PHYSICAL METHODS
OF INVESTIGATION

EPR Spectra of Solutions
of Platinum Superoxo Hydroxo Complexes

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Abstract—EPR spectra of platinum superoxo hydroxo complexes in alkaline solutions were studied at various alkali concentrations. The EPR parameters for new platinum complexes were determined; the g-factors and hyperfine coupling constants were interpreted in terms of the ligand field theory. The structure of the platinum coordination sphere in the superoxo hydroxo complexes is discussed based on the EPR data.

In a previous study [1], dealing with ozonization of the platinum hexahydroxo complex in alkaline solutions with alkali concentrations of 1 to 4 mol/l, we discovered a blue platinum compound, which was classified as a superoxo hydroxo complex. The EPR spectra in [1] virtually coincided with those reported in [2] for the derivative of pentavalent platinum resulting from ozonization or electrochemical oxidation of alkaline solutions of hexahydroxoplatinate(IV). Based on the resolved structure of the EPR spectra of solutions of compounds identified as $M[Pt^V(OH)_6]$ (M = Li, K, Rb, Cs), it was concluded [2] that the unpaired electron of Pt(V) is involved in substantial hyperfine coupling (HFC) with the alkali-metal ions. This is surprising, especially for solutions in which the salts are dissociated. The coupling between the unpaired electron and, for example, potassium or lithium nuclei, whose nuclear spin is 3/2, should result in four equidistant components with equal intensities in the EPR spectra; this was not observed in the spectra of frozen solutions reported in [2]. The EPR spectra of paramagnetic platinum (usually Pt(III)) complexes exhibit hyperfine structure (HFS) from the ^{195}Pt isotope ($I = 1/2$, natural abundance 33.8%); i.e., for each main component of the g-tensor, the spectrum may contain two equidistant satellites, whose intensity is about 25% of the central peak intensity. The spectra reported in [2] cannot be assigned to individual mononuclear platinum(V) complexes, because they have additional components. These facts, together with those reported in [1], indicate that the EPR spectra observed can by no means be attributed to the platinum(V) hydroxo complex and can be due only to the corresponding superoxo complex.

However, some features of these spectra had precluded [1] the possibility of drawing unambiguous conclusions on the structure of the "blue" complex. The same holds true for the "pink" complex, first prepared in [3], which is stable in more concentrated solutions of KOH. More detailed investigation of this aspect is the subject of the present study.

EXPERIMENTAL

The initial alkaline solutions of Pt(IV) were prepared by dissolving $M_2[PtCl_6]$ (M = Na, K) or $PtO_2 \cdot xH_2O$ in aqueous NaOH or KOH or in solutions of NaOD or KOD in D_2O (alkali concentration 0.1–20 mol/l) followed by boiling. The resulting solutions of $Pt(OH)_6^{2-}$ were oxidized by ozone, excess $Na_2S_2O_8$, or by hypochlorites or subjected to electrochemical oxidation. The total content of platinum in the solution was $(0.5–10.0) \times 10^{-3}$ mol/l.

The EPR spectra of the solutions were recorded on a RADIOPAN SE/X-2544 spectrometer in the X-band (frequency ~9.1 GHz) at 77 K. A typical feature of the compounds studied discovered in recording the spectra is that the upper levels of the unpaired electron are saturated when the microwave radiation power delivered to the sample is more than several milliwatts. When this level is exceeded, the intensity ratio of the components in the spectrum changes, which might lead to errors in their interpretation.

Virtually all of the EPR spectra of Pt ozonization products consist of a large number of components. Therefore, in discussing the results, much attention is paid to the principles used to interpret the spectra. In the case of complex spectra, computer simulation of EPR spectra and comparison with the experimental spectra is the most adequate method for determination of spectral parameters (g-factors, HFC constants, etc.).

The spectra with $S = 1/2$ were interpreted using the EPR-D5 program package, version 3.0 (Komozin, P.N. and Berngardt, E.A., GEOKhI RAN, 1996), based on the theory of g-tensor and HFC for low-spin d^5 complexes [4]. It enables automatic calculation of EPR

parameters and the contents of individual complex species from a superposition of signals of several complexes.

