

sides, the Os(IV) species derives from  $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$  with the trans dioxo moiety  $\text{O}=\text{Os}=\text{O}$ . It is probable that the reduction occurs with retention of trans configuration in the Os(IV) state, which is inert. Nevertheless it is possible that isomerization occurs in the Os(III) state.

**Registry No.**  $[\text{Os}^{\text{VI}}\text{O}_2\text{Cl}_4]^{2-}$ , 39162-54-4;  $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$ , 67378-38-5;  $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2]_2\text{O}^{2-}$ , 74355-72-9;  $[\text{Os}^{\text{IV}}\text{Cl}_6]^{2-}$ , 16871-52-6;

$[\text{Os}^{\text{IV}}\text{Cl}_5(\text{H}_2\text{O})]^-$ , 59683-36-2;  $[\text{Os}^{\text{III}}\text{Cl}_4(\text{H}_2\text{O})_2]^-$ , 80642-48-4;  $[\text{Os}^{\text{III}}\text{Cl}_3(\text{H}_2\text{O})]^{2-}$ , 74009-23-7;  $[\text{Os}^{\text{III}}\text{Cl}_6]^{3-}$ , 62792-05-6;  $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})(\text{OH})]^-$ , 80695-88-1;  $[\text{Os}^{\text{IV}}\text{Cl}_4(\text{OH})_2]^{2-}$ , 20617-39-4.

**Supplementary Material Available:** Calculations of  $\text{p}K_1$  and  $\text{p}K_2$  values and of resolved UV-vis spectra and a listing of observed and calculated absorbances obtained during the deprotonation of  $\text{Os}^{\text{IV}}\text{Cl}_4(\text{H}_2\text{O})_2$  (5 pages). Ordering information is given on any current masthead page.

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## Water Exchange and Solvolysis in Dimethyl Sulfoxide of Square-Planar Tetraaquaplatinum(II). A Platinum-195 NMR Study

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Isotopic shifts of  $-1.00$ ,  $-0.81$ , and  $-0.63$  ppm have been observed for the platinum-195 NMR signals from the complexes  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ ,  $\text{trans-PtCl}_2(\text{H}_2\text{O})_2$ , and  $\text{trans-PtCl}_2(\text{OH})_2^{2-}$ , respectively, when an  $^{16}\text{O}$  ligand is exchanged for  $^{18}\text{O}$ . The resolved isotopic shifts indicate that there are four equivalent slow-exchanging aqua ligands in the hydrated platinum(II) ion, corresponding to a coordination number of 4. Axial interaction of fast-exchanging water is probably not very significant. The exchange frequency for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  at  $25^\circ\text{C}$  is  $2.3 \times 10^{-3} \text{ s}^{-1}$ , corresponding to a second-order rate constant for water exchange of  $4.5 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ . The activation parameters are  $\Delta H^\ddagger = 100 \pm 10 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = 40 \pm 30 \text{ J mol}^{-1} \text{ K}^{-1}$ .  $^{195}\text{Pt}$  spin-lattice relaxation in  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  is mainly due to chemical shift anisotropy. Solvolysis of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  in dimethyl sulfoxide solvent has been studied with use of UV spectrophotometry. The rate constant at  $25^\circ\text{C}$  for the substitution of the first aqua ligand by  $\text{Me}_2\text{SO}$  is  $1.1 \times 10^{-3} \text{ s}^{-1}$ , and the activation parameters are  $\Delta H^\ddagger = 90 \pm 1.5 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = 2 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ . The kinetic parameters for the water exchange and the dimethyl sulfoxide solvolysis of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  indicate that the mechanism for these two reactions is mainly dissociative. In combination with previous kinetic data for the reaction of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  with various entering ligands X it is thus likely that there is a gradual change of mechanism from mainly dissociative to mainly associative when the ligands X are changed in the order  $\text{H}_2\text{O}$ ,  $\text{Me}_2\text{SO}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ .

### Introduction

No studies of water exchange of square-planar platinum(II) aqua complexes have been reported so far. A number of paramagnetic metal ions with labile water in the inner coordination sphere have been investigated with use of the effect of the paramagnetic metal ion on the line width of the  $^{17}\text{O}$  NMR resonance.<sup>1,2</sup> For metal ions with a relatively inert coordination sphere, on the other hand, there is no generally applicable method to monitor the water exchange. For a few systems of Co(III), Cr(III), Rh(III), and Ir(III), precipitation of sparingly soluble salts followed by mass spectrometric analysis has been used to follow the exchange of inner-sphere  $\text{H}_2^{16}\text{O}$  for bulk  $\text{H}_2^{18}\text{O}$ .<sup>3</sup> This method has also been used to monitor exchange between oxo anions and solvent water.<sup>4</sup> It will probably not be possible to find a precipitating agent for the platinum(II) aqua complexes that does not interfere with the exchange.

Platinum-195 chemical shifts are very sensitive to the environment of the platinum.<sup>5-9</sup> Oxygen isotope effects like

those reported<sup>10</sup> for the  $^{55}\text{Mn}$  and  $^{95}\text{Mo}$  resonances from the complexes  $\text{MnO}_4^-$  and  $\text{MoO}_4^-$  should therefore be expected in the chemical shifts of platinum coordinated to oxygen. The present study shows that such oxygen isotope effects exist and can be utilized to determine both the coordination number of  $\text{Pt}(\text{aq})^{2+}$  and the rate and activation parameters for the water exchange of platinum(II) aqua species. In this context, a determination of the activation parameters for the solvolysis of tetraaquaplatinum(II) in dimethyl sulfoxide will also be reported.

