

# [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup>: Preparation, Characterization, Determination of Acid-Dissociation Constants, and Kinetics and Mechanism of Acid-Catalyzed Aquation

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Herein we report on the preparation and characterization and on some aspects of the chemistry of [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup> (1) and [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>=CHCO<sub>2</sub>H)(H<sub>2</sub>O)]<sup>2+</sup> (2) in aqueous solution. The pK<sub>a</sub> values, as determined by titration, for 1 are 3.20, 6.78, and 9.8 and for the corresponding Os(III) form are 1.76, 3.46, and 7.40. In each case they refer to deprotonation of η<sup>1</sup>-acrylic acid, η<sup>2</sup>-acrylic acid, and an ammonia, respectively. For 2, the values are 2.75, 5.27, and 8.57, and for the corresponding Os(III) form the values are 1.42, 3.65, and ≈8. Here they refer to deprotonation of the coordinated H<sub>2</sub>O, of the η<sup>2</sup>-acrylic acid, and of an ammonia, respectively. Particularly for Os(II) they illustrate the powerful electron-withdrawing effect of the alkene link. The 3+/2+ redox potentials of 1 and 2 in acid are 0.59 and 0.69 V vs (SHE), respectively, and they change with pH in accord with the value of pK<sub>a</sub>. The aquation of 1 to form 2 is accelerated by HPF<sub>6</sub>, but the effect reaches a limit. This behavior together with other observations lead us to the conclusion that opening of the η<sup>2</sup>-bond precedes protonation and that protonation then takes place at the πd electrons, thereby labilizing for substitution. With HCl and HO<sub>3</sub>SCF<sub>3</sub>, complications occur which we ascribe to addition of the anions to the β carbon after the η<sup>2</sup>-linkage opens. In these cases protonation of the πd electrons leads to the formation of monohydrides of Os(IV) (paramagnetic), without loss of the η<sup>1</sup>-ligand.

## Introduction

The acrylic acid–osmium ammine system was selected in the expectation that it would provide an additional example of linkage isomerization accompanying electron transfer and was attractive because of the simplicity of composition. Experience with other osmium ammine systems<sup>1,2</sup> made it seem likely that when the metal is in the 2+ oxidation state it would, because of the great propensity for back-bonding, bind at the alkene in preference to the nearby polar group, but on 1 electron oxidation it would seek the polar site. Early results showed that the metal does not relocate on oxidation, even when the carbonyl is deprotonated. The title complex however offered elements of interest distinct from those which motivated the study, and we undertook to investigate some basic reactions: acid–base titration, electrochemistry, and acid-catalyzed aquation. We deal not only with [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup> (1) but also with the product of aquation [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>=CHCO<sub>2</sub>H)(H<sub>2</sub>O)]<sup>2+</sup> (2). The results illustrate the influence of the metal center on the properties of the associated ligands when, as is the case in the lower oxidation state, back-bonding is an important contribution to the interaction and when, on 1 electron oxidation, much of the capacity is lost and the metal center acts mainly by inductive effects.

**Glossary of Numbered Species:** [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup> (1), [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>=CHCO<sub>2</sub>H)(H<sub>2</sub>O)]<sup>2+</sup> (2), [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>2</sup>-(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>)]<sup>2+</sup> (3).

## Experimental Section

**Materials and Reagents.** Osmium tetroxide (Nat. Colonial Metal, Inc), hydrazine (98%, Aldrich), trifluoromethanesulfonic acid (HOTf) (98%, Aldrich), lithium trifluoromethanesulfonate (LiOTf), acrylic acid (99%, Aldrich), and DCl (20% in D<sub>2</sub>O, Aldrich) were used as supplied; DPF<sub>6</sub> ≈ 7 M solutions were obtained by mixing stoichiometric amounts of DCl (20%) in D<sub>2</sub>O and TlPF<sub>6</sub> and removing the TlCl precipitated. Hexafluorophosphoric acid (HPF<sub>6</sub>) solutions were prepared from an aqueous 60% solution, newly purchased (Aldrich) and kept refrigerated.

**Syntheses.** Ammonium hexachloroosmate(IV), (NH<sub>4</sub>)<sub>2</sub>[OsCl<sub>6</sub>], was prepared from osmium tetroxide by the procedure of Dwyer and Hogarth.<sup>3</sup>

**Bis(dinitrogen)pentaammineosmium(II) dichloride**, [Os(NH<sub>3</sub>)<sub>5</sub>(N<sub>2</sub>)<sub>2</sub>]Cl<sub>2</sub>, was prepared by the procedure of Magnuson and Taube.<sup>4</sup>

**(Dihydrogen)aquotetraammineosmium(II) bis(tetraphenylborate)**, [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-(H<sub>2</sub>))(H<sub>2</sub>O)](B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>)<sub>2</sub>, was prepared by the procedure of Li and Taube.<sup>5</sup>

