

IRON(III) COMPLEXES OF SALICYLIDENE AMINO ACIDS

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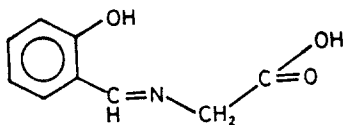
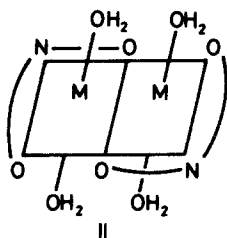
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Several iron(III) complexes of tridentate dibasic salicylidene/substituted salicylidene amino acids (ONO donor set) have been prepared and characterized. All iron(III) compounds possess dimeric pseudo - octahedral structure established on the basis of elemental analysis, magnetic moment studies, superimposable infrared spectra of these complexes with those of nickel(II), cobalt(II), manganese(II), magnesium(II) and zinc(II) complexes, and thermogravimetric analysis.

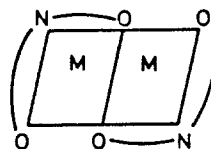
The stability of salicylideneamino acid Schiff bases (I) is observed only in the presence of suitable metal ion [1]. Nickel(II), cobalt(II), manganese(II), magnesium(II) and zinc(II) complexes of salicylideneamino acids have dimeric pseudo - octahedral structures through coordination of aqua molecules in the trans apical sites (structure II) [2-7]. The manganese(II) salicylidene leucine Schiff base, however, gave a four-coordinated anhydrodimer (structure III). The enhanced stability of these metal complexes may be attributed to the two chelate rings at the metal atom [1]. There is a report on a dimeric iron(III) complex, [(Salgly) Fe(gly)Fe(salgly)] OH (structure IV, Slagly H₂ salicylidene glycine, gly H = glycine) containing terminal salicylidene glycine and a bridging glycinate ion [8]. We have been unable to confirm this reported synthesis, all variations of which led to the hitherto unidentified dimeric iron(III) complex containing bridging salicylidene glycinate ion with coordinated aqua molecules (structure V).

In this communication we describe the preparation of several iron(III) complexes of tridentate dibasic salicylidene amino acids. These complexes have been characterized on the basis of elemental analysis, magnetic susceptibility measurements, infrared spectra and TG analysis.

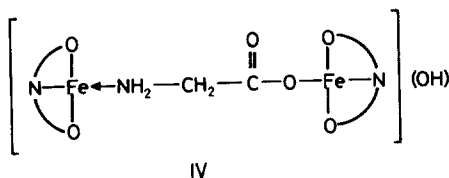
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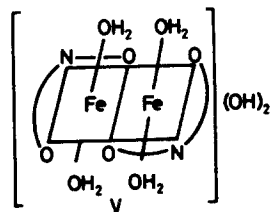
II



III



IV



V

Structures: Salicylidene glycine and its complexes

Experimental

To a warm solution of salicylaldehyde (1.5 g in 50 ml ethanol) hot aqueous glycine solution (1 g in 15 ml water) was added and the solution was refluxed for 30 minutes. To the clear solution freshly prepared hot aqueous solution of iron(II) sulphate (1 g in 10 ml water) was added and the

resulting solution thus obtained was refluxed for two hours. During heating, the solution turned deep red and then deep red crystals separated gradually from the solution. The whole mixture was then kept in the refrigerator for cooling when huge crystals separated. These were collected by suction, washed with ice cold water, ethanol and finally with ether. The deep red shining crystals thus obtained were dried over silica gel.

A further crop may be obtained from the mother liquor by the addition of anhydrous sodium acetate, yield 3 g.

Similar procedure were adopted for the preparation of the other iron (III) compounds. All the compound are highly crystalline, have deep red colour and are soluble in water and ethanol but more soluble in pyridine. The compounds are insoluble in acetone, dioxane, ether and other common organic solvents. The compounds are neutral to litmus, and they are decomposed by dilute mineral acids and strong alkalies. On warming the aqueous solution, the compound decomposes. The compound on treatment with dilute HCl yields a colourless solution which on treatment with thiocyanate solution gives blood red colour thus indicating the trivalent oxidation state of iron.

