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Iron(III) and Antimony(III) Derivatives of 1-Hydroxy -2-Naphthoic and 3-Hydroxy-2-Naphthoic Acids

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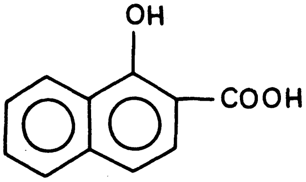
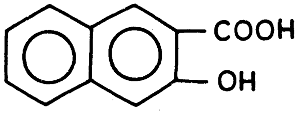
Several iron(III) and antimony(III) derivatives of 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids have been prepared by the interaction of iron or antimony triisopropoxide with the latter in various stoichiometric ratios *viz.* 1 : 1, 1 : 2 and 1 : 3 in benzene medium. The compounds thus prepared were obtained as coloured solids with some of them being hygroscopic. All these compounds were characterized by azeotrope and elemental analyses, as well as by IR and PMR spectral measurements.

INTRODUCTION

The ligating properties of 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic acids have widely been examined in solution[1–6]. Their metal complexes have also been isolated in solid state and characterized in several cases[7,8]. No attempt has, however, been made towards the preparation of their metallo derivatives especially *via* the reactivity of the corresponding metal alkoxide, particularly in view of the fact that these naphthoic acids contain replaceable hydrogen(s). The work described here thus deals with the preparation of several iron(III) and antimony(III) derivatives of 1-hydroxy-2-naphthoic acid (LH_2) (I) and 3-hydroxy-2-naphthoic acid ($L'H_2$) (II) by alcoholysis reaction involving the interaction of the corresponding metal isopropoxides with LH_2 or $L'H_2$ in appropriate



(I)



(II)

stoichiometric ratios *viz.* 1:1, 1:2 and 1:3 in benzene medium. The amount of isopropanol liberated during the course of reaction was fractionated out azeotropically and estimated to monitor the completion of the reaction in each case. The compounds thus prepared were 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 PMR spectral measurements.

EXPERIMENTAL

Due to highly hygroscopic nature of the metal alkoxides, stringent precautions were taken to exclude moisture throughout the experiments, using glasswares with interchangeable joints. The alcohol interchange reactions were performed in a fractionating column (30 cm long) packed with Rasching rings and fitted to a total condensation variable take-off stillhead. Special weighing tubes and measuring pipettes were used for the analytical sampling of the compounds.

Benzene (BDH, AR), isopropanol (BDH, Glaxo AnalaR) and solvent ether (E. Merck) were dried by standard procedures.[9] 1-Hydroxy-2-naphthoic acid (E.Merck) and 3-hydroxy-2-naphthoic acid (Koch-Light) were used after recrystallization from 50% (*v/v*) aqueous-ethanol. Iron and antimony triisopropoxides were prepared by known methods.[10,11]

Iron(III) was estimated as ferric oxide[12], while antimony(III) was first oxidized to antimony (V) and then estimated iodimetrically.[13] The IR spectra were recorded on a Perkin-Elmer Model 983 Spectrometer in the region 4000–400 cm^{-1}, using KBr pellets, while the PMR spectral measurements were taken in dmso-d_6 solution on a Varian EM 390, 90 MHz Spectrometer, using TMS as an internal standard.

Reaction Between Iron Triisopropoxide and LH_2; 1:1 Molar Ratio

A mixture $Fe(OPr^i)_3$ (1.1670 g; 5.01 m mole) and LH_2 (0.9420 g; 5.01 m mole) suspended in dry benzene (60 ml) taken in a R.B. flask was refluxed on a wax bath (95–100°C), using a fractionating column. After *ca.* 10 h of reflux, the isopropanol liberated during the course of reaction was removed azeotropically, and determined by an oxidimetric method.[14,15] On completion of the reaction, the excess of solvent from the reaction mixture was removed *in vacuo*, when the product, $Fe(OPr^i)$ (L) isolated as a black solid. It was then filtered under suction, washed with dry benzene (3–4 times) and then by dry ether (2–3 times) to remove unreacted $Fe(OPr^i)_3$ and LH_2, if any, and then dried in vacuum yield ~ 80.0 – 86.1%). The product was found to be soluble in dimethylformamide and dimethylsulphoxide but insoluble in other common organic solvents like ethanol, benzene, toluene, ether, carbon tetrachloride etc. Similar procedure was adopted for the preparation and purification of other derivatives. The analytical and spectral data are recorded in Tables 1–3.

