Mössbauer, infrared and thermal decomposition studies of Iron(III) complexes with substituted malonic acids

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Iron(III) complexes with alkyl (methyl, ethyl and dimethyl) and phenyl substituted malonic acids have been synthesized. Mössbauer spectra of all the complexes exhibit small quadrupole doublet with $\Delta E_Q = 0.43-0.84 \text{ mm s}^{-1}$. Isomer shift ($\delta$) values are in the range 0.62-0.76 mm s$^{-1}$ (w.r. to SNP) indicating iron(III) to be in high spin state. This assertion is further supported by magnetic moment data. Nature of alkyl group does seem to affect the electron density at the iron nucleus. Infrared spectral studies indicate monodentate nature of the carboxylate group which leads to tris type chelate complexes in all cases except in the case of malonic acid where diaquobis(malonato)ferrate(III) is formed. Thermogravimetric (TGA) data show two-stage decomposition; first two ligand molecules are lost at 120°C and finally $\text{Fe}_2\text{O}_3$ is formed at 230°C. This is supported by Mössbauer spectral evidence.

Materials and Methods

All the chemicals used were of AR or GR grade (Aldrich USA or Fluka, Switzerland). The complexes were prepared by mixing 0.56 g of iron powder (electrolytic grade; S. Merck) in a warm aqueous solution of the carboxylic acid (0.03 M). Evolution of gas started which ceased at the end of the reaction. Later, the solution was digested on a water bath for about 2 hr so as to complete the reaction. After digestion, the solution was filtered and kept overnight when coloured crystals of the complexes were obtained. These were separated from the mother liquor and dried in vacuo over fused CaCl$_2$. Compositions of the complexes were determined from C, H and Fe analyses (Table 1). Fe was determined spectrophotometrically using 1,10-phenanthroline.

Mössbauer spectra were recorded using a constant acceleration transducer driven Mössbauer spectrometer in conjunction with a PC based 1K Multichannel Analyzer (Nucleonix, Hyderabad). A 5 mCi $^{57}\text{Co(Rh)}$ source (obtained from BARC, Bombay) was used. All the spectra were recorded at room temperature and were visually fitted with Lorentzian line shape. The spectrometer was calibrated using natural iron foil and recrystallised sodium pentacyanonitrosylferrate(II) dihydrate (SNP) as the standard. For recording Mössbauer spectra of thermal decomposition products, the compounds were heated at 150, 200 and 400°C for 4 hr in a muffle furnace and cooled at room temperature.

Reflectance spectra were recorded using a Shimadzu model UV-240 spectrophotometer employing MgO as the reference. Infrared spectra (4000-200 cm$^{-1}$) in KBr medium were recorded on a Pye-Unicam IR spectrophotometer. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out at heating rates of 20° and 10°C per min respectively employing a Perkin-Elmer Ther-
Table 1—Analytical data of the complexes of various substituted malonic acids

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found (calc.), %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>Light green</td>
<td>17.02 (17.78)</td>
</tr>
<tr>
<td>2</td>
<td>Light green</td>
<td>11.68 (11.54)</td>
</tr>
<tr>
<td>3</td>
<td>Grey</td>
<td>13.69 (13.75)</td>
</tr>
<tr>
<td>4</td>
<td>Middle buff</td>
<td>12.47 (12.47)</td>
</tr>
<tr>
<td>5</td>
<td>Grey</td>
<td>12.85 (12.47)</td>
</tr>
<tr>
<td>6</td>
<td>Brown</td>
<td>9.29 (9.16)</td>
</tr>
</tbody>
</table>

Results and Discussion

All the complexes were found to be coloured solids and stable under atmospheric conditions. Unlike earlier results from our laboratory on mono- and dicarboxylate complexes, our attempts to prepare tris type complexes from ferric nitrate and the sodium salt of the corresponding carboxylic acid failed. Jagannathan et al., have reported the preparation of Fe(II) salts by mixing iron powder with hot aqueous solution of malonic or maleic acids. Therefore, we also attempted to follow this route. But instead of Fe(II) salts we got Fe(III) complexes in which three carboxylate ligands are bonded to form an octahedron except in the case of malonic acid where two distinct complexes H₂[Fe(II){CH₂(COO)₂}·2H₂O]·H₂O and H[Fe(III){CH₂(COO)₂}·2H₂O]·H₂O are formed. It seems that with alkyl substituted malonic acids, iron first gets oxidized to Fe(III) and then tris type complexes of general formula H₃[Fe[RCH(COO)₂]₃] are formed. However, in the case of malonic acid, a mixture of hydrogen diaquo-bis(malonato)ferrate(III) monohydrate, H[Fe(III){CH₂(COO)₂}·2H₂O]·H₂O and hydrogen diaquo-bis(malonato)ferrate(II) monohydrate, H₃[Fe(II){CH₂(COO)₂}·2H₂O]·H₂O are formed where unlike other cases, only two malonate ligands are coordinated and the other two positions, possibly trans, are occupied by two water molecules. This is evident from the complex nature of Mössbauer spectra.

