

# MÖSSBAUER STUDY OF IRON (III) SALICYLATES

K. MAHESH, N. D. SHARMA\* and D. C. GUPTA

*Department of Physics, Kurukshetra University, Kurukshetra—132119*

*and*

D. M. PURI

*Department of Chemistry, Kurukshetra University, Kurukshetra—132119*

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Mössbauer infrared and magnetic studies of different basic salicylates of iron(III) are reported. Comparison of observed isomer shift and quadrupole splitting with the earlier work allows us to assign the trinuclear chain structure to the complexes wherein the central iron atom in the chain is considered to be octahedrally coordinated in case of salicylate and 4-aminosalicylate derivatives, and pentacoordinated for the thiosalicylate with the terminal iron atoms in tetrahedral symmetry. The Mössbauer parameters and  $\mu_{\text{eff}}$  - values indicate the high spin state of the central iron atom and low spin state for the terminal ones.

## INTRODUCTION

TAKASHIMA and Tateishi (1965) reported a preliminary Mössbauer study for the iron (III) salicylate at room temperature. Due to the absence of further work on this complex and to obtain more detailed information, it was considered worthwhile to prepare a series of three complexes of iron (III) salicylate, (i) basic ferric salicylate, (ii) basic ferric thiosalicylate and (iii) basic ferric 4-aminosalicylate and make a Mössbauer study of the same. Comparison of our data with that of Takashima and Tateishi (1965) and from the measured range of values of Mössbauer and magnetic parameters, it is possible to support the trinuclear structure in conformity with that proposed by them for the basic ferric salicylate.

## MATERIALS AND METHODS

Ferric chloride (BDH) was analysed before use. The organic ligands—salicylic acid, thiosalicylic acid and 4-amino salicylic acid were of high purity and were used as such. Molecular weight of the the complexes has been determined using Gallankamp Semi-micro Ebulliometer. Infrared spectra were recorded on Beckman IR-20 spectrophotometer in nujol mull.

The method of preparation of the complexes was essentially the same as followed by Takashima and Tateishi (1965). To an aqueous solution of the sodium-salts of the different salicylic acids, about 40ml of ether and an aqueous solution of iron (III) chloride was added. The mixture was allowed to stand for several hours. The precipitate formed was filtered and dried over calcium chloride. The effect of the presence of ether causes the solubility of the complex compounds to decrease, thus increasing the yield. Further, it helps in increasing the purity of the complex by keeping

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\*Present address : Mosul University, Mosul, IRAQ.

TABLE I  
Chemical analysis of the complexes

Sl. No.	Acid	Analysis				Molecular formula of the complexes	Colour		
		Fe (%)		C (%)				H (%)	
		Found	Cal.	Found	Cal.			Found	Cal.
1.	Basic ferric salicylate	13.66	13.79	49.89	50.64	3.14	3.18	$[\text{Fe}_2(\text{OC}_6\text{H}_4\text{COOH})_6(\text{OH})_2] \cdot (\text{OC}_6\text{H}_4\text{COOH})$	Red solid.
2.	Basic ferric thiosalicylate	16.09	16.23	39.19	40.03	3.84	3.43	$[\text{Fe}_2(\text{SC}_6\text{H}_4\text{COOH})_6(\text{OH})_2] \cdot \text{OH} \cdot 3\text{H}_2\text{O}$	Dirty yellow
3.	Basic ferric 4-amino-salicylate	11.45	11.81	41.69	41.45	3.74	3.63	$[\text{Fe}_2(\text{OC}_6\text{H}_3(\text{NH}_2)\text{COOH})_6(\text{OH})_2] \cdot (\text{OC}_6\text{H}_3(\text{NH}_2)\text{COOH}) \cdot 9\text{H}_2\text{O}$	Dark violet red.

the organic complexing agent soluble. Chemical analysis for the complexes was done by standard methods for iron, hydrogen and carbon and is given in Table I.

The Mössbauer spectra of the complexes were taken at room temperature on the constant velocity cam drive set-up using single channel analyser and separate scalar-recorder for positive and negative velocities. The counts accumulated at each velocity point were 70,000 or more. The source used was a 5mCi—Co<sup>57</sup> in stainless steel matrix. The isomer shifts ( $\delta_{Fe}$ ) given refer to metallic iron.

