Template Synthesis of Cobalt(II,III), Nickel(II) and Copper(II) Macrocyclic Compounds with 2,8-Dithio-3,7-diaza-5-oxanonandithioamide-1,9 in Gelatin-Immobilized Matrix

Oleg V. Mikhailov*, Albina I. Khamitova and Vladimir I. Morozov

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

Abstract

Low-temperature template synthesis of macrocyclic coordination compounds with 2,8-dithio-3,7-diaza-5-oxanonandithioamide-1,9 in the triple systems M(II)-dithiooxamide- formaldehyde (M= Co, Ni, Cu) in the cobalt(II)-, nickel(II)- and copper(II) hexacyanoferrate (II) gelatin-immobilized matrices has been carried out.

Introduction

The processes of template synthesis which afford the possibility of constructing chelate complexes of d-elements with macrocyclic ligands from simpler fragments (so-called ligand synthons), are known to occur in solutions and solid phase mostly under rather drastic conditions. It could be believed nevertheless that the specific conditions formed upon complexing in 3d-metal-containing gelatin-immobilized matrices, for example in metal(II)hexacyanoferrate(II) ones ($M_2[Fe(CN)_6]$-GIM) [1-7], would enable at least certain template processes to occur under soft conditions, primarily at room temperature. We report in this communication that we have been able to perform such synthesis involving $M_2[Fe(CN)_6]$-GIM (M =Co, Ni, Cu) and such ligand synthons as dithiooxamide H_2N-C(=S)-C(=S)-NH_2 and formaldehyde CH_2O to give macrocyclic coordination compounds of Co(III), Ni(II) and Cu(II) with a novel before unknown (N,N,S,S)- tetradentate ligand -2,8-dithio- 3,7-diaza-5- oxanonandithioamide-1,9.

Experimental

Cobalt(II)-, nickel(II)- and copper(II) metalhexacyanoferrate(II) GIMs were synthesized as described in [1-7].

Synthesis of $CoC_6S_4N_4O_3H_{11}$. This synthesis occurs on contact of $Co_2[Fe(CN)_6]$ -GIM with alkaline solutions (pH=11-12) containing dithiooxamide and formaldehyde.

The concentration of cobalt(II) hexacyanoferrate(II) in the matrix was 0.1-2.0 mol dm^{-3}, the concentration of dithiooxamide and formaldehyde in the solution was ($3.0\ 10^{-3}$ -$5.0\ 10^{-2}$) mol l^{-1} and ($1.5\ 10^{-3}$ -$1.0\ 10^{-1}$) mol l^{-1}, 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 *Bacillus 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, ethanole and dried at the room temperature. Found (%): Co, 16.0; C, 19.4; S 15.2; N, 33.9; O, 12.7; H, 2.8. $CoC_6S_4N_4O_3H_{11}$, calc. (%): Co, 15.75; C, 19.25; S, 14.96; N, 34.27; O, 12.83; H, 2.04. Characteristic bands of the IR-spectra (cm^{-1}): 700 (ν(C=S)); 1100 (ν(C-O-C)); 1645 (ν(C=N)); 2855, 2915 (ν(CH_2)); 3470 (ν(NH)).

Synthesis of $NiC_6S_4N_4OH_8$. This synthesis was carried out as it described for cobalt complex but on the contact with alkaline solutions (pH=11-12) containing dithiooxamide and formaldehyde was $Ni_2[Fe(CN)_6]$ -GIM. Found (%): Ni, 17.5; C, 21.3; S, 37.5; N, 16.5; O, 4.8; H, 2.4; $NiC_6S_4N_4OH_8$, calc. (%): Ni, 17.32; C, 21.25; S, 37.83; N, 16.52; O, 4.72. Characteristic bands of the IR-spectra (cm^{-1}): 680 (ν(C=S)); 1110 (ν(C-O-C)); 1640 (ν(C=N)); 2865, 2940 (ν(CH_2)); 3450 (ν(NH)).

Synthesis of $CuC_6S_4N_4OH_8$. It was carried out as in the previous cases but on the contact with alkaline solutions (pH=11-12) containing dithiooxamide and formaldehyde was $Cu_2[Fe(CN)_6]$ -GIM. Found (%): Cu, 18.5; C, 20.9; S, 37.3; N, 16.1; O, 4.8; H, 2.4. $CuC_6S_4N_4OH_8$, calc. (%): Cu, 18.45; C, 20.96; S, 37.21; N, 16.34; O, 4.69; H, 2.35. Characteristic bands of the IR-spectra (cm^{-1}): 650 (ν(C=S)); 1120 (ν(C-O-C)); 1640 (ν(C=N)); 2860, 2910 (ν(CH_2)); 3430 (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. The mathematical processing of kinetical relationships was carried out by means of computer Pentium - 166MMX (Intel) according to procedure described in [8].

