

Synthesis and Chemical Characterization of Metals (Al, Cr, Co, Mn and VO) Complexes with Acetylacetone (β -diketone)

Muhammad Saeed
QAU Islamabad
Islamabad, Pakistan

Ziab Khalid
QAU Islamabad
Islamabad, Pakistan

Rabia Saleem
UAF FSD
Faisalabad Pakistan

The research is financed by Asian Development Bank. No. 2006-A171(Sponsoring information)

Abstract

In this Article, we focused on synthesis, chemical reactivity and physical properties of metal acetylacetone complexes. Metals (Mn, Cu, Co, V, Al) were obtained from their salts, and reacted with acetylacetone acting as a ligand. Products were recrystallized using methanol or pet ether and their melting point was determined. Synthesis and Metal (acetylacetone) complex structures $[Al(CH_3COCHCOCH_3)_3]$, $[VO(CH_3COCHCOCH_3)_2]$, $[Mn(CH_3COCHCOCH_3)_2]$, $[Cu(CH_3COCHCOCH_3)_2]$, $[Cr(CH_3COCHCOCH_3)_3]$ are discussed in this article. Complexation was confirmed by FTIR as a characterizing technique. UV/VIS spectrum were taken for all complexes and their maximum absorbance as a function of wavelength was taken. Further confirmation was obtained by NMR (Nuclear Magnetic Resonance). Solubilities in different organic solvents were tested. Melting Points and Yields of metal-acac complexes are also given in this article. Material Safety Data Sheet of Urea, Chromium chloride hexahydrate and acetylacetone has been discussed in this report.

Keywords: Metals (Al, Cu, Cr, Mn, VO), Acetylacetone(acac), FTIR, NMR, UV/VIS, Recrystallization.

Introduction

Acetylacetone (2,4-pentanedione) is an organic compound, a β -diketone, that exists as an equilibrium mixture of tautomeric keto and enol forms. In basic solution, it is deprotonated to form the acetylacetonate anion (acac) (Figure 1).

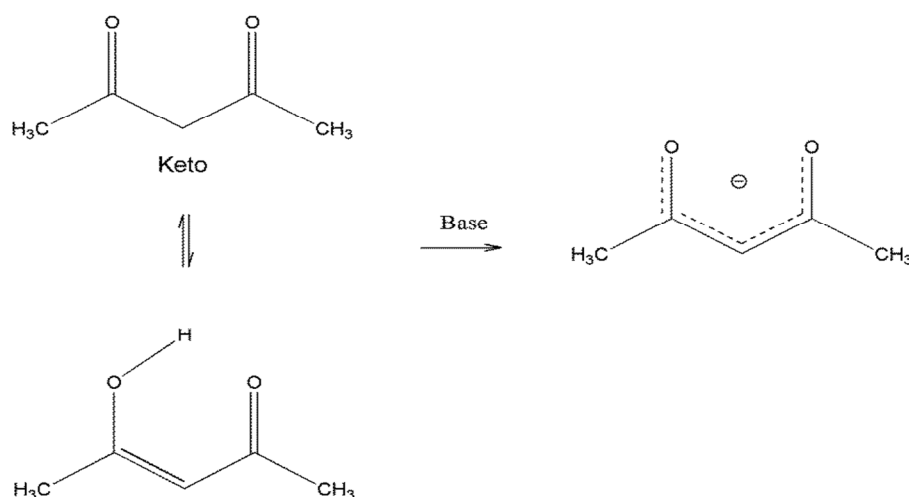


Figure 1: Keto-enol equilibrium of acetylacetone and formation of acetylacetonate anion.

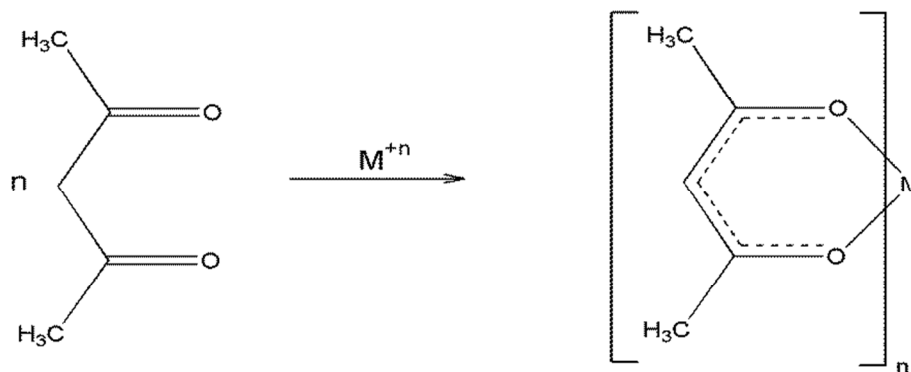


Figure 2: Acetylacetonate forms neutral complexes with most metals.

