ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 3, pp. 384–397. © Pleiades Publishing, Ltd., 2012.
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Study of Sorption of Platinum and Palladium Cyanometallate Complexes as the Key to Understanding the Mechanism of Binding the $[Au(CN)_2]^-$ Anion with Carbon Adsorbents

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Received June 16, 2011

Abstract—Goldcarb WSC-207C GR activated carbons with platinum and palladium complexes adsorbed from aqueous solutions of $K_2[Pt(CN)_4]$, $K_2[Pt(CN)_6]$, and $K_2[Pd(CN)_4]$ were studied by the methods of X-ray photoelectron spectroscopy and IR spectroscopy with Fourier transformation, and also by MALDI mass-spectrometry. Platinum and palladium cyanide complexes are not reduced onto surface of active charcoal while adsorption. A certain part of the $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ anions directly bound to active centers on the activated carbon is oxidized more deeply and functions as particles-anchors, forming oligomers resembling Krogmann salt. A correspondence between the structure of the complex cyanometallate ion and a mode of its binding with active carbon is found. The adsorption of complex species with a linear structure or a square planar structure is defined by a possibility of the formation of donor-acceptor and metallophilic bonds. The mode of the anion $[Au(CN)_2]^-$ binding with the surface of active carbon was considered.

DOI: 10.1134/S107036321203005X

In last 30 years a stable interest arose to the application of activated carbons in hydrometallurgical processes. First of all, it is connected with industrial usage of coals as main adsorbents for extraction of gold(I) from cyanide solutions and pulps. In spite of it the reason of a selective sorption of gold(I) cyanide complex on carbon adsorbents is not yet elucidated at present. Unlike the corresponding complexes of gold, adsorption of platinum and palladium cyanide complexes is by no means studied though the knowledge of specificity of their behavior in relation to carbon adsorbents can present both theoretical and practical interest. This interest is connected, firstly, with the study of mechanisms of binding complexes of noble metals with active carbons and also with the search for methods improving kinetic and capacity properties of carbon adsorbents and increasing their selectivity. Results of such studies promote the improvement of the process of mining and refining platinum metals and gold.

Depending on the nature of a central atom and its ligand environment, and also on the composition of a solution and conditions, in which transition metal complexes contact carbon adsorbents, partial or complete reduction of a metal center and (or) chemisorption, which is accompanied by a change in its oxidation state, can occur at the adsorption. To predict a possible result of the interaction between activated carbon and complexes of noble metals, it was suggested to use a comparison of working and stationary potentials of coal in a solution with appropriate redox potentials of complex compounds [1]. The nature of adsorbate at the adsorption of transition metal complex compounds on activated carbons depends on several factors. The composition and structure of a sorbed ion, the value of a solution pH, its composition and temperature, the presence of dissolved oxygen in the system, the chemical composition of the adsorbent surface, and also the duration of the contact between an adsorbate and the activated carbon material [1–6] are recognized among these factors.

There is a great number of published examples describing behavior of Pt(IV), Pt(II), Pd(II), and Au(III) chloride complexes during adsorption on carbon adsorbents of various nature in different conditions [5, 7–11]. Transformations, which Pd(II), Pt(II), and Pt(IV) chloride complexes undergo on their adsorption on activated carbon materials from acid aqueous solutions, in many respects remind the processes occurring in the same conditions with the $[AuCl_4]^-$ anion. The similarity lies in the fact that central atoms in $[MCl_4]^{2-}$ and $[MCl_6]^{2-}$ complexes of platinum and palladium can be reduced to a metal state on contact with carbon adsorbents (see [7, 8] and references therein). It was found by the EXAFS method that the reduction of the $[PdCl_4]^{2-}$ anion to metal is preceded by its binding with the active center on the adsorbent surface [12]. A similar chemical process occurs on the activated carbon surface also in the case of reduction of a gold(III) chloride complex [12].

After the adsorption of the anion $[PdCl_4]^{2-}$ from solution, depending on sorption conditions and the carbon adsorbent nature, it is possible to detect on its surface both Pd(0) as the main reaction product with an insignificant admixture of Pd(II) [7] and Pd(II) compounds, which can contain a Pd(0) admixture in some cases [11, 13, 14]. However it follows from the X-ray photoelectron spectroscopy (XPS) data that both adsorbed compounds, to which the oxidation state Pd(II) is assigned [13], are characterized by different values of $Pd3d_{5/2}$ binding energy (336.8 and 339.7 eV) and it is more likely that the higher value corresponds to Pd(IV) rather than Pd(II). Metal palladium precipitated on the surface of the activated carbon granule is oxidized upon a long-term keeping (about one day) in concentrated HCl solutions in air and diffuses inside the adsorbent granule, but does not pass back in a solution [5]. It was assumed [13, 14] on the basis of a Cl:Pd ratio determined in adsorbate in the case of $H_2[PdCl_4]$ adsorption on a surface of a carbon carrying agent at pH 1–2 that the complex $PdCl_2·A$ (A is the active sorption center of active carbon possessing ligand properties) is mainly formed. It is supposed that an element of a π-system of the carbon carrying agent acts as the active center A [13, 14].

The adsorption of the anion $[PtCl_6]^{2-}$ on activated carbon fibers from acid solutions results in the formation of metal platinum in dominating amounts and also of Pt(II) and Pt(IV) compounds of undetermined composition on the adsorbent surface. The total fraction of platinum(II, IV) complexes is about 25% of the initial amount of the metal [9]. When $[PtCl_6]^{2-}$ anions are adsorbed from alkaline solutions, hydrated platinum(II) oxide is formed in the coal phase [4].

From 1 M HCl solutions the ion $[PtCl_4]^{2-}$ is adsorbed onto SKN activated carbon in the form of Pt(II) compounds, whereas the absorption of the complex anion by the same coal from 0.01 M HCl solutions results in the formation of metal platinum with an admixture of, apparently, a Pt(II) compound on their surface [11].

The reduction of chloride complexes of platinum metals, silver, and gold from aqueous solutions on the surface of activated carbons in many respects is connected with the fact that the majority of carbon adsorbents have lower redox potentials than the potentials of $[MCl_n]^{m-}/[MCl_k]^{l-} + (n - k)Cl^-$ pairs. Values of the latter in standard conditions are as follows (V): 0.726 ($M = Pt$, $n = 6$, $m = 2$, $k = 4$, $l = 2$), 0.758 ($M = Pt$, $n = 4$, $m = 2$, $k = 0$, $l = 0$), 0.60 ($M = Pd$, $n = 4$, $m = 2$, $k = 0$, $l = 0$), and 1.002 ($M = Au$, $n = 4$, $m = 1$, $k = 0$, $l = 0$) [15]. Comparing these potentials with the working potentials of activated carbons shows that potentially many of them can play the role of reducing agents with respect to complex compounds [1, 7, 8, 11]. It is natural that the reduction of a complex anion $[MCl_n]^{m-}$ is accompanied by the oxidation of carbon adsorbents themselves [1, 7, 11]. The capability of platinum and palladium chloride complexes to be reduced on a surface of activated carbon materials is used for concentrating metals for the analysis of solutions and for the preparation of supported catalysts [7, 10, 13].

