HARVARD EDUCATIONAL AND SCIENTIFIC REVIEW

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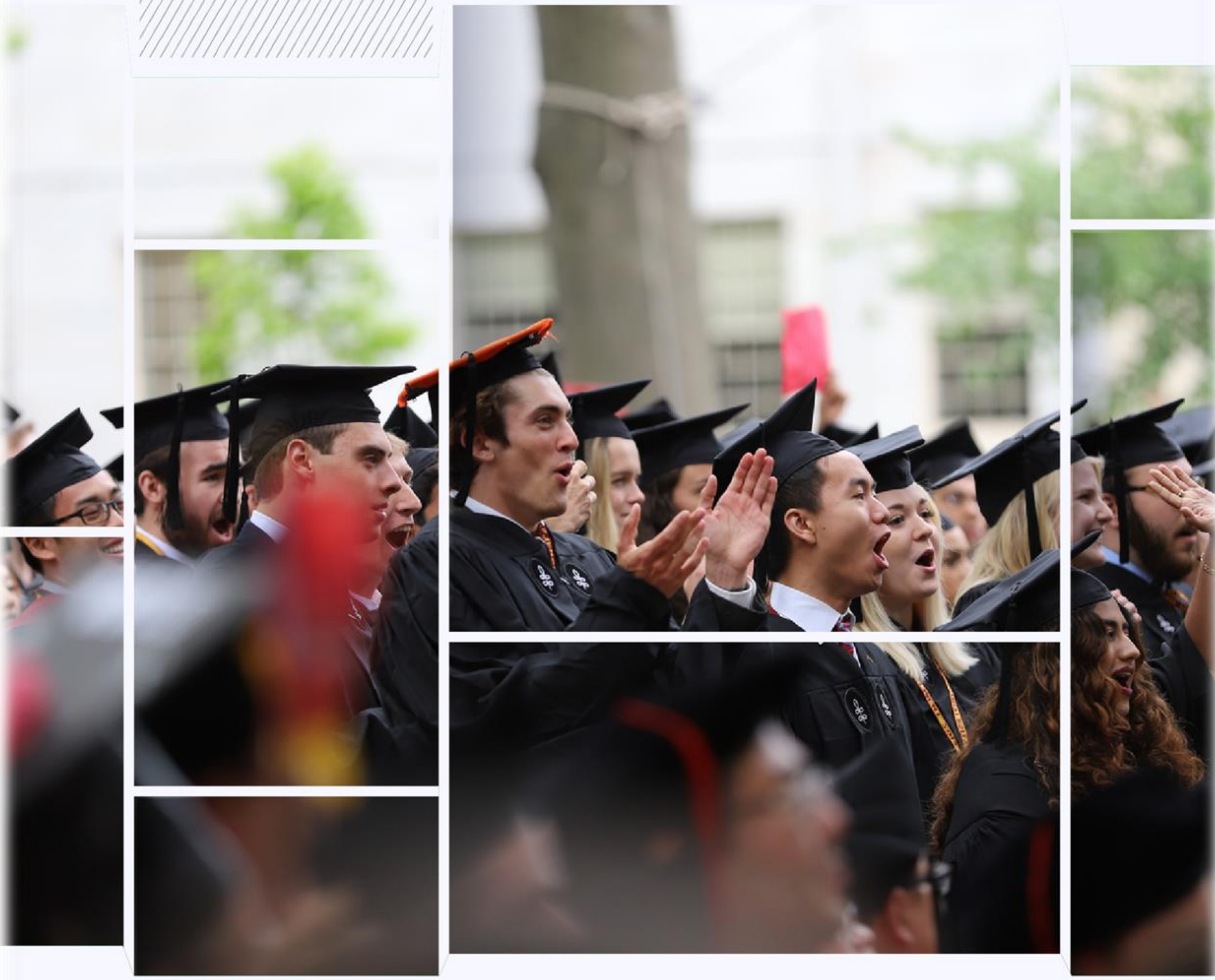

Harvard Educational and Scientific Review
International Agency for Development of Culture, Education and Science
United Kingdom
Street: 2 High Street City: Ashby Phone number 079 6425 7122
Zip code DN16 8UZ Country United Kingdom
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Har. Edu.a.sci.rev. 0362-8027
Vol.2. Issue 3 Pages 74-82.

