

# Mössbauer, Infrared & Magnetic Studies on Hexacarboxylatoferrate(III) Complexes

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Mössbauer and infrared spectroscopic studies of some trisodium hexacarboxylatoferrate(III) complexes,  $\text{Na}_3[\text{Fe}(\text{OCOR})_6]$ , ( $\text{R} = -\text{H}, -\text{CH}_3, -\text{C}_2\text{H}_5, n\text{- and } i\text{-C}_3\text{H}_7, -\text{C}_6\text{H}_5, -\text{C}_6\text{H}_5\text{CH}_2, -(\text{C}_6\text{H}_5)_2\text{CH}, -\text{C}_{10}\text{H}_7\text{CH}_2, o\text{- and } m\text{-CH}_3\text{C}_6\text{H}_4, o\text{-, } m\text{- and } p\text{-NH}_2\text{C}_6\text{H}_4, o\text{- and } p\text{-ClC}_6\text{H}_4, -2,4\text{ and } -2,6\text{ Cl}_2\text{C}_6\text{H}_3\text{ and } -2,3\text{ and } 2,4\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3$ ) have been carried out at room temperature. Unidentate coordination of the carboxylate group is supported by the difference in  $\nu_s(\text{OCO})$  and  $\nu_a(\text{OCO})$  modes. All the complexes exhibit isomer shift ( $\delta$ ) values in the range of 0.60-1.01  $\text{mms}^{-1}$  (with respect to sodium nitroprusside) and a quadrupole doublet with  $\Delta E_Q$  in the range of 0.22 to 0.94  $\text{mms}^{-1}$ . For aliphatic carboxylate complexes,  $\delta$  varies in a very narrow range of 0.69-0.88  $\text{mms}^{-1}$  but it varies in a large range for substituted benzoate complexes. Variation in  $\Delta E_Q$  values has been attributed to distortion in octahedral geometry and restriction in free rotation around  $\text{C}_6\text{H}_5\text{-C}$  bond as a result of substitution in the benzene ring. Magnetic moments indicate all the complexes to be of high spin.

Carboxylate ion ( $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$ ) acts as a unidentate, bidentate or a bridging ligand, depending on the nature of metal ion, carboxylic acid and the reaction conditions<sup>1-3</sup>. Iron is known to form simple and some basic salts with formic and acetic acids<sup>4-8</sup>. Formation of hexaformate complexes has also been reported<sup>4,9</sup>. A recent review has described the polynuclear nature of some metal carboxylates<sup>10</sup>. In some compounds with M-M quadrupole bonds, syn-syn bridging  $\text{RCOO}^-$  ligand is extremely common<sup>11</sup>. All these unusual features prompted us to undertake the study of hexacarboxylates of higher fatty acids<sup>12</sup>. Recently Brar *et al.*<sup>13</sup> have studied hexaformate complexes,  $\text{M}_3[\text{Fe}(\text{OCOH})_6] \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$  and  $\text{Cs}$ ). We have presently synthesized complexes with the general formula  $\text{Na}_3[\text{Fe}(\text{OCOR})_6]$  where  $\text{R} = -\text{H}, -\text{CH}_3, -\text{C}_2\text{H}_5, n\text{- and } i\text{-C}_3\text{H}_7, -\text{C}_6\text{H}_5, -\text{C}_6\text{H}_5\text{CH}_2, -(\text{C}_6\text{H}_5)_2\text{CH}, -\text{C}_{10}\text{H}_7\text{CH}_2, o\text{- and } m\text{-CH}_3\text{C}_6\text{H}_4, o\text{-, } m\text{- and } p\text{-NH}_2\text{C}_6\text{H}_4, o\text{- and } p\text{-ClC}_6\text{H}_4, 2,4\text{- and } 2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{ and } 2,3\text{- and } 2,4\text{-}(\text{CH}_3)_2\text{C}_6\text{H}_3$  and studied their Mössbauer and infrared spectra with a view to throw light on the effect of nature of ligand and the substitution of higher alkyl or substituted benzyl groups on the octahedral geometry of these hexacarboxylate complexes.

