Greenwood & Earnshaw

2nd Edition

Chapter 23

Group 6

Chromium, Molybdenum & Tungsten

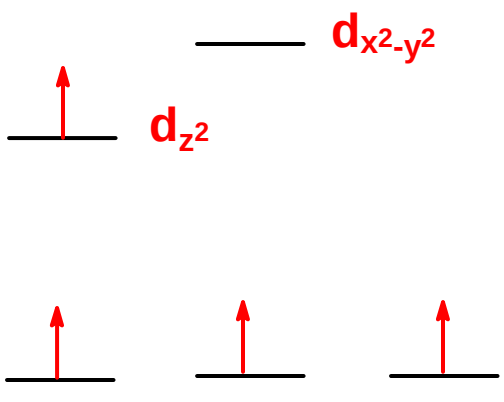
Chromium, Molybdenum & Tungsten

- **First row d electrons fall below valence shell, +6 oxidation state is now highly oxidiziing. Those of 5^{th} & 6^{th} period non-oxidizing.**
- **First row +3 oxidation state most stable.**
- **Melting points: Cr/Mo lower than V/Nb, but W highest of all metals. Can be seen in energy of atomization.**
- **Electrical resistivity Cr lower than V, Much larger drop in resistivity is seen in 5^{th} & 6^{th} period.**
- **Chromium has an extensive aqueous chemistry in oxidation states II-VI.**
- **Coordination chemistry Cr very important in the development of Crystal Field Theory and Ligand Field Theory.**
- **Mo(III) also has an extensive coordination chemistry.**
- **Mo,W form complex series of polymetallates**

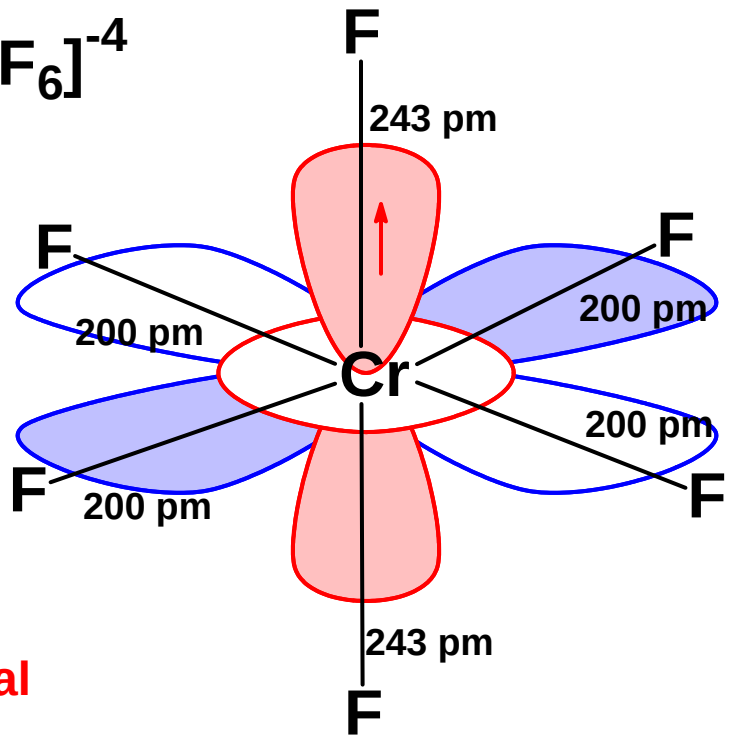
Chromium, Molybdenum & Tungsten

High Spin Cr(II) Jahn-Teller Distortions

Cr^{2+} - d^4 electron configuration in octahedral crystal field predict a single ^5E to $^5T_2$ transition. Experiment shows two absorptions - a Jahn-Teller distortion of the O_h crystal field.



$[CrF_6]^{-4}$



Elongation of the "axial" fluorines will lower the energy of the d_{z^2} atomic orbital relative to the $d_{x^2-y^2}$ atomic orbital

The complex undergoes a "tetragonal distortion breaking the degeneracy of the e_g set as a result of their unequal filling. The electron goes to the orbital having the lowest ligand interaction (coulomb repulsion).