TABLE 1
ANALYTICAL DATA OF THE VARIOUS IRON (III) AND ANTIMONY(III) DERIVATIVES OF 1-HYDROXY-2-NAPHTHOIC 3-HYDROXY -2-NAPHTHOIC ACIDS

S. NO.	Compound/(molar ratio)/Colour	m.p. (°C)	Azeotropic analysis Pr^iOH found (calcd)	Analysis % Found (Calcd.)		
				C	H	Metal
1.	$Fe(OPr^i)(L)$ (1:1)(Black)	>300	0.58 (0.60)	55.59 (55.85)	4.33 (4.35)	18.50 (18.55)
2.	$Fe(OPr^i)(LH_2)$ (1:2)(Black)	>300	0.50 (0.52)	61.09 (61.37)	4.31 (4.33)	11.36 (11.41)
3.	$Fe(LH_3)$ (1:3)(Black)	>300	0.95 (0.99)	63.92 (64.20)	3.41 (3.43)	9.01 (9.05)
4.	$Sb(OPr^i)(L)$ (1:1)(Yellow)	180	0.38 (0.39)	45.63 (45.82)	3.56 (3.57)	33.34 (33.17)
5.	$Sb(OPr^i)(L'H)_2$ (1:2)(White)	157	1.08 (1.12)	53.85 (54.09)	3.83 (3.81)	21.82 (21.93)
6.	$Sb(LH)_3$ (1:3)(White)	135	1.13 (1.17)	57.79 (58.01)	3.09 (3.10)	17.78 (17.82)
7.	$Fe(OPr^i)(L')$ (1:1)(Black)	>300	1.09 (1.12)	55.52 (55.85)	4.33 (4.35)	18.52 (18.55)
8.	$Fe(OPr^i)(L'H)_2$ (1:2)(Black)	>300	0.98 (1.02)	61.10 (61.37)	4.32 (4.33)	11.36 (11.41)
9.	$Fe(L'H)_3$ (1:3)(Black)	>300	1.15 (1.20)	63.90 (64.20)	3.42 (3.43)	9.02 (9.05)
10.	$Sb(OPr^i)(L')$ (1:1)(Yellow)	220 d	0.67 (0.69)	45.60 (45.82)	3.56 (3.57)	33.17 (32.17)
11.	$Sb(OPr^i)(L'H)_2$ (1:2) (Yellow)	198	0.99 (1.01)	53.85 (54.09)	3.83 (3.81)	21.82 (21.93)
12.	$Sb(L'H)_3$ (1:3) (Yellow)	210	1.00 (1.01)	57.73 (58.01)	3.09 (3.10)	17.75 (17.82)

Abbreviations: $OPr^i = OC_3H_7$, LH_2 or $L'H_2 = C_{11}H_8O_3$

RESULTS AND DISCUSSION

The various reactions occurring between iron or antimony triisopropoxide and LH_2 may be illustrated as under:

$$M(OPr^i)_3 + LH_2 \rightarrow M(OPr^i)(L) + 2Pr^iOH \quad (1)$$

$$M(OPr^i)_3 + 2LH_2 \rightarrow M(OPr^i)(LH_2) + 2Pr^iOH \quad (2)$$

$$M(OPr^i)_3 + 3LH_2 \rightarrow M(LH)_3 + 3Pr^iOH \quad (3)$$

where, M = Fe or Sb.

Identical reactions followed in case of $L'H_2$.

