Complexation of Nickel(II) with Dioximes in Ni₂[Fe(CN)₆] Gelatin-Immobilized Matrix Implants

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Abstract—The complexation of Ni(II) with α -dioximes, which occurs due to the contact of Ni₂[Fe(CN)₆] gelatin-immobilized matrix implants with water-alkaline (pH 12.0 ± 0.1) solutions of dimethylglyoxime, α -benzyldioxime, and nioxime (H₂L) used as ligands, was studied. It was shown that in each system, the [Ni(HL)₂], [Ni(H₂L)₂]²⁺, and [Ni(H₂L)]²⁺ coordination compounds were formed, while in the Ni(II)–dimethylglyoxime system at pH > 13, the [NiL(OH₂)₂] complex was additionally formed.

INTRODUCTION

The complexation of Ni(II) with dimethylglyoxime and its analogs has long ago and repeatedly been studied by numerous researchers beginning with L.A. Chugaev [1]. Generalizing data on these studies are presented, for example, in monograph [2]. These studies established that in an alkaline medium, dimethylglyoxime (I), α -benzyldioxime (II), and nioxime (III) form bischelate coordination compounds with Ni(II).

Complexation in systems containing Ni(II) and some of the α -dioxime in the metal-containing gelatinimmobilized matrix systems, in general, and in the nickel(II) hexacyanoferrate(II) systems, in particular, has not been discussed in the literature to date. Previously [3–9], we studied complexation in the Ni₂[Fe(CN)₆] gelatin-immobilized matrices (GIM) in the Ni(II)–dithiooxamide [3–5], Ni(II)–*N*,*N*-diphenylthiooxamide [6, 7], Ni(II)–*N*,*N*-diphenyldithiooxamide [5], and Ni(II)–quinoxaline-2,3-dithiol systems [7–9], which contain N,S-donating ligands capable of forming two deprotonated forms (HL⁻ and L^{2–}).

The authors of these works noted that, when the system contains an N,S-donating ligand capable of producing the L^{2-} form (dithiooxamide, *N,N*'-diphenyl-thiooxamide, quinoxaline-2,3-dithiol) in an aqueous solution, the character of complexation and the amount and stoichiometric composition of the coordination compounds that are formed in the Ni₂[Fe(CN)₆] GIM differ substantially from those for complexation in the same systems in solutions or in the solid phase. When the ligand exhibits no tendency to give the L^{2-} form in solution (N,N'-diphenyldithiooxamide), the indicated distinctions in complexation in a solution, solid phase, and gelatin-immobilized matrix are not observed.

These conclusions were further confirmed in paper [10], which was devoted to studying processes in the $Ni_2[Fe(CN)_6]$ –GIM systems containing Ni(II) and 8-mercaptoquinoline, as well as its various 5-substituted derivatives.

In this connection, it seems interesting to reveal the regularities of complexation in the Ni₂[Fe(CN)₆] gelatin-immobilized implants in the binary systems containing Ni(II) and N,O-donating ligands capable of forming two deprotonated forms (HL⁻ and L²⁻) in an aqueous solution. The α -dioximes can serve as examples of such compounds.

The interest in studying complexation in such systems is dictated by the following circumstances. On the one hand, the coordination compounds of Ni(II) with dimethylglyoxime, according to data in [11], are promising supports for nonsilver photographic images, which are mainly formed at the stage of "toning." The chemistry of this stage consists in the complexation between Ni(II) and an organic compound. On the other hand, dimethylglyoxime, α -benzyldioxime, and nioxime can play the role of a ligand and also of one of the so-called ligand synthons during template synthesis, resulting in supramolecular metal-capsulated coordination compounds [12].

