Greenwood & Earnshaw

2nd Edition

Chapter 22

Group 5

Vanadium, Niobium & Tantalum

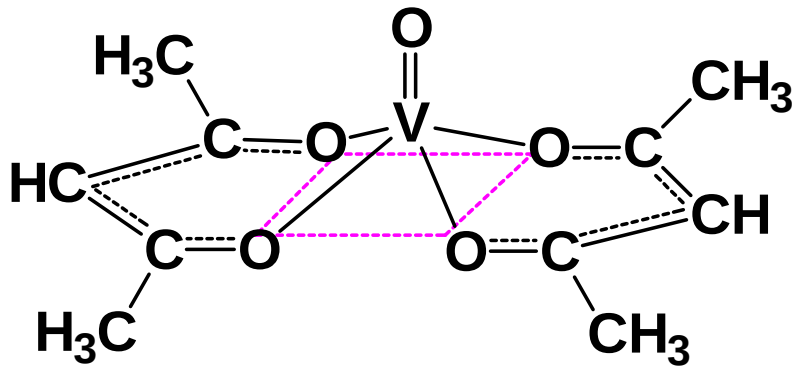
Vanadium, Niobium, Tantalum

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

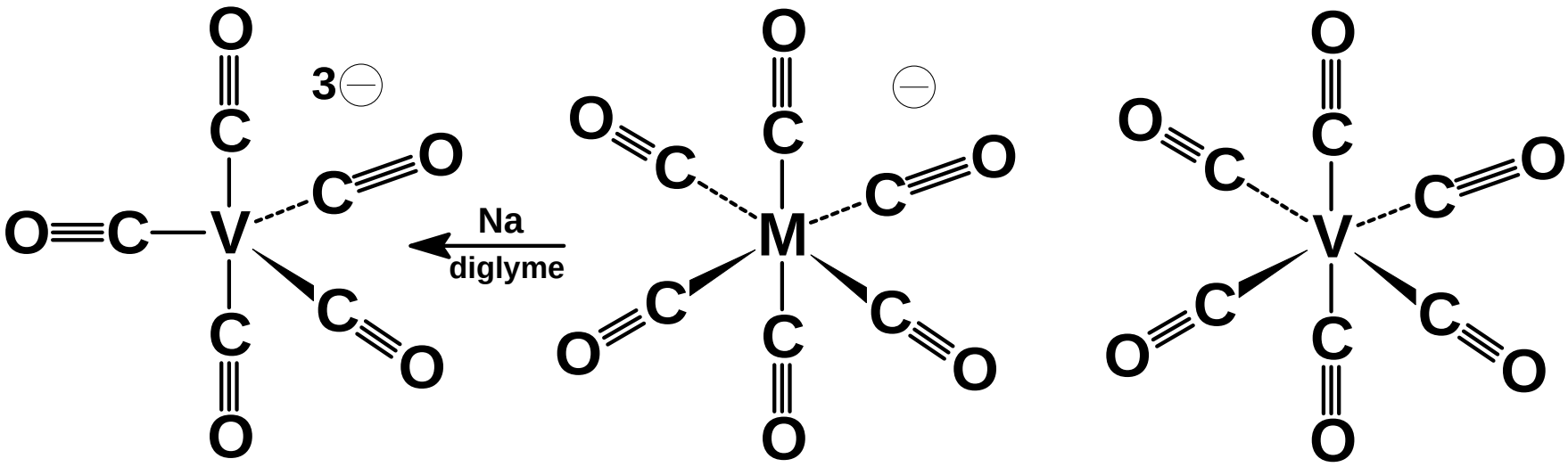
$VO(acac)_2$

$d_{V=O}$ ~ 157-168 pm

d_{V-O} ~ 207-218 pm



Binary Carbonyls of V, Nb, Ta



[NVE = 18] [NVE = 18] [NVE = 17]

Reduction of MX_2 or MX_3 with sodium in atmosphere of CO.

