

Coordination Compounds of Tin, Selenium and Bismuth. Complexes of Tin(IV), Selenium(IV) and Bismuth(III) with Schiff Bases

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ABSTRACT

Tin, selenium and bismuth metal complexes containing Schiff bases ligands derived from ortho-benzaldehyde, dimethyl ketone, diethyl ketone and di(o-aminophenyl) disulphide have been prepared from the direct reaction of Schiff base and metals in 1:2 molar ratio to give:

$\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_4$, $\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_4$, $\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_4$,
 $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_3$, $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$, $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_3$,
 $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_4$, $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_4$ and $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_4$.

The reaction of the above metals with a mixture of iodine and Schiff bases give in (1:1:3) molar ratio the compounds $\text{SnI}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_3$, $\text{SnI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$, $\text{SnI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_3$, $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_2$, $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_2$, $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_2$, $\text{SeI}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_3$, $\text{SeI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$ and $\text{SeI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_3$. The compounds were characterized by microanalysis, infrared, UV/Visible spectroscopy and conductivity measurement.

(IV)

(IV)

(III)

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1:2

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$\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_4$, $\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_4$, $\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_4$,
 $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_3$, $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$, $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_3$,
 $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3-o)_4$, $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_4$ and $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_4$.

(: :) (3:1:1)

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$\text{SnI}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_3$, $\text{SnI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$, $\text{SnI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_3$,
 $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{CH-C}_6\text{H}_4\text{OCH}_3\text{-}o)_2$, $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_2$, $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_2$,
 $\text{SeI}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_3$, $\text{SeI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$ and $\text{SeI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_3$.

INTRODUCTION

Compounds of both main group and transition metals with sulphur donor ligands are a subject of current interest. They arise in part because of their varied structures and because of their biological activities (Mustafa and Taqa, 2001, Buttrus, 1998, Buttrus et al., 2001, Zeena, 2001). Substituted disulfide derivatives of main group metals have received much less attention than those of the corresponding transition metals.

The chemistry of $\text{Sn}(\text{SR})_4$, $\text{R}_x\text{Sn}(\text{SR}')_{4-x}$, tin (II)thiolate and of the corresponding lead compounds have been reviewed (Abel and Armitage, 1967, Schumann, et al., 1971, Harrison and Stobart, 1973, Abel et al., 1973) The electro- chemical oxidation of a metal in a non-aqueous solution of disulphide is a convenient and direct route to neutral thiolate complexes of elements such as zinc, cadmium, mercury, tin, lead, indium and thallium (Hencher et al., 1982, Hencher et al., 1985). The direct reaction between indium or tin metal with $(\text{C}_6\text{H}_5)_2\text{E}_2$ ($\text{E}=\text{S}, \text{Se}$) to give the neutral compounds $\text{In}(\text{EC}_6\text{H}_5)_3$ or $\text{Sn}(\text{EC}_6\text{H}_5)_4$ have been used by (Tuck and Yang, 1971).

The synthesis of dihalobis(2-pyridinethiolato)tin(IV) by an oxidative-addition reaction of di-2-pyridyldisulfide to tin(II) halide represents an example of preparing other similar dihalodithiolatotin(IV) compounds (Masaki and Matsunami, 1987).

Although many disulfide compounds are reduced by reaction with metal ions *via* the oxidation of $\text{M}(\text{I})$ to $\text{M}(\text{III})$ ($\text{M}=\text{Cu}(\text{I}), \text{Ir}(\text{I}),$ and $\text{Rh}(\text{I})$) or the use of $\text{Ni}(\text{II})$ under certain conditions (Livingstone et al., 1973) this is not always the case. Some thiumdisulfide compounds, $[\text{R}_2\text{NC}(\text{S})\text{S}]_2$ ($\text{R}=\text{Et}$ or Me) have been shown to coordinate unaltered. However, disulfide of the type $[\text{Et}_2\text{NC}(\text{S})\text{S}]_2$ may be readily reduced by reaction with lead thiolates or with $\text{Rh}[\text{Ph}_2\text{PC}(\text{S})\text{NPh}](\text{PPh}_3)$ (Thewissen and Noltes, 1982).

