Synthesis, Mössbauer, infrared spectroscopic and thermal decomposition studies of some iron(III) carboxylate complexes

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Several new iron(III) carboxylate complexes with the general formula \( \text{Na}_3[\text{Fe(OCOR)}_6] \) where \( \text{R} = (\text{CH}_3)_3\text{C} -, \text{CH}_3(\text{CH}_2)_8 -, \text{CH}_3(\text{CH}_2)_{10} -, 2,5\text{-Cl}_2\text{C}_6\text{H}_3 -, 2,5\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3 -, 2\text{-MeOC}_6\text{H}_4 - \) and \( 3\text{-MeOC}_6\text{H}_4 - \) have been synthesized. Also, iron(III) complexes with pyridine 2,6-dicarboxylic acid and quinic acid have been synthesized. Infrared data suggest unidentate nature of the carboxylate ligands in all cases. Mössbauer spectra of all the complexes exhibit quadrupole doublet except for quinic acid complex where a triplet has been observed. Isomer shift \( (\delta) \) values are in the range 0.58-0.74 mm s\(^{-1}\) (with respect to sodium nitroprusside as a standard) suggesting iron(III) in high spin state. Quadrupole splitting \( (\Delta E_Q) \) values are in the range of 0.30-2.71 mm s\(^{-1}\) and its variation is attributed to varying distortions in octahedral geometry. Thermogravimetric (TGA) studies show a single stage, but slow decomposition yielding a mixed sodium iron oxide or sodium ferrate \( (3\text{Na}_2\text{O.Fe}_2\text{O}_3) \). Magnetic moment and reflectance spectral data have also been reported.

Carboxylate ion \( (\text{C}=\text{O}^-) \) is a unique ligand which can act as a unidentate, bidentate or bridging ligand depending on the nature of metal ion, carboxylic acid and the reaction conditions. Iron is known to form simple and some basic salts with formic and acetic acids. Earlier we have studied several iron(III) carboxylate complexes of mono- and di-carboxylic acids by Mössbauer and infrared spectroscopy. In order to further study the effect of more bulky groups on the octahedral geometry, we report here synthesis and structural investigations on some new carboxylate complexes with the general formula \( \text{Na}_3[\text{Fe(OCOR)}_6] \) where \( \text{R} = (\text{CH}_3)_3\text{C} -, \text{CH}_3(\text{CH}_2)_8 -, \text{CH}_3(\text{CH}_2)_{10} -, 2,5\text{-Cl}_2\text{C}_6\text{H}_3 -, 2,5\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3 -, \text{CH}_3(\text{CH}_2)_{10} -, 2\text{-MeOC}_6\text{H}_4 - \) and \( 3\text{-MeOC}_6\text{H}_4 - \). Also iron(III) complexes with pyridine 2,6-dicarboxylic acid and quinic acid have been synthesized and their spectral studies carried out. We have also studied the thermal decomposition behaviour of the complexes.

Materials and Methods

All the chemicals used were of AR, GR or high purity grade. Quinic acid \( (1,3,4,5\text{-tetrahydroxycyclohexane 1-carboxylic acid}) \), pyridine 2,6-dicarboxylic acid and heptanoic acid were Fluka AG (puram) reagents. Sodium salts of the acids were prepared by mixing equimolar \( (0.1 \text{ M}) \) aqueous solutions of the acids and sodium hydroxide. In case of trimethylacetic acid (Fluka, AG) and heptanoic acid, reaction was carried out with sodium metal pieces in dry benzene till the evolution of hydrogen ceased. Sodium salt so formed was then filtered and dried.

Preparation of complexes

The complexes were prepared by mixing 0.1 \( M \) ferric nitrate with 0.6 \( M \) aqueous solution of the corresponding sodium carboxylate. Trisodium tris(pyridine 2,6-dicarboxylicato)ferrate(III) complex was prepared by reacting 0.81 g ferric nitrate with 1.13 g monosodium pyridine 2,6-carboxylate in 1:1 water-ethanol mixture.

Sodium salt of quinic acid could not be prepared and, hence, its complex was prepared by treating 0.056 g iron powder (electrolytic grade, S. Merck) with a warm aqueous solution of 1.92 g \( (3 \text{ mM}) \) acid. The resultant solution was slowly evaporated on a water bath.

