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# Effect of Coordination of Lead(II) Nitrilo-Tris-Methylenephosphonate Complexes on Their Thermal Behavior in the Compact State and in the Chemisorbed Layers on Steel Surface according to Thermogravimetry and X-ray Photoelectron Spectroscopy In Situ

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**Abstract**—The thermal decomposition of two lead(II) complexes with the same ligand, nitrilo-tris-methylenephosphonic acid $N(CH_2PO_3)_3H_6$, but with different coordination modes, in the compact state and as chemisorbed layers on a steel surface, was studied by TGA and X-ray photoelectron spectroscopy. Using these methods, the thermal decomposition was conducted in the spectrometer chamber with simultaneous recording of the electronic spectra in situ. The differences in the thermochemical behavior of lead(II) complexes were elucidated.

**Keywords:** lead(II) nitrilo-tris-methylenephosphonates, thermal decomposition, thermogravimetry, X-ray photoelectron spectroscopy in situ, chemisorption

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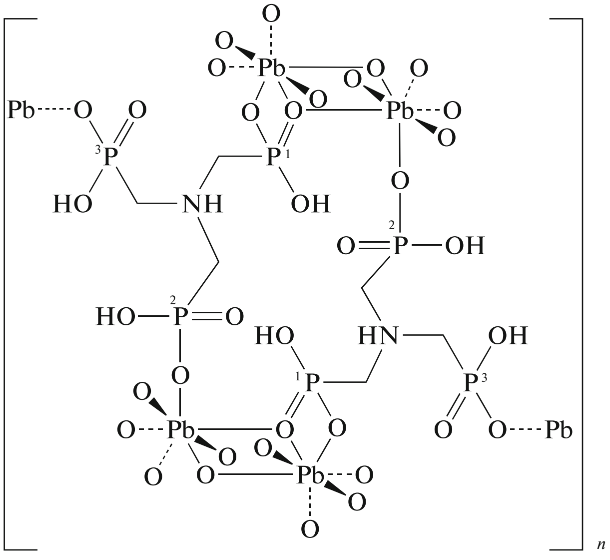
## INTRODUCTION

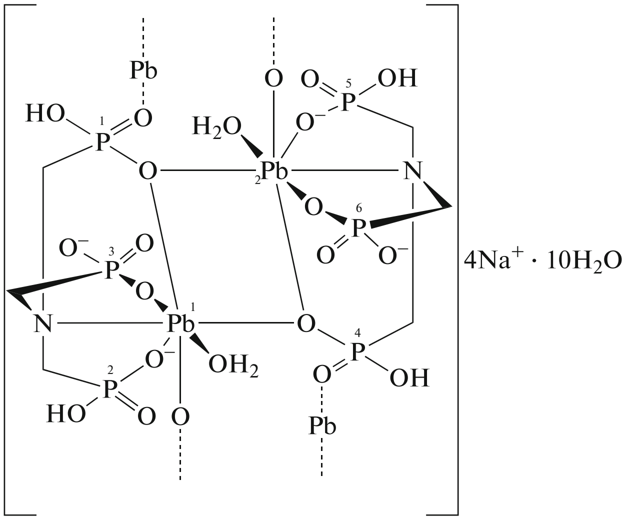
The effect of coordination of the central atom on the reactivity and mechanisms of reactions of complex compounds is an important problem of coordination chemistry. Metal complexes of nitrilo-tris-methylenephosphonic acid (N(CH2PO3)3H6; below NTP) are of considerable practical interest, as some compounds of this class act as steel corrosion inhibitors in aqueous media [1–5] and as bactericidal agents [6]. The activity of NTP complexes as corrosion inhibitors is usually attributed to the inner-sphere substitution reactions that occur on contact with metal surface and to the formation of heteropolynuclear metal complexes [7, 8]. Hence, for the preparation of corrosion inhibitors with a pre-specified high stability and efficiency based on NTP derivatives, it is necessary to study the chemistry of interactions of NTP complexes with the steel surface and the thermal stability and the mechanism of thermal decomposition of the complexes.

Lead(II) is a rare example of a complexing agent with a filled *s*-level and vacant *p*- and *d*-levels of the valence electron shell, which accounts for a number of specific structural features of the coordination compounds it forms. In particular, the 6*s* lone pair of Pb(II) can be located either symmetrically or asymmetrically, the degree of asymmetry of the 6*s* pair position and, hence, of the Pb(II) coordination environment increases with increasing electronegativity of the donor coordination sites [9, 10].

