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High-pressure proton NMR study of acetonitrile exchange kinetics on $[Rh_2(CH_3CN)_{10}]^{4+}$ and ^{17}O NMR investigation of aqueous solutions of $[Rh_2(H_2O)_{10}]^{4+}$*

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Abstract

The ^1H NMR spectrum of $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2](BF_4)_4$ supports the presence in solution of this dinuclear species with a 4/1 equatorial/axial ratio. The lability of the axial acetonitrile is high on the NMR time scale, suggesting a dissociative mechanism of exchange with bulk acetonitrile. In contrast the equatorial acetonitrile exchange rate is slow and has been followed by ^1H NMR isotopic labelling: $k^{298} = 3.1 \times 10^{-5}$ s^{-1}, $\Delta H^{\ddagger} = 65.6$ kJ mol^{-1}, $\Delta S^{\ddagger} = -111.0$ J K^{-1} mol^{-1}, and $\Delta V^{\ddagger} = -4.9$ cm^3 mol^{-1}. It is suggested that a concerted migration of the a-CH_3CN molecule to the equatorial plane and release of an e-CH_3CN molecule to the bulk takes place through a contracted transition state. The ^{17}O NMR spectrum of the dinuclear Rh(II) aqua-ion is consistent with the entity $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$. This aqua-ion is not very stable and decomposes, within 1 h at 339 K, forming metallic Rh and $[Rh(H_2O)_6]^{3+}$. The equatorial water exchange rate constant is estimated to be $10 < k^{298} < 50$ s^{-1}, whereas the axial water exchange rate is larger than 10^4 s^{-1} at 298 K. It is believed that the water exchange mechanisms for the dinuclear Rh(II) aqua-ion are similar to those suggested for the acetonitrile analogue.

Introduction

High-pressure NMR has quickly developed into a powerful means of studying solvent exchange reaction mechanisms [2, 3]. In particular, its use has helped to show that a gradual mechanistic changeover occurs along the series of both divalent and trivalent high-spin first-row hexasolvated transition-metal ions [4], and that a sterically controlled crossover of solvent-exchange mechanism takes place for tetrasolventoberyllium(II) [5]. Although complete kinetic and mechanistic information is now available for many ions containing only one metallic cation, such detailed knowledge is rare for polymetallic ions. The study of the properties of $[M_2]^{n+}$ cores surrounded only by weakly coordinated, often neutral, ligands has been of increasing interest for some years [6]. The main reasons for this interest are that such species may serve as versatile starting materials in the preparation of other complexes of the M_2 unit and that these complexes have potential activity for carbonylation and hydrogenation reactions [7]. Therefore it is important to have reliable information concerning the lability of the solvates of $[M_2]^{n+}$ species, and in particular the mechanism for solvent exchange. In this paper, the acetonitrile-exchange kinetics for $[Rh_2(CH_3CN)_{10}]^{4+}$ in neat acetonitrile, obtained from proton NMR spectroscopy is reported. The variable-temperature ^{17}O NMR spectra of $[Rh_2(H_2O)_{10}]^{4+}$ in aqueous acidic solution are presented and structural and kinetic information are obtained for this aqua-ion.

Experimental

Materials and preparation of solutions

^{17}O enriched water (Yeda, 15.57 at.% ^{17}O, normalised in ^1H) was used without further purification. Deuterated nitromethane, CD_3NO_2, (Glaser, >99 at.% D) was dried over molecular sieves. Deuterated acetonitrile, CD_3CN, (Ciba-Geigy, 99.0 at.% D) was kept over calcium hydride for 24 h, and then distilled three times on the vacuum line. $[Be(H_2O)_4](ClO_4)_2$ was prepared and its composition determined as previously reported [5].

