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Preparation of Iron(II) Water-Soluble Compounds Based on Iron(0), (1-Hydroxyethylidene)diphosphonic Acid, and Organic Amines

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Abstract—The reaction of aqueous suspension of finely dispersed iron with one equivalent of (1-hydroxyethylidene)diphosphonic acid (H_4L) results in poorly soluble iron(II) (1-hydroxyethylidene)diphosphate $FeH_2L·H_2O$. The reaction with two equivalents of the acid gives a water-soluble compound $Fe(H_3L)_2$, which undergoes disproportionation up to $FeH_2L·H_2O$ and H_4L. The reaction of a $FeH_2L·H_2O$ aqueous suspension with an organic amine results in the dissolution of the complex. Heating the $FeH_2L·H_2O$ aqueous suspension in a pressure reactor at 150°C in the presence of KF catalytic amounts causes the formation of a new crystal phase and X-ray-amorphous admixtures.

Keywords: (1-hydroxyethylidene)diphosphonic acid, carbonyl iron, reduced iron, 2-aminoethanol, 2-amino-2-(hydroxymethylpropane)-1,3-diol

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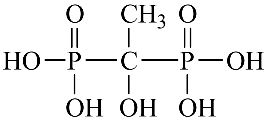
Tetrabasic (1-hydroxyethylidene)diphosphonic acid (H_4L) is one of most effective complexons forming highly stable complexes with metals.



$$HO-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH$$

H_4L

Chemical compounds of this acid with biometals (sodium, potassium, magnesium, calcium, zinc, manganese, iron, cobalt, copper, and molybdenum) appear promising for use in the food industry, medicine, animal husbandry, and crop production. Water-soluble iron complexes [1, 2] showed good results in the fight against yellow disease of plants. This disease is caused by the deficiency of the iron water-soluble form. In principle, the soil may contain a great deal of this metal, but it is converted to insoluble carbonates, and plants do not obtain it for their development.

(1-Hydroxyethylidene)diphosphonic acid forms metal complexes of different solubility. Copper and zinc compounds have a high solubility, whereas manganese, iron, and cobalt compounds are poorly soluble in water. First of all iron in the oxidation state 2+ is required for plant nutrition. Most abundant, affordable, and cheapest source of iron(II) is its sulfate $FeSO_4·7H_2O$ (copperas). It is sufficiently soluble (26.3 g per 100 mL at 20°C), resistant to oxidation, and usually is a part of combined fertilizers and microfertilizers. Iron(II) nitrate and iron(II) chloride are not used because they are oxidized in air and turn into salts of iron(III).

Thus, the range of available derivatives of bivalent iron resistant to fast oxidation in air is limited. In this connection the search for convenient procedures for production of such derivatives appears to be urgent. In the present communication we present the method for preparation a difficultly soluble inoxidable in air coordination compound of bivalent iron and for transfer it into aqueous solutions using solubility promotors.

The iron(II) complex was synthesized by the reaction of a metal iron suspension with (1-hydroxyethylidene)diphosphonic acid in aqueous medium at the equimolar ratio of the reagents. Carbonyl iron and reduced iron were used.

$$Fe^0 + H_4L = FeH_2L + H_2. \tag{1}$$

After intensive stirring of the mixture at 70°–90° within 1.0–1.5 h a white precipitate of difficultly soluble iron(II) (1-hydroxyethylidene)diphosphate, $FeH_2L\cdot H_2O$ (**1**), was formed, which was filtered off, washed on the filter with distilled water, and dried in an inert atmosphere. The color changed from white to blue-green during drying. One molecule of crystallization water enters into the composition of the compound. Heating the compound in a vacuum up to 200°C resulted in discoloration caused by the final dehydration. The initial blue-green color returns on keeping the compound in air. Its solubility is modest (0.14 g in 100 mL of solution). The color test for Fe^{2+} and Fe^{3+} showed that prolonged (up to 90 day) storage in air access did not lead to oxidation. Addition of a $K_3Fe(CN)_6$ solution causes the Turnbull's blue precipitation (color reaction for the Fe^{2+} cation), whereas addition of an ammonium thiocyanate solution (color reaction for the Fe^{3+} cation) does not give a red coloring.

