



SYNTHESIS AND STUDIES OF BROMIDE COMPLEXES OF COPPER (II) AND CADMIUM (II) WITH ARSENIC CONTAINING LIGANDS

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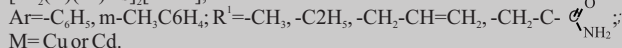
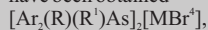
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ABSTRACT

The interaction of $K_2[MBr_4]$ (where $M = Cu(II)$ or $Cd(II)$) with tetrasubstituted arsonium nitrates in aqueous-alcoholic solutions has been studied. As a result of the reaction, tetrabromocuprates (II) or tetrabromocadmates (II) of arsonium

have been obtained



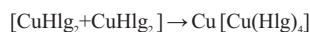
$M = Cu$ or Cd .

The composition and structure of synthesized compounds was established by elemental analysis, as well as various physical and chemical methods of analysis. The IR-spectrum of the synthesised compounds indicates the quaternization of the atom of arsenic and its presence in the complex cation. The cationic-anionic composition of the samples under study has been established by determining the molar conductivity in dimethyl formamide. These analyses indicate the formation of three ions as a result of dissociation.

KEYWORDS : quaternization of the atom of arsenic, arsonium salts, thermogravimetric analysis, cationic-anionic composition.

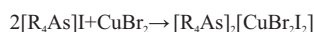
INTRODUCTION

Copper (II) belongs to a group of elements that easily form complex compounds. Among the set of complex anions, it is necessary to mark out the $[Cu(Hlg)_4]^{2-}$ ion, which is formed in concentrated aqueous solutions of copper (II) halides and determines the green color of these solutions [1].

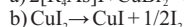
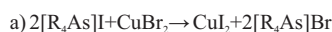
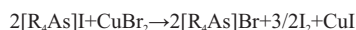


After the further dilution, the above-mentioned anions are transformed into the hydrate form $[Cu(H_2O)_4]^{2+}$, as a result of which a green shade of solutions turns into a bluish-gray color. The selection of cations, which could facilitate precipitation of $[Cu(Hlg)_4]^{2-}$ ions in the form of insoluble complex compounds is associated with a set of technical difficulties [2].

In this regard, we considered it possible to obtain copper (II) cationic-anionic complexes, the anion of which would contain mixed ligands:



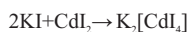
However, all attempts appeared to be futile. As a result of the interaction of an aqueous solution of copper (II) bromide and an aqueous-alcoholic solution of tetrasubstituted arsonium iodide, a white powdery substance has been precipitated, which turned out to be copper (I) iodide. It worth mentioning that in case of using saturated solutions of the aforementioned compounds, arsonium ions have been partly precipitated as well. At the same time, it was not possible to obtain target product in a pure form by means of application of common purification methods, like recrystallization, reprecipitation, etc. As it appears, the formation of copper (I) iodide is conditioned by the following successive reactions [4]:

**COMBINED CHEMICAL EQUATION**

As for the deposition of arsonium cations in saturated solutions, it is possible that in this case it conditioned by a co-precipitation. The evidences were obtained, that under these conditions the formation of the four-substituted arsonium iodide and copper (II) bromide does not occur due to the thermodynamic state of copper (II) iodide.

According to the published scientific papers [3], the end products of the

chemical interaction between cadmium iodide and arsonium salts are the corresponding tetraiodocadmates. The yield of final products of the reaction is significantly increases if the process takes place in a aqueous-alcoholic solution in the presence of an excess of cadmium iodide, which apparently participates in the formation of intermediate products:



These intermediate substances undergo following transformation, as a result of which tetraiodocadmates (II) are precipitated.

EXPERIMENTAL PROCEDURE

The IR spectra were recorded on an UR-20 spectrometer in the interval 400-3700 cm^{-1} using KBr tablets. The specific electrical conductivity of the samples under study in dimethyl formamide was measured at room temperature (25°C) on an "Impulse" conductometer with an accuracy of $\pm 1.5\%$. The temperature stability was maintained with an accuracy of $\pm 0.5\%$. Molar electro-conductivity was calculated according to the formula $\mu = 1000\chi/s$ ($Ohm^{-1} \cdot cm^2 \cdot mol^{-1}$), where χ and c are the specific electro-conductivity and concentration of the solution, respectively.

