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Mössbauer Spectra of Ferrous Fumarate

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Mössbauer spectra of ferrous fumarate $Fe(HCCOO)_2$ show two lines, at various temperatures. The results are explained on the basis of the earlier proposed polymeric distorted octahedral structure.

Introduction

Mössbauer investigations for ferrous complexes of various monobasic and dibasic organic acids *e.g.* formic acid,[1] oxalic acid[2-4] and gluconic acid[5] etc. have been reported in literature. But so far no studies have been done with complexes of fumaric acid which is a peculiar dibasic acid having trans configuration. It acts almost as a monobasic acid and bidentate ligand.[6] Recently Prabhakaran and Patel[7] have studied its magnetic and spectral properties and suggested a polymeric and distorted octahedral structure. We have studied the Mössbauer spectra of this compound at four temperatures, from room temperature down to that of liquid nitrogen, for a better understanding of its geometry and structure.

Experimental Section

Ferrous fumarate was obtained through the courtesy of Professor C.C. Patel of Indian Institute of Science, Bangalore. The experimental details of the velocity drive, sample mounting and cryoscopic arrangements were the same as reported earlier.[8] ^{57}Co in Cu matrix (~ 1 mC) was used as a source. It was kept stationary and always at room temperature. The data were analysed by least squares fit using CDC 3600 computer at TIFR, Bombay.

Results and Discussion

Ferrous fumarate gave a two line spectrum indicating large quadrupole splittings at all the temperatures. A representative spectrum at room temperature is shown in Figure 1. The parameters derived from these spectra are given in Table I. The values of Debye-Waller factors (f_a) for the compound at different temperatures were calculated using the relation

$$A = 0.6\pi\left(\frac{C}{E_0}\right)f_s[\Gamma' + 0.20n\sigma_0\Gamma f_a]$$

where all the notations have their usual meaning. The value of f_s for the source at room temperature was taken to be 0.71 from literature.[9]

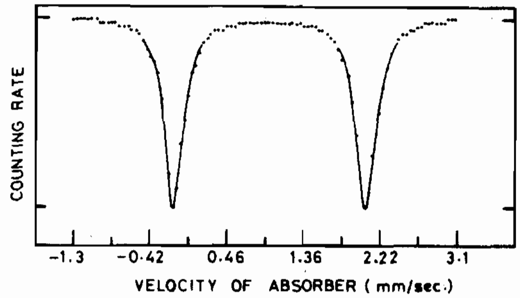

Figure 1. Mössbauer spectra of ferrous fumarate at room temperature.

Recently Prabhakaran and Patel[7] have proposed a polymeric and distorted octahedral structure for the compound (Figure 2). They have indicated, by X-ray diffraction studies, that ferrous fumarate has orthorhombic nature of the unit cell. The observed value of magnetic moment is 5.18 B.M. suggesting that Fe^{2+} forms a high spin compound with distorted octahedral or tetrahedral structure. Infrared evidence shows that the carboxylate group of the fumaric acid acts as a bidentate ligand. Beside this a band at 10,530 cm^{-1} in the electronic absorption spectrum has been assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition. On the other hand tetrahedral ferrous compounds give a spin allowed *d–d* band at a much lower energy (~ 5500 cm^{-1}).

Edward, Johnson, and Williams[10] have suggested from the studies of several tetrahedral iron(II) compounds, that a comparative study of compounds having similar isomer shift data can indicate their coordination number. The value of isomer shift in-

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(3) F. de S. Barros, P. Zory, and L.E. Campbell, *Phys. Lett.*, *7*, 153 (1963).
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(5) K. Kisganska, M. Kopcewicz, S. Ligenza, and J. Pickoszewski, *Nuckleonika*, *13*, 969 (1968).
(6) L. Korecz and K. Burger, *Acta. Chem. Acad. Sci. Hung.*, *58*, 253 (1968).
(7) C.P. Prabhakaran and C.C. Patel, *Ind. J. Chem.*, *7*, 266 (1969).
(8) A.N. Garg and P.S. Goel, *J. Inorg. Nucl. Chem.*, *31*, 697 (1969); *ibid.*, *32*, 1547 (1970); A.N. Garg, Ph.D. Thesis, Indian Institute of Technology Kanpur, 1970.
(9) R.M. Housley, J.G. Dash, and R.H. Nussbaum, *Phys. Rev.*, *136*, A464 (1964).
(10) P.R. Edwards, C.E. Johnson and R.J.P. Williams, *J. Chem. Phys.*, *47*, 2074 (1967).

