

NEW NITROGEN CONTAINING DERIVATIVES OF GLYCOL  
AND COMPOUNDS ON THEIR BASIS

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Interaction of urea with monomethylolurea and glyoxal has been investigated. The obtained products are forming the monomeric and oligomeric complexes as well of chelate type by interaction with acetates of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ . The synthesized compounds have been studied by IR, PMR spectroscopy and elemental analysis.

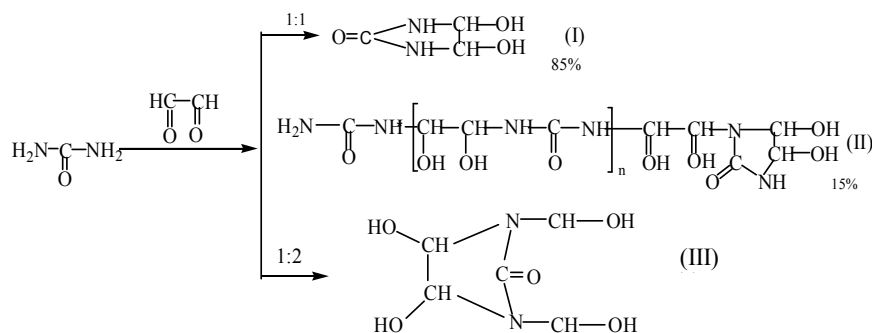
**Keywords:** urea, glyoxal, monomethylolurea, chelate complex, elemental analysis, IR spectroscopy, PMR spectroscopy, derivative.

**Introduction.** Amino-, amidoalcohols and their functional derivatives are very often used in organic synthesis and also for the obtaining resins and polymers of target destination on their basis [1, 2]. Derivatives of urea containing alcohol functional groups are very interesting for application.

It is well known from literature, that methylol derivatives of urea and resins and polymers synthesized on their basis can be widely used in woodworking industry as a cheap and accessible products for making different kinds of furniture [3].

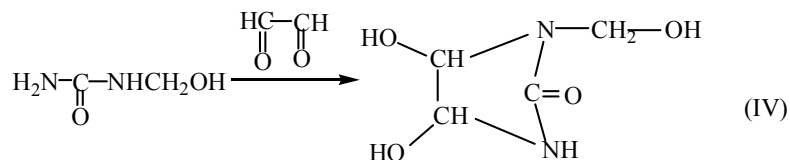
There is a lack of information about obtaining methylol derivatives of urea by interaction of urea and glycol. This article is about that reaction.

Depending on molar ratio of urea/glycol the following compounds have been synthesized:



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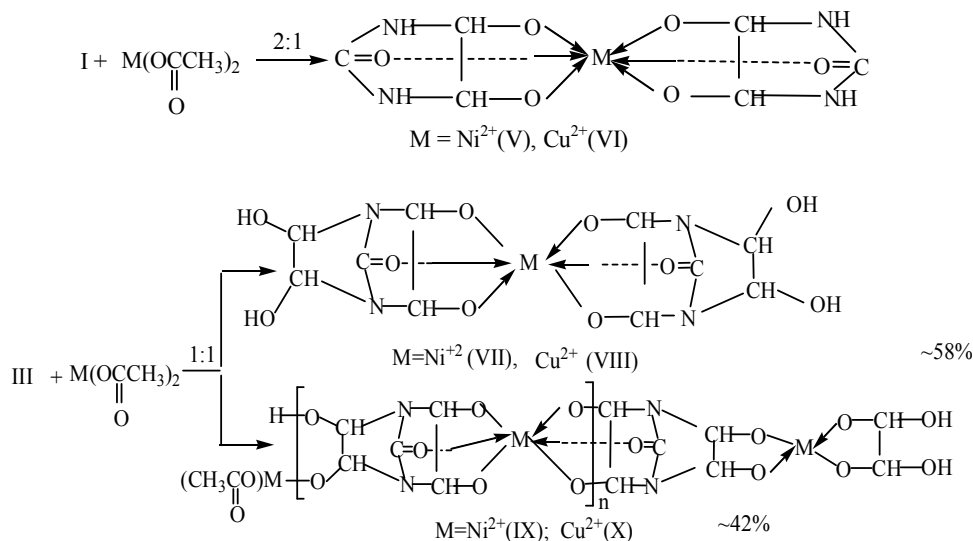
Later a reaction was occurred between monomethylolurea and glyoxal:



Scheme 2.

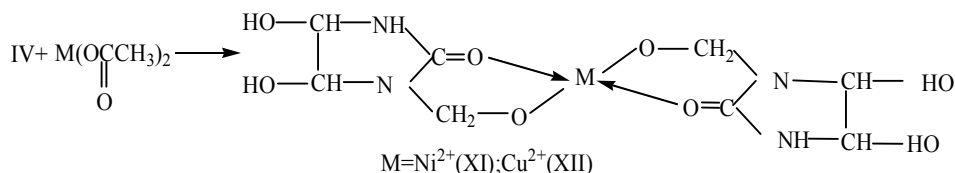
I, II, and IV compounds in the presence of metals acetates can be transformed into complex compounds of chelate type.

