Low-Temperature Template Synthesis of Nickel-Containing Heterocyclic Compound with 2,8-Dithio-3,5,7-triazanonandithioamide-1,9 in Gelatin-Immobilized Matrix

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Abstract

Template synthesis of nickel-containing heterocyclic compound with 2,8-dithio-3,5,7-triazanonandithioamide-1,9 in the nickel(II)hexacyanoferrate(II) gelatin- immobilized matrix at room temperature has been carried out.

Introduction

As known the template synthesis which afford the possibility of constructing metal-heterocyclic compounds of d-elements from simpler fragments (so-called ligand synthons), occurs 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) [1-5], would enable at least certain template processes to occur under soft conditions, primarily at room temperature. Indeed, such process was shown to take place [6-7] in the M(II) -dithiooxamide-formaldehyde (M= Co, Ni, Cu) and in the M(II)-dithiooxamide-acetone (M= Ni, Cu) triple systems in the corresponding $M_2[Fe(CN)_6]$-GIM. In principle, just one more ligand synthon for template synthesis in the M(II) -dithiooxamide-formaldehyde system, ammonia NH_3 is. We report in this communication that we have been able to perform such synthesis in the Ni(II)-dithiooxamide-formaldehyde-ammonia quaternary system in the $Ni_2[Fe(CN)_6]$-GIM and, as a result, to observe a formation of macrocyclic coordination compound of nickel(II) with a novel before unknown (N,N,S,S)- tetradentate ligand -2,8-dithio- 3,5,7-triazanonandithioamide-1,9.

Experimental

$Ni_2[Fe(CN)_6]$-GIM was synthesized as described in [1-5]. The synthesis of $NiC_6S_4N_5H_9$ occurs on contact of $Ni_2[Fe(CN)_6]$ -GIM with alkaline solutions (pH=11-12) containing dithiooxamide, formaldehyde and ammonia. The concentration of nickel(II)hexacyanoferrate(II) in the matrix was 0.1-2.0 mol· dm^{-3}, the concentration of dithiooxamide, formaldehyde and ammonia the solution was $(3.0\cdot 10^{-3} -5.0\cdot 10^{-2})$ mol· l^{-1}, $(1.5\cdot 10^{-3} -1.0\cdot 10^{-1})$ mol· l^{-1} and $(3.0\cdot 10^{-3} -5.0\cdot 10^{-2})$ 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, ethanol and dried at room temperature. Found (%): Ni, 17.6; C, 21.2; S, 37.7; N, 20.5; H, 2.4; O was not found. $NiC_6S_4N_5H_9$, calc. (%): Ni, 17.36; C, 21.31; S, 37.94; N, 20.71; H, 2.68. Characteristic bands in the IR-spectra (cm^{-1}): 675 (ν(C=S)); 1645 (ν(C=N)); 2860, 2940 ($\nu(CH_2)$); 3460 (ν(NH)). Mass spectrometry data: the molecular mass of compound synthesized is 338.2.

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 $\pm$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 previously described [8].

Results and Discussion

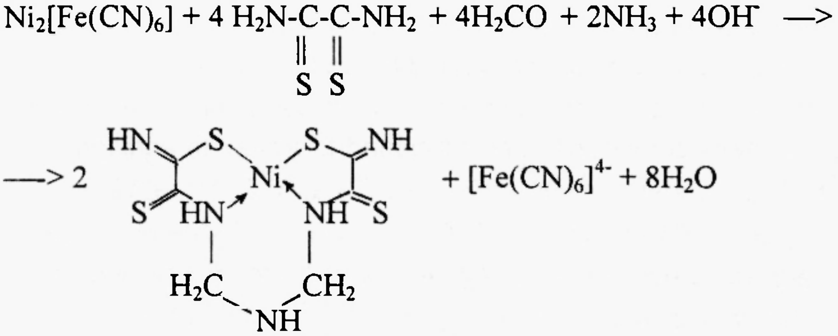
The analysis of $D^{\nabla} = f(C_F, C_L^0, t)$ kinetic curves of complexing where D^{∇} is the absorbance of the metal-chelate GIM, corresponding to C_F is the concentration of metal(II) hexacyanoferrate(II) in the matrix, C_L^0 is the dithiooxamide concentration in solution, t is the duration of the complexing process, for the various dithiooxamide: formaldehyde: ammonia molar ratio in the range 1: (0.5-2.0): (0.5-1.5) according to methodology [8], provides clear evidence that an addition of two dithiooxamide molecules, two formaldehyde ones and one ammonia molecule per Ni^{II} ion occurs in the course of the process. The resulting compound colours the polymeric masses of the GIM, which becomes brown. The UV-VIS-spectra of this compound contains 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 a violet compound (λ_{max} =580 nm) with spectral characteristics similar to those of the Ni(II)-dithiooxamide complex [1,2,5,6] is formed; at in absence of ammonia, a brown compound having $NiC_6S_4N_4OH_8$ composition, is formed as it was shown in our earlier work [6]. No doubt in this connection that formaldehyde as well as ammonia together with dithiooxamide and Ni^{II} 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 [5] allowed us to isolate dark-brown compound $NiC_6S_4N_5H_9$. According to the data mass spectrometry, the molecular mass of compound synthesized is 338.2 which accords with calculated value (338.127).

