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NOVEL NITROGEN CONTAINING COORDINATION COMPOUNDS FOR HUMAN AND ENVIRONMENT PROTECTION

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Abstract:

Novel nitrogen containing coordination compounds of some d-metals Ag(I), Hg(II), Zn, Fe(II), Cu(II), Mn(II), Cd(II), Ni(II) and Co(II) are synthesized and studied. The optimal conditions of the synthesis have been established. The essence of this method is that nitrates, chlorides and sulfates of mentioned metals form stable, but water-soluble coordination compounds with 2,2-dipyridyl and ethylenediamine. It was established that their extraction from mother solution in chemically pure form for further transformations is not necessary: corresponding d-metals tetrasulphantimonite(V) dipyrilidates and ethylenediamine complexes are instantaneously precipitated during treatment by these solutions' precipitator – sodium tetra sulphantimonite. It was showed that the obtained coordination compounds are finely dispersed substances, insoluble in water and ethanol. The composition and structure of synthesized coordination have been established by elemental analyses. The study of IR spectra of these compounds showed that group in studied substances represents exteriorly spherical tetrasulphantimonite (V) ion. Analysis of synthesized compounds thermographs shows that thermal destruction of studied samples begins at $\sim 150^\circ$, runs stage-by-stage and deligation (removal of ligand) is completely finished approximately at $400-500^\circ$. Bioscreening of obtained compounds was carried out. Their antimicrobial, antiviral and parasiticide activity has been established. Area of their application has been established.

Key-words: Industrial waste, stibium, coordination compound, bioscreening, composite, use.



1. Aims and scope of the paper

Transformation of stibium containing industrial waste into stable coordination compound with specific properties with the purpose of their further application belongs to a variety of topical issues of applied and coordination chemistry. Successful solution of this problem will not only create new raw materials resource base, but also will solve important ecological problem – will protect environment from pollution by stibium containing waste. The presented work is devoted to this problem, in which reaction responsive stibium compounds extracted from arsenic production waste are considered, on the basis of which new nitrogen containing bioactive coordination compounds are obtained.



2. Methodology of research/ approach

Spectral analysis: IR spectra were obtained with a spectrophotometer FT-IR “THER-MO NICOLET” in Ge plates and UR-20 (400-4000 cm^{-1}) in liquid paraffin. Thermogravimetric analysis carried out due to F.Paulik, I.Paulik & L.Erdey’s systems Q 1500 type thermal analyzer by Hungarian firm MOM, heating rate 100/min, sensibility DTA 1/10 [18]. Melting points were determined by apparatus Meelting Point Meter MPM-HV2, Germany; metal content _ on atomic absorptive spectro-photometer Perkin Elmer 603.

X-ray pattern of four samples Fe(II), Ni(II), Ag(I) and Hg(II) given here was studied by use of the method of homology. For that purpose table data of American card-catalogue ASTM-20-1917 and ASTM-20-1918 have been used by us, those are basically in good correlation with X-ray reflection of complexes received by us.

Microbiological study was carried out by using of internet-system program PASS C&T.

Standard microbiological methods for study of antibacterial activity of synthesized compounds have been used.



3. Results and Discussions

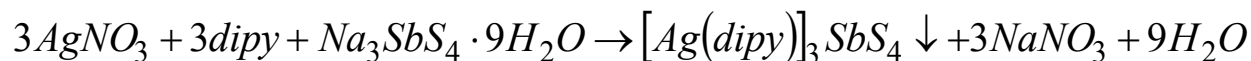
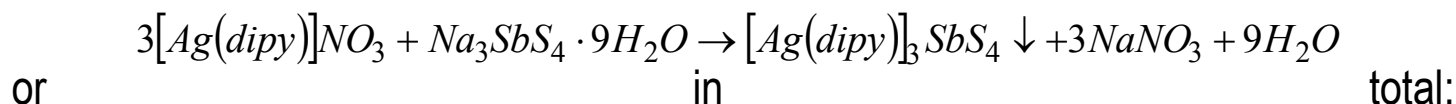
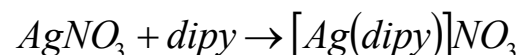
2,2'-dipyridyl as a ligand, for a great while is studied during the synthesis of coordination compounds [1]. The reason of this study is not uniform and contains both pure chemical and applied aspects. The ample opportunities of 2,2'-dipyridyl ($\text{NH}_4\text{C}_5\text{-C}_5\text{H}_4\text{N}$) for creation of different types coordination compounds.

