



Electrochemical and Computational Chemistry Study of $\text{Mn}(\beta\text{-diketonato})_3$ complexes



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ABSTRACT

Nine different $\text{Mn}(\beta\text{-diketonato})_3$ complexes, with $\beta\text{-diketonato}$ = dipivaloylmethanato, acetylacetonato, benzoylacetato, dibenzoylmethanato, trifluoroacetylacetonato, trifluorobenzoyletonato, trifluorofuroylacetonato, trifluorobenzoylacetato and hexafluoroacetylacetonato, were synthesized. The effect of the various substituents on the $\beta\text{-diketonato}$ backbone of these complexes, on the ease of oxidation and reduction of the central metal in the nine different $\text{Mn}(\beta\text{-diketonato})_3$ complexes, was studied by means of electrochemistry. It was found that, when adding aromatic substituents to the backbone of the $\beta\text{-diketonato}$ ligands of the complexes, the reduced/oxidized species were stabilized. It was also found that, when adding more electron withdrawing groups to the backbone of the $\beta\text{-diketonato}$ ligands of the complexes, that $\text{Mn}(\beta\text{-diketonato})_3$ complex was more easily reduced at a higher potential. Good linear relationships and trends were obtained between the mean value of peak oxidation and reduction potential of the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ redox couple, and various electronic parameters and DFT calculated energies.

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1. Introduction

$\text{Mn}(\beta\text{-diketonato})_3$ complexes can be used as homogeneous and heterogeneous catalysts in various reactions, of which selected examples are given below: Some of the most dominant compounds of numerous potent pharmaceutical drugs and various functional materials, are known as azaheterocycles (nitrogen-containing heterocycles). The construction of azaheterocycles from readily available starting materials, is still investigated. It was found, that the application of catalytic amounts of $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$, enabled the formation of substituted pyridines and 2-azabicyclo [3.3.1]non-2-en-1-ol derivatives, from easily obtainable vinyl azides and cyclopropanols, including a range of substituents [1]. Secondly, oxidative coupling of phenols to dimeric products, in the past used to be catalyzed by ferric chloride and ferricyanide, however this procedure has been limited, due to the formation of unwanted quinones. Instead, complex $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$ was found to be a successful alternative to the ferri-compounds, since it is soluble in organic solvents, and produces the biphenols which can be isolated in good yields under relatively mild conditions, before further oxidation to quinones can take place [2]. Thirdly, the oxidation reaction of alcohols with CCl_4 , at a temperature of 473.15 K, can also be catalyzed by $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$. Among

the following catalysts MnCl_2 , MnO_2 , $\text{Mn}(\text{OAc})_2$ and $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$, the latter showed the highest activity during the reaction of CCl_4 with alcohols [3]. Fourthly, $\text{Mn}(\text{acac})_3$ showed high activity in the autoxidation of ethyl linoleate (a model compound for the binder molecule in household alkyd paint), which is far superior to commercial manganese-containing paintdrying catalysts [4]. Further, an environmentally friendly and chemoselectively heterogeneous silica functionalized $\text{Mn}(\text{acac})_3$ catalyst, gave excellent yields in the selective oxidative synthesis of 2-arylbenzimidazoles and 2-arylbenzothiazoles [5]. There are not many examples of the application of other $\text{Mn}(\beta\text{-diketonato})_3$ complexes other than $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$. However, $\text{Mn}(\text{C}(\text{CH}_3)_3\text{COCHCO}(\text{CH}_3)_3)_3$ or $\text{Mn}(\text{dpm})_3$ also showed catalytic activity in the conversion of a variety of α,β -unsaturated ketones into α -hydroxy ketones [6], while another complex such as $\text{Mn}(\text{CF}_3\text{COCHCOCF}_3)_3$, or $\text{Mn}(\text{hfaa})_3$ (9), is a strong neutral oxidant, which oxidizes organic compounds with a low redox potential or a weak C-H or O-H bond, such as 9,10-dihydroanthracene (DHA), toluene, 2,4-di-*tert*-butyl phenol, and *p*-methoxytoluene [7].

