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SYNTHESIS, STUDY AND USE OF NEW TYPE BIOLOGICALLY ACTIVE ARSENIC-ORGANIC COMPLEX COMPOUNDS

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Abstract. The interaction of tetra substituted arsonium iodides with zinc iodide and potassium cyanide have been studied. By using of the data of physical, chemical and elemental analysis methods the composition and structure of synthesized compounds have been established. New composite materials of multifunctional application for individual and environmental protection, based on the silicon-organic carbofunctional oligomers and obtained complex compounds have been created. It was shown that the created composites could be used as protective covers (film materials and impregnating compositions) resistant to biocorrosion and as a biologically active polymer materials for protection of archaeological and museum exhibits.

Keywords: arsenic salt, complex compounds, bioactivity, d^{10}-elements, antibiocorrosive cover.

1. Introduction

As it is known, zinc represents the most important element in many respects for all living organisms. It is essential for synthesis of enzyme carbon hydrate existing in erythrocytes, which is important for respiration processes. Zn^{2+} ions produce complex compounds with the ligands containing nitrogen and oxygen donor atoms, which are of interest in many respects because they are included in composition of active center of vitally important enzyme.

Zinc is included in various animal organs. It participates in production of active form of insulin and is used for assignment of hormonal activation of synthesized insulin. Based on this fact our purpose was synthesis of bioactive complexes, which contain such biologically active elements as arsenic, zinc, nitrogen and organic radicals. Following from the above mentioned we decided that coexisting of these elements will increase physiological activity of synthesized complexes.

Application of arsonium salts for synthesis of coordination compounds is the priority in chemistry of arsenic-organic compounds. They easily form cationic-anionic complexes [1], soluble salts of tetraalkyl(aryl)arsonium are successfully used for precipitation of ions (their common salts are highly soluble in water) [2]. It is known that d^{10}-elements easily form pseudo-halogen acid-complexes with different composition and structure. Based on these facts, we have tried to ascertain the coordination sequence of ligands and biologic activity of such compounds [3].

At present, many synthetic polymer materials are susceptible to attack by various microorganisms which leads to products damage or destruction. Growth and colonization of microorganisms on material surfaces may cause an epidemiologically dangerous situation in environment, caused by large-scale propagation of microorganisms.

Protection of cultural inheritance is a global problem. Historical buildings, archaeological artifacts, museum exhibits – all of them need protection from the influence of various aggressive microorganisms.

One of the ways to preserve synthetic and natural polymeric materials and cultural inheritance is creation of novel coatings providing antibacterial protection. Antibiocorrosive covers contain two components: biologically active compound and polymer matrix, where the biologically active compound is dropped [4].

2. Experimental

Potassium-tetrasubstituted arsonium tetracyanozincate(II). In Erlenmeyer flask, in the aqueous solution of 0.74 g of zinc iodide and 0.73 g potassium cyanide under permanent stirring

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iodmethylentributylarsonium in alcohol solution was added. The flask was leaved for 2 days. Later precipitate was filtered, washed and dried in vacuum-drier over P_2O_5. 1.23 g of potassium-tetra substituted arsonium tetra cyanozincate (II) was obtained (86.5 % from theor.). Other cationic-anionic complexes were synthesized by analogy. Some characteristics of the synthesized compounds are presented in Table 1.

Table 1

Some characteristics of synthesized complex compounds $[R_2As(R`)CH_2I]K[Zn(CN)_4]$

R	R'	Melting point, K	Molar electro conductivity, $Om^{-1}\cdot cm^2\cdot mol^{-1}$	Found, %				Brutto-formula	Calculated, %			
				As	Zn	N	I		As	Zn	N	I
C_4H_9	C_6H_5	423–424	83.6	11.86	10.24	8.85	20.41	$C_{19}H_{25}AsKZnN_4I$	12.19	10.56	9.10	20.65
C_4H_9	C_4H_9	443–444	92.0	12.56	11.02	9.24	20.98	$C_{17}H_{29}AsKZnN_4I$	12.60	10.92	9.41	21.34
iso-C_4H_9	*iso*-C_4H_9	507–508	95.1	12.43	10.78	9.71	21.56	$C_{17}H_{29}AsKZnN_4I$	12.60	10.92	9.41	21.34
C_5H_{11}	C_6H_5	395–396	80.3	11.81	9.84	8.65	19.65	$C_{38}H_{58}AsKZnN_4I$	11.66	10.10	8.70	19.75
C_6H_5	C_6H_5	509–510	77.6	11.33	9.90	8.50	19.21	$C_{23}H_{17}AsKZnN_4I$	11.45	9.92	8.54	19.38