According to the X-ray diffraction analysis, compound **1** exists in a crystalline form. Tightly interlocked crystals in the form of long threads precipitated from the aqueous solution. The aggregates can be arranged both in parallel to each other and disorderly. The phenomenon of the formation of metal (1-hydroxyethylidene)diphosphates in the form of thready crystals and their aggregates is common for manganese(II) [3], cobalt(II) [4], and iron(II) derivatives.

The presence or absence of an X-ray amorphous admixture significantly affects the character of precipitates deposited from aqueous solutions. The presence of amorphous phase slows down the process of crystals precipitation, they have time to regroup into two-dimensional formations (sheets stacked in piles), which might be strong enough. Mechanical impact causes the initial desintegration of the piles into sheets, and only thereafter the sheets fall apart to fine powders. The amorphous component was virtually nonexistent in compound **1**. Thread-like crystals formed strong aggregates, which grouped in parallel formations due to van der Waals forces. Some of them formed pieces with disordered arrangement of threads. Mechanical impact resulted in the disintegration of long aggregates up to shorter species.

Heating $FeH_2L\cdot H_2O$ aqueous suspension in a pressure reactor at 150°C in the presence of catalytic amounts of KF gave rise to the formation of a pale milky liquid, which was separated into two parts by filtration. A finely dispersed precipitate on the filter formed an exfoliated thick hard film changing color from white to green on drying. The film easily separated from the filter in the form of a large green disk after drying. The filtered off compound was different from initial compound **1** in its crystal structure and contained a substantial fraction of an amorphous phase. This latter served as a binder in the formation of a layered film containing long flat rectangular formations (crystals or their aggregates) embedded in the amorphous matrix.

Atomic force microscopy data confirms the amorphization of the microcrystalline structure and the presence of long rectangular crystals embedded in the amorphous matrix. Their surface is not perfectly flat, the height difference along the crystal is 220 nm on the length of 5 μm. It could be caused either by amorphous phase overgrowths or by etching surface during the pressure reactor processing. The roughness in the transverse direction reaches 500 nm.

It is known from the published data [5–7] that the syntheses of (1-hydroxyethylidene)diphosphates of transition and rare earth metals in the aqueous phase at elevated temperatures with additives of organic amines and in a pressure reactor can give crystals suitable for X-ray experiments. To intensify such a process, small additions of potassium fluoride were often used. Our previous experiments [4] have shown that the addition of 2-aminoethanol did not result in the conversion of the whiskers to good faceted crystals. Hydrothermal action on compound **1** without amine addition destroyed bunches of whisker crystals, led to the formation of amorphous microparticles, and resulted in the formation of an X-ray amorphous phase. The resulting pale-dairy liquid partially passed through the filter, and had various crystallographic forms. According to the X-ray microanalysis, the ratio of iron and phosphorus in the precipitate remained intact.

The use of two forms of iron did not show any advantage of carbonyl iron compared with reduced iron. Reaction durations in both cases are approximately the same (1.0–1.5 h). At the Fe : H_4L = 1 : 2 ratio iron was dissolved completely within 1 h. When cooled to 25°C, the solution underwent no changes, but on further heating an abundant curdy precipitate of FeH_2L was formed. After filtration and evaporation of the filtrate (1-hydroxyethylidene)-diphosponic acid was obtained. Thus, the reaction of iron with a twofold excess of the acid can be described by Eqs. (2), (3).

