The *d*-Block Elements. General properties

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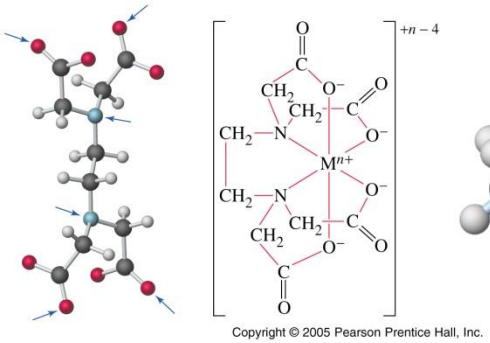
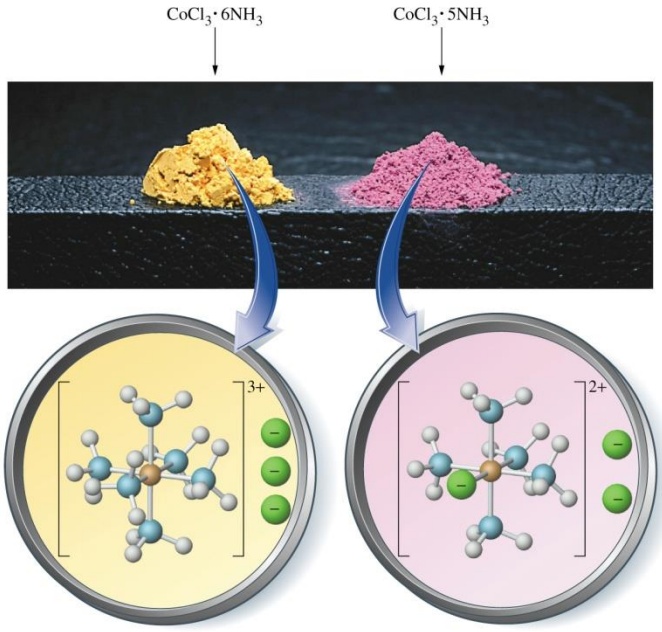
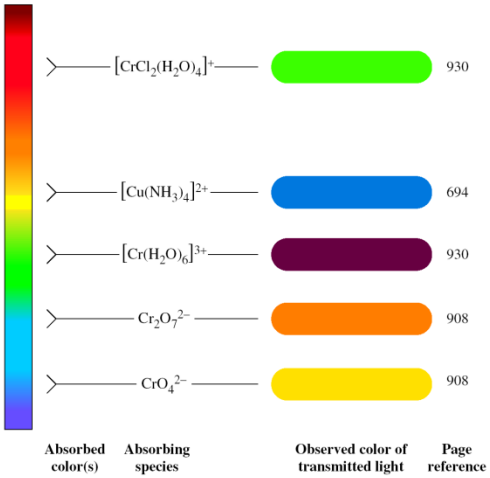
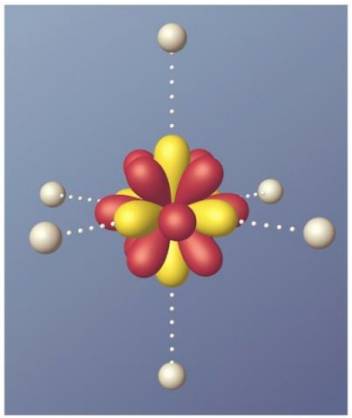
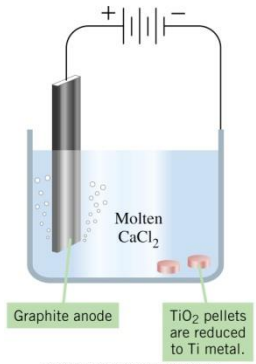










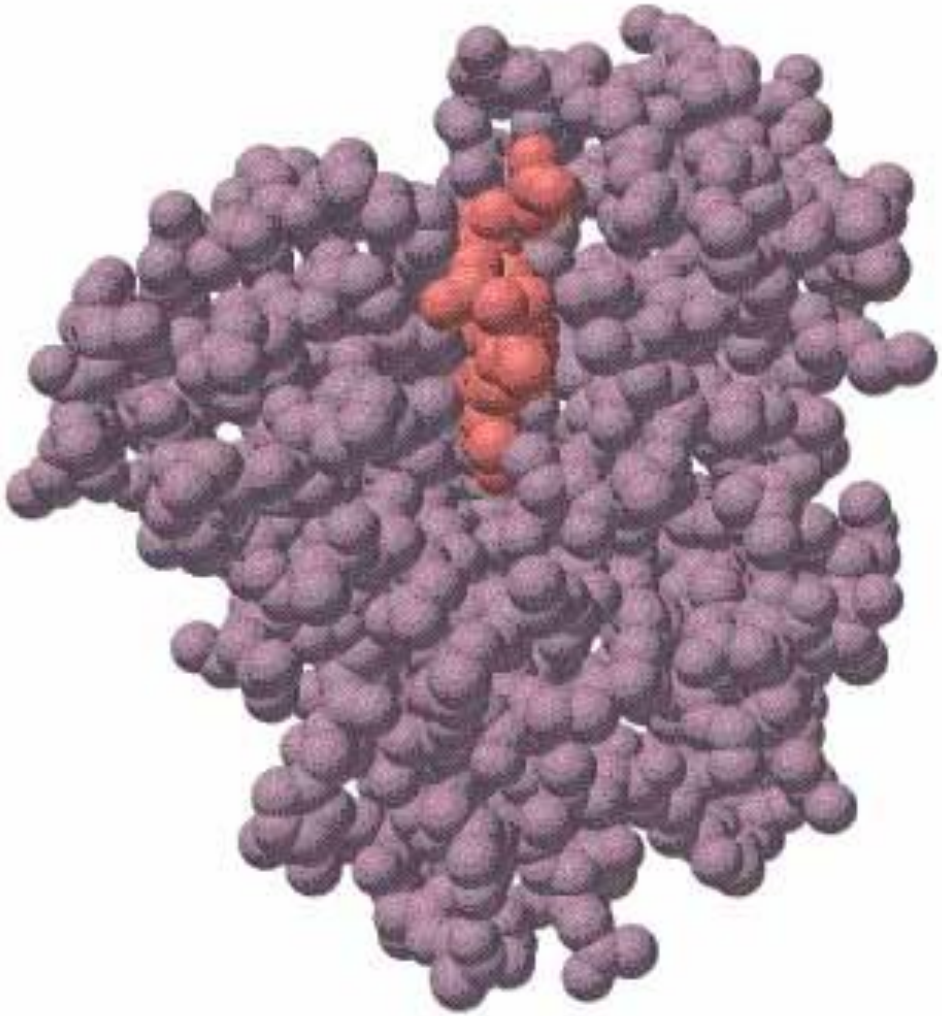
Why Study Descriptive Chemistry of Transition Metals