OBTAINING NEW SULFUR-CONTAINING COMPLEXONES BASED ON THIOCARBAMIDE AND MONOCHLOROACETIC ACID

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Abstract: In order to synthesize sulfur-retaining complexes, the processes of condensation of thiourea with monochloroacetic acid and its salts have been studied. It has been established that mono - and polycarboxymethylene derivatives are formed by the interaction of thiourea with monochloroacetic acid in an acidic medium. The composition and structure of the products obtained were confirmed by element analysis and IR spectroscopy.

Keywords: sulfur-preserving complexes, thiourea, monochloroacetic acid, condensation, mono- and polycarboxymethylene derivatives, element formation, IR spectroscopy.

Introduction. Complexons containing a sulfur atom as the main center are of practical importance due to the specificity of interaction with the genes of metals that have an affinity for sulfur. The extremely toxic and unstable thioglycolic acid was used as the initial reagent in the synthesis of sulfur-containing ligands, the methods for obtaining which are very complex and time-consuming, which largely hindered the development of the synthetic chemistry of these compounds [1].

The main properties of polydentate compounds is the ability to form complexonates with most metal ions in aqueous solutions, the stability of which, as a rule, is so high that the corresponding cation is not detected using classical methods. Synthetic availability and broad possibilities for modifying the structure of molecules of complexones and complexes based on them open up great prospects for creating compounds with a predetermined set of properties for solving both theoretical problems and specific national economic problems.

The purpose of this work is to obtain new sulfur-containing complexones based on thiocarbamide and to find ways to use the obtained complexones.

Modern methods for obtaining polydentate compounds are based on two main areas: hydroxyalkylation or carboxyalkylation of amines and the introduction of complex fragments into a molecule containing mobile hydrogen or halogen atoms [2,3].

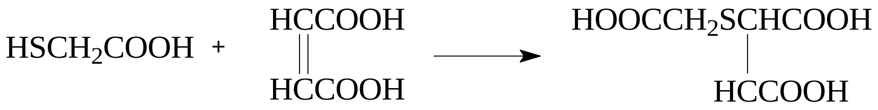
Methods for the synthesis of carboxyl-containing complexones are quite diverse and are widely used in the technology of obtaining these practically important compounds.

Sulfur-containing ligands of the complexone type are of considerable interest; in connection with their synthesis, some attention has been paid in recent years.

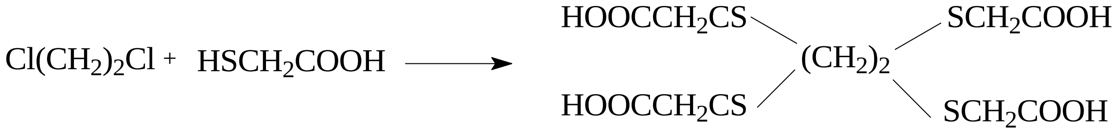
Thiodiacetic acid is obtained with a yield of 65% by heating thioglycolic acid with monochloroacetic acid in an alkaline medium in a stream of nitrogen. Its preparation is also described by the interaction of sodium sulfide with monochloroacetic acid in an alkaline medium with a yield of 27%. A modification of the described method is the Williamson reaction, which consists in the interaction of a sulfide with an ester of α-haloacetic acid [2].

Based on thioglycolic acid, methylenedi (thioacetic) acid is obtained by interaction with formaldehyde in the presence of gaseous hydrogen chloride in benzene [3] (yield about 30%). This acid was obtained with sodium hydrosulfite and formaldehyde (yield 30%).

