

*Inorganic Chemistry*

## Mixed Ligand Pseudo-Halogen Acid-Complexes of Fourthly Substituted Arsonium

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**ABSTRACT.** One of the most important properties of tertiary-substituted arsonium salts with the difference of cations represents inclination to forming the coordination compounds. They can construct cationic-anionic complexes in the alcohol-water solutions. The novelty is in the following: without educing the outlet of arsonium nitrates in the individual condition and by the interaction of cadmium iodated(V) the coordination compounds of  $[R_2As(R)CH_2I]$   $[Cd(IO_3)_2 \cdot CN]$  composition are received. It was established that the spatial arrangement of ligands into the anions and thus hybridization of electronic orbitals of cadmium is stipulated by existence of ligands of iodated-ions. The formation of cyanide admixture of mixed ligand arsonium and purity was established by physical and chemical research methods. © 2017 Bull. Georg. Natl. Acad. Sci.

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

Cyanide and tiocyanide complexes represent considerably easily extragenic substances, than corresponding halogen admixture [1]. Also, the pseudo-halogens of metals have the great perspective of usage in nonferrous-metals industry, galvanic technique and etc. Formation of complex admixtures that are less solvable in water but considerably good soluble in organic solutions gives possibility to separate metal ions from each other [1, 2]. Mixed cylindrical complexes having great perspective and practical value are not yet studied well. The polyfunctionality of compounds as a rule gives possibility to use them in

practice. In this connection there exists great probability that these compounds have high and specific biological activity, because they contain arsenic in their structural units, various organic radicals, cyanide groups, cadmiums etc. [3, 4].

The goal of presented work was to receive the coordination compounds of cadmium(II) diiodattocyanide in chemically pure form and study their physical and chemical properties. For outlet substances cadmium iodate (V), potassium cyanide and arsonium iodate were taken in such quantities, which insure molar relation 1:1:1. Cadmium iodate was

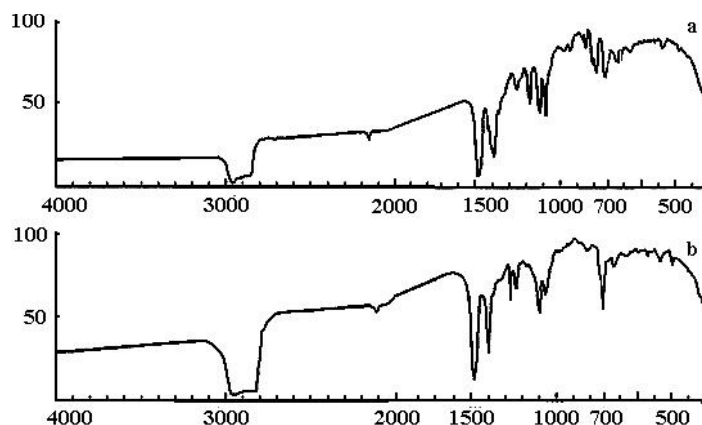
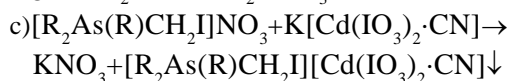
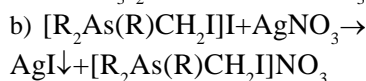
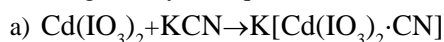


Fig. 1. IR spectrum of absorption in the liquid paraffin:

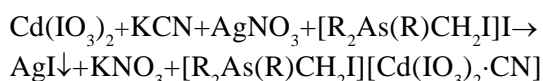
a)  $[(i\text{-}C_4H_9)_3AsCH_2I][Cd(IO_3)_2 \cdot CN]$ ; b)  $[(C_3H_7)_3AsCH_2I][Cd(IO_3)_2 \cdot CN]$ .

solved in the water solution containing potassium cyanide (a-reaction) and afterwards the received mass for reaction was treated by alcohol-water solutions of fourthly substituted arsonium (c-reaction) nitrate. The latter represents filter received consequently by interaction of iodinemethylnetrialkyl (aryl)arsonium iodides with mercury nitrate in the alcohol-water solution. As a result of reaction white colored narrow crystalline compounds are received, physical and chemical analyses of which shows that synthesized substances represent diiodatocyanocadmates(II) of iodinemethylnetrialkyl(aryl)arsonium [5-8].

