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# Water-Soluble Double Potassium and Ammonium Salts of Iron(III) and Manganese(II) with (Hydroxyethylidene)diphosphonic Acid

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**Abstract—**A method to multifold increase the water solubility of diiron(III) tris[(hydroxyethylidene)-diphosphonate) tetrahydrate $Fe_2(H_2L)_3{\cdot}4H_2O$ and manganese(II) (hydroxyethylidene)diphosphonate dihydrate $MnH_2L{\cdot}2H_2O$, prepared by the reaction of 1-hydroxyethylidene-1,1-diphosphonic acid with iron(III)hydroxide and basic manganese carbonate. The method involves conversion of the phosphonates into their double salts $Fe_2K_6L_3{\cdot}4H_2O$ [$Fe_2(NH_4)_6L_3{\cdot}4H_2O$] and $MnK_{1.3}H_{0.7}L{\cdot}2H_2O$ [$Mn(NH_4)_2L{\cdot}2H_2O$] by treatment of their aqueous suspensions with potassium or ammonium hydroxides. The solubility of the iron salt increases from 0.2 to 4.0 g per 100 mL solution (20 times) and that of the manganese salt increases from 0.1 to 4.8 g per 100 mL solution (45 times).

**Keywords**: double salts, (hydroxyethylidene)diphosphonic acid, solubility

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We previously described [1] two environmentally friendly methods of synthesis of water-soluble Fe(III) and Mn(II) chelates of (hydroxyethylidene)diphosphonic acid ($H_4L$), intended for use as microfertilizers for drip irrigation. The iron salts $Fe_2(H_2L)_3{\cdot}4H_2O$ and $Fe(H_3L)_3{\cdot}4H_2O$ were synthesized from $Fe(OH)_3$ gel, and the manganese compounds $MnH_2L{\cdot}2H_2O$ and $Mn(H_3L)_2{\cdot}4H_2O$, from commercial $MnCO_3{\cdot}m Mn(OH)_2{\cdot}nH_2O$. Increased acid content, i.e. the transition from $Fe_2(H_2L)_3{\cdot}4H_2O$ to $Fe(H_3L)_3{\cdot}4H_2O$ and from $MnH_2L{\cdot}2H_2O$ to $Mn(H_3L)_2{\cdot}4H_2O$, leads to solubility enhancement. A freshly prepared sample of amorphous diiron (hydroxyethylidene)diphosphonate $Fe_2(H_2L)_3{\cdot}4H_2O$ showed excellent solubility (33.0 g per 100 mL solution) but it decreased 165 times (to 0.2 g) after a 6-week storage at room temperature in a dry state. Moreover, the dissolution time of a dry substance sharply increased (up to 2 days). Thus, the metal-enriched and the most cost-effective $Fe_2(H_2L)_3{\cdot}4H_2O$ and $MnH_2L{\cdot}2H_2O$ chelates are poorly soluble compounds and not completely meet the requirements for practical application.

Our attempts to estimate the content of the P(O)OH groups in the iron and manganese salts by acid−base titration showed that slow (indicator-controlled) addition of a 0.094 N solution of KOH to salt suspension results in rapid dissolution of the salt, while rapid pouring of concentrated alkali to salt suspension caused precipitation of Fe(III) hydroxide and Mn(IV) oxide. The use of KOH and ammonia is associated with potassium and nitrogen are essential for plant nutrition [2].

(Hydroxyethylidene)diphosphonic acid ($H_4L$) is a tetrabasic acid [3, 4].

$$\underset{H_4L}{(HO)_2(O)PC(CH_3)(OH)P(O)(OH)_2}$$

The first two acid dissociation constants (p$K_a^1$ 1.7, p$K_a^2$ 2.47) allow $H_4L$ to be classed with strong acids [3]. The fact that the acidity at further stages gets lower (p$K_a^3$ 7.28, p$K_a^4$ 10.29) is a well-known feature of polybasic acids. Therefore, titration of all the four P(O)OH groups in the presence of acid−base indicators is hardly practical. Titration with a strong base in the presence of phenolphthalein detects 2.6–2.9 acid groups in $H_4L$ instead of four, on account of a decrease in the total acidity with accumulation of the $P(O)O^-$ groups which are stronger electron donors than P(O)OH.

