

## Synthesis and characterization of iron(III) complexes of salicylaldehyde 4-methoxybenzoyl hydrazone

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Iron(III) complexes of salicylaldehyde 4-methoxybenzoyl hydrazone, ( $H_2smbhon$ ), have been isolated and the reactions of  $[Fe(smbhon)(Cl)(H_2O)]_2$  with  $SnCl_2$  and  $CH_3CN$  are discussed. These complexes have been characterised by elemental analyses, molar conductance values, magnetic susceptibilities, molecular weights and spectroscopic (electronic, infrared and Mössbauer) data. Depending on the reaction conditions, the ligand may function as a dibasic tridentate, monobasic or neutral bidentate ligand.

The chemical properties of hydrazones have been investigated extensively due to their chelating capacity<sup>1</sup>, pharmacological activity<sup>2-4</sup> and analytical applications<sup>5</sup>. Although iron(III) complexes with different types of aroylhydrazones<sup>1</sup> are known, those with salicylaldehyde 4-methoxybenzoyl hydrazone ( $H_2smbhon$ ) are not reported. In view of the above and also as a part of our studies on the metal complexes of aroyl hydrazone ligands<sup>6-9</sup>, we report herein the synthesis and characterization of some new iron(III) complexes of a tridentate ONO donor ligand (Structure I) formed by the condensation of salicylaldehyde with 4-methoxybenzoyl hydrazide.

### Materials and Methods

All the chemicals used were of AR grade. Solvents were purified whenever necessary. IR spectra were recorded on KBr discs with a Perkin-Elmer 1330 spectrophotometer and the electronic spectra on a Hitachi spectrophotometer model 200-20. Conductance measurements were made with a conductivity bridge of Leeds and Northrup Co. Cat. No. 4959. The magnetic susceptibility measurements were made with a Gouy balance at room temperature. Mössbauer spectra at room temperature were recorded by an ECIL MBS-35 spectrometer connected with a 250 channel MCA at constant acceleration mode. Molecular weights were determined by Rast's method.

### Preparation of salicylaldehyde 4-methoxybenzoyl hydrazone ( $H_2smbhon$ )

4-Methoxybenzoate obtained from 4-methoxybenzoic acid<sup>10</sup>, was converted to acid hydrazide ( $Hmbhin$ ) on treatment with 85% hydrazine

hydrate<sup>11</sup>. To this acid hydrazide ( $Hmbhin$ ) (1.66 g, 0.01 mol) solution was added salicylaldehyde (1.22 g, 0.01 mol) in dry ethanol (40 cm<sup>3</sup>) and the mixture heated under reflux for 4 h to give a yellow solution. It was filtered and the filtrate reduced *in vacuo* when light yellow micro-crystalline compound precipitated out on cooling. It was filtered off, washed with cold and dry ethanol and dried *in vacuo* over fused  $CaCl_2$  (Yield 85%; m.p. 178-180°C).

### Preparation of the complexes

#### $[Fe(smbhon)(Cl)(H_2O)]_2$ (1)

To a solution of  $H_2smbhon$  (2.03 g, 0.0075 mol) in methanol (15 cm<sup>3</sup>), solution of  $FeCl_3 \cdot 6H_2O$  (2.03 g, 0.0075 mol) in methanol (15 cm<sup>3</sup>) was added and the resulting green solution heated under reflux for 3 h (pH ~ 4.5). The separated green crystals were filtered off and washed with methanol and dried *in vacuo*, (Yield, 70%).

#### $[Fe(smbhon)(H_2O)_2]_2 Cl_2$ (2)

Similar reaction between  $FeCl_3 \cdot 6H_2O$  (2.03 g, 0.0075 mol) in methanol (15 cm<sup>3</sup>) and  $H_2smbhon$  (2.03 g, 0.0075 mol) in methanol (15 cm<sup>3</sup>) at pH ~ 9 yielded a green crystalline compound on concentration and cooling (Yield, 60%).

#### $[(H_2smbhon)_2FeCl_2]Cl$ (3)

Analogous reaction between  $FeCl_3 \cdot 6H_2O$  and  $H_2smbhon$  in 1:2 molar ratio afforded this green compound at pH ~ 4 in ~ 60% yield.

#### $[(smbhon)(Hsmbhon)Fe.Fe(smbhon)(Cl)(H_2O)]$ (4)

Similarly, this green compound was isolated in ~ 50% yield when  $H_2smbhon$  and  $FeCl_3 \cdot 6H_2O$  was reacted in 2:1 molar ratio at pH ~ 9.