Recently we reported the synthesis of $\text{Sn}(\text{IV})$ and $\text{Bi}(\text{IV})$ dithiocarbamate complexes via the thermal oxidative addition reaction of tin and bismuth metals with $\text{N}, \text{N}, \text{N}', \text{N}'$ -tetraalkylthiuram disulfide.

In this paper the oxidative addition reaction of the S-S linkage of Schiff base $(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_2$, $(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_2$, $(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_2$ with tin, selenium and bismuth metals alone and to metals in the presence of iodine are described.

EXPERIMENTAL

General data:

IR spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer over the range $200\text{-}4000\text{cm}^{-1}$ using CsI pellets. Conductance measurements were carried out at room temperature in DMF solution (10M^{-3}) using a Jenway 4070 conductivity meter. Metals, toluene, orthoaminothiophenol, dimethylketone and diethylketone were commercial products (Fluka) and used as supplied. UV/visible spectra were recorded on a

UV/160 Shimadzu UV/Visible recording spectrophotometer. C.H.N. microanalyses were carried out using a 1106 Carlo Erba analyzer in Department of Chemistry/ College of Science/Mosul University. The disulfides ($\text{RC}_6\text{H}_4\text{S}$)₂, R=*o*-NH₂ were synthesized by standard methods (Stewart and Mathes, 1949).

Preparation of Schiff bases:

The condensation of the disulfide with aldehyde and ketone in alcoholic solution to yields the corresponding Schiff bases were applied (Livingstone and Nolan, 1973).

Preparation of (SC₆H₄N=CHC₆H₄OCH₃-*o*)₂:

Orthomethoxybenzaldehyde (1mole) was refluxed with (1mole) of (SC₆H₄NH₂-*o*)₂ in (40ml)ethanol for 2h offers a pale yellow crystal. This was recrystallized from ethanol to 85% yield.

Preparation of (SC₆H₄N=C(CH₃)₂)₂:

A mixture of dimethylketone and (SC₆H₄NH₂-*o*)₂ (1mole)was refluxed for 4 h. A precipitate was formed, which was recrystallized from ethanol to 60% yield.

Preparation of (SC₆H₄N=C(CH₂CH₃)₂)₂:

Diethylketone (2mole) was refluxed with (1mole) (SC₆H₄NH₂-*o*)₂ in (40 ml) ethanol for 4h. A red precipitate was formed and recrystallized from ethanol, to give yield of 67%.

Synthesis of complexes:

Syntheses of Tin (IV) complexes:

Sn(SC₆H₄N=CHC₆H₄OCH₃-*o*)₄, Sn(SC₆H₄N=C(CH₃)₂)₄ and Sn(SC₆H₄N=C(CH₂CH₃)₂)₄

A mixture of finely cut tin metal (1.0mmole) and the Schiff base (2mmole) in toluene (50ml) was refluxed for 7h. The unreacted tin was removed by filtration, and the resultant orange or black solution was reduced to ca. 1/3 of their volume. The resulting solids were collected by filtration, washed with petroleum ether (b.p.60-80°C) and dried in vacuo.

SnI(SC₆H₄N=CHC₆H₄OCH₃-*o*)₃, SnI(SC₆H₄N=C(CH₃)₂)₃, and SnI(SC₆H₄N=C(CH₂CH₃)₂)₃

Small pieces of tin metal 1.0mmole) were refluxed with (1.5 mmole) of Schiff base and iodine (0.5mmole) in toluene (50mL). A yellow solution was formed after 10h after which time the solution was filtered while hot to remove any trace of unreacted metal. The collected solids were washed with petroleum ether (p.b 60-80°C) and dried in vacuo.