### Experimental Section

**Chemicals and Solutions.** A solution of tetraaquaplatinum(II) perchlorate (15.1 mM) in perchloric acid (1.00 M; Baker p.a.) was prepared from potassium tetrachloroplatinate(II) (Johnson and Matthey) and anhydrous silver perchlorate (F. Smith) as described previously.<sup>11</sup> The solution was concentrated to  $C_{\text{Pt}} = 44.2 \text{ mM}$  and  $C_{\text{HClO}_4} = 2.85 \text{ M}$  by freezing out water at  $-18^\circ\text{C}$ . The UV spectrum of the concentrated solution was identical with the spectrum of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  reported previously,<sup>11</sup> and its platinum concentration was determined spectrophotometrically at  $273 \text{ nm}$  ( $\epsilon = 56.5 \text{ cm}^{-1} \text{ M}^{-1}$ ). The molarity of  $\text{H}_2^{16}\text{O}$  was calculated from the concentrations and the density of the solution ( $1.1787 \text{ g cm}^{-3}$ ) to be  $87.5 \pm 0.2\%$  relative to pure water. The original concentration of potassium from  $\text{K}_2\text{PtCl}_4$  is reduced somewhat in the final solution because some solid potassium perchlorate is also precipitated during the freezing out of water. This is negligible for the determination of the water molarity.

A  $44.2 \text{ mM}$  solution of  $\text{trans-PtCl}_2(\text{H}_2\text{O})_2$  was prepared by adding solid sodium chloride (to give  $0.2 \text{ M}$ ) to the  $44.2 \text{ mM}$  tetraaquaplatinum(II) solution and aging for 1 h at room temperature. According to the chloride anation rate constants for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ ,  $\text{PtCl}(\text{H}_2\text{O})_3^+$ , and  $\text{trans-PtCl}_2(\text{H}_2\text{O})_2$ ,<sup>12</sup> the trans complex is accumulated to almost 100% within this time and remains unchanged for several hours. This was confirmed by a constant intensity of the

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Table I. Platinum-195 NMR Chemical Shifts and Oxygen Isotopic Shifts for the Various Complexes<sup>a</sup>

complex	$\delta^b$	$\Delta\delta^c$
0.2 M $\text{H}_2\text{PtCl}_6$	0	
0.1 M $\text{K}_2\text{PtCl}_6$	-1620, -1618 <sup>6</sup>	
44 mM <i>trans</i> - $\text{PtCl}_2(\text{H}_2\text{O})_2$	-630	-0.81
44 mM $\text{Pt}(\text{H}_2\text{O})_4^{2+}$	+31, +24 <sup>d</sup>	-1.00
40 mM <i>trans</i> - $\text{PtCl}_2(\text{OH})_2^{2-}$	-675	-0.63
40 mM $\text{Pt}(\text{Me}_2\text{SO})\text{Cl}_3^-$	-2990, -3000 <sup>8</sup>	
40 mM $\text{Pt}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$	-2009	

<sup>a</sup> Solvent water, where not otherwise stated. <sup>b</sup> Positive chemical shift is to the high-frequency (low-field) side of the  $\text{PtCl}_6^{2-}$  reference. <sup>c</sup> The observed chemical shift for each  $^{18}\text{O}$  introduced into the complex. <sup>d</sup> Solvent 50:50 vol %  $\text{Me}_2\text{SO}-\text{H}_2\text{O}$ .

platinum NMR signal from *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  during this interval of time.

A solution of *trans*- $\text{PtCl}_2(\text{OH})_2^{2-}$  was prepared immediately before use by addition of a small volume of sodium hydroxide (ca. 5 M) to the *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  solution to give a final pH of 13. The intensity of the platinum-195 NMR signal from the dihydroxo complex decreased markedly within 1 h probably due to base hydrolysis and/or polynuclear complex formation.

A 40 mM solution of  $\text{Pt}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$  in perchloric acid (2 M) was prepared by reaction between dimethyl sulfoxide (40 mM) and a slight excess of tetraaquaplatinum(II) (44 mM) and also from  $\text{KPt}(\text{Me}_2\text{SO})\text{Cl}_3$  and silver perchlorate as described previously.<sup>13</sup> The platinum-195 chemical shifts for these two preparations were identical.

Isotopic water (Norsk Hydro) contained  $\text{H}_2^{16}\text{O}:\text{H}_2^{17}\text{O}:\text{H}_2^{18}\text{O}$  in the relative amounts 15.95:21.72:62.32 mol %. Spectral grade dimethyl sulfoxide (BDH) was freshly distilled under reduced pressure at 70 °C.