In the present work the study is performed on the adsorption of platinum(II), (IV) and palladium(II) cyanide complexes on WSC-207C GR Goldcarb activated carbon preliminarily washed with a 1 M $HClO_4$ solution and distilled water. The adsorption experiments were carried out at room temperature by contacting aqueous solutions of individual compounds $K_2[Pd(CN)_4]$, $K_2[Pt(CN)_4]$, or $K_2[Pt(CN)_6]$ with weighed samples of activated carbon at shaking. Values of pH of the solutions were defined by the acidity of distilled water and in all cases were within the range of 6.2–6.4.

The XPS study of products of adsorption of tetracyanometallate complexes containing platinum(II) and palladium(II) as central atoms has shown that cyanide complexes are not reduced up to a metal state on the surface of Goldcarb WSC-207C GR activated carbon. No reduction was found either on the adsorption of platinum(IV) cyanide complex. On the adsorption of $[Pt(CN)_6]^{2-}$ anions from a solution only one compound was detected on the adsorbent surface, whereas on the contact of activated carbon with solutions containing $[Pd(CN)_4]^{2-}$ or $[Pt(CN)_4]^{2-}$ ions at least two platinum compounds and two palladium compounds were found on the coal surface.

The $Pt4f_{7/2}$ binding energy for Pt(II)compounds is normally within the range of 73.6±0.8 eV, whereas for Pt(IV) it is 76.3±1.5 eV. For dinuclear Pt(III) compounds with a Pt(III)-Pt(III) bond the $Pt4f_{7/2}$ binding energy, as a rule, is 75.0±0.2 eV [16].

We have found that the $Pt4f_{7/2}$ binding energy in the initial complex $K_2[Pt(CN)_6]$ is 76.95 eV. This experimental result agrees well with published values of the binding energy for Pt(IV) cyanide complexes. In particular, for $K_2[Pt(CN)_6]$ the published values of the $Pt4f_{7/2}$ binding energy are 76.3 [17] and 76.86 eV [18], and for *trans*-$K_2[Pt(CN)_4Cl_2]\cdot 3H_2O$ it is 76.6 eV [19]. After adsorption on the activated carbon surface a peak of $Pt4f_{7/2}$ in XPS spectra is observed at 77.2 eV. It unambiguously points to the absence of reduction of complexes on their extraction by coal from solutions. It is necessary to note that the standard electrode potential for the system $[Pt(CN)_6]^{2-}/\{[Pt(CN)_4]^{2-} + 2CN^-\}$ is not determined at present, but the known trends in the variation of standard potentials and stability of complex ions for the systems $[PtX_6]^{2-}/\{[PtX_4]^{2-} + 2X^-\}$ (X = Cl, Br, SCN, I) suggest that its value for the cyanide system is close to 0.3 V.

The study of activated carbon containing adsorbed $K_2[Pt(CN)_6]$ by time-of-flight MALDI mass-spectrometry shows that this compound is present on the adsorbent surface in the form of the hexacyanoplatinate (IV) complex without replacement of cyanide ligands in its inner sphere. This is proved by the signals in the region of negatively charged ions with the following *m*/z values: 389.90–394.01 $\{K[Pt(CN)_6]\}^-$, 337.04–340.90 $\{K[Pt(CN)_4]\}^-$, 272.02–276.01 $\{Pt(CN)_3\}^-$, and 246.09–250.00 $\{Pt(CN)_2\}^-$ (Fig. 1, monoisotopic masses are denoted in the figure). The peaks are assigned on the basis of a correspondence between experimental spectra and those theoretically calculated in view of natural isotope composition of platinum. The fact that one sharp $Pt4f_{7/2}$ peak is observed in the XPS spectra suggests that the $[Pt(CN)_6]^{2-}$ anion is the only form of the platinum(IV) complex on the adsorbent surface, and it is bound to the adsorbent in the same way in all cases.

In the mass spectrum of $K_2[Pt(CN)_6]$ taken under the same conditions the heaviest ions are the $\{[Pt(CN)_6]\}^-$ anion free from the potassium ion (*m*/z 351.39–355.40) and the product of its partial disintegration $\{[Pt(CN)_4]\}^-$ (*m*/z 299.34–303.37) (Fig. 2). In this connection it should be noted that the ions $\{K[Pt(CN)_4]\}^-$ and $\{K[Pt(CN)_6]\}^-$ were detected in the mass spectra of $K_2[Pt(CN)_4]$ and $K_2[Pt(CN)_6]$ measured by the secondary ions mass-spectrometry (SIMS) method [18]. In the SIMS mass spectra of activated carbons with the cyanide complex $Na[Au(CN)_2]$ adsorbed on them [19] a signal of the $\{Na[Au(CN)_2]\}^-$ ion was also detected and, when the coal was pretreated by crown ethers, of the ions $\{(NaL)[Au(CN)_2]\}^-$ (L is 12-crown-4 or 18-crown-6). It has allowed us the assumption that the ions Na^+ and $[Au(CN)_2]^-$ are intimately bound with each other on the coal surface [19]. The difference, which we have found in the mass spectra of the free complex $K_2[Pt(CN)_6]$ and that adsorbed on the activated carbon surface, points, first of all, to differences in structures of the crystalline complex and the complex deposited on the adsorbent.

The main part of the metal in adsorbed platinum(II) cyanide compounds (93.7%) is characterized by the $Pt4f_{7/2}$ binding energy of 73.3 eV. The second platinum compound contained on the activated carbon surface in a minor amount (6.3%), is characterized by the $Pt4f_{7/2}$ binding energy of 75.0 eV. We found the value of the $Pt4f_{7/2}$ binding energy of 73.5 eV for the sample of $K_2[Pt(CN)_4]\cdot 3H_2O$ used in this work. Published values of the $Pt4f_{7/2}$ binding energy for $K_2[Pt(CN)_4]$ are as follows: 73.01 [17], 73.19 [18], 73.7 [20], and 73.8 [21], and that for $K_2[Pt(CN)_4]\cdot 3H_2O$, 74.2 [22]. These data allow a suggestion that platinum oxidation state in the predominant part of adsorbate is +2. However for the well studied Krogmann salt $K_2[Pt(CN)_4Cl_{0.3}]\cdot aH_2O$ ($2 < a \leq 3$) [abbreviation KCP(Cl) is accepted in the English-language literature], in which platinum atoms are in the formal oxidation state +2.33, $Pt4f_{7/2}$ binding energy is 73.0 eV [22]. In such compounds a metal–metal bond is realized due to overlapping d_{z^2} orbitals of platinum atoms [23]. The shortest Pt–Pt distance in KCP compounds falls in the range 2.80–3.00 Å [24], which is comparable to the length of the metal–metal

