954 *Inorg. Chem.* **1989**, *28*, 954-960

Contribution from the Departments of Chemistry, The University, Newcastle upon Tyne NE1 7RU, England, U.K.,
and University of St. Andrews, St. Andrews KY16 9AG, Scotland, U.K.

Oxidation of Hexaaquairidium(III) and Related Studies: Preparation and Properties of Iridium(III), Iridium(IV), and Iridium(V) Dimers as Aqua Ions

Sylvia E. Castillo-Blum,[†] David T. Richens,[*,‡] and A. Geoffrey Sykes[*,†]

Received November 14, 1988

The aqueous (acidic) solution chemistry of Ir in its higher oxidation states III, IV, and V and interconversions between these states have been explored for the first time. Procedures used involve electrochemical or chemical (Ce(IV)) oxidation of $[Ir(H_2O)_6]^{3+}$ (0.1–7.0 mM) in 2.0 M H^+ ($HClO_4$ or CF_3SO_3H), to give a brown-green product that titrates for Ir(V). Subsequent electrochemical or chemical (I^-, Fe^{2+}, Eu^{2+}) reduction of the Ir(V) gives first blue-purple Ir(IV) and then pale yellow Ir(III), where the latter is not $[Ir(H_2O)_6]^{3+}$. The strongly oxidizing Ir(V) and Ir(IV) are unstable, with half-lives (25 °C) of typically ~5 h and ~1 day, respectively, and initial studies were therefore on the stable Ir(III) products. Cation-exchange chromatography yields two components, $Ir(III)_A$ and $Ir(III)_B$, here characterized as dimers. A further 30% of the Ir(III) remains on the ion-exchange column as a higher oligomer. Oxygen-17 NMR studies on $Ir(III)_A$ (two H_2O resonances in a 1:1 ratio) and $Ir(III)_B$ (1:4 ratio), together with the behavior observed in cation-exchange chromatography, allow the formulas $[(H_2O)_4Ir(OH)_2Ir(H_2O)_4]^{4+}$ and $[(H_2O)_5IrOHIr(H_2O)_5]^{5+}$ to be assigned. Conversion of $Ir(III)_A$ to $Ir(III)_B$ is slow and requires ~2 h at 60 °C in 7 M CF_3SO_3H. When this mixture is heated further to 100 °C, $[Ir(H_2O)_6]^{3+}$ is obtained within ~10 h. Electrochemical oxidation of $Ir(III)_A$ and $Ir(III)_B$ yields respectively blue and purple Ir(IV) products. Spontaneous conversion of blue to purple Ir(IV) (25 °C) occurs via a conjugate-base form ($K_a = 1.7$ M) with rate constant $k = 1.02 \times 10^{-2}\ s^{-1}$. Similar NMR studies on blue Ir(IV) equilibrated with 5–10% enriched H_2O ($t_{1/2} \sim 1$ min), gives two resonances of equal intensity, which transform to a single peak as purple Ir(IV) is formed. The evidence obtained is consistent therefore with double- and single-bridged dimeric structures, where the most likely formulas are $[(H_2O)_4Ir(OH)_2Ir(H_2O)_4]^{6+}$ for the blue compound and $[(H_2O)_5IrOIr(H_2O)_5]^{6+}$ for the purple one. All Ir(III) and Ir(IV) solutions are oxidized by Ce(IV) to give the same Ir(V) spectrum, suggesting rapidly equilibrating species in this oxidation state. In the initial oxidation of $[Ir(H_2O)_6]^{3+}$ to Ir(V) a transient brown but no blue-purple intermediate is observed. Dimerization most likely occurs in the Ir(V) state, with oxo ligand(s) labilizing the coordinated H_2O's. Formulas for the Ir(IV) and Ir(V) products are closely related to those established for $Ir(III)_A$ and $Ir(III)_B$. Interconversions are summarized in the reaction scheme given in Figure 11.

Introduction

Little is known about the solution chemistry of Ir in its higher oxidation states. In spite of numerous studies on the oxidation of Ir(III), some leading to the formation of blue and purple products, these have not been well characterized, and the chemistry is poorly defined.[1-9] There are few examples of compounds in the IV or V states,[10-12] and those that are known are noted for their strong oxidizing properties. The lead-in compound used to establish the chemistry described is hexaaquairidium(III) ion, first prepared by Beutler and Gamsjäger in 1976.[13] Later, in an extension of their work, the same group determined first and second acid dissociation pK_a values ($I = 1.0$ M, 25 °C) of 4.37 and 5.20, respectively.[14] The incorporation of $[Ir(H_2O)_6]^{3+}$ into an alum and the X-ray crystal structure thereof has been reported.[15] Studies on complexation reactions[16,17] and water exchange[18] have demonstrated the extreme inertness of the ion. It is in fact the most inert hexaaqua ion so far identified[16] and remains of considerable interest since it is the only hexaaqua ion fully characterized in the third-row transition series.[19]

To date no quantitative redox studies on $[Ir(H_2O)_6]^{3+}$ have been carried out, and there are no clearly identified aqua/hydroxo/oxo ions of Ir in the IV and V states. In the present studies we report on such oxidations that give in the first place a brown-green Ir(V) product. The approach used has been to investigate the products of the reduction of Ir(V), where a blue-purple mix of two Ir(IV) ions and then a pale yellow mix of two Ir(III) products (not the hexaaqua ion) are obtained. An oligomeric form is also present. Oxygen-17 NMR supports the assignment of bis(μ-hydroxo) and mono(μ-hydroxo) Ir(III) dimers as proposed in an earlier communication.[20]

Experimental Section

Preparation of Solutions. Solutions of hexaaquairidium(III) were prepared by the procedure reported previously,[13,14] involving treatment of $Na_2[IrCl_6]\cdot 6H_2O$ (Johnson Matthey, 2.0-g amounts) with NaOH (10 mL, 0.2 M) at 35 °C for 3 h. Following adjustment of the pH to 8 by dropwise addition of 4.0 M $HClO_4$ (BDH AnalaR), a precipitate of iridium(III) hydroxide, $[Ir(OH)_3(OH_2)_3]$, was separated by centrifugation. After the precipitate was dissolved in 1.0 M $HClO_4$, the resulting solution was loaded (at 0.1 M H^+) onto a Dowex 50W-X2 cation-exchange column (10 cm × 1 cm) (Sigma Chemicals) from which, after prewashing with 0.2 M $HClO_4$, pure $[Ir(H_2O)_6]^{3+}$ could be eluted with 2.0 M $HClO_4$ or CF_3SO_3H (trifluoromethanesulfonic acid). Solutions of $[Ir(H_2O)_6]^{3+}$ were standarized by UV–vis absorption spectroscopy, peak maxima λ/nm (ϵ/M^{-1} cm^{-1}) at 267 (36.4) and 313 (32.5) in 2.0M H^+.[17] The slightly lower ϵ value for the 267-nm peak[20] represents an

---

[†] The University, Newcastle upon Tyne.

[‡] University of St. Andrews.

(1) Bardin, M. B.; Ketrush, P. M. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1973**, *18*, 693.

(2) Tikhonova, L. P.; Zayats, V. A. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1976**, *21*, 1184.

(3) Pilipenko, A. T.; Falendysh, N. F.; Parkhomenko, E. P. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1975**, *20*, 1683.

(4) Tikhonova, L. P.; Zayats, V. Ya.; Svarkovskaya, I. P. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1979**, *24*, 1502.

(5) Pshenitsyn, N. K.; Ginzburg, S. I.; Salskaya, L. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1959**, *4*, 130.

(6) Bardin, M. B.; Houng, Th. T.; Kelrush, P. M. *Zh. Anal. Khim.* **1976**, 1282.

(7) Rose, D.; Liver, F. M.; Powell, A. R.; Wilkinson, G. *J. Chem. Soc. A* **1969**, 1690.

