



## Studies of Fe(III) and Mn(II) Complexes of Valerohydroxamic Acid and Isovalerohydroxamic Acid

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The Fe<sup>3+</sup> and Mn<sup>2+</sup> complexes of valerohydroxamic and isovalerohydroxamic acids were prepared with good yield. Infrared studies of the isolated solid indicates chelation *via* ketonic oxygen. The solution studies of the systems, reveals the formation of a single specie, with a 1:2 and 1:3 metal-ligands ratios for Mn<sup>2+</sup> and Fe<sup>3+</sup> systems, respectively. The electronic studies of the complexes indicates a *d-d* and <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>A<sub>1g</sub>, <sup>4</sup>E<sub>g</sub> transitions for Mn<sup>2+</sup> and Fe<sup>3+</sup> complexes, respectively. They do not show any activity towards the test organisms, with exception of iron(III) valerohydroxamate, which shows partial activity against *Staphylococcus aureus* (Sa) and *Candida albicans* (Ca) at a dosage of 1000 µs/mL.

**Key Words:** Fe(III), Mn(II), Valerohydroxamic acid, Isovalerohydroxamic acid, Complex.

### INTRODUCTION

There is a great deal of attention on the metal complexes of monohydroxamic acids, due to its biological importance. Hence there is an increase search for chelators as an oral source for iron anemia and manganese deficiency, which are of tremendous requirement in normal function of the body and growth<sup>1-3</sup>.

Many reports<sup>3,4</sup> about in the literature on the hydroxamic complexes of Fe<sup>3+</sup> and Mn<sup>2+</sup>, with scanty reports on their solution studies. We are reporting the synthesis and solution studies of Fe<sup>3+</sup> and Mn<sup>2+</sup> complexes with valerohydroxamic acid and isovalerohydroxamic acid and their biological activity.

### EXPERIMENTAL

All chemicals used are products of BDH Ltd., with the exception of ethyl valerate and ethyl isovalerate which are product of Aldrich chemical company Ltd. The elemental analysis were carried out by titrimetry method according to standard methods<sup>5</sup>. The absorption spectra were recorded on a 620sp UV-visible spectrophotometer, while the IR in CCl<sub>4</sub> were recorded on a Perkin-Elmer 370 spectrometer in the range 4000-400 cm<sup>-1</sup>. The microbial screening was made by Agar-diffusion methods.

**Preparation of the ligands:** Valerohydroxamic acid and isovalerohydroxamic acid were prepared as described<sup>6</sup>.

### Preparation of the complexes

**[Fe(VA)<sub>3</sub>]:** 1.625 g (0.01 M) FeCl<sub>3</sub> in 10 mL dry ethanol was added to a solution of 3.51 g (0.03 M) valerohydroxamic acid (VA) in 10 mL dry ethanol. The mixture was stirred and its pH raised to 8 by the addition of sodium ethoxide. The solution was filtered to remove NaCl and was concentrated under room temperature and crystallization was achieved after 48 h in a deep freezer. The dark red precipitate was filtered and dried over fused-calcium chloride gel in a vacuum dessicator for 3 weeks, with a yield of 55.69 %.

The isovalerate complex of Fe(III), was similarly prepared using 3.54 g (0.03 M) isovalerohydroxamic acid (IVA) with a yield of 40.84 %.

**[Mn(VA)<sub>2</sub>]:** A solution of 1.98 g (0.01 M) MnCl<sub>2</sub>·4H<sub>2</sub>O in 20 mL dry ethanol was added to a solution of 2.34 g (0.02 M) valerohydroxamic acid (VA) in 10 mL dry ethanol. The mixture was well stirred and its pH raised to 6.1 by the addition of sodium ethoxide. The mixture was filtered and the filtrate concentrated under room temperature. The solution was kept in a deep freezer for 48 h and the precipitate was filtered and dried over CaCl<sub>2</sub> in a vacuum desiccator, with a yield of 27.5 %.

Similar procedure was followed with 2.34 g (0.02 M) isovalerohydroxamic acid with a yield of 22.65 %.

**Solution studies:** Nine solution containing 1:1-1:3 metal to ligand ratio (increasing in 0.025 M) were used for the determination of the number of species present in solution at equilibrium, spectro photometrically by the isosbestic point method and graphical matrix rank analysis. The solution of

