New Aqua Ions of Iridium in Oxidation States (III), (IV), and (V)

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The electrochemical preparation and characterisation in terms of oxidation state, spectra, stability, and reduction potentials of Ir^{IV} and Ir^V aqua ions in 2 M $HClO_4$, and related binuclear Ir^{III} ions, is described.

Beutler and Gamsjäger first prepared the mononuclear aqua Ir^{III} ion in 1976.[1] Since then it has been demonstrated that the ion is hexa-aqua, with a pK_a of 4.37,[2,3] but as yet no redox studies have been reported. Here we describe experiments in which $[Ir(H_2O)_6]^{3+}$ in 1.0—4.0 M $HClO_4$ is oxidised, and aqua ions of Ir^{IV} and Ir^V, not monomeric and almost certainly binuclear, are obtained. There are at present few well characterised complexes of Ir^{IV} and Ir^V.[4—6]

Solutions of hexa-aquairidium(III), typically 0.02 M in 2 M $HClO_4$, peaks λ/nm (ε/M^{-1} cm^{-1}) at 310(32.5) and 265(41), were prepared by the procedure described.[1] To obtain the brown-green Ir^V ion a solution of $[Ir(H_2O)_6]^{3+}$ (0.1—7.0 mM) in 1—2 M $HClO_4$ was electrochemically oxidised for 10—15 min (at 0 °C) at a constant current of 1.0 A using a Pt gauze working electrode (~4 cm^2), and a Pt wire counter electrode. Anodic and cathodic solutions (each ~25 ml) were separated by a fine (No. 4) sinter. Stirring of the anodic solution was achieved using a stream of N_2 gas. Alternatively controlled potentiometric oxidation at 1.6 V vs. normal hydrogen electrode (n.h.e.) was employed. A further method in which electrolytic oxidation of an iridium wire electrode,[7] current 1.0 A in 2 M $HClO_4$ at 0 °C, whereby iridium(V) concentrations of 0.05 M were obtained in 2—3 h has also been used.

By reversing the polarity of the Pt gauze electrode reduction of Ir^V to Ir^{IV} was achieved. At a current of 1.0 A (at 0 °C) maximum purple colour intensity was observed after 1—2 min. Alternatively controlled potentiometry at 1.35 V vs. n.h.e. was used. Delays during which the Ir^V could undergo

spontaneous decay were avoided. Further reduction at a current of 1.0 A (or by controlled potentiometry at 0.65 vs. n.h.e.) gave a pale yellow Ir^{III} solution in 10—20 min.

Solutions of Ir^V and Ir^{IV} (1—2 mM) at 0 °C (to maximise stability), with N_2 bubbled through solution (10 ml) to remove any O_2, were titrated iodometrically. Excess of NaI (1 ml of 0.10 M) was added to reduce to Ir^{III}, and the I_3^- formed titrated against 0.010 M $Na_2S_2O_3$. From an average of three determinations Ir^V gave an oxidation state of 5.10 ± 0.05, and Ir^{IV} of 3.98 ± 0.02.

Spectra of the Ir^V and Ir^{IV} ions in 1—4 M $HClO_4$ are shown in Figure 1. Peak positions λ/nm (ε/M^{-1} cm^{-1}) are for Ir^V 447 (1260) and 640 (358), and for (purple) Ir^{IV} 547 (1500). Freshly prepared Ir^V in 2 M $HClO_4$ decays spontaneously to another Ir^{IV} containing product brown-purple in colour, with a peak at 494 nm, which we have not further studied. The decay, $t_{\frac{1}{2}}$ ~5 h at 25 °C, involves oxidation of H_2O, where O_2 can be detected by its reduction wave at 0.65 V. The purple Ir^{IV} generated electrochemically from Ir^V is more stable, and spontaneous decay to Ir^{III} in at least two stages requires >1 week.

