Preparation of Amorphous Water-Soluble Complexes of Biometals with (1-Hydroxyethylidene)diphosphonic Acid, 2-Aminoethanol, and 2-Amino-2-(hydroxymethyl)propane-1,3-diol

V. V. Semenov^a, N. V. Zolotareva^a, B. I. Petrov^a, E. V. Baranov^a, V. I. Titova^b, L. D. Varlamova^b, E. Yu. Geiger^b, I. D. Korolenko^b, and E. V. Dabakhova^b

^a G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, ul. Tropinina 49, Nizhni Novgorod, 603950 Russia e-mail: vvsemenov@iomc.ras.ru

^b Nizhni Novgorod State Agricultural Academy, pr. Gagarina 97, Nizhni Novgorod, 603107 Russia

Received December 8, 2014

Abstract—Multifold enhancement of solubility in water of Fe(III) and Mn(II) complexes with (1-hydroxyethylidene)diphosphonic acid has been achieved by their transformation into the corresponding salts via interaction of aqueous suspensions of the poorly soluble complexes with 2-aminoethanol and 2-amino-2-(hydroxymethyl)propane-1,3-diol. Molecular structure of tris(2-hydroxyethanaminium)(1-hydroxyethylidene)diphosphonate has been determined. Potential agricultural efficiency of the prepared iron and manganese derivatives as well as zinc and copper complexes with (1-hydroxyethylidene)diphosphonic acid as a microfertilizer has been estimated.

Keywords: (1-hydroxyethylidene)diphosphonic acid, iron, manganese, 2-aminoethanol, microfertilizer, agricultural efficiency

DOI: 10.1134/S1070363215050199

High solubility of metal complexes in water is a key factor of their efficient application as microfertilizer. Long-term storage of concentrated aqueous solutions (commercial form of many microfertilizers) under conditions of alternating temperature often results in precipitation of crystalline coordination compounds that are dissolved extremely slowly. We have earlier suggested a method to enhance the solubility of iron and manganese salts of (1-hydroxyethylidene)diphosphonic acid H₄L via the controlled treatment with potassium and ammonium hydroxides [1]. The so formed mixed salts are transformed into colored gels upon water removal, and their further drying yields transparent glass, easily grinded into a powder. Long-term storage of concentrated solutions of the mixed salts over winter and spring does not result in precipitation, probably due to the amorphous structure of the coordination compounds.

Herein we present a new method to enhance the solubility of iron and manganese salts via their treatment with 2-aminoethanol I and 2-amino-2-(hydroxymethyl)propane-1,3-diol **II**. The so prepared compounds as well as zinc and copper derivatives with (1-hydroxyethylidene)diphosphonic acid, readily soluble in water, were tested as microfertilizers.

Amines [2] and aqueous ammonia [3] formed poorly soluble mixed salts with (1-hydroxyethylidene)diphosphonic acid bound to transition or rare-earth metals. The crystalline compounds were isolated from the hot aqueous solutions under conditions of hydrothermal synthesis. On the contrary, the presence of one or three hydroxyl group(s) favored formation of amorphous compounds, readily soluble in water.



The following poorly soluble salts were used as models to test the solubility enhancement [4]: diiron(III) tris[(1-hydroxyethylidene)diphosphonate] tetrahydrate $Fe_2(H_2L)_3$ ·4 H_2O (solubility in water of 0.2 g in 100 mL of the solution) and manganese(II) (1-hydroxy-ethylidene)diphosphonate dihydrate MnH₂L·2H₂O (0.1 g per 100 mL) [4].

Six free acid groups were present in the $Fe_2(H_2L)_3$. 4H₂O molecule, capable of the salt formation with the amine. On top of that, neutral 2-aminoethanol ligand, being more nucleophilic, could replace four water molecules initially forming coordination bonds with iron. Hence, one molecule of the iron complex was expected to bind up to ten molecules of 2-aminoethanol I. The interaction of Fe₂(H₂L)₃·4H₂O suspension with a large excess of compound I (1 : 87 mol/mol) vielded the iron derivative containing nine 2-aminoethanol molecules, Fe₂(H₂L)₃·9H₂NCH₂CH₂OH (III). The product was a light-brown powder, readily soluble in water and 2-aminoethanol but poorly soluble in methanol. Evidently, one of the six acid groups remained unbound. The assumption was further supported by the result of the interaction of (1-hydroxyethylidene)diphosphonic acid with 2-aminoethanol. The isolated crystalline compound IV was a salt containing three fragments of the amine, $C(CH_3)(OH)$. $[P(O)O^{-}NH_{3}^{+}CH_{2}CH_{2}OH]_{3}[P(O)(OH)]$ (Fig. 1), as evidenced by the data of elemental analysis and X-ray diffraction analysis (Tables 1 and 2).