Monomeric and oligomeric products of chelate type are formed by reacting equal moles of compound III with acetates of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  (Scheme 3).



Scheme 3.

Monomeric and oligomeric products of chelate type are formed by reacting equal moles of compound III with acetates of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  (Scheme 4).



Scheme 4.

The compounds I–XII have been studied by IR, PMR spectroscopy and elemental analysis. The physical and chemical parameters of the compounds I–XII are given in shown below (see Table).

In provided Table it is shown, that there are displacements of absorption region in IR spectra of chelate connections, because of coordination  $>\text{C}=\text{O}$  and

–OH functional groups with shifted above metals. For  $>C=O$  displacement is from  $1695\text{ cm}^{-1}$  to  $1670\text{ cm}^{-1}$ , for –OH it is from  $1035\text{--}1085\text{ cm}^{-1}$  to  $1000\text{--}1020\text{ cm}^{-1}$ .

Comp.	Temp. swim., °C	IR spectroscopy, $\nu, \text{cm}^{-1}$	PMR spectroscopy, $\delta, \text{m.d.}$	Elemental composition, found / calculated, %			
				C	H	N	M
1	2	3	4	5	6	7	8
I	110±0.1	1085–1150 (OH), 1420–1440 $\left( \begin{array}{c} > \text{N} - \text{C} - \text{N} < \\    \\ \text{O} \end{array} \right)$ , 1520 (Ni–H), 1600–1675 $\text{O}=\text{C} \begin{array}{l} \text{N} \\ \diagup \\ \diagdown \\ \text{N} \end{array}$ ]	3.45–3.72 d (2H, CH)  4.2–4.54 s (2H, OH)  7.15–7.75 d (2H, NH)	$\frac{30.6}{30.5}$	$\frac{4.9}{5.08}$	$\frac{23.5}{23.73}$	–
II	~190*	1039–1085, 3300 (–OH), 1420–1430 $\left( \begin{array}{c} > \text{N} - \text{C} - \text{N} < \\    \\ \text{O} \end{array} \right)$ , 1695 ( $>C=O$ ), 1605–1680 $\text{O}=\text{C} \begin{array}{l} \text{N} \\ \diagup \\ \diagdown \\ \text{N} \end{array}$ ]	3.41–37.8 d (10H, CH)  4.15–4.48 s (10H, CH)  5.18 s (2H, NH <sub>2</sub> )  7.25–7.8 d (10H, CH)	30.3	5.2	23.8	–
III	90±0.1	1055–1085, 1125–1205, 3300–3400 (OH), 1415–1430 $\left( \begin{array}{c} > \text{N} - \text{C} - \text{N} < \\    \\ \text{O} \end{array} \right)$ , 1695 (C=O), 1600–1650 $\text{O}=\text{C} \begin{array}{l} \text{N} \\ \diagup \\ \diagdown \\ \text{N} \end{array}$ ]	3.41–3.82 d (4H, CH)  4.18–4.56 s (4H, 6H)	$\frac{34.2}{34.09}$	$\frac{4.3}{4.54}$	$\frac{15.7}{15.91}$	–
IV	90±0.1	1085–1135, 3300 (OH), 1230 (CH <sub>2</sub> OH), 1420–1435 $\left( \begin{array}{c} > \text{N} - \text{C} - \text{N} < \\    \\ \text{O} \end{array} \right)$ , 1595–1660 $\text{O}=\text{C} \begin{array}{l} \text{N} \\ \diagup \\ \diagdown \\ \text{N} \end{array}$ ] 1695 (C=O), 3150 (N–H)	2.31–2.55 d (2H, CH <sub>2</sub> )  3.47–3.81 d (2H, CH)  4.27–4.58 s (3H, OH)  7.31–7.92 d (1H, NH)	$\frac{32.3}{32.43}$	$\frac{5.5}{5.4}$	$\frac{18.7}{18.92}$	–
V	~140*	440–460 (Ni–O), 1010–1020 (OH, coord.), 1410–1420 $\left( \begin{array}{c} > \text{N} - \text{C} - \text{N} < \\    \\ \text{O} \end{array} \right)$ , 1670 ( $>C=O$ )	3.43–3.64 d (4H, CH)  4.65–4.86 s (2H, OH)  7.45–8.21 d (4H, NH)	$\frac{24.4}{24.57}$	$\frac{3.5}{3.41}$	$\frac{19.0}{19.11}$	$\frac{20.1}{20.14}$
VI	~160*	460–470 (Cu–O), 1000–1010 (OH, coord.), 1410–1420 $\left( \begin{array}{c} > \text{N} - \text{C} - \text{N} < \\    \\ \text{O} \end{array} \right)$ , 1670 ( $>C=O$ ) 3160 (N–H)	–	$\frac{24.1}{24.24}$	$\frac{3.45}{3.37}$	$\frac{18.7}{18.85}$	$\frac{21.1}{21.21}$

