International Journal of Science and Research (IJSR)
ISSN: 2319-7064
SJIF (2019): 7.583

Sterically Hindered Organoantimony Compounds of TRIS (α-NAPHTHYL) Antimony (III)(α-$C_{10}H_7)_nSbX_{3-n}$(n=1,2) & TRIS (α-Naphthyl) Antimony (V) (α-$C_{10}H_7)_nSbX_{5-n}$ (n=2,3,4) Derivatives

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Abstract: ***Several new hitherto unreported penta-coordinate tris(α-naphthyl)- antimony(iii) & antimony (v) halothiocyanato, Interpseudohalide, Interhalogen of the general formulas(α-$C_{10}H_7)_nSbX_{3-n}$ and (α-$C_{10}H_7)_nSb_{5-n}$ (n=1,2 where OOCR = $C_6H_5CONHCH_2COO^-$,$C_6H_4(OH)COO^-$,$C_6H_5C_2H_4COO^-$,$(C_6H_5)_2(OH)C.COO$,etc.X=halogens) have been prepared by the metathesis reaction of (α-$C_{10}H_7)_nSbX_{3-n}$ with the appropriate metals salts of the carboxylic acid. The halothiocyanate derivatives were also obtained by the addition of the tris(α-naphthyl)-antimony(iii) & antimony(v). The newly synthesized compounds have been characterised by conventional methods. The failure to replace the second halogen atom in (α-$C_{10}H_7)_nSbX_{3-n}$ may be attributed to steric hindrance offered by the naphthyl groups bound to antimony as well as the bulky nature of the organic ligand.***

Keywords: Tris(α-naphthyl)- antimony(iii) & antimony (v), Halothiocyanato, Interpseudohalide, Interhalogen, Carboxylate

1. Introduction

Despite a considerable interest in the synthesis, reaction and biological activity of hydrocarbon and halophenyl and haloalkyl based organometallic derivatives of Group 15 elements, sterically congested derivatives either of the elements (As, Sb and Bi) have not attracted much attention. It is more surprising in the light of the fact that sterically bulky groups such as cyclohexyl, naphthyl, mesityl*etc.* are known to render thermal stability as well as hydrolytic stability to the compounds. Also, as in case of organotinanalogs, corresponding antimony compounds of cyclohexyl and naphthyl has been found to exhibit biologically activity. It may also be noted that significant changes in structure and bonding have also been observed on changing the nature and contents of organic groups bound to antimony of the oxidation state of antimony *i.e.* +III or +V [1]. This behaviour is more visible in case of organoantimony carboxylates [2], pseudohalides [3] and other related derivatives. Organoantimony (III) compounds are generally pyramidal; three coordinate and biologically more potent while antimony (V) compounds [4] show lesser activity and have penta coordinate around antimony resulting in TBP or square planar geometry (SP).

Although in recent years considerable interest has been shown in hydrocarbons and polyhalogenated derivatives of antimony(III) and antimony(V), corresponding sterically congested compounds bearing cyclohexyle fused, aromatic rings and mesityl groups have been little studied [5-12]. Earlier we have reported, oxidative addition, reductive cleavage, metathetical, insertion and anionic exchange reactions of tris (α-naphthyl) antimony(V) compounds [8,13-16]. It may be noted that the reactions of (α-$C_{10}H_7)_nSbCl_{3-n}$(n=1,2,3) have not attracted any attention probably due to the difficulty encountered in the preparation of (α-$C_{10}H_7)_3SbCl_{3-n}$(n=1,2) which has now been obtained via redistribution reaction. Further, it may be noted that cyclohexyl based derivatives of group 14 have got potential biological activity and that is true for Group 15 elements as well and this aroused author's interest to synthesize newer (α-naphthyl)antimony(III) halides and their derivatives. Further, as compared to organoantimony(V) derivatives/ organoantimony (III) derivatives are better antitumoral, antifungal and antibacterial agents [5-8]. It may be noted that organometallic compounds especially those of group 14 containing cyclohexyl group have been found to possess significant antimicrobial, insecticidal and anti-tumor activity [13-15]. In case of Group 15 elements both phenyl and cyclohexyl antimony (III) and antimony (V) derivatives have been shown to possess considerable biological activity as has been reported from this laboratory [5-8]. Thus the present study deals with the:Oxidative addition reaction of freshly generated halo-pseudohalides [10], X(SCN) [X = Cl, Br] with (α-naphthyl)$_3$Sb and (α-naphthyl)$_n$$SbCl_{3-n}$ with interhalogens.Metathetic reactions of (α-naphthyl)$_2$SbCl and (α-naphthyl)$SbCl_2$ with sodium salts of carboxylic acids.The principal objective of this work was to explore the effect of bulky (α-naphthyl) groups present on antimony, on the structural and chemical behaviour of antimony(III) compounds *vis-a-vis* alkyl and aryl analogues of antimony(III). Further, it would be more relevant in the presence of bulky organic ligand (amide, oxime, carboxylic acid) and should present interesting steric hinderance related problem like solubility, lack of dimerisation and other solution studies [10-12]. The newly synthesized compounds apart from elemental and melting point data have been identified by solid state IR spectra and some solution phase studies.