The EPR parameters of compounds were determined by optimization using the specified interpretation model (spin Hamiltonian and the line contour) until the best fit of the theoretical spectrum to the experimental spectrum was attained. In the calculation using the ERD-D5 package, some instrumental errors, for example, the drift of the zero line of the spectrum, are also automatically compensated. After optimization based on finite steps of the parameter variation had been completed, the errors of parameter determination were estimated. The root-mean-square deviations of the points of the theoretical spectrum from the experimental spectrum allow one to judge the adequacy of the given model corresponding to a particular complex composition and structure.

The line shape plays an important role in the simulation of spectra. The Lorentzian shape is theoretically substantiated for an EPR signal of an isolated paramagnetic center. An experimental EPR spectrum is normally described as a convolution of Gaussian and Lorentzian line shapes. The EPR-D5 package uses a Lorentzian line; the nonuniform broadening of the real signal is taken into account by introducing a nonresolved hyperfine structure; this is better defined from the physical viewpoint and accelerates the calculation. And, if the model has been chosen correctly, it provides additional information on the structure of the complex. Analysis of selected best-resolved components of the spectra of the complexes under consideration demonstrated that EPR signals are described quite well by a purely Lorentzian contour; i.e., it does not include nonresolved structure from any type of nuclei.

For compounds with $S > 1/2$, the theoretical EPR spectra were simulated using the SimFonia program from the WinEPR package (Bruker software) until the maximum visual coincidence with the experimental spectrum was attained.

RESULTS AND DISCUSSION

The structure and the content of the platinum oxidation products observed in the EPR spectra scarcely depend on the nature of the oxidant used but are determined by the alkali concentration and vary with time.

"Pink" complexes. The simplest EPR spectral pattern is observed in a study of the so-called "pink" complexes, which exist at alkali concentrations of more than 5 mol/l [3]; in this case, the spectral pattern is almost the individual signal of a paramagnetic compound (species **I**, Fig. 1).

A typical HFS from one ^{195}Pt nucleus is resolved in the region of components with the smallest g values. Owing to computer analysis, the line shape for the nonresolved low-field spectrum component could also be estimated. The experimental EPR parameters of this compound are presented in the table.

The spectrum can formally be assigned to a Pt(V) complex with $S = 1/2$ and rhombic anisotropy of the g-tensor irrespective of the site where the unpaired electron is located. The two g-tensor components are relatively close and, in the first approximation, its anisotropy can be regarded as axial anisotropy with $g_\parallel(g_z) > g_\perp(g_x + g_y)$; in the case of complexes with the low-spin d^5 configuration, this corresponds to the ^2E ground state (if the electron is localized in the d_{xz}, d_{yz} orbital) [4, 5]. Such systems with an unpaired electron in degenerate orbitals are distorted due to the Jahn–Teller effect [5], which may account for the rhombic anisotropy of the g-tensor.

According to the theory considered in [4], for low-spin d^5 complexes with the lower Kramers doublet

$$\psi^\pm = a(-id_{yz}^\pm) + b(\mp d_{xz}^\pm) + c(\pm id_{xy}^\mp),$$

the expressions for the g-tensors and HFC can be written as follows:

$$g_x = g_e(+a^2 - b^2 - c^2) - 4kbc,$$

$$g_y = g_e(-a^2 + b^2 - c^2) - 4kac,$$

$$g_z = g_e(-a^2 - b^2 + c^2) - 4kab,$$

$$A_x = K_k(+a^2 - b^2 - c^2)$$
$$+ P[(2a^2 + 2c^2 + 2ab - 2ac)/7 + 4k_e(-bc)], \quad (1)$$

$$A_y = K_k(-a^2 + b^2 - c^2)$$
$$+ P[(2b^2 + 2c^2 + 2ab - 2bc)/7 + 4k_e(-ca)],$$

$$A_z = K_k(-a^2 - b^2 + c^2)$$
$$+ P[(2a^2 + 2b^2 + 4c^2 - 2ac - 2bc)/7 + 4k_e(-ab)].$$

where $g_e = 2.0023$, k is the orbital contraction factor, which takes into account the orbital mixing (the cova-

Parameters of the EPR spectra (77 K): g-factors and HFS constants (A_i, 10^{-4} cm^{-1})