Synthesis of Bismuth(III) complexes:

Bi(SC₆H₄N=CHC₆H₄OCH₃-*o*)₃,Bi(SC₆H₄N=C(CH₃)₂)₃ and Bi(SC₆H₄N=C(CH₂CH₃)₂)₃

A mixture of finely cut bismuth metal (1.0mmole) and the Schiff base (1.5mmole) in toluene (50mL) was refluxed vigorously for 7hr. The mixture was evaporated in vacuo and the residue was triturated with n-pentane (10mL) to give solid complex which was collected by filtration and dried in vacuo.

BiI(SC₆H₄N=CHC₆H₄OCH₃-o)₂ BiI(SC₆H₄N=C(CH₃)₂)₂ and BiI(SC₆H₄N=C(CH₂CH₃)₂)₂

Finely cut bismuth metal (1.0mmole) was refluxed with Schiff base (1.0mmole) and iodine (0.5mmole) in toluene (50mL) for 10hr. The reaction mixture was filtered; the yellow solution was reduced to ca. 10 ml by evaporation under reduced pressure. The solid was collected by filtration, washed with petroleum ether (60-80°C) and dried in vacuo.

Syntheses of Selenium(IV) complexes:

Se(SC₆H₄N=CHC₆H₄OCH₃-o)₄, Se(SC₆H₄N=C(CH₃)₂)₄ and Se(SC₆H₄N=C(CH₂CH₃)₂)₄

A mixture of small pieces selenium metal (1mmole) and the Schiff base (2mmole) in toluene(50ml) was refluxed for 10hr. the unreacted of selenium were removed by filtration, and the resultant red solution were reduced to ca. 1/3 of their volume and cooled to room temperature. The solid obtained was then collected by filtration, washed with petroleum ether (60-80°C) and dried in vacuo.

SeI(SC₆H₄N=CHC₆H₄OCH₃-o)₃ SeI(SC₆H₄N=C(CH₃)₂)₃, and SeI(SC₆H₄N=C(CH₂CH₃)₂)₃

Small pieces of selenium metal (1.0 mmole) were refluxed with (1.5 mmole) of the Schiff base and iodine (0.5 mmole) in toluene (50 ml). A yellow solution was formed after 5hr. The solution was filtered while hot to remove any traces of unreacted metal. The collected solution were washed with petroleum ether (b.p60-80°C) and dried in vacuo.

RESULTS AND DISCUSSION

The method described in this work represents simple and direct syntheses of a number of complexes of the formula Sn(SC₆H₄N=CHC₆H₄OCH₃-o)₄, Sn(SC₆H₄N=C(CH₃)₂)₄, Sn(SC₆H₄N=C(CH₂CH₃)₂)₄, Bi(SC₆H₄N=CHC₆H₄OCH₃-o)₃, BiSC₆H₄N=C(CH₃)₂)₃, Bi(SC₆H₄N=C(CH₂CH₃)₂)₃, Se(SC₆H₄N=CHC₆H₄OCH₃-o)₄, Se(SC₆H₄N=C(CH₃)₂)₃ and Se(SC₆H₄N=C(CH₂CH₃)₂)₄ compounds.

The reaction of metals with a mixture of iodine and Schiff bases give the compounds SnI(SC₆H₄N=CHC₆H₄OCH₃-o)₃, SnI(SC₆H₄N=C(CH₃)₂)₃, SnI(SC₆H₄N=C(CH₂CH₃)₂)₃, BiI(SC₆H₄N=CHC₆H₄OCH₃-o)₂, BiI(SC₆H₄N=C(CH₃)₂)₂, BiI(SC₆H₄N=C(CH₂CH₃)₂)₂, SeI(SC₆H₄N=CHC₆H₄OCH₃-o)₃, SeI(SC₆H₄N=C(CH₃)₂)₂ and SeI(SC₆H₄N=C(CH₂CH₃)₂)₃ compounds by thermal oxidative addition reaction. These reactions are simple compared with those used for the preparation of compounds of main group elements involving methathetical reactions of MCl_n with the corresponding sulfides (Chadha, et al., 1987, Gilman and Abbott, 1949).