$$Fe^0 + 2H_4L = Fe(H_3L)_2 + H_2, \tag{2}$$

$$Fe(H_3L)_2 = FeH_2L + H_4L. \tag{3}$$

Iron(II)(1-hydroxyethylidene)diphosphate was transferred in solution by treatment with water-soluble organic bases: 2-aminoethanol $H_2NCH_2CH_2OH$ **2,** 2-amino-2-(hydroxymethyl)propane-1,3-diol **3**, and 1,2-bis(2-aminoethoxy)ethane **4**. Dissolution of the $FeH_2L·H_2O$ suspension with addition of 1 mol of a base with stirring for 1–2 h at 70–90°C was accompanied by deepening the green color of the reaction mixture. After solution evaporation amine complexes **5–7** were obtained in the form of dark green (almost black) powders easily and quickly dissolved in water. Initial compound $FeH_2L·H_2O$ **1** after drying at 110°C exists in the crystalline form, whereas isolated amine derivatives **5–7** are X-ray amorphous.

$H_2NCH_2CH_2OH$
2

$H_2NC(CH_2OH)_3$
3

$H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$
4

$FeH_2LH_2NCH_2CH_2OH$
5

$FeH_2LH_2NC(CH_2OH)_3$
6

$FeH_2LH_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$
7

Within a series of related compounds, amorphous compounds have much greater solubility compared to crystalline compounds. This pattern is used in the pharmaceutical industry to obtain soluble forms of drugs. It also plays a positive role in the preparation of combined and microfertilizers, the commodity form of which is usually a near-saturated aqueous solution of salts and coordination compounds of metals.

When preparing solutions of combined fertilizers and microfertilizers it seems inappropriate to isolate pure iron(II)(1-hydroxyethylidene)diphosphate and then to dissolve it again. The stage of the isolation can be easily excluded by adding a solubility promoter (an organic base) to white curdy precipitate formed in the Fe^0 reaction with H_4L. A check showed that for effective and rapid dissolution of the precipitate it is necessary to add 1–2 mol of the base per 1 mol of $FeH_2L·H_2O$. The dissolution of the $FeH_2L·H_2O$ suspension was most effective on addition of two equivalents of compound **3** and one equivalent of compound **4**. Obviously the lesser amount of compound **4** is caused by the presence of two amine groups able to coordinate with the transition metals and to form amine salts with remaining free P(O)OH groups.

Filtering and drying the solid phase consisting of whisker crystals with the X-ray amorphous admixture results in the formation of a flat firm layered disc, easily separated from the paper filter. Surface texture, as shown by the microscopy data, consists of long whiskers fastened by the amorphous phase. Aqueous solutions of amorphous amine compounds **5–7** show a different behavior on drying. When drying up, a solution layer (1–2 cm) flats out, the dissolved compound concentration and the viscosity increase. In the last stage a thick swelled elastic film with wound-up edges is obtained. This is because of strongly differing rates of the solvent removal from the top and bottom (adjacent to the vessel bottom) film layers. The top layer dries up quickly, whereas the bottom layer remains swelled and more voluminous. Soluble amorphous compounds form fragile transparent films twisted in a spiral and breakable on mechanical action. Fractures occur without any priority in any directions, as is the case with a vitreous body. The texture of the glassy surface is smooth, not structured, and has fractal located cracks.

EXPERIMENTAL

The IR spectra of compounds in mineral oil mulls (1400–400 cm^{-1}) and in fluorated oil (4000–1400 cm^{-1}) placed between the KBr plates were recorded on an IR Fourier Spectrometer SMF 1201. The X-ray studies were performed on a Shimadzu XRD-7000 X-ray diffractometer. The electron microscopy experiments were fulfilled on a Tescan VEGA II scanning electron microscope. The microrelief was studied at the 500–50000-fold magnification, accelerating voltage of

20 kV, and operating distance of 2–8 mm, using secondary electron (SE) detectors and back scattered electrons (BSE). Relative concentrations of certain chemical elements (Fe, P) along a specified line on the electronic image of the material surface were estimated using an Oxford Instruments INCA Energy 250 energy dispersive spectrometer in the scan mode. Surface characteristics were determined on a Solver PRO-M (NT-MDT, Russia) scanning probe microscope by atomic-force microscopy in the semi-contact mode in air. Silicon probes of the NSG01 NT-MDT company were used. Optical microscopy measurements were performed on a LeicaDM 4000 microscope.