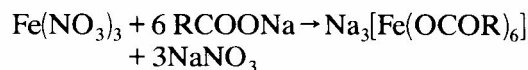
## Materials and Methods

### Preparation of complexes

All the chemicals used were of AR or high purity

grade. Sodium salts of the acids were prepared by treating equimolar amounts of the acids with sodium hydroxide or sodium metal in dry benzene.

The complexes were prepared by mixing (0.1 M) ferric nitrate with a slight excess of the calculated amount of the corresponding sodium carboxylate in aqueous medium.



In most cases coloured complexes separated out immediately but in some cases the mixture had to be cooled in a freezing mixture for 3-4 days; e.g. complexes of *n*- and *i*-butyric acids were oily liquids which solidified on cooling in a freezing mixture. All complexes were dried *in vacuo* over fused  $\text{CaCl}_2$ . Analytical data were found to be in good agreement with the proposed formula (Table 1) and no water molecules were found to be associated in any case.

### Mössbauer, infrared and magnetic measurements

Mössbauer spectra were recorded on a constant acceleration driven Mössbauer spectrometer employing a 25 mCi  $^{57}\text{Co}(\text{Rh})$  source. Natural iron was used as a calibrant while sodium nitroprusside (SNP) was used as standard. All measurements were carried out at room temperature only and all spectra were fitted with Lorentzian line equation visually. Infrared spectra were recorded in KBr on a Perkin-Elmer model 580 spectrophotometer. Magnetic

Table 1 — Analytical Data of Various Carboxylato Complexes,  $\text{Na}_3[\text{Fe}(\text{OCOR})_6]$ 

R	Colour	Fe (%)		C (%)		H (%)	
		Calc.	Found	Calc.	Found	Calc.	Found
H	Middle buff	14.43	13.38	18.23	18.58	1.52	1.20
$\text{CH}_3$	Middle buff	11.66	10.96	30.07	30.25	3.76	3.57
$\text{C}_2\text{H}_5$	Middle buff	9.92	9.81	38.38	36.76	5.33	5.15
<i>n</i> - $\text{C}_3\text{H}_7$	Brick red	8.63	8.78	44.52	42.18	6.49	5.59
<i>i</i> - $\text{C}_3\text{H}_7$	Pale rose	8.63	7.95	44.52	43.41	6.49	6.69
$\text{C}_6\text{H}_5\text{CH}_2$	Golden brown	5.97	5.69	61.61	59.62	4.49	4.47
$(\text{C}_6\text{H}_5)_2\text{CH}$	Middle buff	4.02	3.94	72.47	68.70	4.74	4.05
$\text{C}_{10}\text{H}_7\text{CH}_2$	Golden brown	4.52	4.10	69.97	66.62	4.33	4.51
$\text{C}_6\text{H}_5$	Pale rose	6.56	7.20	59.23	59.77	3.53	3.87
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	Pale cream	5.97	5.94	61.61	60.67	4.49	4.47
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$	Middle buff	5.97	6.32	61.61	61.25	4.49	4.79
<i>o</i> - $\text{NH}_2\text{C}_6\text{H}_4$	Black	5.94	5.63	53.57	49.74	3.83	4.02
<i>m</i> - $\text{NH}_2\text{C}_6\text{H}_4$	Portland grey	5.94	6.27	53.57	52.90	3.83	4.26
<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4$	Brown	5.94	5.76	53.57	53.40	3.83	3.88
<i>o</i> - $\text{ClC}_6\text{H}_4$	Portland grey	5.28	5.29	47.62	50.62	2.27	1.98
<i>p</i> - $\text{ClC}_6\text{H}_4$	New ivory	5.28	4.95	47.62	50.20	2.27	2.40
$(2,3)(\text{CH}_3)_2\text{C}_6\text{H}_3$	Golden yellow	5.48	5.67	63.60	60.86	5.30	5.20
$(2,4)(\text{CH}_3)_2\text{C}_6\text{H}_3$	Golden yellow	5.48	5.01	63.60	60.56	5.30	4.95
$(2,4)\text{Cl}_2\text{C}_6\text{H}_3$	New ivory	4.42	4.57	39.84	40.15	1.42	1.40
$(2,6)\text{Cl}_2\text{C}_6\text{H}_3$	Pale cream	4.42	4.28	39.84	39.58	1.42	1.18