(8) Fine, D. A. *J. Inorg. Nucl. Chem.* **1970**, *12*, 2731.

(9) Ginsburg, S. I.; Yuz'ko, M. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1965**, *10*, 444. Ginsburg, S. I.; Yuz'ko, M. I.; Sal'skaya, L. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1963**, *8*, 429.

(10) Dwyer, F. P.; Gyarfas, E. C. *J. Proc. R. Soc. N.S.W.* **1950**, *84*, 122. Desideri, P.; Pantani, F. *Ric. Sci. Part 2: Sez. A* **1961**, *1*, 265.

(11) Hepworth, M. A.; Robinson, P. L.; Westland, G. J. *J. Chem. Soc.* **1954**, 4269; **1958**, 611. Robinson, P. L.; Westland, G. J. *J. Chem. Soc.* **1956**, 4481.

(12) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 808. Gilbert, T. M.; Bergmann, R. G. *Organometallics* **1983**, *2*, 1458. Isobe, K.; Vazquez de Miguel, A.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 929.

(13) Beutler, P.; Gamsjäger, H. *J. Chem. Soc., Chem. Commun.* **1976**, 554.

(14) Gamsjäger, H.; Beutler, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1415.

(15) Armstrong, R. S.; Beattie, J. K.; Best, S. P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1973.

(16) Castillo-Blum, S. E.; Sykes, A. G.; Gamsjäger, H. *Polyhedron* **1987**, *6*, 101.

(17) McMahon, M. R.; McKenzie, A.; Richens, D. T. *J. Chem. Soc., Dalton Trans.* **1988**, 711.

(18) Preliminary results from an oxygen-17 NMR study of the water exchange on $[Ir(OH_2)_6]^{3+}$ in aqueous CF_3SO_3H solution indicate a half-life of >100 years at 25 °C ($[H^+] = 4.7$ M): Richens, D. T.; Zbinden, D.; Helm, L.; Merbach, A. E. Unpublished results, 1988.

(19) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley-Interscience: New York, 1988.

(20) Castillo-Blum, S. E.; Richens, D. T.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1986**, 1120.

improvement in procedures. Sodium perchlorate, manganese perchlorate hexahydrate and iron(II) perchlorate hexahydrate (BDH AnalaR) were used as supplied. Samples of europium(III) and lanthanium(III) perchlorates were prepared by dissolution of the oxide (Fluka puriss) in solutions of 1.0 M $HClO_4$, followed by recrystallization twice from water. Perchlorate solutions were standarized by exchange onto an Amberlite IR 120H cation-exchange column (10 cm × 1 cm), followed by titration of the liberated H^+ with NaOH. Solutions of $HClO_4$ and CF_3SO_3H were standarized by titration with NaOH. Background concentrations of H^+ in solutions of $[Ir(H_2O)_6]^{3+}$ were similarly determined by difference. Solutions of europium(II) perchlorate were prepared by amalgamated zinc reduction of Eu(III) in $HClO_4$ under nitrogen. Solutions of Ce(IV) were obtained by making up ammonium cerium(IV) nitrate, $(NH_4)_2[Ce(NO_3)_6]$ (BDH AnalaR), in solutions of $HClO_4$. Sodium iodide and sodium thiosulfate (BDH AnalaR) were used as supplied. A 1.2-g sample of iridium wire (o.d. 0.5 mm) was supplied by Johnson Matthey. Samples of $H_2{}^{17}O$ (20 atom %) were obtained from Yeda Co. Ltd., Israel.

Electrochemistry. Cyclic voltammetry measurements (25 °C) on solutions 5.0 mM in Ir, 2.0 M H^+, were carried out by using a standard three-electrode cell design employing platinum-disk (area 0.04 cm^2) working, Pt-wire counter, and saturated calomel reference electrodes, with either a Chemical Electronics Model DD50 SU potentiostat/sweep generator and JJ Lloyd PL 51 XY plotter or a Princeton Applied Research Model 170 electrochemistry system. Reduction potentials were determined from the average values of the anodic and cathodic peak potentials and reported relative the normal hydrogen electrode (NHE).

Electrochemical generation of the Ir(V) solution was achieved by two methods, both employing a two-compartment cell (each 25 cm^3) separated by a fine sinter (No. 4): (i) oxidation of a solution of $[Ir(H_2O)_6]^{3+}$ (0.1–7.0 mM) in 2.0 M $HClO_4$ using a platinum-gauze working electrode (area 24 cm^2) at 0 °C; (ii) oxidation of an Ir wire anode immersed in 2.0 M $HClO_4$ at 0 °C. For method i oxidation was achieved either at constant current (1.0 A for 10–15 min) by using a two-electrode circuit with a Pt-wire counter electrode and a Farnell Model E301 stabilized power supply or at constant potential (+1.6 V vs NHE) by using Pt-wire counter and saturated calomel reference electrodes with either of the potentiostats described. In method ii, oxidation was carried out with a two-electrode circuit at 1.0 A for 2–3 h by using the Farnell power supply and Pt-wire counter electrode. Separation of the anodic and cathodic compartments was essential to avoid side reactions occurring as a result of contamination.

Coulometric measurements were carried out at constant potential by using the three-electrode cell design and potentiostats described. Integration of the current–time curves was performed by paper weighing of the corresponding area in comparison to that for a standard solution of 5.0 mM $Na_2[IrCl_6]$ in 2.0 M $HClO_4$, which is one-electron reduced to $[IrCl_6]^{3-}$. Background currents were subtracted. Duplicate runs were reproducible to ±6%.

Reduction of Ir(V) to Ir(IV) and then Ir(III) was performed either at constant current (by reversing the polarity of the electrodes) or at constant potential by adjusting to the required value at the working electrode.

Spectrophotometry. Ultraviolet and visible spectra were recorded on a Perkin-Elmer Lambda 5G recording spectrophotometer using 0.1- and 1.0-cm quartz cells with electronic thermostating (±0.1 °C) and auto-cell change facilities for kinetic measurements. Measurements of pH were performed with a Radiometer PHM62 pH meter and Russell CWR/322 combination glass/Ag/AgCl electrodes having narrow stems.

Oxygen-17 NMR Measurements. These were carried out on solutions (0.05–0.1 M in Ir) at 54.24 MHz in 10-mm-o.d. tubes on a Bruker AM-400 instrument. Total spectral widths of between 40 and 83 KHz and 1K–4K data points for the FID's (10^4–10^5 transients added) were used. The pulse width varied between 7 and 14 μs. Addition of Mn^{2+} (0.1 M) removed the large ^{17}O resonance line of bulk water by paramagnetic exchange broadening.[21] Corrections for small shifts in the bound oxygen resonances due to the presence of added Mn^{2+} were made. Chemical shifts are reported relative to bulk water by using ClO_4^-, (^{17}O = +288 ppm from bulk water) as reference. Oxygen-17 enrichments of between 5 and 10 atom % were used. The temperature of the probe (25 ± 0.5 °C) was measured by a substitution technique[22] and maintained by using a stream of compressed air. Line shapes were simulated by fitting to Lorentzian distributions using a nonlinear least-squares program. Integrations were performed by using Lorentzian line simulations and were referenced to those from the anions ClO_4^- or $CF_3SO_3^-$ present in large excess and at natural abundance (0.037%) or, occasionally, bulk water.

