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## COORDINATION COMPOUNDS OF TIN AND BISMUTH. COMPLEXES OF TIN(IV) AND BISMUTH(III) WITH N,N-DIALKYLDITHIOCARBAMATES

I. A. Mustafa<sup>a</sup> & Amer A. Taqa<sup>b</sup>

<sup>a</sup> Chemistry Department, College of Science, University of Mosul, Mosul, Iraq

<sup>b</sup> Department of Dental Basic Science, College of Dentistry, University of Mosul, Mosul, Iraq Version of record first published: 20 Aug 2006.

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## COORDINATION COMPOUNDS OF TIN AND BISMUTH. COMPLEXES OF TIN(IV) AND BISMUTH(III) WITH N,N-DIALKYLDITHIOCARBAMATES

I. A. Mustafa<sup>1,\*</sup> and Amer A. Taqa<sup>2</sup>

<sup>1</sup>Chemistry Department, College of Science, and <sup>2</sup>Department of Dental Basic Science, College of Dentistry, University of Mosul, Mosul, Iraq

#### ABSTRACT

Tin and bismuth metals react with N,N,N',N'-tetraethylthiuramdisulfide,  $[Et_2NC(S)S]_2$ , and N,N,N',N'-tetramethylthiuramdisulfide,  $[Mt_2NC(S)S]_2$ , in refluxing toluene to give the compounds  $Sn(S_2CNR_2)_4$  (R = Et, Me) in high yield. Under similar conditions bismuth gives  $Bi(S_2CNR_2)_3$ . The reaction of metallic tin with a mixture of iodine and  $[R_2NC(S)S]_2$ gives the compounds  $SnI(S_2CNR_2)_3$  and  $SnI_2(S_2CNR_2)_2$ . Similarly, with mixtures of  $[R_2NC(S)S]_2$  and  $I_2$ , bismuth yields  $BiI(S_2CNR_2)_2$  and  $BiI_2(S_2CNR_2)$ . Adducts of  $Bi(S_2CNR_2)_3$ with 1,10-phenanthroline and 2,2'-bipyridyl were also prepared. The compounds and adducts were characterized by microanalyses, infrared, UV/Visible spectroscopy and conductivity measurements.

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<sup>\*</sup>Corresponding author.

#### **INTRODUCTION**

Interest in complexes of both main group and transition metals with sulfur donor ligands arises in part because of their varied structures and because of their biological activity<sup>1-6</sup>. Direct electrochemical syntheses were used to prepare simple thiolato complexes of zinc, cadmium, mercury<sup>7</sup>, lead<sup>8</sup>, indium and thallium<sup>9</sup>. An alternative route to the electrochemical synthesis involves reaction between the disulfide ligand and the main group metal in refluxing toluene<sup>6,10</sup>.

Although many disulfide compounds are reduced by reaction with metal ions *via* the oxidation of M(I) to M(III)  $(M = Cu(I)^{11}, In(I)^{12}, Ir(I)$  and Rh(I)<sup>13</sup>) or the use of Ni(II) under certain conditions<sup>14</sup>, this is not always the case, some thiuramdisulfide compounds,  $[R_2NC(S)S]_2$  (R = Et or Me), have been shown to coordinate unaltered<sup>15</sup>. However, disulfides of the type  $[Et_2NC(S)S]_2$  may be readily reduced by reaction with lead thiolates<sup>16</sup> or with Rh[Ph\_2PC(S)NPh](PPh\_3)<sub>2</sub><sup>13</sup>. In this paper the oxidative addition of the -S-S- linkage of  $[R_2NC(S)S]_2$  (R = Et or Me) to tin and bismuth metals, reactions of thiuramdisulfide with different molar ratio of iodine and tin or bismuth metal, are discussed. Also reported is the preparation of the bismuth compound adducts with the neutral donor bases 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bipy).

#### **EXPERIMENTAL**

#### **General Data**

Tin and bismuth metals,  $[Me_2NC(S)S]_2$ ,  $[Et_2NC(S)S]_2$ , toluene and other reagent were used as supplied (Fluka). C, H, N microanalyses were carried out using a 1106 Carlo Erba analyzer. Infrared spectra were recorded on a Perkin-Elmer 580 infrared spectrophotometer using CsI pellets. UV/Visible spectra were recorded on a UV/160 Shimadzu UV/Visible recording spectrophotometer. Conductance measurements were carried out at room temperature in DMF solution (10<sup>-3</sup> M) using a Jenway 4070 conductivity meter.