In all the cases coloured complexes separated out immediately and these were dried \( \text{in vacuo} \) over fused \( \text{CaCl}_2 \). C, H analyses (Table 1) were carried out at the analytical laboratories of Regional Sophisticated Instrumentation Centre, Lucknow. Fe was determined spectrophotometrically using 1,10-phenanthroline reagent.
Table 1 – Analytical data of various carboxylate complexes

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Na$_3$[Fe(OCOR)$_6$]</th>
<th>Colour</th>
<th>Found (Calc) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R =</td>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>1</td>
<td>(CH$_3$)$_3$C$-$</td>
<td>Middle buff</td>
<td>7.23 (7.66)</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$(CH$_2$)$_3$-</td>
<td>Brick red</td>
<td>7.42 (7.13)</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3$(CH$_2$)$_6$-</td>
<td>Middle buff</td>
<td>4.24 (4.20)</td>
</tr>
<tr>
<td>4</td>
<td>2,5-Cl$_2$C$_6$H$_3$-</td>
<td>Middle buff</td>
<td>5.02 (4.62)</td>
</tr>
<tr>
<td>5</td>
<td>2,5-(CH$_3$)$_2$C$_6$H$_3$-</td>
<td>Middle buff</td>
<td>5.89 (5.75)</td>
</tr>
<tr>
<td>6</td>
<td>2-MeO C$_6$H$_4$-</td>
<td>Golden yellow</td>
<td>5.85 (5.43)</td>
</tr>
<tr>
<td>7</td>
<td>3-MeOC$_6$H$_4$-</td>
<td>Brick red</td>
<td>5.12 (5.43)</td>
</tr>
<tr>
<td>8</td>
<td>Na$_3$[Fe(R)$_3$]</td>
<td>Brown</td>
<td>7.80 (7.95)</td>
</tr>
<tr>
<td>R = pyridine, 2,6-dicarboxylic acid</td>
<td></td>
<td></td>
<td>(8.88)</td>
</tr>
<tr>
<td>9</td>
<td>H$_3$[Fe(II)[C$_6$H$_4$O$_2$]$_3$] or H$_3$[Fe(III)[C$_6$H$_4$O$_2$]$_3$]</td>
<td>Grey</td>
<td>9.11 (8.90)</td>
</tr>
</tbody>
</table>

Physical measurements

Mössbauer spectra were recorded using a constant acceleration transducer, driven Mössbauer spectrometer in conjunction with a PC based 1 K Multichannel Analyzer (Nucleonix, Hyderabad). A 5 mCi $^{57}$Co(Rh) source (procured from the Isotope Group, BARC, Bombay) was used. All the spectra were recorded at room temperature and visually fitted with Lorentzian line shape. The spectrometer was calibrated using natural iron foil. Sodium nitroprusside dihydrate (SNP) was used as the standard.

Infrared spectra (4000-2000 cm$^{-1}$) were recorded in KBr medium on a Perkin-Elmer-157 IR spectrophotometer. Thermogravimetric (TGA) and differential thermal gravimetric analyses (DTG) were carried out at a heating rate of 10°C per min using Perkin-Elmer Thermogravimetric Analyzer System Model TGS-2 and Thermal Analysis Data Station-TADS 3600 of RSIC, Nagpur.

Results and Discussion

All the complexes are coloured solids and stable under atmospheric conditions. Fe(III) in an octahedral environment will be surrounded by six or three carboxylate ligands with central iron atom having an electronic configuration $t^3_d$ $e^2_g$. Due to the large size of the carboxylate ligands, especially with long chain alkyl groups, geometry is likely to be distorted quite significantly.

All the complexes exhibit a well resolved quadrupole doublet except the quinic acid complex where a three line spectrum is observed. Mössbauer spectrum of quinic acid complex can be re-
solved into two sets of doublets, one corresponding to Fe(II) and another more intense to Fe(III). Typical Mössbauer spectra of substituted benzoate and heptanoic acid complexes are shown in Fig. 1. Similarly, Mössbauer spectra of pyridine 2,6-dicarboxylic acid and quinic acid complexes are shown in Fig. 2. Isomer shift (δ), quadrupole splitting (ΔEQ) along with magnetic moment and electronic spectral bands are given in Table 2.

