**Figure 1.** dsd graphs for 7-vertex deltahedra.

polyhedra and the chemical significance of the intermediate polyhedron, Figure 1 indicates a variety of other possible dsd processes for the degenerate isomerization of the pentagonal bipyramid and the capped octahedron. Distinguishing between these diverse dsd processes is likely at best to be extremely difficult experimentally, although differences in symmetry might be exploited in very carefully designed low-temperature NMR experiments on specially constructed systems in order to obtain some relevant information.

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**Activation Parameters and Mechanism for Water Exchange of Tetraaquaplatinum(II) Studied by High-Pressure Oxygen-17 NMR Spectroscopy[1]**

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Solvent-exchange reactions at metal ions are fundamental for the understanding of complex formation and some redox reactions.

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(1) High-Pressure NMR Kinetics. 21. Part 20: ref 3.

Although substitution reactions of square-planar complexes have been extensively investigated, only two studies of their solvent exchange seem to have been published so far.[4,5] Platinum-195 NMR was recently used to follow the kinetics of water exchange of $Pt(H_2O)_4^{2+}$.[4] Similar rates for entry of water and dimethyl sulfoxide and for transfer of a chloride ligand from $HgCl^+$ to $Pt(H_2O)_4^{2+}$ were found, and the approximate activation entropies for the water exchange and the entry of dimethyl sulfoxide were slightly positive. Those observations led to the conclusion that the intimate mechanism of substitution in $Pt(H_2O)_4^{2+}$ might change from $I_a$ to $I_d$ for those entering ligands.[4] On the other hand, dimethyl sulfide exchange of *trans*-$Pd(Me_2S)_2Cl_2$, studied by proton NMR spectroscopy, has negative entropies and volumes of activation, compatible with an associative activation for the exchange.[5]

A more comprehensive investigation of the water exchange of $Pt(H_2O)_4^{2+}$, including a variable-pressure study, seemed very desirable in view of these results. Since up to 0.5 M solutions of the complex can now be prepared,[6] the slow water exchange at $Pt(H_2O)_4^{2+}$ can be followed with good accuracy by use of the increase in height of the oxygen-17 NMR signal from coordinated water obtained when platinum(II) perchlorate solutions are mixed with oxygen-17-enriched water. We report here the result of such studies.

**Experimental Section**

**Chemicals and Solutions.** Ca. 10 mM solutions of tetraaquaplatinum(II) perchlorate in aqueous perchloric acid (1.00 M; Baker p.a.) were prepared from potassium tetrachloroplatinate(II) (Johnson and Matthey) and anhydrous silver perchlorate (G. F. Smith, reagent quality) as described previously.[6,7] These solutions were concentrated by repeated evaporation, partial neutralization of excess acid with potassium hydrogen carbonate (Merck p.a.), and separation of excess perchlorate as the potassium salt. Further details are given elsewhere.[6] The procedure gave platinum stock solutions (10–15 mL) for the NMR experiments, with the following concentrations of $[Pt(H_2O)_4](ClO_4)_2$ and $HClO_4$, respectively: 0.549, 3.31 *m*; 0.581, 3.51 *m*; 0.580, 3.60 *m*. The stock solutions were kept under nitrogen in a refrigerator. Their UV spectra agreed with those published for other concentrated platinum(II) perchlorate solutions.[6] Polynuclear hydrolysis was negligible. The solutions were analyzed for perchloric acid by use of a glass electrode, and platinum concentrations were determined spectrophotometrically at 275 nm, where the molar absorptivity of $Pt(H_2O)_4^{2+}$ is 56.5 $cm^{-1}$ $M^{-1}$.[7] Distilled oxygen-17-enriched water (8–20 atom %, normalized in $^1H$) was from Yeda.

**Instrumentation.** All oxygen-17 NMR spectra were recorded on a Bruker CXP-200 spectrometer equipped with a 4.7-T wide-bore cryomagnet working at 27.11 MHz. The accumulated free-induction decays were stored on a DIABLO hard disk system. The temperature was held constant within ±0.3 °C by flushing air or nitrogen through the probe. It was measured by a substitution technique using a platinum resistor.[8] Exchange rate measurements under pressure were performed at 297 K with a high-pressure probe described elsewhere.[9] For fast exchange at higher temperatures, a fast-injection apparatus was used. It is described elsewhere.[10] Absorption spectra were recorded by use of Cary 14 and Perkin-Elmer Hitachi 340 instruments.