Work is in progress to characterise further the Ir^{III} solutions obtained by electrochemical reduction of Ir^{IV}. Two closely related products Ir^{III}_A, shoulder at 318(50), and Ir^{III}_B shoulders at 265 (130) and 310 (80), Figure 2, can be separated by
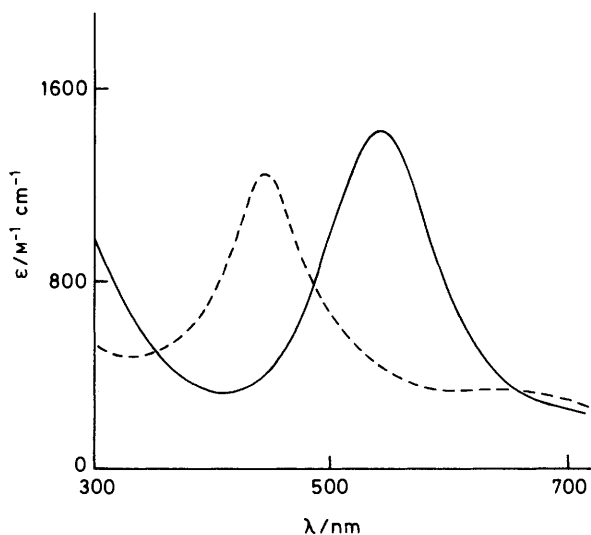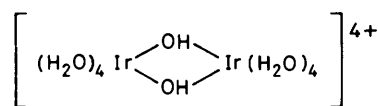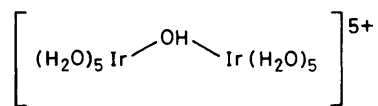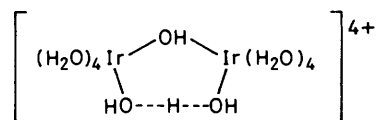

Figure 1. U.v.–visible spectra of Ir^V (---) and (purple) Ir^{IV} (——) generated electrochemically from $[Ir(H_2O)_6]^{3+}$ (0.1—7.0 mM) or by anodic oxidation of an Ir electrode in 2 M $HClO_4$.
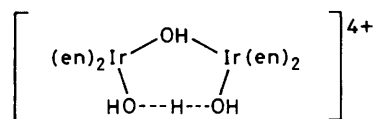

(I)

(II)

(III)

(IV)

en = ethylenediamine
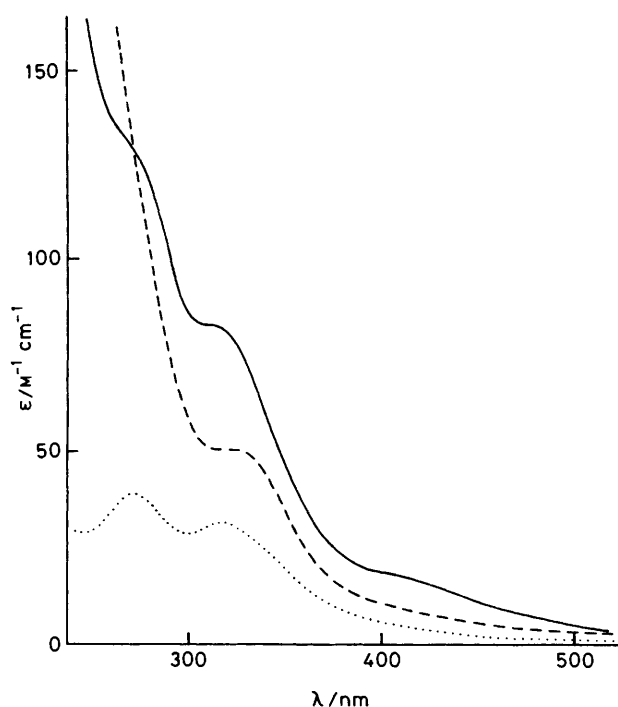
Figure 2. A comparison of u.v.–visible spectra of the Ir^{III}_A and Ir^{III}_B ions, $[(H_2O)_4Ir(OH)_2Ir(H_2O)_4]^{4+}$ (– – –) and $[(H_2O)_5IrOH Ir(H_2O)_5]^{5+}$ (——) (ε values per dimer), with $[Ir(H_2O)_6]^{3+}$ ($\cdots$) in 2 M $HClO_4$ solutions.

column chromatography and eluted with 2 M $HClO_4$. Elution characteristics as compared to binuclear and trinuclear aqua Cr^{III} ions of known charges 3+ through to 5+, and charge per metal determinations for Ir^{III}_B,[8] suggest dimeric bridged structures (I) and (II) for Ir^{III}_A and Ir^{III}_B respectively.

