Enzyme-assisted matrix isolation of novel quinoxaline-2,3-dithiol nickel(II) complexes

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The complexation reaction occurring on the nickel(II) hexacyanoferrate(II), Ni$_2$[Fe(CN)$_6$], matrix immobilized in the gelatin layer, containing an alkaline solution of quinoxaline-2,3-dithiol has been studied. It has been shown that three different complex forms can be obtained: (Ni$_2$L)$_2$[Fe(CN)$_6$] (I), Ni$_2$(H$_2$O)$_2$ (II) and Ni(HL)$_2$ (III) (where HL and L are partially and fully deprotonated forms of ligand respectively), while the reaction carried out in solution produces only one compound, Ni(HL)$_2$. Chelate I (of an orange-yellow colour) is formed at ligand concentration ($C_L$) < 10$^{-3}$ mol dm$^{-3}$, hexacyanoferrate(II) nickel(II) concentration ($C_F$) > 3.0 $\times$ 10$^{-2}$ mol dm$^{-3}$ and a short (1-2 min) contact time of an immobilized matrix with ligand solution. Chelate II (of a pink-red colour) is formed at $C_L$ > 5.0 $\times$ 10$^{-3}$ mol dm$^{-3}$ and $C_F$ < 2.0 $\times$ 10$^{-2}$ mol dm$^{-3}$ and chelate III (blue-green colour) is formed upon the reaction of acidic solutions (pH 5) and the gelatin layer containing chelate II. Chelate I has only "a wing" of an electron transfer intensive band, the maximum of which is in the near UV region, and an indistinct shoulder at 430-440 nm, chelate II has $\lambda_{\text{max}}$ = 535 nm and chelate III has $\lambda_{\text{max}}$ = 630 nm and $\lambda_{\text{max}}$ = 700 nm. It has also been pointed out that complexation on the immobilized Ni$_2$[Fe(CN)$_6$] matrix in the Ni(II)-quinoxaline-2,3-dithiol system enables one to obtain more complex forms than with complexation in the same system in aqueous solutions.

Complexation reaction of Ni(II) with quinoxaline-2,3-dithiol(A) has been investigated to a limited extent$^1$-$^3$; mainly the attention has been focused on the possibility of using quinoxaline-2,3-dithiol as an analytical reagent for the determination of nickel. According to published reports, Ni(II) on reaction with quinoxaline-2,3-dithiol in aqueous solution forms only one insoluble chelate complex. This complex has nickel ion:ligand ratio of 1:2 and contains a partially deprotonated form of quinoxaline-2,3-dithiol. However, we have found that under specific conditions which have not been employed in preparative coordination chemistry earlier, it is possible to obtain other nickel(II) complexes with quinoxaline-2,3-dithiol. This paper deals with synthesis and study of these new chelate complexes.

Experimental

The object of this investigation was to study the complexation reactions occurring in Ni(II)-quinoxaline-2,3-dithiol system in a new medium, a nickel(II) hexacyanoferrate(II), Ni$_2$[Fe(CN)$_6$], matrix immobilized in a thin gelatin layer. For the preparation of a Ni$_2$[Fe(CN)$_6$] immobilized matrix, first the matrix was prepared starting from elemental silver. For this purpose, a photosensitive silver halide material on a transparent support was exposed to measured amounts of visible radiation. Then the exposed photographic material was processed in an alkaline solution of methanol or hydroquinone. Unreduced silver halide was removed from the photographic layer by an aqueous solution of sodium thiosulphate (Na$_2$S$_2$O$_3$). This gave an elemental silver matrix immobilized in gelatin (where gelatin was a binding agent for the photographic layer). To remove soluble impurities diffusing into the gelatin layer during both the processing stages, the matrix obtained was washed with running water. After washing, the silver matrix was treated with a solution containing hexacyanoferrate (III), chloride ions and a Ni(II) complex of citric acid. Silver contained in the matrix was transformed into silver chloride, and simultaneously the precipitation of nickel hexacyanoferrate (II) was observed, according to Eq. (1).

$$6[\text{Ni(HCt)}_3]^{-} + 4[\text{Fe(CN)}_6]^{3-} + 4\text{Ag} + 4\text{Cl}^- \rightarrow 3\text{Ni}_2[\text{Fe(CN)}_6] + [\text{Fe(CN)}_6]^{3-} + 4\text{AgCl} + 18\text{HCt}^3^-$$

... (1)

(where HCT$^3$ is the anion of citric acid). After washing with running water, the processed matrix was treated with an aqueous solution of sodium thiosulphate for the second time in order to remove silver chloride from the gelatin layer (Eq. 2),

$$\text{AgCl} + 2\text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag(S}_2\text{O}_3)_2]^{3-} + \text{Cl}^-$$

... (2)
As a result, silver was completely removed from the gelatin layer. However, \( \text{Ni}_2[\text{Fe}(\text{CN})_6] \) remained in the layer and formed an immobilized matrix. Finally, the gelatin layer with the matrix was washed with large amounts of water. The detailed procedure employed to obtain the \( \text{Ni}_2[\text{Fe}(\text{CN})_6] \) matrix is described in an earlier work.

