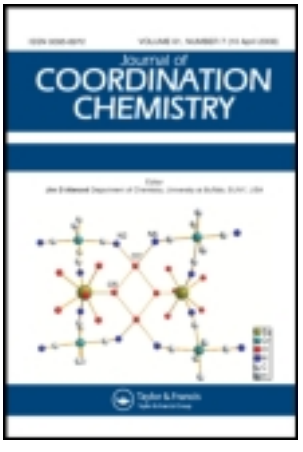

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Microwave-assisted synthesis, characterization, antimicrobial, and pesticidal activity of bismuth and antimony complexes with coumarin-based ligands

Latika Dawara [a] & R.V. Singh [a]
[a] Department of Chemistry , University of Rajasthan , Jaipur 302 004, India
Published online: 26 Feb 2011.

To cite this article: Latika Dawara & R.V. Singh (2011) Microwave-assisted synthesis, characterization, antimicrobial, and pesticidal activity of bismuth and antimony complexes with coumarin-based ligands, Journal of Coordination Chemistry, 64:6, 931-941, DOI: 10.1080/00958972.2011.557721

To link to this article: http://dx.doi.org/10.1080/00958972.2011.557721

Journal of Coordination Chemistry
Vol. 64, No. 6, 20 March 2011, 931–941

Microwave-assisted synthesis, characterization, antimicrobial, and pesticidal activity of bismuth and antimony complexes with coumarin-based ligands

LATIKA DAWARA and R.V. SINGH*

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India

(*Received 15 April 2010; in final form 3 December 2010*)

Reactions of 3-acetylcoumarin with thiosemicarbazide and semicarbazide hydrochloride resulted in the formation of 3-acetylcoumarinthiosemicarbazone ($C_{12}H_{11}N_3O_2S$ or L^1H) and 3-acetylcoumarinsemicarbazone ($C_{12}H_{11}N_3O_3$ or L^2H), respectively. Bi(III) and Sb(III) complexes have been synthesized by mixing metal salts in 1 : 1 and 1 : 2 molar ratios with these ligands using microwave as well as conventional heating for comparison. The authenticity of these ligands and their complexes has been established with elemental analysis, melting points, molecular weights, IR, ^{1}H-NMR, UV, mass spectral, and X-ray powder diffraction studies. The ligands coordinated to metal as monobasic bidentate manner and tetra- and pentacoordinated geometry have been proposed around the metals. Both ligands and complexes have been screened for antimicrobial activities. The pesticidal activities of ligands and complexes against the *Corcyra cephalonica* have also been tested.

Keywords: Bismuth(III) and antimony(III) complexes; Antimicrobial and pesticidal activity; Thiosemicarbazone; Semicarbazone; Spectral studies

1. Introduction

Microwave synthesis attracts considerable attention. The main advantage of microwave heating is the almost instantaneous ''in-core'' heating of the materials in a homogeneous and selective manner, coupled with the significantly shorter reaction time. This implies considerable saving of energy [1]. Coumarin derivatives constitute an important class of heterocyclic compounds with anticoagulant (e.g., warfarin and acenocoumarol) [2], anticoagulant insecticide (e.g., coumaphos) [3], antibacterial (e.g., novobiocin and clorobiocin) [4], and pharmacological properties. Schiff-base complexes of main group elements containing semicarbazones and thiosemicarbazones have remained a topic of research interest [5], mainly due to the biological applications of ligands and compounds derived from them. Semicarbazones and thiosemicarbazones can act as neutral or charged ligands, showing tautomerism in keto/thione or enol/thiol form. Coordination through oxygen or sulfur and azomethine nitrogen is observed in the formation of a five-membered chelate ring. Semicarbazones and thiosemicarbazones

*Corresponding author. Email: rvsjpr@hotmail.com

ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2011.557721

have attracted special attention due to their biological activities. These compounds present a wide variety of biological activities, such as antitumor [5], fungicidal, bactericidal, and antiviral [6]. Some drugs have increased activity when administered in the form of metal complexes and a number of metal chelates inhibit tumor growth. In the treatment of cancer, the active species is not the semicarbazones or thiosemicarbazones but their metal chelates [7]. Coordination chemistry, biological effects, and toxicology of antimony and bismuth complexes, such as their requirements in pharmacological activities, are the areas of increasing research interest [8]. Antimony compounds exhibit a broad spectrum of biological activities, chemotherapeutic applications, and cytotoxic activities [9]. Bi(III) exhibits variable coordination numbers and often an irregular coordination geometry. Comparison of the relationships between specific structural features and bioactivity for bismuth(III) thiosemicarbazones and their related ligands suggests that the primary role of the ligands is to transport the bismuth into susceptible microbes [10]. For inorganic medicines of antimony, antimony potassium tartrate, and stibophen are antiprotozoal and anthelmintic agents [11]. Compared with the studies of bismuth(III) compounds only few antimicrobial activities [12–15] and structural studies had been reported for antimony(III) complexes with thiosemicarbazones and semicarbazones [16].