2. Results and Discussion

(i) Redistribution Reactions

In an anhydrous oxygen free atmosphere tris-(α-naphthyl)antimony(III) chlorides were obtained by the redistribution reactions of tris-(α-naphthyl) antimony(III) with antimony trichloride in the sense of equation shown below:

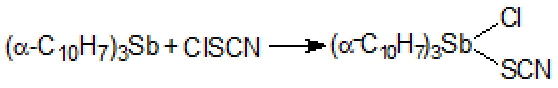
$$(\alpha\text{-}C_{10}H_7)_3Sb + 2SbCl_3 \xrightarrow[\Delta]{\text{neat}} 3(\alpha\text{-}C_{10}H_7)SbCl_2 \quad (1)$$

$$2(\alpha\text{-}C_{10}H_7)_3Sb + SbCl_3 \xrightarrow[\Delta]{\text{neat}} 3(\alpha\text{-}C_{10}H_7)_2SbCl \quad (2)$$

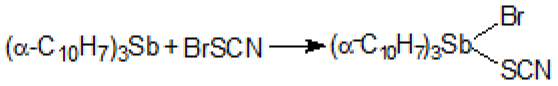
Both the halides thus obtained are brown solid, are much more stable than the phenyl analogues and had comparatively higher melting point. They are soluble in organic solvents.

(ii) Oxidative Addition Reactions

Freshly generated solution of X-SCN (X=Cl, Br) were found to add tris(α-naphthyl)antimony(III) at –5°C in carbon tetrachloride.



$$(\alpha\text{-}C_{10}H_7)_3Sb + ClSCN \longrightarrow (\alpha\text{-}C_{10}H_7)_3Sb{<}^{Cl}_{SCN} \quad (3)$$



$$(\alpha\text{-}C_{10}H_7)_3Sb + BrSCN \longrightarrow (\alpha\text{-}C_{10}H_7)_3Sb{<}^{Br}_{SCN} \quad (4)$$

The reactions were carried out in dark to retard the polymerization of (XSCN). Both the halo-thiocyanato derivatives are coloured solid and can be stored at room temperature without decomposition. They are sharp melting and soluble in organic solvents such as chloroform; acetonitrile *etc.*

(iii) Metathetical Reactions

$(\alpha\text{-}C_{10}H_7)_nSbCl_{3-n}$ (n=1,2) were subjected to metathetical reaction with metallic salt of pseudohalides.

$$(\alpha\text{-}C_{10}H_7)_2SbCl + MSCN \longrightarrow (\alpha\text{-}C_{10}H_7)_2SbSCN + MCl \quad (5)$$

$$(\alpha\text{-}C_{10}H_7)SbCl_2 + 2MSCN \longrightarrow (\alpha\text{-}C_{10}H_7)Sb(SCN)_2 + 2MCl \quad (6)$$

The azido derivative was obtained in presence of phase transfer catalyst (18-crown-6).

$$(\alpha\text{-}C_{10}H_7)_2SbCl + NaN_3 \xrightarrow[\text{reflux temperature}]{\text{Benzene}} (\alpha\text{-}C_{10}H_7)_2SbN_3 \quad (7)$$

$$(\alpha\text{-}C_{10}H_7)SbCl_3 + NaN_3 \xrightarrow[\text{reflux temperature}]{\text{Benzene}} (\alpha\text{-}C_{10}H_7)Sb(N_3)_2 \quad (8)$$

A series of mono and di-carboxylates which were expected to be biologically active was prepared by the metathetical reaction.

$$(\alpha\text{-}C_{10}H_7)_nSbCl_{3-n} + MOOCR \longrightarrow (\alpha\text{-}C_{10}H_7)_nSb(OOCR)_{3-n} + MCl \;\ldots\; (9)$$