$[Rh_2(CH_3CN)_{10}](BF_4)_4$ was prepared according to the method of Dunbar and Pence [8]. 0.2 g of $Rh_2(CH_3COO)_4(CH_3OH)_2$ [9] was dissolved in a mixture

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of 5 ml of 1 M $(CH_3)_3OBF_4$ in CH_2Cl_2 (Fluka, purum) and 10 ml of CH_3CN (Fluka, puriss p.a., freshly distilled over CaH_2). The resulting solution was refluxed for several days, until the appearance of orange crystals. These crystals were recovered by filtration, washed with dry CH_2Cl_2 and dried under vacuum (10^{-3} torr). *Anal.* Calc. for $[Rh_2(CH_3CN)_{10}](BF_4)_4$: C, 24.93; H, 3.14; N, 14.54. Found: C, 25.41; H, 3.36; N, 13.58%. The solutions used for the NMR kinetic measurements were all 0.0113 m (mol/kg of solvent) in $[Rh_2(CH_3CN)_{10}]^{4+}$ and were prepared in a dry-box by weighing the desired amount of $[Rh_2(CH_3CN)_{10}](BF_4)_4$ in a 0.0292 m solution of tetramethylammonium perchlorate (TMAP) in CD_3CN. Chemical shifts were measured with respect to TMAP ($\delta = +3.14$ ppm). TMAP was also used as an intensity reference. In the variable pressure experiments, a small amount of non-deuterated acetonitrile (2%) was added for better shimming.

Aqueous solutions of $[Rh(H_2O)_6](ClO_4)_3$ were prepared according to Ayres and Forrester [10] and were standardised spectrophotometrically by using the known spectrum of $[Rh(H_2O)_6]^{3+}$, with peaks at 311 nm ($\epsilon = 67.4$ M^{-1} cm^{-1}) and 396 nm ($\epsilon = 62$ M^{-1} cm^{-1}) [11]. Aqueous solutions of $[Cr(H_2O)_6]^{2+}$ were prepared by dissolution under argon (333 K, 24 h) of 2 g of electrolytic chromium (BDH, 99.5%) in a mixture of 7 ml of CF_3SO_3H and 50 ml of H_2O. The resulting blue solution was kept under argon and was standardised spectrophotometrically ($\epsilon = 4.82$ M^{-1} cm^{-1} at 715 nm [12]). Preparation of solutions of $[Rh_2(H_2O)_{10}]^{4+}$ in aqueous CF_3SO_3H was based on the method of Maspero and Taube [13]: 20 ml of degassed 23.5×10^{-3} M $[Rh(H_2O)_6]^{3+}$ in 2 M $HClO_4$ were mixed under argon with 1 ml of 0.57 M $[Cr(H_2O)_6]^{2+}$. The resulting solution was loaded on a Dowex 50W-X2 column. After washing with 200 ml of 1 M CF_3SO_3H, the green aqua-ion $[Rh_2(H_2O)_{10}]^{4+}$ was eluted with a solution of 3 M CF_3SO_3H. The $[Rh_2(H_2O)_{10}]^{4+}$ concentration was determined by UV–Vis spectroscopy ($\epsilon = 63$ M^{-1} cm^{-1} at 402 nm and $\epsilon = 46.5$ M^{-1} cm^{-1} at 648 nm [14]). 1.5 ml of 0.2 M $Mn(CF_3SO_3)_2$ in ^{17}O enriched water purged with argon was added to 1.5 ml of $[Rh_2(H_2O)_{10}]^{4+}$ (5×10^{-3} M) in a 10 mm NMR tube which was then sealed for the relaxation rate measurements.

Proton NMR measurements

For the variable temperature study, the spectra were recorded on a wide-bore Bruker AC-200 spectrometer working at 4.7 T. Samples in 5 mm o.d. tubes were thermostated with a flux of nitrogen and the temperature was measured by a substitution technique [15]. The field was locked by using the deuterium signal of the solvent. The variable-pressure measurements were performed on a Bruker AM-400 (9.4 T), using the high-pressure probe and the sample vessel described previously [16]. For all experiments, 4–20 scans of a sweep of 800–4000 Hz were recorded on 16 K data points, with a repetition rate of 7 s. The chemical shifts are referenced to TMS.