TABLE-1  
PHYSICO-CHEMICAL AND ANALYTICAL DATA

Compound	Formula	Colour	m.f. (g)	Yield (%)	m.p. (°C)	M <sup>2+</sup> (%)	Elemental analysis (%)			BM (SCM <sup>2</sup> mol <sup>-1</sup> )
							C	H	N	
VAH	C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>	White	117	58.00	77.78	–	10.270 (10.26)	0.854 (0.855)	11.99 (11.96)	–
Fe(VA) <sub>3</sub> ·H <sub>2</sub> O	C <sub>15</sub> H <sub>32</sub> N <sub>3</sub> O <sub>7</sub> Fe	Brownish red	422	55.69	170.00	13.88 (13.27)	40.84 (40.65)	7.62 (7.58)	9.86 (9.95)	5.480
Mn(VA) <sub>2</sub> ·H <sub>2</sub> O	C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O <sub>5</sub> Mn	Light brown	305	27.50	161.00	18.37 (18.03)	39.38 (39.34)	7.20 (7.21)	9.22 (9.19)	0.016
IVAH	C <sub>5</sub> H <sub>11</sub> NO <sub>2</sub>	White	117	62.00	76.77	–	10.28 (10.26)	0.856 (0.855)	11.98 (11.96)	–
Fe(IVAH) <sub>3</sub> ·H <sub>2</sub> O	C <sub>15</sub> H <sub>32</sub> N <sub>3</sub> O <sub>7</sub> Fe	Brownish red	422	40.84	165.00	13.71 (13.27)	40.81 (40.65)	7.60 (7.58)	9.88 (9.95)	5.540
Mn(IVA) <sub>2</sub> ·H <sub>2</sub> O	C <sub>10</sub> H <sub>22</sub> N <sub>2</sub> O <sub>5</sub> Mn	Light brown	305	22.65	162.00	18.48 (18.03)	39.41 (39.34)	7.18 (7.21)	9.20 (9.19)	0.012

$5 \times 10^{-2}$  M of the metal ion and ligands were used in an ionic strength of  $0.1 \text{ mol dm}^{-3}$ , made up of  $0.01 \text{ M HNO}_3$  and  $0.09 \text{ M NaNO}_3$ . The nature of the species in solution was determined by Job's method<sup>7</sup>, spectrophotometrically, by using nine solutions in the ratio of 2:22-22:2 metal/ligand volume ratio at  $750 \text{ nm}$  from a stock solutions of  $5 \times 10^{-3} \text{ M}$  of an ionic strength of  $0.1 \text{ M dm}^{-3}$ .

## RESULTS AND DISCUSSION

The pK<sub>a</sub> value which gives the basicity of the ligand in aqueous medium at  $25 \text{ °C}$  and ionic strength of  $0.10 \text{ mol dm}^{-3}$  as been determined to be  $9.50$  for valerohydroxamic acid and  $9.51$  for isovalerohydroxamic acid, as previously reported are quite high, complying that they may be good bases. The solution studies for the four systems were all similar, with Fig. 1, showing the visible absorption spectra of solutions containing a constant Fe<sup>3+</sup> and variable ligand molar concentration for VAH system, while Fig. 2 shows the graphical rank matrix analysis of the absorbance data generated from similar solutions for the Mn<sup>2+</sup> IVAH system. The absence of an isosbestic point in Fig. 1 and the shape of Fig. 2, are in accordance with a system containing one specie<sup>7</sup>.

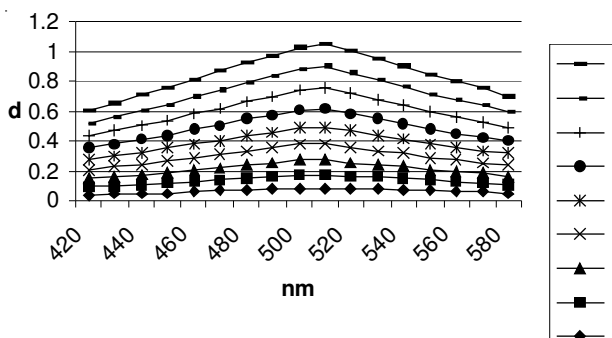


Fig. 1. Isosbestic point search for Fe<sup>3+</sup>-IVAH system

The nature of species in the system were determined by Jobs method at  $520 \text{ nm}$  wavelengths, with a maxima at  $0.667$  mol fraction values for the Fe<sup>3+</sup> systems and  $0.337$  mol fraction values for the Mn<sup>2+</sup> systems, corresponding to a 1:3 and 1:2 metal/ligand ratios, respectively as given below.

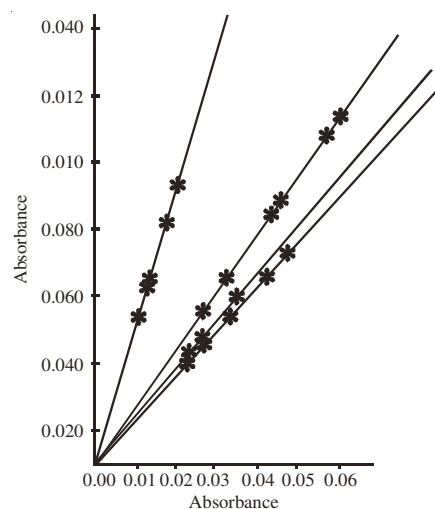
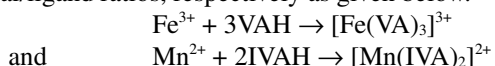


Fig. 2. Graphical rank matrix analysis for the Mn<sup>2+</sup>/VAH system, (i/m) nm: 770/610, 850/750, 750/700, 800/780

Some physio-chemical properties and analytical data for the isolated complexes are given in Table-1. The low values of the conductivities, implies that the complexes are non-electrolytes.