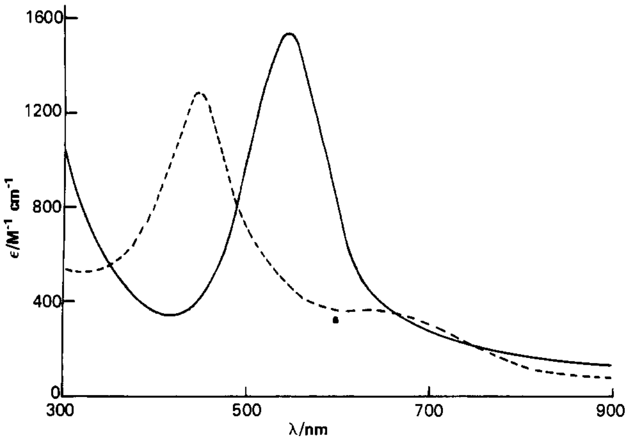


Figure 1. UV–vis absorbance spectra (ε's/Ir) for solutions of Ir(V) (---) and Ir(IV) (purple) (—) in 2.0 M $HClO_4$.

Results

Preparation of Ir(V). On electrochemical oxidation, solutions of $[Ir(H_2O)_6]^{3+}$ in 2.0 M $HClO_4$ are rapidly converted to brown-green solutions via a brown intermediate. No blue-purple intermediates were observed. A similar brown-green solution is obtained by dissolution of an iridium wire anode in 2.0 M $HClO_4$ at constant current (1.0 A) for 2–3 h at 0 °C,[23] and by chemical oxidation of $[Ir(H_2O)_6]^{3+}$ in 2.0 M $HClO_4$ with a 20-fold excess of Ce(IV). In all cases, solutions of Ir(V) were characterized by absorption maxima λ/nm (ε/M^{-1} cm^{-1}) at 447 (1260) and 640 (358) (Figure 1). The oxidation state of Ir(V) samples, generated at 0 °C to maximize stability, was verified by iodometric titration to Ir(III) with an excess of I^-, and titration of the liberated I_3^- with sodium thiosulfate. Prior to titration N_2 was bubbled through solutions (~10 mL) to remove any O_2. From an average of three determinations, the oxidation state was found to be (5.10 ± 0.05).

Coulometric measurements at +1.6 V vs NHE (0 °C) on solutions of $[Ir(H_2O)_6]^{3+}$ (5.0 mM) in 2.0 M $HClO_4$ further confirmed the presence of Ir(V), the conversion requiring 2.04 ± 0.05 equiv/Ir (average of three determinations) following background corrections.

Freshly prepared Ir(V) in 2 M $HClO_4$ decays spontaneously to a brown-purple Ir(IV)-containing product with a peak at 494 nm that we have not further studied. The decay $t_{1/2}$ ~ 5 h at 25 °C involves oxidation of H_2O, where O_2 can be detected by its reduction wave at 0.65 V.

Reduction of Ir(V). When the polarity of the Pt-gauze electrode was reversed at a constant current of 1.0 A, reduction of Ir(V) to Ir(IV) and Ir(III) was achieved. At 0 °C a deep blue-purple solution of Ir(IV) was obtained within 1–2 min. This solution might be described as purple, but since there is a blue component, we use here the description blue-purple and retain purple for the product obtained after standing (see e.g. Figure 5 below), or on oxidation of chromatographically pure $Ir(III)_B$. Solutions of the blue-purple product are characterized by a peak at ~555 nm, whereas the purple product has an absorption peak at 547 nm (ε = 1500 M^{-1} cm^{-1} per Ir) (Figure 1). Following maximization of the peak, the oxidation state was obtained by iodometric titration. From an average of three determinations, a value of 3.98 ± 0.02 was obtained. The purple Ir(IV) product undergoes spontaneous decay to Ir(III) in at least two stages requiring ~1 week.

Blue-purple solutions were also obtained from Ir(V) by controlled-potential reduction at +1.35 V vs NHE or by chemical reduction with Fe^{2+} or Eu^{2+}. Coulometric measurements established the consumption of 0.98 ± 0.06 electron equiv/Ir (average of three runs), thus verifying the formation of Ir(IV).

Further constant current reduction at 1.0 A, for 10–20 min at 0 °C gave pale yellow Ir(III) solutions. Alternatively, con-

---

(21) Hugi-Cleary, D.; Helm, L.; Merbach, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 4444.

(22) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.

(23) Details of this procedure were communicated to us in 1985 by (now the late) Prof. G. Biedermann, K.T.H., Stockholm.

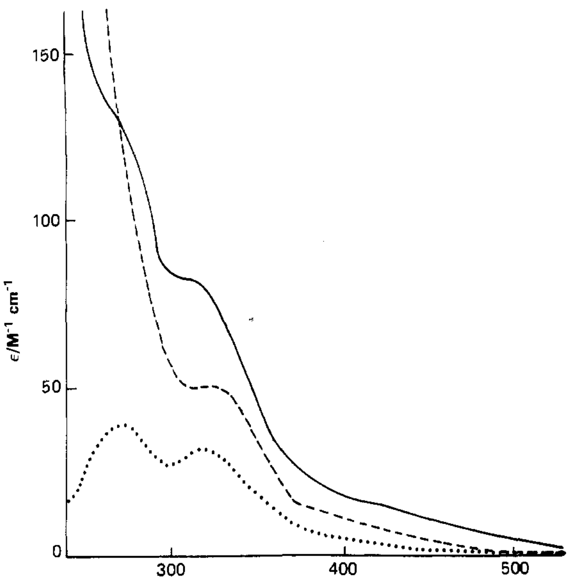


Figure 2. UV-vis absorbance spectra (ε's/Ir) for solutions of $[Ir(OH_2)_6]^{3+}$ (···), $Ir(III)_A$ (- - -), and $Ir(III)_B$ (—) in 2.0 M $HClO_4$.

trolled-potential reduction at +0.7 V vs NHE could be used. Coulometry at +0.7 V confirmed the further consumption of 1 electron equiv/Ir in the conversion of Ir(IV) to Ir(III). The UV-vis spectrum of the Ir(III) solution does not correspond to that of $[Ir(H_2O)_6]^{3+}$. The stability of the products allowed further investigation by ion-exchange chromatography.

Separation of Ir(III) Products. The $[H^+]$ of pale yellow Ir(III) solutions was adjusted to 0.1 M prior to loading on a Dowex 50W-X2 cation-exchange column (10 cm × 1 cm). After the column was washed with 0.5 M $HClO_4$, two yellow bands separated which successively eluted with 2.0 M $HClO_4$. From a starting solution of $[Ir(H_2O)_6]^{3+}$ (<7.0 mM) in 2.0 M $HClO_4$, ~70% of the total iridium was recovered in the two yellow bands. The remaining 30%, held as a greenish yellow band, was not eluted with 10 M $HClO_4$ and is polymeric. Larger amounts of the polymer were produced if the electrolysis was carried out at higher iridium concentrations.[24] The concentration of Ir in each yellow band, $[H^+]$ = 2.0 M, was determined by oxidation of Ir(V) and standardizing at the 447-nm peak (ϵ = 1260 $M^{-1}\ cm^{-1}$).

The products $Ir(III)_A$ (~25%) and $Ir(III)_B$ (~45%) (in order of elution) gave UV-vis spectra as shown in Figure 2. At $[H^+]$ = 2.0 M $Ir(III)_A$ gives a shoulder at 318 nm (ϵ = 50 $M^{-1}\ cm^{-1}$) assigned to the transition ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and $Ir(III)_B$ shoulders at 265 nm (ϵ = 130 $M^{-1}\ cm^{-1}$) and 310 nm (ϵ = 80 $M^{-1}\ cm^{-1}$) assigned as ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and ${}^1A_{1g} \rightarrow {}^1T_{1g}$, respectively (all ε's per Ir). Both spectra were more intense than that corresponding to $[Ir(H_2O)_6]^{3+}$ for which similar assignments have been made. The elution behavior of $Ir(III)_A$, $Ir(III)_B$, and $[Ir(H_2O)_6]^{3+}$ alongside that of monomer and dimer forms of chromium(III)[25,26] suggest charges of 4+ for $Ir(III)_A$ and 5+ for $Ir(III)_B$ in 2.0 M $HClO_4$. In a further experiment an equimolar mixture of $[Cr(H_2O)_6]^{3+}$, $[(H_2O)_4Cr(OH)_2Cr(H_2O)_4]^{4+}$, $Ir(III)_A$, and $Ir(III)_B$ was separated on a Dowex X2 column by slow displacement elution (1 drop every 30 s) by using 0.05 M La^{3+} in 0.1 M $HClO_4$. The ions in order of elution were Cr^{3+} closely followed by $Ir(III)_A$, with $Cr_2(OH)_2{}^{4+}$ and $Ir(III)_B$ eluting later in the same fractions. Under these conditions charges of 3+ to 4+ for $Ir(III)_A$ and 4+ for $Ir(III)_B$ were suggested, implying some acid dissociation of both Ir(III) species at $[H^+]$ ~ 0.1 M. A higher charge is indicated for $Ir(III)_B$ as compared to $Ir(III)_A$. The behavior observed is consistent with dimeric structures.

