PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2016, № 3, p. 25–29

Chemistry

AMINO ALCOHOLS AND CHELATES ON THEIR BASIS

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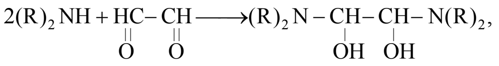
Interactions of amines and amino alcohols with glyoxal have been investigated and the compositions and structures of synthesized compounds have been studied. Alcoholates as well as chelates of Ni^{2+} and Mn^{2+} ions respectively have been prepared on the basis of products of the above reactions. The compositions and structures of the synthesized metal-organic compounds were studied by IR spectroscopy and elemental analysis.

***Keywords*:** amino alcohols, glyoxal, metal-organic compounds, elemental analysis.

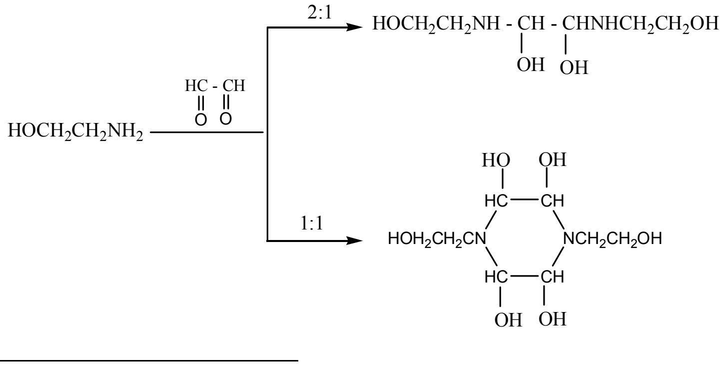
Introduction. One of the basic methods for preparing amino alcohols is the direct interaction of aliphatic and aromatic amines with the corresponding aldehydes (Mannich reaction) [1, 2]. The reactions between mono- and bifunctional amines as well as polyfunctional aldehydes are of specific interest. In this respect it is worth mentioning the investigations of interactions between amines and dialdehydes, particularly with glyoxal, carried out by the authors [3, 4]. In the paper the results of investigations of interaction between mono-, diamines and glyoxal, which have been used later for synthesis of new chelates having practical applications are presented. Synthesized compounds and chelates based on the can be used as thermo reactive resin hardeners and polymer modifiers. Dimethylamine, mono- and diethanolamine were used as mono- and diamines.

Reactions occurred with different mole ratios of amines and glyoxal:



$$2(R)_2NH + \underset{\displaystyle O}{\underset{\|}{HC}}-\underset{\displaystyle O}{\underset{\|}{CH}} \longrightarrow (R)_2N-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-N(R)_2,$$

$R = –C_2H_5$ (I); $HOCH_2CH_2 –$ (II).



(III)

(IV)

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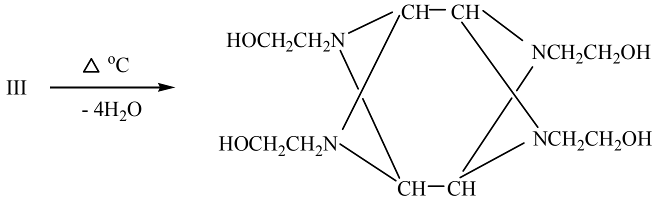
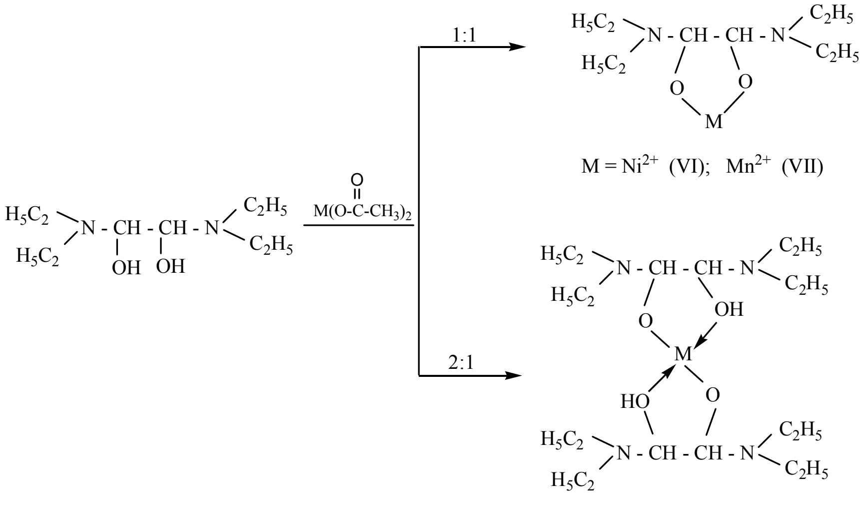
Spiro structural pyrazine compound is formed by thermal treatment of (III):



