TABLE 1 — YIELD OF FORMALDEHYDE IN THE ^{60}Co γ-RAY IRRADIATED BARIUM, CALCIUM AND LEAD FORMATES

Total dose Mrad	$Ba(HCOO)_2$		$Ca(HCOO)_2$		$Pb(HCOO)_2$	
	ppm (HCHO)	G (HCHO)	ppm (HCHO)	G (HCHO)	ppm (HCHO)	G (HCHO)
5·00	48·7	12·5	30·7	7·9	—	—
10·00	70·0	9·7	61·5	7·9	—	—
12·09	—	—	—	—	21·8	2·3
15·00	99·1	8·3	83·3	7·1	—	—
25·00	110·9	5·8	108·8	5·6	—	—
50·40	—	—	—	—	37·2	1·0
125·00	—	—	—	—	32·7	0·3

amount of elementary carbon was also produced. The analysis of solid products of thermal decomposition of the formates[4] supports the observations.

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Mössbauer Study of Acetate & Chloride-Acetate of Fe(III)

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Mössbauer study of the high spin monochloro bisacetate of Fe(III) [Fe(CH₃COO)₂Cl], the triacetate [Fe₃(CHCOO)₃](CH₆COO)₃.6H₂O, and the basic acetate [Fe₃O(CH₃COO)₆.3H₃O](CH₃COO) has been made at room temperature. Monochlorobisacetate Fe(III) is assigned a square-pyramidal structure with sp^3d bonding and the results obtained for the triacetate and the basic acetate of Fe(III) are in agreement with those reported.

MATHUR and Gupta[1] studied the Mössbauer spectra of Fe(acac)$_2$Cl and Fe(acac)Cl$_2$ (acac = acetylacetone) to determine the bonding and the structure of these Fe(III) high spin complexes. However, a reexamination of the spectrum of Fe(acac)$_2$Cl by Cox[2] showed that this complex has a square-pyramidal structure in which Fe(III) is pentacoordinated, instead a symmetrical tetrahedral structure assigned by Mathur and Gupta[1]. In view of some ambiguity regarding the structrue[3-5] of the basic ferric acetate, we have prepared chloride

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acetate derivative of Fe(III) and have studied its Mössbauer spectrum. Our observations agree with those of Duncan et al.[4] and Malathi and Puri[5].

The Mössbauer spectra were taken on a constant velocity cam drive set-up in transmission geometry. The source was a 5 mCi ^{57}Fe in stainless steel (SS) matrix. The counts accumulated at each velocity were 7×10^4 or more. The infrared spectrum of Fe(CH$_3$COO)$_2$Cl was also recorded to obtain information on bond formation.

The Mössbauer spectra, at room temperature, are shown in Fig. 1 and the derived parameters along with those of others are given in Table 1. The δ-values listed in Table 1 characterize these complexes to be high spin complexes[6]. A comparison of δ (Table 1) of Fe(CH$_3$COO)$_2$Cl complex with Fe(acac)$_2$Cl studied by Cox[2] shows that both are high spin complexes. The doublet asymmetry observed by us suggests a positive V_{zz} in conformity with that
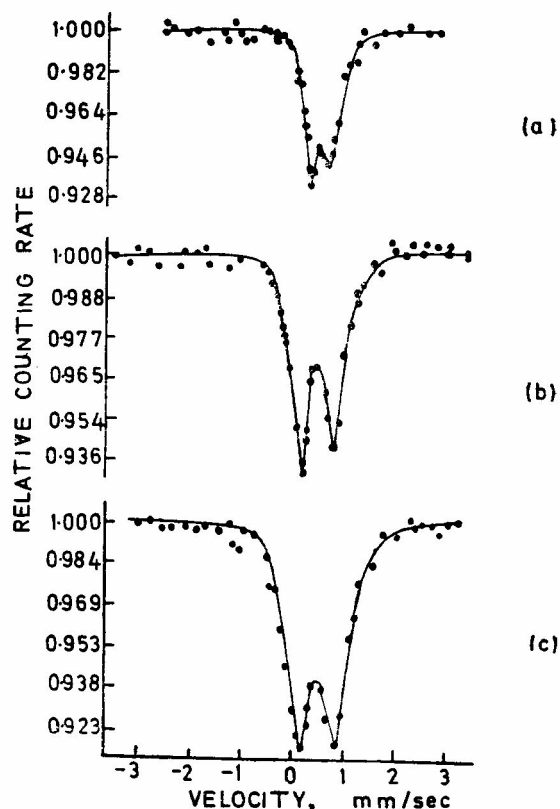

