

Synthesis, Characterization and Antifungal Activity of Iron (III) Derivatives of N-[O-Hydroxy Substituted (Or H) Benzyl] Glycines

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ABSTRACT: Several iron (III) derivatives of N-[o-hydroxy substituted (or H) benzyl] glycines have been prepared by alcoholysis reactions involving interaction of iron triisopropoxide with the latter in 1:1, 1:2 and 1:3 molar ratios in benzene medium. The amount of isopropanol liberated during the course of reaction was fractionated out azeotropically and estimated to monitor the completion of reaction in each case. The compounds thus prepared were generally obtained as coloured solids and amongst them those containing isopropoxy group were found to be hygroscopic. All these compounds were characterized, by azeotrope and elemental analysis as well as by IR and mass (in several representative cases) spectral measurements. Antifungal activity of the ligands and its metal derivatives were also recorded.

Key words: Iron derivatives, N-[o-hydroxy substituted (or H) benzyl] glycines, alcoholysis reaction, Antifungal activity.

I. INTRODUCTION

N-[o-hydroxy substituted (or H) benzyl] glycines act as potential ligands as evidenced by considerably higher stability of their metal (II) complexes examined in solution^[1,2] earlier. However, work on preparation and characterization of their metallo derivatives is rather scant^[3]. The facile reactivity of metal alkoxides towards protonated organic compounds provides a simple and convenient method of preparing a variety of metallo-organic / organometallic derivatives. In a systematic programme of work in these laboratories it was, therefore, thought worthwhile to prepare their metallo derivatives via the reactivity of the corresponding metal alkoxide in view of the fact these complexones contain replaceable hydrogen(s). The ligating tendency of N-[o-hydroxy substituted (or H) benzyl] glycines

indicates its coordination to Fe(III) and their derivatives widely uses as agro fungicides. The effect of substituent such as methyl, methoxy, ethoxy, present in the phenyl ring on of fungitoxicity of benzal derivatives has been studied. But so far no attempt has been made to investigate the N-[o-hydroxy substituted (or H) benzyl] glycines derivatives which display a vital role in fungitoxicity.

The work described here thus relates to the preparation and characterization of iron (III) derivatives of several N-[o-hydroxy substituted (or H) benzyl] glycines (I) viz. (i) N-(2-hydroxy benzyl)glycine (H₂hbg), (ii) N-(2-hydroxy-3-methyl benzyl)glycine (H₂hmbg-3), (iii) N-(2-hydroxy-6-methyl benzyl)glycine (H₂hmbg-6) and (iv) N-(2-hydroxy-5-methyl benzyl)glycine (H₂hmbg-5). These derivatives were prepared by alcoholysis reactions involving interaction of iron triisopropoxide with (I) in appropriate stoichiometry viz. 1:1, 1:2 and 1:3 in benzene as a reaction medium, which were obtained as coloured solids and amongst them those containing isopropoxy group were found to be hygroscopic. All these derivatives were characterized by elemental and azeotrope analysis, as well as by IR spectra were recorded for all the derivatives prepared, the mass spectra were taken only in several representative cases. NMR measurements were not possible because of insolubility of these derivatives in appropriate solvent. Antifungal activities of some derivatives (1:1 derivatives) with ligands were recorded.

II. EXPERIMENTAL

2.1. Materials

Benzene (Qualigens, AR), isopropanol (Qualigens, AR), solvent ether (Qualigens, AR) was dried by standard procedures^[4]. The various N-[o-hydroxy substituted (or H) benzyl] glycines

were prepared and purified by methods reported earlier [3]. Iron triisopropoxide was prepared by already known method [5,6].

2.2. Apparatus / instruments

Melting points were determined digital m.p. apparatus and are uncorrected. The IR spectra were recorded on a Bruker IFS 66v FT-IR spectrometer in the region 4000-400cm⁻¹, using KBR pellets. The electrothermal digital m.p apparatus and are uncorrected. The IR spectra were recorded on a micromass Quarto II triple quadrupole mass spectrometer. The samples were introduced into the ESI source through a syringe pump at 0.4 ml/h. the ESI capillary was 305 kv² and the voltage was 25-50v.