In all cases, iron is surrounded by three alkyl substituted malonate ligands to form an octahedral complex. Obviously, it is likely to form a six-membered stable ring with the central iron atom acquiring the configuration $t_{2g}^{3}e_{g}^{2}$. Reflectance spectra of all the complexes except complex 1 (see Table 1) exhibited two bands of low intensity at 18000 and 25000 cm⁻¹ corresponding to $^{6}A_{1g} \rightarrow ^{4}T_{2g}$ and $^{6}A_{1g} \rightarrow ^{4}T_{2g}$ spin forbidden transitions respectively. In the case of alkyl substituted malonic acids a further distortion in geometry is expected.

Typical Mössbauer spectra of malonato and substituted malonato complexes are shown in Fig. 1. All the complexes exhibited a well resolved quadrupole...
Table 2—Mössbauer spectral and magnetic data for various carboxylato ferrate(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Mössbauer parameters</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a Hydrogen diaquobis(malonato) ferrate(III) monohydrate</td>
<td>$\delta$ = 0.62 mm s$^{-1}$, $\Delta E_Q$ = 0.83 mm s$^{-1}$</td>
<td>5.40</td>
</tr>
<tr>
<td>1 b Hydrogen diaquobis(malonato) ferrate(II) monohydrate</td>
<td>$\delta$ = 1.58 mm s$^{-1}$, $\Delta E_Q$ = 2.76 mm s$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>2 Sodium tris(malonato)ferrate(III) trihydrate</td>
<td>$\delta$ = 0.69 mm s$^{-1}$, $\Delta E_Q$ = 0.58 mm s$^{-1}$</td>
<td>5.64</td>
</tr>
<tr>
<td>3 Hydrogen tris(methylmalonato)ferrate(III)</td>
<td>$\delta$ = 0.75 mm s$^{-1}$, $\Delta E_Q$ = 0.64 mm s$^{-1}$</td>
<td>5.44</td>
</tr>
<tr>
<td>4 Hydrogen tris(dimethylmalonato)ferrate(III)</td>
<td>$\delta$ = 0.64 mm s$^{-1}$, $\Delta E_Q$ = 0.43 mm s$^{-1}$</td>
<td>5.37</td>
</tr>
<tr>
<td>5 Hydrogen tris(ethylmalonato)ferrate(III)</td>
<td>$\delta$ = 0.76 mm s$^{-1}$, $\Delta E_Q$ = 0.62 mm s$^{-1}$</td>
<td>5.35</td>
</tr>
<tr>
<td>6 Hydrogen tris(phenylmalonato)ferrate(III) monohydrate</td>
<td>$\delta$ = 0.66 mm s$^{-1}$, $\Delta E_Q$ = 0.63 mm s$^{-1}$</td>
<td>5.65</td>
</tr>
</tbody>
</table>

*Relative to SNP as a standard.

**Error within ±0.02 mm s$^{-1}$.

Mössbauer spectrum of the complex 1 can be resolved into two sets of doublets, one corresponding to Fe(II) complex, $\text{H}_2\text{[Fe(II)CH}_2\text{(COOH)}\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$ and the other, more intense to Fe(III) complex, $\text{H}[\text{Fe(III)}\text{CH}_3\text{(COOH)}\text{H}_2\text{O}]\cdot\text{H}_2\text{O}$. Mössbauer parameters, $\delta$ (w.r. to SNP as a standard) and $\Delta E_Q$ alongwith magnetic moment data are given in Table 2.