**Bis(acrylic acid)tetraammineosmium(II) Bis(hexafluorophosphate)**, [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> (1). This preparation was carried out under a nitrogen atmosphere in a Vacuum Atmospheres Corp. glovebox. [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-H<sub>2</sub>)(H<sub>2</sub>O)](B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>)<sub>2</sub> (362 mg, 4.0 × 10<sup>-4</sup> mol) and acrylic acid (285 mg, 4.0 × 10<sup>-3</sup> mol) were dissolved in 5 mL of acetone. The solution was kept under stirring for 4 h. After that a solution of 280 mg (8.0 × 10<sup>-4</sup> mol) of TlPF<sub>6</sub> in 2 mL of acetone was added. A white solid was removed by filtration, and 50 mL of ether was added to the filtrate, yielding a yellow solid. This was collected on a medium-porosity frit, washed with ether, and dried under vacuum. The yield was 108 mg (40%). Anal. Calcd for OsC<sub>6</sub>H<sub>20</sub>O<sub>4</sub>N<sub>4</sub>P<sub>2</sub>F<sub>12</sub>: C, 10.41; H, 2.89; N, 8.09. Found: C, 10.82; H, 2.94; N, 8.98. <sup>1</sup>H NMR spectrum (200 MHz) in D<sub>2</sub>O vs TSP as internal standard: δ 3.58 ppm (s, broad, 12H, 4NH<sub>3</sub>), 3.7–4.3 (m, 3H, η<sup>2</sup>-olefinic protons), 5.7–6.4 (m, 3H, η<sup>1</sup>-olefinic protons). Cyclic voltammetry: E<sub>1/2</sub> = 0.59 V vs SHE, 0.50 M LiOTf aqueous solution.

**(Acrylic acid)aquotetraammineosmium(II)**, [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CH<sub>2</sub>=CHCO<sub>2</sub>H)(H<sub>2</sub>O)]<sup>2+</sup> (2), in solution was prepared by keeping a 3 × 10<sup>-2</sup> M HOTf solution of 1 at room temperature overnight. The reaction under these conditions is slow but quantitative. Cyclic voltammetry: E<sub>1/2</sub> = 0.69 V vs SHE, 0.50 M LiOTf aqueous solution. The preparation in D<sub>2</sub>O gives a product with <sup>1</sup>H NMR signals at δ 3.50 ppm (s, broad, 12H, 4NH<sub>3</sub>), and 3.8–4.4 (m, 3H, olefinic protons).

**Bis(ethylene)tetraammineosmium(II) Bis(hexafluorophosphate)**, [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>2</sup>-(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> (3). The procedure for this preparation is given by Li and Taube.<sup>6a</sup> [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-H<sub>2</sub>)(acetone)](PF<sub>6</sub>)<sub>2</sub> (50 mg, 8.2 × 10<sup>-5</sup> mol) (this compound was obtained by simple substitution of the B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup> counterion by the reaction with TlPF<sub>6</sub> in acetone) was dissolved in 2 mL of acetone. The solution was kept under 30 psi of ethylene for 4 h. During that time there is seen a gradual color change from light yellow to brown. A 10-mL volume of ether was then added

(3) Dwyer, F. P.; Hogarth, J. W. *Inorg. Synth.* 1957, 5, 206.

(4) Magnuson, R. H.; Taube, H. *J. Am. Chem. Soc.* 1975, 97, 5129.

(5) Li, Zai-Wei; Taube, H. *J. Am. Chem. Soc.* 1991, 113, 8946.

(6) (a) Unpublished results (b) Li, Zai-Wei; Yeh, A.; Taube, H. *J. Am. Chem. Soc.* 1993, 115, 10384.

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(1) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* 1987, 109, 1883.

(2) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* 1988, 110, 5403.

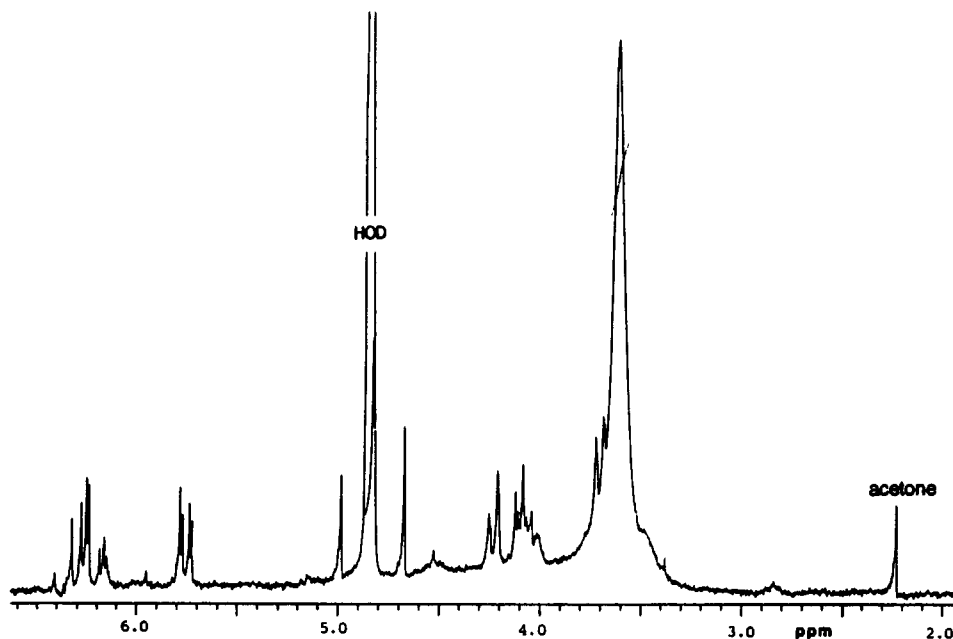


Figure 1. <sup>1</sup>H NMR spectrum of [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)](PF<sub>6</sub>)<sub>2</sub> in D<sub>2</sub>O. The sharp peaks around the solvent peak are side bands.

