Lecture 5: Outcomes

• Introduction to Molecular Magnetism

• To understand the difference between bulk and molecular magnetic properties

• Understand the J value and what its sign and magnitude tells us about the M…M magnetic interaction within a compound.

• Understand concept of the superexchange mechanism
• Up until now we had considered monomeric transition metal ions.

• In polynuclear complexes the individual paramagnetic ions can interact.

• These ions are said to magnetically coupled and are undergoing Magnetic Exchange.

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**Molecular Magnetism**

- The study of magnetic properties of *isolated molecules* and *assemblies of molecules*

The same (magnetic) concepts also apply for *polymetallic complexes* (a.k.a. ‘clusters’ or ‘cages’) of paramagnet metals, i.e. molecules containing more than one metal containing unpaired electrons. These involve interactions amongst a finite number of separate spins…

("cluster" = complex with more than one metal ion)
Polymetallic Paramagnetic (clusters)

This is an example of a polymetallic paramagnetic complex:

\[ \text{[Fe}_5\text{O}_2\text{(OMe)}_2\text{(bta)}_4\text{(btaH)}\text{(MeOH)}_4\text{Cl}_5] \]

Bridging organic ligands link the metal centres

Terminal Cl\(^-\) ions complete coordination at metal centres

Bridging O ions (OH\(^-\), O\(^{2-}\), "OMe) link transition metals together

Terminal solvent molecules complete coordination at metal centres

In this complex the organic ligand is:

Benzotriazole (btaH)

Molecular Magnetism

Historically, this field took off with the magnetic properties of copper(II) acetate hydrate.

Chemists assumed it was a monometallic complex (i.e. \([\text{Cu(II)}\text{(OAc)}_2\text{(H}_2\text{O})_2]\)]

For example:

Chelating acetate ligands (\(\sim \text{O}_2\text{CCH}_3\))

OR

6 coordinate octahedral complex

5 coordinate square based pyramidal complex

4 coordinate, square planar also plausible
Magnetic measurements "did not make sense"

- $\chi$ was temperature dependent and did not follow Curie Law ($T$ independent) as expected for a monometallic Cu complex (i.e. $S = \frac{1}{2}$).

- Copper acetate essentially DIAMAGNETIC at ~ 90 K

I.e., Experiment shows copper acetate looks diamagnetic at lower T !! But how can this be ? Copper acetate was supposed to follow Curie Law...

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The crystal structure explained why……

- It's actually a DINITURAL complex!
- The four acetate ligands bridge the Cu$^{2+}$ centres
- H$_2$O molecules bond terminally to the Cu$^{2+}$ centres

Cu...Cu ~ 2.65 Å

- Clearly, the two Cu$^{2+}$ metal ions (each $S = \frac{1}{2}$) are interacting magnetically.
- Doing so in a way that yields a smaller $\chi_M$ (or $\mu_{\text{eff}}$) per Cu than expected for $S = \frac{1}{2}$, and eventually $\chi_M$ (or $\mu_{\text{eff}}$) → 0.

Critical discovery in the development of modern theories for antiferromagnetic coupling.
**Cu(II) dimeric complex:**
- Each Cu centre is $d^9$ therefore has one unpaired $e\^-$ each
- Their spins can interact in one of two ways…

**Align ant-parallel** ($S = \frac{1}{2} - \frac{1}{2} = 0$)

**Align parallel** ($S = \frac{1}{2} + \frac{1}{2} = 1$)

**OR**

- **Antiferromagnetic interaction**
- **Ferromagnetic interaction**

**YOU ALWAYS GET BOTH CASES, BUT WHICH IS THE GROUND SPIN STATE ($S$)?**

**NOTE:** $S$ (capital letter) is the Total Spin Quantum number of the complex in the ground state.

- Only one of them can be the ground state ($S' = 0$ or $1$). Where $S'$ are the Total Spin States for the complex.
- If the two unpaired electrons interact ferromagnetically: $S' = 1$ is the ground state.
- Likewise if they interact antiferromagnetically: $S' = 0$ is the ground state.

**Note:** $S_A$ and $S_B$ = local spin on CuA and CuB respectively. $S'$ = total spin.

- The energy difference is equal to $J$
- **IMPORTANT** The $J$ value describes the magnetic exchange interaction between two metal centres.
It is an example of an antiferromagnetically-coupled dinuclear complex, and thus $\chi_M$ and $\mu_{\text{eff}} \to 0$ as $T \to 0$.

$T_N = \text{Néel temp.} \approx 280 \text{ K}$. This is a very high value, indicating very strong coupling (interaction) between the Cu$^{2+}$ ions.

