

## Mössbauer and Thermal Studies of Sodium Ferrite Synthesized from Sodium / Potassium Hexakis (Trimethylacetato) Ferrate (III) Complexes

LANJEWAR R. B.<sup>1</sup> AND LANJEWAR M. R.<sup>2</sup>

<sup>1</sup> Department of Chemistry, Dharampeth M.P. Deo Memorial Science College, Nagpur 440033 (M.S.)

<sup>2</sup> Department of Chemistry, Shri Shivaji Science College, Congress Nagar, Nagpur 440012 (M.S.)

e-mail: [rb\\_lanjewar@rediffmail.com](mailto:rb_lanjewar@rediffmail.com), [mr\\_lanjewar@rediffmail.com](mailto:mr_lanjewar@rediffmail.com)

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### ABSTRACT

*The thermal analysis of sodium and potassium hexakis (trimethylacetato) ferrate (III) complexes has been carried out in flowing air atmosphere from ambient temperature to 500 °C. Various physicochemical techniques i.e. TGA-DTG, IR and Mössbauer spectroscopy etc have been carried out to characterize the intermediate and end products. After dehydrations, the anhydrous complexes undergo decomposition to yield  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and metal oxalate in the temperature range 200-500°C. A subsequent oxidative decomposition of metal oxalates leads to the formation of respective alkali metal carbonate/oxides in successive stages. Finally, nanosized ferrites have been obtained as result of solid state reaction between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and fraction of MCO/ MCO<sub>3</sub>. The temperature of ferrite formation is much lower than possible in the conventional ceramic method.*

Key Words: Mössbauer Spectroscopy, ferrites, Carboxylates, Thermolysis, Nanoferrites

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### Introduction

Recently, the preparation and characterization of nanostructure materials has received much attention due to their importance in material technology. Mössbauer spectroscopy provides useful information about the new solid state structure afforded by nanostructure materials<sup>1</sup>. The particle size and chemical properties are depending on the preparation methods and heating treatment. The study of the mode of thermal decomposition of metal ferricarboxylates is of technical importance as their end products i.e. ferrite finds extensive application in satellite communication bubble devices audio-video and digital recording as permanent magnets. The precursor method has achieved a great importance in synthesizing stoichiometrically pure and single phase fine particles of ferrites. The ceramic method which is most common technique for bulk preparation of ferrites involves high temperature sintering of reactant oxides coupled with frequent milling<sup>2</sup>. The precursor technique, involves thermolysis of metal ferricarboxylates precursors and provide better route to prepare nanoferrites at lower temperature in shorter time<sup>3,4</sup>. This

novel techniques has been employed for the production of alkalimetal ferrites from their trimethylacetate precursors.

## Experimental

All the chemicals used were of AR, GR or high purity grade. Trimethylacetic acid was puriss (Koch-Ligh, England) grade. Its alkalimetal salts were prepared by reaction with equivalent amount of the respective alkali metal hydroxides and evaporating the resulting solution on a water bath. The complexes were prepared by mixing 0.1M ferric nitrate (GR. S.Merck) with 0.6M aqueous solution of the corresponding alkalimetal trimethylacetate. Hydrogen hexakis (trimethylacetato) ferrate(III) was prepared by reacting 0.56 g (0.1 M) iron powder (electrolytic grade E. Merck) with trimethyl acetic acid under warm condition. . The resulting solution was slowly evaporated on a water bath for 3-5 hr and recrystallized from acetone. In all cases buff coloured complexes separated out immediately, which were dried in vaccum over fused  $\text{CaCl}_2$ . The identities of the complexes are established by elemental/ chemical analysis.

## Physical measurements

The Mössbauer spectra were recorded on transducer driven Mössbauer spectrometer in constant acceleration mode (ELCENT) at room temperature. A  $\sim 5$  mCi  $^{57}\text{Co(Rh)}$  source was used. The spectrometer was calibrated using a natural iron foil. The isomer shift values were reported with respect to metallic iron. The spectra were fitted with Lorentzian line shapes by using least square fitting procedure. Infrared spectra were obtained on a sample in KBr pallets using Hitachi Nicolet Model\_I 5040 FTIR spectrophotometer. The thermogravimetric (TGA-DTA) were carried out using Seiko Instrument Inc.SSC/5200. The DSC Curve was recorded between 273K and 785K on RIGAKU Thermoflex Apparatus at scanning rate  $5 \text{ Kmin}^{-1}$ .