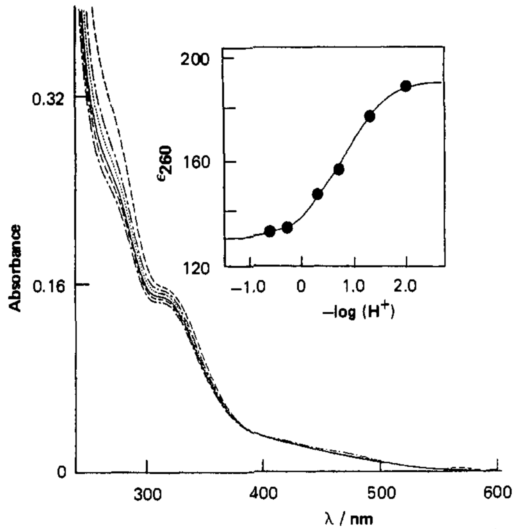


Figure 3. UV-vis absorbance spectra for solutions of $Ir(III)_B$ (0.1–19.8 mM) as a function of $[H^+]$ (0.01–1.98 mM), I = 2.0 M ($NaClO_4$). The $[H^+]$ was adjusted by dilution into aqueous $NaClO_4$.

Acid Dissociation Constants for Ir(III) Dimers. Spectrophotometric changes in the $[H^+]$ range 0.01–2.0 M were observed for both Ir(III) species. At 25 °C with $Ir(III)_B$, $[H^+]$ range 2.0 × 10^{-3} to 2.0 M, I = 2.0 M ($NaClO_4$), a significant increase in absorbance was observed below 330 nm on decreasing the $[H^+]$. The absorbance at 260 nm (maximum change) of solutions obtained on diluting $Ir(III)_B$ (0.05 M) in $HClO_4$ with $NaClO_4$, I = 2.0 M, was recorded as a function of $[H^+]$. The data obtained (Figure 3) were fitted to (1) by using an iterative procedure, with

$$\epsilon_{obs} = \frac{\epsilon[H^+] + \epsilon_{OH}K_a}{[H^+] + K_a} \qquad (1)$$

K_a, ϵ (for the aqua form), and ϵ_{OH} (for the conjugate base) as adjustable parameters. This gave, at 25 °C, K_a = 0.16 ± 0.03 M, ϵ = 130 ± 5 $M^{-1}\ cm^{-1}$/Ir and ϵ_{OH} = 190 ± 8 $M^{-1}\ cm^{-1}$/Ir, corresponding to a single acid dissociation process. An isosbestic point was detected at 396 nm (Figure 3), and the changes observed were reversible.

For solutions of $Ir(III)_A$, similar increases in absorbance at <330 nm were observed on lowering the $[H^+]$ to <0.2 M. The changes were however too small to allow a precise measure of K_a, which is <0.1 M.

Charge/Ir Determinations. These were estimated for both $Ir(III)_A$ and $Ir(III)_B$ by using a modified Cady and Connick method[27] as described by Finholt et al.[26] Freshly prepared samples of $Ir(III)_A$ and $Ir(III)_B$ (100 cm^3 each of 5.0 mM in Ir) were separately loaded onto a small Dowex 50W-X2 column (3 cm × 1 cm). Following washing of the column with 0.1 M $HClO_4$, the samples were eluted with 0.1 M La^{3+} in 0.1 M $HClO_4$ by the slow displacement method. About 1–2 cm^3 of solution free from La^{3+} contamination could be obtained (tested by dropwise addition to 0.1 M oxalic acid), which was then diluted to pH >1.0. The free $[H^+]$ was determined by pH measurement using a glass electrode. Values were typically between 1.5 and 1.7. The total charge was determined by loading a known amount (usually ~10 cm^3) of the diluted solution onto a further small Dowex 50W-X2 column (3 cm × 1 cm) and titrating the liberated H^+ (corresponding to total charge) with NaOH. The charge/Ir was then evaluated by (2). The value for $Ir(III)_B$ of 2.08 ± 0.01, determined at pH

$$\text{charge/Ir} = \frac{\text{moles of total charge} - \text{moles of free } H^+}{\text{moles of Ir present}} \qquad (2)$$

---

[24] The color of the Ir(V) obtained from $[Ir(H_2O)_6]^{3+}$ at >7.0 mM with $[H^+]$ < 1.0 M is more brown than brown-green, with loss of the peak at 640 nm and shift of the 447-nm maximum to 450 nm. Larger amounts of oligomeric Ir(III) product were detected on subsequent reduction.

[25] Thompson, M.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 2279.

[26] Finholt, J. E.; Thompson, M.; Connick, R. E. *Inorg. Chem.* **1981**, *20*, 4151.

[27] Connick, R. E.; Cady, H. H. *J. Am. Chem. Soc.* **1957**, *59*, 4242; **1958**, *80*, 2646.

Table I. Cyclic Voltammetric Data (25 °C) for Ir(III)$_A$ and Ir(III)$_B$ as a Function of [H$^+$] and Scan Rate (I = 2.0 M (NaClO$_4$))

[H$^+$], M	scan rate, V s^{-1}	$E°$(IV/III), V vs NHE	E_p, mV	$E°$(V/IV), V vs NHE
		Ir(III)$_A$		
1.98	0.100	+1.260	80	+1.49[a]
1.98	0.050	+1.259	70	
1.98	0.020	+1.262	55	
1.00	0.100	+1.235		
		Ir(III)$_B$		
1.95	0.100	+1.230		+1.58[a]
1.00	0.100	+1.213		
0.01	0.200	+1.089	50	
	0.100	+1.089	43	
	0.050	+1.090	38	
	→0	+1.089	→29.5	

[a] Cathodic peak not well-defined. Values only at [H$^+$] = 2.0 M are reported.

Table II. First-Order Rate Constants (k_{obs}) for the Spontaneous Conversion of Blue Ir(IV) (0.5–5.0 mM Ir(IV)) to Purple Ir(IV) (I = 1.0 M (NaClO$_4$))

T, °C	[H$^+$], M	k_{obs}, s^{-1}	T, °C	[H$^+$], M	k_{obs}, s^{-1}
0	0.12	0.027	25	0.12	0.60
	0.42	0.022		0.42	0.47
	0.72	0.019		0.72	0.44
	1.00	0.017		1.00	0.40

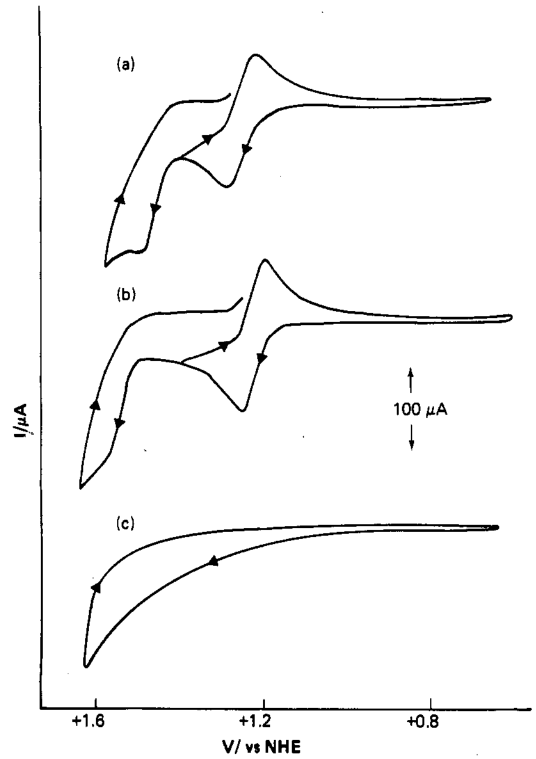


Figure 4. Cyclic voltammograms (25 °C) for solutions of (a) Ir(III)$_A$, (b) Ir(III)$_B$, and (c) [Ir(OH$_2$)$_6$]$^{3+}$. Scan rates = 0.1 V s^{-1}, concentrations ~ 5 mM, and I = 2.0 M (NaClO$_4$).