Table 2 — Magnetic and Mössbauer Spectral Data of Various Hexacarboxylato Complexes,  $\text{Na}_3[\text{Fe}(\text{OCOR})_6]$  at Room Temperature

R	Mössbauer parameters		$\mu_{\text{eff}}$ B.M.
	Isomer shift* $\delta$ (mms <sup>-1</sup> )	Quadrupole splitting $\Delta E_Q$ (mms <sup>-1</sup> )	
H	0.70	0.22	5.60
$\text{CH}_3$	0.88	0.36	5.10
$\text{C}_2\text{H}_5$	0.60	0.69	6.15
<i>n</i> - $\text{C}_3\text{H}_7$	0.69	0.66	5.27
<i>i</i> - $\text{C}_3\text{H}_7$	0.69	0.44	5.51
$\text{C}_6\text{H}_5\text{CH}_2$	0.72	0.54	6.03
$(\text{C}_6\text{H}_5)_2\text{CH}$	0.60	0.50	5.49
$\text{C}_{10}\text{H}_7\text{CH}_2$	0.66	0.53	5.35
$\text{C}_6\text{H}_5$	0.64	0.43	6.25
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	0.66	0.94	5.28
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$	0.66	0.63	5.80
<i>o</i> - $\text{NH}_2\text{C}_6\text{H}_4$	0.72	0.53	5.90
<i>m</i> - $\text{NH}_2\text{C}_6\text{H}_4$	0.66	0.63	5.27
<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4$	0.64	0.65	5.25
<i>o</i> - $\text{ClC}_6\text{H}_4$	0.69	0.56	5.26
<i>p</i> - $\text{ClC}_6\text{H}_4$	0.71	0.60	5.28
$(2,3)(\text{CH}_3)_2\text{C}_6\text{H}_3$	0.88	0.65	5.10
$(2,4)(\text{CH}_3)_2\text{C}_6\text{H}_3$	1.01	0.69	6.30
$(2,4)\text{Cl}_2\text{C}_6\text{H}_3$	0.69	0.50	5.10
$(2,6)\text{Cl}_2\text{C}_6\text{H}_3$	0.98	0.48	6.07

\*Sodium nitroprusside as standard.

moments were calculated from magnetic susceptibility measurements using Guoy balance<sup>14</sup> and  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the standard.

## Results and Discussion

All the complexes are coloured solids and stable but decompose on storage for long periods. The  $\text{Fe}^{3+}$  is in an octahedral environment with six carboxylates surrounding central iron atom having an electronic configuration  $t_{2g}^3 e_g^2$ , where all five 3d-electrons remain unpaired. Although a regular octahedron is expected but due to large size of the carboxylate ions and the alkyl groups attached to it a distorted geometry may be formed. In the complexes studied here alkyl groups are widely different and hence distortions may be correlated with the nature of alkyl group attached to the carboxylates. If phenyl group is the substituent, then rotation around local  $\text{C}_6\text{H}_5 - \text{C}$  bond may get restricted, thus affecting the local symmetry.

Mössbauer spectra of all the complexes exhibit a well-resolved quadrupole doublet and the values of the parameters,  $\delta$  and  $\Delta E_Q$  are given in Table 2. The line-widths are found to be in the range of 0.21–0.50 mms<sup>-1</sup> but most of them are around 0.40 mms<sup>-1</sup>, which is as expected for  $\text{Fe}^{3+}$  complexes<sup>15</sup>. Some unusually large line-widths may be due to electronic-spin relaxation effects<sup>16</sup>. Mössbauer spectrum of phenylacetato complex at room temperature is shown in Fig. 1 as a typical case.

