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Microwave-Assisted Synthesis, and Stereochemical and Biological Aspects of Some Antimony(III) and Bismuth(III) Complexes with Biologically Potent Bidentate Schiff Bases

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Microwave-Assisted Synthesis, and Stereochemical and Biological Aspects of Some Antimony(III) and Bismuth(III) Complexes with Biologically Potent Bidentate Schiff Bases

Karuna Mahajan, Monika Swami, and R. V. Singh

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Tetra- and pentacoordinated antimony and bismuth derivatives have been prepared by the interactions of monophenylantimonydichloride(III), trichlorostibane, and trichlorobismuthane with the sodium salts of 3-(indolin-2-one)hydrazinecarbothioamide (L^1H) and 3-(indolin-2-one)hydrazinecarboxamide (L^2H), under microwave irradiation as well as by conventional heating. These compounds were further characterized by analytical and spectroscopic techniques including UV, IR, 1H NMR, and ^{13}C NMR spectra. Newly synthesized complexes with their corresponding ligands were also tested for their antifungal and antibacterial activities.

Keywords Antifungal and antibacterial activities; microwave irradiation; Schiff bases

INTRODUCTION

Microwave (MW) irradiation is an efficient and environmentally benign method to activate various transformations; the main benefits of performing reactions under microwave irradiation are the significant rate enhancements and the higher product yields.¹ The use of microwaves with proper control of power and reaction temperature is more efficient than conventional heating.² Microwave heating has not been restricted to organic chemistry, as various aspects of inorganic chemistry³ and polymer chemistry have also been investigated. Bose et al.⁴ claimed that the method overall is more cost-effective (only simple glassware needed) and environment-friendly (less solvent needed). To demonstrate the versatility of microwave chemistry, a variety of inorganic reactions have been carried out using a domestic microwave oven or commercial ovens.

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Thiosemicarbazones and semicarbazones are versatile organic compounds. They are often observed as mixtures of structural isomers (E- and Z-forms) in solution,⁵ and they coordinate to the metal atom either as a neutral ligand or as a deprotonated ligand through two or three heteroatoms.⁶ Metal complexes of semicarbazones and thiosemicarbazones have aroused considerable interest in view of their industrial and biological importance. Their biological activities are considered due to their ability to form chelates with metal ions.⁷⁻¹⁰

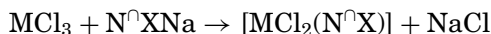
Bismuth compounds have been widely used in clinical settings for centuries because of their high effectiveness and low toxicity in the treatment of a variety of microbial infections, including syphilis, gastritis, and colitis.¹¹ Most obvious has been the widespread use of bismuth compounds, mainly colloidal bismuth subcitrate (CBS) and bismuth subsalicylate (BSS), in the treatment of duodenal ulcers,¹² and chronic¹³ and acute diarrhea in children.¹⁴ Bismuth compounds are environmentally friendly reagents, as they are relatively nontoxic and fairly insensitive to small amounts of water. The biochemical, toxicologic, and environmental effects of bismuth compounds have been well documented and show that they are attractive candidates for the use in green chemistry.¹⁵

Antimony(III) complexes are very interesting due to their fascinating structures, bonding variations,^{16,17} and potential applicability as biocides.¹⁸⁻²⁰ Organic antimony salts are used medically to treat some tropical diseases,²¹ especially in the treatment of all forms of leishmaniasis.²² Among the antimony derivatives containing nitrogen and oxygen/sulfur donor sites, their thiosemicarbazone and semicarbazone derivatives have been studied extensively from their analytical points of view and biological applications.^{23,24}

Taking these facts into consideration, and our interest in biologically active coordination compounds of antimony(III) and bismuth(III), we report in this article the synthesis of these metal salts/compounds with monobasic bidentate thiosemicarbazones and semicarbazones of 1H-indol-2,3-dione and their biological activities against many microbes.

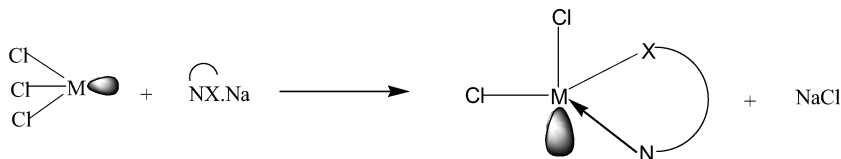
RESULTS AND DISCUSSION

The unimolar and bimolar reactions of PhSbCl_2 , SbCl_3 , and BiCl_3 with the monobasic bidentate thiosemicarbazone and semicarbazone ligands have been carried out in methanol.