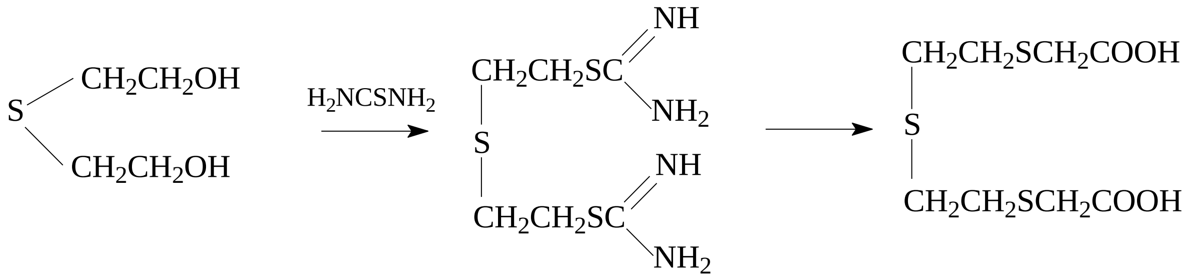
Carboxymethyl thiosuccinic acid is obtained by the interaction of thioglycolic acid with maleic acid in the presence of sodium hydroxide [4]:



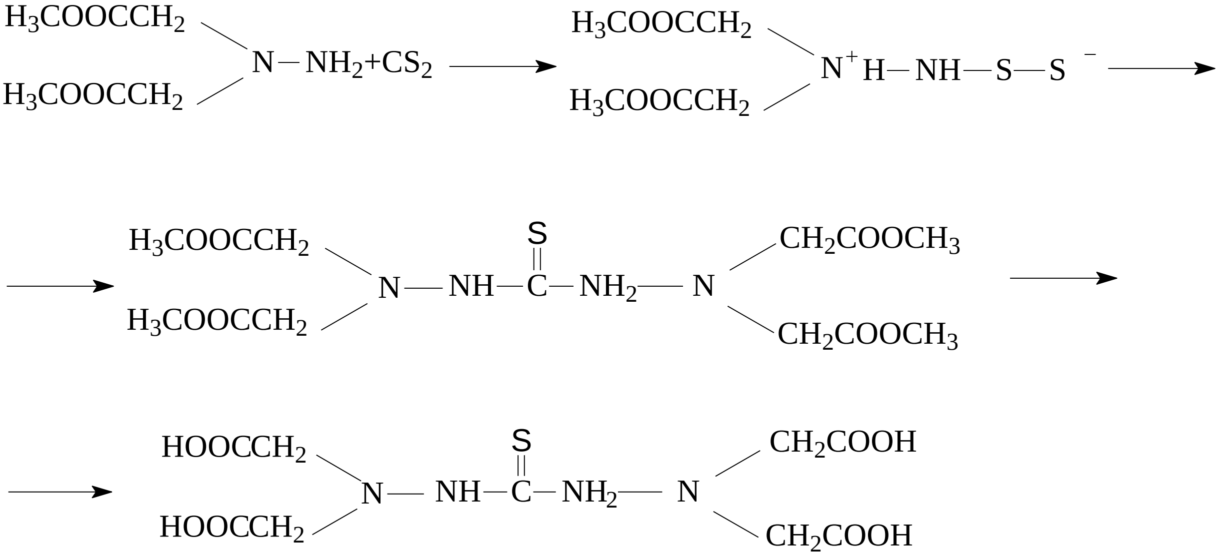
Ethylenetetra (thioacetic) acid is synthesized by the reaction of thioglycolic acid with tetrachloroethane [5,6]:



Diethylenetrithiodiacetic acid was obtained in 58% yield by reacting thiodiglycol with thiourea via thiuronium salt followed by condensation of 2, 2-dimercaptodiethyl sulfide with monochloroacetic acid [7]:



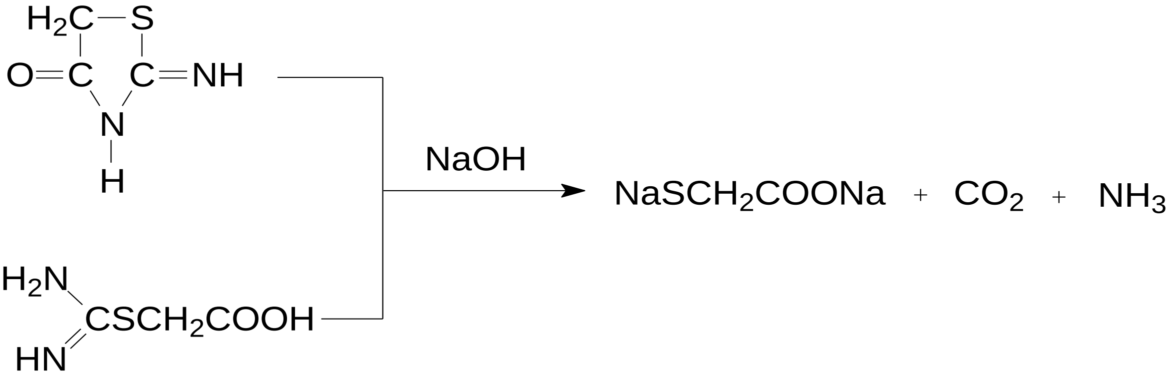
The action of carbon disulfide on the dimethyl ester of N,N-hydrazine diacetic acid was obtained [8] dithiocarbazic acid, which, under the action of alcohol and saponification, gives thiocarbodihydrazidetetraacetic acid:



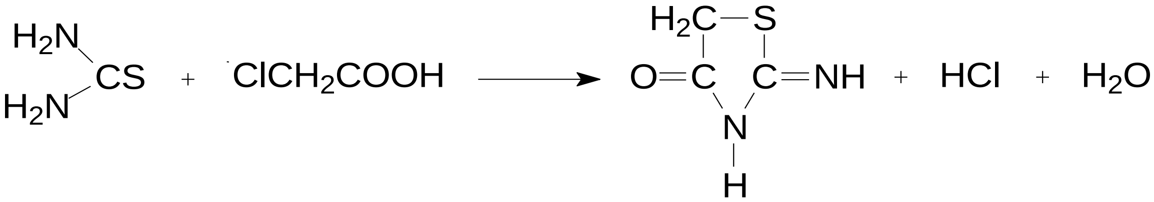
Methylenetrithioacetic acid was obtained by the interaction of thioglycolic and formic acids in a stream of gaseous hydrogen chloride [9].

One of the disadvantages of the methods discussed above for the production of sulfur-containing complexones is the use of thioglycolic acid as a starting reagent, a highly toxic and unstable compound that easily oxidizes to form dithiodiacetic acid. Oxidation of thioglycelic acid is also a side reaction in the preparation of complexones based on it, which makes it difficult to isolate the final products from the reaction mixture. In addition, the known methods for obtaining thioglycolic acid are complex and time-consuming. In this regard, of interest is the shown possibility of replacing thioglycolic acid complexones in the synthesis with stable and accessible reactive sulfur-containing compounds - iminothiazolidone and its non-cyclic analogue - (amidinothio) acetic acid [11, 12].

In this regard, we first proposed (amidinothio) acetic acid and its cyclic derivative, iminothiazolidone, as starting reagents for the preparation of sulfur-containing complexoids - derivatives of thioglycolic acid, which quantitatively decompose in an alkaline medium to the sodium salt of thioglycolic acid according to the scheme below



According to the data available in the literature, the synthesis of iminothiazolidone is carried out in two ways: by condensation of tumourea with monochloroacetic acid in an aqueous or aqueous-alcoholic medium and subsequent neutralization of the reaction solutions under fairly mild conditions with alkaline agents, which are sodium hydroxide or acetate



and condensation of thiourea with sodium salt of monochloroacetic acid. However, it is known that cyclization of organic acids, including carbolic acids, is observed, as a rule, in an acidic medium. The data of physicochemical studies confirming the identity of the compounds obtained by the interaction of thiourea with monochloroacetic acid and its sodium salt are not given. And in connection with this, it seemed interesting to us to study the nature of the final reaction products occurring in alkaline and acidic media.

