New heterometallic di-μ-hydroxo chromium(III)–iridium(III) and rhodium(III)–iridium(III) dinuclear aqua ions

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The synthesis and solution characterisation of bis(μ-hydroxo) heterometallic chromium(III)–iridium(III) and rhodium(III)–iridium(III) dinuclear aqua ions, namely $[(H_2O)_4Cr(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$ and $[(H_2O)_4Rh(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$ have been performed. Formation of such dinuclear ions is facilitated in alkaline media. Oxidation of the iridium(III) to iridium(IV) in basic solutions was avoided by working under oxygen-free conditions. Separation and purification of the dinuclear ions has been carried out by ion-exchange chromatography. Solution characterisation included metal analyses, charge determination and UV/VIS absorption spectroscopy.

The synthesis and characterisation of the first heterometallic hydrolytic dinuclear aqua ion containing chromium(III) and rhodium(III) linked by two hydroxo bridges was recently reported, and its structure confirmed by X-ray diffraction studies.[1] Kinetic and thermodynamic studies related to the cleavage of the double bridge have been done by Crimp and Spiccia.[2] On the other hand, the hydrolytic polymerisation process of chromium(III) has been extensively studied by other groups,[3–11] where a dimer, trimer, tetramer and pentamer of chromium(III) have been characterised. Kinetic and thermodynamic studies have also been presented. Cervini *et al.*[12] have reported the crystal structure of a doubly bridged rhodium(III) dimer, and oligomerisation of rhodium has been investigated by NMR spectroscopy.[13] Two dimers of iridium(III) have been obtained from solutions of iridium(IV) and characterised by ^{17}O NMR studies.[14]

Rhodium(III) and iridium(III) are two of the more inert metal centres, therefore the synthesis of heterometallic dinuclear species containing these ions is not straightforward. Appropriate reaction conditions were obtained by various test procedures.

It is possible to obtain homometallic dimers, trimers, and higher oligomers, as well as heterometallic polynuclear species, when solutions of two metal ions are mixed at high pH. In the present work we describe a synthetic procedure that yields the bis(μ-hydroxo) dinuclear ion containing chromium(III) and iridium(III) as the only product, and the optimum conditions for obtaining the corresponding rhodium(III)–iridium(III) dinuclear species.

Experimental

Materials

All reagents were AR grade and used as received. Cation-exchange chromatography was carried out on Dowex 50W X2 resin (Sigma Chemicals). All solutions were prepared with distilled water.

Instruments and methods

A Hewlett-Packard 8452 diode-array spectrometer, fitted with a Peltier temperature controller (±0.1 K), was used to record UV/VIS spectra. Chromium analysis of a $[Cr(H_2O)_6]^{3+}$ solution was carried out by atomic absorption spectroscopy using a Varian Spectra 10Dq Plus instrument. The content of iridium

in $[Ir(H_2O)_6]^{3+}$ solutions was determined by its conversion into $[IrCl_6]^{2-}$, as previously described.[15] The concentration was determined from its absorbance maximum in the UV/VIS spectrum λ_{max}/nm 486 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 4075[16]). The metal contents of solutions of heterometallic dinuclear species were determined by the inductively coupled plasma (ICP) technique using a Jobin-Ybon JY24 instrument. The magnetic moment of $[(H_2O)_4Cr(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$ was determined in solution by the shift of proton resonance lines of the acetone spectrum, as reported by Evans,[17] using a 300 MHz Varian Plus spectrometer; the ^1H NMR resonance signals were collected using a frequency of 300.235 MHz.

Syntheses

$[Ir(H_2O)_6]^{3+}$. The preparation from $Na_2[IrCl_6]\cdot6H_2O$ (Strem Chemicals 99%, 1.0 g) was as described by Beutler and Gamsjäger.[18,19] Solutions of hexaaquairidium(III) were standardised spectrophotometrically after its conversion into hexachloroiridate(IV) as described by Zinser and Page.[15] The UV/VIS spectrum of the latter has a peak at 486 nm.

$[Rh(H_2O)_6]^{3+}$. The preparation was from an aqueous solution (10 cm³) of $RhCl_3\cdot xH_2O$ (1 g, 4.48 mmol), to which concentrated $HClO_4$ (70%, Mallinckrodt AR; 15 cm³) was added. The procedure has been described by Ayres and Forrester.[20] The complex was purified by cation-exchange chromatography using a Dowex 50W X2 column (10 × 1 cm). The spectrum was in agreement with that reported by Cervini *et al.*;[21] peaks at λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 308 (66) and 396 (62).

$[Cr(H_2O)_6]^{3+}$. The procedure involved the reduction of CrO_3 (0.9971 g, 9.9714 mmol) in 1.0 mol dm⁻³ $HClO_4$ (92.1 cm³) with H_2O_2 (30%, 7.8 cm³), as described in the literature.[22] The UV/VIS absorption spectrum gives peaks at λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) 408 (15.6) and 574 (13.4). The solution was standardised by atomic absorption spectrometry.

