STABILIZATION OF AN AQUEOUS SOLUTION OF A LIQUID MICRO FERTILIZER CONTAINING TRILON B AS A CHELATING AGENT. STRUCTURE OF THE MOLECULAR CRYSTAL OF SODIUM CARBAMIDE ETHYLENEDIAMINETETRAACETATE HYDRATE $NaH_3L^1 \cdot (H_2N)_2CO \cdot H_2O$

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Abstract. Chemical analysis methods were used to identify the causes for precipitation and fouling with a gray-green deposit of a vessel for the storage of liquid micro fertilizer consisting of ammonium heptamolybdate, potassium chloride, ammonium vanadate, boric acid, chromium trichloride, sodium selenate, and Trilon B as a chelating ligand. The precipitate represented the crystalline 1 : 1 complex of Trilon B with carbamide $NaH_3L^1 \cdot (H_2N)_2CO \cdot H_2O$ (H_4L^1 = ethylenediaminetetraacetic acid). The deposit on the vessel bottom and wall was formed upon transformation of the molybdenum complex $Na_4(MoO_3)_2L^1 \cdot 8H_2O$ into insoluble coordination polymer in an acid medium. Neutralization of the solution to pH 6–7 and a decrease in the concentration of Trilon B gave a violet micro fertilizer solution that was stable during storage. The molecular structure of the $NaH_3L^1 \cdot (H_2N)_2CO \cdot H_2O$ crystal was determined.

INTRODUCTION

Metal complexonates [1] are valuable microfertilizers, the effectiveness of which significantly exceeds the action of the corresponding inorganic metal salts. Biometals (metals of life) include ions of the following metals: sodium, potassium, magnesium, zinc, manganese, iron, cobalt, copper and molybdenum. Complexonates of these biometals are practically non-toxic, sufficiently soluble in water, stable in a wide range of pH values, adsorbed by soil and not destroyed by microorganisms. One of the most widely used complexing agents, forming highly stable water-soluble complex compounds with metals, is ethylenediaminetetraacetic acid (H_4L^1, **EDTA**).

Metal complexonates have a positive effect [2] on seed germination, growth and yield increase of many agricultural plants. Seed treatment with complexonates of trace elements leads to an increase in germination and acceleration of germination, changes in the vegetation period, and increases yield. Metal complexonates are very promising for pre-sowing seed treatment with the use of film-forming preparations. Metal complexes and metal complexonates are of no less importance in seed dredging. Introduction of complexonates into the shell of dragees has a positive effect on the yield and quality of root crops. Increase in yield of many agricultural crops [3] is achieved by introducing complexonates of trace elements by foliar feeding.

The most common commercial form of microfertilizers are solutions of biometallic salts close to saturated. They should not precipitate during long-term storage. Before use in the field, they are diluted with water many times. The present work presents the results of studying the cause of formation of undesirable solid phases from a newly created effective microfertilizer intended for seed pre-sowing treatment. The required set of trace elements was determined experimentally, but the experimentally achieved result could not be realized due to instability of the solution during storage. Chemical analysis made it possible to find out the causes of instability and eliminate them.

EXPERIMENTAL PART

In the work we used the EDTA dynatrium salt — $Na_2H_2L \cdot 2H_2O$ dihydrate (**trilon-B**) of "pure" grade, GOST 10652–73, heptamolybdate of ammonium

four-water, potassium chloride, ammonium vanadate, boric acid, chromium three-chloride six-water, sodium selenium sulfate (JSC Khimreaktiv, Nizhny Novgorod); EDTA was obtained by treatment of the EDTA dinatrium salt with hydrochloric acid.

Synthesis of $NaH_3L^1 \cdot (H_2N)_2CO \cdot H_2O$ (I). To 90 mL of distilled water was added 14.3 g (3.86×10^{-2} mol) of trilon-B and 17.75 g (2.95×10^{-1} mol) of urea under stirring. After 2 days, a white precipitate precipitated from the clear colorless solution, which was filtered off, washed with cold water, and dried in air. yield was 2.09 g (5.33×10^{-3} mol, 14%) of compound I.

IR spectrum (ν, cm^{-1}): 3434 s, 3244 sh, 3020 sl, 2719 sr, 2633 sr, 1688 pl, 1629 s, 1352 sr, 1310 sr, 1280 sl, 1182 sr, 1075 sl, 1051 sl, 1021 sl, 964 sl, 926 sl, 908 sr, 810 sr, 720 sr, 547 sl, 500 sl.

Found, %:   C 33.33,   H 5.34,   N 13.72.
For $C_{11}H_{21}N_4NaO_{10}$
calculated, %:   C 33.66,   H 5.40,   N 14.28.

Synthesis of 1,2-*bis*(3,5-dioxopiperazin-1-yl)ethane (H_2L^2) (a) To a suspension of 4.0 g (1.38×10^{-2} mol) of EDTA in 50 mL of H_2O, there was added 7.00 g (1.17×10^{-1} mol) of urea under with stirring. After 2 h of heating at 80–90°C, the suspension dissolved. The mixture was heated during 7 h, evaporated, and the residue was dried at 110°C. The brown solid was poured into methanol, crushed after swelling, washed with methanol, filtered, air-dried. The yield was 1.45 g (5.70×10^{-3} mol, 41%) of compound H_2L^2 as a light gray soft powder.

IR spectrum (ν, cm^{-1}): 3455 sr, 3387 s, 3256 sr, 3166 sr, 1700 s, 1656 s, 1620 pl, 1599 pl, 1462 s, 1373 sr, 1355 sl, 1319 s, 1268 s, 1206 s, 1116 sr, 1099 sr, 908 sl, 878 sr, 848 s, 678 s, 619 sr, 550 sr, 529 s, 500 sr. $C_{10}H_{14}N_4O_4$, M=254.1. Mass spectrum m/e: 254.12 (14%), 127.16 (100%), 99.19 (50%), 71.19 (19%).

