Chapter 21
d-block metal chemistry: the first row metals

Occurrence, extraction, and uses

Physical properties

Inorganic Chemistry

PERIODIC TABLE OF THE ELEMENTS

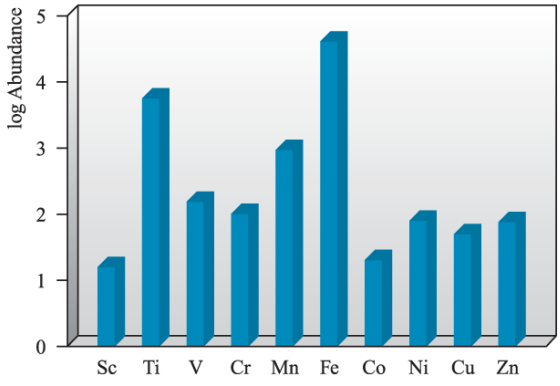
1												13	14	15	16	17	18
1 H 1.008	2															1 H 1.008	2 He 4.003
3 Li 6.941	4 Be 9.012	← Transition Metals →										5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
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	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
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 (97.91)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	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	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209.0)	85 At (210.0)	86 Rn (222.0)
87 Fr (223.0)	88 Ra (226.0)	103 Lr (262.1)	104 Rf (261.1)	105 Db (262.1)	106 Sg (263.1)	107 Bh (264.1)	108 Hs (265.1)	109 Mt (266.1)	110 (269.1)	111 (272.1)	112 (277.1)						

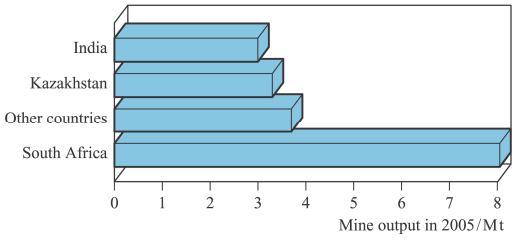
Lanthanides	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (144.9)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
Actinides	89 Ac (227.0)	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237.0)	94 Pu (244.1)	95 Am (243.1)	96 Cm (247.1)	97 Bk (247.1)	98 Cf (251.1)	99 Es (252.1)	100 Fm (257.1)	101 Md (258.1)	102 No (259.1)

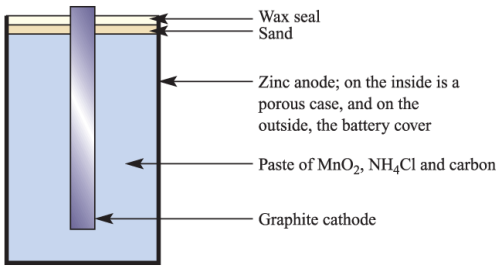
Introduction to the first row d-block metals

- Chemistry of the first member of the triad is distinct from the two heavier members
- Electronic spectra and magnetic properties of many complexes of 1st row transition metals can frequently be rationalized using **crystal or ligand field theory**, but the effect of spin-orbit coupling are more important for the heavier elements.
- Complexes of heavier metal ions show a wider range of coordination numbers than 1st row metal ions
- Trends of oxidation states are not consistent for all members of a triad
  - The maximum oxidation state is +6 for Cr, Mo, and W, though its stability is greater for Mo and W than Cr
- Metal-metal bonding is more important for the heavier metals than for those in the first row.

Relative Abundances of first row d-block metals

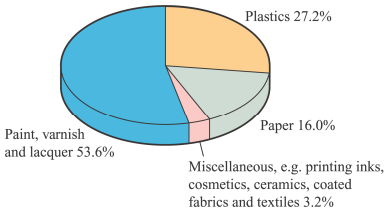


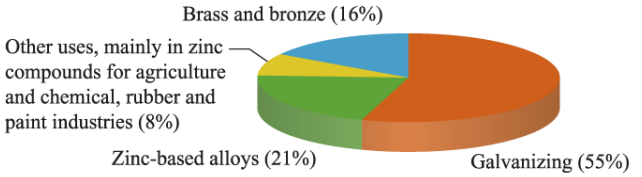




Schematic representation of the dry battery cell ('acid' version).

Modern bronze: 88%Cu:12%Sn
Commercial bronze: 90%Cu:10%Zn
High brass: 65%Cu:35%Zn
Manganese brass: 70%Cu:29%Zn:1.3%Mn



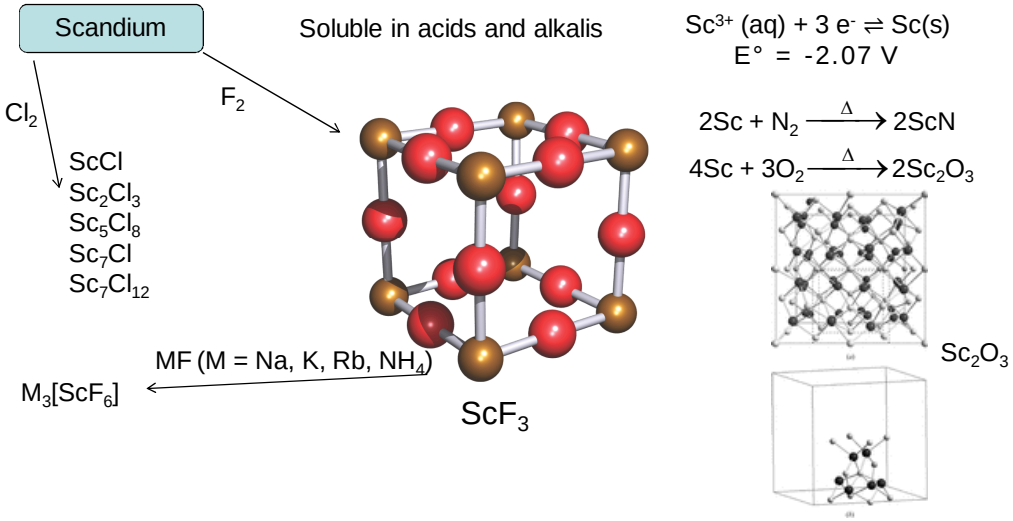


Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic number, Z	21	22	23	24	25	26	27	28	29	30
Physical appearance of pure metal	Soft; silver-white; tarnishes in air	Hard; lustrous silver coloured	Soft; ductile; bright white	Hard; blue-white	Hard; lustrous silver-blue	Quite soft; malleable; lustrous, white	Hard; brittle; lustrous blue-white	Hard; malleable and ductile; grey-white	Malleable and ductile; reddish	Brittle at 298 K; malleable 373–423 K; lustrous blue-white
Melting point / K	1814	1941	2183	2180	1519	1811	1768	1728	1358	693
Boiling point / K	3104	3560	3650	2945	2235	3023	3143	3005	2840	1180
Ground state valence electronic configuration (core = [Ar]):										
Atom	$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$	$4s^2 3d^{10}$
M^+	$4s^1 3d^1$	$4s^2 3d^1$	$3d^4$	$3d^5$	$4s^1 3d^5$	$4s^1 3d^6$	$3d^8$	$3d^9$	$3d^{10}$	$4s^1 3d^{10}$
M^{2+}	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$	$3d^{10}$
M^{3+}	[Ar]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$