(n=1,2) where OOCR = $C_6H_5CONHCH_2COO^-$, $C_6H_4(OH)COO^-$, $C_6H_5C_2H_4COO^-$, $(C_6H_5)_2(OH)C.COO^-$, *etc.*

All the reaction proceeds smoothly to give almost quantitative yield of the product at the refluxing temperature of the medium. The analytical data of these carboxylate derivatives are collected in the table (1-3). All the compounds are amorphous solids and insensitive to air and moisture. They are sharp melting and moderately soluble in common organic solvents.The products can be crystallised from petroleum-ether (40-60°C) or carbon tetrachloride (1:1). In general the melting points of the complexes are on higher side. This could reasonably be assigned to the bulkier nature of naphthyl group which engender higher thermal and hydrolytic stability. This is not surprising since cyclohexyl group bound to antimony have been found hydrolytically stable.The constancy in the melting points after repeated crystallisation as well TLC runs in polar solvents with a single spot excluded the presence of mixtures of reactants. The analytical data given in table 2 correspond well with the proposed formulation of the complexes.The newly synthesized compounds have been found non-electrolyte and monomeric in nature on the basis of the molecular weight data in freezing benzene and conductivity measurements of 10^{-3} M solutions in acetonitrile at room temperature.

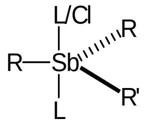
Infrared spectra

All the complexes were characterised by diagnostic infrared absorption data in the region 4000-400 cm^{-1}. IR absorptions corresponding to α-naphthyl group bound to antimony are in close conformity with the reported values of analogustris(α-naphthyl) antimony [13-14]. The diagnostic IR absorption bands of the newly synthesized compounds have been identified and are listed **in table 3.**The infrared spectra of all the compounds show almost identical absorption due to α-naphthyl groups. The Sb-C stretching frequency corresponding to Y-mode was observed in the range 426-405 cm^{-1} as a medium to weak band. The antimony-halogen frequency in the spectra of the carboxylates was not observed in the range 4000-400 cm^{-1}. In the IR-spectra of these compounds the carboxylate bands are observed in the characteristic region [ν_{asym}(OCO) between 1667 and 1633 cm^{-1}, ν_{sym}(OCO) between 1384 and 1300 cm^{-1}]. On the basis of Δν (OCO) (separation values 274-338 cm^{-1}) it is reasonable to assume that there is no interaction between the carbonyl oxygen atom of the carboxylate group and the antimony atom which indicate in the presence of monodentate ester type-OCO group [15]. The absorption bands due to –NCS and $-N_3$ groups compare very well with those reported earlier for other covalent organometallic pseudohalides [16-18]. Other important features in favour of nitrogen linkage are the appearance of the C-S symmetric stretching of weak to medium intensity at (835, 793 cm^{-1})

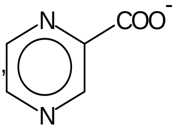
and a weak bond due to δ(N–C–S) bonding is observed at (463, 485 cm^{-1}). These modes of vibrations favour an iso structures (–N=C=S) [13].

^{1}H NMR Spectra

^{1}H NMR spectra of the representatives compounds were recorded on Brucker DRX-300 (300 MHzFTNMR) spectrometer, using $CDCl_3$ as solvent with chemical shift being reported as δ(ppm) using tetramethylsilane (TMS) as reference. The multiplets appearing in the range δ (7.10-7.69) ppm may be attributed to the protons of α-naphthyl ring. Thus, on the basis of spectral data in combination with the molecular weight and conductance measurement it may be concluded that the newly synthesized compounds possess a monomeric covalent constitution with trigonal-bipyramidal geometry around antimony. The three α-naphthyl group occupy the equatorial positions and the electronegative group(s) (ligands or chlorine) occupies apical or axial positions [19].



R = α-$C_{10}H_7$ (Naphthyl)

L = NCS, N_3, o-$OHC_6H_5COO^-$, R'CH(OH)COO^-, 

R' = C_6H_5, *p*-$CF_3C_6H_4$, or *p*-$OCH_3C_6H_4$

Experimental

Typical experiments for the preparation of bis(α-naphthyl) antimony(III) carboxylate, bis(α-naphthyl) antimony(III) and pseudohalides (Ps = N_3 or NCS) and tris(α-naphthyl) antimony -chloro and –bromo –thiocyanate [(α-$C_{10}H_7)_3$SbBrSCN and (α-$C_{10}H_7)_3$SbClSCN] are given below. Detail for other reactions alongwith analytical data are given in **Tables 1-3**.