Table 2

The quantities of initial compounds for obtaining of tetrasubstituted arsonium tetracyanozincates (II)

For the reaction iodomethylenetrialkyl(aryl)arsonium was taken								Yield		
$[R_2As(R')CH_2I]I$				ZnI_2		KCN		$[R_2As(R')CH_2I]K[Zn(CN)_4]$		
R	R′	g	mol	g	mol	g	mol	g	mol	%
C_4H_9	C_6H_5	2.5	0.0046	0.74	0.0023	0.73	0.0112	1.23	0.0020	86.5
iso-C_4H_9	*iso*-C_4H_9	2.5	0.0048	0.77	0.0024	0.75	0.0116	1.21	0.0020	84.3
C_5H_{11}	C_6H_5	3.0	0.0053	0.85	0.0026	0.83	0.0128	1.36	0.0021	79.6
C_4H_9	C_4H_9	2.5	0.0048	0.77	0.0024	0.75	0.0116	1.17	0.0019	80.9
C_6H_5	C_6H_5	3.5	0.0060	0.97	0.0030	0.95	0.014	1.66	0.0025	83.2

Preparation of the antibiocorrosion covers: to bioactive complex compounds (≤ 3 %) and oligo-organosiloxane MF-AMA (modifier for matrix compound ≤ 10 %) in composition with ED-26 (matrix) the hardening agent – hexamethylenediamine (≤ 5%) was added. The mixture was stirred until obtaining a homogenous mass. Later, the produced thin layers on the surface of the selected material (lead, plastic, *etc*.) were kept in air for 24–48 h at room temperature [5].

3. Results and Discussion

Our purpose was to study hydro-chemical interaction of tetra substituted arsonium and zinc iodides in potassium cyanide solution.

Experiments were carried out at room temperature. In the aqueous solution of zinc iodide and potassium cyanide, under permanent stirring, alcoholic solution of tetra substituted arsonium iodide was added, initial compounds were taken in molar ratio $[R_3AsCH_2I]I : ZnI_2 : KCN$ = 2:1:4. 10–20 % of KCN surplus in comparison with the theoretical amount was used. Instantly after mixing the solutions of initial compounds white crystalline substance was formed (Table 2).

As cadmium iodide easily forms acid-complexes with tetra substituted arsonium iodide [8, 9], we expected to obtain cationic-anionic coordination compounds according to the scheme:

$$2[R_3AsCH_2I]I + ZnI_2 \rightarrow [R_3AsCH_2I]_2[ZnI_4] \quad (1)$$

However, based on elemental analysis it was established that 1 atom-mole arsenic corresponds to 1 atom-mole of iodide [but not 3, as according to the scheme (1)].

Like that in the presence of excess amount of potassium cyanide, formation of the products of interaction of iodmethylentrialkyl(aryl)arsonium iodide and zinc iodide can be explained by the scheme:

$$[R_3AsCH_2I]I + ZnI_2 + 4KCN \rightarrow \\ \rightarrow [R_3AsCH_2I]K[Zn(CN)_4] \quad (2)$$

The composition of synthesized compounds has been established by physical, chemical, and elemental analysis methods. Namely, in the solution of dimethylformamide the molar electro-conductivity has been studied. The values of the molar electro-conductivity

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in the interval of 77–92 $Om^{-1}\cdot cm^2\cdot mol^{-1}$ have changed (Table 1).

