Organic Chemistry

# Synthesis and Characterization of Mixed-Ligand Complexes of Arsenic-Organic Compounds

## Tea Lobzhanidze\*, Ioseb Metskhvarishvili\*\*, Kristine Giorgadze\*

(Presented by Academy Member Shota Samsoniya)

ABSTRACT. Unlike the other coordination compounds, one of the most important features of the tetrasubstituted arsonium salts is their tendency to produce cationic and anionic complexes in alcohol-water solution. The mixed-ligand complexes have great prospects of application. Most likely, these compounds have high and specific biological activity. The arsonium salt and cadmium bromate are used as initial materials of reaction in the molar ratio of 1:1. The reaction is carried out at room temperature in alcohol-water solution. The structure and composition of synthesized mixed-ligand complexes of arsenic organic compounds were tested with elemental analysis and other physical and chemical methods of research. © 2018 Bull. Georg. Natl. Acad. Sci.

Key words: arsenic-organic compounds, bioactivity, d<sup>10</sup>-elements, bromate

Nowadays, in the arsenic-organic chemistry the priority direction is to use arsonium salts for obtaining the coordination compounds [1-4]. As is known, d¹¹¹-elements are capable to produce coordination compounds with arsonium salts providing corresponding acido complexes of various structure and composition. The goal of the present work is to study the interaction of arsonium salts with cadmium bromate (V), to isolate the reaction products in the individual condition, to determine chemical composition and to study the chemical and physical properties and structure.

The iodides and cadmium bromate (V) of iodinemethylenetrialkyl(aril)arsonium were used

as initial products. Soon after interaction of the reacting substances a whitish crystalline substance precipitated, and the goal was achieved according to equation [5-8]:

$$\begin{split} &[R_2As(R`)CH_2I]I + Cd(BrO_3)_2 \\ \rightarrow &[R_2As(R`)CH_2I][Cd(BrO_3)_2 \cdot I] \end{split}$$

#### **Results and Discussion**

Composition and structure of synthesized complexes are also confirmed by their electric conductivity. Since their  $\mu$  in the dimethylformamide (synthetic compounds do not solve in water, alcohol and other aprotic solvents) fluctuate within 75-93 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup> (Table 1)

<sup>\*</sup>Department of Chemistry, Faculty of Exact and Natural Sciences, Ivane Javakhishvili Tbilisi State University, Tbilisi, Georgia

<sup>\*\*</sup> Laboratory of Cryogenic Techniques and Technologies, Ilia Vekua Sukhumi Institute of Physics and Technology, Tbilisi, Georgia

#	[R <sub>2</sub> As(R`)CH <sub>2</sub> I] [Cd(BrO <sub>3</sub> ) <sub>2</sub> ·I]		Melting temperature	μ, molar electroconductivity,	Was found, %			Bruto- formula	Calculated, %		
	R	R'	t,0C	om -1 cm 2 mol-1	As	Cd	Hlg		As	Cd	Hlg
1	$C_3H_7$	$C_3H_7$	224-225	92.1	8.61	13.28	47.95	$C_{10}H_{23}AsCdBr_2I_2O_6$	8.73	13.0	48.22
2	izo-C <sub>3</sub> H <sub>7</sub>	izo-C <sub>3</sub> H <sub>7</sub>	197-198	90.4	8.85	12.83	48.02	$C_{10}H_{23}AsCdBr_2I_2O_6$	8.73	13.0	48.22
3	C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	73-74	87.8	8.38	12.01	45.39	$C_{15}H_{25}AsCdI_2Br_2O_6$	8.14	12.21	44.98
4	izo-C <sub>4</sub> H <sub>9</sub>	izo-C <sub>4</sub> H <sub>9</sub>	183-184	77.6	8.30	12.61	47.75	C <sub>13</sub> H <sub>29</sub> AsCdI <sub>2</sub> Br <sub>2</sub> O <sub>6</sub>	8.32	12.48	45.97
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	139-140	75.2	7.98	11.55	42.92	$C_{19}H_{17}AsCdI_2Br_2O_6$	7.80	11.70	43.10