(i)Reaction of bis(α-Naphthyl)antimony(III)chloride with sodium salt of salicylic acid

In an oxygen and moisture free atmosphere a solution of bis(α-naphthyl) antimony(III) chloride (0.411 g, 1 mmole) and sodium salt of salicylic acid (0.160 gm, 1 mmole) in carbon tetrachloride (20 ml) was stirred at room temperature for 20 h. The sodium chloride thus formed was filtered off. The filtrate was concentrated *in vacuo* (2-3 ml) followed by addition of n-hexane (5 ml) afforded white crystalline solid which was characterised as bis(α-naphthyl) antimony(III) salicylate.Melting Point: 192°C Yield: 25%

(ii) Reaction of bis(α-naphthyl)antimony(III) chloride with sodium salt of 2-Pyrazine carboxylic acid

In an atmosphere of dry nitrogen a solution of bis(α-naphthyl) antimony(III) chloride (0.411 gm, 1 mmole) and sodium salt of 2-pyrazine carboylic acid (0.146 gm, 1 mmole) in dry benzene (20 ml) was stirred at room temperature for 24 h. The sodium chloride, thus formed was filtered off. The complete solvent was evaporated under vaccum to afford white crystalline solid. The compound was recrystallised from mixture of petroleum-ether (60-80°C) and n-hexane in the ratio (3:1) and was characterised as bis(α-naphthyl) antimony(III) 2-pyrazine carboxylate.Melting Point: 170°C Yield 70%

(iii) Reaction of bis(α-naphthyl)antimony(III) chloride with sodium salt of 2,5-dinitrobenzoic acid

In an atmosphere of dry nitrogen a solution of bis(α-naphthyl) antimony(III) chloride (0.411 gm.1 mmole) in dry carbon tetrachloride (20 ml) and sodium salt of 2,5-dinitrobenzoic acid (0.293 g, 1 mmol) in the same solvent was stirred at room temperature for 12 h. The sodium chloride, thus formed was filtered off. The complete solvent was evaporated under vacuum to afford off white crystalline solid. The compound was recrystallised from n-hexane and characterised as bis(α-naphthyl)antimony(III)2,5-dinitrobenzoxylate. Melting point 85°C Yield: 80%

(iv) Reaction of bis(α-naphthyl)antimony(III) chloride with KSCN

The solution of bis(α-naphthyl)antimony(III) chloride (0.411 gm 1 mmole) and excess of potassium thio-cyanate (0.97 gm, 1 mmole) in carbon tetrachloride (25 ml) was stirred at room temperature for 12 h. The reaction mixture was further refluxed for 2 h to ensure the completion of reaction. The potassium chloride thus formed was filtered off. The complete removal of solvent from filtrate under vacuum afford white crystalline solid which was recrystallised from a mixture of acetone and absolute ethyl alcohol (1:1). The compound was characterised as (α-$C_{10}H_7)_2$Sb(NCS).Melting point: 232°C Yield: 40%

(v)Reaction of bis(α-naphthyl)antimony(III) chloride with sodium azide

In an oxygen and moisture free atmosphere, a solution of bis(α-naphthyl)antimony(III) chloride (0.411 gm 1 mmole) and excess of sodium azide (0.130 gm, 2.0 mmole) in carbon tetrachloride (20 ml) was refluxed with continuous stirring for 12 h. The sodium chloride, thus formed was filtered off. The solvent was completely removed from filtrate *in vacuo* affording off white crystalline solid. The compound was recrystallised from a mixture of benzene and n-hexane and was characterised as (α-$C_{10}H_7)_2$Sb(N_3). Melting point: 224°C Yield: 43%.

