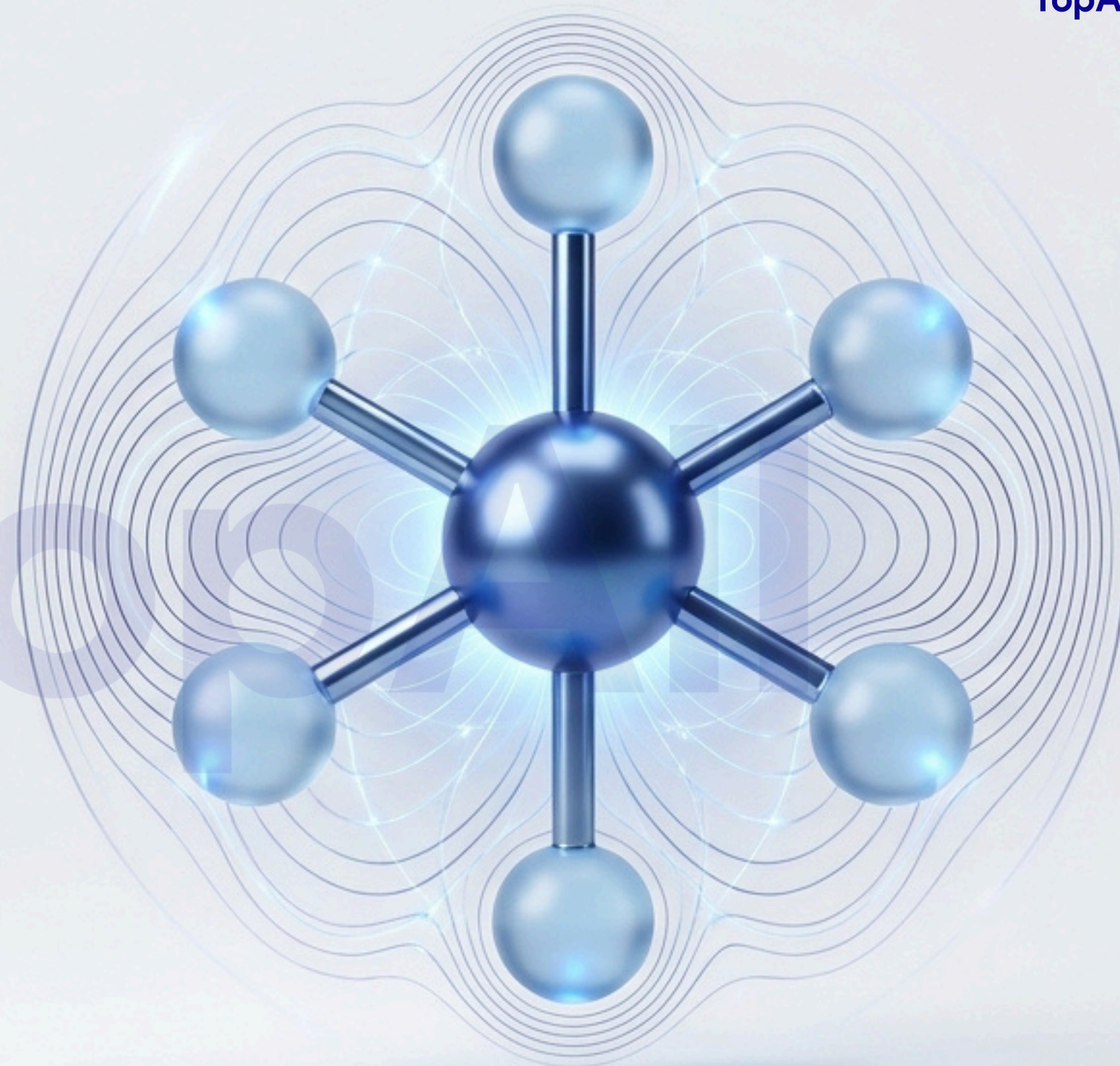


COORDINATION CHEMISTRY 5.5.2

Magnetic Properties of Coordination Compounds

Decoding Geometry Through Unpaired Electrons

Magnetic susceptibility experiments aren't just about magnetism—they are the key to unlocking the hidden structures, electron configurations, and hybridization of metal complexes.



