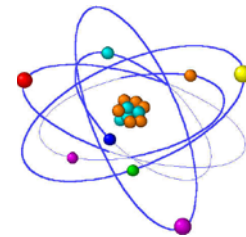


# Inorganic Chemistry Laboratory



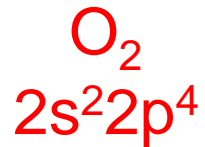
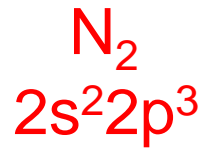
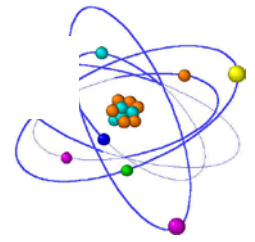
Lab 8

Experiment 12 (p.117)

The Paramagnetic Complex  $\text{Mn}(\text{acac})_3$

# Electron Configurations

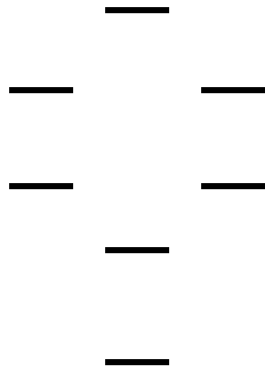
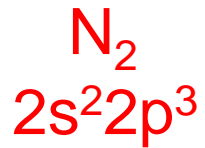
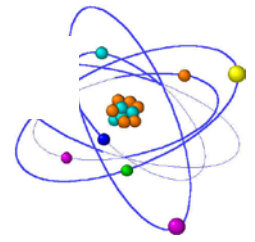
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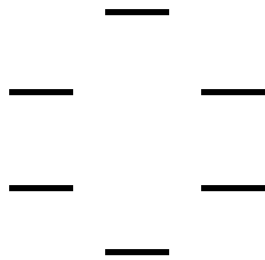
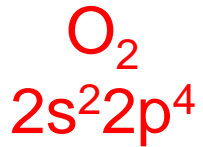
What are some consequences of the different electron configurations?

# Electron Configurations

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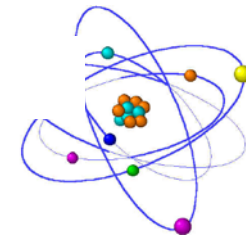


What are some consequences of the different electron configurations? What physical properties will be influenced?



# Magnetism and Electron Configuration

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Two types of magnetism based on electron configuration.

**Paramagnetic**

Unpaired electrons

**Diamagnetic**

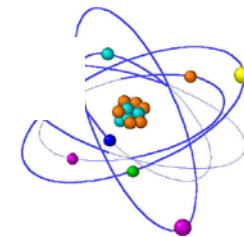
All electrons paired

*d*-Electron configurations of coordination compounds are experimentally determined by measuring **magnetic susceptibility**,  $\chi$ .

**paramagnetic** – *having unpaired e<sup>-</sup>; the substance is attracted to (or adds to) the external field*

**diamagnetic** – *lacking unpaired e<sup>-</sup>; the substance is repelled by (or subtracts from) the external field*

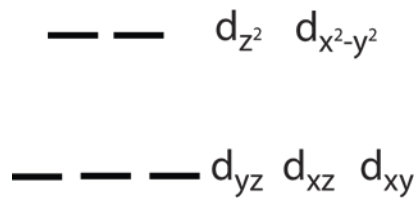
# Transition Metals and Magnetism



What factors affect the magnetism of transition metals?