**Table 1.**Some physical and chemical constants of iodide-bromate-cadmiums (II) of tetra substituted arsonium

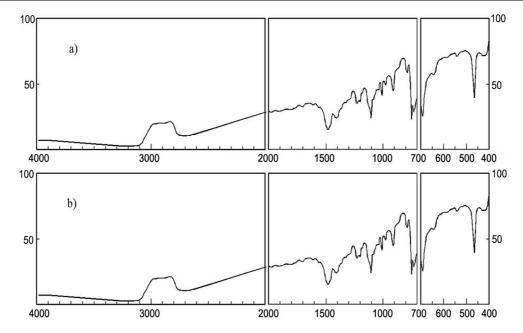


Fig. 1. IR spectrum of absorption in the Vaseline oil: a)  $[(C_3H_7)_3A_5CH_2I][Cd(BrO_3)_2\cdot I];$  b)  $[(C_4H_9)_2A_5(C_6H_5)CH_2I][Cd(BrO_3)_2\cdot I].$ 

indicating that the study samples represent binary ionic coordination compounds that are dissociated in the dimethylformamide according to the following scheme: [9]:

$$[R_2As(R)CH_2I][Cd(BrO_3)_2\cdot I] \leftrightarrows$$

$$[R_2As(R)CH_2I]^+ + [Cd(BrO_3)_2\cdot I]$$

The analysis of the absorption IR spectrum shows that they have almost all the absorption lines that are characteristic of the tetrasubstituted arsonium iodides indicating the ionic structure of the synthesized compounds. The only difference is that there are observed absorption lines 428; 790;

810 cm<sup>-1</sup> that are characteristic of the bromate ions [10].

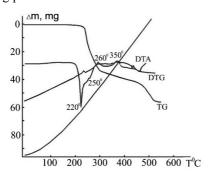
To illustrate the above said, we provide the IR spectra of iodidedibromatecadmiates (II) of iodinemethylenetributylphenylarsonium (Fig. 1, a) and iodidedibromatecadmiates (II) of iodinemethylenetripropylarsonium (Fig. 1, b).

The thermostability of synthesized materials were studied by thermodynamic method. As an example, we provide the results of thermal decomposition of iodidedibromatecadmiates (II) of iodinemethylenetripropylarsonium (Fig. 2.). The

	Loaded substances							Received			
#	[R <sub>2</sub> As(R`)CH <sub>2</sub> I]I					BrO <sub>3</sub> ) <sub>2</sub>	$[R_2As(R)CH_2I][Cd(BrO_3)_2\cdot I]$				
	R	R`	gg	mol	gg	mol	g	mol	%		
1	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	1,5	00031	1.22	0.0031	2.35	0.0027	86.4		
2	izo-C <sub>3</sub> H <sub>7</sub>	izo-C <sub>3</sub> H <sub>7</sub>	1,5	0.0031	1.22	0.0031	2.31	0.0026	85.0		
3	C <sub>4</sub> H <sub>9</sub>	$C_6H_5$	2,0	0.0037	1.44	0.0037	2.83	0.0030	82.2		
4	izo-C <sub>4</sub> H <sub>9</sub>	izo-C <sub>4</sub> H <sub>9</sub>	2,5	0.0048	1.87	0.0048	3.81	0.0042	87.1		
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	3,0	0.0052	2.01	0.0052	4.21	0.0043	83.9		

**Table 2.** The yield of target products of iodide-bromate-cadmiums (II) of tetra substituted arsonium

Fig.2 shows that the weight loss starts above the melting point.



**Fig. 2.** Thermogram of [(izo-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>AsCH<sub>2</sub>I][Cd(BrO<sub>3</sub>)<sub>2</sub>I].