**Instrumentation.** NMR spectra were recorded with use of a modified Fourier transform Varian XL-100 spectrometer at 21.5 MHz. The spectral width was 5000 Hz, the pulse width 30  $\mu\text{s}$  (70°), and the repetition time 0.1 s. The Varian instrument, a Fourier transform spectrometer equipped with an Oxford Instruments 6 T wide-bore superconducting magnet, and a Nicolet 360 Fourier transform spectrometer with an Oxford Instruments 8.5 T 12 mm bore superconducting magnet were used for spin-lattice relaxation time measurements. The tetraaquaplatinum(II)-dimethyl sulfoxide reaction was monitored with a thermostated Zeiss PMQ II spectrophotometer with a recorder, and UV spectra were obtained by a Beckman 25 double-beam spectrophotometer.

**NMR Measurements and Chemical Shifts.** Table I summarizes the chemical shifts for the various complexes. The isotopic shifts of *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$  and *trans*- $\text{PtCl}_2(\text{OH})_2^{2-}$  were measured with use of preparations that started from tetraaquaplatinum(II) solutions that had first been equilibrated in  $^{18}\text{O}$ -enriched water (1 mL of the 44 mM solution + 1 mL of the isotopic water). It is not possible to introduce the  $\text{H}_2^{18}\text{O}$  by direct exchange of the *trans* complexes, since isotopic equilibrium is too slowly established compared to the decay rates of these complexes.

The signals from the various complexes equilibrated in  $^{18}\text{O}$ -enriched water (platinum stock solution to isotopic water 1:1) are shown in Figure 1. The spectrum of tetraaquaplatinum(II) displays four well-resolved equidistant signals from the complexes coordinating zero, one, two, and three  $\text{H}_2^{18}\text{O}$  ligands. The *trans* complexes give three signals, which are not so well separated. Their isotopic shifts were determined by the curve-fitting procedure described below.

The spin-lattice relaxation times  $T_1$  for tetraaquaplatinum(II) were measured by inversion recovery at the three different fields ( $B_0$ ) 2.36, 6.0, and 8.5 T, giving  $39 \pm 2$ ,  $8.8 \pm 1$ , and  $4.6 \pm 0.2$  ms, respectively.

**Water-Exchange Kinetics.** The kinetics were started by mixing 0.50 mL of  $^{18}\text{O}$  enriched water contained in a calibrated Misco-pipet and 2.00 mL of the tetraaquaplatinum(II) solution (44.2 mM) in a 12-mm NMR tube. The resulting concentrations were  $\text{H}_2^{16}\text{O}:\text{H}_2^{17}\text{O}:\text{H}_2^{18}\text{O} = 81.3:4.83:13.83$  mol % and  $C_{\text{Pt}} = 35.4$  mM,  $C_{\text{HClO}_4} = 2.27$  M.

Since the platinum NMR chemical shifts are very temperature dependent (ca. 1 ppm  $\text{K}^{-1}$ ), the solutions had to be carefully pre-thermostated before mixing. The Misco-pipet with the  $^{18}\text{O}$  solution

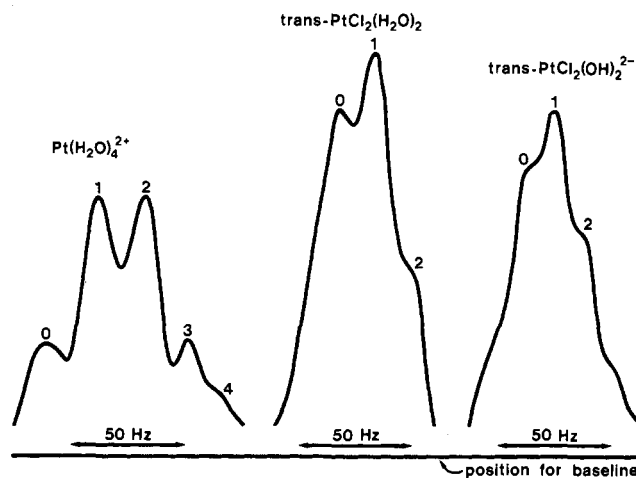
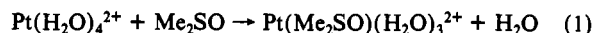


Figure 1. Platinum-195 NMR spectra of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ , *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ , and *trans*- $\text{PtCl}_2(\text{OH})_2^{2-}$  equilibrated in isotopic water. The mole fraction of  $^{16}\text{O}$  compared to  $^{18}\text{O}$  is ca. 1.6:1. The numbers denote number of  $\text{H}_2^{18}\text{O}$  coordinated. The base line noise was about 5% of the highest peak.

was sealed by a piece of Teflon tape and placed into the NMR tube with the platinum solution. The tube with the two solutions was left in the magnet for ca. 30 min to attain temperature equilibrium. Mixing was accomplished by blowing the solution in the Misco-pipet into the platinum solution. Accumulation of the spectra could then be started within a few seconds after mixing, without any broadening of the signals due to drift in the temperature.

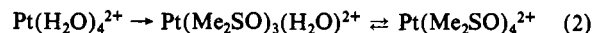
The temperature could only be varied between 18 and 28 °C, the upper limit being given by the rate of exchange and the time needed to accumulate a spectrum (ca. 32 min) and the lower one by the broadening of the  $^{195}\text{Pt}$  signals due to faster relaxation.

