

## Synthesis of new Bismuth (III) compound and adducts of benzothiazol disulfide derivatives and their complexes with Co(II), Ni(II) and Cu(II)

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### الخلاصة

يتفاعل فلز البزموت مع ثنائي بنزوثيازي ازل ثنائي الكبريتيد  $(C_7H_4NS_2)_2$  في التولوين ليعطي المركب  $Bi(S_2C_7H_4N)_3$  خلال تفاعل الأوكسدة المضافة وبصورة مشابهة فان مزيج البزموت و  $(C_7H_4NS_2)_2$  واليود وبنسبة مولية 1:1:0.5 في التولوين يؤدي إلى تكوين المركب  $Bi(S_2C_7H_4N)_2I$ . تم تحضير مركبات الإضافة لمركبات البزموت الجديدة مع ثلاثي فنيل فوسفين و 1,10-فينانثرولين من خلال تفاعل الإضافة المباشرة بين مركبات البزموت والليكاندات أعلاه . المعقدات ثلاثية النوى ذوات الصيغة العامة  $[Bi(S_2C_7H_4N)_3(MCl_2)_2]$  تم تحضيرها من خلال التفاعل ال مباشر ما بين  $CuCl_2.4H_2O$  أو  $NiCl_2.6H_2O$ ،  $CoCl_2.6H_2O$  مع مركبات البزموت . مركبات البزموت ومركبات الإضافة والمعقدات تم تشخيصها بالطرق الفيزيائية والكيميائية وبالطرق الطيفية.

### Abstract

Bismuth metal react with dibenzothiazole disulfide  $(C_7H_4NS_2)_2$  in refluxing toluene to give the compound  $Bi(S_2C_7H_4N)_3$  through oxidative addition reaction, similarly, a mixture of bismuth,  $(C_7H_4NS_2)_2$  and iodine in 1:1:0.5 molar ratio in refluxing toluene lead to the formation of  $Bi(S_2C_7H_4N)_2I$ . Adducts of new bismuth compounds with triphenylphosphine and 1,10-phenanthroline have been synthesized by direct reaction between the bismuth compounds and the neutral ligand. Trinuclear complexes of the general formula  $[Bi(S_2C_7H_4N)_3(MCl_2)_2]$  were prepared by a direct reaction of  $CoCl_2.6H_2O$ ,  $NiCl_2.6H_2O$  or  $CuCl_2.4H_2O$  with bismuth compound. The bismuth compounds their adducts and the complexes have been characterized physico-chemically and spectroscopically.

## **Introduction**

The past decade has seen a period of intense activity in study of the complexation of transition metal and main group metal ions with thioether ligands<sup>(1-4)</sup>.

Coordinated thiolato sulfur atoms tend to make bridges with a variety of metal ions, and considerable attention has been focused on the S-bridged polynuclear structure derived from [M(thiolato-S)<sub>2</sub>(amine-N)<sub>2</sub>]-type (M=Ni(II), Pd(II)) mononuclear complexes<sup>(5-8)</sup>.

The synthesis of dihalobis (2-pyridinethiolato) tin(IV) by an oxidative addition reaction of di-2-pyridyldisulfide to tin (II) halides represents an example of preparing other similar dihalodithiolato tin(IV) compounds<sup>(9)</sup>. In our previous studies<sup>(10,11)</sup> we have describe a direct reaction between bismuth or tin metal with (RC<sub>6</sub>H<sub>4</sub>S)<sub>2</sub>, (R=*o*-NH<sub>2</sub>, *p*-Me, *p*-Bu.t) refluxing toluene to give the corresponding comounds Bi(SC<sub>6</sub>H<sub>4</sub>R)<sub>3</sub> and Sn(SC<sub>6</sub>H<sub>4</sub>R)<sub>4</sub> respectively.

