

COORDINATION  
COMPOUNDS

## Platinum(IV) Superoxo Complexes<sup>1</sup>

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**Abstract** – The products of reaction of platinum(IV) hydroxo complexes with ozone in alkaline solutions were studied using various physicochemical methods: electronic spectroscopy, electron spin resonance, and cyclic voltammetry. The arguments presented suggest that the blue solutions obtained contain superoxo Pt(IV) complexes.

One of the most efficient ways to stabilize higher oxidation states in the transition elements is complex formation in aqueous-alkaline media [1]. In this case, hydroxyl ions offer advantages over other ligands and produce a stronger decrease in  $E^0$  of a redox system than other, rather weakly polarizable ligands, which form complex ions in acid and neutral media. This circumstance is the one favoring stabilization of the highest oxidation states in neptunium, plutonium, americium(VII) [2], and iron(VIII) [3]. Hence, in alkaline media, heavy  $d$  transition metals, platinum especially, are expected to form rather stable compounds containing elements in their highest oxidation states (e.g., oxo or hydroxo complexes). Obtaining these elements in their highest oxidation states is still a problem.

In this connection, we attempted to oxidize platinum(IV) hydroxo complexes with ozone in alkaline medium, and observed the formation of intensely blue solutions.

This paper aims at investigation of the compounds thus prepared in order to establish the composition and geometry of the blue complexes.

### EXPERIMENTAL

Solutions of platinum(IV) hydroxo complexes were prepared by treating solutions of potassium [hexachloroplatinate(IV)] with a potassium hydroxide solution under reflux until the initially formed precipitate dissolved. Ozonization was performed at room temperature by bubbling air containing 1% ozone through this solution at a flow rate of 30 l/h.

Spectrophotometric study of the solutions was performed on a double-beam Specord UV-VIS spectrophotometer in the 13000 - 50000  $\text{cm}^{-1}$  range (quartz cells,  $l = 10$  mm,  $\text{H}_2\text{O}$  or  $\text{KOH}$  reference solutions). Electrochemical experiments (i.e., cyclic voltammetry) were made on a PA-3 polarographic analyzer using a

procedure similar to that described in [4]. ESR spectra of the solutions were taken on an EPRV experimental setup ( $X$ -band;  $H = 9.2$  GHz) made in the Design Department of the Institute of Chemical Physics, Russian Academy of Sciences.

Hydroxoplatinate(IV) solutions containing  $(1.5 - 6.0) \times 10^{-3}$  mol/l platinum in 1 - 4 mol/l aqueous  $\text{KOH}$  are faint yellow. Upon ozonation, these solutions change their color to intense blue. Properties of these solutions will be considered below.

### RESULTS AND DISCUSSION

**Pt(IV) hydroxo complexes** used as the initial compounds in the ozonation have been studied in detail earlier [5 - 7]. In this work, the compositions of hydroxo complexes were determined using only the electronic spectroscopic data. The results of spectroscopic study of alkaline solutions of hydroxo complexes appear in Table 1.

Note that the interpretation of the absorption spectra made in [5] seems to be controversial. The theoretical evaluation made in [5]<sup>2</sup> fails to fit the experimental data: the  $\text{PtCl}_5\text{OH}^{2-}$ ,  $\text{PtCl}_4(\text{OH})_2^{2-}$ , and  $\text{Pt}(\text{OH})_6^{2-}$  ions, which were considered in [5], demonstrate in the spectra absorption bands that were not assigned in [5].

For this reason, we made special assignment for the absorption spectra of  $\text{Pt}(\text{OH})_6^{2-}$  ions using the recommendations [9].

First of all, within the framework of the strong-field model,<sup>3</sup> the  $5d^6$  states for a complex of octahedral geometry are characterized by the lowest  $^1A_1$  term. The

<sup>2</sup>The Mulliken-Wolfsberg-Helmholz (MWH) technique with allowance for the symmetry.  $10Dq = 27600 \text{ cm}^{-1}$  for hexahydroxo platinum(IV) complex as calculated according to [5]. This value is inconsistent with that expected from the ligand-field theory.

<sup>3</sup>For the Pt(IV) ion, the spin-orbit coupling constant is much greater than zero.