Because of the fact that nitrogen atoms hold in molecule such position that optimum conditions are created for formation of 5-member cycle, α,α' -dipyridyl from the very beginning became the focus of scientists' interest, and due to this fact coordination compounds with metal halogenides, nitrates, sulfates and almost every other soluble salt, containing it, are studied in details.

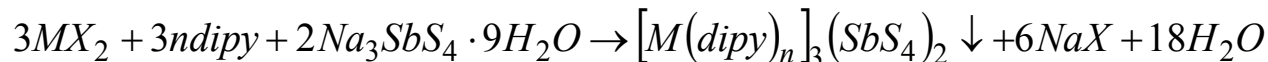
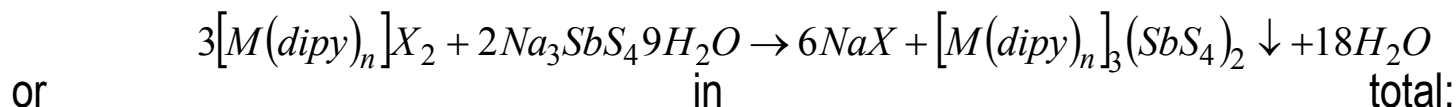
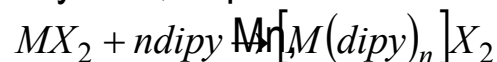
Sodium tetra thio-arsenates(V) water solutions action with the products of interaction of d-metals soluble salts with bidentate ligand 2,2'-dipyridyl leads us to the formation of appropriate coordination compound [2]. Having used the same method we implemented the synthesis of coordination compounds tetra sulphantimonates(V) with 2,2'-dipyridyl.



Salts dissolved in d-metals water are used as basic substances: Ag(I) and Hg(II) nitrates, Zn(II), Fe(II) and Cu(II) sulfates, Mn(II), Cd(II), Ni(II) and Co(II) chlorides; sodium tetra sulphantimonate is used as precipitator, while 2,2-dipyridyl (C₅H₄N)₂ (shortly dipy) is used as nitrogen containing ligand. Synthesis of d-metal tetra sulphantimonates coordination compound with 2,2'-dipyridyl was carried out by exchange reaction, as result of which tetra sulphantimonates complexes of corresponding d-metals are precipitated, formation of which can be explained by the unity of the following consecutive reactions:



As to other metals(II) dypiridylates, in particular when M = Fe, Co, Ni, Zn, Cd, Hg, Cu, then:



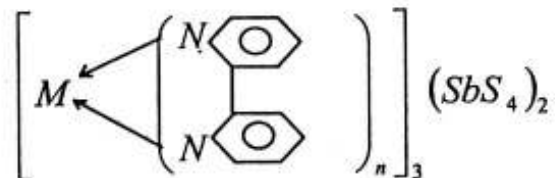


The essence of this method comprises in the fact that nitrates, chlorides and sulfates of mentioned metals form stable, but water-soluble coordination compounds with 2,2'-dipyridyl. That's why their extraction from mother solution in chemically pure form for further transformation is not necessary: corresponding d-metals tetra sulphantimonate(V) dipyridylates and ethylene diamine complexes are instantaneously precipitated during treatment by these solutions' precipitator – sodium tetra sulphantimonate.

Received coordination compounds represent finely dispersed substances, insoluble in differently colored water and ethanol. All of them are extracted without crystallization water, except of Fe(II) dipyridylate, which adds 3 molecules of water. They have no certain melting temperature, since they resolve before melting. Composition of synthesized complexes was established by elemental analysis: stibium was determined by Evins method, sulfur – by gravimetric method, metal – by volumetric method, and nitrogen – by Dumas micro method. Composition and structure of synthesized complexes, except of elemental analyses, was determined by us of physical-chemical research methods. Study of IR spectra of these complexes adsorption (Fig. 1) shows that group in studied substances represents exteriorly spherical tetra sulphantimonate(V) ion. In the long-wave 380 and 384 cm^{-1} spectral region absorption band are observed, that correspond to ν_3 oscillation of ion [3].



Comparison of free (incoordinate) ligand – 2,2'-dipyridyl spectrum with d-metal tetrasulphantimonates (V) dipyridylates spectra shows displacement of high frequency absorption bands. Free ligands absorption band is at 1584cm^{-1} , while in the complexes it is displaced to $1600\text{-}1610\text{ cm}^{-1}$, that is related to heterocyclic nitrogen coordination with metals atoms [4-6]. By taking into account the abovementioned we come to a conclusion that formulas of synthesized coordination compounds can be presented by the following form:



For Fe(II) complex, as for crystalline hydrate, absorption band are observed in 1630cm^{-1} region, that points at the presence of crystallization water in the compounds.