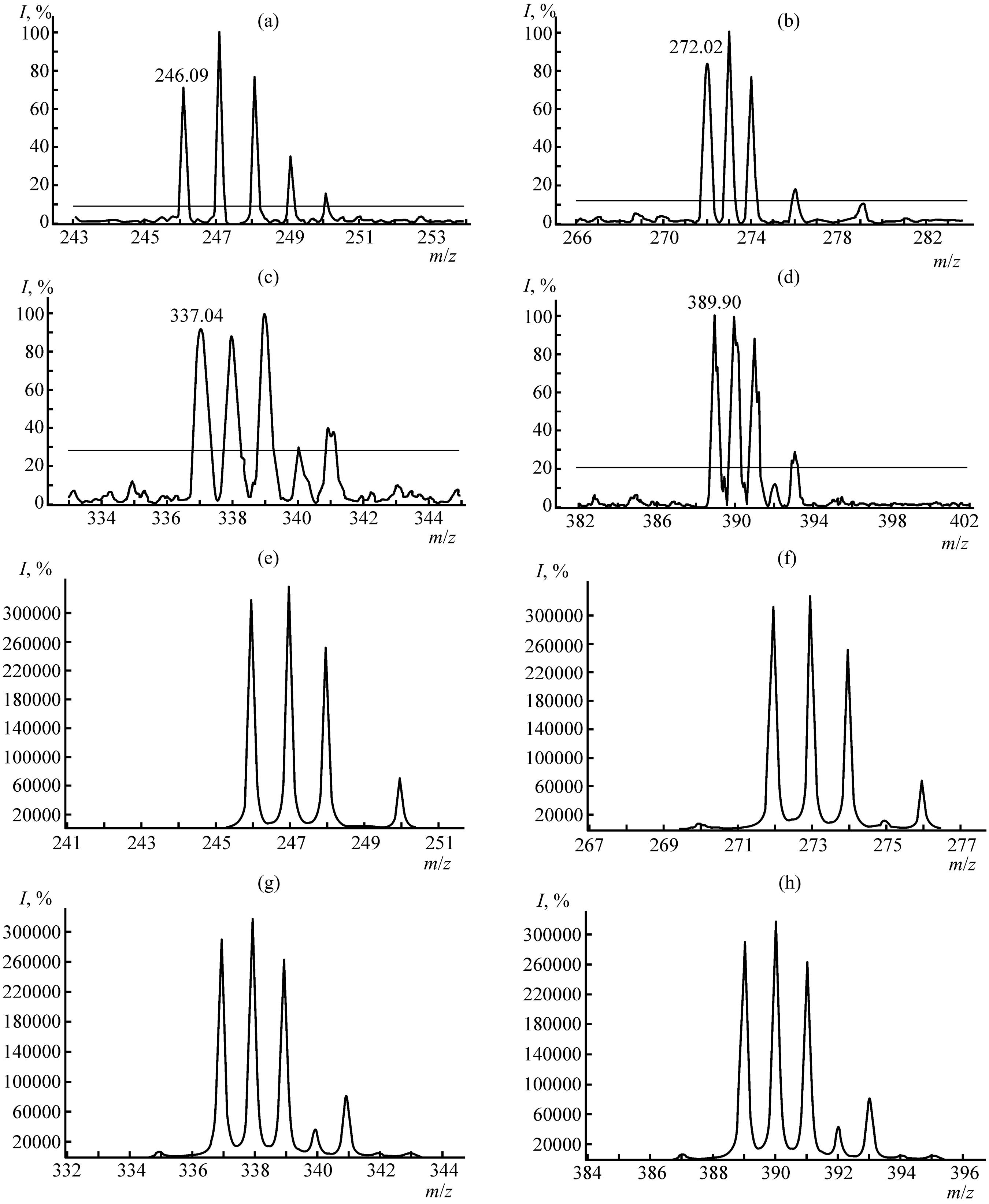

Fig. 1. (a–d) Fragments of mass spectrum of activated carbon with $K_2[Pt(CN)_6]$ adsorbed on it and (e–h) mass spectrum theoretically calculated for these fragments. (a), (e) $[Pt(CN)_2]^-$; (b) $[Pt(CN)_3]^-$; (c), (d) $\{K[Pt(CN)_4]\}^-$; (d), (h) $\{K[Pt(CN)_6]\}^-$.

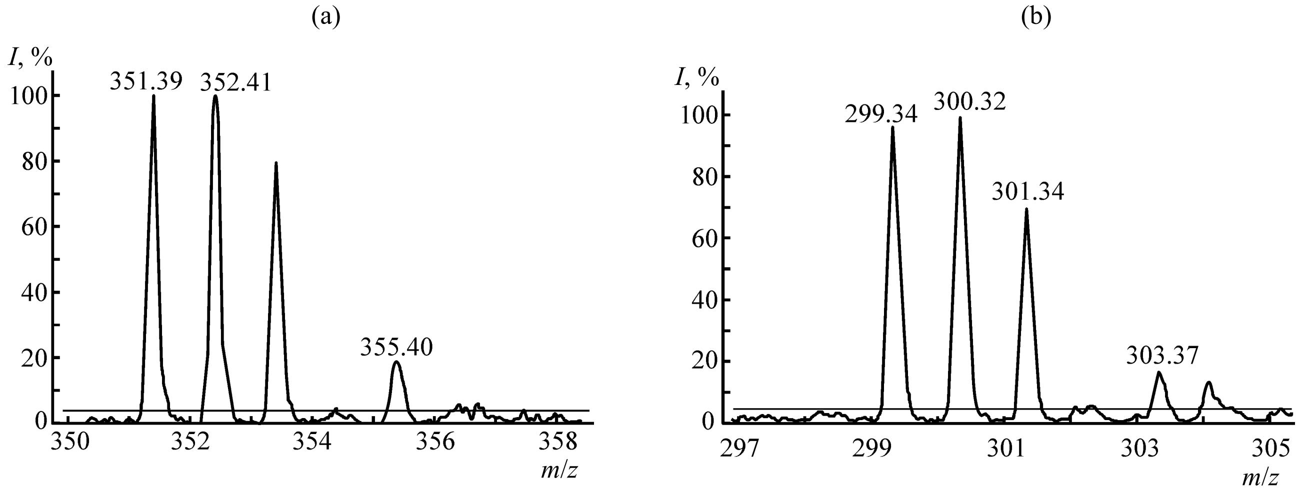

Fig. 2. Fragments of mass spectrum of $K_2[Pt(CN)_6]$. (a) $Pt[(CN)_6]^-$ and (b) $[Pt(CN)_4]^-$.

bond in the metal platinum crystal lattice (2.78 Å). Thus, the XPS results do not provide an unambiguous answer to the problem of the oxidation state of central atom in the main adsorbed platinum complex.

The adsorbed compound with the $Pt4f_{7/2}$ binding energy of 75.0 eV formally corresponds to a platinum complex with a Pt(III)–Pt(III) bond. It is known that a rather stable dinuclear anion $[Pt_2(CN)_{10}]^{4-}$ with a Pt(III)–Pt(III) bond can be formed on the oxidation of the $[Pt(CN)_4]^{2-}$ complex anion by Tl(III) cyanide compounds [17, 25, 26] or on the electrochemical reduction of aqueous solutions containing Cu^{2+} and $[Pt(CN)_6]^{2-}$ ions [18]. All cyanide ligands in this complex are terminal [26]. The measured $Pt4f_{7/2}$ binding energy in the $Cu_2[Pt_2(CN)_{10}]$ complex indicates the equivalence of platinum atoms, but it proves to be too high (76.18 eV [18]) as compared with usually observed values in Pt(III) complexes with metal–metal bonds [16, 27]. In our opinion it is improbable that a species adsorbed on a carbon adsorbent in the case under study would be a $[Pt_2(CN)_{10}]^{4-}$ anion.

To refine the structure of the platinum adsorbate on the surface of activated carbon particles, we used vibration spectroscopy methods. In the IR spectrum of $K_2[Pt(CN)_4]$, which we have synthesized and used as an adsorptive agent, there is one band in the region of 1900–2300 cm^{-1} with a maximum at 2136 cm^{-1} belonging to the stretching vibrations $\nu(C\equiv N)$. The measurement of the IR spectrum of platinum cyanide complex coated on a black surface of activated carbon presents certain technical difficulties. Therefore in the further studies we used the IR Fourier-spectroscopy method.

