International Journal of Chemical Synthesis & Chemical Reactions
Vol. 3: Issue 1
www.journalspub.com

Synthesis, Spectral Characterization and Biocidal Activities of Triphenyl Antimony (V) Halide and Methoxide Complexes

Ashish Kumar[1*], *Brij Kishore Tiwari*[1], *Tasneem Sultan*[2], *Narendra Deo Pandey*[3], *Sahid Suhail Narvi*[3]
[1]Department of Applied Sciences, G.L. Bajaj Institute of Technology and Management, Greater Noida, UP, India
[2]Department of Chemistry, Meerut College, Meerut, UP, India
[3]Department of Chemistry, NIT, Allahabad, UP, India

ABSTRACT

The schiff base ligands N-mono(salicyclidene)-σ-phenylenediamine (spdH) and N-mono(2-hydroxy-1-naphthalidene)-σ-phenylenediamine (hnpdH) and their triorganoantimony (V) complexes were synthesized by conventional method, were characterized by UV, IR and ^1H NMR spectral studies which proposed that in the complexes of the ligands spdH and hnpdH, antimony is seven coordinated and in sp^3d^3 hybridization state with pentagonal bipyramidal geometry.

Keywords: halide, methoxide complexes, triphenylantimony (V)

Corresponding Author
E-mail: ashish2009chemistry@gmail.com

INTRODUCTION

Organo-antimony compounds have a diversity of applications in both biological and non-biological fields [1–3]. It has been reported that the organo-antimony (V) carboxylates possess potential *in vitro* activity against certain cancer cells [4].

Antimony (V) complexes of lapachol have been synthesized by the reaction of Ph_3SbCl_2 or Ph_3BiCl_2 with lapachol and characterized by IR, and NMR spectroscopy and X-ray crystallography. Such complexes inhibited the growth of a chronic myelogenous leukemia cell line and show remarkable cytotoxic activity [5].

Islam *et al.* synthesized the organo-antimony (V) complexes of ligand acetylsalicyclic acid and 3-acetoxy benzoic acid, the structural analysis show that the metal complexes show five coordinated extremely distorted trigonal bipyramidal geometry and show the antileishmanial and antibacterial activities [6].

Fahmi *et al.* synthesized Sb(III) complexes of with N and S atom containing donor ligands like N′-[1-(2-oxo-2H-chrome-3yl-ethylidene]-hydrazinecarbodithionic acid methyl ester and N′-[1-(2-oxo-2H-chrome-3yl-ethylidene]-hydrazinecarbodithionic acid benzyl ester in such complexes the ligands coordinated to organo-antimony in a monobasic bidentate manner through sulfur and nitrogen donor atom and tetra and pentacoordinated environments around the antimony have been proposed. On screening, their biological activity they were found active against *Corcyra cephalonica* [7].

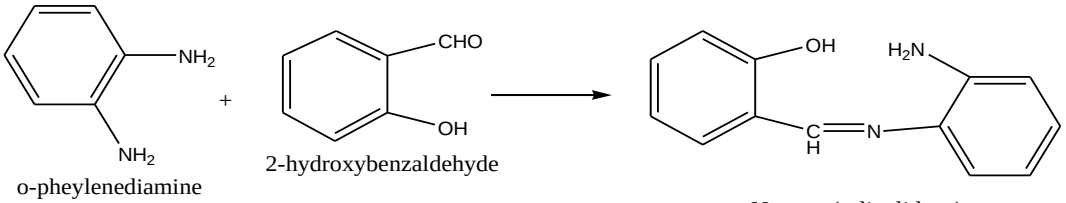
The present paper exploring the synthesis of triphenyl antimony (V) complexes of Schiff base N-mono(salicyclidene)-σ-phenylenediamine (spdH) and N-mono(2-hydroxy-1-naphthalidene)-σ-phenylenediamine (hnpdH) and their *in vitro* antimicrobial activity is tested against the bacteria

Staphylococcus aureus, Escherichia coli, Proteius vulgurais and *Klebsiella pneumoniae.*