Thermogravimetric analysis was carried out on Paulik-Paulik-ErdeyQ-1500D derivatograph (heating rate 10°C/min, normal air, mass of the samples 0.1 g, platinum crucible). The determination of arsenic was carried out by B.S. Evans's method [9], copper - by iodometric method [10], and - by brom titrimetric method [11].

Tetrabromocadmate (II) of triphenylmethylarsonium. In the aqueous solution of 0.72 g of lead (II) nitrate under permanent stirring 2 g. of triphenylarsonium iodide dissolved in 50 ml of ethanol is added. The yellow sediment is formed instantly. After 2-3 hours, the precipitate is filtered through a Shott's filter #4.

At the same time 0,6 g of cadmium bromide and 0,53 g of potassium bromide is dissolved in 25 ml. of distilled water. The resulting solution is added to the pre-prepared filtrate and left for 24 hours. The next day, the precipitate is filtered using distilled water and alcohol. Then the precipitate is dried in a vacuum-drier over phosphorus pentoxide and paraffin. As a result, 1,80 g. of tetrabromocadmate (II) of triphenylmethylarsonium (colourless crystalline substance) with the melting point of 137-138°C is obtained.

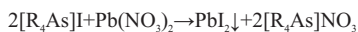
Tetrabromocuprates (II) of triphenylmethylarsonium. 1.44 g of lead (II) acetate is dissolved in 40 ml of distilled water. Under permanent stirring, a solution obtained by addition of 3,5 g. of triphenylmethylarsonium iodide to 50 ml. of ethanol is added to this

solution. The yellow sediment is formed instantly, which is left for 4 hours and then filtered.

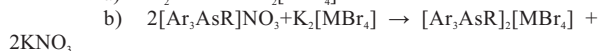
At the same time, the mixture of 0.85 g of copper (II) bromide and 1.82 g of potassium bromide is prepared (the latter is taken in double quantities, in comparison with the theoretical calculation). Then the precipitate obtained during mixing solutions of triphenylmethylarsonium iodide and lead (II) acetate is added to this mixture. As a result, a fine-crystalline precipitate is formed. After 12 hours, the precipitate is filtered and washed three times using distilled water and alcohol. Then the precipitate is dried in a vacuum-drier over phosphorus pentoxide and paraffin. As a result, 2.28 g. of tetrabromocuprate (II) of triphenylarsonium (fine-crystalline substance of greenish colour) with the melting point of 87-88°C is obtained.

RESULTS AND DISCUSSION

Within the framework of this study, we investigated the possibility of obtaining some tetrabromocuprats (II) and tetrabromocadmates (II) of tetrasubstituted arsonium. The aim of the study was to obtain a precipitate of a complexing agent in the form of tetrabromocuprate (II) and tetrabromocadmate (II) of arsonium. Iodides of tetrasubstituted arsonium are used as the initial reagent. In order to prevent the formation of diiodocuprates (I) of tetrasubstituted arsonium, as well as tetraiodocadmates (II) or mixed diiododibromocadmates (II) of tetrasubstituted arsonium, the initial iodides were previously transformed to the corresponding nitrates according to the following reaction:



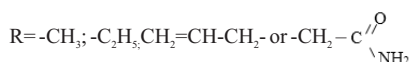
It has been established, that as a result of the interaction of aqueous solutions of copper bromide or cadmium bromide and potassium bromide with aqueous-alcoholic solutions of nitrates of tetrasubstituted arsonium, the sediment of white color is precipitated. As analysis indicates, the precipitate represents tetrabromocuprates (II) and tetrabromocadmates (II) of arsonium, the formation of which is conditioned by the following sequential reactions:



COMBINED CHEMICAL EQUATION



M=Cu or Cd; Ar=-C₆H₅ or m-CH₃C₆H₄



It should be noted that the latter reaction can serve as a basis for the separation of complex salts of copper and cadmium from compounds.

Thus, a significant yield of arsonium complexes with copper (II) bromide and cadmium (II) bromide is obtained as a sediment. Any change in the reaction conditions (like addition of quaternary arsonium nitrate in a fourfold or sixfold amount or a variation of the sequence of addition of reagents), regardless of the nature of the substituent in the benzene ring and the size of the radicals located next to the atom of the arsenic, had any influence on the final result. In all cases, cationic-anionic complex compounds are formed that contain one molecule of copper (II) bromide or cadmium (II) bromide and two molecules of quaternary arsonium bromide (Table 1).

