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Electrophilic Substitution Ni(II) → M(II) in $Ni_2[Fe(CN)_6]$ Gelatin-immobilized Matrix Materials

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Abstract—The electrophilic substitution reactions Ni(II) → M(II) (M = Co, Cu, Zn, Cd) occurring in nickel(II) hexacyanoferrate(II) gelatin-immobilized matrix materials on their contact with aqueous solutions of corresponding chlorides MCl_2 were studied. During contact, Ni(II) is partly substituted by the other metal to form heteronuclear hexacyanoferrates(II) of nickel(II) and corresponding double-charged ions, and none of the studied reactions involves complete substitution of Ni(II) until the mononuclear hexacyanoferrate(II) $M_2[Fe(CN)_6]$ has formed.

During the last decade in the literature there appeared a series of publications, including the reviews [1–6], devoted to the synthesis and application of the so-called gelatinimmobilized matrix materials and complex formation in their bulk. However, most emphasis in these publications was put on nucleophilic substitution reactions or template synthesis, whereas electrophilic substitution reactions remained unexplored. The exceptions are communications [7, 8], in the first of which electrophilic substitution reactions were used to develop a general methodology for preparing metal hexacyanoferrate, and in the second, for preparing metal sulfide gelatin-immobilized matrix materials. No systematic investigations were as yet undertaken in this field, and the present study is aimed at filling this gap. Theoretically, reactions of this type may result in formation of heteronuclear hexacyanoferrates(II) containing atoms of three different *d* metals, which up to now, 30 years after the publication of the basic monograph [9], remain scarcely studied.

As a result of a 2-min or longer contact between nickel(II) hexacyanoferrate(II) gelatinimmobilized matrix implantants with aqueous solutions of Co(II), Cu(II), Zn(II), or Cd(II) chlorides, the initial light green color noticeably changes to emerald green, brown, bluish green, and greenish yellow, respectively. The kinetic curves $D = f(c_F, c^0_M, \tau)$ in the coordinate sections [c_F = const, varied c^0_M, variable τ] and [c^0_M = const, varied τ, variable c_F], where D is the optical density of the gelatin-immobilized matrix corresponding to the concentration of nickel(II) hexacyanoferrate(II) in the gelatin bulk (c_F, mol dm^{-3}), concentration of the *d*-metal (M) ion in the solution of this metal chloride contacting the matrix (c^0_M, M), and the contact time (τ, min) for the systems $Ni_2 \cdot [Fe(CN)_6]–CoCl_2$, $Ni_2[Fe(CN)_6]–CuCl_2$, $Ni_2 [Fe(CN)_6]– ZnCl_2$, and $Ni_2[Fe(CN)_6]–CdCl_2$ are presented in Figs. 1–4, respectively. In all cases, already at $t > 2$ min, D reaches a certain peak value and then remains practically unchanged on further contact of the $Ni_2(CN)_6]$ gelatin-immobilized matrix with the solution of MCl_2. This result can be explained either by formation of mechanical mixtures of nickel(II) and M(II) hexacyanoferrates, their proportion in each of these mixtures being established constant in a relatively short period of time or by formation of heteronuclear Ni(II) and M(II) *dd*-hexacyanoferrates(II) of a definite stoichiometric composition. By the shape of the kinetic cures $D = f(c_F, c^0_M, \tau)$, the above systems can be divided into two groups. The first includes $Ni_2[Fe(CN)_6]–CoCl_2$ and $Ni_2[Fe(CN)_6]–CuCl_2$, the saturation curves of which, i.e. the $D = f(c_F, c^0_M, \tau)$ plots in the coordinate section [c^0_M = const, varied τ, variable c_F] at τ 4–10 min (where, as noted above, D is independent of τ), fall between the $D = f(c_F)$ plots for hexacyanoferrates of nickel(II) and of that *d* metal M whose ions are present in the solution of MCl_2 contacting the matrix. Therewith, the former two curves locate closer to the curve of for the respective metal than to that for nickel(II) (Figs. 1 and 2). For the systems of this group, the UV and visible spectra of gelatin-immobilized matrices, obtained at τ > 6 min, are similar to the spectra of pure $M_2[Fe(CN)_6]$ and it is only at λ 600–800 nm that they become similar to those of nickel(II) hexacyanoferrate(II) (Fig. 5). The second group includes $Ni_2[Fe(CN)_6]–ZnCl_2$ and $Ni_2[Fe(CN)_6]–CdCl_2$, whose saturation curves are similar in shape with the $D = f(c_F)$ curve for $Ni_2[Fe(CN)_6]$ and lie both above this curve and the