### Magnetic moments

Magnetic moments of the carboxylato complexes lie in the range of 5.10–6.30 B.M. indicating five unpaired electrons and high spin state of  $\text{Fe}(\text{III})$ . High

Table 3 — Infrared Data of Various Hexacarboxylatoferate(III) Complexes,  $\text{Na}_3[\text{Fe}(\text{OCOR})_6]$ 

R	$\nu_{\text{as}}\text{OCO}$	$\nu_{\text{s}}\text{OCO}$	$\nu\text{C}=\text{O}$	$\delta\text{OCO}$	$\nu\text{C}-\text{C}$	$\nu\text{Fe}-\text{O}$	$\nu\text{C}-\text{H}$	$\Delta\nu_{\text{max}}^*$	Direction of shift*		Other bands
									$\nu_{\text{as}}\text{OCO}$	$\nu_{\text{s}}\text{OCO}$	
H	1580b	1400m	1070m	740sh	920w	420m	2880w	180	ae	1	780m
$\text{CH}_3$	1580m	1370m	1010m	720w	—	420w	2900m	210	ae	1	—
$\text{C}_2\text{H}_5$	1580m	1380m	1070m	660w	810w	410m	2960w	260	ae	1	340w
<i>n</i> - $\text{C}_3\text{H}_7$	1580m	1375w	1095w	665w	890w	400s	2960m	205	ae	1	340w
<i>i</i> - $\text{C}_3\text{H}_7$	1580m	1380w	1100s	660w	930w	400s	2960w	200	ae	1	770m, 840m
$\text{C}_6\text{H}_5\text{CH}_2$	1600w	1330w	1070m	660w	950m	395w	3020w	270	h	1	320w, 840m, 1170w
$(\text{C}_6\text{H}_5)_2\text{CH}$	1595m	1400w	1075w	665w	870w	420s	3040w	195	h	1	325m
$\text{C}_{10}\text{H}_7\text{CH}_2$	1590m	1380w	1070w	660w	870w	430m	3040w	210	h	1	315w
$\text{C}_6\text{H}_5$	1595m	1380w	1070s	670s	935m	420w	3060w	215	h	1	325s, 1170s
<i>o</i> - $\text{CH}_3\text{C}_6\text{H}_4$	1600m	1400w	1080w	660s	920w	420m	2960w	200	h	1	860s, 1155s
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4$	1570w	1380w	1080s	660m	930w	410w	2920w	190	ae	1	840m, 1160w
<i>o</i> - $\text{NH}_2\text{C}_6\text{H}_4$	1600w	1380w	1125w	660m	855w	400vw	—	220	h	1	320m, 1160s, 3460w
<i>m</i> - $\text{NH}_2\text{C}_6\text{H}_4$	1565m	1380m	1060w	660s	—	420vw	—	185	ae	1	320w, 790s, 3400w
<i>p</i> - $\text{NH}_2\text{C}_6\text{H}_4$	1600w	1380w	1125m	660w	850m	400w	—	220	h	1	330w, 1170s, 3460w
<i>o</i> - $\text{ClC}_6\text{H}_4$	1590m	1400s	1040s	645s	850w	420m	2980w	190	h	1	320m, 1160m
<i>p</i> - $\text{ClC}_6\text{H}_4$	1590s	1400m	1090s	680s	850s	410s	2940w	190	h	1	1170m
$(2,3)(\text{CH}_3)_2\text{C}_6\text{H}_3$	1570s	1385s	1110b	685w	850w	490s	2940w	185	ae	1	1175b, 2725w
$(2,4)(\text{CH}_3)_2\text{C}_6\text{H}_3$	1580m	1380s	1110w	780s	880w	430m	2920b	200	ae	1	600s, 1150s
$(2,4)\text{Cl}_2\text{C}_6\text{H}_3$	1580m	1400s	1100s	760w	860m	420s	2920w	180	ae	1	330m, 1160w
$(2,6)\text{Cl}_2\text{C}_6\text{H}_3$	1565b	1375w	1080b	760w	—	450b	2920w	190	ae	1	1195w
$\text{Na}(\text{OCOCH}_3)$	1578	1414						164			

\*Compared with ionic carboxylate such as sodium formate or sodium acetate, s-strong, m-medium, w-weak, vw-very weak, sh-shoulder.

ae = almost equal, l = lower, h = higher.

