

## USING OF ACYL-BISTHIUREAS AS NEW LIGANDS FOR SPECTROPHOTOMETRIC DETERMINATION OF BI(III)

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### **Abstract**

*A simple, accurate, sensitive and reliable method for the selective determination of Bi(III), which is based on spectrophotometric measurement of water soluble yellow bismuth-ligand complexes have been developed. The linear calibration ranges and limit of detection for the proposed method was  $1.00 \times 10^{-6}$  –  $1.00 \times 10^{-3}$  and  $2.00 \times 10^{-8}$  mol/L, respectively. The complexes were prepared in mixing of sample with the organic-solvent solution of chelating agent. The influence of the organic solvent amount was studied. Chelating agent were firstly synthesized though the reaction of thiosemicarbazides with aroyl isothiocyanates. The mentioned ligands are bithiureas with sulfur, nitrogen and oxygen donor atoms. The quantum-chemical calculations were carried out for detailed understanding of the complex formation reaction for received compounds.*

**Keywords:** *Bismuth, Bis-thiourea, Spectrophotometry,*

### **Introduction**

Development of fast and reliable methods for determination of small quantities of Bismuth in natural samples is an important task. Bismuth is widely used in different parts of industry. Bismuth is a metal that is mostly consumed in the production of low-melting alloys and metallurgical additives [Carlin, 2008], as a substitute for the toxic lead in ammunition [Pamphlett et al, 2000]. Bismuth-containing pigment based on platelet-shaped crystals of bismuth oxide chloride (BiOCl) and greenish yellow pigment based on bismuth orthovanadate (BiVO<sub>4</sub>) have been known for a long time [Völz et al, 2006].

Some bismuth-containing complex oxides could be activated by visible light and mineralize organic pollutants [Liu et al, 2010]. Furthermore, visible light-responsive photocatalysts like Bi<sub>2</sub>WO<sub>6</sub>, BiVO<sub>4</sub> and Bi<sub>2</sub>MoO<sub>6</sub> were also described [Zhang et al, 2012].

Human exposure mainly occurs during production and use of pharmaceuticals such as Pepto-Bismol (Bismuth Subsalicylate) and Bismuth Citrate, an over-the counter drug to treat minor upsets of the digestive system [Larsen et al, 2003; Mahony et al, 2005].

Bismuth containing drugs is used for eradication of *Helicobacter pylori* in peptic ulcers [Malfertheiner et al, 2010; Andrews et al, 2011; Gisbert, 2011], treatment of syphilis and tumors [11 Rosenblat et al 2010], reduction of the renal toxicity of cisplatin [Leussink et al, 2003; Luo et al, 2012].

In recent years, bismuth has been promoted as a “green element”, however, the bio-availability and toxicity of bismuth is still not very well described. Bi-containing compounds are considered to be slightly adsorbed through both respiratory and gastrointestinal tracts but information on uptake and metabolism is still scarce. [Urgast et al, 2012].

In one investigation was shown that Bi<sup>3+</sup> ions, at concentration of 60 µg/ml, may reduce normal sperm metabolism by inhibition of sperm creatine kinase, which probably is an important cause of infertility in men. [Ghaffari et al, 2011].

There are some reports that the digestion of bismuth and its compounds may result in kidney damage, gingivitis, rheumatic pain, fever and problems in hepatic function [Itoh et al, 1999; Agrawal et al, 2004].

Unlike organic pollutants, metals cannot be degraded easily and accumulate throughout the food chain, producing potential human health risks and ecological disturbances [Nordberg et al, 2005]. That is why, the elaboration of bismuth-detection techniques is actual.

There are many techniques for the determination of Bismuth in various types of samples – such as flame atomic absorption spectrometry (FAAS) [CHATTOPADHYAY et al, 1991., ŞAHAN et al, 2010], inductively coupled plasma mass spectrometry (ICP-MS) [PAVLÍČKOVÁ et al, 2003], atomic fluorescence spectrometry [RAHMAN et al, 2000], potentiometric analysis [OSTAPCZUK et al, 1993] and spectrophotometry [BENDIGO et al, 1951; SATAKE et al, 1977]. Some of these techniques such as ICP-MS usually have enough sensitivity for the determination of Bi at trace level, but suffer from matrix interferences and is not available in many laboratories due to its high cost. FAAS is simple, low cost, highly selective, but due to the relatively poor sensitivity, direct determination of trace amounts of bismuth is problematic.

The sensitivity and detection limit for the analyte determination can be significantly improved by the combination of a separation/preconcentration with the instrumental technique of analysis. 2-Mercaptobenzothiazole (MBT), with sulfur and nitrogen donor atoms, as a chelating agent has been used for the separation and preconcentration of bismuth [SHAKERIAN et al, 2014]. The objective of our studies is improving of photometric determination of Bi(III) by complexation with variation of ligands nature.