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**Table 1.** Electronic spectra of hexacoordinate platinum(IV) complexes\*

Ion	Absorption bands ( $\nu \times 1000 \text{ cm}^{-1}$ ), their intensities ( $\epsilon, \text{l M}^{-1} \text{ cm}^{-1}$ ), and assignment			
	$^1A_1 \rightarrow ^3T_1$	$^1A_1 \rightarrow ^3T_2$	$^1A_1 \rightarrow ^1T_1$	$^1A_1 \rightarrow ^1T_2$
PtF <sub>6</sub> <sup>2-</sup>	22.5	24.4	31.4	36.4
[10, 11]	(20)	(40)	(280)	(240)
PtCl <sub>6</sub> <sup>2-</sup>	20.7	21.5	26.4	28.3
[6, 15]	(27)	(32)	(200)	(294)
Pt(OH) <sub>6</sub> <sup>2-</sup>	22.57	—	32.7	—
[5]	(20)		(300)	
Pt(OH) <sub>6</sub> <sup>2-</sup>	22.5	(24.3)**	31.8	37.0
(Our data)	(25)		(400)	(450)

Notes: \* The spin-orbit coupling constants  $\xi = \sqrt{\epsilon_{3T_1} 2 \{E_{3T_1} - E_{1T_1}\}^2 / \epsilon_{1T_1}}$  were calculated from the relation  $\xi$  given by Gray [8] with allowance for the free-orbital  $\xi$  value for the Pt(IV) ion (i.e.,  $5100 \text{ cm}^{-1}$ ). The calculated values are 3364, 2962, and 3288 for the fluoride, chloride, and hydroxide, respectively. In fact, these values support the similarity between the properties of the fluoro and hydroxo complexes: e.g., the degrees of ionization are 0.65 and 0.64 for the F<sup>-</sup> and OH<sup>-</sup> derivatives, respectively.

\*\* Assessment.

following  $d-d$  transitions will appear in the spectra:  $^1A_1 \rightarrow ^3T_1$ ,  $^1A_1 \rightarrow ^3T_2$ ,  $^1A_1 \rightarrow ^1T_1$ ,  $^1A_1 \rightarrow ^1T_2$  (all corresponding to the transitions from  $(t_{2g})^6$  to the  $(t_{2g})^5(e_g)$  configuration) [9]. The singlet transitions are spin-allowed, and the triplet ones, spin-forbidden. Actually [10], all of these transitions may appear in the spectra, but their intensities differ by about an order of magnitude. This situation is exactly the one observed in spectra of PtCl<sub>6</sub><sup>2-</sup> and PtF<sub>6</sub><sup>2-</sup> ions [11].

Taking into account that the OH<sup>-</sup> ions are located between H<sub>2</sub>O and F<sup>-</sup> ions in the spectrochemical series [12], the fluoro complex PtF<sub>6</sub><sup>2-</sup> appears to be a satisfactory model for assignment of the Pt(OH)<sub>6</sub><sup>2-</sup> absorption bands. The observed absorption bands (Table 1) for the hydroxo complex have distinctly different intensities. This makes it possible to interpret these spectra as proposed in Table 1.

The assignment for the spectra of the hydroxo complexes in Table 1 seems to be self-consistent. In fact, it is usually assumed [14] that  $E(^1T_1) = 10Dq - C$  ( $C = 6B$  for the PtF<sub>6</sub><sup>2-</sup> ion [10])<sup>4</sup> and the difference between the  $^1T_2$  and  $^1T_1$  terms is  $18B$ . Then, for  $Dq$  we obtain an energy of  $3300 \text{ cm}^{-1}$ , with the  $B$  parameter being  $300 \text{ cm}^{-1}$ . The  $Dq$  value for the PtF<sub>6</sub><sup>2-</sup> ion is about the same, if not less, than the one for the Pt(OH)<sub>6</sub><sup>2-</sup> ion ( $Dq = 3350 \text{ cm}^{-1}$ ), just as expected from the spectrochemical series. Calculation of the  $B$  parameters for

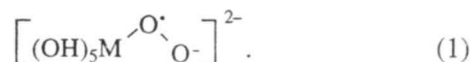
<sup>4</sup>  $C = 6B$  for the hexafluoroplatinate(IV) ion [10].

platinum(IV) hydroxo complex from the nepheloxetic parameter  $\beta$  (Jørgensen, [15]) demonstrates that the  $B$  value obtained is quite reasonable. Similarly, for  $Dq$ : calculation from the spectrochemical parameters  $f$  and  $q$  [15] gives  $Dq = 3370 \text{ cm}^{-1}$ , the value almost coinciding with the found one.

