**Literature Discussion: Molecular Magnets with Lanthanide Metal-Metal Bonding**

A recent *Science* paper by Gould et al. reported a series of dilanthanide complexes with exceptional magnetic properties due to the presence of metal-metal bonding. These “molecular magnets” were composed of two lanthanide ions (Y, Gd, Tb, or Dy) held in close proximity by three bridging iodide ligands, capped by two CpiPr5 ligands, as shown below. The paper claims that a single electron occupies a bonding orbital shared equally between the two metal ions, making these compounds the first molecules ever reported to have metal-metal bonding between two lanthanides!



**READ** the research article describing these exceptional molecular magnets:

Gould, C.A. et al. “Ultrahard magnetism from mixed-valence dilanthanide complexes with metal-metal bonding.” *Science* **2022**, *375*, 198-202.

Glossary of important terms:

* *coercivity / coercive magnetic field (HC)* – the intensity of applied magnetic field required to demagnetize a strongly magnetized (“saturated”) material. Materials with a high HC are said to be magnetically “hard” while materials with a low HC are said to be “soft”.
* *exchange coupling* – a quantum mechanical phenomenon that lowers the energy of a system when two nearby electrons can be exchanged indistinguishably (i.e. when they have parallel spins).
* *magnetic anisotropy* – a change in a material’s magnetic properties depending on the direction of an applied field. A material with strong magnetic anisotropy will be easy to magnetize along certain directions, but more difficult to magnetize along others.
* *magnetic hysteresis* – process of applying a magnetic field to magnetize a material, then reversing the direction of the applied field to demagnetize it. The shape of a hysteresis loop can be used to determine the coercivity and response of a magnetic material to temperature.

**CONSIDER** the following questions, which we will discuss during class:

1. Why have compounds featuring metal-metal bonding between lanthanides been challenging to isolate until now?
2. The molecular magnets (CpiPr5)2M2I3 (M = Y, Gd, Tb, Dy) are described as “mixed-valence dilanthanide complexes”. What is meant by the term “*mixed-valence*”? How are the valence electrons distributed between the two metal ions? What evidence does the paper present for where the valence electrons are located?
3. Because the single bonding electron is shared equally by both metal atoms in (CpiPr5)2M2I3, its spin aligns with other unpaired f electrons on the lanthanide atoms, giving rise to the magnetic properties observed in these molecules. Sketch a simple MO diagram of the (M)25+ dinuclear core of each of the (CpiPr5)2M2I3 molecules. (Use electron configurations as given on the pre-discussion worksheet!)
4. Taking the gadolinium complex **1-Gd** as an example, how many parallel unpaired electrons are present in **1-Gd** in the ground state, according to our MO diagram? Calculate the spin multiplicity and the spin-only magnetic moment that we would expect. What evidence does the paper present that such high-spin ground states exist in these molecules?
5. The paper boasts that compounds **1-Dy** and **1-Tb** have the largest magnetic coercivities “yet reported for any molecule or molecule-based material” at relatively high (liquid nitrogen!) temperature. What properties of these molecules combine to produce such record-breaking magnetic behavior?

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**Literature Discussion Worksheet**

**COMPLETE** the following preparatory exercises (to be turned in at the start of class):



1. The reaction scheme for the synthesis of the molecular magnets is shown above (see Figure 1A in the paper). Potassium graphite acts as a one-electron reductant to the precursor molecule (CpiPr5)2M2I4 and abstracts an iodide ion, forming the (CpiPr5)2M2I3 product that features a trigonal bipyramidal core structure of two lanthanides bridged by three iodides. For the (CpiPr5)2M2I4 precursor and the (CpiPr5)2M2I3 molecular magnet as shown, determine:
	1. the oxidation state(s) of M
	2. the point group (You may assume that the CpiPr5 ligands are freely rotating and do not affect the symmetry.)
2. Which atomic orbitals on each lanthanide interact to form the metal-metal bond? Sketch the bonding interaction of the two relevant orbitals in the (CpiPr5)2M2I3 molecular magnets. To what irreducible representation would this MO belong, in the symmetry you identified in Question 1? What type of metal-metal bonding (σ/π/δ) do these molecules exhibit?
3. The ground state electron configurations for the free Y, Gd, Tb, and Dy atoms are given below:

Y: [Kr] 5s24d1
Gd: [Xe] 6s24f75d1
Tb: [Xe] 6s24f9
Dy: [Xe] 6s24f10

Construct electron diagrams for each of these metal atoms. (You may assume Aufbau ordering of the orbital energies: 5s < 4d < 5p < 6s < 4f < 5d < 6p.) Predict which electrons are likely to be lost in the M(III) ion of each metal atom.

1. Define Hund’s Rule. Explain how this rule is demonstrated by your electron diagrams from Question 3.