PHYSICAL METHODS
OF INVESTIGATION

EPR Spectroscopy of Transformations of Iridium(III) and Iridium(IV) Hydroxo Complexes in Alkaline Media

D. A. Pankratov[a], P. N. Komozin[b, †], and Yu. M. Kiselev[a]

[a] *Moscow State University, Moscow, 119992 Russia*
e-mail: pankratov@radio.chem.msu.ru
[b] *Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,*
ul. Kosygina 19, Moscow, 119991 Russia
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Abstract—Processes that occur in strong alkaline solutions of iridium(III) and iridium(IV) hydroxo complexes have been studied by EPR and electronic absorption spectroscopy. It has been demonstrated that dissolution of iridium compounds in alkaline solutions should be accompanied by a series of complicated transformations involving oxygen, which lead to the formation of several binuclear iridium(III, III), (III, IV), and (IV, IV) dioxygen complexes.

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Most research into the chemistry of platinum metals has focused on their complexes [1]. However, the chemistry of their hydroxo complexes is still one of the least studied fields. There are both objective (experimental complexity of operation in alkaline and strong alkaline media, tendency to polymerization of many hydroxo compounds, and others) and subjective reasons for this situation. In particular, it is believed that the chemistry of platinum metal hydroxo complexes is insufficiently diverse. Nevertheless, we previously showed the possibility of the existence of platinum(IV) hydroxo complexes as mono- and binuclear superoxo complexes [2, 3] of different composition forming under oxidative conditions in strong alkaline media.

The chemistry of iridium hydroxo complexes is a blank spot in the chemistry of platinum group hydroxo compounds. It is traditionally believed that there are hexahydroxoiridium(III) and -iridium(IV) complexes that can interconvert into each other and polymerize in solutions and precipitate from them as hydroxides. Interconversions of iridium hydroxo complexes have been mainly studied by electrochemical methods; i.e., on the one hand, redox transformations occurred under external voltage, and on the other hand, similar studies were carried out after forced removal of oxygen from the reaction solution. As is shown below, oxygen is always involved in redox reactions that occur on dissolving iridium compounds in alkaline solutions. This work deals with interconversions of iridium complexes in strong alkaline media.

[†] Deceased.

EXPERIMENTAL

The electronic absorption spectra of solutions were recorded on a Specord UV/VIS spectrophotometer in the wavelength range 200–800 nm in quartz cells with a reference solution corresponding to the medium of the analyte solution.

The electron paramagnetic resonance spectra of solutions frozen to 77 K in quartz cells were recorded on a Radiopan SE/X-2544 radiospectrometer (X-band, 9.2 GHz).

Solutions of hydroxoiridates were prepared by introducing an aliquot of an aqueous solution of hexachloroiridic acid (prepared from pure grade hexachloroiridic acid hydrate $H_2IrCl_6 \cdot nH_2O$, 38.7% Ir) into a potassium hydroxide solution of a desired concentration. To do this (for example, to prepare 10 mL of a solution), a weighed portion of KOH (pure for analysis grade) corresponding to a required alkali concentration, was dissolved in 5–7 mL H_2O and heated almost to boiling on a water bath with simultaneous bubbling of an inert gas to remove oxygen from a solution. Into the solution thus obtained, 1–2 mL of a preliminarily prepared dark brown solution of H_2IrCl_6 with a metal concentration of ~10 mg/mL was introduced, and the solution was brought to the final volume with degassed water. The resulting solution was pale brown and could contain (at very high iridium contents) some amount of a pale green precipitate. Then, the solution was heated almost to boiling on a water bath (the precipitate dissolved) and cooled to 0–20°C by water or ice. All operations were carried out in an inert atmosphere. The solution thus prepared was of yellow-brown color, which could change to violet with deposition of dark blue precipitates of hydrated iridium hydroxide.