**[(smbhon) Fe(NO<sub>3</sub>) (H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>H<sub>2</sub>O (5)**

This black solid compound was isolated in ~60% yield following a method similar to that used for (1) and using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in place of FeCl<sub>3</sub>·6H<sub>2</sub>O.

**[(H<sub>2</sub>smbhon) (Hsmbhon) Fe(NO<sub>3</sub>)<sub>2</sub>] (6)**

When the preparation of (3) described above was repeated using Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (2.02 g, 0.005 mol), this black compound was isolated in ~75%.

**Reaction of [Fe(smbhon) (Cl) (H<sub>2</sub>O)]<sub>2</sub> (1) with SnCl<sub>2</sub>**

Solid anhydrous SnCl<sub>2</sub> (0.95 g, 0.005 mol) was added to the solution of (1) (1.89 g, 0.0025 mol) in dry pyridine (10 cm<sup>3</sup>) under nitrogen atmosphere and heated under reflux for 3 h and filtered. The black filtrate was kept in a refrigerator for 3 days to obtain a black compound [Fe(smbhon) (SnCl<sub>3</sub>) (py)<sub>2</sub>] (7). The compound was recrystallised from diethylether/pet. ether (60°-80°C) mixture (containing few drops of py) (Yield, 60%).

Reaction with CH<sub>3</sub>CN: The complex (1) (1.89 g, 0.0025 mol) was taken in dry CH<sub>3</sub>CN (10 cm<sup>3</sup>) and heated under reflux for 3 h. The separated black crystals of [Fe(smbhon) (CH<sub>3</sub>CN) (H<sub>2</sub>O)<sub>2</sub>]Cl (8) were filtered off and washed with MeOH-CH<sub>3</sub>CN mixture (40:60 v/v) (Yield, 60%).

## Results and Discussion

The reaction of 4-methoxybenzoyl hydrazide (Hmbhin) with salicylaldehyde in ethanol or

methanol yielded the ligand salicylaldehyde 4-methoxybenzoyl hydrazone, H<sub>2</sub>smbhon (Structure I). The reactions of H<sub>2</sub>smbhon with FeCl<sub>3</sub>·6H<sub>2</sub>O and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O under different reaction conditions yielded coloured iron(III) hydrazone complexes (1) to (6). The complex (1) smoothly reacted with anhydrous SnCl<sub>2</sub> in dry pyridine to yield a heterometallic compound, (7) containing both Fe and Sn. Similarly, the complex (8) was formed when the complex (1) was refluxed in dry CH<sub>3</sub>CN. In the complex (8), CH<sub>3</sub>CN acts as a ligand. The elemental analyses, molar conductance values, molecular weights and magnetic moments of the complexes are listed in Table 1 which support the formulations of the isolated chelates. The present results support that the aroyl hydrazone, H<sub>2</sub>smbhon functions as a dibasic tridentate ligand in the complexes (1), (2), (5), (7), (8); both dibasic tridentate and monobasic bidentate ligand species are present in the complex (4), while in the complex (6), both neutral bidentate and monobasic bidentate ligand species are found to be present. Similar behaviour of the hydrazone ligand was observed by us previously<sup>12</sup>.