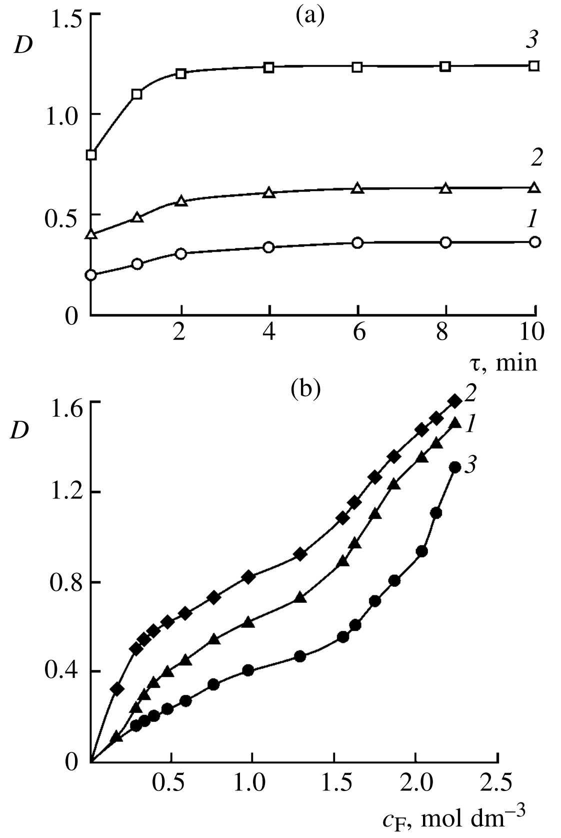

Fig.1. Curves $D = f(c_F, c^0_M, \tau)$ (a) in the coordinate section [c^0_M = const, varied c_F, variable τ] at c^0_M 7.0×10^{-2} M and c_F = (*1*) 0.40, (*2*) 1.00, and (*3*) 1.90 mol dm^{-3} and (b) in the coordinate section [c^0_M = const, varied τ, variable c_F] (*1*) at c^0_M 7.0×10^{-2} M and τ 6 min, and for (*2*) $Co_2[Fe(CN)_6]$ and (*3*) $Ni_2[Fe(CN)_6]$ in the system $Ni_2[Fe(CN)_6]$–Co(II). The optical densities are measured after a blue filter with a transmission maximum at 450 nm.

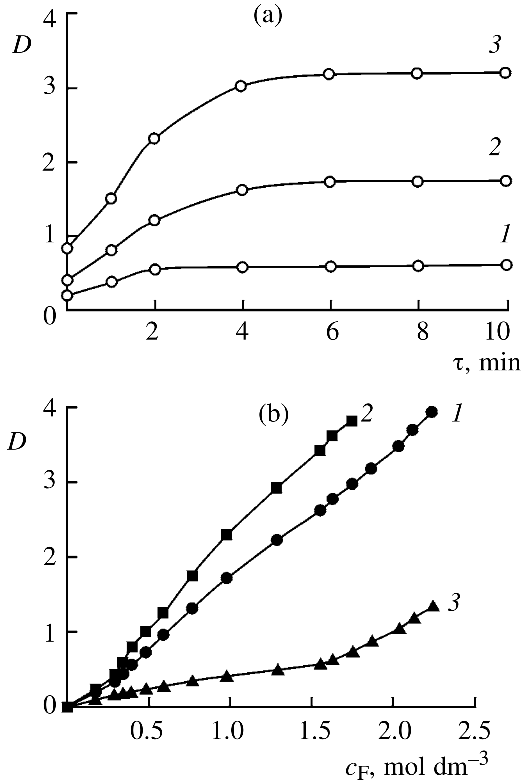

Fig. 2. Curves $D = f(c_F, c^0_M, \tau)$ (a) in the coordinate section [c^0_M = const, varied c_F, variable τ] at c^0_M 7.0×10^{-2} M and c_F (*1*) 0.40, (*2*) 1.00, and (*3*) 1.90 mol dm^{-3} and (b) in the coordinate section [c^0_M = const, varied τ, variable c_F] (*1*) at c^0_M 7.0×10^{-2} M and τ 6 min, and for (*2*) $Cu_2[Fe(CN)_6]$ and (*3*) $Ni_2[Fe(CN)_6]$ in the system $Ni_2[Fe(CN)_6]$–Cu(II). Optical densities are measured after a blue filter with a transmission maximum at 450 nm.

same curve for the corresponding mononuclear hexacyanoferrate(II) $M_2[Fe(CN)_6]$ (Figs. 3 and 4). The absorption maxima in the electronic absorption spectra of the products formed in gelatin-immobilized matrices in both $Ni_2[Fe(CN)_6]$–$ZnCl_2$ and $Ni_2[Fe(CN)_6]$–$CdCl_2$ at $\tau > 6$ min are shifted red relative to those for mononuclear hexacyanoferrates(II) and appear at λ 650–700 nm, which is typical for “normal” hexacyanoferrates(II) ($M_2[Fe(CN)_6]$) of cadmium(II), zinc(II), and nickel(II). Noteworthy, however, that the spectral curves of the reaction products both are similar in shape and lie nearer to the spectral curve for the starting $Ni_2[Fe(CN)_6]$ (Fig. 6).