The complexes are air-stable at room temperature and insoluble in common organic solvents. They are, however, soluble in dimethyl formamide (DMF) and donor solvents. Their melting points, elemental analysis and conductivities are listed in (Table 1). The most important diagnostic features of the IR spectra are listed in (Table 2).

The IR bands of the free ligands (SC₆H₄N=CHC₆H₄OCH₃-o)₂, (SC₆H₄N=C(CH₃)₂)₂, (SC₆H₄N=C(CH₂CH₃)₂)₂ are elaborated and elucidated for comparison. Medium absorption bands of the ν(C-S) bands were observed in the 850-1050cm⁻¹ for the free ligands and is only slightly increased upon forming the complexes (Table 2) which indicates that the metal compounds M(SC₆H₄N=CR)_x [R=C₆H₄OCH₃-o, (CH₃)₂, (CH₂CH₃)₂, x=3,4] had formed. Bands which are not present in the spectra of the ligands

appear at $425\text{-}510\text{cm}^{-1}$ and $320\text{-}380\text{cm}^{-1}$ in the spectra of the metal complexes, these bands are in the region expected for both $\nu(\text{M-N})$ and $\nu(\text{M-S})$ respectively (Buttrus et al., 2001). The higher energy bands seem likely to be associated with $\nu(\text{M-N})$ and the lower frequency with $\nu(\text{M-S})$ modes. The ir spectra of the complexes reveal bands between $520\text{-}540\text{cm}^{-1}$ it is tentatively assigned as $\nu(\text{M-O})$ for methoxy group (Sivasubraai et al., 1982).

A strong band in the $1620\text{-}1632\text{cm}^{-1}$ region is characteristic of the azomethine group $\nu(\text{C=N})$ (Wissam *et al.*, 1985). In the complexes as a shift of C=N frequency towards higher wave number takes place in the complexes, and this may be ascribed to the increase in the bond order of the carbon nitrogen link.

Molar conductivities for 10^{-3} M solutions of the complexes in DMF solvents at ambient temperature ($25\text{ }^{\circ}\text{C}$) were in the ranges $5.2\text{-}14.4\text{ ohm}^{-1}\text{ cm}^{-1}\text{ mol}^{-1}$ (Table 1), suggesting nonconductive species (Kettle, 1975) i.e., non-ionic complexes in the solvent used.

The UV/visible spectra of the complexes are similar to one another but different from these of the free ligands (Table 1). The broad band observed in the range $240\text{-}367\text{ nm}$ are due to $\pi\text{-}\pi^*$ or $n\text{-}\pi^*$ transitions of the free Schiff base, while a new additional for almost all complexes in the range $379\text{-}420\text{ nm}$. This band may be attributed to the charge transfer from filled ligand orbitals to the vacant metal orbitals.

It may be concluded that the tin, selenium and bismuth complexes obtained in this study might well have octahedral structure in the complexes $\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_4$, $\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_4$, $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$, $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_3$, $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_3$ and $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_4$ (Fig.1), probably with some distortion. Hexa-coordinated complexes of tin and bismuth were described elsewhere (Mustafa and Taqa, 2001, Buttrus, 1998, Buttrus et al., 2001). On the other hand, the metals are hexa or hepta coordinated in the complexes (Figs.1,2,3). $\text{Sn}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_4$, $\text{Bi}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_3$, $\text{Se}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_4$, $\text{SnI}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_3$, $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{CH-C}_6\text{H}_4\text{OCH}_3\text{-}o)_2$ and $\text{SeI}(\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-}o)_3$ as shown in Figure 1, hepta compounds of bismuth were described elsewhere. Bismuth might well have tetrahedral geometry in the complexes $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2)_2$, $\text{BiI}(\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2)_2$ (Fig.5).