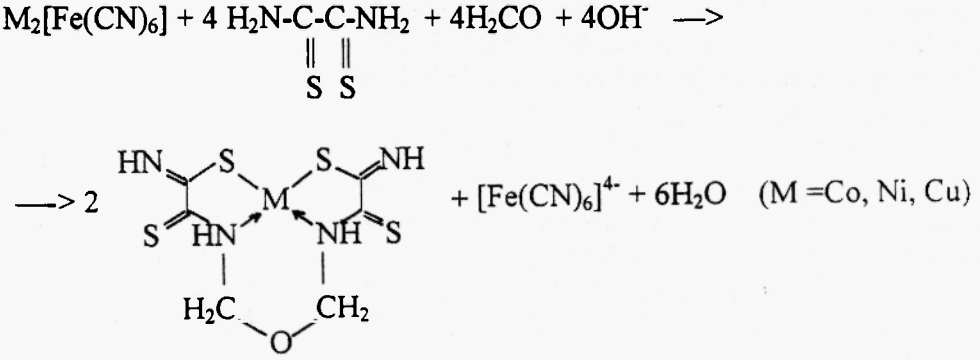
Results and Discussion

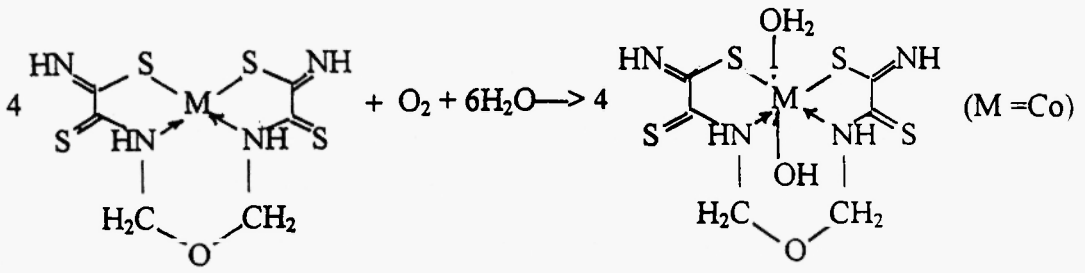
The analysis of $D^{\nabla} = f(C_F, C_L^0, t)$ kinetic curves of complexing where D^{∇} is the optical density of the metal-chelate GIM corresponding to concentration of metal(II) hexacyanoferrate(II) in the matrix (C_F), dithiooxamide in solution (C_L^0) and the duration of the complexing process t for the various dithiooxamide: formaldehyde molar ratio in the range 0.5-2.0, provides clear evidence that an addition of two dithiooxamide molecules and two formaldehyde ones per M^{II} ion takes place in the course of the process. The resulting compounds colour the polymeric masses of the GIM, which becomes brown (Co,Ni) or greenish-brown (Cu). The UV-VIS-spectra of these compounds contain only a shoulder due to the intense charge transfer band, whose maximum is in the UV region. It should be noted especially that at in absence of formaldehyde, 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 [1]; 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 [1,2,5,6]; 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 [3,7] are 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 $MC_6S_4N_4OH_8$ (M= Ni, Cu) and $MC_6S_4N_4O_3H_{11}$ (M =Co). These compounds are almost insoluble in water, ethanol, acetone, chloroform, benzene and tetrachloromethane, and poorly soluble in dimethylformamide, dimethylsulfoxide and hexamethylenephosphortriamide. The substances having $CoC_6S_4N_4O_3H_{11}$ and $NiC_6S_4N_4OH_8$ formulas are diamagnetic and give an ESR signals neither at low (77 K, liquid nitrogen) nor at room temperatures. This circumstance allows to assume that

