

Greenwood & Earnshaw

2nd Edition

Chapter 24

Group 7

**Manganese, Technetium &
Rhenium**

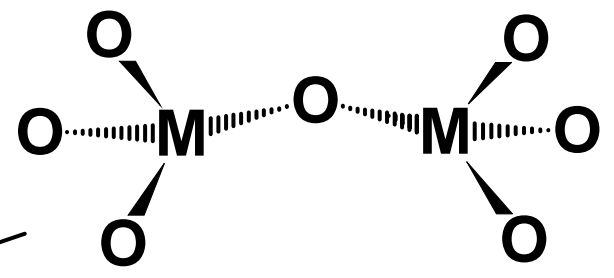
Manganese, Technetium & Rhenium

- Manganese very common (0.106%), ocean-bed nodules, used in steel manufacture to remove Sulfur and Oxygen, used to color glass.
- Technetium has no stable isotopes, longest lived, 2.11×10^5 years, a beta emitter, isolated from spent nuclear fuel rods, few uses.
- Rhenium very rare (.0007 ppm), isolated from Mo flue dusts, UTK sole source from 1940-50. Used principally in catalysts.
- Mn(VII) is highly oxidizing, Tc & Re less so.
- Electronegativity trends are sharply reversed.
- MP lower for Mn vs Cr, Tc higher than Mo, Re 2nd only to W. Enthalpies of atomization lower for Mn/Re than Cr/W.
- Electrical resistivities are anomalously high for Mn and higher for Re than W.

Oxides & Oxoanions of Mn, Tc, Re

Mn is very electropositive, pyrophoric powders, reacts with water to produce hydrogen.

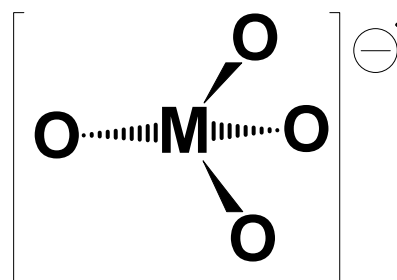
Mn(VII) to Mn(II) have extensive aqueous chemistry. Principally as oxoanions in higher oxidation states.



M	mp °C	bp
Tc	119.5	310.6
Re	300.3	360.3
Mn	powerful oxidizer explosive	

MnO_4^- **Deep Violet**

TcO_4^-
 ReO_4^- } **Colorless**



All have intense charge transfer bands, only Mn is in the visible, others UV.

Oxides

MnO "rock salt" str.
antiferromagnetic

MnO_2 Most important oxide.

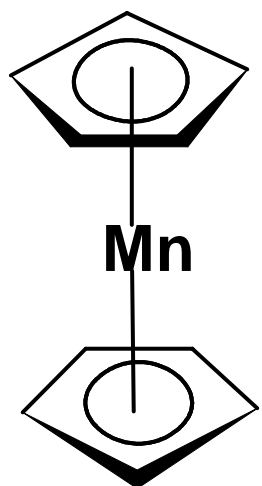
Mn_2O_3 Does not have corundum str.

ReO_3 Octahedral, 1 e
in conduction band
very low resistivity
 $10 \mu\Omega \text{ cm}$.

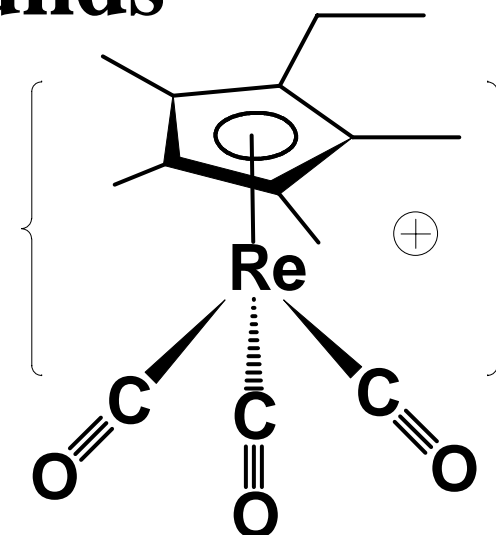
TcO_2 } Most stable oxide Tc.
 ReO_2 } Have distorted rutile str.

Mn_3O_4 Spinel structure,
mixed valence.

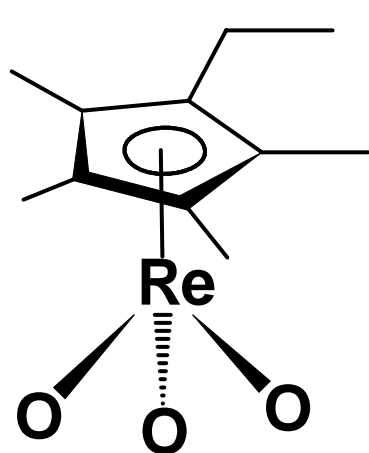
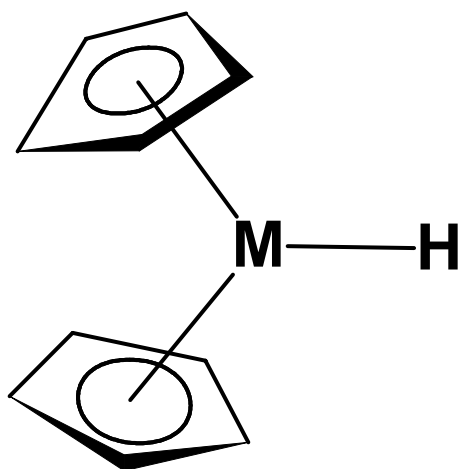
Organometallic Compounds



Dicyclopentadienylmanganese, NVE = 17 paramagnetic, 5 unpaired electrons; ReCp_2 compound unstable above 20K. amber colored manganocene is a zig-zag polymer with bridging Cp units at $\sim 159^\circ\text{C}$ it turns pink adopts the monomeric "sandwich" structure which persists in the gas phase and in hydrocarbon solvents. $[\text{MCp}^*_2]$ M = Mn, Re are known and are low spin intermediate substitution show spin equilibria.

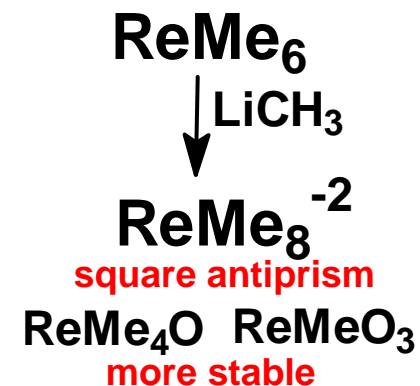


$[\text{MCp}_2\text{H}]$ M = Tc, Re known.



H_2O_2
Re(VII)

H_2O_2
Tc(IV)



$[\text{Tc}_2(\text{C}_5\text{Me}_5)\text{O}_3]_n$