Experimental part. The synthesis of carboxymethylene derivatives of thiourea was carried out in the following sequence: to 15.2 g (0.2 mol) of thiourea dissolved at 40–45°C in 30 ml of water, a solution of 18.9 g (0. 2 mol) of monochloroacetic acid in 30 ml of water. The reaction mixture is heated to 90 - 95 °C, kept at this temperature for 20 - 30 minutes, then cooled to 15 - 20 °C. The precipitate formed is filtered off, dissolved in 240 ml of boiling water, and a solution of 28 g (0.34 mol) of sodium acetate in 30 ml of water (pH 4–5) is added. The precipitate is filtered off, washed with ice water and dried.

Elemental analysis results, empirical formula CH_7N_2OS:
found: C=31,40; H=3,70; N=24,67; S=27,57.
computed: C=31,03; H=3,43; N=24,14; S=27,58.

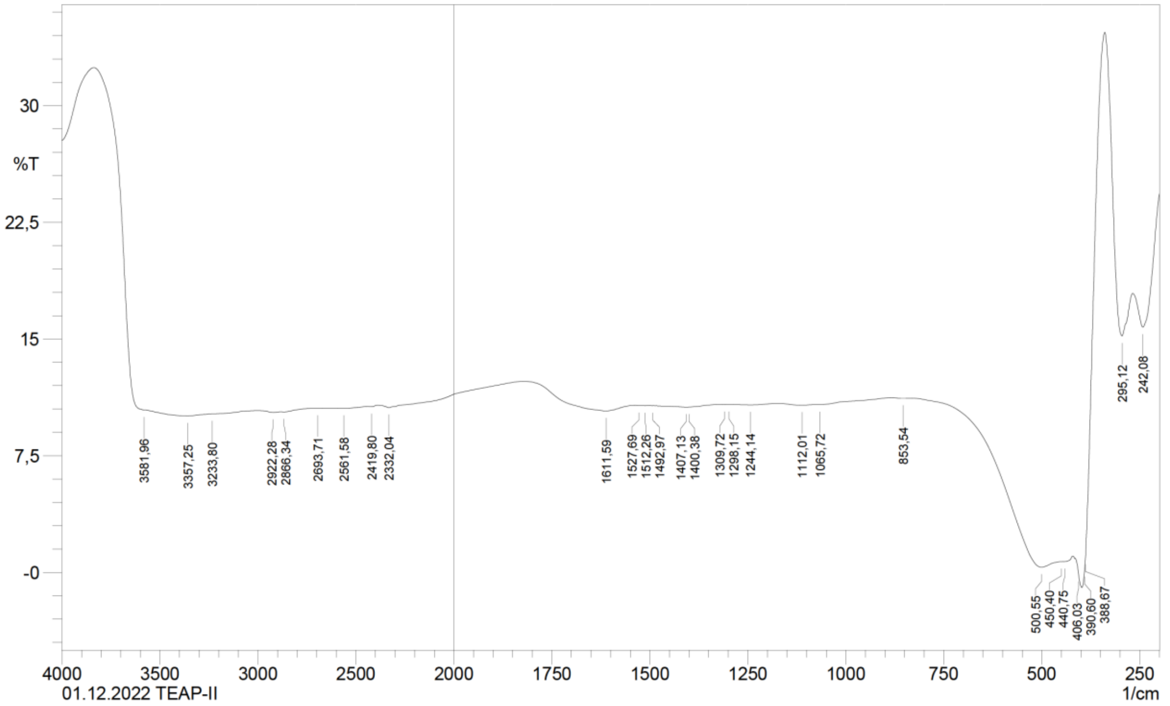
Condensation of thiourea with sodium salt of monochloroacetic acid. To a solution of 18.9 g (0.2 mol) of monochloroacetic acid in 10 ml of water, neutralized with a solution of 8 g (0.2 mol) of NaOH in 20 ml of water, a preliminarily prepared solution of 15.2 g (0.2 mol) thiourea in 30 ml of water. The reaction mixture is heated to 50 - 60 °C. Maintain at this temperature for 10 - 15 minutes, then cool to 15 - 20 °C. The precipitate that formed was filtered off and dried.

