# Hydroxides

$$M^{+}OH^{-}_{(s)} + nH_2O \rightarrow M^{+}_{(aq)} + OH^{-}_{(aq)}$$

for metals with more ionic bonds → Base

$$MOH + nH_2O \rightleftarrows MO^{-}_{(aq)} + H_3O^{+}_{(aq)}$$

for more covalent M-O bonds of the non-metals → Acid

Amphoteric Hydroxides also exist

# Alkoxides

The basic formula of an alkoxide is $OR^-$ where R is an organic group such as an alkyl group.

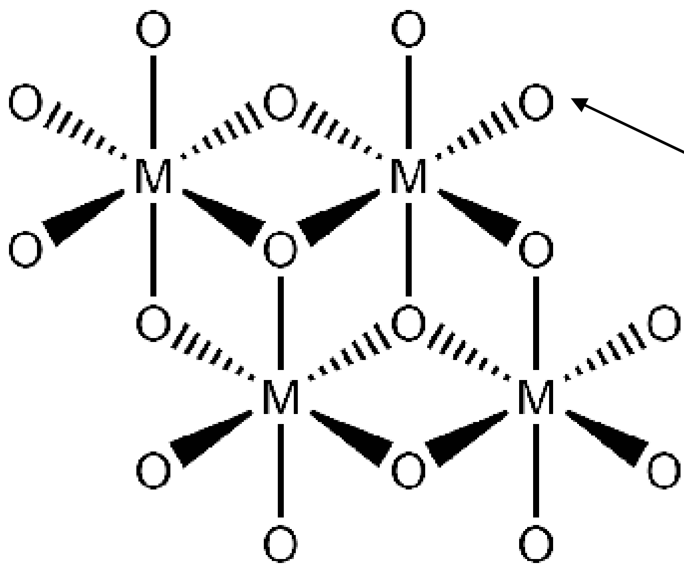
They are very reactive in water and hydrolyze quickly…

$$OR^{-} + H_2O \rightleftarrows OH^{-} + ROH$$

(forms an alcohol)

$M(OR)_4$ is a common metal alkoxide type of compound (or we also say "complex").
*e.g.*, $Ti(OR)_4$

It has an interesting molecular structure that stabilizes the molecule.

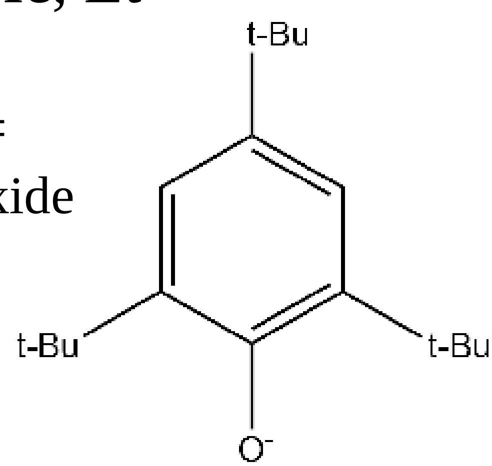



These represent $OR^-$ groups

the more bulky R groups on $OR^-$ ligands lead to compounds with low coordination numbers

$M(OR)_4$ when R = Me, Et

"$M(OR)_2$" when R =
2,3,5-tritetrabutylphenoxide



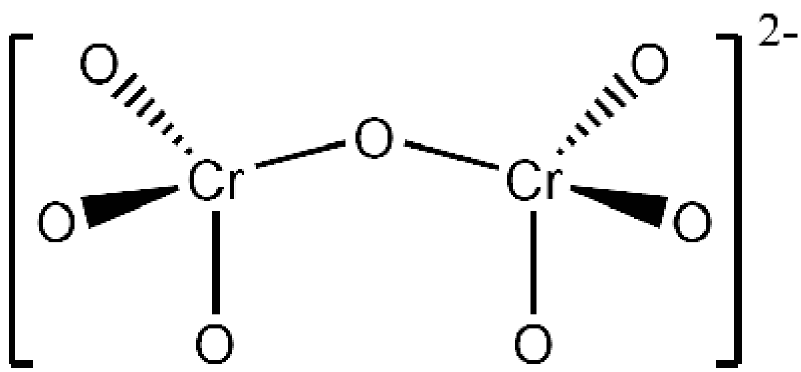
## Polynuclear or Polymeric Oxides/Hydroxides