Trinuclear complexes of the general formula [Sn(SC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-*o*)<sub>4</sub>(MCl<sub>2</sub>)<sub>2</sub>] {M=Ni(II),Pd(II) or Pt(II)} were prepared by a direct reaction of NiCl<sub>2</sub>.6H<sub>2</sub>O, Na<sub>2</sub>PdCl<sub>4</sub> or K<sub>2</sub>PtCl<sub>4</sub> with the tin compound<sup>(12)</sup>.

In view of these interesting results and as continuation of our studies on transition and non-transition metal complexes with sulfur-containing ligands<sup>(13-15)</sup> we have prepared the bismuth compound Bi(S<sub>2</sub>C<sub>7</sub>H<sub>4</sub>N)<sub>3</sub>, also, the derivatives with iodine and their adducts with neutral ligands, as well as the trinuclear complexes of general formula [Bi(S<sub>2</sub>C<sub>7</sub>H<sub>4</sub>N)<sub>3</sub>(MCl<sub>2</sub>)<sub>2</sub>].

## **Experimental**

### **General**

IR spectra were recorded on Tensor 27 Co.Brucker (FT.IR) Spectrophotometer in the (4000-250 cm<sup>-1</sup>) range using Nujol mulls or CsI disc. The metal content was estimated spectrophotometrically using Shimadzu AA670. Conductivity measurements were made on 10<sup>-3</sup> M solution of the complexes in dimethylsulfoxide (DMSO) solvent at ambient temperature using conductivity meter model 4070 Jenway. Electronic spectra were recorded on Shimadzu UV/Vis. Spectrophotometer UV-160 for 10<sup>-3</sup> M solution of the complexes in DMSO using 1cm quartz cell. The magnetic measurements were carried out at 25°C on the solid by Faraday's method using Burker BM6 instrument.

### **Starting material**

Bismuth metal, toluene and dibenzothiazoldisulfide were commercial products (Fluka) and used as supplied.

### Preparation of Bismuth (III) compounds.

- 1-  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3$ .** Finely cut bismuth metal (0.21 g, 1.0 mmol) and the disulfide  $(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_2$  (0.48 g, 1.5 mmol) in toluene ( $30 \text{ cm}^3$ ) was refluxed for 8h. The reaction mixture was filtered through celite and the resultant solution was reduced to ca  $10 \text{ cm}^3$ , of its volume by evaporation under reduced pressure. The solid thus obtained after cooling in an ice-bath, was collected by filtration, washed with petroleum ether (60-80°C) and dried in vacuo.
- 2-  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_2\text{I}$ .** Finely cut bismuth metal (0.21 g, 1.0 mmol) was refluxed with the disulfide (0.33 g, 1.0 mmol) and iodine (0.064 g, 0.50 mmol) in toluene ( $30 \text{ cm}^3$ ) for 4h. The reaction mixture was filtered through celite and the resultant brown solution was reduced to ca  $10 \text{ cm}^3$  of its volume by evaporation under reduced pressure. The solid thus obtained after cooling in an ice-bath, was collected by filtration, washed with petroleum ether (60-80°C) and dried in vacuo.

### Preparation of $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3$ adducts:

- 3-  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3 \cdot 2\text{PPh}_3$ .** The bismuth compound  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3$  (0.49 g, 10. mmol) was added to a solution of the ligand  $\text{PPh}_3$  (0.52 g, 2.0 mmol) in ethanol ( $20 \text{ cm}^3$ ) at room temperature. The reaction mixture was stirred for 4h., during which time a precipitate formed. It was collected by filtration, washed with ethanol, diethylether and dried in vacuo.
- 4-  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3 \cdot \text{Phen}$ .** The bismuth compound  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3$  (0.49 g, 10. mmol) was stirred with 1,10-phenanthroline (0.18 g, 1.0 mmol) in benzen ( $20 \text{ cm}^3$ ) for ca 2h., during which time a dark yellow oily layer was separated from the colourless solution and colourless layer was decanted. The oily layer was triturated with diethylether ( $30 \text{ cm}^3$ ) until it solidified and the resultant yellow solid was filtered, washed with ether and dried in vacuo.