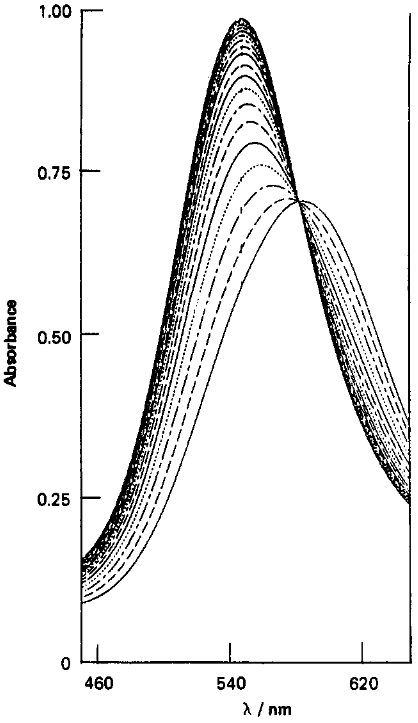


Figure 5. UV–vis scan absorbance spectra (25 °C) for the blue to purple Ir(IV) conversion (0.6 mM) at 584 nm as a function of time over a period of ~1 h in 0.5 M HClO$_4$.

1.6, is consistent with a dimeric ion of 4+ charge formed by acid dissociation (K_a = 0.16 M) of a μ-hydroxo 5+ dimer present at higher [H$^+$]. The charge/Ir value for Ir(III)$_a$ of 1.09 ± 0.03 suggests that at pH >1.6 a bis(μ-oxo) structure (or equivalent) may be present. This would support a 4+ bis(μ-hydroxo) dimer in ~2 M HClO$_4$.

Electrochemistry. Cyclic voltammograms obtained for solutions of Ir(III)$_A$ and Ir(III)$_B$ (5.0 mM in Ir) in 2.0 M HClO$_4$ indicate quasi-reversible oxidation to Ir(IV) and a further quasi-reversible wave for oxidation to Ir(V) (Figure 4). Formal reduction potentials (25 °C) were estimated from the average value of the anodic and cathodic peak potentials at a scan rate of 0.1 V s^{-1} and are shown in Table I for the V/IV and IV/III couples of both Ir(III)$_A$ and Ir(III)$_B$ in 1.0 and 2.0 M H$^+$.

For the Ir(III)$_A$ and Ir(III)$_B$ oxidations the anodic/cathodic peak separations approach the theoretical limit of 29.5 mV for a two-electron process at 25 °C,[28,29] as the scan rate is decreased toward zero. From variations with [H$^+$] it can be concluded that the oxidation to Ir(IV) involves one to two protons and two electrons.

Consistent with reduction potentials in Table II, controlled-potential oxidation of Ir(III)$_B$ at +1.4 V vs NHE in 2.0 M HClO$_4$ using the Pt-gauze electrode gives rise to a purple Ir(IV) solution having a single absorption maximum at 547 nm (ϵ = 1700 M^{-1} cm^{-1}/Ir). However, the corresponding oxidation of Ir(III)$_A$ gives a blue Ir(IV) product, λ_{max} = 584 nm (ϵ = 1190), which spontaneously converts to the purple form obtained from Ir(III)$_B$. An isosbestic point was observed at 580 nm (Figure 5), consistent with the interconversion of two related dimeric forms.

Kinetics of the Blue to Purple Ir(IV) Change. Conversion of blue to purple Ir(IV) (0.5–5.0 mM) was followed at 550 nm as a function of [H$^+$] in the range 0.12–0.99 M, I = 1.0 M (NaClO$_4$), at 0 and 25 °C. The observed absorbance increase conformed to first-order kinetics, with plots of ln ($A_\infty - A_t$) vs time being linear for at least 3 half-lives. The dependence of rate constants k_{obs} (Table II) on [H$^+$] was as in (3), indicating a single reaction

$$k_{obs} = \frac{kK_a[\mathrm{Ir(IV)}]}{[\mathrm{H}^+] + K_a[\mathrm{Ir(IV)}]} \qquad (3)$$

pathway involving deprotonated blue Ir(IV) with acid dissociation constant K_a. Consistent with (3), a plot of k_{obs}^{-1} vs [H$^+$] was linear at both temperatures (Figure 6), from which k = (1.02 ± 0.08) × 10^{-2} s^{-1} at 25 °C, $\Delta H^\ddagger$ ~ 19 kcal mol^{-1}, $\Delta S^\ddagger$ ~ −2.5 cal K^{-1} mol^{-1}, and K_a for blue Ir(IV) = 1.7 ± 0.3 M at 25 °C. Spectrophotometric changes (Figure 7) were also observed for purple Ir(IV) as a function of [H$^+$] in the range 0.02–2.0 M, implying different degrees of protonation. These changes were reversible over ~10 min periods.

---

[28] Weissberger, A.; Rossiter, B. W. *Physical Methods of Chemistry, Part IIA, Electrochemical Methods*; Wiley-Interscience: London, 1971; p 20.

[29] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

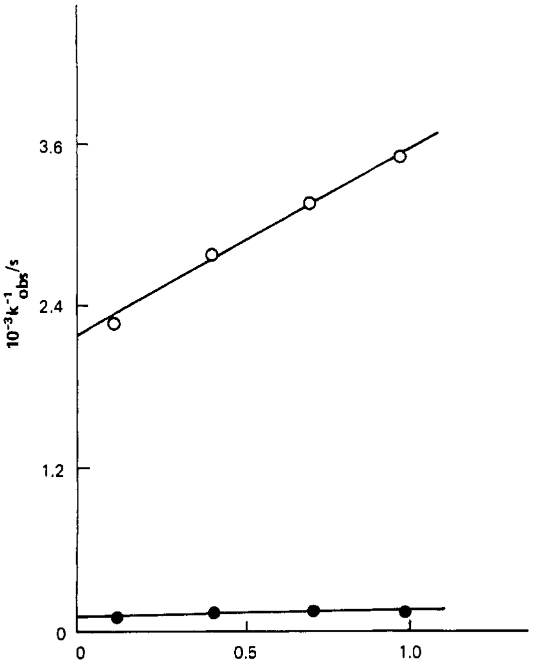


Figure 6. Plots of k_{obs}^{-1} vs [H$^+$] for the blue to purple Ir(IV) conversion at 0 °C (○) and 25 °C (●), I = 1.0 M (NaClO$_4$).