**NMR Measurements.** The water exchange was followed by mixing weighed quantities (ca. 0.5–0.8 g for measurements at ambient pressure; ca. 1.3–1.6 g for high-pressure measurements) of platinum stock solutions and oxygen-17-enriched water and recording the NMR spectra as a function of time. Accumulation time for a single spectrum varied between 1200 and 12.9 s for measurements at ambient pressure, depending on the exchange rate, and was 240 s for the high-pressure measurements. Further details are given in the captions of Figures 1 and 2.

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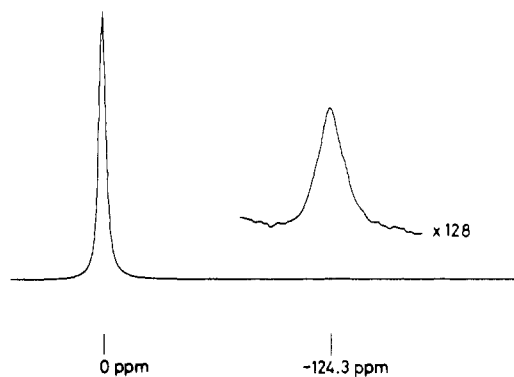
**Figure 1.** 27.11-MHz $^{17}$O NMR spectrum of a 0.25 $m$ [Pt(H$_2$O)$_4$]-(ClO$_4$)$_2$ and a 1.5 $m$ HClO$_4$ solution in 10% $^{17}$O-enriched water at 297.6 K obtained by use of the high-pressure probe at 228 MPa. The bulk (reference) and coordinated water (expanded vertical scale) are isotopically equilibrated. The spectrum is the result of 8000 scans using a repetition rate of 30 ms and a pulse width of 15 $\mu$s in the quadratic detection mode; 1K data points were used over a total spectral width of 20 000 Hz and an exponential filter of 40 Hz.
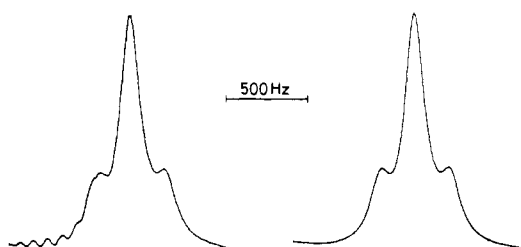


**Figure 2.** 27.11-MHz $^{17}$O NMR spectrum of coordinated water of the same solution described in the caption of Figure 1, but at 332 K in a 10-mm tube, obtained by use of the commercial high-resolution probe and showing $^1J_{^{17}O-^{195}Pt}$ coupling. The experimental spectrum (left) is the result of 108 000 scans using a repetition rate of 85 ms and a pulse width of 15 $\mu$s in the quadratic detection mode. 4K data points were used over a total spectral width of 25 000 Hz, without exponential filtering. The computer-fitted spectrum is shown to the right: $1/T^b_{2Q} = 455.2 \pm 2.1$ s$^{-1}$; $^1J_{^{17}O-^{195}Pt} = 423.8 \pm 1.4$ Hz.

**Kinetic Analysis.** The rate law for an isotopic exchange reaction at an aqua ion (eq 1) can be expressed according to eq 2, commonly referred
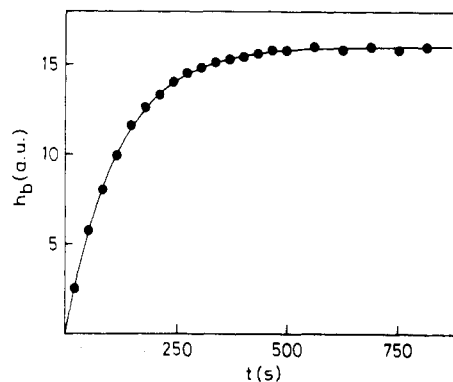
$$M(H_2O)_n^{2+} + nH_2{}^*O \overset{k_{ex}}{\rightleftharpoons} M(H_2{}^*O)_n^{2+} + nH_2O \qquad (1)$$
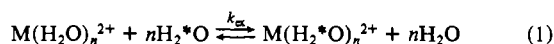
$$-dx/dt = k(x - x_\infty)/(1 - x_\infty) \qquad (2)$$

to as the McKay equation[11] (cf. supplementary material). In this equation, the kinetic isotopic effects, probably never larger than 2%, have been neglected. $k$ represents the rate constant for the exchange of a particular water molecule,[12] and $x$ and $x_\infty$ represent the mole fractions of labeled water coordinated to the metal at the time of sampling and at exchange equilibrium, respectively.

