

COMPLEXES OF SILVER, LEAD, CALCIUM WITH BISPHOSPHONIC LIGANDS

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It is interesting in chemical terms and promising in the applied production of new complexes of metals with bisphosphonic ligands with a popular set of consumer properties. To date, little has been studied chemistry of bisphosphonic acid complexes with the basic structure of 1-hydroxymethylene-bisphosphonic acid with a side chain containing 11 carbon atoms and ending with an amino group. The main objective is to obtain new bisphosphonates of s-, p-, d- and f-elements, their characterization by a complex of physical and chemical research methods (NMR and IR spectrometry, RSA, DTA, optical microscopy, laser diffraction) and to identify new applications of bisphosphonic acids and their salts. In the course of the work, complexes of Ag, Pb, Ca, with 1-hydroxymethylene-bisphosphonic acid ($H_2N(CH_2)_x C(OH)(H_2PO_3)_2$) and its derivatives, the side chain ends with an amino group, its length is 11 carbon atoms. Crystal structures of metal-bisphosphonate complexes with the general formula $H_2N(CH_2)_{10}C(OH)(HPO_3)_x M$ ($M = Ag, Pb, Ca$) were determined. The complexes were characterized by IR spectroscopy and ^{31}P solid-state NMR spectroscopy, RSA. The areas of practical use of the complexes are outlined. It is shown, by the example of wastewater in Kuopio, Finland, that bisphosphonic acids can be used for wastewater treatment of enterprises from heavy metals ($M = Pb, Zn, Cd$, etc.).

Keywords: bisphosphonate ligands, synthesis, complexes with metals, 11-amino-1-hydroxyundecylene-1,1-bisphosphonic acid, waste water treatment.

КОМПЛЕКСЫ СЕРЕБРА, СВИНЦА, КАЛЬЦИЯ С БИСФОСФОНОВЫМИ ЛИГАНДАМИ

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Представляется интересным в химическом плане и перспективным – в прикладном получении новых комплексов металлов с бисфосфоновыми лигандами, обладающих востребованным комплексом потребительских свойств. К настоящему времени мало изучена химия комплексов бисфосфоновых кислот, имеющих базовую структуру 1-гидроксиметилена-бисфосфоновой кислоты с боковой цепью, содержащей 11 атомов углерода

и оканчивающейся аминогруппой. Основной задачей является получение новых бисфосфонатов *s*-, *p*-, *d*- и *f*-элементов, их характеристика физико-химическими методами (ЯМР- и ИК-спектроскопия, рентгеноструктурный анализ, дифференциальный термический анализ, оптическая микроскопия, лазерная дифракция) и выявление новых областей применения бисфосфоновых кислот и их солей. В ходе работы получены комплексы Ag, Pb, Ca, с 1-гидроксиметилен-бисфосфоновой кислотой ($H_2N(CH_2)_x C(OH)(H_2PO_3)_2$) и ее производными, боковая цепочка оканчивается аминогруппой, а длина составляет 11 атомов углерода. Определены кристаллические структуры комплексов состава $H_2N(CH_2)_{10}C(OH)(HPO_3)_x M$ ($M = Ag, Pb, Ca$). Комплексы охарактеризованы методами ИК-спектроскопии, твердофазной ^{31}P -ЯМР-спектроскопии, проведен рентгеноструктурный анализ образцов. Намечены области практического применения полученных комплексов. На примере сточных вод в г. Куопио, Финляндия, показано, что бисфосфоновые кислоты можно применять для очистки сточных вод предприятий от тяжелых металлов ($M=Pb, Zn, Cd$ и др.).

Ключевые слова: синтез, бисфосфонатные лиганды, комплексы с металлами, 11-амино-1-гидроксидецилиден-1,1-бисфосфоновая кислота, очистка сточных вод.