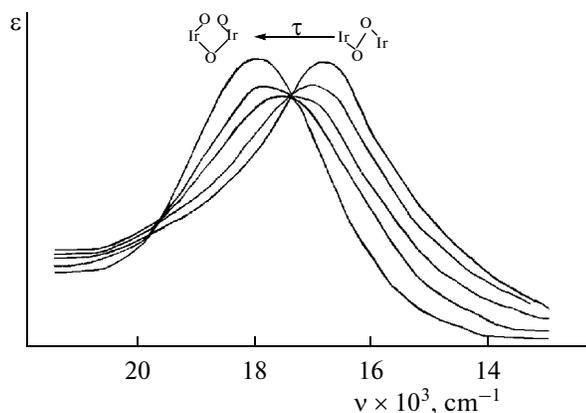**Fig. 1.** Isosbestic point for iridium alkaline solutions ($\tau >$ 60 min).

Fig. 2. EPR spectra of iridium-containing solutions: (*1*) H_2IrCl_6 solution; (*2*) solution 1 + 3 M KOH, $\tau = 0$; (*3*) solution 2 heated to 100°C, $\tau = 10$ s; (*4*) solution 3 heated to 100°C, $\tau = 600$ s; (*5*) solution 4 + O_2 (0°C), blue; (*6*) solution 5 + O_2 (80°C), violet (iridium concentrations in solutions *2* and *6* were not changed).

The hydroxoiridate solutions readily react with oxygen (or air) and become intensely colored. This is clearly observed if a hydroxoiridate solution is placed in a high narrow beaker (tube) and allowed to stand in air: the surface layer of the solution rapidly becomes blue while the pale yellow-brown color persists for some time in the rest of the solution. In this work, we have shown that the interaction of yellow-brown solutions of hydroxoiridates with oxygen leads to the formation of at least two types of complexes.

Blue solutions of complexes form when oxygen is bubbled through strongly cooled solutions of hydroxoiridates prepared by the above procedure. These solutions are unstable (no more than 3 h) and readily (more rapidly on heating) form violet solutions containing a hydroxoiridate complex of the second type. The color change is observed always and is evidently irreversible. The UV/Vis spectra show an isosbestic point at 17090 cm^{-1} (Fig. 1). The UV/Vis spectra of the resulting violet solutions do not change in time, except the decrease in their intensity caused by deposition of dark blue precipitates of iridium hydroxide.

These data are evidence that alkaline iridium solutions can contain several complex species, and the observed absorption spectra are a superposition of the spectra of each of them. Therefore, some absorption bands are poorly pronounced and can be masked by other stronger and broader bands, which can be a reason for the errors in the determination of their positions and intensities and in the assignment of them to a definite compound. In addition, some limitations are imposed by the presence of a broad and very strong absorption band at 44000 cm^{-1} and higher, which arises from potassium hydroxide contained in solutions in considerable concentrations.

In particular, whereas the spectra of aqueous solutions of hexachloroiridic acid show well-defined absorption bands, they are observed only as shoulders at 24000, 28400, and 31200 cm^{-1} in the spectra
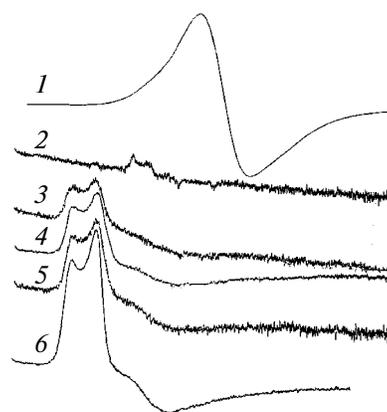
recorded immediately after the introduction of the above solution into 3 M KOH.

The spectra of pale yellow-brown solutions (at low iridium concentrations, solutions are nearly colorless) obtained after heating to 100°C in an inert atmosphere show one strong absorption band at 31900 cm^{-1} and one very weak band at 41600 cm^{-1}. After exposure of this solution to oxygen at low temperature, the spectra of the resulting blue solutions show new bands at 16880 and 31700 cm^{-1}. As the blue solution turns violet, these bands are shifted to 17950 and 31900 cm^{-1}, respectively. In addition, the spectra show weak absorption b ands as shoulders at 21400 and 28000 cm^{-1}.