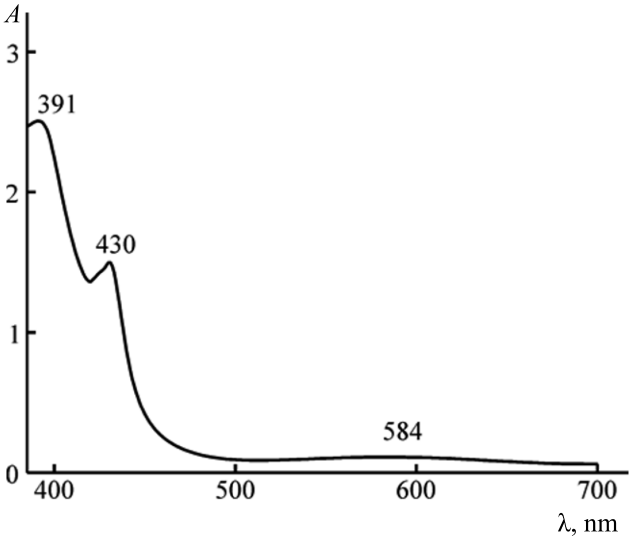

**Fig. 1.** Electronic absorption spectrum of aqueous $Fe_2K_6L_3\cdot 4H_2O$.

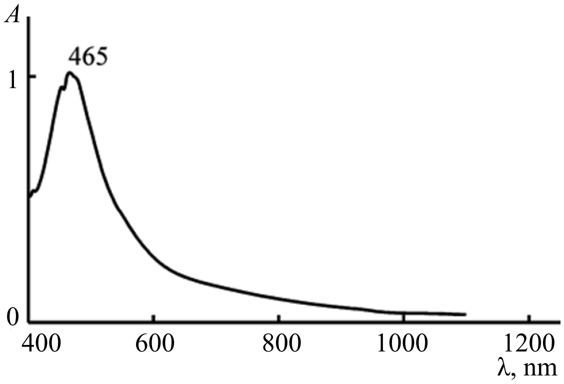

**Fig. 2.** Electronic absorption spectrum of aqueous $MnK_{1.3}(H_{0.7}L)\cdot 2H_2O$.

Titration poorly soluble diiron(III) tris[(hydroxyethylidene)diphosphonate] tetrahydrate $Fe_2(H_2L)_3\cdot 4H_2O$ and manganese(II) (hydroxyethylidene)diphosphonate dihydrate $MnH_2L\cdot 2H_2O$ was performed by slowly adding a 0.79 N solution of KOH to salt suspension in the presence of phenolphthalein under magnetic stirring. The green color of the iron salt solution does not interfere with the observation of the color change of the indicator, whereas the light rose color of the manganese salt makes it difficult to determine the end point. The end points for all the six P(O)OH groups in the iron compound are well-defined. Complete dissolution of a $Fe_2(H_2L)_3\cdot 4H_2O$ sample occurs already after 5 equiv of KOH have been added. The respective value for $MnH_2L\cdot 2H_2O$ is 1.3. Gradual dilution of the KOH solution to a calculated volume (6 mol per mole iron salt and 2 mol per mole manganese salt) produces no $Fe(OH)_3$ gel precipitation only with the iron salt. With the manganese salt, the solution darkens due to formation of Mn(II) hydroxide and its rapid oxidation to Mn(IV) oxide which is an amorphous black powder. After the complex has dissolved completely, a little alkali can be added to solution and then continue with its workup.

Titration of $H_4L$ and its iron and manganese salts with ammonia seems to have no chance to success, because the end point is impossible to detect (and even roughly estimate). Gradual addition of a required volume of a fairly concentrated (9.5 N) solution of $NH_4OH$ to salt under vigorous stirring causes no hydroxide precipitation. On addition of equivalent quantities of ammonium hydroxide, the starting compounds dissolve completely.