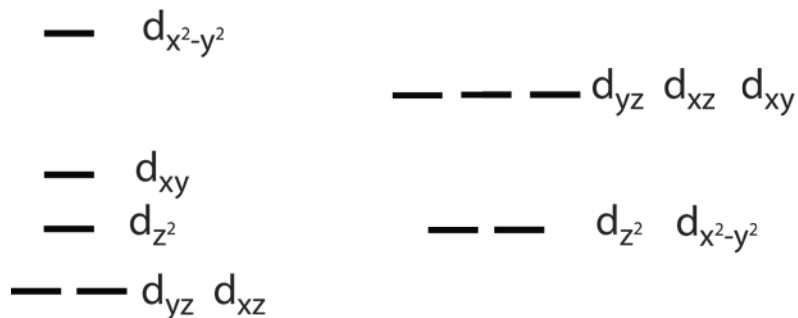
## 1. Oxidation State

Consider  $\text{Cu}^+$  vs.  $\text{Cu}^{2+}$



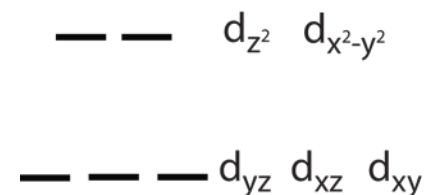
## 2. Coordination Geometry

Consider Square Planar vs. Tetrahedral  $\text{Ni}^{II}\text{L}_4$

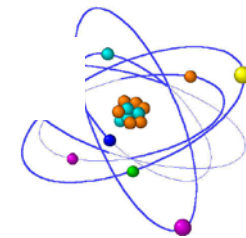


## 3. Ligand Identity

D-orbital Splitting Octahedral ( $\Delta_o$ )

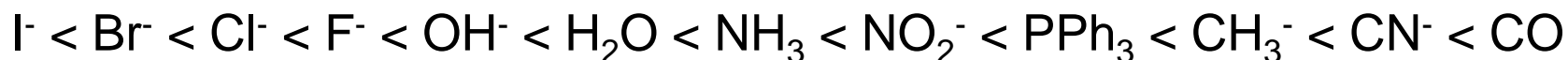


# Transition Metals and Magnetism



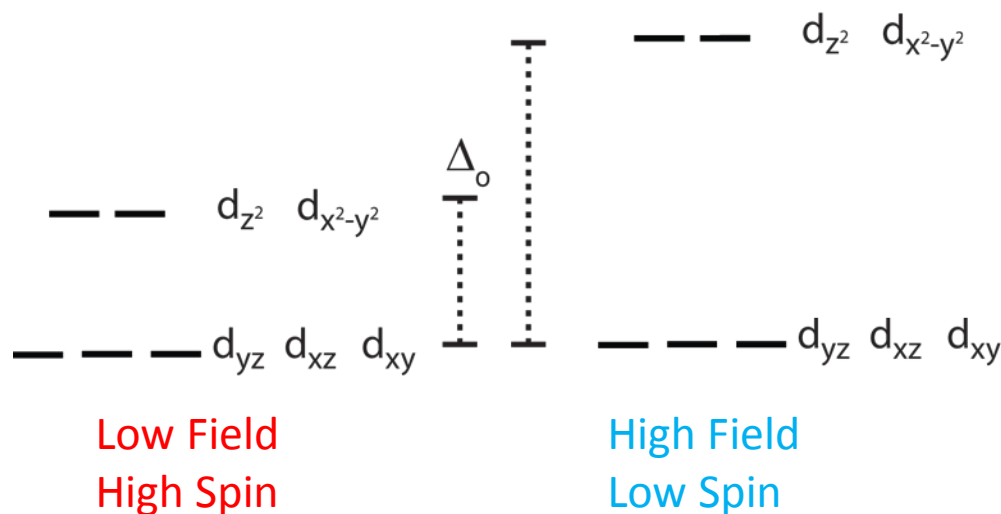
## Spectrochemical Series

Strong  $\sigma$  donors or  $\pi$  acceptors induce bigger energy gaps in d orbitals ( $\Delta_o$ )