**Magnetic moments**

Magnetic moments of all the complexes showed the presence of five unpaired electrons ($\mu_{\text{eff}} = 5.35$-5.65 B.M.) indicating high spin state of Fe(III). The $\mu_{\text{eff}}$ values are slightly lower than expected (5.9 B.M.) which may possibly be due to partial quenching.

**Mössbauer parameters**

Isomer shift ($\delta$) values for all the complexes are in the range 0.62-0.76 mm s$^{-1}$ indicating Fe(III) to be in high spin state$^{12}$. The minimum value of 0.62 mm s$^{-1}$ is observed for the bis(malonato)ferrate(III) and the maximum value of 0.76 mm s$^{-1}$ is obtained for tris(methyl/ethyl malonato)ferrate(III) complexes. For phenyl substituted malonato complex, however, $\delta$ becomes 0.66 mm s$^{-1}$ indicating that electron donor or withdrawal character does affect the s-electron density and hence the $\delta$ value. Similar type
of behaviour has been observed earlier for monocarboxylatoferrate(III) complexes. Quadrupole splitting also varies in a large range ($\Delta E_0 = 0.43-0.83$ mm s$^{-1}$) indicating varying distortion depending upon the nature of alkyl group. Surprisingly hydrogen tris(dimethylmalonato)ferrate(III) complex exhibits the minimum $\Delta E_0$ value of 0.43 mm s$^{-1}$; it also exhibits a lower $\delta$ value. $\Delta E_0$ for this complex is lower than even that for sodium tris(malonato)ferrate(III) trihydrate complex. Presumably, in this case two methyl groups do not allow the chelate ring to oscillate like a swing but instead keep it tight enough so as to cause the minimum distortion. In other cases, however, distortion increases becoming maximum for diaquo bis(malonato)ferrate(III) complex. For diaquo bis(malonato)ferrate(II) complexes, high value of quadrupole splitting, ($\Delta E_0 = 2.76$ mm s$^{-1}$) is due to high spin state of Fe(II) (electronic configuration, $t^6g^5$) which compares well with 2.68 mm s$^{-1}$ observed by Ravi et al. Probably malonic acids with more bulky groups as substituents need to be further investigated to understand this aspect.

Earlier we had observed a single broad line spectrum, resolved into a doublet, for the sodium tri(malonato)ferrate(III) trihydrate complex, $\text{Na}_3[\text{Fe(CH}_2\text{C}_2\text{O}_4]_3\text{H}_2\text{O}$ with $\Delta E_0 = 0.58$ mm s$^{-1}$. Bassi et al. had observed a single line spectrum with $\Gamma = 1.08-1.39$ mm s$^{-1}$ for alkali metal tris(malonato)ferrate(III) complexes. However, Ravi et al. have reported $\delta = 1.41$ mm s$^{-1}$ and $\Delta E_0 = 2.68$ mm s$^{-1}$ for ferrous malonate dihydrate salt, Fe$(\text{CH}_2\text{C}_2\text{O}_4]_2\text{H}_2\text{O}$. Therefore, in the Mössbauer spectrum of hydrogen diaquo bis(malonato)ferrate(III) monohydrate complex the parameters, $\delta = 1.48$ mm s$^{-1}$ and $\Delta E_0 = 2.76$ mm s$^{-1}$ compare well with those for the Fe(II) malonate dihydrate. All the other complexes, however, gave well resolved doublet indicating the formation of a single complex.

Infrared spectra

The carboxylate group may act as a unidentate, bidentate or bridged ligand depending on the nature of metal ion and reaction conditions. The most prominent vibrational bands affected by coordination are $\nu_{\text{w}}(\text{COO})$, $\nu_{\text{s}}(\text{COO})$ and $\delta(\text{COO})$. These intense and well defined bands are observed in the regions 1690-1590, 1430-1400 and 800-710 cm$^{-1}$ respectively. Another important band observed in the region 580-515 cm$^{-1}$ is due to Fe-O stretching vibrations. It has been suggested that the magnitude of separation, $\Delta \nu = |\nu_{\text{w}}(\text{COO})-\nu_{\text{s}}(\text{COO})|$ should be higher for unidentate carboxylate ligand as compared to that for simple ionic carboxylates. In all the dicarboxylate complexes studied here $\Delta \nu$ values (170-230 cm$^{-1}$) are higher than that for sodium acetate (164 cm$^{-1}$) which is purely ionic. This indicates unidentate nature of all the substituted malonate ligands.