For comparison we considered alkaline solutions of K_3IrCl_6 obtained in an inert atmosphere. They are characterized by rather strong absorption bands at 28800 and 24100 cm^{-1}, a weak band at 32100 cm^{-1}, and very weak bands at 37600 and 18000 cm^{-1}. The spectra change rapidly when solutions are exposed to air during measurement of the spectra.

The EPR spectra of yellow-green solutions frozen immediately after introducing a hexachloroiridate solution into an alkali solution show no signal corresponding to the iridium(IV) chloro or hydroxo complex (compare *1*, *2*, and *3* in Fig. 2). However, even short heating of the solution at ~50°C leads to the appearance of a signal (even if rather weak) analogous to that observed for an iridium(IV) hydroxo complex. As the duration or temperature of heating in an inert atmosphere increases, this signal builds up to some constant time-independent value (Fig. 2, *3* and *4*). Oxygen bubbling through the previous, nearly colorless, solution accompanied by the change in its color to blue has almost no effect on both the EPR line shape and intensity (Fig. 2, *6*). For violet solutions obtained from blue solutions on heating in an oxygen flow, the intensity of this signal increases twofold.
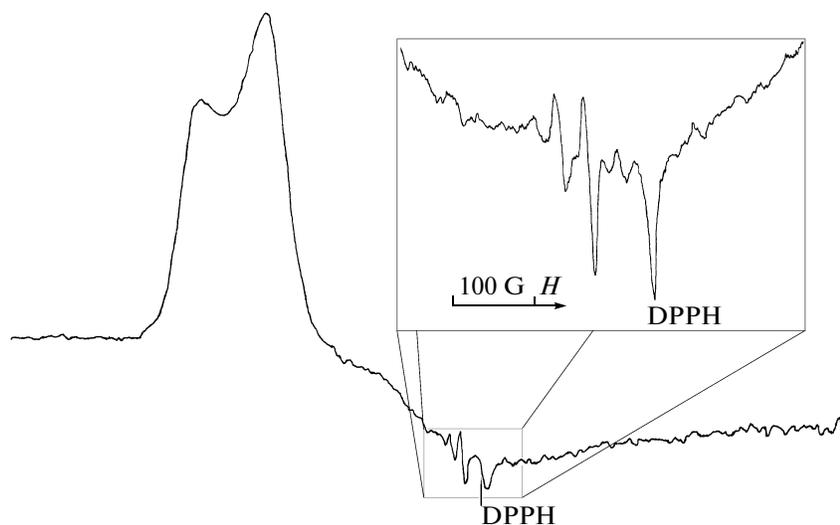
Fig. 3. EPR spectrum of an iridium(IV) solution in 3 M KOH.

The EPR spectra of violet and blue complexes are almost identical, expect for that, in the spectra of the violet complexes, the third *g* tensor component and, hence, the rhombic anisotropy ($g = 2.71 \pm 0.2$, 2.45 ± 0.02, 1.94 ± 0.04), is more clearly pronounced. The high-field component is considerably broadened, which is likely caused by an unresolved hyperfine structure (HDS) due to the iridium nuclei ($I = 3/2$).

It is worth noting that, for many alkaline iridium solutions, the EPR spectra often showed signals reflecting the presence of a paramagnet (Fig. 3) similar to that observed for platinum superoxo compounds [4, 5]. The area under the corresponding signal for the same sample changed to zero after several freeze–thaw cycles.

RESULTS AND DISCUSSION

Let us examine the above data taking into account the fact that EPR spectroscopy is a more informative method for studying alkaline solutions of hydroxoiridates and products of their interaction with oxygen since it is more sensitive to the presence of a paramagnet, whereas electronic absorption spectroscopy is less suitable for these systems since the compounds in question give rise to weak absorption bands with close energies. In addition, it is worth noting that most hydroxoiridate solutions evidently contain several iridium complexes (rather than one), which are likely to differ in structure, composition, combination of ligands in the inner sphere, and oxidation state of the central atom. In addition, the situation is complicated by polymerization of complexes and, hence, the presence of polymer homologues existing in solutions of complexes.