The acac anion can act as a ligand towards metal ions, typically forming a bidentate complex where the metal is bound to the two oxygen atoms, thus forming a 6-membered ring. Metal acac compounds are typically isolated as crystalline solids that are neutral, hence an M^{n+} metal forms a complex with n acac ligands (Figure 2)¹.

Hazards:

Acetylacetonate is a mild irritant to the skin and mucous membranes. It is also a flammable liquid. Manganese(II) chloride tetrahydrate is harmful if swallowed, inhaled, or absorbed through the skin. Sodium acetate trihydrate is not generally considered dangerous. The normal precautions should be observed. Potassium permanganate is a powerful oxidizing agent and should be handled with care. It is harmful if swallowed, inhaled, or absorbed through the skin. It is extremely destructive to the mucous membranes and skin. Cyclohexane is irritating to skin. It may cause lung damage if swallowed and vapors may cause drowsiness and dizziness. It is a highly flammable liquid. Petroleum ether is irritating to skin. It may cause

lung damage if swallowed and vapors may cause drowsiness and dizziness; serious damage to health is associated with prolonged exposure through inhalation (such as impaired fertility). Petroleum ether is a highly flammable liquid.²

Materials and Instruments:

Acetylacetonate(Daejung/ Kosdaq-listed company), Hydrated aluminium sulphate(Repacked), Hydrated Chromium chloride(Uni-chem), Urea(Fluka-Garantie), Cyclohexane(Emplura), Concentrated sulphuric acid(Riedel-deHaen) NICOLET 6700 FTIR used to record IR spectra, Spectrophotometer used to record UV Vis spectra, Melting point apparatus model mP-D mitamuraikenkogyo (Japan) for determination of melting points of compounds, NMR (Nuclear magnetic resonance) for characterization.

1. Aluminum (Al^{+3}) Complex:

Tris(acetylacetonato)aluminum(III), $[Al(C_2H_7O_2)_3]$, has been prepared starting from industrial alum, $Al_2(SO_4)_3 \cdot 16H_2O$ and characterized by chemical, IR, and UV-Vis. The central metal is hexacoordinated to three bidentate acetylacetonate ligands.³

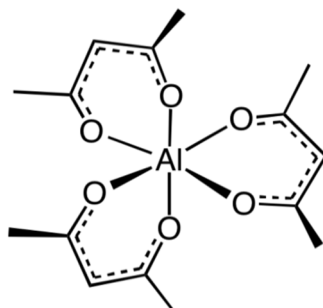


Figure 3: Tris(acetylacetonato)aluminum(III) complex, $[Al(C_2H_7O_2)_3]$

¹ Seco, M. Acetylacetonate: A Versatile Ligand. *J. Chem. Ed.* **1989**, 9, 779-780.

² *Crystallographic Study of Manganese(III) Acetylacetonate: An Advanced Undergraduate Project with Unexpected Challenge, Journal of Chemical Education*, Vol. 82 No. 3 March 2005.

³ *Indian Journal of Chemistry*. Vol. 49, December 2010, pp. 1607

a. key words:

Inorganic chemistry, Aluminum acetylacetonate, Alumina, Alum, FT-IR spectroscopy, and UV-Vis spectroscopy.

b. Abstract:

Herein, we report the synthesis and characterization of Aluminum (Al^{3+}) with acetylacetonate (acac). More specifically, the coordination reactions of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ with acetylacetonate. These aluminum compounds were characterized via FTIR spectroscopy and UV-Vis spectroscopy.

c. Experimental:

$[\text{Al}(\text{acac})_3]$ was prepared using alum, A solution of alum $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ (0.1M) was prepared using doubly distilled water. The solution was acidic. To this solution, an ammoniacal solution of acetylacetonate was added in small proportions with continuous swirling till the solution became neutral or slightly basic (pH 7-8). The reaction mixture was allowed to stand for 15 minutes. The pale yellow precipitate formed, was filtered, washed with doubly distilled water and dried under vacuum. The complex was recrystallized using n-hexane as solvent. ¹

d. Physical Appearance, MP & Solubility:

Color of complex, milk white.