causing the precipitation of a light brown solid, which was collected in a medium-porosity frit, washed with ether, and dried under vacuum. The yield was 30% (26 mg). <sup>1</sup>H NMR in acetone-*d*<sub>6</sub>: δ 3.68 ppm (s, broad, 12H, 4NH<sub>3</sub>), 3.94 (s, 8H, olefinic protons). Cyclic voltammetry: *E*<sub>1/2</sub> 1.5 V vs SHE, 1 M (TBA)PF<sub>6</sub>-acetone solution.

**Apparatus and Techniques.** <sup>1</sup>H NMR spectra were obtained on Varian XL-400 (400 MHz) and Gemini (200 MHz) spectrometers. In D<sub>2</sub>O, TSP (3-(trimethylsilyl)propionic-2,2,3,3-*d*<sub>4</sub> acid, sodium salt) and DSS (3-(trimethylsilyl)-1-propanesulfonic acid, sodium salt) 99% were used as internal reference standards.

**Electrochemical experiments** were performed under nitrogen by using a PAR Model 173 potentiostat driven by a PAR Model 175 universal programmer. Cyclic voltammograms were recorded by use of a platinum or glassy-carbon working electrode, a Pt<sup>0</sup> counter electrode, and a saturated calomel reference electrode (SCE) (0.243 V vs SHE, standard hydrogen electrode). The ionic strength was kept constant using lithium trifluoromethanesulfonate (LiOTF) as supporting electrolyte.

**Electronic spectra** in the UV-vis range (190–820 nm) were recorded on a Hewlett-Packard Model 8452A diode-array spectrophotometer.

**Kinetic measurements** were performed using a stopped-flow system for semirapid reactions, Model SFA-11, from Hi-Tech Scientific Ltd. The acid-assisted aquation of **1** was performed by measuring the disappearance of the starting material as a function of time. Deaerated solutions of the metal complex and of hexafluorophosphoric (HPF<sub>6</sub>) acid were mixed and the reactions followed by spectrophotometric changes at 20 °C. The final acid concentrations were in the range of 0.06–0.50 M, with the ionic strength kept constant at 0.5 M by NaPF<sub>6</sub>, and the total concentration of Os(II) was ca. 2.5 × 10<sup>-4</sup> M. Species **1** has a molar extinction coefficient of 4.51 × 10<sup>3</sup> M<sup>-1</sup> cm<sup>-1</sup> at 250 nm, and the resulting aquo complex, **2**, has ε(250 nm) = 3.51 × 10<sup>2</sup> M<sup>-1</sup> cm<sup>-1</sup>. The rate constants have an estimated error of 5%. All the experiments were done under a nitrogen atmosphere using glovebag techniques.

**Determinations of p*K*<sub>a</sub> values** of the coordinated ligands in the complexes **1** and **2** were done by cyclic voltammetry and spectrophotometry with an acid–base titration at 0.50 M LiOTF (OTF = trifluoromethanesulfonate). In general, the experimental results for a single titration can be expressed by the Henderson–Hasselbach equation,<sup>7</sup> pH = p*K*<sub>a</sub> – log([HA]/[A<sup>-</sup>]), where [HA] and [A<sup>-</sup>] are the equilibrium concentrations of the protonated and deprotonated species, respectively. A plot of pH vs log([HA]/[A<sup>-</sup>]) gives a straight line with slope close to unity. The Os(III) complexes were obtained by chemical oxidation with the equivalent of AgPF<sub>6</sub> in acetone solution. After removal of Ag<sup>0</sup>, the solvent was evaporated under vacuum and the dry compound was dissolved in a 0.50 M LiOTF aqueous solution. The dependence of the redox potential on the pH also can provide a convenient measure of the p*K*<sub>a</sub> values in both oxidation states, and such experiments were performed. The pH values of the solutions were measured under nitrogen using a VWR Scientific

Table 1. Summary of p*K*<sub>a</sub> Data for 1<sup>2+/3+</sup> and 2<sup>2+/3+</sup>

complex	type <sup>a</sup>	p <i>K</i> <sub>a1</sub>	p <i>K</i> <sub>a2</sub>	p <i>K</i> <sub>a3</sub>
1 <sup>2+</sup>	UV	3.20	6.78	9.8
	cv	3.70	6.10	9.30
1 <sup>3+</sup>	UV	1.76	3.46	
	cv	2.50	4.50	7.40
2 <sup>2+</sup>	UV	2.75	5.27	8.57
	cv	2.85	6.00	
2 <sup>3+</sup>	UV	1.42	3.65	≈8
	cv	1.75	3.65	

<sup>a</sup> UV = spectrophotometric titration; cv = cyclic voltammetric titration.