The hydroxoiridates forming on interaction of hexachloroiridic acid with alkali solutions in an inert atmosphere are considered to be initial hydroxo complexes. A relatively small number of studies have focused on the interaction of hexachloroiridates(IV) with aqueous solutions [6–8]. In most papers, the easily reversible reaction of reduction of the iridium(IV) complex to iridium(III) has been documented [6]. In particular, it has been shown by spectrophotometry [7] that, in alkaline media, the reaction of reduction of hexachloroiridate(IV) to hexachloroiridate(III) precedes to the substitution of hydroxide ions for the chloride ions in the inner sphere. Mass spectrometry [8] has demonstrated that this reduction is accompanied by oxygen release by the scheme

$$2IrCl_6^{2-} + 2OH^- = 2IrCl_6^{3-} + 1/2\,O_2 + H_2O, \qquad (1)$$
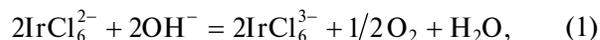
i.e., one-fourth of a mole of oxygen is released for every mole of hexachloroiridate(IV). Then, according to [9], the inner coordination sphere of the complex changes (more rapidly on heating) to form a yellow-green solution of hydroxoiridate(III), which is oxidized with oxygen to produce colorless solutions [9]. The reduction reaction is instantaneous, while the subsequent two reactions are slow.

Our EPR data confirm that the first stage of iridium reduction that occurs on dissolving the chloroiridate in an alkali solution is almost instantaneous and leads to yellow-green solutions, whereas the rates of formation of the iridium hydroxo complex and its oxidation are low and depend, among other factors, on temperature. It is worth noting that, according to [9], iridium(III) is oxidized by the oxygen, both existing in the solution and forming at the first stage. According to our observations, the physicochemical properties of complexes that form on heating of the above-described solutions to 100°C both in an inert gas flow (which should facilitate removal of the dissolved oxygen from solutions) and without it are identical. How-

Electronic spectra of cobalt [11], platinum [3], and iridium dioxygen compounds ($1000 \, cm^{-1}$, ε, L mol/cm, is parenthesized)

Sample	Assignment of absorption bands				
	$\pi_h^* \to \pi_v^*$	$d\pi \to \pi_v^*$	$d \to d$	$\pi_h^* \to d_{z^2}$	$\pi_v \to \pi_v^*$
$Co(CN)_5 O_2^{3-}$	–	19.95 (80)	25.0 (1000)	31.25 (4000)	–
$Co_2(CN)_{10} O_2^{5-}$	12.2 (13)	20.59 (745)	26.8 (1500)	32.2 (17250)	44.4 (13800)
Pt–(I) (3 M KOH)	13.5 (40)	16.8 (100)	22.0 (100)	36.1 (>1000)	41.0 (>2000)
Pt–(II) (9 M KOH)	13.86 (~10)	19.88 (30)	26.43 (90)	35.8 (>2000)	39.5 (>4000)
$\left[(OH)_5 Ir^{IV} \left(\mu\text{-}O_2^- \right) Ir^{IV} (OH)_5 \right]^{3-}$ (3 M KOH)	13.9 (10)	16.9 (80)	22.4 (30)	31.7 (1000)	41.5 (1500)
$\left[(OH)_4 Ir^{IV} \left(\mu\text{-}O_2^{2-} \right)(\mu\text{-}OH) Ir^{IV} (OH)_4 \right]^{3-}$ (3 M KOH)	13.6 (8)	18.0 (80)	22.5 (30)	31.9 (1000)	

ever, this should be observed only if the oxygen formed in reduction is bound by the complex-forming atom.

Formation of blue iridium solutions has been documented by many researchers [8]. However, only some of them have attributed this to the iridium interaction with air oxygen. Most frequently, the blue color of solutions was explained by polymerization and it was believed that blue (or violet) solutions contained hexahydroxoiridate(IV). The transition from the blue form to the violet one has been reported only in few papers. We have shown that the formation of intensely colored blue or violet solutions is only possible when oxygen is involved. Initially, the blue species forms, which is unstable and irreversibly converts into the violet species. This is consistent with the hypsochromic shift of absorption bands in the corresponding UV/Vis spectra. Formation of violet solutions is equilibrium and quantitative and proceeds to the end, which is reflected by the presence of the isosbestic point in the electronic spectra.