1	2	3	4	5	6	7	8
VII	~150*	440–450 (Ni–O), 1010–1020 (OH, coor.), 1050–1085 (OH) 1425–1440 $\left( \begin{array}{c} > \text{N}-\text{C}-\text{N} < \\    \\ \text{O} \end{array} \right)$ , 1580–1640 $\text{O}=\text{C} \left\langle \begin{array}{c} \text{N} \\ \text{N} \end{array} \right\rangle$ 1670 (>C=O)	3.34–3.44 d (8H, CH) 4.27–4.5 s and 4.63–4.78 s (4H, OH and 2H, OH coor.)	$\frac{29.2}{29.34}$	$\frac{3.51}{3.42}$	$\frac{13.5}{13.69}$	$\frac{14.3}{14.42}$
VIII	~170*	465–480 (Cu–O), 1000–1020 (OH, coor.), 1050–1080 (OH) 1420–1430 $\left( \begin{array}{c} > \text{N}-\text{C}-\text{N} < \\    \\ \text{O} \end{array} \right)$ , 1590–1630 $\text{O}=\text{C} \left\langle \begin{array}{c} \text{N} \\ \text{N} \end{array} \right\rangle$ 1670 (>C=O)	–	$\frac{29.1}{29.05}$	$\frac{3.7}{3.39}$	$\frac{13.7}{13.56}$	$\frac{15.3}{15.25}$
IX		440–450 (Ni–O), 1010–1020 (OH, coor.), 1050–1085 (OH) 1420–1440 $\left( \begin{array}{c} > \text{N}-\text{C}-\text{N} < \\    \\ \text{O} \end{array} \right)$ , 1580–1640 $\text{O}=\text{C} \left\langle \begin{array}{c} \text{N} \\ \text{N} \end{array} \right\rangle$ 1750 $-\text{C} \left\langle \begin{array}{c} \text{O} \\ \text{O} \end{array} \right\rangle$ 2800 (CH)	1.81–2.21 s (3H, CH <sub>3</sub> ) 3.41–3.53 d (16H, CH) 4.21–4.38 s (2H, OH) 4.55–4.61 s (7H, OH coor.)	27.3	2.9	14.2	7.5
X		470–480 (Cu–O), 1010–1020 (OH, coor.), 1055–1085 (OH) 1420–1440 $\left( \begin{array}{c} > \text{N}-\text{C}-\text{N} < \\    \\ \text{O} \end{array} \right)$ , 1585–1665 $\text{O}=\text{C} \left\langle \begin{array}{c} \text{N} \\ \text{N} \end{array} \right\rangle$ 1740 $-\text{C} \left\langle \begin{array}{c} \text{O} \\ \text{O} \end{array} \right\rangle$ 2800–2850 (CH)	–	27.1	2.8	14.1	7.8
XI	130*	440–450 (Ni–O), 1050–1090 (OH), 1420–1440 $\left( \begin{array}{c} > \text{N}-\text{C}-\text{N} < \\    \\ \text{O} \end{array} \right)$ , 2800–2950 (CH <sub>2</sub> CH), 1660 (>C=O)	1.85–2.12 d (4H, CH <sub>2</sub> ) 3.41–3.38 d (4H, CH) 4.31–4.41 s (4H, OH) 7.31–8.24 d (2H, NH)	$\frac{27.3}{27.19}$	$\frac{3.7}{3.97}$	$\frac{15.6}{15.86}$	$\frac{16.6}{16.71}$
XII	145*	465–480 (Cu–O), 1050–1085 (OH), 1420–1440 $\left( \begin{array}{c} > \text{N}-\text{C}-\text{N} < \\    \\ \text{O} \end{array} \right)$ , 1580–1650, 1660 (>C=O)	–	$\frac{26.8}{26.89}$	$\frac{3.8}{3.92}$	$\frac{15.8}{15.67}$	$\frac{17.5}{17.65}$

\* softening temperatures of corresponding compounds.

**Experimental Part.** IR and PMR spectrum of the compounds I–XII were recorded by spectrophotometer Nicolet FTIR Nexus and the unit Varian Mercury respectively. Content of metal ions in complex compounds V–XII were defined by atom-absorbition photometer AAS-3. Urea of chemically pure grade, 38% aqueous solution of formaldehyde, 40% aqueous solution of glyoxal,  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  of pure grade are used for analysis. Monomethylolurea is received according to [4].