(b) 2.00 g (6.89×10^{-3} mol) of EDTA and 0.83 g (1.38×10^{-2} mol) of urea were mixed and pounded in a mortar. The resulting mixture was heated for 5 h at 175–200°C in an argon stream. The solidified dark gray melt was crushed, mixed with 70 mL H_2O, filtered, the precipitate was washed with water and methanol, and dried in air. The yield was 0.90 g (3.54×10^{-3} mol, 51%) of H_2L^2 compound as a cream-colored powder. The IR and mass spectra are identical to the product obtained in aqueous medium.

Stabilized solution of microfertilizer. To 150 ml of distilled water, powdered components were added under stirring in the following order: trilon-B (10.06 g), $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (2.96 g), KCl (13.62 g), NH_4VO_3 (0.50 g), H_3BO_3 (7.30 g), $CrCl_3\cdot6H_2O$ (1.50 g), Na_2SeO_4 (0.12 g), $(H_2N)_2CO$ (17.75 g). From ammonium vanadate the solution became yellow, from chromium chloride at first green, but after 1–2 h acquired violet color. A solution of 0.65 g KOH in 5 mL of H_2O was added dropwise to the violet solution. The yield was 194 mL of violet solution with density 1.123 g/mL at 20°C.

Microfertilizer solution with increased acidity. The solution with increased acidity was prepared in order to form and collect scale on the walls of the vessel for subsequent analyses. To the above solution instead of KOH, 2 ml of 30% H_2SO_4 was added, stirred for 30 min and poured into a fluoroplastic beaker. A thin transparent solid film appeared on the surface after 10–12 h. The thickness of the film increased with time. Its thickness increased with time. According to optical microscopy it did not contain crystalline formations. After 5 days the solution was filtered. Wet scale from the walls and bottom of the beaker was removed with a spatula, combined with the filtered film, mixed with 30 ml of H_2O, the operation was repeated 3 times. The water-washed suspension was filtered, dried in air and in a desiccator at 110°C.

Scale annealing was carried out in a quartz tube placed in a quartz tube heated by an electric furnace. A slow flow of argon was blown through the tube.

Reaction of ammonium heptamolybdate with trilon-B. To 2.96 g of ammonium heptamolybdate solution (2.40×10^{-3} mol, 1.68×10^{-2} g-at Mo) in 30 mL H_2O was added a solution of 3.12 g (8.38×10^{-3} mol) of Trilon-B in 20 mL H_2O. The clear colorless solution was evaporated and the residue was dried for 3 h at 110°C. The yield was 5.50 g (6.77×10^{-3} mol, 80%) of $Na_4(MoO_3)_2L^1\cdot8H_2O$ complex as a white solid mass rubbing to a white fine powder.

IR spectrum (ν, cm^{-1}): 3428 sr, 1694 s, 1647 s, 1402 sr, 1349 sr, 1316 sr, 1212 sl, 1137 sl, 1008 sl, 964 sr, 947 sr, 896 s, 812 s, 777 s, 750 sr, 720 pl, 583 sr, 562 sr, 482 sl.

Found, %:   C 15.03,   H 3.12,   N 3.87.
For $C_{10}H_{28}NO_{22}Na_4Mo_2$
calculated, %:   C 14.79,   H 3.48,   N 3.45

Solubility of the complex is 6.17 g in 100 mL of H_2O at 22°C.

A solution of 3.40 g $Na_4(MoO_3)_2 L^1\cdot8H_2O$ in 60 mL H_2O was divided into 3 parts of 20 mL each and 1, 2, and 4 mL of a solution of 6% H_2SO_4 was added, respectively. After 2 h the solutions became cloudy, the turbidity increased with increasing acidity of the solution. After 12 h a precipitate appeared at the bottom, a thin white layer was formed on the vessel walls, the IR spectrum of which after drying was identical to the spectrum of the scale precipitated from the microfertilizer solution.

IR spectra of compounds in the form of suspension in vaseline (1400–400 cm^{-1}) and fluorinated (4000–1400 cm^{-1}) oils between KBr plates were recorded on a FSM 1201 Fourier transform infrared spectrometer. Elemental analysis was performed on an automatic elemental analyzer Vario EL cube (Elementar Analysensysteme GmbH) in CHNS configuration, carrier gas – helium grade 6.0. Optical microscopy was performed on a
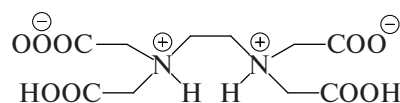
Micromed 3 microscope manufactured by Ningbo Shept Heng Optics and Electronics Co., Ltd., PRC; Observational Instruments LLC, St. Petersburg. X-ray phase analysis (XRF) was performed on a Shimadzu XRD-7000 X-ray diffractometer, thermogravimetric analysis (TGA) was performed on a TGA/DSC3+ METTLER TOLEDO synchronous thermal analysis instrument, heating rate was 5 deg/min, argon feed rate was 20 ml/min. Measurements were performed in the temperature range from +25 to +500°C. The mass spectra of compounds were recorded using a Trace GC Ultra/Polaris Q chromatography-mass spectrometer (Thermo Electron Corporation, USA) equipped with a direct input system; mass analyzer is ion trap. Mass spectra in positive ion mode were recorded at an ionizing electron energy of 70 eV in the mass number range of 50−700. Electron microscopy was performed on a Tescan VEGA II scanning electron microscope. The relative concentration of individual chemical elements (C, N, O, S, Cl, Na, K, V, Cr, Mo) was estimated on an Oxford Instruments INCA Energy 250 energy dispersive spectrometer in the scanning mode along a given line on the electronic image of the material surface.