Table I. Mössbauer parameters for ferrous fumarate.

Temperature (°K)	Isomer shift* δ(mm/sec)	Quadrupole splitting ΔE_Q(mm/sec)	Linewidths (FWHM) Γ_1 and Γ_2 (mm/sec)		Debye-Waller factor (fa)
300	1.40 ± 0.01	2.183 ± 0.01	0.276,	0.290	0.143
200	1.31 ± 0.01	2.330 ± 0.01	0.328,	0.336	0.101
160	1.32 ± 0.01	2.242 ± 0.01	0.232,	0.232	0.179
80	1.263 ± 0.014	2.148 ± 0.01	0.450,	0.334	0.175

* These values, originally calculated from spectra taken with ^{57}Co (Cu) source at room temperature, were converted relative to sodium nitroprusside dihydrate as standard by adding 0.48 mm/sec.

creases as the coordination number of the iron atom increases. For ferrous formate[1] and ferrous oxalate,[4] which have the same carboxylate ligands attached to the iron atom, the isomer shift values are reported to be ~1.40 mm/sec at room temperature. Ferrous fumarate gives $\delta=1.40\pm0.01$ mm/sec, thus consistent with its having the octahedral symmetry.

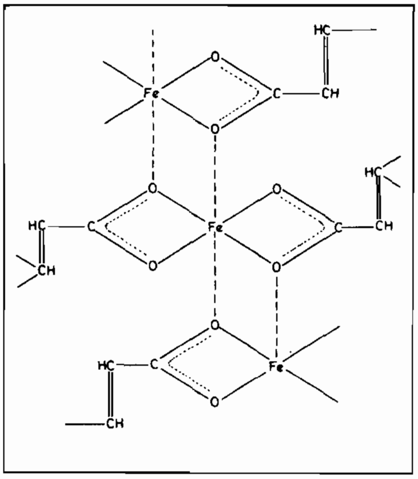

Figure 2. Structure of ferrous fumarate (see Prabhakaran and Patel, *Ind. J. Chem.*, *7*, 266 (1969).

In general, the value of quadrupole splitting is larger for an octahedral than for a tetrahedral compound. Experimental data for tetrahedral compounds having similar ligands, are not available for comparison. But the ΔE_Q value for ferrous fumarate is definitely larger in comparison with that of the other tetrahedral compounds. This also supports an octahedral symmetry.

In high spin octahedral complexes the energy separation (10 Dq) between t_{2g} and e_g levels is ~10,000 cm^{-1} which is comparable to the observed value of 10,530 cm^{-1} in the present case. The electronic configuration is $t_{2g}^4\ e_g^2$ and the ground state is ^{5}D. Thus the sixth odd *d*-electron will be responsible for net EFG at the iron nucleus. However, lattice contribution will also be there due to distortions in the octahedral symmetry.

Ferrous fumarate gives very large value of quadrupole splitting ($\Delta E_Q=2.18\pm0.01$ mm/sec at room temp.) which is well within the characteristic range of high spin ferrous compounds. As shown in Figure 3, the value of ΔE_Q increases slightly as we decrease the temperature and then again decreases approaching almost the same value at liquid nitrogen temperature. This very small temperature dependence suggests that Δ, the energy difference between the t_{2g} ground level and the next higher t_{2g} level is quite large. Ingalls[11] has reported similar behaviour for other octahedral compounds $FeC_2O_4 . 4H_2O$ and $FeCl_2 . 4H_2O$. Axtman, Hazony and Hurley[12] have estimated that in such cases $500\ cm^{-1} < \Delta < 800\ cm^{-1}$. The first excited state is so much raised relative to the ground state that the odd electron population is not affected by lowering the temperature. Ingalls[12] and Hoy and Barros[1] have calculated the ground state orbital wave function for ferrous oxalate and ferrous formate to be $|XY>$ and since ferrous fumarate shows similar behaviour, the same ground state wave function can be assumed for this compound as well.