## Result and Discussion:

Mössbauer Parameters, IR frequencies and Magnetic moments for alkalimetal hexakis (trimethylacetato) ferrate(III) complexes and its thermal decomposition products are given in Table.1 .IR spectrum of sodium and potassium hexa(trimethylacetato) ferrate(III) shows two prominent bands in the range  $1590\text{-}1570 \text{ cm}^{-1}$  and  $1430\text{-}1410 \text{ cm}^{-1}$  due to  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  respectively. The magnitude of separation  $[\Delta\nu = \nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})]$  in each case is more than that for sodiumtrimethylacetate ( $140 \text{ cm}^{-1}$ ) suggesting unidentate coordination<sup>5</sup>. Similarly, the direction of shift for  $\nu_{\text{as}}(\text{OCO})$  mode is towards higher wavenumbers whereas that of  $\nu_{\text{s}}(\text{OCO})$  is towards lower wavenumbers compared to their respective positions in simple ionic carboxylates<sup>6</sup>. A sharp band of medium intensity at  $600 \text{ cm}^{-1}$  is assigned to  $\delta(\text{OCO})$ . Another sharp and distinct band observed at  $430 \pm 10 \text{ cm}^{-1}$  is due to  $\nu(\text{Fe-O})$ . The broad band

centered at about  $3315\text{ cm}^{-1}$  due to  $\nu(\text{OH})$  of lattice water and a small but distinct shoulder at  $2900\text{ cm}^{-1}$  due to  $\nu(\text{C-H})$  of the trimethylacetate group.

**Table.1.** Mössbauer Parameters, IR frequencies and Magnetic moments for alkalimetal hexakis (trimethylacetato) ferrate(III) complexes and its thermal decomposition products.

Complex	Temperature °C	Isomer shift, ( $\delta$ ), $\text{mms}^{-1}$	Quadrupole splitting , ( $\Delta E_Q$ ) $\text{mms}^{-1}$	Magnetic field kOe	$\mu_{\text{eff}}$ B.M.	$\nu_{\text{as}}(\text{OCO})$ $\text{cm}^{-1}$	$\nu_{\text{s}}(\text{OCO})$ $\text{cm}^{-1}$	$\Delta\nu$ $\text{cm}^{-1}$
Na	25	0.74	0.65		5.22	1590	1410	180
	200	0.65	0.40					
	250	0.63	0.80					
	350	0.74	--	508				
K	25	0.63	0.31		5.36	1580	1420	160
	200	0.74	0.81					
	350	0.68		516				

$$\Delta\nu = [\nu_{\text{as}}(\text{OCO}) - \nu_{\text{s}}(\text{OCO})]$$

Mössbauer spectra of the precursors exhibit a doublet with isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E_Q$ ) values are in the range of  $0.66\text{--}0.74\text{ mms}^{-1}$  and  $0.31\text{--}0.40\text{ mms}^{-1}$  respectively. These parameters are in close agreement to those reported for high spin Fe(III) complexes with octahedral geometry<sup>7</sup>. The coordination number of six for iron is satisfied by six trimethylacetate ligands which bind to iron through oxygen atoms of the carboxylate groups. The outer cation ( $\text{Na}^+$ ,  $\text{K}^+$ ) and water molecules seems to be responsible for linkage together the complex ion  $[\text{Fe}\{(\text{OCOC}(\text{CH}_3)_3)_6\}]^{3-}$ . The high spin nature of iron(III) moiety has been confirmed by its effective magnetic moments in the range of  $5.22\text{--}5.80\text{ B.M.}$ , deduced from magnetic susceptibility measurements.

In order to confirm the formation of the intermediate and the end products, their Mössbauer spectra were recorded after heating the complexes at different temperatures. When the complexes were heated at  $200\text{ }^\circ\text{C}$  for 4hr, isomer shift ( $\delta$ ) remain unaffected but the quadrupole splitting ( $\Delta E_Q$ ) almost double compared to room temperature. On further heating at  $350\text{ }^\circ\text{C}$  for 4hr, it gives characteristics six line spectrum (Fig.1) with ( $\delta$ ) values in the range of  $0.25\text{--}0.44\text{ mms}^{-1}$ . This suggests that while the oxidation state of iron remain affected, one or two ligands are lost at  $200\text{ }^\circ\text{C}$ , causing an increase in  $\Delta E_Q$ . Abras et al<sup>8</sup> have suggested a decrease in the number of ligands for iron(III) benzoate at  $200\text{ }^\circ\text{C}$ . Later, on further heating at  $350\text{ }^\circ\text{C}$  (Fig.1), alkali metal ferrate or  $\alpha\text{-Fe}_2\text{O}_3$  seems to be formed. The corresponding magnetic fields are in the range of  $497\text{--}516\text{ kOe}$  characteristics of alkali metal ferrates.

Typical TGA and DTG plots of sodium hexakis (trimethylacetato) ferrate(III) are shown in Fig.2. The complexes undergoes dehydration at 300 °C as shown by an inflexion in the TG curve at a mass loss of 68.34%.

