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Synthesis and Study of Tetrathioarsenates of d^{10}-Metals

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Abstract: For the first time in hydrochemical conditions tetrathioarsenates of d10-metals by composition Ag_3AsS_4 and $M_3(AsS_4)_2 \cdot H_2O$, where M-Zn, Cd or Hg and X=(Zn) or 2(Cd, Hg), were synthesized. Their composition, constitution, reaction of dehydration and thermal shock resistance in 20-1000 interval were studied by means of thermal analysis, UR-spectroscopy, X-ray crystal determination and derivatographic research.

Keywords: Tetrathioarsenate, IR-spectra, X-ray Crystal Determination

1. Introduction

Among the inorganic compounds of Arsenic (V) d-metals tetraoxoarsenates are well studied [1-8]. Their search was very intensive in last century and now the all methods of their synthesis are developed in detail. This compounds were obtained by hydrochemical, hydrothermal and solid-phase methods. Among this, it is known method of separation of goal-products from alloys in individual condition. But separation-study of all desirable salts by this method is impossible because of their low thermal stability. Therefore, from abovementioned methods hydrochemical method has advantage, because it does not need favorable conditions to be created and moreover it is easy to obtain chemically pure goal-products.

From inorganic compounds of Arsenic (V), as physiologically active compound, metal tetra okcoarsenates have wide application. It concerns both full and alkali salts of transition metals. As for d-metals tetraoxoarsenates with the general (common) formula M3(AsS4)2·nH2O, almost completely uninvestigated not only because of revelation of physiologic activity, but also chemical point of view. Therefore, the aim of our research is the study of for d-metals tetraoxoarsenates synthesis and characteristics of their physical-chemical properties.

2. Research Methods and Initial Data

An attempt to obtain and research tetrathioarsenates of d10-metals by modern physic-chemical methods has been made. To produce tetrathioarsenates of d10-metals we use hydrochemical method as one of the easiest to be implemented for obtaining final products in individual state. As initial substances there were used water soluble salts of d10-metals and sodium tetrathioarsenate (V) which was obtained in the following reaction [1]:

$$3Na_2S + As_2S_3 + 2S + 16H_2O \rightarrow 2Na_3AsS_4 \cdot 8H_2O \quad (1)$$

Based on many experiments it was established that formation of the product for special purpose runs from the following reactions:

$$a)\ Na_3AsS_4 + 3AgNO_3 \rightarrow Ag_3AsS_4 + 3NaNO_3 \quad (2)$$

$$b)\ 2Na_3AsS_4 + 3MX_2 + nH_2O \rightarrow M_3(AsS_4)_2 \cdot 2nH_2O + 6NaX \quad (3)$$

where M=Zn, Cd and Hg; X=CH_3COO, NO_3; n=4 or 2.

Reactions were carried out in water solution. Mixing the initial compounds the fine crystalline substances were precipitated immediately.

Based on experiments it was established, that with change of succession and mixing intensity final substances of different composition were formed: when in Na3AsS4·8H2O we gradually added water solutions or d10-metal salt, we obtained mixed salts according to the following reaction:

$$Na_3AsS_4 + 3MX_2 + nH_2O \rightarrow NaMAsS_4 \cdot nH_2O + 2NaX \quad (4)$$

So, to avoid this process, salts of d10-metals were taken on 5-10 % more than theoretical and the reaction was carried out

by adding to the latter the solution of sodium tetrathioarsenate (V).

The composition and structure of synthesized products, except for element analysis has been presented by IR-spectroscopy. X-ray crystal determination and derivatographic research. Charge of starting materials and yield of synthesized products are given in Table 1 and the results of thermal analysis are illustrated in table 2, which shows that all compounds, except silver tetratioarsenates (v), contain water of cristalization.

Table 1. *Charge of starting materials and yield of synthesized products*

	Charge os starting materials					Yield of Ag3AsS4					
	Na3AsS4·8H2O		MX_2·H2O			and M3(AsS4)2·nH2O					
	g	mole	M	X	Y	g	mole	n	g	mole	%
1	3000	0.0072	Ag	NO_3	–	3.94	0.0232	–	3.88	0.0067	98.45
2	3000	0.0072	Zn	CH_3COO	2	2.50	0.0114	4	2.43	0.0036	94.34
3	3000	0.0072	Cd	CH_3COO	2	3.05	0.0115	2	2.81	0.0036	93.67
4	3000	0.0027	Hg	NO_3	1	3.93	0.0115	2	3.63	0.0036	95.56

Table 2. *Results of chemical analysis*

Found, %				Compound	Calculated			
M	As	S	H_2O		M	As	S	H_2O
61.36	14.29	24.35	–	Ag_3AsS4	61.48	14.23	24.29	–
29.028	22.13	37.75	10.84	$Zn_3(AsS4)_2·4H_2O$	29.11	22.25	37.96	10.68
43.42	19.08	32.58	42.92	$Cd_3(AsS4)_2·2H_2O$	43.28	19.25	32.85	4.62
57.22	14.66	25.04	3.08	$Hg_3(AsS4)_2·2H_2O$	57.65	14.37	24.53	3.45

In the IR-spectra of all samples there appeared bands for ≡ As – S band: of deformative in the region 470 cm-1 [2] valency vibration in the region 430 cm-1 [3]. Presence of water of crystallization observed by week band at 1630 2δ (H2O) and rather intensive ν(OH) – broad – at 3110 cm-1 and 3530 cm-1 region [3].