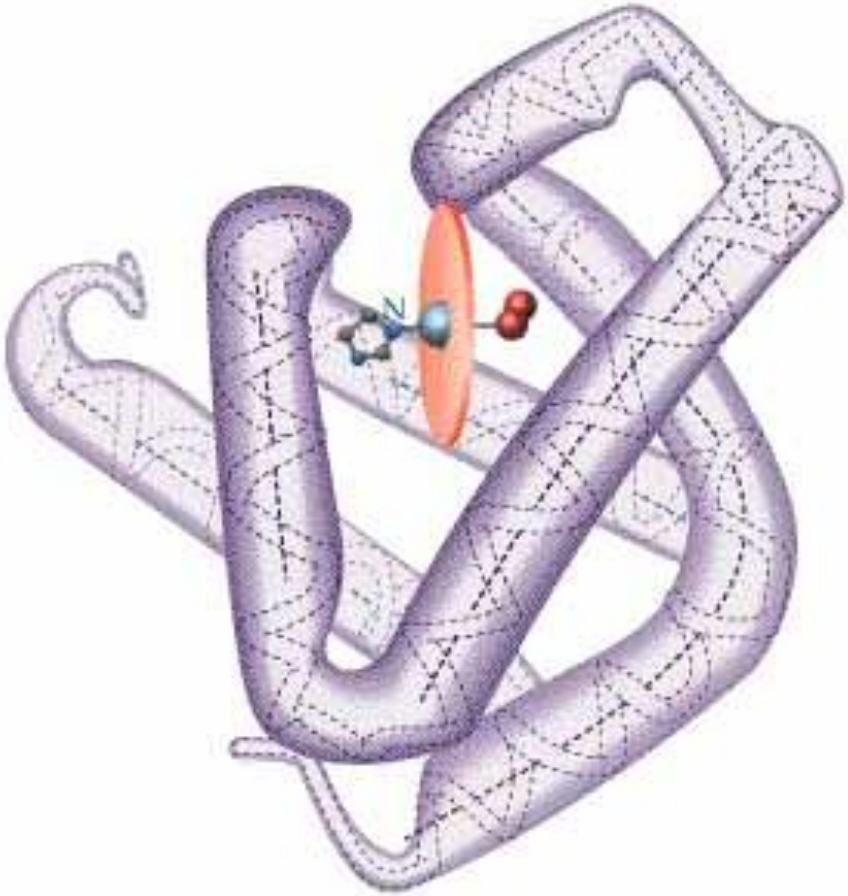
- **Transition metals are found in nature**
  - Rocks and minerals contain transition metals
  - The color of many gemstones is due to the presence of transition metal ions
    - Rubies are red due to Cr
    - Sapphires are blue due to presence of Fe and Ti
  - **Many biomolecules contain transition metals that are involved in the functions of these biomolecules**
    - Vitamin B12 contains Co
    - Hemoglobin, myoglobin, and cytochrome C contain Fe