We performed the synthesis and X-ray diffraction study of Pb(II) complexes with the same ligand, but different coordination modes. Depending on the pH of the reaction medium, NTP is coordinated to Pb(II) by either only the phosphonate $PO_3H$ groups (complex **I**) or the N atom and the $PO_3$ groups (complex **II**).



**(I)**



**(II)**

According to X-ray diffraction data, all the acid residues of the ligand and all Pb(II) atoms in **I** are symmetrically equivalent. In **II**, two acid residues of the ligand and two Pb(1) and Pb(2) atoms are symmetrically non-equivalent; therefore, differences can be detected by structure-sensitive methods.

On going from **I** to **II**, the asymmetry of the Pb(II) coordination environment markedly decreases as a result of replacement of one O atom by less electronegative N atom. According to the distortion theorem [11, 12], a decrease in the distortion of the coordination polyhedron results in a decrease in the average distance between the Pb atom and the coordination sphere atoms. This may presumably lead to higher strength or, at least, to different reactivities of complexes **I** and **II**.

Various types of thermogravimetric analysis (TGA) have long proven to be efficient for investigation of thermochemical transformations. However, most often, TGA is unable to reliably identify the changes of atomic and molecular structure and is inapplicable for investigation of thin surface layers.

This communication presents the results of a comparative study of the thermal stability and mechanism of thermal decomposition of complexes **I** and **II** and their adsorption layers on the steel surface using both TGA and structure-sensitive X-ray photoelectron spectroscopy (XPS) in situ.

## EXPERIMENTAL

**Synthesis of I.** A solution of twice recrystallized NTP (0.025 mol) was added with continuous vigorous stirring to a solution of analytical grade lead(II) acetate (0.025 mol). The reaction mixture was heated to 95–100°C and filtered, and compound **I** was crystallized upon cooling and evaporation of the filtrate.

**Synthesis of II.** A solution of NTP (0.025 mol) and NaOH (0.1 mol) was added with continuous vigorous stirring to basic lead(II) carbonate freshly precipitated from lead(II) acetate with excess sodium carbonate (analytical grade). The reaction mixture was heated until lead(II) carbonate completely dissolved and then filtered. Compound **II** was isolated by evaporation at room temperature.

The thermogravimetric analysis of **I** and **II** was carried out under argon on a Shimadzu DTG-60H automated diffractometer in the 30–500°C range at a heating rate of 3°C/min.

X-ray photoelectron spectra of complexes **I** and **II** and their adsorption layers on the steel surface were recorded on a domestic RES-3 X-ray photoelectron spectrometer developed at the Physical-Technical Institute (Ural Branch, Russian Academy of Sciences). A specific feature of this instrument is the use of a magnetic iron-free energy analyzer with a nonuniform magnetic field. The energy analyzer solenoids are located outside the vacuum chamber containing the sample, toroidal focusing section, and the collector of photoelectrons. Therefore, evolution of thermal decomposition products does not affect the operation of energy analyzer, which allows in situ investigation of the chemical transformations that occur on sample heating. Excitation was performed by Al$K_\alpha$ radiation ($h\nu$ = 1486.6 eV). Samples of free complexes **I** and **II** were deposited as several micrometer-thick compact layers on a gold (99.9%) substrate. The adsorption layers on the steel surface were fabricated by immersing the steel 20 (GOST 1050-2013) substrates into 1% aqueous solutions of complexes **I** and **II** for 10–15 min followed by removal of the remaining solution with fil-