- dimers, trimers, cages, etc.
- cyclic structures
- chains
- sheets

## Polynuclear Oxo Anions

oxygen atoms shared between various polyhedra

Ex #1 dichromate

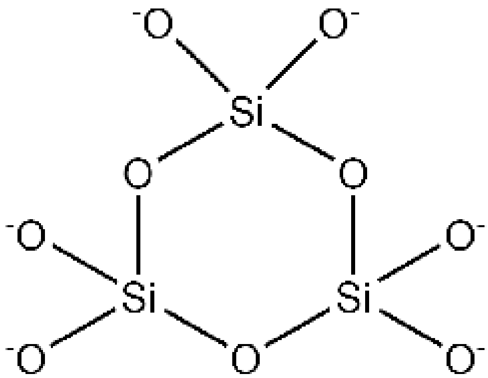


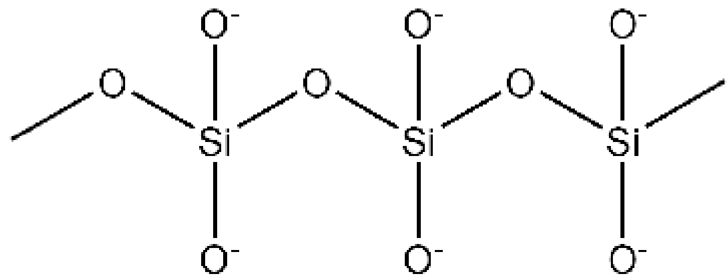

Dimer

$Cr_2O_7^{2-}$

(two tetrahedra sharing one atom)

Ex #2





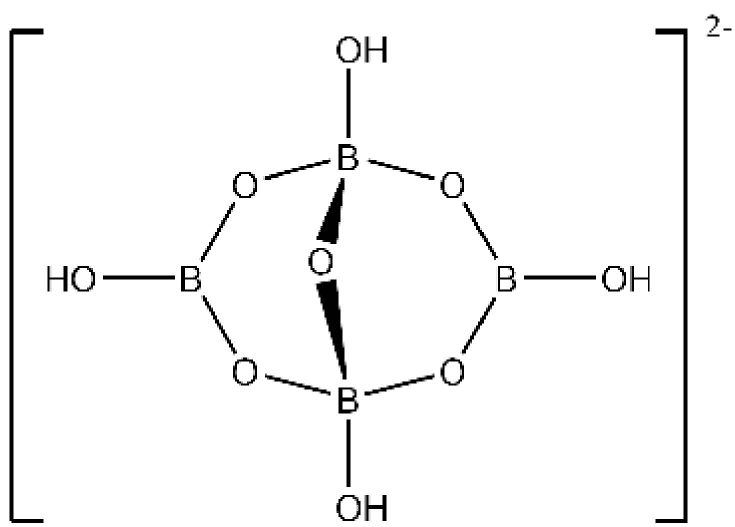
(tetrahedra sharing an edge)

Ring anion
$Si_3O_9^{6-}$

Chain
$SiO_3^{2-}$

Ex #3

tetramer
$B_4O_5(OH)_4^{2-}$



Common anion in borates

Basic Idea:

- Silicates are minerals composed of different types of shared $SiO_4$ units
- Borates are minerals in the same vein, but with $BO_4$ units shared in various ways

The structure that results is based on a complicated interplay of concentrations, pH, temperature and pressure (which affect solubilities).