Why can we say this? The tendency to align the spins ($\uparrow \downarrow$) is sufficient to overcome thermal energy even at ~ 280 K.

The larger $T_N$ = the larger the inter-metal (M•••M) interaction between their unpaired electrons.

A closer look at the J value

Consider two transition metal ions connected with two bridging ligands (L):

If the interaction is ANTI-FERROMAGNETIC = $J < 0$

If the interaction is FERROMAGNETIC = $J > 0$

The magnetic properties of a complex depend greatly on SIGN and MAGNITUDE of J.

Note: This J IS NOT associated with Spin-Orbit Coupling

For example…
Large + $J = $ Strongly ferromagnetic complex
Large − $J = $ Strongly antiferromagnetic complex

NOTE: Units of J: cm$^{-1}$ or K
THE SHAPE OF THESE CURVES TELLS US ABOUT STRENGTH OF J

Plots for AF Copper Dimer - $\chi T$

$\chi_M T$ vs $T$

Less obvious: lack of maximum makes fitting data imprecise. Also, as $\chi T$ zero at low $T$, fit will be very sensitive to impurities.

Plots for F Copper Dimer - $\chi T$

$\chi_M T$ vs $T$

$\chi T$ very dependent on $J$: still no maximum so it will be more difficult to get a precise $J$ cf. moderate negative $J$ value.

Units: $\text{cm}^{-1}$
Magnetic exchange mechanisms

There must be a way for the unpaired electrons to interact......

* Single unpaired electron on Cu²⁺ in dx²−y² orbital

Paramagnetic centres M can interact via two mechanisms:

1) Direct exchange: Not possible in above complex (the orbitals are too far apart and don’t point in the right direction).

Direct overlap of the ‘magnetic orbitals’ (orbitals containing the unpaired electron(s)). Akin to a metal-metal bond (see next slide).

Gives rise to bonding (symmetric) and anti-bonding (anti-symmetric) Molecular Orbitals (MOs from MO theory).

More on Direct Overlap

We must consider what a strong metal-metal bond would look like:

Consider 2 x ML₅ fragments with 1 upe in each (i.e. Mn(CO)₅)

σ Bond formation

• However, when two atomic orbitals overlap they produce 2 x MOs: 1 x bonding (attractive) and 1 x anti-bonding (repulsive) MO.

ΔE = ν large cf. kT. Tens of thousands of cm⁻¹.

i.e. All molecules have σ² ground state.

• Such a molecule is described as metal-metal bonded with no upe’s.
• Thus the σ* orbital is too high in energy (thermally inaccessible) to be populated even at 300 K.
There are therefore 2 energy states possible but the excited state is very high in energy \((\text{vs. } kT)\). We can draw them:

\[
\begin{align*}
\sigma^* & \quad \Delta E \quad \sigma \\
\text{Ground state } S = 0 & \quad \sigma \quad \text{bond} \quad \sigma & \quad \Delta E \quad \sigma^* \\
\text{Excited state } S = 1 & \quad \text{No bond}
\end{align*}
\]

Which can also be represented by:

\[
\begin{align*}
\text{energy} & \quad \Delta E = \text{very large} \\
S = 1 & \quad \text{energy} \\
S = 0 & \quad \text{energy}
\end{align*}
\]

• Thus diamagnetic, metal-metal bonded compounds are a sub-set of paramagnetism, with \(S = 0\) as their ground state and very high lying excited states (i.e. \(S = 1\) in previous slide).
• As a result the \(S = 0\) state is occupied at room temperature.
• However if direct overlap is \textit{weak}, \(\Delta E\) will be small enough that the excited state can be thermally populated.

For example consider overlap of orbitals with \(\delta\) symmetry:

\[
\begin{align*}
\delta^* & \quad \delta \\
\text{dx}^2-\text{y}^2 & \quad \text{dx}^2-\text{y}^2 \\
\text{along } z & \quad \text{along } z
\end{align*}
\]

\(\delta\) overlaps are inherently weak due to their side-on nature. However does not have to be \(\delta\) overlaps to lead to weak overlap observed in a complex:

\[
\begin{align*}
\delta^* & \quad \delta \\
\text{dx}^2-\text{y}^2 & \quad \text{dx}^2-\text{y}^2 \\
\text{Ground state, } S = 0 & \quad \text{Accessible excited state} \\
\Delta E = \text{not large} & \quad S = 1
\end{align*}
\]
Which can also be represented by:

\[ \Delta E \]

\[ \Delta E = \text{not very large} \]

\[ S = 1 \]
\[ S = 0 \]

The bigger \( \Delta E \) the higher the Neél Temperature \( (T_N) \).

