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Synthesis and Characterization of Some Trivalent and Tetravalent Derivatives of 2-Hydroxy-1-naphthoic Acid

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Abstract: The trivalent derivatives (B, Al, As, Sb & Fe) and tetravalent derivatives (Si, Ti & Se) of 2-hydroxy-1-naphthoic acid have been prepared by the interaction of their corresponding isopropoxide with letter in different molar ratio viz. 1:3 & 1:4 in benzene medium. The prepared compounds generally obtained as coloured solids and amongst them those containing isopropoxy groups were found to be hygroscopic. All these compound were characterized by azeotrope and elemental analysis as well as by IR, PMR and mass spectral measurements. These spectral data have facilitated in elucidating the mode of bonding of the said metals and non-metals in these compounds with 2-hydroxy-1-naphthoic acid.

Keywords: Tri- and tetravalent derivatives, 2-Hydroxy-1-naphthoic acid, Alcoholysis reaction.

Introduction

The reactivity of metal / non metal alkoxides provides a simple and convenient method for preparations of a variety of metallo-organic / non-metallo-organic compounds.

The ligating properties of 2-hydroxy-1-naphthoic acid containing hydroxy groups (-OH) adjacent to the carboxylic acid group(-COOH) have seen extensively examined¹⁻³ owing to the favorable geometry of donor sites for stable 6-membered metal chelating ring formation.

These prepared trivalent and tetravalent compounds of 2-hydroxy-1-naphthoic acid (abbreviated as 2,1hna or LH₂) (structure a) by alcoholysis reaction involving the interaction of the corresponding metal/non-metal isopropoxide with 2,1hna in appropriate stoichiometric ratios *viz.* 1:3 and 1:4 (1:1 and 1:2 were reported earlier⁴) in benzene as a reaction medium.

Experimental

Materials

All the chemicals used during the study were of analytical grade reagents. The solvents were dried by standard procedures.⁵ 2-Hydroxy-1-naphthoic acid were used after re-crystallization from 50% (v/v) aqueous ethanol. B, Al, Fe, As or Sb triisopropoxides and Si and Se tetraisopropoxides were prepared by already reported methods⁶. Titanium tetraisopropoxides were used as such.

General Procedure for the synthesis of trivalent and tetravalent derivatives

The tri/tetravalent isopropoxide and 2,1 hna in appropriate stoichiometry in dry benzene are refluxed on a wax bath at 90-100°C. After several hrs (Table 1) of reflux, the isopropanol-benzene was fractionated out and the amount of isopropanol liberated was estimated by an oxidimetric method^{7,8} to monitor the completion of the reaction. This yielded colored solid which was washed with dry benzene followed by dry ether and finally dried under suction.

Characterization

Melting points were recorded on an electro thermal CAT No. IA 8103 digital m.p. apparatus. The IR spectra was recorded on a Bruker IFS 66 v FT-IR spectrometer, using KBr pellets in the region 4000-400 cm⁻¹, while the PMR spectra were taken in DMSO- d₆ solution and recorded on a JEO GSX 400 NB FT-NMR 400 MHz spectrometer, using TMS as an internal standard. The electrospray mass spectra were recorded on a Micromass Quatro II triple quadrupole mass electrospray spectrometer.

Results and Discussion

The reaction occurring between tri and tetravalent metal and non- metal isopropoxide and LH₂ may be illustrated as under:

(Where M = Bi, Al, Fe, As & Sb)

(M = Si, Ti & Se)

IR and PMR spectrum of trivalent (III) and tetravalent (IV) compounds^{9,11}

The IR and PMR spectrum are already known⁴. M(III) (LH₂)₃, M(IV) (LH₂)₄ shows weak and medium absorption in the region 3100-2880 cm⁻¹ indicate the overlapping of free hydroxy and νC-H of the aromatic ring, while the other absorptions in the region 3100-2880 cm⁻¹ corresponds to the overlapping of νC-H of the aromatic ring and isopropoxide group in case of M(IV) (LH₂)₃ (OPrⁱ). The absorption in the region 1645-1620 cm⁻¹ shows the overlapping of ν_{as}COO and νC=C of the aromatic ring and other absorption at 1440 -1420 cm⁻¹ assigned to ν_sCOO of the carboxylate group. Thus a shift of 10-20 cm⁻¹ ν_s COO in comparison to the ligand suggests bonding of the carboxylate oxygen to the corresponding metal / non-metal. Further the separation value (ν_{as}COO-ν_sCOO)

$\Delta\nu\text{COO}$, $185\text{--}230\text{ cm}^{-1}$ suggests the presence of a bridged or coordinated carboxylate group. The weak absorptions in the region $1390\text{--}1360\text{ cm}^{-1}$ in $\text{M(IV)}(\text{LH}_2)_3(\text{OPr}^i)$ exhibits C-H bending of the gem-dimethyl structure of the isopropoxy group and other absorption in the region $1345\text{--}1210\text{ cm}^{-1}$ because of the $\nu\text{ C-O}$ of the hydroxyl group, while the absorption in the region $1160\text{--}1140\text{ cm}^{-1}$ in $\text{M(IV)}(\text{LH}_2)_3(\text{OPr}^i)$ correspond to $\nu\text{C-O}$ of the isopropoxy group. The new bands around $1360\text{--}1350\text{ cm}^{-1}$ and $580\text{--}475\text{ cm}^{-1}$ correspond to $\nu\text{B-O}$ and $\nu\text{M-O}$ ($\text{M} = \text{Br, Al, Sb, Fe, As, Si, Ti \&, Se}$).