The synthesis reactions were carried out at room temperature. After mixing the reagents and forming a sediment, the latter was separated by filtration. The resulting precipitate was then thoroughly washed, dried and subjected to analysis.

The synthesized compounds represent a finely crystalline substance of bright green (tetrabromocuprate (II) of triarylalkylarsonium) and white (tetrabromocadmate (II) of triarylalkylarsonium) colors, which are insoluble in water, alcohol, acetone and ether. They are relatively well soluble in dimethyl sulfoxide and dimethyl formamide. The composition and structure of the synthesized compounds was established by elemental analysis method, IR spectroscopy and by studying the molar electro-conductivity.

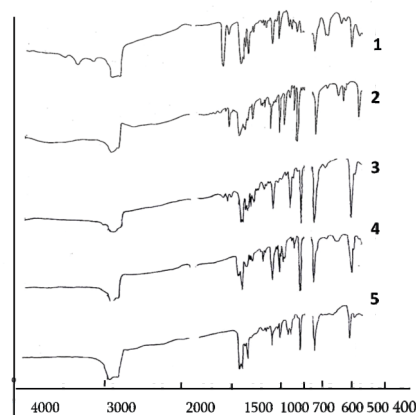
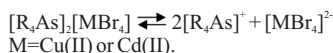


FIGURE 1. IR-SPECTRA

1. Tetrabromocuprate (II) of triphenylacetamidarsonium
2. Tetrabromocuprate (II) of tri-m-tolylmethylarsonium
3. Tetrabromocadmate (II) of triphenylmethylarsonium
4. Tetrabromocadmate (II) of triphenylallylarsonium
5. Tetrabromocadmate (II) of diphenyl-n-butylmethylarsonium

In the IR-spectra of synthesized compounds the characteristic absorption band has been detected at 620 cm⁻¹ (Figure 1), which indicates the quaternization of the atom of arsenic and hence its presence in the cationic complex. The IR-spectra of the studied samples (with the exception of the absorption bands of tetrabromocuprate and tetrabromocadmate) are mainly identical to the IR-spectrum of the original cations of arsonium iodide [5, 6]. The absorption band observed at 1030-1300 cm⁻¹ has been assigned to the stretching vibrations of the C-H aromatic bond, and the absorption band at 1410-1605 cm⁻¹ has been attributed to C=C bond of the core of the aromatic nucleus [7]. The similarity of IR spectra of initial iodides of tetrasubstituted arsonium and synthesized complex compounds confirms the ionic composition of the latter.



The coordination formulas and, correspondingly, the cationic-anionic composition of the synthesized compounds, are also confirmed by the results of the molar electro-conductivity study of their solutions (Table 1). Dimethyl formamide was used as the solvent due to the fact that the samples under study are insoluble in water. The values of molar electro-conductivity of synthesized compounds have changed in the interval of 80-131 ohm⁻¹.cm².mol⁻¹, which indicates the formation of three ions as a result of their dissociation in dimethyl formamide [8]. Consequently, it can be concluded that the synthesized compounds are cationic-anionic complexes that undergo dissociation in dimethyl formamide according to the following formula:



According to the thermal analysis results, it was established that, despite the significant difference in composition, the thermolysis of the samples under study proceeded almost identically. As an example, the derivatogram of tetrabromocuprate (II) of triphenylmethylarsonium is presented (Fig. 2). According to this derivatogram, the process of thermal decomposition of the sample consists of several stages, during which at least three endothermic effects are observed. The first endothermic effect, was observed at 190-400°C interval and the sample lost 41.0% of its mass, which may be attributed to the loss of triphenylmethylarsonium bromide [(C₆H₅)₃AsCH₃]Br (theoretically 39.1%). As it is known, arsonium salts belong to thermally stable compounds [9]. Thus, it can be assumed that in the indicated temperature interval, the separation of the products of decomposition of arsonium salts, rather than the salts itself, occurs. [(C₆H₅)₃AsCH₃]Br \rightleftharpoons (C₆H₅)₃As + CH₃Br

This is also proved by the fact that in the 190-400°C interval the first observed endothermic effect combines two relatively smaller endothermic effects (Fig. 2), which could not be explained by separation of certain constituents from triphenylmethylarsonium bromide.

Yield, melting point, molar electro-conductivity (μ) and elemental analysis data of substituted cations of tetrabromocuprates (II) and tetrabromocadmates (II) of arsonium $[\text{Ar}_2(\text{R})(\text{R}^1)\text{As}]_2[\text{MBr}_4]$.