#### RESULTS AND DISCUSSION

The values of the isomer shift and the quadrupole splitting are determined from Mössbauer spectra of these complexes at room temperature. These are given in Table II alongwith those of Takashima and Tateishi (1965) (reported only for the basic ferric salicylate). The 4s occupation by the ligands (Danon, 1966) corresponding to the observed  $\delta_{Fe}$ -values is also shown in Table II. The four resonance dips observed in the spectrum of each complex have been analysed in terms of the inner and outer doublets. In conformity with the similar observations by Takashima and Tateishi (1965) in case of basic ferric salicylate and from the observed range of values of Mössbauer parameters, it is possible to assign the trinuclear chain structure to all these complexes in which iron occupies two non-equivalent sites in the chain.

(i) *IR Analysis*—The recorded infrared spectra for the three complexes at room temperature are shown in Fig. 1((a,b,c). The Fe-S bond formation in basic ferric thiosalicylate was confirmed by the absence of -SH frequency otherwise present at 2600–2550  $\text{cm}^{-1}$  in the free acid (Bellamy, 1958). The covalent linkage between the iron atom and thiosalicylic acid is through the sulphur atom. The observation of lowering of the carbonyl frequency from 1720–1680  $\text{cm}^{-1}$  (for free acid) to 1630–1610  $\text{cm}^{-1}$ , suggests coordination of the carbonyl oxygen to the iron atom. In the ferric 4-aminosalicylate complex, the observed-NH<sub>2</sub> vibrations

TABLE II  
Measured Mössbauer parameters

Sample	Inner doublet			Outer doublet		
	$\Delta E_Q$ (mm/sec)	$\delta_{Fe}$ (mm/sec)	Partial 4s population by ligands (a)	$\Delta E_Q$ (mm/sec)	$\delta_{Fe}$ (mm/sec)	Partial 4s population by ligands (a)
Basic ferric salicylate	0.64	0.55	0.300	1.60	0.49	0.370
	0.35*	0.58*	0.320	1.20*	0.60*	0.305
Basic ferric thio- salicylate	0.80	0.59	0.370	2.28	0.35	0.440
Basic ferric 4-amino- salicylate	1.52	0.61	0.340	3.2	0.71	0.290
Uncertainty range	$\pm 0.04$	$\pm 0.04$	—	$\pm 0.04$	$\pm 0.04$	—

\*Determined from the calibration plot (Danon, 1966)

\*Values reported by Takashima and Tateishi (1965)

Other values mentioned refer to the present work.