Why Study Descriptive Chemistry of Transition Metals

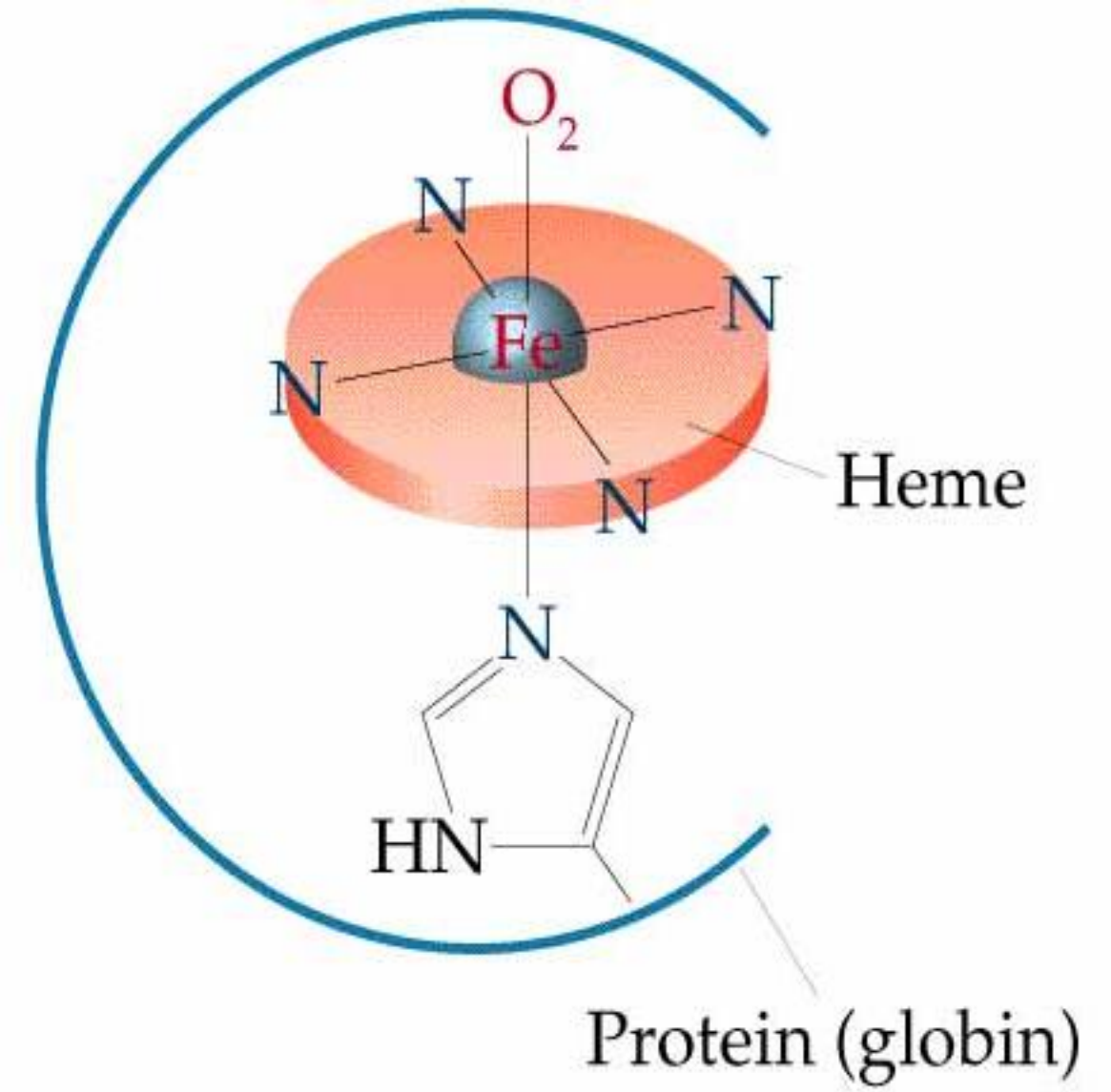
- **Transition metals and their compounds have many useful applications**
  - Fe is used to make steel and stainless steel
  - Ti is used to make lightweight alloys
  - Transition metal compounds are used as pigments
    - TiO_2 = white
    - $PbCrO_4$ = yellow
    - $Fe_4[Fe(CN)_6]_3$ (prussian blue)= blue
  - Transition metal compounds are used in many industrial processes