In order to understand and improve the catalytic application of $\text{Mn}(\beta\text{-diketonato})_3$ complexes, a fundamental knowledge of the activity of these complexes towards oxidation and reduction is important. Considering different $\text{Mn}(\beta\text{-diketonato})_3$ complexes, it seems as if, with only one exception [8], $\text{Mn}(\text{CH}_3\text{COCHCOCH}_3)_3$ (2), is the only $\text{Mn}(\beta\text{-diketonato})_3$ complex that has previously been studied by electrochemistry [4,9–14]. In this study we therefore

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present an electrochemical study of a series of four new and five known Mn(β -diketonato)₃ complexes, with β -diketonato = dpm (1), acac (2), ba (3) (new), dbm (4), tfaa (5) (new), tfth (6) (new), tffu (7), tfba (8) (new) and hfaa (9), see Scheme 1. The different β -diketonato ligands (RCOCHCOR')⁻ were chosen to contain R and R' groups with differing electron donating and withdrawing power, in order to illustrate the influence of these groups on the redox properties of the different Mn(β -diketonato)₃ complexes.

2. Material and methods

2.1. General

The melting points were determined by an Olympus BX51 microscope, which is fitted with a Linkam THMS600 hot stage that is connected to a Linkam TMS94 temperature programmer. The melting points given were measured at the onset temperature of melting. MALDI-TOF-MS (matrix assisted laser desorption/ionization time-of-flight mass spectrometry) spectra (Mass spectrometry of Mn(tfba)₃ was done by the use of Gas chromatography-mass spectrometry (GC-MS)) were collected by a Bruker Microflex LRF20 in the positive reflection mode, with the minimum laser power required to observe signals. Mn(acac)₃ complex (2) was obtained from Sigma-Aldrich (cat: M228–4).

2.2. Synthesis of Mn(β -diketonato)₃ complexes (1), (3)–(9)

The Mn(β -diketonato)₃ complexes (1), (3)–(8) were synthesized by a procedure adapted from literature [15]: 0.011 mol of the respective β -diketone (for (4) the β -diketone was dissolved in 0.005 dm³ ethanol) was added to a solution of potassium permanganate (0.25 g, 0.00159 mol) dissolved in a minimum amount of water, followed by vigorous stirring over a steam bath for five minutes. The mixture was left to cool for ten minutes, filtered and washed with water to obtain the desired Mn(β -diketonato)₃ complex. On the other hand, the Mn(β -diketonato)₃ complex (9) was prepared following a procedure adapted from [16]: A reaction mixture of Mn₂O₃ (0.418 g, 0.00265 mol), Hhfaa (0.003 dm³, 0.02119 mol) and dry THF (0.002 dm³) was refluxed under Ar for 24 h. Excess solvent and Hhfaa were removed under vacuum. The dark green residue was then sublimed under vacuum, at 60 °C. The yellow Mn(hfaa)₃ was subsequently collected from the cold finger. Mn(β -diketonato)₃ complexes are high spin paramagnetic complexes [17] and cannot be characterized by NMR. References to previously published compounds are given.

2.2.1. Characterization data for Mn(C(CH₃)₃COCHCOC(CH₃)₃)₃, (1) Mn(dpm)₃ [6]

Yield 24%. Colour: Brown. Melting point > 310 °C. MS Calculated: Mr = 604.74 g/mol Found: 604.97 g/mol. Elemental analysis; Calculated MnC₂₇H₅₇O₆: C, 65.5; H, 9.5. Found: C, 65.4; H, 9.7.

2.2.2. Characterization data for Mn(C₆H₅COCHCOCH₃)₃, (3) Mn(ba)₃

Yield 70%. Colour: Green. Melting point 184.3 °C. MS Calculated: Mr = 538.48 g/mol, Found: 538.72 g/mol. Elemental analysis; Calculated for MnC₃₀H₂₇O₆: C, 66.9; H, 5.1 Found: C, 67.3; H, 5.8.

2.2.3. Characterization data for Mn(C₆H₅COCHCOC₆H₅)₃, (4) Mn(dbm)₃ [18]

Yield 80%. Colour: Black. Melting point 235.7 °C. MS Calculated: Mr = 724.68 g/mol Found: 724.95 g/mol. Elemental analysis; Calculated for MnC₄₅H₃₃O₆: C, 74.6; H, 4.6 Found: C, 74.5; H, 4.7.