Taking into consideration that in the course of the process under study the CN^- group remains unchanged, the resulting products can be assigned the general frrmula $Ni_nM_mFe_k(CN)_l$, where *n*, *m*, *k*, and *l* are positive numbers (not necessarily integers). The elemental and X-ray fluorescence analyses of the compounds isolated from the matrices under the above-described conditions suggest the molecular formulas $Ni_{1.61}Co_{0.38}Fe_{0.98}(CN)_{6.00}$, $Ni_{1.38}Cu_{0.57}Fe_{0.98}(CN)_{6.00}$, $Ni_{1.36}Zn_{0.57}Fe_{0.99}(CN)_{6.00}$, and $Ni_{1.66}Cd_{0.42}Fe_{0.91} \cdot (CN)_{6.00}$, which is close to the stoichiometric compositions $Ni_{13}Co_3[Fe(CN)_6]_8$, $Ni_{11}Cu_5[Fe(CN)_6]_8$, $Ni_{11}Zn_5[Fe(CN)_6]_8$, and $Ni_{12}Cd_3[Fe(CN)_6]_7(CN)_2$, respectively. With these data, it is easy to show that the experimental ratios between the numbers of nickel and iron atom (*n* : *k*) for the products of the reaction $Ni_2[Fe(CN)_6] + MCl_2$ are 1.65 (Co), 1.42 (Cu), 1.38 (Zn), and 1.81 (Cd). Had the above-noted observation that the $D = f(\tau)$ curves rather fast attain a plateau

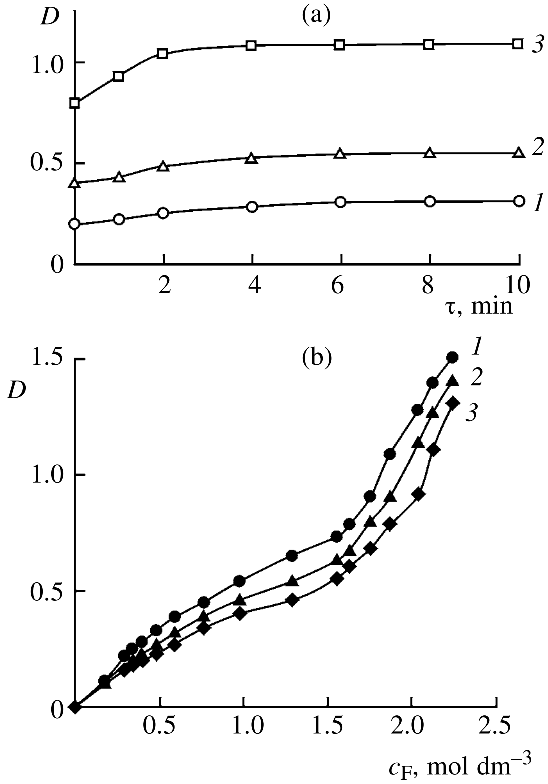

Fig. 3. Curves $D = f(c_F, c^0_M, \tau)$ (a) in the coordinate section [c^0_M = const, varied c_F, variable τ] at c^0_M 7.0×10^{-2} M and c_F (*1*) 0.40, (*2*) 1.00, and (*3*) 1.90 mol dm^{-3} and (b) in the coordinate section [c^0_M = const, varied τ, variable c_F] (*1*) at c^0_M 7.0×10^{-2} M and τ 6 min, and for (*2*) $Zn_2[Fe(CN)_6]$ and (*3*) $Ni_2[Fe(CN)_6]$ in the system $Ni_2[Fe(CN)_6]$–Zn(II). Optical densities are measured after a blue filter with a transmission maximum at 450 nm.