Ni₂[Fe(CN)₆] GIM were synthesized according to a described procedure [3–6]. The obtained implants were brought in contact with water-alkaline solutions of the ligands with concentrations from 5.0×10^{-3} to 5×10^{-1} mol/l and with unchanged pH, 12.0 ± 0.1 . The duration of the implant–ligand solution contact was varied from 1 to 10 min at constant temperature (20.0 ± 0.1)°C. After the complexation was completed, the polymeric layers were washed with running water for 15 min and dried for 2–3 h at room temperature.

For the obtained metallocomplex gelatin-immobilized implants, we measured the absorbances (D^{\triangledown}) corresponding to the starting concentration of Ni₂[Fe(CN)₆] in the matrix $(c_{\text{Fe}}, \text{mol/dm}^3)$, the concentration of the ligand in a solution $(c_{\text{H}_2\text{L}}, \text{mol/l})$, and the time the implant was in contact with the solution (in fact, the time of complexation between Ni(II) and the corresponding ligand) (τ, min) . Then, the $D^{\blacktriangledown} = f(c_{\text{Fe}}, c_{\text{H}_2\text{L}}, \tau)$ functions were plotted in the two-dimensional coordinate cut-away views $[c_{\text{Fe}} = \text{const}, \text{variables } \tau_{\text{H}_2\text{L}}, \tau)$ variables τ] and $[c_{\text{H}_2\text{L}} = \text{const}, \text{varied } \tau, \text{variables } c_{\text{Fe}}]$. Further, according to a procedure described in [13], the stoichiometric coefficients of elementary steps of complexation in the studied binary systems were determined.

NiCl₂ · 6H₂O, K₃[Fe(CN)₆], trisubstituted sodium citrate Na₃C₆H₅O₇, and Na₂S₂O₃ · 5H₂O (analytical grade) were used for the preparation of solutions. In order to prepare alkaline solutions of **I**, **II**, and **III**, the corresponding α -dioximes (analytical grade) were used. Coordination compounds formed in the metal-lochelate GIM were isolated following a described procedure [4].

Mathematical analysis of the $D^{\vee} = f(c_{\text{Fe}}, c_{\text{H}_2\text{L}}, \tau)$

kinetic curves was performed on a Pentium-166MMX PC. Absorbances were measured on a Macbeth TD 504 photometer in the 0.1–5.0 interval with an accuracy of $\pm 2\%$ (rel. units). Electronic absorption spectra were recorded on Specord UV-VIS (Carl Zeiss) and PU-8710 (Philips) spectrophotometers in the 400- to 800-nm range.

RESULTS AND DISCUSSION

The contact of $Ni_2[Fe(CN)_6]$ GIM with alkaline solutions of dimethylglyoxime, α -benzyldioxime, and nioxime at pH 9–13 accompanied by the complexation process in the gelatin bulk results in the accumulation of substances, which color is pink-purple in the case of I and impart various shades of red-brown in the case of II and III.

Figures 1 and 2 present typical $D^{\triangledown} = f(c_{\text{Fe}}, c_{\text{H},\text{L}}, \tau)$ curves describing the kinetics of the process in the Ni(II)-dimethylglyoxime and Ni(II)-nioxime systems, respectively. These curves have simple shape and are characterized by a monotonic increase in D^{\blacktriangledown} with c_{Fe} , $c_{\rm HJL}$, and τ ; they do not contain any pronounced bents or inflections. The electronic absorption spectra of the gelatin layers obtained at the indicated pH values and any combination of c_{Fe} , $c_{\text{H}_{2}\text{L}}$, and τ are identical and coincide with the spectra of aqueous suspensions of nickel(II) bisdioximates. Both these facts indicate that the formation of one Ni(II) coordination compound with the corresponding ligand prevails in each system. Since a similar situation is also observed for the Ni(II)- α -benzyldioxime system, we shall further discuss the details of complexation for one of the three studied systems, namely, Ni(II)-dimethylglyoxime.