Species	Medium	g_1	g_2	g_3	A_1	A_2	A_3
I	$c_{OH^-} > 5$	2.169(4)	2.014(1)	1.977(2)	52(12)	53(2)	63(4)
II	$0.5 < c_{OH^-} < 5$	2.187(2)	2.086(1)	1.926(1)	78(5)	51(5)	69(3)
III	$0.5 < c_{OH^-} < 5$	2.177(4)	2.055(1)	1.954(2)	,69(7)	53(3)	68(5)

lence of the metal–ligand bond and configurational interaction). K_k is the contact contribution, P is a dipole–dipole interaction parameter, and $k_e = 2k/g_e = 0.99885k$. Substitution of experimental g_i or A_i ($i = x, y, z$) values into the equations gives wave function coefficients a, b, c; the secular equation

$$(E_{xz} - E)a + (\lambda/2)b + (\lambda/2)c = 0,$$

$$(\lambda/2)a + (E_{yz} - E)b + (\lambda/2)c = 0,$$

$$(\lambda/2)a + (\lambda/2)b + (E_{xy} - E)c = 0$$

can be used to calculate the energies of d orbitals E_{ij} expressed in the units of the spin–orbit interaction λ of the complex.

It is impossible to determine the sign of the g-tensor components from the experimental spectrum; therefore, their substitution into equation (1) can lead, depending on the sign of the component $g_i < g_e$, to two fundamentally different solutions corresponding to a great (i) or small (ii) splitting of d orbitals.

	a	b	c	k	E_{xz}/λ	E_{yz}/λ	E_{xy}/λ
(a) $g_x = 1.977$	0.997	0.074	0.015	0.568	14.3	7.5	–21.8
(b) $g_x = -1.977$	0.588	0.583	0.561	1.001	0.03	0.02	–0.04

Note that the assignment of g_i values close in magnitude (2.014, 1.977) to either g_x or g_y component of the g-tensor is equivalent to redefinition of the X and Y axes of the complex, i.e., to the change in the order of arrangement of the levels E_{xz} and E_{yz}, which is insignificant in this particular case.

Experimental data on the EPR spectra of low-spin d^5 complexes [5] indicates that for complexes with a slight distortion of the octahedral symmetry, in which all the d_π orbitals of the metal atom are virtually degenerate (solution a), it is impossible to obtain a spectrum in which the lines would be so narrow as those observed in the spectrum shown in Fig. 1. Thus, the solution that implies great axial splitting accompanied by some rhombic anisotropy ($g_x > 0$) is the most likely. The orbital contraction factor, $k = 0.568$, is much smaller than the value $k = 1$, expected for the case where the unpaired electron is fully localized on the d_{xz} and d_{yz} orbitals. Unfortunately, the available experimental data are insufficient for estimating the contribution of configurational interaction to the k factor; however, it can be suggested that electron delocalization from the d orbitals to the ligand plays the crucial role in the decrease in k.

The character of the metal–ligand bond can be estimated more correctly by analyzing the HFS constants. Even the first juxtaposition of the obtained results with the data for known Pt(III) complexes [6, 7] shows that,
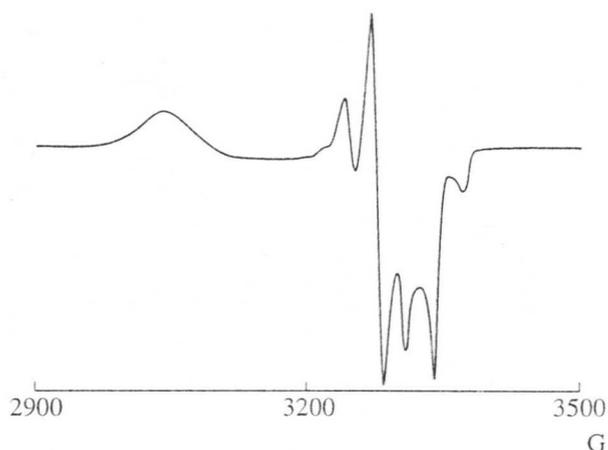

Fig. 1. EPR spectrum (77 K) of the "pink" solution after ozonization of the Pt(IV) hydroxo complex in KOH ($c_{OH^-} = 15$ mol/l).