Thus, there are serious reasons to suppose that hydroxyl-containing ions of octahedral configuration [i.e., hexahydroxoplatinato(IV) complexes] exist in the initial solutions of the hydroxo complexes. Note further that the spectrum as given in Table 1 also appears after decomposition of the aforementioned deep-colored compound. This makes it possible to assume that the products of the corresponding conversion also correspond to the composition Pt(OH)<sub>6</sub><sup>2-</sup>.

**Blue solutions** contain paramagnetic species ( $g_{\perp} = 2.053 \pm 0.002$ ) according to the ESR spectroscopic data (the spectra were taken at 200 K, so that they may be treated as being obtained from a substance incorporated in a glassy isotropic matrix). The absorption spectra of the same complex, taken at 20°C, exhibit the absorption bands given in Table 2.

These results are interpreted satisfactorily assuming that the ozonation of the alkaline solutions of platinum(IV) hexahydroxo complexes yields mononuclear superoxo derivatives of the type



Evidence is the set of bands at 16800, 22000, and  $36100 \text{ cm}^{-1}$  present in the absorption spectra of the blue solutions, and the intensities of these bands.

**Table 2.** Electronic absorption spectra of the superoxo complexes and the blue platinum(IV) compound<sup>1)</sup> ( $\nu$ , in parentheses).

Complex	Assignment				
	$\pi_h^* - \pi_v^*$ <sup>2)</sup>	$d\pi - \pi_v^*$ (a) <sup>3)</sup>	$d-d$ <sup>4)</sup>	$\pi_h^* - d_{z^2}$ (b) <sup>3)</sup>	$\pi_v \rightarrow \pi_v^*$
[Co(CN) <sub>5</sub> O <sub>2</sub> ] <sup>3-</sup> <sup>5)</sup> [20]	- <sup>6)</sup>	19.95 <sup>7)</sup> (~80)	25.0 <sup>7)</sup> (1000)	31.25 <sup>7)</sup> (~4000)	-
[Co <sub>2</sub> (CN) <sub>10</sub> O <sub>2</sub> ] <sup>5-</sup> [20]	12.2 (13)	20.59 (745)	26.8 (~1500)	32.20 (17250)	44.4 (13800)
[Co <sub>2</sub> (NH <sub>3</sub> ) <sub>10</sub> O <sub>2</sub> ] <sup>5+</sup> [20]	12.5 (110)	14.89 (927)	20.8 (~309)	33.10 (20200)	44.4 (21000)
[Co <sub>2</sub> en <sub>4</sub> (OH)O <sub>2</sub> ] <sup>4+</sup> [19]	-	14.8 (500)	20.3 (460)	-	-
[Co <sub>2</sub> en <sub>4</sub> (NH <sub>2</sub> )O <sub>2</sub> ] <sup>4+</sup> [19]	-	14.3 (280)	20.8 (310)	-	-
Blue platinum complex <sup>8)</sup>	13.5 (40)	16.8 (100)	22.0 <sup>9)</sup> (100)	36.1 (>1000)	41.0 (>2000)

Notes: <sup>1)</sup> $\nu \times 1000 \text{ cm}^{-1}$ ,  $\epsilon$ , l/(M cm).

<sup>2)</sup> The intraligand transition band (forbidden according to Laporte).

<sup>3)</sup> The charge-transfer band: (a) metal-to-ligand; (b) ligand-to-metal.

<sup>4)</sup> The  $d-d$  transition in the cobalt(III) complexes ( $^1A_{1g} \rightarrow ^1T_{1g}$ ).

<sup>5)</sup> Mononuclear complex in solution.

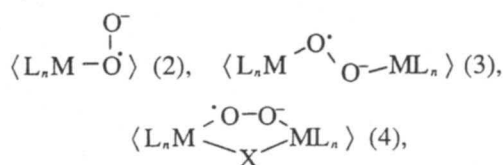
<sup>6)</sup> Not observed in the spectra either of solutions or of single-crystalline samples.