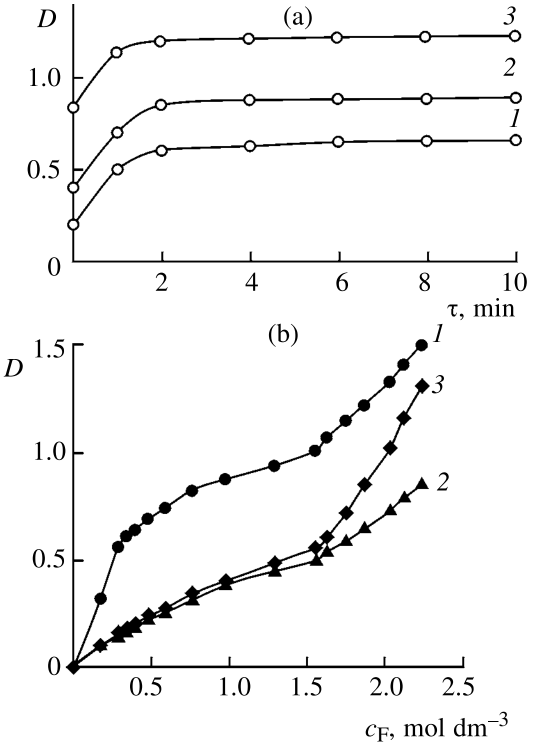

Fig. 4. Curves $D = f(c_F, c^0_M, \tau)$ (a) in the coordinate section [c^0_M = const, varied c_F, variable τ] at c^0_M 7.0×10^{-2} M and c_F (*1*) 0.40, (*2*) 1.00, and (*3*) 1.90 mol dm^{-3} and (b) in the coordinate section [c^0_M = const, varied τ, variable c_F] at (*1*) c^0_M 7.0×10^{-2} M and τ 6 min, and for (*2*) $Cd_2[Fe(CN)_6]$ and (*3*) $Ni_2[Fe(CN)_6]$ in the system $Ni_2[Fe(CN)_6]$–Cd(II). Optical densities are measured after a blue filter with a transmission maximum at 450 nm.

with increasing τ (see Figs. 1–4) been associated with the process of sorbtion of M(II) ions with the gelatin-immobilized nickel(II) hexacyanoferrate(II), this ratio would has been close to 2.00. This fact can be considered indirect evidence for the substitution of Ni(II) by M(II) in the $Ni_2[Fe(CN)_6]$ crystal lattice points in all the systems studied.

In the IR spectra of the above described reaction products for the systems $Ni_2[Fe(CN)_6]$–$CoCl_2$ and $Ni_2[Fe(CN)_6]$–$CdCl_2$, the stretching vibration frequencies of the cyano group are shifted red by 20–30 cm^{-1} relative to that of nickel(II) hexacyanoferrate(II) and equal 2070 and 2082 cm^{-1}, respectively. In two other studied systems, the position of the ν(CN) band in the region of 2102–2100 cm^{-1} remains unchanged, while its intensity increases considerably. The same increase in the intensity not attended with any shift of the signal is also observed for the ν(Fe–C) band at 594 cm^{-1} in the spectra of the products of the substitution of Ni(II) by Co(II) and Cu(II) in nickel(II) hexacyanoferrate(II). At the same time, the ν(Fe–C) band of the products formed in the systems $Ni_2\cdot[Fe(CN)_6]$–$ZnCl_2$ and $Ni_2[Fe(CN)_6]$–$CdCl_2$ is shifted red by 5–10 cm^{-1} to 600 and 602 cm^{-1}, respectively. In addition, the medium-intensity δ(Fe–CN) band in the IR spectra of the products formed by the substitution of Ni(II) by Cu(II), Zn(II), and Cd(II) in $Ni_2\cdot[Fe(CN)_6]$ gelatin-immobilized matrix is slightly shifted to 500, 492, and 496 cm^{-1}, respectively. In the system $Ni_2[Fe(CN)_6]$–$CoCl_2$, the δ(Fe–CN) band does not change its position but increases in intensity. The above-noted features of the IR spectra of the isolated substances led us to conclude that each of them is an individual compound, rather than a mixture of two mononuclear hexacyanoferrates(II) or a solid solution of one of them in another. Evidence for this conclusion was obtained from their X-ray analysis which