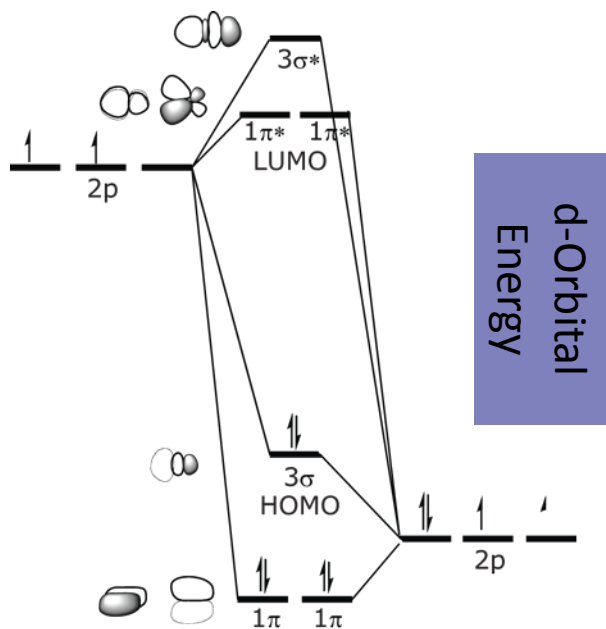
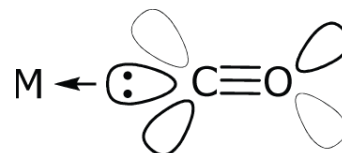
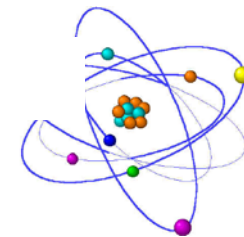


Consider  $\text{Fe}^{2+}$   
 $\text{Fe}(\text{OH})_6^{4-}$  vs.  $\text{Fe}(\text{CN})_6^{4-}$

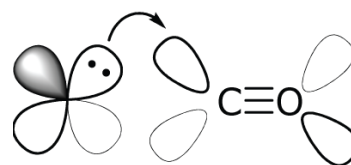
Why does CO induce such large  $\Delta_o$ ?



# Transition Metals and Magnetism



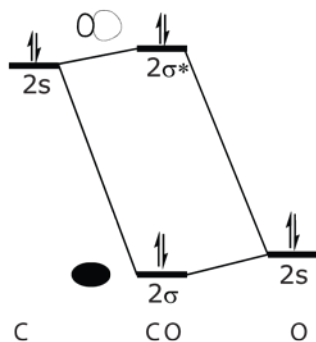
$\sigma$ -donation



and

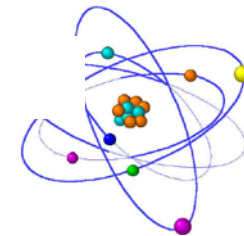


$\pi$ -accepting

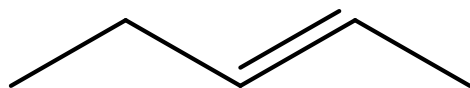


# Manganese Acetylacetonate (acac)

---



How will this molecule coordinate to a metal ion?



Bidentate through both oxygen atoms

How many acac ligands will manganese accept assuming octahedral geometry?

Three

If this complex is neutral, what is the charge on Mn?

$\text{Mn}^{3+}$

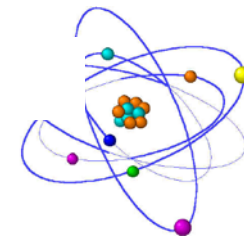
How many d electrons?

Four



# Mn(acac)<sub>3</sub> Synthesis

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Slow addition of acac  
(aqueous)