Model 34100-632 pH-meter with a combined glass electrode. The p*K*<sub>a</sub> values have an estimated error of 5%.

Microanalyses were performed by Desert Analytics Corp.

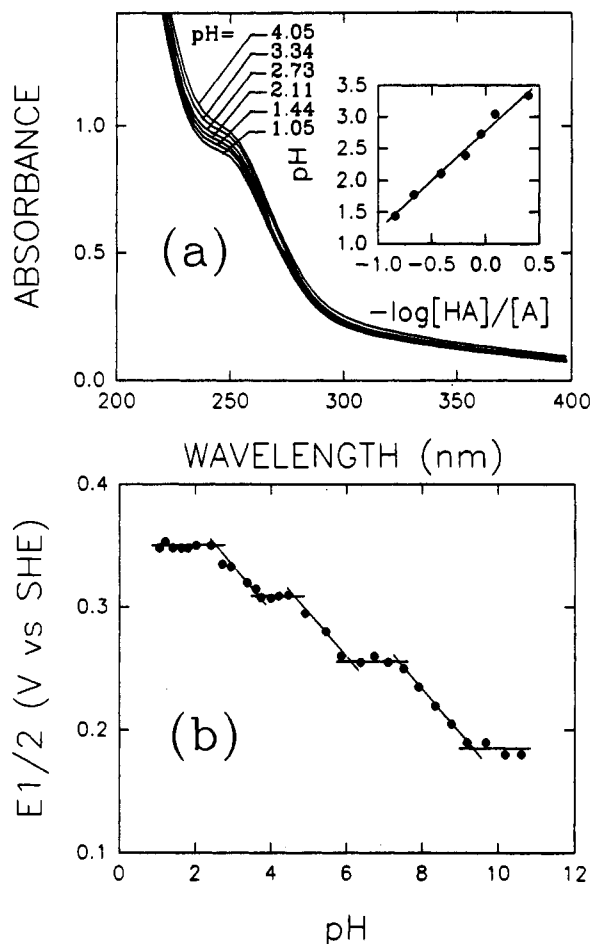
## Results

**[Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup>: Composition and Mode of Coordination.** The elemental analysis together with the proton NMR spectrum, Figure 1, support the bis-substituted formulation. Although the spectrum taken in D<sub>2</sub>O shows a small acetone peak at 2.22 ppm, the integrated signal is too small to justify including acetone in the formula.

**Reactivity of the Coordinated Ligands: p*K*<sub>a</sub> Values.** The p*K*<sub>a</sub> values for the coordinated ligands in the Os(II) and Os(III) oxidation states of the complexes **1** and **2** were determined by acid–base titration in a 0.50 M LiOTF aqueous solution. Table 1 summarizes the p*K*<sub>a</sub> values found. Figure 2 shows the interesting detail of the dependence of the redox potential on the pH for 1<sup>2+/3+</sup> and also illustrates the determination of the p*K*<sub>a</sub> values for 2<sup>2+</sup> by the use of the Henderson–Hasselbach plot. We believe that the p*K*<sub>a</sub> values obtained by the spectrophotometric method are more reliable than those found by cyclic voltammetry due to the fact that the slopes in the *E*<sub>1/2</sub> vs pH plot are somewhat smaller than the expected 60 mV/pH unit. Nevertheless the data are valuable in confirming the existence of the several stages of deprotonation.

**Chemical Behavior of [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup> in Dilute Acid Solutions: Acid-Catalyzed Aquation.** When the PF<sub>6</sub><sup>-</sup> salt of **1** is dissolved in a dilute acid solution and the cyclic voltammogram is taken, a new species is formed, exhibiting a reversible wave with *E*<sub>1/2</sub> = 0.69 V vs SHE. Figure 3 shows the net electrochemical changes as a function of time, observed in an acid solution, pH = 1.53, 0.50 M LiOTF, at room temperature. It must be kept in mind that the bulk solution is in the Os(II)

(7) Skoog, D. A.; West, D. M. *Analytical Chemistry—An Introduction*, 2nd ed.; Holt, Rinehart and Wiston, Inc.: San Francisco, CA, 1974.



**Figure 2.** (a) Typical spectrophotometric changes as a function of pH for the  $2^{2+}$  ion complex. The inset shows the Henderson-Hasselbalch plot for determination of  $pK_a$  values. (b) Redox potential dependence on pH for  $1^{2+}/3^{+}$ .

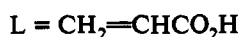
state; thus, the appearance of a new species must represent a reaction of the reduced form of the complex.

To get more information about the reaction, we have prepared a sample at pH = 2.16 in  $D_2O$ , and the  $^1H$  NMR spectrum was taken from time to time. Figure 4 shows the main changes recorded. The appearance of the characteristic signals of free acrylic acid and the change in those of the metal complex shows that the  $\eta^1$ -bound ligand is replaced by  $D_2O$ .

**Kinetics of Aquation.** The rate of aquation of **1** was followed by spectrophotometric measurements at  $\lambda = 250$  nm where the molar extinction coefficients for **1** and **2** are  $4.51 \times 10^3$  and  $3.51 \times 10^2$   $M^{-1} cm^{-1}$ , respectively.