It is known that α -dioximes, depending on pH of the medium, can exist in four forms:

 $(\mathbf{R}^1, \mathbf{R}^2 = \mathbf{H}, \text{alkyl}, \text{aryl}, \text{aralkyl}, \text{and others})$

Since the pK_b , pK_{a1} , and pK_{a2} values [2] for α dioximes lie in the 0.1–2.5, 9.5–10.8, and 11.2–12.3 intervals, respectively, we can expect that, during the contact of Ni₂[Fe(CN)₆] GIM with alkaline solutions of dimethylglyoxime, Ni(II) complexes with HL⁻ or L²⁻ will be accumulated in the polymer bulk.

When the gelatin-immobilized implats obtained as a result of this contact are decomposed with proteolytic enzymes, the dark pink substance can be isolated from the GIM. According to chemical analysis data, this substance has the molecular formula $C_8H_{14}N_4O_4N_i$ corre-

sponding to the Ni(II) complex with dimethylglyoxime $Ni(HL)_2$. In the case of the two other studied systems, coordination compounds similar in composition were isolated from the gelatin bulks (table).

A computer-simulation analysis of the $D^{\blacktriangledown} = f(c_{\text{Fe}}, c_{\text{H}_2\text{L}}, \tau)$ kinetic plots for all systems studied showed that, although complexes with the molar ratio Ni(II) : ligand = 1 : 2 are formed during complexation, the limiting stage of the process is the formation of the 1 : 1 complexes. However, all our attempts to isolate com-



Fig. 1. Kinetic curves for the Ni(II)–dimethylglyoxime system: a, plot of D^{\triangledown} vs. τ at $c_{\text{Fe}} = (1-3)$ 0.55 and (1'-3') 1.50 mol/dm³ and (1, 1') $c_{\text{H}_2\text{L}} = 2.5 \times 10^{-2}$, (2, 2') 5.0 × 10^{-2} , and (3, 3') 2.0 × 10^{-1} mol/l; b, plot of D^{\blacktriangledown} vs. c_{Fe} at $c_{\text{H}_2\text{L}} = (1-3)$ 2.5 × 10^{-2} and (1'-3') 2.0 × 10^{-1} mol/l, $\tau = (1, 1')$ 1, (2, 2') 2, (3, 3') 4, and (4, 4') 6, and (5, 5') 10 min $(\lambda_{\text{max}} = 540 \text{ nm})$.

pounds in which Ni(II) : $HL^- = 1 : 1$ failed. This is caused, most likely, by the fact that in the Ni(HL)₂ complexes, where $H_2L = I$ –III, in addition to two five-membered Ncontaining metallocycles typical of α -dioximates, two six-membered N,O-containing metallocycles also appear due to the formation of intramolecular hydrogen bonds, which substantially increases the stability of the Ni(HL)₂ complexes. The [NiHL]⁺ complexes do not and cannot contain such additional six-membered cycles.

Taking into account the above said, we can suggest that, in the studied systems, the following complexation process is realized in the $Ni_2[Fe(CN)_6]$ GIM:





Fig. 2. Kinetic curves for the Ni(II)–nioxime system: a, plot of *D*[♥] vs. τ at $c_{\text{Fe}} = (1-3) 0.55$ and $(1'-3') 1.50 \text{ mol/dm}^3$ and $c_{\text{H}_2\text{L}} = (1, 1') 2.5 \times 10^{-2}$, $(2, 2') 5.0 \times 10^{-2}$, and $(3, 3') 2.0 \times 10^{-1} \text{ mol/l}$; b, plot of *D*[♥] vs. c_{Fe} at $c_{\text{H}_2\text{L}} = (1-3) 2.5 \times 10^{-2}$ and $(1'-3') 2.0 \times 10^{-1} \text{ mol/l}$ and $\tau = (1, 1') 1$, (2, 2') 2, (3, 3') 4, (4, 4') 6, and $(5, 5') 10 \text{ min} (\lambda_{\text{max}} = 540 \text{ nm})$.