Table1: Physical properties and analysis data of the complexes.

Complexes	Empirical formula	Formula weight	Color	Yield%	m.p C°	Analysis ^a			Ω_M mol ⁻¹ cm ²
						C%	H %	N%	
Sn[SC ₆ H ₄ N=CHC ₆ H ₄ OCH ₃ -o] ₄	C ₅₆ H ₄₈ N ₄ O ₄ S ₄ Sn	1086	Orange	73	>350	61.83 (61.85)	4.417 (4.42)	5.15 (5.15)	14
SnI[SC ₆ H ₄ N=CHC ₆ H ₄ OCH ₃ -o] ₃	C ₄₂ H ₃₆ N ₃ O ₃ SnI	971.69	Yellow	77	107	51.66 (51.78)	3.70 (3.81)	4.32 (4.35)	7
Se[SC ₆ H ₄ N=CHC ₆ H ₄ OCH ₃ -o] ₄	C ₅₆ H ₄₈ N ₄ O ₄ S ₄ Se	1074	Maroon	70	186	64.18 (64.16)	4.58 (4.58)	5.34 (5.440)	8
SeI[SC ₆ H ₄ N=CHC ₆ H ₄ OCH ₃ -o] ₃	C ₄₂ H ₃₆ N ₃ O ₃ SeI	932	Brown	78	234	54.07 (54.11)	3.86 (3.89)	4.50 (4.61)	5
Bi[SC ₆ H ₄ N=CHC ₆ H ₄ OCH ₃ -o] ₃	C ₄₂ H ₃₆ N ₃ O ₃ S ₃ Bi	935	Gold yellow	84	300d	53.90 (54.01)	3.85 (3.83)	4.49 (4.48)	12
BiI[SC ₆ H ₄ N=CHC ₆ H ₄ OCH ₃ -o] ₂	C ₂₈ H ₂₄ N ₂ O ₂ S ₂ BiI	820	Green	80	130	40.97 (40.99)	2.92 (2.95)	3.41 (3.43)	11
Sn[SC ₆ H ₄ N=C(CH ₃) ₂] ₄	C ₃₆ H ₄₀ N ₄ S ₄ Sn	774.69	Brown	95	365d	55.76 (55.78)	5.16 (5.19)	7.22 (7.22)	9
SnI[SC ₆ H ₄ N=C(CH ₃) ₂] ₃	C ₂₇ H ₃₀ N ₃ S ₃ SnI	737.69	Pale orange	92	86	43.92 (43.94)	4.06 (4.10)	5.69 (5.66)	9
Se[SC ₆ H ₄ N=C(CH ₃) ₂] ₄	C ₃₆ H ₄₀ N ₄ S ₄ Se	735	Brown	90	160	58.77 (58.67)	5.44 (5.55)	7.61 (7.64)	6
SeI[SC ₆ H ₄ N=C(CH ₃) ₂] ₃	C ₂₇ H ₃₀ N ₃ S ₃ SeI	698	Orange	75	170	46.41 (46.43)	4.29 (4.31)	6.01 (6.04)	8
Bi[SC ₆ H ₄ N=C(CH ₃) ₂] ₃	C ₂₇ H ₃₀ N ₃ S ₃ Bi	701	Orange	83	165	46.21 (46.22)	4.27 (4.27)	5.99 (6.02)	5
BiI[SC ₆ H ₄ N=C(CH ₃) ₂] ₂	C ₁₈ H ₂₀ N ₂ S ₂ BiI	664	Red	79	212	32.53 (32.55)	3.01 (3.05)	4.21 (4.240)	10
Sn[SC ₆ H ₄ N=C(CH ₂ CH ₃) ₂] ₄	C ₄₄ H ₅₆ N ₄ S ₄ Sn	886.69	Orange	70	102	59.54 (59.56)	6.31 (6.31)	6.31 (6.35)	11
SnI[SC ₆ H ₄ N=C(CH ₂ CH ₃) ₂] ₃	C ₃₃ H ₄₂ N ₃ S ₃ SnI	821.69	Orange	93	285d	48.19 (48.21)	5.11 (5.13)	5.11 (5.11)	6
Se[SC ₆ H ₄ N=C(CH ₂ CH ₃) ₂] ₄	C ₄₄ H ₅₆ N ₄ S ₄ Se	847	Orange	81	>350	62.33 (62.35)	6.61 (6.62)	6.61 (6.61)	13
SeI[SC ₆ H ₄ N=C(CH ₂ CH ₃) ₂] ₃	C ₃₃ H ₄₂ N ₃ S ₃ SeI	782	Pale yellow	85	109	50.63 (50.66)	5.37 (5.38)	5.37 (5.31)	14
Bi[SC ₆ H ₄ N=C(CH ₂ CH ₃) ₂] ₃	C ₃₃ H ₄₂ N ₃ S ₃ Bi	785	Brown	90	205	50.44 (50.47)	5.35 (5.33)	5.35 (5.36)	8
BiI[SC ₆ H ₄ N=C(CH ₂ CH ₃) ₂] ₂	C ₂₂ H ₂₈ N ₂ S ₂ BiI	720	Dark Brown	64	90	36.66 (36.68)	3.88 (3.90)	3.88 (3.89)	7