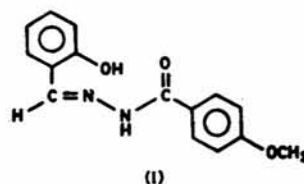


Table 1—Characterization data of iron(III) complexes

Compound	M.pt. (°C)	Found (Calcd.), %					Mol. wt. Found (calcd.)	$\mu_{\text{eff}}$ (BM)	$\Lambda_{\text{M}}$ (cm <sup>2</sup> Ohm <sup>-1</sup> mol <sup>-1</sup> )
		C	H	N	Cl	Fe			
[Fe(smbhon)Cl(H <sub>2</sub> O)] <sub>2</sub> (1)	250 (dec.)	47.16 (47.70)	3.62 (3.71)	6.92 (7.42)	8.95 (9.40)	15.08 (14.80)	748 (754.7)	5.3	5.60
[Fe(smbhon) (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub> (2)	300 (dec.)	45.23 (45.53)	4.14 (4.04)	6.85 (7.08)	8.59 (8.98)	14.00 (14.12)	796 (790.7)	5.38	58.9
[(H <sub>2</sub> smbhon) <sub>2</sub> FeCl <sub>2</sub> ]Cl (3)	270 (dec.)	50.85 (51.25)	3.70 (3.98)	7.45 (7.97)	14.78 (15.16)	8.25 (7.95)	688 (702.35)	5.90	38.46
[(smbhon) (Hsmbhon) Fe- Fe(smbhon) (Cl) (H <sub>2</sub> O)] (4)	300 (dec.)	55.55 (55.65)	4.20 (4.02)	8.50 (8.65)	3.50 (3.66)	11.75 (11.51)	938 (970.2)	5.4	6.40
[(smbhon)Fe(NO <sub>3</sub> ) (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> H <sub>2</sub> O (5)	> 300	40.00 (40.92)	3.94 (4.09)	9.85 (9.55)	—	13.05 (12.69)	420 (439.5)	5.80	16.2
[(H <sub>2</sub> smbhon) (Hsmbhon)- Fe(NO <sub>3</sub> ) <sub>2</sub> ] (6)	245 (dec.)	50.50 (50.07)	3.59 (3.76)	10.88 (11.68)	—	8.20 (7.77)	741 (718.85)	5.60	10.5
[Fe(smbhon) (SnCl <sub>3</sub> ) (Py) <sub>2</sub> ] (7)	230 (dec.)	41.94 (42.43)	3.26 (3.11)	7.58 (7.92)	15.35 (15.06)	7.50 (7.89)	698 (707.05)	5.85	8.9
[Fe(smbhon) (CH <sub>3</sub> CN) (H <sub>2</sub> O) <sub>2</sub> ]Cl (8)	275 (dec.)	45.80 (46.75)	3.98 (4.35)	10.06 (9.62)	8.25 (8.13)	12.95 (12.80)	420 (436.35)	5.7	29.60

All the iron compounds excepting (2), (3) and (8) isolated in the present study behave as non-electrolytes in DMSO ( $\Lambda_M$  of  $10^{-3} M$  solution at room temperature varies between  $5\text{--}16 \text{ cm}^2 \text{ Ohm}^{-1} \text{ mol}^{-1}$ )<sup>13</sup> (Table 1). However, the values of 38.46 and 29.6 for the complexes (3) and (8) in the same solvent suggest 1:1 electrolytic nature of these two complexes whereas the value 58.9 for the complex (2) indicates 1:2 electrolytic nature in solutions.

It is evident from Table 1 that the complexes (3), (5) to (8) have the values for effective magnetic moments characteristic of high spin pseudooctahedral iron(III) state ( $d^5$  system). Therefore, it can be concluded that H<sub>2</sub>smbhon behaves towards iron(III) as a ligand with a relatively weak ligand field. The complexes (1), (2) and (4) with  $\mu_{\text{eff}}$  values 5.3, 5.38 and 5.4 B.M. respectively may attain the oxo-bridged dimeric structure in the solid state where, the antiferromagnetic exchange interaction may be present between the two metal centres<sup>14</sup> causing the reduction of the room temperature magnetic moment values.

The lowering of magnetic moments in the complexes (1), (2) and (4) may be due to two reasons. Firstly, the presence of only one axial ligand in a 5-coordinate square pyramidal sphere would generate a greater splitting of the  $^5T_2$  state (of  $O_h$  Parentage) thereby reducing the orbital contribution to  $\mu_{\text{eff}}$  (ref.15). Secondly, the presence of antiferromagnetic coupling through the bridging oxygen may also result in the lowering of magnetic moment, as reported earlier in many 5-coordinate di-iron(III) (each unit) complexes derived from Schiff base ligands<sup>16-18</sup>. The intensity of the IR band  $\sim 840 \text{ cm}^{-1}$  is characteristics of four-membered iron-oxygen ring indicating that interaction is substantial<sup>19</sup>. Earlier, Rastogi *et al*<sup>14</sup> have reported some di-iron(III) complexes of the above type.

The electronic spectra of the present iron(III) complexes have been measured in DMSO and show several absorption bands in the range  $14,700\text{--}35,710 \text{ cm}^{-1}$ . The maxima observed above  $29,400 \text{ cm}^{-1}$  are probably due to the  $d\text{-}\pi^*$  interactions and those at higher wavelengths are characteristic of the intraligand  $\pi\text{-}\pi^*$  transitions<sup>14</sup>. The absence of maxima belonging to the  $d\text{-}d$  transitions is not unusual for iron(III) complexes<sup>20,21</sup>. Besides, the presence of a number of broad maxima, especially in the region  $25,640\text{--}30,300 \text{ cm}^{-1}$ , indicates that the levels of electronic transitions in the complexes are not well defined. The optical absorption spectra of antiferromagnetically coupled high spin iron(III) complexes [(1), (2) and (4)] exhibiting an enhancement of the intensity of the long wavelength