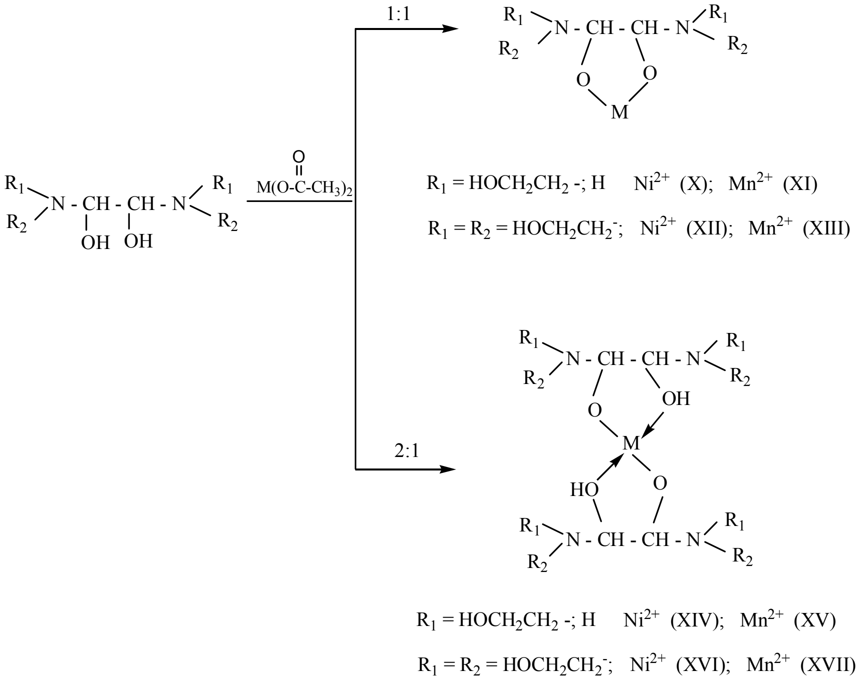
(V)

Chelate complexes based on I–III and metal acetates have been prepared:



M = Ni^{2+} (VI); Mn^{2+} (VII)

M = Ni^{2+} (VIII); Mn^{2+} (IX)



$R_1 = HOCH_2CH_2$ -; H Ni^{2+} (X); Mn^{2+} (XI)

$R_1 = R_2 = HOCH_2CH_2^{\cdot}$; Ni^{2+} (XII); Mn^{2+} (XIII)

$R_1 = HOCH_2CH_2$ -; H Ni^{2+} (XIV); Mn^{2+} (XV)

$R_1 = R_2 = HOCH_2CH_2^{\cdot}$; Ni^{2+} (XVI); Mn^{2+} (XVII)

The compounds (I–XVII) listed above have been studied by IR spectroscopy and elemental analysis.