The above equations can be explained by the following structural equation as shown below:



where, X = S/O, M = Sb/Bi, and N^\capX is the donor set of the ligands.

After removing the solvent under reduced pressure, colored solid compounds were obtained, which were found to be sparingly soluble in CH_2Cl_2 , CHCl_3 , and CCl_4 and highly soluble in methanol. The molecular weight determinations show them to be monomeric in nature. The molar conductances of 10^{-3} M solutions of the complexes in dry DMF lie in the $12\text{--}15\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ range, indicating that they are non-electrolytes. The isolated complexes are presented in Tables I and II together with their analytical data.

Electronic Spectra

The electronic spectra of the ligands show two maxima at ca. 274 nm and ca. 316 nm due to $\pi\text{--}\pi^*$ transitions of the aromatic ring, and which appear almost at the same positions in the spectra of their antimony and bismuth complexes. Another band observed at around 336 nm in the spectra of the ligands can be assigned to $n\text{--}\pi^*$ transitions of the $>\text{C}=\text{N}$ chromophore. This band shows a hypsochromic shift²⁵ (ca. 20 nm) in the spectra of the antimony and bismuth complexes due to the polarization within the chromophore ($>\text{C}=\text{N}$) caused by the metal–ligand interaction.

IR Spectra

The assignment of the important characteristic bands in the IR spectra (Table III) of these new antimony(III) and bismuth(III) derivatives were made by comparing them with the IR spectral data of the corresponding ligands. The IR spectra of the ligands display two sharp bands around 3360 cm^{-1} and 3430 cm^{-1} assignable to ν_{asym} and ν_{sym} NH_2 vibrations, respectively, which remain unaltered in the antimony and bismuth complexes, indicating their non-involvement in coordination. The ligands show a medium intensity band at $3284\text{--}3122\text{ cm}^{-1}$ due

TABLE I Synthetic and Analytical Data of Antimony(III) and Bismuth(III) Complexes of Hydrazinecarbo-
thioamide (L'H)

S. No.	Reactants in g			Molar ratio	Empirical formula of complexes	Color	Mp (°C)	Elemental Analysis (%)					Mol. Wt. Found (Calcd.)
	Starting Material	Ligand	Na					N Found (Calcd.)	S Found (Calcd.)	Cl Found (Calcd.)	Sb/Bi Found (Calcd.)		
1	—	L'H	—	—	C ₉ H ₈ ON ₄ S	Dark Green	217	25.13 (25.43)	14.12 (14.55)	—	—	204 (220.2)	
2	PhSbCl ₂ (0.69)	L'H (0.55)	0.06	1:1	SbC ₁₅ H ₁₂ ON ₄ SCl	Light Green	210	12.55 (12.35)	8.86 (7.07)	7.86 (7.82)	26.56 (26.85)	449 (453.5)	
3	PhSbCl ₂ (0.54)	L'H (0.89)	0.09	1:2	SbC ₂₄ H ₁₉ O ₂ N ₈ S ₂	Brown	172 ^a	16.85 (17.58)	10.45 (10.06)	—	18.76 (19.10)	649 (637.3)	
4	SbCl ₃ (0.55)	L'H (0.53)	0.06	1:1	SbC ₉ H ₇ ON ₄ SCl ₂	Reddish brown	186	13.12 (13.60)	7.84 (7.78)	17.45 (17.21)	29.43 (29.56)	417 (411.9)	
5	SbCl ₃ (0.57)	L'H (1.09)	0.12	1:2	SbC ₁₈ H ₁₄ O ₂ N ₈ S ₂ Cl	Green	178	8.99 (18.81)	10.45 (10.89)	5.78 (5.95)	20.56 (20.69)	596 (595.6)	
6	BiCl ₃ (0.64)	L'H (0.45)	0.05	1:1	BiC ₉ H ₇ ON ₄ SCl ₂	Greenish yellow	169	11.16 (11.22)	5.97 (6.42)	14.12 (14.21)	41.77 (41.87)	504 (499.1)	
7	BiCl ₃ (0.71)	L'H (1.98)	0.10	1:2	BiC ₁₈ H ₁₄ O ₂ N ₈ S ₂ Cl	Brown	185	15.98 (16.41)	8.83 (9.39)	5.78 (5.99)	29.96 (30.60)	684 (682.9)	

^aDecomposition temperature of the complexes.