In the work we used pure grade (1-hydroxyethylidene)diphosphonic acid $H_4L\cdot H_2O$ (PAO "Khimprom," technical specifications 2439-363-05783441-2002), pure grade 2-amino-ethanol (OOO "Sintez Oka," technical specifications 2423-002-78722668-2010), special-purity grade carbonyl iron R-20 (mail box M-5168, technical specifications 6-09-3000-73, class 6-2), and pure grade reduced metal iron (Cherkassy chemical factory, technical specifications 6-09-2227-72).

Iron(II) (1-hydroxyethylidene)diphosphonate (1). *a.* (1-Hydroxyethylidene)diphosphonic acid (48.84 g, 2.18×10^{-1} mol) in 175 mL of water was added with stirring to a suspension of 6.10 g (1.09×10^{-1} g-atom) of carbonyl iron in 100 mL of distilled water and heated up to 40–45°C. After 4 h iron was completely dissolved and a blue-green weakly opalescent solution was formed. Subsequent heating up to 90°C resulted in the formation of an abundant white curdy precipitate. After 24 h the mixture was filtered, the precipitate was washed with distilled water, dried in an argon flow and then in a vacuum with heating up to 150°C. Yield 25.40 g (9.14×10^{-2} mol, 84%), blue-green mass, easy-to-grind into powder. IR spectrum, ν, cm^{-1}: 3491 w, 3259 w, 2320 w, 1638, 1301 sh, 1173 sh, 1131, 1045, 944, 821, 658, 571, 541, 458. Found, %: C 8.23; H 3.07; Fe 19.78; P 21.94. $C_2H_8FeO_8P_2$. Calculated, %: C 8.65; H 2.90; Fe 20.10; P 22.29.

The filtrate was evaporated to 30.0 g of a brown resin, a portion of which (2.50 g) was dissolved in glacial acetic acid. After 48 h white crystals precipitated from the solution, which were identified as (1-hydroxyethylidene)diphosphonic acid by the data of IR spectroscopy and acid-base titration.

b. (1-Hydroxyethylidene)diphosphonic acid (16.04 g, 7.3×10^{-2} mol) in 100 mL of water was added with stirring to the reduced iron suspension (4.00 g, 7.2×10^{-2} g-atom) in 100 mL of distilled water, and heated up to 60–75°C. After 1.5 h iron was completely dissolved, and the viscosity of the mixture increased due to the formation of a large amount of white precipitate. After 24 h the mixture was stirred, then filtered, washed with distilled water, dried in an argon flow and then in a vacuum with heating up to 150°C. Yield 12.80 g (4.61×10^{-2} mol, 64%), blue-green mass, easy-to-grind into powder. IR spectrum, ν, cm^{-1}: 3495 w, 3262 w, 2322 w, 1640, 1300 sh, 1175 sh, 1130, 1048, 945, 820, 660, 570, 540, 457. Found, %: C 8.53; H 3.03; Fe 19.90; P 22.04. $C_2H_8FeO_8P_2$. Calculated %: C 8.65; H 2.90; Fe 20.10; P 22.29.

