Group 10

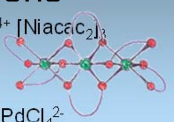
Ni, Pd, Pt

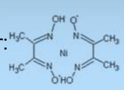
Elements

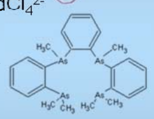
	Ni	Pd	Pt
Occurrence ppm.	**100**	**0.001**	**0.0005**
Mp °C	**1455**	**1594**	**1774**
El. resistivity μΩcm	**6.8**	**9.9**	**9.9**
E° (M^{2+}/M) V	**-0.25**	**0.95**	**1.18**
Common ox.-state	**+2**	**+2**	**+2, +4**
M^{2+} typical geometries	**tetrahedral square planar octahedral**	**square planar**	**square planar**
M(IV) geometry	**octahedral**	**octahedral**	**octahedral**
pK M_{aq}^{2+}	**9.86**	**~2.5**	**~4**

Geometric variations

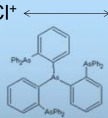
- Octahedral: $Ni(H_2O)_6^{2+}$, $PdCl_6^{2-}$, $Ptbipy_3^{4+}$ [$Niacac_2$]$_3$



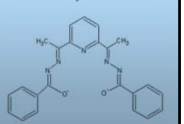
- Tetrahedral: $NiCl_4^{2-}$
- Square planar:  $Ni(DMG)_2$, $PdCl_4^{2-}$
- Square pyramidal: Pd(TPAs)Cl^+ ←→



- Trigonal bipyramid Pt(QAS)I^+



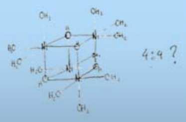
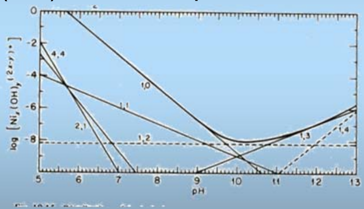
- Pentagonal bipyramid Ni(DAPBH)aq_2



Ni^{2+} - H_2O

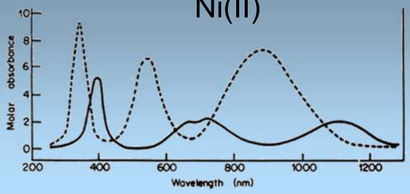
- $Ni(H_2O)_6^{2+}$

  $Ni^{2+} \leftrightarrows Ni(OH)^+ + H^+$ pk~9.9

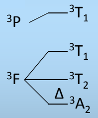



Ni(II)

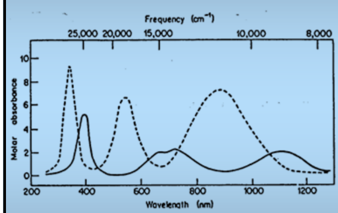
d8



	$Niaq_6^{2+}$		$Nien_3^{2+}$	
transition	λ/nm	$\sigma/10^{-3}cm^{-1}$	λ/nm	$\sigma/10^{-3}cm^{-1}$
$^3A_2 \rightarrow {}^3T_2$	1180	8.5	890	11.25
$^3A_2 \rightarrow {}^3T_1$	702	14.0	545	18.4
$^3A_2 \rightarrow {}^3T_1$	400	25.3	345	29.0



Absorption Spectra

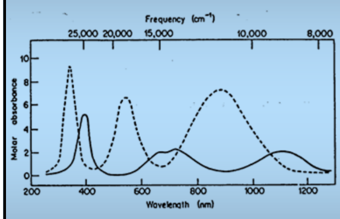


$Ni(H_2O)_6^{2+}$ ——— $Nien_3^{2+}$--------

aq:H_2O	λ_1	λ_2	λ_3
$Niaq_6^{2+}$	1180	715	395
$Niaq_4en^{2+}$	1020	635	373
$Niaq_2en_2^{2+}$	950*	570	355*
$Nien_3^{2+}$	890	542	340

Absorption Spectra

Average environment rule prediction



aq:H_2O	λ_1	λ_2	λ_3
$Niaq_6^{2+}$	1180	715	395
$Niaq_4en^{2+}$			
$Niaq_2en_2^{2+}$			
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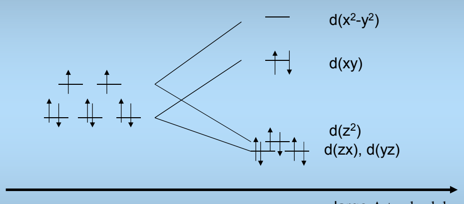
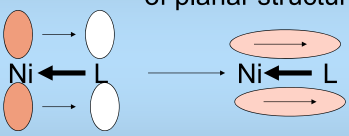
$Ni(H_2O)_6^{2+}$ ——— $Nien_3^{2+}$--------

Square planar d^8



π-back bonding

Extra stabilisation of planar structure



$d(z^2)$ filled — π empty

σ-lone pair bonding + π-backbonding

Ni^{2+} colours

- Octahedral: green to blue violet ε~5-10
  think of $Nien_n(H_2O)_{6-2n}^{2+}$
- Square planar: red to yellow ε~50
  think of $Ni(DMG)_2$
- Tetrahedral: blue ε~100
  think of $NiCl_4^{2-}$

Substitution in sq. pl. ML_4

- Trans-influence (bond length trans to L)
- Trans-effect: trans ligand effect on kinetics
  - e.g. $PtI_3NH_3^- + NH_3 \rightarrow cis\text{-}PtI_2(NH_3)_2 + I^-$

Trans-effect series of ligands: H_2O, OH^-,NH_3 ,py<Cl^-<Br^-<SCN^-<I^-< NO_2^-< $C_6H_5^-$< $SC(NH_2)_2$< CH_3^- <NO, CN^- ,CO

Ni in biology

$2.4 \cdot 10^9$ years ago: rise in O_2 in atmosphere

Coincides with decrease of $[Ni^{2+}]$ in oceans (from 400 to 9 nM).

Ni^{2+} in Chlorophyll-like cofactor F-430 in methane producing archaebacteria. CH_4 removes O_2

- Ni in Urease (plants, bacteria)
  $(NH_2)_2CO + H^+ \leftrightarrows 2NH_4^+ + HCO_3^-$

Pd

- Hydrogenation catalyst
  $2Pd_s + H_2 \rightarrow PdH_{\sim 1}$("interstitial" hydride)
- Binding of CO to the surface of Pd_s
- $PdCl_4^{2-}$ catalyst for
  $\frac{1}{2}O_2 + CH_2{=}CH_2 \rightarrow CH_3CHO$ using
  $PdCl_4^{2-} + CH_2{=}CH_2 \rightarrow [PdCl_3(\eta^2\text{-}C_2H_4)]^- + Cl^-$,
  cf. Zeise's salt $K[PtCl_3(\eta^2\text{-}C_2H_4)]$

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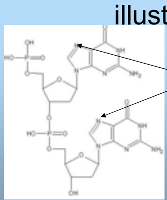
Pt in cancer chemotherapy

cis-$[PtCl_2(NH_3)_2]$: From 197x in clinical use
5-years survival 91%(certain cancer types)
Mechanism: bidentate binding to DNA
illustrate: dpGdpG+ cis-$[PtCl_2(NH_3)_2]$



$Pt(NH_3)_2$
gives "kink" relative to DNA angles

preventing DNA from replicating

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