This compound is almost insoluble in water, ethanol, acetone, chloroform, benzene and tetrachloromethane, and poorly soluble in dimethylformamide, dimethylsulfoxide and hexamethylenephosphortriamide; the DTA data indicates that it is very stable and do not undergoes pyrolysis up to 600°C. The compound studied is diamagnetic and gives no ESR signals either at low (77 K, liquid nitrogen) or at room temperatures; such a fact allows us to assume that nickel in it has an oxidation degree equal to +2 with planar D_{2h}- or C_{2h}-coordination of donor centers around metal atom. The UV-VIS spectra of dimethylformamide solution of this compound are almost identical to those of their source GIM. Thus indicates that the immobilized compound is the same as that was isolated from immobilized matrices.

The IR spectra of the substance 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 nickel. In addition, the IR spectra of the compounds under study contains $\nu(C=S)$ at 675 cm^{-1} (usually observed at 705-570 cm^{-1}) and $\nu(C=N)$ band at 1645 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 $\nu(Ni\text{-}S)$ and $\nu(Ni\text{-}N)$ 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 $\nu(CH_2)$ at 2940 and 2860 cm^{-1} (according to literature data [9], these bands lie within the 2945-2915 and 2870-2845 cm^{-1} ranges, respectively). These $\nu(CH_2)$ bands are absent in the IR spectra of dithiooxamide and in any of the coordination compounds of Ni(II) with this ligand known to date [3]. Thus, one may conclude that compound under examination contain at least one CH_2- structural group; it is quite evident that the formation of Ni(II) coordination compounds with some novel ligand takes place. However, a band due to the stretching vibrations of the bridging C-O-C group at 1120-1100 cm^{-1} which, according to [6] is observed in a product of template synthesis in the Ni(II) - dithiooxamide-formaldehyde system, is absent in the IR spectra of compound studied.

Because compositions of compounds formed at the complexing in the Ni(II) - dithiooxamide-formaldehyde system ($NiC_6S_4N_4OH_8$ [6]) and Ni(II) -dithiooxamide-formaldehyde -ammonia one ($NiC_6S_4N_5H_9$) are different, it is obvious that in formation of this novel ligand, dithiooxamide and formaldehyde as well as ammonia participate. 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 and ammonia for at least 2 days, and no indications of a chemical process between dithiooxamide, formaldehyde and NH_3 was observed. Therefore, we have no doubt that the reaction between the reagents indicated above does not occur at all in absence of a metal ion. A similar plhenomenon is possible only in template synthesis [10,11]. Besides, dithiooxamide, formaldehyde and ammonia act as ligand synthons.

By taking into considerattion the all foregoing, the following scheme of template synthesis proceeding at an interaction between Ni(II), dithiooxamide, formaldehyde and ammonia in the $Ni_2[Fe(CN)_6]$-GIM and leading to formation of metalheterocyclic compound - (2,8-dithio-3,5,7-triazanonandithioamide-1,9)nickel(II), may be written:



$$Ni_2[Fe(CN)_6] + 4\,H_2N\text{-}\underset{\underset{S}{\|}}{C}\text{-}\underset{\underset{S}{\|}}{C}\text{-}NH_2 + 4H_2CO + 2NH_3 + 4OH^- \longrightarrow$$

It should be specially mentioned that processes of template synthesis between Ni(II), dithiooxamide, formaldehyde and ammonia occurs *only in GIM;* we failed to obtain these coordination compounds in the reaction of $Ni_2[Fe(CN)_6]$ 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. It is interesting that compound under examination is not formed at interaction between NH_3 and $NiC_6S_4N_4OH_8$ synthesized by method described in [6], either in solution or GIM.

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