- Eventually, if all oxygens are shared in a $SiO_4^{n-}$, solid, it becomes silica, $SiO_2$

- replace some $Si^{4+}$ ions with $Al^{3+}$, and it is possible to make structures like the silicates, except the anion charge is retained:
  "$SiO_2$" neutral
  "$SiAlO_2$" is negatively charged $SiAlO_2^-$
  $\rightarrow$ <u>Aluminosilicates</u>
  Minerals with open frameworks that can allow molecules to pass through

Ion exchangers (solution)
Molecular sieves (gas)

## Zeolites

$[(Al,Si)O_2]_n$ framework

Basic composition of Zeolites is:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot z\, H_2O$$

number of $AlO_2^+$ units

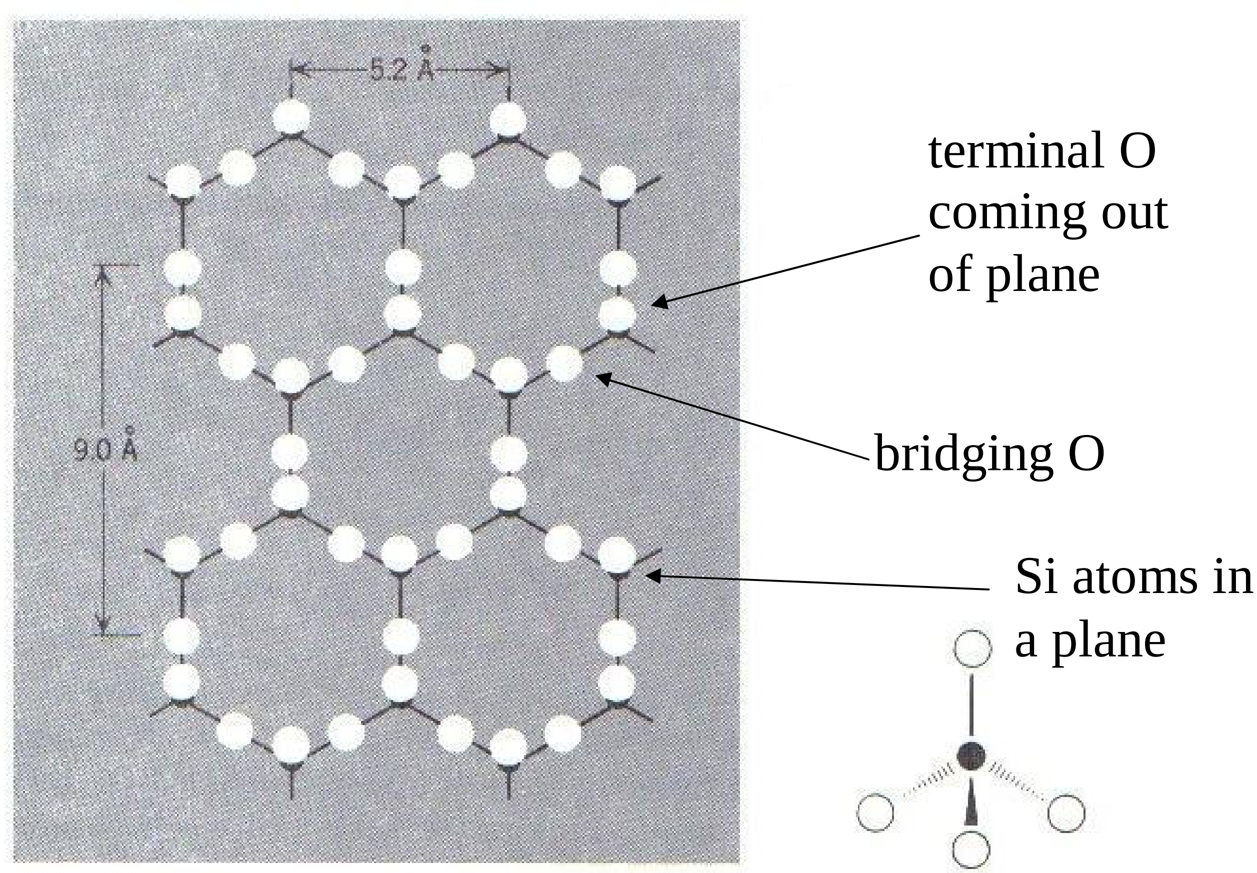
charge of metal cation

number of $SiO_2$ units

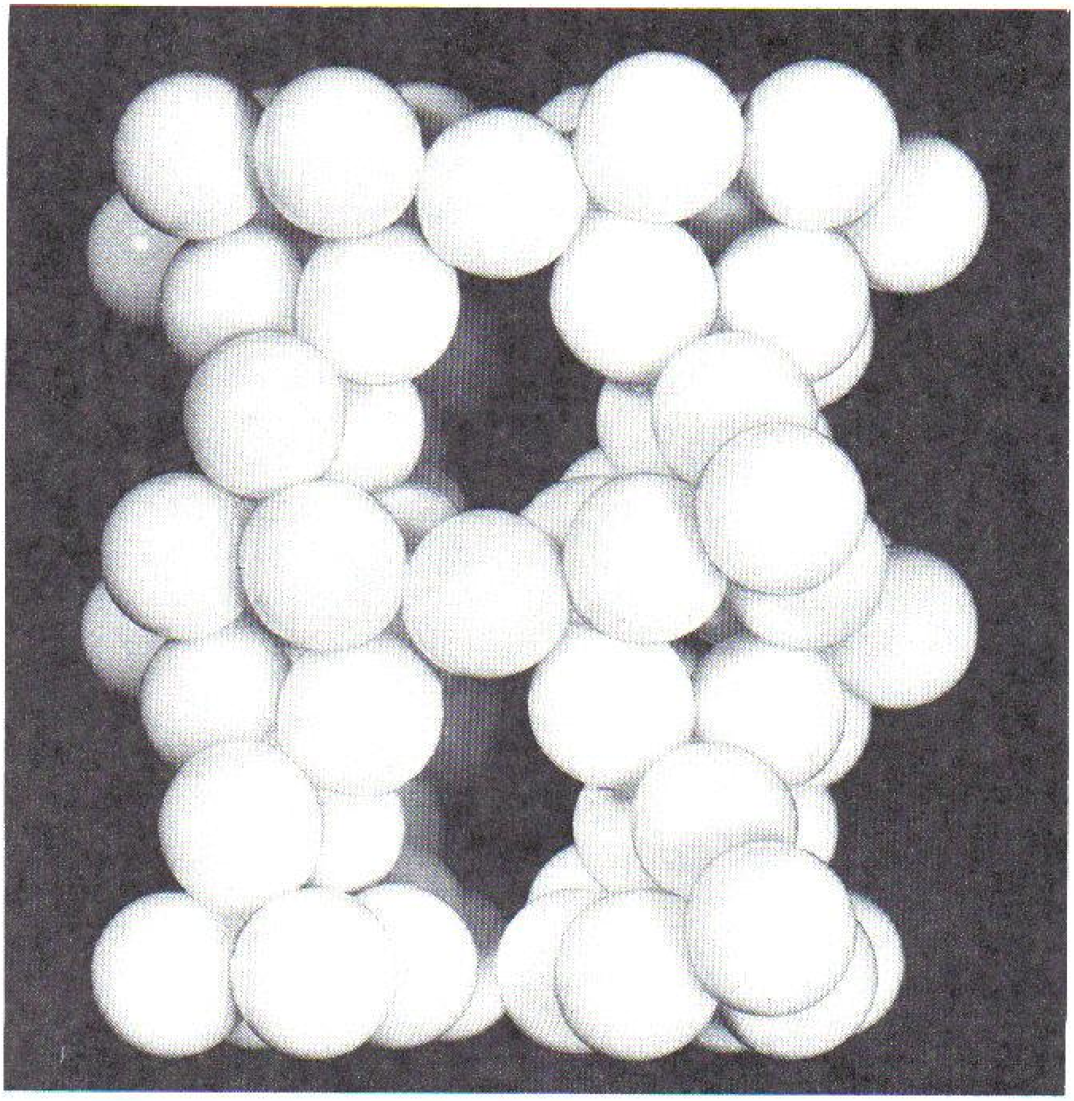
z – degree of hydration
lots of water can fill void space