Myoglobin, a protein that stores O_2 in cells

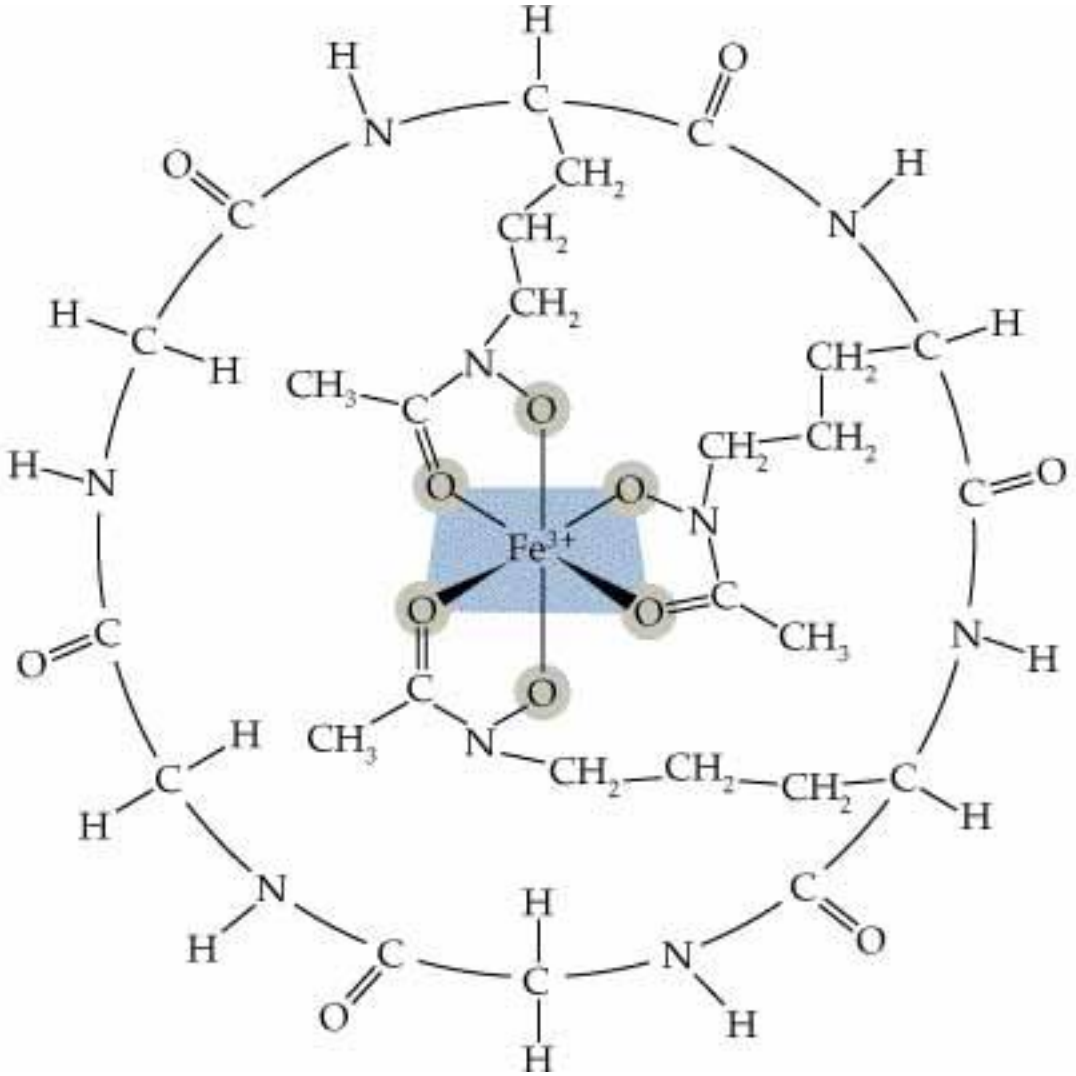




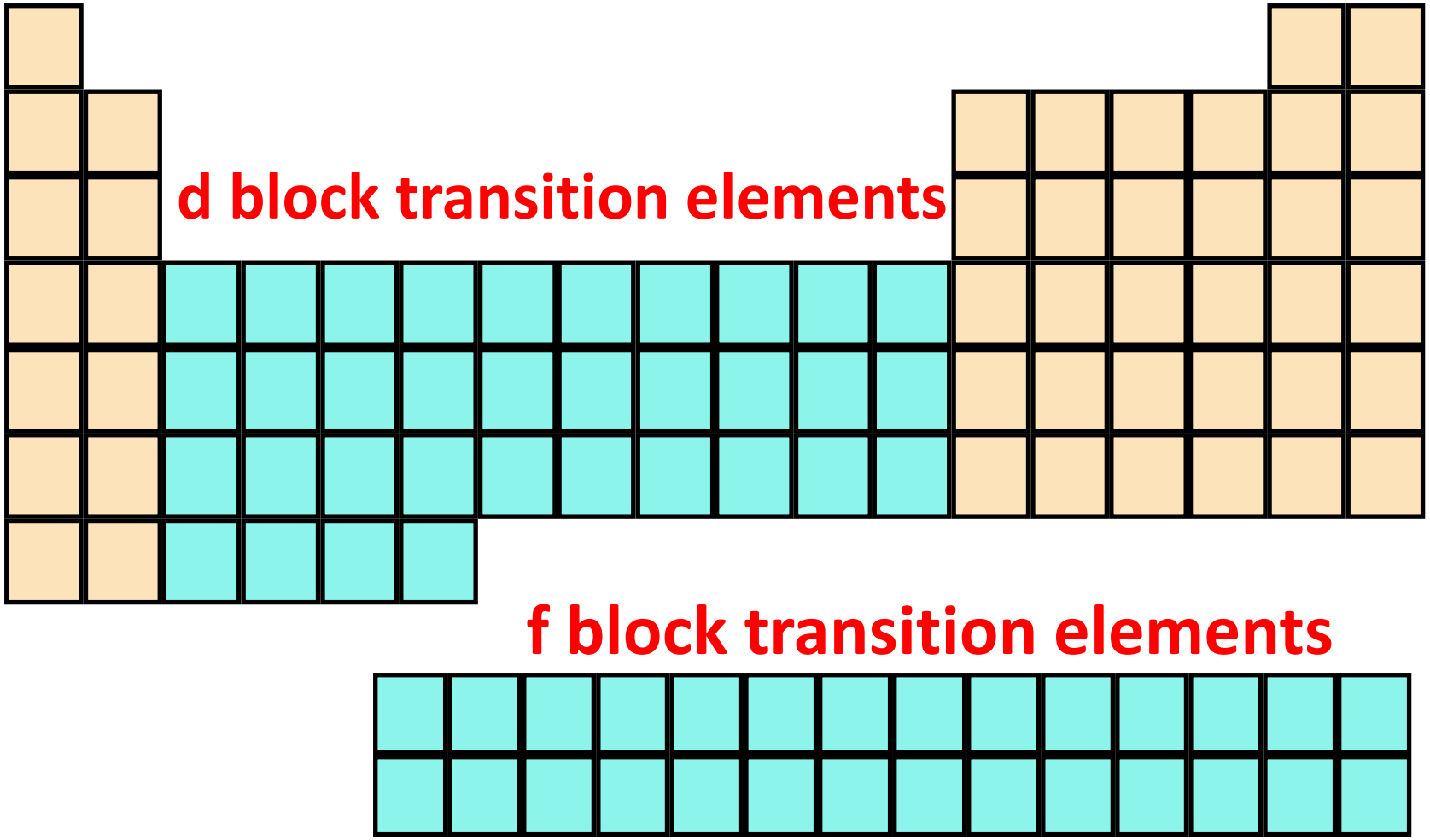
Coordination Environment of Fe^{2+} in Oxymyoglobin and Oxyhemoglobin



Ferrichrome (Involved in Fe transport in bacteria)



