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LETTERS
TO THE EDITOR

Reaction of Gelatin-immobilized Lead(II) Hexacyanoferrate(II) with Dithioxamide

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Reactions of gelatin-immobilized hexacyanoferrates(II) of *d*-elements with dithioxamide ($H_2N–CS–CS–NH_2$) have been repeatedly considered [1–3], but no data concerning specific features of complex formation in any systems consisting of a *p*-element ion and dithioxamide have so far been available. The only exception is the reaction between gelatin-immobilized lead(II) hexacyanoferrate(II) ($Pb_2[Fe(CN)_6]$) and dithioxamide in alkaline medium, which has been used to form silver-free images with attendant substantial increase in the photographic sensitivity [4]. In this connection it seemed important to investigate processes that take place on contact of gelatin-immobilized $Pb_2[Fe(CN)_6]$ with dithioxamide under the specific conditions created in lead(II) hexacyanoferrate(II) gelatin-immobilized matrices. We found that treatment of the latter [the concentration of lead(II) hexacyanoferrate(II) the matrix (c_f) was 0.1–1.5 mol dm^{-3}] with aqueous alkaline (pH > 12) dithiooxamide solutions ($c_L^0 < 10^{-5}$ M) produces a practically complete decomposition of the immobilized lead(II) hexacyanoferrate(II) into soluble anionic hydroxo complexes of Pb(II). This process is accompanied by a significant decrease in the optical density (*D*) of the implantant. Similar effect is observed on treatment of the lead(II)-hexacyanoferrate(II) matrices with aqueous solutions of NaOH and KOH with the same pHs. Such results implies that in the conditions under study complex formation is preceded by formation of Pb(II) hydroxo complexes.

In both cases, no significant accumulation of lead(II) hydroxide, expected to precede the formation of hydroxo complexes of this element, was observed in the immobilized matrix. Analysis of the $D = f(c_F, c_L^0, \tau)$ kinetic curves (τ is the time of matrix–solution contact) for the above range of c_F and c_L^0 and $\tau >$ 2 min revealed no dithioxamide addition. According to [5, 6], in the Pb(II)–OH$^-$ system at pH 11–13, the lead hydroxo complex $[Pb(OH)_3]^-$ is accumulated. The complex is readily soluble in water and can be easily removed from the polymeric matrix. In view of this fact, we can propose the following total reaction scheme:

$$Pb_2[Fe(CN)_6] + 6OH^- \longrightarrow [Pb(OH)_3]^- + [Fe(CN)_6]^{4-}. \quad (1)$$

On treatment of the same $Pb_2[Fe(CN)_6]$-gelatine-immobilized matrix (c_F 0.1–1.5 mol dm^{-3}) with alkaline dithioxamide solution (pH > 12, $c_L^0 > 2.5 \times 10^{-2}$ M) we observed, already at $\tau > 2$ min at 20°C, that the matrix changed its initial yellowish color to brownish black. Therewith, the *D* values steadily increased with c_F, c_L^0, and τ to reach certain limiting values. After destruction of the resulting matrices, a black material was obtained and identified as lead(II) sulfide by elemental analysis. The electronic spectrum of any matrices containing this compound coincides with the spectrum of gelatine-immobilized lead(II) sulfide, reported in [7]. This is in complete agreement with the elemental analysis and shows that the compound contained in the matrix and isolated from it are identical to each other. In the solution contacting with the matrix we found hexacyanoferrate(II) and oxalate anions and ammonia. Therefore, we can state that the reaction between gelatine-immobilized $Pb_2[Fe(CN)_6]$ and dithioxamide is described by Eq. (2).

$$Pb_2[Fe(CN)_6] + H_2N–CS–CS–NH_2 + 6OH^-$$
$$\longrightarrow 2PbS + [Fe(CN)_6]^{4-} + C_2O_4^{2-} + 2NH_3 + 2H_2O. \quad (2)$$

In the c_L^0 range 10^{-5}–10^{-2} M, the initially yellowish polymeric layer of the matrix gets yellowish brown just upon a very short contact (τ ~2 min). After destruction of the resulting matrices, a brown material was obtained and firmly identified as lead(II) sulfide. No other elements in amounts exceeding those for admixtures were found. But the $D = f(c_F, c_L^0, \tau)$ dependences for the indicated c_L^0 range occurred to be more complicated and cannot be unambiguously explained in terms of our mathematical model [8]. Presumably, whereas at $c_L^0 > 2.5 \times 10^{-2}$ M the gelatine-immobilized PbS is formed directly in the polymer bulk, at c_L^0 10^{-5}–10^{-2} M lead sulfide formed at the matrix–solution interface by the reaction between any of the water-soluble Pb(II) hydroxo complexes and dithioxamide, leading to the same products as reaction (2).

Synthesis of the starting $Pb_2[Fe(CN)_6]$-gelatine-immobilized matrixes had not been reported and was carried out by our original procedure, starting from silver-containing gelatine-immobilized matrices. The latter were treated with a solution containing 17.0 g l^{-1} of lead(II) trioxonitrate(V), 10.0 g l^{-1} of potassium hexacyanoferrate(III), and 1.5 g of 68% nitric acid for 3 min at 25°C.

The process is described by Eq. (3), the immobilized chemical compounds are shown in braces.

$$\{4Ag\} + 4[Fe(CN)_6]^{3-} + 2Pb^{2+} \longrightarrow \{2Ag_2Pb[Fe(CN)_6]\} + 2[Fe(CN)_6]^{4-}. \quad (3)$$

The martrix was then washed with running water for 5 min at 15–20°C and treated with 25% aqueous sodium thiosulfate for 5 min at 20°C. The silver(I) contained in the matrix was bound in a water-soluble complex $[Ag(S_2O_3)_2]^{3-}$ and removed to leave the target lead(II) hexacyanoferrate(II) in the matrix [reaction (4)].

$$\{2Ag_2Pb[Fe(CN)_6]\} + 8S_2O_3^{2-} \longrightarrow \{Pb_2[Fe(CN)_6]\} + 4[Ag(S_2O_3)_2]^{3-} + [Fe(CN)_6]^{4-}. \quad (4)$$

Finally, the matrix was washed with running water for 15 min and dried for 2–3 h at room temperature.

The isolation of immobilized chemical compounds from corresponding matrices was carried out according to the procedure described in [9]. Its use for isolating the immobilized substance from our obtained lead(II) hexacyanoferrate(II) matrices gave a yellowish material identified as $Pb_2[Fe(CN)_6]$ by elemental analysis. Found,%: C 11.3; Fe 9.1; N 13.5; Pb 67.0. $C_6FeN_6Pb_2$. Calculated,%: C 11.50; Fe 8.92; N 13.42; Pb 66.16.

For the compound isolated from the matrices formed at $c_L^0 >$ 2.5×10^{-2} M, found, %: Pb 86.3; S 13.6; for the compound isolated from the matrixes formed at c_L^0 $10^{-}5$–10^{-2} M, found, %: Pb 86.7; S 13.3. PbS. Calculated, %: Pb 86.60; S 13.40.

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