^a Calculated values in parentheses

d : Decomposition

() :found

Table 2: IR absorption (cm^{-1})^a and Electronic data for complexes.

Complexes	N (C-S)	ν (M-S)	ν (M-N)	ν (M-O)	ν (C=N)	UV/Visible bands maximum in nm Λ max(nm) ϵ max ($\text{dm}^3\text{mole}^{-1}\text{cm}^{-1}$)		
$\text{Sn}[\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-o}]_4$	950m	350s	495m	495m	1650s	249(40160)	343(29239)	400(2500)
$\text{SnI}[\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-o}]_3$	945m	320s	510w	540w,530s	1660s	267(37435)	346(28901)	388(25773)
$\text{Se}[\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-o}]_4$	940s	325s	470s	540w,520m	1635s	282(35460)	339(29498)	400(25000)
$\text{SeI}[\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-o}]_3$	950m	335m	500w	555m	1635s	240(41841)	345(28985)	379(26385)
$\text{Bi}[\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-o}]_3$	1065m	325w	490m	540m	1620s	278(35971)	339(29498)	385(25974)
$\text{BiI}[\text{SC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{OCH}_3\text{-o}]_2$	1010s	330w	445w	535m	1610m	288(34723)	342(29239)	400(25000)
$\text{Sn}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2]_4$	950w	380w	440w	---	1630m	290(34482)	330(30303)	397(25188)
$\text{SnI}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2]_3$	1030m	380w	465w	-----	1630m	299(33444)	367(27247)	-----
$\text{Se}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2]_4$	1025s	330w	490m	-----	1630s	273(36630)	343(29154)	420(23809)
$\text{SeI}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2]_3$	1030w	335m	500w	-----	1625m,1648m	301(33222)	357(28011)	-----
$\text{Bi}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2]_3$	1000m	320w	460m	-----	1625m,1648m	300(33333)	367(27247)	-----
$\text{BiI}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2]_2$	945s	330w	420s	-----	1625m	295(33898)	339(29498)	399(25062)
$\text{Sn}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2]_4$	955w	355w	450w	-----	1525m	257(38910)	335(29850)	420(23809)
$\text{SnI}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2]_3$	970w	335w	425m	-----	1630s,1640w	268(37313)	343(29154)	385(25979)
$\text{Se}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2]_4$	960w	320w	435m	-----	1620vs,1640m	283(35335)	364(27472)	-----
$\text{SeI}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2]_3$	965w	330w	440s	-----	1625m,1650w	270(37037)	330(30303)	393(25445)
$\text{Bi}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2]_3$	940w	380m	470w	-----	1670m	267(37453)	330(30303)	393(25445)
$\text{BiI}[\text{SC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_2\text{CH}_3)_2]_2$	950w	410m	465w	-----	1640m	276(37453)	346(28901)	388(25773)