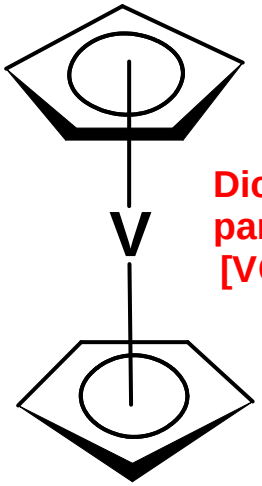
Paramagnetic (1.83 BM), $1e^-$ blue-green, pyrophoric crystals $V_{(g)}$ + CO matrix, Unique species

$V_2(CO)_{12}$ ← add Noble Gas in Condensing Matrix

$V + N_2 \xrightarrow{\text{Frozen } N_2 \text{ matrix}} V(N_2)_6$

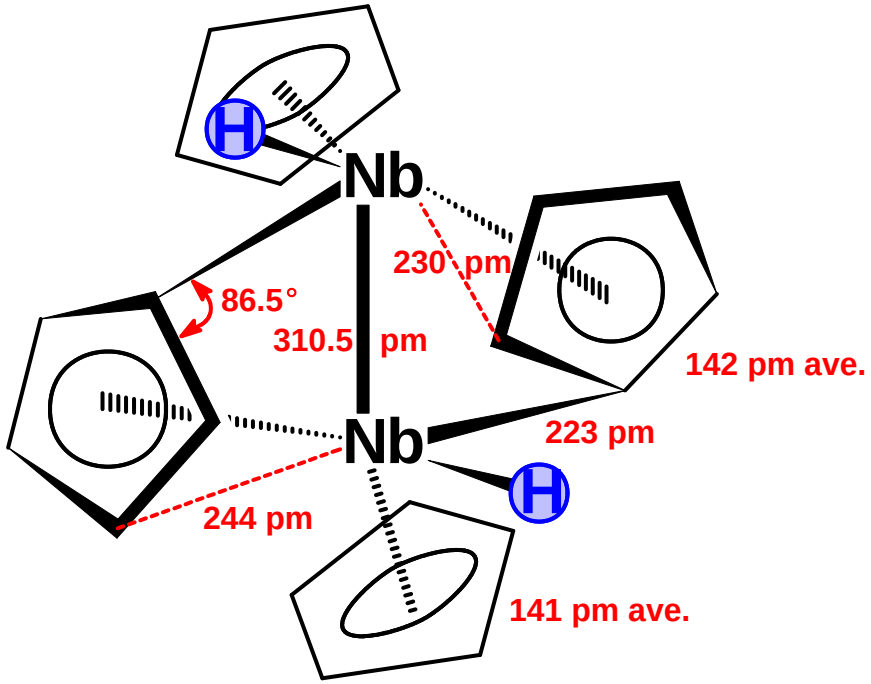
The hexakis(dinitrogen) compound is probably isoelectronic and isostructural with the hexacarbonyl.

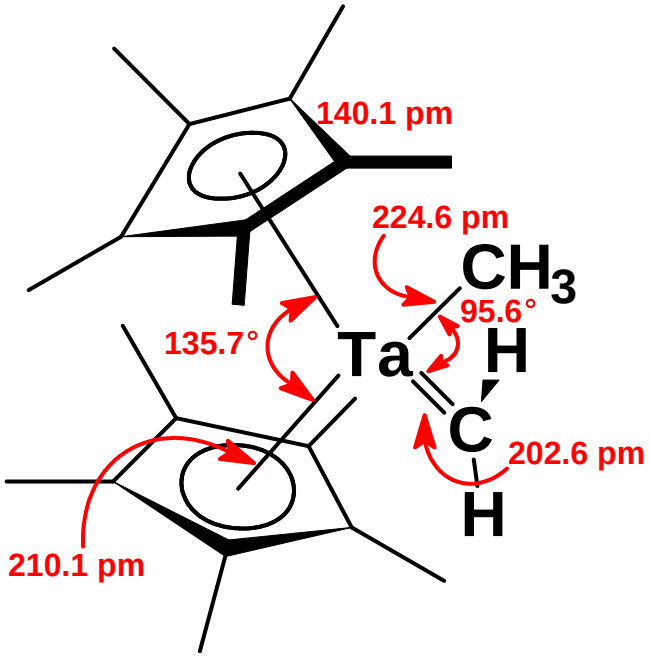
Cyclopentadienyls of V, Nb, Ta



Dicyclopentadienylvanadium, violet
paramagnetic, 3 unpaired electrons
$[VCp_2Cl_n]$ n = 1, 2, 3 also possible

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





Note the plane of the CH_2 group
is perpendicular to the C-Ta-C
plane and the Cp rings are eclipsed.