Compound	Colour	Temp. swim., °*C*	IR spectroscopy, *ν*, *cm*$^{-1}$	Elemental composition, found / calculated, %			
				C	H	N	M
I	dark mustard shade	119	1050–1060, 3550–3600 (>CH–OH), 2850–2950 (–CH_3), 1180–1250 (>N–CH<)	58.70 / 58.82	11.60 / 11.76	13.90 / 13.72	–
II	light mustard shade	107.5	1050–1060, 3550–3600 (>CH–OH), 1120, 1180–1210 (>NH–CH_2–), 1240, 2010–2180 2850–2900 (–CH_2–), 3300–3450 (–CH_2–OH)	44.50 / 44.77	8.60 / 8.99	10.10 / 10.45	–
III	white	90.4	1030–1050, 3550–3600 (>CH–OH), 1230, 2010–2180, 2850–2920 (–CH_2–), 3340 (>NH)	39.80 / 40.00	8.60 / 8.88	15.30 / 15.55	–
IV	mustard shade	117.5	1080–1100, 1115–1200 (tertiary >NH), 1050–1070, 3300–3400 (–OH), 2860–2950 (–CH_2–)	40.20 / 40.34	7.28 / 7.56	11.60 / 11.76	–
V	light yellow	145.6	1060–1080, 1120–1200 (tertiary >N–), 1040–1050, 3300–3350 (–OH), 2850–2900 (–CH_2–)	49.80 / 50.00	8.50 / 8.33	19.20 / 19.44	–
VI	dark green	217	680 (Ni–O), 1180–1210 (>N–), 2820–2950 (–CH_3)	45.70 / 45.98	8.30 / 8.43	10.60 / 10.73	22.70 / 22.60
VII	creamy-white	180	510 (Mn–O), 1180–1210 (>N–), 2850–2950 (–CH_3)	46.60 / 46.69	8.60 / 8.56	11.00 / 10.89	21.30 / 21.40
VIII	green	205	670 (Mn–O), 170–1205 (>N–), 3200–3350 (–OH), 2800–2900 (–CH_3)	51.40 / 51.61	9.70 / 9.89	12.10 / 12.04	12.80 / 12.69
IX	dark creamy-white	150	500 (Mn–O), 1180–1200 (>N–), 2810–2920 (–CH_3), 3200–3300 (–OH)	51.90 / 51.86	9.90 / 9.98	12.30 / 12.15	11.80 / 12.63
X	green	–	670 (Ni–O), 1180–1210 (>N–), 2850 (–CH_2–), 3300–3490 (–OH)	30.50 / 30.64	5.50 / 5.10	11.80 / 11.91	25.10 / 25.11
XI	creamy-white	–	510 (Mn–O), 1175–1210 (>N–), 2800–2900 (–CH_2–), 3300–3450 (–OH)	31.20 / 31.17	5.30 / 5.19	12.30 / 12.12	22.90 / 22.80
XII	green	–	680 (Ni–O), 1170–1200 (>N–), 3300–3400 (–CH_2CH_2 OH),	36.70 / 36.92	6.90 / 6.77	8.50 / 8.61	18.00 / 18.15
XIII	creamy-white	–	515 (Mn–O), 1170–1200 (>N), 2850 (–CH_2–), 3200–3350 (–OH)	37.20 / 37.38	6.60 / 6.89	8.60 / 8.82	17.20 / 17.13
XIV	dark green	200	680 (Ni–O), 1160–1190, (>N–), 1080 (–OH), 2890–2900 (–CH_2–), 3200–3350 (–OH)	34.90 / 35.05	5.70 / 5.84	13.50 / 13.62	14.50 / 14.35
XV	nude	100	500 (Mn–O), 1160–1190 (>N–), 1080 (–OH), 2890–2900 (–CH_2–), 3200–3350 (–OH)	35.20 / 35.38	5.80 / 5.90	13.70 / 13.76	13.40 / 13.51
XVI	green	120	680 (Ni–O), 1160–1180 (>N–), 1040–1090 (–OH), 2890 (–CH_2–), 3200–3350 (–OH)	40.40 / 40.47	7.60 / 7.76	9.50 / 9.44	10.10 / 9.95
XVII	dark nude	85	510 (Mn–O), 1180–1190 (>N–), 1040–1100 (–OH), 2890 (–CH_2–), 3200–3350 (–OH)	40.60 / 40.75	7.60 / 7.81	9.60 / 9.51	9.30 / 9.34

Experimental Part. IR spectra of compounds I–XVII were recorded by spectrophotometer Specord I–75 using a CaF_2 prism. The elemental compositions of shifted compounds were defined by the method of elemental analysis and spectrophotometer AAS-3. Chemically pure grade diethylamine was used. Mono- and diethanolamine were purified by distillation in vacuum (1.502 *mm* Hg): $n_d^{20} = 1.012\ g \cdot cm^{-3}$ and $n_d^{20} = 1.0966\ g \cdot cm^{-3}$ fractions were used for monoethanolamine and diethanolamine respectively. 40% glyoxal solution, $Ni(OC(O)CH_3)_2$ and $Mn(OC(O)CH_3)_2$ of GR grade have been used in our investigations.

N,N'-bis(diethyl)dihydroxyethane (I). The reactor was charged by 18.25 *g* (0.25 *mol*) diethylamine and while continued stirring 40% aqueous solution of glyoxal was gradually added. Continuing stirring the mixture temperature was increased to 45–55°*C* and at this temperature the reaction was continued for 90–120 *min*. Then it was dehydrated in vacuum (14–15 *mm* Hg) and dark mustard shade mass with high viscosity was repeatedly washed with chloroform and then acetone. Mustard shade powder was dried in vacuum (1.5–2 *mm* Hg) at 70–75°*C* to constant weight. Output is 73%. Compound I dissolves in water, ethanol and esters.

N,N'-bis(aminodiethanol)dihydroxyethane (II). The reactor was charged by 21.4 *g* (0.2 *mol*) diethanolamine and while stirring for 5 *min* 40% aqueous solution of glyoxal was added gradually and continued stirring at 50–55°*C* temperature about 90–120 *min*. Then it was dehydrated in vacuum (14–15 *mm* Hg) and mustard shade powdery product was extracted which was repeatedly washed with chloroform and acetone and dried in vacuum (1.5–2 *mm* Hg) to constant weight. Output is 87%.