Formation of final products is explained by the following totality of sequence reactions:



Or in summarized form:

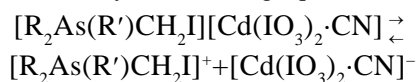


where R and R' are organic radicals and herewith  $R=R'$  or  $R \neq R'$ .

## Results and Discussion

The coordination formulas of the synthesized complex compounds were established by the data of molar electroconductivity of the dilute solutions. As the diiodatocyanocadmiate (II) of the iodinemethylen-

trialkyl (aryl) arsonium is not solvable in water, its molar electro conductivity was studied in the solution of dimethylformamide. Results are presented in Table 1. The Table shows that molar electroconductivity of the investigated samples fluctuate in the frames of  $58\text{--}84\text{Om}^{-1}\text{cm}^2\text{mol}^{-1}$  that corresponds to double ionic electroconductivity of electrolytes [9]. Basing on this fact it can be concluded that synthesized compounds represent cationic-anionic complexes, which are dissociated in the dimethylformamide solution by the following equation:



Structure of the investigated samples was established by the IR spectrum. Outlet of iodinemethylnetrialkyl (aryl)arsonium iodides and IR spectral analyses of the synthesized compounds show the creation of fourthly substituted diiodatocyanocadmates(II) ( Fig. 1). Absorption stripes of  $As-C_{alip}$  bindings are observed in the range of  $625\text{cm}^{-1}$ , which means that the arsenic is in  $sp^3$  hybridized condition [10].

Absorption stripes of oscillations for phenyl group are observed in the  $1580, 1700, 3000\text{--}3080\text{cm}^{-1}$  regions. Concerning the valence oscillations of bonds of  $(IO_3^-)$  and  $(CN)$  groups, their corresponding absorption stripes are in the  $750\text{ cm}^{-1}$  and  $2150\text{ cm}^{-1}$  regions.

Thus, this investigation shows that IR spectrum of initial substances and final products almost do

**Table 1.**  
Some physical and chemical constants of diiodatocyanadmiates(II) of iodinemethylenetrialkyl(aryl)arsonium

#	[R <sub>2</sub> As(R)CH <sub>2</sub> I] [Cd(IO <sub>3</sub> ) <sub>2</sub> ·CN]		Melting temperature, t, °C	μ, molar electroconductivity, Ωm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	Was found, %			Brutto-formula	Calculated, %		
	R	R'			As	Cd	I		As	Cd	I
1	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	218-219	83.5	8.75	13.36	45.46	C <sub>11</sub> H <sub>23</sub> AsCdI <sub>3</sub> O <sub>3</sub> N	8.99	13.48	45.71
2	Izo-C <sub>3</sub> H <sub>7</sub>	Izo-C <sub>3</sub> H <sub>7</sub>	160-161	79.1	9.12	13.29	45.39	C <sub>11</sub> H <sub>23</sub> AsCdI <sub>3</sub> O <sub>3</sub> N	8.99	13.48	45.71
3	C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	53-54	58.9	8.61	12.45	42.73	C <sub>16</sub> H <sub>25</sub> AsCdI <sub>3</sub> O <sub>3</sub> N	8.37	12.55	42.55
4	Izo-C <sub>4</sub> H <sub>9</sub>	Izo-C <sub>4</sub> H <sub>9</sub>	119-120	75.5	8.21	13.01	43.42	C <sub>14</sub> H <sub>29</sub> AsCdI <sub>3</sub> O <sub>3</sub> N	8.56	12.83	43.52
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	108-109	74.2	7.89	12.21	40.33	C <sub>20</sub> H <sub>17</sub> AsCdI <sub>3</sub> O <sub>3</sub> N	8.01	12.01	40.73

