

Greenwood & Earnshaw

2nd Edition

Chapter 27

Group 10

Nickel, Palladium & Platinum

Nickel, Palladium & Platinum

•Nickel (99 ppm) is 22nd most abundant element & 7th most abundant transition metal. World production 1,000,000 tonnes/y most recovered in association with platinum group metals. Richest single source: Sudbury Basin, Canada, possibly of meteoric origin, 18%, next former USSR 25%. Used iron alloys, stainless steels, armor plating, Alnico permanent magnets, German Silver (Ni,Cu,Zn); Monel (Ni 68%/Cu 32%), Nichrome (Ni 60%/Cr 40%), Nickel-Cadmium batteries, Alkaline dry cells, catalysts (Repe synthesis).

•Palladium (0.015 ppm) and platinum (0.01 ppm) are much rarer most coming from South Africa (3rd major source of Ni also Ag, Au). Palladium used hydrogenation catalysts, Pd - H₂/D₂/T₂ separations/purifications, Wacker process. Platinum has extensive use as catalysts (HNO₃ production, oxidation catalysts, petroleum reforming, hydrogenations, etc.), jewelry (“*platina*”). ¹⁹⁵Pt I = 1/2.

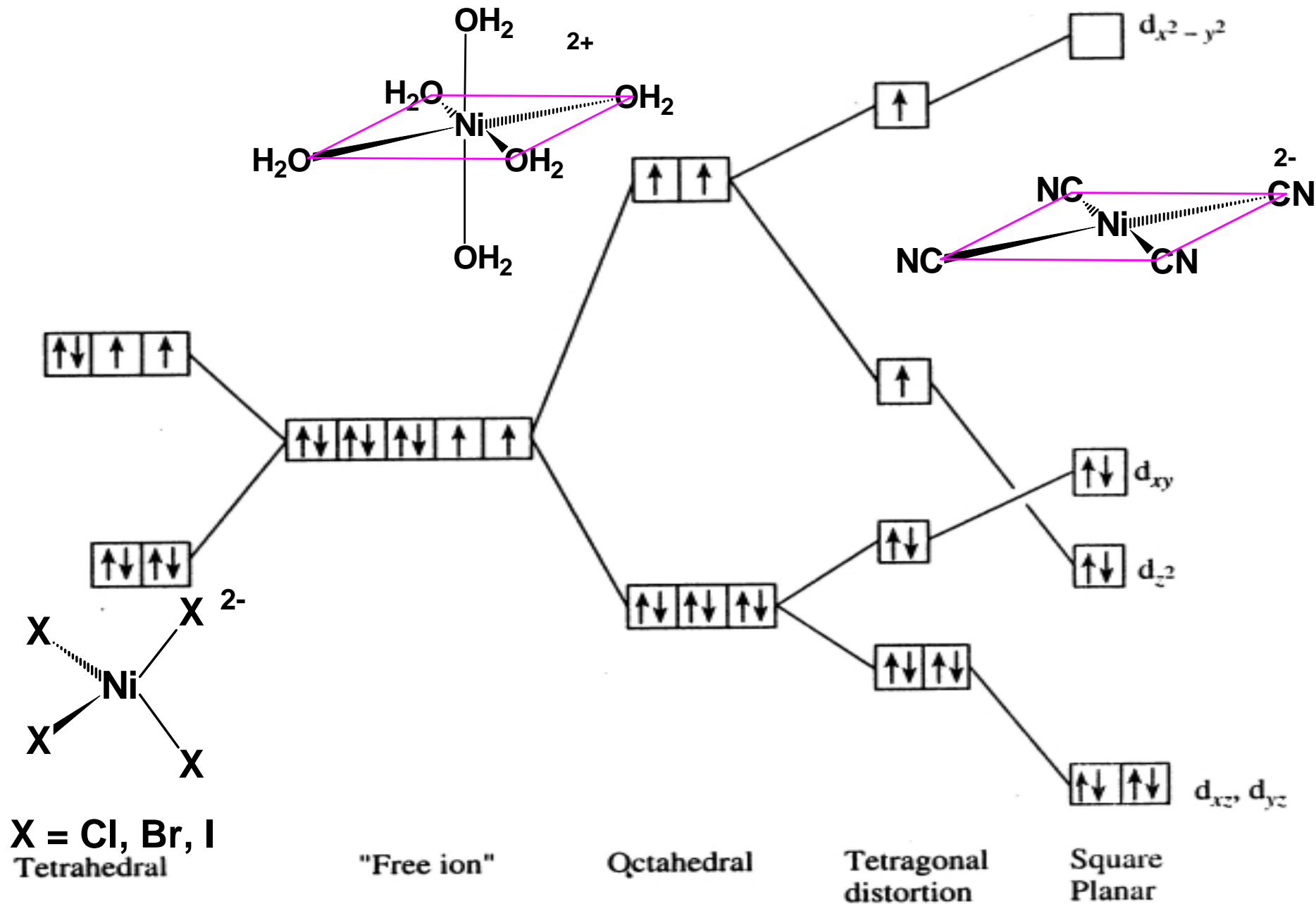
Nickel, Palladium & Platinum

- Note the diversity in electron configurations of elements:

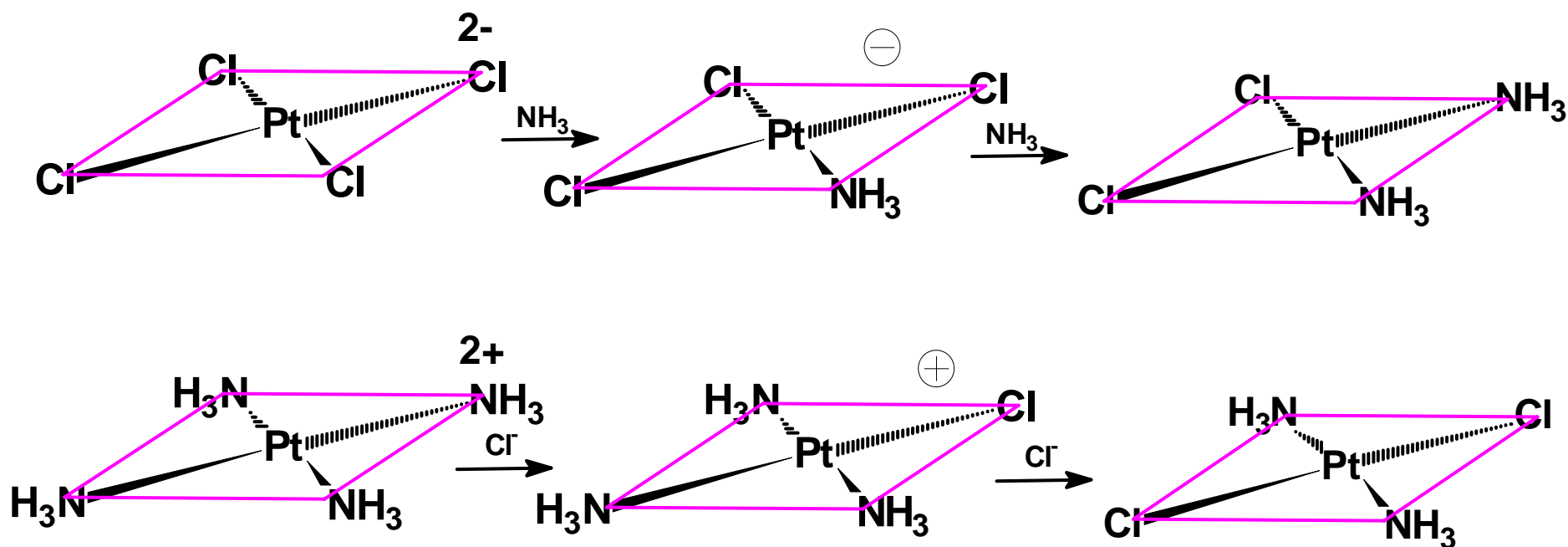


- Electronegativities mirror Groups 8 & 9.
- Limited oxidation states at both ends: Pt(V) to M(II).
- All three metals have *fcc* metal structure, all resist atmospheric oxidation; all dissolve in molten alkali metal oxides. Platinum very prone to B, Si, Pb, P, As, Sb, Bi melts under reducing conditions.
- Metals all have high melting points but are not refractory, showing a decrease in all periods. Enthalpy of atomizations show a parallel decrease: Ni ~ Co > Fe > Mn.
- Most stable oxidation states: Ni(II), Pd(II), Pt(II), Pt(IV), latter two are kinetically inert, Pt(IV) is class “a” Pd(II) & Pt(II) class “b” all have an extensive aqueous complex chemistry.

Ni(II) Coordination Chemistry



Pd(II) & Pt(II) Coordination Chemistry



Weakest trans labeling effect

F^- , OH^- , H_2O , NH_3 , py < Cl^- < Br^- < I^- ~ SCN^- , NO_2^- , $C_6H_5^-$ <

$S=C(NH_2)_2$, CH_3^- , < H^- , PR_3 , AsR_3 < CN^- , CO , C_2H_4

Strongest trans labeling effect

Pd(II) & Pt(II) Coordination Chemistry

Trans Effect

- “Trans effect” – Kinetic - Strong π -acceptor character drains electron density from the metal and from the trans-ligand's π orbitals thus encouraging nucleophilic attack.
- “Trans influence” – Thermodynamic – Strong σ -donor ligands produce an axial polarization of the metal and ligand lone pair inducing a positive charge on the near-side of the metal and a negative charge on the far-side which weakens the trans-ligand attachment to the metal.
- Pt(II) and Pd(II) bromides and iodides are insoluble. Most common compounds are the $[\text{MX}_4]^{2-}$ complexes.

Pd(IV) & Pt(IV) Coordination Chemistry

- **Virtually all are octahedral, kinetically inert, and diamagnetic, t_{2g}^6 .**
- **K_2PtCl_6 is the most common compound of Pt.**

Other Coordination Chemistry

- **Ni(III) is rather well represented. K_3NiF_6 is another octahedron with an axial elongation due to a Jahn-Teller distortion caused by the $t_{2g}^6 \cdot e_g^1$ electron configuration.**
- **The M(III) oxidation state is rather poorly represented in Pd & Pt.**
- **Some compounds claimed to be Pt(III) such as Wolfram's red salt have been shown to be mixed valent.**