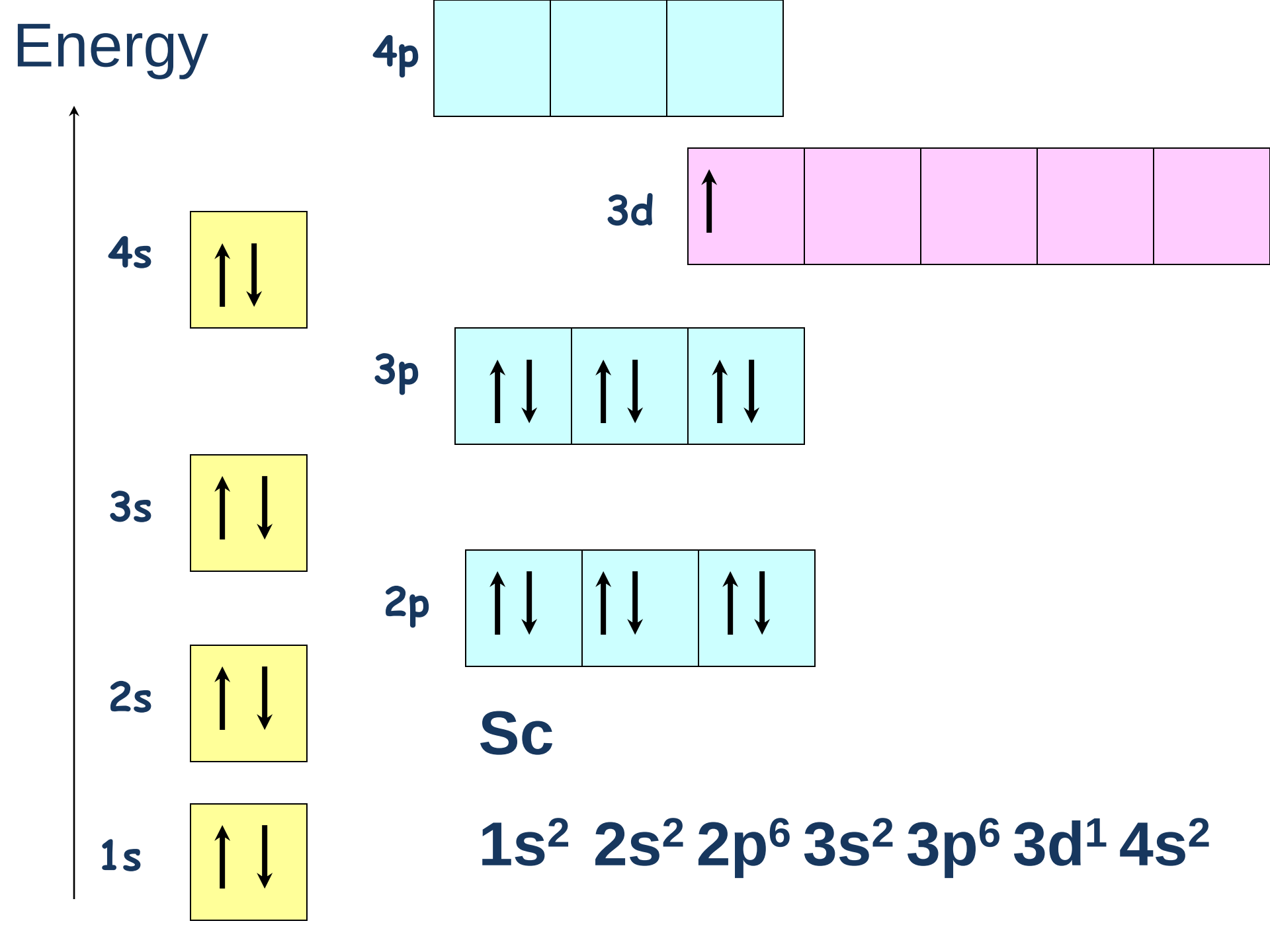
Periodic Table



d-Block Transition Elements

IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg

Most have partially occupied d subshells in common oxidation states


Energy
4p
3d
4s
3p
3s
2p
2s
1s
Sc
1s² 2s² 2p⁶ 3s² 3p⁶ 3d¹ 4s²

Electronic Configurations

Element	Configuration
Sc	$[Ar]3d^1 4s^2$
Ti	$[Ar]3d^2 4s^2$
V	$[Ar]3d^3 4s^2$
Cr	$[Ar]3d^5 4s^1$
Mn	$[Ar]3d^5 4s^2$

$$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$$

Electronic Configurations

Element	Configuration
Fe	$[Ar]\ 3d^6 4s^2$
Co	$[Ar]\ 3d^7 4s^2$
Ni	$[Ar]\ 3d^8 4s^2$
Cu	$[Ar] 3d^{10} 4s^1$
Zn	$[Ar] 3d^{10} 4s^2$

$$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$$

General Properties of the *d*-Block Elements and Their Trends

- Fourth-period *d*-block elements form ionic bonds with somewhat less ionic character than do the metals of the *s*-block.
- Lower oxidation states (+2, +3) usually correspond to ionic character.
- For Co through Zn, relative energies of the 4*s* and 3*d* subshells are such that few (or no) 3*d* electrons are lost in forming ions.