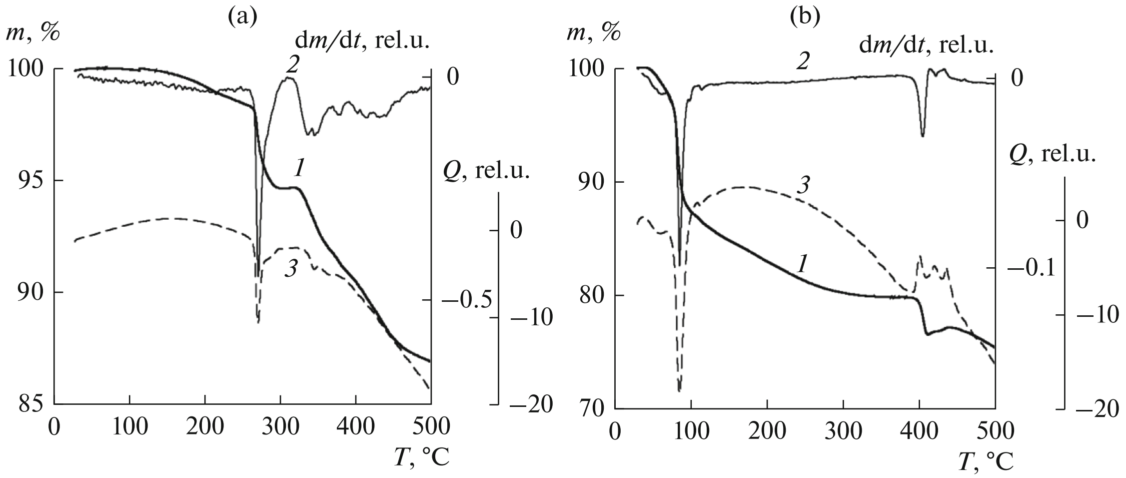


**Fig. 1.** Thermogravimetric analysis of complexes (a) **I** and (b) **II**: (*1*) sample weight, (*2*) weight change, and (*3*) heat effect as functions of temperature.

ter paper. After drying of the obtained layers, the samples were placed into the spectrometer chamber. The residual pressure in the chamber was $10^{-4}$–$10^{-3}$ Pa. The core level C1*s*, N1*s*, O1*s*, P2*p*, Pb4*f*, Na2*s*, and Fe$2p_{3/2}$ spectra and valence band spectrum were recorded at sample temperatures of 75 to 450°C. The energy analyzer was calibrated against the C1*s* spectra (binding energy $E_B$ = 285.0 eV) and Na2*s* ($E_B$ = 63.5 eV). The background and inelastic scattering corrections were applied according to Shirley [13]. The statistic processing of the results was done taking the Poisson distribution law for the photoelectron flux intensity. The ticks show the 95% confidence intervals for experimental spectral intensity.

## RESULTS AND DISCUSSION

The results of TGA of complexes **I** and **II** are presented in Fig. 1. The sample of **I** shows no weight change or thermal effects below 150°C. The P2*p* and Pb4*f* spectra of complexes **I** and **II** under heat treatment in situ are shown in Fig. 2. The maximum intensity of the N1*s* spectrum corresponds to the binding energy $E_B$ = 401.5 eV. The O1*s* spectrum is composed of two components with $E_B$ = 531.9 and 533.8 eV, corresponding to deprotonated and protonated oxygen atoms of the $PO_3H$ groups, respectively. The P2*p* spectrum consists of two components ($E_B$ = 133.1 and 134.2 eV) with 2 : 1 intensity ratio. The full width at half maximum (FWHM) for each component reaches 2.2 eV due to the own spin–orbit splitting of each component into a P$2p_{3/2}$–P$2p_{1/2}$ doublet (Δ = 0.8 eV). The components with $E_B$ = 133.1 and 134.2 eV refer apparently to the phosphorus atoms in different local environments: the binding energy $E_B$ = 133.1 eV is inherent in the P(1) and P(2) atoms that coordinate two Pb atoms, and $E_B$ = 134.2 eV corresponds to P(3) coordinating one Pb atom. The spectrum shows a Pb$4f_{7/2}$–Pb$4f_{5/2}$ doublet with component intensity ratio of 5 : 4. The component binding energies ($E_B$ = 139.0 and 143.8 eV, Δ = 4.8 eV) are typical of Pb(II) compounds [14]. The FWHM of each component is 1.7 eV, which attests to equivalence of all Pb atoms and supports the X-ray diffraction data.

In the 150–260°C range, complex **I** loses $0.5H_2O$ with an exothermic effect, which is indicative of intermolecular condensation of $PO_3H$ groups to give the polyphosphate P–O–P bridge. In the 260–300°C range, one more $H_2O$ molecule is eliminated with a pronounced endothermic effect. The XPS show a change in the structure of **I** in the same temperature range. At 280°C, the O1*s* spectrum has a component with a maximum at $E_B$ = 530.2 eV, corresponding to P–O–P-bridge oxygen atoms. In the P2*p* spectrum, only one component remains with $E_B$ = 134.2 eV and FWHM of 2.2 eV, indicating a substantial structural change. The spectra of other elements do not change in this temperature range.