in our case, the HFS constants are much lower. This points to a substantial decrease in the unpaired electron density in the atomic orbitals of the metal and confirms the above choice of the solution corresponding to $k < 1$. By substituting the a, b, and c coefficients and the k factor into equation (1) for A_i, one can calculate the contact contribution and the dipole–dipole interaction parameter and compare them with the corresponding values for the free ^{195}Pt ions: $K_0 = 11\,478 \times 10^{-4}$ cm^{-1} and $P_0 = 497 \times 10^{-4}$ cm^{-1} [8]. As in the case of the g-tensor, the signs of the HFC tensor components A_i are unknown. However, as far as all three values of the HFS constant have been estimated and only two unknown parameters, K_k and P, are to be found from three independent equations, the signs can be determined unambiguously. When the equations $A_i = f(K_k, P)$ are solved in pairs with all of the possible signs of A_i, only one convergent solution having a physical meaning is obtained ($0 < P/P_0 < 1$): $K_k = 54 \times 10^{-4}$ cm^{-1}, $P = 25 \times 10^{-4}$ cm^{-1}. The ratio $K_k/K_0 > 0$ shows that the contact contribution is due to the slight admixing of the $6s$ orbitals to the $5d$ orbitals of the metal atom. The value $P/P_0 = 0.05$ points to an exceptionally high degree of delocalization of the unpaired electron from the metal d orbitals to the ligand.

Thus, these results cannot be explained in terms of the formation of mononuclear low-spin d^5 aqua hydroxo complexes, which cannot be characterized by such great distortions and degree of electron delocalization from the d_{xy} orbital ($g_\parallel < g_\perp$) [9]. The assumption that the Pt(V) ion exists in the low-spin d^5 configuration does not account for the saturation of the sample by microwave radiation, which is more typical of systems with weak spin–orbit coupling of the unpaired electron, e.g., for radicals. A more probable model is a

Fig. 2. EPR spectra (77 K) of the products of oxidation of the Pt(IV) hydroxo complex in NaOH (c_{OH^-} = 5 mol/l) by excess $Na_2S_2O_8$ at 100°C for (*a*) 1, (*b*) 3, (*c*) 10, (*d*) 20, and (*e*) 40 min.

Pt(IV) complex with an O_2^- group, whose existence in systems of this type has been shown previously [3].

"Blue" complexes. The EPR spectra recorded upon oxidation of platinum(IV) in solutions with a KOH concentration of less than 5 mol/l are more complex and depend on the time of the reaction or storage of solutions. It is significant that the EPR spectra of the final products obtained using different oxidizing reagents (ozone, hypochlorite, or persulfate) but with the same c_{OH^-} are virtually identical. Upon treatment of platinum hydroxo complexes with persulfate, the simplest species corresponding to an initial stage of the process can be detected.

Figure 2 shows the variation of the EPR spectra during the oxidation of platinum in a 5 M solution of NaOH with excess persulfate at 100°C. The "oxidized" products were found to exist in solutions over limited periods of time. When c_{OH^-} > 3 mol/l, the products almost necessarily contain species **I**. Even besides the signal due to this species, the spectral variations observed during the reaction point to the presence of several platinum complexes in the solution. Identification of the EPR signals is hampered by the fact that the use of either KOH or low concentrations of any alkali results in the formation of precipitates, which are responsible for broadened lines in the EPR spectra. The complex spectral patterns, caused by superposition of

EPR signals of several compounds, might be the reason for the erroneous interpretation of the signals made in [2].

An attempt to describe a complex EPR spectrum by a combination of signals with $S = 1/2$ and HFS from one ^{195}Pt nucleus leads to satisfactory results if more than three complexes with rhombic anisotropy of the *g*-tensor are taken into account. However, resolution of the spectrum into signals corresponding to a large number of compounds permits one to interpret almost any EPR spectrum, although the reliability of the thus-obtained information is extremely low. According to Raman spectroscopy data [10, 11], simultaneous existence of more than three complexes in this type of system is relatively unlikely.