The reaction is first order in complex ion concentration as determined from the Guggenheim plots.

$$-d[Os^{II}(NH_3)_4L_2]/dt = k_{obs}[Os^{II}(NH_3)_4L_2] \quad (1)$$



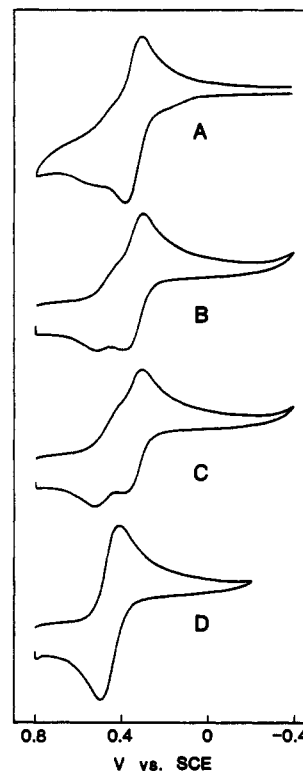
Good pseudo-first-order rate constants,  $k_{obs}$ , were obtained at each concentration of acid ( $[HPF_6] \leq 0.50$  M). It is evident that  $k_{obs}$  reaches a limiting value as the  $[H^+]$  is increased. This kind of behavior can be accounted for by the functional dependence

$$k_{obs} = \frac{a[H^+]}{[H^+] + b} \quad (2)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{a} + \frac{b}{a[H^+]} \quad (3)$$

In Figure 5 the data are plotted in accord with the reciprocal



**Figure 3.** Overall electrochemical changes for the  $[Os(NH_3)_4(\eta^1, \eta^1-(CH_2=CHCO_2H)_2)]^{2+}$  ion complex in aqueous solution, 0.50 M LiOTf, pH = 1.53, as a function of time. See the text for details.

relation and yield for the  $a$  and  $b/a$  values of  $1.52 \times 10^{-2} s^{-1}$  and 8.03, respectively, at 20 °C.

Interesting complications appear in strong acid solutions ( $[H^+] > 6$  M), which are mild when the anion is  $PF_6^-$  but reveal a complete change in stoichiometry when the counterion is  $Cl^-$  or  $OTf^-$ . In 6 M  $HPF_6$ , the aquation to **2** and free acrylic acid is almost quantitative, but the  $^1H$  NMR traces show that a small amount of paramagnetic substance is produced. When either HCl or HOTf is used, the kinetic data even at lower acid concentrations (above 0.5 M) are difficult to interpret and show that the concentration of the anion is as important as that of  $[H^+]$  in determining the rates. At higher levels of acid, the dominant product(s) is (are) paramagnetic. For example, at 10 M HOTf in  $D_2O$ , after the initial rapid reaction phase, only 11% of the complex appears in diamagnetic form (species **2**), and this slowly becomes converted to a paramagnetic substance. Remarkably, despite the acceleration of aquation shown by use of  $HPF_6$  in high concentration, only 7% of the acrylic acid appears free in solution in the experiment at 10 M HOTf.

The paramagnetic nature of the products was shown by the application of the Evans method<sup>8</sup> for determining magnetic susceptibility of solute species. A solution of  $9.0 \times 10^{-2}$  M in **1** and 6 M in DOTf in  $D_2O$  was kept for ca. 1.5 h. Over the range of 269 to 350 K the magnetic moment of the solute calculated from the data remained constant within experimental error at  $(1.15 \pm 0.02) \mu_B$  per osmium. This is to be regarded as a lower limit of the value for the paramagnetic component because it is based on total osmium. In 10 M HOTf (see above), 11% of the immediate product appears in diamagnetic form. The fraction will be considerably greater in 6 M HOTf, and  $\mu_B$  for the paramagnetic form may be as high as that measured for a solution of  $Os(en)_2(H)CH_3OH(CF_3SO_3)_3$  in  $(CD_3)_2CO$ ,<sup>6b</sup> namely  $2.4 \mu_B$ .

Against our initial expectations no linkage isomerization reactions were observed in the time scale of 24 h following the changes in the oxidation states for **1** and **2**. The same conclusion applies to the ester, amide, and nitrile forms.<sup>9</sup>

(8) Loliger, J.; Scheffold, R. *J. Chem. Educ.* 1972, 49, 646.

(9) Nunes, F. S.; Taube, H. *Inorg. Chem.*, preceding paper in this issue.