Table 1. Analytical details of the compounds of 2-hydroxy-1-naphthoic acid.

S.No	Compound molar ratio	Reflux time, h	Colour	M.P $^{\circ}\text{C}$	Azeotrope Analysis Found, Cald.	Elemental Analysis			Mol. Weight*
						C % Found, (Cal),	H % Found, (Cal),	M % Found, (Cal),	
1	$\text{B(LH}_2)_3$ (1: 3)	06	Light yellow	240	0.87 (0.87)	68.20 (69.25)	2.80 (3.69)	0.80 (1.90)	572.35
2	$\text{Al(LH}_2)_3$ (1: 3)	08	Brown	270	0.98 (0.98)	66.25 (67.35)	2.50 (3.60)	3.45 (4.58)	588.51
3	$\text{Fe(LH}_2)_3$ (1: 3)	12	Black	300	0.50 (0.50)	63.30 (64.20)	2.30 (3.43)	8.04 (9.04)	617.38
4	$\text{As(LH}_2)_3$ (1: 3)	08	Yellow	220	0.71 (0.71)	61.50 (62.28)	2.30 (3.33)	10.70 (11.77)	636.44
5	$\text{Sb(LH}_2)_3$ (1: 3)	10	White	250	1.07 (1.08)	4.30 (58.00)	2.10 (3.09)	16.80 (17.81)	683.29
6	$\text{Si(LH}_2)_3$ (OPr ⁱ) (1: 3)	10	White	270	1.62 (1.63)	65.60 (66.65)	3.35 (4.35)	3.70 (4.33)	648.71
7	$\text{Si(LH}_2)_4$ (1: 4)	12	Off white	280	1.98 1.99	67.50 (68.04)	2.63 (3.63)	2.60 (3.60)	
8	$\text{Ti(LH}_2)_3$ (OPr ⁱ) (1: 3)	09	Reddish brown	260	1.00 (1.01)	63.23 (64.68)	3.35 (4.23)	2.55 (7.17)	668.52
9	$\text{Ti(LH}_2)_4$ (1: 4)	10	Reddish brown	240	0.81 (0.82)	65.98 (66.34)	2.10 (3.54)	5.24 (6.01)	
10	$\text{Se(LH}_2)_3$ (OPr ⁱ) (1: 3)	08	Off white	230	0.58 (0.58)	60.80 (61.81)	3.10 (4.03)	10.10 (11.29)	
11	$\text{Se(LH}_2)_4$ (1: 4)	08	Off white	230	0.73 (0.73)	62.70 (63.85)	2.30 (3.41)	8.60 (9.54)	

* Molecular weight obtained by Mass Spectrum in several representative cases.

The multiplet between 7.20-8.15 corresponds to the naphthyl ring protons. The doublet and multiplet in the region 1.20-1.55 and 4.10-4.55 due to $-\text{CH}_3$ and $\equiv\text{CH}$ protons of the isopropoxy group in $\text{M(IV)}(\text{LH}_2)_3(\text{OPr}^i)$. A hump in the region 6.44-5.85 suggests that the hydroxy group remains intact. The signal due to the protons of the carboxylic acid observed in 2.1hna disappear in these compounds and no additional peaks have been observed to occur which indicates the participation of carboxylate groups in bonding with the corresponding metal / non-metal.

Structural Aspects

On the basis of azeotrope and elemental analysis, as well as spectral data of compounds, the main findings of the structures of synthesized compounds are as under.

The compounds $M(LH_2)_3$ (where $M = B, Al, Fe, As \text{ \& } Sb$) contain hexa-coordinated atom in each case as a result of bonding with both the oxygens from each of the three carboxylate groups available from three moles of 2,1 hna. (structure b).

The compounds $M(LH_2)(OPr^i)$ (Where $M = Si, Ti \text{ \& } Se$) contain hepta coordinated atom in each case as a result of bonding with both the oxygens from each of the three carboxylate groups available from three moles of 2,1 hna along with an isopropoxy group (structure c) and $M(LH_2)_4$ compounds (where $M = Si, Ti \text{ \& } Se$) contain octa coordinated atom as a result of bonding with both the oxygens from each of the four carboxylate groups available from four moles of 2,1 hna (structure d).

Structure-a

Structure-b

Structure-c

Structure-d

- a LH_2 (2,1hna)
- b Where $M = B, Al, Fe, As \text{ \& } Sb$
- c Where $M = Si, Ti, Se$
- d Where $M = Si, Ti, Se$

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