Elemental analysis results, empirical formula $C_3H_6N_2O_2S$:
found: C=26,89; H=4,74; N=20.93; S=23,74.
computed: C=26,54; H=1,69; N=20,88; S=23.90.

The discussion of the results. Elemental analysis data indicate different compositions of the obtained products. Depending on the reaction conditions, they are in good agreement with the calculated values for either iminothiazolidone or (amidinothio)acetic acid.

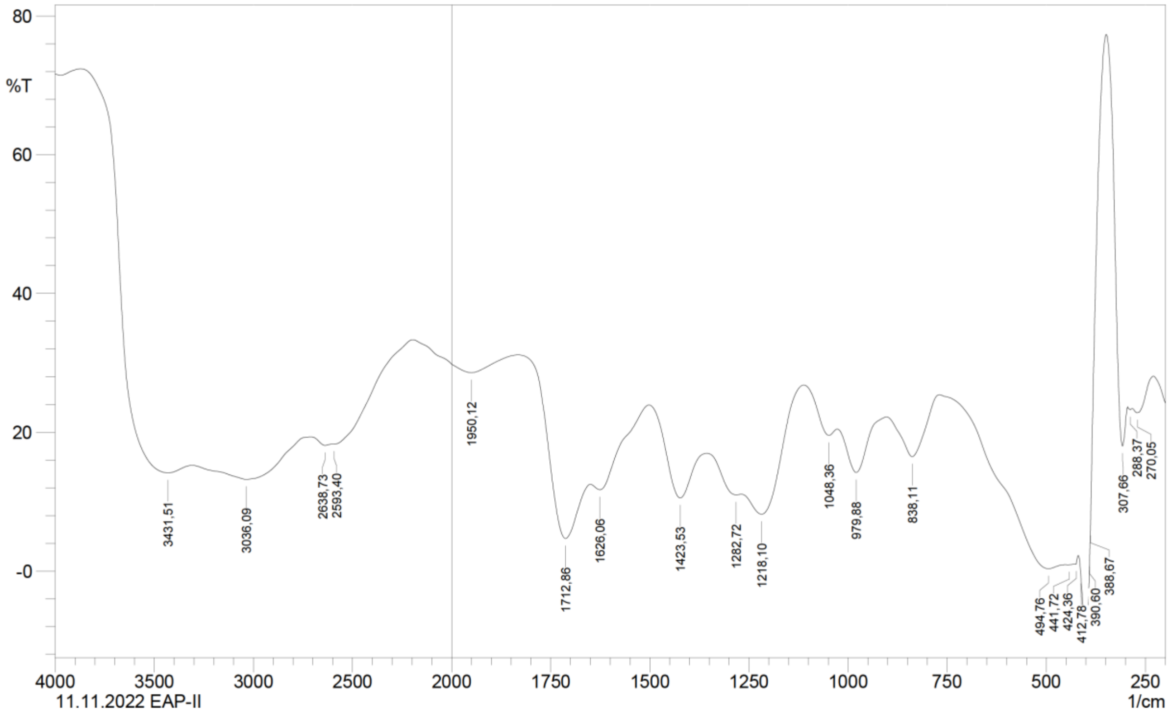
The composition and structure of the obtained products were also established using the IR spectroscopic method (Figs. 1 and 2).

IR spectra were recorded on a SHIMADZU IR spectrophotometer from Nicolet Instrument Corp. Measurement area: 400-4000 cm–1, transparent disk with KBr 7 mm in diameter (test substance about 0.5 mg in 80 mg of KBr powder).