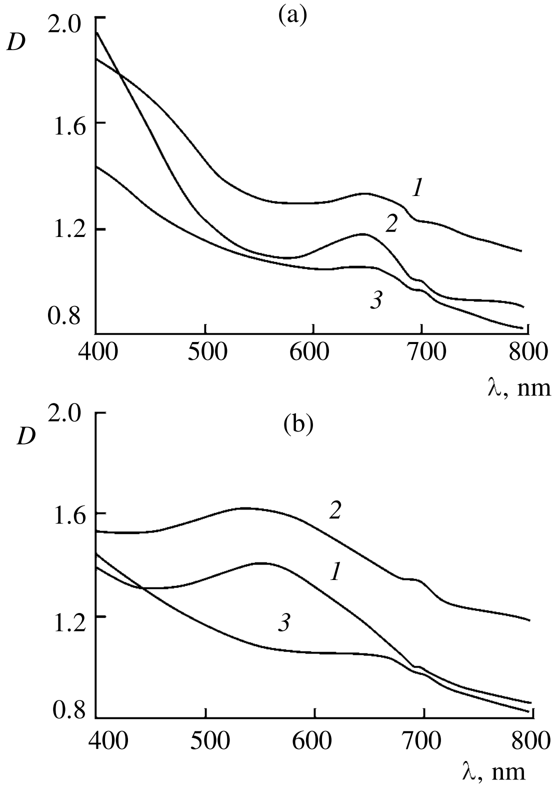

Fig. 5. Electronic absorption spectra of metal hexacyanoferrate(II) gelatin-immobilized matrices. (*a*) (*1*) System $Ni_2[Fe(CN)_6]$–$CoCl_2$, c_F 0.30 mol dm^{-3}, c_M^0 7.0 × 10^{-2} M, and τ 6 min; (*2*) individual $Co_2[Fe(CN)_6]$ (c_F 0.10 mol dm^{-3}); and (*3*) individual $Ni_2[Fe(CN)_6]$ (c_F 0.30 mol dm^{-3}). (*b*) (*1*) System $Ni_2[Fe(CN)_6]$–$CuCl_2$, c_F 0.30 mol dm^{-3}, c_M^0 7.0 × 10^{-2} M, and τ 6 min; (*2*) individual $Cu_2[Fe(CN)_6]$ (c_F 0.30 mol dm^{-3}); and (*3*) individual $Ni_2[Fe(CN)_6]$ (c_F 0.30 mol dm^{-3}).

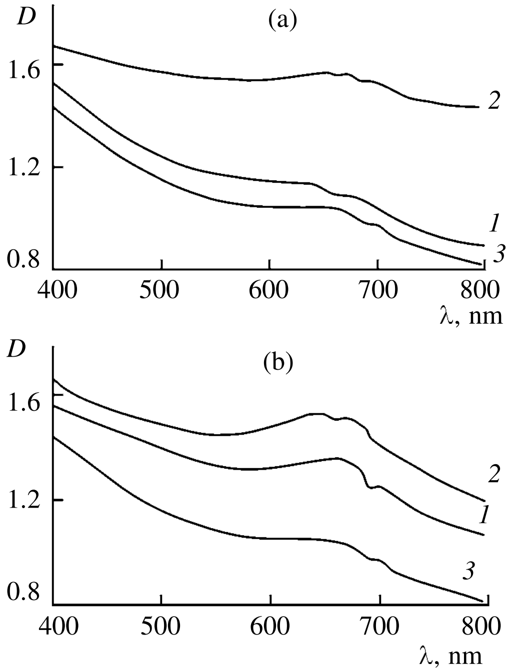

Fig. 6. Electronic absorption spectra of metal hexacyanoferrate(II) gelatin-immobilized matrices. (a) (*1*) System $Ni_2[Fe(CN)_6]$–$ZnCl_2$, (c_F 0.30 mol dm^{-3}, c_M^0 7.0 × 10^{-2} M, and τ 6 min); (*2*) individual $Zn_2[Fe(CN)_6]$ (c_F 0.30 mol dm^{-3}); and (*3*) individual $Ni_2[Fe(CN)_6]$ (c_F 0.30 mol dm^{-3}). (b) (*1*) System $Ni_2[Fe(CN)_6]$–$CdCl_2$ (c_F 0.30 mol dm^{-3}, c_M^0 7.0 × 10^{-2} M, and τ 6 min); (*2*) individual $Cd_2[Fe(CN)_6]$ (c_F 0.30 mol dm^{-3}); and (*3*) individual $Ni_2[Fe(CN)_6]$ (c_F 0.30 mol dm^{-3}).

established appearance of a single *dd*-heteronuclear hexacyanoferrate(II) in each of the $Ni_2[Fe(CN)_6]$–MCl_2 systems studied and ruled out the assumption that the observed phenomena relate exclusively to sorbtion of M(II) by nickel(II) hexacyanoferrate(II) and not to the electrophilic substitution Ni(II) → M(II) in the crystal lattice of $Ni_2[Fe(CN)_6]$. In the last case, the X-ray diffraction patterns of the product of contact of $Ni_2[Fe(CN)_6]$ with MCl_2 would be expected to almost concide with those the starting nickel(II) hexacyanoferrate(II). The interplanar spacings (*d*), relative line intensities (*I*, %), and reflection indices (*hkl*) of the mononuclear and *dd*-heteronuclear hexacyanoferrates(II) are listed in the table. These results provide enough reasons to suggest that, similar to the starting nickel(II) hexacyanoferrate (II), the resulting Ni,Co-, Ni,Cu-, Ni,Zn-, and Ni,Cd-heteronuclear hexacyanoferrates(II) have a cubic face-centered lattice with a likely space group *Fm*3*m*, since the X-ray patterns of each of these compounds contain no other reflections than those with even integral *hkl* indices. These four compounds are isostructural to each other and to the starting mononuclear nickel(II) hexacyanoferrate(II).