Reflectance spectra of these complexes exhibit two bands (Table 2) of low intensity at 19,000 cm⁻¹ and 25,000 cm⁻¹ corresponding to spin forbidden ⁶A₁g → ⁴T₁g and ⁶A₁g → ⁴T₂g transitions respectively. These are in agreement with literature assignments.

Magnetic moments

Magnetic moments of the carboxylate complexes are in the range of 5.29-6.23 B.M. indicating high spin state of Fe(III) with five unpaired electrons. High μₑₑₑ values in some cases may be attributed to (i) some contribution from the alkyl or aryl groups attached to the carboxylate, (ii) non-quenching of orbital contribution, (iii) some other magnetic interactions including magnetically non-equivalent sites in a unit cell and (iv) large distortions in the geometry of the complexes.

Even though there is no direct evidence the possibility of multiple centre bands cannot be ruled out.

Infrared spectra

Infrared spectra of a wide variety of carboxylates of different metal ions have been studied. The most prominent features of infrared spectra of the carboxylate complexes are the sharp and well defined absorptions due to $\nu_{as}(\text{OCO})$, $\nu_{s}(\text{OCO})$ and δ(OCO) observed in the region as 1665-1470, 1430-1340 and 770-600 cm⁻¹ respectively. Their positions and intensities are similar to those reported for other carboxylate complexes. Another important band is due to $\nu(\text{Fe-O})$ observed in the region 540-440 cm⁻¹. Other characteristic bands such as $\nu(\text{C-O})$, $\nu(\text{C-C})$ and $\nu(\text{C-H})$ were also observed in regions 1110-1000, 1290-1210 and 3250-2720 cm⁻¹ respectively. It follows that in all carboxylate complexes studied here $\Delta \nu = [\nu_{as}(\text{OCO}) - \nu_{s}(\text{OCO})]$ is in the range 180-295 cm⁻¹ which is higher than that for the corresponding sodium salt in all the cases indicating unidentate character of the carboxylate ligands.
It has also been shown that the direction of shift of $v_{as}(\text{OCO})$ mode in the coordinated unidentate carboxylate ligand is towards higher wavenumbers, whereas that of $v_s(\text{OCO})$ is towards lower wavenumber compared to their respective positions in simple ionic carboxylates. In the present study, $v_{as}(\text{OCO})$ mode appears either at a higher or at the same wave number and $v_s(\text{OCO})$ appears at a lower wavenumber with respect to the corresponding sodium salt of the acid. Therefore, both criteria, the magnitude of separation as well as the direction of shift, indicate a unidentate nature of carboxylate ligands.

The $v(\text{Fe-O})$ mode in the complexes studied here appears in the region 540–440 cm$^{-1}$ in accordance with that reported in the literature. Bassi et al. have also observed $v(\text{Fe-O})$ for alkali tris(malonato)ferrates(III) in the range 560–530 cm$^{-1}$. In aliphatic carboxylates $\text{Fe-O}$ stretching frequencies increase in the order $(\text{CH}_3)_3\text{C}^- < \text{CH}_3(\text{CH}_2)\text{C}^- < \text{CH}_3(\text{CH}_2)_2\text{C}^-$. On the other hand, for substituted benzoato complexes $v(\text{Fe-O})$ values are higher than those for aliphatic carboxylate complexes. This may be explained in terms of a partial double bond character for $\text{H}_2\text{C}_6-\text{C}$ bond causing a partial change in polarity of the $\text{Fe-O}$ bond.

For pyridine 2,6-dicarboxylic acid complex, additional bands at 1600 and 1430 cm$^{-1}$ are observed corresponding to free uncoordinated carboxylic acid. It suggests only bidentate nature of pyridine 2,6-dicarboxylic acid. Also a characteristic band corresponding to $\text{Fe-N}$ stretching vibration at 400 cm$^{-1}$ is observed. Naik and Curran have also confirmed bidentate nature of pyridine 2,6-dicarboxylic acid in its Sn(IV) complexes, thus leaving one – COOH free.