Herein, we report synthesis and molecular structures of Bi(III) and Sb(III) complexes and their antimicrobial and pesticidal activities as well as the free ligands, and discuss the relationship between the structures and antimicrobial activities.

2. Experimental

2.1. *Materials and methods*

$BiCl_3$ and $SbCl_3$ as well as 3-acetylcoumarin were purchased from Alfa Aesar. Solvents of analytical grade were distilled from appropriate drying agents immediately prior to use. Molecular weights were determined by Rast's camphor method [17]. Chlorine was estimated by Volhard's method. Bismuth was estimated complexometrically. Antimony was estimated by oxidation of Sb(III) to Sb(V) on heating with $KMnO_4$, the excess of which was decolorized with H_2O_2. The remaining H_2O_2 was decomposed, and Sb(V) was then determined iodimetrically. Nitrogen was estimated by Kjeldahl's method and sulfur was estimated by Messenger's method [18]. Electronic spectra were recorded in methanol on a Varian–Cary/5E spectrophotometer at SAIF, IIT, Madras. Infrared (IR) spectra of the ligands and their complexes were recorded on a Nicolet Megna FTIR-550 spectrophotometer as KBr pellets. ^{1}H NMR spectra were recorded on a JEOL-AL-300 FTNMR spectrometer in DMSO-d_6 using TMS as the internal standard.

2.2. *Preparation of the ligands*

Two different routes were employed for the synthesis of the ligands.

2.2.1. Microwave-assisted synthesis. The ligands were prepared by the condensation of 3-acetylcoumarin (2.02 g, 0.01 mol) with thiosemicarbazide (0.978 g, 0.01 mol) or

semicarbazide hydrochloride (1.197 g, 0.01 mol) in the presence of sodium acetate. The reaction mixture was irradiated in the microwave oven in 2–3 mL solvent. The reactions were completed in 5–7 min. The resulting precipitate was then recrystallized with alcohol and dried under vacuum. These were characterized and analyzed before use. Elemental analyses (N and S) were conducted using the methods mentioned above and their results were in good agreement with the calculated values. The structures of the ligands are shown in figure 1.

2.2.2. Conventional thermal method. For comparison, the above ligands were also synthesized by thermal methods. In this method, 100 mL of ethanol was used to dissolve the starting materials and refluxed for 3–4 h. The residue formed was separated, filtered off, washed with water, recrystallized from ethanol, and finally dried in vacuum over fused calcium chloride. A comparison between thermal method and microwave method is given in table 1.

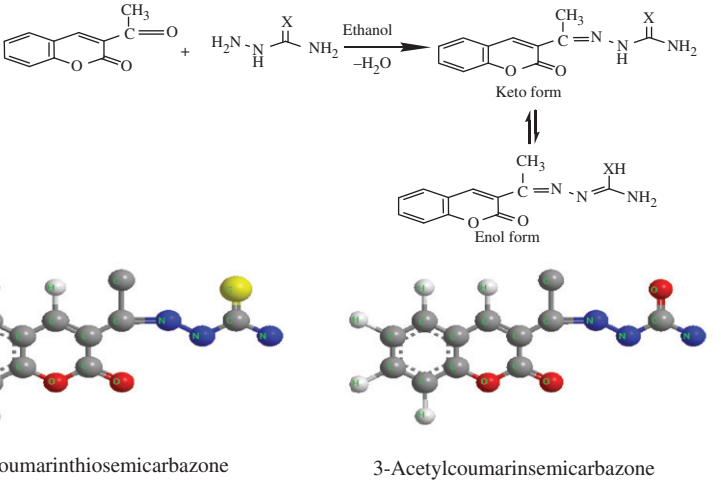

Figure 1. Structures of the ligands.

