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Preparation of Water-Soluble Iron and Manganese Chelates with Oxyethylidenediphosphonic Acid

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Abstract—The following water-soluble iron(III) and manganese(II) chelate complexes were obtained via the reaction of 1-hydroxyethylidene-1,1-diphosphonic acid (H_4L) with ferric hydroxide or basic manganese carbonate: $Fe_2(H_2L)_3·4H_2O$, $Fe(H_3L)_3·4H_2O$, $MnH_2L·2H_2O$, and $Mn(H_3L)_2·4H_2O$. The complexes solubility was of 33.0, 1.40, 0.1, and 0.4 g in 100 mL of water, respectively. The amorphous $Fe_2(H_2L)_3·4H_2O$ underwent structural changes upon storage, its solubility decreasing. The prepared compounds are recommended for use as micro-fertilizers for drip irrigation of crops.

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All plants and animals need constant replenishment of micronutrients. The following elements are referred to as biometals (also known as "metals of life"): sodium, potassium, magnesium, zinc, manganese, iron, cobalt, copper, and molybdenum. They should be introduced into a living organism in the biologically active form, easily transported and digested; for example, the common inorganic salts are not efficient. The metal complexes, especially the phosphorus-containing, are more beneficial: containing ir-replaceable phosphorus along with the biometal, they are non-toxic, sufficiently soluble in water, stable over wide range of pH, adsorbed by soil, and not lysed by microorganisms [1–5]. In modern agriculture the introduction of micronutrients via drip irrigation with dilute aqueous solution has been found cost-effective, moreover, its minimized soil contamination [6]. The optimal concentrations of iron in the watering solution is of 0.014 g/L and that of manganese is 0.008 g/L.

This work aimed to propose the methods to prepare of water-soluble coordination compounds of two biometals: manganese and iron. The ligand used was a readily available phosphorus compound, 1-hydroxy-ethylidene-1,1-diphosphonic acid (hereafter designated as H_4L).

$(HO)_2(O)PC(CH_3)(OH)P(O)(OH)$.

H_4L

This tetrabasic acid is stable at elevated temperature, highly soluble in water, and interacts with metals to form complex compounds of varied solubility. The unique properties of the chelator are due to combination of two phosphonic groups (capable of complex formation even in strongly acidic medium) and hydroxyl group within one molecule. The most prominent feature of H_4L is for sure the extreme stability of its complexes with many metals. In contrast to polyaminopolycarboxylic complexones, H_4L forms stable complexes in strongly acidic media as well.

The iron(III) complex was prepared by reacting ferric hydroxide $Fe(OH)_3$ with H_4L in aqueous medium:

$$2Fe(OH)_3 + 3H_4L \rightarrow Fe_2(H_2L)_3·4H_2O + 2H_2O.$$

Previously, the same complex was prepared via interaction of H_4L disodium salt with iron(III) chloride [7].

The stoichiometry of the above reaction was proved by elemental analysis and IR spectroscopy data, thus, two molecules of $Fe(OH)_3$ reacted with three molecules of H_4L, giving the $Fe_2(H_2L)_3·4H_2O$ complex. Each of the three ligand molecules acted as bidentate chelator. After preparation, the complex could be isolated either by evaporation or by precipitation with acetic acid. The absence of marketable form of iron hydroxide does not impede the technological application of the method, as $Fe(OH)_3$ is easily prepared from

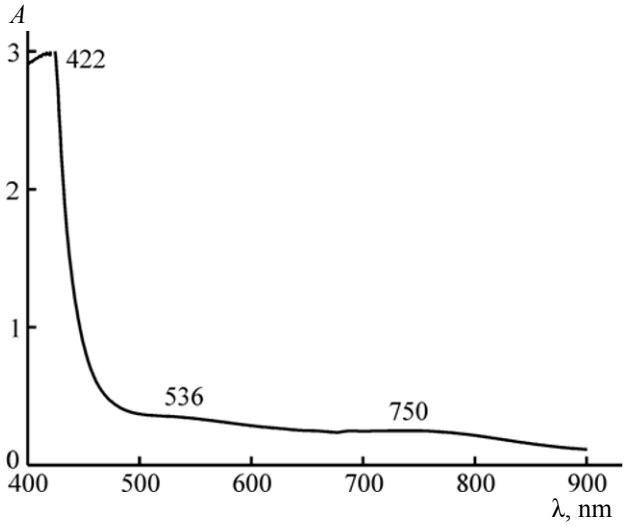

Fig. 1. Electronic absorption spectrum of aqueous solution of $Fe_2(H_2L)_3 \cdot 4H_2O$.