2.3. Preparation of iron (III) derivatives of (I): General procedure

Stringent precautions were taken to exclude moisture throughout the experiments using glass assemblies with interchangeable joint. The alcoholysis reactions were performed in a fractionating column (30cm long) packet with racing rings and fitted to a total condensation variable take-off still head. Guard tubes filled with fused calcium chloride were used, wherever required.

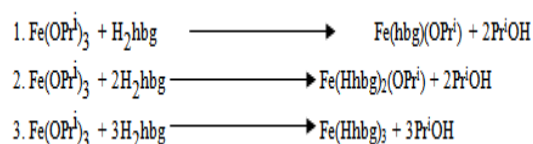
A mixture of Fe (OPrⁱ)₃ and (I) in appropriate stoichiometry in dry benzene take in a R. B. flask, was refluxed on a wax bath (90-100⁰C), using a fractionating column. After several hrs. (Table 1) of reflux, the isopropanol-benzene azeotrope was fractionated out and the amount of isopropanol liberated was estimated by an oxidimetric method [7,8] [liberated isopropanol was oxidized to acetone by a known volume of K₂Cr₂O₇ (N) solution in 12.5% H₂SO₄ which was estimated iodometrically by titrating against standard sodium thiosulphate (N/5) solution] to monitor the completion of the reaction. After the completion of the reaction, the excess of solvent from the reaction mixture was removed in vacuum, when the product isolated as a coloured solid which was washed with dry benzene (3-4 times) followed by dry ether (2-3 times) and finally dried under suction.

III. RESULTS AND DISCUSSION

The relevant analytical details of the various compounds prepared are summarized in Table 1. The molecular weights obtained from the mass spectral data (Table 1) in case of several representative cases are good in agreement with the corresponding calculated values. Since, these

ligands exist in zwitterionic form [3] (Structure 1) there exists a possibility of replacement of isopropoxy group(s) from iron triisopropoxide by

the hydrogen from either the >N⁺H₂ group or hydroxy group or both of them from the ligands with the liberation of isopropanol and the formation of a new class of organo derivatives of iron (III). The various reactions occurring between Fe(OPrⁱ)₃ and H₂hbg are as under:



The 1:1 molar reaction (reaction 1) resulted in the replacement of two of the isopropoxy groups from Fe(OPrⁱ)₃ by one of the

hydrogens from the >N⁺H₂ group, as well as the hydrogen from the hydroxy groups from H₂hbg. In molar reaction (reaction 2) again two of the isopropoxy groups from Fe(OPrⁱ)₃ were replaced by one of the hydrogens from each of the

hydrogens from each of the two >N⁺H₂ groups available from two moles of H₂hbg. The 1:3 molar reaction (reaction 3) resulted in the replacement of all three isopropoxy groups from Fe(OPrⁱ)₃ by one

of the hydrogens from each of three >N⁺H₂ groups available from three moles of H₂hbg.

Similar course of reaction followed in case of the other derivatives viz. H₂hmbg-3, H₂hmbg-6 and H₂hmbg-5.

3.1. IR spectral measurements

3.1.1. N-[o-hydroxy substituted (or h) benzyl] glycines

Though the characterization of these ligands by IR spectral measurements has already been reported by [3] their characteristic IR frequencies are, however, being recorded here again (Table 2) for the purpose of comparison with their corresponding iron (III) derivatives in order to elucidate the structures of the latter.

3.1.2. Iron (III) derivatives of N-[o-hydroxy substituted (or H) benzyl] glycines

1.1. Derivatives

The main observations from the IR measurements are as under:

- (i) The absorption in the region $3600-3300\text{ cm}^{-1}$ due to νOH of the unbonded hydroxyl group^[9] as observed in the ligands is found to be absent here suggesting the bonding of the hydroxyl oxygen to iron(III).
- (ii) The band due to $\nu\text{N-H}$ of the zwitterionic $>\overset{+}{\text{N}}\text{H}_2$ group^[10] as observed in (I) between $2600-2375\text{ cm}^{-1}$ is found to disappear here with the appearance of new νNH band in the region $3400-3100\text{ cm}^{-1}$ indicating deprotonation of the $>\overset{+}{\text{N}}\text{H}_2$ group to $>\text{NH}$, as a result of coordination of the imino nitrogen to iron (III).
- (iii) A shift of $10-20\text{ cm}^{-1}$ in $\nu_{\text{s}}\text{COO}$ as compared to (I) suggest possible bonding of the carboxylate oxygen to iron (III). Further, the separation value, $\Delta\nu\text{COO}$ ($\nu_{\text{as}}\text{COO} - \nu_{\text{s}}\text{COO}$) between $250-230\text{ cm}^{-1}$ shows unidentate bonding of the carboxylate group^[11] to iron (III).
- (iv) The absorption in the region $1390-1380\text{ cm}^{-1}$ corresponds to the gem-dimethyl structure of the isopropoxy group^[9]. Again, the absorption in the region $1150-1020\text{ cm}^{-1}$ indicates $\nu\text{C-O}$ of the isopropoxy group^[12].
- (v) The medium and weak bands in the region $480-450\text{ cm}^{-1}$ may be assigned to $\nu\text{Fe-O}$, while the others in the region $430-420\text{ cm}^{-1}$ correspond to $\nu\text{Fe-N}$.

On of the basis of the foregoing considerations it is inferred that iron (III) in these derivatives viz. $\text{Fe}(\text{hbg})(\text{OPr}^i)$, $\text{Fe}(\text{hmbg-3})(\text{OPr}^i)$, $\text{Fe}(\text{hmbg-6})(\text{OPr}^i)$ and $\text{Fe}(\text{hmbg-5})(\text{OPr}^i)$ exhibits tetra coordination in each case as a consequence of bonding with one of the oxygens from the carboxylate group, as well as the nitrogen from imino group (obtained by deprotonation of $>\overset{+}{\text{N}}\text{H}_2$ group) and the hydroxy oxygen, along with an isopropoxy group, as shown in (Structure 2).

1.2. Derivatives

The IR measurements indicate that:

- (i) A broad band in the region $3600-3000\text{ cm}^{-1}$ derivatives corresponds to the overlapping of

$\nu\text{O-H}$ of the unbonded hydroxy group and $\nu\text{N-H}$ along with aromatic $\nu\text{C-H}$.

- (ii) The appearance of new bond in the region $1720-1700\text{ cm}^{-1}$ may be assigned to $\nu\text{C-O}$ of the carbonyl group, expected of a normal ester type of linkage^[13]. The existence of this linkage is further supported by absorption between $1240-1225\text{ cm}^{-1}$ due to $\nu\text{C-O}$.
- (iii) The absorption in the region $1390-1385\text{ cm}^{-1}$ occurs due to the overlapping of O-H bending of the hydroxy group and C-H bending of gem-dimethyl structure of the isopropoxy group. The presence of $\nu\text{C-O}$ of the isopropoxy group is identified by medium and strong band in the region $1140-1030$.
- (iv) The medium and weak absorptions in the region $540-420\text{ cm}^{-1}$ correspond to $\nu\text{Fe-O}$. these observations suggest that iron (III) in these derivatives viz. $\text{Fe}(\text{Hhbg})_2(\text{OPr}^i)$.
- (v) $\text{Fe}(\text{Hhmbg-3})_2(\text{OPr}^i)$, $\text{Fe}(\text{Hhmbg-6})_2(\text{OPr}^i)$ and $\text{Fe}(\text{Hhmbg-5})_2(\text{OPr}^i)$ is bonded with one of the oxygen from each of the two carboxylate group available from two moles of the ligand having a normal ester type of linkage, along with an isopropoxy group, and thus it exhibits its known trivalency in each case, as shown in (Structure 3).