† Metallic radius for 12-coordinate atom.
‡ See eq. 6.3 for relationship between electrical resistivity and resistance.
* At 290–300 K.

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Enthalpy of atomization, $\Delta_a H^\circ(298\,K)$ / kJ mol^{-1}	378	470	514	397	283	418	428	430	338	130
First ionization energy, IE_1 / kJ mol^{-1}	633.1	658.8	650.9	652.9	717.3	762.5	760.4	737.1	745.5	906.4
Second ionization energy, IE_2 / kJ mol^{-1}	1235	1310	1414	1591	1509	1562	1648	1753	1958	1733
Third ionization energy, IE_3 / kJ mol^{-1}	2389	2653	2828	2987	3248	2957	3232	3395	3555	3833
Metallic radius, r_{metal} / pm[†]	164	147	135	129	137	126	125	125	128	137
Electrical resistivity (ρ) $\times 10^8$ / Ω m (at 273 K)[‡]	56[*]	39	18.1	11.8	143	8.6	5.6	6.2	1.5	5.5
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

[†] Metallic radius for 12-coordinate atom.
[‡] See eq. 6.3 for relationship between electrical resistivity and resistance.
[*] At 290–300 K.



Coordination chemistry of Sc(III)

- Generally reacts with hard donors such as N and O

$[Sc(bpy)_3]^{3+}$ *mer*-$[ScCl_3(OH_2)_3]$ *mer*-$[ScCl_3(THF)_3]$ $[Sc(acac)_3]$

Titanium

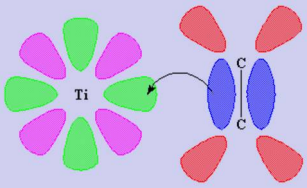
Reactions with nonmetals

TiC TiN TiO_2 TiX_4

Purification of Ti in the chloride process

$TiO_2 + Cl_2 \rightarrow TiCl_4$

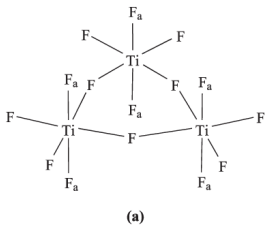
$TiCl_4$ (mp 249 K, bp 409 K)
Lewis acid, used with $AlCl_3$ in Zeigler-Natta catalysis for alkene polymerization



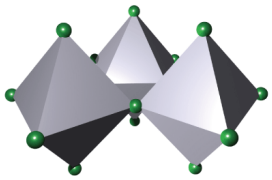
Reactions with mineral acids

$2Ti + 6HCl \xrightarrow{\Delta} 2TiCl_3 + 3H_2(g)$

$2Ti + 6HF \xrightarrow{\Delta} 2[TiF_6]^{2-} + Ti^{2+} + 3H_2(g)$



(a)

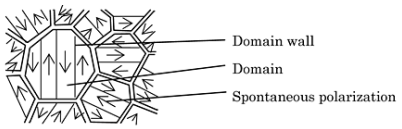

(b)

$TiF_4(s)$

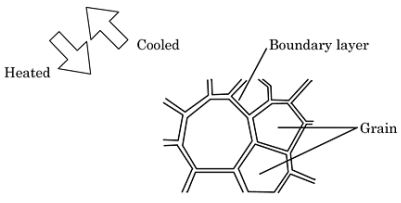
Titanium

$AO + TiO_2 \xrightarrow{\Delta,1600K} ATiO_3$ (A = Ca, Sr, Ba)

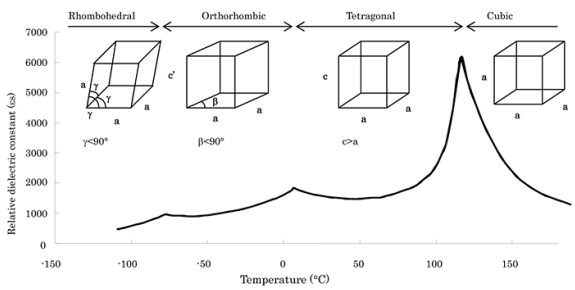
$BaTiO_3$ is ferroelectric
-has an electrical dipole moment even in absence of an external electrical field

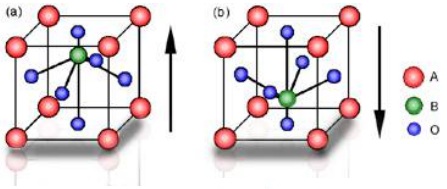


Initial condition of the structure (tetragonal) at temperature below Curie point



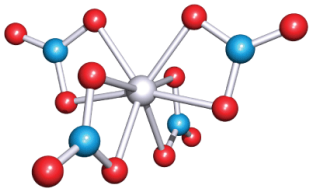
Condition of the structure (cubic) at temperature above Curie point





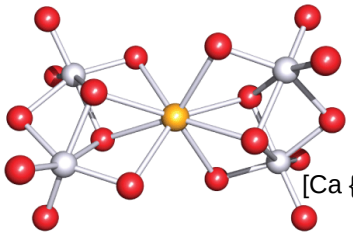
Dodecahedral coordination

$Ti(NO_3)_4$



(a)

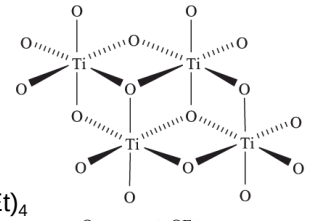
Titanium alkoxides
-used in waterproofing, heat resistant paints
-forming thin films/capacitors



$[Ca\{Ti_2(OEt)_9\}_2]$

(b)