^{17}O NMR measurements

Spectra were recorded at 54.22 MHz on a Bruker AM-400 (9.4 T). Temperature stabilisation and measure were as described above. The number of scans was between 50 000 and 200 000, using repetition rate of 7–20 ms and pulse length of 12 μs in the quadratic detection mode. 2 K data points were used over total spectral width of 50 000 Hz without exponential filtering. The chemical shifts are referenced to the signal of bulk water set to $\delta = 0$ ppm. The transverse relaxation rates were obtained by fitting a Lorentzian line shape to the NMR signal.

Results

Acetonitrile exchange kinetics on $[Rh_2(CH_3CN)_{10}]^{4+}$

The proton NMR spectrum of a 8.4×10^{-3} m solution of $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$ in the diluent CD_3NO_2 at 298 K consists of two resonances, one sharp at +2.72 ppm and one less sharp at +2.39 ppm (measured in respect to incompletely deuterated nitromethane $\delta = +4.30$ ppm). The integration of the signals indicates that the first corresponds to the eight e-CH_3CN in equatorial position and the second to the two axial a-CH_3CN. The solutions of $[Rh_2(CH_3CN)_{10}](BF_4)_4$ in CD_3NO_2 are stable only below 298 K and for less than 12 h. Moreover, this compound is not soluble in other diluents such a CH_2Cl_2. Thus acetonitrile was the chosen solvent for the dynamics study of $[Rh_2(CH_3CN)_{10}]^{4+}$, where both solubility and stability criteria are fulfilled. In CD_3CN, two resonances at +2.71 ppm and +1.97 ppm (coinciding with the multiplet due to partially deuterated acetonitrile) are observed: the former is attributed to the e-CH_3CN, whereas the second has the frequency known for free acetonitrile. As no additional resonance was observed for the a-CH_3CN, it was deduced that these molecules were in fast exchange with the free CH_3CN. These observations are in agreement with those reported previously [8, 17].

The very slow exchange of the equatorial e-CH_3CN on $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$ in CD_3CN (eqn. (1))

$$[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CD_3CN)_2]^{4+} + 8CD_3CN \rightleftharpoons [Rh_2(e\text{-}CD_3CN)_8(a\text{-}CD_3CN)_2]^{4+} + 8CH_3CN \quad (1)$$

was followed by monitoring the decrease in intensity of the proton NMR signal of the bound e-CH_3CN (at +2.71 ppm). The spectra were taken after mixing the complex and acetonitrile, as soon as the temperature equilibrium was reached, at regular intervals of time. The time t dependence of the mole fraction x of bound e-CH_3CN, obtained from integration of the signals of e-CH_3CN and TMAP, was fitted to eqn. (2) [18],

$$x = x_{\mathrm{inf}} + (x_0 - x_{\mathrm{inf}}) \exp[-kt/(1-x_{\mathrm{inf}})] \qquad (2)$$

where x_0 (x at $t=0$) and k (the rate constant for the exchange of a particular solvent molecule [19]) were the adjustable parameters and x_{inf} ($\approx 8 \times 0.013/22.7 = 0.0046$) the value of x at infinite time was obtained from the molality of the complex. The exchange rate constants obtained from variable temperature and variable pressure (at 314.3 K) measurements (Table 1 and Fig. 1) were then analysed according to eqns. (3) and (4), respectively, leading to $k^{298} = (3.1 \pm 0.4) \times 10^{-5}$ s^{-1},

$$k = (k_B T/h) \exp(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT) \qquad (3)$$

$$\ln k_p = \ln k_0 - P\Delta V^{\ddagger}/RT \qquad (4)$$

$\Delta H^{\ddagger} = 65.6 \pm 4$ kJ mol^{-1}, $\Delta S^{\ddagger} = -111.0 \pm 11$ J K^{-1} mol^{-1} and $k_0^{314.3} = (18.8 \pm 0.1) \times 10^{-5}$ s^{-1}, $\Delta V^{\ddagger} = -4.9 \pm 0.2$ cm^3 mol^{-1}.