**Solvolysis Kinetics in Dimethyl Sulfoxide.** Mixing of 40 mM tetraaquaplatinum(II) with an equal volume of dimethyl sulfoxide gives a slow color change from yellow to colorless. The rate of this reaction is approximately first order with respect to both the complex and dimethyl sulfoxide with a second-order rate constant very close to that reported for the process

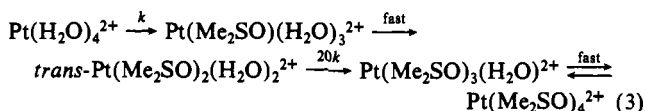


in aqueous 1.00 M perchloric acid.<sup>14</sup> An isosbestic point at 393 nm indicates that only two species (or two rapid-equilibrium mixtures) are present in detectable concentrations during the reaction.

Mixing of 40 mM  $\text{Pt}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$  with dimethyl sulfoxide in the same manner gives a first-order reaction 20 times faster than that observed when  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  is used. If the large *trans* effect of dimethyl sulfoxide compared to that of water (ca.  $2 \times 10^6$ )<sup>13</sup> is also taken into account, it is obvious that the overall process



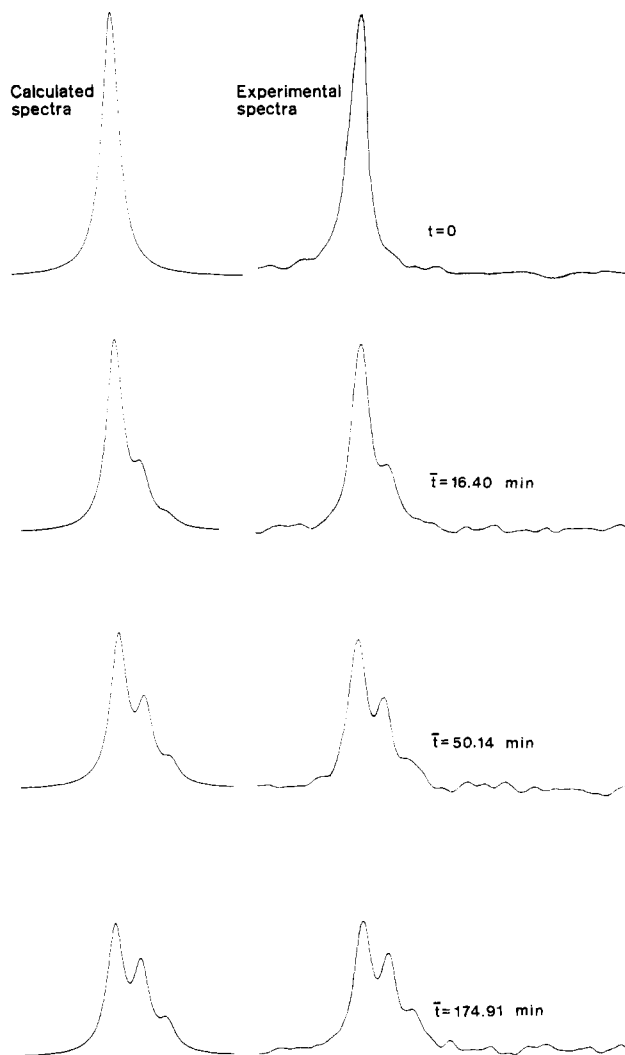
takes place via the consecutive reactions given in eq 3 with reaction 1 being rate determining.<sup>15</sup>



The pseudo-first-order rate constant for step 1 was determined from kinetic runs at 290–310 nm and four temperatures started by mixing 15 mL of thermostated dimethyl sulfoxide with 50 or 100  $\mu\text{L}$  of tetraaquaplatinum(II) stock solution from a Misco-pipet to give  $C_{\text{Pt}}$

(14) L. I. Elding and A.-B. Gröning, *Inorg. Chim. Acta*, 31, 243 (1978).

(15) For further proof that there is no rapid initial conversion of tetraaquaplatinum(II) in the dimethyl sulfoxide solvent, a sample of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  (33.0 mM) equilibrated in isotopic water was mixed with dimethyl sulfoxide in the volume ratio 1:1. After 5 min of thermostating the  $^{195}\text{Pt}$  NMR signal was accumulated for 25 min. The signal only shifted 7 ppm compared to that of an aqueous solution, and the relative intensities from the complexes coordinating zero and one  $\text{H}_2^{18}\text{O}$  ligands were the same as before mixing with dimethyl sulfoxide. In this experiment this ratio was 1:1.



**Figure 2.** Experimental and calculated platinum-195 NMR spectra from the tetraaquaplatinum(II) ion (35 mM) in an isotopic mixture with the composition  $^{16}\text{O}:^{17}\text{O}:^{18}\text{O} = 81.3:4.83:13.83$  mol % as a function of time. The time  $\bar{t}$  denotes the time elapsed from the time of mixing to the midpoint of the interval of accumulation (32 min). The initial spectra refer to pure  $^{16}\text{O}$  water, and the final ones represent isotopic equilibrium.

ca.  $(1-2) \times 10^{-4}$  M and  $\text{C}_{\text{HClO}_4}$  ca. 5–10 mM. The solvent for these experiments was thus almost pure dimethyl sulfoxide, the mole fraction being 0.98–0.99.