TABLE II Synthetic and Analytical Data of Antimony(III) and Bismuth(III) Complexes of Hydrazinecarboxamide (L^2H)

S. No.	Reactants in g			Molar ratio	Empirical formula of complexes	Color	Mp (°C)	Elemental Analysis (%)				Mol. Wt. Found (Calcd.)
	Starting Material	Ligand	Na					N Found (Calcd.)	Cl Found (Calcd.)	(Sb/Bi) Found (Calcd.)		
1	—	L^2H	—	—	$C_9H_8O_2N_4$	Gray	228	27.10 (27.43)	—	—		201 (204.2)
2	$PhSbCl_2$ (0.57)	L^2H (0.43)	0.05	1:1	$SbC_{15}H_{12}O_2N_4Cl$	Reddish brown	216	12.12 (12.81)	7.83 (8.10)	27.24 (27.83)		434 (437.5)
3	$PhSbCl_2$ (0.58)	L^2H (1.76)	0.09	1:2	$SbC_{24}H_{19}O_4N_8$	Brown	156	18.23 (18.52)	—	19.97 (20.12)		599 (605.2)
4	$SbCl_3$ (0.68)	L^2H (0.61)	0.07	1:1	$SbC_{19}H_7O_2N_4Cl_2$	Charry	146	13.96 (14.15)	17.21 (17.91)	30.24 (30.76)		390 (395.8)
5	$SbCl_3$ (0.77)	L^2H (1.38)	0.16	1:2	$SbC_{18}H_{14}O_4N_8Cl$	Light brown	178	19.10 (19.88)	6.02 (6.29)	21.26 (21.61)		559 (563.6)
6	$BiCl_3$ (0.72)	L^2H (0.47)	0.05	1:1	$BiC_9H_7O_2N_4Cl_2$	Cream	245	11.20 (11.59)	7.06 (7.34)	43.01 (43.26)		478 (483.1)
7	$BiCl_3$ (0.61)	L^2H (1.58)	0.08	1:2	$BiC_{18}H_{14}O_4N_8Cl$	Gray	279 ^a	16.86 (17.22)	5.17 (5.45)	31.97 (32.11)		654 (650.8)

^aDecomposition temperature of the complexes.

to ν NH vibrations, which disappears in the spectra of the complexes, suggesting the loss of a proton on the α -nitrogen on complexation with the antimony and bismuth atoms. Sharp and strong bands in both the ligands appear in the region 1611–1615 cm^{-1} , assigned to the stretching mode of the $>\text{C}=\text{N}$ group. However, these bands are lowered^{25,26} by $\sim 10 \text{ cm}^{-1}$ in the complexes, indicating the coordination of azomethine nitrogen to the antimony atom. The formation of $\text{Bi} \leftarrow \text{N}$ bonds is further supported by a shift of 10–10 cm^{-1} toward higher wave number in the position of $\nu >\text{C}=\text{N}$ which appear at 1621–1623 cm^{-1} in the spectra of the complexes. Strong bands at 1690 cm^{-1} (L^2H) and 1050 cm^{-1} (L^1H) are due to $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{S}$, respectively for the free ligands, which shift in the complexes, suggesting complexation through the enolic oxygen and thiolic sulfur, respectively, which is further supported by the appearance of new bands of medium to weak intensity in regions ca. 410–415, 508–510, and 298–305 cm^{-1} due to $\nu(\text{Sb} \leftarrow \text{N})$,²⁷ $\nu(\text{Sb}-\text{O})$,²⁸ and $\nu(\text{Sb}-\text{S})$ ²⁹ vibrations, respectively, in the spectra of the antimony complexes. Bands also appear at ca. 450 cm^{-1} due to a $(\text{Ph}-\text{Sb})$ ⁴³ stretching mode. For bismuth complexes, $\nu(\text{Bi} \leftarrow \text{N})$,³⁰ $\nu(\text{Bi}-\text{O})$,³¹ and $\nu(\text{Bi}-\text{S})$ ³² vibrations appear at ca. 321–329, 428, and 270 cm^{-1} , respectively. The spectra of the ligands as well as complexes show a band at 1670 cm^{-1} due to the presence of $>\text{C}=\text{O}$ group. The absence of any shift in its position indicates that this group does not take part in the bonding.