<sup>7)</sup> Peaks of the absorption bands (and their intensities) somewhat alter their positions on the energy axis. Here, the values for acetonitrile solution are given.

<sup>8)</sup> 3M KOH solution containing  $1 \times 10^{-3}$  mol/l Pt; the peak position remains the same in the 1 - 4 M KOH range.

<sup>9)</sup> The  $d-d$  transition of the  $^1A_1 \rightarrow ^3T_1$  type.

Indeed, for similar cobalt and rhodium compounds [14, 16 - 18] (having  $d^6$  configuration at the central atom), the following three types of complexes can exist:



where complex (2) is mononuclear, and complexes (3) and (4) are bridged binuclear compounds.

The spectra of these superoxo derivatives exhibit absorption bands at 15000, 21000, and 33000  $\text{cm}^{-1}$ .<sup>5</sup> Two of these bands are charge-transfer bands. Hence, for compounds of types (3) and (4), rather high extinction coefficients [of  $\epsilon \geq 500$  l/(M cm)] are typical for the absorption bands in the visible spectral region. Interestingly, bridged system (4) usually displays markedly lower  $\epsilon$  values for the 15000- $\text{cm}^{-1}$  band. In the mononuclear complexes (type 2), this band shows still lower  $\epsilon$  values, of about 100 l/(M cm).

In our case, we observe about the same set of absorption bands. Further, the absorption maxima

<sup>5</sup> Similar peroxy complexes exhibit no absorption band at 15000  $\text{cm}^{-1}$  and are diamagnetic, in contrast to superoxo complexes.

observed in the visible spectral range have low intensities [ $\epsilon$  of about 100 l/(M cm)].

The bridging fragments  $\langle M(O_2^-)M \rangle$  and  $\langle M(O_2^-)(X)M \rangle$  in the cobalt and rhodium compounds have planar geometries [20]. According to quantum chemical calculations [20], this provides rather high extinction coefficients for the charge-transfer bands of the types  $d\pi \rightarrow \pi_v^*$  and  $\pi_v^* \rightarrow d\sigma^*$  ( $d_{z^2}^*$ ). Intensities of these bands will decrease either when one of the two bridges appears to be out the plane or when the M-O-X angle varies (a conclusion based on the Gray's diagrams of the complex molecular orbitals [20]). This explains the low  $\epsilon$  values in a mononuclear (type 2) complex.

Note that transitions in the visible spectral range, similar to the ones we found earlier in platinum compounds, appear in many other complexes containing superoxo bridges, and the spectral doublet at 15000, 21000  $\text{cm}^{-1}$  is their characteristic feature (Fig. 1) [14]. However, the assignment for the 21000- $\text{cm}^{-1}$  line (as well as the position of this line on the energy axis) may vary from one complex to another. For example, in  $[L_5Co(O_2)CoL_5]$  ( $L = NH_3$ ), the peak  $\nu = 20800 \text{ cm}^{-1}$  was interpreted as the forbidden  $^1A_{1g} \rightarrow ^1T_{1g}$  transition [with  $\epsilon = 309$  l/(M cm)] [20]. For  $L = CN$  (ionic charge of 5-), the band at  $\nu = 20590 \text{ cm}^{-1}$  was assigned to the  $d\pi \rightarrow$

$\pi_v^*(O_2^-)$  transition [with  $\epsilon = 745 \text{ l/(M cm)}$ ], and the one at  $26800 \text{ cm}^{-1}$  [ $\epsilon = 1500 \text{ l/(M cm)}$ ], to a forbidden transition of the  ${}^1A_1 \rightarrow {}^1E$  type.

Hence, the component at  $22000 \text{ cm}^{-1}$  in the spectrum of the blue solutions most likely is a spin-forbidden transition of the  ${}^3T_1 \rightarrow {}^1A_1$  type (compare with Table 1). An increase in  $\epsilon$  as compared to that of a similar transition in  $\text{Pt(OH)}_6^{2-}$  can be described in terms of the borrowed-intensity mechanism [9].