Observed Melting point is 188-191° C

$\text{Al}(\text{acac})_3$ is soluble in solvent like Methanol, Ethanol, Acetone, Toluene, Acetonitrile and DMSO but is sp.soluble in water(on heating soluble).

Result and Discussion:

Aluminum is the lightest element to form trivalent ions which have a coordination number of six. Three anionic 0-ketoenolate ligands chelate the ion forming the neutral, water-insoluble, organic solvent soluble complex². After forming the complex The IR spectrum of the tris complex exhibits several signals in the IR region (400 cm^{-1} - 4000 cm^{-1}) indicating the presence of the organic ligand. The anhydrous nature of the complex is evident from the absence of O-H vibration as no signals are observed beyond 3000 cm^{-1} . The signals observed at 410 , 484 cm^{-1} may be assigned to the bending mode of Al-O vibration, while those at 575.5 , 658.7 , 684.38 , 771.29 and 933.7 cm^{-1} are due to $\nu_{\text{Al-O}}$ vibrations.

2. Vanadyl Acetylacetonate Complex(VO^{+2}):

Vanadyl Acetylacetonate $\text{VO}(\text{acac})_2$, has been prepared starting from vanadium pentoxide (V_2O_5) and characterized by chemical, IR, NMR and UV-Vis. The central metal is hexacoordinated to three bidentate acetylacetonate ligands.

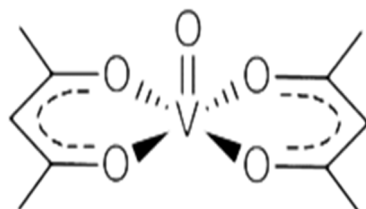


Figure 4: Vanadyl Acetylacetonate $\text{VO}(\text{CH}_3\text{COCHCOCH}_3)_2$

a. key words:

Inorganic chemistry, Vanadyl acetylacetonate, vanadium, Vanadium oxide, NMR, FT-IR spectroscopy, and UV-Vis spectroscopy.

b. Abstract:

Herein, we report the synthesis and characterization of **Vanadyl Acetylacetonate** $\text{VO}(\text{CH}_3\text{COCHCOCH}_3)_2$. These vanadium compounds were characterized via FT-IR spectroscopy, NMR and UV-Vis spectroscopy.

c. Experimental:

To a round-bottom flask, add 5 mL distilled water, followed by slow addition of concentrated H_2SO_4 . Then add 12 mL ethanol then 2.5 g vanadium pentoxide (V_2O_5). Fit the round bottom flask with a condenser and reflux for 90 minutes, which should result in a dark blue-green solution. Allow the mixture to cool and filter using cotton wool, discarding any solid residue. With stirring, add 6mL of acetylacetonate dropwise. To neutralize the solution, add it carefully with stirring to a large conical flask containing 20 g anhydrous sodium carbonate dissolved in 150 mL distilled water. The mixture should be cooled in an ice bath and the resulting precipitate filtered using Buchner filtration. Wash the solid with cold distilled water and dry the product in a vacuum desiccator. Determine the percentage yield of this dry product.

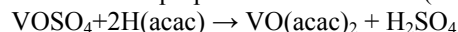
Dissolve a small portion of the product (about 0.5 g) in 6 mL dichloromethane and carefully decant from

¹ Indian Journal of Chemistry. Vol. 49, December 2010, pp. 1608

² F.A. Cotton, Progress in inorganic chemistry 7 Interscience publisher (1966) p.380

any residue. Add 20 mL of petroleum ether, swirl the mixture and allow to stand for 10 minutes. Filter the product using Buchner filtration, rinse with cold petroleum ether and dry in a vacuum desiccator.¹

It can also be prepared from vanadium(IV), e.g. vanadyl sulfate:²

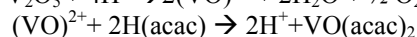
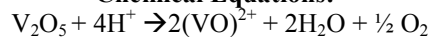


d. Physical Appearance, M.P & Solubility:

Color of complex, blue, Observed Melting point is 184-187° C.

