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CHELATE COMPLEXES ON THE BASIS OF UREA'S TRIAZINE DERIVATIVES AND METAL IONS VARIABLE VALENCE

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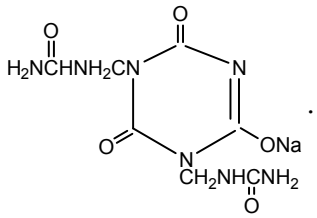
On the basis of the sodium salts and urea derivatives of isocyanuric acid and transition metals new chelate complexes were synthesized. It is shown that the chelate complexes based on disodiom salt 1-monokarbamidilmethyl isocyanurate with Ni^{2+} and Co^{2+} ions have structure of spatially cross-linked clusters, while chelate complexes based on monosodiom salt 1,3-karbamidilmethyl isocianurate have ladder structure. The synthesized chelate complexes are studied by IR spectroscopy and elemental analysis.

Keywords: chelate complexes, ladder structure, 1-monokarbamidilmethyl isocyanurate, 1,3-karbamidilmethyl isocianurate, clusters.

Introduction. New urea derivatives of isocyanuric acid were described in our earlier published work [1]. Mono- and di-substituted urea derivatives of isocyanuric acid, as an active ligands, were used with the purpose to obtain chelate complexes. Synthesis of the corresponding chelate complexes was carried out in interaction sodium mono- and di-substituted salt derivatives of isocyanuric acid with chlorides of Ni(II) and Co(II). In the present study the following sodium salts of urea derivatives of isocyanuric acid were used:

1. 

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Monosodiom salt 1,3-karbamidilmethyl isocianurate (MDKMITS);

$$2n(\text{MDKMITS}) + n\text{MCl}_2 \xrightarrow[-2n\text{NaCl}]{} [(\text{MDKMITS})_2\text{M}]_n,$$

M = Ni^{2+} (I); Co^{2+} (II).

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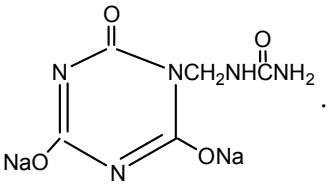
2. 

Disodiom salt 1-monokarbamidilmethyl isocyanurate (DKMITS);

$$2n(\text{DKMITS}) + n\text{MCl}_2 \xrightarrow[-2n\text{NaCl}]{} [(\text{DKMITS})_2\,\text{M}]_n,$$

M = Ni^{2+} (III); Co^{2+} (IV).

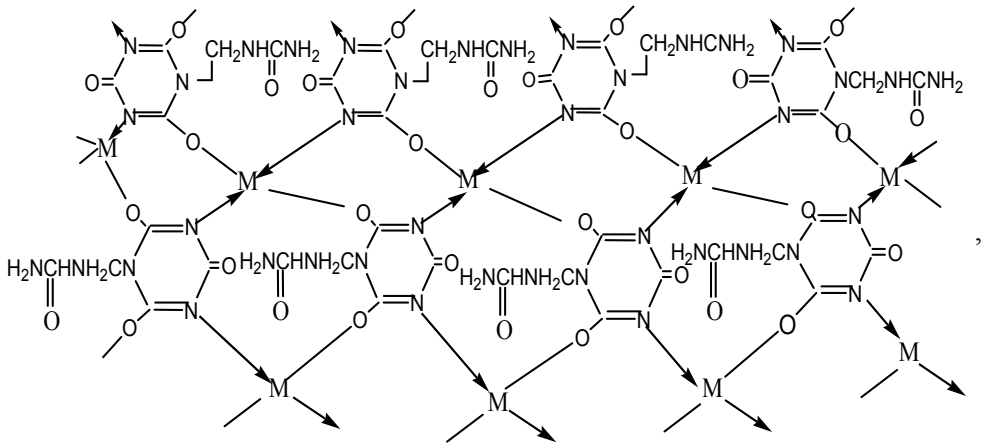
I–IV complexes connection were studied by IR spectroscopy and elemental analysis. The results are shown in the Table.