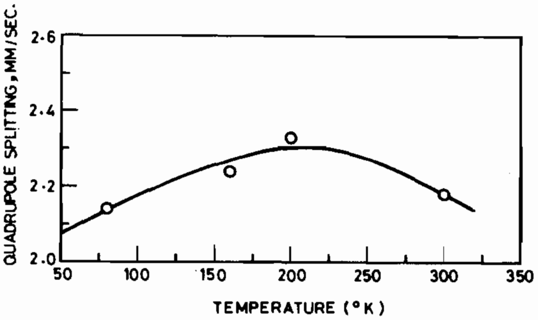

Figure 3. Variation of quadrupole splitting with temperature.

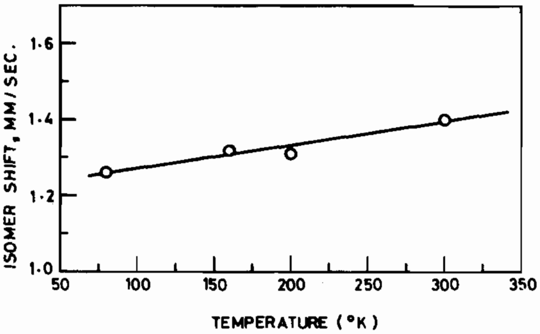

Figure 4. Variation of isomer shift with temperature.

In Figure 4 is shown the variation of isomer shift with temperature. The value of δ decreases with

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(11) R. Ingalls, *Phys. Rev.*, *133*, A787 (1964).

(12) R.C. Axtmann, Y. Hazony, and J.W. Hurley, Jr., *J. Chem. Phys.*, *52*, 3309 (1970).

the decrease in temperature with small temperature gradient, $\partial\delta/\partial T = -6.36 \times 10^{-3}$ mm/sec/°K. This is in opposition to the usually observed variation for normal cases. A plausible explanation for this trend could be given in terms of a possible change in crystal symmetry of the complex at lower temperatures. Perhaps further studies at still lower temperatures may help to elucidate this possibility.

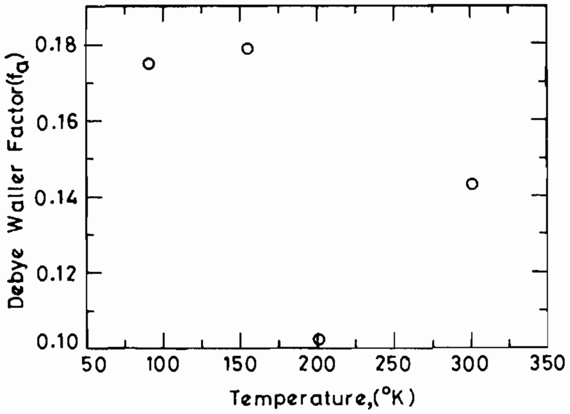

Figure 5. Variation of Debye-Waller factor (fa) with temperature.

The temperature dependence of Debye-Waller factor (f_a) as shown in Figure 5 appears to indicate a general increase with decreasing temperature. This is similar to the observations of Stöckler[13] on polymeric organotin compounds. Lack of data on other polymeric iron compounrs does not permit us to make any more meaningful conclusions.

Acknowledgments. We are grateful to Professor C.C. Patel of the Indian Institute of Science, Bangalore for providing us the compound and to Mr. R. Nagarajan of TIFR, Bombay for computer analysis of the data.

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