¹H NMR Spectra

The ¹H NMR spectra (Table III) of the free ligands and their antimony(III) and bismuth (III) complexes have been recorded in DMSO- d_6 . The $-\text{NH}$ proton of the ligands resonates at δ 11.24 (L^1H) and δ 11.32 (L^2H) region as a singlet. The disappearance^{25–26} of these signals in the spectra of the complexes clearly suggests deprotonation of the functional group during the complexation and coordination through the sulfur (L^1H) and oxygen (L^2H) with the antimony and bismuth atoms in the complexes. A singlet due to the $-\text{NH}_2$ group appears in the region δ 3.42–3.48 ppm. This signal remains unaltered in the spectra of the complexes, suggesting its non-involvement in complexation. The $-\text{NH}$ proton of the indole ring present in the free ligands and their metal complexes resonates in the range of δ 11.90–11.98 ppm. No significant shift has been observed in the position of these signals, showing the non-involvement of this group in the complexation. Aromatic protons present in the ligands as well as in their complexes resonate in δ the 6.24–8.18 ppm range as a complex pattern. Phenyl protons of the ligand moieties have been found to be merged with the signals of the phenyl

TABLE III IR (cm^{-1}) and ^1H NMR Spectra Data (δ , ppm) of the Antimony and Bismuth(III) Complexes

Compounds	$\nu(\text{C}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M} \leftarrow \text{N})$	$\nu(\text{M}-\text{S})$	-NH(Free) (bs)	-NH (ring)	-NH ₂	Aromatic proton (m)	C ₆ H ₅ -Sb (m)
L ¹ H	1615	—	—	—	11.24	11.90	3.42	6.24–8.12	—
PhSbCl(L ¹)	1605	—	413	305	—	11.91	3.41	6.25–8.17	6.63–8.32
SbCl ₂ (L ¹)	1607	—	415	298	—	11.90	3.42	6.26–8.18	—
BiCl ₂ (L ¹)	1623	—	329	270	—	11.90	3.42	6.24–8.15	—
L ² H	1611	—	—	—	11.32	11.98	3.48	6.35–8.16	—
PhSbCl(L ²)	1602	510	410	—	—	11.97	3.47	6.37–8.15	6.58–8.25
SbCl ₂ (L ²)	1604	508	412	—	—	11.98	3.48	6.36–8.12	—
BiCl ₂ (L ²)	1621	428	321	—	—	11.98	3.47	6.34–8.14	—

M = Sb/Bi, bs = broad singlet, and m = multiplet.

protons attached to the antimony atom and observed as a multiplet in the range δ 6.58–8.32 ppm.

^{13}C NMR Spectra

A comparison of the ^{13}C NMR spectra of the antimony(III) and bismuth(III) derivatives with the ligands provides very useful information about the mode of bonding. Considerable shifts (~ 5 to 15 ppm) were observed in the position of the azomethine (δ 157.24 and 161.16 ppm), thiol (164.85 ppm), and amido (178.35 ppm) group carbon atoms in antimony(III) derivatives, further supporting the involvement of these groups in the complexation. In the ^{13}C NMR spectra of the bismuth complexes, the signal for $>\text{C}=\text{N}$ carbon appears at δ 165.34–166.76 ppm, and a downfield shift of ~ 2 –6 ppm in azomethine carbon confirms the complexation. A new set of four signals observed in the spectra of the complexes in the range of δ 130.82–142.15 ppm has been assigned to the phenyl carbons attached to the antimony atom. Further, only one set of signals for the phenyl carbons of Ph_2Sb group has been observed, which indicates that the two phenyl groups are chemically equivalent. The signal for the carbonyl carbon ($\text{C}=\text{O}$) present in the heterocyclic ring appears in the range of δ 165.26–168.26 ppm.

In view of the spectroscopic evidence (UV, IR, and NMR), it may be concluded that the ligand moiety behaves as a monodentate and binds to antimony and bismuth through a nitrogen and sulfur/oxygen atom. A tetra- and pentacoordinated environment^{33–34} around the metal atom may be tentatively proposed for these compounds (Figure 1).

