Synthesis of a Ni(II) macrocyclic ligand complex

- Synthesis of coordination complexes
- Use of metal ion as a template for a cyclization reaction
- Crystallization by choice of appropriate anion
- Microanalysis by EDTA titration
- Acquisition and analysis of electronic absorption spectrum
- Use $^1$H NMR and infrared spectra to characterize structural changes
  - Use of KBr pellets and Nujol mulls for obtaining solid state IR spectra
- Determination of magnetic susceptibility by NMR method

\[
\text{[Ni(OH$_2$)$_6$](BF$_4$)$_2$ + 3 en} \rightarrow \text{[H$_2$N\textsubscript{3}N\textsubscript{6}]$_2$N\textsubscript{3}NH$_2$ (BF$_4$)$_2$} \quad \text{low kinetic stability}
\]

\[
\text{[H$_2$N\textsubscript{3}N\textsubscript{6}]$_2$N\textsubscript{3}NH$_2$} \rightarrow \text{[H$_2$N\textsubscript{3}N\textsubscript{6}]$_2$N\textsubscript{3}NH$_2$} \quad \text{high kinetic stability}
\]
Diastereoisomers of macrocyclic complex

[Chemical structures of trans and cis isomers]

major isomer
less soluble

Mechanism of the cyclization reaction
Reactions of macrocyclic complex

Reduction

\[
\begin{array}{c}
\text{Ni}^2+ \\
\text{H}_2\text{Ni}\text{N}_2\text{H}_2 \\
1) \text{NaBH}_4 \\
2) \text{NH}_4\text{PF}_6 \\
\end{array}
\]

Oxidation

\[
\begin{array}{c}
\text{Ni}^2+ \\
\text{H}_2\text{Ni}\text{N}_2\text{H}_2 \\
1) \text{HNO}_3 \\
2) \text{NH}_4\text{PF}_6 \\
\end{array}
\]

Complexes are not destroyed by harsh conditions because of high kinetic stability of macrocyclic ligand-metal complexes

Infrared spectra

- Sample holder
- Sample preparation
  - Solution
  - KBr pellet
  - Nujol mull
- Qualitative analysis
  - Group frequencies
  - Fingerprint region
Chelate ring conformations

Analysis for nickel content: murexide indicator for EDTA titrations

Indicator - violet  Complexed indicator - yellow
Effect of ligand on absorption spectra (and color)

Energy changes for formation of $ML_6^{n+}$

$M^{n+} + 6 L \rightarrow ML_6^{n+} \rightarrow ML_6^{n+} \text{(octahedral)}$

Electrostatic attraction

differential repulsions of d orbitals

e-e repulsion

$\Delta E$

$d_{z^2}$, $d_{x^2-y^2}$, $d_{xz}$, $d_{xy}$, $d_{yz}$
Energy level diagram for complex with $\sigma$ donor ligands

Comparison of level diagrams for complexes with $\sigma$ only and $\sigma$ plus $\pi$ donor ligands
Energy level diagram for complex with $\sigma$ and $\pi$ acceptor ligands

Energy level diagrams for complexes with $\sigma$ only, $\sigma$ plus $\pi$ donor, and $\sigma$ plus $\pi$ acceptor ligands
Effect of $\pi$-donor and $\pi$-acceptor interactions on $\Delta$ in octahedral complexes

Energy of d-orbitals prior to interaction with ligands

- $\sigma$ bonding only
- $\sigma + \pi$ donor
- $\sigma + \pi$ acceptor

Comparison of angular overlap splittings for octahedral, square planar and tetrahedral ligand fields

Purcell and Kotz, *Inorganic Chemistry*, p. 546
Scaling factors for M-L interaction in angular overlap model

Structural preference energies based on angular overlap (MO) model
Effect of ligand on absorption spectra (and color)

Transitions in $d^1 (d^9)$ and $d^2 (d^8)$ complexes
The Racah repulsion parameters

- The different free ion terms for an electron configuration have different energies due to variations in electron-electron repulsion.
- The different energies can be expressed using a small number of electrostatic parameters, A, B and C.
- These parameters are integrals related to the extent of electron-electron repulsion. The larger they are, the greater the repulsion.
- A, B and C are called Racah parameters; energy differences between states depend only upon B and C.