(vi) Reaction of tris(α-naphthyl)antimony(III) chloride with ClSCN

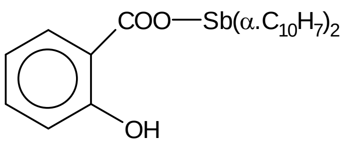
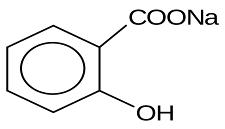
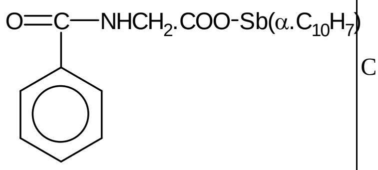
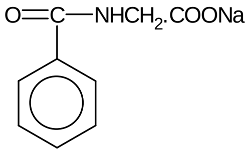
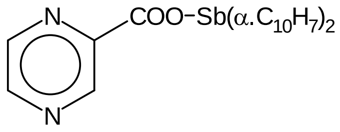
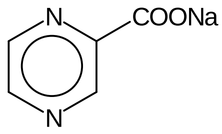
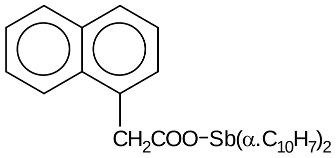
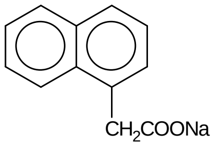
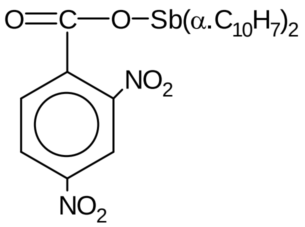
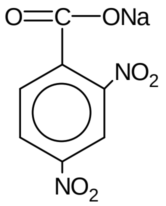
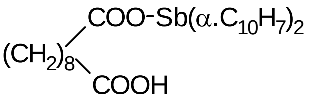
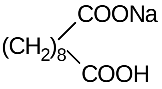
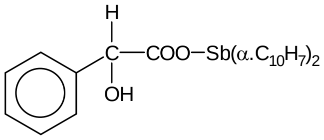
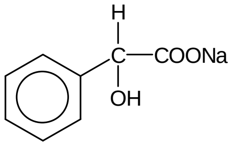
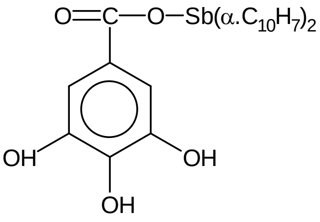
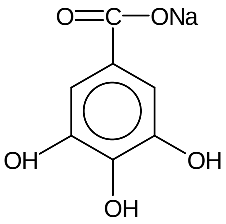
A freshly generated solution of ClSCN (0.93 gm, 1 mmol) in carbon tetrachloride at –5°C was added to precooled (–5°C) stirring solution tris(α-naphthyl)antimony (0.503 gm, 1 mmol) in the same solvent during 2 h. The reactantswere stirred for 1 h at initial temperature and then allowed to come at room temperature. The solution was evaporated under reduced pressure and cooled overnight.Melting point: 134°C Yield: 65%

(vii) Reaction of tris(α-naphthyl)antimony(III) chloride with BrSCN

A freshly generated solution of BrSCN (0.137 gm, 1 mmol) in carbon tetrachloride at –5°C was added to precooled (–

$5^{o}C$) stirring solution tris(α-naphthyl)antimony (0.503 gm, 1 mmol) in the same solvent during 2 h. The reactants were stirred for 1 h at initial temperature and then allowed to come at room temperature. The solution was evaporated under reduced pressure and cooled overnight. Melting point: $154^{o}C$ Yield: 60%

Table 1: Preparation and properties of sterically hindered organoantimony(III) derivatives carboxylate and pseudohalides

Compd. No.	Complex	Organo-metallic halide (g)	Ligand (g)	Molar Ratio/ Solvent (ml)	m.p. (^{o}C)	Yield (g) %	Colour	Recrys-tallisation solvent
1.		(α-$C_{10}H_7)_2SbCl$		1:1 (CCl_4) 20 ml	192	25	Off white	Pet Ether/ n-Haxene
2.		(α-$C_{10}H_7)_2SbCl$		1:1 (CCl_4) 20 ml	210	60	Off white	Pet Ether (60-80^{o}C)
3.		(α-$C_{10}H_7)_2SbCl$		1:1 (CCl_4) 20 ml	170	70	Light brown	n-hexane/ Pet ether (40-60^{o}C)
4.		(α-$C_{10}H_7)_2SbCl$		1:1 (CCl_4) 20 ml	98	50	Off white	n-hexane
5.		(α-$C_{10}H_7)_2SbCl$		1:1 (CCl_4) 20 ml	85	80	Off white	n-hexane
6.	 $(CH_2)_8(COO\text{-}Sb(\alpha.C_{10}H_7)_2)(COOH)$	(α-$C_{10}H_7)_2SbCl$	 $(CH_2)_8(COONa)(COOH)$	1:1	105	35	Off white	Pet Ether (40-60^{o}C)
7.		(α-$C_{10}H_7)_2SbCl$		1:1 (CCl_4) 20 ml	72	75	Off white	Pet Ether (40-60^{o}C)
8.		(α-$C_{10}H_7)_2SbCl$		1:1 (CCl_4) 20 ml	120	25	Off white	Pet Ether (40-60^{o}C) n-hexene
9.	(α-$C_{10}H_7)_2Sb(SCN)$	(α-$C_{10}H_7)_2SbCl$	KSCN	1:1 (CCl_4) 20 ml	232	40	Off white	Benzene/ n-hexane
10.	(α-$C_{10}H_7)_2Sb$ (N_3)	(α-$C_{10}H_7)_2SbCl$	NaN_3	1:1 (CCl_4) 20 ml	224	43	Off white	Benzene/ n-hexane