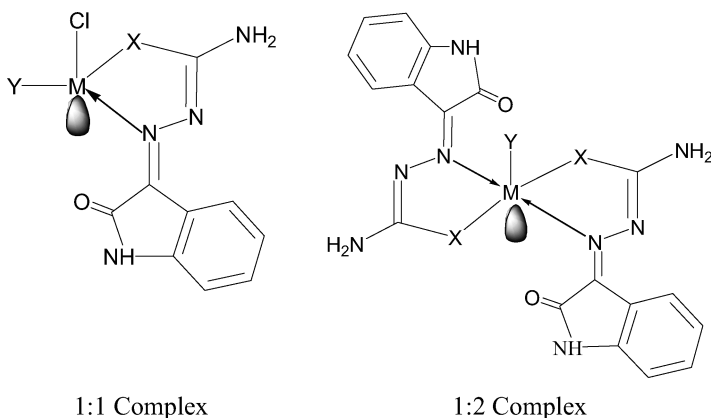


FIGURE 1 Structures of the metal complexes. Where, $\text{X} = \text{O/S}$, $\text{Y} = \text{Cl/Ph}$, and $\text{M} = \text{Sb/Bi}$.

Mode of Action

Antimicrobials can attack various targets in microorganisms, as a consequence of which, organisms are either destroyed or have their growth inhibited. Since the complexes inhibit the growth of microorganisms, it is assumed that the production of the enzymes is being affected, and hence the microorganisms are unable to utilize food for themselves, or the intake of ion decreases and consequently the growth ceases. The bonding of the chelated metals to the nitrogen bases of DNA and RNA and the inhibition of DNA synthesis through the blockage of the enzyme ribonucleotide diphosphate reductase (RDR)³⁵ are also responsible for the activity.

DISCUSSION

The free ligands and their antimony and bismuth heterochelates were tested against some fungi and bacteria to study their growth inhibitor potential towards the test organisms. Upon closer examination, a common feature that appears is enhanced bioactivity due to the following indicators:

1. The chelation reduces the polarity and increases the lipophilic nature of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane. This can be well ascribed to Tweedy's chelation theory.³⁶
2. The enhanced activity of the complexes depends on fineness of the particle size of the metal ion and the presence of the bulkier organic moieties. Furthermore, halogen atoms directly attached to metal ion increase toxicity to some extent, and when this halogen atom is being replaced by a bulky ligand moiety, it enhances the activity of the whole molecule to a considerable extent.³⁷
3. The toxicity of antibacterial compounds against different species of bacteria depends either on the difference in ribosomes or the impermeability of the cell to the antimicrobial agent.³⁸
4. It is also noteworthy that concentration plays an important role in inhibiting the growth of microorganisms. At lower concentration, inhibition is less severe. Due to this fact, the activities of the organisms will be slowed down, while at higher concentration, more enzymes will become inhibited leading to a quicker death of the organisms. Lower concentration of compounds can check the sporulation in fungi, and a higher concentration inhibits the growth of organisms almost completely.

5. It is also evident that the complexes having sulfur as a donor atom in the ligand system display higher activity than those that do not have it.³⁹
6. Replacement of bismuth with antimony in its compounds reduced the compounds' antibacterial activities,^{40,41} and we have also confirmed that antimony analogues of a compound have substantially lower levels of activity.

CONCLUSION

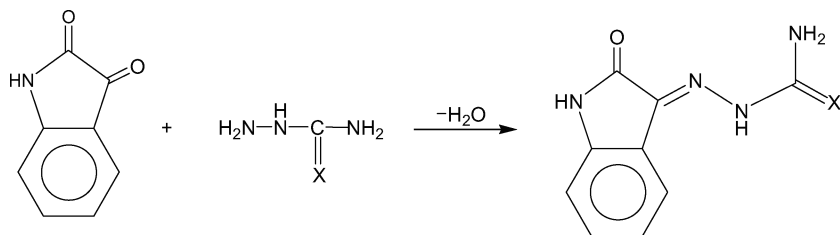
Microwave irradiation (MWI) is an efficient and environmentally benign method to accomplish various inorganic syntheses to afford products in higher yields in shorter reaction periods. Antimony(III) and bismuth(III) complexes obtained by 1:1 and 1:2 molar reactions were found to be tetra- and pentacoordinated, but due to the stereochemically active lone pairs of electrons present on the metal atom, pseudo trigonal bipyramidal and distorted octahedral geometries have been tentatively proposed for the said complexes. Antimicrobial activity of the complexes and the ligand showed that the former are more active than the parent ligand. The data given in Table III reveal that $\text{PhSb}(\text{L}^1)_2$ and $\text{BiCl}(\text{L}^1)_2$ complexes were found to be more toxic than the other complexes, and the bismuth complexes display better results than the antimony complexes.