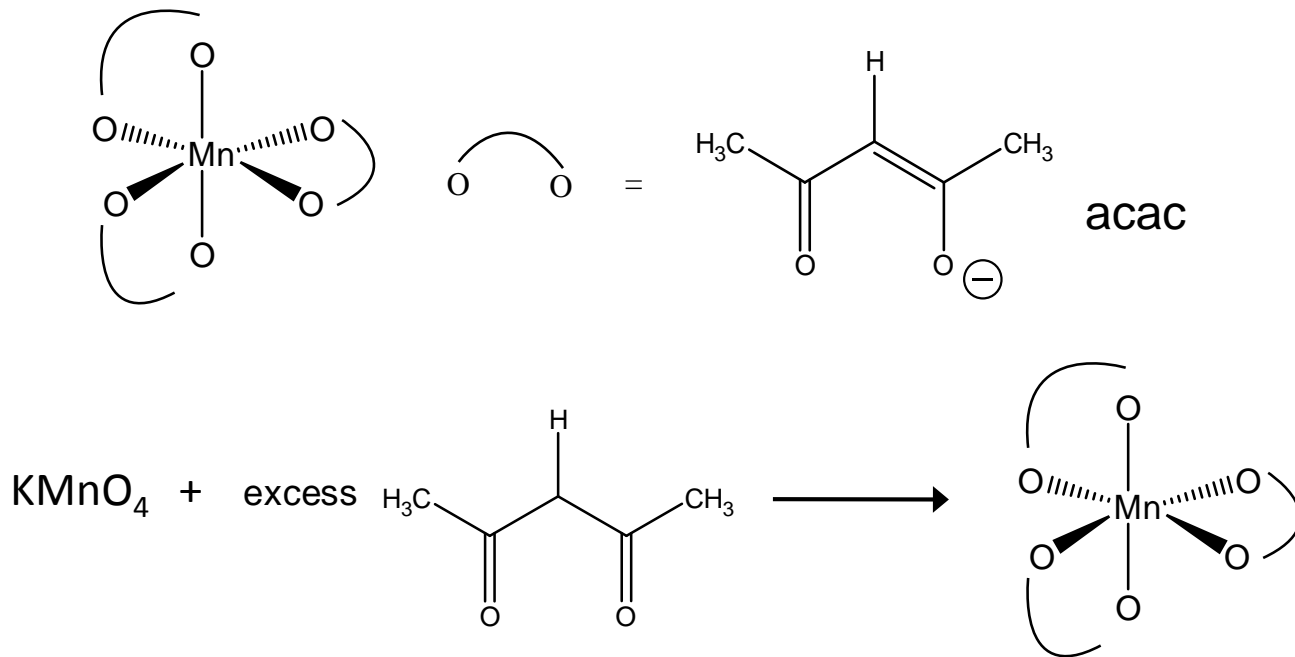


Dry on frit

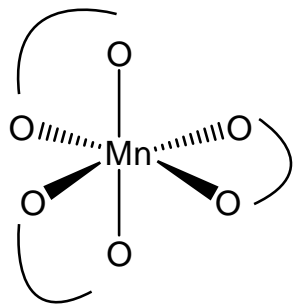
Rapid addition results in  
foam...what might this be?

# The Paramagnetic Complex $[\text{Mn}(\text{acac})_3]$ – Magnetic Susceptibility

## Tris(acetylacetonato)manganese(III)



# [Mn(acac)<sub>3</sub>]: Possible *d*-Electron Configurations



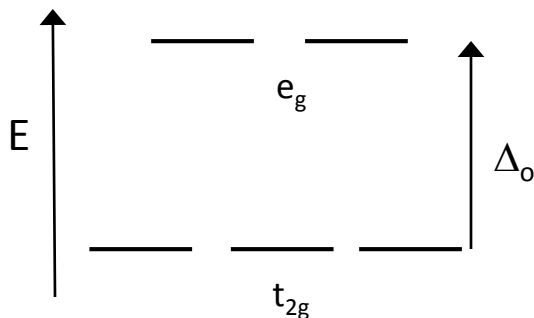
Mn<sup>3+</sup> electron configuration? [Ar] 3*d*<sup>4</sup>

*Remember: 4s e- are lost first (lower Z\*)*

*d*-orbital splitting in an octahedral ligand field?

Possible *d*-electron configurations?