In 1865 the first synthesis of bisphosphonates was carried out in Germany [1], whose biological characteristics were first studied more than 40 years ago [2]. These compounds, characterized by two P–C bonds connected to a carbon atom, thus form geminal compounds with a structure containing P–C–P bonds. Bisphosphonates are analogs of inorganic pyrophosphates, widely distributed in nature [3, 4]. Bisphosphonic acids can be obtained at different ways, using such methods as Burthorn's reaction, Witting-Horner reaction, Abdu reaction, etc. [5–7]. Solid metal-phosphonate complexes are usually obtained at elevated temperature [8–10]. Small changes in the structure of bisphosphonates can lead to significant changes in their physicochemical, biological, medical and toxicological characteristics. Chemistry of metal phosphonates is of interest in connection with the prospect of their use in catalysis, ion exchange, biotechnology, in the production of optically active and magnetic materials [11–14].

The purpose of this work is the development new methods of synthesis, determination of composition, structure and identification of potential applications of $H_2N(CH_2)_{10}C(OH)(HPO_3)_x M$ ($M = Ag, Pb, Ca$) complexes.

Experimental

The raw materials are bisphosphonate ligand, 11-amino-1-hydroxyundecylidene-1,1-bisphosphonic acid – $H_2N(CH_2)_{10}C(OH)(H_2PO_3)_2$ and metal nitrates.

Synthesis of 11-amino-1-hydroxyundecylidene-1,1-bisphosphonic acid. A mixture of 11-amino-undecylenic acid (157 g), phosphorous acid (64 g) and methane sulfonic acid (375 ml) was heated to 65 °C with gradual addition of PCl_3 (140 ml) for 20 min. The mixture was hold at 65 °C for 48 h, and then cooled to 0 °C with vigorous stirring. The obtained precipitate was filtered off in

a yield of 270 g (83%) in the form of a white crystalline powder. 1H NMR (D_2O , 500 MHz, δ , ppm): 2.52 (t, 2H, $3J_{HH} = 7.0$), 1.81 (m, 2H), 1.49 (m, 2H), 1.36 (m, 2H), 1.29–1.18 (m, 14H); ^{31}P NMR (D_2O , 202 MHz, δ , ppm): 20.4. Found, %: C – 37.86; H – 7.77; N – 3.92; O – 32.07; P – 17.65. Calculated, %: C – 38.04; H – 7.84; N – 4.03; O – 32.25; P – 17.84.

The substance is insoluble in acetone, chloroform, limitedly soluble in water, ethanol and hexane, and is highly soluble in strongly acidic and strongly alkaline solutions.

Synthesis of metal complexes. Synthesis was carried out by two methods: autoclave and reflux condensation. In both cases, the reagents were mixed in a molar ratio of 1: 1. The synthesis was carried out for 24 h to obtain solid crystalline powders, which were filtered off and dried. NMR of the resulting compounds was carried out on a Bruker AMX400 NMR spectrometer. To establish the structure parameters, XRD were used (Bruker AXS-D8 Advance Powder Diffractometer, CuK_α radiation and three-circle Bruker AXS diffractometer, MoK_α radiation).

Synthesis of complex I ($M = Ag$). A solution of bisphosphonic acid 0.347 g (1 mmol) and 0.17 g (1 mmol) of silver nitrate in 50 ml of water was heated under reflux for 24 h. The precipitate formed (a colorless crystalline powder) was filtered off, washed and dried. Similarly, 0.347 g (1 mmol) of Lime was mixed with 0.21 g (1 mmol) of lead nitrate, diluted with water and refluxed for 24 h. The resulting precipitate (white crystalline powder) was filtered, washed and dried.

Similarly, synthesis was carried out with nitrates of lead (II) and calcium (III).

Results and Discussion

The structure of the obtained complexes are presented in Fig. 1–3.