It can be shown that for the equilibrium constant K_{298} of the overall process (1) under the normal conditions, in accordance with the Guldberg and Waage law, Eq. (2) is valid.

$$Ni_2[Fe(CN)_6](c.) + M^{2+}(s.) \longrightarrow M_2[Fe(CN)_6](c.) + Ni^{2+}(s.), \quad (1)$$

$$K_{298} = K_s\{Ni_2[Fe(CN)_6]\}/K_s\{M_2[Fe(CN)_6]\}. \quad (2)$$

Here K_s is the solubility constant of the corresponding compound. Considering validity of the general rela-

X-ray powder diffraction data for mono- and heteronuclear *dd*-hexacyanoferrates(II)

Compound	*d*, Å	*I*, %	*hkl*
$Ni_2[Fe(CN)_6]$	5.02	94	200
	3.56	100	220
	3.04	8	311
	2.51	68	400
	2.25	14	420
	2.04	15	422
	1.78	11	440
	1.60	11	620
$Cu_2[Fe(CN)_6]$	5.68	7	111
	4.98	94	200
	3.52	100	220
	3.00	8	311
	2.88	12	222
	2.49	60	400
	2.23	16	420
	2.03	21	422
	1.77	15	440
	1.68	7	600
	1.58	13	620
$Ni_{11}Cu_5[Fe(CN)_6]_8$	5.05	100	200
	3.57	95	220
	2.53	68	400
	2.26	36	420
	2.06	26	422
	1.79	24	440
	1.685	21	600
	1.60	23	620
$Co_2[Fe(CN)_6]$	5.00	69	200
	3.54	100	220
	2.99	90	311
	2.51	39	400
	2.25	6	420
	1.78	14	440
	1.59	18	620
$Ni_{13}Co_3[Fe(CN)_6]_8$	5.04	100	200
	3.56	82	220
	2.52	49	400
	2.27	17	420
	2.06	11	422
	1.79	16	440
	1.69	21	600
	1.60	12	620
	1.46	3	444
	1.41	5	640
$Zn_2[Fe(CN)_6]$	6.41	15	
	6.25	14	
	5.41	98	
	4.48	46	
	4.07	100	
	3.75	6	
$Zn_2[Fe(CN)_6]$	3.61	42	
	3.45	12	
	3.09	27	
	2.70	15	
	2.51	18	
	2.31	14	
	2.18	16	
	2.09	5	
	2.02	9	
$Ni_{11}Zn_5[Fe(CN)_6]_8$	5.07	93	200
	4.50	5	
	4.16	16	
	3.58	100	220
	2.89	13	
	2.52	49	400
	2.26	41	420
	2.07	21	422
	1.79	24	440
	1.69	15	600
	1.60	31	620
	1.52	8	
$Cd_2[Fe(CN)_6]$	5.08	80	
	3.86	27	
	3.59	100	
	3.41	24	
	3.11	6	
	3.01	11	
	2.53	43	
	2.27	21	
	2.03	24	
	1.80	10	
	1.61	13	
$Ni_{13}Cd_3[Fe(CN)_6]_7–(CN)_2$	5.03	100	200
	4.71	3	
	3.56	79	220
	3.44	3	
	3.18	5	
	2.76	8	
	2.52	56	400
	2.26	24	
	2.06	20	
	1.96	3	
	1.79	12	
	1.69	11	
	1.60	20	
	1.53	7	
	1.50	2	
	1.42	7	
	1.35	8	642

tionship $K_s = 4S^3$, where S is solubility (mol l^{-1}), for hexacyanoferrates(II) $M_2[Fe(CN)_6]$ and using the known equation (3), we find Eq. (4).