X-ray crystallography of the single crystal I was performed on an automatic four-circle Agilent Xcalibur E diffractometer (MoC_α-radiation, ω-scanning, λ = 0.71073 Å). Diffraction data collection, initial indication of reflections, refinement of unit cell parameters, and integration of the experimental intensity set were performed in the CrysAlisPro software [4]. The SCALE3 ABSPACK algorithm [5] was used for empirical absorption recording. The structure was decoded by direct methods using the "dual-space" algorithm in the SHELXT program [6] and refined by full-matrix MNC using F^2_{hkl} in the anisotropic approximation for non-hydrogen atoms using the SHELXTL software package [7, 8]. The hydrogen atoms of the H(1A) and CH_2-groups are placed in geometrically calculated positions and refined isotropically in a "rider" model with fixed thermal parameters $U_{iso}(H) = 1.2U_{eq}(C)$. The remaining H atoms are localized from Fourier difference synthesis of the electron density and refined in the isotropic approximation. Graphical representations of the molecular and crystal structure of I were obtained in the OLEX2 program [9].

The structure I is registered with the Cambridge Structural Data Bank (CCDC No. 2343187 and available at https://www.ccdc.cam.ac.uk/structures/).

RESULTS AND DISCUSSION

Liquid microfertilizer for seed pre-sowing treatment was prepared on the basis of ethylenediaminetetraacetic acid (EDTA) (Scheme 1), a well-known chelating ligand having a betaine structure in the crystalline state and in solution [1].

Scheme 1. Ethylenediaminetetetraacetic acid (H_4L^1)

EDTA dissolves very poorly in aqueous medium, therefore, its well-soluble dynatrium salt $Na_2H_2L^1$ was used for preparation of solutions. Table 1 shows the composition of liquid microfertilizer.

In the proposed composition, the ratio of trilon-B to the sum of cations (Mo^{6+}, V^{5+}, Cr^{3+}) is 1.13, which should ensure their complete chelation. The prepared solution was found to be of limited stability. After 1 month of storage, there was observed the formation of gray with green tinge deposit on the bottom and walls of the vessel, 1 month later − white precipitation. To clarify the cause of the observed phenomena was mixed at separate components taken in slightly higher concentrations than in the solution of microfertilizer. It turned out that the white precipitate was formed in the solution containing trilon-B and urea in 2−3 days. The presence of ammonium heptamolybdate in the solution slowed down its formation and reduced its amount, which was to be explained by a decrease in the concentration of trilon-B due to the consumption for the formation of a stable chelate complex with molybdenum. Indeed, mixing of trilon-B with ammonium heptamolybdate resulted in the formation of a clear stable solution. At the same time, a similar solution of trilon-B with chromium chloride quickly produced a small amount of greenish precipitate, which further dissolved. The presence of urea in the solution prevented its formation. Trilon-B did not form precipitates when mixed with boric acid, potassium chloride, vanadium and selenium compounds. Counteraction to precipitation of chromium complex by urea is explained by its known [10] ability to give a well-soluble compound − trihydrate hexa(urea) chromium(III)trichloride [$Cr(OCN_2H_4O_6)$]$Cl3\cdot3H_2O$.

The IR spectrum of the crystalline precipitate (compound I) precipitated from the microfertilizer solution was completely identical to the spectrum of crystals isolated in the reaction of trilon-B with urea. Fig. 1 shows the IR spectra of the precipitate, trilon-B and urea. The resulting spectrum of the precipitate was a hybrid of the spectra of the parent compounds in the characteristic valence vibration region of N-H and O-H bonds 3500−3200 cm^{-1} and N-H deformation vibrations, as well as C=O valence vibrations 1700−1600 cm^{-1}. In the range of 1470−500 cm^{-1} it is more similar to the spectrum of trilon-B.

According to elemental analysis, the ratio of trilon-B and urea in the crystals was 1 : 1. Their structure was established by X-ray diffraction analysis as urea sodium ethylenediaminetetraacetate hydrate $NaH_3L^1\cdot(H_2N)_2CO\cdot H_2O$ (I). The main crystallographic

Table 1. Content of active and useful substances in 1 L of microfertilizer solution

Effective substance (ES)*	m, g/l	N · 10, mol/L	Useful substance (US)** in ES, wt. %	US in solution, g/l
$Na_2H_2L \cdot 2H_2O$***	59.58	1.61	N, 7.53	4.49
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	15.42	0.13	Mo, 54.34. N, 6,80	8.38 1.05
KCl	70.94	9.53	K_2O, 63.17	44.81
NH_4VO_3	2.60	0.22	V, 43.55 N, 11.97	1.13 0.31
H_3HE_3	38.02	6.14	B, 17.48	6.65
$CrCl_3 \cdot 6H_2O$	7.81	0.29	Cr, 19.51	1.52
Na_2SeO_4	0.63	0.03	Se, 41.80	0.26
$(H_2N)_2CO$	92.44	15.42	N, 46.65	43.12

* Salt, boric acid, urea.

** US – biometal, nitrogen, conversion to K_2O is adopted for potassium.

*** Trilon-B.

characteristics, X-ray diffraction experiment parameters and refinements for I are given in Table 2, the main bond lengths and angles in Table 3. The structure of I in the crystal is presented in Fig. 2.

In the crystal, coordination compound I has a polymer structure of dimensionality 2D. In the 2D coordination polymer, sodium atoms bind four bridging molecules of ethylenediaminetetraacetate each and are coordinated by six oxygen atoms of EDTA – O(1,3–7). Accordingly, each bridging EDTA ligand coordinates four sodium atoms each by all four carboxylate groups.

The pair of bridging bidentate groups –COO with O(3,4) and O(5,6) atoms have the coordination type $\mu_2 - \kappa O: \kappa O'$, while the other pair of carboxylate groups with coordinating atoms O(1) and O(7) is characterized by a monodentate type of coordination (κO).