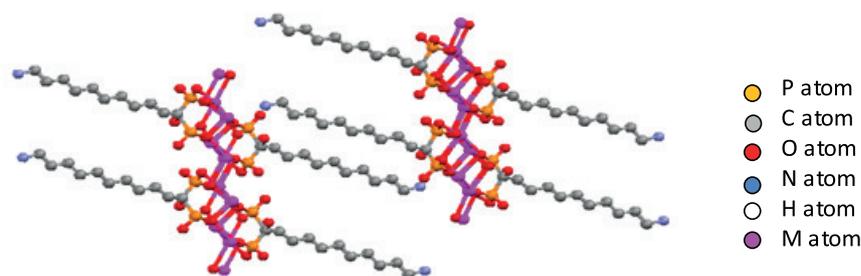


Fig. 1. The structure of complex **I**

d , Å: Ag1-O1 2.229(7), Ag2-O4 2.217(3), P1-O1 1.462(2), P2-O4 1.525(9), P1-C1 1.851(9), P2-C1 1.834(8)
 ω , grad.: Ag1-O1-P1 114.4(3), Ag2-O4-P2 124.7(3), P1-C1-P2 115.7(6).

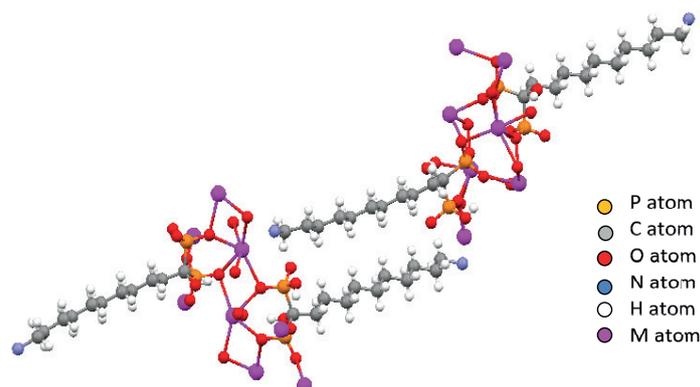


Fig. 2. The structure of complex **II**

d , Å: Pb1-O1 2.329(6), Pb1-O4 2.437(6), P1-O1 1.535(6), P1-O2 1.553(7), P1-C1 1.856(9), P2-O4 1.534(6),
 P2-O5 1.480(6), P2-C1 1.853(9)
 ω , grad.: O1-Pb1-O4 79.3(2), P1-O1-Pb1 137.6(4), P2-O4-Pb1 141.2(4).

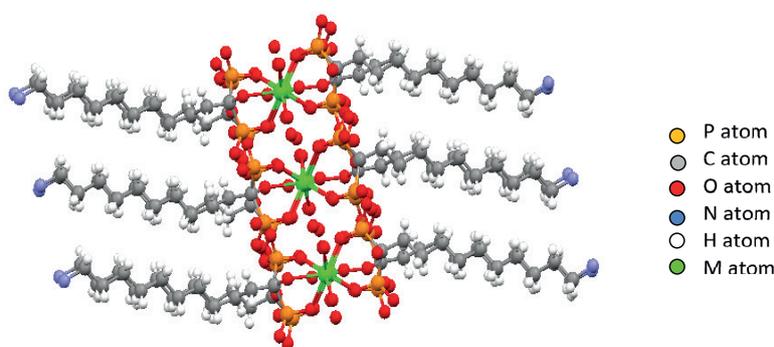


Fig. 3. The structure of complex **III**

d , Å: Ca1-O1 2.388(0), Ca1-O8 2.284(5), P1-O1 1.515(8), P3-O8 1.498(1), P1-C1 1.857(1), P3-C12 1.848(5)
 ω , grad.: O1-Ca1-O8 80.7(9), Ca1-O1-P1 121.6(0), Ca1-O8-P3 139.4(4).

Fig. 1 (M = Ag), 2 (M = Pb), 3 (M = Ca) is carried out using the Mercury program. The results of chemical analysis of compounds **I–III** are shown in Table 1. Crystallographic characteristics of compounds are presented in Table 2.