Octahedral d^8 (e.g. Nickel(II)).

\[ ^3\text{T}_{2g} \leftarrow ^3\text{A}_{2g}, \quad \nu_1/B = \Delta/B \]

\[ ^3\text{T}_{1g}(F) \leftarrow ^3\text{A}_{2g}, \quad \nu_2/B = \tfrac{1}{2}\{15 + 3(\Delta/B) - \sqrt{225 - 18(\Delta/B) + (\Delta/B)^2}\} \]

\[ ^3\text{T}_{1g}(P) \leftarrow ^3\text{A}_{2g}, \quad \nu_3/B = \tfrac{1}{2}\{15 + 3(\Delta/B) + \sqrt{225 - 18(\Delta/B) + (\Delta/B)^2}\} \]

From this the ratio \( \nu_2/\nu_1 \) would become:

\[ \tfrac{1}{2}\left\{15 + 3(\Delta/B) - \sqrt{225 - 18(\Delta/B) + (\Delta/B)^2}\right\} \]

\[ \Delta/B \]

And the range of \( \Delta/B \) required is from ~5 to ~17.
Correlation between magnetic moment and unpaired electrons

- A moving charge generates a magnetic dipole the magnitude of which is determined by the angular momentum resulting from the motion of the charge.
- An electron associated with an atom has spin angular momentum and in some cases orbital angular momentum.
- The spin-only magnetic moment (in units of the Bohr magneton) is given by $\mu_{s.o.} = 2[S(S+1)]^{1/2}$ where $S = \Sigma s_i$ and $s_i$ are the spin quantum numbers of the unpaired electrons.
- The 2 is derived from the magnetogyric ratio (the precise value is 2.0023 for a free electron), which is the ratio of the magnetic moment to spin angular momentum.
- Complexes of certain coordination numbers and geometries of some transition metal ions may have modest orbital contributions to the magnetic moment such that $\mu_{\text{eff}}$ is slightly greater than the predicted spin-only value.

<table>
<thead>
<tr>
<th>Unpaired e-</th>
<th>$\mu_{s.o.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.73</td>
</tr>
<tr>
<td>2</td>
<td>2.83</td>
</tr>
<tr>
<td>3</td>
<td>3.87</td>
</tr>
<tr>
<td>4</td>
<td>4.90</td>
</tr>
<tr>
<td>5</td>
<td>5.92</td>
</tr>
</tbody>
</table>

Relationship between magnetic susceptibility and magnetic moment

- In the presence of a magnetic field magnetic dipoles which are otherwise randomly oriented tend to align with the field and the sample achieves net magnetic polarization.
- The tendency of a sample to achieve net magnetic polarization in proportion to the applied magnetic field is its magnetic susceptibility. This is defined as $\kappa = I/H$ where $I$ is the intensity of magnetization (the extent to which the magnetic dipoles are aligned) and $H$ is the applied magnetic field.
- $\kappa$ is the volume susceptibility so that division by the density $\rho$ give the specific or mass susceptibility, $\chi$. The molar susceptibility $\chi_M = \chi \times MW$.
- The magnetic moment is determined from $\chi_M$ after correction for the diamagnetic contributions of the electron pairs of the constituent atoms. Thus $\chi_M^{\text{corr}} = \chi_M + \Sigma \chi_d$. $\chi_d$ values are tabulated and are often referred to as Pascal’s constants.
- Finally $\mu_{\text{eff}} = \left[3k/\pi\mu_B^2\right]^{1/2}[\chi_M^{\text{corr}}T]^{1/2} = 2.83[\chi_M T]^{1/2}$ (cgs)
  $\mu_{\text{eff}} = \left[3k/\pi\mu_o\mu_B^2\right]^{1/2}[\chi_M^{\text{corr}}T]^{1/2} = 798[\chi_M T]^{1/2}$ (SI)
**Measurement of \(X_g\) by NMR**

- Use NMR method in which the difference in the shift of a standard resonance in the presence and absence of the paramagnetic substance is measured.
- Both shifts are determined simultaneously using a special set of concentric tubes.
- The difference in shifts is due to the enhancement of the applied field by the presence of the paramagnetic substance.
- The difference in shift of the standard resonance is related to the mass susceptibility by
  \[
  \chi = -\frac{3f}{4m} \Delta f + \chi_o + \frac{\chi_o (d_o - d_s)}{m}
  \]
  where
  - \(f\) is the frequency separation between the lines in the presence and absence of the paramagnetic species in Hz
  - \(f\) is the frequency of the spectrometer in Hz
  - \(m\) is the mass of substance contained in 1 mL of solution
  - \(\chi\) is the mass susceptibility of the solvent
  - \(d_o\) is the density of the solvent; \(d_s\) is the density of the solution
- The last term is generally ignored for reasonable concentrations of moderate to highly paramagnetic species.

**Paramagnetic compounds and NMR**

\(^1\)H NMR spectrum at 100 MHz; resonances marked with \(x\) are due to free ligand impurity

*Inorg. Chem.* 1968, 12, 1408

Benzyl alcohol with addition of shift reagent a)

*Chem. Commun.* 1970, 422
Chiral shift reagents

2-phenyl-2-butanol without added shift reagent

J. Am. Chem. Soc. 1971, 93, 5913