It has also been suggested that the shift of $\nu_{\text{s}}(\text{COO})$ mode of coordinated unidentate carboxylate ligand should be higher as compared to the corresponding mode in simple ionic carboxylate. In the present study, it is observed that $\nu_{\text{s}}(\text{COO})$ modes appear either at the same or higher wavenumber than in ionic salts. Similarly, $\nu_{\text{w}}(\text{COO})$ mode appears at the lower wavenumber with respect to that for sodium acetate. This further confirms the unidentate nature of the carboxylate ligand.

The $\nu$Fe-O mode in the compounds studied here appears in the region 580-515 cm$^{-1}$ in accordance with literature reports. There is however, no regularity with respect to size of alkyl group except that $\nu$Fe-O is lowest for tris(dimethylmalonato)ferrate(III) complex (i.e. 515 cm$^{-1}$) suggesting a possible change in the polarity of Fe-O bond.
Fig. 3—Mössbauer spectrum of hydrogen tris(dimethylmalonato)ferrate(III) complex heated at 400°C for 4 hr.

$\nu$ (C-O), $\nu_{as}$(C-C), $\nu_{s}$(C-C) and $\nu$(C-H) modes observed in the range 1090-1040, 1230-1170, 950-880 and 3000-2960 cm$^{-1}$ respectively, are in agreement with those reported in the literature.$^{23,24}$

Thermal decomposition

Thermal decomposition of iron carboxylates has been of interest to many workers$^{25-28}$ because of the wide applicability of these carboxylates as medicinal agents, catalysts etc. In all the present cases, decomposition behaviour seems to be similar; all the complexes decompose in two stages. The TGA, DTG and DTA curves obtained for hydrogen tris(ethylmalonato)ferrate(III) complex are shown in Fig. 2 as a typical case. There are significant mass losses first at 180°C and then at 230°C. The mass loss at 230°C corresponds to the formation of Fe$_3$O$_4$ in all the cases and there is no further mass loss beyond this temperature. In order to confirm the formation of Fe$_3$O$_4$, complexes were heated at 400°C for 4 hr and their Mössbauer spectra were recorded. A typical six line spectrum obtained for the end product of hydrogen tris(dimethylmalonato)ferrate(III) is shown in Fig. 3. It gives an isomer shift of 0.67 mm s$^{-1}$ which compares well with 0.63 mm s$^{-1}$ for α-Fe$_3$O$_4$. However, first mass loss at 180°C corresponds to the loss of two carboxylate ligands in each case. Vithal and Jagannathan$^6$ have proposed loss of one ligand molecule in the thermal decomposition of maleato complex. Somewhat similar observation has been reported by Saha and Mitra$^9$ for several malonato complexes. Therefore, the possible mechanism of decomposition could be represented as follows:

$$\text{H}_3\text{Fe}[\text{RCH(COO)}_2]^+ \rightarrow \text{[Fe}((\text{COO})_2\text{CHR(OH)} + 2\text{RCH(COOH)}_2]$$

At 180°C

$$2[\text{Fe}((\text{COO})_2\text{CHR(OH)} + 2\text{RCH(COOH)}_2] \rightarrow \text{Fe}_3\text{O}_4 + \text{CO}_2 + ..$$

Abras et al.$^{24}$ have studied the thermal decomposition of potassium tris(malonato)ferrate(III) trihydrate and suggested the formation of α-Fe$_3$O$_4$ and K$_2$CO$_3$. When the corresponding sodium compound was heated at 200°C for 4 hr it still gave a two line spectrum with $\Delta E_0 = 0.77$ mm s$^{-1}$. On further heating at 400°C for 4 hr, it exhibited a six line spectrum with $\delta = 0.75$ mm s$^{-1}$. Thus, the formation of α-Fe$_3$O$_4$ in all the cases is confirmed. In the case of DTA, two peaks are observed, one endothermic at 150°C and another flat, broad exothermic peak at 230°C. At 150°C, it may possibly involve melting whence two carboxylate ligands escape and later it undergoes oxidative decomposition. Randhawa et al.$^4$ have also observed endothermic and exothermic peaks for magnesium tris(malonato)ferrate(III) decahydrate. Thus, basically there seems to be a two step decomposition ultimately yielding Fe$_3$O$_4$ as the final product.

Acknowledgement

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References