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 4*s*-population by ligands	V_{zz}
		$Fe(CH_3COO)_2Cl$		
1	$0{\cdot}30 \pm 0{\cdot}03$	$0{\cdot}42 \pm 0{\cdot}03$	0·310	+
		$Fe(acac)_2Cl$		
2	1·0	0·32	0·370*	+
		$[Fe_3O(CH_3COO)_33H_2O](CH_3COO)$		
3	$0{\cdot}68 \pm 0{\cdot}03$	$0{\cdot}45 \pm 0{\cdot}03$	0·290	0
	$0{\cdot}63 \pm 0{\cdot}03$	$0{\cdot}40 \pm 0{\cdot}02$	0·315*	0
	$0{\cdot}43 \pm 0{\cdot}73$	$0{\cdot}43 \pm 0{\cdot}45$	0·30-0·275*	0
	0·61	$0{\cdot}38 \pm 0{\cdot}01$	0·325	
		$[Fe_3(CH_3COO)_6](CH_3COO)_3.6H_2O$		
4	$0{\cdot}61 \pm 0{\cdot}03$	$0{\cdot}40 \pm 0{\cdot}03$	0·310	+
	$0{\cdot}69 \pm 0{\cdot}03$	$0{\cdot}38 \pm 0{\cdot}02$	0·325*	0

*As read from the calibration plot (7).

of Cox[2] for $Fe(acac)_2Cl$. Furthermore, it was possible to establish the lines in the quadrupole spectrum of $Fe(CH_3COO)_2Cl$ (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 $Fe(CH_3COO)_2Cl$ 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 $[Fe_3O(CH_3COO)_6 3H_2O]CH_3COO$ 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.

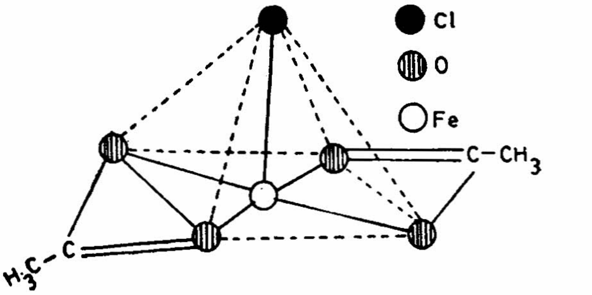

Fig. 2 — Proposed square-pyramidal structure for monochlorobisacetate Fe(III)

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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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values of Q^*, and E have been calculated from the data reported in our previous paper[1].

Eq. (1) relates the water flux J_w when pressure, difference ΔP and temperature difference ΔT are simultaneously operating on the system.

$$J_w = -L_{11}\frac{v}{T}[\Delta P-\Delta P_0\{1-\exp(-\Delta P/\Delta P_0)\}] + L_{12}\left(\frac{-\Delta T}{T^2}\right) \quad ...(1)$$

$$J^q = L_{21}\left(\frac{-v\Delta P}{T}\right)+L_{22}\left(\frac{-\Delta T}{T^2}\right) \quad ...(2)$$

Assuming the validity of Eq. (2) which relates[2] the heat flux, J_q, in the presence of both ΔP and ΔT, and Onsager's reciprocal relation, the equation showing connection between heat of transport and thermo-osmotic pressure can be written as (Eq. 3):

$$\left(\frac{[\Delta P-\Delta P_0\{1-\exp(-\Delta P/\Delta P_0)\}]}{\Delta T}\right)_{J_{w=0}} = -\frac{Q^*}{vT} \quad ...(3)$$

In the region where $\Delta P \gg \Delta P_0$ Eq. (3) reduces to linear form

$$\left(\frac{\Delta P-\Delta P_0}{\Delta T}\right)_{J_{w=0}} = -\frac{Q^*}{vT} \quad ...(4)$$

In Eqs. (1) to (4), ΔP_0 is the extrapolated intercept on the ΔP-axis, v is the specific volume of water and L_{ik} are the phenomenological coefficients. For the sake of simplicity the present discussion is confined to the linear region where Eq. (4) holds good. The values of Q^* have been calculated from Eq. (4).

It is evident from Eq. (4) that $(\overline{\Delta P-\Delta P_0/\Delta T})J_{w=0}$ should decrease with increase in temperature. This is found to be true. Although L_{12} has been shown[1] to be more or less invariant with T, both L_{11} and specific volume increase with increase in temperature. The values of Q^* are recorded in Table 1. The values of heat of transport, defined[2] as $Q^* = L_{21}/L_{11}$, show a decreasing trend with increase in temperature.

The activation energy for water flow through bentonite has been calculated by a procedure similar to that used earlier[3]. The value of E estimated from the temperature-dependence data of water flow comes out to be 10·13 kcal/mole which is very high in comparison to the values of Q^* given in Table 1. A similar trend has been noticed earlier[3,4] and the explanation provided earlier holds good for the present system also.

The very low values of heat of transport in the present system suggest that molecules involved in diffusion jumps do not have to gather appreciable energy by forming bonds again at new equilibrium sites. But instead the flow appears to be governed by such fraction of water molecules as are quite free from bonds of any kind and are mobile. This is achieved through thermal motion when some of the hydrogen bonds in hydrogen-bonded water molecules break down. It also appears that the mechanism of heat of transport is not related to activation energy in the present case. These interpretations are in agreement with the previous views[3,4] that activation energy in such a system reflects changes in hydrogen bond rather than any specific mechanism of flow.

TABLE 1 — DEPENDENCE OF $(\overline{\Delta P-\Delta P_0/\Delta T})J_{w=0}$ AND Q^* ON TEMPERATURE

Temperature (°K)	$(\overline{\Delta P-\Delta P_0/\Delta T})J_{w=0}$ $\times 10^{-5}$ (dyne cm^{-2} deg^{-1})	Q^* (cal/mole)
308	0·0893	0·0658
313	0·0627	0·0469
318	0·0480	0·0369
323	0·0387	0·0299

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Sorption of Radioiodine on Bismuth Hydroxide

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The sorption characteristics of bismuth hydroxide for the removal of radioiodine from aqueous solutions have been evaluated under different conditions of *p*H, time and amounts of sorbent used. Effect of competing anions such as chloride, nitrate, sulphate and phosphate on the sorption equilibrium has also been studied. The distribution coefficient (*K_d*), has been found to be of the order of 4×10^4 suggesting the utility of the sorbent in the decontamination of radioactive waste waters generated in the nuclear power plants.

RADIOIODINE (^{131}I) is produced as a result of fission process in nuclear reactors. In the event of fuel failures, iodine finds its way into the coolant and consequently appears in the radioactive liquid effluents. Its removal is important from the radiation safety point of view.

Sorption of ^{131}I on a number of sorbents has been described in a series of papers[1-8]. Removal of radioiodine by coprecipitation with lead sulfate was tried by Cohen[9]. Bismuth hydroxide has a tendency to adsorb strongly the acid anions. Based on this, its sorption characteristics for the removal of radioiodine from aq. solutions were studied in detail and the results are reported in this note.

The sorbent was prepared by the dropwise addition of $1M$ NaOH to $0{\cdot}1M$ bismuth nitrate with constant stirring at $28 \pm 3°$. After the precipitation was complete at *p*H 5·6, the mixture was kept overnight for settling. It was filtered through Whatman No. 42 filter paper, washed with distilled water,