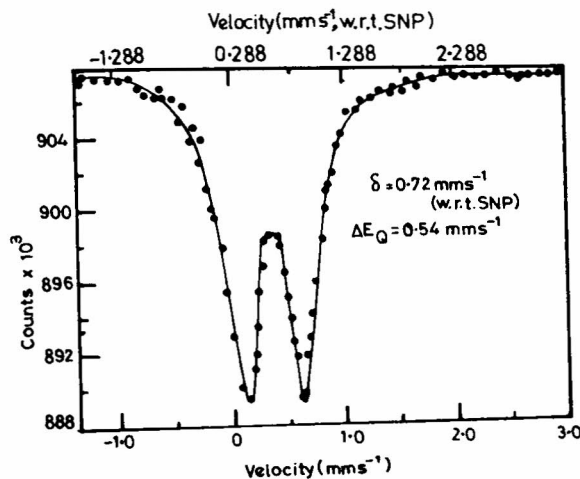


Fig. 1 — Mössbauer spectrum of phenylacetato complex at room temperature

$\mu_{\text{eff}}$  values in some cases may be attributed to (i) some contribution from the alkyl or aryl part of the ligands<sup>14</sup> or (ii) non-quenching of orbital contribution or (iii) from some other magnetic interactions including magnetically non-equivalent sites in a unit

cell<sup>17</sup>. However, the possibility of multiple-centre bonds cannot be ruled out altogether even though there is no direct evidence for it.

#### Infrared spectra

Infrared spectra of a wide variety of carboxylates of different metal ions have been recorded and discussed<sup>2,16-22</sup>. Most important vibrational modes affected by coordination are  $\nu_{\text{as}}(\text{OCO})$ ,  $\nu_{\text{s}}(\text{OCO})$  and  $\delta(\text{OCO})$  which are observed in the regions 1600-1565, 1400-1330 and 740-645  $\text{cm}^{-1}$  respectively (Table 3). It has been suggested that the magnitude of separation,  $\Delta\nu [= \nu_{\text{s}}(\text{OCO}) - \nu_{\text{as}}(\text{OCO})]$  should be higher for unidentate carboxylate ligands as compared to those for simple ionic carboxylates<sup>20-24</sup>. In Table 3 are given  $\Delta\nu$  values and the direction of shifts in  $\nu_{\text{as}}(\text{OCO})$  and  $\nu_{\text{s}}(\text{OCO})$  for individual carboxylate complexes. It is observed that in all carboxylate complexes studied here  $\Delta\nu$  values (180-270  $\text{cm}^{-1}$ ) are always higher than that for sodium acetate (164  $\text{cm}^{-1}$ ) which is purely ionic carboxylate. This indicates unidentate nature of the carboxylate ligand.

It has also been shown that the shift of  $\nu_{as}(\text{OCO})$  modes of coordinated unidentate carboxylate ligand should be almost equal or higher whereas that of  $\nu_s(\text{OCO})$  should be lower as compared to the corresponding modes in simple ionic carboxylate<sup>2,22</sup>. In all the cases studied here it is observed that  $\nu_{as}(\text{OCO})$  modes appear either at higher wavenumber or at the same wavenumber with respect to sodium acetate as reference. Similarly,  $\nu_s(\text{OCO})$  modes appear at lower wavenumber in all the hexacarboxylato complexes as compared to that of sodium acetate. Therefore, the criterion of direction of shifts also indicates a unidentate nature of the carboxylate ligands<sup>21,23</sup>. Though, the two criteria of the magnitude of separation ( $\Delta\nu$ ) and the direction of shift in  $\nu\text{-CO}$  modes are basically qualitative in nature, these are definitely indicative of the coordinating nature of the carboxylate ligands.