As can be seen from the presented data, complexes **I** and **II** are formed by the interaction of one ligand molecule with one metal ion. They are formed pillared layered two-dimensional structures: the initial chains are connected by hydrogen bonds. The complex of calcium (**III**) differs from complexes

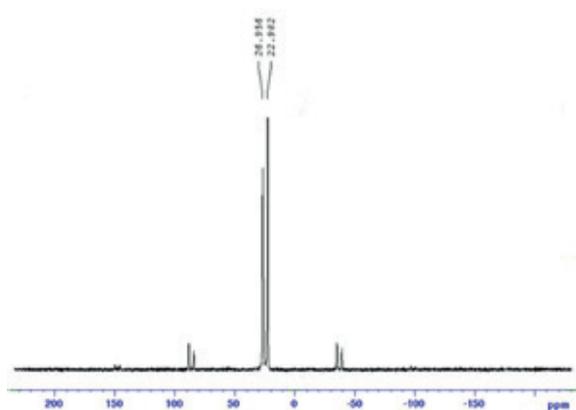
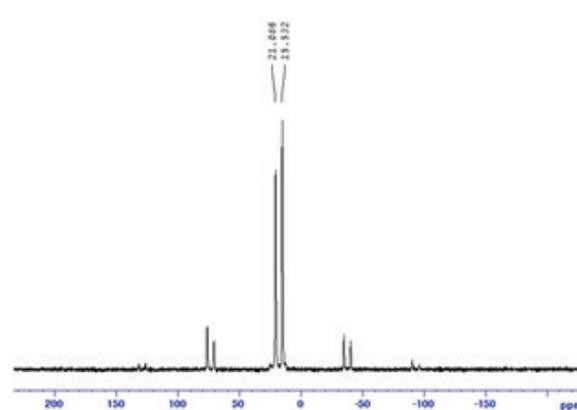
I and **II** in the structure of the chains: in this case one metal ion combines two ligand molecules. Compounds **I–III** have similar ^{31}P NMR spectra due to the protonation of one of the phosphonic groups. In Fig. 4 and 5 are ^{31}P NMR spectra of the compounds obtained. The ^{31}P NMR spectrum contains two main peaks at 22.982 and 26.956 ppm for compound **I**, and 15.532 and 21.086 ppm for compound **II**, corresponding to two phosphorus atoms with different coordination, due to the deprotonation of one of the phosphonic groups.

Table 1. Metal complexes with bisphosphonic acids

Number of complex	Formula	Chemical analysis
Complex I	$H_2N(CH_2)_{10}C(OH)(H_2P_2O_6)Ag_2$	Calculated, %: C – 23.55, H – 4.49, N – 2.50, O – 19.96, P – 11.04. Found, %: C – 23.4, H – 4.28, N – 2.62, O – 21.3, P – 11.5.
Complex II	$H_2N(CH_2)_{10}C(OH)(HPO_3)_2Pb$	Calculated, %: C – 23.91, H – 4.56, N – 2.54, O – 20.27, P – 11.22. Found, %: C – 23.8, H – 4.75, N – 2.46, O – 19.9, P – 11.5.
Complex III	$[H_2N(CH_2)_{10}C(OH)(H_3P_2O_6)]_2Ca$	Calculated, %: C – 36.07, H – 7.16, N – 3.82, O – 30.57, P – 16.91. Found, %: C – 35.2, H – 7.32, N – 3.58, O – 31.1, P – 16.6.

Table 2. Crystallographic data of complexes I, II and III

Parameters	I	II	III
Space group	P-1	P 21	P-1
Crystal system	Triclinic	Monoclinic	Triclinic
$a, \text{Å}$	5.610(2)	5.1136(6)	10.2195(3)
$b, \text{Å}$	7.254(3)	7.6588(9)	17.3940(6)
$c, \text{Å}$	40.983(4)	41.9070(4)	20.7457(7)
α	90.416(11)	90.243(3)	102.1790(2)
β	91.499(11)	90.0000	91.8880(2)
γ	100.217(13)	90.0000	90.0310(2)
Crystal size, mm ³	0.16×0.18×0.10	0.20×0.16×0.16	0.18×0.20×0.16
$V, \text{Å}^3$	1640.67	1641.25	3602.65
R_1 и $wR_2, I > 2\sigma(I)$	0.0402 and 0.0902	0.0511 and 0.0944	0.0432 and 0.0862


 Fig. 4. ³¹P NMR spectrum of complex I.

