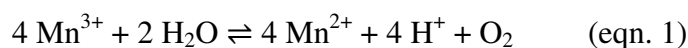


Preparation of Tris(2,4-pentanedionato)manganese(III)

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. KMnO_4 .¹ The target complex of this experiment is the acetylacetonatomanganese(III) complex, aka tris(2,4-pentanedionato)manganese(III) and often abbreviated as $\text{Mn}(\text{acac})_3$. This complex 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!).²



In this experiment a solution of manganese(II) chloride (MnCl_2) is oxidized with potassium permanganate in the presence of acetylacetonone 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;

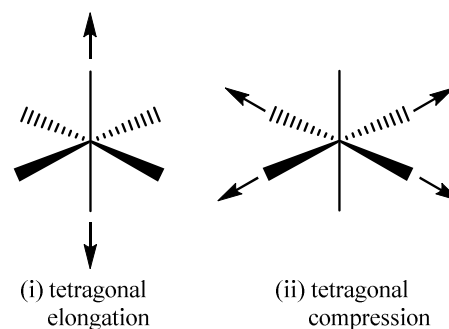


Figure 1.

(i) *tetragonal 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 ($\lambda_{\text{max}} = 500 \text{ nm}$).³

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 *non-innocent 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.⁴

Procedure³

In a 125-mL conical flask prepare a solution of 0.66 g manganese(II) chloride tetrahydrate and 1.80 g of sodium acetate trihydrate in 25 mL of deionized water. To this solution add by pipette 2.5 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 0.14 g of potassium permanganate in 10 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 1.80 g of 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 subsequently cool to room temperature. Filter the crude dark solid on a small Buchner funnel and wash with three 5-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 2.0 mL of toluene contained in a 25-mL conical flask. Filter the solution through a Hirsch funnel to remove any undissolved crude solid. 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 5 mL of petroleum ether to the solution to precipitate the product. Collect the recrystallized product in a clean Hirsch 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. For your introduction, give a clear and detailed account of the importance of manganese redox chemistry in a single biological process of your choice, e.g. the photosynthetic oxygen evolving complex, Mn-superoxide dismutase etc.
3. Write balanced equations for the preparation and report theoretical and percentage yields?

Due to issues with Recrystallization report at least the **crude %** yield. [Hint: The synthesis is described by two reaction equations with the intermediate species being $\text{Mn}(\text{acac})_2$]

4. Use ChemDraw to draw the structure of $\text{Mn}(\text{acac})_3$ and determine its point group.
5. Is it possible to draw optical isomers of $\text{Mn}(\text{acac})_3$?
6. How do you account for the single absorption band in the electronic spectrum of $\text{Mn}(\text{acac})_3$?

References

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2. Blankenship, R. E., *Molecular Mechanisms of Photosynthesis*. Blackwell Science: 2002.
3. This synthetic procedure has been scaled down from an Inorganic Synthesis preparation Charles, R. G., *Inorg. Synth.*, **1963**, 7, 183.
4. Richert, S. A., Tsang, P. K. S., Sawyer, D. T., *Inorg. Chem.*, **1989**, 28, 2471.