Fig. 1 — Mössbauer spectra of (a) monochlorobisacetate, (b) the triacetate and (c) the basic acetate of Fe(III)

TABLE 1 — EXPERIMENTALLY OBSERVED MÖSSBAUER
PARAMETERS FOR Fe(III) COMPLEXES AT ROOM TEMPERATURE

Sr. No.	ΔE_Q (mm/sec)	δ (mm/sec) relative to Fe	Fractional 4s- population by ligands	V_{zz}
	Fe(CH$_3$COO)$_2$Cl			
1	0·30±0·03	0·42±0·03	0·310	+
	Fe(acac)$_2$Cl			
2	1·0	0·32	0·370*	+
	[Fe$_3$O(CH$_3$COO)$_3$3H$_2$O](CH$_3$COO)			
3	0·68±0·03	0·45±0·03	0·290	0
	0·63±0·03	0·40±0·02	0·315*	0
	0·43±0·73	0·43±0·45	0·30-0·275*	0
	0·61	0·38±0·01	0·325	
	[Fe$_3$(CH$_3$COO)$_6$](CH$_3$COO)$_3$.6H$_2$O			
4	0·61±0·03	0·40±0·03	0·310	+
	0·69±0·03	0·38±0·02	0·325*	0

*As read from the calibration plot (7).

Fig. 2 — Proposed square-pyramidal structure for mono-chlorobisacetate Fe(III)

of Cox[2] for Fe(acac)$_2$Cl. Furthermore, it was possible to establish the lines in the quadrupole spectrum of Fe(CH$_3$COO)$_2$Cl (Fig. 1a) to π or σ transitions without resorting to the study of the angular dependence of the ratios of the areas in monocrystals. This complex being a polycrystalline powder its Mössbauer spectrum was also recorded by placing it in an external magnetic field of ≈ 15 kOe. This only resulted in slight broadening of the two lines, and indicated that the magnetic interaction was comparable in magnitude to quadrupole interaction. An analysis[8,9] of broadening of the lines showed that the left-hand line in the spectrum (Fig. 1a) corresponded to $\frac{3}{2}\rightarrow\frac{1}{2}$ transition resulting in positive V_{zz}. The positive V_{zz} was explained on the basis of a square-pyramidal array of ligands which have more negative charge in the x-y plane than in the pyramidal axis. Thus it was possible to propose square-pyramidal structure for the Fe(CH$_3$COO)$_2$Cl complex as shown in Fig. 2. sp^3d is the expected[10] hybridization in this structure involving $d_{x^2-y^2}$ orbital which is at a higher energy level as compared to the d_{z^2} orbital.

Our results on basic ferric acetate [Fe$_3$O(CH$_3$COO)$_6$ 3H$_2$O]CH$_3$COO at room temperature support the work of Duncan et al.[4] and Malathi and Puri[5] who proposed an equilateral triangular structure with iron sites in octahedral symmetry and contradicted the linear chain structure of Takashima and Tateshi[3]. Recently Rumbold and Wilson[10] have also reported Mössbauer study of basic ferric acetate and our values of δ and ΔE_Q agree with those reported by these workers. However, they have reported a line asymmetry of about 9% which they ascribed to Goldanskii-Karyagin effect. In the case of ferric acetate we too observed a doublet asymmetry of about 10%. The possibility of these asymmetries arising from accidental preferred crystal orientation in the samples have been excluded. These asymmetries may be attributed to the localized distortions
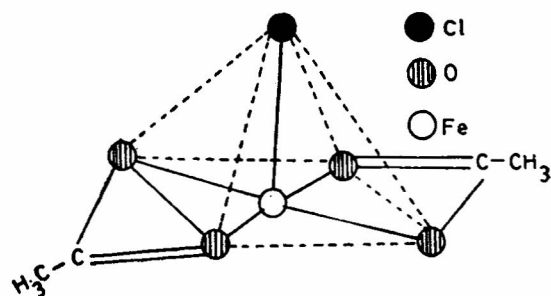
in the octahedral symmetry of the three iron sites which may render the sites to be slightly inequivalent.

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Heat of Transport of Water in Bentonite

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The values of heat of transport of water, as calculated from the thermo-osmotic pressure data, in the bentonite-water system have been found to be extremely low in comparison to the activation energy of flow processes. The activation energy in the present case may be related to changes in hydrogen bonding rather than any specific mechanism of flow.

THERMO-OSMOSIS of water through bentonite has been reported earlier[1]. It has been shown that heat of transport of water in such a system may vary in a complex exponential with the difference in applied pressure. However, the values of heat of transport were not calculated. In order to discuss the very low values of heat of transport, Q^*, in comparison to the activation energy, E, the

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