Ethan-1-ol-2-aminiumiron(II) (1-hydroxyethylidene)diphosphonate (5). To a FeH_2L suspension (5.22 g, 2.00×10^{-2} mol) in 100 mL of distilled water 10 mL of 2-aminoethanol **2** aqueous solution (1.23 g, 2.00×10^{-2} mol) was added with stirring. The mixture was stirred for 30 min at 25°C, the iron complex suspension was dissolved almost completely, then the mixture was heated for 1 h at 60–70°C up to obtain a transparent dark green solution, which was cooled and filtered. The filtrate was evaporated, the remainder was heated in a vacuum up to 200°C. Yield 5.07 g (1.58×10^{-2} mol, 79%), dark green (almost black) powder. IR spectrum, ν, cm^{-1}: 3600–2200 w, 1620, 1519, 1271, 1093, 1003, 812, 667, 574, 476. Found, %: C 14.27; H 4.13; Fe 17.42; P 19.32. $C_4H_{13}FeNO_8P_2$. Calculated, %: C 14.97; H 4.08; Fe 17.40; P 19.30.

Tris(hydroxymethyl)methanaminiumiron(II) (1-hydroxyethylidene)diphosphonate (6) was obtained similarly from a $FeH_2L\cdot H_2O$ (3.90 g, 1.40×10^{-2} mol) suspension and 2-amino-2-(hydroxymethyl)propane-1,3-diol **3** (1.70 g, 1.40×10^{-2} mol). Yield 4.95 g (1.30×10^{-2} mol, 93%), dark green (almost black) powder. IR spectrum, ν, cm^{-1}: 3600–2300 w, 2725 sh, 2678 sh, 1629, 1516, 1298, 1117–1060 w, 944 sh, 818, 664, 565, 470. Found, %: C 19.22%; H 4.03; Fe 15.04; P 16.72. $C_6H_{17}FeNO_{10}P_2$. Calculated, %: C 18.91; H 4.50; Fe 14.66; P 16.26.

2,2'-(Ethylenedioxy)diethylaminium iron(II) (1-hydroxyethylidene)diphosphonate (7) was obtained similarly from a $FeH_2L\cdot H_2O$ (4.40 g, 1.58×10^{-2} mol) suspension and 1,2-bis(2-aminoethoxy)ethane (2.35 g, 1.58×10^{-2} mol). Yield 5.61 g (1.37×10^{-2} mol, 87%), dark green powder. IR spectrum, ν, cm^{-1}: 3700-2600 w, 1626, 1531, 1301 sh, 1355 sh, 1104, 1030, 1000, 812, 670, 586, 479. Found, %: C 23.87; H 5.13; Fe

13.37; P 15.08. $C_6H_{17}FeNO_{10}P_2$. Calculated, %: C 23.55; H 5.43; Fe 13.69; P 15.18.

Pressure reactor processing of iron(II) (1-hydroxyethylidene)diphosphonate (1). To a suspension of 2.0 g of reduced iron in 50 mL of distilled water 8.02 of (1-hydroxyethylidene)diphosphonic acid was added. After 20 h the resulting precipitate was filtered off, washed with distilled water, loaded in a pressure reactor, 200 mL of water and two KF crystals were added, and the mixture was heated at 150°C for 25 h. The resulting milky white suspension was filtered on a Büchner funnel, the precipitate was dried on the filter within 5 h at 110°C. The precipitate (4.55 g) was obtained in the form of a thin green, layered disk easily exfoliated from the paper filter. IR spectrum, ν, cm^{-1}: 3650–2400 w, 1638, 1307, 1170, 1104, 1048, 1072, 973 sh, 947 sh, 821, 661, 580, 553, 482, 461. X-ray phase analysis: two reflexes at the reflection angles 2θ 7.5° and 8.3°. X-ray microanalysis: P : Fe = 2.5 : 1.0 (in initial compound **1** P : Fe = 2.6 : 1.0). The filtrate was evaporated. The remainder was a thick light green film (1.70 g) easily ground to a light green powder. IR spectrum, ν, cm^{-1}: 3650-2000 w, 1635, 1122, 1060, 935, 810, 744, 658, 562, 482, 458. X-ray phase analysis: four reflexes at the angles 2θ 18.6, 36.5, 38.1, and 38.2° and an amorphous halo in the intervals of 2θ 5°–16° and 25°–36°.

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