Table 1. Comparison between microwave and thermal methods.

	Yield (%)		Solvent (mL)		Time	
Compound	Thermal	Microwave	Thermal	Microwave	Thermal (h)	Microwave (min)
$L^1H(N^{\cap}SH)$	84	90	100	3	3	5
$L^2H(N^{\cap}OH)$	85	92	100	2	4	7
$[Cl_2Bi(N^{\cap}S)]$	72	83	40	4	14	5
$[ClBi(N^{\cap}S)_2]$	75	82	35	3	16	7
$[Cl_2Bi(N^{\cap}O)]$	73	80	30	2	15	5
$[ClBi(N^{\cap}O)_2]$	69	77	45	4	13	5
$[Cl_2Sb(N^{\cap}S)]$	71	78	30	3	15	6
$[ClSb(N^{\cap}S)_2]$	65	81	45	2	14	8
$[Cl_2Sb(N^{\cap}O)]$	74	86	40	4	16	6
$[ClSb(N^{\cap}O)_2]$	68	79	35	3	17	5

2.3. *Preparation of the metal complexes*

2.3.1. Microwave method. For synthesis of complexes, $SbCl_3$ or $BiCl_3$ and sodium salt of the ligands (prepared by adding the corresponding weight of sodium metal to 3-acetylcoumarin thiosemicarbazone/semicarbazone) in 5 mL of dry methanol in 1 : 1 and 1 : 2 molar ratios were irradiated inside a microwave oven at 700 W for 5–8 min. The products were recovered from the microwave oven and dissolved in a few milliliters of dry methanol. The white sodium chloride formed during the course of the reaction was removed by filtration, and the filtrate was dried under reduced pressure. The resulting product was repeatedly washed with petroleum ether and finally dried at 40–60°C/0.5 mmHg for 3–4 h. The purity was further checked by thin layer chromatography using silica gel-G.

2.3.2. Thermal method. These chloroantimony(III) and chlorobismuth(III) complexes were also synthesized by thermal methods. The reaction mixtures were heated under reflux for 13–17 h, filtered to remove NaCl and the solvent was removed by the same procedure mentioned above. The physico-chemical properties and analytical data of these complexes are listed in table 2.

2.4. *Microbiological studies*

2.4.1. Antifungal activity. The antifungal activities of the standard fungicide (Flucanazone), ligands, and complexes were tested for their effect on the growth of microbial cultures and studied for their interaction with *Aspergillus niger* and *Fusarium oxysporum* using Czapek's agar medium having composition glucose 20 g, starch 20 g, agar–agar 20 g, and distilled water 1000 mL. To this medium was added requisite amount of the compounds after being dissolved in methanol to get 50, 100, and 200 ppm. The medium was then poured into Petri plates and spores of fungi were placed on the medium using inoculum's needle. These Petri plates were wrapped in polythene bags containing a few drops of alcohol and were placed in an incubator at 30 ± 2°C. The 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 fungal colony after 96 h and the percentage inhibition was calculated by the equation:

$$\% \text{ Inhibition} = (C - T/C)100,$$

where C and T are the diameters of the fungal colony in the control and test plates, respectively [19].

2.4.2. Antibacterial activity. Antibacterial activities were tested against *Escherichia coli* and *Bacillus subtilis* using the paper disc method [20]. Each compound was dissolved in DMSO and the solutions of 500 and 1000 ppm were prepared separately. Paper discs of Whatman filter paper (No. 42) of 2 cm were cut and sterilized in an autoclave. Paper discs soaked in the desired concentration of the complex solutions were placed aseptically in Petri dishes containing nutrient agar media (agar 20 g + beef extract 3 g + peptone 5 g) seeded with *E. coli* and *S. aureus* bacteria, separately.

Table 2. Analytical data and physical properties of the ligands and their metal complexes.