$TiCl_4$ + NaOEt → $Ti(OEt)_4$

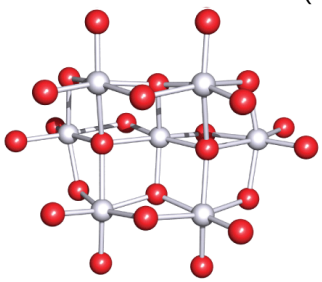


O represents OEt group

(c)

$Ti(OEt)_4$ + EtOH

$CuCO_3$



(d) $[Ti_7(\mu_4\text{-}O)_2(\mu_3\text{-}O)_2(OEt)_{20}]$

Vanadium

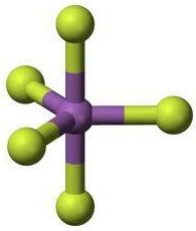
Reactions with halogens:
VF_5
VCl_4
VX_3 (X = Br or I)

V^{2+} (aq) + 2 e^- ⇌ V(s)
E° = -1.18 V

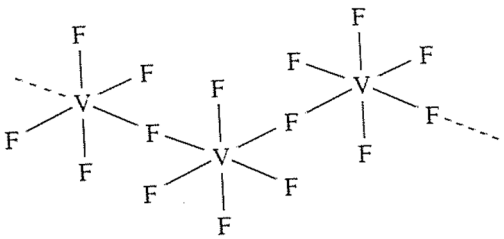
$2VBr_3 \rightarrow VBr_2 + VBr_4$

Typical oxidation states:
+5,+4,+3,+2, 0

Vanadium(V)



VF_5 (gas phase)

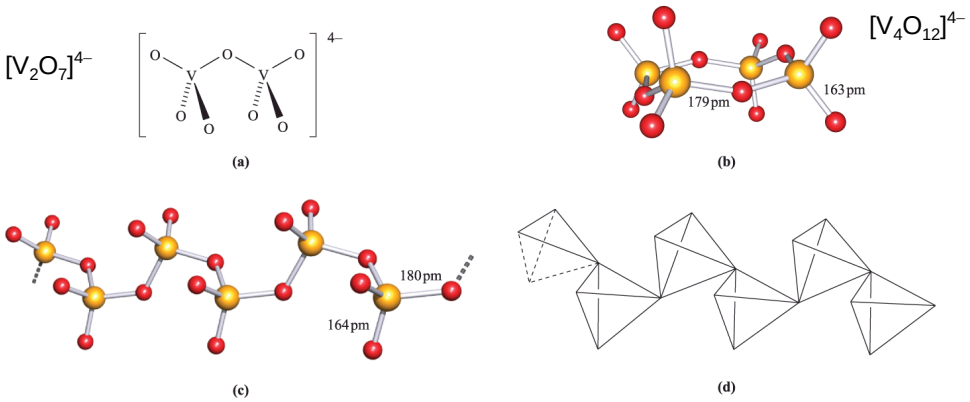


VF_5 (s) (polymeric)

Vanadium(V) oxide is **amphoteric**, sparingly soluble in water, but soluble in alkalis and in strong acids

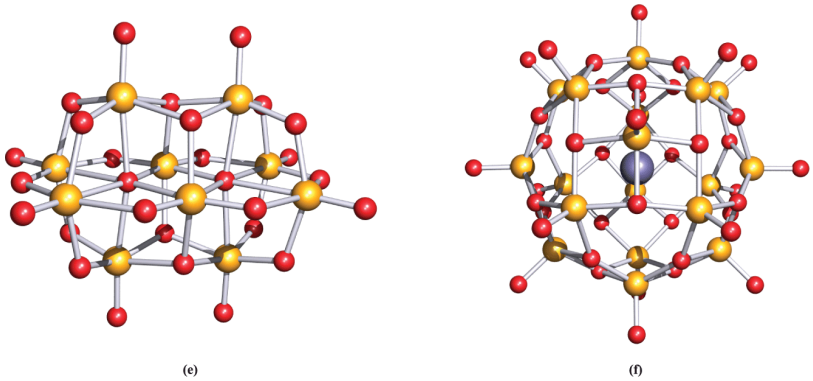
		$[VO_4]^{3-} + H+ \rightleftharpoons [VO_3(OH)]^{2-}$
pH 14	$[VO_4]^{3-}$	
		$2\ [VO_3(OH)]^{2-} \rightleftharpoons [V_2O_7]^{4-} + H_2O$
	$[VO_3(OH)]^{2-}$ (in eq. w/ $[V_2O_7]^{4-}$)	$[VO_3(OH)]^{2-} + H^+ \rightleftharpoons [VO_2(OH)_2]^-$
	$[V_4O_{12}]^{4-}$	$4\ [VO_2(OH)_2]^- \rightleftharpoons [V_4O_{12}]^{4-} + 4\ H_2O$
pH 6	$[H_nV_{10}O_{28}]^{(6-n)-}$	$10\ [V_3O_9]^{3-} + 15\ H^+ \rightleftharpoons 3[HV_{10}O_{28}]^{5-} + 6H_2O$
	V_2O_5	$[HV_{10}O_{28}]^{5-} + 5H^+ \rightleftharpoons [H_2V_{10}O_{28}]^{4-}$
pH 0	$[VO_2]+$	$[H_2V_{10}O_{28}]^{4-} + 14H^+ \rightleftharpoons 10\ [VO_2]^+ + 8\ H_2O$

Isopolyanions (homopolyanions) are complex metal oxoanions (polyoxometallates) of type $[M_xO_y]^{n-}$

