Mixed-ligand complexes of osmium(III/IV)8-quinolinolates with one ketoximate ligand

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Summary
A group of mixed-tris chelates of type \([\text{OsAQ}_2]\) \(\text{[A=isonitrosoacetophenonate (A1)}\) and isonitroso-propiophenonate (A2); \(\text{Q=deprotonated 8-quinolinol (Q1)}\) and 2-methyl-8-quinolinol (Q2)\] have been prepared by two distinct synthetic approaches. \([\text{OsAQ}_2]^+\), obtained by \(\text{Ce IV}^+\) oxidation of \([\text{OsAQ}_2]\), can be regenerated by hydrazine hydrate reduction of the former. The complexes, characterized by physico-chemical, magnetic and spectroscopic methods, exhibit several spin-allowed and spin-forbidden charge transfer transitions in their electronic spectra. In MeCN solution the \(\text{OsN}_3^0\) unit displays a nearly-reversible \(\text{OsIV-OsIII}\) change and an \(\text{OsIV}^{2+}-\text{OsIII}\) couple in the \(ca. -1.0-+0.3\) V range versus s.c.e. The stability of the metal oxidation levels is discussed in terms of the chemical and electrochemical results.

Introduction
In recent years we have investigated \(^1-^4\) the binding of osmium(II), (III) and (IV) to 8-quinolinolates (OsQ) using different bidentate chelators, L, in varied matrices of general formula \([\text{OsL}_3\text{Q}_3]^{n+}\) \((n=\text{number of co-ligand L}; \ z=\text{overall charge})\). The present work extends over ketoxime ligands (HA) such as \(\alpha\)-hydroxyiminoacetophenone (HA1) and \(\alpha\)-hydroxyiminopropiophenone (HA2). Direct reaction of HA with \([\text{OsX}_2\text{Q}_2]\) \((X=\text{Cl or Br})\) yields complexes of the type \([\text{OsAQ}_2]\) \((3)\). An alternative route to \((3)\) consists of catalytic nitrosation of ketones \(\text{[PhC}O\text{(OCH}_2\text{R)}\), namely acetophenone \((R=\text{H})\) and propiophenone \((R=\text{Me})\) with \([\text{OsX(NO)}\text{Q}_2]\). Oxidation of \((3)\) with aqueous cerium(IV) ions yields \([\text{OsAQ}_2]^+\), isolated as the perchlorate salt \((4)\) which, on subsequent reduction with hydrazine hydrate, reverts to \((3)\). Details of the synthesis, characterization, and chemical and electrochemical link-up of metal oxidation states in \((3)\) and \((4)\) are presented in this paper.

**Experimental**

**Materials**
Literature methods were used to prepare \([\text{OsX}_3\text{Q}_3]\) \(^5\) and \([\text{OsX(NO)}\text{Q}_2]\) \(^6\). \(\alpha\)-Hydroxyiminooacetophenone (HA1) and \(\alpha\)-hydroxyiminopropiophenone (HA2) were obtained by standard methods \(^7\). Purification of MeCN and preparation of the supporting electrolyte \([\text{Et},\text{N}[\text{ClO}_4]\)] for electrochemical work were done following published procedures \(^8\). All other chemicals and solvents used for preparations, spectroscopic and other measurements were of analytical grade and available commercially.

**Caution!** Perchlorates of heavy metal ions with organic ligands are potentially explosive. The synthesis described below involves the use of perchlorate ions. Due care must be exercised to avoid explosion hazards, although we have not encountered any such problems to date.