EXPERIMENTAL

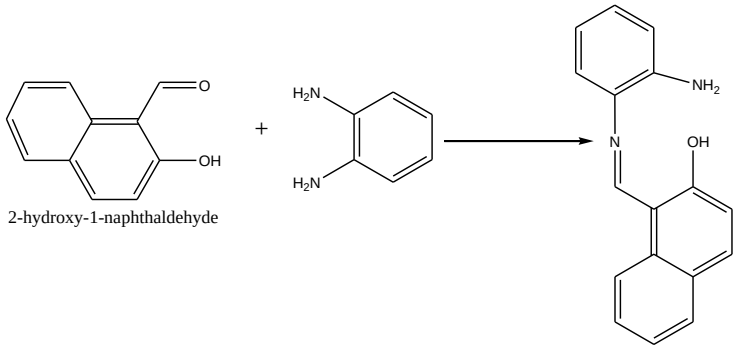
Synthesis of Schiff Base Ligands: N-Mono(salicyclidene)-σ-phenylenediamine (spdH) and N-Mono(2-hydroxy-1-naphthalidene)-σ-phenylenediamine (hnpdH)

In 60 ml ethanolic solution of 0.54 g, 5 mol, σ-phenylenediamine add dropwise with continues stirring 30 ml ethanolic solution of 0.61 g, 5 mol salicylaldehyde. The mixture was refluxes on water bath for 2 hours. On cooling on ice bath the product separated out which recrystallized by hot acetonitrile [8].



o-pheylenediamine 2-hydroxybenzaldehyde N-mono(salicylidene)o-phenylenediamine

N-mono(2-hydroxy-1-naphthalidene)-σ-phenylenediamine (hnpdH) was prepared in a similar way as above from 2-hydroxy-1-naphthaldehyde and o-phenylenediamine [9].



2-hydroxy-1-naphthaldehyde N-mono(2-hydroxy-1-napthalidene)o-phenylenediamine

Preparation of Triphenyl Organoantimony (V) Complexes of Schiff Base Ligand, spdH and hnpdH by Conventional Method

In a mixture of 5 m mol solution of sodium salt of schiff base (spdH/hnpdH) in benzene adds 100 ml benzene solution of triphenyl antimony (V) dichloride (2.03 g, 5 m mol). The resultant mixture was refluxed for two hours and resulting complex was precipitated by adding dry petroleum ether (temp 40–60°C), which was recrystallized from benzene–hexane mixture (Table 1).

$$SpdH + Ph_3SbCl_2Ph_3SbCl \longrightarrow (spd) + HCl$$
$$hnpdH + Ph_3SbClPh_3 \longrightarrow SbCl(hnpd) + HCl$$

Table 1. *Reaction of R_3SbX_2 with sodium salt of Schiff bases.*

Reactants taken (g)			Product (g)	Yield (%)	Color
R_3SbX_2	Na	Schiff base			
Ph_3SbCl_2 2.03	0.11	spdH 1.06	Ph_3SbCl(spd) 1.15	40	Yellow
Ph_3SbCl_2 2.14	0.12	hnpdH 1.32	Ph_3SbCl(hnpd) 1.24	38	Red

Preparation of Triphenylantimony (V) Methoxide Complexes of Schiff Base spdH and hnpdH by Conventional Method

Reflux for 2 hours with constant stirring, 5 mmol solution of Schiff base ligand (spdH/hnpdH) in benzene (50 ml) was added dropwise to a solution of triphenyl–antimony(V) dimethoxide (2.17 g, 5 mmol) in benzene (50 ml). Concentrate on cooling gave orange–red crystals (Table 2).

$$SpdH + Ph_3Sb(Ome)_2 \longrightarrow Ph_3SbOme(spd)$$
$$hnpdH + Ph_3Sb(Ome)_2 \longrightarrow Ph_3SbOme(hnpd)$$

Table 2. *Reaction of $R_3Sb(OMe)_2$ with Schiff bases.*

Reactants taken (g)		Product (g)	Yield (%)	Color
$R_3Sb(OMe)_2$	Schiff base			
$Ph_3Sb(OMe)_2$ 2.31	spdH 1.09	$Ph_3SbOMe(spd)$ 0.98	32	Yellow
$Ph_3Sb(OMe)_2$ 2.17	hnpdH 1.37	$Ph_3SbOMe(hnpd)$ 1.30	39	Orange–red

RESULT AND DISCUSSION

Elemental Analysis

Analytical data indicates 1:1 metal ligand stiochiometry for all metal complexes (Table 3).

