Preparation and Ultraviolet–Visible Spectrum of Hexa-aquairidium(III)

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Summary Hexa-aquairidium(III) has been prepared in aqueous perchloric media and its u.v.–visible spectrum recorded.

THE preparation of $[Ir(OH_2)_6]^{3+}$ has apparently not been described so far. While $[RhCl_6]^{3-}$ can be aquated to $[Rh(OH_2)_6]^{3+}$ by boiling for several hours with concentrated perchloric acid, a similar procedure with $[IrCl_6]^{3-}$ leads to a deep blue solution containing Ir presumably in a mixed valence state. The difficult preparation of $[Ir(OH_2)_6]^{3+}$ arises mainly from the following properties of the $5d^6Ir^{III}$ co-ordination centre: it shows pronounced (b) class behaviour,[1] it is as a rule even more substitution inert than $4d^6Rh^{III}$,[2] and moreover it is sensitive towards oxidation. Our procedure is based on the observation that the Ir–Cl bonds of $[IrCl_6]^{3-}$ are markedly labilized in alkaline media.

When $[NH_4]_2[IrCl_6]$ (1 g) was dissolved in NaOH (0·1M; 600 ml) the colour changed from red to green within a few minutes. In aqueous alkaline media $[IrCl_6]^{2-}$ is reduced spontaneously evolving oxygen, probably according to equation (1).[3] The solution was kept at 35—40 °C for 3–4 h.

$$2\,[IrCl_6]^{2-}(\text{red}) + 2\,OH^- = 2\,[IrCl_6]^{3-}\,(\text{green}) + 0{\cdot}5\,O_2 + H_2O \qquad (1)$$

Complete substitution of Cl^- by OH^- was indicated by a gradual colour change from green to light yellow. Immediately after the first tinge of blue appeared 200 mg of ascorbic acid were added to avoid air oxidation. The solution was cooled to 5 °C and maintained at this temperature for 30 min, then the pH was brought to *ca.* 8 with 0·1M $HClO_4$. A light yellow precipitate consisting of iridium(III) hydroxide hydrate was formed. The solid product was thoroughly washed with H_2O and dissolved in 40 ml of 0·1M $HClO_4$. The solution was diluted with 50 ml of H_2O and chromatographed on an ion-exchange column of Dowex 50A × 8 (mesh 50/100) resin in the H^+ form to separate mono- and poly-nuclear Ir^{III} cations. On elution with 2M $HClO_4$ the Ir^{III} product was found to be free from chloride when the first 5—10 ml were rejected.

In the middle fraction of the eluate a single Ir^{III} species, namely $[Ir(OH_2)_6]^{3+}$ was present. This was confirmed by an extensive investigation of homogeneous and heterogeneous hydrolysis reactions of Ir^{3+} to be reported elsewhere.[4]† On prolonged elution with 2M $HClO_4$ polynuclear Ir^{III} products were found but not studied in detail. A similar ion-exchange procedure was used by Sasaki and Sykes[5] for the preparation of $[Mo(OH_2)_6]^{3+}$.

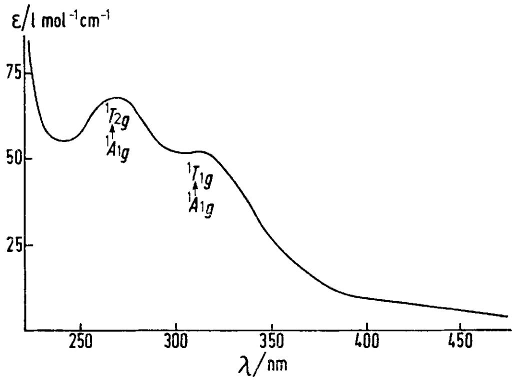

FIGURE. U.v.–visible spectrum of $[Ir(OH_2)_6]^{3+}$ in aqueous 1·0M $HClO_4$.

Stock solutions of $[Ir(OH_2)_6]^{3+}$ were prepared from the strongly acid eluate by reprecipitating iridium(III) hydroxide hydrate with NaOH at pH *ca.* 8 and dissolving it in the appropriate amount of 0·1M $HClO_4$. Total iridium was determined according to the method of Zinser and Page.[6] At pH 2—3 stock solutions were stable for a month or longer until oxidation of Ir^{III} became significant.

The u.v.–visible spectrum of $[Ir(OH_2)_6]^{3+}$ (Figure) shows prominent absorption bands at 265 and 310 nm; these correspond according to the spectrochemical series with those for the well characterized complexes $[Ir(NH_3)_6]^{3+}$ (maxima at 214 and 251 nm)[7] and $[IrCl_6]^{3-}$ (356 and 415 nm).[8,9] In these octahedral complexes the *d–d* bands mentioned can be assigned to the two spin-allowed transitions ($^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$). Jørgensen[8] has predicted a wavelength of 317 nm for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition for the then hypothetical $[Ir(OH_2)_6]^{3+}$ which is very close to the value observed.

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† Oxygen-18 experiments and/or *X*-ray data would be desirable to confirm the octahedral geometry of $[Ir(OH_2)_6]^{3+}$ and these are currently under investigation.

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