#### Syntheses

Sn(S<sub>2</sub>CNMe<sub>2</sub>)<sub>4</sub> and Sn(S<sub>2</sub>CNEt<sub>2</sub>)<sub>4</sub>

A mixture of finely cut tin metal (0.119 g, 1 mg atom) and the disulfide (2 mmol) in toluene (40 mL) was refluxed vigorously for 5h. The mixture

#### TIN AND BISMUTH COMPLEXES

was evaporated *in vacuo* and the residue was triturated with *n*-pentane (10 mL) to give an orange solid, which was collected by filtration and dried *in vacuo*; yield 0.54 g for the methyl derivative and 0.62 g for the ethyl derivative, respectively.

#### SnI(S<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub> and SnI(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>

A mixture of finely cut tin metal (0.119 g, 1 mg atom), the disulfide (1.5 mmol) and iodine (0.127 g, 0.5 mmol) in toluene (30 mL) was refluxed vigorously for 5 h. The mixture was filtered to remove traces of unreacted tin metal (0.007 g). A yellow solid obtained after the volume of the filtrate was reduced to *ca*.1/3 and cooled to room temperature. The solid was collected and dried *in vacuo*; yields 0.50 g and 0.55 g, respectively.

#### SnI<sub>2</sub>(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> and SnI<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>

These were prepared by the same method as above except that 0.254 g (1 mmol) of iodine was used along with the disulfide (1 mmol); yields 0.50 g and 0.54 g, respectively.

#### $Bi(S_2CNMe_2)_3$ and $Bi(S_2CNEt_2)_3$

A mixture of small pieces of bismuth metal (0.21 g, 1 mg atom) and the disulfide (1.5 mmol) in toluene (50 mL) were refluxed for 3 h. The unreacted traces of bismuth (0.01 g) were removed by filtration, and the resultant yellow solutions 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 (b.p. 60-80 °C) and dried *in vacuo*; yields 0.50 g and 0.55 g, respectively.

BiI(S<sub>2</sub>CNMe<sub>2</sub>)<sub>2</sub> and BiI(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>

Small pieces of bismuth metal (0.21 g, 1 mg atom) were refluxed with 1.5 mmol of the disulfides and iodine (0.127 g, 0.5 mmol) in toluene (30 mL). A yellow solution was formed after 3.5 h, after which time the solution was filtered while hot to remove any traces of unreacted metal (0.01 g). The collected solids were washed with petroleum ether (b.p. 60-80 °C) and dried *in vacuo*; yields 0.47 g and 0.53 g, respectively.

BiI<sub>2</sub>(S<sub>2</sub>CNMe<sub>2</sub>) and BiI<sub>2</sub>(S<sub>2</sub>CNEt<sub>2</sub>)

These were prepared by the same method as above except that 0.254 g, 1 mmol iodine was used along with the disulfides (0.47 mmol); yields 0.47 g and 0.52 g, respectively.

#### Bi(S<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub>.phen and Bi(SCNEt<sub>2</sub>)<sub>3</sub>.phen

The reaction of Bi(S<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub> (0.57 g, 1 mmol) or Bi(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub> (0.65 g, 1 mmol) and 1,10-phenathroline (phen) (0.18 g, 1 mmol) in methanol (20 mL) yielded a yellow oil which became a solid after stirring for 4 h at ambient temperature. This solid was collected, washed with methanol (10 mL) and dried *in vacuo*; yields 0.61 g and 0.65 g, respectively.

#### Bi(S<sub>2</sub>CNMe<sub>2</sub>)<sub>3</sub>.bipy and Bi(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>.bipy

 $Bi(S_2CNMe_2)_3$  (0.57 g, 1 mmol) or  $Bi(S_2CNEt_2)_3$  (0.65 g, 1 mmol) was stirred with 2,2'-bipyridine (bipy) (0.16 g, 1 mmol) in benzene (30 mL) for 3 h during which time a deep yellow oil was formed. The colorless solution was removed and the oil was triturated with diethylether (40 mL). The resultant solid was dried *in vacuo*; yields 0.58 g and 0.63 g, respectively.