TABLE 1. Temperature and pressure dependence of the e-CH_3CN exchange rate constant, k, on 0.013 m $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$ in neat acetonitrile, obtained from ^1H NMR

T (K)	10^4k (s^{-1})	P (MPa)	10^4k (s^{-1})
293.5[a]	0.23 ± 0.01	0.1[b]	1.89 ± 0.07
298.4	0.35 ± 0.01	42.0	2.03 ± 0.08
306.1	0.56 ± 0.03	82.5	2.21 ± 0.04
320.9	1.94 ± 0.07	123.0	2.37 ± 0.06
325.5	2.27 ± 0.07	157.0	2.50 ± 0.08
340.3	10.9 ± 0.4	195.0	2.76 ± 0.06
343.3	16.1 ± 0.5		
354.3	22.1 ± 1.1		

[a]At 200 MHz, in neat CD_3CN. [b]At 400 MHz and 314.3 K, in 98% CD_3CN and 2% CH_3CN.

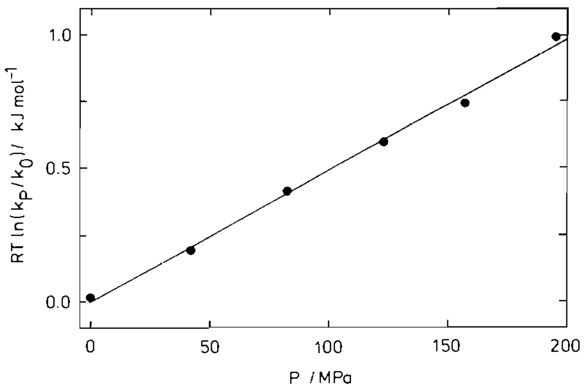

Fig. 1. Pressure effect on the normalized natural logarithm of the rate constant for e-CH_3CN exchange on 0.013 m $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$ in neat acetonitrile.

Solution behaviour of $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$

The ^{17}O NMR spectra of an acidic solution of $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$ in ^{17}O enriched water at 298 K exhibit two resonances, an intense one due to the bulk water (0 ppm) and a small one at −162 ppm. The addition of Mn^{2+}, an efficient relaxation agent for the free water resonance [20], results in the removing of this signal, but no other signal is revealed. A known amount of $[Be(H_2O)_4](ClO_4)_2$ dissolved allows the use of the resonance of $[Be(H_2O)_4]^{2+}$ at +3 ppm as an internal intensity reference [5]. It was deduced that the signal at −162 ppm corresponds to eight water molecules per dinuclear Rh(II) unit, and was attributed to the eight e-H_2O molecules. No signal due to the two a-H_2O molecules is seen from −400 to +500 ppm, even at the lowest temperature (272.3 K). If the signal corresponding to the a-H_2O molecules was narrower than 3000 Hz at 298 K, it would have been detected. The rate constant for the exchange of these a-H_2O has thus been estimated as greater than 10^4 s^{-1} at 298 K. The rate constant, k, for the exchange of a particular equatorial water molecule can be obtained from the transverse relaxation rate of the e-H_2O, $1/T_2^{b}$ (Table 2), according to eqn. (5), where $1/T_{2Q}^{b}$ is the quadrupolar

$$1/T_2^{b} = k + 1/T_{2Q}^{b} \qquad (5)$$

relaxation rate. The temperature dependence of $1/T_{2Q}^{b}$ is given by eqn. (6).

$$1/T_{2Q}^{b} = (1/T_{2Q}^{b})^{298} \exp[E_Q^{b}/R(1/T - 1/298.15)] \qquad (6)$$