Halides or Cr, Mo & W

- **CrF_6 – 400°C, 200;atm F_2, disproportionates at lower pressure.**
  $CrF_6 \rightarrow CrF_5 + F_2$
- **MoF_6 – Highly oxidizing, volatile, octahedral molecule.**
- **WF_6 – Not highly oxidizing, volatile, octahedral molecule.**
- **MoF_5, WF_5 – Cyclic tetramers, octahedral M, bridging fluorine.**
  WF_5 – readily disproportionates to $WF_6 + WF_4$
- **$CrCl_3$ – $MoCl_3$ – have layer structures, Cr(III) occupying 2/3 of octahedral sites of alternate layers, 1/3 empty giving a cleavage plane resulting in mica-like flake cleavage. Mo(III) isostructural.**
- **WCl_3 – A cluster compound based on $M_6X_{12}^{n+}$ (see Gp 5 Nb, Ta) with 6 additional Cl atoms at each metal apex.**
- **WBr_3 – Cluster Compound based on M_6X_8 ; $[W_6Br_8]^{6+}$ $(Br_4^{2-})(Br^-)$.**

Metal – Metal Bonding

$Cr + \text{dilute HCl} \longrightarrow Cr^{+2}$

octahedral high spin d^4 complexes
~4.9 BM, nearly all are "sky blue"

$Cr + \text{dilute } CH_3COOH \longrightarrow$

Red or pink, nearly diamagnetic,
anhydrous or hydrated species.
Sulfates are violet colored.

$Mo(CO)_6 + \text{dilute } CH_3COOH \longrightarrow [Mo_2(CH_3COO)_4]$

completely diamagnetic

$\downarrow$ HCl conc.

