Ionophoric binding of alkaline earth metal ions (M$^{2+}$) by \textit{tris}(arylazo oximato)osmium(II) anions, [OsA$_3$]$^{-}$

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Summary

High-yield synthetic routes to trinuclear complexes of the type [M(OsA$_3$)$_2$] (M = Mg, Ca, Sr or Ba; A = anion of arylazo oxime) by reaction of Na[OsA$_3$] and M(ClO$_4$)$_2$, or of [HOsA$_3$] with MCO$_3$, are described. The new complexes have been characterized on the basis of spectroscopic and physico-chemical results. The alkaline earth metal ions are held in an O$_6$ matrix of two \textit{facial} [OsA$_3$]$^{-}$ units, each behaving as a tridentate (O, O, O) ligand. Quantitative transport of one equivalent of M$^{2+}$ from the aqueous to the organic (CH$_2$Cl$_2$) phase can be achieved with two equivalents of [OsA$_3$]$^{-}$. When the aqueous phase is acidified with two mol of H$^+$, [M(OsA$_3$)$_2$] decomposes into M$^{2+}$ and [HOsA$_3$], and M$^{2+}$ returns to this phase in its free state.

Introduction

Ionophoric transport of Group IIA(2) metal ions (M$^{2+}$) from the aqueous to the organic phase is attracting attention in connection with biological membrane action$^{1-3)}$. The transport of metal ions is effective in the presence of an anionic chelating agent and the pendant oximato oxygen triad is correctly disposed$^{(9)}$ to occupy a triangular face of a separate polyhedron. Two such units should be able to complete an O$_6$ coordination octahedron around M$^{2+}$, and Ph/R as the non-polar group might enhance the solubility of the final species in the organic phase. With this background in mind, we have successfully synthesized and characterized complexes of the type [M(OsA$_3$)$_2$] (M = Mg, Ca, Sr or Ba; A = anion of arylazo oxime) by reaction of Na[OsA$_3$] and M(ClO$_4$)$_2$, or of [HOsA$_3$] with MCO$_3$, are described. The new complexes have been characterized on the basis of spectroscopic and physico-chemical results. The alkaline earth metal ions are held in an O$_6$ matrix of two \textit{facial} [OsA$_3$]$^{-}$ units, each behaving as a tridentate (O, O, O) ligand. Quantitative transport of one equivalent of M$^{2+}$ from the aqueous to the organic (CH$_2$Cl$_2$) phase can be achieved with two equivalents of [OsA$_3$]$^{-}$. When the aqueous phase is acidified with two mol of H$^+$, [M(OsA$_3$)$_2$] decomposes into M$^{2+}$ and [HOsA$_3$], and M$^{2+}$ returns to this phase in its free state.

Experimental

Materials

Arylazo oximes were obtained by the reported method$^{(10)}$. The Na[OsA$_3$]$^{-}$3H$_2$O complex was prepared as described previously$^{(9)}$; Na[OsA$_3$] and Na[OsA$_3$] were synthesized similarly. [HOsA$_3$] complexes were isolated by adding a stoichiometric excess of HC$_1$ to the sodium salt of [OsA$_3$]$^{-}$ in aqueous EtOH. All the [HOsA$_3$] complexes, Na[OsA$_3$] and Na[OsA$_3$] were analysed (C, H, N) and found to have \textit{facial} geometry by spectroscopic and electrochemical measurements, and/or comparison of their properties with well-known \textit{facial}$^{(9)}$ Na[OsA$_3$]$^{-}$3H$_2$O. Hydrated alkaline earth metal perchlorates were freshly prepared by treating the corresponding metal carbonates with 70% aqueous HClO$_4$, and were stored in a desiccator over H$_2$SO$_4$. Determination of M$^{2+}$ ions was made following available procedures$^{(11)}$. Mg$^{2+}$, Ca$^{2+}$ and a mixture of Mg$^{2+}$ and Ca$^{2+}$ were estimated by EDTA titration; gravimetric procedures (as sulphates) were applied to the separation (from Mg$^{2+}$) and determination of Sr$^{2+}$ and Ba$^{2+}$. The purification of solvent (MeCN), and preparation of supporting electrolyte ([Et$_2$N][ClO$_4$]), for electrochemical work were performed using the literature method$^{(12)}$. All other chemicals and solvents were of analytical grade and were used without further purification.

Measurements

I.r. (KBr discs, 4000–300 cm$^{-1}$), electronic (in MeCN, 10$^{-3}$ M and 1H-n.m.r. (in CDCl$_3$; Me$_4$Si as an internal standard) spectra were recorded using a Perkin-Elmer 783 spectrometer, a Hitachi 330 spectrophotometer and a Brucker 270 MHz spectrometer, respectively. Mass spectra were taken on a Perkin-Elmer model 240C elemental analyser. Solution electrical conductivity (in MeCN and MeOH, 10$^{-3}$ M) and pH measurements were made on a Philips PR 9500 conductivity bridge and a Systronics 335 digital pH meter, respectively. Molecular weights were determined in CHCl$_3$ using a Knauer vapour pressure osmometer with benzil as calibrant. Electrochemical measurements (MeCN at 25°C) were carried out under dry N$_2$ with a PAR 370-4 electrochemistry system as described elsewhere$^{(13)}$. Cyclic voltammetry (c.v.) the following parameters and relation were used: scan rate (v), 50 mV s$^{-1}$; formal potential, $E^\circ$ = 0.5($E_{pc} + E_{pa}$), where $E_{pc}$ and $E_{pa}$ are cathodic and anodic peak potentials, respectively; $\Delta E_{pc}$, peak-to-peak separation. In differential pulse voltammetry (d.p.v.): scan rate (v), 10 mV s$^{-1}$; modulation amplitude ($\Delta E$), 25 mV; $E^\circ$ = $E_{pc} + 0.5(\Delta E)$, where $E_{pc}$ is the d.p.v. peak potential. The agreement between $E^\circ$ data obtained by the two techniques is invariably good (within ±5 mV). The potentials are referenced to a S.C.E. and are uncorrected for the junction contributions.