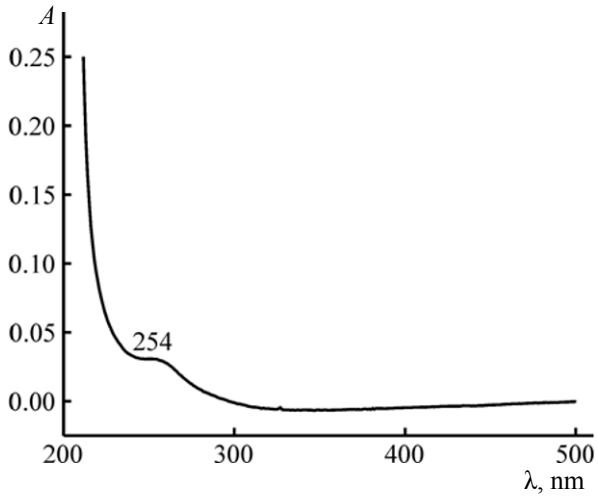

Fig. 2. Electronic absorption spectrum of aqueous solution of H_4L (c = 0.13 mol L^{-1}).

affordable ferric chloride and aqueous ammonia. The freshly prepared gel, in contrast to Fe_2O_3 and Fe_3O_4 oxides, is highly reactive towards H_4L. The ease of $Fe(OH)_3$ gel preparation from ferric chloride [8] and of the product purification from by-produced ammonium chloride has made for the final choice of this approach.

According to the proposed method, the freshly prepared $Fe(OH)_3$ gel should not be dried nor stored before the complex synthesis. Heating and aging reduced the gel reactivity towards H_4L due to partial transformation into the oxide Fe_2O_3, inert towards H_4L. After washing the gel with distilled water, aqueous H_4L was added; no heating was observed. The reaction proceeded slowly upon stirring and heating to 80–90°C. Within 3.0–3.5 h, the reaction mixture changed from brown (suspension of iron hydroxide) to transparent light-green (dissolved iron–H_4L complex); thus, the end point of the reaction was easily determined visually. The optimal reagents ratio was strictly stoichiometric, $Fe(OH)_3$: H_4L = 2 : 3. With 7–10% excess H_4L the reaction progressed faster, within 1.5 h. However, the decrease in reaction time was accompanied with overconsumption of the acid. The target compound was isolated as light-green powder by evaporation, drying of the so obtained viscous mass at 95–105°C, and crushing in a porcelain mortar.

Another method of the product isolation and purification was precipitation by two-fold volume of glacial acetic acid (an equal volume of acetic acid could be alternatively added after partial evaporation of water from the reaction mixture); the complex product rapidly precipitated. That method gave pure product, but seemed less efficient than evaporation and drying.

The highly pure iron complex was obtained after additional washing of the crude powder with methanol. Methanol and ethanol readily dissolved H_4L admixture (the only possible impurity), but not the iron complex. Gravimetric analysis showed only very small weight loss after washing (0.05–0.1%); there was practically no difference in IR and elemental analysis data of the crude and purified powders. Thus, both the isolation methods gave sufficiently pure complex product.

The electron absorption spectra of aqueous solutions of $Fe_2(H_2L)_3 \cdot 4H_2O$ and H_4L are shown in Figs. 1 and 2, respectively. In the iron complex spectrum, three absorption bands were observed: at λ_{max} = 422 nm (strong), λ_{max} = 536 nm (weak), and λ_{max} = 750 nm (weak). The first band was assigned to metal-ligand charge transfer, and the two weak bands were typical of Fe(III) cation [9]. The *d*-*d* transition bands were very weak, as in the cases the other *d*-metal cations optical spectra. The complex color was due to weak band at 536 nm in the green spectral region. The absorption spectrum of H_4L aqueous solution contained the only weak band at λ_{max} = 254 nm due to $n \rightarrow \pi$ transition of P=O group.