The iodidedibromatecadmiates(II) of iodinemethylenetripropylarsonium loses 55.92% of its mass in the interval of 195-285°C that indicates the removal of the entire "organic". Therefore, [(Iso- $C_3H_7$ )<sub>3</sub>AsCH<sub>2</sub>I] I (theoretically – 56.18%) is isolated in this interval. It would be more realistic to say that it is not the tetrasubstituted arsonium isolated in this interval rather its products of decomposition. The thermolysis of the "inorganic" is more complicated. Particularly, the mass loss in the 300-500°C temperature interval is 28.57%. In this interval Br<sub>2</sub>O<sub>5</sub> (theoretically 28.81%) is isolated. Therefore, the thermolysis of the synthesized substance is carried out according to the following scheme:

$$[(Iso-C_3H_7)_3AsCH_2][Cd(BrO_3)_2I] \xrightarrow{195-285^{\circ}C} \\ -(Iso-C_3H_7)_3As; \\ -CH_2I_2 \xrightarrow{-(Iso-C_3H_7)_3As;} \\ Cd(BrO_3)_2 \xrightarrow{-(Iso-C_3H_7)_3As} CdO \xrightarrow{t^{\circ}} \cdots$$

By X-ray diffractometer, where recording passes on the  $CuK_{\alpha}$  radiation, investigation of samples

proved that all synthesized samples are crystalline and do not contain initial components even as an admixture (Table 3).

## **Experimental Part**

iodidedibromatecadmiates(II) of Iodinemethylenetributylarsonium. 2.5g Iodinemethylenetributylarsonium iodide is dissolved in ethyl alcohol and the water solution of 1.87 g of cadmium bromate(V) is prepared; the latter is added by the alcohol solution of iodinemethylenetributylarsonium iodide. As soon as they are mixed a white crystalline substance is produced, which is delayed for twenty-four hours and is filtered the next day; the precipitant is rinsed with distilled water, alcohol and then is dried in vacuum-exicator using phosphorous pentoxide until a steady mass is received. As a result, 3.81g (87.1%) iododibromatecadmiates of iodinemethylenetributylarsonium is obtained. Analysis allowed to find, %: As 8.30; Hlg 45,75; Cd 12,61. C<sub>13</sub>H<sub>29</sub>AsCdI<sub>2</sub>Br<sub>2</sub>O<sub>6</sub> and to compute, %: A8.32; HL 45.97; C. 12.48.

Table 3. X-ray diffraction

$[(C_3H_7)_3AsCH_2I]_2[Cd(BrO_3)_2I]$					
I/Io Intensity	d <sub>α</sub> /n				
100	8.84				
30	5.37				
35	4.09				
20	3.95				
20	3.785				
40	3.708				
40	3.49				
10	3.19				
10	3.03				
10	2.88				
10	2.68				
15	2.03				

In the same way, the other iodide-bromatecadmiums (II) of tetrasubstituted arsonium are obtained (Table 2). The substances used for reaction and the yield of target products are given in Table 2, and the other physical and chemical constants in Table 1 and Table 3.

ორგანული ქიმია

# დარიშხანორგანული შერეულლიგანდიანი კომპლექსების სინთეზი და გამოკვლევა

თ. ლობჟანიძე $^*$ , ი. მეცხვარიშვილი $^{**}$ , ქ. გიორგაძე $^*$ 

\* ივანე ჯავახიშვილის სახელობის თბილისის სახელმწიფო უნივერსიტეტი, ქიმიის დეპარტამენტი, ზუსტ და საბუნებისმეტყველო მეცნიერებათა ფაკულტეტი, თბილისი, საქართველო \*\* სოხუმის ილია ვეკუას ფიზიკა-ტექნიკის ინსტიტუტი, კრიოგენული ტექნიკისა და ტექნოლოგიების ლაბორატორია, თბილისი, საქართველო

(წარმოდგენილია აკადემიის წევრის შ. სამსონიას მიერ)