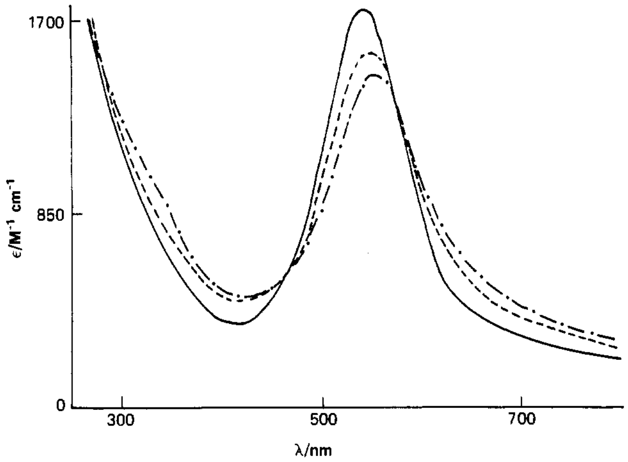


Figure 7. UV–vis absorbance spectra (ε's/Ir) for (0.20–20 mM blue Ir(IV) at 25 °C as a function of [H$^+$]: 2.0 M (—); 0.2 M (- - -); 0.02 M (-·-), I = 2.0 M (NaClO$_4$).

Conversion of the blue to purple Ir(IV) could also be followed by ^{17}O NMR employing 5 atom % ^{17}O-enriched samples (see below).

Oxygen-17 NMR Studies. Extremely slow exchange is observed for water ligands on both Ir(III)$_A$ and Ir(III)$_B$, and direct ^{17}O-enrichment at the Ir(III) state was only feasible at elevated temperatures (>100 °C). Interestingly for solutions in CF$_3$SO$_3$H, this resulted in the eventual conversion of Ir(III)$_A$ and Ir(III)$_B$ to [Ir(H$_2$O)$_6$]$^{3+}$, which gives a single ^{17}O-bound water resonance at −152 ppm relative to bulk water as zero. The latter assignment was verified by using 0.4 M solutions of [Ir(H$_2$O)$_6$]$^{3+}$ at natural abundance (0.037 atom %). Conversion of Ir(III)$_A$ to Ir(III)$_B$ (under conditions of 7.0 M H$^+$, at 60 °C for 2 h) with ultimate conversion to [Ir(H$_2$O)$_6$]$^{3+}$ (100 °C, 10 h) is consistent with double- and single-μ-hydroxo-bridged structures, respectively.

Rapid enrichment ($t_{1/2}$ ~1 min) of bound water was observed for both blue and purple Ir(IV). Thus electrochemical oxidation of a solution of Ir(III)$_A$ (0.05 M) in 2.0 M HClO$_4$, containing 5 atom % H$_2$^{17}O and 0.1 M Mn^{2+}, resulted in the rapid appearance of two bound water resonances of blue Ir(IV) at +43 ppm and −46 ppm vs bulk water (Figure 9a) having equal intensity. No resonances were observed that could be assigned to bridging μ-oxo or hydroxo groups in the expected range −200 to +1000 ppm. Virtually concurrent with the appearance of two blue Ir(IV) resonances was the growth of a single ^{17}O resonance at −9 ppm assigned to the bound water ligands of purple Ir(IV). (Figure 8a–d). Once conversion to purple Ir(IV) was complete (Figure 8), rapid reduction to Ir(III) was performed by addition of 1 equiv of Eu^{2+} per Ir. The resulting UV–vis spectrum of the yellow solution confirmed the presence of Ir(III)$_B$ (Figure 2). A single broad ^{17}O resonance due to bound water ligands was obtained at −145 ppm from bulk water (Figure 9). However on close analysis of the line shape (inset) two overlapping Lorentzians of 1:4 intensity were identified. This confirms a single μ-hydroxo-bridged dimeric structure for Ir(III)$_B$, and a single μ-oxo (or hydroxo) structure is relevant therefore in the case of Ir(IV). The latter is supported by the single resonance for purple Ir(IV) (Figure 8d), which we were unable to further resolve.

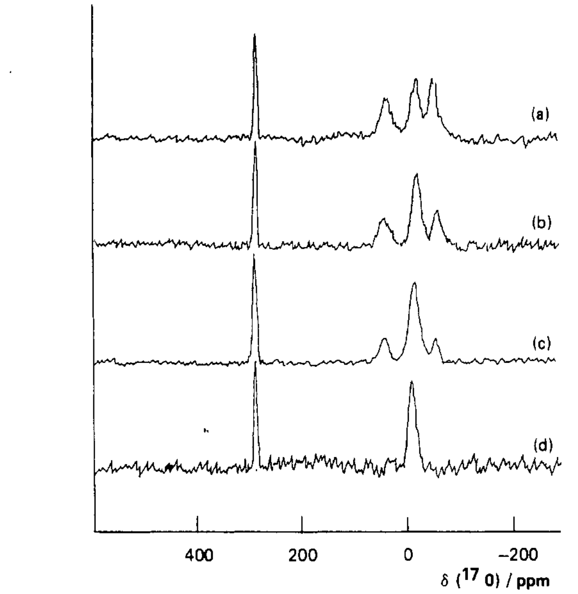


Figure 8. 54.24-MHz ^{17}O NMR spectra (25 °C) for a solution of blue Ir(IV) (0.05 M) as a function of time: (a) 10 min; (b) 15 min; (c) 20 min; (d) 1 h, I = 2.0 M (HClO$_4$); ^{17}O enrichment was 5 atom %, with 0.1 M Mn^{2+} added. The line at +288 ppm is from the natural abundance of ClO$_4^-$.

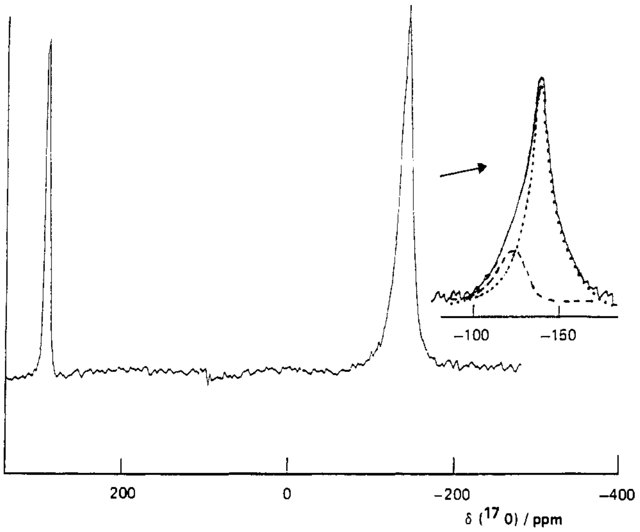


Figure 9. 54.24-MHz ^{17}O NMR spectrum (25 °C) of Ir(III)$_B$ (0.05 M) in 2.0 M HClO$_4$, 5 atom % ^{17}O, with 0.1 M Mn^{2+} added (the reference line at +288 ppm is from the natural abundance of ClO$_4^-$). The inset is a simulation of the bound water region using Lorentzian lines.

Owing to the irreversibility of the spontaneous blue to purple Ir(IV) conversion, enrichment of Ir(III)$_A$ via the above scheme using Ir(IV) was not possible. However, a bound water-enriched sample of Ir(III)$_A$ was obtained as a byproduct during the

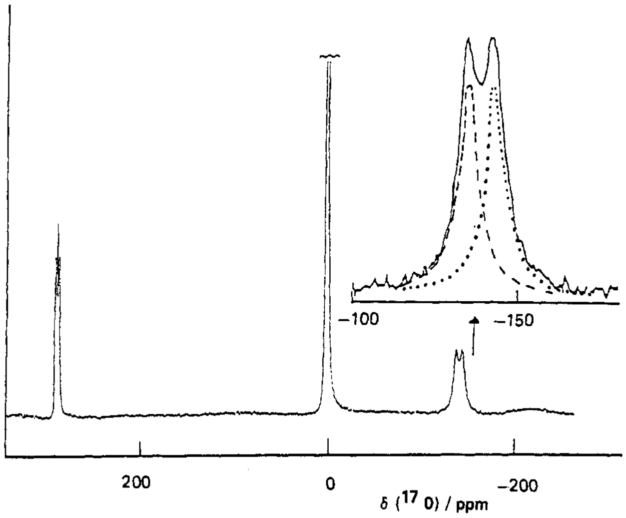
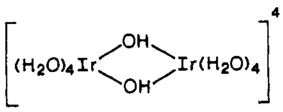
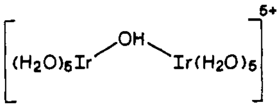


