

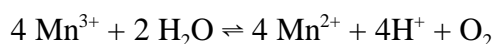
**Tris(2,4-pentanedionato)manganese(III)**  
[Acetylacetonatomanganese(III)]

## Introduction

Manganese is a first row transition metal that has a tremendous variety of oxidation states that appear in its compounds. The oxidation numbers range from Mn(–III) in compounds like  $\text{Mn}(\text{NO})_3\text{CO}$  to Mn(VII) in  $\text{KMnO}_4$ . Compounds of manganese range in oxidation number between these two extremes. This experiment involves the preparation of a Mn(III) complex of acetylacetonone (also named 2,4-pentanedione) which is a useful starting material for the preparation of other Mn(III) compounds. Manganese(III) complexes are relatively stable and can be prepared directly by reactions of the hydrous manganese(III) oxide or by oxidation of the hydrous manganese(II) oxide with air or an oxidizing agent. In aqueous solution Mn(III) is readily hydrolyzed



and is most stable in acid solutions. Manganese(III) is also slowly reduced by water.



In this experiment a solution of manganese(II) chloride is oxidized with potassium permanganate in the presence of acetylacetonone giving the brown acetylacetonemanganese(III),  $\text{Mn}(\text{acac})_3$ .

Because the ground state for octahedral complexes like that of  $\text{Mn}(\text{acac})_3$  is a  ${}^5E_g(t_{2g}^3e_g^1)$  there exists considerable Jahn-Teller distortion. Therefore, the complexes are not “pure” octahedral. Two forms of  $\text{Mn}(\text{acac})_3$  are known: one with substantial tetrahedral elongation (two Mn-O bonds at 212 pm, and four at 193 pm), the other with moderate tetragonal compression (two Mn-O bonds at 195 pm and four at 200 pm). The electronic spectrum of  $\text{Mn}(\text{acac})_3$  shows a broad band at approximately  $20,000 \text{ cm}^{-1}$  (500 nm).<sup>1</sup> The complex forms lustrous crystals which are black to dark brown by reflected light and green by transmitted light.<sup>2</sup>

The  $\text{Mn}(\text{acac})_3$  complex can be reversibly oxidized to  $\text{Mn}(\text{acac})_3^+$  (0.96 V vs SCE), or reduced to  $\text{Mn}(\text{acac})_3^-$  (–0.06 V vs SCE) in acetonitrile solution (0.1 M tetraethylammonium perchlorate). It has been shown that many electron transfer reactions like those above are ligand-centered rather than metal-centered.<sup>3</sup> This implies that in many transition metal complexes electron transfer reactions are facilitated by stabilization of the ligand-radical product via covalent bond formation with an unpaired *d* electron of the transition metal center. The covalent bond energy is proportional to the negative shift in the potential for the ligand oxidation relative to that for the free ligands anion.<sup>3</sup> The  $\text{Mn}(\text{acac})_3$  prepared here may be used in a later magnetic susceptibility experiment.

This synthetic procedure has been scaled down (semi-microscale) from an Inorganic Synthesis preparation.<sup>2</sup>

## Procedure

In a 250-mL conical flask prepare a solution of 1.00 g (5.05 mmol) manganese(II) chloride tetrahydrate and 2.72 g (17.1 mmol) of sodium acetate trihydrate in 40 mL water. To this solution add by digital pipet 3.79 mL (4.10 g or 40.0 mmol) acetylacetone. Place a small magnetic stirring bar in the solution and place the flask on a magnetic stirrer in the hood. To the stirred mixture add dropwise a solution of 0.21 g (1.3 mmol) of potassium permanganate in 10 mL water. (*Note 1*: Because of the color intensity of the permanganate solution it is difficult to determine if all the solid has dissolved; therefore, stir thoroughly and check for undissolved solute.) After the addition of the potassium permanganate solution continue stirring for 5 minutes. Prepare a solution containing 2.72 g (17.1 mmol) sodium acetate trihydrate in 10 mL of water and add this in approximately 1-mL portions to the stirred solution of crude  $\text{Mn}(\text{acac})_3$ . Heat the reaction mixture to *near* boiling (hot plate) for 10 minutes and cool to room temperature. Filter the dark solid on a small Buchler funnel and wash with three 10-mL portions of water. (*Note 2*: Do not use sintered glass filters for this step.) Spread out the product on a porcelain dish and dry the product in a drying oven at 60 °C to 70 °C for at least one-half hour.

Weigh the dry product and determine the percent yield. Under the hood dissolve the dried acetylacetonatomanganese(III) in 4.0 mL of benzene contained in a 25-mL conical flask. Filter the solution through a 30-mL medium porosity glass filter. Transfer the filtrate to a 30-mL beaker and cool in an ice bath, being careful not to get any water in the benzene solution. Add 15 mL of petroleum ether to the solution to reprecipitate the product. Collect the recrystallized product on a 30-mL medium porosity filter funnel and place in a drying oven at 60 °C. (*Note 3*: Place the filtrate in a proper lab waste container, not down the drain.) Weigh the recrystallized product and calculate the percent yield from starting material.

## Laboratory Report

1. Submit your sample in a clearly labeled bottle. Write balanced equations for the preparation and report theoretical and percentage yield?
2. Draw the structure of  $\text{Mn}(\text{acac})_3$ ? What is the point group of the molecule? Is it possible to draw optical isomers of  $\text{Mn}(\text{acac})_3$ ?
3. How do you account for the single absorption band in the electronic spectrum of  $\text{Mn}(\text{acac})_3$ ?

## References

1. Cotton, F. A., Wilkinson, G., Murillo, C. A., Bochmann, M., *Advanced Inorganic Chemistry*, 6<sup>th</sup> Ed., Wiley and Sons, New York, 1999.
2. Charles, R. G., *Inorg. Synth.*, **1963**, 7, 183.
3. Richert, S. A., Tsang, P. K. S., Sawyer, D. T., *Inorg. Chem.*, **1989**, 28, 2471.