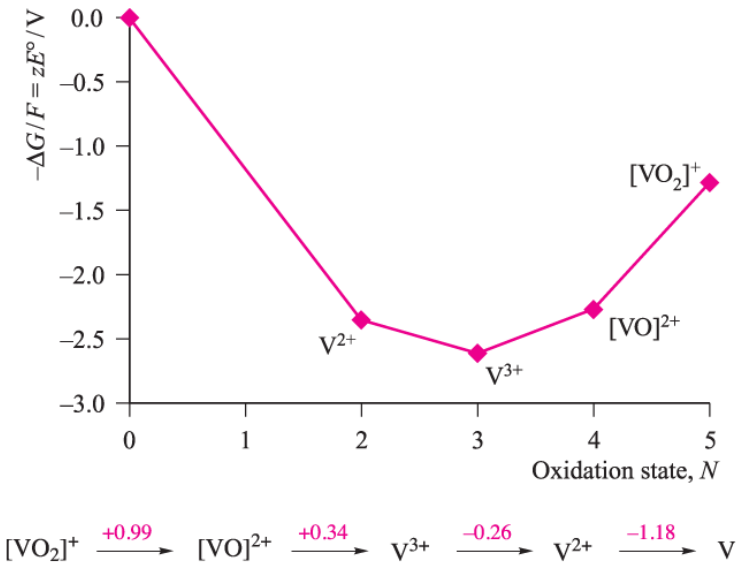


part of one chain in $[n\text{-}C_6H_{13}NH_3][VO_3]$
metavanadate

$[V_{10}O_{28}]^{6-}$ $[V_{18}O_{42}]^{4-}$



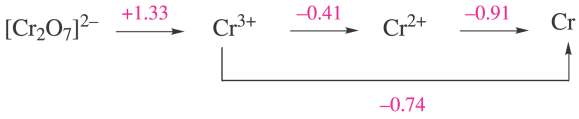
(e) (f)



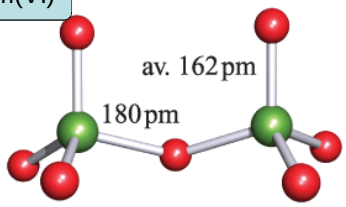
chromium

Reactions with nitrogen:
CrN, Cr_2N, Cr_3N, Cr_3N_2
Sulfur: Cr_2S_3

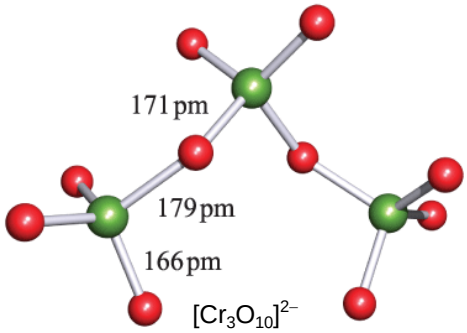
Typical oxidation states:
+6,+3,+2, 0



chromium(VI)



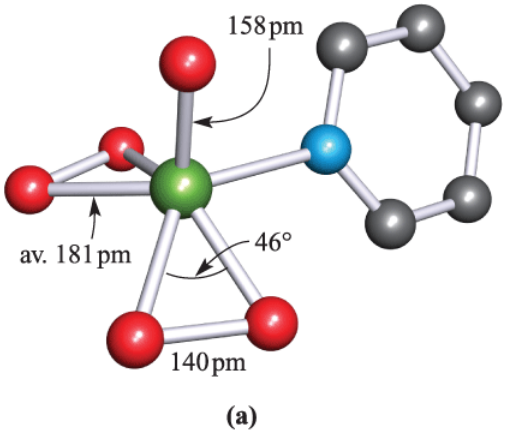
$[Cr_2O_7]^{2-}$



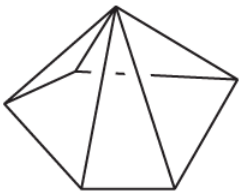
$[Cr_3O_{10}]^{2-}$

(a) Tetrahedral coordination **(b)**

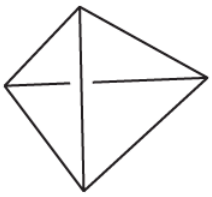
$[CrO_4]^{2-} + 2H^+ + 2H_2O_2 \rightarrow [Cr(O)(O_2)_2] + 3H_2O$
Unstable in aqueous solution, but stabilized as a pyridine adduct



(a)



(b)



(c)

$[Cr(O)(O_2)_2(py)]$

chromium(III)

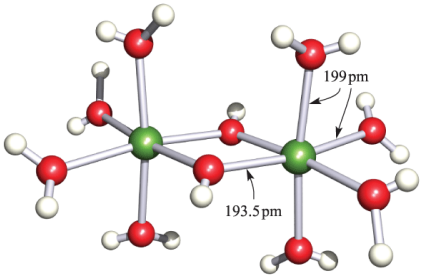
octahedral complexes
$[CrF_6]^{3-}$
$[Cr(acac)_3]$

$Cr + 3\ Cl_2 \rightarrow 2CrCl_3$

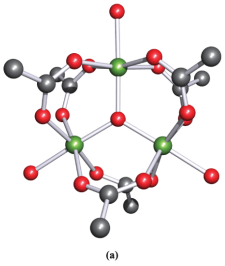
O_2, Δ ↓ Cr_2O_3

HF, 750 K ↓ $2CrF_3$

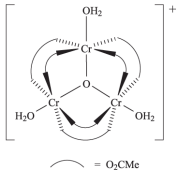
$Cr:Al_2O_3$



$[Cr_2(OH_2)_8(\mu\text{-}OH)_2]^{4+}$



(a)

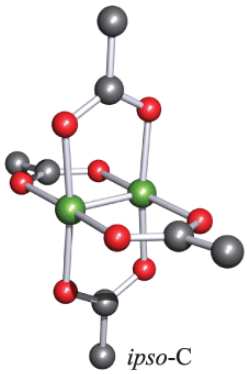


(b)

$[Cr_3L_3(\mu\text{-}O_2CR)_6(\mu_3\text{-}O)]^+$

Chromium-chromium multiple bonds

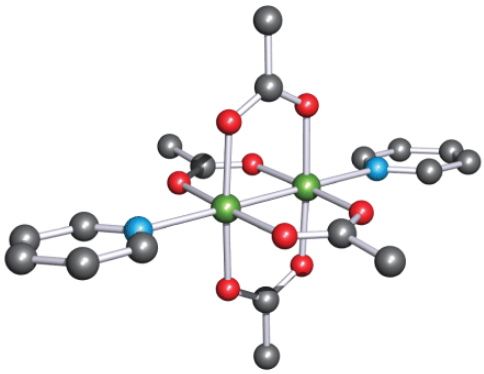
$[Cr_2(\mu\text{-}O_2CR)_4]$ or $[Cr_2L_2(\mu\text{-}O_2CR)_4]$



Cr–Cr = 197 pm

(a)