Figure 10. 54.24-MHz ^{17}O NMR spectrum (25 °C) of Ir(III)$_A$ (0.1 M) in 2.0 M $HClO_4$, 0.7 atom % ^{17}O, no Mn^{2+} added (the reference lines at +288 ppm (ClO_4^-) and 0.0 ppm (bulk water) are both from natural abundance). The inset is a simulation of the bound water region using Lorentzian lines.

preparation of ^{17}O-enriched samples of $[Ir(H_2O)_6]^{3+}$.[18] This sample in 2.0 M $HClO_4$ was obtained at natural abundance in bulk water following ion-exchange chromatography. The sample, verified as Ir(III)$_A$ from its UV–vis spectrum and electrochemical oxidation to blue Ir(IV), showed in addition to the natural-abundance ^{17}O resonances of bulk water (0 ppm, no Mn^{2+} added) and ClO_4^- (+288 ppm), two sharp lines of equal intensity at −137 and −143 ppm (Figure 10). The low signal intensity here was due to the lower ^{17}O enrichment (0.7 atom %) present for the bound water ligands. The two bound water resonances gave two overlapping Lorentzians of equal intensity consistent with a bis(μ-hydroxo) dimeric structure for Ir(III)$_A$.[30] Again no peaks in the region assignable to μ-hydroxo (oxo) bridging groups were observed. Small line widths are observed in Figure 10 in the absence of Mn^{2+}, which can give rise to a broadening of H_2O resonances. The well-resolved quartet for ClO_4^- (coupling to $^{35,37}Cl$, $I = {}^3/_2$) is noted in Figure 10.



Ir(III)$_A$



Ir(III)$_B$

Solutions of Ir(V) were also generated in the presence of enriched $H_2{}^{17}O$, but no bridging or bound water oxygen resonances were observed. This is most likely due to the considerable lability coupled with the inherent paramagnetism of Ir(V), leading to rapid exchange broadening of the bound H_2O resonances.

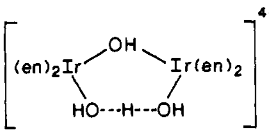
Chemical Oxidation to Ir(V). A 20-fold excess of cerium(IV) ($E° = 1.7$ V)[31] rapidly ($t_{1/2} < 1$ min) oxidizes $[Ir(OH_2)_6]^{3+}$, as well as the dimeric Ir(III) and Ir(IV) ions, in 2.0 M $HClO_4$ to brown-green Ir(V).

Discussion

The scheme in Figure 11 summarizes the solution chemistry described in this paper. The initial step involves electrochemical (10–15 min at 0 °C) or chemical, e.g. Ce(IV) ($t_{1/2} < 1$ min), oxidation of $[Ir(H_2O)_6]^{3+}$,[8] where brown-green Ir(V) is obtained.[24] A further method involving electrolytic oxidation of an Ir-wire electrode is capable of giving higher concentrations of Ir(V) over 2–3 h, but some aging (and resultant contamination) of solutions can occur over such time intervals.[8,23] Reversing the polarity of the electrode reduces Ir(V) to blue-purple Ir(IV) and then pale yellow Ir(III) solutions.

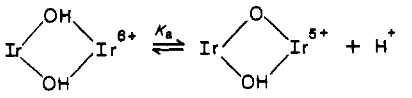
Two yellow Ir(III) products were separated by ion-exchange chromatography, with a further ~30% of a more highly charged oligomeric Ir(III) form that is held at the top of columns. From the elution profile as compared to monomeric and dimeric Cr(III) aqua ions, charges in the range 3+ to 5+ are indicated. Furthermore from NMR studies on ^{17}O-enriched samples, Ir(III)$_A$ has two different types of coordinated H_2O of equal abundance, consistent with a bis(μ-hydroxo) 4+ structure, and Ir(III)$_B$ has two different H_2O's of 4:1 relative abundance, consistent with a μ-hydroxo 5+ structure. Only on heating in the presence of high (7 M) acid could these two forms be interconverted (CF_3SO_3H rather than the potentially oxidizing $HClO_4$ was used[16]), and (eventually) $[Ir(H_2O)_6]^{3+}$ regenerated. It is concluded that the sequence of changes Ir(III)$_A$ → Ir(III)$_B$ → $[Ir(H_2O)_6]^{3+}$ is in order to decreasing hydrolysis. The highly inert nature of the Ir(III) state[16] is clearly apparent in these studies.

From spectrophotometric studies on the μ-hydroxo (5+) Ir(III)$_B$ an unusually high acid dissociation constant (K_a) of 0.16 M has been obtained. This compares with 0.1 M for $[(H_2O)_5CrOHCr(H_2O)_5]^{5+}$ [32] and 0.016 M for $[(en)_2(H_2O)IrOHIr(H_2O)(en)_2]^{5+}$,[33] both single-bridged μ-hydroxo dimers of 5+ charge. It has been confirmed by X-ray crystallography that the H-bonded $H_3O_2^-$-bridged form is present in the latter case.[33]

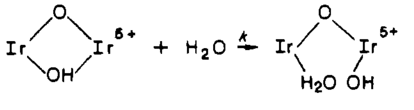


Therefore on acid dissociation a similar structure seems likely in the case of Ir(III)$_B$. There are now a number of examples of $H_3O_2^-$ bridging, and the subject has recently been reviewed.[34] In the case of Ir(III)$_A$, UV–vis absorbance changes occur at $[H^+] < 0.2$ M, and a smaller K_a applies for this ion.

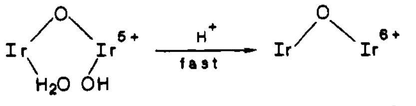
The above evidence for bis(μ-hydroxo) 4+ and μ-hydroxo 5+ structures for Ir(III)$_A$ and Ir(III)$_B$, respectively, provides a basis for discussion of the Ir(IV) and Ir(V) structures. We have not as yet been able to obtain crystalline products, due to the dilute nature of solutions from column chromatography, the substitution inertness of Ir(III) (making the introduction of other ligands difficult), and (spontaneous) decay of Ir(IV) ($t_{1/2}$ ~ 1 day) and Ir(V) states ($t_{1/2}$ ~ 5 h). Electrochemical oxidation of Ir(III)$_A$ and Ir(III)$_B$ provides evidence for Ir(IV) analogues, blue and purple, respectively. Cyclic voltammetry measurements both indicate quasi-reversible 2e oxidations with accompanying loss of protons. Particularly interesting is the metastable nature of the blue solutions, which convert to purple solutions in a single rate-determining step. The rate law for eq 5 is consistent with



(4)



(5)



(6)

a reaction proceeding solely via the conjugate base of blue Ir(IV), $K_a = 1.7$ M. There are two possible sites for acid dissociation, a terminal H_2O or (if present) a bridging OH^-. In the first case acid dissociation of a terminal H_2O and labilization of a hydroxo

---

(30) Richens, D. T.; Helm, L.; Pittet, P.-A.; Merbach, A. E. *Inorg. Chim. Acta* **1987**, *132*, 85. Similar features have been observed for bound ^{17}O-enriched water of $[(H_2O)_4Mo(\mu\text{-}OH)_2Mo(H_2O)_4]^{4+}$.

(31) Latimer, W. *Oxidation States of the Elements and their Potentials in Aqueous Soltuion*, 2nd ed.; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1982.

(32) We are most grateful for comments from Professor J. E. Finholt.

(33) Galsbol, F.; Larsen, S.; Rasmussen, B.; Springborg, J. *Inorg. Chem.* **1986**, *25*, 290.