### Calculations and Results

#### Water Exchange and Coordination Number of $\text{Pt}(\text{aq})^{2+}$ .

The experimental spectrum of the equilibrated solution shown in Figure 2 (bottom) consists of three lines, which can be identified as the signals from  $\text{Pt}(\text{H}_2^{16}\text{O})_n^{2+}$ ,  $\text{Pt}(\text{H}_2^{16}\text{O})_{n-1}(\text{H}_2^{18}\text{O})^{2+}$ , and  $\text{Pt}(\text{H}_2^{16}\text{O})_{n-2}(\text{H}_2^{18}\text{O})_2^{2+}$ . The intensities of the signals were obtained by means of a least-squares fitting of the sum of three Lorentzian lines of equal line width and with equal spacing to the digitized experimental spectra (ca. 50 points). With use of the intensity of the initial platinum signal (top curve) as the known parameter, the fractions of the three complexes at equilibrium could be calculated. The agreement with the statistical distribution for a four-coordinated complex is very good (cf. Table II), whereas the distributions calculated for five- and six-coordinated complexes are outside the experimental errors. Since the isotopic water contained  $\text{H}_2^{17}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ -coordinated complexes are also present in the equilibrium mixture. These give no contribution to the platinum signal, however, probably due to a large spin coupling constant to the  $^{17}\text{O}$  nucleus, but their presence is established as a 15%

**Table II.** Calculated and Experimental Mole Fractions (%) of the Various Complexes

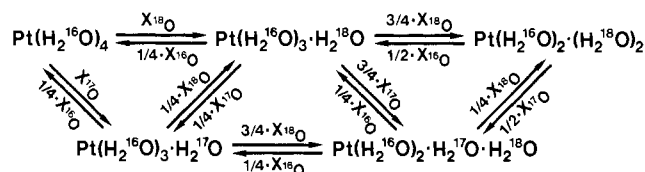
	$\text{Pt}(\text{H}_2^{16}\text{O})_n$	$\text{Pt}(\text{H}_2^{16}\text{O})_{n-1}(\text{H}_2^{18}\text{O})$	$\text{Pt}(\text{H}_2^{16}\text{O})_{n-2}(\text{H}_2^{18}\text{O})_2$
calcd <sup>a</sup>			
CN = 6	29	29	10
CN = 5	36	30	10
CN = 4	44	30	7
exptl	46	30	9

<sup>a</sup> CN = coordination number.

**Table III.** Rate Constants for Water Exchange<sup>a</sup>

$t/^\circ\text{C}$	$10^4 k'_{\text{ex}}/\text{s}^{-1}$ <sup>b</sup>	$10^4 k''_{\text{ex}}/\text{s}^{-1}$ <sup>b</sup>	$10^4 k_{\text{ex}}/\text{s}^{-1}$ (mean)
18.0	$9 \pm 1.2$	$8.2 \pm 0.4$	$8.6 \pm 0.8^c$
27.6	$33 \pm 1.6$	$32 \pm 3$	$32.5 \pm 2.4$

<sup>a</sup> Standard state of water: unit mole fraction. <sup>b</sup>  $k'_{\text{ex}}$  was calculated from the variation of the  $\text{Pt}(\text{H}_2^{16}\text{O})_4$  signal with time and  $k''_{\text{ex}}$  from the  $\text{Pt}(\text{H}_2^{16}\text{O})_3(\text{H}_2^{18}\text{O})$  signal. <sup>c</sup> The first-order value at 25 °C is  $(2.3 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$ , and the second-order value, obtained by division with water molarity (55 M), is  $(4.5 \pm 0.5) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ .



**Figure 3.** Reaction model. The rate constants are defined in units of  $k_{\text{ex}}$ , and  $X$  denotes mole fraction. Complexes with more than one  $\text{H}_2^{17}\text{O}$  or less than two  $\text{H}_2^{16}\text{O}$  have negligible concentrations.

decrease of the integrated area of the final signal compared to that of the initial one. This is close to the statistically expected decrease of 18%.

The spectra in Figure 2 recorded before attainment of chemical equilibrium are a time average over the accumulation period (32 min). The fractions of the three contributing complexes were calculated as a function of time as described above, with use of line width and shift from the initial and final spectra as known parameters. The fractions of  $\text{Pt}(\text{H}_2^{16}\text{O})_4^{2+}$  and  $\text{Pt}(\text{H}_2^{16}\text{O})_3(\text{H}_2^{18}\text{O})^{2+}$  as a function of time gave the water-exchange rate constant  $k_{\text{ex}}$  by using the reaction scheme in Figure 3, where the rate constants are defined in units of  $k_{\text{ex}}$  and  $X$  denotes mole fraction. This gives two independent determinations of the exchange rate constant, denoted  $k'_{\text{ex}}$  and  $k''_{\text{ex}}$ , respectively (see Table III).

Since the relative values of all rate constants in the reaction model are known from the relative concentrations of the isotopes and the statistical factors,  $k_{\text{ex}}$  is the only unknown parameter needed to describe the variation of each complex concentration with time. The exchange-rate constant was calculated from eq 4 with use of a computer program.

$$\langle f(t)_{\text{exptl}} \rangle_i^{t+d} = \langle f(t)_{\text{calcd}} \rangle_i^{t+d} \quad (4)$$

$\langle f(t)_{\text{exptl}} \rangle_i^{t+d}$  is the experimental mean fraction of the complex in the time interval  $[t, t+d]$ , while  $\langle f(t)_{\text{calcd}} \rangle_i^{t+d}$  is a quantity calculated from the reaction model and the initial conditions. The errors in  $k'_{\text{ex}}$  and  $k''_{\text{ex}}$  were obtained by solving eq 4 for the upper and lower limits of  $\langle f(t)_{\text{exptl}} \rangle_i^{t+d}$ , with use of one standard deviation from the least-squares fitting. Complexes with more than one  $\text{H}_2^{17}\text{O}$  or less than two  $\text{H}_2^{16}\text{O}$  never account for more than 2.5% of the total platinum concentration for the isotopic composition used and can therefore be neglected in the calculations.