Preparation of complexes – general

The trinuclear complexes were prepared starting with either the sodium salt or the protonated form of [OsA$_3$]$^{-}$. Preparation of the magnesium compound [Mg(OsA$_3$)$_2$], prepared from Na[OsA$_3$]$^{-}$3H$_2$O, was reported earlier$^{(9)}$, but its synthesis from [HOsA$_3$] is new. All other complexes were hitherto unknown. Details of synthesis for representative cases are presented below. The yields ranged from 80 to 90% (on the basis of osmium
monomer). Experimental details of typical biphasic transport are also delineated.

**Preparation of [Ca(OsA₃₂)₃] (3f)**

Method 1  Ca(ClO₄)₂·6H₂O (0.04 g, 0.115 mmol) was added to a well-stirred EtOH solution (15 cm³) of Na[OsA₃₂] (0.2 g, 0.23 mmol). The green solution changed to green-brown. Stirring was continued for a period of 2 h. The solid residue obtained after evaporation of the mixture was washed copiously with H₂O and finally hexane. Analytically pure material was obtained after drying in vacuo over P₂O₅· (Yield 0.17 g, 85%).

Method 2  A 0.2 g (0.231 mmol) sample of [HOsA₃₂] was dissolved in Me₂CO (25 cm³) and 0.045 g (0.45 mmol) CaCO₃ was suspended in the solution. The mixture was then refluxed for 3 h. The resulting green-brown solution was cooled to 0 °C, filtered through a fine glass-frit and then processed as in method 1 to obtain pure (3f). (Yield 0.16 g, 80%).

**Biphasic transport of M²⁺**

(1) Aqueous to organic phase
(a) Reaction of metal perchlorate and Na[OsA₃₂]
From a stock solution of Ca(ClO₄)₂ in H₂O (3.82 × 10⁻³ m) an aliquot (25 cm³) was shaken for 20 min (from variable time experiments; it was observed that this procedure was sufficient to achieve equilibrium in all the biphasic experiments done in this work) with 25 cm³ of Na[OsA₃₂] solution in CH₂Cl₂. The aqueous phase was collected and Ca²⁺ was estimated. The experiment was repeated with different concentrations (4.02–8.56 × 10⁻³ m) of Na[OsA₃₂].

(b) Reaction of metal hydroxide and [HOsA₃₂]
Standard solutions of [HOsA₃₂] (0.19 × 10⁻³ m) in CH₂Cl₂ and Ba(OH)₂ (1.02 × 10⁻³ m) were prepared in H₂O. From these a series of mixtures were made having the same [HOsA₃₂] (0.09 × 10⁻³ m) but different Ba(OH)₂ (0.00–0.05 × 10⁻³ m) concentrations in stoppered conical flasks. Both the organic and aqueous layers were diluted by adding the respective pure solvents. The flasks were shaken for 20 min and electronic spectra of the CH₂Cl₂ phase were recorded in order to monitor the extent of transport. The ionophore: alkaline earth metal ion ratio was 2:1.

(2) Reverse transport
Solutions of HCl (1.00 × 10⁻³ m) in H₂O and [Ca(OsA₃₂)₃] (0.8 × 10⁻³ m) in CH₂Cl₂ were made. An aliquot (20 cm³) of the latter was taken in a stoppered conical flask and a known vol of the HCl solution added. The aqueous layer was diluted. Several sets of such mixtures were made with the same [Ca(OsA₃₂)₃] concentration but different (0.00–0.40 × 10⁻³ m) HCl concentrations. After shaking (20 min) the layers were separated. Electronic spectra of the organic phase and pH of the aqueous phase were recorded. The complete transport of M²⁺ into the aqueous phase after addition of 2 mol of the acid was confirmed analytically.

**Results and discussion**

Two distinctly different approaches were applied for the preparation of [M(OsA₃)₂] : reaction of (1) Na[OsA₃] with hydrated alkaline earth (M) perchlorates in EtOH; and (2) [HOsA₃] and MCO₃ suspended in refluxing Me₂CO. All analytical data are consistent with the calculated values (Table 1). The air-stable, moisture-insensitive complexes are powders, readily soluble in a range of common organic solvents with a green-brown solution but are insoluble in H₂O. In MeCN and MeOH they behave as non-conductors, as is evident from low conductivities (Table 2). In CHCl₃, conductivity should be less and molecular-weight determination is helpful in proposing trinuclear formulation. Indeed, osmometric molecular weights determined in CHCl₃ agree well with the [M(OsA₃)₃] composition (Table 2). The results with barium compounds are somewhat low, in line with the conductivity values.

I.r. and ¹H-n.m.r. results are consistent with trinucleation. In the i.r., a strong absorption at ca. 1230 cm⁻¹, assignable to the ν(N→O) stretch, is invariably observed for all complexes (Table 2); a shift towards lower