Analysis and measurements

Iron was estimated volumetrically after decomposition of the compound with conc. H_2SO_4 . Nitrogen was estimated by the Dumas method, and chloride was determined as silver chloride. Microanalyses of carbon and hydrogen were done at CDRI, Lucknow (Table 1). Infrared spectra (Table 2) were taken in the form of KBr pellets. Thermogravimetric runs were made by a MOM derivatograph in a stream of air with a 5 deg per minute heating rate (Table 3). About 100 mg of the finely crystalline compounds were heated in each TG run.

Results and discussion

Schiff bases of type (I) containing ONO donor set react with metal(II) [M(II) = Ni(II), Co(II), Mn(II), Mg(II) and Zn(II)] ions to give trans aqua - μ - bis (salicylideneaminoacidato) - di-metal(II) cation (structure IV) [2-7]. Dimeric structures for nickel(II) and cobalt(II) complexes have been established after considering the magnetic moments and electronic spectra of the respective complexes [2-4]. Besides the nickel(II) and cobalt(II) com-

Table 1 Characteristic data of iron(III) complexes of salicylidene aminoacids

Complex	Colour	Magnetic moment, B. M.	Fe, %	Found/Calculated			H, %	Cl, %
				N, %	C, %			
[Fe(salgy)(H ₂ O) ₂](OH) ₂	Deep red	5.94 Found Calc.	19.5 19.5	4.9 4.8	37.2 37.7	3.8 4.1	- -	
[Fe(5cl-salgy)(H ₂ O) ₂] ₂ (OH) ₂	"	5.81 Found Calc.	17.4 17.4	4.4 4.3	33.2 33.7	3.0 3.4	11.1 11.0	
[Fe(SNO ₂ -salgy)(H ₂ O) ₂] ₂ (OH) ₂	"	5.98 Found Calc.	15.7 15.6	7.9 7.8	29.8 30.3	2.9 3.3	- -	
[Fe(2hynaph-gly)(H ₂ O) ₂] ₂ (OH) ₂	"	5.71 Found Calc.	16.6 16.6	4.1 4.1	46.0 46.4	3.7 4.1	- -	
[Fe(sal-α-alan)(H ₂ O) ₂] ₂ (OH) ₂	"	5.77 Found Clac.	18.5 18.6	4.7 4.6	39.6 40.0	4.2 4.6	- -	
[Fe(5cl-sal-α-alan)(H ₂ O) ₂] ₂ (OH) ₂	"	5.71 Found Calc.	16.7 16.7	4.2 4.1	35.5 35.8	3.4 3.8	10.6 10.6	
[Fe(SNO ₂ -sal-α-alan)(H ₂ O) ₂] ₂ (OH) ₂	"	5.89 Found Calc.	15.5 15.4	7.8 7.7	32.8 33.2	3.3 3.6	- -	
[Fe(2hynaph-α-alan)(H ₂ O) ₂] ₂ (OH) ₂	"	5.31 Found Calc.	16.0 15.9	4.0 4.0	47.7 48.0	4.1 4.5	- -	
[Fe(sal-val)(H ₂ O) ₂] ₂ (OH) ₂	"	5.33 Found Calc.	17.0 17.0	4.3 4.2	47.1 47.5	4.8 5.1	- -	
[Fe(5cl-sal-val)(H ₂ O) ₂] ₂ (OH) ₂	"	5.49 Found Calc.	15.4 15.4	3.9 3.8	42.7 43.0	4.1 4.4	9.8 9.7	
[Fe(SNO ₂ -sal-val)(H ₂ O) ₂] ₂ (OH) ₂	"	5.41 Found Calc.	14.4 14.3	7.2 7.2	40.0 40.1	3.8 4.1	- -	

salgyH₂ = salicylidene-glycine; sal-α-alanH₂ = salicylidene-α-alanine; 5-Cl-salgyH₂ = 5-chlorosalicylidene-glycine; 5-Cl-sal-α-alanH₂ = 5-chlorosalicylidene-α-alanine; 5-NO₂-salgyH₂ = 5-nitrosalicylidene-glycine; 5-NO₂-sal-α-alanH₂ = 5-nitrosalicylidene-α-alanine; sal-leucH₂ = salicylideneleucine; 2-hynaph-glyH₂ = 2-hydroxy-1-naphthaldehyde-glycine; 2-hynaph-α-alanH₂ = 2-hydroxy-1-naphthaldehyde-α-alanine; 5-Cl-salvalH₂ = 5-chlorosalicylidene valine; 5-NO₂-salvalH₂ = 5-nitrosalicylidene valine

