Co(II,III), Ni(II) and Cu(II)-Containing Heterocyclic Compounds with 2,7-Dithio-3,6-diazaoctadien-3,5-dithioamide-1,8 Obtained in Gelatin-Immobilized Matrix by Template Synthesis Process

Oleg V. Mikhailov*, Albina I. Khamitova and Liliya S. Mingalieva

Kazan State Technological University, K.Marx Street 68, 420015 Kazan, Russia
Fax: (8432)36 57 68, e-mail: ovm@kstu.ru

• Abstract

Mild template synthesis of heterocyclic coordination compounds of Co(III), Ni(II) and Cu(II) with 2,7-dithio-3,6- diazaoctadien-3,5-dithioamide-1,8 in the M(II)-dithiooxamide-glyoxal triple systems (M= Co, Ni, Cu) in the cobalt(II)-, nickel(II)- and copper(II) hexacyanoferrate(II) gelatin- immobilized matrices has been carried out.

• Introduction

Mild template synthesis was shown to occur in the M(II)- dithiooxamide- formaldehyde and in the M(II)- dithiooxamide- acetone triple systems (M= Ni, Cu) at the contact of corresponding metal(II)hexacyanoferrate(II) gelatin-immobilized matrices ($M_2[Fe(CN)_6]$ -GIM) with aqueous-alkaline solutions containing dithiooxamide and formaldehyde or acetone [1,2]. Dithiooxamide and formaldehyde or acetone were ligand synthons in such a process. We would like to report in this paper that we had found template synthesis proceeding in the triple M(II) -dithiooxamide -glyoxal systems in the $M_2[Fe(CN)_6]$-GIM where M is Co, Ni or Cu.

• Experimental

Cobalt(II)-, nickel(II)- and copper(II) metalhexacyanoferrate(II) GIMs were synthesized as described in [3-5].

Synthesis of $CoC_6S_4N_4O_2H_7$. This synthesis occurs on contact of $Co_2[Fe(CN)_6]$ -GIM with alkaline solutions (pH=11-12) containing dithiooxamide and glyoxal. The concentration of cobalt(II) hexacyanoferrate(II) in the matrix was 0.1-2.0 mol dm^{-3}, the concentration of dithiooxamide and glyoxal in a solution was ($3.0\ 10^{-3}$ -$5.0\ 10^{-2}$) mol dm^{-3} and ($6.0\ 10^{-3}$ -$1.0\ 10^{-1}$) mol dm^{-3}, respectively. The duration of the process was 10-12 min at 18-20°C. The matrix obtained was treated with the solution of proteolytic enzyme *Bazillus mesentericus*, as a result gelatin binding of matrix was split into soluble low mol. wt. compounds whereas coordination compound synthesized was precipitated and then isolated from a mother liquor. Finally, the substance isolated from GIM was washed with distilled water, ethanol and dried at room temperature. Found (%): Co, 16.8; C, 20.4; S 36.1; N, 15.8; O, 8.6; H, 2.2. $CoC_6S_4N_4O_2H_7$, calc. (%): Co, 16.6; C, 20.4; S, 36.2; N, 15.8; O, 9.0; H, 2.0. Characteristic bands of the IR-spectra (cm^{-1}): 690 (ν(C=S)); 1640 (ν(C=N)); 3470 (ν(NH)).

Synthesis of $NiC_6S_4N_4H_4$. This synthesis was carried out as it described for cobalt complex but on the contact with alkaline solutions (pH=11-12) containing dithiooxamide and glyoxal was $Ni_2[Fe(CN)_6]$ -GIM. Found (%): Ni, 18.6; C, 22.7; S, 39.5; N, 17.9; H, 1.3; O is not found. $NiC_6S_4N_4H_4$, calc. (%): Ni, 18.41; C, 22.58; S, 40.20; N, 17.56; H, 1.25. Characteristic bands of the IR-spectra (cm^{-1}): 650 (ν(C=S)); 1640 (ν(C=N)); 3470 (ν(NH)).