The analogous adducts  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_2\text{I} \cdot 2\text{PPh}_3$  (5) or  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_2\text{I} \cdot \text{Phen}$  (6) were prepared similarly.

### Preparation of $[\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3(\text{MCl}_2)_2]$ complexes

M= Co(II), Ni(II), Cu(II)

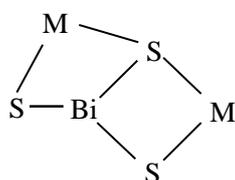
A clear solution of  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3$  (0.49 g, 10. mmol) in methanol ( $10 \text{ cm}^3$ ) was added to a solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  or  $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$  (2.0 mmol) in distilled water ( $10 \text{ cm}^3$ ). The mixture was stirred under reflux for ca. 2h. the formed precipitate, was filtered off washed with methanol, and diethylether then dried under vacuo.

## Results and Discussion

The direct reaction of the ligand dibenzothiazole disulfide with bismuth metal in refluxing toluene using a 1:2 metal to ligand molar ratio afforded the compound  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3$  through an oxidative addition reaction<sup>(15)</sup>, also the reaction of iodine with disulfide and bismuth metal give a product of the formula  $\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_2\text{I}$ . The mechanism of these reactions involves the initial cleavage of the  $-\text{S}-\text{S}-$  bond to form the thiolate ion and the oxidation of bismuth metal from  $\text{Bi}^0$  to  $\text{Bi}^{+3}$ . The reaction of the above compounds with neutral ligands were also reported. Treatment of the bismuth compound in alcohol with aqueous solution of metal chloride in (1:2) molar ratio gave the trinuclear complexes of the type  $[\text{Bi}(\text{S}_2\text{C}_7\text{H}_4\text{N}_2)_3(\text{MCl}_2)_2]$ . The nucleophilicity of the thiolate sulfur atoms in the bismuth compound is responsible for the formation of these new complexes. The physical properties of the compounds and complexes are listed in (Table 1).

The complexes are quite stable in dry air and melt or decompose at above than 135 °C. They are insoluble in most organic solvents but soluble in dimethylformamide.

The most important IR assignment of bismuth compounds and their complexes are listed in Table 2. The infrared spectra of the ligand showed a sharp band at  $1021\text{ cm}^{-1}$  attributed to C – S stretching vibration, which shifts to lower value in the compounds, indicating a coordination between sulfur and bismuth<sup>(16)</sup>, strong band in the  $1580\text{ cm}^{-1}$  region, while were assigned to  $\nu(\text{C}=\text{N})$ , the negligible effect on this frequency after complexation precludes the possibility of sharing of this group. Furthermore, the IR spectra of the adducts with  $\text{PPh}_3$  and Phen show a medium band at  $985\text{-}990\text{ cm}^{-1}$  indicating that the ligand coordinated through sulphur atoms. Further support for this was obtained from the appearance of a new band at  $323\text{-}336\text{ cm}^{-1}$  which assigned  $\nu(\text{Bi-S})$  while the  $\nu(\text{Bi-N})$  and  $\nu(\text{Bi-P})$  for 1,10-phenanthroline and triphenylphosphine are in good agreement with the reported values of  $\text{In.X}_3.1.5\text{phen}$  ( $\text{X}=\text{Cl},\text{Br}$ ) which fall in the  $410\text{-}450\text{ cm}^{-1}$ , while the  $\nu(\text{Bi-P})$  band is observed at  $480\text{-}510\text{ cm}^{-1}$  similar results was found some were else<sup>(18)</sup>. The frequency of  $\nu(\text{C-S})$  band observed at to  $995\text{-}1005\text{ cm}^{-1}$  in the compounds is slightly decreased upon complexation with  $\text{MCl}_2$  to form the corresponding trinuclear complexes. Further support for the formation of new complexes is provided by the appearance of a new band at  $340\text{-}380\text{ cm}^{-1}$  range characteristic of bidentate trithiobismuth<sup>(17)</sup>, as shown below.