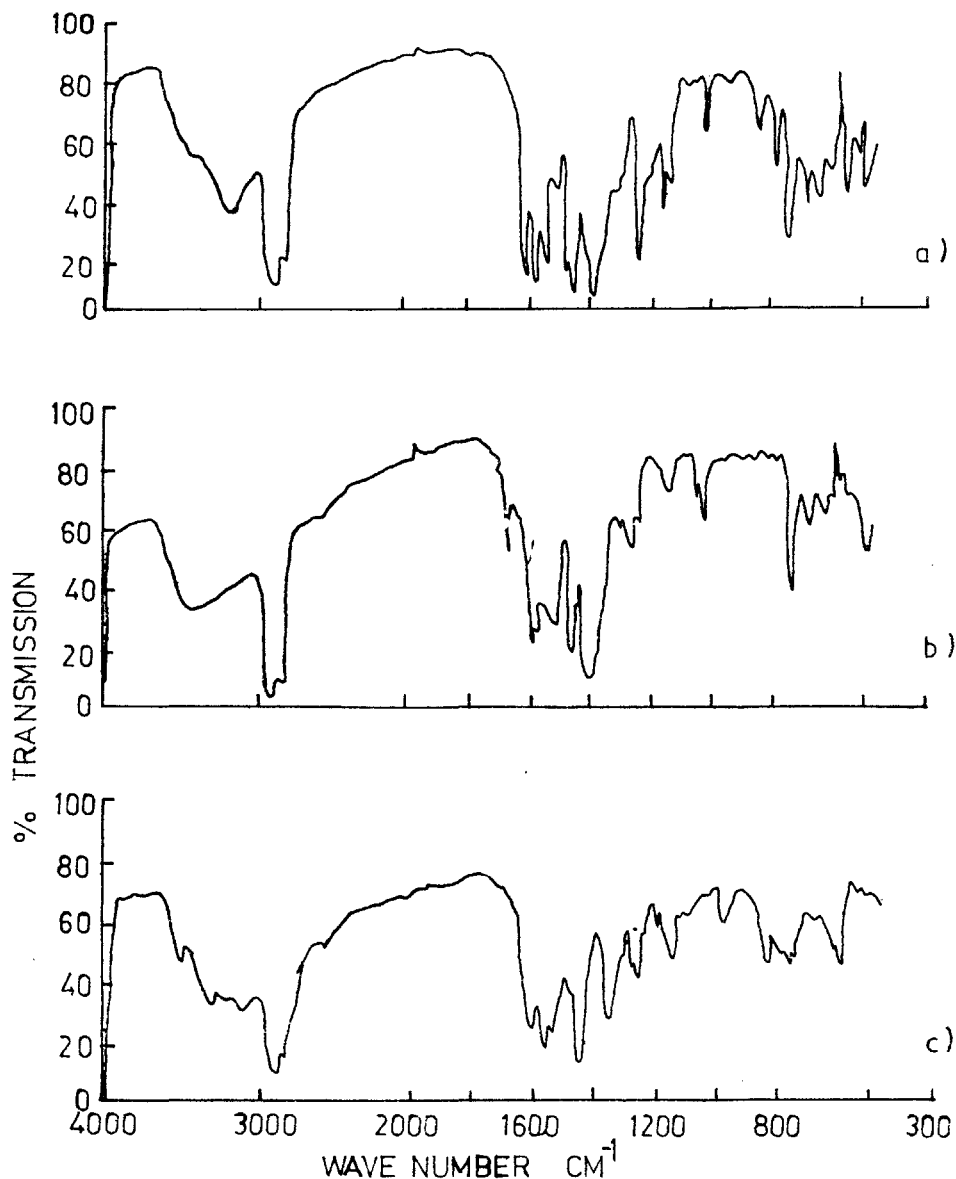


FIG. 1. Infrared spectra of (a) basic ferric salicylate, (b) basic ferric thiosalicylate and (c) basic ferric 4-amino salicylate.

at 3350 and 3290  $\text{cm}^{-1}$  are somewhat lowered as compared to 3370 and 3300  $\text{cm}^{-1}$  in the free acid which indicate the coordination through nitrogen also.

(ii) *Mössbauer measurements*—Mössbauer spectra recorded at room temperature for all the complexes are shown in Fig. 2 (a,b,c) from which different  $\delta_{\text{Fe}}$  and  $\Delta E_Q$  values have been determined (Table II). From the observed range of  $\delta_{\text{Fe}}$ -and  $\Delta E_Q$ -values for the complexes corresponding to inner and outer