At 330–400°C, two feebly pronounced endotherms are observed; the weight losses correspond to elimination of $H_2O$ and $1/2N_2$ from compound **I**. At about 450°C, the slope of the thermal effect curve increases, indicating melting of decomposition products of **I**. The weight of the residue corresponds to the $0.4PbO \cdot 0.6P_2O_5$ composition. According to XPS data, the N1*s* line is absent at 360°C. The O1*s* ($E_B$ = 530.2, 531.9, and 533.8 eV), P2*p* ($E_B$ = 134.2 eV), and Pb4*f* spectra ($E_B$ = 139.0 and 143.8 eV) are characteristic of the lead phosphate glass $0.4PbO \cdot 0.6P_2O_5$ [15].

The thermochemical behavior of complex **II** sharply differs from that of **I**. In the 45–120°C range, all ten molecules of the water of crystallization are eliminated: $-2H_2O$ (45–67°C), $-7H_2O$ (67–110°C), and –

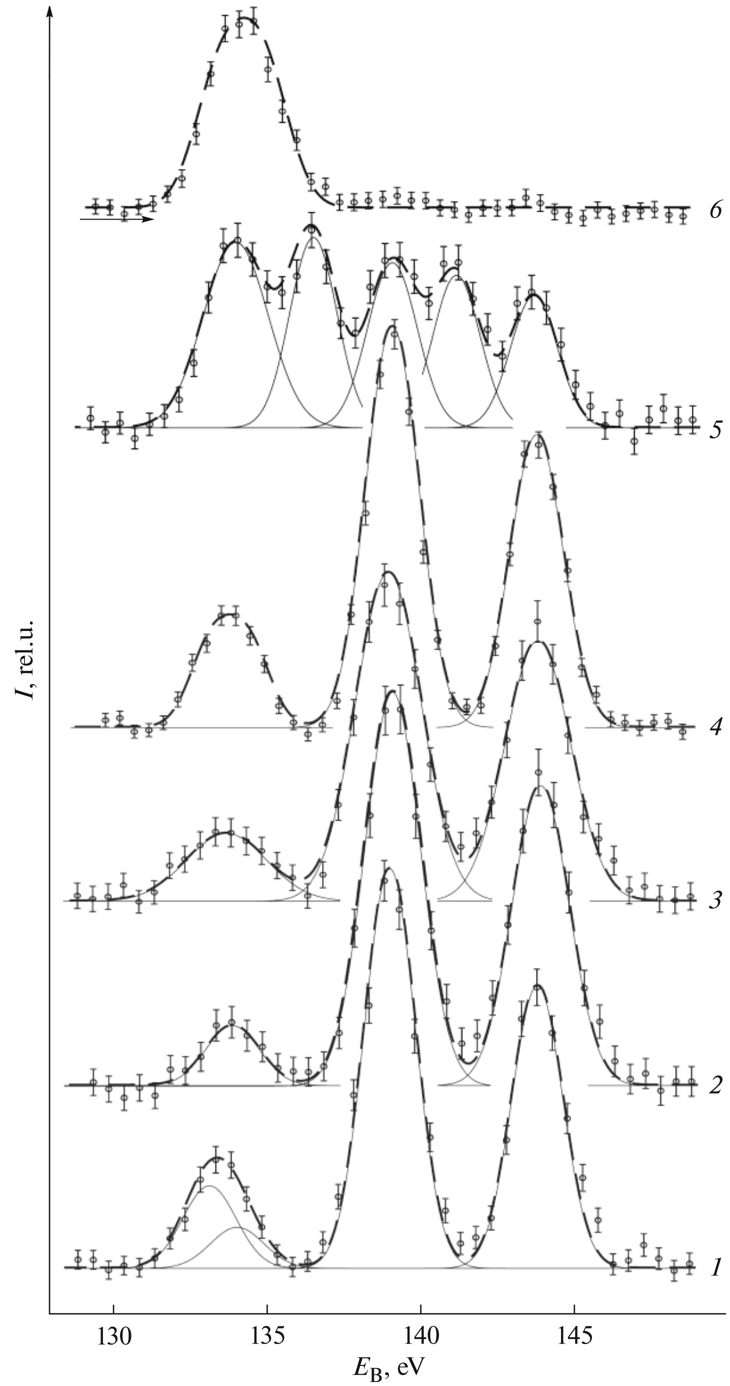


**Fig. 2.** X-ray photoelectron spectra of complexes (*1*–*3*) **I** and (*4*–*6*) **II** at (*1*) 150, (*2*) 280, (*3*, *6*) 360, (*4*) 100, and (*5*) 200°C.