## Material and methods

### Computational investigation

All calculations were performed with MOPAC2012 program [MOPAC2012]. Graphical results were presented with Jmol program [Jmol] and Gabedit [Allouche, 2011].

### Chemical synthesis

Synthesis of Compounds L1,2. (General Method). NH<sub>4</sub>SCN (13 mmol) was dissolved in acetonitrile (100 ml) at 60-70°C. The solution was cooled to 35-40°C and aroyl chloride (10 mmol) was added with stirring. The suspension obtained was stirred for 15-20 min and then a solution of corresponding thiosemicarbazide (10 mmol) in acetonitrile (50 ml) was added. Stirring was continued for 30 min at 45-50°C. Solvent was removed under reduce pressure. The residue was mixed with cold water. The precipitate of product L1,2 was filtered off, washed with water, and dried in the air. The precipitate was recrystallized from suitable solvent and dried in the air.

**N-{{2-(methylcarbamothioyl)hydrazino}carbonothioyl}benzamide (L1)** obtained in 71% yield; m.p. 190-192 °C. IR (cm<sup>-1</sup>): 3250 (N-H); 1700 (C=O); 1480-1600 (C=S, C-N); 1200-1300 (N-N, Ph, C-N). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ = 3.06 (d, 3H, CH<sub>3</sub>N), 6.45-13.10 (NH, Ph, NH, NH, NH). Anal. Calcd for C<sub>10</sub>H<sub>12</sub>N<sub>4</sub>OS<sub>2</sub>, %: C, 44.76; H, 4.51; N, 20.88; O, 0.96; S, 23.90. Found, %: C 44.39; H 4.20; N 19.71; S 22.94.

**N-{{2-(prop-2-en-1-ylcarbamothioyl)hydrazino}carbonothioyl}benzamide (L2)** obtained in 57% yield. m.p. 144-146 °C. IR (cm<sup>-1</sup>): 3250 (N-H); 1700 (C=O); 1480-1600 (C=S, C-N); 1200-1300 (N-N, Ph, C-N). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ = 4.17 (m, 2H, CH<sub>2</sub>N), 5.25-5.38 (dd, 2H, CH<sub>2</sub>=), 5.88 (m, 1H, =CH-), 6.41-13.03 (NH, Ph, NH, NH, NH). Anal. Calcd for C<sub>12</sub>H<sub>14</sub>N<sub>4</sub>OS<sub>2</sub>, %: C, 48.96; H, 4.79; N, 19.03; S, 21.78. Found, %: C 47.84; H, 4.87; N, 18.40; S, 21.19.

### Analytical procedure

For the investigation we used two different samples: TlBiSe2 – semiconductor, and a tablet of “Vicairum” – combined drug for treating stomach.

**TlBiSe2.** A sample was dissolved in 5 ml of concentrated HNO<sub>3</sub>. Mixture was evaporated with boiling, 5 ml of H<sub>2</sub>SO<sub>4</sub> solution (1:1) was added and evaporated again. Obtained residue was diluted with bi-distilled water (about 30 ml) and filtered. Water was added to this solution till average 50.0 ml. An aliquot of 5ml of this solution was dissolved in 95 ml of water to get 100 ml of sample solution.

### Vicairum.

A pill of “Vicairum” was dissolved in 5 ml of concentrated HNO<sub>3</sub>. Mixture was diluted with bi-distilled water (about 30 ml) and filtered. Water was added to this solution till average 100.0 ml. An aliquot of 2 ml of this solution was dissolved in 98 ml of water to get 100 ml of sample solution.

The measurement of analytical signal was carried out in the mentioned manner. Results are presented in the Table.1.

**Table.1.** Determination of Bi (III). (n=3,  $\alpha=4,30$ ,  $\alpha = 0,95$ .)

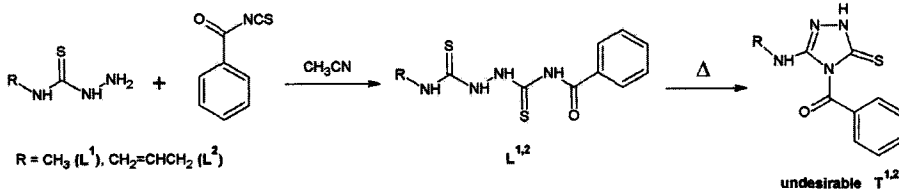
Substance	Weight, g	Mass of Bi in sample, g	Calc $\mu\text{g/ml}$	experiment	$\bar{X}$	$S_r$	$\bar{X}\pm\Delta X$
TlBiSe2	0.10260	0.03753	37.53	36.9 36.7 35.7	36.43	0.018	36.43 $\pm$ 2.76
“Vicairum”	1.05620	0.15079	30.16	28.7 30.1 27.9	28.9	0.039	28.90 $\pm$ 4.79