The \( \text{Ni}_2[\text{Fe}(\text{CN})_6] \) matrix formed was treated with an alkaline solution of quinoxaline-2,3-dithiol (concentration, \( 10^{-3} \text{ to } 10^{-1} \text{ mol.dm}^{-3} ; \text{pH, } 12.0 \pm 0.1 \)). The temperature of the gelatin layer containing the matrix and the contacting solution was 20 ± 0.5°C. The duration of the contact varied from 1 to 10 min. Then the gelatin layer containing the complexes formed was washed with running water and dried for 2-3 hr at room temperature. Optical densities of the gelatin layer in transmitted light were measured on a Macbeth TD-504 densitometer (Kodak, USA). Complexation process was described in terms of \( D' = \frac{F(C_p, C_L, t)}{C_{F(C_p, C_L, t)} - 1} \) coordinates, where \( D' \) is optical density of the gelatin layer, corresponding to the concentration \( C_F \) of nickel hexacyanoferrate (II) in the matrix, ligand concentration, \( C_L \), in the solution and the reaction time, \( t \). Absorption spectra were measured on a Specord spectrophotometer.

Nickel (II) chelate complexes with quinoxaline-2,3-dithiol formed in the gelatin layer were released by processing the above layer in special enzyme solutions (\textit{Bacillus mesentericus}) capable of decomposing the gelatin binding agent but incapable of reaction with Ni(II) complexes contained in the layer. As a result, the gelatin was depolymerized and transferred into the solution; the complex contained in the layer was precipitated and could be easily removed from the solution. The experiments showed that the character of complexation processes proceeding on the matrix did not depend on the type of gelatin used, and the gelatin itself did not participate in the complexation reaction.

**Results and discussion**

At \( C_L < 10^{-3} \text{ mol.dm}^{-3} \), \( C_F > 3.0 \times 10^{-2} \text{ mol.m}^{-2} \) and a short (1-2 min) contact time of the immobilized \( \text{Ni}_2[\text{Fe}(\text{CN})_6] \) matrix with an alkaline solution of quinoxaline-2,3-dithiol, an orange-yellow chelate (I) is formed. The electronic spectrum of this compound in the visible region has only "a wing" of an electron transfer intensive band, the maximum of which is in the near UV-region, and an indistinct shoulder at 430-440 nm. At \( C_F < 2.0 \times 10^{-2} \text{ mol.m}^{-2} \) and \( C_L > 5.0 \times 10^{-3} \text{ mol.dm}^{-3} \), a pink-red chelate (II) is formed (\( \lambda_{\text{max}} = 535 \text{ nm} \)). Upon reaction with acid solutions (\( \text{pH} < 5 \)), the chelate (II) in the gelatin layer is immediately changed into chelate (III) as shown by change of colour from pink-red to cyan-blue (\( \lambda_{\text{max}} = 630 \) and 700 nm). However, chelate (I) does not change its colour upon interaction with acid solutions. The above described colour change indicates that three different insoluble nickel (II) complexes are formed with quinoxaline-2,3-dithiol (Fig. 1).

The analysis of \( D' = \frac{F(C_p, C_L, t)}{C_{F(C_p, C_L, t)} - 1} \) kinetic curves (at fixed \( C_F \) and variable \( C_L \) and \( t \)) shows that on contact with \( \text{Ni}_2[\text{Fe}(\text{CN})_6] \) matrix, one molecule of quinoxaline-2,3-dithiol in the case of chelate (I) formation, and two molecules in the case of chelate (II) per molecule of nickel (II) hexacyanoferrate(II) are coordinated to nickel (II). It can, therefore, be concluded that metal-ligand ratios in chelates (I) and (II) are 2:1 and 1:1, respectively. These ratios are confirmed by the chemical analysis data [Found: Ni, 28.42%; Fe, 6.59%; C, 31.90%; N, 16.83%; H, 1.02%. Req'd for \( \text{Ni}_4 \text{FeC}_2 \text{S}_4 \text{Ni}_3 \text{H}_8 ^{2+} \); Ni, 28.26%; Fe, 6.74%; C, 31.78%; N, 16.85%; H, 0.96%. For the pink-red compound: Found: Ni, 20.51%; C, 33.55%; N, 9.88%; H, 2.90%, Req'd for \( \text{Ni}_2 \text{C}_6 \text{N}_3 \text{H}_8 ^{2+} \); Ni, 20.55%; C, 33.44%; N, 9.75%; H, 2.79%]. In view of all the above mentioned facts, Eqs 3 and 4 can be suggested for the formation of chelates (I) and (II).

![Fig. 1 - Spectral characteristics of thin gelatin layers](image-url)
The cyan-blue compound (III) obtained from the gelatin layer showed the analytical data in conformity with 1:2 (metal: ligand) ratio [Ni, 13.10%; C, 42.96%; N, 12.83%; H, 2.30%. Reqd. for NiS4C16N4H10 Ni, 13.25%; C, 43.15%; N, 12.58%; H, 2.25%]. Spectral characteristics of this compound are consistent with those reported in literature for Ni (II) chelate with quinoxaline-2,3-dithiol, with nickel (II) ion/ligand ratio of 1:2. In this case formation of the compound can be described by the Eq. (5).

The transformation of (II) into (III) is a reversible process. Upon reaction with alkali, chelate (III) is again transformed into chelate (II). Simultaneously, the initial pink colour of the gelatin layer reduces in intensity (Eq. 6).

Thus, in the course of the complexation reaction on the immobilized Ni2[Fe(CN)6]-matrix in Ni (II)-quinoxaline-2,3-dithiol system the formation of three different complex compounds, e.g., (Ni2L)2[Fe(CN)6] (I), NiL(H2O)2 (II) and Ni(HL)2 (III) was observed (where HL- and L2- are partially and fully deprotonated ligand forms, respectively), while complexation in solution is known to produce only one compound, Ni(HL)2.

It is apparent that the complexation process occurring on the Ni2[Fe(CN)6] matrix provides for greater synthetic possibilities compared to that in solutions.

References
2 Clark R E D, Analyst, 83 (1958) 431.