1.3. Derivatives

Here, the findings from the IR measurements are as follows:

- (i) The absorption in the region $3500-3400\text{ cm}^{-1}$ may be assigned to the unbonded hydroxy group.
- (ii) Here, again the band due to $\nu\text{N-H}$ of the zwitterionic $>\overset{+}{\text{N}}\text{H}_2$ group as observed in (I) is found to be absent with appearance of a new $\nu\text{N-H}$ band in the region $3400-3100\text{ cm}^{-1}$ indicating deprotonation of the $>\overset{+}{\text{N}}\text{H}_2$ group to $>\text{NH}$ as a result of bonding the imino nitrogen to the iron (III).
- (iii) A shift of $10-20\text{ cm}^{-1}$ in $\nu_{\text{s}}\text{COO}$ as compared to the corresponding ligand suggest the bonding of the carboxylate oxygen to iron. The separation value, $\Delta\nu\text{COO}$ in the region $230-245\text{ cm}^{-1}$ is indicative of the unidentate bonding of the carboxylate group to iron (III).

(iv) The medium and weak absorptions in the region $480-450\text{cm}^{-1}$ occur due to $\nu\text{Fe-O}$, while the other weak absorptions in the region $420-415\text{cm}^{-1}$ correspond to $\nu\text{Fe-N}$.

It is thus concluded that iron (III) in these derivatives viz. $\text{Fe}(\text{Hhmbg-3})_3$, $\text{Fe}(\text{Hhmbg-6})_3$ and $\text{Fe}(\text{Hhmbg-5})_3$ display hexa-coordination as a result of bonding with one of the oxygens from each of the three carboxylate group and the nitrogen from each of the three imino groups

(obtained by deprotonation of $>\overset{+}{\text{N}}\text{H}_2$ groups) available from three moles of ligand, as shown in (Structure 4).

3.2. ^1H NMR spectrum measurements

3.2.1. N-[o-hydroxyl substituted (or H) benzyl] glycines (abbreviated as I)

The existence of (I) in zwitterionic form is further supported by ^1H NMR spectrum Measurements by the appearance of a singlet at

$\delta 3.00 - \delta 3.85$ corresponding to the $>\overset{+}{\text{N}}\text{H}_2$ group protons. The appearance of any singlet in the region $13.00-7.50$ indicates the absence of the carboxylic acid group. The characteristic ^1H NMR frequencies of the ligands and their derivatives being recorded in (Table-3).

3.2.2. 1:1, 1:2 and 1:3 derivatives of (I)

The singlet in the region $\delta 3.95- \delta 3.35$ due to the $>\overset{+}{\text{N}}\text{H}_2$ protons, as observed in (I) is found to be absent in these derivatives. On the other hand, the appearance of new signal (singlet) in the region $\delta 3.65- \delta 3.50$ shows coordination of the imino nitrogen (obtained by deprotonation of the $>\overset{+}{\text{N}}\text{H}_2$ group) to iron in case of 1:1 and 1:3 derivatives. A singlet in the region $\delta 5.95- \delta 4.50$ due to the unbonded hydroxyl group observed in the ligands is found to be absent here suggesting the bonding of the hydroxyl oxygen to iron (III) in the case of 1:1 derivatives. A doublet in the region $\delta 1.50- \delta 1.10$ and a multiplet in the region $\delta 4.35- \delta 4.15$ occur respectively due to the $-\text{CH}_3$ and $\equiv\text{CH}$

protons of the isopropoxy group in the case of and derivatives.

IV. ANTIFUNGAL ACTIVITY

The antifungal activity of ligands and their 1:1 derivatives has been evaluated by Radial Growth Method ^[14] using Czapek's agar medium having the composition, glucose 20g, starch 20g, agar-agar 20g and distilled water 1000 ml. The principle involved in this technique is to poison the nutrient medium a fungitoxicant and then allowing a test fungus to grow on such a medium.

The test compounds are incorporated in the potato-dextrose agar medium in requisite amount to give a certain concentration (50, 100 and 200 ppm) and thoroughly mixed by constant stirring. The medium is then poured into the petriplates and stored in a refrigerator. A disk of 7mm of fungal culture of a specific age growing on the solid medium is then cut with a sterile cork borer. The plates are incubated at specific temperature, favorable for the growth of test fungus. Suitable checks are kept where the culture discs are grown under the same condition on the agar medium without any fungicide. Three replicates were used in each case. The colony diameter after four days is measured to evaluate the fungitoxicity. The percent inhibition was calculated as: $\% \text{ inhibition} = \frac{(C-T)}{C} \times 100$ where C and T are the diameters of the fungus colony in control and test discs, respectively.