The persistence of the d^5 configuration of iridium after the interaction with oxygen for both blue and violet solutions is confirmed by EPR data. After this interaction, the relative intensity of the EPR signal for blue solutions remains unaltered, while, for violet solutions, it increases twofold, which is evidence of the corresponding change in the concentration of a paramagnet, namely, iridium(IV).

The above data for blue, violet, and initial complexes can be interpreted assuming the possibility of formation of binuclear iridium dioxygen hydroxo complexes analogous to those obtained for platinum [2–5, 10], cobalt [11], and rhodium [12–15]. In particular, taking into account that the intensity of the EPR signal corresponding to the d^5 configuration is maximal for violet solutions and the signals of the superoxo group are not observed, we can state that

these complexes contain the $Ir^{IV} \left(\mu\text{-}O_2^{2-} \right) Ir^{IV}$ moiety. A rather intense $\pi_v^* \to \pi_h^*$ transition in the UV-Vis spectra of these compounds (table) indicates that this moiety is nearly planar (which is not typical of peroxo complexes). This can be caused only by the presence of the second hydroxo bridge. Hence, violet solutions evidently contain the complex of the tentative composition $\left[(OH)_4 Ir^{IV} \left(\mu\text{-}O_2^{2-} \right)(\mu\text{-}OH) Ir^{IV} (OH)_4 \right]^{3-}$ (for simplicity, formation of only hydroxo derivatives of iridium is assumed).

The complexes preceding the violet one slightly differ from it in properties and, evidently, structure. First of all these complexes are also binuclear with a dioxygen bridge (table). The lower intensity of the EPR signal due to iridium(IV) for these solutions can be caused by two factors. The first one is the formation of a complex with iridium atoms of different valence (iridium(III) and (IV)) and a diamagnetic peroxo bridge. The second one is formation of a complex with iridium in the oxidation state +4 with a paramagnetic superoxo bridge, an electron of this bridge interacting with a valence electron of one of the iridium atoms. For blue complexes, the second variant is evidently realized, namely, the planar binuclear superoxo iridium(IV, IV) complex $\left[(OH)_5 Ir^{IV} \left(\mu\text{-}O_2^- \right)(\mu\text{-}OH) Ir^{IV} (OH)_5 \right]^{3-}$ is formed. The first variant implying the formation of the nonplanar peroxo complex like $\left[(OH)_5 Ir^{IV} \left(\mu\text{-}O_2^{2-} \right) Ir^{IV} (OH)_5 \right]^{5-}$, for which the absorption in the short-wavelength range is not observed, is realized in initial solutions.

The possibility of formation of binuclear iridium complexes was previously considered in [16] where oligomers of iridium(III) aqua complexes were oxi-
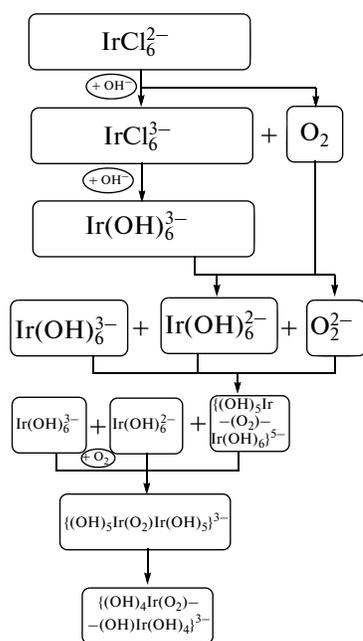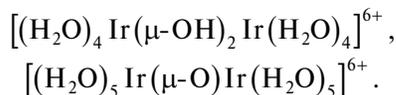
Fig. 4. Schematics of transformation of iridium compounds in alkaline solutions.