In IR-spectra [10] of the synthesized compounds the characteristic absorption bands have been detected at 430 and 515 cm^{-1} (Fig. 1) typical for ν(MC) and δ(MCN) vibrations. The absorption band at 630cm^{-1} of As-C_{alk} was detected indicating sp^3 hybridization state. The absorption band of coordinated CN group ν(CN) at 2160 cm^{-1} has detected. This data is higher than for bi-ionic complexes, but less than for tri-ionic complexes. Analogical occurrence has been registered in [9] and the authors explain this fact by partial coordination of anions by complex-forms. Thus $[Zn(CN)_4]^{2-}$ ions are partially associated with arsonium ions and it causes the decrease of molar electro conduction of the solution. Thus, in the solution the following process can by realized:

$$[R_3AsCH_2I]K\,[Zn(CN)_4] \rightarrow$$
$$\rightarrow K^{+}+\{[R_3AsCH_2I]\,[Zn(CN)_4]\} \qquad (3)$$

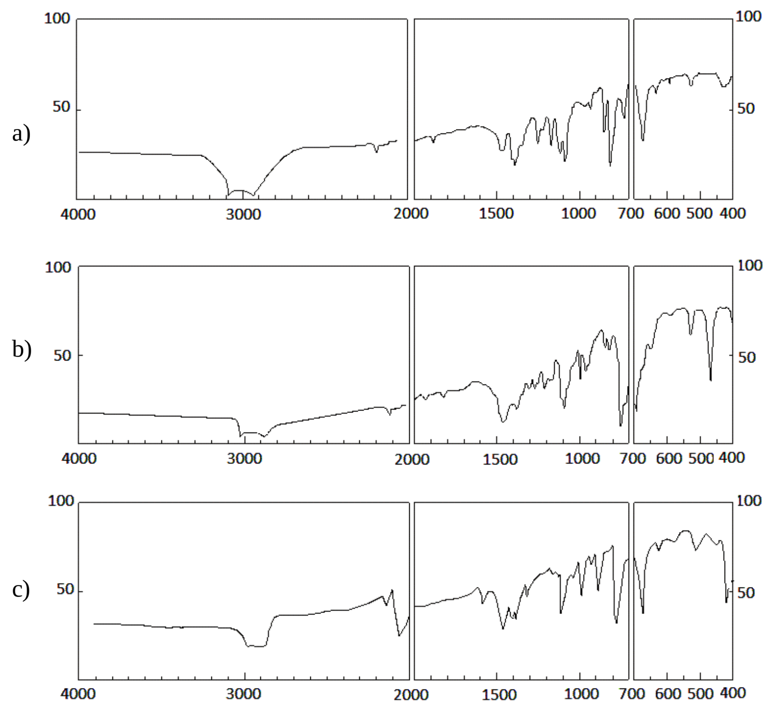

Fig. 1. IR-spectra of absorption in white paraffin oil: $[(iso\text{-}C_4H_9)_3AsCH_2I]K[Zn(CN)_4]$ (a); $[(C_5H_{11})_2As(C_6H_5)CH_2I]K[Zn(CN)_4]$ (b) and $[(iso\text{-}C_3H_7)_3AsCH_2I]K[Zn(CN)$ (c)

Table 3

Results of X-ray analysis of synthesized complex compounds

Complex compound $[(C_5H_{11})_2As(C_6H_5)CH_2I]K[Zn(CN)_4]$	
Intensity, I/I_o	d_α/n
100	12.03
20	10.4
30	5.9
35	4.56
25	4.33
30	4.05
20	3.63
15	3.49
10	3.24
30	3.19
15	3.07
20	2.60
25	2.56
5	2.36
10	2.31
5	2.23

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Thermolysis of the synthesized compounds has been studied (Fig. 2). The sample in 463–593 K interval lost 76.17 % of its mass, that indicates the loss of whole "organics" (theoretically 69.44 %); loss of the mass in 593–753 K interval is equal to 10.78 %, one mole KCN is separated (theoretically 10.92 %). The scheme of thermolysis can be presented as:

$$[R_3AsCH_2I]K[Zn(CN)_4] \xrightarrow[-(C_4H_9)As]{463\text{-}593\ K}$$

$$K[Zn(CN)_4] \xrightarrow[-KCN]{593\text{-}753\ K} Zn(CN)_2 \xrightarrow{T,\ K} \qquad (4)$$