**Physical measurements**
Solution electrical conductivities (in MeCN, \(ca. 10^{-3}\) mol dm \(^-3\)), i.r. spectra (KBr discs, 4000–3000 cm \(^-1\)) and electronic spectra (in MeCN) were recorded using a Philips (India) PR 9500 conductivity bridge, a Perkin-Elmer 783 spectrometer and a Shimadzu UV-160A spectrophotometer, respectively. Magnetic susceptibility measurements (in the solid state at 25°C) were made with a PAR 155 vibrating-sample magnetometer fitted with a L 75 FBAL magnet. E.p.r. spectra were run on a Varian 109C E-line X-band spectrometer fitted with a quartz Dewar for measurements at \(-196\) °C (liquid N\(_2\)). Spectra were calibrated with d.p.p.h. \((g=2.0037)\). Analytical data (C, H and N) were obtained using a Perkin-Elmer Model 240C elemental analyser. Electrochemical measurements (in MeCN) were carried out under dry N\(_2\) with a PAR 370-4 electrochemistry system as described elsewhere \(^9\). In cyclic voltammetry (c.v.) the following parameters and relation were used: scan rate \((\eta)\), \(50\) mV s \(^-1\); formal potential \(E^0\) \(=0.5(E_{pc}+E_{pa})\), where \(E_{pc}\) and \(E_{pa}\) are cathodic and anodic peak potentials, respectively; \(\Delta E_{pa}\), peak-to-peak separation; and in differential pulse voltammetry (d.p.v.); scan rate \((\eta)\), \(10\) mV s \(^-1\); modulation amplitude \((\Delta E)\), \(25\) mV; \(E''=E_p+0.5(\Delta E)\), where \(E_p\) is the d.p.v. peak potential. The agreement between \(E''\) data obtained by the two techniques is invariably good (within \(\pm5\) mV). The potentials are referenced to a s.c.e. and are uncorrected for the junction contributions.

**Preparation of complexes**
The orange–red osmium(III) complexes were prepared by two methods. Details of each procedure, for a particular compound, are given below. Isolation of green
osmium(IV) complexes (4) from the corresponding osmium(III) precursors and conversion of (4) into (3) are also described with a suitable example.

Isonitrosopropiophenonatobis(8-quinolinolato)-osmium(III) ([OsA2Q2]3).

1. Method A. HA2 (0.15g, 0.92 mmol) and CaCO3 (0.09 g, 0.9 mmol) were added to a suspension of [OsCl2Q4] (0.1 g, 0.182 mmol) in 1:1 MeOCH2CH2OH-H2O (20 cm³). The mixture was boiled under reflux for 4 h, the suspension gradually dissolved producing an orange-red solution. This was filtered through a fine glass frit and the filtrate was evaporated under reduced pressure. The solid residue was washed several times with solvent Et2O and dried in vacuo over P4O10; it was then redissolved in a minimum of CH2Cl2 and subjected to chromatography on a silica gel (60–120 mesh, BDH) column (20 x 1 cm). Initially a small green fraction of unreacted [OsCl2Q4] was eluted with CH2Cl2, followed by a slow moving orange-red band eluted with 2:1 PhH–MeCN. On slow evaporation of the eluate, crystals of the desired compound resulted. Analytically pure material was obtained after drying in vacuo over P4O10. Yield 0.075 g (65%).

2. Method B. To a MeOH solution (20 cm³) of 0.1 g (0.184 mmol) of [OsCl(NO)Q2] were added 0.025 g (0.186 mmol) propiophenone and 0.01 g (0.185 mmol) MeONa. The mixture was heated to reflux for 1 h, and the resulting orange-red solution was evaporated under reduced pressure. The solid residue was washed several times with solvent ether and dried in vacuo over P4O10. Yield 0.095 g (80%).

Isonitrosopropiophenonatobis(8-quinolinolato)-osmium(IV) perchlorate, [OsA2Q2]ClO4.

[OsA2Q2]ClO4 (0.1 g, 0.156 mmol) was dissolved in 1:1 CH2Cl2–MeCN (10 cm³) and the mixture was stirred magnetically at room temperature (25°C). To this 10 cm³ of aqueous Ce(SO4)2·4H2O (0.1 g, 0.249 mmol in 1 M H2SO4) was added dropwise. The orange–red solution immediately changed to green. Stirring was continued for a further 15 min, the solution was then filtered through a fine glass frit, evaporated under reduced pressure and dried in vacuo over P4O10. The solid residue was extracted with CH2Cl2 and allowed to evaporate in air; it was then redissolved in MeCN and a saturated aqueous solution (2 cm³) of NaClO4 was added. On evaporation, crystals deposited. For quantitative precipitation the mixture was refrigerated for 6 h. The green crystals which separated on cooling were collected by filtration and washed with chilled H2O. Analytically pure [OsA2Q2]ClO4 was obtained in an almost quantitative yield after drying in vacuo over P4O10.

Conversion: OsIV → OsIII.