DSC studies (Fig. 3) revealed two endo peaks at 50–175°C and 175–270°C, due to the loss of crystal hydrate water. Gravimetry confirmed that the weight loss strictly corresponded to four molecules of H_2O, in line with the elemental analysis.

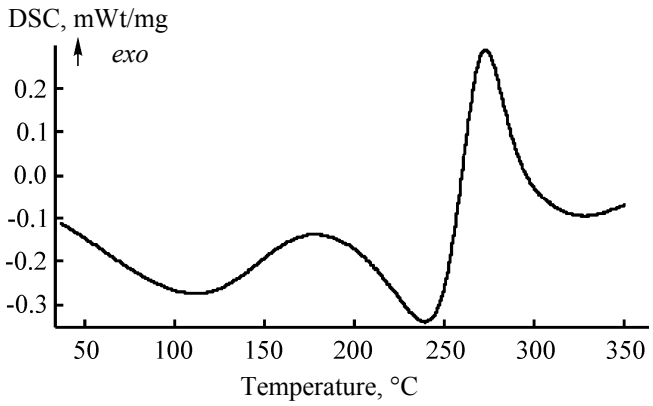

Fig. 3. Differential scanning calorimetry scan of $Fe_2(H_2L)_3 \cdot 4H_2O$.

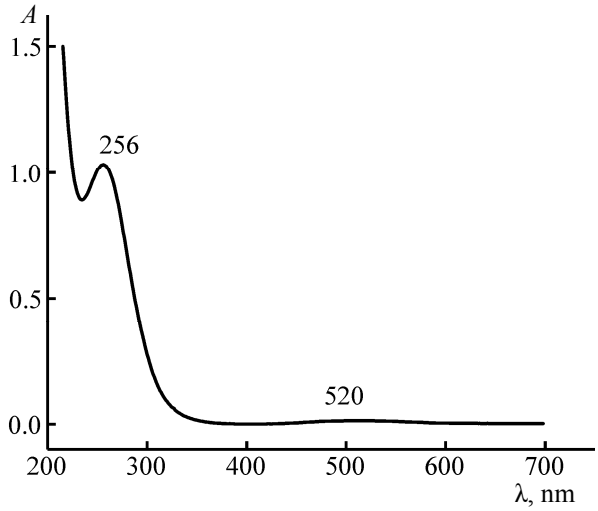

Fig. 4. Electronic absorption spectrum of aqueous solution of $Mn(H_3L)_2 \cdot 4H_2O$.

XRD data indicated that $Fe_2(H_2L)_3 \cdot 4H_2O$ was an amorphous product. Diffraction pattern contained two amorphous halos at the reflection angles of 11–19° and 22–40°.

The freshly prepared $Fe_2(H_2L)_3 \cdot 4H_2O$ was highly water-soluble (>33.0 g per 100 mL). However, after 6 weeks storage at room temperature its solubility decreased to only 0.2 g per 100 mL, and dissolution was slower. In order to overcome that, we attempted to prepare another complex at the ratio of Fe : H_4L = 1 : 3 either by interaction of $Fe(OH)_3$ gel with 3 equivalents of H_4L, or by interaction of $Fe_2(H_2L)_3 \cdot 4H_2O$ with H_4L:

$$Fe(OH)_3 + 3H_4L \rightarrow Fe(H_3L)_3 + 3H_2O,$$

$$Fe_2(H_2L)_3 + 3H_4L \rightarrow 2Fe(H_3L)_3.$$

Both the methods gave the target complex that was isolated by evaporation and drying in the form of tetrahydrate $Fe(H_3L)_3 \cdot 4H_2O$. Its solubility was 1.40 g in 100 mL of water and did not change during storage at room temperature or prolonged heating at 80–90°C. After evaporation and drying, the compound appeared as monolithic light-green mass, giving light-green powder after grinding in porcelain mortar.