# $Si_2O_5^{2-}$ sheets

Si atoms are in a plane connected by 3 oxygen atoms to give a hexagonal motif one oxygen on each Si is not used to bridge



Model of a zeolite showing the channels in the structure. The spheres are O atoms. The Si and Al atoms lie at the centers of the $O_4$ tetrahedra and cannot be seen



# Polynuclear Oxo Anions continued

## "Polyoxoanions" of Transition Metals

$V^{V}$, $Nb^{V}$, $Ta^{V}$, $Mo^{VI}$, $W^{VI}$

form anions with shared $MO_6$ octahedra where corners and edges are shared

Excellent example is $[CrMo_6O_{24}H_6]^{3-}$

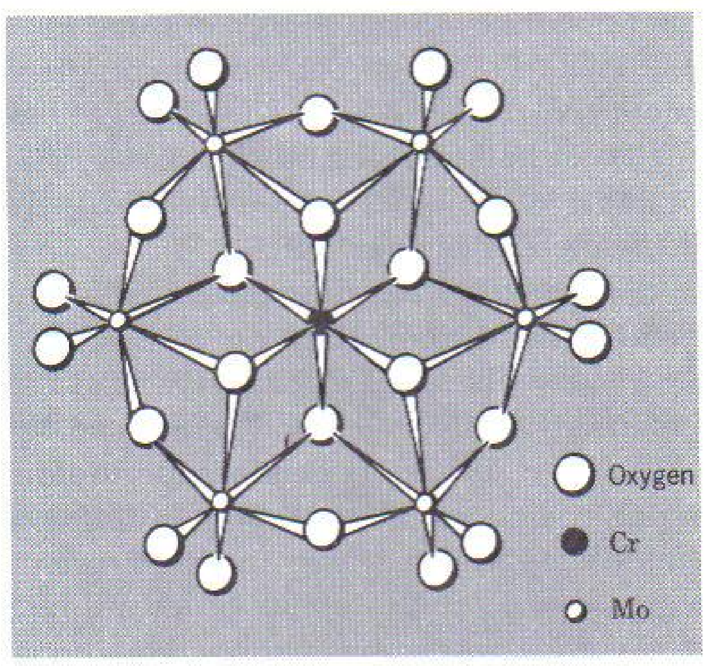
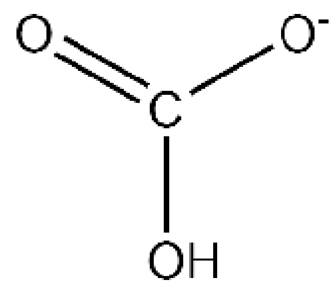



**Figure 5-5** The structure of $[CrMo_6O_{24}H_6]^{3-}$. The hydrogen atoms are probably bound to oxygen atoms of the central octahedron.

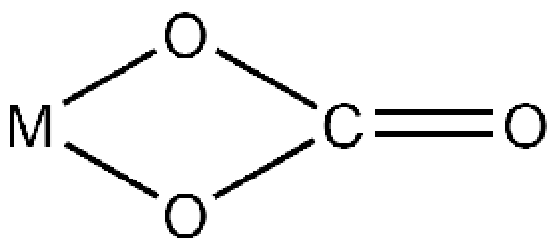
Miscellaneous oxo anions that are worth mentioning specifically because they are ubiquitious are as follows:

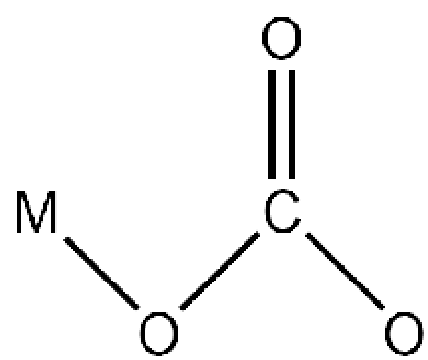
<u>Carbon-based</u>

$CO_3^{2-}$ $HCO_3^-$



coordination modes:

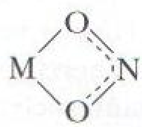




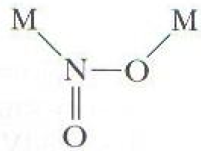
<u>Nitrogen-based</u>

$NO_2^-$ nitrite $NO_3^-$ nitrate

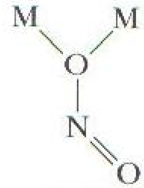
Various binding modes are depicted on page 152-153 of textbook



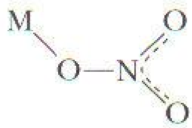
5-X



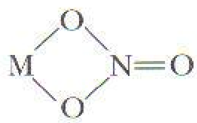
5-XI



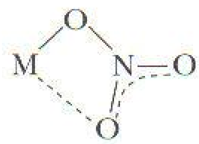
5-XII



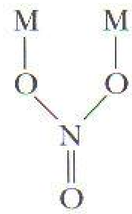
5-XIII



5-XIV



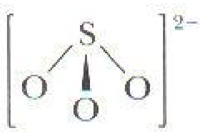
5-XV



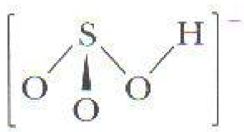
5-XVI

## Sulfur-based

$SO_3^{2-}$ sulfite; $HSO_3^-$ bisulfite
$SO_4^{2-}$ sulfate; $HSO_4^-$ bisulfate



5-XVII



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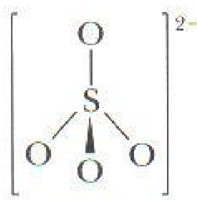

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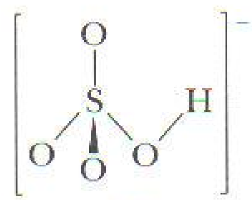
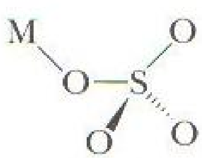
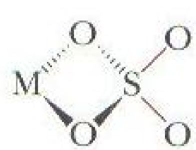