Synthesis of $CuC_6S_4N_4H_4$. It was carried out as in the previous cases but on the contact with alkaline solutions (pH=11-12) containing dithiooxamide and glyoxal was $Cu_2[Fe(CN)_6]$ -GIM. Found (%): Cu, 19.6; C, 22.4; S, 39.4; N, 17.3; H, 1.3. $CuC_6S_4N_4H_4$ calc. (%): Cu, 19.61; C, 22.24; S, 39.60; N, 17.30; H, 1.23; O is not found. Characteristic bands of the IR-spectra (cm^{-1}): 660 (ν(C=S)); 1650 (ν(C=N)); 3440 (ν(NH)).

The transmitted light absorbance of the GIMs (D^{*}) were measured with a Macbeth TD504 photometer (Kodak Co., USA) in the 0.1-5.0 absorbance units range with an accuracy of ±2% (rel.). Electron absorption spectra of the GIMs were recorded using Specord UV-VIS (Karl Zeiss, Germany) and PU-8710 (Philips, The Netherlands) spectrophotometers in the 400-800 nm range. In order to record IR spectra, a UR-20 spectrometer (Karl Zeiss, Germany) was employed. ESR- spectra were measured by ESR230 spectrometer. DTA analysis was made with Q-Derivatograph Paulik-Paulik-Erdey (Hungary). The mathematical processing of kinetical relationships was carried out by means of computer Pentium -166MMX (Intel) according to procedure described in [6].

• Results and Discussion

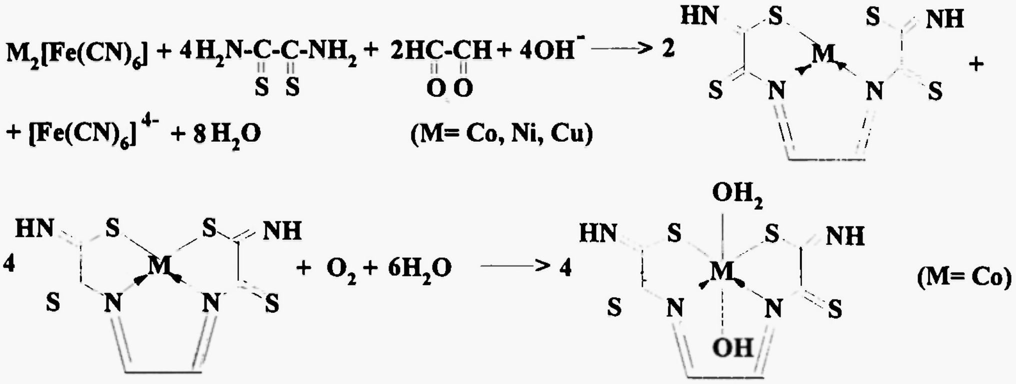
The compounds obtained colour the polymeric masses of the GIM in brown (Co,Ni) or in greenish-brown (Cu); however, the UV-VIS-spectra of these compounds contain only a «wing» of the intense charge transfer band, whose maximum is in the UV region at 350-360 nm. It should be noted especially that at in absence of glyoxal, in the case of $Co_2[Fe(CN)_6]$ -GIM, yellow-brown compound with spectral characteristics similar to those of the $Co(HL)_3$ complex [7], is formed. In the case of $Ni_2[Fe(CN)_6]$, a violet compound (λ_{max} =580 nm) with spectral characteristics similar to those of the $[NiL(OH)_2]$ complex [4,8], is formed. In the case of $Cu_2[Fe(CN)_6]$, a dark-green substance with spectral characteristics similar to those of the known $[Cu(HL)_2]$ chelate [5,9], is formed (HL^- and L^{2-} are singly and doubly deprotonated forms of dithiooxamide). It is apparent that both dithiooxamide and formaldehyde participate in the complexing process that occurs under these specific conditions. Decomposition of the polymeric binder of GIM by enzymes according to the known procedure [6] allowed us to isolate dark-brown compounds having $MC_6S_4N_4H_4$ (M= Ni, Cu) and $MC_6S_4N_4O_2H_7$ (M= Co) compositions. They are almost insoluble in water, ethanol, acetone, chloroform, benzene and tetrachloromethane, and poorly soluble in dimethylformamide, dimethylsulfoxide and hexamethylenephosphortriamide.