VO(acac)₃ is soluble in solvent like Methanol, Ethanol, Acetone, Acetonitrile and DMSO but is insoluble in water & Toluene at room temperature.

Chemical Equations:



e. Result and Discussion:

In the IR spectrum, the intense bands observed at frequencies of 1558 cm⁻¹ and 1377 cm⁻¹ are assigned to the C–O stretching vibrations. Judging from the calculated normal modes, the (CO)vibrations are strongly mixed with the C–C stretching vibrations, which also manifest themselves in the IR spectra at frequencies of 1535 and 1320–1270 cm⁻¹. In the ranges between 1535 and 1320–1270 cm⁻¹, their spectra exhibit bands associated with the bending vibrations of the CH₃ groups. In the range 1200–1000cm⁻¹, their spectra contain bands attributed to the δ(H₃CC) vibrations mixed with the out-of-plane vibrations (distortions of the C–C–C angles), i.e., the vibrations associated with the deviations of the methyl groups from the planes of the ligand rings. The in-plane vibrations of the cyclic fragments manifest themselves at a frequency of 950cm⁻¹. These vibrations involve simultaneous stretching of the C–C bonds and changes in the angles between these bonds. The vibrations of the C–C exo bonds are observed at slightly lower frequencies in the range characteristic of the ν(CC) vibrations. The frequency of the vibrations associated with the deviations of the C–H bonds from the ring planes is approximately equal to 800 cm⁻¹.³

3. Copper (Cu⁺²) Complex:

Bis(acetylacetonato)copper(III), [Cu(C₂H₇O₂)₂], has been prepared starting from industrial alum, CuCl₂·2H₂O and characterized by chemical, IR, and UV-Vis. The central metal is tetra coordinated to two bidentate acetylacetonate ligands.

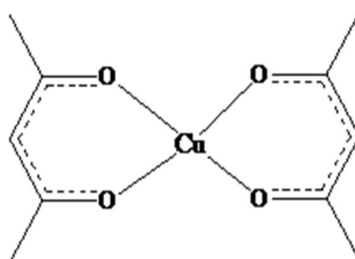


Figure 5: Bis(acetylacetonato)copper(III), [Cu(C₂H₇O₂)₂]

a. key words:

Inorganic chemistry, copper acetylacetonate, copper sulfate, FT-IR spectroscopy & UV-Vis spectroscopy.

b. Abstract:

Herein, we report the synthesis and characterization of Copper (Cu⁺²) with acetylacetonate (acac). These copper compound were characterized via FTIR spectroscopy and UV-Vis spectroscopy.

c. Experimental:

In a conical flask, dissolve 4 g copper(II) chloride (CuCl₂·2H₂O) in 25 mL distilled water. Over a period of 10 minutes with stirring, add a solution of 5 mL acetylacetonate in 10 mL of methanol. To the resulting mixture, add over 5 minutes 6.8 g of sodium acetate dissolved in 15 mL of water. Heat the reaction to 80°C for 15 minutes, followed by cooling in an ice bath. Filter the blue-grey precipitate using Buchner filtration, wash with cold distilled water 100ml and dry in an oven (110°C) for 15 minutes. Determine the percentage yield of the dry product.⁴

d. Chemical Equation:



e. Physical Appearance, MP & Solubility:

Color of complex, blue grey,

Observed Melting point is 283-285°C

¹ Glidewell, C. Metal Acetylacetonate Complexes: Preparation and Characterization. In Inorganic Experiments, Third Edition, 2010; pp 117

² Rowe, Richard A.; Jones, Mark M. (1957). "Vanadium(IV) Oxy(acetylacetonate)". *Inorganic Syntheses* 5: 113–116

³ Crystallography Reports, Vol. 50, No. 2, 2005, pp. 224–229.