Table 2 IR spectral bands of $[M(\text{salgly})(\text{H}_2\text{O})_2]_2$ ($M = \text{Zn(II), Mn(II), Ni(II), Co(II), Mg(II)}$) and $[\text{Fe}(\text{salgly})(\text{H}_2\text{O})_2](\text{OH})_2$

Complex	ν , cm^{-1}
1. $[\text{Fe}(\text{salgly})(\text{H}_2\text{O})_2]_2(\text{OH})_2$	3360-3205 bs, 1655s, 1605s, 1545s, 1475s, 1450s, 1405s, 1340s, 1305s, 1195s, 1150vs, 1135s, 1075m, 1045w, 1000w, 985w, 910m, 820s, 780s, 760w.
2. $[\text{Ni}(\text{salgly})(\text{H}_2\text{O})_2]_2 \cdot 2\text{H}_2\text{O}$	3200bs, 1650vs, 1600s, 1550s, 1465m, 1450s, 1395m, 1340m, 1305vs, 1205s, 1155ms, 1135s, 1095ms, 1040m, 1012w, 970w, 948w, 910w, 858w, 792w, 768m, 750ms.
3. $[\text{Co}(\text{salgly})(\text{H}_2\text{O})_2]_2$	3178vs, 1644s, 1600s, 1545s, 1470ms, 1450s, 1400s, 1335ms, 1290s, 1190s, 1149s, 1130s, 1086m, 1041w, 1010w, 958w, 900w, 798m, 770w, 760w, 743w.
4. $[\text{Mn}(\text{salgly})(\text{H}_2\text{O})_2]_2$	3125bs, 1645s, 1600s, 1548s, 1470vs, 1450s, 1400s, 1335s, 1300s, 1190vs, 1149vs, 1130s, 1060m, 1041w, 1010w, 1149vs, 1130s, 1060m, 1041w, 1010w, 961w, 900w, 854m, 800m, 769w, 759m, 740w.
5. $[\text{Mg}(\text{salgly})(\text{H}_2\text{O})_2]_2$	3400-3200bs, 1660s, 1600m, 1540m, 1475s, 1445s, 1410s, 1340s, 1303s, 1198s, 1155s, 1132s, 1085s, 1042m, 1020m, 958m, 950w, 858w, 770s, 760s, 750s.
6. $[\text{Zn}(\text{salgly})(\text{H}_2\text{O})_2]_2$	3350-3200bs, 1650s, 1610s, 1550s, 1480s, 1450s, 1400s, 1340s, 1310s, 1200s, 1145s, 1135s, 1080m, 1045w, 1000w, 980w, 915m, 815s, 780s, 750w.

bs = broad and strong; vs = very strong; s = strong; ms = medium strong; m = medium; w = weak.