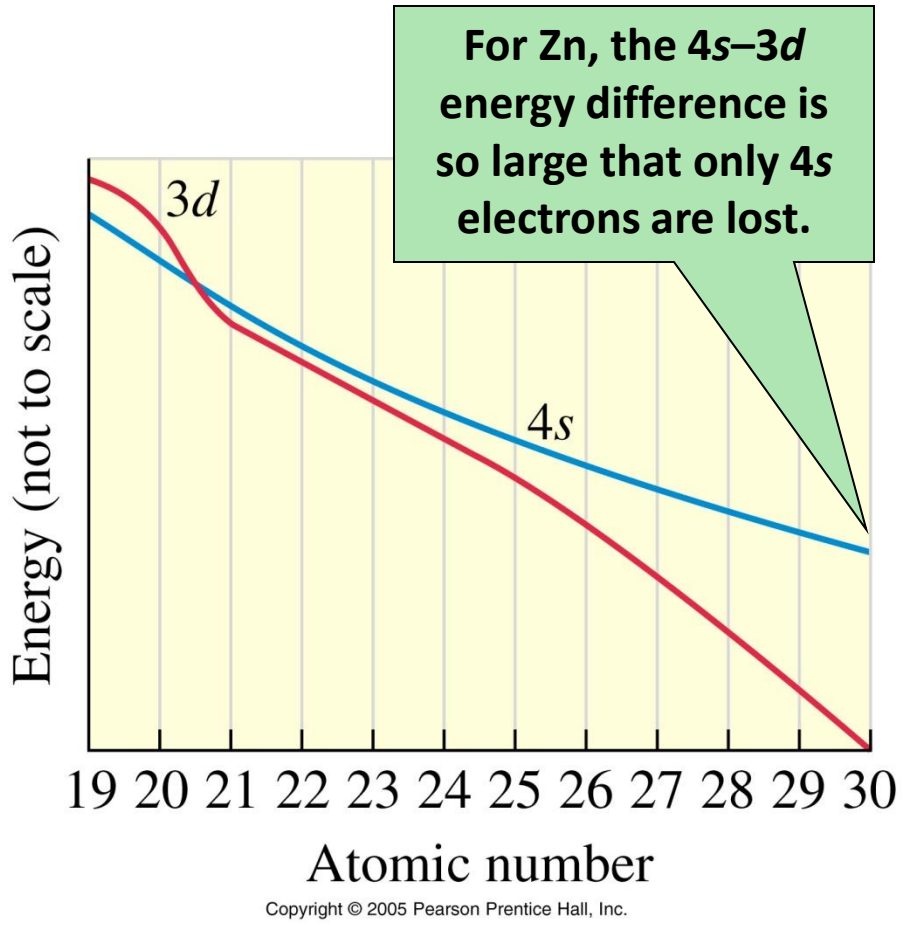


Table 22.1 Selected Properties of the *d*-Block Elements of the Fourth Period

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number	21	22	23	24	25	26	27	28	29	30
Electron configuration[a]	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$
Electronegativity	1.4	1.5	1.6	1.7	1.6	1.8	1.9	1.9	1.9	1.7
Common cations	3+	2+, 3+	2+, 3+	2+, 3+	2+, 3+	2+, 3+	2+, 3+	2+	1+, 2+	2+
Common positive oxidation numbers[b]	3	2, 3, 4	2, 3, 4 5	2, 3, 6	2, 3, 4 6, 7	2, 3, 6	2, 3	2, 3	1, 2	2
Atomic radius, pm	161	145	132	125	124	124	125	125	128	133
$E°$, V[c]	−2.03	−1.63	−1.13	−0.90	−1.18	−0.440	−0.277	−0.257	+0.340	−0.763
Melting point, °C	1397	1672	1710	1900	1244	1530	1495	1455	1083	420
Density, g/cm^3	3.00	4.50	6.11	7.14	7.43	7.87	8.90	8.91	8.95	7.14
Electrical conductivity[d]	3	4	6	12	1	16	25	23	95	27
Thermal conductivity[d]	4	5	7	22	2	19	23	21	93	27

[a] Each atom has an argon core configuration.

[b] The most important oxidation numbers are printed in red.

[c] For the reduction $M^{2+}(aq) + 2\,e^- \longrightarrow M(s)$ [except for Sc, where the ion is $Sc^{3+}(aq)$].

[d] Electrical and thermal conductivities are on an arbitrary scale relative to 100 for silver, the best metallic conductor.

Some Properties of the Fourth Period *d*-Block

- In the fourth-period *d*-block, **only scandium is active enough to displace H_2** from H_2O.
- These elements have moderate to high melting points and moderately high densities.
- **Electrical and thermal conductivities of these elements ar very high.** Copper is second only to silver in electrical conductivity.

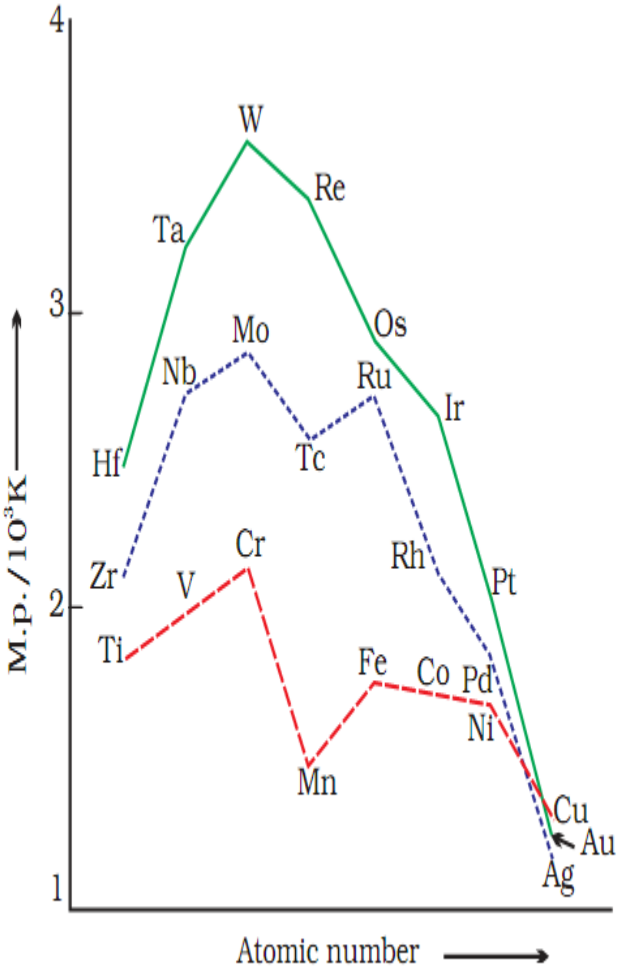
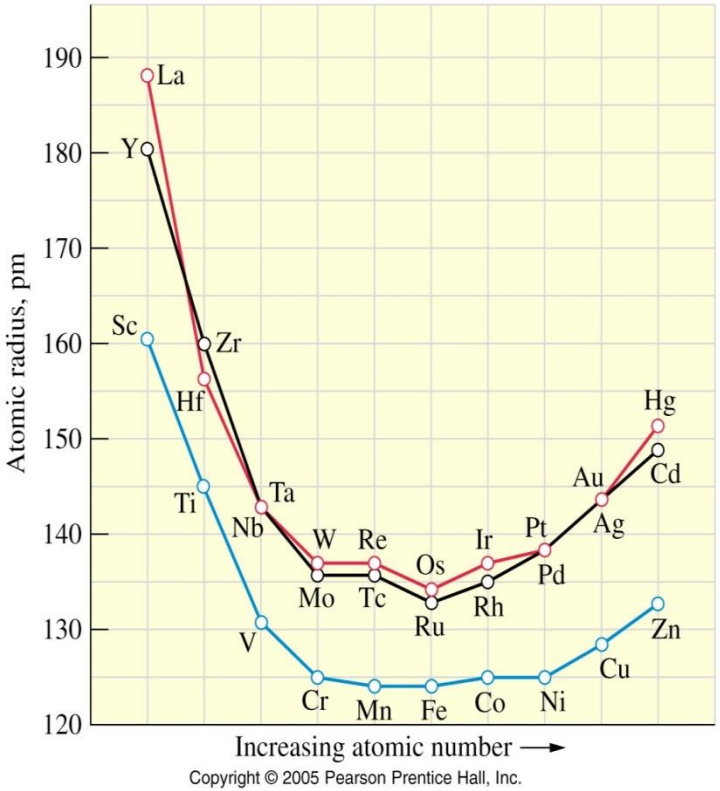