#### **RESULTS AND DISCUSSION**

The method described represents simple and direct syntheses of a number of  $Sn(S_2CNR_2)_4$  and  $Bi(S_2CNR_2)_3$  compounds by thermal oxidative addition reactions. These reactions are simpler than those used for the preparation of  $M(S_2CNR_2)_n$  compounds of main group elements involving metathetical reactions<sup>17-19</sup> of  $MX_n$  with  $NaS_2CNR_2$  or *via* the insertion of  $CS_2$  into  $M(NR_2)_n^{20-22}$ .

The possible reaction involved is that shown in eq (1) giving a +1 oxidation state species, which is then followed by the oxidative insertion reaction of eq (2) or (3).

$$2\mathbf{M} + [\mathbf{R}_2 \mathbf{N} \mathbf{C}(\mathbf{S}) \mathbf{S}]_2 \to 2[\mathbf{M}(\mathbf{S}_2 \mathbf{C} \mathbf{N} \mathbf{R}_2)] \tag{1}$$

$$2[M(S_2CNR_2)] + (n-1)[R_2NC(S)S]_2 \to 2[M(S_2CNR_2)_n]$$
(2)

$$2[M(S_2CNR_2)] + (n-1)[R_2NC(S)S]_2 + mI_2 \rightarrow 2[MI_m(S_2CNR_2)_n] \quad (3)$$

$$Bi(S_2CNR_2)_3$$
 + phen or bipy  $\rightarrow Bi(S_2CNR_2)_3$ .phen or bipy (4)

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The oxidative addition process of eqs (2) and (3) are clearly analogous to known reactions involving the conversions<sup>23</sup>  $In(0) \rightarrow In(III)$  or  $Sn(II) \rightarrow Sn(IV)$ .

The reaction of tris(N,N-dialkyldtiocarbamato)bismuth(III) complexes,  $Bi(S_2CNR_2)_3$ , with phen or bipy (1:1 molar ratio) yields neutral adducts of stoichiometry  $Bi(S_2CNR_2)_3$ .phen and  $Bi(S_2CNR_2)_3$ .bipy respectively [eq (4)].

The compounds and adducts were isolated as colored solids. Their melting points, elemental analyses and conductivities are listed in Table I. The important diagnostic bands of the IR spectra are listed in Table II.

The characteristic IR bands that are sensitive to molecular structure are the stretching modes for the C-N, C-S and M-S bonds. In particular, the v(C-N) band in the region 1450–1550 cm<sup>-1</sup> and the v(C-S) band in the region  $850-1050 \,\mathrm{cm}^{-1}$  are known to depend on the nature of the coordination of the dithiocarbamate ligands to the metal<sup>17,24</sup>. The splitting of v(C-N) and v(C-S) bands is characteristic of a monodentate dithiocarbamate ligand whereas the appearance of a single band in each region is characteristic of bidentate chelation of the dithiocarbamate ligand. The dithiocarbamate ligands  $Sn(S_2CNR_2)_4$ ,  $SnI(S_2CNR_2)_3$ , in  $Bi(S_{2})$ CNR<sub>2</sub>)<sub>3</sub>.phen and Bi(S<sub>2</sub>CNR<sub>2</sub>)<sub>3</sub>.bipy act both as monodentate and as bidentate ligands; the patterns for v(C-N) and v(C-S) are consistent with this (Table II). The IR spectra of the compounds  $Bi(S_2CNR_2)_3$ ,  $BiI(S_2CNR_2)_2$ and BiI<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>) show the pattern characteristic of bidentate dithiocarbamate ligands. The IR spectra of the compounds SnI<sub>2</sub>(S<sub>2</sub>CNR<sub>2</sub>)<sub>2</sub> show the presence of two v(C-S) bands and one strong v(C-N) band. This is an indication of the anisobidentate (unsymmetric) character of the dithiocarbamate ligands<sup>17,25</sup>. Further support for the coordination of these derivative was provided by the appearance of bands at about  $320-390 \, \text{cm}^{-1}$ which are assigned to  $v(Sn-S)^{26}$  and  $v(Bi-S)^{6}$ , while the v(Bi-N) absorption of the phen and bipy adducts are in good agreement with the reported values for similar compounds which fall in the range<sup>6,27</sup> 220-270 cm<sup>-1</sup>.