### Discussions

In our work we decided to combine few donor groups for receiving the new ligand with synergistic effect of atoms. For this purposes we synthesized substituted N,N'-bisthioureas which contain mercapto group for the formation of strong Sulfur-Metal covalent bond, carbonyl and amino group for the additional coordinate bonds and formation of stable complexes.

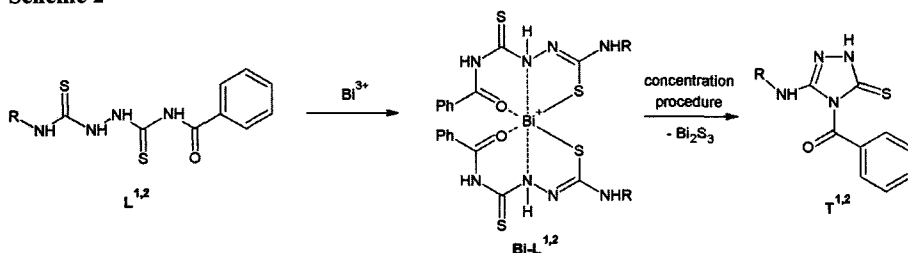
The starting ligands N-{{2-(R-carbamothioyl)hydrazino}carbonothioyl}benzamide L1,2 (Scheme 1) was obtained from N-R-thiosemicarbazide and benzoyl isothiocyanate. We determined physical and chemical characteristics of synthesized organic ligands (stability, solubility, IR spectroscopy spectra, UV spectroscopy spectra, NMR spectra, etc). It was noted that obtained bisthioureas L1,2 are not stable upon heating – the reaction of hydrogen sulfide elimination was occurred with formation of corresponding triazoles T1,2 which are not an object of this study.

### Scheme 1

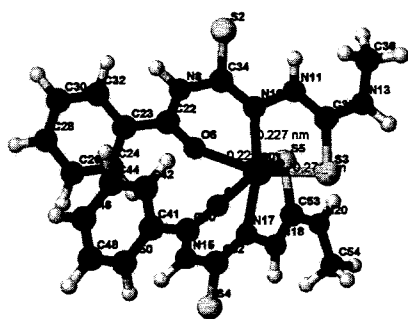


We investigated the reaction conditions of  $\text{Bi}^{3+}$  ions with  $N$ -({2-[( $R$ -amino)carbonothioyl]hydrazino}carbonothioyl)benzamides  $L_{1,2}$  in water solution (Scheme 2). It must be noted that yellow complex is formed in this reaction, but we were unable to separate this complex in necessary minimal quantity for identification. In the case of using highly concentrated solutions black Bismuth Sulfide was precipitated and  $\text{Bi-L}_{1,2}$  formation was not observed.

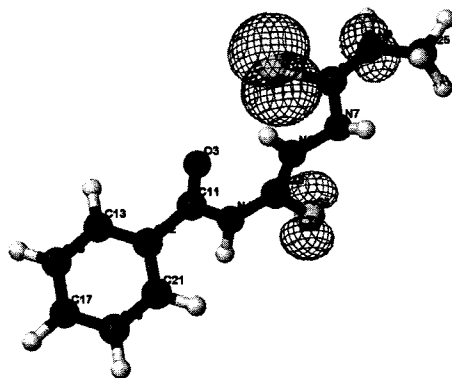
**Scheme 2**



Therefore, for detailed understanding of the complex formation reaction for  $L_{1,2}$  compounds was carried out quantum-chemical calculations. The semi-empirical PM6 method was chosen as a method of calculation, because it was developed for a wide range of compounds and atoms, including transition and heavy metals [Stewart, 2007]. The calculations were carried out using MOPAC2012 [MOPAC2012; Maia et al, 2012]. The picture 1 presents hypothetical structure for  $\text{Bi-L}_1$  complex. Selected PM6 semi-empirical method gives satisfactory settlement for bond lengths of  $\text{Bi-X}$  (where  $X = \text{N}, \text{O}, \text{S}$ ) [Suzuki et al, 2001]. HOMO orbital were calculated to find the reaction center of ligands molecules: As can be seen from the picture 2 HOMO orbital which is response for the reaction with cations located on the Sulfur atom, so at first  $\text{Bi-S}$  bond will be formed with the next formation of  $\text{Bi-N}$  and  $\text{Bi-O}$  coordination bonds.