Figure 2 indicates that even at high temperatures, the kinetic contribution is small. A least-squares analysis of the $1/T_2^{b}$ values, using eqns. (3), (5) and (6), was

TABLE 2. Temperature dependence of the transverse relaxation rate, $1/T_2^{b}$, of the e-H_2O of 2.5×10^{-3} M $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$ in ^{17}O enriched water (7.4 at.%) containing 0.1 M $Mn(CF_3SO_3)_2$ and 1.5 M CF_3SO_3H

T (K)	$1/T_2^{b}$ (s^{-1})
272.3	1999
278.8	1702
283.1	1483
287.8	1258
294.0	985
307.3	823
320.7	744
328.0	611
338.9	564

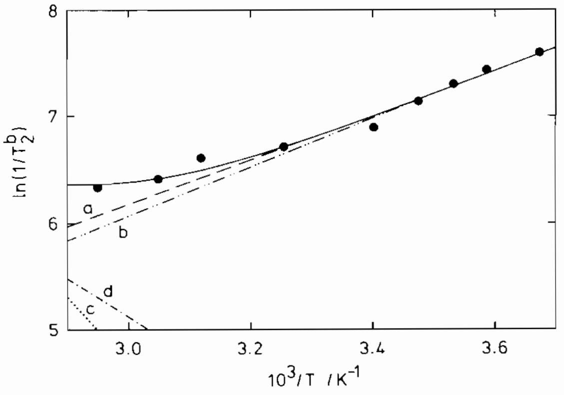

Fig. 2. Effect of temperature on the transverse relaxation rate $1/T_2^b$ of the e-H_2O of 2.5×10^{-3} M $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$ in ^{17}O enriched water (7.5 at.%) containing 0.1 M $Mn(CF_3SO_3)_2$ and 1.5 M CF_3SO_3H, and deduced quadrupolar contribution $1/T_{2Q}^b$ (a: for $\Delta S^\ddagger = -60$ J K^{-1} mol^{-1}; b: for $\Delta S^\ddagger = -120$ J K^{-1} mol^{-1}) and kinetic contribution k (c and d, respectively).

possible only if a value of $\Delta S^\ddagger$ was fixed, $(1/T_{2Q}^b)^{298}$, E_Q^b and $\Delta H^\ddagger$ being the optimised parameters. Good fits could only be obtained for $\Delta S^\ddagger$ values less than -60 J K^{-1} mol^{-1} but an entropy of activation more negative than -120 J K^{-1} mol^{-1} would be very surprising for such a reaction. The optimised values for $\Delta S^\ddagger = -60$ J K^{-1} mol^{-1} (-120) were: $(1/T_{2Q}^b)^{298} = 1493 \pm 50$ s^{-1} (1472 ± 50), $E_Q^b = 17.2 \pm 2$ kJ mol^{-1} (18.8 ± 2), $\Delta H^\ddagger = 49.0 \pm 1$ kJ mol^{-1} (27.8 ± 1). Using the values of $\Delta S^\ddagger$ and $\Delta H^\ddagger$, the k^{298} values calculated were: 14 ($\Delta S^\ddagger = -60$ J K^{-1} mol^{-1}) and 49 s^{-1} ($\Delta S^\ddagger = -120$ J K^{-1} mol^{-1}). The rate constant for the e-H_2O exchange on $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$ was then estimated $10 < k^{298} < 50$ s^{-1}. The fast injection of ^{17}O enriched water to a solution of $[Rh_2]^{4+}$ aqua-ion in a ^{17}O natural abundance solution showed that the appearance of the signal at -162 ppm was complete at 298 K within 5 min, the minimum time required for recording the NMR spectra. Therefore, an estimated lower limiting value of $k^{298} > 5 \times 10^{-3}$ s^{-1} is incompatible with the k^{298} range given above from the transverse relaxation rates.