Sodium atoms have a distorted octahedral environment. Atoms O(3,4,5,6) are located at the base of the octahedron; atoms O(1) and O(7) occupy axial positions. The Na(1) atom is located at the base of the octahedron (Na moving from the O(3–6) plane is 0.086 Å). Note that the angle between the axial substituents
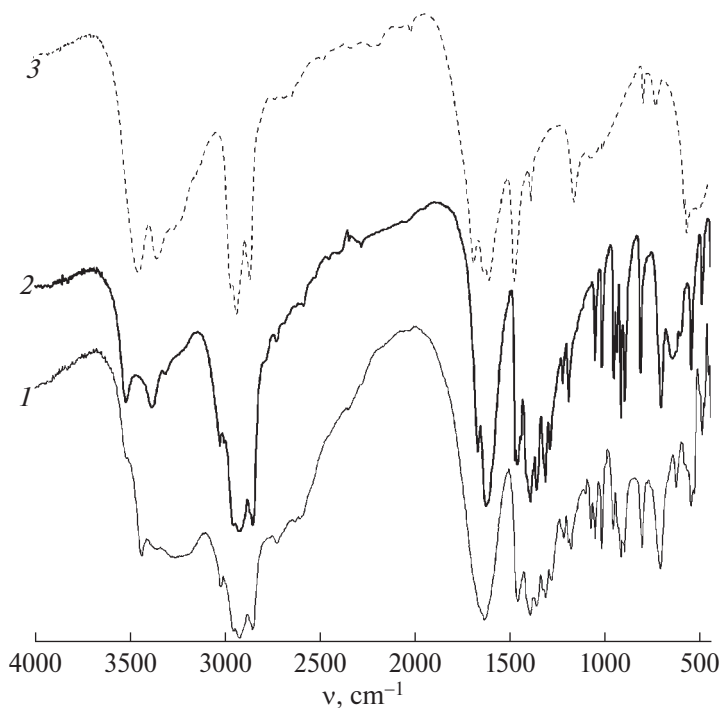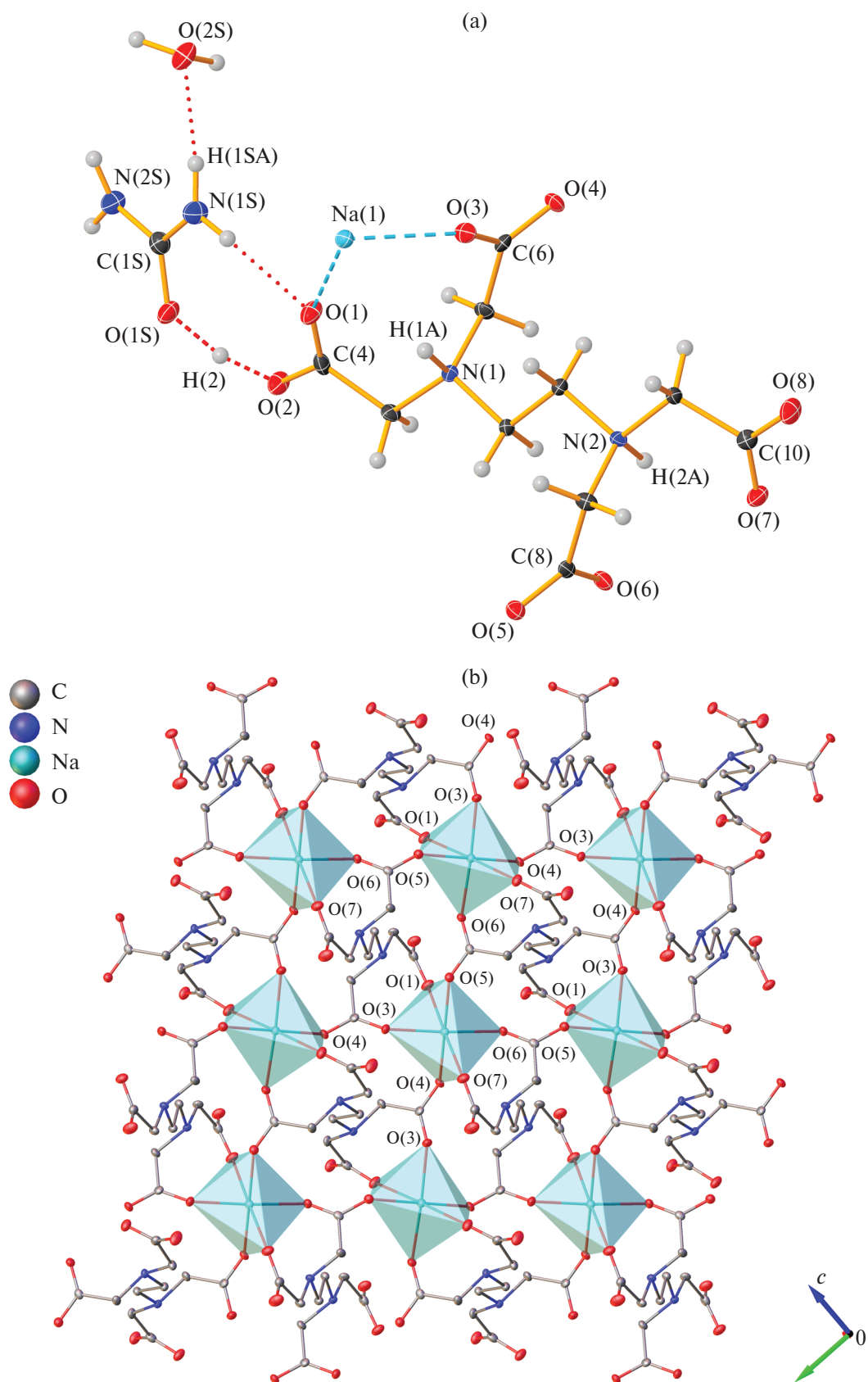

Fig. 1. IR spectra of the crystalline precipitate (compound I) (*1*), trilon-B (*2*) and urea (*3*).