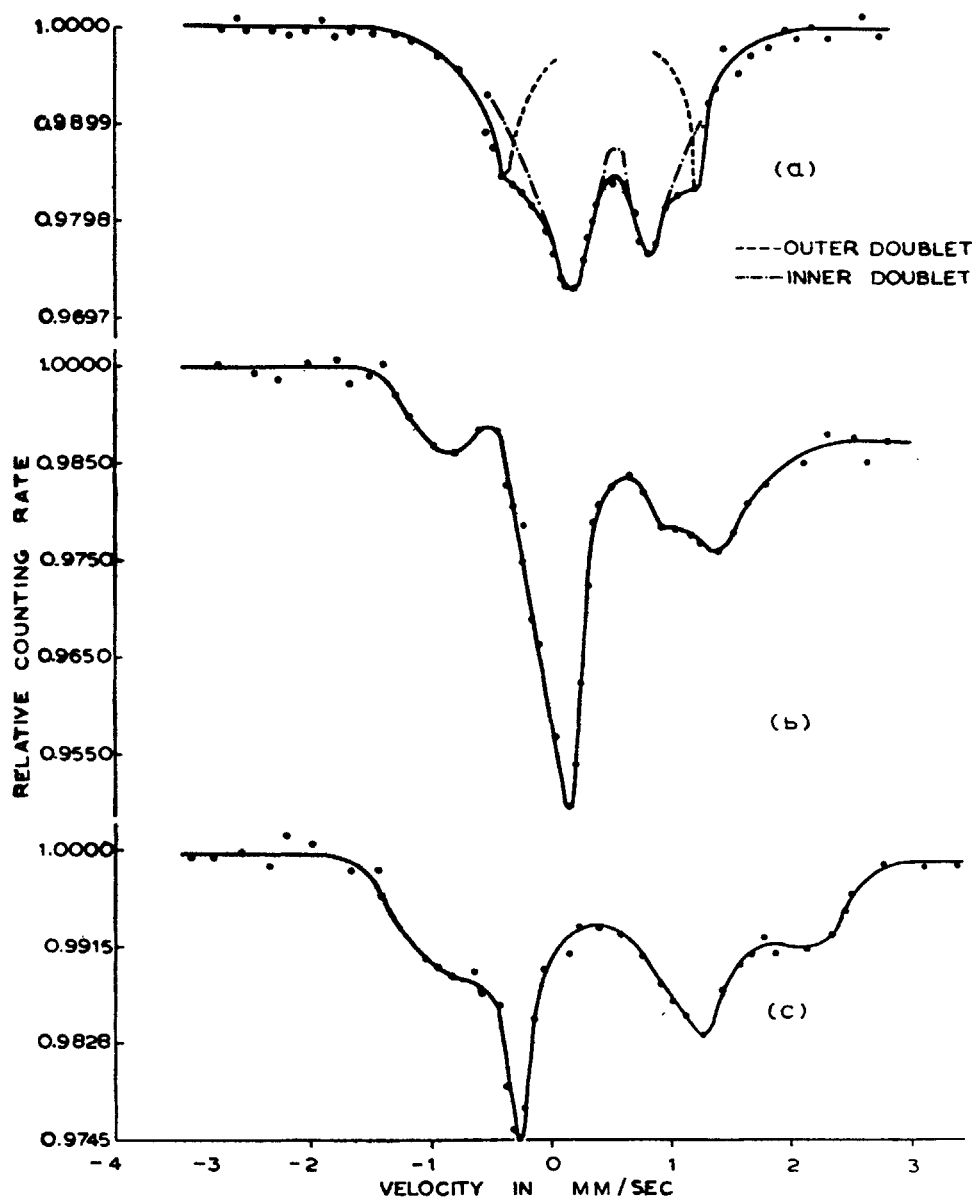


FIG. 2. Mössbauer spectra of (a) basic ferric salicylate, (b) basic ferric thiosalicylate and (c) basic ferric 4-amino salicylate, recorded at room temperature.

doublets, it is possible to characterise these peaks as arising from the high spin (Debrunner, 1973; Reiff, 1971) and low spin (Debrunner, 1973) states of iron, respectively. The relatively large  $\Delta E_Q$ -values for the outer doublet in all the three complexes as compared to those for the inner one show the possibility of octahedral coordination of the central iron atom (Brown, 1967). It should be noted (Fig. 2b) that in case of basic ferric thiosalicylate, the inner doublet shows a pronounced

TABLE III  
Magnetic susceptibility measurements

Sample	$\chi_M$ (emu/gm)	$\mu_{\text{eff}}$ (BM)
Basic Ferric salicylate	$0.92 \times 10^{-6}$	1.81
Basic Ferric thiosalicylate	$0.84 \times 10^{-6}$	1.72
Basic Ferric 4-amino salicylate	$0.89 \times 10^{-6}$	1.67

asymmetry. This shows that while the terminal iron atoms of the trinuclear chain have the tetrahedral ligand symmetry for the basic ferric salicylate and 4-amino ferric salicylate, in case of basic ferric thiosalicylate, they exhibit a penta-coordinated symmetry. As the penta-coordinated iron will be subjected to a large configurational strain resulting in the structural distortions, and thereby causing an effective departure from the cubic symmetry, this effect can manifest in terms of an increased line asymmetry and the quadrupole doublet, as has been observed presently. Comparing the  $\Delta E_Q$ -values of the three complexes, large values of Q.S. are also observed for both the inner and the outer doublets for ferric 4-amino salicylate. In this case, it may be noted that when  $\text{NH}_2$  group is substituted at the para position of the ring, it amounts to the packing of large groups in the solid crystal form. This can distort an otherwise compact structural configuration (Johnson, 1971). It may also be possible that the  $\text{NH}_2$  group acts as a donor constituent of the ligand in preference to the carbonyl group which will then exert a comparatively strong field on the metal iron with the consequent possibility of  $3d$ -orbital augmentation of the low spin central metal ion which could result in more spreaded core and thus, an increase in the I.S. of the outer doublet.

(iii) *Magnetic measurements*—Magnetic susceptibility measurements on these complexes were carried out at room temperature by the Guoy's method. These are reported in Table. III. From these measurements the effective magnetic moment,  $\mu_{\text{eff}}$ , has been determined from the expression (Lewis & Wilkins, 1960).

$$\mu_{\text{eff}} = 2.84 T^{1/2} \chi_M^{1/2} \text{ (BM)}$$

where  $\chi_M$  is the molecular susceptibility and  $T$  the absolute temperature. The range of the values of  $\chi_M$  and  $\mu_{\text{eff}}$  for Fe-atom in the different complexes is indicative of the linear trinuclear configurations (Mobbs & Machin, 1973).

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