The available data on the dissociation constants $(pK_a^1 \ 1.70 \ \text{and} \ pK_a^2 \ 2.47)$ stated that (1-hydroxyethylidene)diphosphonic acid was a strong one [5]. However, the acidic properties were weakened at further dissociation steps $(pK_a^3 \ 7.28 \ \text{and} \ pK_a^4 \ 10.29)$, similarly to the polybasic acids; that explained the absence of coordination of the fourth molecule of 2aminoethanol with (1-hydroxyethylidene)diphosphonic acid.

The crystal of compound IV contained anions of (1-hydroxyethylidene)diphostriply deprotonated phonic acid $C(CH_3)(OH)[P(O)O_2^2][P(OH)(O)O^2]$ and the ammonium cations $HOCH_2CH_2NH_3^+$. The central C^1 atom of the anionic part of the molecule revealed tetrahedral coordination. The bond angles at C^1 atom ranged from 105.62(12)° to 113.39(8)° (Table 1). The P^2-O^6 bond length of 1.593(1) Å was comparable to that of the similar P–OH in the structure of the triply deprotonated (imid-CH₂)C(OH)[P(O)O₂²⁻][P(OH)(O)O⁻] Zolendronic acid (imid standing for imidazole fragment) [1.574(1) Å] [6]. The P^2-O^4 and P^2-O^5 bonds in the $[P(OH)(O)O^{-}]$ fragment were noticeable shortened [1.509(1) and 1.498(1) Å, respectively],

Table 1. Selected bond lengths (*d*) and bond angles (ω) in the molecule of tris(2-hydroxyethanaminium)(1-hydroxyethylidene)diphosphonate **IV**

Bond	<i>d</i> , Å	Angle	ω, deg
$C^1 - C^2$	1.523(2)	$C^{1}P^{1}O^{1}$	110.05(6)
$C^1 - O^7$	1.452(2)	$C^1P^1O^2$	107.78(6)
$C^1 - P^1$	1.853(2)	$C^{1}P^{1}O^{3}$	103.69(6)
$C^1 - P^2$	1.848(2)	$O^1P^1O^2$	111.44(6)
P^1-O^1	1.522(1)	$O^2 P^1 O^3$	110.82(6)
$P^1 - O^2$	1.525(1)	$O^1P^1O^3$	112.68(6)
P^1-O^3	1.538(1)	$C^{1}P^{2}O^{4}$	108.02(7)
$P^2 - O^4$	1.509(1)	$C^{1}P^{2}O^{5}$	111.62(7)
$P^2 - O^5$	1.498(1)	$C^1P^2O^6$	103.40(6)
$P^2 - O^6$	1.593(1)	$O^4 P^2 O^5$	117.12(6)
		$O^5P^2O^6$	109.97(6)
		$O^4 P^2 O^6$	105.68(6)
		$P^1C^1P^2$	113.39(8)
		$C^2C^1O^7$	105.62(12)
		$C^2C^1P^1$	111.9(1)
		$C^2C^1P^2$	110.72(10)
		$P^1C^1O^7$	107.23(9)
		$O^7 C^1 P^2$	107.51(9)

their lengths coinciding with those of the corresponding bonds in the Zolendronic acid [1.501(1) and 1.502(2) Å] [6]. Evidently, equality of the P²–O⁴ and P²–O⁵ bond lengths was due to delocalization of the negative charge and conjugation with the P=O bond in the O⁴–P²–O⁵ fragment (1.483–1.503 Å [7]). The O⁴P²O⁵ angle of 117.12(6)° was remarkably different from the O⁵P²O⁶ [109.97(6)°] and O⁴P²O⁶ [105.68(6)°] angles. The P¹–O¹⁻³ distances in the [P(O) O²₂⁻] fragment were very close [1.522(1)–1.538(1) Å], somewhat longer than the P²–O^{4,5} ones. The P¹–O¹⁻³ bond lengths were close to the average P–O distance in the O=P–O^{2–}₂ fragment with two delocalized negative charges (1.513 Å [7]). The angles between the O¹, O², and O³ atoms at the P¹ atom were close [110.82(6)°– 112.68(6)°].

The interaction of $Fe_2(H_2L)_3 \cdot 4H_2O$ with excess of 2-aminoethanol occurred at slight heating and was complete within 40 min. That was observed as complete dissolution of the complex suspension and formation of the transparent red-brown solution; compound **III** was isolated from it as light-brown powder, poorly soluble in ethanol, DMSO, and acetonitrile. The attempts to re-precipitate the product by addition of large volume of methanol or ethanol to the concentrated aqueous solution were not successful.