Compound	Color	m.p. (°C)	Found (Calcd) (%)				Molecular weight Found (Calcd)
			N	S	Cl	M	
L^1H	Cream	215–218	15.92(16.08)	11.92(12.27)	–	–	260.121(261.300)
L^2H	Yellow	195–200	16.82(17.13)	–	–	–	244.231(245.234)
$[Cl_2Bi(N^{\cap}S)]$	Black	175–179	7.25(7.78)	5.26(5.94)	12.96(13.13)	38.12(38.69)	538.213(540.178)
$[ClBi(N^{\cap}S)_2]$	Brown	181–185	10.25(10.99)	7.98(8.38)	4.25(4.63)	27.16(27.32)	764.012(765.017)
$[Cl_2Bi(N^{\cap}O)]$	Light yellow	162–167	7.91(8.02)	–	13.11(13.53)	39.13(39.87)	522.023(524.112)
$[ClBi(N^{\cap}O)_2]$	Orange	170–174	11.06(11.47)	–	4.29(4.84)	28.21(28.51)	731.300(732.866)
$[Cl_2Sb(N^{\cap}S)]$	Orange	210–213	8.92(9.28)	6.86(7.08)	15.32(15.65)	25.92(26.88)	451.549(452.958)
$[ClSb(N^{\cap}S)_2]$	Brown	232–236	12.03(12.40)	9.03(9.46)	5.15(5.23)	17.24(17.96)	676.321(677.796)
$[Cl_2Sb(N^{\cap}O)]$	Cream	226–229	9.02(9.62)	–	16.12(16.23)	26.93(27.87)	435.721(436.892)
$[ClSb(N^{\cap}O)_2]$	Brown	192–196	12.59(13.02)	–	5.21(5.49)	18.36(18.86)	644.256(645.655)

The Petri dishes were incubated at 37°C and the inhibition zones were recorded after 24 h of incubation. The antibacterial activity of Streptomycin was also recorded using the same procedure, concentrations, and solvent. The % activity index for the complex was calculated by the formula:

$$\%\ \text{Activity index} = \frac{\text{Zone of inhibition by test compound (diameter)}}{\text{Zone of inhibition by standard (diameter)}} \times 100.$$

2.4.3. Determination of minimum inhibitory concentration. Minimum inhibitory concentration (MIC) is the lowest concentration of test agent that inhibited visible growth of bacteria after 24-h incubation at 37°C. The determination of the MIC involves a semiquantitative test procedure, which gives an approximation to the least concentration of an antimicrobial needed to prevent microbial growth. The MIC was determined by the liquid dilution method [21]. Stock solutions of the ligands and their complexes with 10–50 mg mL^{-1} concentrations were prepared with aqueous methanol. Inoculum of the overnight culture was prepared. In a series of tubes, 1 mL of complex solutions with different concentrations were taken and 0.4 mL of the inoculum was added to each tube; 3.5 mL of the sterile water was added to each of the test tubes. These test tubes were incubated for 24 h and observed for the presence of turbidity. The absorbance of the suspension of the inoculum was observed with the help of a spectrophotometer at 555 nm. The end result of the test was the minimum concentration of antimicrobial (test materials) which gave a clear solution, that is no visual growth [22, 23].

2.4.4. Insecticidal activity. Many insects cause damage to stored products and other commodities, such as food, grain, paper, books, furniture, timber, and clothing. A pest is an animal whose population buildup increases above a certain level of economic injury, and its existence conflicts with human welfare, convenience, and profit [24].

Larva of *Corcyra cephalonica* were obtained from stock culture maintained at the storage section of the Division of Entomology, Agricultural Research Institute, Durgapura, Jaipur. Insects were reared on grains of wheat at 27 ± 1°C and 70% relative humidity. Glass jars containing 500 g of wheat grains were labeled to indicate the date of introduction of larvae and new emergence. At alternate days, larvae were shifted to fresh jars so that successive rearing jars can be maintained and insects of known age can be obtained regularly. Insecticidal activity of the synthesized compounds was tested by dipping and spraying methods. All synthetic compounds were weighed and dissolved in methanol to prepare 1000 mg L^{-1} stock solution. Further concentrations, namely 900, 800, 700, 600, 500, 400, 300, 200, and 100 mg L^{-1}, were prepared by serial dilution. One milliliter of each concentration of various compounds was directly poured into each Petri plate (90 mm) using a micropipette. Petri plates with test solution were rotated vigorously to prepare uniformly and were allowed to dry for 3–5 min. Each concentration as well as control in methanol was replicated thrice. Twenty adults (2–5 days old) were released in each Petri plate and were kept at 27 ± 1°C and 70% relative humidity. Mortality was observed after 96 h. Adults were considered dead if they failed to respond to stimulus by touch. Control mortality was corrected by using Abbott's formula [25] and LC_{50} is obtained by graphical method. X^2 is calculated by statistical analysis.