Individuality of investigated substance is testified by results of X-ray phase studies (Table 1).

X-ray pattern of four samples Fe(II), Ni(II), Ag(I) and Hg(II) given here was studied by use of the method of homology. For that purpose table data of American card-catalogue ASTM-20-1917 and ASTM-20-1918 have been used by us, those are basically in good correlation with X-ray reflection of complexes received by us.



Table 1. Results of X-ray phase studies of coordination compounds of d-metals tetra sulphantimonates(V) with dipyriddyate

[Fe(dipy) ₃] ₃ (SbS ₄) ₂ ·3H ₂ O		[Ni(dipy) ₃] ₃ (SbS ₄) ₂		[Ag(dipy)] ₃ SbS ₄		[Hg(dipy) ₂] ₃ (SbS ₄) ₂	
I/Io	dα/n	I/Io	dα/n	I/Io	dα/n	I/Io	dα/n
100	11.05	10	11.0	5	9.15	3	9.8
5	9.31	2	7.08	15	6.18		
5	7.69	2	6.44	32	3.63	33	6.33
4	4.79	2	5.55	25	3.56	6	3.83
5	4.28	1	5.07	100	3.34		
5	4.18	1	4.28	35	3.13	43	3.36
5	3.708	2	3.95	5	2.978	100	3.186
10	3.562	2	3.86	15	2.90	10	2.915
4	3.36	3	3.74	15	2.80	8	2.765
6	3.10	2	3.63	5	2.675	10	2.529
4	2.54	1	2.69	28	2.564	8	2.765
5	2.227	1	2.51	10	2.368	10	2.529
4	2.156	1	2.44	8	2.22	5	2.127
				40	2.054	16	2.057
				10	1.898		
				30	1.758	5	1.953
				30	1.744		



Thermal studies of synthesized compounds assured us that dipyriddy complexes don't contain crystallization water, except of Fe(II) tetra sulphantimonate dipyriddy, that is testified by IR spectroscopic data, too. Thermal behavior of these compounds is almost similar. Thermolysis of Fe(II) tetra sulphantimonate(V) dipyriddyate $[Fe(dipy)_3]_3(SbS_4)_2 \cdot 3H_2O$ was considered as an example. Decay process starts at 80°C, in the 80-150°C temperature range endothermic effects with a maximum at 110°C is observed at DTA curve. Mass loss at that time comprises of 3.57%, that corresponds with the removal of 3 crystallization water (theoretically 2.54%). The further stage of thermolysis at 150-380°C flows very difficult. Three exothermic effects, with maximum 210, 250 are observed at 360°C. Mass loss at that time is equal to 45.00%, that probably corresponds with the removal of 6 molecules of ligand dipyriddy (theoretically 44.03%).

In the 380-530°C temperature range exothermic effect with maximum at 480°C is observed at DTA curve. At this stage mass change comprises of 27.57%, that corresponds with the removal of 3 moles of ligand and 2 moles of sulfur (theoretically 25.03%). After-wards, sample mass experiences 1% loss, that correspond with removal of 1 mole of sulfur (theoretically 1.5%).



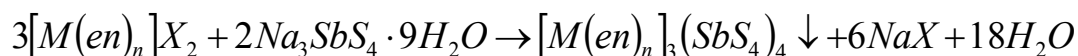
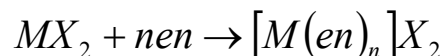
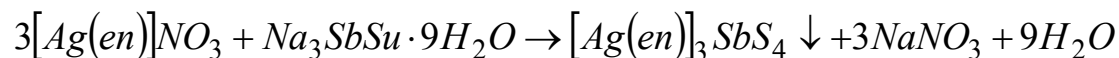
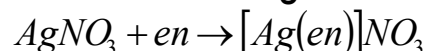
Analysis of synthesized compounds thermographs (Fig. 3) shows, that destruction of samples under investigation begins from $\sim 150^{\circ}\text{C}$, runs on stage-by-stage and removal of ligand finally completes approximately at $400\text{-}500^{\circ}\text{C}$. Little difference observed in their thermolysis is caused: 1) by different amount of ligands; 2) by the presence of crystallization water. E.g. $[\text{Fe}(\text{dipy})_3]_3(\text{SbS}_4)_2 \cdot 3\text{H}_2\text{O}$. Only exception is presented by Hg(II) complex: thermolysis begins at relatively low (100°C) temperature and completes by total decay. This fact is caused by instability of mercuric (II) compounds itself at high temperatures.