The pathogenic fungi used for this investigation are *Aternaria salternata* and *Fusarium oxporum*. The structure activity relationship shows that the presence of isopropoxy group in phenyl ring showed strong activity against all test fungi as shown in Table 4. The chelation theory ^[14] accounts for the metal complexes; the chelation reduces the polarity of the metal atom mainly because of partial sharing of its positive charge with the donor groups and possible p electron delocalization within the whole chelating ring. The chelation increases the lipophilic nature of the central atom, which subsequently favors its permeation through the lipid layer of the cell membrane.

Table 1. Analytical Details of the N-[o-hydroxy substituted (or H) benzyl] glycines and their iron (III) derivatives.

Compound (Molar ratio)	Reflu x	m.p. ($^{\circ}\text{C}$)	Azeotrope	Elemental Analysis % Found (calcd.)	* Mol.
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(Color)	Time (hrs.)	Analysis Pr ⁱ OH (g) found (calcd.)	C	H	N	Fe	Wt. found (calcd.)
H ₂ hbg (off white)	- 50	-	59.50 (59.66)	6.00 (6.12)	7.70 (7.73)	-	-
H ₂ hmbg-3 (off white)	- 190	-	61.45 (62.52)	6.70 (6.71)	7.16 (7.18)	-	-
H ₂ hmbg-6 (off white)	- 88	-	61.30 (61.30)	6.69 (6.71)	7.16 (7.18)	-	-
H ₂ hmbg-5 (off white)	- 148	-	61.45 (61.52)	6.68 (6.71)	7.15 (7.18)	-	-
Fe(hbg)(OPr ⁱ) (1:1) (brown)	6 160	1.07 (1.11)	48.82 (49.00)	5.46 (5.48)	4.75 (4.76)	18.90 (18.99)	294.1 (284.1)
Fe(Hhbg) ₂ (OPr ⁱ) (1:2) (brown)	4 172	0.76 (0.76)	52.90 (53.07)	5.71 (5.73)	5.87 (5.89)	11.72 (11.72)	475.3 (475.3)
Fe(Hhbg) ₃ (1:3) (brown)	18 214	0.91 (0.91)	54.15 (54.37)	5.06 (5.07)	7.02 (7.05)	9.33 (9.36)	-
Fe(Hmbg-3) (OPr ⁱ) (1:1) (dark brown)	6 175	1.24 (1.25)	50.45 (50.67)	5.87 (5.89)	4.55 (4.55)	18.08 (18.12)	-
Fe(Hmbg-3) ₂ (OPr ⁱ) (1:2) (dark brown)	4 190	1.10 (1.10)	54.65 (54.88)	6.18 (6.21)	5.55 (5.57)	11.08 (11.10)	503.3 (503.4)
Fe(Hmbg-3) ₃ (OPr ⁱ) (1:3) (dark brown)	10 210	1.06 (1.07)	56.20 (56.43)	5.66 (5.68)	6.57 (6.58)	8.73 (8.75)	-
Fe(Hhmbg-6) (OPr ⁱ) (1:1) (dark brown)	7 165	1.23 (1.23)	50.45 (50.67)	5.88 (5.89)	4.54 (4.55)	18.09 (18.12)	380.1 (380.1)
Fe(Hhmbg-6) ₂ (OPr ⁱ) (1:2) (dark brown)	5 200	0.96 (0.97)	54.65 (54.88)	6.19 (6.21)	5.55 (5.57)	11.08 (11.10)	-
Fe(Hmbg-6) ₃ (1:3) (dark brown)	12 285	1.16 (1.16)	56.22 (56.43)	5.66 (5.68)	6.56 (6.58)	8.72 (8.75)	-
Fe(Hhmbg-5) (OPr ⁱ) (1:1) (dark brown)	6 190	1.28 (1.29)	50.49 (50.67)	5.88 (5.89)	4.55 (4.55)	18.09 (18.12)	-

Fe(Hhmbg-5) ₂ (OPr ⁱ) (1:2) (dark brown)	5	168	0.93 (0.94)	54.65 (54.88)	6.19 (6.21)	5.56 (5.57)	11.07 (11.10)	503.4 (503.4)
Fe(Hhmbg-5) ₃ (1:3) (dark brown)	10	145	1.08 (1.08)	56.21 (56.43)	5.68 (5.68)	6.56 (6.58)	8.73 (8.75)	

Abbreviation : OPrⁱ = OC₃H₇, H₂hbg = HOC₆H₄CH₂>N⁺H₂CH₂COO⁻, H₂hmbg-3 (or-6 or-5) = HOC₆H₃(CH₃)CH₂CH₂>N⁺H₂CH₂COO⁻
 * Obtained by mass spectral measurements.