For quinic acid an unusual situation seems to exist where one COOH and four OH groups are present. Two bands at 1610 and 1420 cm$^{-1}$ correspond to $v_{as}(\text{OCO})$ and $v_s(\text{OCO})$ respectively suggesting a unidentate coordination for the carboxylate. However, analytical and physical measurements suggest the ligand to be bidentate which is possible only if one of the $-\text{OH}$ groups is also bonded. Besides, a band at 480 cm$^{-1}$ due to $v(\text{Fe-O})$ (from $-\text{COO}$) and another weak band at 360 cm$^{-1}$ due to $v(\text{Fe-N})$ confirm this suggestion. Presence of other free OH groups is confirmed by a broad band at 3250 cm$^{-1}$.

**Mössbauer studies**

A perusal of Table 2 indicates that for aliphatic carboxylate complexes $\delta$ varies in the narrow range of 0.58–0.66 mm s$^{-1}$ and increases in the order: $(\text{CH}_3)_3\text{C}^- < \text{CH}_3(\text{CH}_2)\text{C}^- < \text{CH}_3(\text{CH}_2)_2\text{C}^-$. For substituted benzoato complexes also $\delta$ varies in the range 0.58–0.67 mm s$^{-1}$ indicating only a small change in $\sigma$-electron density at the iron nucleus. It may be attributed to $\pi$-resonance as a result of which some electronic charge may be donated to the $d$-orbitals of Fe resulting in variation
Table 3 - Thermogravimetric data of the carboxylate complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Starting dec. temp. (°C)</th>
<th>DTG peak temp. (°C)</th>
<th>Dec. Process</th>
<th>Constant Wt. Temp. (°C)</th>
<th>Final wt (%)</th>
<th>Possible end product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120</td>
<td>320</td>
<td>(slow)</td>
<td>450</td>
<td>24.8</td>
<td>3Na₂O·Fe₂O₃</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>270</td>
<td>(fast)</td>
<td>480</td>
<td>27.0</td>
<td>3Na₂O·Fe₂O₃</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>260</td>
<td>(fast)</td>
<td>480</td>
<td>17.6</td>
<td>3Na₂Q·Fe₂O₃</td>
</tr>
<tr>
<td>4</td>
<td>200</td>
<td>380</td>
<td>(fast)</td>
<td>460</td>
<td>22.2</td>
<td>2NaCl·NaFe₂O₅</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>450</td>
<td>(very slow)</td>
<td>550</td>
<td>19.17</td>
<td>3Na₂O·Fe₂O₃</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>220</td>
<td>(very slow)</td>
<td>560</td>
<td>36.4</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>200</td>
<td>350</td>
<td>(slow in 250 stages)</td>
<td>550</td>
<td>34.52</td>
<td>—</td>
</tr>
<tr>
<td>8</td>
<td>80</td>
<td>160</td>
<td>(very fast)</td>
<td>600</td>
<td>63.0</td>
<td>Loss of CO₂ at 160°C, later two ligands are lost.</td>
</tr>
<tr>
<td>9</td>
<td>180</td>
<td>240</td>
<td>(very fast)</td>
<td>400</td>
<td>47.7</td>
<td>Fe₂O₃</td>
</tr>
</tbody>
</table>

in δ values. Nature of electron donating or withdrawing groups at α- and/or p-position of the benzene ring may also affect the isomer shift. This is because disubstitution in benzene ring may affect the nature of Fe-O bond to some extent. Similar variations have been observed in alkyl phosphine and phosphite substituted pentacyano ferrate complexes. It is well known that δ values and metal-ligand stretching vibrations are affected by the substitution of alkyl or halide group in the ligand irrespective of low or high spin nature of iron(III) complex.

In case of point charges surrounding Fe(III) ion in octahedral geometry no quadrupole splitting is expected, because the 3d-electrons are equally populated. However, substituted carboxylate ligands are large enough to cause distortion and hence net electric field gradient (EFG) is generated due to ligand contribution giving rise to quadrupole splitting. In the present studies of alkyl and substituted benzoato complexes, ΔE₀ in the range of 0.30-0.88 mm s⁻¹ is observed suggesting small but significant distortions in the octahedral geometry.

Amongst aliphatic carboxylate complexes, ΔE₀ increases from 0.30 for trimethylaceto complex to 0.78 mm s⁻¹ for heptanoic acid complex. On further increase in chain length in dodecanoic acid, it is reduced to 0.60 mm s⁻¹. It means that with increasing chain length, first ΔE₀ increases and then subsides suggesting a decrease in distortion. Probably with increasing chain length, the chain coils causing a decrease in distortion and hence decrease in ΔE₀. Almost a similar observation was made by us for dicarboxylate complexes.