The  $\nu\text{Fe-O}$  modes in the compounds studied presently appear in the region  $490\text{-}395\text{ cm}^{-1}$ . Except for 2,3-dimethylbenzoato and 2,6-dichlorobenzoato complexes in which  $\nu\text{Fe-O}$  modes appear at  $490$  and  $450\text{ cm}^{-1}$  respectively, in most of the other complexes  $\nu\text{Fe-O}$  modes appear  $\sim 400\text{ cm}^{-1}$ . It is also observed that in aliphatic carboxylates (from formato to phenylacetato) there is a continuous decrease in  $\nu\text{Fe-O}$  modes, probably due to the bulk effect. The  $\nu\text{C=O}$ ,  $\nu\text{C-C}$  and  $\nu\text{C-H}$  modes observed in the range  $1125\text{-}1010$ ,  $950\text{-}810$  and  $3060\text{-}2880\text{ cm}^{-1}$  respectively, are in agreement with those reported in the literature<sup>18,19</sup>.

#### Mössbauer parameters

All the complexes give well-resolved doublet with isomer shift values ( $\delta$ ) in the range  $0.60\text{-}1.01\text{ mms}^{-1}$  (sodium nitroprusside as the reference) indicating Fe(III) in high spin state. For aliphatic carboxylate complexes  $\delta$  varies in a narrow range of  $0.60\text{-}0.88\text{ mms}^{-1}$  and increases in the order  $\text{C}_2\text{H}_5 < n\text{-C}_3\text{H}_7 < \text{H} < \text{CH}_3$ . For aryl substituted acetato complexes  $\text{Na}_3[\text{Fe}(\text{OCOCH}_2\text{C}_6\text{H}_5)_6]$ ,  $\text{Na}_3[\text{Fe}(\text{O-COCH}(\text{C}_6\text{H}_5)_2)_6]$  and  $\text{Na}_3[\text{Fe}(\text{OCOCH}_2\text{C}_{10}\text{H}_7)_6]$ ,  $\delta$  values are found to be  $0.72$ ,  $0.60$  and  $0.66\text{ mms}^{-1}$  respectively. The small change in  $s$ -electron density at the iron nucleus may be attributed to  $\pi$ -resonance in benzene ring as a result of which some electronic charge may be donated to the  $d$ -orbitals of the iron atom resulting in variation in isomer shift values. For benzoato complex,  $\delta = 0.64\text{ mms}^{-1}$  is observed which is the lowest amongst benzene substituted complexes. For monosubstituted benzoic acid complexes,  $\delta$  varies in the range of  $0.64\text{-}0.72\text{ mms}^{-1}$ . Substitution at  $o$ -position with  $-\text{CH}_3$ ,  $-\text{NH}_2$  and  $-\text{Cl}$  groups leads to  $\delta$  values of  $0.66$ ,  $0.72$  and  $0.69\text{ mms}^{-1}$  respectively. For disubstituted complexes  $\delta$

values are comparatively higher indicating that  $s$ -electron density at the iron nucleus is affected by disubstitution. Incidentally, disubstituted phenylcarboxylato complexes not only give higher  $\delta$  values but also their  $\nu\text{Fe-O}$  modes appear at higher wavenumbers. Presumably, disubstitution in benzene ring may be affecting the nature of Fe-O bond to some extent. Inoue *et al.*<sup>26</sup> have also observed similar variations in alkyl phosphine and phosphite substituted pentacyanoferrates and explained their observations due to Hammett substituent constants. This mechanism could not be invoked here because substituents are not directly linked to the metal ion. However, the isomer shift values and metal-ligand stretching vibrations are equally affected by the substitution of heavier alkyl groups in ligands irrespective of low or high spin nature of iron(III) complexes<sup>26</sup>.