Thus, obtained results allow us to make a conclusion that molecules of 2,2'-dipyridyl are coordinated with d-metals atoms by means of nitrogen atoms, while group is located in the external (second) sphere of the complex. Since ethylene diamine ($\text{H}_2\text{N-CH}_2\text{-CH}_2\text{-NH}_2$) is one of the best bidentate ligand, we set as a goal the receipt of complex compounds of transition metals(II) tetra sulphantimonates $M^{II}-\text{SbS}_4^{3-}-en-\text{H}_2\text{O}$. the system

Sodium tetra sulphantimonate, $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ ethylene diamine 50% water solution and salts of water-soluble d-metals has been used by us as a mother (basic) substances.



Coordination compounds of d-metal tetra sulphantimonates with ethylene diamine have been received by means of exchange reaction: by the action of sodium tetra sulphantimonate with the products of interaction of 50% ethylene diamine and d-metals salts, without extraction of the latter in individual status. Silver (I), cadmium, zinc, mercuric (II), copper, cobalt and nickel (II) complexes with ethylene diamine have been synthesized according to the following reactions:

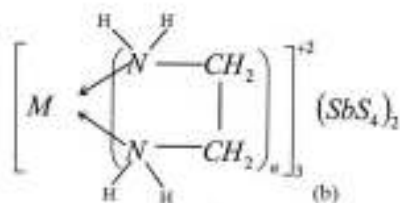
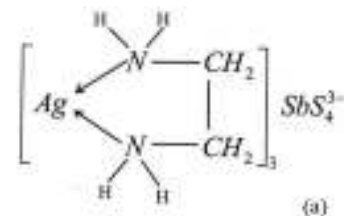


where $M=Zn, Cd, Hg, Cu, Ag, Co, Ni$; $X=Cl^-$, $1/2SO_4^{2-}$, NO_3^- .

Since Fe(II) ethylene diamine complex is extracted from water solution in the form of precipitate, while received precipitate is insoluble in the sodium tetra sulphantimonates, we were not able to obtain Fe(II) tetrasulphantimonate complex by means of exchange reaction with ethylene diamine, as it was achieved during synthesis of other d-metals amminates. Synthesized complexes are finely crystalline compounds of various coloring, they are insoluble in the water, spirit, and other ordinary organic solvents.



Synthesized compounds, except of elemental analysis, have been studied by IR spectroscopy, X-ray graphical studies and thermogravimetric analysis. In IR spectra NH_2 -group absorption bands are significantly replaced in comparison with uncoordinated ligand. For free, uncoordinated ethylene diamine absorption bands in 1595 and 3510 cm^{-1} regions are characteristic, while in coordination compound under investigation absorption bands of this group are located in 1620 and 3370 cm^{-1} region, that is characteristic for valence vibration of $\text{H}_2\text{N} \rightarrow \text{M}$ bond. And since silver (I) coordination number is equal to 2, while in case of other d-metals, proceeding from the quality of their oxidation this number increases up to 4, we should make a conclusion that ethylene diamine plays the role of cyclic bidentate ligand, and synthesized complexes have the following structure:





Individuality of obtained products has been checked by us by means of X-ray phase analysis. Cu(II), Ni(II) and Ag(I) compounds show sufficiently defined X-ray picture, while as to Hg(II), Zn(II) and Co(II) tetra sulphantimonate complexes with ethylene diamine (Table 2), they turn out to be X-ray amorphous [7]. X-ray diagram of American card-catalogue [8] ASTM 20-1692 ($C_5H_8N_2 \cdot 2HCl$ pure ligand) has been used with the purpose of study of received X-ray diagrams. It turns out that in our case correlation takes place, but the certain amount of X-ray reflections is not deciphered (decoded), and for this purpose the method of homology has been used. More perfect X-ray diagram existing in American card-catalogue ASTM 24-1670 partially filled the gap and gave us the picture that is almost similar to Ni(II) and Cu(II) tetrasulphantimonate complexes with ethylene diamine. It may be said that the samples are virtually similar to the references to be compared and represent ethylene diamine complexes. Synthesized compounds' behavior has been studied by us during their heating. Thermolysis begins with removal of ligand, and afterwards the picture of their decay is in exact correlation with the thermolysis of normal salts.