^a w: weak, m:medium, s: strong

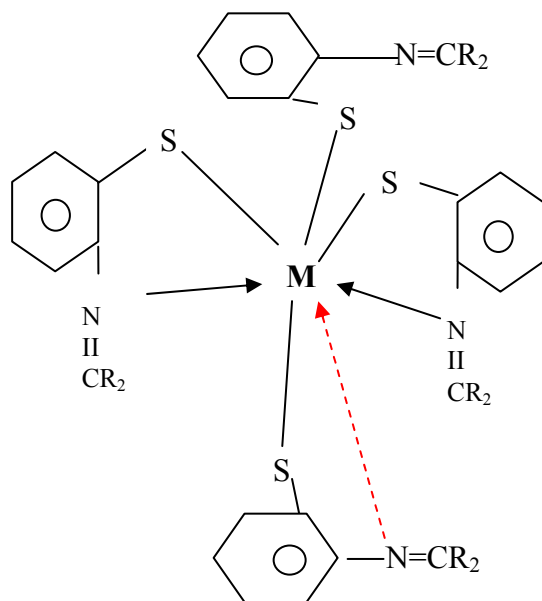


Fig. 1: Suggested structure of $M(SC_6H_4NCR_2)_4$
 $M = Se, Sn, R = CH_3, CH_2CH_3$

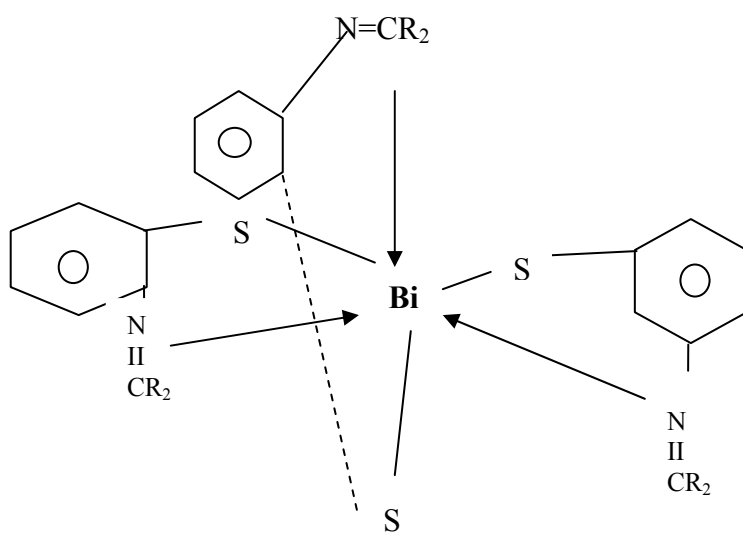


Fig2: Suggested structure of $Bi(SC_6H_4NCR_2)_3$
 $R = CH_3, CH_2CH_3$.