3. Results and discussion

Metal ions interact with the monobasic bidentate ligands having N∩S and N∩O donor sets in 1 : 1and 1 : 2 molar ratios with the formation of $[Cl_2M(N^{\cap}X)]$ and $[ClM(N^{\cap}X)_2]$ (where X = S/O, M = Sb/Bi). These reactions can be represented by the following general equations:

$$MCl_3 + NaN^{\cap}X \xrightarrow[MeOH]{1:1} [Cl_2Bi(N^{\cap}X)] + NaC1,$$

$$MCl_3 + 2NaN^{\cap}X \xrightarrow[MeOH]{} [ClBi(N^{\cap}X)_2] + NaC1.$$

After removing the solvent under reduced pressure, colored solid compounds were obtained, which were found to be soluble in MeOH and DMSO. Molecular weight determinations show them to be monomeric. The molar conductances of 10^{-3} mol L^{-1} solutions of the complexes in dry DMF lie in the 12–15 Ω^{-1} cm^2 mol^{-1} range, indicating that they are non-electrolytes.

3.1. *UV spectra*

Electronic spectra of the ligands in methanol display maxima at ~276 and ~326 nm, which are due to π–π^* electronic transitions and remain almost unchanged in the spectra of the metal complexes. The band at 370 nm is due to n–π^* transitions of the >C=N chromophore and shows a bathochromic shift of 20–30 nm after coordination of azomethine nitrogen to the metal, indicating delocalization of the electronic charge within the chelate ring and thereby stabilizing the resulting complexes.

3.2. *IR spectra*

Absorption frequencies of the ligands and their metal complexes along with their assignments are listed in table 3. IR spectra of L^1H and L^2H display absorption bands

Table 3. IR (cm^{-1}) and ^1H NMR (δ, ppm) spectral data of the ligands and their complexes.

	IR spectral data				^1H NMR spectral data			
Compound	(>C=N)	(M–S)	(M–O)	(M←N)	–NH	$–CH_3$	$–NH_2$	Aromatic protons (m)
($N^{\cap}SH$)	1610	–	–	–	8.49	2.08	3.45	6.42–8.02
($N^{\cap}OH$)	1600		–	–	8.69	2.10	3.43	6.45–8.12
$[Cl_2Bi(N^{\cap}S)]$	1615	235	–	320	–	2.11	3.42	6.48–8.05
$[ClBi(N^{\cap}S)_2]$	1620	265	–	321	–	2.07	3.47	6.72–8.06
$[Cl_2Bi(N^{\cap}O)]$	1605	–	443	326	–	2.04	3.44	6.73–8.09
$[ClBi(N^{\cap}O)_2]$	1607	–	445	328	–	2.06	3.46	6.72–8.15
$[Cl_2Sb(N^{\cap}S)]$	1605	382	–	405	–	2.08	3.47	6.71–8.10
$[ClSb(N^{\cap}S)_2]$	1607	391	–	415	–	2.11	3.48	6.76–8.06
$[Cl_2Sb(N^{\cap}O)]$	1590	–	507	440	–	2.05	3.38	6.65–8.11
$[ClSb(N^{\cap}O)_2]$	1592	–	515	445	–	2.06	3.41	6.85–8.16

at 3150–3250, 1600–1610, and 1080/1690 cm^{-1} assigned to –(NH), (>C=N), and (>C=S)/(>C=O), respectively. Bands at 1720–1725 cm^{-1} due to (>C=O) of lactone of the ligands remain almost unchanged in the complexes, indicating their non-involvement in complexation. The broad band due to –(NH) vibration disappears in the spectra of the complexes, indicating deprotonation on coordination with the metal. The negative shift (10–20 cm^{-1}) of (>C=N) observed in all complexes indicates involvement of azomethine nitrogen in complexation [26]. Bands due to (>C=S) and (>C=O) shift to lower frequencies in the complexes, indicating coordination of sulfur and oxygen to metal. The spectra of the free ligands display sharp bands at 3340–3500 and 3350–3490 cm^{-1} due to the asymmetric and symmetric vibrations of NH_2, respectively, which remain at almost the same positions in spectra of the complexes, suggesting that NH_2 is not involved in chelation. New bands are at 440–450, 507–515, 382–391, 320–328, 235–265, and 443–445 cm^{-1} for (Sb←N) [27], (Sb–O) [28], (Sb–S) [29], (Bi←N) [30], (Bi–S) [31], and (Bi–O) [32], respectively.

