Greenwood & Earnshaw

2nd Edition

Chapter 23

Group 6

Chromium, Molybdenum & Tungsten

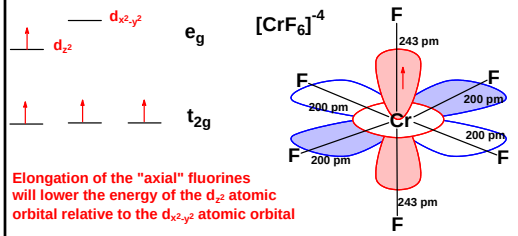
Chromium, Molybdenum & Tungsten

- First row d electrodes fall below valence shell, +6 oxidation state is now highly oxidiziing. Those of 5th & 6th 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 5th & 6th 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 + dilute HCl ⟶ Cr^{+2} — octahedral high spin d^4 complexes ~4.9 BM, nearly all are "sky blue"

Cr + dilute CH_3COOH ⟶ — Red or pink, nearly diamagnetic, anhydrous or hydrated species. Sulfates are violet colored.

$Mo(CO)_6$ + dilute CH_3COOH ⟶ $[Mo_2(CH_3COO)_4]$ completely diamagnetic

↓ HCl conc.

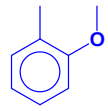
$[Mo_2Cl_8]^{-4}$ Red, diamagnetic, Cl's eclipsed

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

Shortest M≡M

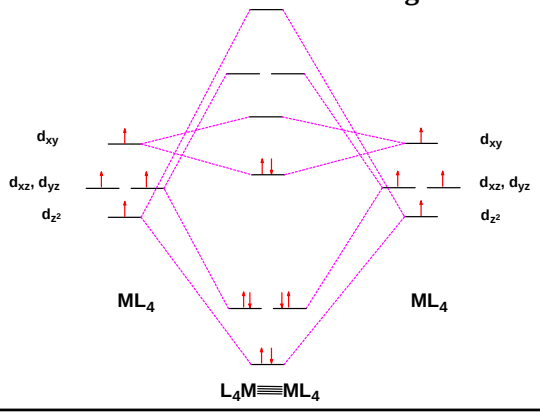
$[Cr_2(o\text{-}C_6H_4O)_4]^{-4}$

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



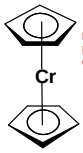
o-C_6H_4O

Metal – Metal Bonding

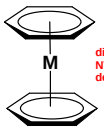


$L_4M{\equiv\equiv}ML_4$

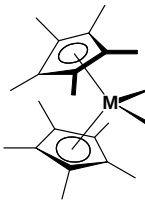
Organometallic Compounds Cr, Mo, W



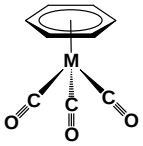
Dicyclopentadienylchromium, NVE = 16 paramagnetic, 2 unpaired electrons; Mo, W compounds polymerize above 10K. $[MCp_2H_2]$ M = Cr, Mo, W known.



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.