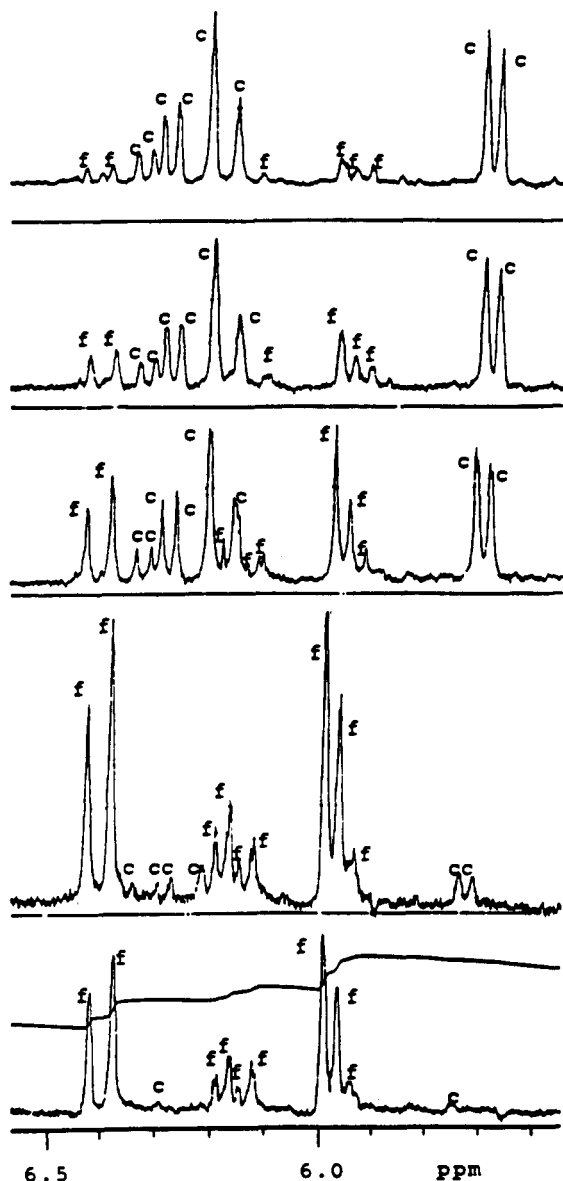


Figure 4. <sup>1</sup>H NMR spectra of [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup> at pH 2.16 in D<sub>2</sub>O, as a function of time: c = coordinated ligand; f = free acrylic acid ligand.

### Discussion

**[Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup>: Preparation, Characterization, and Mode of Coordination.** The success of the preparative method is mainly to be credited to the use of the dihydrogen complex, [Os<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-(H<sub>2</sub>))(H<sub>2</sub>O)]<sup>2+</sup>, as starting material. Taking into account the intensive use of the triflate salt, [Os<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>(OTf)]<sup>3+</sup>, which enabled the recent development of the pentaammineosmium(II) chemistry,<sup>10</sup> it might be expected that the analogous ion, [Os<sup>III</sup>(NH<sub>3</sub>)<sub>4</sub>(OTf)<sub>2</sub>]<sup>3+</sup> would also be a good starting material for the synthetic work. This proved not to be the case. The synthetic problems increase when we use a protonic ligand like acrylic acid. Our attempts to produce the η<sup>2</sup>-complex by reduction of either [Os<sup>III</sup>(NH<sub>3</sub>)<sub>4</sub>(OTf)<sub>2</sub>]<sup>3+</sup> or [Os<sup>III</sup>(NH<sub>3</sub>)<sub>5</sub>(OTf)]<sup>3+</sup> in the presence of acrylic acid led mainly to the production of the corresponding dihydrogen complex and to the reduction of the acrylic acid itself.

The <sup>1</sup>H NMR spectrum of [Os(NH<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>,η<sup>1</sup>-(CH<sub>2</sub>=CHCO<sub>2</sub>H)<sub>2</sub>)]<sup>2+</sup> (Figure 1) shows only one ammine peak, as expected for the trans configuration. The spectrum also clearly distinguishes the two kinds of coordination (η<sup>2</sup> and η<sup>1</sup>) as manifested by the chemical shifts of the olefinic protons. One set of protons

(10) Taube, H. *Pure Appl. Chem.* 1991, 63, 651.

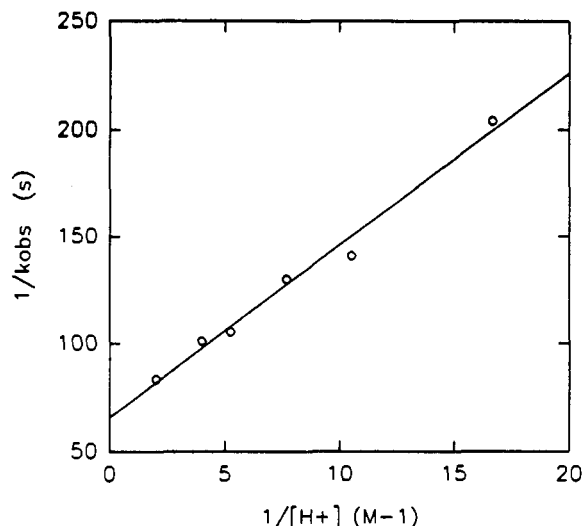
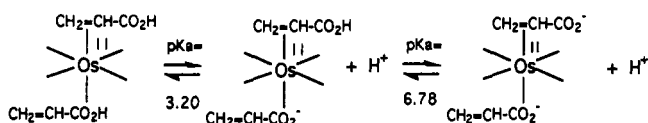


Figure 5. Reciprocal plot of eq 2 for the determination of  $a = k_1 = 1.52 \times 10^{-2} \text{ s}^{-1}$  at 20 °C.