The substances having $CoC_6S_4N_4O_2H_7$ and $NiC_6S_4N_4H_4$ formulas are diamagnetic and do not give an ESR signals either at low (77 K, liquid nitrogen) or at room temperatures. This circumstance allow us to assume that cobalt in the compound synthesized has an oxidation degree equal to +3 with pseudo-O_h-coordination of donor centers around above-mentioned cobalt, nickel has an oxidation degree equal to +2 with planar D_{2h}- or C_{2h}- coordination of donor centers around metal ion. $CuC_6S_4N_4H_4$ compound is paramagnetic ($\mu_{eff.}$= =1.97m_B) and gives ESR signal with $g_{||}$ =2.24, $g_{\perp}$= =2.07 which also typical of planar coordination of donor centers to Cu(II) and the N_2S_2 composition of these centers. The UV-VIS spectra of dimethylformamide solution of all these three compounds are almost identical to those of their source GIM indicating that the immobilized compound is the same as that isolated from these immobilized matrices.

The IR spectra of the substances synthesized have a band in the 3400-3500 cm^{-1} region typical of NH or NH_2 groups uncoordinated to metal ion. Hence, at least a portion of the N atoms in these compounds are not bound to Co, Ni or Cu. In addition, the IR spectra of the compounds under study contain ν(C=S) at 650-700 cm^{-1} (usually observed at 570-705 cm^{-1}) and ν(C=N) bands at 1640-1650 cm^{-1} (usually observed at 1625-1690 cm^{-1}) [10] indicating the presence of (C=S) and (C=N) groups, respectively. The IR spectra obtained in the region <1000 cm^{-1}, where according to [10] ν(M-S) and ν(M-N) (M=Co, Ni, Cu) frequencies should be observed, unfortunately do not allow us to reliably assign the bands which contain in this region, to vibrations indicated. It should be especially noted that ν(C-O-C) band (at 1100-1120 cm^{-1}) and $\nu(CH_2)$ bands (at 2855-2865 cm^{-1}) which were typical for the compounds formed at the template synthesis in the M(II)- dithiooxamide- formaldehyde system [1], are not found for any of compounds obtained. Thus, one may conclude that all three compounds under examination do not contain structural groups indicated. However, the compositions of compounds synthesized here ($MC_6S_4N_4H_4$ in the case of Ni and Cu and $MC_6S_4N_4O_2H_7$ in the case of Co) *do not coincide* with ones of cobalt(II), cobalt(III), nickel(II) and copper(II) chelates with dithiooxamide known from literature cited above ($CoC_4S_4N_4H_6$, $CoC_6S_6N_6H_9$, $NiC_4S_4N_4H_6$ and $CuC_4S_4N_4H_6$).

The analysis of $D^{\blacktriangledown}=f(C_F,C_L^0,t)$ kinetic curves of complexing where $D^{\blacktriangledown}$ is the optical density of the metal-chelate GIM corresponding to concentration of metal(II) hexacyanoferrate(II) in the matrix (C_F), dithiooxamide in solution (C_L^0) and the duration of the complexing process t for the various dithiooxamide: glyoxal molar ratio in the range 0.5-2.0, provides clear evidence that an addition of *two* dithiooxamide molecules and *one* glyoxal molecule per M^{II} ion takes place in the course of the process. It is quite evident that the formation of coordination compounds of metals indicated with some novel ligand which is «assembled» from dithiooxamide and glyoxal fragments, occurs during complexing in the M(II)- dithiooxamide- glyoxal systems (M= Co, Ni, Cu). It should be noted especially in this connection that the UV-VIS absorption spectra of aqueous solutions of dithiooxamide of any concentrations in the range of 400-700 nm at pH>10 did not change even on addition of significant amounts of glyoxal for at least 2 days, and no indications of a chemical process between dithiooxamide and glyoxal was observed. Therefore, we have no doubt that the reaction between the reagents indicated above does not occur in the absence of a metal ion. A similar phenomenon is possible only in template synthesis [11-13]. Besides, dithiooxamide and glyoxal act in it as ligand synthons. The DTA data indicate that all these compounds are very heat-resistant and do not undergo pyrolysis even at 600°C; the fact indicated is circumstantially evidences in favour of such a supposition.