Table 3. *Microanalysis of Schiff base ligands and Sb(V) metal complexes.*

Ligand/complexes	C% (Calc./found)	H% (Calc./found)	N% (Calc./found)	Metal% (Calc./found)
spdH	73.58/73.51	5.66/5.72	13.21/13.47	–
hnpdH	77.86/77.62	5.34/5.46	10.69/11.01	–
$Ph_3SbCl(spd)$	62.52/62.59	4.75/4.78	4.56/4.59	19.80/19.89
$Ph_3SbOMe(spd)$	64.94/64.96	5.28/5.30	4.59/4.58	19.95/19.93
$Ph_3SbCl(hnpd)$	65.03/65.10	4.7/4.62	4.21/4.22	18.31/18.32
$Ph_3SbOMe(hnpd)$	67.29/67.33	5.19/5.20	4.24/4.23	18.44/18.42

UV Spectral Studies

The electronic spectra of free ligands and their complexes show bands at 285–320 nm assigned to π-electronic transition with aromatic ring. An addition band appeared due to presence of chromophore–C=N- at 350–385 nm which shifts towards lower wavelength (bathochromic effect) due to coordination of azomethine nitrogen with the metal atom [10].

IR Spectral Studies

For the given compounds, infrared spectra have been recorded within the range of 4000–400 cm^{-1}. The bands of interest are assigned on the basis of earlier publications [11, 12]. Important data are listed in Table 4.

The IR spectra of ligand spdH and hnpdH show medium intensity band at 2700–2900 cm^{-1} attributable to ν (OH) and such band is disappeared in the spectra of corresponding antimony(III) metal complex. These observations indicate the replacement of hydrogen atom of –OH group of ligand and formation of Sb–O bond in complexes [13].

The $–NH_2$ group symmetrical and asymmetrical stretching vibrations of the ligand spdH and hnpdH are observed at a considerably lower wave- number in the complexes which confirm that N atom of $–NH_2$ group is involve in bonding with antimony. The ligand spdH and hnpdH and their complexes show broad band at 1620 cm^{-1} due to –C=N group stretching

vibrations which suggested that such group in not participated in coordination with metal atom [14].

Table 4. *Important IR frequencies (cm^{-1}) of ligands and their Sb(V) metal complexes.*

Ligand/complexes	–OH	ν(NH_2)		ν(C=N)	ν(C–O)	νSb–Ph	νSb–OMe
		Sym	Asym				
spdH	2700 2900	3340	3430	1620	1280	–	–
hnpdH	2750 2960	3380	3480	1620	1310	–	–
Ph_3SbCl(spd)	–	3060	3360	1610	1290	450 465	
Ph_3SbOMe(spd)	–	3190	3380	1620	1300	445 450	1050
Ph_3SbCl(hnpd)	–	3330	3410	1620	1300	440 455	
Ph_3SbOMe(hnpd)	–	3140	3380	1620	1305	427 440	1065

^{1}H NMR Spectral Studies

^{1}H NMR spectra of ligand spdH show a sharp triplet at δ 4.0 ppm suggested the presence of –OH group and disappearance of such signal in the spectra of Sb(V) complex indicate that –OH group is involved in bonding via deprotonation. the appearance of singlet at δ 5.0 ppm indicate the presence of $–NH_2$ group and the downfield shifting of such signal show the involvement of such group in bonding while the involvement of azomethine group in bonding is exhibited by the downfield shifting of proton attached with carbon atom of this group from δ 8.39 ppm

The ^{1}H NMR spectra of ligand hnpdH is characterized by the presence of following characteristics signal one triplet at δ 4.52 ppm of –OH group, one singlet at δ 4.0 ppm of $–NH_2$ group and doublet of proton attached with carbon atom of azomethine group at δ 8.20 ppm and downfield shifting of $–NH_2$ group and proton attached with carbon atom of azomethine group up to 1.5 ppm suggested that N-atom of $–NH_2$ group and azomethine group is involve in bonding while disappearance of –OH group signal indicate that –OH group is involved in bonding via deprotonation (Table 5) [15].