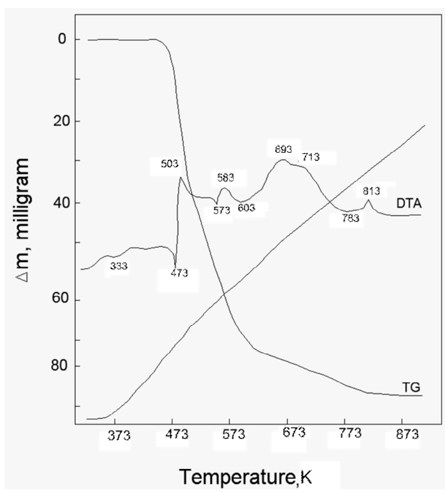


Fig. 2. DTA and TGA curves of $[(C_4H_9)_3AsCH_2I]K[Zn(CN)_4]$

Antibiocorrosive covers contain two components – biologically active compounds and polymer matrix, where the biologically active compound is dropped [8]. Some polyfunctional hetero-chained organic polymers, such as polyurethane elastomers, polyurethane-acrylates, ionomers, *etc*., have been successfully used as a matrix for creation of antibiocorrosive covers. The polymer matrix for the antibiocorrosive covers may be also obtained based on polyepoxide resins in mass in the presence of active diluents. The use of the organic polyepoxide resins ED-20 and ED-26 did not give the satisfactory results for creation of the matrix for antibiocorrosive coatings. For modification of the above-mentioned coatings, we have used silicon-organic oligomers with fluorine alkyl radicals at silicon atoms [5].

$$nMe_3SiO[i\text{-}(MeHSi)_a(Me_2SiO)_b(MePhSiO)_c]_mSiMe_3 + $$
$$+ \ mb\ CH_2{=}CHC(O)OCH_2(CF_2)_5CF_2H \longrightarrow$$
$$\longrightarrow Me_3SiO[\underset{\displaystyle CH_2CH_2C(O)OCH_2(CF_2)_5CF_2H}{\underset{|}{MeSiO}})_a(MeSiO)_b(MePhSiO)]_mSiMe_3$$

where: $a = 0.3$, $b = 0.4$, $c = 0.3$; $m = 10$ (5)

Addition of fluoride acrylate containing oligomers to polyether amide and polyepoxide (ED-26) improves hydrophobic properties and thermal characteristics, but fixation of the above mentioned oligomers is difficult. To simplify the process of hardening of silicon-organic modifiers, we have synthesized the new fluorine-containing carbofunctional oligoorganosiloxane with methacrylic groups at silicon atoms (MF-1-AMA-F$_3$):

$$Me_3SiO[(Me_2SiO)_a\left(\begin{matrix}Me\\|\\SiO\\|\\R\end{matrix}\right)_{3n}(\underset{\displaystyle (CH_2)_3-O(O)C-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2}{\underset{|}{SiMeO}})_b(SiMePhO)_c]_mSiMe_3$$

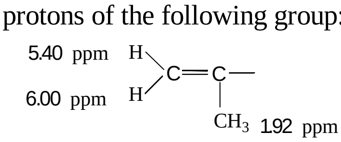
where, $R = CH_2CH_2CF_3$ (6)

$a = 0.3$, $b = 0.4$, $c = 0.3$; $m \approx 10$

In the IR spectra of synthesized compounds together with absorption bands (1040–1090 cm^{-1}, 1425 cm^{-1}, 1440 cm^{-1}, 1330 cm^{-1}, 2970 cm^{-1}, 1605 cm^{-1}, 3080 cm^{-1}) related to SiOSi, $SiCH_3$, SiC_6H_5, CH_3 and C_6H_5 groups absorption bands related to $H_2C{=}C$ (in acrylic groups), C=O (in ester groups) and C–F group (in CF_2 groups) (1640 cm^{-1}, 1720 cm^{-1}, 1330 cm^{-1}) were found. In IR spectra a week maximum of absorption related to Si–H group was also observed, confirming non-complete (100 %) conversion of Si–H groups. The synthesized oligomer is viscous liquids soluble in acetone, dioxane, benzene, and toluene.