$H_2O$ (110–120°C). The maximum intensity of the N1*s* spectrum corresponds to $E_B = 399.6$ eV, which is 1.9 eV lower than that for complex **I**; the shift of the N1*s* spectrum to lower energy is caused by involvement of the nitrogen atom in the coordination to Pb(II). The FWHM of the O1*s* line ($E_B = 532.1$ eV) is 2.6 eV, which is indicative of non-equivalent oxygen atoms in structure **II**. The P2*p* spectrum ($E_B = 132.1$ eV, FWHM of 2.3 eV) contains only one component split into a P2$p_{3/2}$–P2$p_{1/2}$ spin–orbit doublet; this confirms the similarity of the local atomic environments of all phosphorus atoms in **II**. The position of the Pb4$f_{7/2}$–Pb4$f_{5/2}$ doublet ($E_B = 138.7$ and 143.5 eV) is generally typical of Pb(II) compounds [14]; however, the FWHM of each component, which reaches 2.2 eV, attests to non-equivalence of the Pb(1) and Pb(2) atoms; this is consistent with X-ray diffraction data. The Na2*s* spectrum is represented by one narrow line with $E_B$ = 63.8 eV.

At 120–300°C, $2H_2O$ are eliminated from the Pb(II) coordination sphere and $2H_2O$ are evolved upon the intermolecular condensation of $PO_3H$ groups to give P–O–P bridges. At 200°C, the intensity of Pb4*f* doublet components with $E_B$ = 138.7 and 143.5 eV inherent in Pb(II) decreases, and new more intense components with $E_B$ = 136.0 and 140.8 eV, corresponding to lead metal, appear.

At 390–410°C in the TGA experiment, $N_2$ is eliminated; after that, the sample weight gain is observed (two peaks in the d*m*/d*t* curve), apparently due to partial oxidation of lead metal with the oxygen impurity present in argon. The spectra recorded in vacuum show the elimination of nitrogen and evaporation of lead metal, which is manifested as a decrease in the N1*s* and Pb4*f* line intensity to zero. The FWHM of the P2*p* spectrum increases to 3.2 eV, which is indicative of differences in the local atomic environments of phosphorus atoms. The Na2*s* spectrum varies during the thermal decomposition of complex **II**. The products of decomposition of **II** are identified spectroscopically as sodium metaphosphate and metaphosphite.

Thus, comparison of the TGA data with the results of XPS in situ carried out in parallel provide more in-depth and reliable knowledge of the thermochemical behavior of lead complexes with different coordination modes. According to X-ray diffraction data, the replacement of N atom by the more electronegative O atom in the Pb(II) coordination sphere decreases its asymmetry and reduces the average distance between the Pb atom and the coordination sphere atoms. Contrary to expectations, this structural change does not lead to increasing chemical stability of the lead coordination environment: compound **II** eliminates lead metal at 200°C, whereas on heating of complex **I**, the Pb–O bonds are retained up to 360°C.

The preliminary data obtained in this way can be used to perform an in situ XPS study of the structure and mechanism of thermal decomposition of thin layers of complexes **I** and **II** chemisorbed on the steel surface, which cannot be investigated by TGA.

The P2*p*, Pb4*f*, and Fe2$p_{3/2}$ spectra of a complex **I** layer chemisorbed on the steel surface are shown in Fig. 3. At 75°C, the N1*s* and O1*s* spectra of a layer of **I** on the steel surface are similar to the spectra of free complex **I**. The P2*p* spectrum contains only one component with $E_B$ = 132.1 eV and FWHM of 1.8 eV. The electron density on the phosphorus atoms of complex **I** deposited on the steel surface becomes equal via the interaction of phosphorus with the surface iron atoms, that is, complex **I** chemically reacts with the steel surface to give surface donor-acceptor complexes. The Pb4$f_{7/2}$–Pb4$f_{5/2}$ doublet has $E_B$ = 137.8 and 142.6 eV, which is indicative of a slight increase in the electron density on the Pb(II) atoms upon the reaction of **I** with the steel surface. The FWHM of each component, which reaches 2.0 eV, attests to the possible non-equivalence of the local environment of some Pb atoms. The Fe2$p_{3/2}$ spectrum is not observed at 75°C; this indicates that the thickness of the chemisorbed layer of **I** exceeds the analytic depth of the XPS method (4–6 nm).