*Compounds I and II.* The reactor was charged by 36.5 mL 40% aqueous solution of glyoxal (0.25 mol) and 15 g urea (0.25 mol). The mixture was stirred in room temperature during 5–10 min. Then the mixture temperature was increased to 55–60°C and stirred about 90 min. 30 min later from the beginning of the reaction homogenic mixture became light brown and a small amount of precipitate was carried out. After all the reaction mixture was transferred into container with water, continued stirring, then was filtered. The oligomeric product II was gained, which doesn't solute in water. Water was removed from the filtrate under vacuum (10–15 mm Hg). Light yellow mass with high viscosity was washed with warm ethanol in order to separate the reaction product from unreacted urea and glyoxal. The compounds I and II were dried under vacuum (1.2–2 mm Hg) at 65–70°C to constant weight with 73% output, in which 85% is the compound I and 15% is the compound II. Compound I is a light brown product and solutes in dimethylsulfoxide (DMSO), dimethylformamide (DMFA), ethanol and water. Compound II is a light yellow product and solutes in DMSO and particularly in DMFA.

*Compound III.* Is carried out similarly to the above example, but the difference is that 15 g (0.25 mol) urea was reacted with 73 mL 40% (0.5 mol) aqueous solution of glyoxal. At the end of the reaction the water was removed under vacuum (10–15 mm Hg) and the high viscosity mass was dissolved in ethanol–acetone mixture (1:1), where the unreacted urea was precipitated. The reaction product was filtrated from the filtrate under vacuum in order to remove the mixture ethanol–acetone. The light brown product was dried under vacuum (1.5–2 mm Hg). The output is 86.5%. Compound III solutes in water, DMSO, DMFA.

*Compound IV.* 13.5 g (0.15 mol) monomethylolurea and 8.5 g (0.15 mol) glyoxal (22.5 mL 40% aqueous solution) were stirred at the room temperature 30 min. Then the temperature was increased to 55–60°C at this temperature stirring continued for 25–30 min. After that the water was removed under vacuum (10–15 mm Hg), and light brown shade mass of high viscosity was repeatedly washed with methanol and acetone and dried under vacuum (1.5–2 mm Hg) bringing to constant weight with 68% output. Compound IV solutes in water, DMSO and DMFA.

*Chelate compounds V and VI.* 11.8 g (0.1 mol) compound I in the presence of 5–6 mL acetone vigorously was grinded with 12.45 g (0.05 mol)  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and 9.95 g (0.05 mol)  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  until receiving a homogeneous mass. During the grinding acetic acid was released. The grinding was continued until no more acetic acid released. In the case of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  solid light green compound was gained. In the case of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  dark blue compound was gained. The compounds V and VI repeatedly were washed with warm ethanol in order to remove unreacted metal

acetates and compound I. Dried under vacuum (1.5–2 mm Hg) to constant weight. Output of compound V is 58.9%, of compound VI is 63.0%.

*Chelate compounds VII–X.* 8.8 g (0.05 mol) compound II and 12.45 g (0.05 mol)  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  or 9.95 g (0.05 mol)  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  intensively was grinded in the presence of 5–6 mL acetone with mild heat until receiving a homogeneous mass. While grinding the acetic acid was released as it is described above. The ending of the process is evaluated by the discontinuation of acetic acid release. In the case of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  solid light green compound was gained. In the case of  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  dark blue compound was gained. The received compounds were repeatedly washed by warm ethanol in order to remove unreacted metal acetates and compound II. The mixture of compounds VII and IX also the compounds VIII and X separately were dissolved in DMFA and filtered. In the first case into filtrate chelate compound VII is transferred and the oligomeric product IX is precipitated. In the second case compound VIII is transferred into filtrate and the compound X is precipitated. From the filtrates with compounds VII and IX under vacuum (1.5–2 mm Hg) DMFA was removed. The compounds VII and IX also the precipitates (compounds VIII and X) were repeatedly washed with warm ethanol and dried under vacuum (10–15 mm Hg) at 65–70°C bringing to constant mass. The general output of compounds is 82%, in which VII is ~ 58% and IX is ~ 42%. The general output of compounds VIII and X is 73%, in which VIII is ~ 58% and X is ~ 42%. The compounds VII and X solute in DMFA and DMSO and the compounds VIII and X solute in DMSO.

*Compounds XI and XII.* Compounds XI and XII are carried out similarly to the above example, but the difference is that the 7.45 g (0.05 mol) compound III was reacted with the 12.45 g (0.05 mol)  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  or 9.95 g (0.05 mol)  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ . After reaction compounds XI and XII were washed with warm ethanol and dried under vacuum (1.5–2 mm Hg) bringing to constant weight. The compound XI has light green color. Output is 57%. The compound XII has dark blue color. Output is 62%.

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