$[Cr_2(\mu\text{-}O_2CC_6H_2\text{-}2,4,6\text{-}{}^iPr_3)_4]$

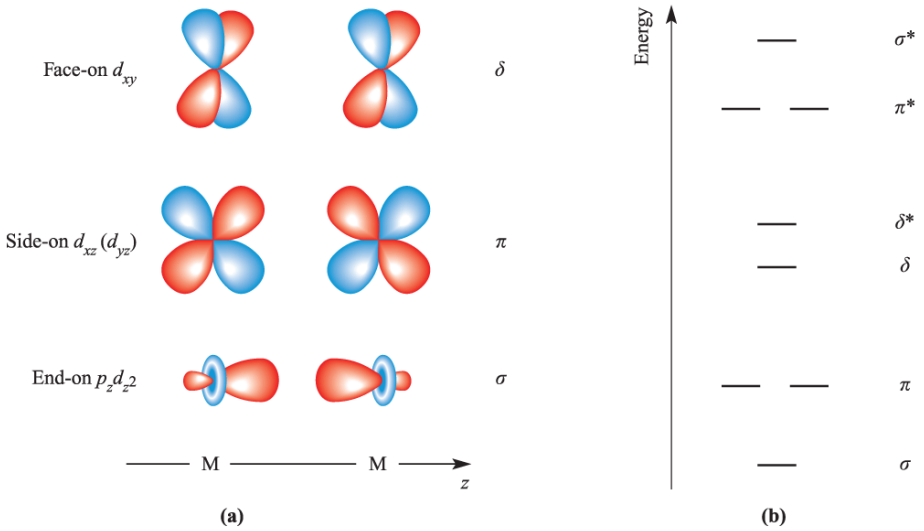


Cr–Cr = 237 pm

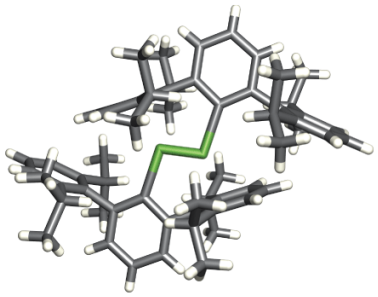
(b)

$[Cr_2(py)_2(\mu\text{-}O_2CMe)_4]$

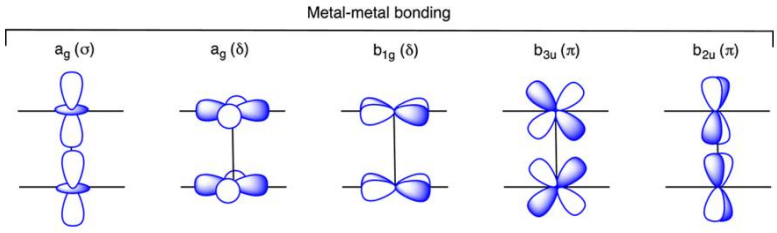
σ, π and δ components of a metal–metal quadruple bond



$[Cr_2L_2]\cdot MeC_6H_5$



σ, π and δ components of a metal–metal quintuple bond



DOI: 10.1021/acs.inorgchem.5b02059

manganese

Typical oxidation states:
+7,+6,+5, +4,+3,+2,+1, 0

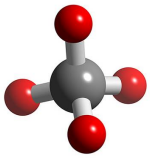
Reactions with halogens:
$Mn + 2HCl \rightarrow MnCl_2 + H_2$
$3Mn + 2O_2 \rightarrow Mn_3O_4$
$3Mn + N_2 \rightarrow Mn_3N_2$
$Mn + Cl_2 \rightarrow MnCl_2$

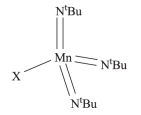
$M^{3+}(aq) + e^- \rightleftharpoons M^{2+}(aq)$

- M = Mn, E^o = +1.54 V
- M = Cr, E^o = -0.41 V

Manganese(VII)

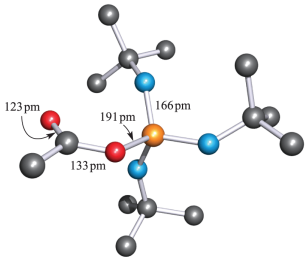
Much of Mn(VII) chemistry is related to MnO_4^-





e.g. X = Cl, O_2CMe, OC_6F_5

(a)



(b)

$[Mn(N^tBu)_3(O_2CMe)]$

$[MnO_4]^-(aq) + e^- \rightleftharpoons [MnO_4]^{2-}(aq)$ E^0 = +0.56 V

$[MnO_4]^-(aq) + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O$ E^0 = +1.69 V

$[MnO_4]^-(aq) + 8H^+ + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$ E^0 = +1.51 V

Manganese(VI)

$4[MnO_4]^- + 4[OH]^- \rightarrow 4[MnO_4]^{2-} + 2H_2O + O_2$

Unstable with respect to disproportionation

$[MnO_4]^{2-} + 4H^+ \rightarrow 2[MnO_4]^- + MnO_2 + 2H_2O$

Manganese(V)

K_3MnO_4

Unstable with respect to disproportionation

$2[MnO_4]^{3-} + 2H_2O \rightarrow [MnO_4]^{2-} + MnO_2 + 4OH^-$

$3[MnO_4]^{3-} + 8H^+ \rightarrow [MnO_4]^- + 2MnO_2 + 4H_2O$

Manganese(IV)

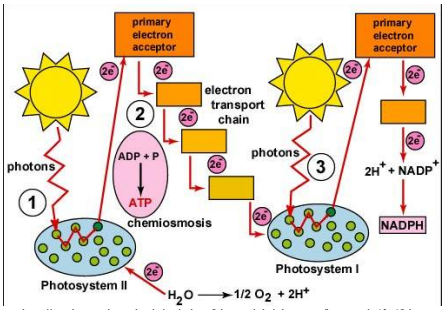
$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

$2CaCO_3 + MnO_2 \rightarrow Ca_2MnO_4 + 2CO_2$

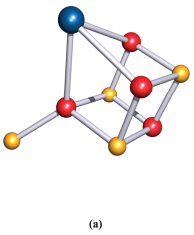
$K_2MnF_6 + 2SbF_6 \rightarrow MnF_2 + 2KSbF_6 + F_2$

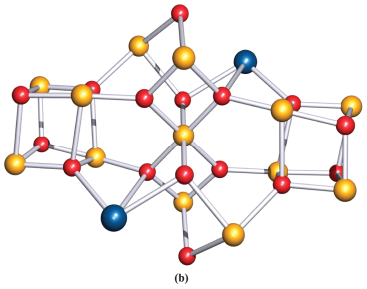
Multinuclear manganese complexes have been studied as models for the enzyme *Photosystem II* (PSII)