[OsA2Q2]ClO4 (0.1 g, 0.135 mmol) was dissolved in MeCN (10 cm³) and the solution was stirred magnetically at 25°C N2H4·H2O (0.01 g, 0.2 mmol) in MeCN was then added dropwise. The green solution changed to orange-red and, on evaporation under reduced pressure, a dark solid deposited; this was extracted with CH2Cl2 (3 x 5 cm³). On slow evaporation of this extract, pure [OsA2Q2] was obtained in an almost quantitative yield. Analytically pure material was obtained after recrystallization from 1:2 PhH:MeCN followed by drying in vacuo over P4O10.

Results and discussion

Two distinctly different approaches to the osmium(III) compound are: reaction of HA with [OsX2Q2] via chelative halide displacement and reaction of ketone PhCl(OCH3)R (R = H or Me) with [OsX(NO)Q2] through chelative nitrosation (Equations 1 and 2, respectively):

\[ \text{[OsX}_2\text{Q}_2] \xrightarrow{\text{HA} \cdot \text{CaCO}_3} \text{[OsA}_2\text{Q}_2] \]

+ other products

\[ \text{[OsX(NO)}_2\text{Q}_2] \xrightarrow{\text{PhCOCH}_2\text{R} \cdot \text{MeONa}} \text{[OsA}_2\text{Q}_2] \]

+ other products

Reaction 1, the usual method applied earlier(2-4), proceeded slowly. Use of an excess of HA in the presence of CaCO3, as a heterogeneous base(9), and under reflux in a high boiling (b.p. ca. 125°C) solvent (MeOCH2CH2OH) resulted in reaction within a reasonable time. The reducing behaviour of the alcoholic solvent converted osmium(IV) into osmium(III). On the other hand, Reaction 2 is relatively fast and its progress was monitored using the v(NO) decrease at ca. 1900 cm⁻¹. However, Reaction 2 became very slow, or did not proceed at all, in the absence of MeONa. The disappearance of the v(NO) band at ca. 1900 cm⁻¹ and the growth of v(N→O) at 1260 cm⁻¹ confirmed that the reaction was occurring at the nitrosyl(10) centre. Mild conditions and better yields showed Reaction 2 to be superior to Reaction 1. Oxidation of the orange-red [OsA2Q2] (3) with aqueous cerium(IV) ion yielded the corresponding green osmium(IV) cation [OsA4Q4]+, isolated as the perchlorate (4). Hydrazine hydrate quantitatively reduced osmium(IV) complexes to the corresponding osmium(III) precursors. Both oxidation and reduction steps were facile.

Analytical data for the osmium(III) and osmium(IV) complexes are consistent with the calculated values (Table 1). The air-stable complexes are powders, soluble

Table 1. Microanalytical data and conductivity values

<table>
<thead>
<tr>
<th>Compound</th>
<th>Found (Calcd.) (%)</th>
<th>( \Lambda_m ) (Ω⁻¹ cm² mol⁻¹)</th>
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<tbody>
<tr>
<td>[OsA2Q2] (3a)</td>
<td>49.5 2.9 6.8 130 4</td>
<td>3.2 (6.3)</td>
</tr>
<tr>
<td>[OsA2Q2] (3b)</td>
<td>51.6 3.5 6.7 120 5</td>
<td>3.2 (6.6)</td>
</tr>
<tr>
<td>[OsA2Q2] (3c)</td>
<td>50.5 3.3 6.6 5</td>
<td>3.6 (6.9)</td>
</tr>
<tr>
<td>[OsA2Q2] (3d)</td>
<td>51.8 3.6 6.5 4</td>
<td>3.2 (6.6)</td>
</tr>
<tr>
<td>[OsA4Q4] (4a)</td>
<td>42.8 2.3 5.8 120 130</td>
<td>2.5 (5.8)</td>
</tr>
<tr>
<td>[OsA4Q4] (4b)</td>
<td>44.4 2.9 5.9 130</td>
<td>2.9 (5.6)</td>
</tr>
<tr>
<td>[OsA4Q4] (4c)</td>
<td>43.8 2.7 5.5 125</td>
<td>2.7 (5.7)</td>
</tr>
<tr>
<td>[OsA4Q4] (4d)</td>
<td>45.2 3.0 5.5 120</td>
<td>3.2 (5.5)</td>
</tr>
</tbody>
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