ოთხჩანაცვლებული არსონიუმის მარილების ერთ-ერთ უმნიშვნელოვანეს თვისებას, სხვა კოორდინაციული ნაერთებისაგან განსხვავებით, წარმოადგენს კატიონურ-ანიონური კომპლექსების წარმოქმნისადმი მიდრეკილება. კერძოდ, ისინი წარმოქმნიან სპირტ-წყალხსნარებში კატიონურ-ანიონურ კომპლექსებს. შერეულლიგანდიან კომპლექსნაერთებს გამოყენების დიდი პერსპექტივა გააჩნია. სახელდობრ, არსებობს დიდი ალბათობა, რომ ამ ნაერთებს ჰქონდეთ მაღალი და სპეციფიკური ბიოლოგიური აქტივობა. საწყის სარეაქციო მასალად გამოიყენება არსონიუმის მარილი და კადმიუმის ბრომატი, მოლური თანაფარდობით 1:1. რეაქცია ტარდება ოთახის ტემპერატურაზე, სპირტ-წყალხსნარებში. სინთეზირებული დარიშხანორგანული შერეულლიგანდიანი კომპლექსების აღნაგობა და შედგენილობა ტესტირებული იყო როგორც ელემენტური ანალიზით, ასევე კვლევის სხვა ფიზიკურ-ქიმიური მეთოდებითაც.

### REFERENCES

- Ermolaev A.V., Smolentsev A.I. Mironov Y.V. (2015) Use of [Re6Q8(CN)6]4– (Q = S, Se, Te) cluster anions and Cu(I) cationic complexes with 2,2'-bipyridine for the construction of new cyano-bridged coordination compounds. Polyhedron, 102: 417–423.
- 2. Griffith W.P. (1975) Cyanide complexes of the early transition metals (groups IVa-VIIa). Coordination Chemistry Reviews, 17: 177-247.
- 3. Rezanka T., Sigler K. (2008) Biologically active compounds of semi-metals. Phytochemistry, 69: 585–606.
- 4. Zhu C., Guo-Qiang C., Zhi-Xiang S., Sai-Juan C., Zhen-Yi W. (2001) Expanding the use of arsenic trioxide: Leukemias and beyond Seminars in Hematology, 38: 26-36.
- Gigauri R.D., Goderdzishvili L.I., Chernokalski B.D., Injia M., Sabin-Guss I. (1980) Sintez i kompleksoobrazovanie iodidov etildi-(m-tolil) alkilarsoniia s iodidom rtuti(II). Soobshchenie AH GSSR, 99: 605-608 (in Russian).
- 6. Lobzhanidze T., Gigauri R. (2008) Synthesis of Tetraiodozincates and Cadmiates of Iodomethylenetrialkyl(aryl)arsonium and their Physical and Chemical Properties "Chemistry of Advanced Compounds and Materials", 217-223. Book Editors: Nodar Lekishvili, Nova Science Publishers, inc. New-York.
- 7. Gigauri R.D., Robaqidze N.I., Injia M. (2001) Vzaimodeistvie iodidov **bis**[trialkil(aril)arsokii]-1,4-digidronaftalinov s iodidom rtuti (II). *Journal of General Chemistry JOCH*, 71: 568-570 (in Russian).
- 8. Tsintsadze G.V., Tsivadze A.Y., Jashiashvili T.K. (1981) Smeshannie psevdogalogenidnye i psevdogalogenidogalogenidnye soedinenii metallov. Tbilisi (in Russian).
- 9. Peyronel G., Malavasi W., Pignedoli A. (1982) Copper (I), silver (I) and mercury(II) halide complexes of the 3,5-diamino-1,2,4-dithiazolium halides (thiouret hydrohalides). *Spectrochimica Acta*, 38: 1069-1072.
- Nakamoto K. (2009) IR and Raman Spectra of Inorganic and Coordinating Compounds, 6th Edition: 772, P.A. Willey and Sons.

Received January, 2018