### Scheme 1



appears as a multiplet in the range of δ 3.7–4.3 ppm. This corresponds to an upfield shift of ≈2 ppm compared to the signals of the free acrylic acid. The result shows that the Os(II) is η<sup>2</sup>-π bound to one of the acrylic acid ligands. This conclusion is consistent with previous results involving the η<sup>2</sup>-π coordination mode in pentaammineosmium(II) complexes containing unsaturated ligands.<sup>11</sup> The other set of olefinic protons has chemical shifts very close to those of the free ligand at δ 5.7–6.4 ppm, as is expected for an η<sup>1</sup>-binding to the carboxylic group, reflecting the small influence of metal coordination at oxygen on the shift of the olefinic protons.

An additional item supporting this mode of coordination is provided by the reduction potential of the complex. The value of  $E_{1/2}$  found at 0.5 M LiOTf for 1 is 0.59 V vs SHE (100 mV/s). On the other hand,  $E_{1/2}$  for the bis(ethylene) complex, 3, is 1.5 V vs SHE (1 M (TBA)PF<sub>6</sub>, CH<sub>3</sub>CN, 100 mV/s). The large difference in the redox potentials leaves no doubt about the mode of coordination for the bis(acrylic acid) complex.

**Assignment of the pK<sub>a</sub> Values.** Free acrylic acid has a pK<sub>a</sub> of 4.25.<sup>12,13</sup> Because of the strong tendency of Os(II) for back-bonding,<sup>14</sup> η<sup>2</sup>-binding leads to a shift of electron density from the metal to the ligand. As a consequence we would expect a pK<sub>a</sub> higher than 4.25 for this ligand, in line with the value of 6.78 found for 1. Darenbourg et al.<sup>15a</sup> also have reported a significant decrease in the acidity of acrylic acid upon complexation to iron tetracarbonyl. A pK<sub>a</sub> of 5.16 was found for the coordinated acrylic acid in the complex [Fe(CO)<sub>4</sub>(CH<sub>2</sub>=CHCO<sub>2</sub>H)]. We conclude that the pK<sub>a</sub> value of 3.20 refers to the η<sup>1</sup>-acrylic acid ligand, as illustrated by the Scheme 1.

A decrease in pK<sub>a</sub> for a carboxylic acid on binding to a cation is expected, but the change by only 1.1 units on attachment to a dication is surprisingly small. It is possible that acrylic acid bound in the η<sup>1</sup>-form, by virtue of some conjugation between the two double bonds, does act as a π acid. In the limit this would

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require a coplanar arrangement of the framework of the molecule, a consideration which is an incentive for the determination of the structure of the molecule by X-ray diffraction. Encountering a situation in which an effect of this kind is revealed involves an element of chance. If the capacity of the metal for back-bonding is great,  $\eta^2$ -attachment prevails, and of course if it is small, evidence of back-bonding by  $\eta^1$ -attachment will not be found. In this connection, it should be pointed out that acrylic acid behaves differently from ethylene, which produces a bis- $(\eta^2)$  complex. The difference compared to acrylic acid may be a consequence of the alternative binding site which the latter offers.

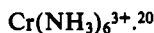
A decrease in  $pK_a$  for all dissociable protons on one-electron oxidation is expected, because of the increase in charge, and reinforced by the decrease in capacity for back-bonding. We ascribe the highest  $pK_a$  values to dissociation of ammine protons. The  $pK_a$  value of 6.6 reported<sup>15b</sup> for  $[\text{Os}(\text{NH}_3)_4\text{Cl}(\text{N}_2)]^+$  provides precedent for the large enhancement of the acidity of  $\text{NH}_3$  when a  $\pi$  acid is co-ligand. Consider that  $pK_a$  for  $\text{H}_2\text{O}$  bound to  $[\text{Os}(\text{NH}_3)_5]^{2+}$  is almost certainly  $>12$ ; for  $[\text{Ru}(\text{NH}_3)_5]^{2+}$  it has been measured as  $>12$ ,<sup>16,17</sup> and because Os(II) is much less electron withdrawing than Ru(II), an even higher value is expected. The  $pK_a$  for  $[\text{Os}(\text{NH}_3)_6]^{2+}$  would be very many orders of magnitude higher, yet the replacement of a  $\sigma$  donor by a  $\pi$  acid, which in fact is negatively charged as is an additional coligand, lowers the  $pK_a$  of a bound ammonia into the range of a weak acid.

The electron-withdrawing effect of  $\eta^2$ -acrylic acid is manifested also in the  $pK_a$  data for **2**. The complex with an  $\eta^2$ -bound ester in place of acrylic acid has been prepared,  $[\text{Os}(\text{NH}_3)_4(\eta^2\text{-CH}_2=\text{CHCO}_2\text{CH}_3)(\text{H}_2\text{O})]^{2+}$ ,<sup>9</sup> and the first  $pK_a$  is measured as 4.3. The comparison with 2.75 for **2** makes it certain that we are dealing with proton dissociation from coordinated water (parenthetically, the increase in  $pK_a$  by 1.5 units on replacing H by  $\text{CH}_3$ , in the absence of prior related measurements, seems large and qualitatively can be attributed to greater electron release into the  $\pi$  system by  $\text{CH}_3$  compared to H). We refer again to the lower limit of  $pK_a$  for  $[\text{Os}(\text{NH}_3)_5(\text{H}_2\text{O})]^{2+}$  in drawing attention to the effect of acrylic acid in extracting electron density from the complement in the complex.