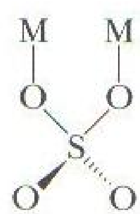
5-XX



5-XXI



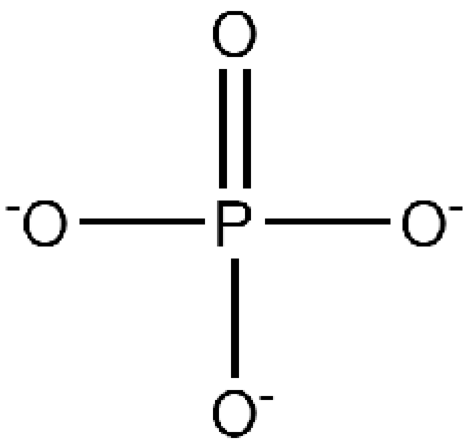
5-XXII



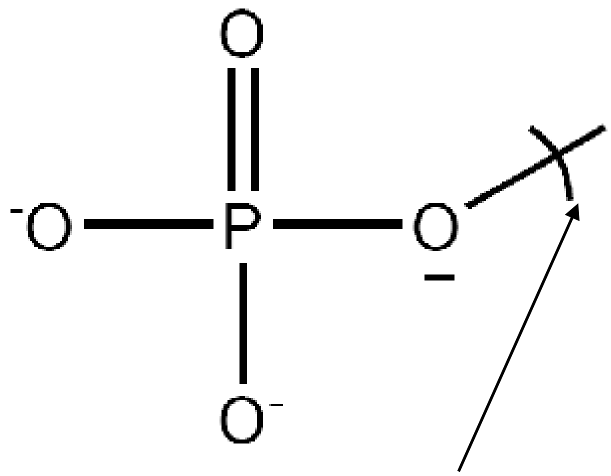
5-XXIII

# Phosphates

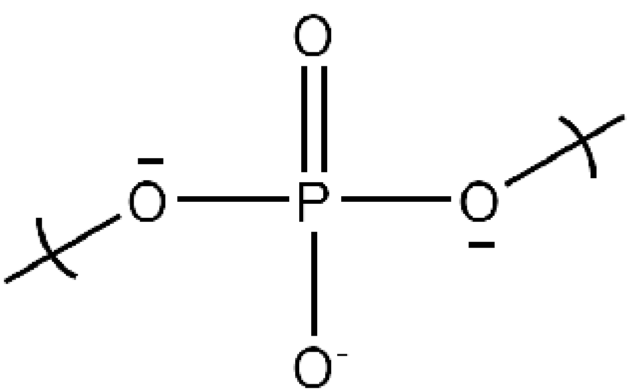
Also important in chemistry as discrete anions and in condensed (polymeric) phases as minerals



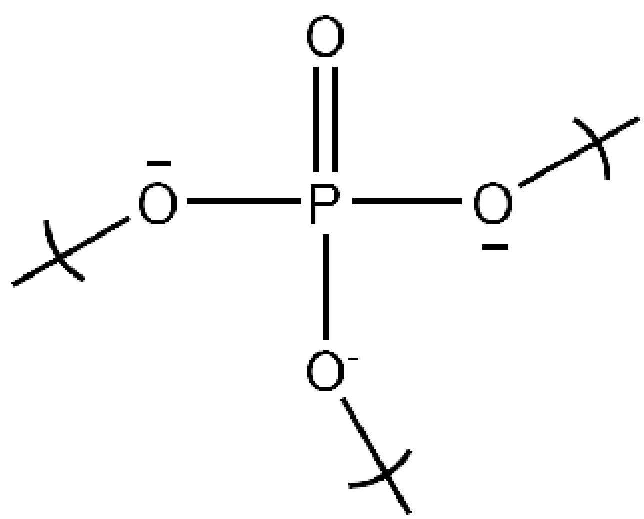
$PO_4^{3-}$
(one of four resonance forms)



binds as an end unit at one O

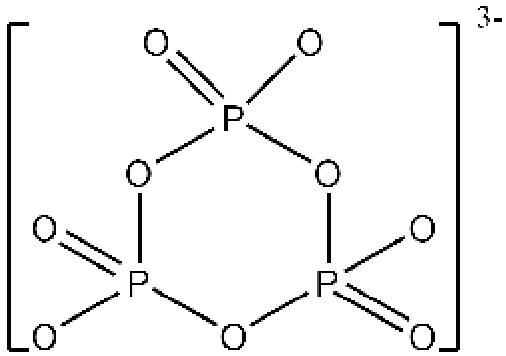


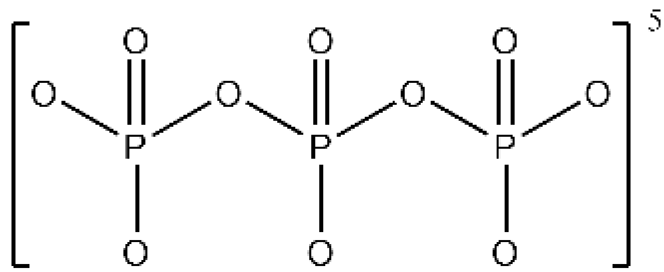
binds as a middle unit



binds as a branching unit

These "Building Blocks" can assemble into linear or cyclic structures





$P_3O_9^{3-}$
metaphosphates

$P_3O_{10}^{5-}$
polyphosphates

widely used as water softeners due to their ability to stabilize $Ca^{2+}$, $Mg^{2+}$ and other ions that make water "hard" ($MgCO_3$, $CaCO_3$ scum)

## <u>Other types of Oxo Anions</u>

- Halogen-Containing Anions
  Halogen-Oxides
  (1) $XO_3^-$ halates (X formal ox. state = ?)
  e.g. $ClO_3^-$ chlorate
  (2) $XO_4^-$ perhalates (X formal ox. state = ?)
  $ClO_4^-$ perchlorate is most well-known

$XO_4^-$ not particularly stable, especially as in the perchlorate anion, $ClO_4^-$

→ these are strong oxidizing agents stabilized in water, dangerous when dry and especially with organic compounds around

• Transition Metal Oxides (Discrete)