Table 2. Crystallographic data, X-ray diffraction parameters experiment and clarification of the structure of compound I

Communication	d, Å	Angle	ω, deg
Na(1)−O(1)	2.453(4)	O(1) Na(1) O(7)	178.26(15)
Na(1)−O(3)	2.306(3)	O(4) Na(1) O(5)	176.05(16)
Na(1)−O(4)	2.361(3)	O(3) Na(1) O(6)	175.33(17)
Na(1)−O(5)	2.397(3)	O(1) Na(1) O(3)	88.94(12)
Na(1)−O(6)	2.348(3)	O(1) Na(1) O(4)	96.18(12)
Na(1)−O(7)	2.431(4)	O(1) Na(1) O(5)	79.99(12)
O(1)−C(4)	1.236(5)	O(1) Na(1) O(6)	86.39(12)
O(2)−C(4)	1.276(5)	O(3) Na(1) O(7)	92.80(12)
O(3)−C(6)	1.246(5)	O(4) Na(1) O(7)	83.40(12)
O(4)−C(6)	1.257(5)	O(5) Na(1) O(7)	100.40(12)
O(5)−C(8)	1.265(5)	O(6) Na(1) O(7)	91.87(12)
O(6)−C(8)	1.242(5)	O(3) Na(1) O(4)	100.89(12)
O(7)−C(10)	1.240(5)	O(3) Na(1) O(5)	80.12(12)
O(8)−C(10)	1.259(5)	O(4) Na(1) O(6)	79.44(12)
O(1S)−C(1S)	1.289(4)	O(5) Na(1) O(6)	99.25(12)
O(1S)...H(2)	1.30(11)		
H(2)...O(2)	1.17(11)		
H(1SA)...O(2S)	2.04(3)	N(1S)...H(1SB)...O(1)	175(4)
H(1SB)...O(1)	2.13(5)	O(1S)...H(2)...O(2)	161(9)

Table 3: Basic bond lengths and angles in connection I

Parameter	Value
Gross formula	$C_{11}H_{21}N_4O_{10}Na$
M	392.31
Temperature, K	100(2)
Syngony	Monoclinic
Sp. group	Pc
a, Å	10.1574(5)
b, Å	9.4792(4)
c, Å	9.2234(4)
β,°	115.678(5)
V, Å^3	800.36(7)
Z	2
ρ(calc.), mg/cm^3	1.628
μ, mm^{-1}	0.165
Crystal size, mm	0.217 × 0.185 × 0.084
F(000)	412
Data acquisition area at 2θ, deg	2.15−29.13
Number of reflections measured/independent	13892 / 4293
R_{int}	0.0527
$R_1/wR_2\,(I > 2\sigma(I))$	0.0431/0.0846
R_1/wR_2 (all data)	0.0643/0.0937
Absolute structural parameter	0.2(4)
S	1.031
Residual electron density (max/min), e/Å^3	0.293/-0.252

(a)

O(2S)

H(1SA)

N(2S)   N(1S)   Na(1)   O(3)   O(4)

C(1S)   O(1)   C(6)

O(1S)   O(1)   H(1A)

H(2)   C(4)   N(1)   O(8)

O(2)   N(2)   C(10)

H(2A)

O(7)

C(8)   O(6)

O(5)

(b)

C
N
Na
O

O(4)

O(3)
O(1)

O(3)

O(6) O(5)
O(7)
O(1)   O(4)

O(7)   O(4)
O(6)
O(1)   O(5)   O(3)
O(3)   O(1)
O(4)
O(6) O(5)
O(4)   O(7)

O(3)

c

0

(c)

Fig. 2. Fragment of the structure of the independent region of the crystal $NaH_3L^1 \cdot (H_2N)_2 CO \cdot H_2O$ (I) (thermal ellipsoids of atoms are given with 50% probability) (a); fragment of the 2D-polymer structure of I in projection along the *a-axis* (hydrogen atoms, water and urea molecules are not shown) (b); fragment of crystal packing I (contacting H atoms are shown, water and urea molecules are highlighted in yellow and green, respectively (c).

is 178.26(15)°, which is slightly larger than the similar angles between the equatorial substituents (175.33(17)° and 176.05(16)°, Table 3). The Na−O distances in the equatorial plane range in value from 2.306(3)−2.397(3) Å and are shorter than the analogous distances of the axial substituents (Na(1)−O(1) 2.453(4), Na(1)−O(7) 2.431(4) Å). The sum of the angles between the substituents in the equatorial plane is 359.7°; and the angles between the axial and equatorial substituents vary between 79.99(12)° − 100.40(12)°.

The C−O distances in the three carboxylate groups with C(6), C(8) and C(10) atoms are equalized, while in the C(4) O(1) O(2) group the lengths of C−O bonds are markedly differentiated and are 1.236(5) and 1.276(5) Å, respectively, indicating protonation of the carboxylate group. Note that the H(2)...(2) distance is 1.17(11) Å, which is noticeably longer than the lengths of the O−H and N−H covalent bonds in this structure (0.81(4) −1.05(5) Å). The H(2)...O(1S) distance of the urea molecule also has a comparable value (1.30(11) Å). High errors of the O(2)...H(2)...O(1S) distances, as well

as a significant value of the isotropic displacement of the H(2) atom (0.17(4) Å^2) compared to the hydrogen atoms of water and amino groups (0.01(1) ... 0.06(2) Å^2) do not allow the position of the H(2) atom to be accurately localized between the O(2) atoms of the carboxylate group and the O(1S) atoms of urea. A similar situation for a proton migrating between two oxygen atoms was found and studied in detail in multitemperature neutron and X-ray diffraction studies of a molecular co-crystallizate of urea and phosphoric acid [11]. The C(1S)-O(1S) bond length in the urea molecule, equal to 1.289(4) Å, is slightly longer than the analogous bond length of unsocrystallized urea (1.258(2) Å at 123 K [12]), which further confirms the presence of the H(2) proton and, consequently, the interaction of the urea molecule with it.