TABLE 2

CHARACTERISTIC INFRARED FREQUENCIES (cm^{-1}) OF 1-HYDROXY-2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS AND THEIR IRON(III) AND ANTIMONY(III) DERIVATIVES

S. No.	Compound	νOH	νC–H	ν_{as}COO	ν_{s}COO	ΔνCOO	C–H bending of *gem* dimethyl	OH bending	νC–O	νM–O
1.	LH_2	3200–2400 (mb)*	—	1640 (vsb)	1420 (m)	—	—	1310 (m)	1260 (m)	—
2.	$L'H_2$	3300 (mb)	3100–2780 (mb)	1670 (b)	1405 (m)	—	—	1320 (m)	1260 (m), 1225 (s)	—
3.	$Fe(OPr^i)(L)$	—	3080–2860 (mb)	1600 (sb)	1410 (m)	210	1360 (m)	—	1265 (m), 1220 (m)	470 (mb), 425 (s)
4.	$Fe(OPr^i)(LH)_2$	3500–3220 (b)	3080 (w), 2940 (w), 2875 (w)	1585 (s)	1420 (s)	165	1365 (m)	—	1270 (m)	490 (m) 450 (m)
5.	$Fe(LH)_3$	3350–3180 (b)	3140 (mb), 3000 (m), 2880 (m)	1600 (vs)	1435 (m)	165	—	1330 (m)	1280 (s)	480 (mb)
6.	$Sb(OPr^i)(L)$	—	3060–2580 (mb)	1630 (vs)	1430 (s)	200	1360 (sh)	—	1250 (m), 1210 (s)	590 (m), 540 (m)
7.	$Sb(OPr^i)(LH)_2$	3350–3120 (mb)	3080 (m), 2960 (w)	1610 (vs)	1415 (m)	195	1360 (sh)	1310 (mb)	1310 (mb), 1270 (m)	585 (mb)
8.	$Sb(LH)_3$	3300–3100 (b)	3060–2830 (mb)	1630 (vs)	1430 (m)	200	—	1310 (m)	1260 (m)	580 (m)
9.	$Fe(OPr^i)(L')$	—	3060 (m), 3000 (m), 2880 (m)	1605 (s)	1425 (mb)	185	1360 (s)	—	1270 (m), 1220 (w)	490 (w), 455 (s)

S. No.	Compound	νOH	νC–H	ν_{as}COO	ν_{s}COO	ΔνCOO	C–H bending of *gem* dimethyl	OH bending	νC–O	νM–O
10.	Fe(OPr^i)(L′H)$_2$	3300 (mb)	3060 (m), 2940 (m), 2840 (w)	1630 (s)	1450 (s)	180	1360 (m)	1300 (m)	1250 (wb)	485 (s), 450 (s)
11.	Fe(L′H)$_3$	3400–3220 (mb)	3000 (w), 2870 (m), 2800 (m)	1630 (sb)	1420 (s)	190	—	1360 (s) 1320 (m)	1250 (s)	540 (m), 460 (s)
12.	Sb(OPr^i)(L′)	—	3050–2820 (mb)	1630 (vsb)	1440 (s)	190	1385 (mb)	—	1280 (s), 1215 (s, sh)	580 (w), 550 (vw)
13.	Sb(OPr^i)(L′H)$_2$	3280 (s)	3040–2600 (mb)	1630 (sb)	1440 (m)	190	1385 (m)	1350 (s)	1275 (sh), 1215 (m)	620 (m), 580 (vw)
14.	Sb(L′H)$_3$	3320 (s)	3060–2720 (mb)	1640 (vsb)	1440 (s)	200	—	1350 (m)	1280 (sh), 1210 (s)	580 (vw), 560 (vw)

*Overlapping of νO–H and νC–H

Abbreviations: vw = very weak, w = weak, m = medium, b = broad, wb = weak broad, mb = medium broad, sb = strong broad, vsb = very strong broad, s = strong, sh = shoulder.