(34) Ardon, M.; Bino, A. *Struct. Bonding (Berlin)* **1987**, *65*, 1 and references therein.

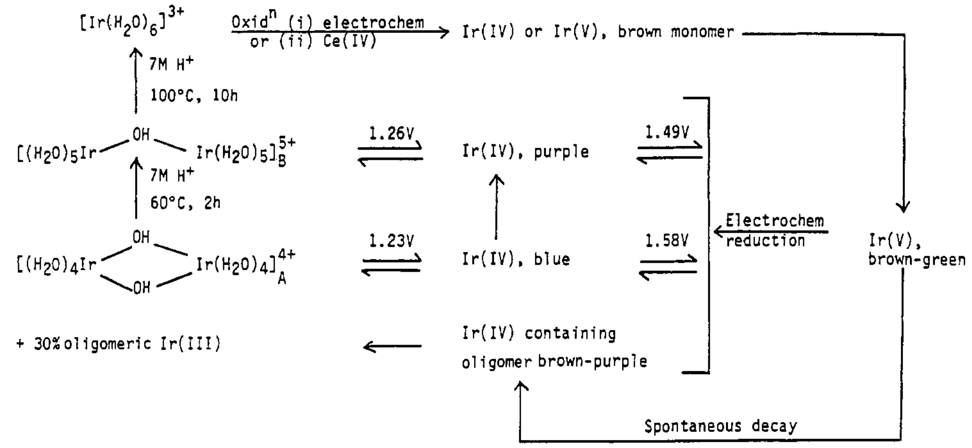


Figure 11. Reaction scheme summarizing the interconversion of Ir(III), Ir(IV), and Ir(V) in aqueous $HClO_4/NaClO_4$ solutions.

bridge can be considered. Alternatively the conversion of μ-OH to μ-O followed by cleavage of the second μ-OH is possible (eq 4–6). An increase in the Ir–O–Ir bond angle as acid dissociation occurs will result in ring strain, and favor bridge cleavage. The high charge (6+) on the two Ir(IV)'s is supported by ion-exchange behavior. Thus solutions of blue and purple Ir(IV) in 2 M $HClO_4$ give a narrow band at the top of a Dowex 50W-X2 column that is not eluted by >5 M H^+. These structures are also supported by the NMR ^{17}O studies. Likely formulas are therefore $[(H_2O)_4Ir(OH)_2Ir(H_2O)_4]^{6+}$ for the blue compound and $[(H_2O)_5IrOIr(H_2O)_5]^{6+}$ for the purple one. In the former case a bis(μ-oxo) structure is not entirely excluded, but seems less likely in view of the $[H^+]^{-1}$ dependence for the blue–purple change.

Electrochemical and chemical oxidations of all Ir(III) and Ir(IV) species yields as far as we can tell identical brown-green Ir(V) solutions. Rapid interconversions of the different Ir(V) forms are implied. It would be surprising if relevant structures did not include dimeric and polymeric forms, because on reduction $Ir(III)_A$, $Ir(III)_B$, and oligomeric Ir(III) are formed in rapid processes. There is no evidence for regeneration of $[Ir(H_2O)_6]^{3+}$, and it can be concluded that monomeric Ir(V) (and Ir(IV)) are present at most in very small amounts.

This has interesting implications with regard to the initial oxidation of monomeric $[Ir(H_2O)_6]^{3+}$, because a brown intermediate but no blue-purple intermediate is observed. It is likely that the brown intermediate corresponds to monomeric Ir(IV) or Ir(V), and that dimerization (and further oligomerization) occur in the Ir(V) state. The suggestion here is that Ir(III) ($5d^6$) is more inert than Ir(V). This is most readily accounted for by Ir(V) having terminal oxo ligand(s). Thus monomeric Ir(V) might be expected to have at least one such ligand. From studies on aqua VO^{2+} and TiO^{2+} it is now well established that oxo groups labilize the trans coordination position.[35-38] Monomeric Ir(IV), with a relatively large radius as compared to V(IV) and Ti(IV), is probably hydrolyzed to a mixture of $Ir^{4+}/IrOH^{3+}$ rather than IrO^{2+} and is not expected to be as labile as Ir(V). No NMR ^{17}O information was forthcoming as to the structure of the Ir(V) species, but it seems likely that these are related to the Ir(III) and Ir(IV) products, and are μ-oxo and/or μ-hydroxo dimers with the possibility of additional terminal oxo ligands. In the context of these studies, we note a similar series of reactions of the $Ru(III)_2$ complex $[(bpy)_2(H_2O)RuORu(H_2O)(bpy)_2]^{4+}$, which can be oxidized in one-electron steps to the Ru(V,V) analogue $[(bpy)_2(O)RuORu(O)(bpy)_2]^{4+}$.[39] Also of interest is the existence of μ-oxo ligands in the Ru(III,IV,III) trimer $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$.[40] No mixed-valence forms have been identified in the present work. This aspect would be of further interest, possibly in studies with bipyridine (bpy) coordinated to the Ir.

Little has so far been said about the higher oligomer forms (i.e. greater than dimers) that feature in the reaction scheme shown in Figure 11. We have no information as to whether a single oligomer, e.g. trimer, or a mixture of higher oligomers is obtained. The oligomers are present for all three oxidation states and are not eluted from ion-exchange columns. Aging of Ir(V) solutions ($t_{1/2} \sim 5$ h at 25 °C) for example leads to an accumulation of a brown-purple oligomeric form of Ir(IV), with a peak at 494 nm ($\epsilon = 994\ M^{-1}\ cm^{-1}$/Ir). This reaction yields O_2 (detected electrochemically), and oxidation of H_2O is indicated. A much slower decay of Ir(IV) solutions is observed ($t_{1/2} \sim 1$ day).

We are aware of fairly extensive Russian work in which the preparations of aqua–Ir(IV) (at the 10^{-6} M level) and Ir(V) have been reported,[1-6,9] but find no significant links with the present work. Although several colorimetric assays of Ir have been developed on the basis of intense purple colors resulting from Ir(IV) in $HClO_4$, H_2SO_4, and H_3PO_4 solutions,[41] little or no detail as to the solution chemistry has so far emerged. The formation of $[IrCl_6]^{2-}$ from the reaction of Ir(IV) in 11 M $HClO_4$ with saturated NaCl at 100 °C is the basis of the Zinser and Page procedure for the determination of Ir.[42]

Acknowledgment. We are most grateful to Professor H. Gamsjäger (University of Leoben, Austria) for help in the early stages of this work and to Professor A. E. Merbach (University of Lausanne, Switzerland) for use of a Bruker AM-400 NMR spectrometer and access to samples of ^{17}O-enriched water. Dr. L. Helm (University of Lausanne) helped in the recording of ^{17}O NMR spectra. S.E.C.-B. thanks the National Autonomous University of Mexico (U.N.A.M.) for postgraduate support, and D.T.R. acknowledges the British Council and Nuffield Foundation for grants. We thank Johnson Matthey for the generous loan of iridium samples.

---

(35) Schlund, A.; Wendt, H. *Ber. Bunsen-Ges. Phys. Chem.* **1968**, *72*, 652.
(36) Thompson, G. A. K.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1977**, *16*, 2880.
(37) Saito, K.; Sasaki, Y. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 179–216.
(38) Comba, P.; Merbach, A. E. *Inorg. Chem.* **1987**, *26*, 1315.
(39) Ellis, C. D.; Gilbert, J. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5070.
(40) Smith, P. M.; Fealey, T. *J. Chem. Soc., Commun.* **1971**, 331.
(41) Pshenitsyn, N. K.; Ginsburg, S. I.; Sal'skaya, L. G. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1960**, *5*, 399.
(42) Zinser, E. J.; Page, J. A. *Anal. Chem.* **1970**, *42*, 787.