In crystal I, 2D-coordination polymers of sodium ethylenediaminetetetraacetate are packed in parallel layers along the crystallographic axis *a* (Fig. 2b). Intermolecular hydrogen bonds O...H with the participation of water and urea molecules are realized

between the polymer layers. Among them, in addition to the noted H(2)...O(1S)UREA bond of 1.30(11) Å, other the shortest O...H bonds were found, the lengths of which are 1.772(18), 1.85(2) ($H^{H_2O}...O^{2D-MOF}$) and 2.04(3) Å ($O^{H_2O}...H^{UREA}$) (highlighted by black dotted lines in Fig. 2b).

Fig. 3 shows the thermal analysis of compound I, trilon-B, and urea. Binding of volatile urea into the complex led to an increase in the thermal stability of the resulting compound I compared to trilon-B. The TGA and DTG curves for them had a largely similar appearance. The mass of urea is 15.3% of the complex mass. The distinctly pronounced first step of weight loss of about 15% on heating to 240°C is due to the removal of the $(H_2N)_2CO$ fragment. Further thermal decomposition proceeded similarly with some lag in weight loss for compound I compared to trilon-B. The DSC curves for them had only very weakly expressed endothermic peaks against the background of uniformly rushing upward lines, which indicated that external heating caused internal processes occurring not with absorption but with heat release. The curve below for compound I indicated that the addition and subsequent detachment of urea from trilon-B led to some rearrangement of the structure of the complex, complicating thermal decomposition under external heat energy supply. Trilon-B has two water molecules in its composition, which is 9.7% of its mass. They were sufficiently firmly retained and removed gradually only when the temperature reached 150°C. The faster and deeper thermal decomposition of hydrated Trilon-B compared to compound I should be attributed to the influence of water molecules. Its displacement by urea led to an increase in the thermal stability of the resulting compound I. The thermal decomposition of urea ignited in vacuum or in air does not require comments, since it has been thoroughly studied [13, 14].

Thus, the reason for the formation of the crystalline precipitate was clarified. It was not possible to predict its formation on the basis of available literature data, despite the highly studied reactions of trilon-B and urea. For general chemical reasons it seemed pointless
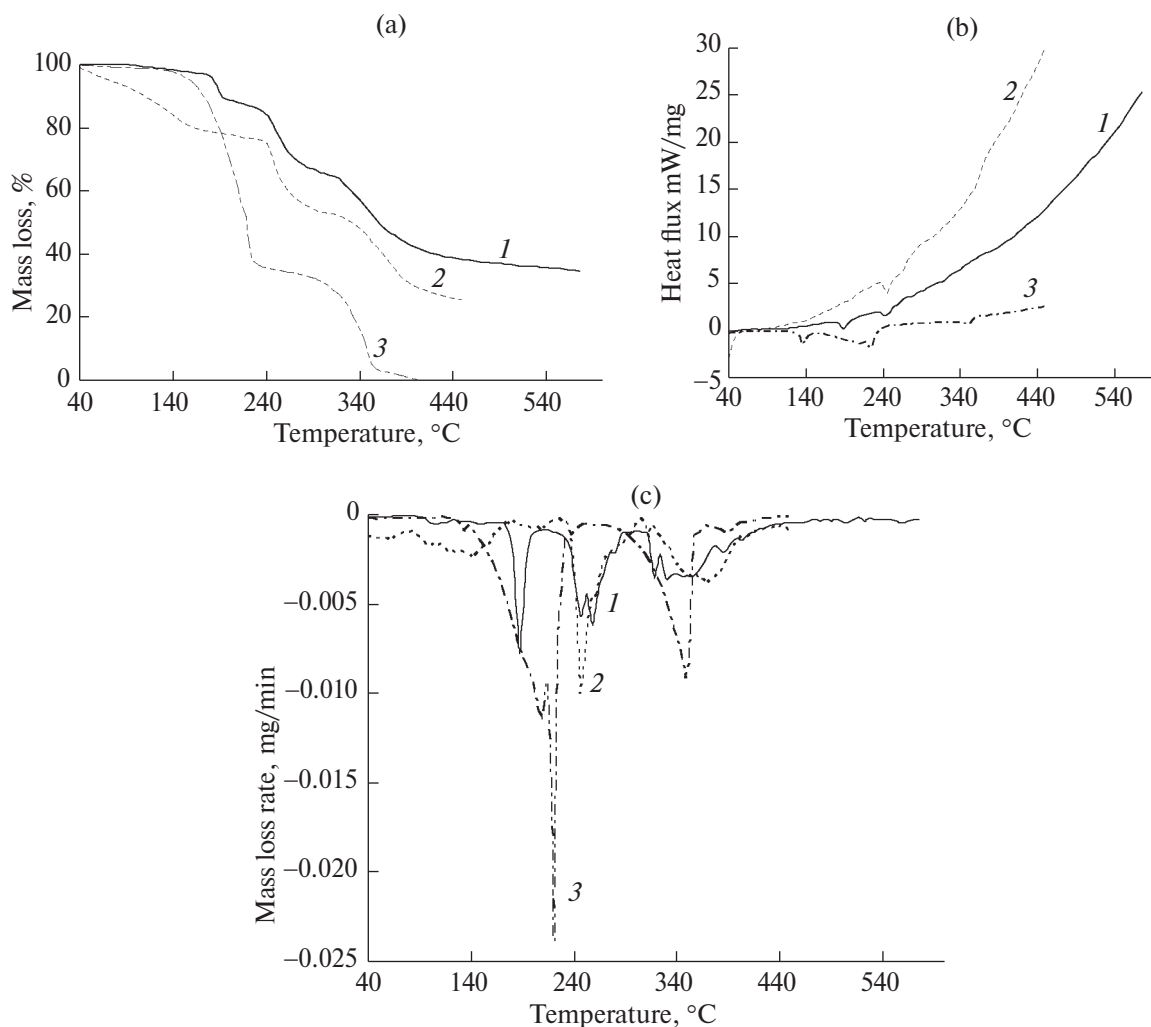

Fig. 3. Thermal analysis of compound I (*1*), trilon-B (*2*) and urea (*3*): TGA (a), DSC (b), DTG (c).

to attempt to react these components. The Chemical Abstracts search engine "SciFinder" did not produce any references to the joint presence of: "Trilon-B-Urea" (Ethylenediamine-N, N, N', N'-tetraacetic acid disodium salt − Urea). At the same time, the interaction with urea of ethylenediamine-tetraacetic acid has been investigated in detail. The product of this reaction − 1,2-*bis*(3,5-dioxopiperazin-1-yl)ethane (H^2L^2) and its derivatives were in demand because they showed anticarcinogenic activity [15].

