

Greenwood & Earnshaw

2nd Edition

Chapter 22

Group 5

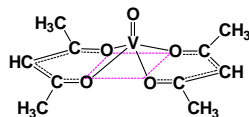
Vanadium, Niobium & Tantalum

Vanadium, Niobium, Tantalum

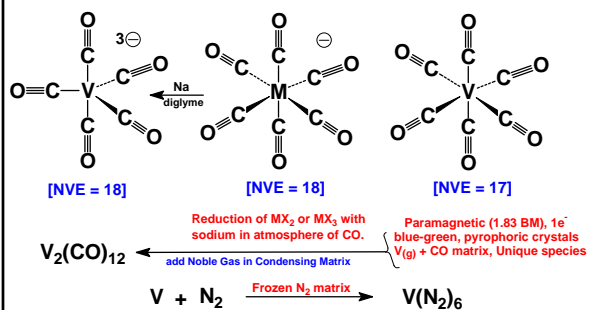
- Electronegativity starting to trend upward going down group.
- Melting points in 5th and 6th period markedly higher – refractory.
- Greater stability of highest oxidation state in 5th and 6th period .
- Ionic radius of 5th and 6th period virtually identical.
- Electrical resistivity trending downward, 5th and 6th period drop.
- Metallic bonding very high in 5th and 6th period.

•Oxides are complex: M_2O_5 , MO_2 , V_2O_3 , MO . VO_4^{3-} ~ silicates, T_d – complex structures. V(IV) – “Vanadyl” a “class A” cation, sq. pyramidal geometry, very common:

$VO(acac)_2$
 $d_{V-O} \sim 157-168 \text{ pm}$
 $d_{V-O} \sim 207-218 \text{ pm}$

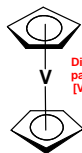


Binary Carbonyls of V, Nb, Ta

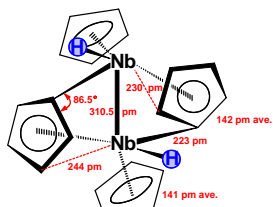
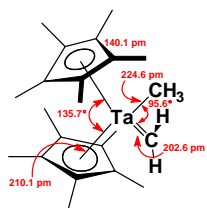


The hexakis(dinitrogen) compound is probably isoelectronic and isostructural with the hexacarbonyl.

Cyclopentadienyls of V, Nb, Ta



Dicyclopentadienylvanadium, violet paramagnetic, 3 unpaired electrons
 $[\text{VCp}_2\text{C}_n]$ $n = 1, 2, 3$ also possible



The Nb-Nb bond is suggested by the diamagnetism of the complex.

Note the plane of the CH_3 group is perpendicular to the C-Ta-C plane and the Cp rings are eclipsed.