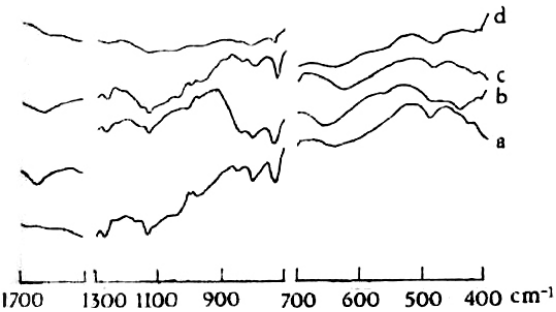

Figure 1. *IR spectra of synthesized compounds:$Ag_3As_3(a)$;$Zn_3(AsS_4)·4H_2O$ (b); $Cd_3(AsS_4)_@·2H_2O$ (c); $Hg_3(AsS_4)_2·2H_2O$*

According to the X-ray determination (Tab. 3) the obtained fine-crystal monophase substances don't contain starting materials as admixture. As it was expected, results of X-ray analysis show similarities of the natural sulphosalts to the synthesized products. The calculations show that they crystallize in a rhombic crystal system. Different results by the character of interflatness distance distribution indicate the different regulation degree of mentioned compounds. That should be exposed by the following summary group: for

$$Ag_3AsS_4 - D_{2n}^{15}\text{-}P_{cab};\ Cd_3(AsS_4)_2·2H_2O \text{ and}$$

$$Zn_3(AsS_4)_2·4H_2O - D_{2n}^{16}\text{-}P_{bnm};$$

$$Hg_3(AsS_4)_2·2H_2O \text{ and } Hg_3(AsS_4)_2·2H_2O\ \ D_{2n}^{16}\text{-}P_{mmn}.$$

Chemical behavior of tetrathioarsenates (V) of d10-metals was studied by heating. For example decomposition of Zn3(AsS4)2·4H2O (Fig.2, b) begins with separation of water of crystallization. This process presents on a DTA curve profound endothermic effects of 60-2300 C interval with maximum of 1000 C interval with maximum of 1000 C. At that time, sample mass decreases by 10 %, that corresponds to separation of 4 mole of water (theoretically – 9.4%). In 230-3500C interval sample loses 8.7% of its own mass, that is probably due to separation of 2 mole sulphur. Next mass decrease takes place in 350-7850C interval, that shows separation of

$$Zn_3(AsS_4)_2·4H_2O \xrightarrow[4H_2O]{65-230^0C} Zn_3(AsS_4)_2 \xrightarrow[2S]{230-350^0C} 3ZnS·As_2S_3 \xrightarrow[As_4S_4]{350-755^0C}$$

So decomposition of sample can be presented by the following scheme:

The same processes take place in decomposition of silver (I) and cadmium tetrathioarsenate (V). The other process takes place in decomposition of mercuric(II) tetrathioarsenate (V), which at 800 C presents endothermic effect on DTA curve in 80-2200 C interval at maximum 1700C. In this interval sample mass decreases by 4% (theoretically – 3.4%), due to separation of 2 moles of sulphur. In 320-4000 C interval sample loses 38 % of its mass (theoretically – 38.4 %), which corresponds to 2 mole mercury. Above 4000 C entire decomposition takes place:

Table 3. *Experimental x-ray diffraction parameters for synthesized products*

Ag_3AsS_4			$Zn_3(AsS_4)_2 \cdot 4H_2O$			$Cd_3(AsS_4)_2 \cdot 2H_2O$			$Hg_3(AsS_4)_2 \cdot 2H_2O$		
I/I0	**d, Å**	**hkl**	**I/I0**	**d, Å**	**hkl**	**I/I0**	**d, Å**	**hkl**	**I/I0**	**d, Å**	**hkl**
20	7.50	011	30	7.68	011	20	5.644	111	20	7.628	100
20	6.67	110	20	6.65	110	20	5.352	002	10	4.457	011
25	5.717	111	15	5.91	111	30	4.811	020	20	3.814	200; 111
30	5.340	002	50	4.44	102	50	4.496	200	100	3.351	210
90	4.972	020	30	4.23	120	40	3.972	121	95	3.322	020
100	4.561	200	30	4.00	121	30	3.779	211	40	3.186	002
50	4.439	021	70	3.582	022; 003	80	3.542	022; 003	35	3.044	120
100	4.320	120	80	3.458	202	80	3.461	202	40	2.921	211; 021
100	4.065	210; 121	90	3.363	013	80	3.366	103	65	2.095	103
40	3.645	022; 003	90	3.344	103; 220	60	3.329	013; 122	20	1.953	113; 222
40	3.515	202	80	3.186	212	100	3.186	212; 220	50	1.753	411
30	3.427	103	100	3.162	221	80	3.132	221	15	1.446	430
50	3.326	013; 122	90	3.136	031	80	3.096	031	15	1.415	431; 403
50	3.271	212; 221	35	2.936	301	25	2.931	130	20	1.366	341
30	3.157	031	35	2.758	311; 123	25	2.850	310	20	1.330	050
30	3.038	300; 130	35	2.678	302	40	2.429	223			
40	2.865	301	30	2.50	321	50	2.058	224; 323			
60	2.831	311	20	2.28	322; 141	40	1.933				
60	2.614	302	35	2.22	330	40	1.898	403; 422			
100	2.574	320	20	2.14	331	50	1.877	340			
50	2.415	223	75	2.08	323; 402	45	1.76	342			
40	2.388	232	90	2.056	420; 332	50	1.74	404; 432			
40	2.085	224; 323	50	1.940	430						
30	2.058	420; 332	60	1.89	422; 340						
50	1.970	314; 304	75	1.758	432						
40	1.930	403; 340									
30	1.858	431									
40	1.730	404									
20	1.713	334									
a=9,122 Å			a=9,050 Å			a=8,992 Å			a=7,628 Å		
b=9,944 Å			b=9,699 Å			b=9,632 Å			b=6,644 Å		
c=10,68 Å			c=10,746 Å			c=10,704 Å			c=6,372 Å		

$$Hg_3(AsS_4)_2 \cdot 2H_2O \xrightarrow[-2H_2O]{80-220^0C} Hg_3(AsS_4)_2 \xrightarrow[-2S]{220-320^0C} Hg_3As_2S_6$$

$$\xrightarrow[-211g]{350-400^0C} Hg_3As_2S_6 \xrightarrow{>400^0C} \text{full decomposition.}$$

Synthesis of tetrathioarsenate (V), of silver (I). In dilute solution of 3.94 g silver nitrate interacted with 3.00 g of sodium tetrathioarsenate (V) dissolved in 20 ml of water. Black compound precipitated immediately. Next day precipitations were filtered, washed by water and dried by P2O5 in vacuum desiccator to the constant mass. In the same way other tetrathioarsenate (V) were obtained. From the synthesized product tetrathioarsenate (V) of silver (I) and mercury (II) are black substances, zinc is yellow, and cadmium is dark yellow. All the compounds are insoluble in alkalis except zinc tetrathioarsenate (V) and elaborated by acid (HCl, H2SO4) they change arsenic (V) pentasulphide.

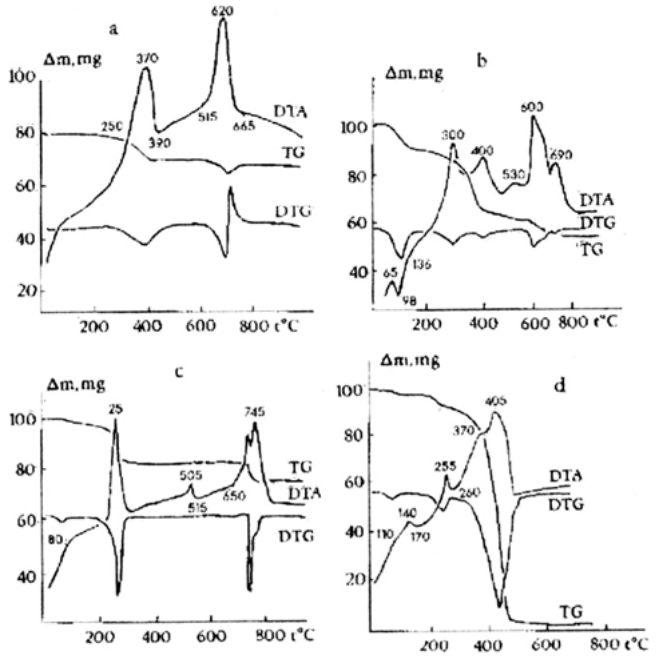

Figure 2. *Thermogravigrams of Synthesized Compounds:Ag_3AsS_4 (a); $Zn_3(AsS_4)_2 \cdot 4H_2O$ (b); $Cd_3(AsS_4)_2 \cdot 2H_2O$ (e);$Hg_3(AsS_4)_2 \cdot 2H_2O$ (d)*

3. Conclusion

As a result of our research, there was established, that d-metals (II) tetra thioarsenates can be easily obtained using hydrochamical method, if the metals soluble salts can be taken for reaction ~10% more, in comparison with theoretical. All synthesized compounds, except silver(I) tetrathioarsenates are crystal hydrates with clearly defined individuality, that is proved not only by results of chemical analysis bus also by the physical-chemical research methods. Synthesized small-crystalline substances are solid compounds with different tints. They are not insoluble in water, alcohol and in other organic solvent. During alkali treatment they are transformed by formation of Arsenic(V) sulphide. Experiment shows that this compound practically don't react with alkali except copper (II) tetrathioarsenate, which gradually dissolves in much alkali at high temperature.

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