Turning back to the  $\langle L_5\text{Co(O}_2^-)\text{CoL}_5 \rangle$  complexes, note that the absorption at  $\nu = 12500 \text{ cm}^{-1}$  is considered to be an electro-dipole-forbidden transition  $\pi_h^* \rightarrow \pi_v^*$  [with  $\epsilon$  ranging between 13 - 110  $\text{l/(M cm)}$ ] [20]. It is possible that the weak absorption at  $13500 \text{ cm}^{-1}$  [ $\epsilon = 40 \text{ l/(M cm)}$ ] observed in the spectrum of the blue solutions corresponds to the same transition.

If we accept the assignment in Table 2, then we easily see the ultraviolet shift of the metal-to-ligand charge-transfer bands for the platinum(IV) compound as compared to the cobalt(III) derivatives (Table 2). The blue shift of the metal-to-ligand charge-transfer band indicates destabilization of the half-filled  $\pi_v^*$  orbital of  $O_2^-$ . A similar effect for the ligand-to-metal charge-transfer band arises from stabilization of the  $\pi_h^*$  orbital of the same ion. All this is accompanied by a slight increase in the energy separation  $\pi_v^* \rightarrow \pi_h^*$ , but not a large one (by only about 0.1 eV).

Provided that the assignment for the spectra of the blue solutions<sup>6</sup> is valid, one should assume that the formation of these solutions was accompanied by the formation of a molecular orbitals system showing no marked differences from that described for the cobalt compounds having the same electronic configuration ( $d^6$ ) of the central atom (Fig. 2 [20]; arrows show the transitions observed in absorption spectra). If we take into account the energies of the  ${}^1A_1 \rightarrow {}^1T_1$ ,  ${}^1T_2$  transitions for  $\text{Co(NH}_3)_6^{3+}$  and  $\text{Co(CN)}_6^{3-}$  [14] and  $\text{Pt(OH)}_6^{2-}$  (Table 1), and the data from Table 2, we can easily see that the  $d\pi-d_z$  energy separation<sup>7</sup> increases,

with substituting  $O_2^-$  for the L ligand in the corresponding  $\langle ML_6 \rangle$  ions, by 6200, 12200, and  $5900 \text{ cm}^{-1}$  for Co(III) compounds containing  $L = \text{CN}$  or  $\text{NH}_3$ , and Pt(IV), respectively. This correlates with the position of the  $O_2^-$  ion in the spectrochemical series [20] and with the difference between the sizes of the Co(III) and Pt(IV) ions. The increase in size in going from Co to Pt decreases the corresponding ionization potentials. The

<sup>6</sup> The platinum-ligand bonds are usually more covalent than the cobalt- or rhodium-ligand bonds.

<sup>7</sup> Comparable with the  $t_{2g}-e_g$  splitting in octahedral complexes.

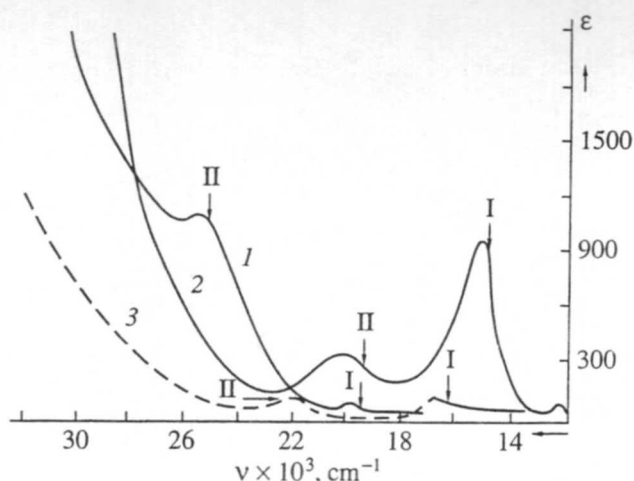


Fig. 1. Electronic spectra for (1) the mononuclear (type 2) complex where  $M = \text{Co}$ ,  $L = \text{CN}^-$  [26], (2) the binuclear (type 3) complex where  $M = \text{Co}$ ,  $L = \text{NH}_3$  [20], and (3) the blue platinum complex: I, metal-to-ligand charge-transfer transition; II,  $d-d$  transition.