Solutions of the dinuclear Rh(II) aqua-ion were stable only for a few days and less when heated above 300 K. At $T = 338.9$ K, the aqua-ion was decomposed just after the time required for the recording of the spectra, excluding its study at higher temperatures. The resulting decomposition products were $[Rh(H_2O)_6]^{3+}$ and metallic rhodium deposited as a mirror on the walls of the NMR tubes. The concentration of $[Rh(H_2O)_6]^{3+}$, obtained from the integration of its ^{17}O NMR signal at -130.5 ppm [21], indicated that the stoichiometry of this decomposition could be given by eqn. (7).

$$3[Rh_2(H_2O)_{10}]^{4+} \longrightarrow 4[Rh(H_2O)_6]^{3+} + 2Rh + 6H_2O \quad (7)$$

Discussion

The solid-state X-ray structure of $[Rh_2(CH_3CN)_{10}](BF_4)_4$ [17] has been shown to be $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$, where for each Rh atom, the axial acetonitrile is at a larger distance (2.191 Å) from the metal than the four equatorial ones (mean: 1.987 ± 0.006 Å). A longer metal–axial ligand bond distance is also observed for $[Mo_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$ [6], *cis*-$[Mo_2(O_2CCH_3)_2(e\text{-}CH_3CN)_4(a\text{-}CH_3CN)_2]^{2+}$ [22, 23] and *cis*-$[Rh_2(O_2CCH_3)_2(e\text{-}CH_3CN)_4(a\text{-}CH_3CN)_2]^{2+}$ [23].

The ^1H NMR spectrum of $[Rh_2(CH_3CN)_{10}]^{4+}$ in CD_3NO_2 shows two signals in a 4/1 ratio which have been assigned to the equatorially (2.72 ppm) and axially (2.39 ppm) bounded acetonitrile molecules, respectively. The signal of the a-CH_3CN appears at a higher frequency than that known for free CH_3CN (1.97 ppm) in the same diluent. This indicates that the two axial CH_3CN are bound to the $[Rh_2]^{4+}$ core in nitromethane solution and necessarily in neat acetonitrile. For the dinuclear Rh(II) aqua-ion, the ^{17}O NMR signal corresponding to eight equivalent water molecules per $[Rh_2]^{4+}$ unit brings the first direct evidence for the presence of eight equatorial water molecules in the entity $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$, also proposed for the Mo analogue [24].

The e-H_2O exchange on $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$ is much faster than the e-CH_3CN exchange on $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$ ($k_{H_2O}/k_{CH_3CN} \approx 10^6$). Such a trend has been observed for $[Ru(H_2O)_6]^{2+}$/$[Ru(CH_3CN)_6]^{2+}$ ($k_{H_2O}/k_{CH_3CN} = 2 \times 10^8$) [25] and $[Ru(\eta^6\text{-}C_6H_6)(H_2O)_3]^{2+}$/$[Ru(\eta^6\text{-}C_6H_6)(CH_3CN)_3]^{2+}$ ($k_{H_2O}/k_{CH_3CN} = 3 \times 10^5$) [18]. The increased inertness of these acetonitrile Ru(II) solvates has been attributed to the strong electron back-donation onto the acetonitrile ligands [25], leading to a higher stability.

It might be expected that the exchange rate for the axial ligand would be faster than for the equatorial ones, since a larger bond distance generally increases the lability, as observed for $[VO(H_2O)_5]^{2+}$ [26] or $[Cu(H_2O)_6]^{2+}$ [27]. This is indeed the case for $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$ in acetonitrile, where the exchange of a-CH_3CN is too fast to be measured, while that of the e-CH_3CN is slow enough to be followed by isotopic labelling. A similar situation applies for the aqua-ion $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$: the exchange of the two a-H_2O ($k^{298} > 10^4$ s^{-1}) is at least a factor of 10^3 faster than the exchange of the e-H_2O ($k^{298} = 10$–50 s^{-1}). This order of magnitude for the axial solvent molecules exchange is expected since, for the dirhodium(II)tetraacetate in water or acetonitrile the rates of axial solvent molecules substitution by phosphines are in the range $1-9\times10^5$ s^{-1} at 298 K [28].