Parameter	Value
Gross formula	$C_8H_{29}N_3O_{10}P_2$
Molecular mass	389.28
Crystal system	Monoclinic
Space group	P2(1)/n
<i>a</i> , Å	10.6190(5)
b, Å	8.7304(4)
<i>c</i> , Å	18.4489(9)
β, deg	90.8920(10)
$V, Å^3$	1710.16(14)
Ζ	4
$d_{\rm calc}, {\rm g/cm}^3$	1.512
μ , mm ⁻¹	0.307
<i>F</i> (000)	832
$2\theta_{\text{max}}$, deg	52
Number of measured reflections	14075
Number of independent reflections	3342
R _{int}	0.0351
Goodness of fit	1.026
R_1 [for reflections with $I > 2\sigma(I)$]	0.0339
wR_2 [for reflections with $I > 2\sigma(I)$]	0.0904
R_1 (for all reflections)	0.0376
wR_2 (for all reflections)	0.0930
Residual peaks of electronic density,	0.391/-0.377
max/min, <i>e</i> , Å ³	

 Table 2. Basic crystallographic and structure refinement

 parameters of compound IV

The electronic absorption spectrum of compound III (Fig. 2) contained a weak band assigned to the d-d transition in the Fe³⁺ cation at 430 nm, and a set of poorly resolved stronger bands in UV region, assigned to the ligand and the metal-ligand transitions [8].

Interaction of $Fe_2(H_2L)_3 \cdot 4H_2O$ with 2-aminoethanol in aqueous medium was performed at the reactants ratios of 1 : 7 and 1 : 4. In the first case, the iron complex was completely dissolved after 2 h stirring at 20°C, whereas in the latter case the solution remained turbid due to the lack of 2-aminoethanol. Filtration, water removal, and drying in vacuum gave compounds of the same composition, $Fe_2(H_2L)_3 \cdot 5H_2NCH_2CH_2OH \cdot$ $4H_2O$ (V). The solvent evaporation led to formation of yellow-orange glassy layer that could be easily ground in the orange powder, readily and completely soluble in water. Electronic absorption spectra of the products were identical to that shown in Fig. 2.

Hence, two types of compounds could be prepared from the poorly soluble $Fe_2(H_2L)_3 \cdot 4H_2O$ iron complex and 2-aminoethanol. In anhydrous medium and in the excess of compound **I**, five of six free P(O)OH acid groups reacted with $H_2NCH_2CH_2OH$ to form the ammonium salt. Simultaneously, all the four water molecules were replaced from the coordination sphere of iron, and the product **III** was of the $Fe_2(H_2L)_3$. $9H_2NCH_2CH_2OH$ composition. The reaction in an aqueous medium yielded the hydrated complex **V**, $Fe_2(H_2L)_3 \cdot 5H_2NCH_2CH_2OH \cdot 4H_2O$.



Fig. 1. General view of molecule IV in the crystal. Ellipsoids are given with probability of 30%; some hydrogen atoms are not shown for the sake of simplicity.



Fig. 2. Electronic absorption spectra of aqueous solution of compound III at (1) 2.74×10^{-3} and (2) 1.60×10^{-4} mol/L.

The prepared complex salts were infinitely soluble in water and did not form solid precipitate upon cooling of the concentrated solutions. The Fe₂(H₂L)₃· 4H₂O complex did not react with excess of the primary amine containing no hydroxyl groups. For example, vigorous stirring of suspension of 1.8 g of the iron complex in 20 mL of (3-aminopropyl)triethoxysilane (EtO)₃Si(CH₂)₃NH₂ at heating to 100°C did not result in the complex dissolution. Similarly, 2.0 g of the iron complex was not dissolved in a large excess (20 mL) of iminodiethanol; however, addition of 4 mL of water at heating to 50°C resulted in complete dissolution of the suspension to form transparent red-brown solution.

Whereas compound III was readily soluble in 2-aminoethanol, vigorous stirring of a light-pink suspension of MnH₂L·2H₂O in 2-aminoethanol yielded a finely dispersed dark-grey insoluble MnH₂L·xH₂NCH₂CH₂OH· yH₂O salt VI that strongly densified the reaction mixture and complicated isolation of the pure reaction product. Addition of water (10 mL per 1 g of the starting MnH₂L·2H₂O) resulted in dissolution of the formed salt VI in the mixed 2-aminoethanol-H₂O solvent. In view of that, preparation of manganese complex with 2-aminoethanol was performed only in aqueous medium. White aqueous suspension of the manganese complex became transparent and turned red 15 min after addition of excess of 2-aminoethanol; the color was changed to dark-cherry after 12 h. The solvent evaporation and heating in vacuum yielded the manganese salt dihydrate MnH2L·2H2NCH2CH2OH· 2H₂O (VII), brown powder, readily soluble in water and poorly soluble in methanol. Precipitate was not formed during the long-term storage of concentrated solution of complex VII at alternating temperatures as well as upon addition of a large volume of methanol. Electronic absorption spectrum of solution of com-



Fig. 3. Electronic absorption spectra of aqueous solution of the manganese complex VII.

pound **VIII** (Fig. 3) contained a weak band corresponding to Mn^{2+} cation at 450 nm (21740 cm⁻¹, ${}^{4}T_{2g}$) [8] and a stronger absorption band at 230–370 nm assigned to the presence of the ligand.