A deprotonated form of Ir^{III}_B detectable from absorbance changes ~280 nm, forms rapidly (pK_a ~0.8) at 25 °C, $I = 2.0$ M $(LiClO_4)$, on adjusting the $[H^+]$. The anomalously low pK_a is explained by the existence of the H-bonded form (III), the analogue of which has been identified for solutions of $[(H_2O)_5CrOHCr(H_2O)_5]^{5+}$ (pK_a ~1.0),[9] and has been characterised crystallographically in the case of the μ-hydroxo-[aquabisethylenediamineiridium(III)][hydroxobisethylene-diamineiridium(III)], (IV).[10]

We have not so far been able to interconvert Ir^{III}_A and Ir^{III}_B which are extremely inert, and there is at present no simple route to regenerate $[Ir(H_2O)_6]^{3+}$. On decreasing the $[H^+]$ solutions of purple Ir^{IV} give a shift in peak to $\lambda_{max.}$ 560 nm at pH 3 which is reversible over ~10 min. Oxidation of Ir^{III}_A yields a blue Ir^{IV} product with a peak at 584 nm, which is rapidly converted into the purple Ir^{IV} product which can be obtained by direct oxidation of Ir^{III}_B. Cyclic voltammetry experiments on 2 M $HClO_4$ solutions at 25 °C indicate formal reduction potentials of 1.49 and 1.26 V (Ir^{III}_A) and 1.58 and 1.23 V (Ir^{III}_B) per electron for the corresponding Ir^V and Ir^{IV} ions respectively. Potential step coulometry on $[Ir(H_2O)_6]^{3+}$

at 0.3 to 1.6 V confirms the presence of the Ir^V state, the conversion requiring 2.04 ± 0.05 equivalents per Ir. Formation of Ir^{IV} in controlled potential experiments at 1.4 V indicates a 0.98 ± 0.06 electron change per Ir. Consistent with the reduction potentials a 20-fold excess of Ce^{IV} in 2 M perchloric acid (reduction potential ~1.7 V)[11] will oxidise $[Ir(H_2O)_6]^{3+}$ and the two dimeric Ir^{III} ions (0.1 to 1.0 mM) to the Ir^V state. Reduction of Ir^V or Ir^{IV} to Ir^{III} is observed with I^-, Fe^{2+}, or ascorbate.

It has also been demonstrated that $[Ir(H_2O)_6]^{3+}$ is extremely inert, probably the most inert hexa-aqua ion in the Periodic Table.[12] The rapidity of the Ce^{IV} oxidation of $[Ir(H_2O)_6]^{3+}$ to brown-green Ir^V (stopped-flow time range) has interesting implications, since neither the Ir^V nor the Ir^{IV} ion are monomeric, and there must therefore be accompanying substitution processes. A transient brown (but no purple) colouration is noted in the electrochemical oxidation of $[Ir(H_2O)_6]^{3+}$ to Ir^V. This suggests that monomeric Ir^{IV} and Ir^V are generated in the stepwise oxidation of $[Ir(H_2O)_6]^{3+}$, and that one or both have sufficient lability to permit rapid formation of binuclear forms. Such lability most likely results from terminal oxo ligands. It is well established from studies on the aqua ions of VO^{2+}, and TiO^{2+} that such oxo groups labilise the *trans* co-ordination position.[13—15] Because purple Ir^{IV} does not appear to be formed in the oxidation of $[Ir(H_2O)_6]^{3+}$ to Ir^V, it seems likely that dimerisation occurs in the Ir^V state to give the brown-green Ir^V product.

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