2.2.4. Characterization data for Mn(CF₃COCHCOCH₃)₃, (5) Mn(tfaa)₃

Yield 69%. Colour: Dark brown-black. Melting point 116.7 °C. MS Calculated: Mr = 514.18 g/mol, Found: 514.50 g/mol. Elemental analysis; Calculated for MnC₁₅H₁₂O₆F₉: C, 35.0; H, 2.4 Found: C, 34.6; H, 2.3.

2.2.5. Characterization data for Mn(CF₃COCHCOC₄H₉S)₃, (6) Mn(tfth)₃

Yield 97%. Colour: Brown. Melting point 157.5 °C. MS Calculated: Mr = 718.45 g/mol, Found: 718.72 g/mol. Elemental analysis; Calculated for MnC₂₄H₁₂O₆F₆S₃: C, 40.1; H, 1.7 Found: C, 40.7; H, 1.99.

2.2.6. Characterization data for Mn(CF₃COCHCOC₄H₉O)₃, (7) Mn(tffu)₃ [19]

Yield 73%. Colour: Black. Melting point 170.6 °C. MS Calculated: Mr = 670.27 g/mol, Found: 670.72 g/mol. Elemental analysis; Calculated for MnC₂₄H₁₂O₉F₉: C, 43.0; H, 1.8 Found: C, 42.25; H, 1.78.

2.2.7. Characterization data for Mn(CF₃COCHCOC₆H₅)₃, (8) Mn(tfba)₃

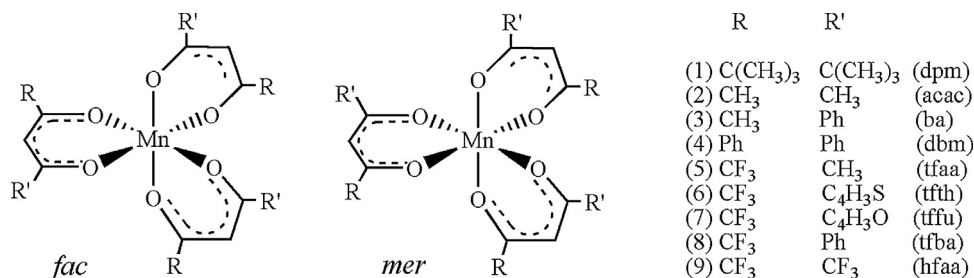
Yield 98%. Colour: Black. Melting point 89.7 °C. MS Calculated: Mr = 700.38 g/mol, Found: 703.25 g/mol. Elemental analysis; Calculated for MnC₃₀H₁₈O₆F₉: C, 51.4; H, 2.6 Found: C, 51.6; H, 3.0.

2.2.8. Characterization data for Mn(CF₃COCHCOCF₃)₃, (9) Mn(hfaa)₃ [16,20]

The yield and melting point could not be determined due to the hygroscopic nature of Mn(hfaa)₃

2.3. Electrochemistry

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were conducted by the use of a Princeton Applied Research PARSTAT 2273 voltammograph, where the data was recorded using PowerSuite (Version 2.58). The three electrodes used during measurements are; a Pt auxiliary electrode, reference electrode Ag/Ag⁺ (0.010 mol dm⁻³ AgNO₃ in CH₃CN) mounted on a Luggin capillary, and a glassy carbon working electrode (surface area 1.257 × 10⁻⁵ m²). The working electrode was polished on a Bühler polishing mat, first with 1 micron and then with 1/4 micron diamond paste. The electrochemistry measurements were performed in solvent CH₃CN (while dichloromethane was used for complex (1), since (1) could not be dissolved in CH₃CN),



Scheme 1. Mn^{III}(β -diketonato)₃ complexes of this study. Two isomeric forms are possible for complexes containing an unsymmetrically substituted β -diketonato ligand, i.e. when group R \neq R' (therefore for unsymmetrical complexes (3), (5), (6), (7) and (8)).

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