Table 2. Results of X-ray phase studies of coordination compounds of d-metals tetra sulphantimonates (V) with ethylene diamine

$[\text{Cu}(\text{en})_2]_3(\text{SbS}_4)_2$		$[\text{Ni}(\text{en})_3]_3(\text{SbS}_4)_2$		$[\text{Ag}(\text{en})]_3\text{SbS}_4$	
I/Io	$d\alpha/n$	I/Io	$d\alpha/n$	I/Io	$d\alpha/n$
3	5,67	5	8.29	2	9.5
4	5,41	5	7.69	1	8.23
1	5,10	4	5.69	2	3.18
2	4,796	4	5.38	6	2.82
10	4,70	10	5.10	10	2.58
1	4,23	5	4.74	3	2.42
5	3,95	6	4.04	2	2.37
5	3,70	9	3.91	1	2.20
1	3,59	9	3.75	2	2.07
1	3,70	6	3.53	1	2.20
3	3,528	10	3.36	2	2.07
2	3,30	5	3.186		
4	3,028	4	2.529		
4	2,80	3	2.449		
2	2,734				
1	2,64				
2	2,584				
1	2,413				
2	2,127				
2	2,02				
	1,824				

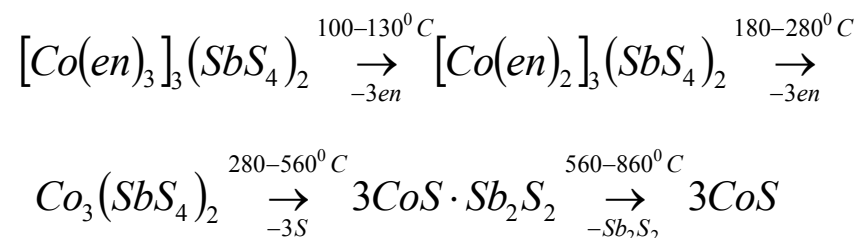


X-ray diagram of American card-catalogue [8] ASTM 20-1692 ($C_5H_8N_2 \cdot 2HCl$ pure ligand) has been used with the purpose of study of obtained X-ray diagrams. It turns out that in our case correlation takes place, but the certain amount of X-ray reflections is not deciphered (decoded), and for this purpose the method of homology has been used. More perfect X-ray diagram existing in American card-catalogue ASTM 24-1670 partially filled the gap and gave us the picture that is almost similar to Ni(II) and Cu(II) tetrasulphantimonate complexes with ethylene diamine. It may be said that the samples are virtually similar to the references to be compared and represent ethylene diamine complexes.

Synthesized compounds' behavior has been studied by us during their heating. Thermolysis begins with removal of ligand, and afterwards the picture of their decay is in exact correlation with the thermolysis of normal salts. Let consider the thermolysis of $[Co(en)_3]_3(SbS_4)_2$ as a sample. Removal of 9 moles of ligand occurs at 100-280°C temperature range in 3 stages: 100-130°C, 130-180°C and 180-280°C. At the first stage the mass decreases by 15.00% (theoretically 14.79%), at the second – by 16.42%, and at the third – by 15.01%. It may be said that removal of 3-3 moles of ligand corresponds with each of these stages. After 280°C, as it was mentioned, the process of thermolysis flows as well as in case of normal (neutral) salts. In the 280-560°C temperature range the mass decreases by 7.14%, that corresponds with the removal of 3 moles of sulfur (theoretically 7.89%). At DTA curve two exothermic effect are observed within this range, with peaks at 340 and 520°C.



Further decay of the samples continues above 520°C, endothermic effect is observed at DTA curve with peak at 820°C, mass loss comprises of 24.28%, that should be caused by removal of stibium sulfide form (theoretically 25.27%). On the assumption of abovementioned probable scheme of thermolysis of Co(II) tetrasulphantimonate(V) ethylene diamine complex can be presented as follows:



As well as in other cases, here the process of thermolysis differs from corresponding processes of other ethylene diamine complexes, that during heating experiences total decay without any residue. Decay of sample begins from 120°C, and becomes especially intense in the 210-270°C temperature range. At that time mass loss is equal to 9.33% (theoretically 8.21%), that corresponds with removal of 2 moles of en. In the 270-450°C temperature range exothermic peak has several maximums at DTA curve, that points out that complex process runs on. During this process total loss of remained mass takes place.