$[Mo_2Cl_8]^{-4}$

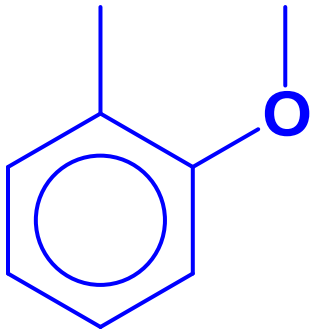
Red, diamagnetic, Cl's eclipsed

$d_{Mo\text{-}Mo} = 224$ pm

Shortest M≡M

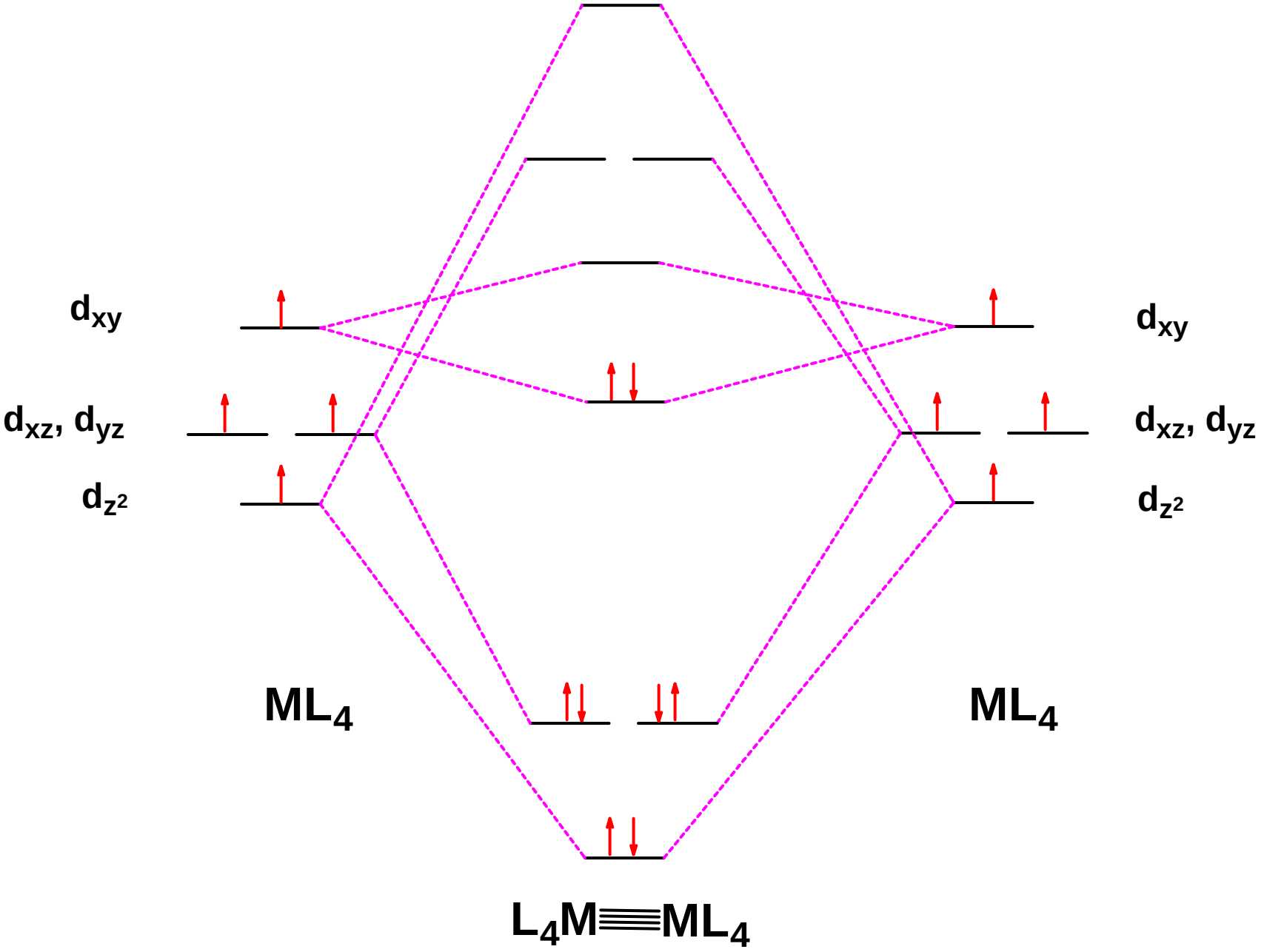
$[Cr_2(o\text{-}C_6H_4O)_4]^{-4}$

$d_{Cr\text{-}Cr} = 183$ pm

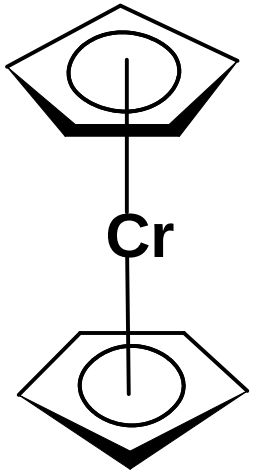


$o\text{-}C_6H_4O$

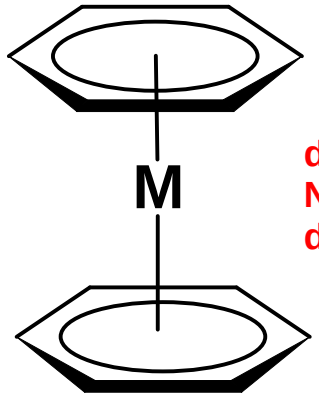
Metal – Metal Bonding



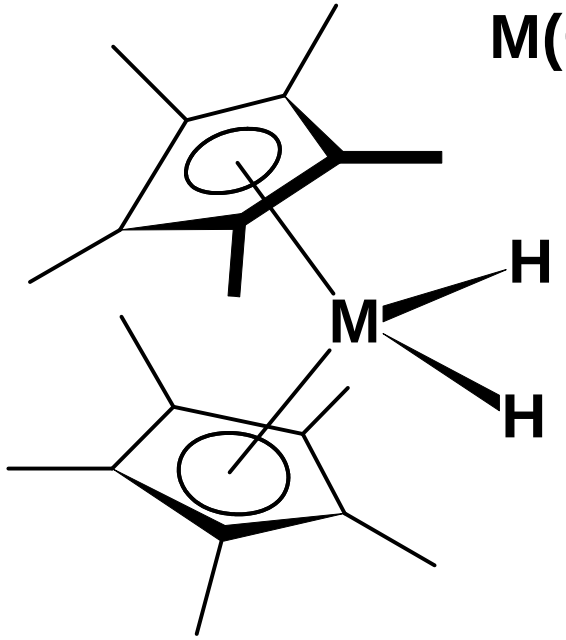
Organometallic Compounds Cr, Mo, W



Dicyclopentadienylchromium, NVE = 16
paramagnetic, 2 unpaired electrons; Mo, W compounds polymerize above 10K.
$[MCp_2H_2]$ M = Cr, Mo, W known.

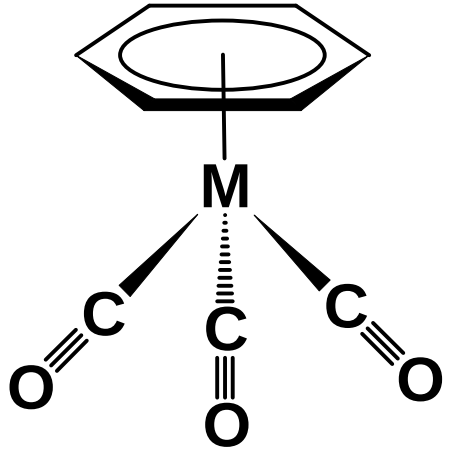


dibenzenechromium
NVE = 18, Mo & W derivatives known



$M(CO)_3(CH_3CN)_3$
or
$M(CO)_6$

reflux



hexaalkylborazine chromium tricarbonyls have also been prepared.