Fig. 8.1: Trends in melting points of transition elements

Atomic Radii of the *d*-Block Elements

- Size does not appear to increase significantly between fifth and sixth period elements.
- The electrons in 4*f* orbitals are not very good at screening valence electrons from the nucleus.
- Thus, the strength of attraction of valence electrons to the nucleus is greater than expected in the sixth period. The phenomenon is known as the ***lanthanide contraction***.



Characteristic properties:

<u>Color:</u> 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→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→L transitions) or ligand to the metal ion (L→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:

Paramagnetism: When there are unpaired electrons in the d sub-shell, these will lead to paramagnetism. Thus, in $[Cr(H_2O)_6]^{3+}$ 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.

Variable oxidation states: Most d-block metal ions display variable oxidation states. Thus, for example, Mn displays oxidation states from Mn(-III) (in $[Mn(CO)(NO)_3]$) through Mn(0) (in $[Mn_2(CO)_{10}]$) to Mn(VII) (in $[MnO_4]^-$).

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 oxidat-ion states become progressIvely less stable as the divalent state becomes dominant

Oxidation States of Transition Elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
							+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		
		+5	+5	+5	+5				
			+6	+6	+6				
				+7					

loss of ns e⁻s

loss of ns and (n-1)d e⁻s

Electronic Configurations of Transition Metal Ions

- Electronic configuration of Fe^{3+}

$$Fe - 3e^- \rightarrow Fe^{3+}$$

$[Ar]3d^64s^2$ $[Ar]3d^5$

valence ns e⁻'s removed first, then n-1 d e⁻'s

- Electronic configuration of Fe^{2+}
- $Fe - 2e^- \rightarrow Fe^{2+}$

$[Ar]3d^64s^2$ $[Ar]3d^6$

valence ns e⁻'s removed first

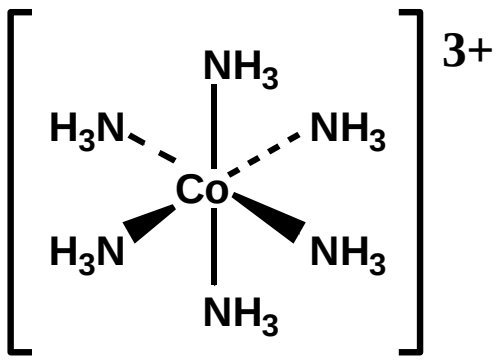
Characteristic properties:

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:

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

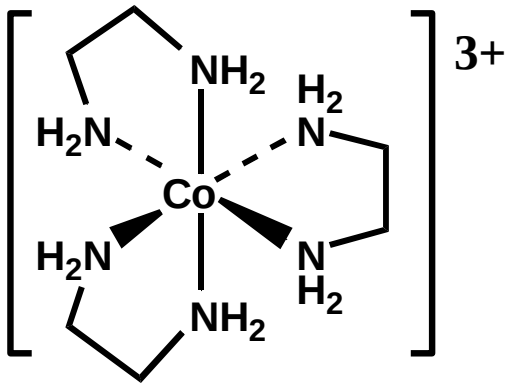
The reason why the d-block cations are such strong Lewis acids will become clear as the course proceeds.