$d\text{-}d$  bands may be partly due to the absence of the spin-forbidden nature of the transition<sup>22</sup>. The extinction coefficients of these bands ( $\epsilon \sim 20\text{--}50$  per Fe atom) are much higher than those expected for 'spin forbidden'  $d\text{-}d$  transitions in monomeric high spin iron(III) complexes. The enhancement in intensities of these bands has been attributed to an exchange interaction coupling of the two iron atoms<sup>23</sup>. The electronic spectral data of the di-iron complexes (1), (2) and (4) support oxo-bridged dinuclear complex formation, in agreement with the  $\mu_{\text{eff}}$  values and the Mössbauer data.

The infrared spectra of the iron complexes has been recorded in KBr phase. The free ligand show band for  $\nu_{\text{NH}}$  at  $3280\text{--}3310 \text{ cm}^{-1}$  which disappeared in the complexes (1), (2), (5), (7) and (8) suggesting that the ligand acts in the enol form and coordinates with the metal ions after deprotonation. Disappearance of the bands in the range  $3300\text{--}3500 \text{ cm}^{-1}$  in the complexes (1), (2), (5), (7) and (8) indicate the involvement of the bond formation by phenolic OH group after deprotonation. However, the presence of H<sub>2</sub>O in the complexes (1), (2), (5) and (8) complicates this interpretation. A clear picture in this regard is obtained from the IR spectral data of the complex (7). Further, the presence of medium to weak and broad bands in the region  $3300\text{--}3500 \text{ cm}^{-1}$  in the complex (3), (4) and (6) suggest non-involvement of phenolic OH in complex formation. The phenolic C-O in the free ligand is observed  $\sim 1265 \text{ cm}^{-1}$ , which is shifted to the  $1270\text{--}1300 \text{ cm}^{-1}$  range in the chelates (1), (2), (5), (7) and (8) (ref.24). The magnetic susceptibility data suggest dinuclear structure for the complexes (1), (2) and (4). In these di-iron complexes, the two Fe-atoms are probably bridged by the oxygen atoms as the Fe-O-Fe vibration in these complexes is observed  $\sim 840 \text{ cm}^{-1}$  (ref.25). The shift of the  $\nu_{\text{C-O}}$  (phenolic) to higher energy is an evidence of the formation of a phenolic oxygen bridge<sup>26,27</sup>. The present di-iron(III) complexes (1), (2) and (4) show a shift of  $\sim 5\text{--}35 \text{ cm}^{-1}$  in the  $\nu_{\text{C-O}}$  (phenolic) mode suggesting thereby the involvement of the phenolic oxygen in bridge formation.

The complexes (1), (2), (5), (7) and (8) show an additional sharp and strong band  $\sim 1595\text{--}1620 \text{ cm}^{-1}$  which is diagnostic of the azine chromophore ( $>C=N-N=C<$ )<sup>28</sup>. The vibration observed  $\sim 1550\text{--}1510 \text{ cm}^{-1}$  and  $1380\text{--}1330 \text{ cm}^{-1}$  are characteristics of  $\nu_{\text{NCO}^-}$ . The  $\nu_{\text{C=N}}$  for the free ligand appearing at  $1600\text{--}1620 \text{ cm}^{-1}$  in the free ligand shifting to  $\sim 1590\text{--}1600 \text{ cm}^{-1}$  in the complexes suggests coordination through the azomethine nitrogen. Hence, in these complexes, the ligand behaves as a dibasic tridentate ONO donor.



Coordination of pyridine in complex (7) can be inferred from the IR absorption band  $\sim 750\text{ cm}^{-1}$  (ref.29).

The absorption band at  $\sim 1430\text{ cm}^{-1}$  and  $1245\text{ cm}^{-1}$  in the nitrate complexes (5) and (6) are assignable to the  $\nu_1(\text{NO stretching})$  and  $\nu_4(\text{NO}_2\text{ asymmetric stretching})$  vibrations respectively<sup>30</sup>. Thus  $\text{NO}_3^-$  is coordinated in unidentate manner in these complexes.