3.3. *^{1}H NMR spectra*

Further evidence for coordination was obtained from ^{1}H NMR spectra. The ^{1}H NMR spectra of the ligands (DMSO-d_6) exhibit a broad peak at 8.49–8.69 ppm due to –NH. The –NH signal disappears in the complexes, suggesting that this proton has been lost *via* thioenolization and ketoenolization of >C=S and >C=O with coordination of sulfur and oxygen. Other protons, namely CH_3 and NH_2 resonate nearly at the same position in complexes as in free ligands (table 3).

3.4. *Mass spectra*

Mass spectroscopy, mainly applied in the analysis of biomolecules, has been increasingly used as a powerful structural characterization technique in coordination chemistry. The EI mass spectrum of [$Cl_2Sb(N^{\cap}S)$] complex was studied as a representative case. The peaks of appreciable intensity were observed at m/z values 454.5379, 438.4360, 367.8567, 244.1285, 200.0572, 185.1061, 171.0575, 145.0778, 129.0924, 113.0687, and 89.0714. The molecular ion peak for [$Cl_2Sb(N^{\cap}S)$] was observed at m/z 454.537, in good agreement with its molecular weight, for a monomer. Fragmentations are given in table 4 and graphs in Supplementary material.

3.5. *X-ray structure determination*

Lattice dynamics of the finely powdered product, [$ClBi(N^{\cap}O)_2$], has been deduced on the basis of X-ray powder diffraction. The observed interplanar spacing values (“d” in Å) have been measured from the diffractogram and the Miller indices h, k, and l have been assigned to each d value and 2-theta angles are reported. The results show that the compound belongs to “orthorhombic” crystal system having unit cell parameters as $a = 32.5689$, $b = 12.9898$, $c = 18.5623$, maximum deviation of 2-theta = 0.021 and alpha = 90, beta = 90, gamma = 90 at wavelength = 1.540598. We have tried to isolate a single crystal of bismuth(III) suitable for X-ray diffraction but could not succeed. However, Silvestru *et al.* [33] have recently reported the single crystal structure of

Table 4. m/z values for mass spectral studies of $[Cl_2Sb(N^{\frown}S)]$.

Formula	m/z
$[Cl_2SbC_{12}H_{10}O_2N_3S]$	454.5379
$[Cl_2SbC_{12}H_8O_2N_2S]^+$	438.4360
$[SbC_{12}H_8O_2N_2S]^+$	367.8567
$[C_{12}H_8O_2N_2S]^+$	244.1295
$[C_{11}H_8O_2N_2]^+$	200.0572
$[C_{10}H_5O_2N_2]^+$(base peak)	185.1061
$[C_{10}H_5O_2N]^+$	171.0575
$[C_9H_5O_2]^+$	145.0778
$[C_9H_5O]^+$	129.0924
$[C_9H_5]^+$	113.0687
$[C_7H_5]^+$	89.0714

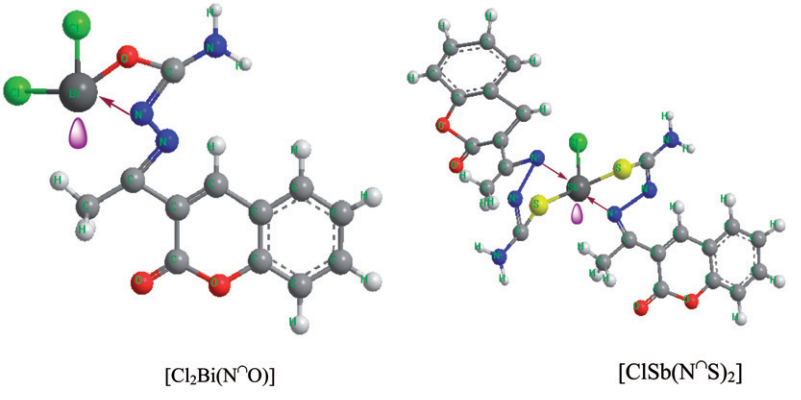

Figure 2. Structures of the complexes.

pentacoordinated bismuth(III) complex in which the ligand adopts the most stereochemically favorable orientation (graph I and table in "Supplementary material").

On the basis of the above discussion, the structures shown in figure 2 have been proposed for the complexes.