The transformations that occur can be described by Eqs. (1)–(4):

$$Fe_2(H_2L)_3 + 6KOH = Fe_2(K_2L)_3 + 6H_2O, \quad (1)$$

$$Fe_2(H_2L)_3 + 6NH_4OH = Fe_2[(NH_4)_2L)]_3 + 6H_2O, \quad (2)$$

$$MnH_2L + 1.3KOH = MnK_{1.3}H_{0.7}L + 1.3H_2O, \quad (3)$$

$$MnH_2L + 2NH_4OH = Mn(NH_4)_2L + 2H_2O. \quad (4)$$

Transition metal complexes of $H_4L$ have high stability constants [5], whereas $K^+$ cations can hardly form complexes with EDTA and other chelating agents [3]. In this connection we can suggest that the P(O)OFe and P(O)OMn groups undergo no transformation in our experimental conditions.

Figures 1 and 2 show the electronic absorption spectra of aqueous solutions of the potassium salts of iron and manganese complexes. The spectrum of the iron compound (Fig. 1) contains three bands at 391, 430, and 584 nm. The latter, weakest band is assignable to the *d–d* transition in the iron cation, and the shorter-wave band at 430 nm, to the metal–ligand transition. The band at 390 nm cannot be assigned to the $P(O)O^-$ anion equilibrated by the potassium cation. The UV spectrum of the potassium salt of $H_4L$ contains a weak absorption band at 261 nm.

The EAS spectrum of aqueous solution of the manganese compound (Fig. 2) shows a well-defined band at 465 nm and structureless absorption until

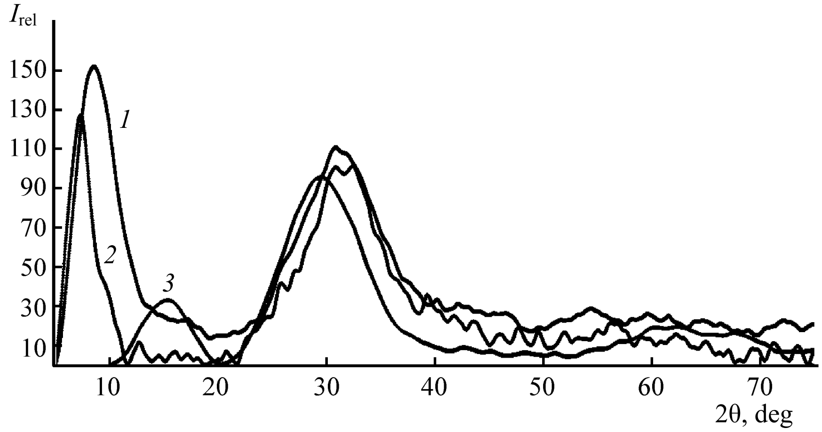

**Fig. 3.** X-ray phase analysis of potassium salts of (*1*) iron and (*2*) manganese complexes and (*3*) $Fe(H_3L)_3{\cdot}4H_2O$.

1000 nm. The *d–d* bands in the Mn(II) cation coordinated to organic ligands are hardly identifiable [6], because even if the ligand has even very weak UV absorption tail, it obscures visible absorption bands. In the EAS of the sparingly soluble $Mn(H_3L)_2{\cdot}4H_2O$ complex we observed [1] a very weak band at 520 nm characteristic of Mn(II) cations; the stronger band at 465 nm, too, appears to belong to the metal–ligand transition.

According to powder X-ray diffraction data (Fig. 3), the potassium derivatives of iron and manganese complexes are amorphous substances. The X-ray diffraction patterns of the complexes are similar to each other and show two amorphous halos in the ranges of reflection angles 9° and 32° (iron, Fig. 3, curve *1*) and 7° and 33° (manganese, Fig. 3, curve *2*). The sparingly soluble complex $Fe(H_3L)_3{\cdot}4H_2O$ prepared previously from $Fe(OH)_3$ gel and $H_4L$ [1], too, is amorphous. Its X-ray pattern (Fig. 3, curve *3*) differs from the two mentioned ones by that the small-angle halo is shifted to larger angles. The soluble manganese complex $Mn(H_3L)_2{\cdot}4H_2O$ obtained in [1] is a crystalline substance.