It is further observed from Table 2 that within the series of substituted benzoato complexes, large variation in ΔE₀ is observed. 2,5-Dichlorobenzoato complex exhibits large ΔE₀ (0.88 mm s⁻¹) compared to 2,5-dimethylbenzoato complex (0.54 mm s⁻¹). Similarly, 3-methoxybenzoato complex gives larger ΔE₀ = 0.56 mm s⁻¹ compared to 2-methoxybenzoato complex (0.36 mm s⁻¹). These observations clearly suggest that not only the nature of substituent but also the position of substitution affects the distortion in geometry quite significantly.

In the case of pyridine 2,6-dicarboxylic acid complex the δ value (0.56 mm s⁻¹) lies within the range expected for typical iron(III) high spin complexes. However, it exhibits quite a large ΔE₀ = 1.92 mm s⁻¹ suggesting a large distortion presumably due to free carboxylic acid group. Naik and Curran have also observed large ΔE₀ for Sn(IV) complexes of this ligand.

In the case of quinic acid complex a three line spectrum (Fig. 2B) has been observed. It can be
resolved into two doublets arising due to Fe(II) and Fe(III) states. It seems that besides the Fe(III) complex, Fe(II) complex is also formed. In that case larger $\Delta E_Q(=2.71 \text{ mm s}^{-1})$ may be due to Fe(II) state while the smaller $\Delta E_Q(=1.11 \text{ mm s}^{-1})$ may be due to Fe(III) complex. Such a large $\Delta E_Q$ in Fe(III) complex indicates large distortion because of cyclohexane ring. The observed $\delta$ values of 0.74 and 1.54 mm s$^{-1}$ also correspond to Fe(III) and Fe(II) states respectively. As suggested in preceding section on IR, iron may be bound through carboxylate and hydroxyl groups at 1 and 5 positions respectively. At this stage it is difficult to say if it is a mixture of two complexes or both the states of iron exist in the same complex. Surprisingly, its magnetic moment is quite high.

Thermal decomposition studies

In most studies on thermal decomposition of carboxylate complexes, sodium ferrate NaFeO$_3$ has been identified as the end product$^{26-29}$. Table 3 lists the thermal decomposition data. In all the cases no weight loss was observed around or below 100°C except in the case of pyridine 2,6-dicarboxylic acid complex. It indicates absence of water molecules in all the carboxylate complexes. For all the three aliphatic carboxylate complexes a constant weight was obtained at 450°C and this corresponds to Na$_3$FeO$_5$ or 3Na$_2$OFe$_2$O$_5$. Formation of sodium ferrate is confirmed by the characteristic six line Mössbauer spectrum. When trimethylacetic acid complex was heated at 200°C for 4 hr, $\Delta E_Q$ increased from 0.30 to 0.62 mm s$^{-1}$. On further heating at 350°C for 4 hr, it gave a six line spectrum with $\delta=0.70 \text{ mm s}^{-1}$ confirming the formation of Na$_3$FeO$_5$. In the case of 2,5-dimethylbenzoato complex also final weight corresponding to the same composition. For 2,5-dichlorobenzoato complex, decomposition was very fast as shown in Fig. 3, yielding a DTG peak at 380°C and a constant weight of 22.2% at 460°C. This may be assigned to the final product having the composition 2NaClNaFeO$_2$. In the case of two methoxy benzoates and quinic acid complexes, all giving about 35-47% final weight, it is difficult to assign any possible composition for the final product.

For pyridine 2,6-dicarboxylic acid complex, a two stage decomposition is observed, similar to the case of malonic acid complexes$^{19}$. Presumably in the first stage a CO$_2$ molecule belonging to the free carboxylic acid is knocked out at 160°C. Later two ligands seem to be lost, yielding simple iron complex with pyridine carboxylate. A similar observation has been made by Allan et al.$^{29}$ for pyridine 2,3-dicarboxylic acid complexes of Mn, Fe, Co and Ni which ultimately yield metal oxide.

When quinic acid complex was heated at 220°C for 4 hr, it gave a six line Mössbauer spectrum with $\delta=0.72 \text{ mm s}^{-1}$ which corresponds to the formation of $\alpha$-Fe$_5$O$_3$ as in other previously reported cases$^{26,29}$.

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