IR spectra and elemental analysis data of connections I–IV

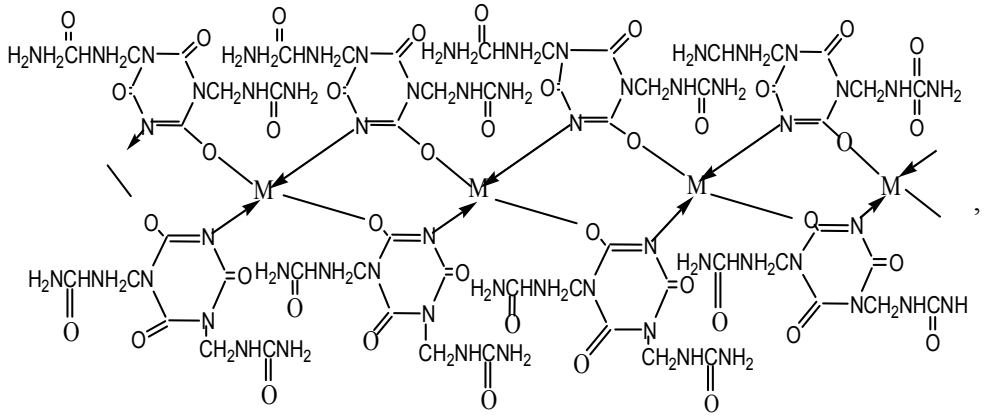
Complex	Temper. swim*, temper. softness**, ^0C	IR spectr., v, cm^{-1}	Color	The elemental composition found / calculated, %			
				C	H	N	Na
I	115±0.5* >270**	763–779 (simm. triaz.) 530–550 (Ni–O) 1415–1430 >N–C–N< 1685–1695 (>C=0) 2950 (–CH_2–) 1580–1625 (–N=C–)	dark green	27.6	3.5	32.3	9.7
				27.86	3.32	35.50	9.78
II	110±0.5* >280**	760–780 (simm. triaz.) 650–670 (Co–O) 1420 >N–C–N< 1675–1690 (>C=0) 2890–2950 (–CH_2–) 1565–1630(–N=C–)	maroon	27.9	3.2	32.4	9.6
				27.86	3.32	32.50	9.78
III	>350**	720–750 (simm. triaz.) 520–540 (Ni-O) 1430 >N–C–N< 1655–1685 (>C=0) 2900 (–CH_2–) 1570–1630 (–N=C–)	light green	23.4	1.7	27.3	22.7
				23.25	1.94	27.13	22.86
IV	>360**	730–760 (simm. triaz.) 590–620 (Co–O) 1424 >N–C–N< 1630–1670 (>C=0) 2850–2950 (–CH_2–) 1560–1615(–N=C–)	light pink	23.1	2.08	27.0	22.9
				23.25	1.94	27.13	2.86

As follows from the Table, in the mixing IR spectra the agreement of functional groups –N=C–, >C=0, >N–C–N< in complexes I–IV are result of coordination of the complex-forming ions. The temperatures of softening and decomposition of studied complexes leads to the conclusion that complexes III–IV have a cluster type spatial structure and the complexes structure of I–II is not ladder like.

The structures of I–IV can be represented as follows:

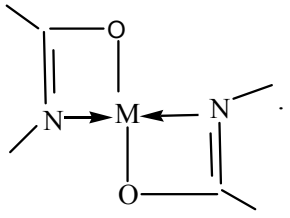


where M = Ni^{2+}(I), Co^{2+}(II),



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

Formation of complexes of four members of the chelated cycles can be described as:



The results of our studies show that complexes of chelate rings with four members are not formed, it should be noted that due to lower formation energy the systems of chelate rings with seven or eight members are more profitable [2, 3]. The possibility of formation of cluster type complexes based on isocyanuric acid derivatives and variable valence metals was described in [4].

Experimental Part. IR spectrum of the compound is recorded by Spekord-75IR spectrophotometer of almost ready combination of petrolatum with appropriate composition I–IV. For recording the IR syntheses was used a prism of CaF_2. Preparation of the MDKMITS and DKMITS compounds is described in [1]. Atomic adsorptions of Ni- and Co- containing complexes are defined by Spectrophotometer AAS-3. "Chemically Pure" $NiCl_2$ and $CoCl_2$ are used.

Synthesis of Chelate Complexes I and II. Reactor separated 7.37 *g* of the compound MDKMITS (0.025 *mol*) and 50 *mL* solvent mixture (30 *mL* of DMF and 20 *mL* of water), shaking until a homogeneous mass will be obtained, then adding slowly 1.62 *g* (0.012 *mol*) $NiCl_2$ (or $CaCl_2$) and adjusting the reaction temperature up to 105–110^0C. The temperature of reaction is maintained constant during 2.5–3 *h*. The reaction mass has a dark green color in the case of $NiCl_2$, and is maroon in the case of $CoCl_2$. Afterwards the mixture at 55–60^0C was vacuum (10–15 *mm* Hg) evaporated and washed repeatedly with a solvent mixture of water–ethanol (1:1). Finally the mixture is vacuum dried (1.5–2 *mm* Hg) to a constant weight.

Yield of compound I is 58.0%, of compound II is 63.0%.

Synthesis of Compound III and IV. In a solvent mixture (30 *mL* DMF and 20 *mL* water) under intensive stirring at 110–115^0C during 2.5–3 *h* leads to an interaction between the 6.12 *g* (0.025 *mol*) DKMITS and 3.25 *g* (0.025 *mol*) $NiCl_2$ (or $CoCl_2$). The reaction mass has a light green color in the case of $NiCl_2$, and is light pink in the case of $CoCl_2$. Afterwards the mixture at 50–55^0C in vacuum (10–12 *mm* Hg) repels mortar and the residue washed repeatedly with a solvent mixture of water–ethanol (1:1). Finally the mixture is vacuum dried (1.5–2 *mm* Hg) to a constant weight.

Yield of compound III is 63.0%, of compound IV is 59.5%.

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