dized electrochemically in acid solutions. This yielded blue and purple compounds [16], which were described, on the basis of UV-Vis and NMR data, as binuclear aquairidium(IV) complexes with two hydroxo bridges and one oxo bridge, respectively:

$$\left[(H_2O)_4 Ir(\mu\text{-OH})_2 Ir(H_2O)_4\right]^{6+},$$

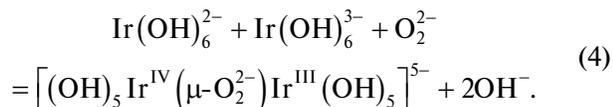$$\left[(H_2O)_5 Ir(\mu\text{-O}) Ir(H_2O)_5\right]^{6+}.$$

Thus, the processes that occur when hexachloroiridate(IV) interacts with alkaline solutions and oxygen can be described as follows. First, the hexachloroiridate(IV) ion is reduced according to Eq. (1). Then, hydroxide ions are substituted for the chloride ions in the iridium(III) inner sphere, which decrease the redox potential of the system:

$$IrCl_6^{3-} + 6OH^- = Ir(OH)_6^{3-} + 6Cl^-. \qquad (2)$$

After that (or simultaneously), one-half of the resulting iridium(III) hydroxo complex is oxidized to iridium(IV) by the oxygen formed in reaction (1):

$$2Ir(OH)_6^{3-} + O_2 = 2Ir(OH)_6^{2-} + O_2^{2-}, \qquad (3)$$
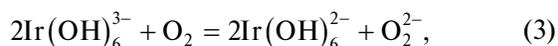
in its turn, one-half of the iridium(IV) complex is involved in formation of the binuclear peroxo complex:

$$Ir(OH)_6^{2-} + Ir(OH)_6^{3-} + O_2^{2-}$$
$$= \left[(OH)_5 Ir^{IV}\left(\mu\text{-O}_2^{2-}\right) Ir^{III}(OH)_5\right]^{5-} + 2OH^-. \qquad (4)$$

Thus, the initial solutions should contain equimolar amounts of hexahydroxoiridate(III) and hexahydroxoiridate(IV) and the peroxo complex

$\left[(OH)_5 Ir^{IV}\left(\mu\text{-O}_2^{2-}\right) Ir^{III}(OH)_5\right]^{5-}$ (which can be formally considered as the superoxo complex $\left[(OH)_5 Ir^{III}\left(\mu\text{-O}_2^-\right) Ir^{III}(OH)_5\right]^{5-}$), which accounts for some inconsistencies in the observed properties of solutions.

The following processes occur when oxygen is bubbled through cooled solutions: the oxidation of the hexahydroxoiridate(III) ion by Eq. (3), the oxidation of iridium(III) in the peroxo complex, and the oxidation of the peroxo bridge to the superoxo bridge. Depending on conditions, intermediate iridium complexes should form in solutions, although the superoxo complex $\left[(OH)_5 Ir^{IV}\left(\mu\text{-O}_2^-\right) Ir^{IV}(OH)_5\right]^{3-}$ can be considered the final form of the blue complex. At elevated temperatures or as time elapses, the superoxo bridge is reduced and the complex $\left[(OH)_4 Ir^{IV}\left(\mu\text{-O}_2^{2-}\right)(\mu\text{-OH}) Ir^{IV}(OH)_4\right]^{3-}$ with two bridges forms.

The described chain of transformations is schematically shown in Fig. 4, where the area of each block is proportional to the number of moles of a reagent involved in reaction.

It follows from this scheme of reactions occurring in alkaline solutions that almost all solutions should contain several different iridium complexes and these solutions should not be treated as those containing individual complexes. In addition to the aforementioned complexes, solutions can contain other dioxygen compounds, including paramagnetic superoxo compounds and oxygen adducts, which is supported by the presence of corresponding weak signal of oxygen radicals in some EPR spectra. Let us remind once more that, for simplicity, in the above analysis, we did not consider the possibility of formation of mixed-ligand hydroxo aqua or hydroxo chloro complexes.

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