Table 2. Characteristic Infrared frequencies (cm⁻¹) of N-[o-hydroxy substituted (or H) benzyl] glycines and its iron (III) derivatives.

Ligand	Fe (III) Derivatives			Assignments
H ₂ hbg, H ₂ hmbg-3, H ₂ hmbg-6, H ₂ hmbg-5	Fe(hbg)(OPr ⁱ), Fe(hmbg-3)(OPri), Fe(hmbg-6)(OPr ⁱ), Fe(hmbg-5)(OPr ⁱ)	Fe(Hhbg) ₂ (OPr ⁱ), Fe(Hhmbg-3) ₂ (OPr ⁱ), Fe(Hhmbg-6) ₂ (OPr ⁱ), Fe(Hhmbg-5) ₂ (OPr ⁱ)	Fe(Hhbg) ₃ Fe(Hhmbg-3) ₃ Fe(Hhmbg-6) ₃ Fe(Hhmbg-5) ₃	
3600-3000 (mb)	-	-	-	Overlapping of νO-H and νC-H of aromatic ring
-	3400-3000 (wb)	-	-	Overlapping of νN-H and νC-H
-	-	3600-3000 (wb)	3500-3400 (wb)	Overlapping of unbonded νO-H, νN-H and νC-H
2910-2840 (wb,mb)	2910-2840 (wb)	2900-2820 (mb,wb)	2920-2800 (mb, wb)	νC-H of -CH ₂ - and -CH ₃
-	-	1720-1700 (s,m)	-	νC=O of carbonyl group
2600-2375 (s,m)	-	-	-	νN-H of >N ⁺ H ₂ group
1640-1630 (sb)	-	-	-	Overlapping of ν _{as} COO ⁻ and aromatic νC=C
-	1630-1625 (sb)	1620-1615 (sb, mb)	1630-1625 (mb, sb)	Overlapping of ν _{as} COO ⁻ aromatic νC=C and N-H deformation
1400-1405 (s)	1390-1385 (w, m)	-	-	ν _s COO ⁻

-	-	1390-1385 (wb, mb)	-	Overlapping of O-H bending of hydroxy group and C-H bending of gem-dimethyl structure of the isopropoxy group.
-	-	-	1390-1385 (wb, mb)	Overlapping of $\nu_s\text{COO}^-$ and O-H bending of hydroxy group.
-	-	1215-1210 (m)	-	$\nu\text{C-O}$ of the ester type of linkage
-	1150-1020 (w,m)	1140-1030 (w, m,)	-	$\nu\text{C-O}$ of the isopropoxy group
1120-650 (m,w)	1000-750 (w, m)	980-785 (w, m)	945-790 (w, m)	In-plane bending vibrations and out-of-plane bending vibrations
-	480-450 (m, w)	540-420 (m, w)	490-440 (m, w)	$\nu\text{Fe-O}$
-	430-425 (w)	-	420-415 (w)	$\nu\text{Fe-N}$

Abbreviations : s = strong, m = medium, w = weak, sb = strong broad, mb = medium broad, wb = weak broad.