On the basis of the above mentioned polymer matrix and the complex compounds, we have prepared the antibiocorrosive covers. The obtained compositions are available, their creation do not need any technical equipments. The basic properties of protective layers (homogeneity, viscosity, compatibility of polymer matrix components with bioactive compounds), physical and chemical characteristics (water absorption $\leq$ 0.2 %), and adhesion strength $\geq$ 4.0 MPa) are in compliance with the compositions of protective layers of objective types [5].

In the ^{1}H NMR spectrum of the hydrosilylation product (Fig. 3) the resonance signals with chemical shifts of 1.92 ppm, 5.40 ppm and 6.00 ppm were identified, related to the protons of the following group:



(7)

In the spectrum one can also observe the resonance signals of phenyl-protons with chemical shifts in the range of 7.0–7.6 ppm. Resonance signals with chemical shifts of 1.2 ppm typical of the protons of methylene groups, as well as resonance signals with chemical shifts of 1.1 ppm related to the CH_2–CH_2 (α) and CH_3–CH (β)fragments of feasible derivation of Markovnikov and anti-Markovnikov addition products were also observed.

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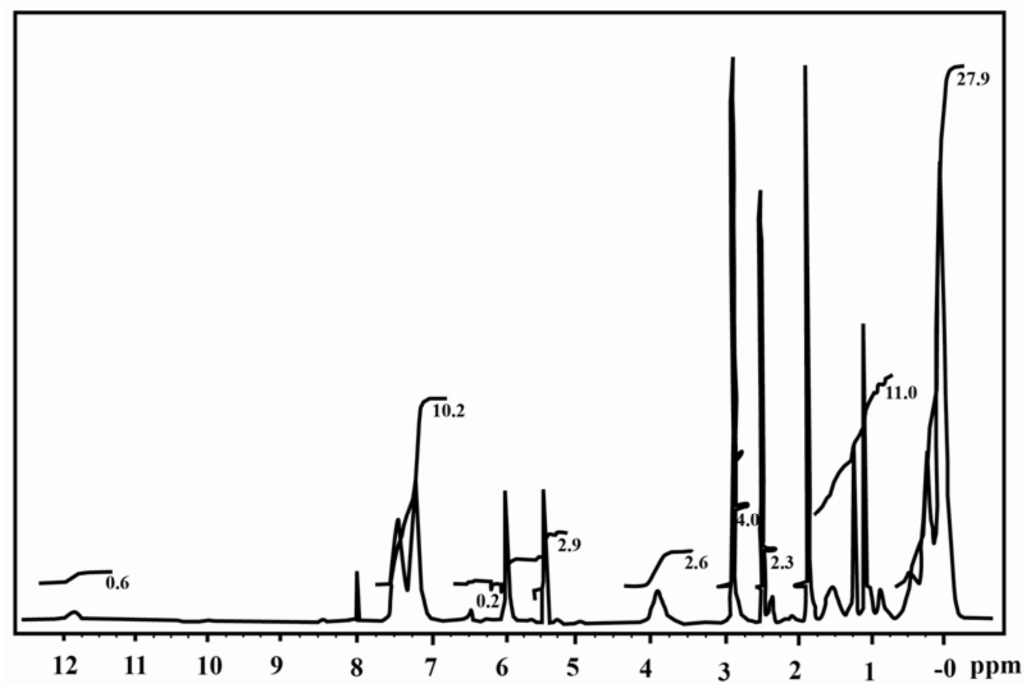

Fig. 3. ^{1}H NMR spectrum of the hydrosilylation product

In the ^{13}C NMR spectrum of the same sample one can observe the presence of the resonance signal with the chemical shift 65.75 ppm related to the carbon of the OCH_2 group and the resonance signal with the chemical shift 17.71 ppm related to the carbon of CH_3-group, which also indicates formation of both (Markovnikov and anti-Markovnikov) products:

$$\underset{12.63\text{ ppm}}{Si-CH_2}-\overset{21.61\text{ ppm}}{CH_2}-\underset{65.75\text{ ppm}}{CH_2}-O\ ,$$
$$\underset{18.60\text{ ppm}}{CH_3}-\overset{28.95\text{ ppm}}{\underset{|\atop Si}{CH}}-\underset{65.75\text{ ppm}}{CH_2}-O \qquad (8)$$

By the ratio of integral intensity of corresponding resonance signals we determined the ratio of *a* and *b* adducts (39.13 : 60.87).