$$\Delta G^0_{298} = -RT\ln K_{298}, \quad (3)$$

$$\Delta G^0_{298} = -3RT\ln\frac{S_{Ni}}{S_M}. \quad (4)$$

Here S_{Ni} and S_M are the solubilities of $Ni_2[Fe(CN)_6]$ and $M_2[Fe(CN)_6]$ in water, respectively. Taking into account that, according to [9], S_{Ni} (2.7×10^{-5} mol l^{-1}) is higher than the respective values for the other mononuclear hexacyanoferrates(II) $M_2[Fe(CN)_6]$, we can state that for any of the above M(II) ion process (1) is thermodynamically allowed. The same qualitative conclusion follows from the ΔG^0_{298} values calculated directly with data in [10]: –424.3, –33.0, –488.7, and –1684.5 kJ for Co(II), Cu(II), Zn(II), and Cd(II), respectively. In this connection, we can note that in none of the $Ni_2[Fe(CN)_6]$–MCl_2 systems studied, complete substitution of Ni(II) by M(II) and formation of the corresponding mononuclear hexacyanoferrate(II) of the composition $M_2[Fe(CN)_6]$ occur; this fact is evidence that the *dd*-heteronuclear hexacyanoferrates(II) resulting from the contact of $Ni_2[Fe(CN)_6]$ with MCl_2 are more stable than both the starting $Ni_2[Fe(CN)_6]$ and $M_2[Fe(CN)_6]$. This result is not unexpected, since, as already noted, mixed hexacyanoferrates(II) containing alkali metal ions and some of the *d*-metal ions M(II) are generally more stable than the corresponding mononuclear hexacyanoferrates(II) $M_2[Fe(CN)_6]$ [9]; moreover, the high kinetic inertness of the $[Fe(CN)_6]^{4-}$ anion, too, favors accumulation of mixed products. However, the substitution Ni(II) → M(II) inevitably produces some strains in the crystal lattice of nickel(II) hexacyanoferrate(II), which, on the substitution of Ni(II) with equal amounts of foreign M(II) ions will be the stronger, the greater the difference in the ionic radii and in the types of the $Ni_2[Fe(CN)_6]$ and $M_2[Fe(CN)_6]$ unit cells. In our case, the electrophilic substitution Ni(II) → M(II) takes place within a very small and severely limited reaction space of the gelatin-immobilized matrix [5, 6] which contains, as readily shown from the medium size of voids between the polypeptide chains of the gelatin molecules, no more than a hundred unit cells of the corresponding hexacyanoferrate(II). The reaction would thus be expected to proceed for as long as the strains developing in the crystal structure of the gelatin-immobilized coordination polymer $Ni_2 \cdot [Fe(CN)_6]$ allow the new structure resulting from this process to be adequately accomodated within these voids. In addition, it should also be taken into account that, according to [9,11,12], in the coordination lattice of $Ni_2[Fe(CN)_6]$, as well as in the isostructural cupric hexacyanoferrate(II), there are two types of Ni atoms. The former has an O_h enviroment of the CN groups, while in the latter, an D_{4h} enviroment with the CN groups located in the vertices of the biantiprism. Most likely, the reactions involve exchange of only one of these types of nickel atoms by other *d*-metal atom. In this connection, the following predictions can be made.

As the *a* parameters of the unit cells of $Ni_2 \cdot [Fe(CN)_6]$, $Cu_2[Fe(CN)_6]$, and $Co_2[Fe(CN)_6]$ are 10.18, 10.03, and 9.93 Å, respectively, and all these hexacyanoferrates(II) have cubic crystal lattices of the *Fm*3*m* type, then the degree of the substitution Ni(II) → M(II) in the case of Cu(II) must be higher than in the case of Co(II).

Mononuclear Zn(II) and Cd(II) hexacyanoferrates have crystal lattices differing from that of the starting $Ni_2[Fe(CN)_6]$, but the ionic radius of Zn(II) is markedly smaller than that of Cd(II); consequently, the insertion of zinc(II) ions into the cubic lattice of nickel(II) hexacyanoferrate(II) will produce weaker strains than the insertion of cadmium(II) ions. It can be noted that, according to [9], in spite of the lack of isomorphism between $Zn_2[Fe(CN)_6]$ and $Ni_2[Fe(CN)_6]$, Zn(II) can rather easily insert into the crystal lattice of the latter, and the degree of the substitution N(II) → M(II) in the case of Zn(II) must be higher than in the case of Cd(II).

Both of these conclusions are in full agreement with the experimental results. Moreover, as judged the elemental analyses, the stoichiometric composition of the synthesized heteronuclear cadmium(II)–nickel(II) hexacyanoferrate(II) $\{(Ni_{12}Cd_3[Fe(CN)_6]_7 \cdot (CN)_2\}$ differs from the other heteronuclear hexacyanoferrates $Ni_nM_m[Fe(CN)_6]_8$ ($n + m = 16$) obtained in the present work.

Noteworthy is the fact that the heteronuclear hexacyanoferrate(II) $\{Ni_{11}Cu_5[Fe(CN)_6]_8\}$ obtained by the substitution Ni(II) → Cu(II) differs in stoichiometric composition from the mixed copper(II)–nickel(II) hexacyanoferrate(II) $NiCu[Fe(CN)_6]$ reported in [9]. This provides good evidence for a specific role the gelatin-immobilized matrix plays in the reactions in hand, which we repeatedly emphasized in our previous publications dedicated to nucleophilic substitution reactions [2, 3, 6, 13, 14].

