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NITROGEN-CONTAINING CHELATE COMPLEXES AND MONOMERS BASED ON THEM

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By the interaction between N-methylolthiourea and Co^{2+}, Mn^{2+} acetates are obtained compounds that were later used for the synthesis of vinyl bifunctional groups containing polymerizable chelate complexes. These compounds are recommended to be used as crosslinkers for obtaining, on the basis of water-based soluble monomers, spatially cross-linked water-swellable copolymers with applied purpose. There are dynamics of water absorption of copolymers from the time of their stay in water.

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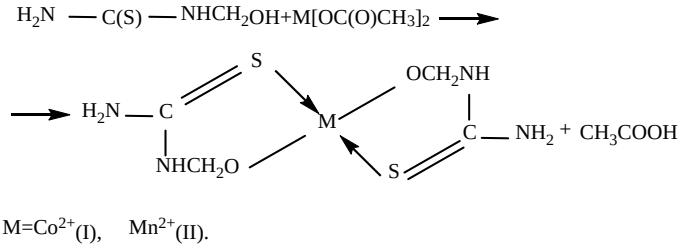
***Keywords*:** applied purpose, chelates, complexes, monomers, copolymer, unsaturated, water absorption, thiocarbamide, methylol.

Introduction. There is a fairly large amount of information in the literature on thio-urea derivatives and their applied purposes. In particular, in [1–3], there is a number of thiourea derivatives, which are recommended for use as plant growth stimulants, pesticides, herbicides, fungicides, bactericides, etc. In 1944, Professor of Yerevan State University, M.T. Dangyan published an extensive scientific article on thiourea derivatives and their applied importance [4]. Functionally active thiourea derivatives are also mentioned in [5].

Considering all mentioned above, the development of the synthesis of new reactive thiourea derivatives and chelate complexes based on them is of both scientific and applied interest.

Carrying out the reaction between N-methylolthiourea and Co^{2+} and Mn^{2+} acetates, the following chelate compounds were obtained, the dimensional structure of which is represented as:



M=Co^{2+}(I), Mn^{2+}(II).

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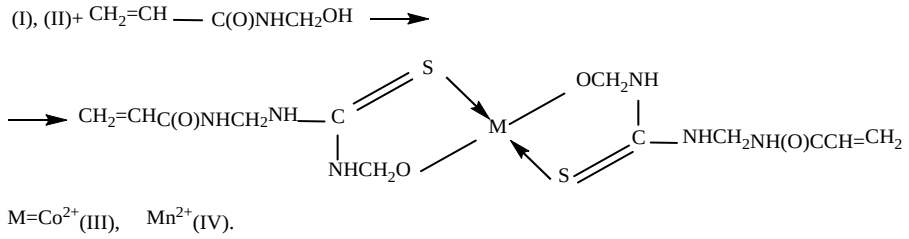
By the reaction of (I) and (II) with N-methylolacrylamide were obtained acrylamidyl functional groups containing derivatives of chelate compounds (I), (II).



Compounds (III) and (IV) were studied by IR spectroscopy and elemental analysis. These data are presented in the Tab. 1.

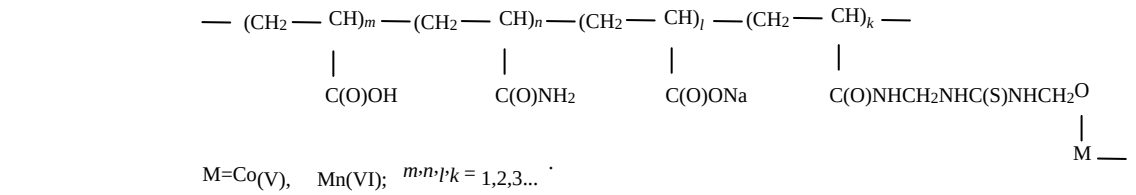
Table 1

Elemental Composition and IR Spectra of Compounds (I)–(IV)