Study of synthesized complex thermographs shows that removal of ethylene diamine in all compounds occurs in 2 or 3 stages. For Cu(II), cadmium and Ag(I) tetrasulphantimonates complexes with ethylene diamine (as well as in case of normal salts) mass increase is observed in the process of thermolysis. Thus, the investigations show that in case of d-metal ethylene diamine complexes treatment by sodium tetra sulphantimonates water solution corresponding compounds $[Ag(en)]_3SbS_4$ and $[M(en)_n]_3(SbS_4)_2$, are received in the form of precipitate, where $n=2, 3$.

We have carried out the preliminary virtual (theoretical) bioscreening of obtained structures by using of internet-system program PASS C&T [9]. The estimation of probability of activity of compounds is carried out via parameters Pa (active) and Pi (inactive); when $Pa > 0.5-0.7$, the compound also will show activity experimentally and probably will be analog of known pharmaceutical agents too. Evaluated relative bioactivities of some synthesized compounds are given in Table 3.



Table 3. Relative bioactivity of some synthesized compounds

Compound	Antiseborrheic	Urethanasase Inhibitor	Antiprotozoal (Leishmania)	Anthelmintic (Nematodes)	Antiviral (Arbovirus)	Antiviral (Picornavirus)	Anticarcinogenic	Neurotoxin	Antibacterial activity enhancer	Antineurotoxic	Cytoprotectant	Antineoplastic (brain cancer)	Hematotoxic	Antianemic
	P _a / P _i													
[Fe(dipy) ₃](SbS ₄) ₂ ·3H ₂ O	0.865/ 0.021	0.820/ 0.005	0.518/ 0.070	0.586/ 0.053	0.687/ 0.046	0.605/ 0.035	0.554/ 0.037	0.719/ 0.029	0.695/ 0.010	0.672/ 0.041	0.661/ 0.035	0.637/ 0.047	0.622/ 0.117	0.523/ 0.066
[Ag(dipy) ₃](SbS ₄) ₂	0.824/ 0.041	0.766/ 0.011	0.569/ 0.134	0.496/ 0.105	0.636/ 0.089	0.543/ 0.071	0.498/ 0.068	0.670/ 0.065	0.657/ 0.025	0.581/ 0.071	0.615/ 0.063	0.522/ 0.084	0.505/ 0.178	0.440/ 0.118
[Mn(dipy) ₃](SbS ₄) ₂	0.865/ 0.021	0.820/ 0.005	0.586/ 0.008	0.586/ 0.053	0.687/ 0.046	0.605/ 0.035	0.554/ 0.037	0.719/ 0.029	0.695/ 0.010	0.672/ 0.041	0.661/ 0.035	0.637/ 0.047	0.622/ 0.117	0.523/ 0.066
[Ag(en) ₃](SbS ₄) ₂	0.768/ 0.066	0.651/ 0.034	0.542/ 0.045	0.543/ 0.075	0.681/ 0.049	0.659/ 0.016	0.521/ 0.054	0.663/ 0.070	0.640/ 0.034	0.636/ 0.052	0.650/ 0.041	-	0.605/ 0.125	0.586/ 0.037



4. Concluding Remarks

I. Novel nitrogencontaining coordination compounds of some d-metals Ag(I), Hg(II), Zn, Fe(II), Cu(II), Mn(II), Cd(II), Ni(II) and Co(II) are synthesized and studied. The optimal conditions of the synthesis have been established. The essence of this method is that nitrates, chlorides and sulfates of mentioned metals form stable, but water-soluble coordination compounds with 2,2-dipyridyl and ethylenediamine.

II. It was established that their extraction from mother solution in chemically pure form for further transformations is not necessary: corresponding d-metals tetrasulphantimonite(V) dipyridilates and ethylenediamine complexes are instantaneously precipitated during treatment by these solutions' precipitator – sodium tetra sulphantimonite.

III. It was showed that the obtained coordination compounds are finely dispersed substances, insoluble in water and ethanol. The composition and structure of synthesized coordination have been established by elemental analyses. The study of IR spectra of these compounds showed that group in studied substances represents exteriorly spherical tetra sulphantimonite (V) ion.

IV. Analysis of synthesized compounds thermographs shows that thermal destruction of studied samples begins at $\sim 150^{\circ}$, runs stage-by-stage and deligation (removal of ligand) is completely finished approximately at $400-500^{\circ}$.

V. Bioscreening of obtained compounds was carried out. Their antimicrobial, antiviral and parasiticide activity has been established. Area of their application has been established.



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