2-Amino-2-(hydroxymethyl)propane-1,3-diol II was less reactive towards iron and manganese complexes as compared to 2-aminoethanol I. Dissolution of the $Fe_2(H_2L)_3$ ·4H₂O complex in the aqueous phase in the presence of compound I occurred at room temperature, whereas in the case of compound II the dissolution was possible only upon heating to 80-90°C. After water removal, transparent strong green-yellow glass was obtained; it could be ground into powder only after prolonged (14 h) annealing in air at 110–115°C. The subsequent heat treatment at 200°C in vacuum resulted in mass loss of about 16%, due to drying and elimination of small amount of the starting compound II. According to the elemental analysis data, the obtained water-soluble complex VIII contained six molecules of 2-amino-2-(hydroxymethyl)-propane-1,3diol and four water molecules: Fe₂(H₂L)₃·6H₂NC(CH₂OH)₃· $4H_2O.$

White suspension of the MnH₂L·2H₂O manganese complex was dissolved in water in the presence of compound **II** faster (within 20 min) and at lower temperature (50°C) as compared to the Fe₂(H₂L)₃· 4H₂O iron complex. Each of the acid groups bound a single molecule of the amine, and two water molecules were incorporated into the metal coordination sphere in the so formed MnH₂L·2H₂NC(CH₂OH)₃·2H₂O complex **IX**. In contrast to the corresponding iron compound, the manganese complex **IX** was easily ground into the fine-dispersed light-grey powder after water evaporation and drying at 110°C.

A special feature of (1-hydroxyethylidene)diphosphonic acid and 2-amino-2-(hydroxymethyl)propane1,3-diol derivatives was formation of glassy and resinlike substances. Interaction of those reactants at the molar ratio of 1 : 4 or 1 : 3 in various organic solvents (methanol, ethanol, acetone, toluene, or dimethylsulfoxide) resulted in fast formation of white suspension of the salt that was transformed into a colorless viscous resin precipitating at the flask bottom under the reaction conditions. In the case of highboiling DMSO as solvent, the reaction product isolated after separation the solvent off and heating at 70-80°C remained resin-like. In the cases of other solvents, solidified melts were so obtained; they could hardly be peeled off the flask and were softened upon heating to 100-120°C. Their heating at 200°C in vacuum resulted in the melting and expansion; however, no solid or liquid products were condensed at the cold walls of the reactor.

The product cooling gave a transparent glassy substance that could be broken into smaller pieces and ground into white powder in a porcelain mortar. According to the elemental analysis data, the obtained salt **X** was of the H₄L·4NH₂C(CH₂OH)₃ composition, with four molecules of compound **II** being bound to a single molecule of the four-basic (1-hydroxy-ethylidene)diphosphonic acid. The salt **X** was formed at the reactants ratio of 1 : 4 or 1 : 3 in any of the above-mentioned solvents. Solubility of compound **X** in methanol was of 1.8 g in 100 mL.

Hence, the products of the reaction between (1hydroxyethylidene)diphosphonic acid with amines I and II were significantly different. The salt IV readily crystallized, whereas the resin-like compound X turned into amorphous glass upon heating. Likely, the latter compound was a coordination polymer due to formation of strong intermolecular hydrogen bonds between the P= $O^{\delta-}$ and $^{\delta+}H-O-C$ fragments. The three electronegative hydroxyl groups (OH, $\sigma_I = 0.25$) [9] were linked to the same carbon atom in the molecule of 2-amino-2-(hydroxymethyl)propane-1,3-diol; therefore, their acidity was significantly enhanced to exceed that of the hydroxyl group in the 2-aminoethanol molecule (CH₂OH, σ_I 0.05). The salt formation induced the appearance of positive charge at the nitrogen atom and further increase of the acidic properties of compound II. In the 2-aminoethanol molecule, nitrogen atom was separated from the hydroxyl group by an additional methylene bridge, and the positive charge was better compensated.

Polymeric structure and the strong hydrogen bonding of the salt \mathbf{X} caused its poor solubility in the organic solvents and good solubility in water.

According to X-ray diffraction analysis data, the coordination compounds of iron and manganese (III, V, and VII–IX) were X-ray amorphous (Fig. 4). The diffraction patterns were identical and contained peaks of amorphous halo at the reflection angles of 5–8, 17–20, and 30° – 33° . The peaks of the manganese compounds were somewhat shifted towards lower 20 values. The middle amorphous halo was absent in the diffraction pattern of compound V.

The suspensions of somewhat better water-soluble solid complexes of iron $Fe(H_3L)_3 \cdot 4H_2O$ and manganese $Mn(H_3L)_2 \cdot 4H_2O$ readily passed into the aqueous solution upon addition of 2-aminoethanol. Synthesis, isolation, and drying (see Experimental section) yielded the hydrated compounds of iron and manganese containing six [Fe(H_3L)_3 \cdot 6H_2NCH_2CH_2OH \cdot 2H_2O, XI] or three [Mn(H_3L)_2 \cdot 3H_2NCH_2CH_2OH \cdot 4H_2O, XII] molecules of 2-aminoethanol. Of all the prepared complexes, only compound XII was crystalline and revealed sufficiently high solubility in the aqueous medium (yet the solubility was lower than that of the amorphous compounds).

