

Note

**Fast water exchange on a Pt(II) center: variable temperature and pressure
¹⁷O NMR study at 14.1 tesla of the ionic arylplatinum species
[Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(OH₂)]⁺(OSO₂CF₃)⁻**Urban Frey ^{a,*}, David M. Grove ^b, Gerard van Koten ^b^a Institut de Chimie Minérale et Analytique, University of Lausanne, BCH, CH-1015 Lausanne, Switzerland^b Department of Metal-Mediated Synthesis, Debye Institute, Utrecht University, Padualaan 8, 3584 CH Utrecht, Netherlands

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Abstract

The water-soluble ionic aryl platinum species [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(OH₂)]⁺ undergoes water exchange at a rate 10⁷ times faster than the coordination complex [Pt(OH₂)₄]²⁺; a clear-cut example of the *trans* effect of the C-bonded organic group. Lineshape analysis of high pressure ¹⁷O NMR data acquired in a 14.1 tesla magnet are indicative for an associative mode of activation for this water exchange. © 1998 Elsevier Science S.A.

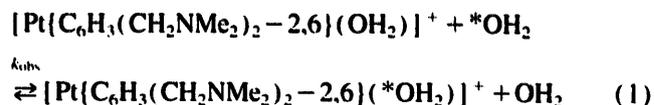
Keywords: Variable pressure; Solvent exchange; Kinetics; Platinum complexes; Aryl complexes; Aqua complexes

1. Introduction

The reactivity and the mechanistic behavior of square-planar d⁸ metal complexes remains a topic of considerable activity due, in particular, to the large number of (homogeneous) catalytic processes that involve these metal ions [1]. Our studies of such d⁸ species containing the terdentate *N,C,N'*-chelating monoanionic ligand [C₆H₃(CH₂NMe₂)_{2-2,6}]⁻ [2], have shown that the unique properties of this ligand and the presence of the fourth coordination site fixed *trans* to a M–C_{ipso} bond can not only result in stabilization of unusual species, including reaction intermediates [2], and the uncommon Ni(III) oxidation state [3], but can also be appropriate for catalytic activity [4]. In our ongoing studies of these and related square-planar organometallic species we are now examining in detail spectroscopic and kinetic aspects [5]. To this end much is known about the kinetics of solvent exchange on homoleptic square-planar palladium(II) and platinum(II) solvates [6]. It has been shown that the exchange rates for a series of such platinum(II) solvates with water, sulfide and isonitrile ligands span more than 10 orders of magnitude and in particular that the C-bonded isonitrile

solvate Pt(CNMe)₄²⁺ has an exchange rate that is 11 orders of magnitude faster than the corresponding aqua complex.

We now report kinetic data for the water exchange reaction of the ionic arylplatinum complex [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(OH₂)]⁺(OSO₂CF₃)⁻ (Eq. (1)) based on linewidth



data obtained from a variable temperature and pressure ¹⁷O NMR study that includes, to the best of our knowledge, the first high pressure NMR measurements, up to 200 MPa, performed in a 14.1 tesla cryomagnet. The kinetic parameters obtained in this study, the activation entropies and volumes, support an associative mode of activation, which is the normal mechanism for substitution on square-planar complexes. The rate constants and activation parameters demonstrate the great extent to which a simple water exchange reaction is influenced by the *trans* Pt–C_{ipso} bond and this information is in agreement with the results of a recent kinetic study of substitution reactions on [Pt{C₆H₃(CH₂NMe₂)_{2-2,6}}(OH₂)](OSO₂CF₃) with entering nucleophiles (Cl⁻, Br⁻, I⁻, N₃⁻, NCS⁻, thiourea, dimethylthiourea, tetramethylthiourea) that showed very fast replacement of the water molecule [7].

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2. Experimental

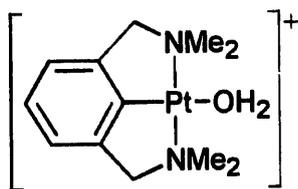
2.1. Materials and solutions

The complex $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\text{OH}_2)](\text{OSO}_2\text{CF}_3)$ (**1**) was prepared according to a literature procedure [8]. ^{17}O enriched water (Enritech Ltd.), trifluoromethanesulfonic acid (Ventron) and manganese(II) perchlorate hexahydrate (Fluka, p.a.) were used without further purification. The solutions used for the NMR measurements were freshly prepared by weight by adding the solvent directly to the reagent. Consequently, concentrations are given in terms of molality (M), in moles per kilogram of solvent. The concentrations of the solutions were 0.02 M in complex, 0.1 M $\text{Mn}(\text{ClO}_4)_2$ and 10 atom % H_2^{17}O for the variable temperature and pressure study. The pH was adjusted to 4 with trifluoromethanesulfonic acid.