The EPR spectra of the products resulting from platinum oxidation for 0.5 to 1 min with the alkali concentration ranging from 0.5 to 5 mol/l, irrespective of the alkali used (NaOH, KOH, NaOD, KOD), always exhibit the predominant signal with a relatively simple shape (Fig. 2, *a*). A short-term storage of the solution under ambient conditions makes the EPR spectrum more complicated. The high reproducibility of the spectra indicates that the initial step of the process yields a single oxidized species **II** or several simple species in a constant ratio.

Let us pay attention to the interpretation of the last spectrum. Note that the weak nonreproducible signals at $g = 2.0$ (3150–3250 G) were considered beforehand as artifacts.

The spectral pattern corresponds to a compound with a rhombic anisotropy of the *g*-tensor, each component of which is structured. The structure of five lines with a ratio of integrated intensities of 1 : 8 : 18 : 8 : 1 can be distinguished especially clearly at the edges of the spectrum (Fig. 3). A quintet with this ratio could not arise from the HFS caused by one ^{195}Pt nucleus (an identical spectrum is also observed in completely deuterated systems, which contain no nuclei capable of inducing HFS, apart from platinum).

Two models, describing most adequately the observed EPR spectra, can be proposed for the structure of the platinum compounds considered.

According to one model, the solution contains species with the total spin $S = 3/2$, in which each unpaired electron is located predominantly at one platinum atom and is partly involved in the exchange interaction. In terms of such an interpretation, three central lines in each quintet are due to the fine structure from three electrons, while the low-intensity outer satellites are due to the HFS from the ^{195}Pt nucleus. Figure 4 shows the experimental and theoretical spectra, calculated within the framework of this assumption for tetragonal (*D*) and rhombic (*E*) zero-field splitting parameters equal to $18(2) \times 10^{-4}$ and $7(2) \times 10^{-4}$ cm^{-1}, respectively. Some differences between the intensities of the central components of the quintets in the experimental and theoretical spectra of the system with $S = 3/2$ can be attrib-
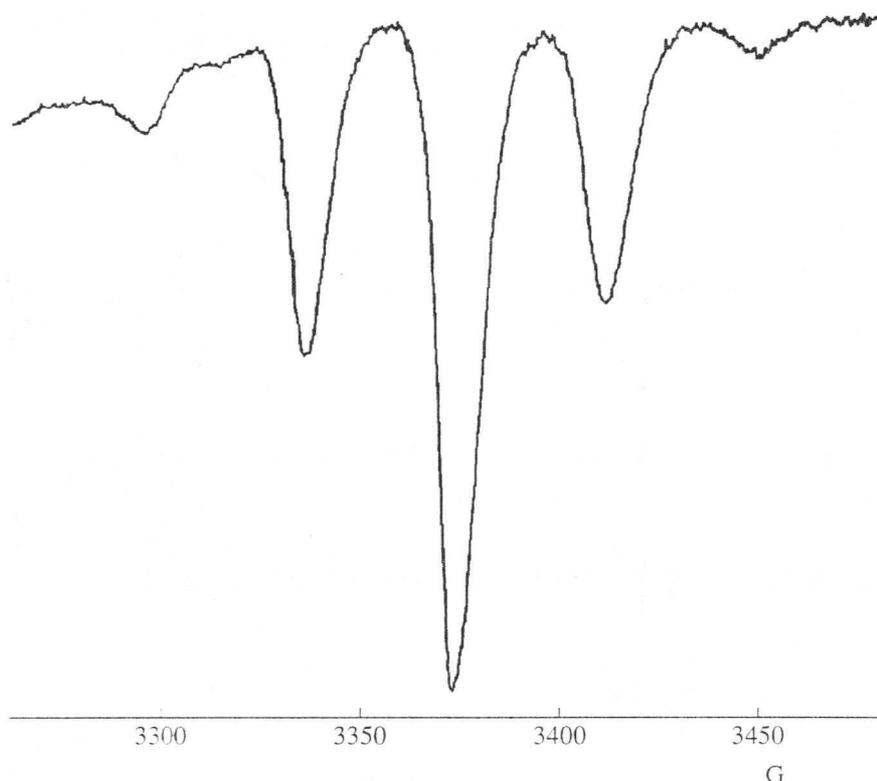
Fig. 3. Fragment of the EPR spectrum (77 K) of the compound formed at the initial stage of oxidation of platinum hydroxo complex in 2 M NaOD.

uted to the presence (about 30%) of a compound (Fig. 4, d) with $S = 1/2$ but with identical g-tensor and HFS values.