N'N-bis(aminoethanol)dihydroxyethane (III). 15.25 *g* (0.25 *mol*) monoethanolamine and 18 *mL* 40% aqueous solution of glyoxal (0.125 *mol*) were stirred and heated to 55–60°*C* and at this temperature stirring continued for 90–120 *min*. Then it was dehydrated in vacuum (10–15 *mm* Hg) and the remaining mass was washed with chloroform and acetone. Yellow shade powdery product was dryed in vacuum (1.5–2 *mm* Hg) to constant weight. Output is 89%.

N,N'-bis(tetrahydroxy)aminoethylpirazine (IV). The reaction and the extraction of product were accomplished according to the example III, the only difference is that 15.25 *g* (0.25 *mol*) monoethanolamine was reacted with 36 *mL* 40% aqueous solution of glyoxal (0.25 *mol*). Output is 64%.

Spiro compound (V). 9 *g* (0.05 *mol*) compound III was heated at 115–125°*C* in vacuum (14–15 *mm* Hg) for about 30–60 *min*. Afterwards it was cooled and washed with acetone and ethanol. The dark-mustard precipitate was filtered and dryed in vacuum (1.5–2 *mm* Hg) to constant weght. Output is 41%.

Compound VI (or VII). 10.2 *g* (0.05 *mol*) compound I in the presence of 5 *mL* acetone vigorously was grinded with 8.65 *g* (0.05 *mol*) $Ni(OC(O)CH_3)_2$ (or 0.05 *mol* $Mn(OC(O)CH_3)_2$) in stainless steel reactor under the pressure 0.5–1.0 *MPa* at 60–65°*C* until receiving a homogenous mass (25–30 *min*). Afterwards the mixture was cooled and reactor contents were transferred into another reactor with acetone (20–25 *mL*) and with continued stirring heated to 40–45°*C*. Then the hot filtration was accomplished. The precipitate was repeatedly washed with chloroform and acetone and then dried in vacuum (1.5–2 *mm* Hg) to constant weight. Output of compound VI is 58%, of compound VII is 48.5%.

Compound VIII (or IX). The interaction between 10.2 *g* (0.05 *mol*) compound I and 4.425 *g* (0.025 *mol*) $Ni(OC(O)CH_3)_2$ (or 10.2 *g* compound I and 4.325 *g* (0.05 *mol*) $Mn(OC(O)CH_3)_2$) and the extraction of reaction products were accomplished according to the method described above. Output of compound VIII is 50%, of compound IX is 48.5%.

Compound X (or XI). The interaction between compound III and $Ni(OC(O)CH_3)_2$ (or $Mn(OC(O)CH_3)_2$) and the extraction of reaction products were accomplished according to the method described above, but the difference is that 9.0 *g* (0.05 *mol*) III reacted with 8.85 *g* (0.05 *mol*) $Ni(OC(O)CH_3)_2$ (or 8.65 *g* (0.05 *mol*) $Mn(OC(O)CH_3)_2$). Output of compound X is 58%, of compound XI is 53%.

Compound XII (or XIII). The interaction between II and $Ni(OC(O)CH_3)_2$ (or II and $Mn(OC(O)CH_3)_2$) and the extraction of reaction products were accomplished according to the method described above, but the difference is that 9.0 *g* (0.05 *mol*) II reacted with 4.425 *g* (0.025 *mol*) $Ni(OC(O)CH_3)_2$ (or 4.325 *g* (0.025 *mol*) $Mn(OC(O)CH_3)_2$). Output of compound XII is 64%, of compound XIII is 62%.

Compound XIV (or XV). The interaction between II and $Ni(OC(O)CH_3)_2$ (or II and $Mn(OC(O)CH_3)_2$) and the extraction of reaction products were accomplished according to the method described above, but the difference is that 13.4 *g* (0.05 *mol*) II reacted with 8.85 *g* (0.05 *mol*) $Ni(OC(O)CH_3)_2$ (or 8.65 *g* (0.05 *mol*) $Mn(OC(O)CH_3)_2$). Output of compound XIV is 71%, of compound XV is 75%.

Compound XVI (or XVII). The interaction between II and $Ni(OC(O)CH_3)_2$ (or $Mn(OC(O)CH_3)_2$) and the extraction of reaction products were accomplished according to the method described above, but the difference is that 13.4 *g* (0.05 *mol*) compound II reacted with 4.425 *g* (0.025 *mol*) $Ni(OC(O)CH_3)_2$ (or 4.025 *g* (0.025 *mol*) $Mn(OC(O)CH_3)_2$). Output of compound XVI is 78%, of compound XVII is 75%.

Received 15.07.2016

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