$[(H_2O)_4Cr(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$. A solution of hexaaquairidium(III) (6.5×10^{-3} mol dm⁻³, 5 cm³) in 2.0 mol dm⁻³ $HClO_4$ was adjusted to pH 13 by dropwise addition of a saturated NaOH solution (and stirring). The solution was cooled to 0 °C and hexaaquachromium(III) (0.098 mol dm⁻³, 0.33 cm³) in $HClO_4$ at pH ≈ 2.0 was added. The resulting solution was vigorously stirred for 15 min, with the temperature kept at 0 °C. The reaction was followed spectrophotometrically, and
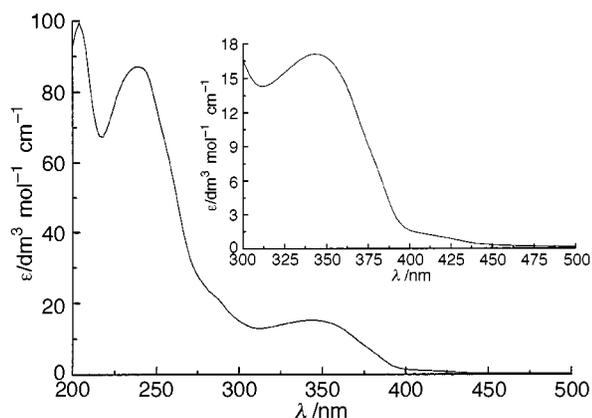
Fig. 1 The UV/VIS absorption spectrum of $[(H_2O)_4Cr(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$ in 2.0 mol dm^{-3} HClO$_4$

Fig. 2 Addition spectra of $[Ir(H_2O)_6]^{3+}$ plus $[Cr(H_2O)_6]^{3+}$(——) and $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ plus $[(H_2O)_4Ir(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$ (– – –)

when no further changes were observed the pH of the solution was lowered to 2 by addition of 4.0 mol dm^{-3} HClO$_4$. A green solution was obtained. Ion-exchange chromatography was used to separate the products. The solution was diluted with distilled water to a final pH of 3 and then loaded onto a Dowex 50W X2 cation-exchange column (4 × 1.5 cm) (Sigma Chemicals). On addition of 2.0 mol dm^{-3} HClO$_4$ a green band moved down the column and was collected. The UV/VIS spectrum has peaks at 244 (94), 346 (15.2) and 418 nm (1.12 dm^3 mol^{-1} cm^{-1}).

$[(H_2O)_4Rh(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$. Solutions of hexaaquairidium(III) and hexaaquarhodium(III) (both 5.2 × 10^{-3} mol dm^{-3}, 5 cm^3) at pH 13 were introduced into the two separate compartments of a reaction cell which was connected to a vacuum line. Oxygen was removed from the solutions by alternately freezing and thawing, while bubbling argon through the cell. This procedure was carried out three times at liquid-nitrogen temperature. The solutions were taken to 20 °C, mixed, and left to react for 4 h. The reaction was followed spectrophotometrically and when no further changes in the spectrum were observed the pH was adjusted to 2 by addition of a 4.0 mol dm^{-3} oxygen-free solution of HClO$_4$. A yellow solution was obtained. Ion-exchange chromatography was used to separate the reaction products. The solution was diluted with distilled water to a final pH of 3 and then loaded onto a Dowex 50W X2 cation-exchange column (4 × 1.5 cm) (Sigma Chemicals). Several fractions were collected by eluting with 2.0 mol dm^{-3} HClO$_4$. A fraction analysing for a 1:1 Rh:Ir complex gave a UV/VIS spectrum having peaks at 232 (3690), 248 (3620), 344 (574) and 410 nm (121 dm^3 mol^{-1} cm^{-1}). Yield 43.49%.

Results

Synthesis of chromium(III)–iridium(III) dinuclear ion

It is known that the oligomerisation reaction of inert metal ions can be promoted in alkaline solutions. Therefore the approach to the synthesis of heterometallic chromium(III)–iridium(III) and rhodium(III)–iridium(III) dinuclear ions involved raising the pH of acidic solutions of the hexaaqua ions.

The optimum conditions for the synthesis of the bis(μ-hydroxo) heterometallic chromium(III)–iridium(III) were pH ≈ 13, temperature 0 °C and reaction time 15 min. The dimerisation process was stopped by adding 4.0 mol dm^{-3} HClO$_4$. The green product eluted as a single band from a cation-exchange column. Its UV/VIS spectrum is shown in Fig. 1.