It may be concluded that there is an octahedral geometry round the tin atom in the present compounds of tin (Fig. 1). Hexa-coordinated compounds of tin were described elsewhere<sup>17,28</sup>. On the other hand, bismuth is hexa-coordinated in the complexes  $Bi(S_2CNR_2)_3$  and hexa- or hepta-coordinated in  $Bi(S_2CNR_2)_3$ .phen and  $Bi(S_2CNR_2)_3$ -bipy. The coexistance in one structure of a monodentate and a bidentate dithiocarbamate ligand has been established earlier<sup>17,26</sup>.

The adducts of  $Bi(S_2CNR_2)_3$  with phen or bipy might contain one or two monodentate  $CS_2^-$  groups, thus giving rise to the possibility of octahedral or pentagonal-bipyramidal structures (Fig. 2). Compounds of hexaand hepta-coordinated bismuth were described elsewhere<sup>18–22</sup>.

	- - - -	t					Analysis <sup>a</sup>		
Compound	Empirical Formula	Formula Weight	Colour	Yield%	Melting Point (°C)	C%	H%	N%	$\Delta_{\rm M} \mod \Omega^{-1}$ cm <sup>2</sup> mol <sup>-1</sup>
$Sn(S_2CNMe_2)_4$	$C_{12}H_{24}S_8N_4Sn$	599.18	Pale	06	163 (d)	24.15 (24.03)	4.10 (4.00)	9.54 (9.34)	8.7
Sn(S,CNEt,)4	$\mathrm{C}_{20}\mathrm{H}_{40}\mathrm{S}_{8}\mathrm{N}_{4}\mathrm{Sn}$	711.18	orange Orange	87	154	33.91 (33.74)	5.65 (5.62)	7.86 (7.87)	21.2
$SnI(S_2CNMe_2)_3$	C <sub>9</sub> H <sub>18</sub> S <sub>6</sub> N <sub>3</sub> ISn	605.96	Yellow	87	228	17.93 (17.82)	3.02 (2.97)	6.99 (6.93)	9.6
$SnI(S_2CNEt_2)_3$	C <sub>15</sub> H <sub>30</sub> S <sub>6</sub> N <sub>3</sub> ISn	689.69	Yellow	85	197	26.20 (26.09)	4.39 (4.35)	6.20 (6.09)	24.7
SnI <sub>2</sub> (S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	$C_6H_{12}S_4N_2I_2Sn$	612.74	Orange	87	175	11.90 (11.75)	2.00 (1.96)	4.56 (4.57)	15.3
SnL <sub>2</sub> (S <sub>2</sub> CNEt <sub>2</sub> )	C., H., S., N. L. Sn	668 74	yellow Orange	86	141 (4)	(7 00 717 07	3 04 (2 99)	4 23 (4 18)	19.4
	10777. 17607.110		vellow	0					
Bi(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub>	$C_9H_{18}S_6N_3Bi$	569.36	Yellow	91	192	19.12 (18.97)	3.02 (3.16)	7.42 (7.37)	12.6
Bi(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub>	C <sub>15</sub> H <sub>30</sub> S <sub>6</sub> N <sub>3</sub> Bi	653.36	Yellow	88	188	27.70 (27.55)	4.64 (4.59)	6.45 (6.43)	8.8
Bil(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub>	$C_6H_{12}S_4N_2IBi$	567.14	Bright	85	161	12.51 (12.49)	2.10 (2.08)	4.87 (4.86)	17.4
			yellow						
Bil(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>2</sub>	$C_{10}H_{20}S_4N_2IBi$	632.14	Yellow	87	152	19.12 (18.98)	3.20 (3.16)	4.48 (4.43)	15.8
$Bil_2(S_2CNMe_2)$	$C_3H_6S_2NI_2Bi$	582.92	Deep	84	147	6.20 (6.17)	1.05 (1.03)	2.42 (2.40)	18.9
			yellow						
$Bil_2(S_2CNEt_2)$	$C_5H_{10}S_2NI_2Bi$	610.92	Deep	89	139	9.80 (9.82)	1.66 (1.63)	2.28 (2.29)	22.0
			yellow						
Bi(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub> .phen	$C_{21}H_{26}S_6N_5Bi$	749.36	Yellow	92	203	33.68 (33.63)	3.51 (3.47)	9.39 (9.34)	15.1
Bi(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> .phen	$C_{27}H_{38}S_6N_5Bi$	833.36	Yellow	93	198	38.98 (38.88)	4.61 (4.56)	8.50 (8.40)	12.3
Bi(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub> .bipy	$C_{19}H_{26}S_6N_5Bi$	725.36	Deep	91	242	31.62 (31.43)	3.44 (3.45)	9.72 (9.65)	14.9
			yellow						
Bi(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> .bipy	$C_{25}H_{38}S_6N_5Bi$	809.36	Deep	92	234	37.17 (37.06)	4.76 (4.69)	8.64 (8.65)	11.6
			yellow						