We studied the thermal-oxidative stability of the synthesized organosiloxane by DTA and TGA analysis methods. We established that their destruction is starting at 553–563 K. The intensive destruction process proceeds above 723 K.

The created composites may be recommended as a protective covers with versatile application (film materials and impregnating compositions) stable to biocorrosion and as a biologically active polymer materials for protection of archaeological and museum exhibits. We manufactured antibiocorrosive covers for goods from different materials based on the synthesized bioactive compounds dropped into the aforementioned polymer matrix. Their water absorption ability (0.1–0.15 %), and adhesion strength (≥ 4.2 MPa) are in compliance with the compositions of protective layers of objective types.

4. Conclusions

The interaction of tetra substituted arsonium iodides with zinc iodide and potassium cyanide have been studied. Using physical, chemical and elemental analyses the composition and structure of synthesized compounds have been established.

The created composites may be recommended as: a) protective coatings (film materials and impregnating compositions) stable to biocorrosion; b) materials with antimycotic properties for prophylaxis and treatment of mycosis; c) biologically active polymer materials for archaeological and museum exhibits protection and d) for human protection during their contact with micro-organisms.

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References

[1] Robaqidze N.: PhD thesis. Javakhishvili Tbilisi State University, Tbilisi 1997.
[2] Gigauri R., Goderdzishvili L., Chernokalski B. *et al.*: Sobsheniya Acad. Nauk Gruzinskoi SSR, 1980, **99**, 605.
[3] Brostow W., Gahutishvili M. *et al.*: Chem. Eng. J., 2010, **159,** 24.
[4] Grekov A., Veselov V. *et.al.*: Pat. 14952A Ukraine. Publ. March 04, 1997.
[5] Lekishvili N., Barbakadze Kh., Zurabishvili D. *et al.*: Oxid. Commun., 2010, **1**, 104.
[6] Lobzhanidze T., Gigauri R., Rusia M. and Kikalishvili M.: Georg. Eng. News, 2002, **3**, 116.
[7] Lobzhanidze T. and Gigauri R.: Synthesis of Tetraiodozincates and Cadmiates of Iodomethylenetrialkyl(aryl)arsonium and their Physical and Chemical Properties. Nova Sci. Publ., New York 2008.
[8] Gigauri R., Robaqidze N. and Injia M.: Zh. Obshchei Khimii, 2001, **71**, 568.
[9] Peyronel G., Malavasi W. and Pignedoli A.: Spectrochim. Acta., 1982, **38**, 1069.
[10] Nakamoto K.: IR and Raman Spectra of Inorganic and Coordinating Compounds. 3rd edn., John&Willey, New York 1978.

СИНТЕЗ, ДОСЛІДЖЕННЯ ТА ВИКОРИСТАННЯ НОВОГО ТИПУ БІОЛОГІЧНО АКТИВНИХ АРСЕНО-ОРГАНІЧНИХ КОМПЛЕКСНИХ СПОЛУК

Анотація*. Вивчено взаємодію тетра-заміщених йодидів арсенію з йодидом цинку і ціаністим калієм. За допомогою фізичного, хімічного та елементного методів аналізу встановлено склад і структуру синтезованих сполук. На основі кремній-органічних карбофункціональних олігомерів та отриманих комплексних сполук створені нові композиційні матеріали багатофункціонального призначення для охорони навколишнього середовища. Показано, що створені композити можуть бути використані як захисні покриття (плівкові матеріали та просочувальні композиції), стійкі до біокорозії і як біологічно активні полімерні матеріали для захисту археологічних та музейних експонатів.*

Ключові слова*: миш'якова сіль, комплексні сполуки, біологічна активність, d^{10}-елементи, антибіокорозійне покриття.*

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