The temperature dependence of  $k_{\text{ex}}$  gave  $\Delta H^\ddagger = 100 \pm 10 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = 40 \pm 30 \text{ J mol}^{-1} \text{ K}^{-1}$  for the water exchange at 25.0 °C.

Table IV. Rate Constants for the Solvolysis of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> in Dimethyl Sulfoxide (Eq 1)

<i>t</i> /°C	10 <sup>4</sup> <i>k</i> <sub>exptl</sub> /s <sup>-1</sup>	<i>t</i> /°C	10 <sup>4</sup> <i>k</i> <sub>exptl</sub> /s <sup>-1</sup>
25.2	11.0 ± 0.3	37.3	49.7 ± 0.6 <sup>a</sup>
30.5	22.0 ± 0.3	43.2	92.2 ± 0.5

<sup>a</sup> The second-order value at 25.0 °C is  $7.9 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , in good agreement with the value  $8.4 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$  determined for aqueous 1.00 M perchloric acid.<sup>14</sup>

**Solvolytic in Dimethyl Sulfoxide.** First-order rate constants were obtained by fitting the function  $A \exp(-k_{\text{exptl}}t) + B$ , *A* and *B* being constants, to the experimental curves. Duplicate runs were reproducible within 2%. The experiments are summarized in Table IV. The second-order rate constant for reaction 1 at 25 °C, obtained by division with the molarity of Me<sub>2</sub>SO in the solutions used (14 M), is  $(7.9 \pm 0.4) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ , in good agreement with the value previously determined for an aqueous 1.00 M perchloric acid medium.<sup>14</sup>

An Arrhenius plot of the data of Table IV is perfectly linear, giving  $\Delta H^\ddagger = 90 \pm 1.5 \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = 2 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$  for the solvolysis of Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> in dimethyl sulfoxide.

## Discussion

**Coordination Number of Pt(aq)<sup>2+</sup>.** The determination of the coordination number for the hydrated platinum(II) ion in Table II using the relative intensities of the various complexes at isotopic equilibrium implies that there are four equivalent slow-exchanging ligands in the complex. These are probably arranged in a square plane around the platinum (cf. for instance the kinetic or thermodynamic properties of the tetraaquaplatinum(II) ion<sup>12,14</sup> or its UV-visible absorption spectrum<sup>11,16</sup> compared to those of the other square-planar chloro-aqua complexes).

Additional, fast-exchanging ligands coordinated axially cannot be detected in the present measurements, if the exchange frequency of these ligands is so high that no further splitting of the NMR signal occurs. However, the observation<sup>15</sup> that the NMR signal from the Pt(aq)<sup>2+</sup> species is only changed 7 ppm—a shift comparable with that caused by a small change of temperature (1 ppm K<sup>-1</sup>)—when the solvent is changed from water to 50:50 vol % water-dimethyl sulfoxide is an indication that there is probably no significant axial interaction of more weakly bound fast-exchanging ligands in the square-planar Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>. A change from axially coordinated water to dimethyl sulfoxide should change the signal considerably—the change of shift when a dimethyl sulfoxide ligand substitutes water in the square plane is very large—2040 ppm (cf. Table I).

**Reaction Mechanism.** Table V gives rate constants for the reactions between Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> and various entering ligands. The values vary more than five orders of magnitude. The rate constants for the halides, thiocyanate, and ethene are much larger than those for water, dimethyl sulfoxide, and HgCl<sup>+</sup>, the latter three being approximately equal.

In the case of the five fast-reacting ligands, the rate is strongly dependent on the nature of the entering ligand, but there is no indication of saturation for large concentrations.<sup>12</sup>

This indicates that bond making is important in the formation of the transition state, but that there is no accumulation of intermediates with increased coordination number. The kinetics for the reaction between Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> and these ligands is thus compatible with what is usually described as an I<sub>a</sub> mechanism.

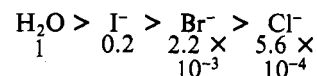
In the case of water, dimethyl sulfoxide, and HgCl<sup>+</sup>, on the other hand, the rate (cf. Table V) is surprisingly insensitive to the nature of the ligand, although these three ligands usually

behave very differently. For instance, the ratio between the stability constants for Pt(Me<sub>2</sub>SO)(H<sub>2</sub>O)<sub>3</sub><sup>2+</sup> and Pt-(H<sub>2</sub>O\*)(H<sub>2</sub>O)<sub>3</sub><sup>2+</sup> is greater than  $5 \times 10^5$ ,<sup>13</sup> and dimethyl sulfoxide is much more efficient than water as entering ligand in square-planar complexes, when a halide is the leaving group.<sup>14</sup> Thus, dimethyl sulfoxide reacts  $4.4 \times 10^3$  times faster than water with PtCl<sub>4</sub><sup>2-</sup>,<sup>14</sup> and about  $2 \times 10^4$  times faster with PtBr<sub>4</sub><sup>2-</sup>.<sup>17</sup> The similar rates for entry of water, dimethyl sulfoxide, and HgCl<sup>+</sup> into Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> rather indicate a common, dissociative rate-determining step. The activation enthalpies for water exchange,  $100 \pm 10 \text{ kJ mol}^{-1}$ , and for the solvolysis in dimethyl sulfoxide,  $90 \pm 1.5 \text{ kJ mol}^{-1}$ , are also equal within experimental errors.