TABLE 3

PROTON MAGNETIC RESONANCE SPECTRAL DATA (δ value) OF 1-HYDROXY-2-NAPHTHOIC AND 3-HYDROXY-2-NAPHTHOIC ACIDS AND SOME OF THEIR IRON(III) AND ANTIMONY(III) DERIVATIVES

S. NO.	Compound	–COOH and –OH (Hydrogen bonded)	Naphthyl ring protons	–OH	Isopropoxy (*gem* dimethyl protons)
1.	LH_2	9.90–10.50 (m)	8.60 (d), 7.40–7.90 (m)	—	—
2.	$L'H_2$	9.90–12.90 (m)	8.58 (s), 7.34–7.99 (m)	—	—
3.	$Fe(OPr^i)(L)$	—	6.75–8.52 (m)	—	1.00–1.10 (d)
4.	$Fe(OPr^i)(L'H)_2$	—	6.80–8.25 (m)	6.00 (s)	0.98–1.05 (d)
5.	$Sb(OPr^i)(L')$	—	6.95–8.20 (m)	—	1.05–1.12 (d)
6.	$Sb(L'H)_3$	—	7.30–8.60 (m)	6.05 (s)	—

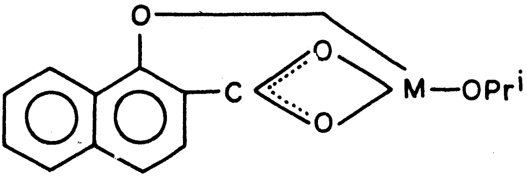
Abbreviations: s = singlet, d = doublet, m = multiplet.

Infrared Spectra

The derivative, $Fe(OPr^i)(L)$ shows a medium broad band between 3080–2860 cm^{-1} which may be assigned νC–H of the aromatic ring and isopropoxy group[16,17]. The band due to νOH of the hydroxy group, as observed in LH_2, is found to be absent here indicating the participation of the hydroxy group in bonding with iron. The overtones in the region 2000–1700 cm^{-1} occur due to substitution in the aromatic ring[18]. A strong broad band at 1600 cm^{-1} indicates the overlapping of $\nu_{as}COO$ and aromatic νC═C[17], while the medium bands at 1580 cm^{-1} and 1470 cm^{-1} may be attributed to the aromatic skeletal vibrations[17]. The appearance of another medium band at 1410 cm^{-1} corresponds to ν_sCOO[19]. A shift of 10 cm^{-1} in ν_sCOO, as compared to LH_2, shows the bonding of the carboxylate oxygen with iron. Further, the separation value, $\Delta\nu COO(\nu_{as}COO–\nu_sCOO)$ of 210 cm^{-1} suggests the presence of a bridged or coordinated carboxylate group[20–22]. A medium shouldered band at 1360 cm^{-1} corresponds to C–H bending of the isopropoxy group[17,20], while the bands at 1265 cm^{-1} and 1220 cm^{-1} occur because of νC–O[16,17]. The medium bands at 1125 cm^{-1} and 1000 cm^{-1} may be assigned to the aromatic C–H–in–plane bending[16], while those at 925 cm^{-1}, 850 cm^{-1} and 785 cm^{-1} correspond to the aromatic C–H out-of-plane bending. A medium band at 470 cm^{-1} and a strong band at 425 cm^{-1} may be attributed to νFe–O[23,24]. The bands below 700 cm^{-1} appear because of the skeletal vibrations. It is thus evident that the iron atom in $Fe(OPr^i)(L)$ [Structure (III)] shows tetra-coordination as a result of bonding with both the oxygens from the carboxylate group and the oxygen from the hydroxy group, along with an isopropoxy group.

