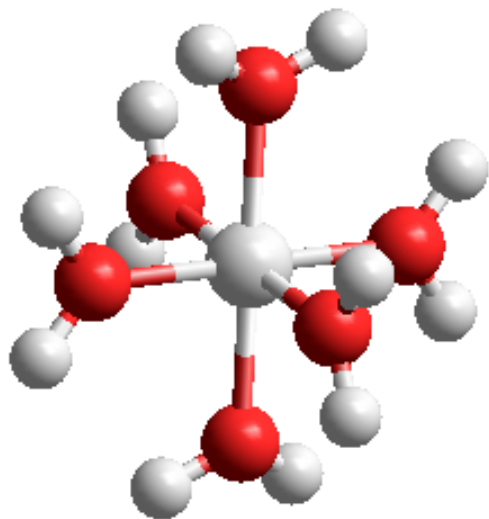


tetrahedral

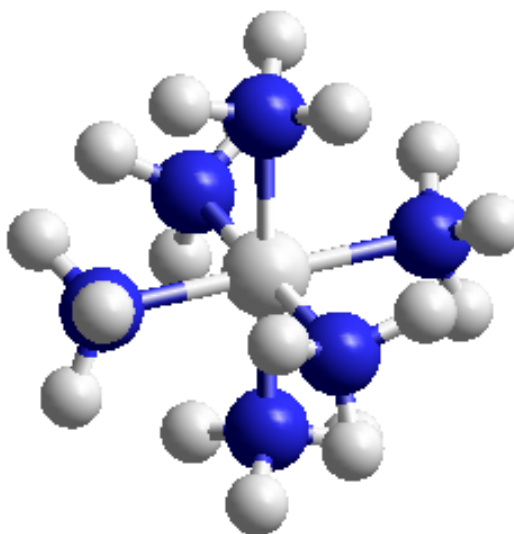
M = Zn(II)

Coordination geometries:

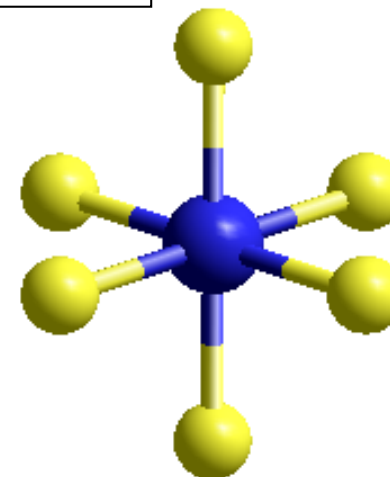
octahedral



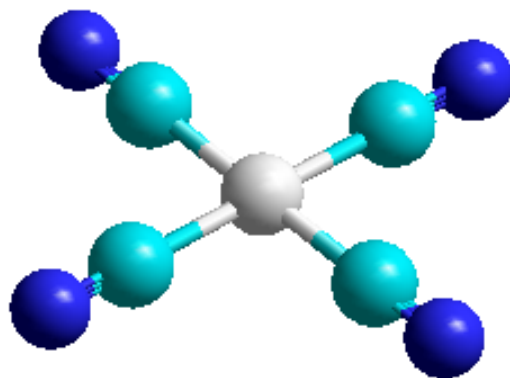
octahedral



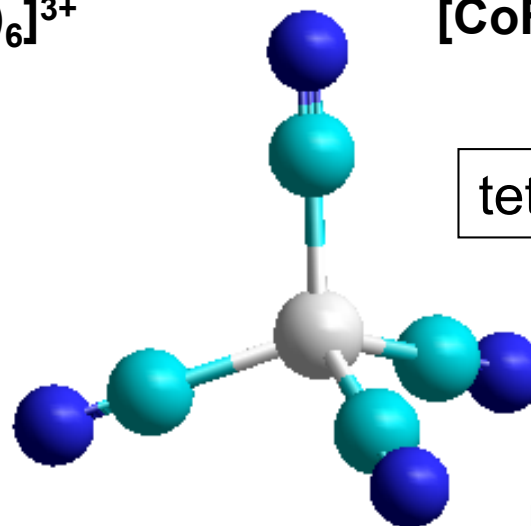
octahedral



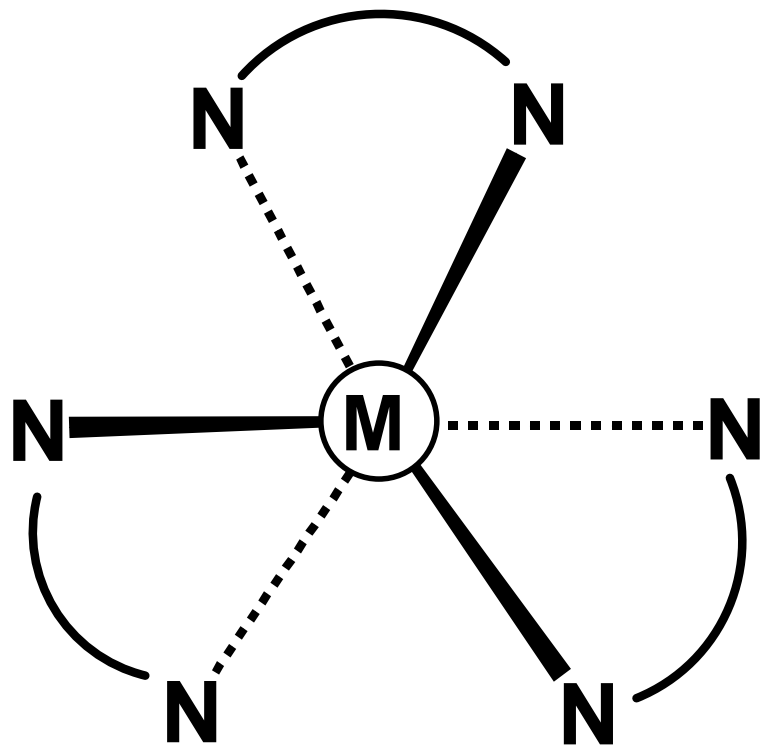
square
planar



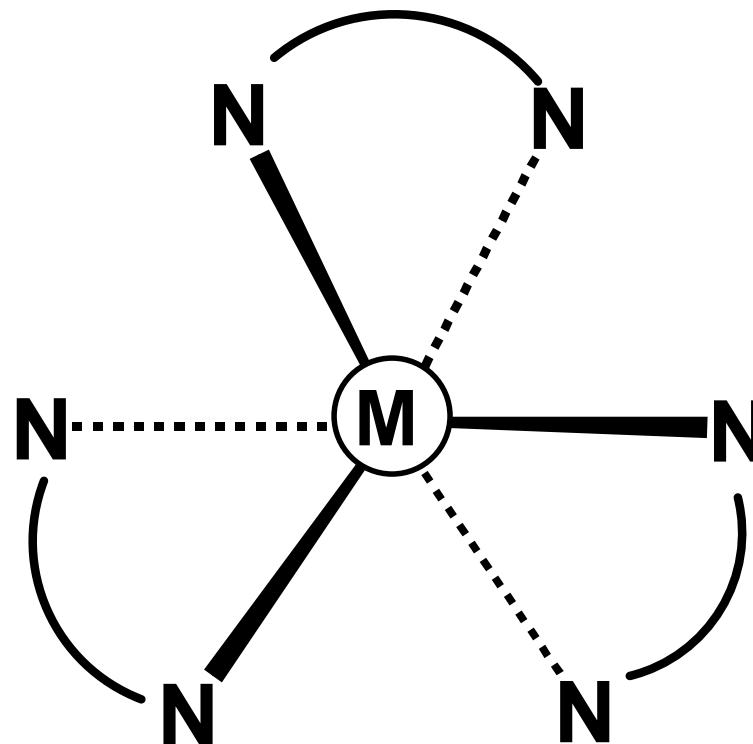
tetrahedral



Optical isomerism:



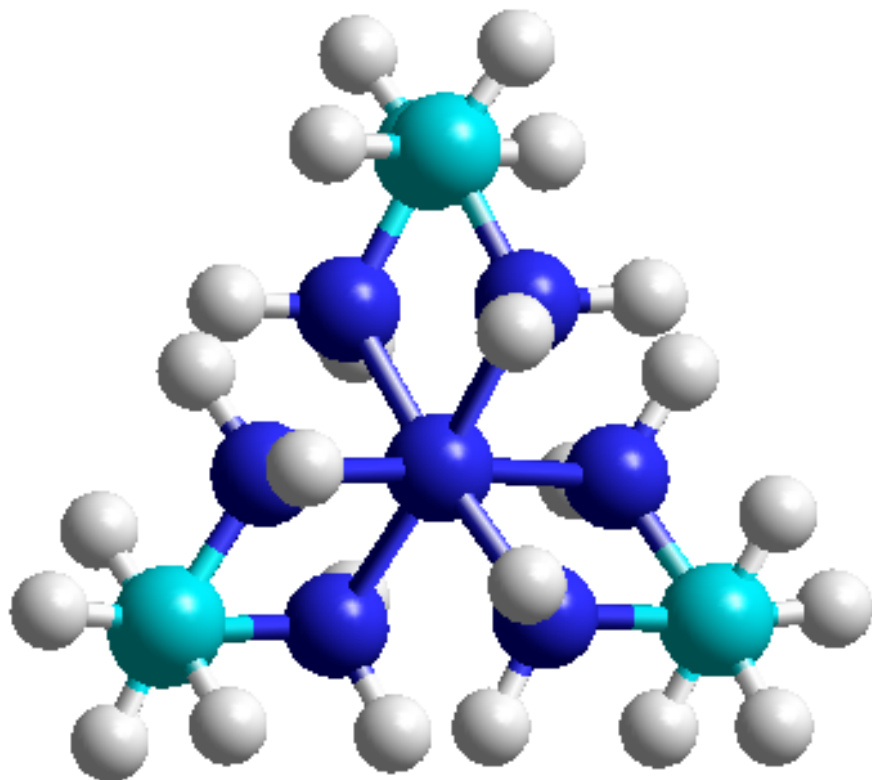
Λ (lambda) form



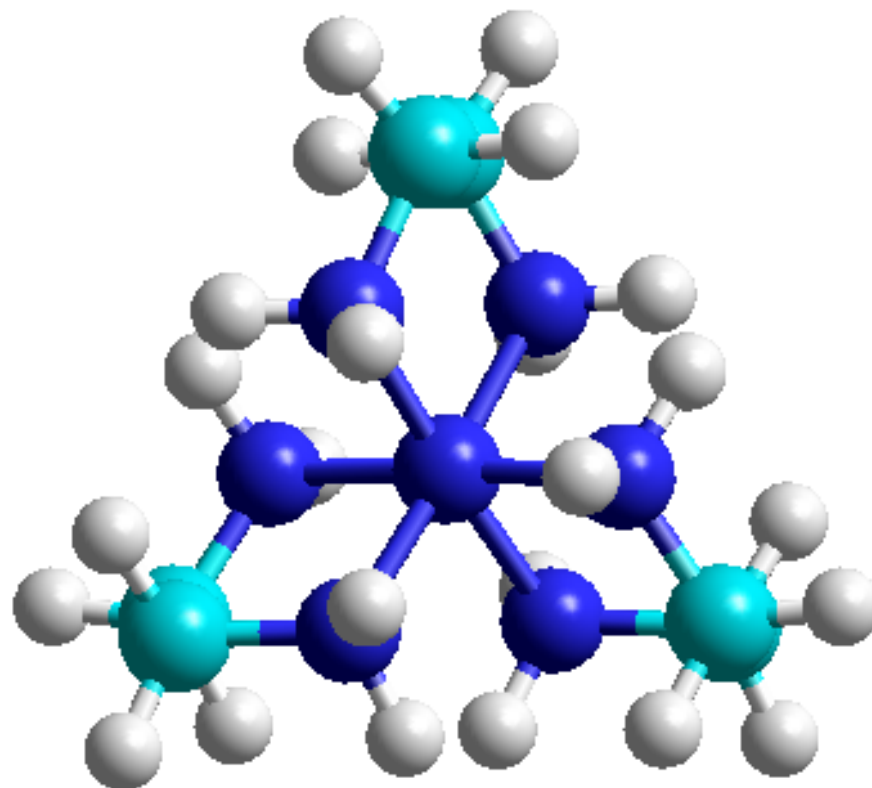
Δ (delta) form

tris-chelate complexes of the D_3 point group where chelate = ethylenediamine, 1,10-phenanthroline, oxalate, etc. exist as pairs of optical isomers.

Optical isomerism:



Λ (lambda) form



Δ (delta) form

The tris-ethylenediamine Co(III) complexes (D_3 point group) exist as pairs of optical isomers.