 Fig. 5. ³¹P NMR spectrum of complex II.

IR spectra of samples I and II are presented in Fig. 6 and 7. Both samples have many similar absorption bands: 3202–3186 cm^{-1} and 2930–2943 cm^{-1} correspond to asymmetric and symmetric stretching vibrations of NH_2 groups, 2912–2921 cm^{-1} and 2849–2910 cm^{-1} correspond to asymmetric and symmetric valence vibrations of CH_2 groups, 2450–

2413 cm^{-1} is responsible for the valence vibration of PO–H group, 1638–1623 cm^{-1} correspond to deformation vibrations of NH_2 group, absorption bands in the interval 1160–1100 cm^{-1} correspond to stretching vibrations of phosphorus compounds with oxygen, also there are absorption bands of 550–541 cm^{-1} , characteristic of hydroxyl groups.

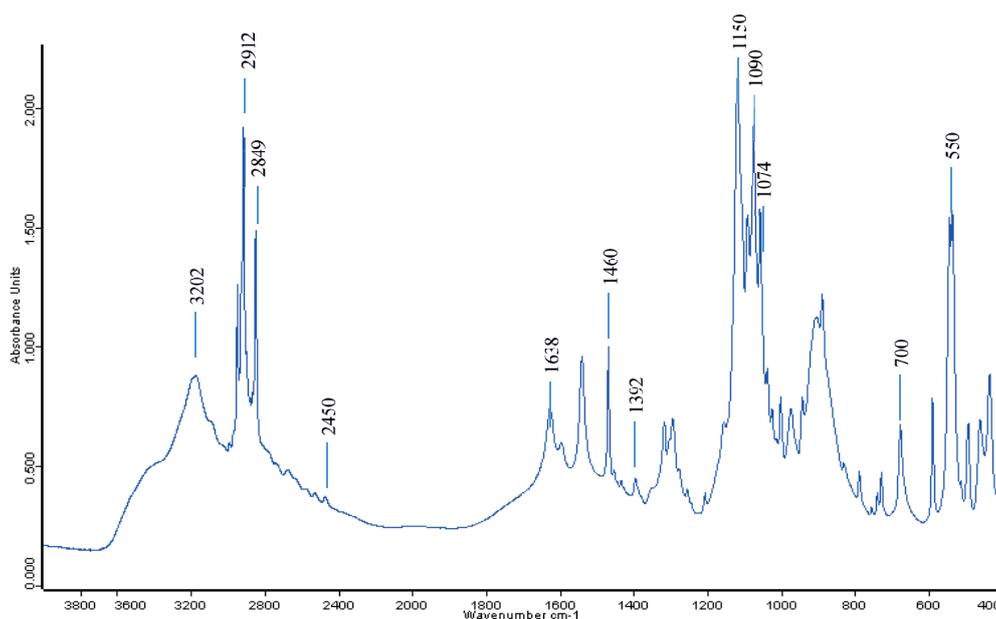


Fig. 6. IR spectrum of complex **I** (cm^{-1}):

$\nu_{\text{as}}(\text{NH}_2)$ 3202; $\nu_{\text{s}}(\text{NH}_2)$ 2930; $\nu_{\text{as}}(\text{CH}_2)$ 2912; $\nu_{\text{s}}(\text{CH}_2)$ 2849; $\nu(\text{PO-H})$ 2450; $\delta(\text{NH}_2)$ 1638; $\nu(\text{C-N})$ 1460; $\nu(\text{C-O})$ 1392; $\nu(\text{P=O})$ 1150; $\nu(\text{P-O})$ 1090; $\nu(\text{C-C})$ 1074; $\nu(\text{C-P})$ 700; $\nu_{\text{def}}(\text{O-H})$ 550.