⁴ Glidewell, C. Metal Acetylacetonate Complexes: Preparation and Characterization. In Inorganic Experiments, Third Edition, 2010; pp 117

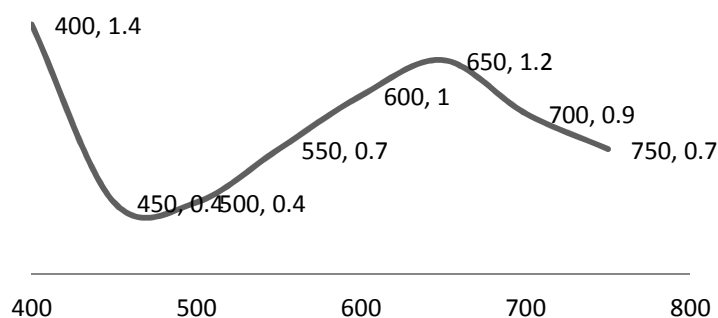
Cu(acac)₂ is soluble in solvent like Methanol, Acetone, Toluene, Acetonitrile and DMSO but is insoluble in water & Ethanol.

f. Calculation:

g. Result and Discussion:

The 1575.93cm⁻¹ and 1520 cm⁻¹ bands are assigned to $\nu(\text{C}-\text{C})$ coupled with $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ coupled with $\nu(\text{C}-\text{C})$ respectively. The band at 3015.5cm⁻¹ shows $\nu(\text{C}-\text{H})$. The bands of 2970cm⁻¹ shows $\nu(\text{C}-\text{H})$ and another small band 453.30cm⁻¹ indicates the stretching vibration of Cu-O for acac complex. 1738.62cm⁻¹ strong peak may be due to the impurity.

Cu-acac Complex λ_{max} : 657nm



4. Chromium (Cr⁺³) Complex:

Tris(acetylacetonato)Chromium(III), [Cr(C₅H₇O₂)₃], has been prepared starting from CrCl₃.6H₂O and characterized by chemical, IR, and UV-Vis. The central metal is hexacoordinated to three bidentate acetylacetonate ligands.

a. key words:

Inorganic chemistry, Chromium acetylacetonate, IR, and UV-Vis.

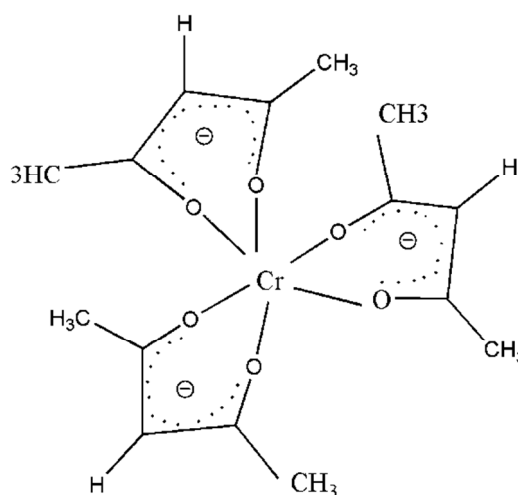
b. Abstract:

Chromium(III) ion is the most stable oxidation state free chromium ion in aqueous solution and it exists as hexaaquachromium(III) ion. Chromium(III) forms stable with various ligands including oxygen and nitrogen donor ligands. Due to its high crystal field stabilization energy, reactions of chromium(III) ion are slow and once Cr(OH)₃ is formed it remains unreacted and hence special care must be taken in the synthesis of chromium(III) complexes in basic solutions.

To avoid excess base and hence the formation of the inert Cr(OH)₃, acetylacetonate is deprotonated by low concentration of Ammonia produced from the hydrolysis of Urea.

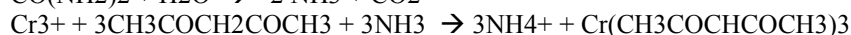
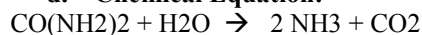
c. Experimental:

To a conical flask, add 1.4 g chromium(III) chloride (CrCl₃ • 6 H₂O) and dissolve it in 50 mL distilled water. In 3 or 4 portions, add 10 g urea with stirring. Add 3 mL acetylacetonate, cover with a watch glass and heat to 80-90°C. Initially the solution should be very dark, but as the reaction proceeds, maroon crystals start to form. After 90 minutes of heating cool the reaction mixture and filter the precipitate using Buchner filtration. Do not rinse the product. Dry the product in air and record the percent yield. Dissolve a small sample in boiling petroleum ether, decant the solution, and reduce the volume by half. Cool the solution in an ice bath, filter the crystals using Buchner filtration and suck dry at the water pump. The resulting purple complex is a d³ paramagnetic compound.