3.6. *Biological activity*

Antimicrobial activities of the ligands and their corresponding metal complexes on selected fungi, *A. niger* and *F. oxysporum*, and two bacteria, *E. coli* and *B. subtilis*, were carried out (graphs II and III in "Supplementary material"). The complexes show moderate activity as compared to the standard fungicide and bactericide, but all the complexes are more active than their respective ligands and thus indicated that complexation enhances the activity of the ligand. This may be explained by the chelation theory [34]. The variation in the activity of different complexes against various organisms depends either on the permeability of the cells of the microbes or on the differences in ribosome in microbial cells [35].

Table 5. MIC (mg mL^{-1}) of the ligands and complexes.

Compounds	*B. subtilis*	*F. oxysporum*
($N^{\cap}SH$)	22	29
($N^{\cap}OH$)	24	32
[$Cl_2Bi(N^{\cap}S)$]	12	23
[$ClBi(N^{\cap}S)_2$]	10	21
[$Cl_2Bi(N^{\cap}O)$]	15	26
[$ClBi(N^{\cap}O)_2$]	13	24
[$Cl_2Sb(N^{\cap}S)$]	11	21
[$ClSb(N^{\cap}S)_2$]	9	19
[$Cl_2Sb(N^{\cap}O)$]	14	23
[$ClSb(N^{\cap}O)_2$]	12	20

Table 6. Pesticidal data of ligands and their metal complexes.

Compounds	Correct motility (%)	X^2	LC_{50} (mg L^{-1})
($N^{\cap}SH$)	61.11	0.960	410
($N^{\cap}OH$)	55.55	0.274	630
[$Cl_2Bi(N^{\cap}S)$]	66.66	0.302	305
[$ClBi(N^{\cap}S)_2$]	72.22	0.736	210
[$Cl_2Bi(N^{\cap}O)$]	61.11	0.242	350
[$ClBi(N^{\cap}O)_2$]	77.77	0.570	240
[$Cl_2Sb(N^{\cap}S)$]	83.33	0.195	165
[$ClSb(N^{\cap}S)_2$]	88.88	0.152	100
[$Cl_2Sb(N^{\cap}O)$]	66.66	0.116	200
[$ClSb(N^{\cap}O)_2$]	77.77	0.160	135
Control	–	1.142	–

3.7. *Minimum inhibitory concentration*

MIC values calculated for the ligands and their Bi(III) and Sb(III) complexes are shown in table 5. The ligands and their metal complexes inhibit the growth of the tested organisms between 9 and 30 MIC (mg mL^{-1}) against selected bacteria and fungi.

3.8. *Pesticidal*

Data reported in table 6 reveal that of the 10 compounds tested, $ClSb(N^{\cap}S)_2$ was highly effective as insecticide with LC_{50} 100 mg L^{-1} against *C. cephalonica*. Other compounds showed good insecticidal activity. Broad conclusions may become possible only after a critical appraisal of a larger data set.

4. Conclusion

On the basis of the analytical data and spectral studies, the ligands coordinate to metal monobasic bidentate giving four- and five-coordinate geometries around the metal. The complexes showed better antimicrobial and pesticidal activities than parent ligands.

The compounds also inhibit the growth of fungi and bacteria dependent on concentration. In the present case we have used Flucanazone for antifungal activity and Streptomycin for antibacterial activity. The results showed that the compounds are more active than the ligands but less active than these standard drugs.

Acknowledgment

The authors are grateful to U.G.C., New Delhi, for financial assistance through grant no. 34(324)/SR-I.