#	Ar	R	R1	Melting point T, °C	Yield, %	Molar electro-conductivity in dimethyl formamide at 250C μ , Ohm ⁻¹ cm ² mol ⁻¹	Found, %		Brutto-formula	Calculated, %	
							As	Br		As	Br
1	C6H6	C6H5	CH3	156-157	61.1	87.6	14.18	30.92	C38H36As2CuBr4	14.63	32.20
2	m-CH3C6H4	m-CH3C6H4	CH3	117-118	63.5	84.3	13.06	28.48	C44H48As2CuBr4	13.52	28.84
3	C6H5	C6H5	C2H5	87-88	57.1	80.0	13.94	29.84	C40H40As2CuBr4	14.24	30.38
4	C6H5	C6H5	CH2-CH=CH2	88-89	62.0	89.4	13.68	29.35	C42H40As2CuBr4	13.92	29.70
5	m-CH3C6H4	m-CH3C6H4	C2H5	159-160	60.3	82.8	12.82	27.93	C46H52As2CuBr4	13.19	28.13
6	C6H5	C6H5		137-138	56.6	83.2	13.12	28.36	C40H38As2N2O2CuBr4	13.50	28.79
7	m-CH3C6H4	m-CH3C6H4		122-123	69.2	88.2	12.26	26.24	C46H50As2N2O2CuBr4	12.55	26.77
8	C6H5	C6H5	CH3	137-138	75.1	122.5	13.65	29.77	C38H36As2CdBr4	13.79	29.79
9	C6H5	C6H5	CH2-CH=CH2	132-133	77.3	128.4	13.21	28.30	C42H40As2CdBr4	13.32	28.42
10	C6H5	C4H9	CH2-CH=CH2	147-148	78.6	128.0	13.24	28.98	C38H48As2CdBr4	13.81	29.47
11	C6H5	i-C3H7	CH2-CH=CH2	135-136	80.2	126.4	14.02	30.32	C36H44As2CdBr4	14.18	30.25
12	C6H5	n-C4H9	CH3	129-130	78.8	130.5	14.33	30.68	C34H44As2CdBr4	14.51	30.95
13	m-CH3C6H4	m-CH3C6H4	CH2-CH=CH2	140-141	81.5	125.6	12.35	26.75	C48H32As2CdBr4	12.40	26.45
m	m-CH3C6H4	m-CH3C6H4	CH3	171-172	82.2	123.9	12.63	27.60	C44H48As2CdBr4	12.95	27.63

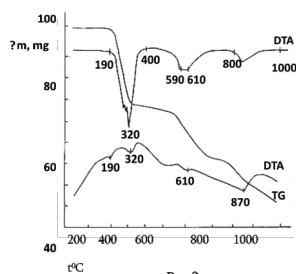
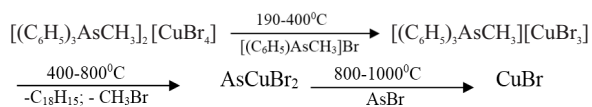


Fig. 2.
DTA and TGA curves of tetrabromocuprate (II) of triphenylmethylarsonium

The second endothermic effect is observed at 800-1000°C temperature interval and accompanied with the loss of mass equal to 16,6%. It should be noted that the sublimation of arsenic starts at 612°C and after reaching 800°C the process of evaporation becomes so intensive, it could be observed visually. On the other hand, copper (II) bromide undergoes decomposition in this temperature range [9]:



It can be assumed that at this stage bromine is partially separated and arsenic if completely separated from the sample under study. Consequently, the process of thermal decomposition of tetrabromocuprate (II) of triphenylmethylarsonium can be described by the following formula



A similar regularity is observed during the thermolysis of other tetrabromocuprates (II) and tetrabromocadmates (II) of tetrasubstituted arsonium.

CONCLUSIONS

Thus, it was demonstrated for the first time that as a result of interaction between potassium tetrabromocuprates (II) or potassium tetrabromocadmates (II) with nitrates or acetates of triaryl(diaryl)alkylarsonium in an aqueous-alcoholic solution the precipitate of tetrabromocuprates (II) or tetrabromocadmates (II) of tetrasubstituted arsonium is formed. It is confirmed that the samples obtained are tri-ionic compounds the composition and structure of which were established by elemental analysis, as well as by modern

physicochemical methods of analysis.

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