IR spectra of the metal complexes and the salts of (1-hydroxyethylidene)diphosphonic acid with 2-aminoethanol and 2-amino-2-(hydroxymethyl)propane-1,3diol were identical and contained three absorption regions at 3700–2000, 1700–1500, and 1200–900 cm⁻¹. The bands were assigned using the information provided in [10, 11]. In particular, the strong broad overlapping bands at 3700–2000 cm⁻¹ corresponded to stretching of O–H bonds in alcohol hydroxyl groups as well as N–H and O–H bonds in the H₃N⁺–C and P(O–H) groups. The two medium-intensity bands at 1620 and 1530 cm⁻¹ were assigned to the N–H deformation vibration, whereas the very strong structured band with maximum at 1050 cm⁻¹ was due to vibrations of the C–O, C–N, and P(O)OH fragments.

The reactions with amines **I** and **II** were more convenient ways to prepare water-soluble forms of iron and manganese coordination compounds as compared to the earlier developed procedure of accurate titration of the poorly soluble salts with (1hydroxyethylidene)diphosphonic acid by potassium or ammonium hydroxides [1]. Good results were achieved only in the cases of the amines containing hydroxyl groups, becoming readily water-soluble organic amines. In the absence of the C(OH) groups in the amines they did not react with the compounds of iron and manganese. That was observed as preservation of the two-phase system upon prolonged vigorous stirring of the complex aqueous suspension in the presence of the amine at 80-90°C.

owing to the presence of the latter. The required amine

amount could be easily calculated taking into account

the number of P(O)OH groups in the coordination

compounds (6 mol per 1 mol of Fe₂(H₂L)₃·4H₂O and 2 mol per 1 mol of MnH₂L·2H₂O. The experiments

revealed that the complexes could be dissolved even with a slight lack of the amine (10-15%) with respect

to the calculated amount. The sharp solubility

enhancement was due to both formation of the salts via the free (not bound to the cation) groups of the protic

acid and to the presence of hydroxyl groups in the

During the 2014 vegetation period, we performed a series of model, laboratory, and vegetation tests to estimate the agricultural efficiency of the novel microfertilizers. Spring rape was utilized as a biological model. Aqueous solutions of the (1-hydroxyethylidene)diphosphonic acid complexes with copper, zinc, manganese, and iron were prepared. The copper $Cu(H_3L)_2$. 5H2O and zinc ZnH2L·4H2O compounds revealed sufficiently high solubility in aqueous media. Due to the higher solubility of the Fe(H₃L)₃·4H₂O and $Mn(H_3L)_2 \cdot 4H_2O$ salts as compared to that of $Fe_2(H_2L)_3$. 4H₂O and MnH₂L·2H₂O, the following pairs of iron and manganese complexes with (1-hydroxyethylidene) diphosphonic acid (with and without 2-aminoethanol as the solubility promotor) were selected for the tests: Fe(H₃L)₃·4H₂O and Fe(H₃L)₃·6H₂NCH₂CH₂OH·2H₂O XI; Mn(H₃L)₂·4H₂O and Mn(H₃L)₂·3H₂NCH₂CH₂OH· 4H₂O XII. Moreover, the readily soluble MnH₂L· 2H2NCH2CH2OH·2H2O VII complex was tested as well.

The one-year results concluded on the possibility of application of the prepared compounds as microfertilizers. The suggested form of zinc-containing fertilizer (ZnH₂L·4H₂O) showed much better results when applied to spring rape than zinc sulfate. The highest effect was achieved out-root fertilization, vielding additional 105 g of the total mass (including 55 g of pods) per 5 kg of soil in the vegetation vessel as compared to the zinc-free reference test. Copper compounds were more efficient in the case of the seeds treatment. The novel fertilizer formulation Cu(H₃L)₂. 5H₂O was 1.4 times more efficient towards rape pods

yield than conventional copper sulfate. Compounds VII and XII when used for out-root fertilization were the most efficient of the manganese compounds; the total biomass increase was of 91 and 45 g/vessel, respectively, and the increase of pods mass was of 58 and 45 g/vessel, respectively. The iron complexes showed no advantages over iron sulfate.

Fig. 4. X-ray powder diffraction patterns of compounds

(1) III, (2) V, (3) VII, (4) VIII, and (5) IX.

The amine should be introduced into the reaction mixture after complete dissolution of the metal compound (iron hydroxide or basic manganese carbonate) during commercial production of the aqueous solutions of iron and manganese aminium(1hydroxyethylidene)diphosphonates. The so prepared concentrated solutions were stable upon long-term storage under conditions of alternating temperatures, revealing no precipitation of crystalline solids.