At 150°C, a component with $E_B$ = 133.5 eV and FWHM of 1.8 eV appears in the P2*p* spectrum, which attests to oxidation of some phosphonate groups to phosphate groups. The electron density on the phosphorus atoms of complex **I** deposited on the steel surface becomes equal via the interaction of phosphorus with the surface iron atoms, that is, complex **I** chemically reacts with the steel surface to give surface donor-acceptor complexes. The Pb4$f_{7/2}$–Pb4$f_{5/2}$ doublet has $E_B$ = 137.8 and 142.6 eV, which is indicative of a slight increase in the electron density on the Pb(II) atoms upon the reaction of **I** with the steel surface. The FWHM of each component, which reaches 2.0 eV, attests to the possible non-equivalence of the local environment of some Pb atoms. The Fe2$p_{3/2}$ spectrum contains components with $E_B$ = 707.5 and 710.5 eV, corresponding to iron metal and Fe(II), respectively. It is known [16, 17] that upon the reaction of iron salts with phosphonate ligands, Fe is stabilized in the oxidation state +2; apparently, the oxidized state of iron observed in the spectrum is caused by interaction with the phosphonate groups of complex **I**.

The P2*p* spectrum at 200°C has only one component with $E_B$ = 133.5 eV and FWHM of 2.2 eV, which corresponds to the oxidized state of phosphorus atoms in iron polyphosphates. The intensity of the Pb4*f* spectrum drops below the statistical error, indicating that lead is reduced to the metallic state and evaporates. The peak corresponding to iron metal in the Fe2$p_{3/2}$ spectrum grows, which attests to a decrease in the thickness of the Fe(II)-containing polyphosphate layer. At 300°C, the intensity of both the P2*p* spectrum and the Fe(II) peak sharply decrease, while the intensity of the iron metal spectrum considerably increases because of destruction of the iron phosphate surface layer.

The spectra of the surface layer of complex **II** on steel (Fig. 4) point to sharp differences between its properties and those of complex **I**. The binding energy of the N1*s* line (401.5 eV) is 1.9 eV higher than that for free complex **II** and attests to the destruction of the N–Pb bond upon the interaction of **II** with the steel surface. The O1*s* spectrum is identical to the spectrum of free complex **II**, which means the retained structure of phosphonate groups. The P2*p* spectrum shows one component with $E_B$ = 131.8 eV and FWHM of 2.0 eV, which is indicative of participation of phosphonate groups in the formation of surface donor-acceptor complexes. Lead is present in both the oxidized ($E_B$ =