The positive activation entropies for the two reactions,  $40 \pm 30$  and  $2 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively, are also more consistent with dissociative activation.<sup>18</sup> For associative water-exchange processes, activation entropies are expected to be substantially negative.<sup>19</sup> For the dimethyl sulfoxide solvolysis, the activation parameters might be influenced by strong hydrogen bonding to the leaving aqua ligand.<sup>20</sup> The entropy change for an associative process in dimethyl sulfoxide solvent should be considerably more negative than that in aqueous solution (cf. thermodynamic data<sup>21</sup>), so the small positive entropy change for reaction 1 is also more in accordance with a dissociative process.

Another indication that dissociative activation might be important in the case of reactions between dimethyl sulfoxide and aqua complexes of platinum(II) is the fact that steric hindrance in the activation process increases the rate. For associative processes, steric hindrance in the complex is expected to decrease the rate. Thus, the reaction in dimethyl sulfoxide between *trans*-Pt(Me<sub>2</sub>SO)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> and Me<sub>2</sub>SO to form Pt(Me<sub>2</sub>SO)<sub>3</sub>(H<sub>2</sub>O)<sup>2+</sup> is 20 times faster than the reaction between Me<sub>2</sub>SO and Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup>. The higher reactivity of the *trans* complex is in accordance with the *cis*-effect order Me<sub>2</sub>SO > H<sub>2</sub>O (ca. 5:1) observed previously.<sup>13</sup> One possible explanation for the *cis* effect of dimethyl sulfoxide in this case might be a mutual repulsion between the dimethyl sulfoxide ligands in the complex and the leaving water in a dissociative step.

It is worthwhile to compare the rate constants for acid hydrolysis of Pt(H<sub>2</sub>O)<sub>3</sub>X<sup>+</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>; rate constants  $2.8 \times 10^{-7}$ ,  $1.1 \times 10^{-6}$ , and  $8 \times 10^{-5} \text{ s}^{-1}$ , respectively<sup>12,22</sup>) with the water exchange rate constant for Pt(H<sub>2</sub>O)<sub>3</sub>(H<sub>2</sub>O\*)<sup>2+</sup>,  $5 \times 10^{-4} \text{ s}^{-1}$  (the first-order rate constants from Table III divided by the statistical factor of 4). The leaving ligand order corrected for statistics is



With the exception of water, this is the entering ligand order given in Table V.

The ratio between chloride and water of  $5.6 \times 10^{-4}$  mainly reflects the smaller stability of a complex bound aqua ligand in Pt(H<sub>2</sub>O)<sub>4</sub><sup>2+</sup> compared to that of a chloride ligand in PtCl(H<sub>2</sub>O)<sub>3</sub><sup>2+</sup>, the ratio in stability constants being ca.  $5 \times 10^{-6}$ .<sup>12</sup> Thus, the difference in reactivity between these two leaving ligands might be due mainly to a ground-state effect, in a process where activation via bond breaking is predominant.

The trend in the halide series can be described as an increasing importance of bond making with the entering aqua

(17) Ö. Gröning, unpublished results.

(18) Reference 1, p 320.

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(20) J. M. G. Cowie and P. M. Toporowski, *Can. J. Chem.*, **39**, 2240 (1961).

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(23) L. I. Elding and Ö. Gröning, submitted for publication in *Inorg. Chem.*

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Table V. Rate Constants and Relative Rate Constants for Reactions between Various Ligands, X, and  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  at 25.0 °C

	X							
	$\text{H}_2\text{O}^a$	$\text{Me}_2\text{SO}^a$	$\text{HgCl}^+{}^b$	$\text{C}_2\text{H}_4^c$	$\text{Cl}^-{}^d$	$\text{Br}^-{}^d$	$\text{I}^-{}^d$	$\text{SCN}^-{}^d$
$k_X/\text{M}^{-1} \text{ s}^{-1}$	$4.5 \times 10^{-5}$	$8.4 \times 10^{-5}$	$9.2 \times 10^{-5}$	$1.0 \times 10^{-2}$	$2.7 \times 10^{-2}$	$2.1 \times 10^{-1}$	9.4	1.3
$k_X/k_{\text{H}_2\text{O}}$	1	2	2	200	600	$5 \times 10^3$	$2 \times 10^5$	$3 \times 10^4$

<sup>a</sup> This work. <sup>b</sup> Reference 23. <sup>c</sup> Reference 24. <sup>d</sup> Reference 12.