Thus, to obtain a powdered iron complex preserving the solubility after prolonged storage the ratio of Fe : H_4L = 1 : 3 was better. However, $Fe_2(H_2L)_3 \cdot 4H_2O$ powder losing the solubility with time could be recommended for application in the form of concentrated solution, after partial evaporation of the reaction mixture.

The manganese(II) complexes with H_4L were previously prepared via reaction of manganese(II) acetate with H_4L disodium salt [7]. We propose a procedure based on the reaction of manganese carbonate with H_4L at the ratio of 1 : 1 or 1 : 2. Using the basic manganese carbonate $MnCO_3 \cdot mMn(OH)_2 \cdot nH_2O$ instead of acetate salt led to nonwaste production of two manganese complexes with different solubility. At the reagents ratio of 1 : 1, $MnH_2L \cdot 2H_2O$ was formed, while the reaction at 1 : 2 ratio gave better soluble $Mn(H_3L)_2 \cdot 4H_2O$:

$$MnCO_3 \cdot Mn(OH)_2 + 2H_4L = 2MnH_2L + CO_2 + 3H_2O,$$

$$MnCO_3 \cdot Mn(OH)_2 + 4H_4L = 2Mn(H_3L)_2 + CO_2 + 3H_2O.$$

The yields were 85 and 83%, correspondingly. The commercially available form of $MnCO_3 \cdot mMn(OH)_2 \cdot nH_2O$ is black-brown fine powder. Using it as received slightly increased the reaction time due to slow dissolution of larger particles fraction. After milling in ball mill, reaction was accelerated. The end point of the reaction was clearly noticed by disappearance of the original black particles of basic manganese carbonate that was converted into white complex. In the excess of H_4L the interaction was faster; however, the violent release of carbon dioxide and foaming the aqueous solution did not occur. Higher solubility of $Mn(H_3L)_2 \cdot 4H_2O$ than that of $MnH_2L \cdot 2H_2O$ led to remaining some of the product (26%) in the filtrate; its evaporation gave additional amount of the product, which was virtually identical to the precipitated one (IR, UV-vis, elemental analysis). The total yield was of 83%.

The prepared complexes solubility in water at 25°C

Compound	In 1 g of complex per 100 mL of solution	In 1 g of metal per 100 mL of solution	In 1 g of metal per 50 L of solution	In 1 g of metal per 50 L of solution
$Fe_2(H_2L)_3 \cdot 4H_2O$[a]	33.0	4.8	16500	2400
$Fe_2(H_2L)_3 \cdot 4H_2O$[b]	0.2	0.029	100	15
$Fe(H_3L)_3 \cdot 4H_2O$	1.4	0.12	700	60
$Mn(H_2L) \cdot 2H_2O$	0.1	0.018	50	9
$Mn(H_3L)_2 \cdot 4H_2O$	0.4	0.038	200	19

[a] Freshly prepared complex. [b] After 6 weeks storage.

The powdered manganese complexes were either white or slightly pink. In the electron absorption spectrum of the aqueous solution (Fig. 4) an intense absorption band of the ligand at λ_{max} = 256 nm and a very weak band of Mn(II) cation at λ_{max} = 520 nm were observed. It is known [9] that the *d*–*d*-transition bands of manganese(II) are rarely observed being overlapped by UV absorption band of the ligand. According to the X-ray powder diffraction, $Mn(H_3L)_2 \cdot 4H_2O$ was crystalline. There was no relevant information in the ICSD powder database.

EXPERIMENTAL

IR spectra of suspensions in paraffin oil between KBr plates were recorded with FSM 1201 FTIR spectrometer. Electronic absorption spectra of aqueous solutions were obtained with Perkin-Elmer Lambda 25 spectrophotometer. Thermal analysis was carried out with Netzsch DSC 204 F1 Phoenix differential scanning calorimeter at heating rate of 5°/min under argon, 20 mL/min, in the range of +25 to +350°C. The weight loss upon heating in vacuum was measured with Macben balance. Elemental analysis was performed with "EURO EA" analyzer. X-ray diffraction studies were performed with Shimadzu XRD-7000 X-ray diffractometer.