EXPERIMENTAL

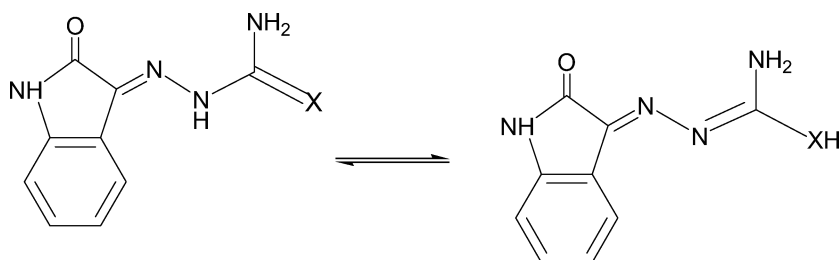
The PhSbCl_2 was prepared according to the method in the literature.⁴² All the reagents were dried and distilled before use. Trichlorobismuthane and 1H-indol-2,3-dione (isatin) were purchased and used as such. All preparations were done under anhydrous conditions.

Preparation of the Ligands

The ligands 3-(indolin-2-one)hydrazinecarbothioamide (L^1H) and 3-(indolin-2-one) hydrazinecarboxamide (L^2H) were prepared by the condensation of 1H-indol-2,3-dione with thiosemicarbazide and semicarbazide hydrochloride (in presence of sodium acetate) in 1:1 molar ratio in EtOH. The reaction mixture was stirred for ca. 30 min, and the separated solid was removed by filtration, recrystallized from EtOH, and dried in vacuo (Scheme 1). The tautomeric forms of the ligand have been shown in Scheme 2.



SCHEME 1 Synthesis of the ligands.



SCHEME 2 Tautomeric forms of the ligands, where, X = S (L^1H) and O (L^2H).

Synthesis of the Antimony(III) and Bismuth(III) Complexes

To a weighed amount of monophenylantimonydichloride, trichlorostibane, and trichloride bismuthane, the sodium salts of the ligands L^1H and L^2H in 1:1 or 1:2 molar ratios were added in dry methanol.

Microwave Method⁴³

In a microwave-assisted synthesis, the reaction mixtures were taken in a 50 mL conical flask, covered with glass wool, and then irradiated for 4–7 min inside the microwave oven. Anhydrous conditions were attained by using a beaker with silica gel or anhydrous CaCl_2 (this beaker was filled with a moisture-absorbing substance known as “Dummy”), which was placed near the reaction vessel during the compound formation inside the microwave oven. The products were recovered from the microwave oven and dissolved in a few mL of dry methanol, whereby the white precipitate of sodium chloride formed during the course of the reaction was removed by filtration, and the products were dried under reduced pressure. The resulting products were repeatedly washed with n-hexane and dried at 40–60°C/0.5 mm of Hg pressure for 3–4 h. The purity was further checked by TLC using silica gel-G.

TABLE IV Comparison Between Conventional and Microwave Method of Synthesis

Compound	Yield (%)		Solvent (mL)		Time	
					(h)	(Min)
	Thermal	Microwave	Thermal	Microwave	Thermal	Microwave
PhSbCl(L ¹)	54	74	15	2	14	8
PhSb(L ¹) ₂	59	78	10	2	15	7
SbCl ₂ (L ¹)	55	75	15	2	12	9
SbCl(L ¹) ₂	60	80	10	2	8	10
BiCl ₂ (L ¹)	61	79	10	2	13	8
BiCl(L ¹) ₂	57	73	10	2	15	15
PhSbCl(L ²)	58	78	15	2	9	10
PhSb(L ²) ₂	65	75	5	2	12	11
SbCl ₂ (L ²)	67	73	15	2	10	15
SbCl(L ²) ₂	57	75	10	2	13	12
BiCl ₂ (L ²)	58	80	5	2	14	13
BiCl(L ²) ₂	49	81	15	2	12	7

Conventional Method

The antimony(III) and bismuth(III) complexes were also synthesized by a thermal method. The contents were boiled under reflux for 14–16 h using a reflux condensor. In the thermal method, instead of 4–7 min, reactions were completed in 14–16 h, and the yield of the products was also less than those obtained in the microwave-assisted synthesis. A drastic reduction in reaction time was thus observed due to the rapid heating capability of microwaves. A comparative study has also been done between the microwave technique and conventional method, and the results are summarized in Table IV.