cobalt in the compound indicated has an oxidation degree equal to +3 with pseudo-O_h-coordination of donor centers around above-mentioned metal ion, nickel, an oxidation degree equal to +2 with planar D_{2h}- or C_{2h}-coordination of donor centers around nickel. $CuC_6S_4N_4OH_8$ compound is paramagnetic ($\mu_{eff.}$ =1.92μ_B) and gives ESR signal with $g_{||}$ =2.21, $g_{|}$ =2.05 which is also typical of planar coordination of donor centers to copper(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 DTA data indicate that all these compounds are very heat-resistant and do not undergo pyrolysis even at 600°C. The IR spectra of the substances indicated 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 cobalt, nickel or copper. In addition, the IR spectra of the compounds under study contain ν(C=S) at 650-700 cm^{-1} (usually observed at 705-570 cm^{-1}) and ν(C=N) bands at 1640-1650 cm^{-1} (usually observed at 1690-1625 cm^{-1}) [9] indicating the presence of (C=S) and (C=N) groups, respectively. Unfortunately, the IR spectra obtained in the region <1000 cm^{-1}, where ν(M-S) and ν(M-N) (M =Co, Ni, Cu) frequencies should be observed [9], do not allow us to reliably assign the bands they contain the stretching vibrations indicated above. It should be especially noted that two medium-intensity peaks belonging to $\nu(CH_2)$ (according to literature data [9], these bands lie within the 2945-2915 and 2870-2845 cm^{-1} ranges, respectively) and a band due to the stretching vibrations of the bridging C-O-C group at 1120-1100 cm^{-1}(usually observed in the 1200-1100 cm^{-1} range) [9] is also present in the spectra of compounds indicated. These bands are absent in the IR spectra of dithiooxamide and in any of the coordination compounds of Co(II), Co(III), Ni(II) and Cu(II) with this ligand known to date [6,7]. Thus, one may conclude that all three compounds under examination contain CH_2-O-CH_2 structural group. Since such groups are present neither in dithiooxamide, nor in any of its complexes with cobalt(II),

cobalt(III), nickel(II) and copper(II), nor in formaldehyde, it is quite evident that the formation of coordination compounds of metals indicated with some novel ligand which is «assembled» from dithiooxamide and formaldehyde fragments, occurs during complexing in the M(II)- dithiooxamide- formaldehyde 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 formaldehyde for at least 2 days, and any indications of a chemical process between dithiooxamide and formaldehyde was not observed. Therefore, we have no doubt that the reaction between the reagents indicated above does not take place at all in the absence of a metal ion. A similar phenomenon is possible only in template synthesis [10-12]. Besides, dithiooxamide and formaldehyde act in it as ligand synthons.

This circumstance attracts attention that composition of coordination compound formed in the case of cobalt is $MC_6S_4N_4O_3H_{11}$ unlike in the cases of nickel and copper ($MC_6S_4N_4OH_8$). Besides, $MC_6S_4N_4O_3H_{11}$ is nothing but $MC_6S_4N_4OH_8(OH_2)(OH)$. By taking into account that an oxidation degree of cobalt in the compound indicated is +3 (see above), and, also, the 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 takes place in our case. With consideration of the all foregoing, the following schemes of template synthesis proceeding at an interaction between M(II), dithiooxamide and formaldehyde 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 formaldehyde 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 (Grant N 96-03-32112), from the Center of Fundamental Sciences of Ministry of Education of Russian Federation (Grant N 97-0-9.2-13) and from International Soros Science Education Program (Grant d98-176) is acknowledged.

References

[1] O.V. Mikhailov and G.K. Budnikov, Bull. Chem. Soc. Jpn, **62**, 4016 (1989)
[2] O.V. Mikhailov, Monatshefte fur Chemie, **121**, 601 (1990)
[3] O.V. Mikhailov, Monatshefte fur Chemie, **122**, 595 (1991)
[4] O.V. Mikhailov, Russ. Chem. Revs., 1995, 64, 657 (1995)
[5] O.V. Mikhailov, Transition Metal Chem., **21**,.363 (1996)
[6] O.V. Mikhailov, Indian J. Chem., **30A**, 252 (1991)
[7] O.V. Mikhailov, Transition Metal Chem., **22**, 535 (1997)
[8] O.V. Mikhailov, Russian J. Coord. Chem., **18**, 1008 (1992)
[9] K. Nakamoto, Infrared and Raman spectra of inorganic and coordination compounds, 4th Edit., Wiley, New York, 1991.
[10] N.V. Gerbeleu and F.K. Zhovmir, Zh. Neorg. Khim., **27**, 547 (1982) (in rus.).
[11] N.V. Gerbeleu and V.B. Arion, Template Synthesis of Macrocyclic Compounds. Kishineu, Stiintsa, 1990 (in rus.)
[12] Shakir Mahammad, S.P.Varkey and F. Farha, Polyhedron, 1994, 14, 2319.

Received on January 25, 2000