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$



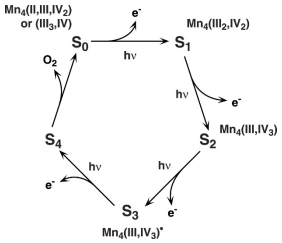
http://student.ccbcmd.edu/~gkaiser/biotutorials/photosyn/images/u4fg43.jpg





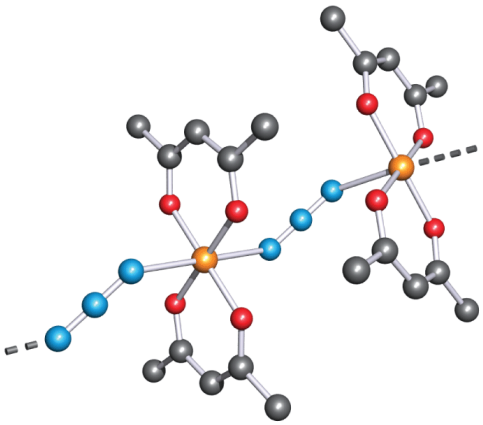
cubane-like Mn_4CaO_4 active site in the oxygen evolving centre (OEC) in Photosystem II

$\{Mn_{13}Ca_2O_{16}\}$



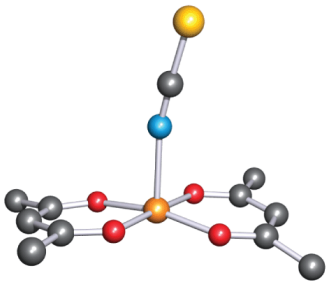
http://www.pnas.org/content/99/13/8631.long

Manganese(III)



(a)

$[Mn(N_3)(acac)_2]$



(b)

$[Mn(NCS\text{-}N)(acac)_2]$

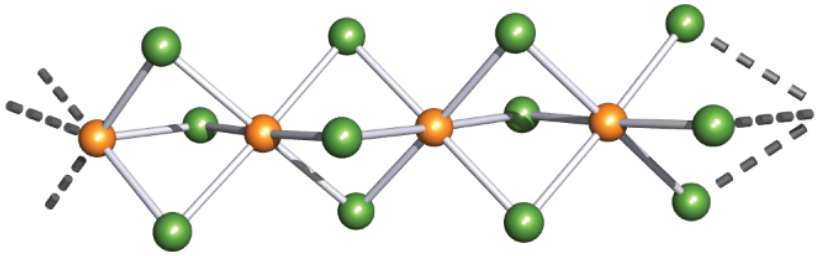
Manganese(II)

$2\ MnO_2 + 2H_2SO_4 \xrightarrow{\Delta} 2MnSO_4 + O_2 + 2H_2O$

Mn(II) salts are generally pale pink or colorless

- d^5 high spin – d-d transitions are spin- and Laporte- forbidden
- Absorptions weaker by factor of ~10^2 than from spin-allowed transitions of other metal ions in first row.

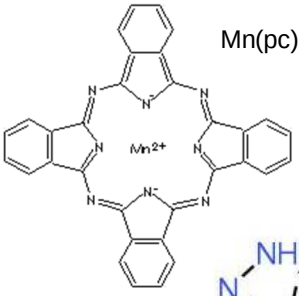
Many Mn(II) complexes are known, some with discrete ions, other in polyhedral chains



Infinite chains of face-sharing $MnCl_6$

$[Me_2NH_2][MnCl_3]$

Manganese(II)



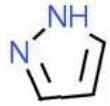
Mn(pc)

tetrahedral: $[MnCl_2(OPPh_3)_2]$, $[Mn(N_3)_4]^{2-}$, $Mn(Se_4)_2]^{2-}$

square planar: Mn(pc)

trigonal bipyramidal: $[MnBr_2\{OC(NHMe_2)_2\}_3]$, MnI

Octahedral: *trans*-$[MnBr_2(Hpz)_4]$, *cis*-$[Mn(bpy)_2(NCS\text{-}N)_2]$, $[Mn(EDTA)]^{2-}$

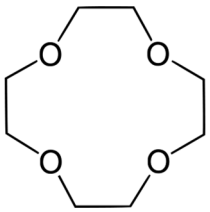


Hpz

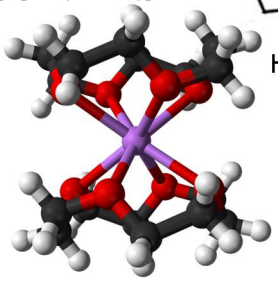
7 coordinate: $[Mn(EDTA)(OH_2)]^{2-}$

Square antiprism: $[Mn(12\text{-crown-}4)_2]$

Dodecahedral: $[Mn(NO_3\text{-}O,O')_4]^{2-}$



12-crown-4



Manganese(I)

Typically stabilized by π–acceptors in organometallic compounds

Iron

Finely divided iron is pyrophoric in air, but bulk metal only oxidizes if heated in dry air
In moist air, iron rusts, forming $Fe_2O_3 \cdot H_2O$

- Rusting is electrochemical, requiring O_2, H_2O, and an electrolyte (SO_2, NaCl, etc.)

$$2\ Fe \rightarrow 2\ Fe^{2+} + 4e^-$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4[OH]^-$$

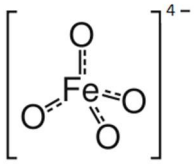
FeF_3, $FeCl_3$, $FeBr_3$, FeI_2, FeS formed by reactions with elements

Iron(VI), iron(V), Iron(IV)

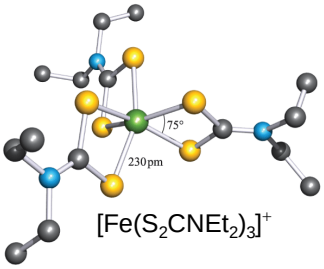
Mossbauer spectroscopy widely used to study iron coordination and oxidation states

Highest oxidation states of iron are in: $[FeO_4]^{2-}$, $[FeO_4]^{3-}$, $[FeO_4]^{4-}$, $[FeO_4]^{3-}$

Jahn-teller distortions for Fe(IV)