In the case of point charges surrounding Fe(III) ion in an octahedral geometry, no quadrupole splitting is expected because all the five electrons are equally populated. However, carboxylate ligands are large enough to cause distortions and hence a net electric field gradient (EFG) is generated due to ligand contribution giving rise to quadrupole splitting. In the presently studied complexes,  $\Delta E_Q$  is in the range of  $0.22$  to  $0.94\text{ mms}^{-1}$  indicating distortions in the octahedral geometry varying with the nature of alkyl group attached to the carboxylate<sup>26</sup>. Some workers<sup>13,27</sup> have attributed variations in  $\Delta E_Q$  values due to change in outer cations in similar type of complexes. In the present studies, variations have been affected in the ligands attached to the central ion. A minimum value of  $\Delta E_Q = 0.22\text{ mms}^{-1}$  was observed for formato complex and a maximum  $\Delta E_Q = 0.94\text{ mms}^{-1}$  for  $o$ -toluato complex. Similar variations have been observed by Inoue *et al.*<sup>26</sup> and attributed to the nature of alkyl group attached to the ligand. In a series of aliphatic carboxylato complexes,  $\Delta E_Q$  values increase in the order  $\text{H} < \text{CH}_3 < i\text{-C}_3\text{H}_7 < n\text{-C}_3\text{H}_7 < \text{C}_2\text{H}_5$ . The difference in  $\Delta E_Q$  value for  $i$ -butyrato and  $n$ -butyrato complexes may be due to the effect of branching in the chain which is expected to cause large distortions. For the substituted acetato complexes [ $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$ ,  $(\text{C}_6\text{H}_5)_2\text{CH}$  and  $\text{C}_{10}\text{H}_7\text{CH}_2$ ],  $\Delta E_Q$  values are found to be almost the same ( $0.54$ ,  $0.50$  and  $0.53\text{ mms}^{-1}$ ). It seems that the substitution in the phenyl nucleus with heavier groups distort the geometry changing local symmetry only to a certain extent after which it remains unaffected. Also the distortion does not seem to be in a regular manner. Gupta *et al.*<sup>8</sup> and Manesh *et al.*<sup>28</sup> have also made similar observations in a series of chloro substituted Fe(III) acetato complexes.

For benzoato complex  $\Delta E_Q = 0.43 \text{ mms}^{-1}$  which is comparatively small for large size of the carboxylato group. Presumably  $\pi$ -electrons in benzene ring may be interacting with  $p\pi$ -orbitals of the carbon atom  $\text{OCO}^-$ , thus restricting the free rotation of the  $\text{C}_6\text{H}_5-\text{C}$  bond.

It would also keep the aryl group planar with respect to carbon atom of the carboxylate ligand. When  $o$ -position is substituted with  $\text{CH}_3$ ,  $\text{NH}_2$  and  $\text{Cl}$  groups  $\Delta E_Q$  values are 0.94, 0.53 and 0.56  $\text{mms}^{-1}$  respectively. The largest value for  $\text{CH}_3$ -substituted complex may be attributed to its bulky nature and the fact that rotation around  $\text{C}_6\text{H}_5-\text{C}$  bond may become free which may not be the case with  $\text{NH}_2$  and  $\text{Cl}$  substituents. It is interesting to see that  $\Delta E_Q$  values for  $m$ -substituted benzoato complexes having  $\text{CH}_3$  and  $\text{NH}_2$  substituents are the same. It means that in  $m$ -position,  $\text{CH}_3$  group no longer influences the  $\Delta E_Q$  due to its bulky character. The  $\Delta E_Q$  of 2,3- or 2,4-dimethylbenzoato and of 2,6-dichlorobenzoato complexes are comparatively small, suggesting that the distortion in the geometry of the complexes is not affected by further substitution in the phenyl ring.

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