The electronic spectrum of the ligand contains three absorption bands in 38700, 33222 and 28818  $\text{cm}^{-1}$  (Table 2) which may be assigned as  $n \rightarrow \pi^*$  or  $\pi - \pi^*$  transitions respectively. The U.V spectral bands of the ligand were observed at higher region upon formation of compounds and their adducts which were observed in 36910-21809  $\text{cm}^{-1}$  ranges, indicating that the bonding of the ligand with the metal ion through sulphur, nitrogen or phosphorus atoms<sup>(19)</sup>.

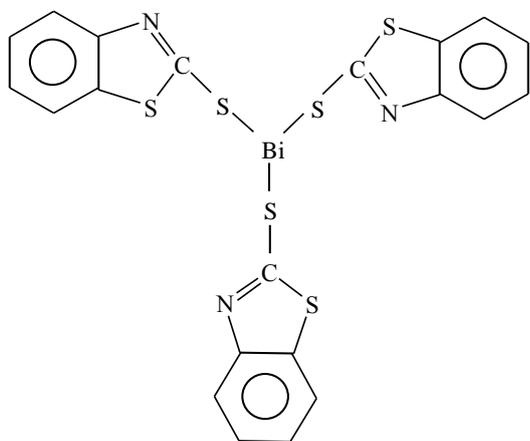
The values of magnetic moment of Co(II) complex(7) is 2.01 B.M. this value correspond to low spin square planar geometry for the complex<sup>(20)</sup>. The electronic spectra of Co(II) complex show a bands at 15797  $\text{cm}^{-1}$ , which may be assigned to  ${}^2A_{1g} \rightarrow {}^2E_g$  transition in square planer geometry and 26525  $\text{cm}^{-1}$  which may be assigned as charge transfer.

The Ni(II) complex (8) was diamagnetic and its electronic spectra showed two bands (Table 2). These bands were assigned to  ${}^1A_{1g} \rightarrow {}^1B_{2g}$  and  ${}^1A_{1g} \rightarrow {}^1E_g$  transition respectively. These results suggest a square planer geometry around the nickel ion<sup>(21)</sup>.

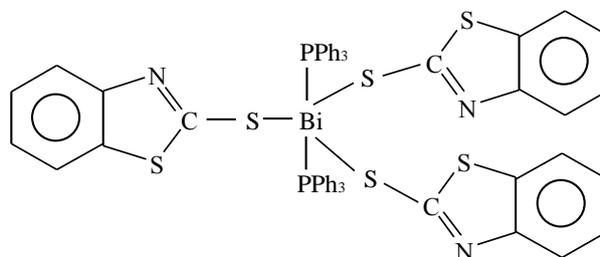
The Cu(II) complex (9) shows a magnetic moment of 2.01 B.M. the electronic spectrum showed broad band centered at 13600  $\text{cm}^{-1}$  correspond to the transition  ${}^2B_{1g} \rightarrow {}^2A_{1g}$  for distorted square planer geometry around Cu(II)<sup>(20)</sup>.

From the above discussion, the following structures can be suggested for the compounds and the complexes.

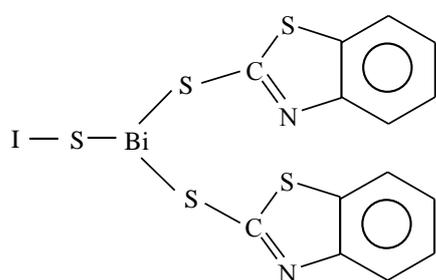




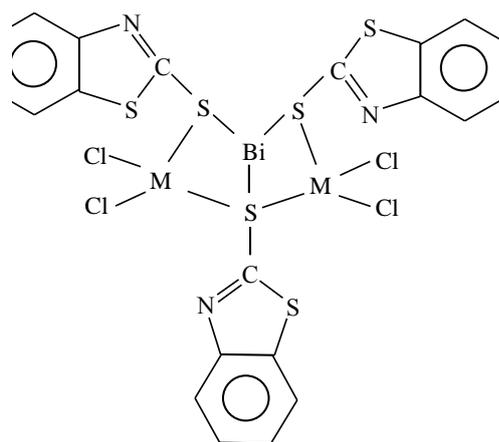
(1)