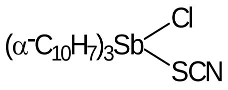
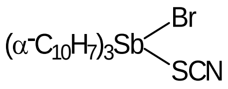
Compd. No.	Complex	Organo-metallic halide (g)	Ligand (g)	Molar Ratio/ Solvent (ml)	m.p. (°C)	Yield (g) %	Colour	Recrys-tallisation solvent
11.		(α-$C_{10}H_7)_3Sb$	Cl(SCN)	1:1 (CCl_4) 20 ml	232	40	Orange	Benzene/ n-hexane
12.		(α-$C_{10}H_7)_3Sb$	Br(SCN)	1:1 (CCl_4) 20 ml	224	43	Orange	Benzene/ n-hexane

Table 2: Elemental Analysis of Sterically Hindered Organoantimony(III) Carboxylates and Pseudohalides

Compd. No.	Emperical Formula	Molecular Weight	Found (Calcd.) %		
			C	H	N
1.	$C_{27}H_{19}O_3Sb$	513.20	63.19 (63.25)	3.73 (3.78)	–
2.	$C_{29}H_{22}O_3NSb$	554.25	62.84 (62.86)	4.00 (4.05)	2.53 (2.58)
3.	$C_{25}H_{17}N_2O_3Sb$	499.17	60.15 (60.20)	3.43 (3.40)	5.61 (5.68)
4.	$C_{32}H_{24}O_2Sb$	550.28	67.66 (67.67)	4.40 (4.45)	–
5.	$C_{27}H_{17}O_6N_2Sb$	587.19	55.23 (55.23)	2.92 (3.00)	4.77 (4.79)
6.	$C_{30}H_{31}O_4Sb$	513.33	70.19 (70.25)	6.09 (6.06)	–
7.	$C_{28}H_{21}O_3Sb$	527.22	63.79 (63.84)	4.01 (4.20)	–
8.	$C_{27}H_{19}O_5Sb$	545.20	59.48 (58.98)	3.51 (3.60)	–
9.	$C_{21}H_{14}N.S.Sb$	434.17	58.09 (57.99)	3.25 (3.31)	3.23 (3.40)
10.	$C_{20}H_{14}N_3Sb$	418.17	57.45 (57.50)	3.38 (3.40)	10.05 (10.23)
11.	$C_{31}H_{21}NClSSb$	596.78	62.39 (62.42)	3.55 (3.58)	2.35 (2.38)
12.	$C_{31}H_{21}NBrSSb$	641.23	58.06 (58.10)	3.30 (3.35)	2.18 (2.20)

Table 3: Characteristic infrared absorption frequencies of (α-naphhyl) antimony III derivatives

Compound No.	NCS/N3	ν_{asy}(CO)/ν_{asy} (OCO) ν_{asy}(C-N) /ν_{asy} (CS) ν_{asy}(Sb-N)	ν_{asy} (CO) / ν N-O / ν(Sb-C)/ /ν_{asy} (OCO) δ N_3/NCS
1.	–	1667 vs	1384 m
2.	–	1655 vs	1280 v.s.
3.	–	1625 vs	1305 m
4.	–	1572	1220 m
5.	–	1710 vs	1312 m
6.	–	1624 vs	1280 w
7.	–	426δb-N) m	40 (Sb-C) w
8.	–	1375 (C-N) m	915 (N-O) w
9.	–	1582 (C-N) m	485(Sb-C) w
10.	2045 w	1260 m	665 m
11.	2056 m	1050 m	470 w
12.	2050 w	1060 w	472 m

vs = very strong; s = strong; m = medium; w = week; vw = very week

Acknowledgement

The author are thankful to the head department of chemistry, Lucknow University, Lucknow for providing the necessary Laboratory facilities, the Director CDRI, Lucknow for obtaining IR,NMR, spectra

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