The model with $S = 3/2$ implies the existence of trimeric complexes in which each platinum atom occurs in the oxidation state +5 (low-spin d^5 configuration) and in a rhombically distorted environment and experiences weak exchange interaction with the two neighbors. A theory for the interpretation of the EPR parameters of similar clusters was developed previously [12]. The hypothesis of the formation of trimeric clusters in the system does not contradict the interpretation of the experimental spectrum as the spectrum of the sum of compounds with $S = 3/2$ and $S = 1/2$, if these compounds are assumed to have the same structure but different numbers of Pt(V) ions, i.e., if the complex with $S = 1/2$ is considered to be the Pt(IV)–Pt(IV)–Pt(V) trimer.

The alternative model that provides interpretation of the EPR spectrum observed at the initial oxidation step assumes the presence of one dimeric compound with a spin of 1/2 in which the unpaired electron is coupled with two equivalent platinum nuclei. The number and the intensity ratio of the observed HFS components is readily interpreted by taking into account the isotope composition of the dimers. The system contains one ^{195}Pt isotope with $I = 1/2$ capable of inducing HFS and

two isotopes, ^{194,196}Pt, with nuclear spins equal to zero. The ^{194,196}Pt–^{194,196}Pt ($I = 0$), ^{194,196}Pt–^{195}Pt ($I = 1/2$), and ^{195}Pt–^{195}Pt ($I = 1$) dimers can coexist in the system and make different contributions to the HFS. Statistical analysis shows that for the natural abundance of ^{195}Pt, equal to 33.8%, the HFS at two equivalent platinum nuclei should consist of five lines with an intensity ratio of 1 : 7.8 : 17.4 : 7.8 : 1, which agrees with the experimental intensity ratio (determined from the areas under the corresponding peaks).

The latter model for the description of the spectrum requires a lesser number of assumptions and, hence, it is preferable. More evidence supporting this model is the fact that no fine structure corresponding to $S > 1/2$ has been observed for analogous rhodium compounds resulting from oxidation in alkaline [13] or acidic [14] solutions.
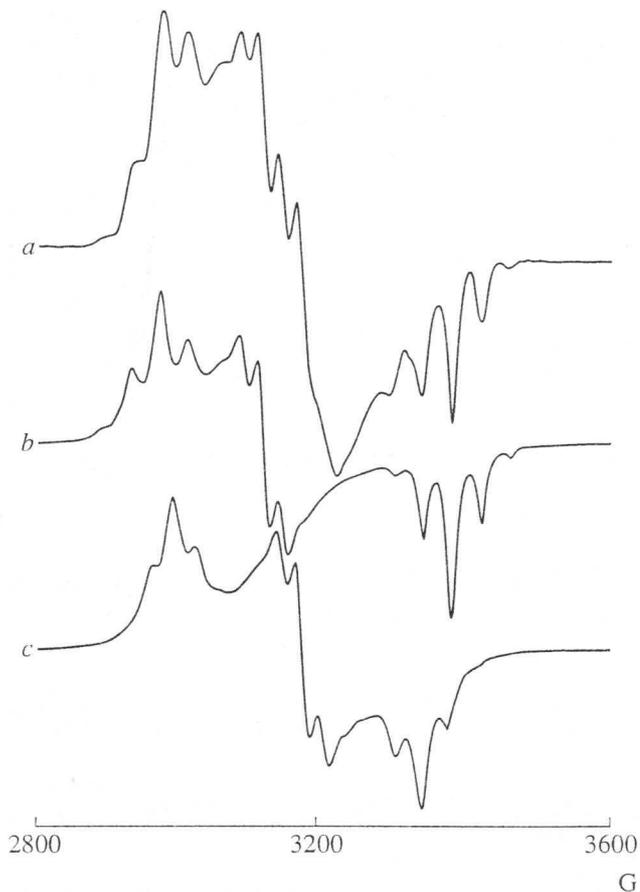
Because the superoxo group coordinated to platinum is known to exist in such systems [15] and resorting to the electronic spectroscopy data, indicating a binuclear structure of compounds [3], one can argue that the complex contains the $[Pt–O_2^- –Pt]^{7+}$ fragment.