In the IR Fourier spectrum of activated carbon with Pt(II) cyanide complex adsorbed on it two bands with maxima at 2125.6 and 2104.3 cm^{-1} were detected in the region of $\nu(C\equiv N)$ stretching vibrations. The position of the $\nu(C\equiv N)$ band in platinum cyanide complexes depends on the central atom oxidation state, the coordination mode (terminal or bridging) of the cyanide ligand [28], and on the nature of a counter ion [29]. Furthermore, the $\nu(C\equiv N)$ position for complexes in the crystalline state can also depend on additional van der Waals interactions arising upon a penetration of polar organic molecules in a crystal lattice of a complex [29]. It is important to note that in the complexes of platinum in an oxidation state higher than Pt(II) with terminal cyanide ligands $\nu(C\equiv N)$ bands are strongly shifted into the near-infrared region as compared to the wave numbers found for corresponding Pt(II) complexes [28]. This shift is the stronger, the higher is the oxidation state of the central atom. In particular, for $K_2[Pt(CN)_4]$ used in the present work $\nu(C\equiv N)$ is 2136 cm^{-1} in agreement with the published data. Values of $\nu(C\equiv N)$ for $K_{1.75}Pt(CN)_4\cdot 1.5H_2O$ and $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ [30] coincide with each other: 2156 cm^{-1} (with a shoulder at 2148 cm^{-1}). For $K_2[Pt(CN)_6]$ synthesized and used in the present work $\nu(C\equiv N)$ is 2192 cm^{-1} that agrees well with the published data [17, 31] for this compound. A similar shift of $\nu(C\equiv N)$ bands into the near-infrared region is also observed, when bridging bonds $Pt^{II}–C\equiv N–Cu^{II}$ [28] or $Pt^{II}–C\equiv N–Pt^{II}$ are formed [32]. These data suggest that cyanide ligands forming a part of predominating adsorbate are terminal and enter into the composition of a platinum(II) complex.

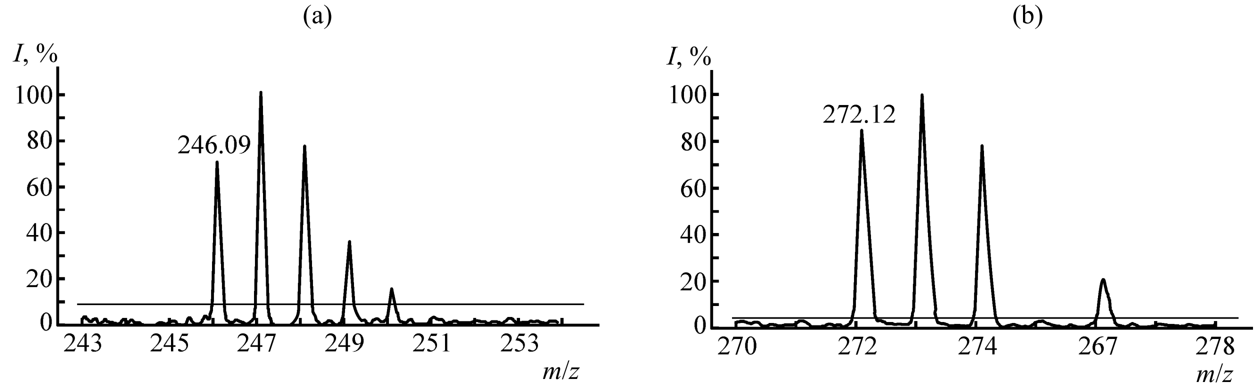

Fig. 3. Fragments of mass spectrum of $K_2[Pt(CN)_4]$ adsorbed on activated carbon. (a) $[Pt(CN)_2]^-$, (b) $[Pt(CN)]_3^-$.

The only factor resulting in the shift of ν(C≡N) into the far-infrared region is the nature of the cation at the $[Pt(CN)_4]^{2-}$ anion in the crystalline state. Values of ν(C≡N) for $[(C_4H_9)_4N]_2[Pt(CN)_4]$ and $[Pt(n\text{-}CNC_6H_4 \cdot C_{10}H_{21})_4][Pt(CN)_4]$ are strongly shifted into the far-infrared region as compared to the corresponding band in the spectrum of $K_2[Pt(CN)_4]$ and are 2118 and 2125 cm^{-1}, respectively [29]. A similar shift of a ν(C≡N) band depending on a size of the cation defining a package of cyanide complex anions in a crystal is observed also in the case of compounds containing the anion $[Pd(CN)_4]^{2-}$ in their composition [33].

When platinum and palladium cyanometallate(II) complexes contact with vapors of volatile organic compounds capable of formation of intermolecular hydrogen bonds with coordinated cyanide ligands, an appreciable shift of ν(C≡N) bands into the near-infrared region occurs [29, 33]. However it was not detected if water acts as an inserted molecule. The IR spectroscopy data for adsorbates on the activated carbon surface indirectly show that by their structure they resemble systems, in which larger particles act as counter-ions in relation to $[Pt(CN)_4]^{2-}$ anions and cyanometallate anions form a stacking structure.

Mass spectra of activated carbon with $K_2[Pt(CN)_4]$ adsorbed on it have peaks with *m*/z 272.12–276.13 and 246.09–250.09 corresponding to the $[Pt(CN)_3]^-$ and $[Pt(CN)_2]^-$ ions. Unlike the mass spectrum of adsorbate, the spectrum of $K_2[Pt(CN)_4]$ itself contains signals with *m*/z values in ranges 337.34–341.36 $\{K[Pt(CN)_4]\}^-$ and 299.34–303.37 $[Pt(CN)_4]^-$ (Figs. 3 and 4). The difference in mass spectra of adsorbate and adsorptive agent suggests that their solid-state structures differ from each other. The presence of the peak of $[Pt(CN)_3]^-$ ion in the mass spectrum shows that $[Pt(CN)_4]^{2-}$ anions somehow bound are present on the activated carbon surface. Furthermore, differences in the mass spectra of $K_2[Pt(CN)_4]$ and $K_2[Pt(CN)_6]$ adsorbed activated carbon point to various character of binding these platinum complexes with a carbon template.

The results of studying the adsorbate formed upon contact of activated carbon with a $K_2[Pd(CN)_4]$ solution remind by the character those obtained on XPS studying a platinum complex adsorbed active charcoal, which is separated out on contact of coal with a $K_2[Pt(CN)_4]$ aqueous solution. In the Pd3*d* spectrum of the studied sample of activated carbon with a palladium compound adsorbed on it two lines in the regions of 338.4 and 343.6 eV are observed, which correspond to the $Pd3d_{5/2}$ and $Pd3d_{3/2}$ components of the doublet. The resolution of the asymmetric $Pd3d_{5/2}$ line allows us to select two components with binding energies of 338.4 (80.3%) and 339.8 (19.7%) eV. The first value of the $Pd3d_{5/2}$ binding energy undoubtedly corresponds to palladium(II) atoms in adsorbate. For comparison we have measured the Pd3*d* spectrum of a surface of a cleansed palladium foil. The measured $Pd3d_{5/2}$ value for metal palladium is 335.1 eV. According to the published data [34], in the case of $PdCl_2$ the $Pd3d_{5/2}$ binding energy increases up to 338.0 eV, and for $K_2[Pd(CN)_4]$ reaches 339.2 eV [35]. The position of the second component with the $Pd3d_{5/2}$ binding energy of 339.8 eV is close to the value characteristic of the Pd(II) atom in $[Pd(CN)_2]_\infty$ (339.6 eV [36]) with a polymeric bridging structure and square-planar ligand surrounding of central atoms [32]. Compounds of Pd(IV) are characterized by even greater values of $Pd3d_{5/2}$ binding energy. In particular, for $K_2[PdCl_6]$ it is 340.5 eV [35]. We failed to find reliable published data on the $Pd3d_{5/2}$ binding energy for Pd(III) complexes.