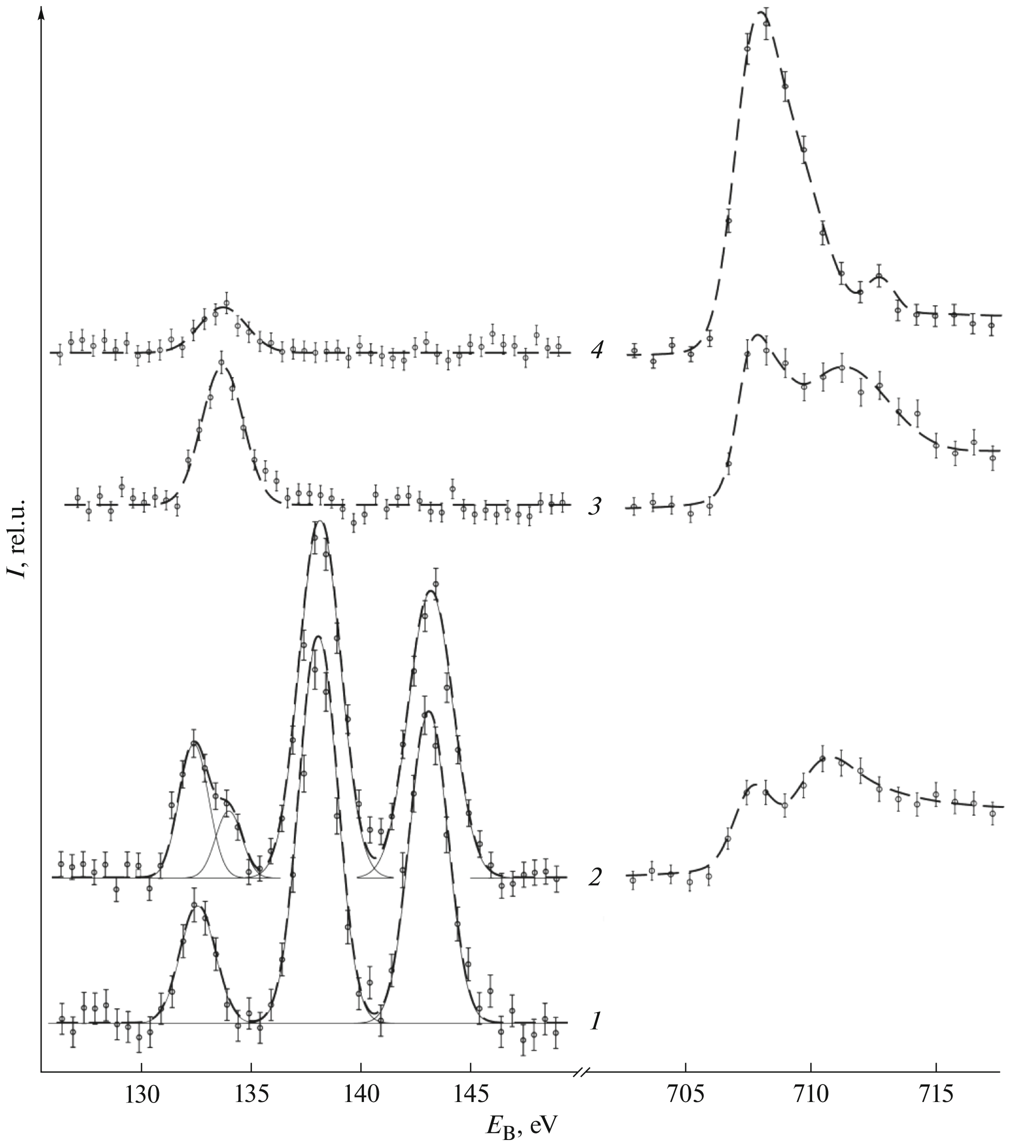


**Fig. 3.** X-ray photoelectron spectra of the adsorption layer of complex **I** on the steel surface at (*1*) 75, (*2*) 150, (*3*) 200, and (*4*) 300°C.

137.8 and 142.6 eV) and metallic states ($E_B = 136.0$ and 140.8 eV). This implies that the interaction of **II** with the steel surface is accompanied by partial inner-sphere replacement of Pb(II) by Fe(II). Apparently, the process starts with the dissociation of the complex anion

$$[Pb_2(H_2O)_2\{N(CH_2PO_3)_3H_2\}_2]^{4-} \rightleftarrows 2Pb^{2+} + 2H_2O + 2N(CH_2PO_3)_3H_2^{4-}, \quad (1)$$

which is followed by adsorption of the lead ion on the steel surface, redox reaction

$$Pb^{2+} + Fe^0 \rightarrow Pb^0 + Fe^{2+}, \quad (2)$$

transfer of the iron ion to the near-surface layer of the electrolyte containing the ligand ion, and stabilization of the iron oxidation state to give the previously studied [18] stable complex

$$N(CH_2PO_3)_3H_2^{4-} + 2H_2O + Fe^{2+} \rightarrow \left[Fe^{II}\{N(CH_2PO_3)_3H_4\}\right] + 2OH^-. \quad (3)$$

A different possible chemical process is initiated by the anodic dissolution of iron in the aqueous medium

$$Fe^0 \rightarrow Fe^{2+} + 2e^-, \quad (4)$$

transfer of iron ions to the near-surface electrolyte layer with their direct exchange reaction with complex **II**