No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	242,08	15,76	4,56	267,15	199,64	49,93	4,1
2	295,12	15,19	9,18	338,52	268,12	49,17	6,62
3	388,67	0,54	0,66	389,64	339,49	40,84	0
4	390,6	0	0,17	391,57	390,6	2,66	0
5	406,03	0	-0,13	407	405,07	385,78	94,84
6	440,75	0,69	0,06	444,61	421,46	48,71	0,94
7	450,4	0,69	0	451,36	445,58	12,49	0
8	500,55	0,33	1,66	840,04	452,33	525,87	18,49
9	853,54	11,2	0,01	885,36	841	42,17	0,01
10	1065,72	10,78	0,03	1077,29	886,33	183,03	0,08
11	1112,01	10,75	0,06	1171,81	1078,25	90,47	0,14
12	1244,14	10,77	0,05	1287,54	1172,77	110,95	0,12
13	1298,15	10,79	0	1302,01	1288,5	13,06	0
14	1309,72	10,79	0	1314,54	1306,83	7,46	0
15	1400,38	10,63	0,01	1404,24	1315,51	86,06	0,01
16	1407,13	10,62	0	1438,96	1405,2	32,84	0
17	1492,97	10,71	0	1500,68	1492	8,42	0
18	1512,26	10,71	0,01	1520,94	1501,65	18,71	0
19	1527,69	10,72	0,01	1536,37	1521,9	14,03	0
20	1611,59	10,38	0,76	1820,88	1537,33	271,83	5,34
21	2332,04	10,6	0,25	2373,51	1821,84	523,94	5,41
22	2419,8	10,65	0,04	2438,13	2388,94	47,77	0,04
23	2561,58	10,54	0,05	2631,02	2439,09	187,21	0,24
24	2693,71	10,55	0,01	2713,96	2631,98	80,06	0,01
25	2866,34	10,32	0,03	2883,7	2714,92	165,59	0,06
26	2922,28	10,29	0,06	3005,22	2884,67	118,79	0,12
27	3233,8	10,19	0	3236,69	3006,19	227,63	0,09
28	3357,25	10,06	0,01	3367,86	3237,66	129,52	0,03
29	3581,96	10,44	0,17	3834,65	3580,04	176,25	4,09

Fig.1. IR spectrum of the condensation product of monochloroacetic acid with thiourea



No.	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	270,05	22,82	1,71	282,58	230,5	31,58	0,86
2	288,37	23,26	0,13	291,26	283,55	4,88	0,01
3	307,66	18,02	18,33	348,17	295,12	23,49	4,58
4	388,67	3,81	1,75	389,64	349,13	14,32	0
5	390,6	0	1,69	391,57	390,6	1,71	0
6	412,78	0	-0,78	413,75	411,82	385,78	94,55
7	424,36	0,99	0,21	425,32	419,54	10,23	0,04
8	441,72	0,91	0,03	447,5	430,14	35,24	0,12
9	494,76	0,34	3,79	769,63	453,29	372,93	23,26
10	838,11	16,49	7,28	902,72	770,6	92,09	9,63
11	979,88	14,2	6,92	1027,14	903,69	91,05	8,19
12	1048,36	19,55	2,46	1111,05	1028,1	53,95	1,75
13	1218,1	8,19	8	1269,22	1112,01	135,49	16,43
14	1282,72	10,98	0,94	1356,02	1270,18	75,2	1,48
15	1423,53	10,53	9,63	1501,65	1356,98	116,99	16,27
16	1626,06	11,72	2,58	1649,21	1502,61	113,13	2,8
17	1712,86	4,69	14,19	1833,42	1650,17	157,26	30,89
18	1950,12	28,6	3,26	2196,05	1834,38	185,19	7,33
19	2593,4	18,31	0,22	2599,19	2197,02	240,13	1,93
20	2638,73	18,11	0,56	2710,1	2600,16	80,39	0,65
21	3036,09	13,23	3,89	3309,03	2711,07	491,05	33,69
22	3431,51	14,16	13,4	3874,19	3309,99	313,06	58,66

Fig.2. IR spectrum of the condensation product of the sodium salt of monochloroacetic acid with thiourea

Due to the fact that both compounds contain the same groups of atoms, the difference between them is due to the presence of a cyclic fragment of iminothiazolidone. In the IR spectra of compounds, this is found primarily in the region of stretching vibrations of the N–H bond (3000–3100 cm^{-1}). The IR spectrum of iminothiazolidone has two bands: 3020 and 3250 cm^{-1}, corresponding to the amino group outside the ring and to the amino group in the ring, respectively.