 $(\mathbf{R}^1 = \mathbf{R}^2 = \text{methyl}, \text{ benzyl}, 1,2\text{-cyclohexylene})$

When acting with aqueous solutions of strong mineral acids with pH < 4 (without pronounced oxidative properties, in particular, diluted H_2SO_4 or HCl) on the GIM containing nickel(II) bis(dimethyl dioximate), the polymer bulk immediately changes its color from purple-pink to bluish green. This is accompanied by a considerable decrease in D^{\P} . When the HCl-treated gelatin layer is decomposed by proteolytic enzymes, it yields a gray-green product, whose chemical composition suggests that it contains two coordination compounds, $[Ni(H_2L)_2]Cl_2$ and $[Ni(H_2L)Cl_2]$, in a molar ratio close to 1 : 3. Both these compounds have long been known [14]. A similar situation is also observed in the systems with **II** and **III**.

Taking into account the composition established above for the compounds formed in the GIM, namely, $Ni(HL)_2$, the processes that occur under the action of acids on these GIM can be described as follows:

Compound	Molecular formula	Content (found/calculated), %			
		С	Н	N	Ni
Ni(II)–dimethylglyoxime					
[Ni(HL) ₂]	C ₈ H ₁₄ N ₄ O ₄ Ni	33.1/33.22	4.9/4.84	19.2/19.38	20.3/20.41
[NiL(OH ₂) ₂]	C ₄ H ₁₀ N ₂ O ₂ Ni	22.7/22.97	5.0/4.78	13.2/13.40	28.1/28.23
[Ni(H ₂ L) ₂]Cl ₂	C ₈ H ₁₆ N ₄ O ₄ Cl ₂ Ni	26.4/26.52	4.7/4.42	15.2/15.47	16.6/16.30
[Ni(H ₂ L)Cl ₂]	C ₄ H ₈ N ₂ O ₂ Cl ₂ Ni	19.3/19.51	3.6/3.25	11.1/11.38	24.2/23.98
$x[Ni(H_2L)_2]Cl_2 +$	<i>x</i> = 0.27	21.5/21.40	3.6/3.57	12.4/12.48	21.7/21.91
$y[Ni(H_2L)Cl_2]$	<i>y</i> = 0.73				
Ni(II)–α-benzyldioxime					
[Ni(HL) ₂]	C ₃₂ H ₃₀ N ₄ O ₄ Ni	65.0/64.81	5.1/5.06	9.6/9.44	10.1/9.90
[Ni(H ₂ L) ₂]Cl ₂	C ₃₂ H ₃₂ N ₄ O ₄ Cl ₂ Ni	57.2/57.71	5.0/4.81	8.4/8.41	8.4/8.81
[Ni(H ₂ L)Cl ₂]	C ₁₆ H ₁₆ N ₂ O ₂ Cl ₂ Ni	47.9/48.32	3.8/4.02	7.0/7.04	15.0/14.76
$x[Ni(H_2L)_2]Cl_2 +$	x = 0.24	50.7/50.57	4.2/4.21	7.3/7.37	13.4/13.33
$y[Ni(H_2L)Cl_2]$	<i>y</i> = 0.76				
Ni(II)-nioxime					
[Ni(HL) ₂]	C ₁₂ H ₁₈ N ₄ O ₄ Ni	42.0/42.28	5.4/5.28	16.6/16.43	17.0/17.23
[Ni(H ₂ L) ₂]Cl ₂	C ₁₂ H ₂₀ N ₄ O ₄ Cl ₂ Ni	35.0/34.82	4.9/4.48	13.2/13.54	14.4/14.19
[Ni(H ₂ L)Cl ₂]	C ₆ H ₁₀ N ₂ O ₂ Cl ₂ Ni	26.9/26.51	3.4/3.68	10.1/10.31	22.0/21.61
$x[Ni(H_2L)_2]Cl_2 +$	<i>x</i> = 0.26	28.5/28.67	4.0/3.98	11.3/11.15	19.8/19.68
$y[Ni(H_2L)Cl_2]$	<i>y</i> = 0.74				