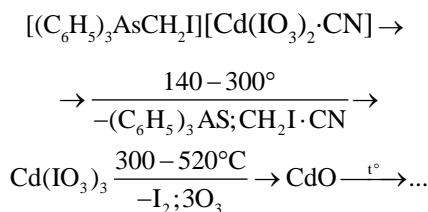
**Table 2.**  
The obtained of cyanodiiodatocadmiates(II) of iodinemethylenetrialkyl(aryl)arsonium, loaded substances and outlet of synthesized complexes

#	Loaded substances										Received	
	[R <sub>2</sub> As(R')CH <sub>2</sub> I]I				AgNO <sub>3</sub>		Cd(IO <sub>3</sub> ) <sub>2</sub>		KCN		[R <sub>2</sub> As(R')CH <sub>2</sub> I][Cd(IO <sub>3</sub> ) <sub>2</sub> ·CN]	
	R	R'	g	mol	g	mol	g	mol	g	mol	g	%
1	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	2.0	0.0042	0.72	0.0042	1.95	0.0042	0.27	0.0042	294	83.5
2	Izo-C <sub>3</sub> H <sub>7</sub>	Izo-C <sub>3</sub> H <sub>7</sub>	2.0	0.0042	0.72	0.0042	1.95	0.0042	0.27	0.0042	2.89	82.0
3	C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub>	1.5	0.0028	0.47	0.0028	1.29	0.0028	0.18	0.0028	1.97	78.6
4	Izo-C <sub>4</sub> H <sub>9</sub>	Izo-C <sub>4</sub> H <sub>9</sub>	1.5	0.0029	0.49	0.0029	1.34	0.0029	0.19	0.0029	2.0	80.4
5	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	2.0	0.0034	0.59	0.0034	1.61	0.0034	0.22	0.0034	2.5	79.7

not differ from each other, if we do not take into account the absorption stripes of  $(\text{IO}_3^-)$  and  $(\text{CN})$  groups. This fact indicates that arsenic is in the cation composition of the investigated sample.

Thermosteadiness of the synthesized diiodoattocyanocadmates(II) was investigated by the thermo-gravimeter analyze method. As an example, the thermogram of diiodoattocyanocadmates(II) of iodmethylenetri- butyl- arso- nium is presented in Fig.2. The mass reduction is 50-71 % in the range of 140-300 °C. In this interval organic fragments are lost. The  $(\text{C}_6\text{H}_5)_3\text{AsCH}_2\text{I}\cdot\text{CN}$  is removed (theoretically 50, 56 %). More difficult is the process of thermolysis with nonorganic fragments. The mass losses are 35, 25 % in the 310-520 °C interval, which means that  $\text{I}_2\text{O}_5$  (theoretically 35, 70 %) is removed.

Thus, thermolysis of the investigated samples can be presented by the following scheme:

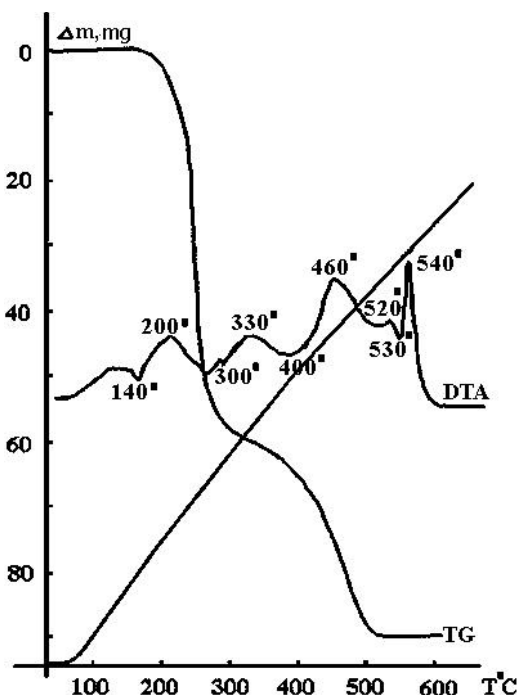


By X-ray diffractometer, where recording passes with the  $\text{CuK}_\alpha$  radiation, investigation of samples proved that all the synthesized samples are crystal-line substanses and do not contain initial components even in admixture (Table 3).