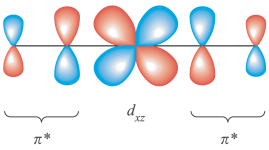


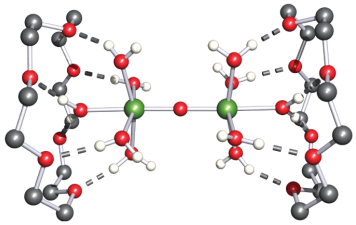
$T_d \rightarrow D_{2d}$



$[Fe(S_2CNEt_2)_3]^+$

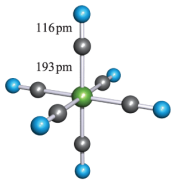
Iron(III)

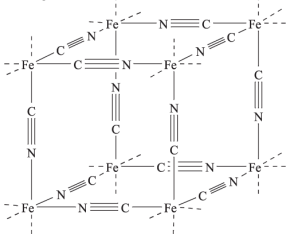


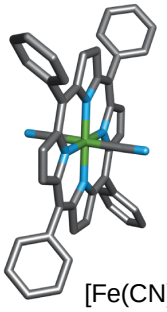


$[(H_2O)_5Fe(\mu\text{-}O)Fe(OH_2)_5]^{4+} \cdot (18\text{-crown-}6)_2$

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





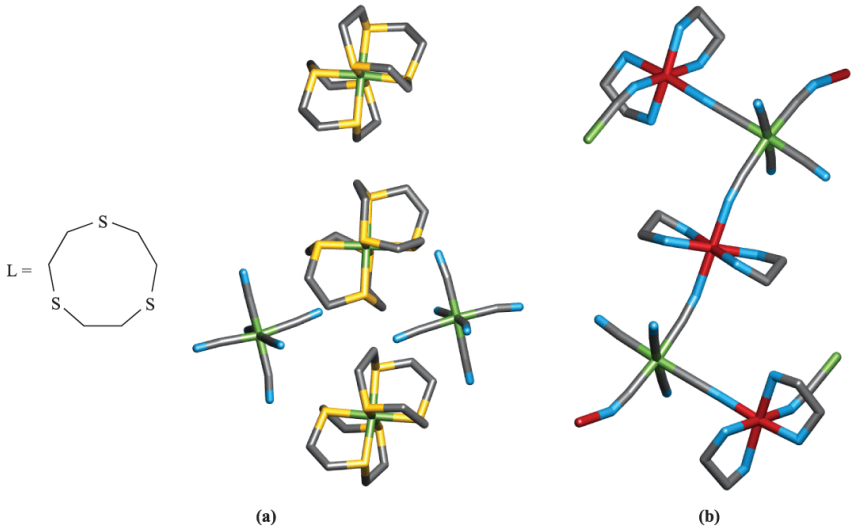


(a) (b) (c)

$[Fe(CN)_2(TPP)]$

Spectrochemical series

$I^- < Br^- < S^{2-} < Cl^- < SCN^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < PPh_3 < CN^- < CO$



$[FeL_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$

Fe(II) and Fe(III) centres are remote from each other ('valence trapped')

polymeric structure of $[Ni(en)_2]_3[Fe(CN)_6]_2{\cdot}2H_2O$

cobalt

Typical oxidation states: +4,+3,+2, 0

Reactions with halogens:
$2Co + 3F_2 \rightarrow 2CoF_3$
$Co + Cl_2 \rightarrow CoCl_2$
$Co + Br_2 \rightarrow CoBr_2$
$Co + I_2 \rightarrow CoI_2$

$M^{2+}(aq) + 2e^- \rightleftharpoons M(s)$

- M = Fe, E^o = -0.44 V
- M = Co, E^o = -0.28 V

cobalt(IV)

Few Co(IV) compounds are characterized
Ba_2CoO_4 and M_2CoO_3 (M = K, Rb, Cs)

$[CoF_6]^{2-}$ low spin, d^5

$[CoF_6]^{3-}$ high spin, d^6

cobalt(III)

Complexation stabilizes the Co(III) oxidation state

$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$ E^0 = +1.92 V

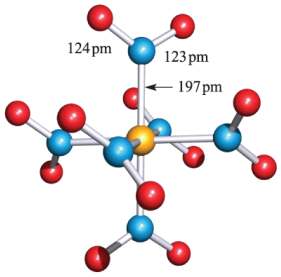
$[Co(bpy)_3]^{3+}(aq) + e^- \rightleftharpoons [Co(bpy)_3]^{2+}(aq)$ E^0 = +0.31 V

$[Co(NH_3)_6]^{3+}(aq) + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}(aq)$ E^0 = +0.11 V

$[Co(en)_3]^{3+}(aq) + e^- \rightleftharpoons [Co(en)_3]^{2+}(aq)$ E^0 = -0.26 V

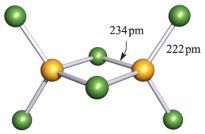
$[Co(CN)_6]^{3+}(aq) + H_2O + e^- \rightleftharpoons [Co(CN)_5(OH_2)]^{2+}(aq) + (CN^-)$ E^0 = -0.83 V

cobalt(III)

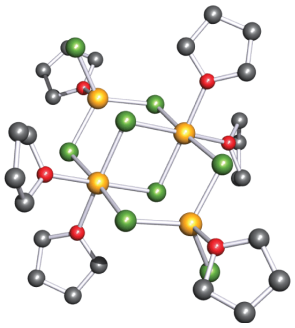


$[Co(NO_2\text{-}N)_6]^{3-}$

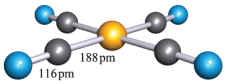
cobalt(II)



$[Co_2Cl_6]^{2-}$

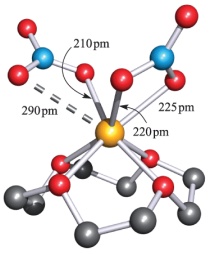


$[Co_4Cl_2(\mu\text{-}Cl)_6(THF)_6]$



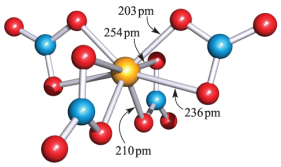
(a)

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



(b)

$[Co(12\text{-}crown\text{-}4)(NO_3)_2]$



(c)

$[Co(NO_3)_4]^{2-}$

nickel

Reactions with fluorine:
$Ni + F_2 \rightarrow NiF_2$
Forms a coating, which prevents further reaction.
Monel metal (68% Ni, 32% Cu)

Oxidation states:
+4,+3,+2,+1, 0

$M^{2+}(aq) + 2e^- \rightleftharpoons M(s)$

- M = Ni, E^o = -0.25 V
- M = Co, E^o = -0.28 V

nickel(IV)

