**Platinum Group Metals**

Rh, Ir, Pd and Pt are all face-centered cubic. They are all oxidized by O_2, F_2 and Cl_2.

Pd has a highest oxidation state of +4 but +2 is the most common, [Pd(H_2O)_4]^{2+} occurs in aqueous solution. The coordination number rarely exceeds six and Pd (II) is a “class b” (soft) metal. Pd⁰ is employed like Pt⁰ as a heterogeneous reduction catalyst dispersed on activated charcoal. Alkynes to alkenes to alkanes, nitro groups to amines.

**The Trans effect**

This refers to a particular effect on selectivity of reaction products. In square planar arrangements the ligand *trans* to the new incoming ligand affects the regiospecificity of the reaction and thus the geometry of the final product, *e.g.* in the following reaction there are two possible products *cis* and *trans*.

![Diagram](image)

Surprisingly only a single major product is formed, in this case. Experimentally a number of square planar reactions were carried out and priority or order of ligands and their *trans* directing effect was measured relative to each other. From this a series was elucidated. Physically this directing effect originates from the fact that the electrons of the ligand *trans* to the incoming group occupies the same orbital, so a “communication” of sorts is set up between the two moieties (there is a stabilization of the pentacoordinate intermediate). That being the case the observed product in the previous was the *cis* product ....Why? The order of ligands described above is listed.

In order of increasing *trans* directing ability:

F⁻, OH, H_2O, NH₃, py, Cl⁻, Br⁻, I⁻, SCN⁻, NO₂⁻, CH₃⁻, H⁻, PR₃⁻, CN⁻, CO < C₂H₄

Therefore in the previous example Cl⁻ > NH₃ so the *cis* product predominates. An example is shown below:

NO₂ > Cl⁻ so the *trans* product predominates.
Exercise

1. Use the trans effect series to suggest synthetic routes to cis- and trans-\([\text{PtCl}_2(\text{NH}_3)_2]\) from \([\text{Pt}(\text{NH}_3)_4]^{2+}\) and \([\text{PtCl}_4]^{2-}\).

Solution

Reaction of \([\text{Pt}(\text{NH}_3)_4]^{2+}\) with HCl leads to \([\text{PtCl}(\text{NH}_3)_3]^{2+}\). Because the trans effect of Cl\(^-\) is greater than that of NH\(_3\), substitution reactions will occur trans to Cl\(^-\) and further addition of HCl will give trans-\([\text{PtCl}_2(\text{NH}_3)_2]\). To synthesize the cis- compound use the starting material \([\text{PtCl}_4]^{2-}\). Reaction with NH\(_3\) leads to \([\text{PtCl}_3(\text{NH}_3)]^{-}\). The second step will involve substitution of one of the two trans Cl\(^-\) ligands with NH\(_3\) to give the cis- \([\text{PtCl}_2(\text{NH}_3)(\text{PH}_3)]\).

2. Give the reactants PH\(_3\), NH\(_3\) and \([\text{PtCl}_4]^{2-}\), propose an efficient route to both cis- and trans-\([\text{PtCl}_2(\text{NH}_3)(\text{PH}_3)]\).

Isolation of palladium and platinum

Ores: Braggite (Pt, Pd, Ni) sulfides, Cooperite (Pt, Pd) sulfides, Sperrylite (PtAs\(_2\)) and Laurite (RuS\(_2\))

Overall process:

1. Crushing of ore followed by floatation (concentration techniques).
2. Gravity filtration followed by roasting of the sulfide aggregates.
3. Chlorination of the solids at 500\(^\circ\)C to make them water soluble.
4. Separation methodology
Actinides

Thorium to lawrencium (14 elements) Z = 90-103. Analogous to lanthanides but the valence electrons are found in the $5f$ orbitals. Thorium, protactinium and uranium are the only naturally occurring species the rest are generated synthetically (known as the trans-uranium elements). All the natural elements are generated by the decay of $^{238}\text{U}$.

\[
\begin{align*}
^{238}\text{U} & \rightarrow ^{234}\text{Th} & ^{234}\text{Th} & \rightarrow ^{234}\text{Pa} & ^{234}\text{Pa} & \rightarrow ^{234}\text{U} \\
\end{align*}
\]

Oxidation states:

- Thorium $+4$
- Pa $+5$ (most stable)
- U $+6$ (higher achievable, $+2$, $+3$ more common)

The metals tarnish in air forming an oxide “coat”. They react with steam evolving $\text{H}_2$ gas. Common compounds include halides, carbides and nitrides.

Lattice structures are:

- Th = FCC, Pa = Cubic, U = Cubic

Isolation of Uranium

Ore is mined in South Africa. The ore is crushed (ground down) and concentrated (floatation). Leaching is then performed with sulfuric acid.

\[
\text{UO}_2^+ + \text{H}_2\text{SO}_4 \rightarrow [\text{UO}_2(\text{SO}_4)_3]^4^-
\]

An extraction process which employs an organic soluble ligand is added to the solution. This will allow the isolation of the uranium by selective solubility into an organic layer. The complex dissolves in a paraffin type hydrocarbon solvent e.g. kerosene. The types of ligands used can form a “ion pair” arrangement with the overall negative complex ion species, e.g. tertiary trioctylamine (alamine 336), $[\text{HN(C}_8\text{H}_{17})_3]^+$. This in turn leads to the complex:

\[
\begin{align*}
\text{R} & = \text{C}_8\text{H}_{17} \\
\end{align*}
\]

The kerosene can be re-used as dilute ammonia will precipitate $\text{UO}_2^+$ (i.e. removes the alamine 336). This “yellow goop” is allowed to dry and form a “cake” this is sometimes sold as is. The material is then “roasted” giving off $\text{H}_2\text{O}$ and $\text{N}_2$. The final product is usually thus $\text{U}_3\text{O}_8$. 