Characterisation of $[(H_2O)_4Cr(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$

The chromium and iridium contents were determined by means of ICP, at two wavelengths 212.68 and 263.97 nm for iridium (where chromium interference is negligible) and at one wavelength for chromium (357.87 nm). The results indicate a 1:1.04
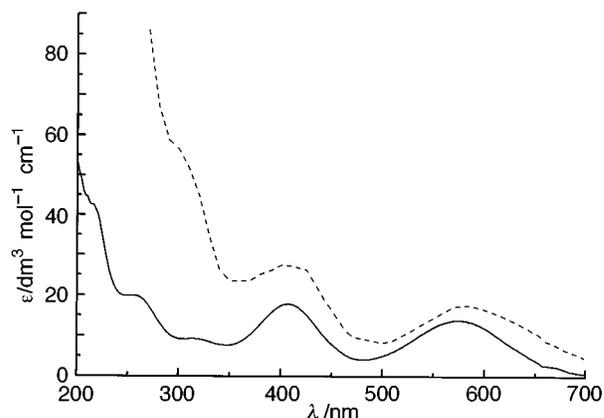
molar ratio of chromium to iridium (average of three determinations).

The charge on the species was also investigated. A small column containing ≈2 g of Dowex cation-exchange resin was saturated with the green solution (pH ≈ 3.0). After washing with distilled water the sample was eluted by displacement with $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ (pH ≈ 3.0).[23] The UV/VIS spectrum of the dinuclear species eluted was in agreement with that reported above.

In a separate experiment, a Dowex 50W X2 cation-exchange resin column (5 g) was saturated with chromium(III)–iridium(III) cation (6.7 × 10^{-3} mol dm^{-3}, 150 cm^3) at pH ≈ 3. The H$^+$ displaced from the column was determined from the difference between the initial moles of H$^+$ present in the chromium(III)–iridium(III) solution and the moles of H$^+$ in the solution eluted from the column. The charge of the species is obtained by dividing by the number of moles of dinuclear cation, equation (1)

$$\text{Charge[Ir–Cr]} = \frac{\text{moles}(H_{el}^+) - \text{moles}(H_{in}^+)}{\text{moles[Ir} - \text{Cr]}} \qquad (1)$$

where H_{el}^+ = protons in the eluted solution, H_{in}^+ = protons in the initial solution. A value of +3.67 was obtained.

The UV/VIS spectrum of the new species was compared both with the addition spectra of $[Ir(H_2O)_6]^{3+}$ plus $[Cr(H_2O)_6]^{3+}$ and with the one obtained from the dimers $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ plus $[(H_2O)_4Ir(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$. The electronic absorption spectrum of the [Ir–Cr] species is different from those obtained by the addition of the hexaaqua monomers or the bis-μ(hydroxo) dimers (Fig. 2).

The magnetic moment of $[(H_2O)_4Ir(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ in 2.0 mol dm^{-3} HClO$_4$ solution was determined by ^{1}H NMR spectroscopy using acetone as inert reference, with the Evans method.[17] The value obtained is 3.86 μ$_B$ (μ$_B$ ≈ 9.27 × 10^{-24} J T^{-1}), which is in agreement with the expected value for Cr^{III} with three unpaired electrons. This also supports the formulation with the dinuclear species containing one chromium atom in oxidation state III per iridium(III) moiety.

Synthesis and characterisation of $[(H_2O)_4Rh(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$

In order to synthesize the rhodium–iridium dinuclear cation several experiments were carried out, varying the conditions. The variables used were pH of the solutions, temperature, time of reaction, molar ratio Rh:Ir and presence/absence of oxygen. Reactions were followed spectrophotometrically. The pH of the solutions was brought to 2.0 by adding 2.0 mol dm^{-3} HClO$_4$ for all the experiments, in order to stop the reaction. The solutions were loaded onto a Dowex cation-exchange column for separation and purification of reaction products. The species that contains one rhodium per iridium was obtained by mixing equimolar solutions of $[Ir(H_2O)_6]^{3+}$ and $[Rh(H_2O)_6]^{3+}$, pH 13, and leaving to react for 4 h at 20 °C.
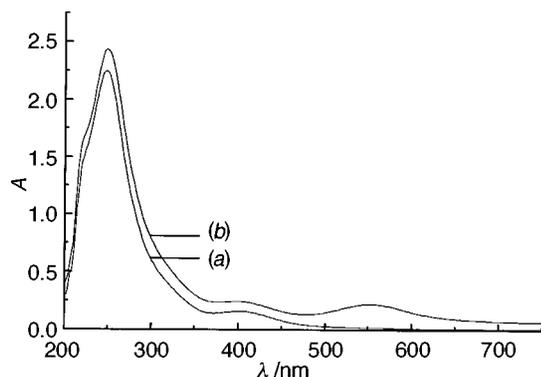
Fig. 3 Spectra for the reaction of $[Rh(H_2O)_6]^{3+}$ with $[Ir(H_2O)_6]^{3+}$. (*a*) Oxygen-free conditions, (*b*) in the presence of oxygen
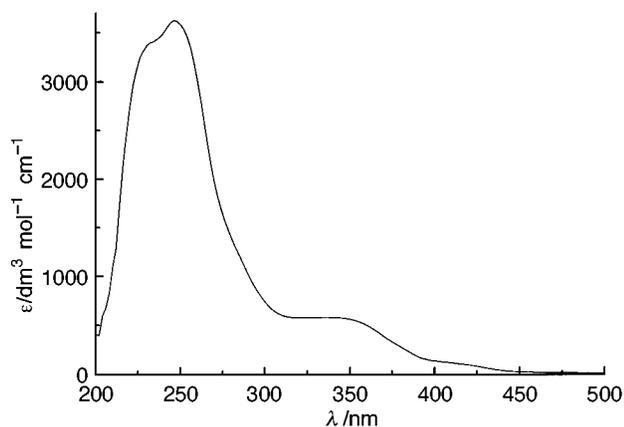
Fig. 4 The UV/VIS absorption spectrum of $[(H_2O)_4Rh(\mu\text{-}OH)_2\text{-}Ir(H_2O)_4]^{4+}$

