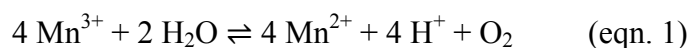


## Preparation of Tris(2,4-pentanedionato)manganese(III)

### Introduction

Manganese is a first row transition metal whose compounds display a tremendous variety of oxidation states ranging from Mn(-III), e.g.  $\text{Mn}(\text{NO})_3\text{CO}$ , to Mn(VII), e.g.  $\text{KMnO}_4$ .<sup>(i)</sup> The target complex of this experiment is the acetylacetonatomanganese(III) complex [aka tris(2,4-pentanedionato)manganese(III), often abbreviated as  $\text{Mn}(\text{acac})_3$ ] and is often used as a synthetic intermediate for the preparation of analogous Mn(III) compounds. Mn(III) complexes are relatively stable, however, will slowly oxidize water with concurrent evolution of dioxygen (equation 1). Thus, it comes as no surprise that nature takes advantage of aqueous manganese redox chemistry in the *oxygen evolving complex* (OEC) of the photosynthetic reaction center to generate dioxygen (the air we breathe today!).<sup>(ii)</sup>



In this experiment a solution of manganese(II) chloride ( $\text{MnCl}_2$ ) is oxidized with potassium permanganate in the presence of acetylacetone giving the brown  $\text{Mn}(\text{acac})_3$  solid. For  $d^4$  transition metal complexes resembling octahedral geometry [such as  $\text{Mn}(\text{acac})_3$ ] the valence shell  $d$ -configuration is described by the  ${}^5E_g$  term symbol ( $t_{2g}^3 e_g^1$ ) which suggests a considerable Jahn-Teller distortion. Therefore, these complexes do not belong to the octahedral point group ( $O_h$ ) but typically belong to the  $D_{4h}$  sub-group of  $O_h$ . The two geometrical forms of  $\text{Mn}(\text{acac})_3$  are shown in Figure 1;

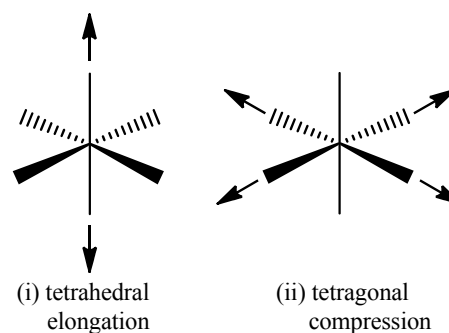


Figure 1.

The two geometrical forms of  $\text{Mn}(\text{acac})_3$  are shown in Figure 1; (i) *tetrahedral elongation* (two axial Mn–O bond lengths of 2.12 Å & four equatorial Mn–O bond lengths of 1.93 Å) and (ii) *tetragonal compression* (two axial Mn–O bond lengths of 1.95 Å & four equatorial Mn–O bond lengths of 2.00 Å). The complex forms lustrous crystals which are dark brown by reflected light and green by transmitted light ( $\lambda_{\text{max}} = 500 \text{ nm}$ ).<sup>(iii)</sup>

The  $\text{Mn}(\text{acac})_3$  complex can be reversibly oxidized to  $[\text{Mn}(\text{acac})_3]^+$   $\{E_{1/2}[\text{Mn}(\text{IV}/\text{III})] = 0.96 \text{ V vs. SCE}\}$ , or reduced to  $[\text{Mn}(\text{acac})_3]^-$   $\{E_{1/2}[\text{Mn}(\text{III}/\text{II})] = -0.06 \text{ V vs. SCE}\}$  in acetonitrile electrolyte solution (0.1 M tetraethylammonium perchlorate). In fact many transition metal complex electron transfer reactions are ligand-centered rather than metal-centered. Such transition metal complex electron transfer reactions are often facilitated by stabilization of the ligand-radical product via covalent bond formation with an unpaired  $d$  electron of the transition metal center (such ligands have become known as *redox-active ligands*). The covalent bond energy is proportional to the negative shift in the potential for the ligand oxidation relative to that for the free ligand.<sup>4</sup>

(note: the  $\text{Mn}(\text{acac})_3$  prepared here will be used in a later magnetic susceptibility experiment)

## Procedure<sup>3</sup>

In a 250-mL conical flask prepare a solution of 1.32 g manganese(II) chloride tetrahydrate and 3.59 g of sodium acetate trihydrate in 50 mL water. To this solution add by pipette 5 mL of 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 0.28 g of potassium permanganate in 15 mL water (due to the color intensity of the permanganate solution it is difficult to determine if it has completely dissolved, therefore, stir thoroughly and check for undissolved solute). After the addition of the potassium permanganate solution, stir for an additional 5 minutes. Meanwhile, prepare a solution containing 3.59 g of sodium acetate trihydrate in 15 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 subsequently cool to room temperature. Filter the crude dark solid on a small Buchner funnel and wash with three 10-mL portions of deionized water. Spread out the crude product on a porcelain dish and dry in an oven at 60 °C to 70 °C for at least 30 minutes.

*Recrystallization:* Weigh the dry product and determine the crude percent yield. Under the hood, dissolve the dried  $\text{Mn}(\text{acac})_3$  in 4.0 mL of toluene contained in a 25-mL conical flask. Filter the solution through a Buchner funnel. Transfer the filtrate to a 30-mL beaker and cool in an ice bath (be very careful not to get any water in the toluene solution). Add 15 mL of petroleum ether to the solution to precipitate the product. Collect the recrystallized product in a Buchner funnel and place in a drying oven at 60°C. Weigh the recrystallized product and calculate the percent yield.

## Laboratory Report

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

## References

- (i) Cotton, F. A., Wilkinson, G., Murillo, C. A., Bochmann, M., *Advanced Inorganic Chemistry*, 6<sup>th</sup> Ed., Wiley and Sons, New York, 1999.
- (ii) Blankenship, R. E., *Molecular Mechanisms of Photosynthesis*. Blackwell Science: 2002.
- (iii) This synthetic procedure has been scaled down (semi-microscale) from an Inorganic Synthesis preparation Charles, R. G., *Inorg. Synth.*, **1963**, 7, 183.
- (iv) Richert, S. A., Tsang, P. K. S., Sawyer, D. T., *Inorg. Chem.*, **1989**, 28, 2471.