Table L Analytical Data of the Compound and Adducts

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<sup>a</sup>Calculated values in parentheses. (d) decomposition.

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$ \begin{array}{llllllllllllllllllllllllllllllllllll$			Π	R a		
	Compound	v(C-N)	v(C-S)	v(M-S)	$v(B_i-N)$	UV/Visible Band Maxima in nm $(\epsilon, dm^3 mol^{-1} cm^{-1}))$
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$Sn(S_2CNMe_2)_4$	1525 s	980 s	385 m	I	262 (12700) 290 (19900) 415 (26650)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$Sn(S_2CNEt_2)_4$	1515 s 11400 s	975 sn 975 s 040 sh	380 m	I	266 (12550) 288 (189800) 908 (24700)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Snl(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub>	1520 S	985 s 986 s	382 m	I	255 (16050) - 418 (26050)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$SnI(S_2CNEt_2)_3$	1490 S 1510 S 1485 s	970 s 976 s 945 s	378 m	I	260 (14980) 285 (20510) 398 (23950)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$SnI_2(S_2CNMe_2)_2$	1490 s	9965 sh	390 m	Ι	260 (15050) 335 (19100) 395 (24250)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	$SnI_2(S_2CNEt_2)_2$	1480 s	980 s 960 s	388 m	Ι	265 (14990) 338 (18200) 380 (24050)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Bi(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub> Bi(S <sub>2</sub> CNHe <sub>4</sub> )	1495 s 1405 s	990 m	350 m 228 m	Ι	260 (12150) - 380 (21050)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Bil(S2CINE12)3 Bil(S2CNMe2)2	1403 s 1505 s	985 s	348 s		255 (12980) 320 (20700) 385 (22300)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$Bil(S_2CNEt_2)_2$	1495 s	975 s	330 m	Ι	260(14080) - 324(20050)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Bil <sub>2</sub> (S <sub>2</sub> CNMe <sub>2</sub> )	1500 s	985 m	325 w	Ι	270 (16030) 330 (24500) 385 (24100)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Bil2(S2CNEt2) Bi(S2CNMe2)3.phen	1490 s 1520 s	970 s 995 m	320 w 330 m	_ 270 m	268 (12650) – – 258 (24200) 328 (26050) 398 (28000)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$		1500 s	960 m			
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Bi(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> .phen	1515 s 1500 s	995 s 965 s	325 m	260 m	$250\ (24100) - 388\ (23010)$
Bi(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> .bipy 1525 s 995 s 325 m 265 m 250 (23950) - 395 (26300)   1485 s 965 sh 325 m 265 m 250 (23950) - 395 (26300)	Bi(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>3</sub> .bipy	1535 s 1505 s	1000 s 960 s	340 m	250 w	255 (24950) 330 (27800) 400 (26500)
	Bi(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub> .bipy	1525 s 1485 s	995 s 965 sh	325 m	265 m	250 (23950) – 395 (26300)

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Figure 1. Suggested structure of SnI(S<sub>2</sub>CNR<sub>2</sub>)<sub>3</sub>.



*Figure 2.* Suggested structure of  $Bi(S_2CNR_2)_3$ , phen or bipy; (a) hepta-coordinated bismuth or (b) hexa-coordinated bismuth.

The UV/Visible spectra of the compounds are similar to one another (Table II). The band observed in the region 260-330 nm might be due to  $\pi$ - $\pi$ \* transitions of the dithiocarbamate ligands, while an additional band was observed for the compounds and the adducts in the range 380-420 nm<sup>17,20,22</sup>. The new band was attributed to the charge transfer transition from the ligand orbital to the vacant metal orbitals.

The molar conductivities of  $10^{-3}$  M solutions of the compounds and adducts indicate the non-electrolyte nature<sup>29</sup> of these compounds and adducts in DMF.

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