**Spectroscopic and magnetic studies:** Fe<sup>3+</sup> is iso electronic with Mn<sup>2+</sup>, but less is known of the details of Fe<sup>3+</sup> spectra, because of the tendency of the trivalent ion to have charge transfer bands in the near-ultra violet region, which have sufficiently strong low-energy wings in the visible to obscure almost completely in many cases, the very weak, spin forbidding *d-d* bands. Hence the band, at  $20408$  and  $20202 \text{ cm}^{-1}$  for Fe<sup>3+</sup> valerohydroxamate and isovalerohydroxamate, respectively are assigned to the  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}, {}^4\text{E}_g$  transition<sup>8</sup> and the bands observed between  $26316$ - $30769 \text{ cm}^{-1}$  are assigned to the *d-d* transition for the Mn<sup>2+</sup> complexes as shown in Table-2.

TABLE-2  
ELECTRONIC BANDS (cm<sup>-1</sup>) IN CHLOROFORM

Compound	Solvent	<i>d-d</i>	${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}, {}^4\text{E}_g$	Symmetry
Fe(VA) <sub>3</sub> ·H <sub>2</sub> O	CHCl <sub>3</sub>	–	20408	Oh
Fe(IVAH) <sub>3</sub> ·H <sub>2</sub> O	CHCl <sub>3</sub>	–	20202	Oh
Mn(VA) <sub>2</sub> ·H <sub>2</sub> O	CHCl <sub>3</sub>	26316-30769	–	Oh
Mn(IVA) <sub>2</sub> ·H <sub>2</sub> O	CHCl <sub>3</sub>	26316-30769	–	Oh

The magnetic moments of these complexes are given in Table-1. The magnetic moment of Fe(III) complexes of VAH and IVAH are in accordance with the high spin octahedral coordination, while the Mn(II) complexes are consistent with that of an octahedral environment.

The infrared spectral bands of the valerohydroxamic acid and isovalerohydroxamic acid and their Fe<sup>3+</sup> and Mn<sup>2+</sup> complexes are shown in Table-3.

Compound	$\nu(\text{OH, NH})$	$\nu(\text{C=O})$	$\Delta\nu(\text{C=O})$	$\nu(\text{C-N})$	$\Delta\nu(\text{C-N})$	$\nu(\text{M-O})$
VAH	3300, 3187	1650	-	1365	-	-
Fe(VA) <sub>3</sub> ·H <sub>2</sub> O	3400	1630	20	1405	10	541
Mn(VA) <sub>2</sub> ·H <sub>2</sub> O	3410, 3200	1580	70	1414	40	538
IVAH	3198	1650	-	1370	-	-
Fe(IVAH)·H <sub>2</sub> O	3420	1636	14	1385	15	570
Mn(IVA)·H <sub>2</sub> O	3351, 3202	1570	80	1410	40	480

The  $\nu(\text{C=O})$  band of the ligands, are lowered by 14-80 cm<sup>-1</sup>. On complexation, the  $\nu(\text{C-N})$  band is increased by about 10-40 cm<sup>-1</sup> which is consistent with chelation by the ketonic oxygen atom. The  $\nu(\text{M-O})$  bands are tentatively assigned in each complex.

**Microbial activity:** The compounds were tested against the following bacteria; *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa* (Ps) and *Candida albicans* (Ca) as given in Table-4.

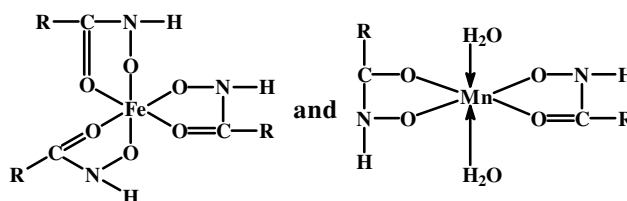
The result indicates partial activity of IVAH against *Escherichia coli* and *Bacillus subtilis* and that of Fe(VA)<sub>3</sub>·H<sub>2</sub>O

Compound	Sa (+)	Ec (-)	Ps (-)	Bs (+)	Ca
VAH	-	-	-	-	-
IVAH	-	+	-	+	-
Fe(VA) <sub>3</sub> ·H <sub>2</sub> O	+	-	-	-	+
Fe(IVAH)·H <sub>2</sub> O	-	-	-	-	-
Mn(VA) <sub>2</sub> ·H <sub>2</sub> O	-	-	-	-	-
Mn(IVA)·H <sub>2</sub> O	-	-	-	-	-

Sa: *Staphylococcus aureus*, Ec: *Escherichia coli*, Ps: *Pseudomonas aeruginosa*, Bs: *Bacillus subtilis*, Ca: *Candida albicans*.

against *Staphylococcus aureus* and *Candida albicans*, while other compounds were negative at 1000 µg/ML.

On the basis of their physico-chemical properties, the following structures are proposed for the complexes.



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