In our experiments, at the time of mixing, there is only one oxygen-17 resonance line from bulk water. The signal from coordinated water molecules containing oxygen-17 is too weak to be observed because of the small natural abundance of this isotope (3.7 $\times$ 10$^{-2}$%). As the reaction proceeds and the concentration of oxygen-17-labeled water bound to platinum increases, a second resonance line appears. Figure 1 shows an example of the two resonances recorded at isotopic equilibrium. The quality of the spectra was excellent, also when recorded under high pressure. The mole fraction of coordinated oxygen-17 water as a function of time is given by eq 3, obtained by integration of eq 2 with the limiting condition $x = 0$ at $t = 0$.

$$x = x_\infty(1 - e^{-kt/(1-x_\infty)}) \qquad (3)$$

The height $h_b$ of the small signal from coordinated oxygen-17 water was used to monitor the exchange kinetics. The spectrometer electronics

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(12) The rates of isotopically labeled solvent exchange of "all n" ligands in M(solvent)$_n^{z+}$ and of a particular one are the same; cf.: Swaddle, T. W. *Adv. Inorg. Bioinorg. Mech.* **1983**, *2*, 121.



**Figure 3.** Kinetics of water exchange at Pt(H$_2$O)$_4^{2+}$ followed by the increase in height $h_b$ (arbitrary unit) of the $^{17}$O NMR signal from coordinated water at 323.8 K and ambient pressure. The solution was prepared by fast injection of 0.7 g of a 0.582 $m$ [Pt(H$_2$O)$_4$](ClO$_4$)$_2$ and a 3.52 $m$ HClO$_4$ solution in normal water into 0.55 g of 20% $^{17}$O-enriched water. The accumulation time for one measurement was 31.8 s.

**Table I.** Water-Exchange Rate Constant of Pt(H$_2$O)$_4^{2+}$, $k_{ex}$, and Quadrupolar Relaxation Rate of Bound Water, $1/T^b_{2Q}$, as a Function of Temperature at Ambient Pressure$^a$

| $T$/K | $k_{ex}$/s$^{-1}$ | $1/T^b_{2Q}$/s$^{-1}$ |
|---|---|---|
| 273.4$^b$ | $(1.09 \pm 0.05) \times 10^{-5}$ | 1942 $\pm$ 75 |
| 278.4$^b$ | $(2.79 \pm 0.22) \times 10^{-5}$ | 1662 $\pm$ 49 |
| 283.2$^b$ | $(5.94 \pm 0.32) \times 10^{-5}$ | 1411 $\pm$ 24 |
| 292.7$^c$ | $(2.10 \pm 0.04) \times 10^{-4}$ | 1066 $\pm$ 15 |
| 300.4$^c$ | $(7.32 \pm 0.15) \times 10^{-4}$ | 886 $\pm$ 20 |
| 312.5$^c$ | $(2.46 \pm 0.12) \times 10^{-3}$ | 739 $\pm$ 15 |
| 323.8$^{c,d}$ | $(8.56 \pm 0.11) \times 10^{-3}$ | 552 $\pm$ 24 |
| 333.6$^{c,d}$ | $(1.52 \pm 0.08) \times 10^{-2}$ | 455 $\pm$ 21 |

$^a$ The concentration of platinum was ca. 0.25 $m$ and that of perchloric acid ca. 1.5 $m$. $^b$ H$_2$ $^{17}$O at 5%. $^c$ H$_2$ $^{17}$O at 10%. $^d$ Fast injection.