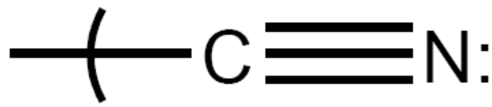
Tetrahedral $MO_4^{n-}$ is very common for the highest oxidation state of the metal (or next to highest)

| | | | |
|---|---|---|---|
| e.g. | $OsO_4^-$ | $Os^?$ | What is formal ox. state? |
| | $ReO_4^-$ | $Re^?$ | |
| Excellent oxidizing agents! | $MnO_4^-$ | $Mn^?$ | |
| | $CrO_4^-$ | $Cr^?$ | |

## <u>Halides and "Pseudohalides"</u>

• Pseudohalides such as $CN^-$ act like halides $OCN^-$, $SCN^-$ (all are good ligands)

Most important one is cyanide $CN^-$



Binds through C atom first

- Halides - ionic versus covalent – ionic are discussed in Chapter 5 (covalent analogs are in Chapter 20) ionic halides are with metals in +1, +2, +3 oxidation states

## Sulfide and Hydrosulfide

- $S^{2-}$ Ionic sulfide compounds are formed with alkali and alkaline earth (they are not stable in $H_2O$)

- $S_n^{2-}$ polysulfides very important ligands for transition metals

# Complex Anions

## Complex Halides

$$AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$$

Lewis Acid      Lewis Base

$$PF_5 + F^- \rightleftharpoons PF_6^-$$

general stability is F > Cl > Br > I

due to strength of A-F
vs A-Cl interactions
vs A-Br
vs A-I

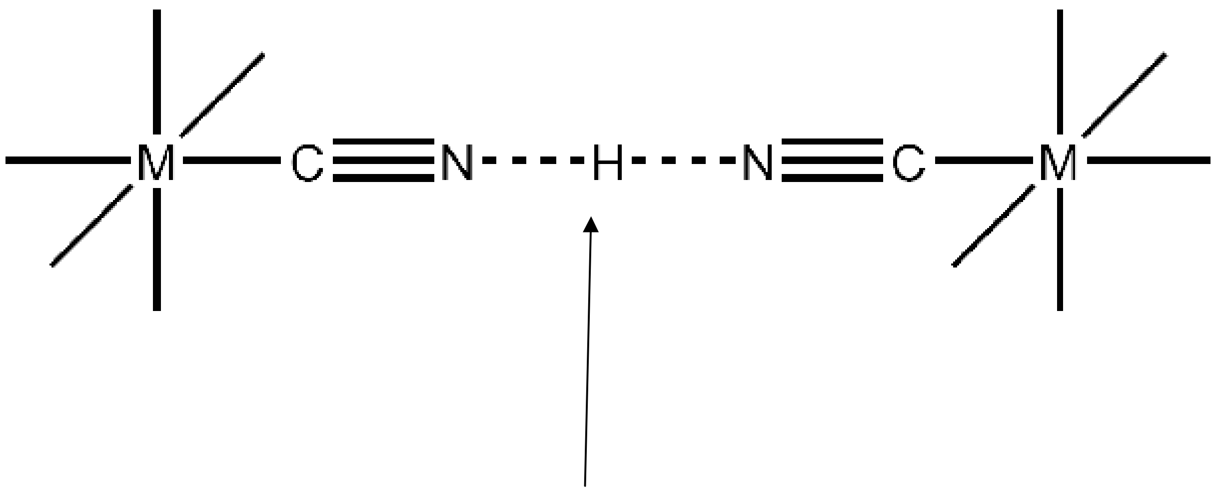
## Complex Transition Metal Anion s

$CN^-$ forms many complex anions in a variety of oxidation states from low to high

$[Fe^{II}(CN)_6]^{4-}$ versus $[Mo^{V}(CN)_8]^{3-}$

Most of these anions are quite stable in $H_2O$, and indeed the acid form of some of them can be made, without releasing HCN.

For example $H_4[Fe(CN)_6]$ exists




$H^+$ is stabilized by H-bonding between molecules