In the case of solvato complexes where solvent molecules S are bound both in axial and equatorial positions, e.g. $[VO(a\text{-}S)(e\text{-}S)_4]^{2+}$, $[TiO(a\text{-}S)(e\text{-}S)_4]^{2+}$, three exchanges are possible: the intermolecular axial solvent exchange, k_{ax}, the intermolecular equatorial solvent exchange, k_{eq}, and the intramolecular axial/equatorial solvent rearrangement, k_{int}. Saito and co-workers have observed that the anation reactions of [VO((2-pyridylmethyl)iminodiacetato)(e-H_2O)] [29] and [VO-(nitrilotriacetato)(e-H_2O)]$^-$ [30], in which the axial position is occupied by the tertiary amino nitrogen group, is much slower than the reaction of equatorial complex formation of $[VO(H_2O)_5]^{2+}$ [31]. They have considered the rate constants for the first reactions as probably representative of the real rate of equatorial substitution, k_{eq}, and therefore, that the other 'equatorial substitution rates' are determined by an intramolecular process in which the ligand at the very labile axial site migrates to the equatorial site. The same mechanism has been proposed for the reactions of complex formation of $[TiO(H_2O)_5]^{2+}$ [31]. Anation reactions at the equatorial sites of the dinuclear Mo_2^{4+} aqua-ion are thought to proceed through a similar mechanism, involving the rapid equilibration of the anion in the axial position followed by a subsequent slower step leading to the anion occupancy of the equatorial position [24].

The exchanges of both the a-DMSO and e-DMSO on $[TiO(e\text{-}DMSO)_4(a\text{-}DMSO)]^{2+}$ [1] have been studied by high-pressure ^1H NMR. A D mechanism has been proposed for the intermolecular a-DMSO exchange, as supported by the first order rate law and the high exchange rate. It has been suggested that the slower e-DMSO exchange results from the concerted migration of the a-DMSO molecule to the equatorial plane and loss of an e-DMSO molecule. However, direct exchange between the e-DMSO and the bulk has not been ruled out. The small positive $\Delta V^\ddagger$ ($+4.8$ cm^3 mol^{-1}) has been considered as indicative of an expanded transition state due to the predominance of the e-DMSO bond breakage.

In the case of $[Rh_2(e\text{-}CH_3CN)_8(a\text{-}CH_3CN)_2]^{4+}$, the a-$CH_3CN$ is very rapidly replaced by a bulk-CH_3CN, most probably through a dissociatively activated mechanism, as proposed for the exchange of other axial ligands [1, 27]. For the exchange of the e-CH_3CN, the pathway involving the concerted migration of the a-CH_3CN and release of an e-CH_3CN is suggested by similarity with the case of $[TiO(DMSO)_5]^{2+}$ [1], although direct intermolecular exchange cannot be excluded. The large negative value of $\Delta S^\ddagger$ (-111.0 J K^{-1} mol^{-1}) and the negative activation volume (-4.9 cm^3 mol^{-1}) indicate a contracted transition state. By comparison with $[Rh_2(e\text{-}CH_3CN)_8\text{-}(a\text{-}CH_3CN)_2]^{4+}$, we propose analogous mechanisms for axial (dissociatively activated) and equatorial (through concerted a-H_2O migration and e-H_2O release) water substitution reactions on $[Rh_2(e\text{-}H_2O)_8(a\text{-}H_2O)_2]^{4+}$.

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Note added in proof

The kinetic measurements performed in the NMR probe-heads, in the dark, were not affected by possible photochemical dissociation of the Rh_2^{4+} core [32].