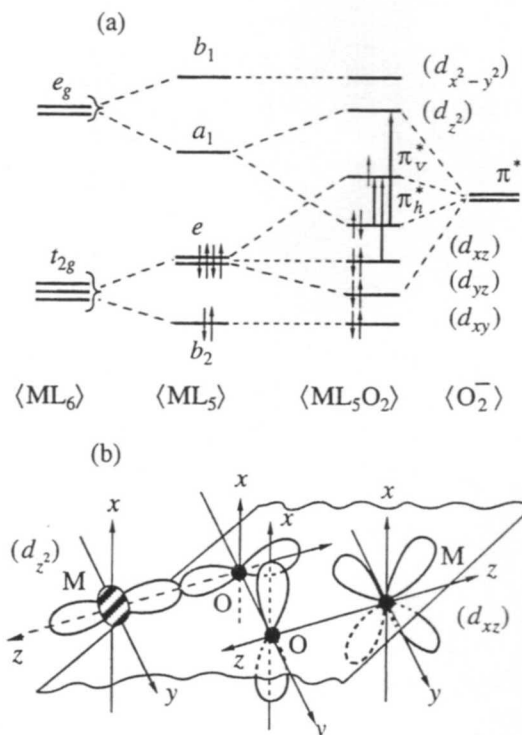
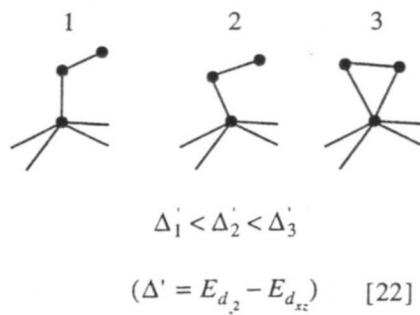
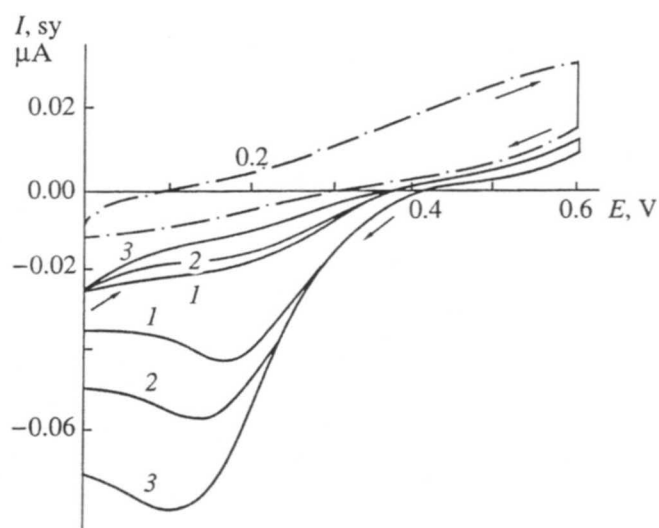


Fig. 2. (a) Molecular-orbital diagram in the  $\langle ML_5O_2 \rangle$  superoxo complexes (according to [14]) and (b) arrangement of some of the orbitals in the  $M-O_2-M$  plane showing how these orbitals interact upon the formation of a superoxo complex.

energy level set becomes deeper, resulting in stabilization of the superoxo platinum(IV) complex even though it contains hydroxyl ions showing moderate  $\pi$ -donating activity. This activity is somewhat greater than that of  $\text{NH}_3$ , and still greater than that of  $\text{CN}$  or ethylenediamine -en-, the ligands conventionally consid-



**Fig. 3.** Hypothetical scheme of configurational transformations in the mononuclear complex containing the  $O_2^-$  superoxo group (according to Hoffman, [22]), resulting in lower intensities of the metal-to-ligand charge-transfer bands.



**Fig. 4.** Cyclic voltammetry traces for the blue platinum complex in alkali solution. Concentrations: Pt, 6 mM; and KOH, 3 M. Potential scan rates: (1) 5, (2) 10, (3) 20 mV/s. Background electrolyte, 3M KOH.

ered to be strong  $\pi$  acceptors.<sup>8</sup> The stabilization is evidenced by the above-marked blue shift of the ligand-to-metal charge-transfer band for platinum(IV) complex relative to the band in the cationic cobalt complex (Fig. 2): this band corresponds to the strengthening of the M–O  $\sigma$  bond (i.e., to the above-mentioned lowering of the  $\pi_h^*$  level by about 0.1 eV).