The amorphous nature of the prepared binary salts is evident on dissolution. Their saturated solutions are transparent colored gels. On drying they form transparent glassy films. Dry gels do not lose solubility and readily dissolve in water.

Precipitation of crystalline metal complexes from aqueous solutions of commercial microfertilizers poses a great problem to their application in drip irrigation and soil dressing. Especially active formation of the solid phase takes place when concentrated solutions are stored in plastic canisters in winter time.

In this connection we decided to test the prepared binary salts. Aqueous solutions of the iron and manganese salts with concentrations of 17 and 20%, respectively, were stored for two winter and one spring months in polyethylene vessels at room temperature. No precipitation was observed. The solutions remained transparent colored liquids. The complete absence of precipitates appears to be associated with the amorphous nature of the salts.

## EXPERIMENTAL

The IR spectra were measured on a FSM 1201 FT-IR spectrometer for suspensions in mineral oil between KBr plates. The EAS spectra were obtained on a Perkin–Elmer Lambda 25 spectrophotometer for aqueous solutions. The X-ray diffraction patters were recorded on a Shimadzu XRD-7000 instrument.

(Hydroxyethylidene)diphosphonic acid of pure grade, Technical Specifications 2439-363-05783441–2002, producer Khimprom (Russia); iron trichloride hexahydrate of pure grade, State Standard 4147–74; manganese carbonate basic $MnCO_3{\cdot}m Mn(OH)_2{\cdot}n H_2O$, State Standard 7205–77, manganese content 44%, producer Unikhim (Russia); and aqueous ammonia, $NH_4OH$, pure grade, State Standard 3760–64 were used in the work.

**Diiron(III) hexapotassium tris[(hydroxyethylidene)diphosphonate)] tetrahydrate $Fe_2K_6L_3{\cdot}4H_2O$.** To a suspension of 2.37 g (0.003 mol) of $Fe_2(H_2L)_3{\cdot}4H_2O$ in 15 mL of distilled water we added dropwise 22.8 mL of 0.79 N (0.018 mol) of KOH in the presence of phenolphthalein under stirring. Dissolution of the poorly soluble salt $Fe_2(H_2L)_3{\cdot}4H_2O$ was observed, and the solution colored light green. The reaction was terminated, when the solution got persistently weakly alkaline or the substance dissolved completely. The resulting solution was evaporated, and the solid residue was washed with ethanol to remove phenolphthalein. Yield 2.86 g (0.003 mol, 97%), dark brown amorphous powder stable in air. IR spectrum, ν, cm$^{-1}$: 3268 (O–H, $H_2O$, COH), 1655 [δ(O–H), PO–H], 1135 br, 1009, 919 sh [P=O, P(O)OH, $PO_3^{2-}$], 813, 668, 578 [δ(P=O)]. $^{31}$P NMR spectrum ($D_2O$): $\delta_P$ 19.22 ppm. EAS spectrum, λ, nm: 391, 430, 584. Solubility 34.8 g (3.9 g per Fe) in 100 mL of distilled water. Found, %: C 6.75; H 2.05; Fe 11.05; K 21.95; P 18.30. $C_6H_{20}Fe_2K_6O_{25}P_6$. Calculated, %: C 7.03; H 1.95; Fe 10.94; K 22.85; P 18.16.