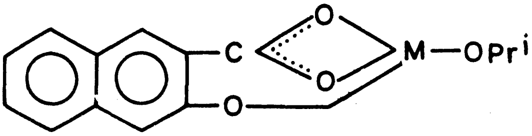
Proton Magnetic Resonance Spectra

The PMR spectrum of $Fe(OPr^i)(L)$ displays a multiplet between δ6.75–8.52 which corresponds to the napthyl ring protons[17,25]. The doublet at δ1.00–1.10



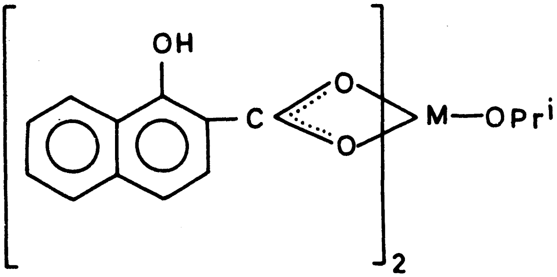
Where M = Fe or Sb

(III)



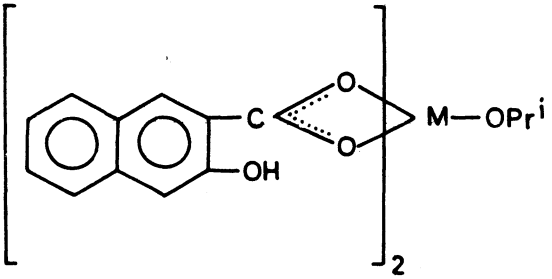
Where M = Fe or Sb

(IV)



Where M = Fe or Sb

(V)



Where M = Fe or Sb

(VI)

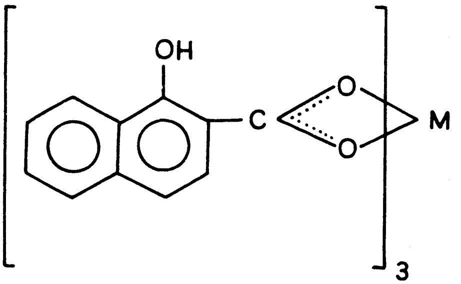
occurs because of the *gem*-dimethyl protons of the isopropoxy group[21]. The signals corresponding to the protons of the carboxylic acid and hydroxy groups, as noted in LH_2, in the region δ9.90–10.50 disappear here with the occurrence of no additional peaks which suggests the participation of both of these groups in bonding with iron. The singlet at δ2.50 may be assigned to dmso impurity. Thus, the conclusions drawn here on the structural aspects of $Fe(OPr^i)(L)$ are in conformity to those inferred earlier from the IR spectral measurements.

The IR and PMR spectral data in respect of the other derivatives were interpreted similarly and the main findings relating to their structures are as under:

The derivatives, $Sb(OPr^i)(L)$ (III) and $Fe(OPr^i)(L')$ or $Sb(OPr^i)(L')$ (IV) contain a tetra-coordinated metal atom in each case showing similar modes of bonding as those observed in $Fe(OPr^i)(L)$.

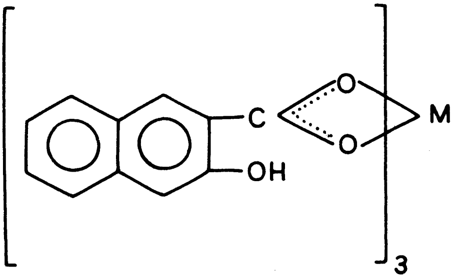
The metal atom is $Fe(OPr^i)(LH)_2$ or $Sb(OPr^i)(LH_2)$(V) and $Fe(OPr^i)(L'H)_2$ or $Sb(OPr^i)(L'H)_2$(VI) exhibits pentacoordination in each case as a consequence of bonding with both the oxygens from each of the two carboxylate groups available from two moles of LH_2 or $L'H_2$, along with an isopropoxy group.

The derivatives, $Fe(LH)_3$ or $Sb(LH)_3$(VII) and $Fe(L'H)_3$ or $Sb(L'H)_3$(VIII) possess a hexa-coordinated metal atom in each case by way of bonding with both



Where M = Fe or Sb

(VII)



Where M = Fe or Sb

(VIII)

the oxygens from each of the three carboxylate groups available from three moles of LH_2 or $L'H_2$.

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