Compounds	Complexes' colours	IR spectra, ν, cm^{-1}	Elemental analysis, %, Founded / Calculated				
			C	H	N	S	M
I	Darkviolet	315–320 (Co–O), 1410–1413 (N–C(S)–N), 3280 (–NH_2), 2850 (CH_2).	17.8 / 17.84	3.6 / 3.72	20.7 / 20.72	29.9 / 29.79	21.8 / 21.93
II	Brown	410–415 (Mn–O), 1405–1415 (N–C(S)–N), 2850 ((CH_2), 3250 (NH_2).	18.2 / 18.11	3.9 / 3.77	21.2 / 21.13	24.3 / 24.15	20.5 / 20.75
III	Pink	320–325 (Co–O), 1410 ((N–C(S)N), 1630 (CH=CH_2), 1695 (C(O)–N).	33.2 / 33.1	4.5 / 4.6	19.5 / 19.31	14.6 / 14.71	13.4 / 13.56
IV	Light black	410–415 ((Mn–O), 1415 (N–C(S)–N), 1640 (CH=CH_2), 1695 (C(O)–N), 2850 (CH_2).	33.3 / 33.41	4.7 / 4.64	19.5 / 19.49	14.7 / 14.85	12.8 / 12.76

The bifunctionality with respect to vinyl groups of compounds (III) and (IV) and their compatibility with water-soluble monomers (acrylic acid, acrylamide and their derivatives) were used to obtain a spatially crosslinked water-swellable copolymer.

In an aqueous medium, with the participation of compounds (III) and (IV), carrying out radical copolymerization between acrylic acid (AA), its sodium salt (Na–AA) and acrylamide (AM), in the presence of ammonium persulfate, spatially crosslinked water-swellable copolymers were obtained, the structure of which can be represented as follows:



M=Co(V), Mn(VI); m,n,l,k = 1,2,3... .

Subsequently, the dependence of water absorption of the crosslinked copolymers on time in water were observed. The results of this dependence are presented in Tab. 2.

Table 2

Dependence of water absorption of copolymers on their composition and stay time in water. Concentration of monomers in the initial mixture: [AA]=1.3 mol/L, [AM]=0.7 mol/L, [Na–AA]=0.7 mol/L, V=50 mL

Mole ratio in copolymer $\frac{[AA]+[Na-AA]+[AM]}{[V] \text{ or } [VI]}$	Water absorption $\frac{g,\ \text{water}}{1\ g\ \text{copolymer}}$ stay time, *min*							
	10	20	30	50	60	80	100	120
135.0	30.0	70.0	100.0	210.0	250.0	320.0	400.0	430.0
54.0	45.0	110.0	180.0	240.0	300.0	330.0	420.0	560.0
27.0	100.0	200.0	240.0	350.0	470.0	530.0	620.0	720.0
18.0	95.0	160.0	220.0	300.0	380.0	420.0	560.0	630.0
13.5	60.0	75.0	110.0	180.0	280.0	330.0	430.0	540.0
5.4	20.0	28.0	35.0	55.0	85.0	110.0	170.0	210.0
2.7	13.0	21.0	30.0	41.0	50.0	57.0	63.0	75.0

As follows from Tab. 2, with an increase in the concentration of the crosslinker, water absorption of the crosslinked copolymer decreases, which is associated with the density of the 3D-structure formed between copolymers macromolecules. The highest water absorption is reached when the mole ratio of the sums of copolymerizable monomers units to crosslinker is 27.

Experimental Part. IR spectra of compounds I–VI were obtained on Nicolet FT-IR Nexus spectrometer. The content of Co^{2+}, Mn^{2+}, Na^{+} in compounds I–VI were determined by atomic absorption spectrophotometer AAS-3. The elemental composition of compounds I–IV was determined according to [6]. $Co[OC(O)CH_3]_2$ and $Mn[OC(O)CH_3]_2$ ("analytical grade"), 27% aqueous formaldehyde solution were used. N-methylolacrylamide was synthesized according to [7]. Thiourea was used after its crystallization from the water. AA was used after distillation, at bp 141°C. AM was purified by recrystallization from the water, at mp 84.5°C. N-methylol-thiourea (MTU) was obtained according to [8].