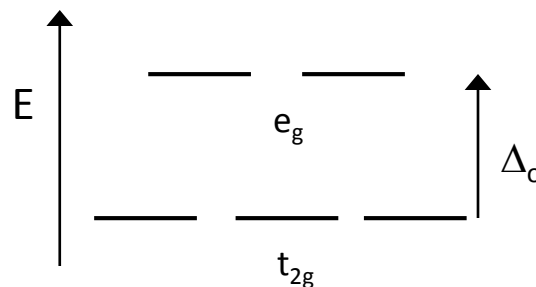
*Two options, depending on strength of Mn—acac interactions (ligand field strength).*



Large  $\Delta_o$

Low-spin complex

Strong-field ligands



Small  $\Delta_o$

High-spin complex

Weak-field ligands

***Our goal: Determine *d*-electron configuration and strong/weak character of acac ligand.***

# A Brief Review of NMR

How does NMR work?

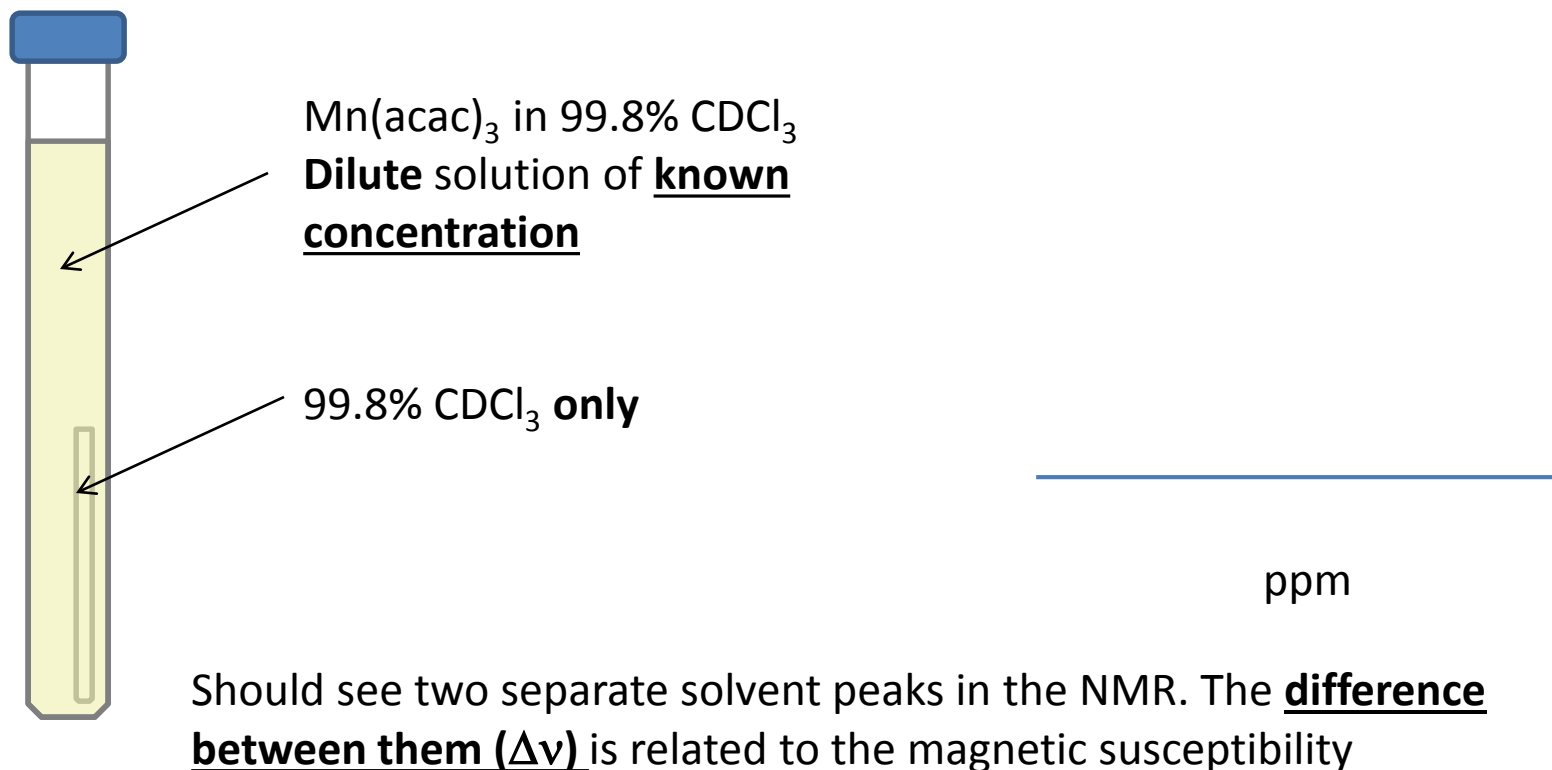
- Nuclei have spins – +1/2 and -1/2 for  $^1\text{H}$ .
- Nuclear “magnets” line up parallel or antiparallel to the external magnetic field.
- The external field is modulated around its “central” value (300 MHz, in our case) by passing current through coils.
- Nuclei in different chemical environments absorb at different frequencies (undergoing spin transitions).
- The *chemical shifts* we report (in ppm) are shifts from the frequency of the external field.