The metal content (rhodium and iridium) was determined for two different samples by means of ICP, and indicated that the molar ratio between rhodium and iridium was 1:1. The charge was determined for two samples and the average value was 4.03.

When the reactions were carried out in the presence of oxygen a purple solution was obtained; its colour faded with time, yielding a yellow solution after a day.

Discussion

In this work two new heterometallic dimers $[(H_2O)_4Cr(\mu\text{-}OH)_2\text{-}Ir(H_2O)_4]^{4+}$ and $[(H_2O)_4Rh(\mu\text{-}OH)_2Ir(H_2O)_4]^{4+}$ have been prepared by mixing metal ions together at high pH.

The procedure described yielded a 1:1 Cr–Ir product with a 4+ charge and magnetic properties consistent with the chromium(III) and iridium(III) components. The UV/VIS absorption spectrum supports the oxidation state III assignment and the charge implies a bis(μ-hydroxo) structure as for the corresponding Cr^{III}_2 and Ir^{III}_2 dimers. In 2.0 mol dm^{-3} HClO$_4$ the UV/VIS spectrum has peaks at 210, 244, 346 and 418 nm which correspond to the expected absorption bands for chromium and iridium. These bands can be assigned to charge transfer M←OH$^-$,[12] $^1T_{2g} \longleftarrow {}^1A_{1g}$ (Ir), $^1T_{1g} \longleftarrow {}^1A_{1g}$ (Ir)[18] and $^4T_{1g} \longleftarrow {}^4A_{2g}$ (Cr),[24] respectively.

The synthesis of the corresponding dinuclear ion containing rhodium(III) and iridium(III) gives various products, and the highest yield for this species was 44%. Working under an argon atmosphere was important since a purple solution resulted otherwise. It is likely that these solutions contain iridium(IV),[14,25] a purple colour being previously observed for the iridium(IV) dimer $[(H_2O)_5IrOIr(H_2O)_5]^{6+}$, absorbance peak at 547 nm.[14] The rhodium(III)–iridium(III) reaction products in the absence (*a*) or presence (*b*) of oxygen are shown in Fig. 3.

The rhodium(III)–iridium(III) containing species has a 1:1 ratio of the two metals and is displaced from the cation-exchange column by $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(H_2O)_4]^{4+}$ consistent with a 4+ charge. The UV/VIS spectrum is shown in Fig. 4, and transitions are assigned according to spectra of the rhodium(III) and iridium(III) aqua ions.[2,12,17] Thus the peak at 232 nm corresponds to M←OH$^-$ charge transfer, the one at 248 nm to a $^1T_{2g} \longleftarrow {}^1A_{1g}$ (Ir) transition, 344 nm to $^1T_{1g} \longleftarrow {}^1A_{1g}$ (Ir), $^1T_{2g} \longleftarrow {}^1A_{1g}$ (Rh), and 410 nm to the $^1T_{1g} \longleftarrow {}^1A_{1g}$ (Rh) transition.

Based on these observations the rhodium(III)–iridium(III) species corresponds to a heterometallic dimer containing two bridging hydroxo groups.
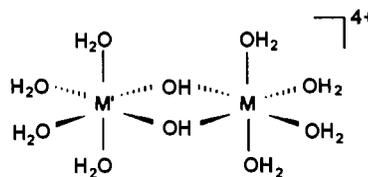
The reaction conditions were determined for preparation of the hydrolytic dimer. Again it is important to stress that oxygen causes oxidation of the iridium(III), and that different products are obtained as a result.

Acknowledgements

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