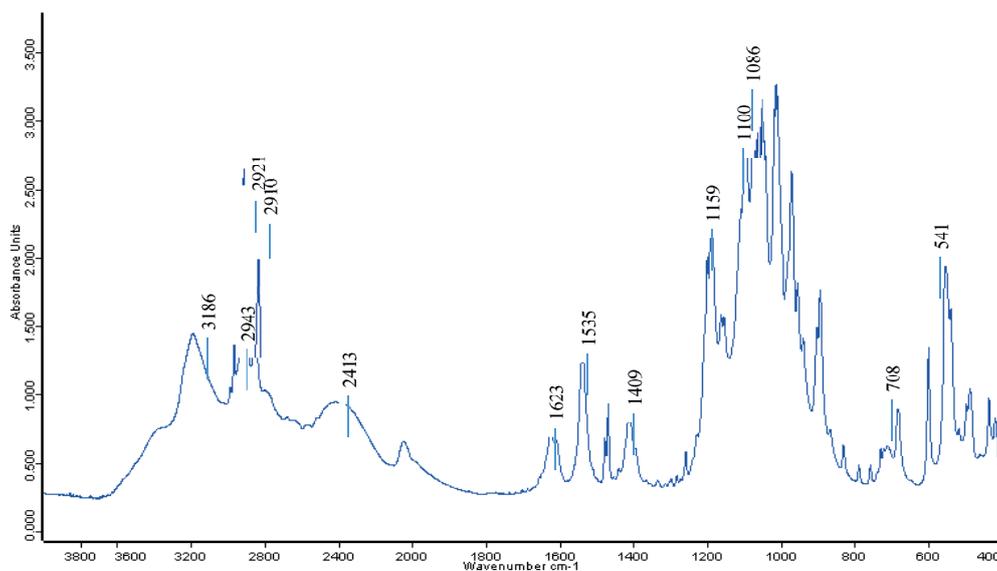


Fig. 7. IR-spectrum of complex **II** (cm^{-1}):

$\nu_{\text{as}}(\text{NH}_2)$ 3186; $\nu_{\text{s}}(\text{NH}_2)$ 2943; $\nu_{\text{as}}(\text{CH}_2)$ 2921; $\nu_{\text{s}}(\text{CH}_2)$ 2910; $\nu(\text{PO-H})$ 2413; $\delta(\text{NH}_2)$ 1623; $\nu_{\text{def}}(\text{O-H})$ 1535; $\nu(\text{C-N})$ 1466; $\nu(\text{C-O})$ 1409; $\nu(\text{P=O})$ 1159; $\nu(\text{P-O})$ 1100; $\nu(\text{C-C})$ 1080; $\nu(\text{C-P})$ 708; $\nu_{\text{def}}(\text{O-H})$ 541.

Bisphosphonic acids have the ability to extract metal ions from solutions. In cooperation with the researcher of the Department of Inorganic Chemistry of the University of Eastern Finland in Kuopio, Yuko Vepsalainen, Lime's ability to extract heavy metal ions from solutions, cadmium, lead and zinc, and silver ions has been studied.

The concentration of metal ions in aqueous solutions at various pH values was determined by atomic absorption spectroscopy on ICAP 6300 DUO. Analysis

error less than 1%. After that, bisphosphonic acid was added to the salt solutions, allowed to react with the reagents, the precipitate was filtered off and the content of metal ions in solutions at different pH was determined by AAS on ICAP 6300 DUO. The concentration of all ions with the addition of bisphosphonic acid is maximum at pH 0–1. Then there is a sharp drop in the concentration of metal ions in the solution. In the pH range from 2 to 6, up to 95–99% of heavy metal ions can be recovered from solutions. The exact pH at which the extraction

of a particular metal ion from the solution is maximum depends on the ability of the bisphosphonic acid to create complex with a particular ion.

On the Fig. 8 shown the content of metal ions in solution at different pH values.