Few Ni(IV) compounds are characterized, K_2NiF_6, $KNiIO_6$

nickel(III)

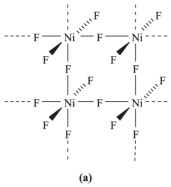
Complexation stabilizes the Ni(III) oxidation state

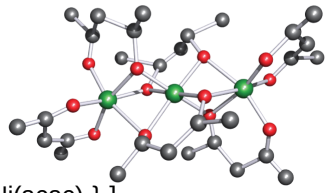
$[NiF_6]^{3-}$ low spin, d^7 (Jahn-Teller distorted)

Ni(III) is a good oxidizing agent, often stabilized by σ–donor ligands

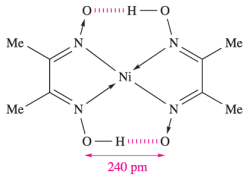
Nickel(II)

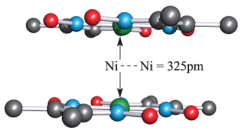
K_2NiF_4

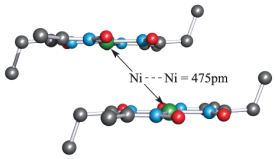




$[\{Ni(acac)_2\}_3]$



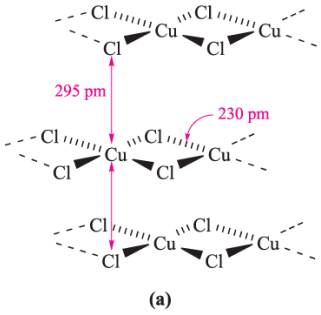




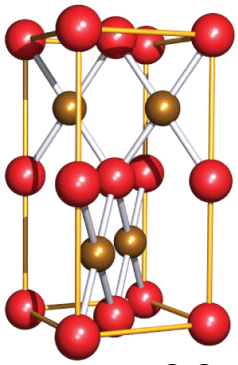
$[Ni(Hdmg)_2]$

bis(ethylmethylglyoximato)nickel(II)

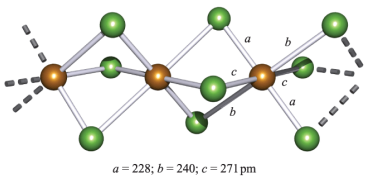
Copper(II)



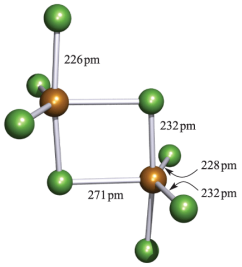
solid state structure of $CuCl_2$



CuO



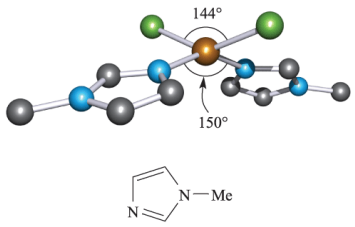
polymeric $^{(a)}[CuCl_3]_n^{n-}$



$^{(b)}[Cu_2Cl_8]^{4-}$

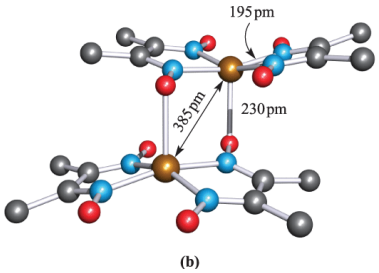
Copper(II)

Flattened tetrahedral



(a)

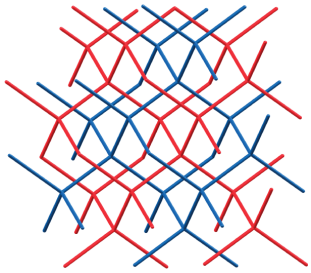
$[CuCl_2(Meim)_2]$



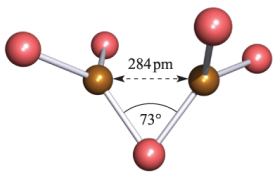
(b)

$[Cu(Hdmg)_2]$ forms dimers

Copper(I)



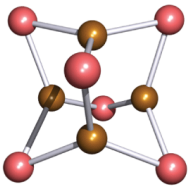
Cu_2O



$Cu–Br_{term} = Cu–Br_{bridge} = 239\,pm$

(a)

$[Cu_2Br_5]^{3-}$

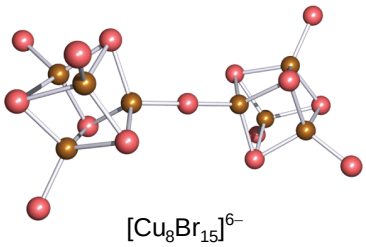


$Cu\cdots Cu = 274\,pm$
$\angle Cu–Br–Cu = 69.5°$

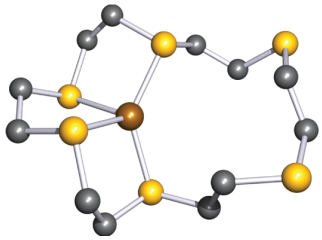
(b)

$[Cu_4Br_6]^{2-}$

Mixed valence Cu



$[Cu_8Br_{15}]^{6-}$



$[Cu(S_6\text{-macrocycle})]$

zinc

Reactions with oxygen:
$2Zn + O_2 \rightarrow 2ZnO$
Reactions w/halogens: ZnF_2, $ZnCl_2$, ZnI_2

Oxidation states:
+2,(+1), 0

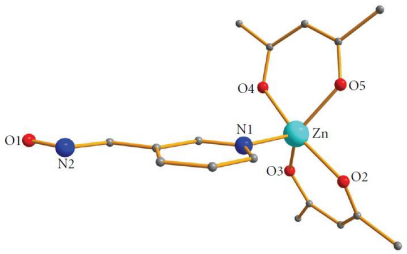
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$ $E^o = -0.76$ V

zinc(II)

Zn^{2+}, Electronic configuration d^{10}, colorless and diamagnetic

Vapors of halides are linear

Adopts tetrahedral, square pyramidal, octahedral coordination



$Zn(acac)_2 \cdot H_2O + (3\text{-py})CHNOH \xrightarrow{MeOH} [Zn(acac)_2\{(3\text{-py})CHNOH\}] \cdot H_2O$

Zinc Halides