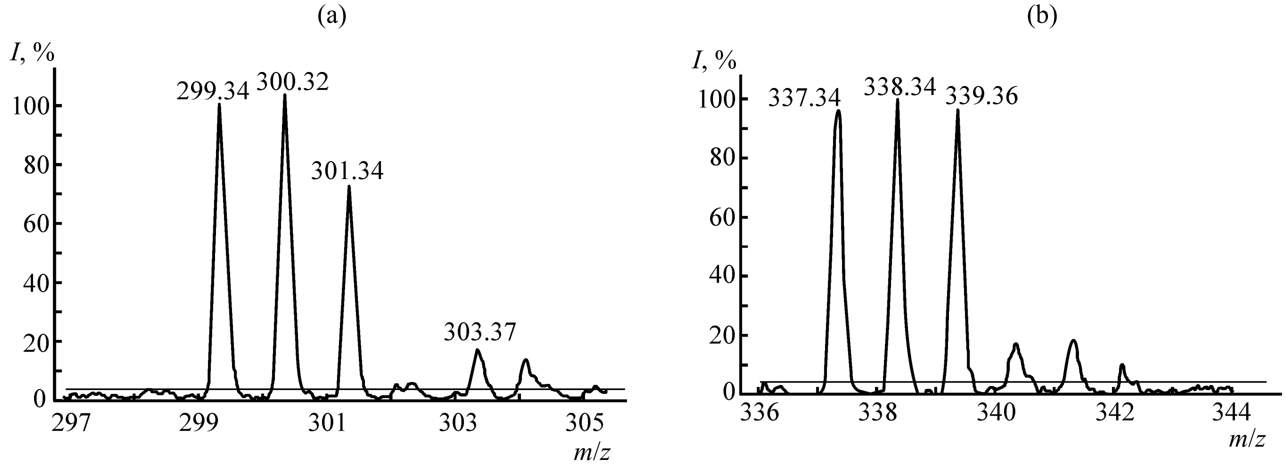

Fig. 4. Fragments of $K_2[Pt(CN)_4]$ mass spectrum. (a) $[Pt(CN)_4]^-$ and (b) $\{K[Pt(CN)_4]\}^-$.

It is no wonder that platinum(II) and palladium(II) cyanide complexes are not reduced. Though experimental values of standard redox potentials E^0 for the pairs $[M(CN)_4]^{2-}/M^0 + 4CN^-$ (M = Pt, Pd) seem to be unknown, they can be estimated approximately on the basis of known standard redox potentials for M^{2+}/M^0 pairs and stability constants of cyanide anions $[M(CN)_4]^{2-}$. The corresponding E^0 values for the systems Pd^{2+}/Pd and Pt^{2+}/Pt are 0.915 [15] and 1.2 V [37], and the values of logarithms of total stability constants log β_4 for $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ are 62.3 [38] and 78 [39]. Thus, E^0 values for the pairs $[M(CN)_4]^{2-}/M^0 + 4CN^-$ are close to –0.93 V (M = Pd) and –1.11 V (M = Pt). We shall also note that the one-electron reduction of the $[Pd(CN)_4]^{2-}$ anion can give the dimeric complex of Pd(I)–$[Pd_2(CN)_6]^{4-}$. The structure of this compound includes a Pd(I)–Pd(I) bond, and the standard potential for the system $[Pd(CN)_4]^{2-}/0.5[Pd_2(CN)_6]^{4-} + CN^-$ was estimated at –0.65 V [40], which indicates that Pd(II) cannot be reduced when adsorbed by this route.

An analysis of the data of the present work and published data shows that the adsorption of platinum(II), platinum(IV), and palladium(II) compounds on activated carbons involves the formation of several types of adsorptive agent structures. In the case of $[MX_4]^{2-}$ chloride complexes, depending on conditions, metals M^0 and also compounds of M^{II} can act as such structures, and it is assumed that the majority of metal ions in these structures are bound to donor centers of an adsorbent and a minor part, to acceptor centers. This is proved by the shift of binding energies to greater or smaller Pt4$f_{7/2}$ or Pd3$d_{5/2}$ binding energies of metal atoms, respectively, in the composition of $[MX_4]^{2-}$ anions of an adsorptive agent [1, 6, 7, 11, 13, 14]. In the case of platinum(IV) chloride complexes the situation becomes even more complicated as in addition to Pt^0 and Pt^{II} complexes Pt^{IV} compounds are also detected on the adsorbent surface in some cases. Unlike platinum and palladium chloride complexes, the behavior of cyanide compounds is not so manifold. The anion $[Pt(CN)_6]^{2-}$ is extremely stable thermodynamically and is more inert than the corresponding platinum(II) complex. For this reason the replacement of a cyanide ligand in it on contact with donor centers of the activated carbon surface is extremely improbable, which is proved by the mass-spectrometry data. Furthermore, the possibility of its entering in a redox reaction with active centers of the adsorbent is also problematic. On the one hand, the central atom Pt(IV) in an anion is in a high oxidation state and further increase in the oxidation state up to Pt(V) or Pt (VI) in these conditions is impossible, and on the other hand, it does not possess a pronounced oxidation power, which is due to the specificity of the cyanide ligand. In this connection it reminds the thermodynamically stable and inert $[RhCl_6]^{3-}$ anion, which is not reduced on the activated carbon surface and is readily desorbed by HCl solutions [6]. Other stable cyanometallate complex of the octahedral structure $\{[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$ [41], and probably $[Cr(CN)_6]^{3-}$ [42]$\}$ depending on the nature of activated carbons (degree of surface oxidation) either are not adsorbed on them at all or are sorbed at certain pH values. In this case they are held on an adsorbent rather weakly and can be desorbed by solutions of acids or alkalis [43]. We have fulfilled special experiments, which have shown that neither $K_3[Fe(CN)_6]$ nor $K_4[Fe(CN)_6]$ in neutral and alkaline (pH 10.5) aqueous solutions are sorbed on a Goldcarb WSC207C-GR activated carbon. In the experiments where $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ ions were adsorbed from a solution by activated carbons, the adsorbent capacity in relation to them reaches a maximum value in a narrow range of pH values (2–4). On the surface of activated carbons in acid solutions the $[Fe(CN)_6]^{4-}$ anion is oxidized by air oxygen to $[Fe(CN)_6]^{3-}$ [43], and in alkaline solutions (pH 13–14) on the contrary $[Fe(CN)_6]^{3-}$ is reduced to $[Fe(CN)_6]^{4-}$ [43, 44]. In the absence of oxygen in a solution the sorption of cyanoferrate ions decreases down to dead stop [43]. Such behavior of hexacyanoferrate anions in redox processes is connected, on the one hand, with rather low value of the potential for the system $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (0.36 V) and, on the other hand, with the fact that on passing from the acid medium (pH 2) to the alkaline medium (pH 12) the value of the stationary potential of activated carbon decreases by more than 0.6 V [1, 6]. For the $[Pt(CN)_6]^{2-}$ anion such redox transformations are impossible. The adsorption of strongly sorbed ions on activated carbons, for example of $[Au(CN)_2]^-$, is also hampered in anaerobic conditions [45]. Thus, dissolved oxygen plays an important role in the adsorption of cyanometallate complexes.