Dry powders of the water-soluble aminium salts were wetted after addition of the minimal amount of water, and turned into transparent viscous liquids 1-2 h later. Further addition of water decreased the viscosity, and the solutions rapidly became the lowviscous colored fluids. In view of that, it was not possible to determined the compounds solubility quantitatively; instead, the prepared complexes should be regarded as the compounds with infinitely high solubility.

EXPERIMENTAL

IR spectra of the suspensions in vaseline oil placed between KBr plates were recorded using a FSM 1201



IR-Fourier spectrometer. Electronic absorption spectra of the aqueous solutions were registered using a Perkin-Elmer Lambda 25 spectrophotometer.

X-ray diffraction data were obtained using a Smart APEX diffractometer (graphitic monochromator, Mo K_{α} radiation, $\lambda 0.71073$ Å, ω - and φ -scans, 100 K). Absorption was accounted for taking advantage of SADABS software [12]. Structure of compound III was solved via direct method and refined via least squares method over F_{hkl}^2 in the anisotropic approximation for all the non-hydrogen atoms. Hydrogen atoms were placed into the geometrically defined positions and refined in *rider* model $[U_{iso}(H) =$ $1.2U_{eq}(C)$, $1.5U_{eq}(O)$]. Positions of hydrogen atoms at the O^6 and O^7 oxygen atoms [OH groups of (1-hydroxyethylidene)diphosphonic acid] and the N^(1Å-C) atoms of HOCH₂CH₂NH₃⁺ molecules were fund via differential Fourier synthesis of the electronic density and refined under isotropic approximation. All computations were performed using SHELXTL v.6.12 software package [13]. The selected bond lengths and angles of compound IV are collected in Table 1. Basic parameters of the X-ray diffraction experiment and the solved structure of compound IV are given in Table 2.

(1-Hydroxyethylidene)diphosphonic acid ("pure" grade, Khimprom, TU 2439-363-05783441-2002) was used; zinc (1-hydroxyethylidene)diphosphonate tetrahydrate [14] and copper bis(1-hydroxyethylidene) diphosphonate pentahydrate [15] were prepared as described in the corresponding references.

Diiron(III) tris[(1-hydroxyethylidene)diphosphonatel nona(2-hydroxyethanaminium) (III). Α mixture of 1.52 g (1.91×10^{-3} mol) of the finely ground $Fe_2(H_2L)_3$ ·4H₂O iron complex and 10 mL (1.67 × 10^{-1} mol) of 2-aminoethanol was stirred at 50°C. After 40 min, 2-aminoethanol was distilled off, and the residue was heated in vacuum during 1 h at 110-130°C. Yield 1.56 g $(1.23 \times 10^{-3} \text{ mol}, 64\%)$, light-brown powder, well soluble in water, poorly soluble in methanol, and insoluble in ethanol, DMSO, and acetonitrile. IR spectrum, v, cm⁻¹: 3500–2200 br, 2127, 1623, 1531, 1278, 1087, 1006, 813, 723, 664. Found, %: C 21.83; H 6.88; N 10.15; Fe 8.90; P 14.80. C₂₄H₈₁N₉Fe₂O₃₀P₆. Calculated, %: C 22.63; H 6.41; N 9.90; Fe 8.77; P 14.59.

Tris(2-hydroxyethanaminium)(1-hydroxyethylidene)diphosphonate (IV). 3.45 g (5.64×10^{-2} mol) of 2-aminoethanol was added to 3.16 g (1.41×10^{-2} mol) of finely ground (1-hydroxyethylidene)- diphosphonic acid in a porcelain mortar, and the mixture was stirred. The formed viscous mass solidified after 15 min. Re-crystallization from hot methanol yielded 5.49 g (0.95×10^{-2} mol, 67%) of the H₄L·3NH₂CH₂CH₂OH salt; well soluble in water and poorly soluble in methanol. IR spectrum, v, cm⁻¹: 3500–2200 br, 2145, 2046, 1596, 1552, 1281, 1084 sh, 1033, 938, 813, 723. Found, %: C 24.26; H 7.47; N 11.06; P 16.31. C₈H₂₉N₃O₁₀P₂. Calculated, %: C 24.68; H 7.51; N 10.79; P 15.91.

Diiron(III) tris(1-hydroxyethylidenediphosphonate) penta(2-hydroxyethanaminium) tetrahydrate (V). 0.68 g (1.12×10^{-2} mol) of 2-aminoethanol was added to a stirred suspension of 1.29 g (1.62×10^{-3} mol) of the finely ground Fe₂(H₂L)₃·4H₂O iron complex in 15 mL of distilled water. 12 h later water was removed, the glassy mass was ground, and the obtained orange powder was incubated in vacuum at 100°C. Yield 1.53 g (1.39×10^{-3} mol, 86%), IR spectrum, v, cm⁻¹: 3700–2000 br, 1623, 1525, 1278, 1087, 1000, 813, 724, 664. Found, %: C 17.91; H 5.36; N 6.74; Fe 10.18; P 16.94. C₁₆H₆₁N₅Fe₂O₃₀P₆. Calculated, %: C 17.45; H 5.58; N 6.36; Fe 10.14; P 16.87.

