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Chemistry

N-ETHYLOL DERIVATIVES OF GLYCOL AND COMPLEXES BASED ON THEM

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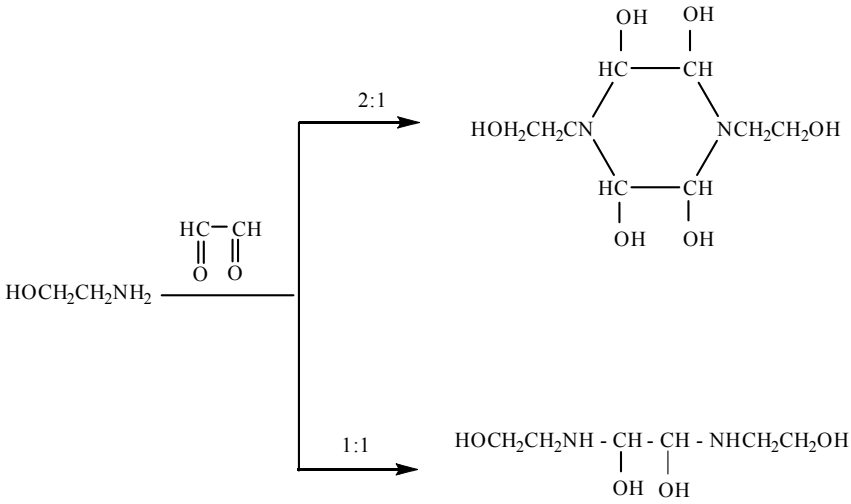
The interactions between mono- and diethanolamines and glyoxal were studied. Co^{2+} and Mn^{2+} chelates having application goals were synthesized based on the obtained amino alcohol derivatives and transition metal acetates. The structure and composition of monomeric ligands as well as chelates on their basis were studied by the methods of IR-spectroscopy and elemental analysis.

Keywords: amino alcohols, metal acetate, elemental analysis, monomeric ligands.

Introduction. Nitrogen containing mono- and diatomic alcohols and complex compounds based on them are of a definite interest both theoretically and practically. Particularly, nitrogen containing amino alcohols and metal complexes on their basis, which due to their high biological activity are widely used in the preparation of compositions having application goals, are described in the works [1–4].

The interactions between ethanol amines (mono- and diethanolamines, MEA and DEA) and glyoxal were performed and depending on their initial molar ratio the following compounds were obtained:



(1)

(II)