Activated carbons are characterized by a highly defective nanoporous structure, which is built from graphemes disordered in space. Our study of Goldcarb WSC207C-GR activated carbon has shown that it is actually a nanoporous adsorbent, as it contains ultramicro- and micropores of 0.8 and 1.4 nm in width, respectively [46]. In the structure of carbon adsorbents there are a rather high amount of defects differing in nature, including the so-called non-hexagonal rings [47]. Similar defects include reactive carbon atoms and are capable to adsorb oxygen molecules, causing thus their dissociation [47]. It was suggested in [48, 49] to consider activated carbon placed in an aqueous solution saturated by air oxygen as an oxygen gas electrode [Eqs. (1) and (2)].

$$\{C_x\cdots O_2\} + 2H_2O \rightarrow \{C_x^{4+}\cdots 4OH^-\}, \quad (1)$$

$$\{C_x\cdots O_2\} + 2H_2O \rightarrow \{C_x^{2+}\cdots 2OH^-\} + H_2O_2. \quad (2)$$

Symbols $\{C_x^{2+}\cdots 2OH^-\}$ and $\{C_x^{4+}\cdots 4OH^-\}$ designate a positively charged template of activated carbon with OH^- counter-ions situated in a plate of a double electrical layer. Under this approach, the adsorption of the $[Pt(CN)_6]^{2-}$ anion and others thermodynamically stable octahedral cyanometallate ions can be considered as a substitution of a hexacyanoplatinate(IV) anion for hydroxide anions according to Eqs. (3) and (4).

$$\{C_x^{4+}\cdots 4OH^-\} + 2[Pt(CN)_6]^{2-} \leftrightarrow \{C_x^{4+}\cdots 2[Pt(CN)_6]^{2-}\} + 4OH^-, \quad (3)$$

$$\{C_x^{2+}\cdots 2OH^-\} + [Pt(CN)_6]^{2-} \leftrightarrow \{C_x^{2+}\cdots [Pt(CN)_6]^{2-}\} + 2OH^-. \quad (4)$$

Such adsorption of anions will be rather weak, and the anion $[Pt(CN)_6]^{2-}$ can be replaced at the treatment of saturated activated carbon by strong acids or alkalis. A possibility of ion-exchange processes (3), (4) is supported by a weak alkalization of solutions accompanying adsorption of $[Au(CN)_2]^-$ [45] and $[PdCl_4]^{2-}$ [13] on coals. However the fraction of $[PdCl_4]^{2-}$ anions attached to activated carbon by such mechanism is rather small [13].

Platinum(II) and palladium(II) cyanometallate complexes could be adsorbed on activated carbons by the considered mechanism. However, as our experiment shows, they are desorbed to an insignificant extent (up to 4–6%) on the treatment of saturated coals by a concentrated HCl solution. At the same time the autoclave desorption of activated carbon with $K_2[Pt(CN)_4]$ adsorbed on it by a solution containing 10 g l^{-1} NaOH and 1 g l^{-1} NaCN at 110°C results in the removal of 86% of the platinum complex at 28 bed volumes of strip solution. It shows that unlike the $[Pt(CN)_6]^{2-}$ anion the main part of $[Pt(CN)_4]^{2-}$ and $[Pd(CN)_4]^{2-}$ ions are bound with activated carbons much more strongly and mainly with other adsorbent centers. It is necessary to exclude π systems of carbon basal surfaces from the list of potentially active centers for binding $[M(CN)_4]^{2-}$ ions (M = Pd, Pt) and $[Au(CN)_2]^-$, as our experiments have shown that reactor graphite having a near-ideal structure does not sorb these ions in appreciable amounts. The complex $K_2[PdCl_4]$ also is not sorbed and reduced on reactor graphite [12].

The dicyanoaurate(I) anion, like platinum(II) and palladium(II) cyanide complex ions, is strongly adsorbed on the activated carbon surface and is not desorbed under the action of strong acids [50]. It is well known that activated carbons contain in their composition paramagnetic centers in concentration of 10^{17}–10^{20} spin/g. When studying the adsorption of the $[Au(CN)_2]^-$ anion on activated carbons, it was found that the limiting capacity of adsorbents correlates with the concentration of paramagnetic centers in them [51].

The simulation of the activated carbon structure by quantum mechanical methods shows that defects in the structure of graphenes can be carbene-like atoms, which are preferably in a triplet state in particles with a considerable number of condensed aromatic rings [52]. Triplet carbenes can be rather stable also in the case of delocalization of unpaired electrons over an aromatic net, they are capable to form polycarbenes possessing paramagnetic properties, and to capture O_2 molecules [53]. A carbene-like atom in the triplet state is a biradical and can act as both a reducing and oxidizing agent, depending on the nature of a species reacting with it. The presence of oxygen dissolved in water favors the appearance of oxidative properties of activated carbons on the adsorption of complexes of transition elements in rather low oxidation states. As a result of the reaction of O_2 molecules with carbene-like centers of activated carbon, reactive species including $OH^{\cdot}$ radicals appear in solution [52, 54]. The treatment of activated carbons by oxidizing agents (nitric acid, chlorine, or bromine in aqueous suspension) results in the complete loss of their adsorption properties with respect to $[Au(CN)_2]^-$ ions in aqueous solutions [45]. Probably it occurs because of practically complete oxidation of the active carbene-like centers.

As shown by the XPS method in the present work, the central atoms of platinum(II) and palladium(II) square-planar cyanide complexes are not reduced on their adsorption. A part of platinum and palladium atoms seems to be in a higher oxidation state formally corresponding to Pt(III) and Pd (III), which are characterized by a coordination number six in compounds with monodentate ligands corresponding to the octahedral structure of the inner sphere of complexes. From the stereochemical point of view the oxidation of a Me(II) center to Me(III) in aqueous solutions is accompanied by addition of two axial water molecules to a $[Me(CN)_4]^{2-}$ plane. These water molecules can easily be replaced by other ligands.

Carbene-like ligand centers located on the surface of micropores of activated carbon in general exhibit a high *trans*-influence and a high capability to form coordination compounds with transition element ions [55]. In particular, they can readily replace a water molecule on the new H_2O–Pd(III)–OH_2 coordinate. These compounds can act as original "anchors," to which $[M(CN)_4]^{2-}$ anions can be added on a surface of activated carbons. A resulting oligomer reminds to an extent crystals of compound of Krogmann salts $K_{1.75}Pt(CN)_4 \cdot 1.5H_2O$ [K(def)CP] or $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ [KCP(Br)]. The "initial" Pt(III) atom in them, as distinct from Krogmann salt, is chemically bound to a carbene center. Further $[Pt(CN)_4]^{2-}$ anions can be added to it with building up a chain of tetracyanoplatinate(II) fragments, between which metallophilic Pt–Pt interactions and the further delocalization of electron density along this chain are realized owing to overlapping of d_{z^2} orbitals of platinum atoms. The capability of $[Pt(CN)_4]^{2-}$ anions to oligomerization in aqueous solutions due to formation of Pt(II)–Pt(II) bonds between anions [56] supports such possibility.