Analytical Methods and Physical Measurements

The molecular weights were determined by the Rast Camphor method. Sulfur and nitrogen were estimated gravimetrically (Messenger's method) as BaSO₄ and by Kjeldahl's method, respectively. Chlorine was determined by Volhard's method.⁴⁴ Antimony was estimated by oxidation of Sb(III) to Sb(V) upon heating with KMnO₄, the excess of which was decolorized with H₂O₂. The remaining H₂O₂ was decomposed, and Sb(V) then was determined iodimetrically.⁴⁵ Bismuth was estimated complexometrically.⁴⁴ Electronic spectra of the complexes were recorded in methanol on a UV-160A Shimadzu spectrophotome-

ter in the range 200–600 nm. Infrared spectra of the ligands and their complexes were scanned in the range 4000–200 cm^{-1} with the help of a model Nicolet Megna FTIR-550 spectrophotometer and a model FT IR-8400 S spectrophotometer on KBr optics as well as Nujol mull. NMR spectra were recorded using a JEOL-AL-300 FT NMR spectrometer in DMSO- d_6 using TMS as the internal standard. The conductivity of the resulting derivatives was determined at room temperature in dry DMF by the Systronics conductivity bridge (Model 305) using a cell having a cell constant of 0.5 cm^{-1} .

Biocidal Activity

Fungicidal and bactericidal screening data (Table V) show that under identical experimental conditions, the compounds possess antimicrobial properties. However, a few compounds possess good activity against microorganisms.

Radial Growth Method for Antifungal Activity⁴³

The antifungal activity was evaluated against *Macrophomina phaseolina* and *Fusarium oxysporum* using the agar plate technique. The compounds were directly mixed with the medium in different concentrations. Controls were also run, and three replicates were used in each case. The linear growth of the fungus was recorded by measuring the diameter of the fungus colony after 4 days. The amount of growth inhibition in each of the replicates was calculated by the equation $100 \cdot (C-T) C^{-1}$, where C and T are the diameters of the fungus colony in the control and the test plates, respectively.

Paper Disc Method for Antibacterial Activity⁴³

Antibacterial activity was evaluated against *Staphylococcus aureus* and *Escherichia coli* by the paper disc plate method. The nutrient agar medium (0.5%, peptone, 0.15% yeast, 0.15% beef extract, 0.35% NaCl, and 0.13% KH_2PO_4) in distilled water (1000 cm^3) was autoclaved for 20 min at 15 psi before inoculation. The 5 mm diameter paper discs of Whatman No.1 were soaked in different solutions (500 and 1000 ppm) of the compounds, dried, and then placed in the Petri plates previously seeded with the test organisms. The plates were incubated for 24 h at $28 \pm 2^\circ\text{C}$, and the inhibition zones around each disc were measured.

TABLE V Antibacterial and Antifungal Screening Data of Antimony(III) and Bismuth(III) Complexes

Compound	Antibacterial screening% inhibition after 1 day (Conc. in ppm)				Antifungal screening% inhibition after 4 days (Conc. in ppm)			
	<i>Escherichia coli</i>		<i>Staphylococcus aureus</i>		<i>Macrophomina phaseolina</i>		<i>Fusarium oxysporum</i>	
	500	1000	500	1000	100	200	100	200
L ¹ H	4	7	7	9	43	49	51	57
PhSb(L ¹)	9	13	-	14	67	76	68	82
PhSb(L ¹) ₂	10	14	11	15	69	80	69	84
SbCl(L ¹) ₂	9	12	10	14	64	72	68	80
BiCl(L ¹) ₂	12	16	13	16	75	86	77	88
L ² H	3	5	6	8	39	45	46	52
PhSbCl(L ²)	7	11	-	13	63	72	68	80
PhSb(L ²) ₂	9	11	10	14	65	74	69	83
SbCl(L ²) ₂	9	10	10	12	63	71	67	78
BiCl(L ²) ₂	11	12	11	16	71	81	75	86

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