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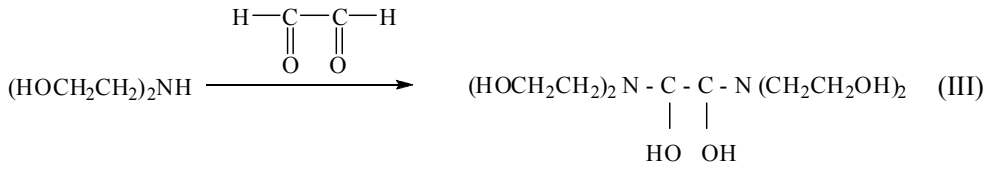
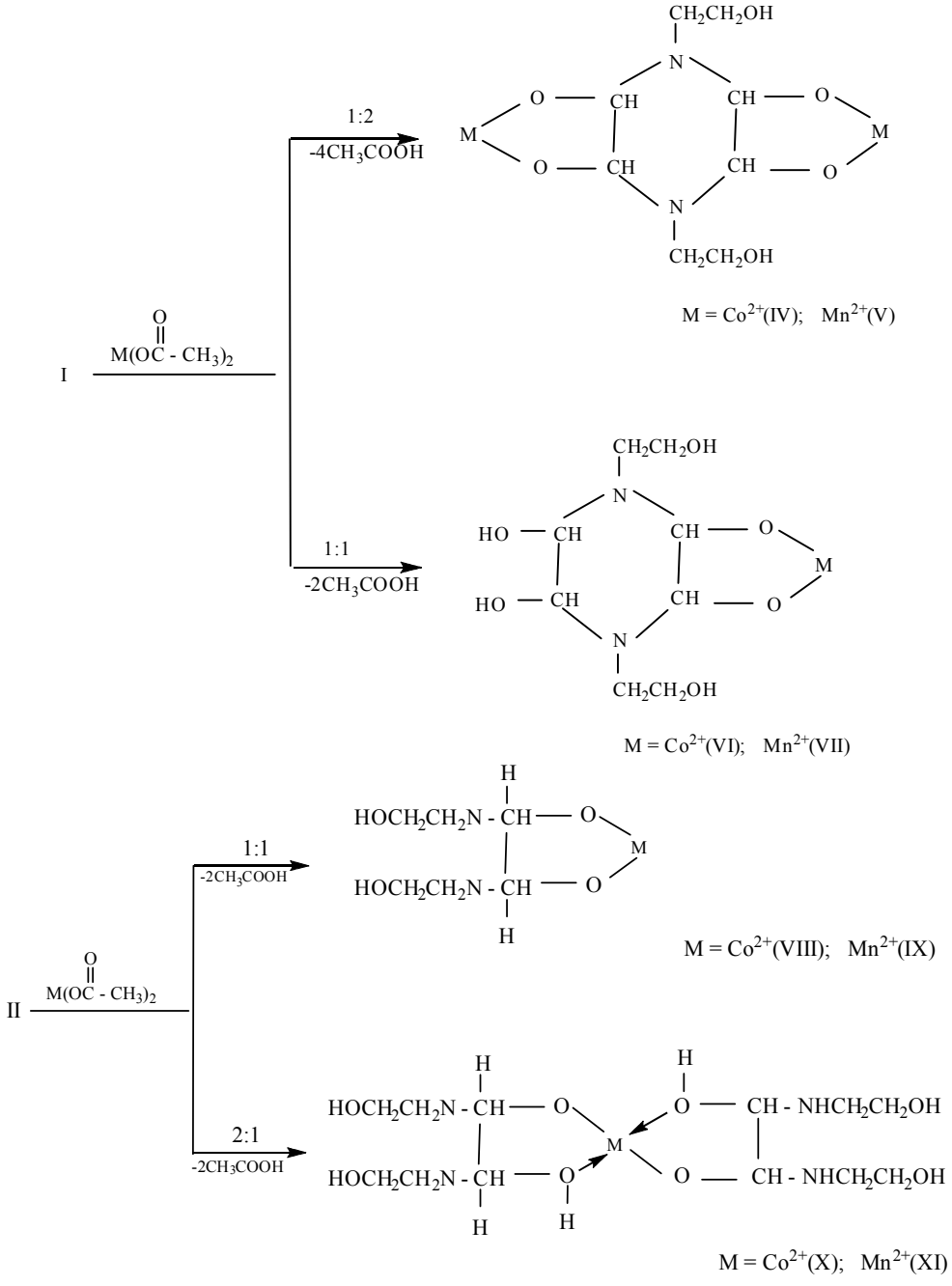
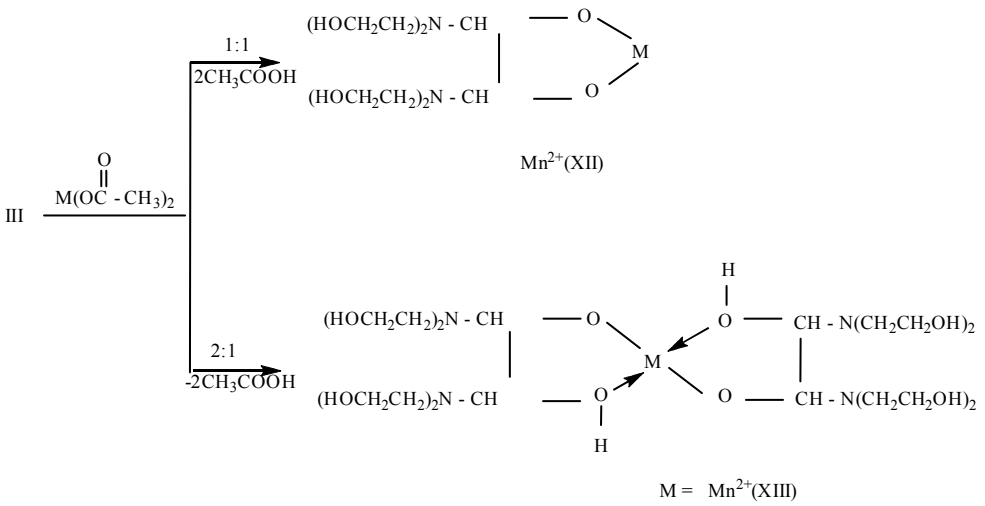


The following compounds were obtained based on compounds I–III and metal acetates:





Characteristics and composition of compounds I–XIII

Comp.	Color	Melting point, °C	IR spectra, ν, cm^{-1}	Elemental composition, found / calculated, %			
				C	H	N	M
I	light yellow	highly viscous state, amorphous	1010–1030 (CH); 1020–1035 (CH_2OH); 1125–1180 ( )CH–OH)	40.50 / 40.34	7.30 / 7.56	11.50 / 11.76	–
II	light yellow	highly viscous state	1020–1035 (CH_2OH); 1080–1110 (C–NH–); 1130–1170 ( )CH–OH)	39.80 / 40.00	9.10 / 8.90	15.40 / 15.55	–
III	light yellow	highly viscous state	all groups as in I	44.90 / 44.78	9.10 / 8.95	10.30 / 10.45	–
IV	dark blue	amorphous decom. temp. 75	all groups as in I, additionally 660 (Co–O)	27.20 / 27.27	4.10 / 3.98	7.90 / 7.95	33.40 / 33.52
V	dark mustard	amorphous decom. temp. 60	all groups as in I, 620–630 (Mn–O)	27.80 / 27.90	4.10 / 4.07	8.20 / 8.14	31.80 / 31.98
VI	blue	amorphous decom. temp. 80	all groups as in I, additionally 658 (Co–O)	32.60 / 32.54	5.50 / 5.42	9.40 / 9.49	19.80 / 20.00
VII	nude	amorphous decom. temp. 67	all groups as in I, additionally 618–630 (Mn–O)	33.10 / 32.99	5.60 / 5.50	9.70 / 9.62	19.10 / 18.90
VIII	blue	140	all groups as in II, additionally 666 (Co–O)	30.30 / 30.38	5.89 / 5.91	11.90 / 11.81	24.70 / 24.89
IX	nude	98	all groups as in II, additionally 618–625 (Mn–O)	30.80 / 30.90	5.90 / 6.00	12.10 / 12.02	23.50 / 23.60
X	blue	150	all groups as in II, additionally 670 (Co–O)	34.60 / 34.53	7.10 / 7.19	13.30 / 13.43	14.10 / 14.15
XI	nude	100	all groups as in II, additionally 610–625 (Mn–O)	34.80 / 34.87	7.10 / 7.26	13.40 / 13.56	13.30 / 13.32
XII	nude	amorphous decom. temp. 110	all groups as in III, additionally 610 (Mn–O)	37.50 / 37.38	6.60 / 6.77	8.50 / 8.61	17.00 / 17.13
XIII	nude	amorphous decom. temp. 115	all groups as in III, additionally 615 (Mn–O)	40.70 / 40.90	7.30 / 7.50	9.60 / 9.54	9.40 / 9.37

The physical properties and elemental composition of compounds I–XIII are given in Table.

Experimental Part. IR spectra of compounds I–XIII were recorded on NICOLET/FT-IR NEXUS spectrometer. 38% glyoxal aqueous solution, $Co(OC(O)CH_3)_2$ and $Mn(OC(O)CH_3)_2$ of GR grade have been used. MEA and DEA have been used after their purification at the temperatures of 142 and 268°*C* respectively.

Preparation of Tetrahydroxy(piperidinyl)diethanol (I). 6.1 *g* (0.1 *mol*) of MEA and 16 *mL* 38% aqueous solution of glyoxal were stirred at the temperature 35–40°*C* for 1–1.5 *h*. During the interaction process the thickening of the light brown reaction mass was observed. Then it was dehydrated in vacuum (10–15 *mm* Hg) and at 50–55°*C*. The remaining viscous mass was washed with chloroform and ether–acetone mixture (2 : 1 by volume) to light brown viscous mass. Then it was dried in vacuum (4.5–5 *mm* Hg) at 50–60°*C* to constant weight. Yield 75%.

Preparation of Bis-N,N'-diethylolethyleneglycol (II). 12.1 *g* (0.2 *mol*) of MEA and 5.8 *g* (0.1 *mol*) 38% aqueous solution of glyoxal were stirred at the temperature 35–40°*C* for 1–1.5 *h*. During the interaction process the reaction medium acquired a light brown color. Then it was dehydrated in vacuum (10–15 *mm* Hg) and at 50–55°*C*. The remaining viscous mass was repeatedly washed with chloroform and ether–acetone mixture (2 : 1 by volume). The transparent viscous mass with the slightly brown color was dried in vacuum (2.5–5 *mm* Hg) at 50–60°*C* to constant mass. Yield is 83%.

Preparation of Bis-N,N'-tetraethylenglycol (III). The reaction between 21 *g* (0.2 *mol*) of compound II and 5.8 *g* (0.1 *mol*) of glyoxal as well as the extraction of reaction products have been carried out according to the method described above. Yield is 83%.