Short Pt(II)–Pt(II) contacts are detected in crystal structures of many compounds containing $[Pt(CN)_4]^{2-}$ fragments. The shortest Pt–Pt distance in $K_2Pt(CN)_4 \cdot H_2O$ is 3.579(1) Å [24], and in the tetranuclear complex $[\{Pt(CN)_4Cu(C_{10}H_8N_2)(NH_3)\}_2]$ containing $[Pt(CN)_4]^{2-}$ fragments located in space in the form of ladder steps this distance is 3.2390(8) Å [57]. Strong Pt–Pt interactions were found in the compounds $[CrX(H_2O)(en)_2][Pt(CN)_4]$ (X = Cl, Br; en is ethylenediamine) [58] and $[Co(NH_3)(H_2O)(en)_2]_2[Pt(CN)_4]$ [59] both in solutions and in the crystalline state.

One-electron oxidation of linear gold(I) complexes results in the formation of Au(II) complexes with inner spheres of triangle, plane square, or octahedron structures distorted tetrahedrally [60]. In this case more stable and most spread gold(II) compounds with an Au–Au bond in an Au_2^{4+} nucleolus can be formed [60]. Thus, one-electron oxidation of aqueous solutions containing linear $[Au(CN)_2]^-$ ions in the vicinity of the activated carbon surface will be accompanied by an increase in the coordination number of new-formed species, water molecules being attached first of all. For example, in the case of the formation of $[Au(CN)_2 \cdot (H_2O)_2]^0$ square-planar species a new coordinate with *trans*-located water molecules in the inner sphere joins to the initial dicyanoaurate(I) anion. As is the case with Pt(III) and Pd(III) compounds, water molecules located on this coordinate in Au(II) compound can be readily replaced by carbene centers of the activated carbon surface. We note that complex anions $[M(CN)_2]^-$ (M = Au, Ag) are also associated in aqueous solutions, and the association is connected with the formation of metallophilic Au(I)–Au(I) and Ag(I)–Ag(I) bonds [61]. The EXAFS study of the $[AuCl_4]^-$ anions adsorption on activated carbons accompanied by its reduction up to Au^0 has revealed that originally compounds reminding a bridging dimer Au_2Cl_6 in their structure are formed on the coal surface [12]. The possibility of the formation of gold–gold metallophilic bonds upon adsorption on activated carbons is confirmed by the value of interatomic distance of 3.01 E determined by the EXAFS method in the adsorbate containing $[Au(CN)_2]^-$ anions and obtained from a $Na[Au(CN)_2]$ aqueous solution [62]. This distance is much shorter than the corresponding distance in the crystal structure of $K[Au(CN)_2]$ (3.64 Å). The Au–Au bond in cyanide complexes adsorbed on activated carbons should differ in strength from that in the case of the addition of $[Au(CN)_2]^-$ anions to polyallylamine [63] or to AM-2B ion exchange resin.

The examination of published data shows that, despite all distinctions in the nature of central atoms, their oxidation states, and geometries of the corresponding complexes, linear or planar cyanide complexes have the capacity for strong adsorption on activated carbon materials. It concerns cyanide compounds of Au(I), Ag(I), Cu(I) [64, 65], Hg(II) [66, 67], Au(III) [68], Pt(II), and Pd(II) (the present work). In none of the mentioned cases a central atom of the complexes is reduced at the adsorption. It is necessary to note that copper(I) cyanide complexes can exist in solutions as linear $[Cu(CN)_2]^-$, distorted planar $[Cu(CN)_3]^{2-}$, and tetrahedral $[Cu(CN)_4]^{3-}$ anions, which can simultaneously be in an equilibrium mixture in a solution. The ratio of components of such mixture is defined by a molar ratio of Cu(I) and anions CN^-, pH value, and temperature of the solution [69]. According to the capability for the adsorption on activated carbon these ions form the series $[Cu(CN)_2]^- > [Cu(CN)_3]^{2-} >> [Cu(CN)_4]^{3-}$ [64, 65, 70, 71], whereas the tetrahedral anion is practically not adsorbed from solutions. The complexes $[Zn(CN)_4]^{2-}$ and $[Cd(CN)_4]^{2-}$ with a tetrahedral configuration have a low affinity to activated coal [41, 72]. The formation of metallophilic bonds for rather light copper(I) atoms is less probable than for heavy Au(I) and Ag(I) atoms. As a result the linear anion $[Cu(CN)_2]^-$ adsorbed on activated carbon is oxidized by air oxygen probably through a stage of formation of a copper(II) compound [4].

In aqueous solutions $Hg(CN)_2$ exists in the form of linear molecules [66], which are perfectly sorbed on activated carbons [73]. On the contrary, the tetrahedral anion $[Hg(CN)_4]^{2-}$ is practically not adsorbed from aqueous solutions [64, 74]. However it is necessary to note that adsorption of $Hg(CN)_2$, unlike adsorption of the $[Au(CN)_2]^-$ ion, is not accompanied by oxygen absorption, though it is considered that the process occurs on the same centers [75] as in the case of the gold complex. For mercury(II) complexes the coordination number four is more characteristic, therefore the extension of the complex coordination sphere does not require oxidation of the central Hg(II) atom and corresponding oxygen consumption.

Unlike gold(I) cyanide complex, which exists only in the form of the linear anion $[Au(CN)_2]^-$, the composition and structure of silver cyanide complexes is defined by a molar ratio of CN^- and Ag^I ions in solutions. When this ratio in a solution exceeds 2.2, $[Ag(CN)_3]^{2-}$ ions can exist together with $[Ag(CN)_2]^-$ anions, and at a 10-fold molar excess of cyanide the tetrahedral anion $[Ag(CN)_4]^{3-}$ can also be present [28, 76]. As a result at a ratio $CN^-/Ag^I \geq 3$ in a solution the capacity of carbon adsorbents with respect to silver(I) noticeably decreases, and the capacity with respect to gold(I) remains practically constant down to the ratio CN^-/Au^I 4.5 [76].

A distinctive feature of linear and planar coordination structures consists in the fact that they can form in space peculiar “stacks” of planar ions or “columns” of complexes with linear structure. In these “columns” alternating $[M(CN)_2]^-$ ions are turned at right angle to each other. “Stacks” remind green Magnus salt $[Pt(NH_3)_4][PtCl_4]$ in their construction with the only difference that they consist of only planar anions. The formation of metallophilic metal-metal bonds is possible in such structures. On the contrary, the formation of metallophilic metal-metal bonds between cyanometallate complex anions with tetrahedral or octahedral structure is impossible. For this reason in the case of thermodynamically stable cyanide complexes having such configurations the ion exchange after Frumkin [Eqs. (3) and(or) (4)] and a nonspecific physical adsorption shall be a more probable mechanism of adsorption on activated carbons.

Both plane and linear constructions on the surface of activated carbons are built from anions, which in our opinion are connected with each other by metallophilic bonds. Similar structures exist only when they are stabilized by counter-ions (cations) and solvent molecules [77]. Doubly charged cations Mg^{2+} and Ca^{2+} positively affect both the kinetics of $[Au(CN)_2]^-$ ions sorption on activated coals and their capacity with respect to gold(I) [78]. Only doubly charged cations of alkaline-earth elements in alkaline cyanide solutions at pH < 12 do not form cyanide or hydroxide anionic complexes. Furthermore, on contact of aqueous solutions of calcium salts with coals they are capable to change a sign of a surface charge of the adsorbent from negative to positive [79]. It suggests that Ca^{2+} cations replace protons and other singly charged cations connected with the surface by acid groups. The greatest content of these defects (carboxylic, phenolic, and other groups) is concentrated in micropores of activated carbons and near them on the adsorbent surface. Defects having the character of carbene-like carbon atoms are concentrated also in the same areas.