Electronic spectra of the blue complex are best of all interpreted in terms of the existence of a mononuclear compound of type (2), even though the  $OH^-$  ions are not the ligands capable of generating steric obstacles to dimerization (steric hindrance is considered an important condition for the existence of monomeric complexes of type (2) in the case of Co(III) compounds [21]. This conclusion is based upon the low intensities of the bands in the visible spectral region and the greater

<sup>8</sup> If we assume that here,  $\sigma$  basicity does not dominate [14].

$d\pi-d_{z^2}$  energy separation. All this indicates distortion of the M–O–O bond system according to the scheme in Fig. 3 (Hoffman calculations [22]), that is, changes of the L–M–L and M–O–O angles. The latter seems to be improbable in a binuclear system including the bridging –O–O– group because configuration (3) is a symmetric one. Generally speaking, the probable existence of binuclear complex (3) is indicated by the set of the absorption bands (Table 2). However, no causes are seen that could prevent the appearance of transitions between the ligand states in the spectrum of mononuclear complexes.

Unfortunately, the ESR data cannot help us in solving this problem and fail to unambiguously show whether the unpaired electron is located on the ligand or on the central atom of the complex compound. However, the suggestion about the presence of the superoxo group becomes reasonable if we compare the  $g$  factors of the blue platinum(IV) complex with those of cobalt(III) complexes of types (2) and (3) and those of alkali metal superoxides (Table 3) especially since the techniques for preparation of both blue platinum(IV) complex and cobalt compounds (in both cases, the configuration of the metal is  $d^6$ ) include ozonization [23], which process is known to be used in generating superoxo groups in complexes [24].

**Properties of the blue platinum complexes.** Solutions of these compounds are unstable and rather quickly decolorize to produce the initial  $Pt(OH)_6^{2-}$  when allowed to stand at room temperature. The same effect is observed upon defrosting the preliminary gasified solutions. This phenomena limits the potentialities of low-temperature experiments performed in the course of recording the ESR spectra.

Cyclic voltametric diagrams of the freshly prepared blue solutions exhibit an irreversible cathode wave with  $E_{max} = 0.18$  V, whose height increases with increasing potential scan rate (Fig. 4). The reduction currents decrease till complete vanishing when the sequential cyclic voltametric diagrams are recorded. A similar decrease and complete vanishing of current occur upon the electroreduction of the blue solutions on a platinum macroelectrode at  $E = 0.0$  to  $-0.10$  V. The vanishing of the reduction wave is accompanied by decoloration of the solution. Apparently, these phenomena arise from reduction of the superoxo ligand in the blue complex. The superoxo ligand is rather weakly bound to the central atom. Therefore, the blue solutions can exist only in aqueous solutions containing oxygen. When oxygen is displaced by argon bubbling, the solutions turn colorless. Reduction of Pt(IV) to Pt(II) in the complexes under study (both blue and colorless) occurs in the range of negative potentials ( $E_{1/2} = -1.58$  V).

Thus, the body of the data available makes it possible to state that ozonization of the hexahydroxoplatinate(IV) produces platinum(IV) complexes with superoxo ligands. These complexes are rather unstable entities generating oxygen upon their decomposition.

**Table 3.** *g* factors for various superoxo compounds\* [23 - 26]

Compound	$g_{\perp}$	$g_{\parallel}$
NaO <sub>2</sub>	2.0029	2.1112
KO <sub>2</sub>	2.002	2.175
CsO <sub>2</sub>	2.0069	
$\langle \text{Co}_2\text{L}_{10}\text{O}_2 \rangle \text{L}=\text{CN}$	2.019	
L=NH <sub>3</sub>	2.023	
$\langle \text{Co}(\text{Me}_2\text{en})_2\text{XO}_2 \rangle^+ : \text{X}=\text{CH}_3\text{CN}$	2.008	2.067
X=MeOH	2.009	2.072
$\langle \text{Co}_2\text{L}_8\text{XO}_2 \rangle \text{L}=\text{CN}$	2.024	
L=CN X=NH <sub>2</sub>	2.034	

\* en - ethylenediamine, Me - methyl.

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