It was more difficult to find out the reasons for the formation of greenish-gray scale on the vessel walls. Coordination compounds obtained in the reactions of trilon-B with metal salts, usually precipitate out of aqueous solutions in the form of fine or coarse crystalline precipitates. Additional experiments in the field of two-component systems: trilon-B-$(NH_4)_6Mo_7O_{24}$, trilon-B-KCl, trilon-B-NH_4VO_3, trilon-B-H_3BO_3, trilon-B-$CrCl_3$, trilon-B-Na_2SeO_4, showed that none of these solutions produced precipitation (wall scaling). According to optical and scanning electron microscopy (SEM) data, the scale scraped off the vessel walls resembled amorphous vitreous matter in appearance. The elemental composition of the thin layer of the sample surface determined by energy dispersive X-ray fluorescence (EDS) analysis showed that the scale contained a high content of carbon, nitrogen, oxygen, potassium, and molybdenum (24, 8, 37, 10, 19%, respectively), while sulfur, chlorine, sodium, vanadium, and chromium were determined at a lower level (0.48, 0.86, 0.27, 1.02, 0.11%, respectively). The high content of carbon, nitrogen and oxygen suggested that the scale on the vessel walls was an organic compound derived from EDTA and urea, and the other elements were contained as adsorbed and incorporated compounds in the organic film in concentrated solution. Such a compound would be the well-known 1,2-*bis*(3,5-dioxopiperazin-1-yl)ethane II (Scheme 2) [15−17], which is insoluble in aqueous medium and obtained from EDTA and formamide [18, 19].
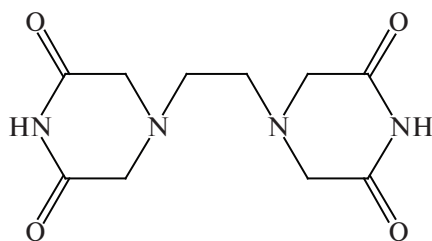
The test showed that the EDTA suspension gradually dissolved in the aqueous urea solution, but the solution did not precipitate or scale on the vessel walls during storage. At the same time, evaporation resulted in the formation of H_2L^2. The mass spectrum of the pure compound H_2L^2 was very simple and contained peaks of the molecular ion ($M = 254$), the product of

the molecule breaking into two equal parts ($M = 127$) by the central C−C bond and a fragment with mass 99. The measured mass spectrum of the scale had a complex appearance and contained three fragments characteristic of the H_2L^2 spectrum, with the fragment with mass 97 (M-2) having an intensity of 100%. However, the IR spectrum of the scale scraped off the vessel walls was not identical to the H_2L^2 spectrum.

It is known [18] that the compound H_2L^2 is insoluble in water and methanol, but reacts quite rapidly with copper(II) acetate, forming a well-soluble complex. Verification showed that it also interacts with chromium chloride and ammonium heptamolybdate. The resulting complexes were well soluble in water, after evaporation and drying their IR spectra did not correspond to the scale spectrum. Thus, the insoluble organic compound H_2L^2 could not be the reason for the formation of a precipitate on the walls of the vessel during its storage.

Testing of the solid phase deposited on the vessel walls by XRD showed that the deposit has a crystalline structure (Fig. 4a). X-ray radiographs of powders dried at 110°C in air and in vacuum did not differ practically. The powder X-ray radiography database contains only natural minerals and well-characterized synthetic inorganic compounds. It is possible to perform some approximation to them only by means of high-temperature treatment of the investigated product due to transformation of complex complexes into simple oxides, carbides, nitrides, etc. Indeed, heating of the scale to 750°C in argon flow with subsequent application of XRD method allowed to find out which metals were deposited in the form of EDTA complexes or some other poorly soluble compounds. The pyrolyzed scale (Fig. 4b) contained potassium molybdate K_2MoO_4 (monoclinic), molybdenum carbide Mo_2C (orthorhombic) and molybdenum nitride Mo_5N_6 (hexagonal) in the 18 : 11 : 1 ratio. The presence of phases of other metals (Cr, V) was not detected.

Thus, the method of powder radiography showed that the cause of fouling is molybdenum(VI) complex. The walls and bottom of the vessel with a solution consisting of Trilon-B, chromium chloride and ammonium heptamolybdate, after 7 days were covered with gray-green scale, which after repeated rinsing with water became white due to the loss of chromium. The resulting solution was acidic (pH 1). It is known that solutions of 3d-metal salts have an acidic reaction as