We note also that the square-planar $[Ni(CN)_4]^{2-}$ anion, for which the formation of metallophilic Ni(II)–Ni(II) bonds is less probable than for complexes of the heavier metals Pd(II) and Pt(II), contacts a surface of activated carbon rather weakly, and the nickel(II) compound is desorbed on washing coal by a dilute HCl solution [78]. The experimental value of heat effect of nickel(II) cyanide complex adsorption from aqueous solutions is 13.8 kJ mol^{-1}, whereas for strongly sorbed $[Au(CN)_2]^-$ anion this value is 257.4 kJ mol^{-1} [80].

When considering adsorption of cyanometallate ions on activated carbons, it is also necessary to take into account the fact that the process of their fixation is connected with a partial or complete dehydration of anions. The probability of anion adsorption by the mechanisms suggested in this work will decrease with the increasing hydration energy of species, which strongly increases as the charge of a species increases, and for the ions $[Au(CN)_2]^-$, $[Ag(CN)_2]^-$, $[Ag(CN)_3]^{2-}$, $[Ag(CN)_4]^{3-}$, $[Ni(CN)_4]^{2-}$, and $[Fe(CN)_6]^{4-}$ it is 186, 190, 710, 1478, 697, and 2612 kJ mol^{-1}, respectively [81].

We note in conclusion that the industrial activated carbons usually contain various amounts of admixtures of inorganic substances [82], many of which possess sorption properties with respect to cyanometallate ions. For example, γ-Al_2O_3 itself in the composition of ash of activated carbons possesses a sorption activity with respect to Fe(II) and Fe(III) hexacyanoferrate complexes [83]. On the contact with aqueous solutions Fe_2O_3, which is present in the composition of activated carbons, partially converts on the surface to FeO(OH) capable to absorb the $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ anions [84]. It brings additional difficulties in comparing sorption properties of various types of activated carbons.

EXPERIMENTAL

Synthesis of $K_2[Pt(CN)_4]$ was carried out according to a procedure [85] from $K_2[PtCl_4]$ and KCN; $K_2[Pd(CN)_4]$ was prepared in the similar way. To obtain $K_2[Pt(CN)_6]$, a modified procedure [30] was applied. For this aim ICN was synthesized [86]. A weighted sample of long colorless needles of cyan iodide (0.60) preliminarily recrystallized from boiling chloroform was mixed with a solution of 1.5 g of $K_2[Pt(CN)_4]$ (molar ratio 1:1) in 6 ml of distilled water. Within 20-30 min ICN dissolution was complete, then the mixture was stirred for 1 h more, and to the resulting solution a solution of 1.2 g of KCN in 6 ml of H_2O was added. In 1.5 h a colorless precipitate started to separate. The resulting suspension was stirred for 24 h. A precipitate formed within a day was filtered on a Hirsch funnel, washed with a small amount of water cooled to 2°C, ethanol, and diethyl ether, and dried in air flow. Yield 1.14 g (67%).

Activated Goldcarb WSC207C GR carbon was preliminarily washed from inorganic compounds by 1 M $HC1O_4$ solution and then by distilled water in a Soxhlet apparatus for a long time (21 day) [87]. Main characteristics of the Goldcarb WSC207C GR coal are given in [46].

Chemical compositions of activated carbon samples with cyanometallate complexes deposited on them and also of platinum and palladium crystalline compounds were studied by the X-ray photoelectron spectroscopy method on a SPECS electron spectrometer (Germany). The spectrometer was equipped with a PHOIBOS-150 hemispherical analyzer, a 9-channel detector of electrons, a FOCUS-500 X-ray monochromator, and an XR-50M source of X-ray characteristic radiation with a double Al/Ag anode. For excitation of XPS spectra AlK_α monochromatic X-ray radiation (hν 1486.74 eV) was used. The relative content of elements in a zone under analysis (the depth of the analysis was 5–10 nm) was determined from the integral intensities of lines in the XPS spectra in view of the photo-ionization cross-section of the corresponding terms [88]. A resolution of the spectra into individual components was applied for the detailed analysis of the spectra. After subtraction of a hum noise by Shirley's method [89] the experimental curve was resolved into a series of lines corresponding to the photoemission of elec-trons from atoms in various chemical environments. The shape of lines was approximated in the form of convolution of Lorentz and Gauss functions.

The IR spectra of initial platinum and palladium cyanometallate complexes in the range of 4000–400 cm^{-1} were taken on a Hitachi 270-30 instrument. Samples were prepared by pressing in tablets with KBr. The IR spectra with Fourier-transformation for studying activated carbon with adsorbed $K_2[Pt(CN)_4]$ were obtained on a Bruker IFS-88 instrument.

Mass-spectrometer experiments were carried out in a mode of recording negatively charged ions on an Axima Perfomance time-of-flight mass-spectrometer (Shimadzu/Kratos Analytical, Great Britain) with a MALD ionization source equipped with a UV laser (337 nm). The ion source voltage was 20 kV, voltage on lenses 6.5 kV, and voltage on a detector 2.1 kV. The detection of ions was carried out over the range of m/z values from 1 up to 2000. Spectra were treated using MALDI-MS Shimadzu Biotech Launchpad v. 2.8 program, signals were processed by the Gauss method. The resolution of the detected signals was 1500. Theoretical isotope distributions were obtained using MassPro v.1.0 program.

Samples for taking mass spectra of $K_2[Pt(CN)_4]$ and $K_2[Pt(CN)_6]$ were prepared as follows. Weighed samples of crystalline complexes were dissolved in a 0.1% aqueous solution of CF_3COOH so that their concentration was 1 mg ml^{-1}. A solution (0.5 μl) of α-cyano-*p*-hydroxycinnamic acid (5 mg ml^{-1}) dissolved in a 0.1% water–acetonitrile (50% of CH_3CN) solution of CF_3COOH and 0.5 μl of a complex compound solution were placed on a target for the matrix-activated laser desorption and then the mixture was dried in air.

When studying activated carbons with deposited Pt (II) and Pt(IV) cyanide complexes, weighed samples of an adsorbent (1 mg) were suspended in 30 μl of 0.1% aqueous solutions of trifluoroacetic acid. From this suspension 0.5 μl of a adsorbent sample was taken and mixed on a target with 0.5 μl of α-cyano-*p*-hydroxycinnamic acid solution prepared from the same components as in the case of studying platinum complexes. The target was dried to dryness in air.

Concentrations of iron cyanide complexes in solutions in the experiments on studying $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ adsorption on activated carbons were determined by atomic absorption spectroscopy on a SpektrAA 220 Varian instrument.

Content of platinum compounds on activated carbon before and after autoclave desorption were determined by the X-ray-luminescent method on an ElvaX energodispersion spectrometer. Fluorescent radiation of Pt (L-series) was excited by filtrated deceleration emission of a through-target X-ray tube with a tungsten anode and recorded using an electrically cooled Si-PIN semiconducting detector. The voltage and current of the tube were 40 kV and 50 μA, respectively. An analytical parameter was determined as a value proportional to the intensity of the fluorescent radiation peak of the PtK_α line.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (grant no. 11-03-01011-a).

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