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Organic Chemistry

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

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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^{10}-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, d^{10}-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]:

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

Results and Discussion

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

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

#	$[R_2As(R`)CH_2I][Cd(BrO_3)_2{\cdot}I]$		Melting temperature t,^{0}C	μ, molar electroconductivity, om $^{-1}$ cm ^{2} ·mol^{-1}	Was found, %			Bruto- formula	Calculated, %		
	R	R′			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_3H_7	izo-C_3H_7	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_4H_9	C_6H_5	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_4H_9	izo-C_4H_9	183-184	77.6	8.30	12.61	47.75	$C_{13}H_{29}AsCdI_2Br_2O_6$	8.32	12.48	45.97
5	C_6H_5	C_6H_5	139-140	75.2	7.98	11.55	42.92	$C_{19}H_{17}AsCdI_2Br_2O_6$	7.80	11.70	43.10

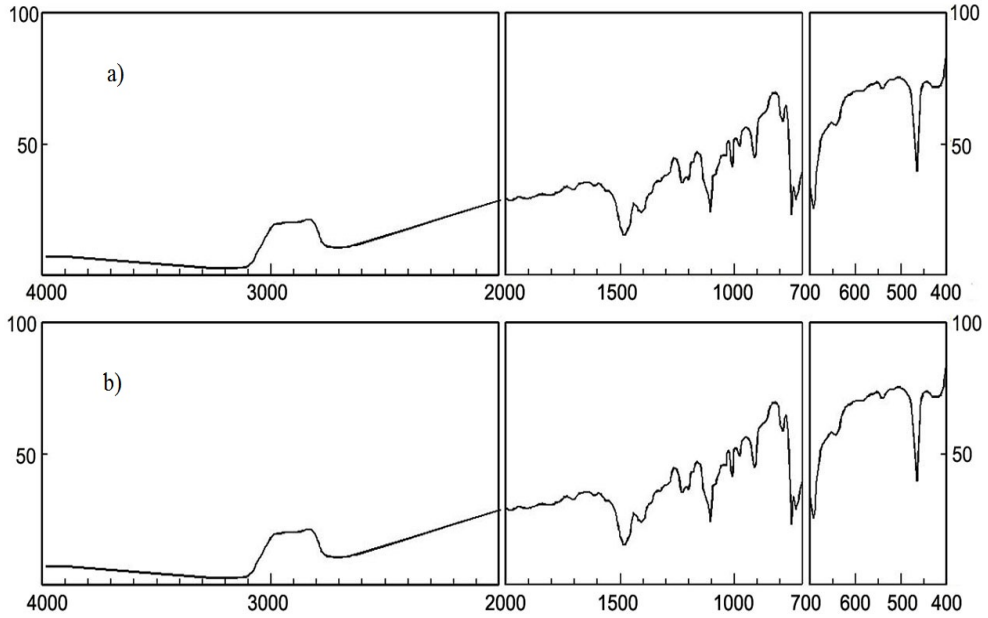

Fig. 1. IR spectrum of absorption in the Vaseline oil: a) $[(C_3H_7)_3AsCH_2I][Cd(BrO_3)_2{\cdot}I]$; b) $[(C_4H_9)_2As(C_6H_5)CH_2I][Cd(BrO_3)_2{\cdot}I]$.

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^{-1} that are characteristic of the bromate ions [10].

To illustrate the above said, we provide the IR spectra of iodidedibromatecadmiates (II) of iodine-methylenetributylphenylarsonium (Fig. 1, a) and iodidedibromatecadmiates (II) of iodine-methylenetripropylarsonium (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

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

#	Loaded substances						Received		
	$[R_2As(R`)CH_2I]I$				$Cd(BrO_3)_2$		$[R_2As(R`)CH_2I][Cd(BrO_3)_2 \cdot I]$		
	R	R`	g	mol	g	mol	g	mol	%
1	C_3H_7	C_3H_7	1,5	00031	1.22	0.0031	2.35	0.0027	86.4
2	izo-C_3H_7	izo-C_3H_7	1,5	0.0031	1.22	0.0031	2.31	0.0026	85.0
3	C_4H_9	C_6H_5	2,0	0.0037	1.44	0.0037	2.83	0.0030	82.2
4	izo-C_4H_9	izo-C_4H_9	2,5	0.0048	1.87	0.0048	3.81	0.0042	87.1
5	C_6H_5	C_6H_5	3,0	0.0052	2.01	0.0052	4.21	0.0043	83.9

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

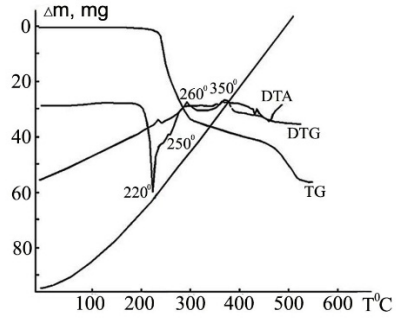

Fig. 2. Thermogram of $[(izo\text{-}C_3H_7)_3AsCH_2I][Cd(BrO_3)_2I]$.

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, $[(Iso\text{-}C_3H_7)_3AsCH_2I]$ 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_2O_5 (theoretically 28.81%) is isolated. Therefore, the thermolysis of the synthesized substance is carried out according to the following scheme:

$$[(Iso\text{-}C_3H_7)_3AsCH_2I][Cd(BrO_3)_2I] \xrightarrow{195\text{-}285^oC} -(Iso\text{-}C_3H_7)_3As;\ -CH_2I_2$$

$$Cd(BrO_3)_2 \xrightarrow[-Br_2O_5]{300\text{-}500^oC} CdO \xrightarrow{t^o} \cdots\cdots$$

By X-ray diffractometer, where recording passes on the CuK_α 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 **Iodinemethyl-enetributylarsonium.** 2.5g Iodinemethylenetr-ibutylarsonium 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 iodinemethylenetributy-larsonium 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%) iododibro-matecadmiates of iodinemethylenetributylarso-nium is obtained. Analysis allowed to find, %: As 8.30; Hlg 45,75; Cd 12,61. $C_{13}H_{29}AsCdI_2Br_2O_6$ 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/I_o Intensity	d_α/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-bromate-cadmiums (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.

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დარიშხანორგანული შერეულლიგანდიანი კომპლექსების სინთეზი და გამოკვლევა

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