We performed special experiments to show that the kind of gelatin used as the polymeric binder in the immobilized matrix systems $Ni_2[Fe(CN)_6]$–MCl_2 has almost no effect on the character of electrophilic substitution in any of the studied systems. This fact allows us to conclude that gelatin as a ligand takes no part in the complex formation.

Unfortunately, the *dd*-heteroluclear hexacyanoferrates(II) formed under our experimental conditions all can be isolated from the corresponding gelatin-immobilized matrix materials only as fine powders unsuitable for single-crystal X-ray diffraction analysis. For this reason, the exact steric structure of these novel compounds is still to be established.

EXPERIMENTAL

The starting nickel(II) hexacyanoferrate(II)–gelatin-immobilized matrix materials were prepared by the procedure described in [13]. The concentration of their contacting aqueous solutions of Ni(II), Co(II), Cd(II), Cu(II), and Zn(II) chlorides was 0.05–0.10 M, contact time 1–10 min at (20.0±0.1)°C. After these operations were complete, the resulting immobilized matrices were washed for 15 min in running water, rinsed with distilled water, and dried at room temperature for 2–3 h. The optical densities of the samples were measured in transmitted light.

pH Measurements were performed on a pH-340 potentiometer.

The optical densities were measured on a Kodak Macbeth TD-504 photometer–densitometer with an accuracy of ±2% in the working interval of 0.1–5.0 units after a blue filter for maximum absorption. On the basis of these results, $D = f(c_F, c^0_M, \tau)$ plots were obtained, where D is the optical density of the gelatin-immobilized matrix, corresponding to the concentration of nickel(II) hexacyanoferrate(II) in the gelatin bulk (c_F, mol dm^{-3}), the concentration of the *d*-metal ion in the solution of its chloride, contacting the matrix (c^0_M, M), and to the contact time (τ, min). Examples of these plots in the coordinate sections [c_F = const, varied c^0_M, variable τ] and [c^0_M = const, varied τ, variable c_F] are presented in Figs. 1–4.

The electronic absorption spectra were registered on a Specord UV-Vis spectrophotometer at wavelengths of 400–800 nm and optical densities of 0.1–2.5 units, measured with accuracies of ±2 nm and ±3%, respectively. Examples of these spectra are given in Figs. 5 and 6.

The X-ray fluorescence analysis was performed on a VRA-20L spectrometer. The measurements were performed in the following conditions: X-ray tube with a tungsten anode; tube voltage 35 kV, current 25 mA; LiF-200 crystal; discriminating mode, level 0.5 V; relaxation time t 1 s; sensitivity 3×10^4 pulse s^{-1}; scan rate 1; automatic spectrum recording; external reference technique. The measured quantity in this case was the fluorescence intensity of the samples.

The IR spectra were measured on a Perkin–Elmer 16PCFT-IR Fourier transform spectrometer at 4000–400 cm^{-1} in Vaseline oil.

The X-ray studies were performed an instrumental and computing complex on the basis of a DRON-4-07 diffractometer (powder technique, Cu radiation, Ni filter, $3° \le 2\varepsilon \le 65°$, step 0.05 2ε). The interplanar spacings d and the I values were computed using the PDOS-1.1 program package. For studying the structure and properties of the *dd*-heteronuclear hexacyanoferrates(II) formed in the gelatin-immobilized matrices, the complexes were isolated from the matrices by treatment with solutions of protein-splitting enzymes (trypsin or *Bazillus mesentericus*) in accordance with the procedure in [15].

Found, %: C 21.9; Co 6.9; Fe 16.9; N 25.6; Ni 28.7. $C_{48}Co_3Fe_8N_{48}Ni_{13}$. Calculated, %: C 21.81; Co 6.69; Fe 17.20; N 25.43; Ni 28.87. Found, %: C 21.9; Cu 11.1; Fe 16.9; N 25.6; Ni 24.6. $C_{48}Cu_5Fe_8N_{48}Ni_{11}$. Calculated, %: C 21.62; Cu 11.91; Fe 17.05; N 25.21; Ni 24.21. Found, %: C 21.8; Fe 17.0; N 25.5; Ni 24.3; Zn 11.4. $C_{48}Fe_8N_{48}Ni_{11}Zn_5$. Calculated, %: C 21.54; Fe 16.99; N 25.12; Ni 24.13; Zn 12.22. Found, %: C 20.2; N 24.5; Fe 14.9; Ni 27.9; Cd 13.5. $C_{44}Cd_3 \cdot Fe_7N_{44}Ni_{12}$. Calculated, %: C 20.44; N 23.85; Fe 15.40; Ni 27.26; Cd 13.05.

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