The g-tensors and HFC constants for **II** do not depend on the model chosen and are presented in the table.
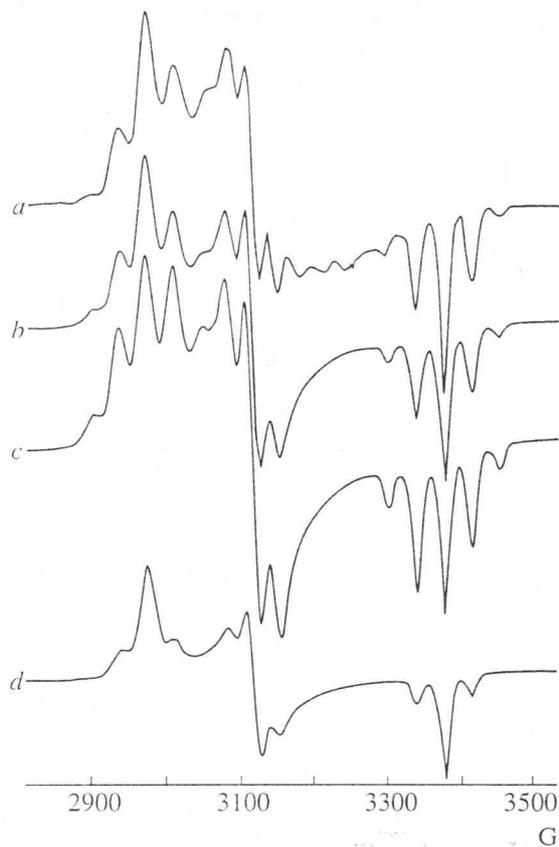
Fig. 4. (*a*) EPR spectrum (77 K) of the compound formed in the oxidation of platinum(IV) hydroxo complex in NaOH (c_{OH^-} = 2 mol/l) by persulfate; the results of computer simulation of EPR signals in the systems with a spin of (*d*) 1/2 and (*c*) 3/2; and (*b*) the superposition of signals with $S = 3/2$ and $S = 1/2$.

Fig. 5. (*a*) EPR spectrum (77 K) of the blue solution obtained after ozonization of the platinum hydroxo complex in KOH (c_{OH^-} = 3 mol/l) and the theoretical signals of individual dimers (*b*) II and (*c*) III.

Interpretation of the electronic structure of compound II in terms of the g-tensor theory of low-spin d^5 complexes is complicated by the fact that the available data do not permit one to choose the g component corresponding to the compound principal axis Z; i.e., it is impossible to elucidate the ground state (the sequence of d orbitals) or to interpret unambiguously the HFS. It only remains to estimate the possible values for d-orbital splitting Δ_i/λ ($\Delta_i = E_i - E_j$, i, j = 1, 2, 3) and the orbital contraction factor. For the reasons discussed above, of the two competing solutions, the latter solution, which corresponds to a great distortion of the complex ($g_{min} > 0$) should be chosen. Then $k = 0.483$, $\Delta_1/\lambda = 3.19$, $\Delta_2/\lambda = 4.93$, and $\Delta_3/\lambda = 8.11$. Attention is attracted by the low value of the k factor, characterizing a very high delocalization of the unpaired electron from the d orbitals of the metal atom to the superoxo group; i.e., as the first approximation, this complex can be regarded as a compound in which two Pt(IV) ions are linked through a superoxo group, containing an unpaired electron, whose behavior is substantially affected by interaction with platinum.