The data obtained suggest that bisphosphonate ligands can also be used to separate the accompanying

metal ions. Bisphosphonates are able to actively extract up to 95–99% of metal ions from solutions to a residual content of several ppm. The ability to reuse bisphosphonate ligands is also key. For example, 11-amino-1-hydroxyundecylidene-1,1-bisphosphonic acid can be used dozens of times to recover metal ions without reducing efficiency.

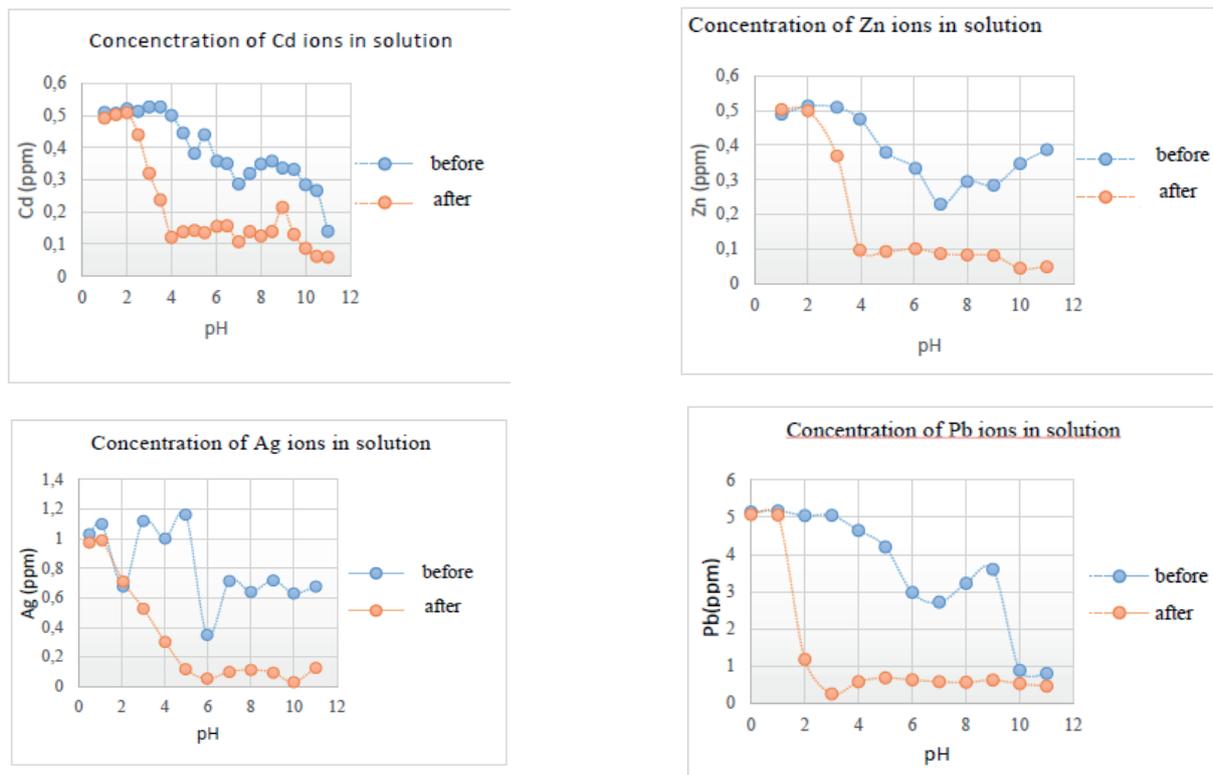


Fig. 8. Concentration of metal ions in solution from pH.

Conclusions

1. A method for the synthesis of metal complexes with bisphosphonate ligands consisting of heat treatment of solutions at 100 °C was developed and implemented;
2. Three new metal complexes with 11-amino-1-hydroxyundecylidene-1,1-bisphosphonic acid, M = Ag,

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Pb, Ca, were obtained, the crystal structures of these complexes were established.

3. It has been shown that this bisphosphonic acid binds easily to metal ions, which can be used in the industry for wastewater treatment from heavy metals, for example, lead, zinc, and calcium.

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