The ligand 1-hydroxyethylidene-1,1-diphosphonic acid was of pure grade (Khimprom, TU 2439-363-05783441-2002); iron trichloride hexahydrate $FeCl_3 \cdot 6H_2O$ was of pure grade (GOST 4147-74); basic manganese carbonate $MnCO_3 \cdot mMn(OH)_2 \cdot nH_2O$ (Unikhim, GOST 7205-77, 44% of manganese) and aqueous ammonia (pure grade, GOST 3760-64) were also used.

Diiron(III) tris(oxyethylidenediphosphonate) tetrahydrate $Fe_2(H_2L)_3 \cdot 4H_2O$. A solution of 35 mL (0.33 mol) of 9.5 N NH_4OH in 30 mL of water was slowly added to a stirred solution of 25.0 g (0.09 mol) of $FeCl_3 \cdot 6H_2O$ in 200 mL of distilled water. The iron hydroxide $Fe(OH)_3$ formed was a fine brown precipitate insoluble in water, it was washed on a Buchner funnel with distilled water to remove chloride ions (controlled with silver nitrate). Then, 30.24 g (0.135 mol) of $H_4L \cdot H_2O$ dissolved in 100 mL of distilled water (23 wt % of H_4L) was added to freshly prepared iron(III) hydroxide. The reaction mixture was heated at 85–90°C upon stirring till complete dissolution of iron(III) hydroxide (3.0–3.5 h). The solution was filtered and evaporated. Yield 34.0 g (0.0427 mol, 95%), a fine-grained light-green powder, stable in air. IR spectrum, ν, cm^{-1}: 3350 (OH, COH, H_2O), 2723 (O–H, PO–H), 1635 (O–H, PO–H), 1080 br [P=O, P(O)OH, PO_3^{2-}], 940, 811, 725, 651, 568 (P=O). Electronic spectrum, λ, nm: 422, 536, 750. Found, %: C 9.20, H 3.39; Fe 14.50; P 23.79. $C_6H_{26}Fe_2O_{25}P_6$. Calculated, %: C 09.05, H 3.27; Fe 14.07;P 23.37. Solubility in water at room temperature: above 33.0 g (4.8 g Fe) in 100 mL in the case of freshly prepared powder. After 6 weeks storage at room temperature, the solubility was down to 0.2 g in 100 mL, the dissolution was slow (during 2–3 days at room temperature).

After heating in vacuum (1 h at 180–200°C) the elemental analysis revealed loss of four molecules of water and formation of $Fe_2(H_2L)_3$. Found, %: C 9.78, H 2.84; Fe 15.56; P 25.89. $C_6H_{18}Fe_2O_{21}P_6$. Calculated, %: C 9.95, H 2.51; Fe 15.46; P 25.68.

Iron(III) tris(oxyethylidenediphosphonate) tetrahydrate $Fe(H_3L)_3 \cdot 4H_2O$. *a.* Prepared as described above for $Fe_2(H_2L)_3 \cdot 4H_2O$, from 30.0 g (0.11 mol) of $FeCl_3 \cdot 6H_2O$. Yield 77.6 g (0.105 mol, 95%), a fine-grained light-green powder stable in air. IR spectrum,

ν, cm^{-1}: 3381 (O–H, COH, H_2O), 2663 (O–H, PO–H), 1635 [δ(O–H, PO–H)], 1104, 1051 br. [P=O, P(O)OH, PO_3^{2-}], 935, 806, 720, 629, 547 [δ(P=O)]. Found, %: C 9.85; H 3.78; Fe 7.00; P 24.26. $C_6H_{29}FeO_{25}P_6$. Calculated, %: C 9.69; H 3.90; Fe 7.54; P 25.03. Solubility in water at room temperature: 1.4 g (0.12 g Fe) in 100 mL.