Table 3. Magnetic resonance spectral data (δ value) of N-(o-hydroxyl) substituted (or H) benzyl] glycines and its iron (III) derivatives

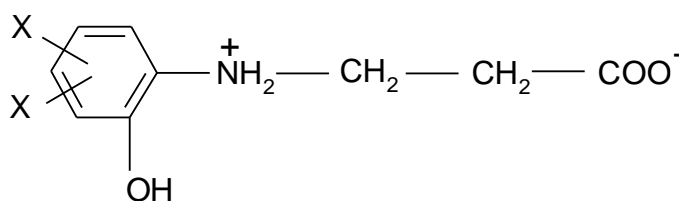
Ligands (I)	Fe(III) derivatives			Assignment
	1:1 (Described in table - 1)	1:2	1:3	
$\delta 7.30 - \delta 6.55$ (m)	$\delta 7.50 - \delta 6.75$ (m)	$\delta 7.20 - \delta 6.35$ (m)	$\delta 6.50 - \delta 6.40$ (m)	Aromatic ring protons.
$\delta 7.20 - \delta 3.15$ (s)	$\delta 3.30 - \delta 3.25$ (s)	$\delta 3.35 - \delta 3.25$ (s)	$\delta 3.35 - \delta 3.20$ (s)	$-\text{CH}_2-$ protons (attached with the benzene nucleus)
$\delta 2.24 - \delta 2.40$ (s)	$\delta 2.70 - \delta 2.68$ (s)	$\delta 2.55 - \delta 2.60$ (s)	$\delta 2.75 - \delta 2.65$ (s)	$-\text{CH}_2-$ protons (of glycine part)
$\delta 3.90 - \delta 3.85$ (s)	-	-	-	$>\text{N-H}$ protons of the $>\text{NH}_2$ group
-	$\delta 3.50 - \delta 3.65$ (s)	$\delta 3.70 - \delta 3.50$ (s)	$\delta 3.75 - \delta 3.65$ (s)	
$\delta 2.25 - \delta 2.20$ (d)	$\delta 2.10 - \delta 2.05$ (d)	$\delta 2.15 - \delta 2.10$ (d)	$\delta 2.11 - \delta 2.00$ (d)	$-\text{CH}_3$ protons attached with the benzene ring

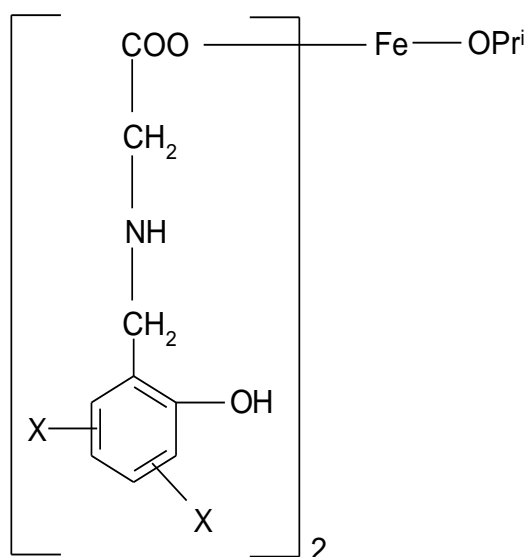
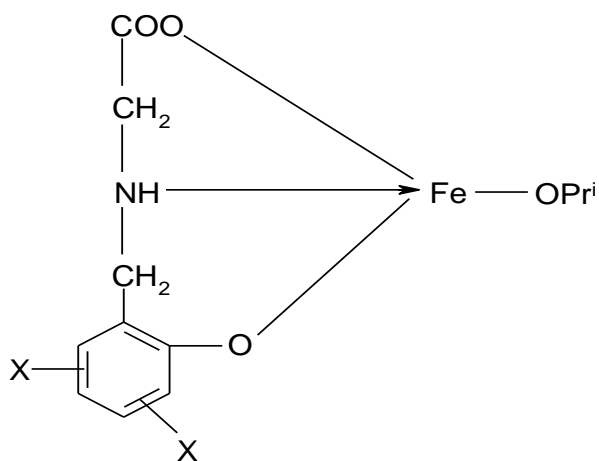
-	$\delta 1.55 - \delta 1.35$ (d) S	-	$\delta 1.35 - \delta 1.15$ (d)	-CH ₂ - protons of the isopropoxy group
-	$\delta 4.35 - \delta 4.25$ (m)	-	$\delta 4.35 - \delta 4.30$ (m)	≡CH protons of the isopropoxy group
$\delta 4.90 - \delta 4.60$ (s)	-	$\delta 4.80 - \delta 4.70$ (s)	$\delta 4.75 - \delta 4.70$ (s)	-OH protons of the hydroxyl group