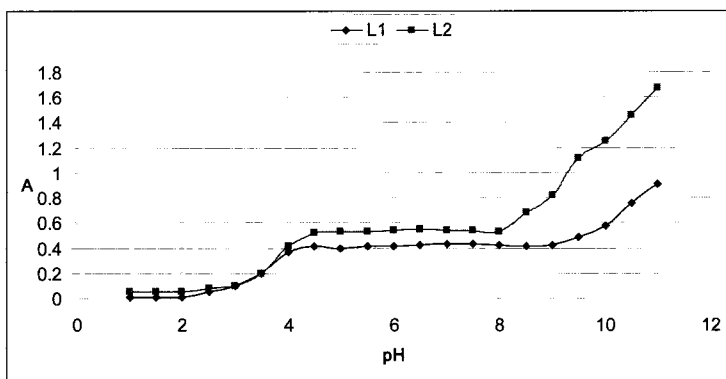
**Picture 1**



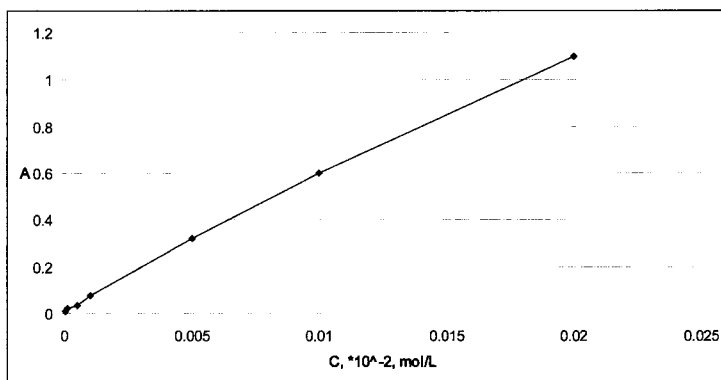
**Picture 2**

Starting 10<sup>-3</sup> M solution of Bismuth was prepared with dissolving of precise sample analytical purity metallic Bismuth in nitric acid. Working standard solutions were prepared by double-distilled water dilution. The solutions of ligands were prepared by dissolving of precise sample of bistiourea (1mmol) in 100ml of solvent (methanol, dioxane, dimethylformamide – DMF),  $C = 10^{-2}$  mol/L. For controlling pH we used 1 M buffer solutions – ammonia buffer ( $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ ) and acetic buffer solution ( $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$ ).

pH is an important factor that influence on the formation of complex. So we investigated the conditions with the formation of maximum amount of complex and maximum optical density. It was established that colored complexes are not produced in acidic conditions with  $\text{pH} < 3$ . In the region of  $\text{pH} = 4-8$  the clear yellow colour was observed, which can be controlled by spectrophotometer, but with further increasing of pH it was still increasing of optical density but this effect was due to formation of opalescence. In the case of L1 – opalescence was observed beginning from  $\text{pH} = 9.5$  and higher, but for L2 this line was even smaller – precipitation begins from  $\text{pH} = 8.5$  (fig.1). According to this we used L1 in our standard technique of Bi(III) determination.



**Figure 1.** Optimal pH region is 4-8.



**Figure 2.** Dependency of optical density with concentration of Bi(III).

It was noted that probes with different solutions of ligands have different optical density. In the case of dioxane, and especially DMF the optical density was much lower. Indeed, when we add pure solvent like dioxane or DMF instead of water during the preparation of probe there were no any color formation. Obviously that these solvents act as destructors of complex. In other investigations we used only methanol solution.

Beer–Lambert–Bouguer law is correct in the range of  $1.00 \times 10^{-6}$ – $2.00 \times 10^{-3}$  and limit of detection for the proposed method is  $2.00 \times 10^{-8}$  mol/L (fig.2).

The weight of sample taken for analysis should be such that the bismuth content is approximately 1 to 10 mg or if this is a solution with concentration diapason  $1.00 \times 10^{-6}$ – $2.00 \times 10^{-3}$  – take 1.00 ml of investigated solution. If the sample is solid or highly concentrated, than it must be prepared according to later described procedure [Bendigo et al, 1951.]. A sample of 1 ml is mixed with 1 ml of methanol solution of ligand L1, 1 ml of buffer solution and 2 ml of bi-distilled water.

This mixture was let to stand for 10 min and than optical density was measured using as a standard the same mixture except that instead of probe we add 1 ml of water.

A photocolorimeter Shimadzu UV-2600 was used in this work. Measurement of the absorbency of the solution was made at 440 nm.

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