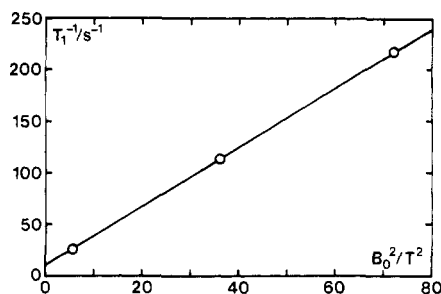


Figure 4. Reciprocal of the platinum-195 spin-lattice relaxation time for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  vs. the square of the magnetic field strength.

ligand in the series  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . This can be rationalized, if the entering aqua ligand is assumed to approach the complex near to the square plane to form the transition state  $\text{Pt}(\text{H}_2\text{O})_4\text{X}^+$ , where the four aqua ligands are arranged in an approximately square plane and the leaving ligand X is displaced out of the plane, before or simultaneous with the attack of water. The order  $\text{I}^- > \text{Br}^- > \text{Cl}^-$  then reflects the increasing polarizability in the halide series. In accordance with this model, a mainly dissociative path for the water exchange might be due to a very low flexibility of the platinum-water bond, which makes formation of a five-coordinated  $\text{Pt}(\text{H}_2\text{O})_5^{2+}$  activated complex less favorable than a formation of three-coordinated  $\text{Pt}(\text{H}_2\text{O})_3^{2+}$  species.

In the case of dimethyl sulfoxide as entering ligand for platinum(II) aqua complexes, steric effects of the  $\text{Me}_2\text{SO}$  ligand in cooperation with the suggested low flexibility of the platinum-water bond might lead to a dissociative path for the  $\text{Me}_2\text{SO}$  entry. It is not likely that steric hindrance from an entering dimethyl sulfoxide ligand should be important in an associative process with initial bond making above or below the square plane, whereas steric hindrance from a dimethyl sulfoxide trying to attack the complex in the square plane combined with the incapability of the aqua ligand to be displaced out of the plane without considerable bond weakening might favor a dissociative process in that case.

**Platinum-195 Spin-Lattice Relaxation Mechanism and Oxygen Isotopic Shifts.** It is obvious from the linear plot of  $T_1^{-1}$  vs. the square of the field strength  $B_0$  (Figure 4) that the platinum-195 spin-lattice relaxation mechanism in the  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  complex is dominated by chemical shift anisotropy. For extreme narrowing conditions ( $\omega\tau_c \ll 1$ ,  $\omega$  being the

Larmor frequency and  $\tau_c$  the rotational correlation time) and the special case of axial symmetry of the species, the relaxation times  $T_1$  and  $T_2$  are given by eq 5, where  $\gamma$  denotes the gy-

$$\frac{6}{7}T_2^{-1} = T_1^{-1} = \frac{2}{15}\gamma^2(\Delta\sigma)^2\tau_c B^2 \quad (5)$$

romagnetic ratio and  $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$  is the chemical shift anisotropy, respectively. The relaxation time  $T_2 = \frac{6}{7}T_1$  gives a line width  $(\pi T_2)^{-1}$  that agrees within 10% with that observed.

From the slope of the plot in Figure 4,  $2.87 \pm 0.03 \text{ T}^{-2} \text{ s}^{-1}$ , the chemical shift anisotropy  $\Delta\sigma$  according to eq 5 can be estimated. An approximate value of  $\tau_c$  can be obtained from the Debye-Stoke-Einstein equation  $\tau_c = 4\pi r^2\eta/(3kT)$  where  $r$  is the effective radius swept out by the tumbling molecule and  $\eta$  is the viscosity of the solvent (here water). If the radius is between 3 and 5 Å (calculated as the sum of the platinum-oxygen bond distance and the radius of the water molecule), we arrive at an order of magnitude for  $\Delta\sigma$  of 40 000–100 000 ppm. The chemical shift anisotropy for these square-planar complexes is thus very large compared to the known chemical shift range for the platinum(II) complexes, which varies about 5500 ppm (cf. Table I and ref 7–9).

The present results give no clear picture of how the magnitudes of the oxygen isotopic shifts are related to the nature of the platinum-oxygen bond. The isotopic shifts for hydroxo ligands are smaller than those for aqua ligands (cf. *trans*- $\text{PtCl}_2\text{L}_2$ ,  $\text{L} = \text{OH}^-$ ,  $\text{H}_2\text{O}$ , in Table I), which suggests that the magnitude does not increase with bond strength. This is also supported by the observation that there is no deviation from Lorentzian line shape in the signal from *trans*- $\text{PtCl}_2(\text{H}_2^{16}\text{O})_2$  (line width 15 Hz), and therefore the isotopic shift due to the natural occurrence of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  must be considerably smaller than the oxygen isotopic shift observed for the aqua ligand in this complex. The sign of the isotopic shift is always negative; i.e., the shielding is larger for coordinated  $^{18}\text{O}$  than for  $^{16}\text{O}$ . Work is in progress at present to determine oxygen isotopic shifts for other platinum complexes.

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**Registry No.**  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ , 60911-98-0; *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ , 13876-96-5; *trans*- $\text{PtCl}_2(\text{OH})_2^{2-}$ , 80642-41-7;  $\text{Pt}(\text{Me}_2\text{SO})(\text{H}_2\text{O})_3^{2+}$ , 80642-42-8;  $\text{Me}_2\text{SO}$ , 67-68-5.