Scheme 2. 1,2-*Bis*(3,5-dioxopiperazin-1-yl)ethane (H_2L^2)(II)
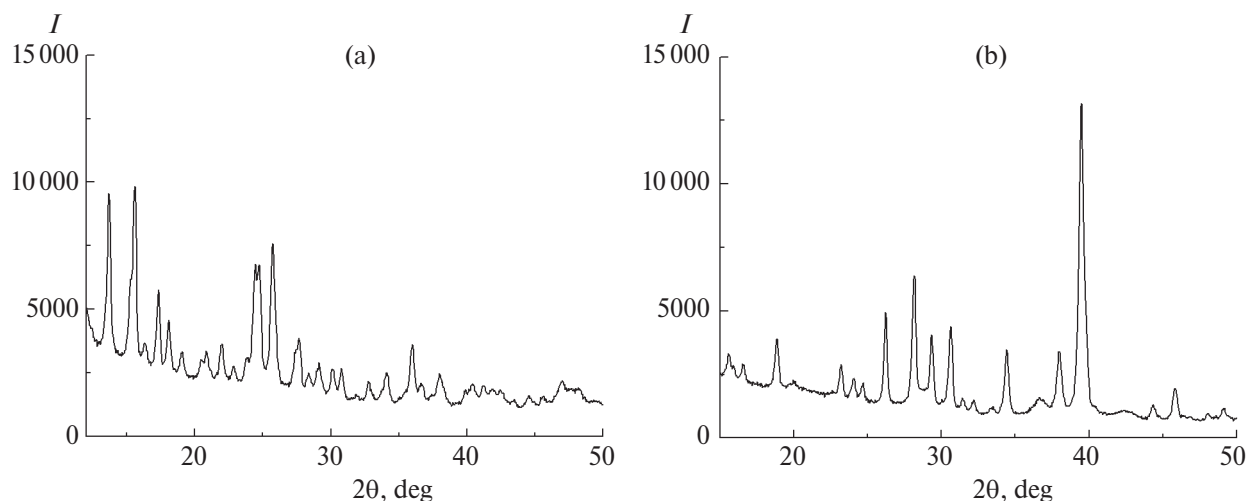
Fig. 4. X-ray radiographs of the solid phase deposited on the walls of the vessel with the microfertilizer solution: dried in vacuum at 110°C (a), heated in argon flow at 750°C (b).

salts of weak base [Cr(OH)$_3$] and strong acid (HCl). According to [20], five coordination compounds of molybdenum have been previously synthesized and characterized. Only one of them Na$_4$(MoO$_3$)$_2$L·8H$_2$O did not contain additional ligands and was a molybdenum(VI) derivative. Obtained by counter synthesis, it was quite well soluble in water (6.2 g in 100 mL), was a fine crystalline white powder, redispersed with methanol, and did not precipitate during storage. However, acidification of the solution to pH 1 caused precipitation after 2 h and adhered to the vessel walls.
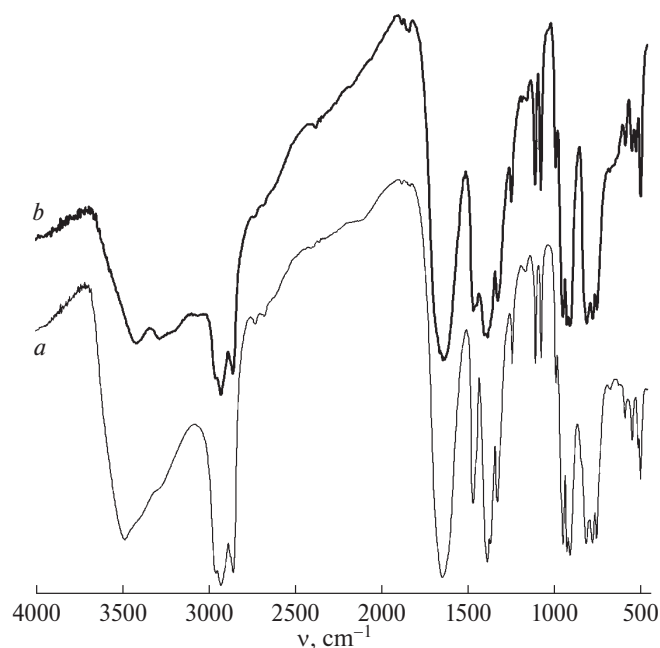

Fig. 5. IR spectra of the scale (a) and the molybdenum compound Na$_4$(MoO$_3$)$_2$L^1·8H$_2$O (b), air-dried without heating.

The IR spectrum (Fig. 5) of the air-dried precipitate was identical to that of the scale extracted from the microfertilizer solution.

It is well known that many metal complexonates lose solubility [1] due to the formation of insoluble coordination polymers. This kind of processes is slow during storage of solutions and faster during changes in acid-base properties.

The identity of IR spectra in the range 1500−400 cm^{-1} ("fingerprint region") is even more apparent than in the region of valence and strain vibrations of O−H, N−H, C=O bonds (characteristic region 3800−1600 cm^{-1}). This is due to some difference in the degree of drying of the products. The molybdenum compound contains eight molecules of crystallohydrate water. The additional adsorbed water causes broadening and increase in absorption intensity in the 3700−3400 cm^{-1} region. Prolonged incubation in an oven at 110°C leads to the appearance in this range of a narrow and less intense single band at 3428 cm^{-1}, belonging to the valence vibrations of the O−H bonds of crystallohydrate water.

The obtained results indicated that stabilization of microfertilizer solution (absence of sediment and scale formation on the bottom and walls of the vessel) is possible at lowering its acidity. Indeed, bringing the pH to 6−7 by adding a calculated amount of NaOH, KOH or Na$_2$CO$_3$ led to the formation of a purple solution that does not precipitate and scale on the walls of the vessel during long-term storage. In order to prevent precipitation of compound I originating from urea and Trilon-B, the content of the latter was reduced to 52.72 g/L (1.25 mol/L)

In conclusion, we note that precipitation during storage of liquid microfertilizer containing nitrogen, potassium, boron, molybdenum, chromium, selenium

as useful substances and trilon-B as chelating ligand is due to high content of urea and trilon-B. Gray-green fouling of the vessel is due to the complex of molybdenum with ethylenediaminetetetraacetic acid, which undergoes polymerization under acidic conditions to form an insoluble coordination polymer. Reducing the concentration of Trilon-B and neutralization of the solution prevents the formation of sediment and fouling of the vessel walls with scale during long-term storage of liquid microfertilizer.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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