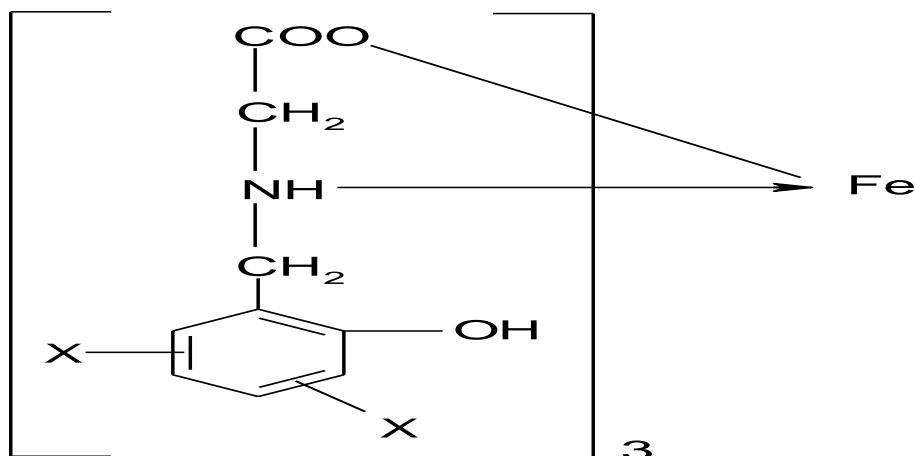
Abbreviations : s = singlet, d = doublet, m = multiplet.

Table 4. Fungicidal screening data of ligands and its derivatives (1:1 derivatives), average percent growth inhibition after 7 days at 30± 2^o c.

Compound	Alternaria alternata			Fusarium oxysporum		
	50	100	200	50	100	200
H ₂ hbg	30	25	20	40	51	55
H ₂ hmbg-3	38	34	27	30	35	34
H ₂ hmbg-6	28	33	35	30	32	32
H ₂ hmbg-5	40	42	46	45	38	39
Fe(hbg)(OPr ⁱ)	45	55	42	47	41	40
Fe(hmbg-3)(OPr ⁱ)	40	57	50	51	56	55
Fe(hmbg-6)(OPr ⁱ)	57	55	50	52	58	60
Fe(hmbg-5)(OPr ⁱ)	59	60	62	59	65	69







Structure-4

REFERENCES

- [1]. Chandra, M. (1983). Transition metal chem. 276.(8, 17, 25).
- [2]. Chandra, M. and Dey, A. K. (1987). Acta chin.Hung. 124.(259).
- [3]. Sivadasan, P. and Chandra, M. (1994). Chim .Acta. turcica. 22.(225).
- [4]. Vogle, A. I. (1978). A Text Book of the practical organic chemistry, 14th edit, Longmans, London.
- [5]. Sarma, P. P and Mehrotra, R. C. (1967). J. Indian chem.soc, 44(74).
- [6]. Bradley, D. C., Gaur, D. P. and Mehrotra, R. C. (1978). Metal Alkoxides, Academic press, London.
- [7]. Bradley, D. C., Halim F. M. A. and Wardlaw, W. (1950). J.Chem. soc, 34(50).
- [8]. Mehrotra, R. C. (1954) J. Indian Chem. soc, 31,(94).
- [9]. Silverstein, R. M., Bassler, G. C. and T.C.Morrill (1981). Spectrometric Identification of Organic Compounds, New York, John Wiley.
- [10]. Bellamy, L. J. (1962). Infrared Spectra of Complex Molecules, London, Methem.
- [11]. Nakamoto, K. (1978). Infrared and Raman Spectra of Inorganic and Coordination Compounds, New York, John Wiley.
- [12]. Ho, Y. K. and Zuckerman, J. J. (1973). Inorg.Chem, 12,(152).
- [13]. Sing, D., Goyal, R. B., and Sing, R. V. (1991) Appl. Organomet. Chem.5, (45).
- [14]. Kumari, A., Sing, R. V. and Tandon, J. V. (1992). Phosphorus, Sulfur and Silicon.66, (195).