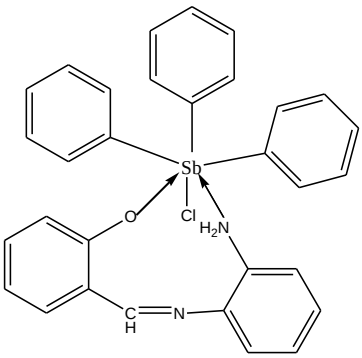
Table 5. *^{1}H NMR spectral data for ligands and complexes.*

Ligand/complex	Chemical shift in δ ppm				
	–OH	Aromatic protons	–CH=N	Sb–OMe	$–NH_2$
spdH	4.0	7.45–6.76	8.39	–	5.0
Ph_3SbCl(spd)	–	7.45–6.76	8.23	–	4.52
$Ph_3Sb(OMe)$(spd)	–	7.52–6.97	8.21	4.00	4.31
hnpdH	4.52	6.52–7.86	8.39	–	4.0
Ph_3SbCl(hnpd)	–	6.25–7.53	7.52	–	3.82
Ph_3SbOMe(hnpd)	–	6.25–7.53	7.59	4.32	3.52

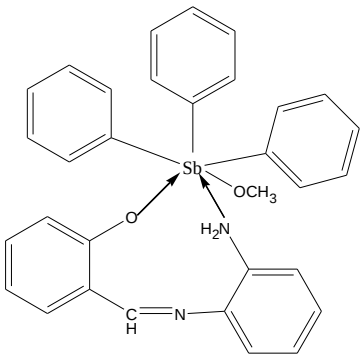
Structure Geometry of Sb(V) Metal Complexes

Taking into consideration all the above facts, it is proposed that the complexes of the ligands spdH and hnpdH antimony is seven coordinated in sp^3d^3 hybridization state with trigonal pentagonal bipyramidal geometry.

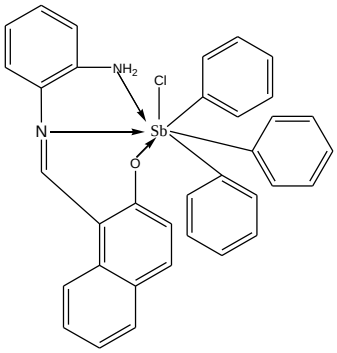
From the Spectral data following structure of antimony metal complexes are proposed



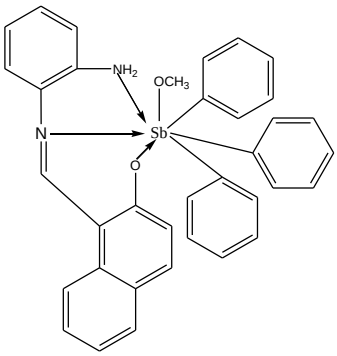
Structure of Ph_3SbCl(spd) complex



Structure of Ph_3SbOme(spd) complex



Structure of Ph_3SbCl(hnpd) complex



Structure of Ph_3SbOme(hnpd)

Antibacterial Screening

In vitro study of the potency of a ligand and its corresponding metal complexes as an antibacterial agent can be measured by filter paper disc method in terms of a *MIC*, *MIC-50* and *MIC*-90 value [16, 17]

The *in vitro* antimicrobial activity of the investigated compounds was tested against the bacteria *S. aureus*, *E. coli*, *P. vulgurais*, *K. pneumoniae* were used. The screening result were compared with Amoxicillin and Gattifloxacin (zone of inhibition Z.I. = 24–26 mm) as a reference drug.