b. 87.6 g (0.39 mol) of $H_4L{\cdot}H_2O$ dissolved in 150 mL of distilled water was added to a stirred suspension of 103.8 g (0.13 mol) of $Fe_2(H_2L)_3{\cdot}4H_2O$ in 100 mL of distilled water. The reaction mixture was heated with stirring until complete dissolution of the original iron(III) complex (3.0–3.5 h). The solution was filtered and evaporated. Yield 187.4 g (0.25 mol, 97%). IR spectrum, ν, cm^{-1}: 3378 (O–H, COH, H_2O), 2716 (O–H, PO–H), 1632 [δ(O–H, PO–H)], 1107, 1051 br [P=O, P(O)OH, PO_3^{2-}], 930, 812, 723, 640, 574 [δ(P=O)]. Found, %: C 9.82; H 4.25; Fe 7.02; P 23.35. $C_6H_{29}FeO_{25}P_6$. Calculated, %: C 9.69; H 3.90; Fe 7.54; P 25.03. Solubility in water at room temperature: 1.4 g (0.12 g Fe) in 100 mL.

Manganese(II) oxyethylidenediphosphonate dihydrate $MnH_2L{\cdot}2H_2O$. 55.10 g (0.246 mol) of $H_4L{\cdot}H_2O$ dissolved in 300 mL of distilled water was added to a suspension of 30.75 g of finely ground $MnCO_3{\cdot}mMn(OH)_2{\cdot}nH_2O$ (44% Mn, 0.246 mol) in 200 mL of distilled water. The mixture was heated at 60–80°C with vigorous stirring during 7 h. Carbon dioxide release was observed, and black-brown basic manganese carbonate was gradually transformed into fine white precipitate, that was subsequently filtered through a Buchner funnel, washed with 200 mL of distilled water, and air-dried. Yield 65.00 g (0.208 mol, 85%). IR spectrum, ν, cm^{-1}: 3349 (O–H, H_2O, COH), 2720 (O–H, PO–H), 1634 [δ(O–H, PO–H], 1077 br [P=O, P(O)OH, PO_3^{2-}], 943, 813, 723, 653, 566 [δ(P=O)]. Found, %: C 7.52; H 4.00; Mn 17.88; P 20.16. $C_2H_{12}MnO_{10}P_2$. Calculated, %: C 7.67; H 3.83; Mn 17.57; P 19.80. Solubility in water at room temperature: 0.10 g (0.02 g manganese) in 100 mL.

Bis(hydroxyethylidendiphosphonate)manganese(II) tetrahydrate $Mn(H_3L)_2{\cdot}4H_2O$. 52.64 g (0.235 mol) of $H_4L{\cdot}H_2O$ dissolved in 150 mL of water was added to a suspension of 14.70 g of $MnCO_3{\cdot}mMn(OH)_2{\cdot}nH_2O$ (44% Mn, 0.118 mol) in 100 mL of water. The mixture was stirred during 2 h at 80°C. Carbon dioxide release was observed, and black-brown basic manganese carbonate was gradually transformed into fine white precipitate, that was filtered through a Buchner funnel, washed with 50 mL of distilled water, and air-dried. Yield 36.21 g (0.067 mol, 57%) of white-pink powder. The filtered solution was evaporated, 10.60 g of pale pink powder was obtained. Total yield: 46.81 g (83%). Water solubility of the precipitate at room temperature: 0.40 g (0.038 g manganese) in 100 mL. The solubility of a substance extracted from the solution: 0.9 g (0.086 g manganese) in 100 mL. For the precipitate: IR spectrum, ν, cm^{-1}: 3572, 3410, 3252 (O–H, H_2O), 2731 (O–H, PO–H), 1631 [δ(O–H, PO–H)], 1207, 1147 br, 1076, 1026 [P=O, P(O)OH, PO_3^{2-}], 939, 819, 721, 648, 555, 482 [δ(P=O)]. Electronic spectrum, λ, nm: 256, 520. Found, %: C 8.60; H 4.60; Mn 10.27; P 23.16 $C_4H_{22}MnO_{18}P_4$. Calculated, %: C 8.94; H 4.10; Mn 10.24; P 23.10.

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