Coordination geometries:



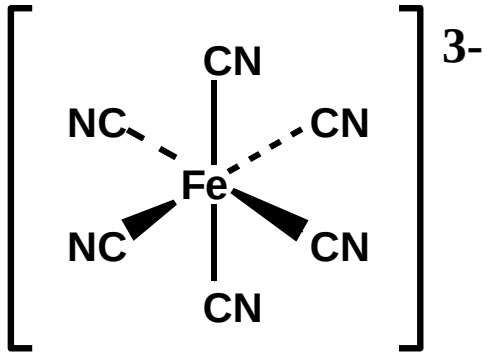
$[Co(NH_3)_6]^{3+}$

octahedral



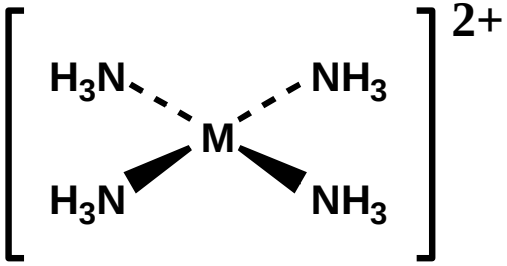
$[Co(en)_3]^{3+}$

octahedral



$[Fe(CN)_6]^{3-}$

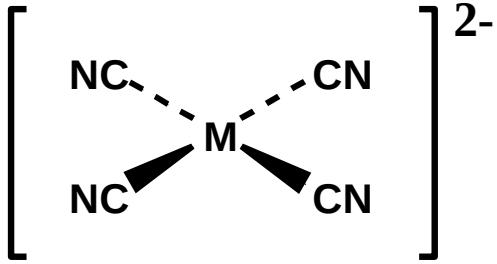
octahedral



$[\ M(NH_3)_4]^{2+}$

square planar

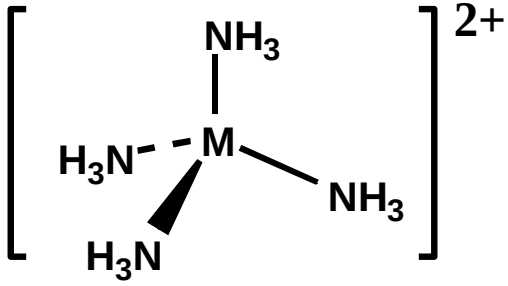
M = Cu(II), Pd(II)



$[M(CN)_4]^{2-}$

square planar

M = Ni(II), Pd(II)



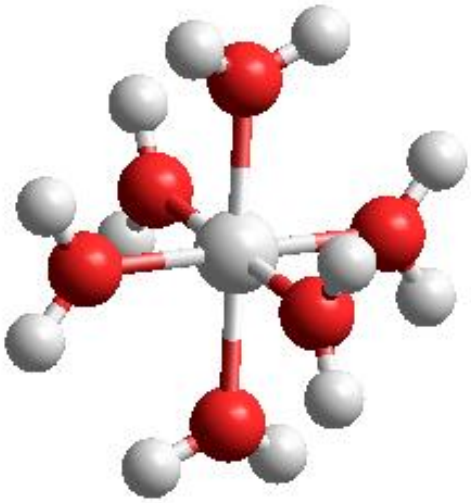
$[M(NH_3)_4]^{2+}$

tetrahedral

M = Zn(II)

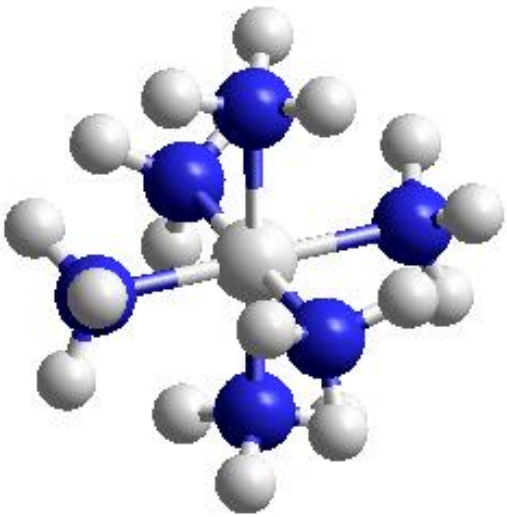
Coordination geometries:

octahedral



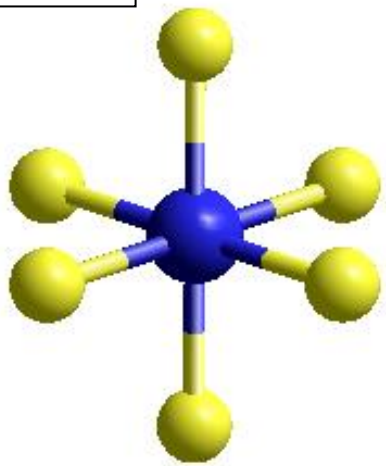
$[Cr(H_2O)_6]^{3+}$

octahedral



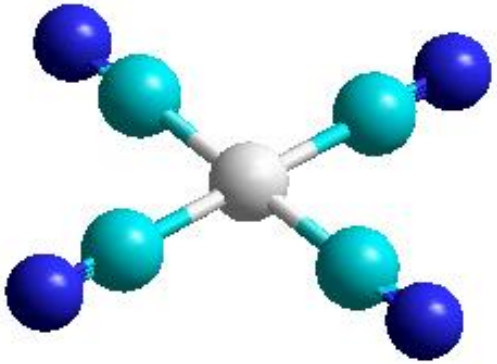
$[Cr(NH_3)_6]^{3+}$

octahedral



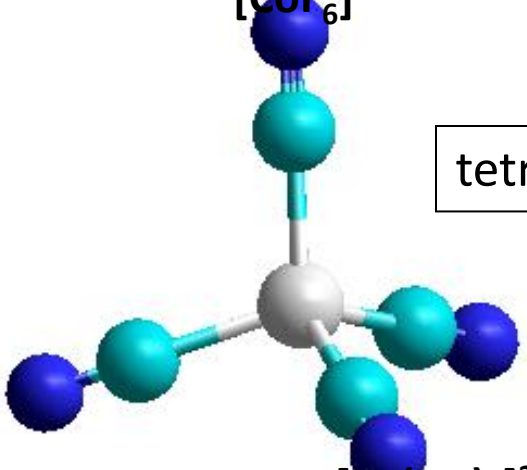
$[CoF_6]^{3-}$

square planar



$[Ni(CN)_4]^{2-}$

tetrahedral



$[Zn(CN)_4]^{2-}$