**Manganese(II) potassium (hydroxyethylidene)-diphosphonate dihydrate $MnK_{1.3}(H_{0.7}L)\cdot 2H_2O$.** To 0.20 g (0.00068 mol) of $Mn(H_2L)\cdot 2H_2O$ in 10 mL of distilled water we added dropwise 1 mL of 0.79 N KOH in the presence of phenolphthalein under vigorous stirring. Dissolution of the poorly soluble salt $Mn(H_2L)\cdot 2H_2O$ was observed, and the solution colored light pink. The solution was evaporated, and the solid residue was washed with ethanol to obtain 0.21 g (0.00061 mol, 91%) of $MnK_{1.3}(H_{0.7}L)\cdot 2H_2O$ as a dark violet powder stable in air. IR spectrum, ν, cm$^{-1}$: 3301 (O–H, $H_2O$, COH), 1652 [δ(O–H), PO–H], 1082 br [P=O, P(O)OH, $PO_3^{2-}$], 996, 953, 817, 658, 562 [δ(P=O)]. EAS spectrum, λ, nm: 465. Solubility 30.2 g (4.8 g per Mn) in 100 mL of distilled water. Found, %: C 6.66; H 2.64; Mn 16.03; P 18.08; K 14.83. $C_2H_{8.7}K_{1.3}MnO_9P_2$. Calculated, %: C 6.97; H 2.53; Mn 15.97; P 18.00; K 14.72.

**Hexaammonium diiron(III) tris[(hydroxyethylidene)diphosphonate)] tetrahydrate $Fe_2[(NH_4)_2L]_3\cdot 4H_2O$.** To 2.34 g (0.0029 mol) of $Fe_2(H_2L)_3\cdot 4H_2O$ in 15 mL of distilled water we added dropwise 1.7 mL of 9.5 N $NH_4OH$ in the presence of phenolphthalein under stirring. Dissolution of the poorly soluble salt $Fe_2(H_2L)_3\cdot 4H_2O$ was observed, and the solution colored light green. The solution was evaporated, and the solid residue was washed with ethanol to obtain 2.4 g (0.0027 mol, 93%) of $Fe_2[(NH_4)_2L]_3\cdot 4H_2O$ as a dark brown amorphous powder. IR spectrum, ν, cm$^{-1}$: 3208 (O–H, $H_2O$, COH), 2698, 2145, 1873, 1668 [δ(O–H), PO–H], 1105 br, 999 [P=O, P(O)OH, $PO_3^{2-}$], 817, 668, 575 [δ(P=O)]. $^{31}$P NMR spectrum ($D_2O$): $\delta_P$ 19.03 ppm. Solubility 15.2 g (1.9 g per Fe) in 100 mL of distilled water. Found, %: C 8.01; H 4.52; N 8.53; Fe 12.35; P 20.55. $C_6H_{44}Fe_2N_6O_{25}P_6$. Calculated, %: C 8.01; H 4.89; N 9.35; Fe 12.47; P 20.71.

**Diamonium manganese(II) (hydroxyethylidene) diphosphonate dihydrate $Mn(NH_4)_2L\cdot 2H_2O$.** To 1.72 g (0.0058 mol) of $Mn(H_2L)\cdot 2H_2O$ in 15 mL of distilled water we added dropwise 1.1 mL of 9.5 N $NH_4OH$ in the presence of phenolphthalein under stirring. Dissolution of the poorly soluble salt $Mn(H_2L)\cdot 2H_2O$ was observed, and the solution colored light pink. The solution was evaporated, and the residue was washed with ethanol to obtain 1.8 g (0.0055 mol, 94%) of $Mn(NH_4)_2L\cdot 2H_2O$ as a dark violet amorphous powder. IR spectrum, ν, cm$^{-1}$: 3222 (O–H, $H_2O$, COH), 2715, 2145, 1860, 1658 [δ(O–H), PO–H], 1075 br [P=O, P(O)OH, $PO_3^{2-}$], 992, 953, 820, 658, 562 [δ(P=O)]. Solubility 26.3 g (4.3 g per Mn) in 100 mL of distilled water. Found, %: C 8.21; H 4.55; N 8.4; Mn 16.28; P 18.31. $C_2H_{16}MnN_2O_9P_2$. Calculated, %: C 7.29; H 4.86; N 8.51; Mn 16.72; P 18.84.

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