¹ Glidewell, C. Metal Acetylacetonate Complexes: Preparation and Characterisation. In Inorganic Experiments, Third Edition; Woolins, D., Ed.; Wiley-VCH: Weinheim, Germany, 2010; pp 118

d. Chemical Equation:



e. Physical Appearance, MP & Solubility:

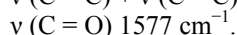
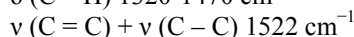
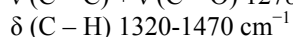
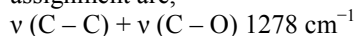
Color of complex **sea blue**

Observed Melting point is 226-229° C

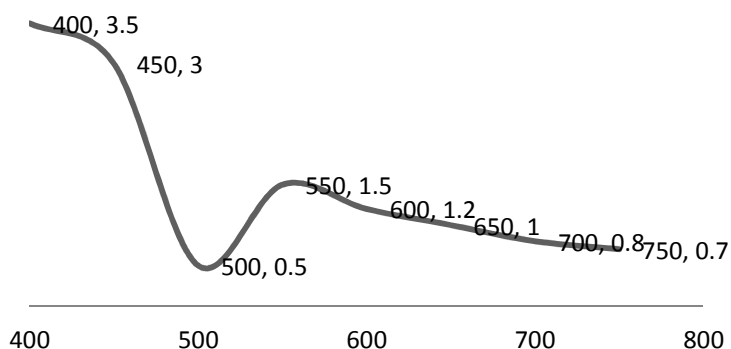
Cr(acac)₃ is soluble in solvent like Methanol, Ethanol, Acetone, Toluene, Acetonitrile and DMSO but is insoluble in water (on heating soluble).

Result and Discussion:

IR spectra of Cr(acac)₃ sample in the region of 1250–1650 cm⁻¹ characteristic for the vibrations of acetylacetonate ligand. The bands of ν (C–C) + ν (C–O), ν (C=C) + ν (C–C) and ν(C=O) vibrations of acetylacetonate ligand are taken for the detailed consideration. The position of the observed bands and their assignment are,



Cr-acac Complex λ_{max}:562nm



5. Manganese (M⁺³) Complex:

Tris(acetylacetonato) Manganese(III), [Mg(C₅H₇O₂)₃], has been prepared starting from MnCl₂·4H₂O and characterized by chemical, IR, and UV-Vis. The central metal is Hexacoordinated to three bidentate acetylacetonate ligands.

a. key words:

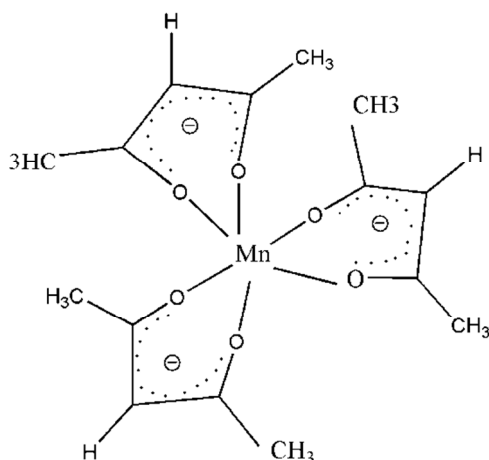
Inorganic chemistry, Chromium acetylacetonate, IR, and UV-Vis.

b. Abstract:

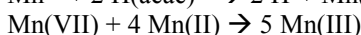
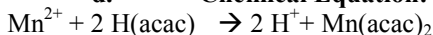
The aim of the synthesis a manganese acetylacetonate complex, is to understand the keto-enol tautomerisation of acetylacetonate and determine the electronic structure of their compound using IR and NMR spectrometer Mn(acac)₃Mn(III) dark brown (these colors are important indicators in this, and many other, inorganic experiments). Mn(acac)₃ forms a D₃ structure but has a “local” coordination environment (MnO₆) that is approximately octahedral.

c. Experimental:

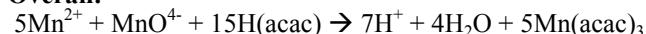
Dissolve 2.6 g of manganese chloride (MnCl₂ · 4 H₂O) and 6.8 g of sodium acetate in 100 mL of distilled water and add 10 mL acetylacetonate. Dissolve 0.52 g of potassium permanganate (KMnO₄) in 25 mL of distilled water and add to the acetylacetonate solution, with stirring, over a period of about 10 minutes. After stirring for 10 minutes, add a solution of sodium acetate (6.3 g) in 25 mL distilled water, with stirring, over a period of about 10 minutes. Continue stirring and heat the flask on a hot plate to 60-70°C for 15 minutes, followed by cooling to room temperature and finally placed in an ice bath. Using Buchner filtration, filter the dark precipitate using small portions of cold distilled water for washing, followed by drying in a vacuum desiccator. Determine the percentage yield of this dry product.¹



d. Chemical Equation:



Overall:



¹ Glidewell, C. Metal Acetylacetonate Complexes: Preparation and Characterisation. In Inorganic Experiments, Third Edition; Woolins, D., Ed.; Wiley-VCH: Weinheim, Germany, 2010; pp 118 & 119

e. Physical Appearance, MP & Solubility:

Color of complex **Brown**

Observed Melting point 251-255° C

Mn(acac)₃ is soluble in solvent like Methanol, Ethanol, Acetone, Toluene, Acetonitrile and DMSO but is insoluble in water (on heating soluble).

Result and Discussion:

The band at ~1250-1650cm⁻¹ indicate the acetylacetonate ligand. The two bands of the stretching vibration C=C and C-CH₃ group have been detected 1253 cm⁻¹. The bending vibration stretch of C=CH is observed at 1185 cm⁻¹. The bands at 928 cm⁻¹ and 1020 cm⁻¹ show that the Mn(III) is bonded to three acetylacetonate ligands. The bending vibration of CH₃ is observed at 1350cm⁻¹ & 1388cm⁻¹ and ν(C=C), δ(C=CH) at 1512cm⁻¹ and 1567cm⁻¹.

ν(C-CH₃) 928cm⁻¹ s

γ(CH₃) 1020cm⁻¹ s

δ(C=CH) 1185cm⁻¹ w

ν(C=C), ν(C-CH₃) 1253cm⁻¹ s

δ(CH₃) 1350 s

δ(CH₃) 1388cm⁻¹ s

ν(C=C), δ(C=CH) 1512 cm⁻¹ s

ν(C=C), δ(C=CH) 1567cm⁻¹ s

ν(C-H) 2920 w

Notes: a Relative intensity: s-strong, m-medium, w-weak

Literature cited:

1. Glidewell, C. Metal Acetylacetonate Complexes: Preparation and Characterization. In Inorganic Experiments, Third Edition, 2010; pp 117
2. Indian Journal of Chemistry. Vol. 49, December 2010, pp. 1607
3. Crystallography Reports, Vol. 50, No. 2, 2005, pp. 224-229.
4. Rowe, Richard A.; Jones, Mark M. (1957). "Vanadium(IV) Oxy(acetylacetonate)". *Inorganic Syntheses* 5: 113-116
5. F.A. Cotton, Progress in inorganic chemistry 7 Interscience publisher (1966) p.380
6. Seco, M. Acetylacetonate: A Versatile Ligand. J. Chem. Ed. **1989**, 9, 779-780.
7. Pass, G. and Sutcliffe, H. Practical Inorganic Chemistry : Preparations , Reaction and Instrumental Methods, Chapman and Hall, London, 1974
8. Bhattacharjee, M.N.; Chaudhuri, M.K.; Khating, D.T. Direct Synthesis of Tris (acetylacetonato)manganese(III). J. Chem. Soc., Dalton Trans. 1982 ,669-670
9. Crystallographic Study of Manganese(III) Acetylacetonate: An Advanced Undergraduate Project with Unexpected Challenge, Journal of Chemical Education , Vol. 82 No. 3 March 2005.
10. Sensors 2006, 6, 1708-1720
11. Coordination Chemistry Reviews, Volume 169, Issue 1, February 1998, Pages 153-186
12. J. Chil. Chem. Soc. vol.58 no.4 Concepción dic. 2013