The higher the \( T_N \) the sooner the \( \chi_m T \) vs. \( T \) curve will deviate from Curie Law.

More specifically \( S = 0 \) begins to dominate earlier (at higher \( T \)).

Example: \([M_2O_2L_6]\) (where \( M = V(IV) \) or \( Mo(V) \))

- Square pyramidal about \( M \), \( d^1 \) with \( 1e^- \) in \( d_{xy} \)

- \( x^2-y^2 \)
- \( z^2 \)
- \( xz, yz \)
- \( xy \)

- When \( M = V \) the \( V...V \) distance is ca. 3 Å — Too large for strong \( d_{xy} / d_{xy} \) overlap
- Therefore \( S' = 0 \) ground state with \( S' = 1 \) (excited) state thermally accessible.

When \( M = Mo \): The 4d orbitals much bigger than 3d orbitals (i.e. in \( V \) above)

- Much greater \( d_{xy} / d_{xy} \) orbital overlap = much larger AF exchange (J)
- No thermal population and DIAMAGNETIC at room temperature.

\( S = 1 \) thermally inaccessible
**Superexchange**

The M–M interaction occurs via an intervening **diamagnetic ligand**

\[ \text{M} - \text{L} - \text{M} \]

*where L = diamagnetic ligand*

Can lead to Ferro- or Antiferromagnetic exchange

This must be what happens in the AF [Cu$_2$(OAc)$_4$(H$_2$O)$_2$] complex!

Acetate bridging ligands are the **diamagnetic ligands** in this instance

**Superexchange: Cu$^{2+}$ dinuclear complexes**

- A Magneto-structural correlation between the **Cu-O-Cu angle** and the sign and magnitude of \( J \) in planar hydroxy-bridged Cu$^{2+}$ dinuclear complexes (below)

<table>
<thead>
<tr>
<th>J value depends on the Cu-O-Cu angle:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Angle &gt; 98.4, ( J &lt; 0 ) (Antiferromagnetic exchange)</td>
</tr>
<tr>
<td>Angle &lt; 98.4, ( J &gt; 0 ) (Ferromagnetic)</td>
</tr>
</tbody>
</table>

- Magneto-structural correlations are where a family of analogous complexes are analysed both structurally and magnetically.

- It is hoped to find a link between a change in structure (i.e. M–M distance, M-L-M angle etc) with a change in magnetic properties (i.e. Antiferro → Ferro)

- This gives us an insight into how we are able to synthesise compounds with predicted and desired magnetic properties.
Magneto-structural correlations observed in family of OH-bridged \([\text{Cu}_2]\) complexes

\[ \theta / \text{degrees} \]

\[ \begin{align*}
\text{Antiferromagnetic} & \quad \theta > 98.4^\circ, J < 0 \\
\text{Ferromagnetic} & \quad \theta < 98.4^\circ, J > 0
\end{align*} \]

Superexchange: \(\text{Cu}^{2+}\) dinuclear complexes

Can be explained using Molecular Orbital (MO) picture:

- Single unpaired \(e^-\) on \(\text{Cu}^{2+}\) in \(d_{x^2-y^2}\) orbital
- If \(\text{Cu-O-Cu} \sim 90^\circ\) then: O will bond with one Cu via \(P_x\) orbital and other with \(P_y\) orbital.

Look at bonding: Two pairs of bonding / antibonding orbitals:

\[ 2 \text{ e}^- \text{ from each O orbital} + 1 \text{ e}^- \text{ from each } d_{x^2-y^2} \text{ orbital} = 6 \text{ electrons} \]

Feed into MO diagram gives 2 unpaired electrons in ground state... **Ferromagnetic exchange**

\[ dx^2-y^2 \]
Mechanisms of exchange: Cu$^{2+}$ dinuclear complexes

- Change angle to approx 180 °:

Oxygen atom only uses 1 orbital to bridge the two Cu$^{2+}$ centres

MO diagram consists of 4 electrons:
2 e- from O orbital ($P_y$) and 1 from each Cu centre ($dx^2-y^2$ orbital).

ANTIFERROMAGNETIC EXCHANGE

Superexchange: Important points

The MO pictures tell us the two extreme scenarios (AF and Ferro)

Does not tell us where the AF ↔ F transition point actually is.

Orthogonality principle:
- If the unpaired electrons are in orthogonal orbitals

FERROMAGNETIC EXCHANGE

It appears to be common that the more obtuse an angle the stronger the ANTIFERROMAGNETIC exchange.