**Table 3.**

**The analysis of X-ray diffraction result for synthesized samples**

[(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> AsCH <sub>2</sub> I][Cd(IO <sub>3</sub> ) <sub>2</sub> CN]	
I/I <sub>0</sub> 060,96603	d <sub>7</sub> /n
100	8.84
25	5.37
30	4.13
40	3.708
30	3.52
5	3.03
5	2.64
5	2.56
-	-
-	-



**Fig. 2.** Thermogram of  $[(\text{C}_6\text{H}_5)_3\text{AsCH}_2\text{I}][\text{Cd}(\text{IO}_3)_2\cdot\text{CN}]$ .

## Conclusion

Thus, perfectly new mixed-ligand cyano-iodatto-cadmates(II) were synthesized and investigated by us. It was determined experimentally that synthesis, composition and structure of complexes of this type is not vastly dependent on the molar relations of reagent substances. The novelty is in the following: the yeild of arsonium nitrates under the individual condition and by the interaction of cadmium iodate(V) coordination the compounds of  $[\text{R}_2\text{As}(\text{R})\text{CH}_2\text{I}][\text{Cd}(\text{IO}_3)_2\cdot\text{CN}]$  composition are received without loss. It was established that special arrangement of ligands in the anions and thus hybridization face of electronic orbitals of cadmium is stipulated by the existence of ligands of iodate-ions.

## Experimental Part

Cyanodiiodattocadmates(II) of iodinemethylentributylarsonium. The 1.5 g iodmethylentributylarsonium iodide solved in the ethylene alcohol under permanent stirring condition is added to 0.49 g water solution of mercury(I) nitrates. Yellow colored sediment

(AgI), is instantly formed, in mother liquid for 2-3 hours and then is filtered by Schottky No.4 filter.

Water solution of 1.34 g cadmium iodate and 0.19 g calcium cyanide are simultaneously prepared and added to the water solution of iodomethyltributylarsonium nitrate. White colored crystalline substance is instantly formed, which we leave for 24 hours and then filter. The sediment is removed before forming the constant mass in the vacuum-exsiccator of phosphorus pent oxygen. The 2.0 g (80.4 %) cyanidiodiodocadmiate(II) of iodomethyltributylarsonium is received, whose melting point is  $t_{\text{melt}} = 119-120^{\circ}\text{C}$ . By analysis it is found,

in %: As 8.21; Hlg 43.42; Cd 13.01.  $\text{C}_{14}\text{H}_{29}\text{AsCdI}_3\text{O}_6\text{N}$ . It is calculated, %: As 8.56; Hlg 43.52; Cd 12.83.

Tertiary substituted arsonium cyanodiodocadmiate(II) was received. Loaded substances and purpose products yield needed for reactions is presented in Table 2 and some physical and chemical constants of the synthesized substances are given in Table 1.

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არაორგანული ქიმია

## ოთხჩანაცვლებული არსონიუმის შერეულლიგანდიანი ფსევდოჰალოგენიდური აციდოკომპლექსები

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ოთხჩანაცვლებული არსონიუმის მარილების ერთ-ერთ უმნიშვნელოვანეს თვისებას, მარტივი კატიონებისგან განსხვავებით კოორდინაციული ნაერთების წარმოქმნისადმი მიდრეკილება წარმოადგენს. კერძოდ, ისინი წარმოქმნიან კატიონურ-ანიონურ კომპლექსებს სპირტ-წყალხსნარებში. ამრიგად, შერეულლიგანდიანი არსონიუმის ციანიდური ნაერთების წარმოქმნა და სისუფთავე დადგენილ იქნა ფიზიკურ-ქიმიური კვლევის მეთოდებით.

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