**Table II.** Water-Exchange Rate Constant of Pt(H$_2$O)$_4^{2+}$, $k_{ex}$, and Quadrupolar Relaxation Rate of Bound Water, $1/T^b_{2Q}$, as a Function of Pressure at 297 K$^a$

| $P$/MPa | $T$/K | $10^4 k_{ex}{}^b$/s$^{-1}$ | $1/T^b_{2Q}$/s$^{-1}$ |
|---|---|---|---|
| 0.1$^c$ | 297.1 | 4.29 $\pm$ 0.42 | 1120 $\pm$ 90 |
| 50$^d$ | 297.3 | 5.02 $\pm$ 0.21 | 1114 $\pm$ 57 |
| 100$^c$ | 297.2 | 5.26 $\pm$ 0.47 | 1121 $\pm$ 80 |
| 150$^c$ | 297.2 | 5.89 $\pm$ 0.25 | 1120 $\pm$ 50 |
| 200$^c$ | 297.0 | 6.08 $\pm$ 0.91 | 1205 $\pm$ 80 |
| 228$^d$ | 297.6 | 6.91 $\pm$ 0.23 | 1105 $\pm$ 35 |

$^a$ The concentration of platinum was ca. 0.25 $m$ and that of perchloric acid ca. 1.5 $m$. $^b$ Calculated for $T = 297.2$ K by using $\Delta H^\ddagger = 89.7$ kJ mol$^{-1}$. $^c$ H$_2$ $^{17}$O at 5%. $^d$ H$_2$ $^{17}$O at 10%.

during the course of a kinetic run was stable as shown by the constancy of the height of the large signal from free water. The data were fitted to eq 4, with $k$ and $h_{b\infty}$ as parameters ($x$ and $x_\infty$, being small, are pro-

$$h_b = h_{b\infty}(1 - e^{-kt/0.98}) \qquad (4)$$

portional to $h_b$ and $h_{b\infty}$, respectively). In the exponential term of eq 3, $x_\infty$ was set equal to $4[\text{Pt(H}_2\text{O)}_4^{2+}]/([\text{H}_2\text{O}] + 4[\text{Pt(H}_2\text{O)}_4^{2+}]) \approx 0.02$.

**Results and Conclusion**

The oxygen-17 resonance of coordinated water consists of three lines: a singlet due to oxygen bound to the platinum isotopes with spin $I = 0$ and a doublet due to spin–spin coupling of the oxygen with the spin $I = {}^1/_2$ platinum-195 isotope of 33% natural abundance. At low temperatures, the multiplet structure is hidden by the fast quadrupolar relaxation of the oxygen-17 spins, leading to broad resonance lines. At higher temperatures, the resonances become sharper and the three peaks can be resolved. This is illustrated by Figure 2.

The quadrupolar relaxation rates of the oxygen-17 water coordinated to platinum given in the tables were obtained by a nonlinear least-squares fit of the experimental spectra of solutions

**Table III.** Exchange Rate Constants and Activation Parameters for Water Exchange of $Pt(H_2O)_4{}^{2+}$ and $Pd(H_2O)_4{}^{2+}$

| complex | $k_{ex,298}/s^{-1}$ | $\Delta H^{\ddagger}/kJ\ mol^{-1}$ | $\Delta S^{\ddagger}/J\ K^{-1}\ mol^{-1}$ | $\Delta V^{\ddagger}/cm^3\ mol^{-1}$ | ref |
|---|---|---|---|---|---|
| $Pt(H_2O)_4{}^{2+}$ | $(3.9 \pm 0.3) \times 10^4$ | $89.7 \pm 2.4$ | $-9 \pm 8$ | $-4.6 \pm 0.2^b$ | this work |
| $Pt(H_2O)_4{}^{2+}$ | $(5.8 \pm 0.6) \times 10^{-4\ a}$ | $100 \pm 10$ | $29 \pm 30^a$ | | 4 |
| $Pd(H_2O)_4{}^{2+}$ | $(5.6 \pm 0.4) \times 10^2$ | $49.5 \pm 1.9$ | $-26 \pm 6$ | $-2.2 \pm 0.2^c$ | 15 |

$^a$ Values from ref 4 recalculated to exchange of a particular water molecule of $Pt(H_2O)_4{}^{2+}$.    $^b$ 297.2 K.    $^c$ 324 K.
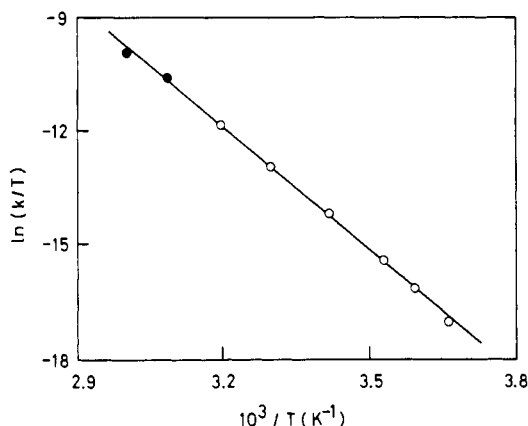