The Magnetic Fingerprint

[Magnetic
Moment Data]

[Count of
Unpaired
Electrons]

[Orbital
Hybridization]

[Molecular
Geometry]

The Principle

The measurable magnetic moment of a coordination compound acts as a diagnostic fingerprint. It directly counts the number of unpaired electrons in the central metal ion.

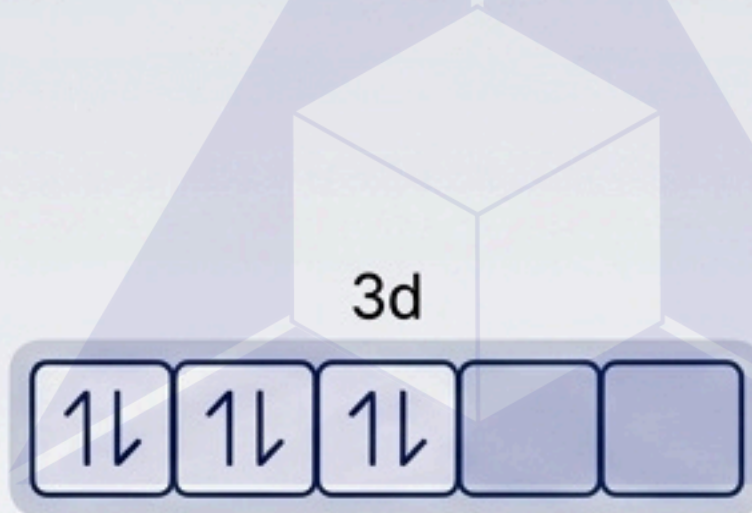
The VBT Link

By knowing the unpaired electron count, Valence Bond Theory (VBT) allows us to reverse-engineer which d-orbitals are empty, dictating the exact hybridization scheme the molecule must adopt.

The Inner vs. Outer Orbital Choice

For metals with 1–3 d-electrons, two vacant orbitals are always available. But for d^4 , d^5 , and d^6 ions, a structural choice must be made based on the ligand environment:

[Inner Orbital] [Low Spin] [d^2sp^3 Hybridization]



Electrons are forced to pair up (violating Hund's rule), leaving two inner 3d orbitals vacant for bonding. This results in fewer unpaired electrons.

[Outer Orbital] [High Spin]

[sp^3d^2 Hybridization]



Electrons remain unpaired. The complex utilizes the higher energy 4d orbitals for bonding, resulting in maximum unpaired electrons.



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$$E=mc^2$$



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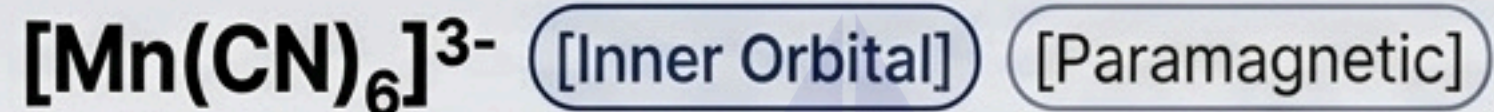
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Key Highlights

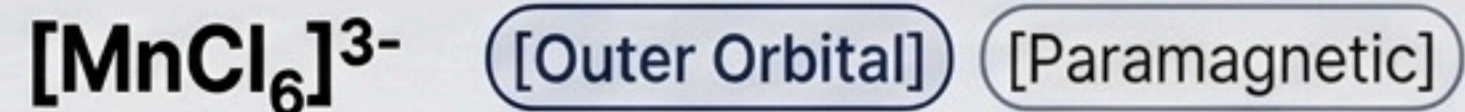
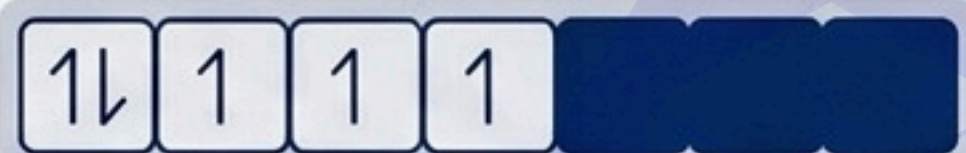
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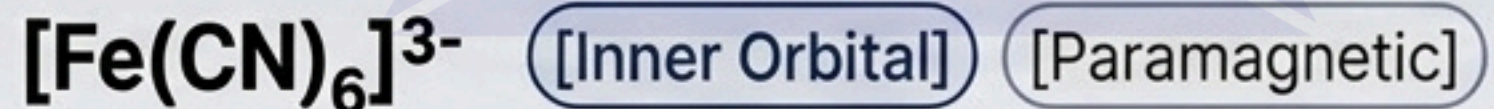
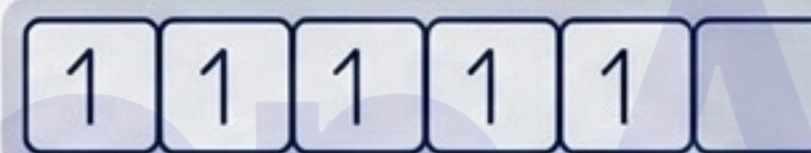
Magnetic Divergence in d^4 and d^5 Systems