Elemental analysis of coordination compounds formed in the Ni(II)– α -dioxime systems in Ni₂[Fe(CN)₆] gelatin-immobilized matrix implants



However, for the Ni(II)–dimethylglyoxime system, the chemical analysis data of the compounds isolated from the metallochelate GIM deviate from the theoretical values calculated for nickel(II) bis(dimethyl dioximate). This deviation is almost insignificant at pH 9–10 but becomes sufficiently great at pH 12 and higher. A similar deviation in the two other systems (with **II** and **III**) was not observed with changes in pH. However, it is remarkable that the electronic absorption spectra of the gelatin-immobilized matrices obtained in the

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Ni(II)–dimethylglyoxime system at pH 9 and 12 are virtually identical. At the same time, the storage of any matrix in a solution of NaOH or KOH with pH > 13 for 3-5 min at 20°C is accompanied by an almost insignificant change in the color of the gelatin matrix layer from purple-pink to carmine red.

The decomposition of the polymeric layer of the immobilized matrix obtained under these conditions allows one to isolate a carmine red substance from it, which, according to chemical analysis data, has a stoichiometric composition $C_4H_{10}N_2O_2Ni$ that coincides with the molecular formula of the [NiL(OH₂)₂] compound.

The analysis of the kinetic curves for this case shows that no additional dimethylglyoxime molecule was added. All these data suggest that, in the case of the Ni(II)–dimethylglyoxime system in an alkaline medium, one more process occurs to a certain extent in addition to reaction (2):



Note that an increase in the concentrations of ligands **I–III** in a solution that is in contact with the matrix even to a very high level $(5.0 \times 10^{-1} \text{ mol/l} \text{ and} \text{ higher})$ does not result in a substantial change in the shape of the kinetic curves in both the Ni(II)–dimeth-ylglyoxime system and other systems considered. It can be assumed that no other nickel(II) metallocomplexes with the studied α -dioximes are formed, in particular, those soluble in water, whose existence in aqueous solutions at pH > 12 is mentioned in [15, 16].

Thus, we can state that, unlike in the previously studied systems with N,S-donating ligands [3–9], in the Ni(II)–dimethylglyoxime, Ni(II)– α -benzyldioxime, and Ni(II)–nioxime systems during complexation in the Ni₂[Fe(CN)₆]–GIM, no other processes occur that differ from those taking place during complexation in solutions and the solid phase. This is probably explained by the fact that the considered N,O-donating ligands are capable of generating the L^{2–} form into a solution at rather high pH, although in insignificant amounts, but still sufficient for complexation with Ni(II). This occurs due to more strongly pronounced proton-donating properties of the N,O-donating ligands

as compared to the N,S-donating ligands [3–10]. As a result, not only the chelates with HL⁻ but also with L²⁻ are formed in a solution. This is why complexation in the Ni(II)- α -dioxime systems in the Ni₂[Fe(CN)₆]-GIM, although providing theoretically more favorable conditions for the formation of metallochelates with the L^{2-} form of the ligands, nevertheless, does not allow one to synthesize any new coordination compounds that are not detected during Ni(II) complexation with α -dioximes in aqueous solutions. In the case of N.Sdonating ligands where the content of the L^{2-} form in solutions is very high and the proton-donating ability of the corresponding Ni(II) metallochelates with the HL⁻ form is poorly pronounced even at very high pH values (14 and higher), the complexes with the L^{2-} form of the ligand in the inner coordination sphere are not formed in a solutions. (However, they are formed during complexation in the $Ni_2[Fe(CN)_6]$ -GIM when the gelatin molecules forming the polymer bulk acquire a negative charge due to the contact with an alkaline solution of the ligand [17]). As a result, some protons can migrate from the inner coordination sphere of the Ni(II) chelates with the HL⁻ and then can be binded by the gelatin molecules; as a consequence, Ni(II) metallochelates with L^{2-} can form.)

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