pounds, other compounds provided superimposable infrared spectra (Fig. 1) and very similar and comparable thermogravimetric curves [2-7]. Since high spin $3d^5$ -iron(III) compounds show very weak forbidden transitions in their electronic spectrum [9-10] and a magnetic moment ($\mu = 5.94$ B.M) which is of little value for identification of the stereochemistry, we compared the present complex $[\text{Fe}_2(\text{salgly})_2(\text{H}_2\text{O})_4](\text{OH})_2$ with reported similar types complexes viz. $[\text{Ni}_2(\text{salgly})_2(\text{H}_2\text{O})_4]$, $[\text{Co}_2(\text{salgly})_2(\text{H}_2\text{O})_4]$, $[\text{Mn}_2(\text{salgly})_2(\text{H}_2\text{O})_4]$, $[\text{Mg}_2(\text{salgly})_2(\text{H}_2\text{O})_4]$ and $[\text{Zn}_2(\text{salgly})_2(\text{H}_2\text{O})_4]$, the dimeric structures of all of them have been established through studies of their distinctive electronic spectra, magnetic moments and infrared spectra (Table 3) [2-7]. All the compounds show a broad strong absorption band in the region of $3200\text{-}3400\text{ cm}^{-1}$ which can be assigned to the $\nu(\text{H}_2\text{O})$ stretching vibration. A strong band at $\sim 1660\text{ cm}^{-1}$ is observed and is assignable to coordinated $\nu(\text{COO})$. The $\nu(\text{C}=\text{N})$ stretching vibration occurs at $1630\text{-}1660\text{ cm}^{-1}$ in free ligands of similar nature and this band undergoes a negative shift in the complex indicating nitrogen coordination of the azomethine moiety [11]. The aromatic $\nu(\text{C}=\text{C})$ stretching vibration appears at $\sim 1545\text{ cm}^{-1}$ [11,12]. The $\nu(\text{C}-\text{N})$ stretching vibration of the $\text{CH}_2\text{-N}$ group appears at about 1340 cm^{-1} [13]. The band at 1300 cm^{-1} is an evidence of a strong bonding of the metal ion with the phenolic oxygen [14]. Elemental analysis and infrared spectra are not consistent with the formula $[(\text{salgly})\text{Fe}(\text{gly})\text{Fe}(\text{salgly})](\text{OH})$ [8].

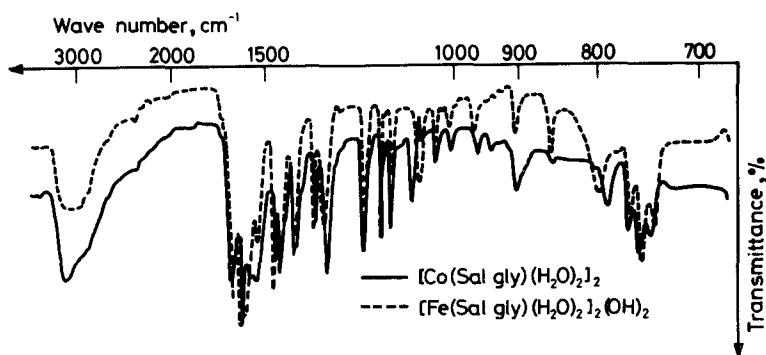
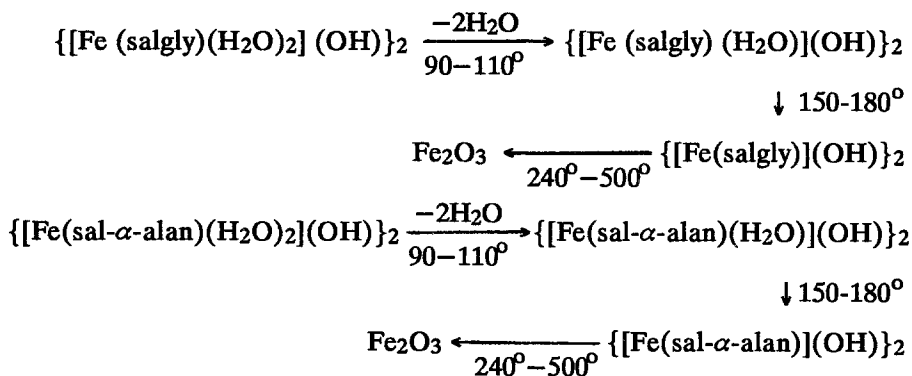


Fig. 1 Infrared spectra of cobalt(II) and iron(III) complexes of salicylidene glycine

The mass loss data obtained from the TG curves of all iron(III) complexes indicate that the coordinated aqua molecules are lost stepwise - two water molecules are removed at about 110° while the remaining two aqua

molecules are lost at 150-180°. The corresponding cobalt(II) complex does so in the range 100-120° (Table 3). Contrary to Behara's claim [4] that the aqua molecules of $[\text{Co}(\text{salgly})(\text{H}_2\text{O})_2]_2$ cannot be easily removed, we found that the water molecules can be removed completely at 120°. No such mass loss can be effected for the corresponding manganese(II), magnesium(II) and zinc(II) complexes at such a low temperature [5-7].