$$2.1 \text{ ppm} = \left( \frac{2.1}{1 \times 10^6} \right) (300 \times 10^6 \text{ Hz}) = 630 \text{ Hz}$$

# The Evans Method for Determining Magnetic Susceptibility

You will determine the degree to which your paramagnetic sample adds to the external field of the NMR magnet.

Compare the solvent peak for  $\text{CHCl}_3$  alone (**0.2%/99.8%  $\text{CDCl}_3$** ) to peak for  $\text{CHCl}_3$  in the presence of the paramagnetic sample



## Calculations: Determining $\chi_M$ , $\chi_M'$ and $n$

**Goal of calculations:** To determine number of unpaired  $d$ -electrons,  $n$

**Strategy:**

1. Determine total magnetic susceptibility,  $\chi_M$ , from the measured frequency difference between the two solvent peaks,  $\Delta\nu$  (Eqn 10).

$$\chi_M = 477 \left( \frac{\Delta\nu}{Q\nu_1c} \right)$$

2. Solve for magnetic susceptibility due to unpaired electrons,  $\chi_M'$  (Eqn 4).

$$\chi_{M,tot} = \chi_M' + \chi_M(\text{metal core}) + \chi_M(\text{ligands})$$

3. Use  $\chi_M'$  and measured temperature (in kelvins) to solve for  $n$  (Eqn 8).

$$\chi_M' T = \frac{1}{8} n(n+2)$$

***d*-electron configuration low- or high-spin?  
acac ligand strong- or weak-field?**

## Experimental Notes

1. Prepare a **dilute** solution of  $\text{Mn}(\text{acac})_3$  of **known concentration**.
  - a) Use the smallest measurable mass ( $\sim 1$  mg); deliver a known volume with a graduated syringe or micropipette.
  - b) Solution should be light yellow/tan. You may need to dilute further; just keep track of exactly what you do so that you can calculate the final molar concentration.
2. I will prepare the capillary tubes containing pure  $\text{CDCl}_3$  (with 0.2%  $\text{CHCl}_3$ ). When your sample is complete, put one in your NMR tube, making sure it drops to the bottom.
3. On your spectrum:
  - a) Zoom in and label your two solvent peaks (maximum precision).
  - b) Make sure you have the recorded temperature.

## Formal Report (Due Thurs., 4/9)

Your report should consist of:

- Your NMR spectrum, with chemical shifts labeled
- Calculations of  $\chi_M$ ,  $\chi'_M$ , and  $n$ 
  - Note: In Table 12-1 (p. 122), the  $\chi_M$  values given have been multiplied by  $10^6$ ; the correct values are on the order of  **$10^{-6} \text{ cm}^3 \text{ mol}^{-1}$** . **This also applies to the value for the metal given in the footnote: it should be  $-13 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ .**
- **Make sure to check you report with the rubric on the course website!**