(3)



(4)



(7-9)

M = Co(II), Ni(II) or Cu(II)

**Fig 1: Suggested structures for the prepared compounds ,adducts and complexes**

Table 1: Physical properties of compounds and complexes

No.	compound	colour	Yield %	M.p (°C)	Analysis % Found(calc.)		$\mu_{eff}$	$\Omega$ ohm <sup>1</sup> .cm <sup>2</sup> .mol <sup>-1</sup>
					Bi	M		
1	Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub>	Yellow	94	184	29.48 (29.56)	---	---	10
2	Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .(phen)	Olive yellow	85	149		---	---	35
3	Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .(2PPh <sub>3</sub> )	Brown	88	198 <sup>d</sup>		---	---	60
4	Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .I	Maroon	70	157 <sup>d</sup>	31.20 (31.28)	---	---	29
5	Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .I.(phen)	Dark brown	87	115 <sup>d</sup>		---	---	70
6	Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .I.(2PPh <sub>3</sub> )	Brown yellow	65	132		---	---	30
7	[Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .(CoCl <sub>2</sub> ) <sub>2</sub> ]	Dark green	70	183 <sup>d</sup>	21.64 (21.61)	12.40 (12.19)	2.10	40
8	[Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .(NiCl <sub>2</sub> ) <sub>2</sub> ]	Brown	64	162 <sup>d</sup>	21.59 (21.61)	12.11 (12.18)	Dia	35
9	[Bi(S <sub>2</sub> C <sub>7</sub> H <sub>4</sub> N) <sub>3</sub> .(CuCl <sub>2</sub> ) <sub>2</sub> ]	Pale olive	91	202 <sup>d</sup>	21.32 (21.41)	12.99 (12.01)	2.01	32

d= decomposition

Table 2: Infrared and electronic data for compounds and adducts

No.	IR band assignments (cm <sup>-1</sup> )						UV.Visible band $\lambda_{max}$ (cm <sup>-1</sup> )
	$\nu$ (C – S)	$\nu$ (C = N)	$\nu$ (M–S)	$\nu$ (M–N)	$\nu$ (M–P)	$\nu$ (M–Cl)	
1	1001 <sub>s</sub>	1580 <sub>m</sub>	329 <sub>m</sub>	---	----	----	259741,33112
2	1005 <sub>s</sub>	1582 <sub>m</sub>	332 <sub>m</sub>	410 <sub>m</sub>	----	----	28089,31948
3	1000 <sub>s</sub>	1579 <sub>m</sub>	335 <sub>m</sub>	----	480 <sub>m</sub>	----	27624,32679
4	985 <sub>s</sub>	1582 <sub>m</sub>	322 <sub>m</sub>	----	----	----	24573,34129
5	989 <sub>s</sub>	1580 <sub>m</sub>	325 <sub>m</sub>	450 <sub>m</sub>	----	----	27777,31654
6	990 <sub>s</sub>	1585 <sub>m</sub>	330 <sub>m</sub>	----	510 <sub>m</sub>	----	27472,33898
7	995 <sub>s</sub>	1580 <sub>s</sub>	330,380	----	----	300	15797,26525,30211
8	998 <sub>s</sub>	1583 <sub>s</sub>	335,375	----	----	310	15948,25510,31347
9	994 <sub>s</sub>	1580 <sub>m</sub>	320,360,380	----	----	315	13600,34722

s= strong, m = medium

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