The uncomplexed ligand exhibits amide-I,  $\nu\text{C}=\text{N}$ , amide II and amide III bands at  $\sim 1600\text{-}1620$ ,  $1565\text{-}1575$ ,  $1490$  and  $1265\text{ cm}^{-1}$  respectively. The negative shift of amide-I ( $\Delta\nu = 10\text{-}15$ ),  $\nu\text{C}=\text{N}$  ( $\Delta\nu = 15\text{-}20\text{ cm}^{-1}$ ) and amide-II ( $\Delta\nu = 10\text{-}20\text{ cm}^{-1}$ ) and a positive shift ( $\Delta\nu = 15\text{-}25\text{ cm}^{-1}$ ) of amide-III in the spectra of the complexes (3) and (6) indicates neutral nature of the ligands and coordination through carbonyl oxygen. These bands are absent in the deprotonated complexes (1), (2), (4), (5), (7) and (8) of the ligand  $\text{H}_2\text{smbhon}$  suggesting enolisation of the *keto* group followed by the complexation through deprotonation. However, the presence of  $\text{H}_2\text{O}$  in the complexes complicates this interpretation. Varied ligating behaviour of  $\text{H}_2\text{smbhon}$  in these complexes (i.e. monobasic bidentate, neutral bidentate, dibasic tridentate, etc.) can also be inferred from the infrared spectral data of these complexes<sup>31</sup>.

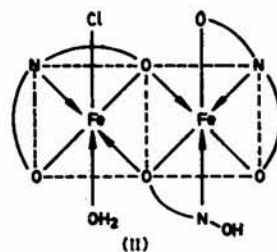
The appearance of a strong band at  $340\text{ cm}^{-1}$  in the complex (7) suggests the presence of  $\sigma$ -bonded  $\text{SnCl}_3^-$  group in this complex<sup>32-34</sup>. The coordinated  $\text{CH}_3\text{CN}$  group in the complex (8) absorbs as a strong band at  $2280\text{ cm}^{-1}$  (ref.35).

The Mössbauer spectral measurements for some of the iron(III) complexes [e.g. complexes (1), (2) and (4) at room temperature] suggests the oxo-bridged dimeric nature of the complexes<sup>36</sup>. The coordination number around iron(III) ion has a direct relation with the value of isomer shift, which follows the order 8-coordinate > 6-coordinate > 4-coordinate<sup>37</sup>.

It has also been observed<sup>37</sup> that as the distortion from octahedral symmetry increases, the isomer shift for six coordinate iron containing minerals decreases toward the four coordinate value.

Recently, Kapoor *et al*<sup>38</sup>, isolated and studied the iron(III) complexes of bis(salicylidine)-oxalyldihydrazine and similar ligands. Low magnetic moments (in the range 4.3-5.2 B.M) and isomer shift (in the range 0.52-0.72 mm/sec) were found for these complexes and iron(III) high-spin octahedral oxo-bridged geometry for these complexes was proposed.

The spectra of the complexes (1) and (2) isolated in the present study, consist of a clear doublet with



isomer shift ( $\delta$ ) =  $0.33 \pm 0.05\text{ mm/sec}$  and  $0.28 \pm 0.05\text{ mm/sec}$  respectively. The isomer shift of these two complexes are low in comparison with the other known iron(III) oxo-bridged complexes which may be due to the lowering of the symmetry. Therefore, high-spin octahedral oxo-bridged structure for these two complexes is tentatively proposed. The very nature of the Mössbauer spectral data for the complexes (1) and (2) suggest that the two iron(III) centres present in each of these complexes are in the same chemical environments. The large values observed for  $\Delta E_Q$  ( $0.90 \pm 0.05\text{ mm/sec}$ ) in the complex (1) may be due to the more asymmetric distribution around iron atoms<sup>39</sup>.

The Mössbauer spectrum of the complex (4), however indicates the presence of two non-equivalent iron(III) sites in it. The site-I has  $\delta = 0.43 \pm 0.05\text{ mm/sec}$  and  $\Delta E_Q = 0.89 \pm 0.05\text{ mm/sec}$ , while site-II has  $\delta = 0.56 \pm 0.05\text{ mm/sec}$  and  $\Delta E_Q = 0.39 \pm 0.05\text{ mm/sec}$ . The magnetic moment value ( $\mu_{\text{eff}} = 5.4\text{ B.M.}$  at room temperature) indicates that the two iron atoms are in high-spin Fe(III) oxidation state, and the following structure may be tentatively suggested for the complex (4) (structure II).

The  $\Delta E_Q$  values indicate that the iron site-I is more distorted with respect to the iron site-II. However, X-ray crystal structure analysis of these complexes may throw more light on the structural features of the iron(III) chelates.

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