Chelate Complexes Based on the I and Acetates of Metal Ions Co^{2+} and Mn^{2+} (IV, V). The interaction between 5.95 *g* (0.025 *mol*) of compound I and 8.85 *g* (0.05 *mol*) of $Co[OC(O)CH_3]_2$ or 8.65 *g* (0.05 *mol*) of $Mn[OC(O)CH_3]_2$ was carried out in 50 *mL* dimethylformamide (DMF) medium at the 110–115°*C* with continuous stirring for 1.5–2 *h*. During the reaction process in the presence of $Co[OC(O)CH_3]_2$ the reaction mass was turned into dark blue color, and in the presence of $Mn[OC(O)CH_3]_2$ it was turned into light mustard color. At the end of reaction DMF was removed under vacuum (10–15 *mm* Hg) and highly viscous masses were washed with ethanol, acetone, chloroform and ether and dried in vacuum (4.5–5 *mm* Hg) at 70–75°*C* to constant weight. Yield is 68% (IV); 72% (V).

Chelate Complexes Based on Compound I and $Co[OC(O)CH_3]_2$ (VI), $Mn[OC(O)CH_3]_2$ (VII). The interaction between 5.95 *g* (0.025 *mol*) of compound I and 4.4 *g* (0.025 *mol*) of $Co[OC(O)CH_3]_2$ or 4.32 *g* (0.05 *mol*) of $Mn[OC(O)CH_3]_2$ was carried out in 50 *mL* DMF medium at the 110–115°*C*. After 15–20 *min* the reaction mass was turned into blue color in the presence of $Co[OC(O)CH_3]_2$ and into light mustard color in the presence of $Mn[OC(O)CH_3]_2$. At the end of reaction DMF was removed under vacuum (10–15 *mm* Hg) and highly viscous masses were repeatedly washed with acetone and chloroform and dried in vacuum (4.5–5 *mm* Hg) at 70–75°*C* to constant weight. Yield is 64% (VI); 69% (VII).

Chelate Complexes Based on Compound II and $Co[OC(O)CH_3]_2$ (VIII), $Mn[OC(O)CH_3]_2$ (IX). The reaction between compound II and $Co[OC(O)CH_3]_2$ or

$Mn[OC(O)CH_3]_2$ and the extraction of reaction products were carried out according to the method described above, the only difference is that 4.5 *g* (0.025 *mol*) of compound II was reacted with 4.4 *g* (0.025 *mol*) of $Co[OC(O)CH_3]_2$ or 4.32 *g* (0.025 *mol*) of $Mn[OC(O)CH_3]_2$. Yield is 74% (VIII); 77% (IX).

Chelate Complexes Based on Compound II and $Co[OC(O)CH_3]_2$ (X), $Mn[OC(O)CH_3]_2$ (XI). The reaction between reagents and the extraction of reaction products were carried out according to the method described above, the only difference is that 4.5 *g* (0.025 *mol*) compound II was reacted with 2.21 *g* (0.0125 *mol*) of $Co[OC(O)CH_3]_2$ or 2.16 *g* (0.025 *mol*) of $Mn[OC(O)CH_3]_2$. Yield is 67% (X);70% (XI).

Chelate Conplexes Based on Compound III and $Mn[OC(O)CH_3]_2$ (XII). The reaction between reagents and the extraction of reaction products were carried out according to the method described above, the only difference is that 6.7 *g* (0.025 *mol*) compound III was reacted with 4.32 *g* (0.025 *mol*) of $Mn[OC(O)CH_3]_2$. Yield is 67%.

Chelate Complexes Based on Compound III and $Mn[OC(O)CH_3]_2$ (XIII). The interaction between 6.7 *g* (0.025 *mol*) of compound III and 2.16 *g* (0.0125 *mol*) of $Mn[OC(O)CH_3]_2$ and the extraction of reaction products were carried out according to the method described above. Yield is 69%.

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REFERENCES

1. **Yeritsyan M. L., Zulumyan N.O., Mirzakhanyan A.V., Isahakyan A.R.** IV International Conference "Chemistry and Chemical Technology". Collected papers, 14–18.09.2015. Yer., p. 231–238 (in Armenian).
2. **Petrosyan G.M., Qaramyan R.A., Yeritsyan L.N., Yeritsyan M.L.** Glycol Derivatives of Urea and Chelates on Their Basis. // J. Physical Chemistry of Polymers, Synthesis, Properties and Applications, 2014, № 20, p. 284–287 (in Russian).
3. **Pomogaylo A.O., Sivost'yanov A.O.** Metal-Containing Monomers and Polymers Based on Them. M.: Khimia, 1988, 384 p. (in Russian).
4. **Neyland O.Ya.** Organic Chemistry. M.: Vischaya Shkola, 1990, p. 644–646 (in Russian).