Synthesis of Compounds I and II. 5.3 *g* (0.05 *M*) of MTU and 4.425 *g* (0.025 *M*) of $Co[OC(O)CH_3]_2$ or 4.32 *g* (0.025 *M*) of $Mn[OC(O)CH_3]_2$ were intensively rubbed with 15 *mL* of ethyl alcohol. The reaction mixture turned purple in the presence of compound (I) and light brown in the presence of compound (II). Then the reaction mixtures were thoroughly washed with dehydrated acetone, chloroform and ether, and were dried under vacuum (1.5–2.0 *mm* Hg) at 70–75°C to

constant weight. The yield was 85% for (I) and 79% for (II). Compounds (I) and (II) start to decompose at temperatures above 150°C.

Synthesis of Compounds III and IV. 3.36 *g* (0.0125 *M*) of (I) or 3.26 *g* (0.0125 *M*) of (II) and 2.25 *g* (0.025 *M*) methylolacrylamide are thoroughly ground with 15 *mL* of ethyl alcohol. The reaction between these compounds is carried out with intensive vigorous stirring at 70–75°C for 1.5 *h*.

The reaction mixture turned pink in the presence of compound (III) and light black in case of compound (IV). Then the reaction mixtures were thoroughly washed with dehydrated acetone, chloroform and ether, and were dried under vacuum (1.5–2.0 *mm* Hg) at 70–75°C to constant weight. The yield was 73% for (III) and 68% for (IV). These compounds have ability to thermal polymerization at temperatures above 155°C.

Copolymerization of AA, Na-AA, AM in the Presence of (III) and (IV). The reactor was filled with 85.6 *mL* of distilled water, 14.4 *mL* (0.07 *M*) of NaOH, 5.68 *g* (0.08 *M*) of AM and calculated amountof (III) or (IV), in order to obtain copolymers with the link composition represented in Tab. 2. The reaction mixture was stirring and bubbling with nitrogen. Then, 0.96 *g* (0.0042 *M*) of $(NH_4)_2S_2O_8$ was added into the reactor. Without stopping bubbling with nitrogen, the copolymerization was continued at 70–75°C for 1.5–2 *h*. At the indicated time, the conversion of monomers was 97%. The swollen copolymer gel was sedimented in ethyl alcohol, dried under vacuum (1.5–2.0 *mm* Hg) at 70–75°C to constant weight.

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ԱԶՈՏ ՊԱՐՈՒՆԱԿՈՂ ԽԵԼԱՏԱՅԻՆ ԿՈՄՊԼԵՔՍՆԵՐ ԵՎ ԴՐԱՆՑ ՀԻՄԱՆ ՎՐԱ ՄՈՆՈՄԵՐՆԵՐ

N-մեթիլոլթիոմիզանյութի և Co^{2+} և Mn^{2+} ացետատների փոխազդեցության արդյունքում ստացվել են միացություններ, որոնք հետագայում օգտագործվել են վինիլային բիֆունկցիոնալ խմբեր պարունակող պոլիմերվելու ընդունակ խելատային կոմպլեքս միացությունների ստացման համար: Այդ միացությունները, որպես կարիչներ առաջարկված է օգտագործել ջրալուծ մոնոմերների հիման վրա տարածական կարված ջրում ուռչող կիրառական նշանակություն ունեցող համապոլիմերների ստացման համար: Ուսումնասիրված է համապոլիմերների ջրակլանման դինամիկան՝ կախված դրանց ջրում լինելու ժամանակից:

В. М. МАВИСАКАЛЯН, М. Л. ЕРИЦЯН

АЗОТСОДЕРЖАЩИЕ ХЕЛАТНЫЕ КОМПЛЕКСЫ И МОНОМЕРЫ НА ИХ ОСНОВЕ

В результате взаимодействия между N-метилолтиомочевиной и ацетатами Co^{2+} и Mn^{2+} получены соединения, которые были использованы для синтеза способных к полимеризации хелатных комплексов, содержащих виниловые бифункциональные группы. Эти соединения рекомендуется использовать в качестве сшивателей для получения на основе водорастворимых мономеров пространственно-сшитых водонабухающих сополимеров, имеющих прикладное значение. Изучены зависимости динамики водопоглощения сополимеров от времени их пребывания в воде.