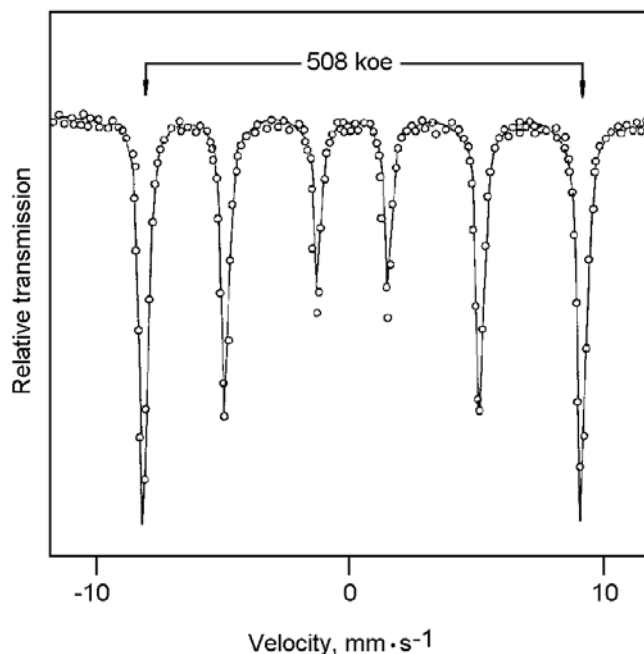


Fig.1. Typical Mossbauer spectra of Sodium hexakis (trimethylacetato) ferrate(III) at after heating at 350°C for 4hr.

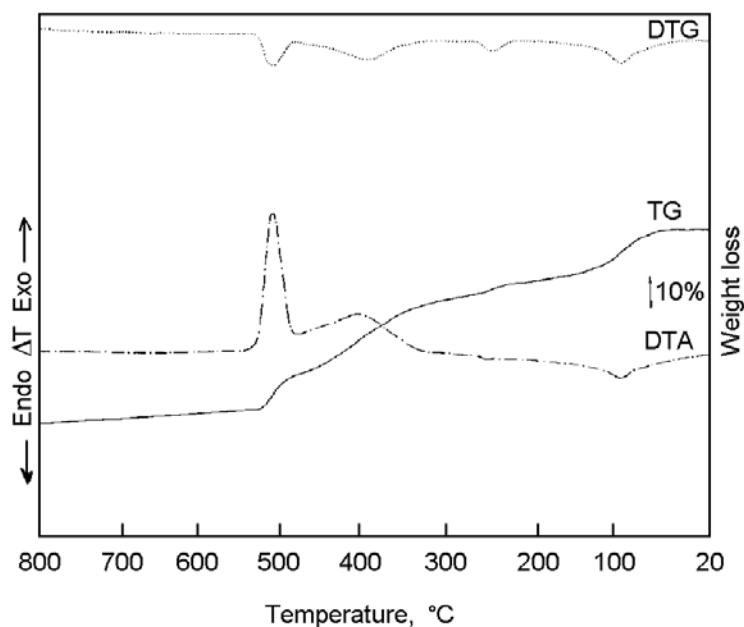


Fig. 2. Simultaneous TG.DTG.DTA thermograms of Sodium hexakis (trimethylacetato) ferrate(III) complex.

The dehydration curve step is accompanied by an endotherm reaction at 120 °C in DSC. DTG also shows a broad peak at 120 °C correspond to this step. The anhydrous compound does not show any arrest in TG and undergoes an abrupt mass loss of 27.34% at 325 °C suggesting the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and sodium oxalates. DSC displays an exotherm reaction at 325 °C with an enthalpy change -267 KJ.mol<sup>-1</sup> for this decomposition step. A respective peak in the DTG lies at 320 °C. These intermediate remain stable upto 600 °C. Mössbauer spectrum of the residue obtained by calcining the parent complex at 350 °C for 4 hr displayed sextets having isomer shift ( $\delta$ ) and quadrupole splitting ( $\Delta E_Q$ ) values of 0.31 and 0.13 mms<sup>-1</sup> respectively. Since the isomer shift is anomalously low as compared to the reported value<sup>9</sup> for pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, these parameters do not represent a fully separated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> + Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> system, but rather a state where probably partially oxalate ligands are coordinated to iron atom.

## Conclusions

The thermolysis of alkalimetal hexakis(trimethylacetato)ferrate(III) complex occurs in four major steps: i) dehydration of original complex, ii) decomposition of anhydrous complex into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and alkalimetal trimethylacetate, iii) decomposition of metal oxalate into metal carbonate and iv) solid state reaction between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and alkalimetal carbonate above 650 °C. to yield ferrite.

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