**Acid-Catalyzed Aquation of 1.** That a transformation of **1** takes place in acid solution was first noted in the electrochemical behavior, Figure 3. The true nature of the reaction however was more readily settled by <sup>1</sup>H NMR spectroscopy (Figure 4), which reveals the accumulation of free acrylic acid and loss from the complex of the  $\eta^1$ -bound form of the acid.

The major points to account for in proposing a mechanism for the aquation are (a) the nature of the variation of  $k_{\text{obs}}$  with  $[\text{H}^+]$  when the anion is  $\text{PF}_6^-$ , (b) the fact that net protonation of **2** is not observed (the <sup>1</sup>H NMR properties of **2** are not altered as  $[\text{H}^+]$  increases), and (c) counterions more nucleophilic than  $\text{PF}_6^-$  cause a profound change in the chemistry (e.g. they promote the formation of paramagnetic products) and in the kinetics.

In general, the nature of the dependence of  $k_{\text{obs}}$  on  $[\text{H}^+]$ , such as is shown in Figure 5, can be accounted for (i) by labile protonation of the substrate, the protonated form reacting in a rate-determining step, a limiting value of  $k_{\text{obs}}$  being reached when the substrate is fully protonated, or (ii) by the slow formation of an intermediate without intervention of the proton, after which the proton intervenes in producing product (mechanism shown in the Scheme 2). Alternative (i) can be rejected on the basis of the <sup>1</sup>H NMR evidence even though it has precedent in offering an explanation for the acid-assisted aquation of the  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  and  $[\text{Ru}(\text{NH}_3)_5\text{py}]^{2+}$  complex ions.<sup>18</sup> The mechanism in these cases is rationalized on the grounds that the coordinated ligands have no free electron pairs exposed to electrophilic attack. The mechanism is also supported by the fact that protons do not assist in the release of  $\text{NH}_3$  from  $\text{Ni}^{2+}$ <sup>19</sup> nor in the aquation of



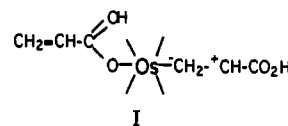
## Scheme 2



$$k_{\text{obs}} = \frac{k_1[\text{H}^+]}{[\text{H}^+] + (k_{-1}/k_2)} \quad (6)$$

The mechanism we propose for catalysis by  $\text{HPF}_6$  takes the form shown in Scheme 2, where  $k_1 = a$  and  $(k_{-1}/k_2) = b$ . The form of eq 6 remains the same if  $\mathbf{1}^*$  and  $(\mathbf{1}^*\cdot\text{H}^+)$  are in labile equilibrium (dissociation constant  $K_d$ ); if  $k_2'$  represents the specific rate of conversion of  $(\mathbf{1}^*\cdot\text{H}^+)$  to products, the only change is that  $k_2$  as above is replaced by  $k_2'K_d$ .

Protonation of Os(II) ammines has been demonstrated,<sup>6b</sup> and the reaction in the case reported is slow; it is expected to be increasingly difficult as the  $\pi$  acid strength of the ligands increases. We propose that the  $k_1$  step corresponds to opening of the three-membered ring to form the intermediate ( $\mathbf{1}^*$ ) shown, where the positive charge may be compensated by the weak nucleophile  $\text{PF}_6^-$ :



After the  $\pi$  acid character of a coligand has been lost, protonation of the d electrons can readily occur. We infer, in analogy to the proposed labilization of  $\text{NH}_3$  in  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  by protons, that this leads to replacement of  $\eta^1$ -acrylic acid by  $\text{H}_2\text{O}$ . In the absence of a strong nucleophile to stabilize the positive charge,  $\eta^2$ -binding is restored and the proton is lost. With stronger nucleophiles ( $\text{Cl}^-$ ,  $\text{CF}_3\text{SO}_3^-$ ) we infer that the open form of the carbon-bound acrylic acid is stabilized and the proton is not ejected because the Os(II) center with a carbanion donating electrons is now electron rich. In effect a monohydride of Os(IV) of coordination number 7 is produced for which there is precedent.<sup>6b</sup> There is also precedent for the paramagnetism, unexpected because the electron count on the metal is 18. The earlier work<sup>6b</sup> also showed that some of the bonds in novel species can be very inert to substitution—e.g. the bonds to  $\text{NH}_3$  or  $\text{NH}_2\text{-R}$  or even to methanol. This can explain why  $\eta^1$ -acrylic acid is not replaced even when the concentration of acid is high. It must be kept in mind that even when  $\text{CF}_3\text{SO}_3^-$  is the counterion, the formation of the paramagnetic product(s) is not quantitative, approximately 10% preceding to the formation of free ligand and the aquo complex. The aquo complex eventually is converted to paramagnetic material but much slowly than is **1**.

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