Let us turn back to platinum compounds in 0.5–5 M solutions of alkali formed upon relatively prolonged oxidation (Fig. 2) or upon storage. Upon choosing a model (spin Hamiltonian) for the complex, complicated spectra can be resolved into signals of individual species. Computer analysis indicates that all the observed EPR spectra are overall spectra of three species, two of which (I and II) were discussed above. The dimeric complex II usually coexists in dilute alkaline solutions with compound III, having a similar structure but slightly different g-factors. This can be explained by differences in the composition of the coordination sphere (for example, H_2O may have been replaced by OH^- groups or vice versa), by the formation of one- or two-bridged complexes (μ-O_2^- or μ-O_2^-, μ-OH^-), or by the presence of different conformations of the binuclear superoxo complex (this follows from the results of quantum-chemical calculations for these systems [16]). Virtually all the conclusions concerning the structure of complex II can be extended to compounds III that have the following ligand field parameters: $k = 0.506$, $\Delta_1/\lambda = 6.97$, $\Delta_2/\lambda = 5.65$, $\Delta_3/\lambda = 12.6$. Figure 5 presents a typ-

ical EPR spectrum of solutions formed upon platinum oxidation and the result of computer simulation of the EPR signals of species **II** and **III**, whose sum describes adequately the experimental spectrum.

Note that the proportions of **II** and **III** in blue solutions (based on the simulation of the EPR spectrum) are nearly equal, whereas complex **I** is present only as an impurity. This is consistent with the Raman spectroscopy data, according to which the solutions in question contain mainly two compounds with the O_2^- group [10, 11].

Thus, oxidation of platinum(IV) hexahydroxo complexes by ozone, hypochlorite, persulfate, or electric current in solutions yields superoxo hydroxo complexes that are present in different concentrations depending on the alkali concentration and exposure duration.

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REFERENCES

1. Kiselev, Yu.M., Pankratov, D.A., Ezerskaya, N.A., *et al.*, *Zh. Neorg. Khim.*, 1994, vol. 39, p. 1340.

2. Burlaku, N.Y., Ketrush, P.M., Shames, A.L., *et al.*, *Mater. Sci.*, 1991, vol. 17, no. 4, p. 47.

3. Kiselev, Yu.M., Pankratov, D.A., Kiseleva, I.N., and Shundrin, L.A., *Zh. Neorg. Khim.*, 1996, vol. 40, p. 2069.

4. Berngardt, E.A. and Komozin, P.N., *Zh. Neorg. Khim.*, 1997, vol. 42, p. 614.

5. Rieger, P.H., *Coord. Chem. Rev.*, 1994, vol. 136/136, p. 203.

6. Kirmse, R., Dietzsch, W., and Sollov'ev, B.V., *J. Inorg. Nucl. Chem.*, 1997, vol. 39, p. 1157.

7. Neubacher, H., Zaplatinski, P., Haase, A., and Lohman, W., *Z. Naturforsch. B*, 1979, vol. 34, p. 1015.

8. Rakitin, Yu.V., Larin, G.M., and Minin, V.V., *Interpretatsiya spektrov EPR koordinatsionnykh soedinenii* (Interpretation of EPR Spectra of Coordination Compounds), Moscow: Nauka, 1993.

9. Komozin, P.N. and Miroshnichenko, I.V., *Zh. Neorg. Khim.*, 1999, vol. 44, no. 3, p. 452.

10. Pankratov, D.A., Sokolov, V.B., and Kiselev, Yu.M., *Zh. Neorg. Khim.* (in press).

11. Pankratov, D.A. and Kiselev, Yu.M., Abstracts of Papers, *XVI Mendeleevskii s"ezd po obshchei i prikladnoi khimii* (XVI Mendeleev Congr. on General and Applied Chemistry), Moscow: Nauka, 1998, vol. 1, p. 239.

12. Berngardt, E.A., Marov, I.N., and Belyaeva, V.K., *Zh. Neorg. Khim.*, 1995, vol. 40, p. 1510.

13. Miroshnichenko, I.V., Sidorov, A.A., and Komozin, P.N., *Zh. Neorg. Khim.*, 1986, vol. 31, p. 2883.

14. Komozin, P.N. and Zakharchenko, E.A., *Zh. Neorg. Khim.*, 1997, vol. 42, p. 1297.

15. Pankratov, D.A. and Kiselev, Yu.M., Abstracts of Papers, *XVI Mezhdunarodnaya Chernyaevskaya konferentsiya po khimii, analizu i tekhnologii platinovykh metallov* (XVI Int. Conf. on Chemistry, Analysis, and Technology of Platinum Metals), Yekaterinburg, 1996, p. 81.

16. Pankratov, D.A., *Cand. Sci. (Chem.) Dissertation*, Moscow: Moscow State Univ., 1998.