This circumstance attracts its attention that composition of coordination compound formed in the case of cobalt ($MC_6S_4N_4O_2H_7$) unlike from one formed in the cases of nickel and copper ($MC_6S_4N_4H_4$). Besides, $MC_6S_4N_4O_2H_7$ is nothing but $MC_6S_4N_4H_4(OH_2)(OH)$. By taking into account that an oxidation degree of cobalt in the compound indicated is +3 (see above), and, also, this fact that Co(II) complexes with (N,S)-donoratomic ligands are oxidized lightly in the corresponding Co(III) ones by an influence of oxygen of air, it may be postulated that Co(II)—> Co(III) redox process occurs. With consideration of the all foregoing, the following schemes of template synthesis proceeding at an interaction between M(II), dithiooxamide and glyoxal in the corresponding metal(II)hexacyanoferrate(II) GIM may be written:



Besides, in the case of cobalt, Co(II) chelate is intermediate and is oxidized at once in the coordination compound of Co(III).

It should be specially mentioned that processes of template synthesis between M(II), dithiooxamide and glyoxal occurs ***only in GIM;*** we failed to obtain these coordination compounds in the reaction of $Co_2[Fe(CN)_6]$, $Ni_2[Fe(CN)_6]$ or $Cu_2[Fe(CN)_6]$ (as Co(II), Ni(II) or Cu(II)) in solution or in the solid phase at room temperature. This fact indicates the specific role of gelatin-immobilized matrix system in template synthesis in our case.

• Acknowledgements

Financial support from the Russian Foundation of Basic Research (Grants NN 96-03-32112 and 00-03-99204) and from the Center of Fundamental Sciences of Ministry of Education of Russian Federation (Grant N 97-0-9.2-13) is acknowledged.

• References

[1] O.V. Mikhailov, A.I. Khamitova and V.I. Morozov, *Heterocyclic Commun.*, **6**, 137 (2000)
[2] O.V. Mikhailov, M.A. Kazymova, T.A. Shumilova and L.R. Vafina, *Heterocyclic Commun.*, **6**, 357 (2000)
[3] O.V. Mikhailov, *Zh. Obtsch. Khim.*, **68,** 1724 (1998)
[4] O.V. Mikhailov, *Monatshefte fur Chemie*, **121**, 601 (1990)
[5] O.V. Mikhailov, *Monatshefte fur Chemie*, **122**, 595 (1991)
[6] O.V. Mikhailov, *Russian J. Coord. Chem.*, **18,** 1008 (1992)
[7] O.V. Mikhailov, M.A. Kazymova, *Transition Metal Chem.*, **24**, 517 (1999)
[8] O.V. Mikhailov, *Transition Metal Chem.*, **21**, 363 (1996)
[9] O.V. Mikhailov, *Transition Metal Chem.*, **22**, 535 (1997)
[10] K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, 4th Edit., Wiley, New York, 1991.
[11] D.H. Bush, *Uspekhi Khimii*, **38**, 822 (1969) (in rus.)
[12] A. Eschenmoser, *Angew. Chem., Int. Edition Engl.*, **27**, 6 (1988)
[13] N.V. Gerbeleu and V.B. Arion, Template Synthesis of Macrocyclic Compounds. Kishineu, Stiintsa, 1990 (in rus.)

Received on April 12, 2001