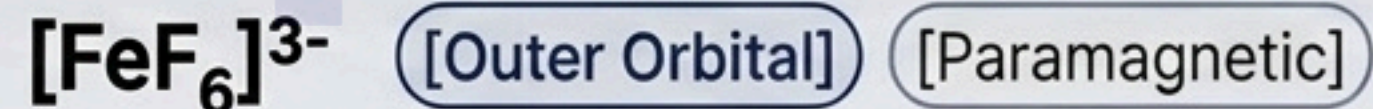
2 unpaired electrons



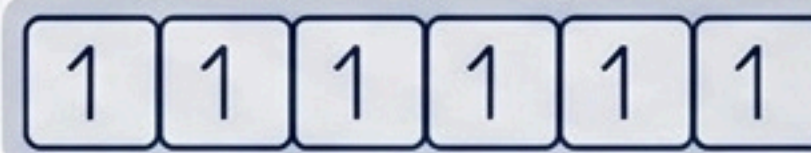
4 unpaired electrons



1 unpaired electron



5 unpaired electrons



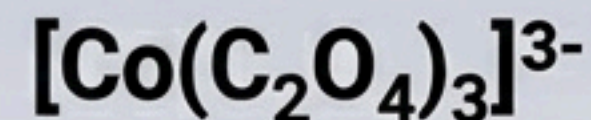
The Cobalt Shift: From Paramagnetic to Diamagnetic



[Outer Orbital sp^3d^2] Paramagnetic 4 Unpaired e^-



The d^6 configuration leaves four electrons completely unpaired, utilizing the outer 4d orbitals for coordination.



[Inner Orbital d^2sp^3] Diamagnetic 0 Unpaired e^-



All six d-electrons are forced to pair up completely to free inner orbitals. This totally erases the magnetic moment of the molecule.

Notice how the choice of ligand radically shifts the fundamental physical property of the molecule from strongly magnetic to entirely non-magnetic.

APPLICATION (EXAMPLE 5.7)

Predicting the Geometry of $[\text{MnBr}_4]^{2-}$

1. The Measurement

The spin-only magnetic moment is measured experimentally at 5.9 BM.

2. The Electron Count

A value of 5.9 BM confirms the presence of exactly 5 unpaired electrons in the d-orbitals of the Mn^{2+} ion.

3. The Structural Fork

The Coordination Number is 4. Therefore, it must be either Tetrahedral (sp^3) or Square Planar (dsp^2).

4. The Final Verdict

Square planar geometry requires an empty d-orbital, forcing electrons to pair. Because all 5 electrons remain unpaired, no pairing occurred. Therefore, the complex must be Tetrahedral (sp^3).

Rules of Magnetic Diagnostics

Magnetic Moment = Structure

Magnetic susceptibility isn't just a physical quirk; it is the primary diagnostic data point that dictates whether an inner or outer orbital hybridization occurs.

The d^4 – d^6 Battleground

Metals with 4, 5, or 6 d-electrons exhibit the most dramatic magnetic variations based on their ligand environment—most notably the shift from highly paramagnetic to entirely diamagnetic in Cobalt.

Data Drives Geometry

As demonstrated with $[\text{MnBr}_4]^{2-}$, simply knowing the magnetic moment allows us to definitively rule out competing molecular geometries without needing a microscope.



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