2.2. Measurements

The variable temperature ^{17}O NMR spectra were recorded by using a Bruker AM-400 spectrometer equipped with a 9.4 tesla wide-bore cryomagnet working at 54.2 MHz. The ambient pressure measurements were performed on solutions in 10 mm NMR tubes in a commercial thermostatted probe in which the temperature was found to be constant within ± 0.2 K as measured by a substitution technique [9]. The variable pressure ^{17}O NMR spectra were recorded by using a Bruker AMX2-600 spectrometer equipped with a 14.1 tesla narrow-bore cryomagnet working at 81.3 MHz. Samples of ~ 1 ml were measured up to 200 MPa by using a newly designed high-pressure probe. This probe, a modified version of the recently presented ^1H NMR high pressure probe [10], was initially constructed to fit into a standard bore 9.4 tesla cryomagnet, is designed to work at hydrostatic pressures up to 200 MPa and in a temperature domain of 253–433 K. A multinuclear matching/tuning circuit allows the observation of nuclei with a resonance frequency between 20 and 160 MHz. The high pressure probe was adapted to fit into a 14.1 tesla cryomagnet. The loss of sensitivity, compared to an ambient pressure commercial probe is only about a factor of 2.

The ^{17}O NMR chemical shifts are referred to water and measured with respect to ClO_4^- at 288 ppm. The analysis of the experimental data using the appropriate equations was performed by a non-linear least-squares program fitting of the desired parameter to the data. The technical details were described previously [11,12].



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3. Results and discussion

The water-exchange reaction on $[\text{Pt}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\text{OH}_2)]^+$ (**1**), (Eq. (1)) was followed by ^{17}O NMR spectroscopy and a lineshape analysis of the resulting NMR spectra afforded the detailed kinetic parameters. The ^{17}O NMR spectrum of a dilute aqueous solution of aqua complex **1**, which has a water-exchange rate that is relatively slow on the NMR time scale, consists of two resonances: an intense peak due to the bulk water and a small peak due to the coordinated water. This small peak is difficult to detect and to analyze by lineshape methods. However, addition of a very efficient relaxation agent such as Mn^{2+} causes the bulk water to relax so rapidly that its resonance becomes extremely large (negligible amplitude), and thus allows the accurate detection and analysis of the bound water signal of **1** at -30 ppm. In the slow exchange limit, the transverse relaxation rate of the ^{17}O NMR signal of water bound to a diamagnetic metal center is given by Eq. (2), where T_{2Q}^b is the quadrupolar relaxation time and τ is the mean lifetime of water in the first coordination

$$1/T_2^b = 1/T_{2Q}^b + 1/\tau \quad (2)$$

sphere. For the water exchange reaction of **1** shown in Eq. (1) a second-order rate law, Eq. (3), was assumed. The temperature dependence of the second-order exchange

$$1/\tau = k_{\text{obs}} = k_2[\text{H}_2\text{O}] \quad (3)$$

rate constant, k_2 , can then be expressed by the Eyring equation [13]. The quadrupolar relaxation rate ($1/T_{2Q}^b$) was assumed to obey an Arrhenius temperature dependence, with $(1/T_{2Q}^b)^{298}$ being the relaxation rate at 298 K and E_Q^b being the corresponding activation energy [12].

For complex **1** the temperature dependence of the observed transverse relaxation rate $1/T_2^b$, as shown in Fig. 1 and table S1, is mainly governed in the temperature domain studied by the kinetic contribution. Therefore, it was not possible to adjust independently E_Q^b and $(1/T_{2Q}^b)^{298}$. In order to fit the data, the parameter E_Q^b was fixed. The known activation energies for the ^{17}O quadrupolar relaxation rate on water coordinated to a square-planar diamagnetic metal center are 16.6 and 18.1 kJ mol^{-1} [12]. The different values for E_Q^b , which were fixed between 15 and 20 kJ mol^{-1} during the fitting procedure, did not significantly change the kinetic parameters within the statistical errors. From the data presented in Fig. 1 we have extracted the values of $(1/T_{2Q}^b)^{298}$, ΔH^\ddagger , ΔS^\ddagger and k_2^{298} that are given in Table 1.

Assuming that the corresponding volume of activation, ΔV^\ddagger , is pressure independent, as is the case for simple solvent exchange reactions, the pressure dependence of $\ln k$ can then be described by the linear Eq. (4), in which $(k_{\text{obs}})_0$ is

$$\ln k_{\text{obs}} = \ln(k_{\text{obs}})_0 - P\Delta V^\ddagger / RT \quad (4)$$

the exchange rate at zero pressure. Due to the small signal to noise obtained for the variable temperature measurements using the 10 mm NMR tubes and a commercial probe in a