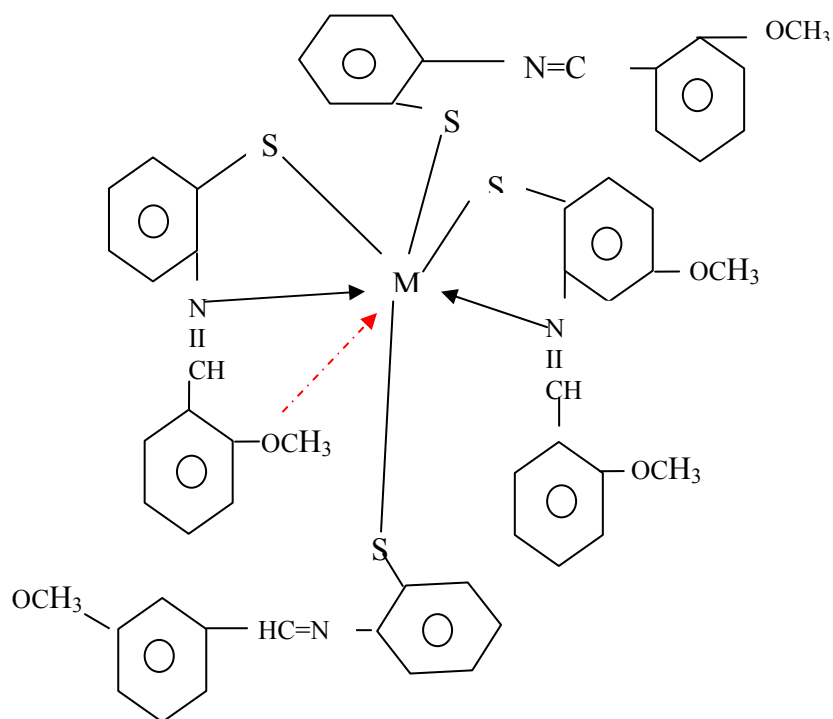


Fig 3: Suggested structure of the complexes $M(SC_6H_4N=CHC_6H_4OCH_3-o)_4$
 $M=Sn, Se$.

s

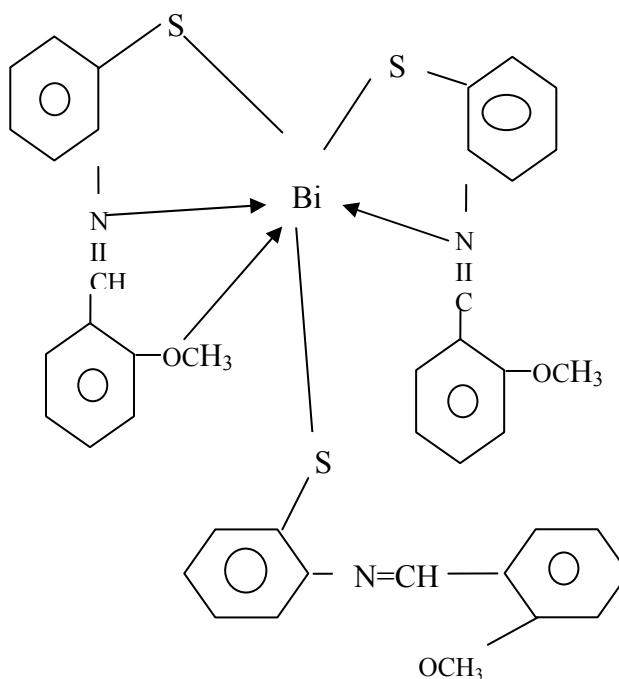


Fig 4: Suggested structure of the complexes $Bi(SC_6H_4N=CHC_6H_4OCH_3-o)_3$.

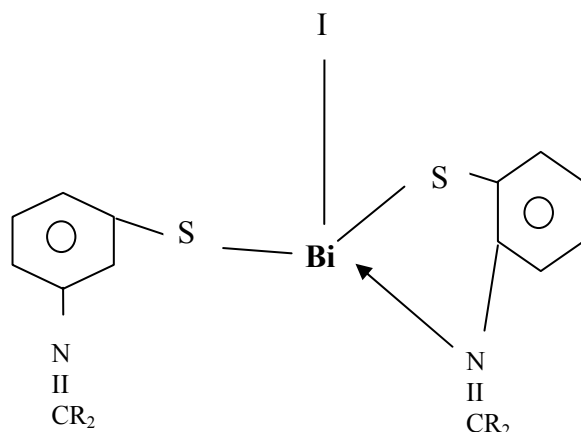


Fig.5: Suggested structure of $\text{BiI}(\text{SC}_6\text{H}_4\text{NCR}_2)_2$
 $\text{R}=\text{CH}_3, \text{CH}_2\text{CH}_3$.

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