Antibacterial Activities

After carrying out comparative analysis of ligands and their complexes (MIC values), it is observed that complexes of Antimony (V) metal exhibits higher antimicrobial activity as compared to their free ligand. The enhanced activity of the complexes can be clarified on the basis of overtones concept.

As per the overtones concept of cell permeability, lipid membrane surrounding the bacterial cell allows the passage of lipid-soluble substances only. It is because of this that, lipo-solubility has become a crucial factor controlling antimicrobial activity.

Upon chelation, polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. It further causes delocalization of π-electrons along the whole chelate ring thereby enhancing lipophilicity of the complexes. The enhanced lipophilicity increases infiltration of the complexes into lipid membranes. The latter then blocks the metal binding sites in the enzymes of bacteria. These complexes also disturb the respiration process of the bacterial cell and thus block the synthesis of the proteins that restricts further growth of the organism (Table 6).

Table 6. *Antibacterial nature of ligands and Sb(V) metal complexes.*

	Bacterial growth inhibition diameter (mm)				**MIC**		
Ligand/complex	***S. aureus***	***E. coli***	***K. pneumoniae***	***P. vulgurais***	**MIC**	**MIC-50**	**MIC-90**
spdH	12	14	18	17	18	22	30
Ph_3SbCl(spd)	13	17	20	19	15	19	27
Ph_3Sb(OMe)(spd)	12	15	18	16	15	20	25
hnpdH	12	15	19	18	16	21	26
Ph_3SbCl(hnpd)	14	13	18	21	14	18	24
Ph_3SbOMe(hnpd)	16	14	20	20	13	15	23

REFERENCES

[1] J.S. Li, G.Q. Huang, Y.T. Wei, C.H. Xiong, D.Q. Zhu. *Appl Organomet Chem*. 1998; 12: 31–8p.

[2] G. Ferguson, B. Kaitner, C. Glidewell, S. Smith, *J Organomet Chem*. 1991; 419: 283–91p.

[3] M. Fujiwara, M. Imada, A. Bala, H. Matsuda. *Tetrahedron Lett*. 1989; 30: 739–42p.

[4] L. Yu, Y.Q. Ma, G.C. Wang, J.S. Li. *Heteroatom Chem*. 2004; 15: 32–6p.

[5] L.G. de Oliveira, M.M. Silva, F.C.S. de Paula, C. Elene. *Molecules*. 2011; 16: 10314–23p

[6] A. Islam, J.G. Da Silva, F. Moan Berbet, S.M. da Silva. *Molecules*. 2014; 19: 6009–30p.

[7] Fahmi et al., *IJPSR*. 2014; 5(12): 5260–6p.

[8] H. Keypour, S. Salehzadeh, R.V. Parish. *Molecules*. 2002; 7: 140–4p.

[9] A.M. Asiri, K.O. Badahdah. *Molecules*. 2007; 12: 1796–1804p.

[10] Y.Q. Ma, J.S. Li, Z. Xuan, R. Liu. *J Organomet Chem*. 2001; 620: 235–42p.

[11] X.Q. Song, Q.L. Xie, X.N. Fang. *Heteroatom Chem*. 2002; 13: 592–8p.

[12] J.S. Li, Y.Q. Ma, J.R. Cui, R.O. Wang. *Appl Organomet Chem*. 2001; 15: 639–45p.

[13] Y.Q. Ma, L. Yu, J.S. Li. *Heteroatom Chem*. 2002; 13: 299–301p.

[14] M.K. Khosa, M. Mazar, S. Ali, K. Shahid, F. Malik. *Turk J Chem*. 2006; 30: 345–54p.

[15] A. Saeed. *Helv Chim Acta*. 2003; 86: 377–83p.

[16] A.L. Barry. Procedures for testing of antimicrobial agents in agar media, In: *Antibiotics in Laboratory Medicine.* V. Lorian, ed., Baltimore, USA: Williams and Wilkins Company; 1980: 1–23p.

[17] A.W. Bauer, et al. Antibiotic susceptibilities testing by standard single disc diffusion method, *Am J Clin Pathol*. 1966; 45: 493–6p.