In the IR spectrum of (amidinothio)acetic acid, a more complex picture is observed in this region, and the NH absorption bands are shifted to a higher frequency region, to 3150 and 3410 cm^{-1}.

The different structure of the products obtained in the presence and in the absence of NaOH is also confirmed by the shift of the stretching vibration bands of the C = N and C – N bonds to a higher frequency region in iminothiazolidone compared to (amidinothio)acetic acid and the presence in the region of 400 – 800 cm^{-1} bands characteristic of stretching and bending vibrations of the ring (the band at 712 cm^{-1} refers to bending vibrations of the C–S bond in the cyclic structure).

The absence of absorption bands of the OH group in the spectrum of the acid is obviously due to strong intermolecular H-bonds, as a result of which these bands are shifted to a lower frequency region and overlap with the absorption bands of NH groups. This is also indicated by a wider absorption range in the region of 3000–3400 cm^{-1} for the acid compared to nminothiazolndone.

An additional confirmation of the formation of compounds with different structures during the reaction under different conditions is a thermographmetric study.

The thermograms of the products of the studied reactions are somewhat different. The onset of decomposition of iminothiazolidone is noted at 163°C, (amidinothio)acetic acid - at 178°C. In the range of 160 - 300 °C, 34 - 38% of the mass of both products is lost. However, for (amidothio)acetic acid, this mass loss occurs in one stage, while its cyclic analogue has two stages of decomposition ($\Delta m1=10\%$ at 210°C and $\Delta m2 = 28\%$ at 257°C). In the future, both thermograms practically coincide, demonstrating a gradual decomposition with a maximum at 420 °C, which ends at 600 °C.

Thus, on the basis of the study, it was concluded that the condensation of thiourea with monochloroacetic acid produces iminothiazolidone, with the sodium salt of monochloroacetic acid - (amidinothio) acetic acid. A mixture of condensation products was added with extractive phosphoric acid produced by OAO Ammophos-Maxam, in a ratio of 1:1, which was conditionally named KMTM and used as inhibitors of mineral salt deposition and compared with industrial products IOMS-1 and OEDP (table).

Table

Dependence of inhibitory activity of KMTM on inhibitor concentration

(T=80 °C)

Inhibitor concentration, mg/l	**Inhibition efficiency, %**			
	Water hardness, mg·eq/l			
	4-5	6-7	8-11	13-15
1,0	77,4	72,5	69,2	71,4
2,0	83,7	79,5	72,7	73,6
3,0	89,5	87,4	85,0	86,1
4,0	90,5	89,1	85,6	86,9
5,0	91,3	90,7	88,5	89,0
6,0	92,1	91,5	89,4	91,3
7,0	92,3	91,6	89,7	91,4
IOMS -1, 4,0	93,0	92,0	91,0	90,0
OEDF, 4,0	90,0	88,0	87,0	86,0

As can be seen from the data in the table, with an increase in the concentration of the inhibitor, its selectivity and effect increase. In water with the highest hardness, at a concentration of 1.0 mg/l, the inhibition efficiency is 71.4%, and at a concentration of 7.0 mg/l - 91.4%.

Conclusion. Thus, purposeful studies have been carried out to develop, study the properties of new improved methods for obtaining complexones based on thiourea with monochloroacetic acid and in the presence of alkaline salts. The reaction of carboxymethylation of thiourea was studied in the temperature range 90 – 95 °C. It has been established that in the synthesis of carboxy derivatives of thiourea, the optimal temperature is 75–80 °C with the alkaline method. The composition and structure of the products obtained were determined using IR spectrophotometry. The inhibitory properties of the synthesized KMTM were studied, it was found that the effective concentration of the resulting product is 7.0 mg/l, at which the efficiency reaches 91.4%.

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