Manganese(II) (1-hydroxyethylidene)diphosphonate bis(2-hydroxyethanaminium) dihydrate (VII) was prepared similarly from 1.78 g (5.70×10^{-3} mol) of the MnH₂L·2H₂O manganese complex, 10 mL of distilled water, and 1.43 g (2.34×10^{-2} mol) of 2aminoethanol. Yield 2.26 g (5.0×10^{-3} mol, 88%). IR spectrum, v, cm⁻¹: 3125 br, 2800–2000 br, 1620, 1528, 1066, 995, 950, 819, 721, 658. Found, %: C 16.96; H 5.94; N 6.84; Mn 13.06; P 14.75. C₆H₂₆N₂MnO₁₂P₂. Calculated, %: C 16.56; H 6.02; N 6.44; Mn 12.62; P 14.24.

Diiron(III) tris[(1-hvdroxvethvlidene)diphosphonate] hexa[1,3-dihydroxy-2-(hydroxymethyl)propan-2-aminium]) tetrahydrate (VIII). 3.11 g (2.56 \times 10^{-2} mol) of 2-amino-2-(hydroxymethyl)propane-1,3diol ground in a mortar was added portionwise to a stirred suspension of 3.39 g (4.26×10^{-3} mol) of the finely ground Fe₂(H₂L)₃·4H₂O iron complex in 25 mL of distilled water. The dissolution was complete after 30 min at 80-90°C. Water was removed; the residue was dried at 110-115°C, ground, and dried in vacuum at 200°C. Yield 5.62 g (3.69·10⁻³ mol, 87%), yellow powder, well soluble in water. IR spectrum, v, cm⁻¹: 3208 br, 2750-2090 br, 1617, 1522, 1054, 813, 723, 664, 580, 473, Found, %: C 24.07; H 6.35; Fe 7.40; P 12.31. C₃₀H₉₂N₆Fe₂O₄₃P₆. calculated, %: C 23.66; H 6.09; Fe 7.34; P 12.21.

Manganese(II) (1-hydroxyethylidene)diphosphonate bis[1,3-dihydroxy-2-(hydroxymethyl)propan-2aminium] dihydrate (IX) was prepared similarly from 4.13 g (1.32×10^{-2} mol) of the MnH₂L·2H₂O manganese complex, 50 mL of distilled water, and 3.35 g (2.77×10^{-2} mol) of 2-amino-2-(hydroxymethyl)propane-1,3-diol. Yield 6.47 g (1.17×10^{-2} mol, 87%), coarsely dispersed light-grey powder. IR spectrum, v, cm⁻¹: 3600–3020 br, 2750–2200 br, 2077, 1609, 1527, 1056, 994, 950, 905 sh, 819, 721, 657, 559, 479. Found, %: C 21.31; H 6.05; Mn 9.82; P 11.07. C₁₀H₃₄N₂MnO₁₆P₂. Calculated, %: C 21.63; H 6.17; Mn 9.89; P 11.16.

Tris[1,3-dihydroxy-2-(hydroxymethyl)propan-2aminium] (1-hydroxyethylidene)diphosphonate (X). 5.3 mL of 0.72 M of (1-hydroxyethylidene)diphosphonic acid solution in ethanol (0.86 g, 3.82×10^{-3} mol) was added dropwise at stirring to a hot solution of 1.39 g (1.15×10^{-2} mol) of 2-amino-2-(hydroxymethyl)propane-1,3-diol in 10 mL of ethanol. 12 h later the solvent was decanted; the residue was dried in air during 7 h at 115°C and in vacuum at 200°C. Yield 1.89 g (2.74×10^{-3} mol, 72%), colorless glassy mass. IR spectrum, v, cm⁻¹: 3650–3000 br, 2800–2000 br, 1617, 1528, 1293, 1125, 1057, 968, 905, 807, 724, 643, 539, 464. Found, %: C 31.87; H 7.97; P 9.03. C₁₈H₅₂N₄O₁₉P₂. Calculated, %: C 31.31; H 7.59; P 8.97.

The reactions in mixed solvents were performed similarly, adding ethanolic solution of (1-hydroxyethylidene)diphosphonic acid to a hot solution or suspension of compound **II** in methanol, acetone, toluene, or DMSO. Compound **II** was completely dissolved in CH₃OH and DMSO and partially dissolved in acetone and toluene.

Iron(III) tris[(1-hydroxyethylidene)diphosphonate] hexa(2-hydroxyethanaminium) dihydrate (XI). 10.22 g (1.67×10^{-1} mol) of 2-aminoethanol was added upon stirring to a suspension of 18.62 g (2.50×10^{-2} mol) of the finely ground Fe(H₃L)₃·4H₂O complex in 200 mL of water. 15 min later the mixture was evaporated; the residue was heated in air during 15 h and in vacuum at 220°C. Yield 24.50 g, light-green powder. IR spectrum, v, cm⁻¹: 3600–2200 br, 1627, 1527, 1272, 1030 br, 914 sh, 804, 725, 660, 570. Found, %: C 19.57; H 6.50; Fe 5.20; P 16.32. C₁₈H₇₁N₆FeO₃₁P₆. Calculated, %: C 19.48; H 6.45; Fe 5.03; P 16.75.