**Figure 4.** Eyring plot for the water-exchange rate constants $k_{ex}$ of $Pt(H_2O)_4{}^{2+}$ in 1.5 *m* $HClO_4$: ●, fast injection.
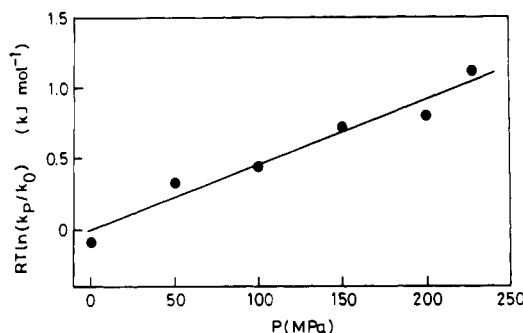


**Figure 5.** Effect of pressure on the water-exchange rate constant $k_{ex}$ of $Pt(H_2O)_4{}^{2+}$ in 1.5 *m* $HClO_4$ at 297.2 K.

in isotopic equilibrium, as in Figure 2. The parameters adjusted were the height $h_b$, the quadrupolar relaxation rate $1/T_{2Q}$, and the coupling constant $^1J_{^{17}O-^{195}Pt}$. Figure 3 shows a typical example of a plot of the height of the NMR signal from coordinated oxygen-17 water vs. time. The water-exchange rate constants listed in Tables I and II were obtained directly from such plots.

Figures 4 and 5 show the temperature and pressure dependencies of the observed exchange rate constants. Activation parameters calculated from those plots are given in Table III. The temperatures of the present experiments could be varied over a wide interval (273–334 K), which gives a much more accurate entropy of activation than that calculated previously.[4]

Negative entropies and negative volumes of activation for solvent-exchange reactions support associative activation, i.e. an A or $I_a$ mechanism. This is well established for octahedral complexes.[13] Although the effect of pressure on many substitution reactions of square-planar complexes has been studied,[14] only a very few activation volumes for symmetric exchange reactions of such complexes are available so far. More detailed mechanistic conclusions based on the present parameters might better be postponed, until more data for solvent exchange have been recorded. It is for example not possible at this stage to use these parameters to discriminate between an associative interchange $I_a$ and a limiting associative A mechanism. However, the slightly negative values for $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ given in Table III do not support

the $I_d$ mechanism for water exchange of $Pt(H_2O)_4{}^{2+}$ suggested recently.[4]

We have just completed a study of the water exchange of the analogous tetraaquapalladium(II) ion.[15] Table III includes the exchange parameters for this complex also. The palladium complex reacts $1.4 \times 10^6$ times faster than that of platinum, and entropies and volumes of activation are negative in this case also.

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**Registry No.** $H_2O$, 7732-18-5; $Pt(H_2O)_4{}^{2+}$, 60911-98-0.

**Supplementary Material Available:** Derivation of eq 2 (4 pages). Ordering information is given on any current masthead page.

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**Circularly Polarized Luminescence from Racemic Terbium(III) Complexes Excited with Circularly Polarized Incident Light**

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The use of lanthanide ions as spectroscopic probes in chemical and biochemical systems[1] has resulted in a significant increase in studies concerned with the elucidation of details of the complex solution structure of these species. In particular, emission spectroscopy has proven to be an extremely important experimental tool, since a number of the lanthanides are highly luminescent, often yielding many well-resolved transitions even in solutions at room temperature.[2] In addition, the intensity and polarization of these transitions are, in general, quite sensitive to small changes in the coordination environment.

A substantial amount of research has been devoted to the measurement of circularly polarized luminescence (CPL)[3] from complexes of lanthanide ions. In CPL one measures the difference in emission intensities between left and right circularly polarized light. By far the most widely studied lanthanides for this kind of work are Eu(III) and Tb(III), because of their large quantum yield for luminescence and their spectral accessibility. All of the solution CPL reported to date for lanthanide ions has necessarily involved the complexation of the cation with one or more optically active ligands.[4] This is due to the fact that no one has yet been able to prepare a stable enantiomerically pure complex in solution that is optically active due only to the configuration of ligands, e.g. a lanthanide complex equivalent to the common tris transition-metal species.

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