Thus, from the mass loss data (Table 3), it is evident that the iron(III) compound after losing two water molecules first favours an intermediate five coordinate square pyramidal dimeric species which on further heating loses the remaining two water molecules and favours square planar geometry. This square planar compound on further heating at higher temperature decomposed to yield Fe_2O_3 [15].



From the above studies it is evident that the formation of dimeric species is not dictated by crystal field stabilisation energy (C.F.S.E.), which is zero for iron(III) ($3d^5$ -system) and those of nickel(II), cobalt(II) and zinc(II) are -12 Dq, -8 Dq and 0 respectively, but by the nature of the donor set (ONO for the present study) and more importantly by the size of the metal ions ($\text{Fe}^{3+} = 0.53 \text{ \AA}$; $\text{Co}^{2+} = 0.72 \text{ \AA}$; $\text{Ni}^{2+} = 0.69 \text{ \AA}$; $\text{Zn}^{2+} = 0.74 \text{ \AA}$; $\text{Mg}^{2+} = 0.80 \text{ \AA}$) [16].

* * *

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Table 3 Thermogravimetric analysis of iron(III), cobalt(II), nickel(II) and manganese(II) complexes of salicylideneamino acids

Complex	% Loss of water*		2nd step	total	calc.	% Total mass loss	
	1st step	2nd step				found (up to °C)	calc. (Fe ₂ O ₃ /Mn ₃ O ₄ /Co ₂ O ₃ /NiO)
[Fe(salgy)(H ₂ O) ₂] ₂ (OH) ₂	6.3 (90-110°)*	6.2 (160-180°)*	12.5	12.5	12.5	72.1 (500°)	72.0
[Fe(5Cl-salgy)(H ₂ O) ₂] ₂ (OH) ₂	5.6 (90-110°)	5.5 (160-190°)	11.1	11.2	11.2	75.0 (500°)	75.1
[Fe(2hynaph-gly)(H ₂ O) ₂] ₂ (OH) ₂	5.4 (100-110°)	5.2 (150-180°)	10.6	10.7	10.7	76.2 (500°)	76.2
[Fe(sal-α-alan)(H ₂ O) ₂] ₂ (OH) ₂	6.1 (90-120°)	6.0 (160-180°)	12.1	12.0	12.0	73.3 (500°)	73.4
[Fe(5Cl-sal-α-alan)(H ₂ O) ₂] ₂ (OH) ₂	5.4 (90-120°)	5.3 (150-170°)	10.7	10.7	10.7	76.0 (500°)	76.1
[Fe(2hynaph-α-alan)(H ₂ O) ₂] ₂ (OH) ₂	5.3 (90-100°)	5.0 (150-180°)	10.3	10.2	10.2	77.2 (500°)	77.2
[Co(salgy)(H ₂ O) ₂] ₂	13.7 (100-120°)	-	13.7	13.4	13.4	68.0 (500°)	70.5
[Ni(salgy)(H ₂ O) ₂] ₂ ·H ₂ O	3.1 (60-100°)	13.0	16.1	16.1	16.1	78.5 (500°)	78.7
[Mn(salgy)(H ₂ O) ₂] ₂	12.1 (160-190°)	-	12.1	13.4	13.4	72.5 (480°)	71.6
[Mn(5Cl-sal-α-alan)(H ₂ O) ₂] ₂	6.0 (90-100°)	6.8 (160-200°)	12.8	12.3	12.3	76.2 (540°)	76.0

*Figures in parentheses indicate the temperature range for the loss of water, °C

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Zusammenfassung – Mit dreizahnigen dibasischen substituierten und unsubstituierten Salizylidenaminosäuren (ONO Donorset) wurden einige Eisen(III)-komplexe hergestellt und diese beschrieben. Mittels Elementaranalyse, TG-Analyse, der Untersuchung des magnetischen Momentes und des Vergleiches von IR-Spektren mit denen von Nickel(II)-, Cobalt(II)-, Mangan(II)-, Magnesium(II)- und Zink(II)-komplexen konnte festgestellt werden, daß alle Eisen(III)-komplexe über eine pseudooktaedrische Dimerenstruktur verfügen.