Manganese(II) bis[(1-hydroxyethylidene)diphosphonate] tris (2-hydroxyethanaminium) tetrahyd**rate (XII)** was prepared similarly form 11.01 g (2.05×10^{-2} mol) of the Mn(H₃L)₂·4H₂O complex, 100 mL of water, and 4 mL (4.08 g, 6.69×10^{-2} mol) of 2-aminoethanol. Yield 11.37 g ($1.58 \cdot 10^{-2}$ mol, 77%), light-brown powder. IR spectrum, v, cm⁻¹: 3600–2100 br, 1624, 1509, 1302, 1272, 1139, 1071, 1021, 988, 929 sh, 893, 787, 725, 663, 642, 580, 538. Found, %: C 17.04; H 6.55; Mn 7.66; P 17.27. C₁₀H₄₃N₃MnO₂₁P₄. Calculated, %: C 16.67; H 6.02; Mn 7.63; P 17.20. Solubility 1.94 g in 100 mL of the solution.

ACKNOWLEDGMENTS

The studies were performed at Analytical Center of Institute of Organometallic Chemistry, Russian Academy of Sciences.

This work was financially supported by Presidium of Russian Academy of Sciences in the frame of the "Targeted synthesis of compounds with desired properties and development of functional materials based thereof" program.

REFERENCES

- Zolotareva, N.V. and Semenov, V.V., Russ. J. Gen. Chem., 2014, vol. 84, no. 4, p. 715. DOI: 10.1134/ S1070363214040197.
- Liu, F.Y., Roces, L., Sa Ferreira, R.A., Garsia-Granda, S., Garsia, J.R., Carlos, L.D., and Rocha, J., *J. Mater. Chem.*, 2007, vol. 17, p. 3697. DOI: 10.1039/B703487C.
- Dong, D.P., Liu, L., Sun, Z.G., Jiao, C.Q., Liu, Z.M., Li, C., Zhu, Y.Y., Chen, K., and Wang, C.L., *Cryst. Growth Des.*, 2011, vol. 11, p. 5346. DOI: 10.1021/ cg2009368.
- Zolotareva, N.V., Semenov, V.V., and Petrov, B.I., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 11, p. 1985. DOI: 10.1134/S1070363213110030.
- Dyatlova, N.M., Temkina, V.Ya., and Popov, K.I., Kompleksony i kompleksonaty metallov (Complexones and Complexonates of Metals), Moscow: Khimiya, 1988.
- Sarkar, A. and Cukrowski, I., Acta Crystallogr. (E), 2011, vol. 67, p. 2980. DOI: 10.1107/S1600536811042206.
- Allen, F.H., Kennard, O., Watson, D.G., Brammer, L., Orpen, A.G., and Taylor, R., *J. Chem. Soc. Perkin Trans.* 2, 1987, no. 12, pp. S1–S19. DOI: 10.1039/ P298700000S1.
- 8. Liver, A.B.P., *Inorganic Electronic Spectroscopy*, Amsterdam: Elsevier, 1984, vol. 2.
- 9. Vereshchagin, A.N., *Induktivnyi effekt. Konstanty zamestitelei dlya korrelyatsionnogo analiza* (Inductive Effect. The Constants of Substituents for the Correlation Analysis), Moscow: Nauka, 1988.

1124

- Kazitsina, L.A. and Kupletskaya, N.B., *Primenenie UF*, *IK i YaMR spektroskopii v organicheskoi khimii* (Application of UV, IR, and NMR Spectroscopy in Organic Chemistry), Moscow: Vysshaya Skola, 1971.
- 11. Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S., *Atlas IK spektrov fosfororganicheskikh soedinenii* (Atlas of the IR Spectra of Organophosphorus Compounds), Moscow: Nauka, 1984.
- 12. Sheldrick, G.M., *SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, Wisconsin, USA, 1998.
- 13. Sheldrick, G.M., SHELXTL v. 6.12.Structure Determination Software Suite. Bruker AXS, Madison, Wisconsin, USA, 2000.
- Urinovich, E.M., Bikhman, B.I., Smirnova, V.A., Selivanova, E.B., Gurevich, M.Z., Zhadanov, B.V., Shugal, N.F., and Adamova, G.M., *Zh. Neorg. Khim.*, 1977, vol. 22, no. 10, p. 2679.
- Kushikbaeva, B.H., Mitrofanova, N.D., Martynenko, L.I., and Spitsyn, V.I., *Dokl. Akad. Nauk SSSR*, 1987, vol. 293, no. 3, p. 627