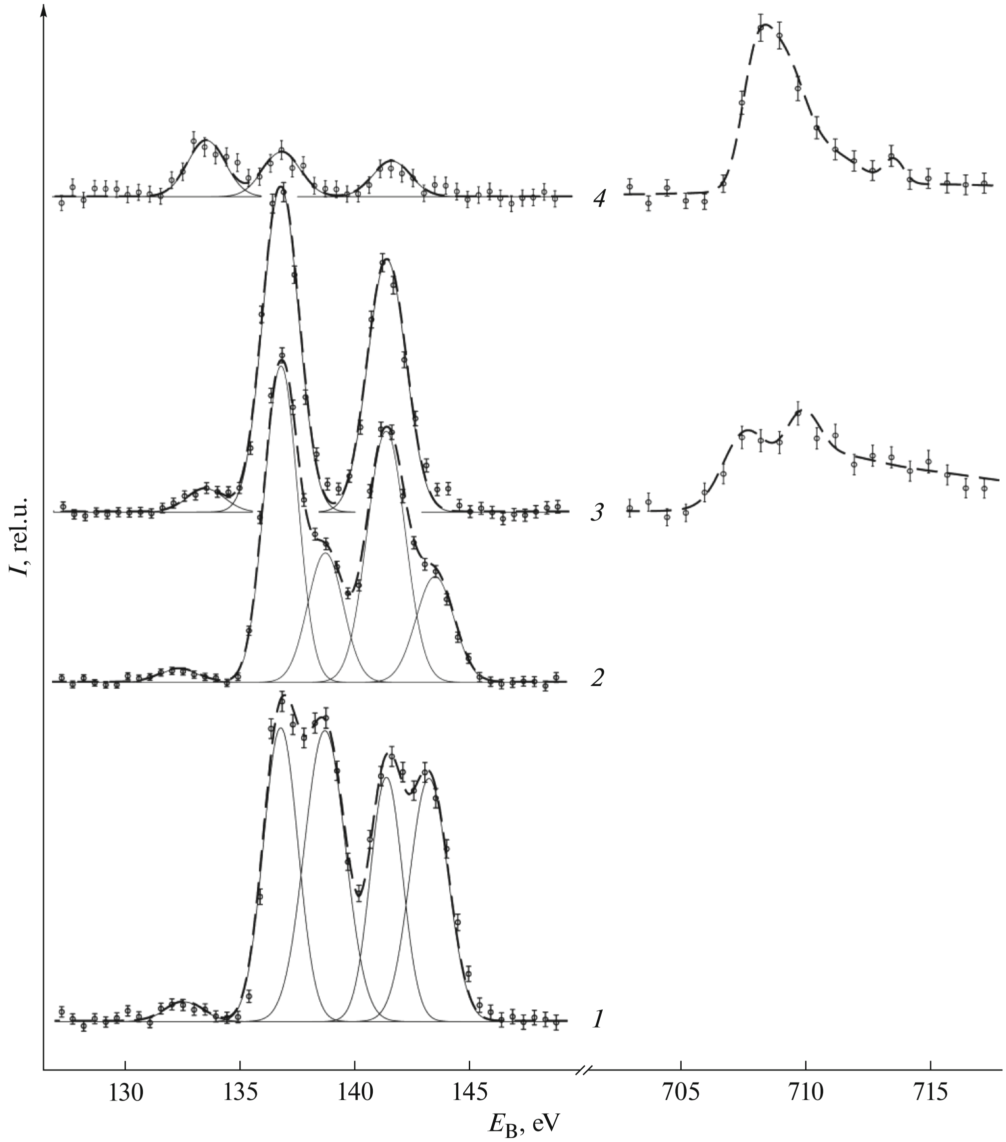


**Fig. 4.** X-ray photoelectron spectra of the adsorption layer of complex **II** on the steel surface at (*1*) 100, (*2*) 200, (*3*) 300, and (*4*) 450°C.

$$\begin{gathered}2Fe^{2+} + 2H_2O \\ + [Pb_2(H_2O)_2\{N(CH_2PO_3)_3H_2\}_2]^{4-} \\ \rightleftarrows 2Pb^{2+} + 4OH^- + 2\left[Fe^{II}\{N(CH_2PO_3)_3H_4\}\right],\end{gathered} \tag{5}$$

the subsequent adsorption of $Pb^{2+}$ ions as a depolarizer, and reduction to $Pb^0$ on the steel surface

$$2e^- + Pb^{2+} \to Pb^0. \tag{6}$$

To reliably distinguish between mechanisms (1)–(3) and (4)–(6). further investigation is required. On heating to 200°C, the intensity of the Pb4*f* spectrum is redistributed, indicating increasing content of lead metal. The $Fe2p_{3/2}$ iron spectrum is not observed since the steel surface is coated by a lead metal layer.

At 300°C, the Pb4*f* spectrum components corresponding to the oxidized state of lead ($E_B$ = 137.8 and 142.6 eV) are completely absent; however, lead metal is retained in the surface layer ($E_B$ = 136.0 and 140.8 eV). The phosphorus atoms are converted to the oxidized state ($E_B$ = 133.2 eV), which means that the phosphonate groups are oxidized to phosphate groups. The intensity of the N1*s* spectrum drops almost to zero. The $Fe2p_{3/2}$ spectrum is observed, indicating the presence of iron metal ($E_B$ = 707.5 eV) and Fe(II) ($E_B$ = 710.8 eV) on the surface.

At a temperature of 450°C, the intensity of the lead metal spectrum is low, but it is still higher than the statistical error of measurements. The rather intense P2*p* ($E_B$ = 133.2 eV) and $Fe2p_{3/2}$ ($E_B$ = 709.5 eV) lines are retained, indicating the formation of an iron phosphate layer on the surface.

Thus, our studies demonstrated the differences between the thermal stabilities and reactivities of complexes **I** and **II**, related to their different structure.

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