References

[1] K.P. Srivastava. *Chem. Indian J.*, **1**, 215 (2003).
[2] D.M. Anderson, S. Shelley, N. Crick, M. Buraglio. *J. Clin. Pharmacol.*, **42**, 1358 (2002).
[3] J. Weick, R.S. Thorn. *J. Econ. Entomol.*, **95**, 227 (2002).
[4] D. Latte, V. Lamour, P.O. Tsvetkov, A.A. Makarov, M. Klich, P. Deprez, D. Moras, C. Briand, R. Gilli. *Biochemistry*, **41**, 7217 (2002).
[5] P. Nagpal, R.V. Singh. *Bioinorg. Chem. Appl.*, **3**, 255 (2005).
[6] P. Tarasconi, S. Capacchi, G. Pelosi. *Bioorg. Med. Chem.*, **8**, 157 (2000).
[7] S. Chandra, L. Gupta, V.P. Tyagi. *Synth. React. Inorg. Met.-Org. Chem.*, **26**, 125 (1996).
[8] K.A. Smith, G.B. Deacon, W.R. Jackson. *Met.-Based Drugs*, **5**, 295 (1998).
[9] M.K. Khosa, M. Mazhar, S. Ali. *Turk. J. Chem.*, **30**, 345 (2006).
[10] G.G. Briand, N. Burford. *Chem. Rev.*, **99**, 2601 (1999).
[11] C.F.J. Barnard, S.P. Fricker, O.J. Vaughan, D.T. Thompson (Eds). *Insights into Speciality Inorganic Chemicals, Medical Applications of Inorganic Chemicals*, pp. 35–61, The Royal Society of Chemistry, Cambridge (1995).
[12] A. Phor, Sushma, I. Singh, R.V. Singh, J.P. Tandon. *Main Group Met. Chem.*, **20**, 663 (1997).
[13] T. Gebel. *Chemico-Biol. Interact.*, **107**, 131 (1997).
[14] S.K. Hadjikakou, C.D. Antoniadis, N. Hadjiliadis, M. Kubicki, J. Binolis, S. Karkabounas, K. Charalabopoulos. *Inorg. Chim. Acta*, **358**, 2861 (2005).
[15] K. Singh, J.P. Tandon. *Monatsh. Chem.*, **123**, 315 (1992).
[16] P.C. Christidis, P.J. Rentzeperis, C.A. Bolos, I.A. Tossidis. *Z. Kristallogr.*, **177**, 83 (1986).
[17] A.I. Vogel. *A Textbook of Organic Quantitative Analysis*, 5th Edn, p. 243, PEL, London (2004).
[18] J.T. Makode, A.S. Aswar. *Indian J. Chem.*, **43A**, 2120 (2004).
[19] A. Chaudhary, R.V. Singh. *J. Inorg. Biochem.*, **98**, 1712 (2004).
[20] S. Gaur, N. Fahmi, R.V. Singh. *Phosphorus, Sulfur Silicon Relat. Elem.*, **182**, 853 (2007).
[21] S.A. Salmon, J.L. Watts, A. Cheryal. *J. Clin. Microbiol.*, **33**, 2435 (1995).
[22] P.M. Davidson, M.E. Parish. *Food Technology*, **43**, 148 (1989).
[23] C.H. Collins. *Microbiological Methods*, p. 296, Butterworths, London (1964).
[24] M. Jain, S. Gaur, S.C. Diwedi, S.C. Joshi, R.V. Singh, A. Bansal. *Phosphorus, Sulfur Silicon Relat. Elem.*, **179**, 1517 (2004).
[25] N.A. Shaki, J. Kumar, Pankaj, A. Pandey, V. Ahluwalia, M.K. Singh, C. Srivastava. *J. Environ. Sci. Health, Part B*, **44**, 344 (2009).
[26] M. Joseph, A. Sreekanth, V. Suni, M.R.P. Kurup. *Spectrochim. Acta, Part A*, **64**, 637 (2006).
[27] G.N. Chremos, R.A. Zingaro. *J. Organomet. Chem.*, **2**, 647 (1970).
[28] T.B. Brill, N.C. Campbell. *Inorg. Chem.*, **l2**, 1884 (1973).
[29] R.K. Sharma, Y.P. Singh, A.K. Rai. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 405 (2001).
[30] L. Agoes, N. Burford, T.S. Cameron. *J. Am. Chem. Soc.*, **118**, 3225 (1996).
[31] G.G. Briand, N. Burford, T.S. Cameron, W. Kwaitkoswki. *J. Am. Chem. Soc.*, **120**, 177 (1998).
[32] M.K. Sharma, M. Sharma, A. Singh, R.C. Mehrotra. *Indian J. Chem.*, **40A**, 1226 (2001).
[33] C. Silvestru, H.J. Breunig, H. Althaus. *Chem. Rev.*, **99**, 3277 (1999).
[34] P. Chaudhary, S. Chauhan, K. Poonia, R.V. Singh. *Spectrochim. Acta, Part A*, **70**, 587 (2008).
[35] S.K. Sengupta, O.P. Pandey, B.K. Srivastava, V.K. Sharma. *Transition Met. Chem.*, **23**, 349 (1998).