

Inorg. Chem., 1997, 36(26), 6009-6020, DOI:10.1021/ic970783y

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[RuH <sub>2</sub> C=CH <sub>2</sub> ]	[Htos]	Ι	Р	$10^{\rm s} \times k_{\rm eq}$
/ m	/ m	/ m	/ MPa	/ s <sup>-1</sup>
0.073	0.097	0.32	0.1	$11.1 \pm 0.1$
0.066	0.094	0.29	0.1	$11.6 \pm 0.1$
0.073	0.108	0.33	38.7	$10.1 \pm 0.1$
0.070	0.107	0.32	79.1	$9.1 \pm 0.2$
0.067	0.104	0.31	121.9	$8.2\pm0.1$
0.070	0.104	0.31	160.0	$7.6 \pm 0.1$
0.069	0.100	0.31	199.6	$6.9 \pm 0.1$

**Table S1.** Effect of pressure on the first order rate constant for the exchange of a particular water molecule coordinated at the equatorial position in  $[Ru(H_2O)_5(H_2C=CH_2)]^{2+}$ .<sup>a)</sup>

 $k_{ex,0}^{292.8} = (1.12 \pm 0.01) \times 10^{-4} \text{ s}^{-1}$ 

 $\overline{a}$  T = 292.8 ± 0.2 K.

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Т	1/T <sub>2</sub> <sup>b</sup>	Т	1/T <sub>2</sub> <sup>b</sup>
/ K	/ s <sup>-1</sup>	/ K	/ s <sup>-1</sup>
 280.2	948	339.9	401
292.8	581	347.9	559
301.1	457	354.7	930
312.6	347	361.9	1575
327.8	305	363.0	1781

**Table S2.** Effect of temperature on the transverse relaxation rate,  $1/T_2^{b}$ , of the <sup>17</sup>O NMR signal of the water molecule coordinated at the axial position in  $[Ru(H_2O)_5(H_2C=CH_2)]^{2^+,a}$ 

<sup>a)</sup> [Ru] = 0.070 m, [Htos] = 0.11 m.

Т	1/T <sub>2</sub> <sup>b</sup>	Т	1/T <sub>2</sub> <sup>b</sup>
/ K	/ s <sup>-1</sup>	/ K	/ s <sup>-1</sup>
276.1	1241	339.6	416
288.4	881	344.8	511
297.0	684	350.1	590
308.4	511	354.4	717
319.0	425	361.6	1150
326.4	387	366.7	1413

**Table S3.** Effect of temperature on the transverse relaxation rate,  $1/T_2^{b}$ , of the <sup>17</sup>O NMR signal of the water molecule coordinated at the axial position in  $[Ru(H_2O)_5(F_2C=CH_2)]^{2+}$ .<sup>a)</sup>

a) [Ru] = 0.073 m, [Htos] = 0.10 m.

## Establishment of equations 12 to 15

Equations (12) - (15) have been established for a solution containing both the complexes  $[Ru(H_2O)_5L]^{2+}$  and  $[Ru(H_2O)_6]^{2+}$  with three sites exchanging with the bulk: equatorial and axial positions in  $[Ru(H_2O)_5L]^{2+}$ , and coordinated water in  $[Ru(H_2O)_6]^{2+}$ . To shorten the typographic effort in the development of the equations, we define the following values:

- E, A, H, S: solvent molecule in equatorial and axial positions in the monocomplex, coordinated in the hexa-aquacomplex and free respectively
- E, \*E, E: solvent molecule in equatorial position in the non-observed isotopic form, observed isotopic form, and all isotopic forms respectively ([E] = [\*E] + [E]) (identical for A, H and S).
- [L]: concentration of free ligand
- $k_{ex}, k_{ax}, k_{eq}$ : rate constant for the water exchange in the hexa-aquacomplex, in the monocomplex in axial and equatorial positions respectively
- $k_{f}, k_{d}$ : second-order rate constant and first order rate constant for the formation and dissociation of the monocomplex, respectively

$$C_{RuL} = [MLAE_4^{n+}]_0$$
 (total concentration of monocomplex) (S1)  

$$C_{hex} = [MH_6^{2+}]_0$$
 (total concentration of hexa-aquacomplex) (S2)  

$$S = [S] + [*S]$$
 (free solvent concentration) (S3)  

$$q = C_{RuL} / S$$
 
$$q_{hex} = C_{hex} / S$$
 (S4)  

$$*W = [*S] / S$$
 (S5)

$$w = [-5]/5$$
  $w = [5]/5$  (85)

$$[*E] = 4[ML*E_4A] + 3[ML*E_3EA] + 2[ML*E_2E_2A] + [ML*EE_3A]$$
(S6)

$$x_{eq} = [*E]/([*E]+[*A]+[*H]+[*S])$$
(molar fraction in equatorial position) (S7)

$$x_{ax} = [MLE_4*A]/([*E]+[*A]+[*H]+[*S]) = [*A]/([*E]+[*A]+[*H]+[*S])$$
(S8)

$$x_{hex} = [*H]/([*E]+[*A]+[*H]+[*S])$$
(S9)

$$x_{s} = [*S]/([*E]+[*A]+[*H]+[*S])$$
(S10)

## Equation for the exchange in axial position:

 $\Rightarrow$ 

$$MLE_4A + *S \xrightarrow{k_{ax}} MLE_4*A + S$$

$$d[MLE_4*A] / dt = k_{ax}[MLE_4A] \cdot W - k_{ax}[MLE_4*A] \cdot W$$
  
=  $k_{ax}(*W(C_{RuL}-[MLE_4*A]) - [MLE_4*A] \cdot W)$   
=  $-k_{ax}([MLE_4*A] - C_{RuL}[*S]/S) = -k_{ax}([MLE_4*A]) - q[*S])$ 

If we divide on both sides by ([\*E]+[\*A]+[\*H]+[\*S])  

$$dx_{ax} / dt = -k_{ax}(x_{ax} - q \cdot x_{S})$$
(12)

Equations for the exchange in equatorial position:

$$MLE_{4}A + *S \qquad \underbrace{\frac{4k_{eq}}{k_{eq}}}_{K_{eq}} \qquad ML*EE_{3}A + S$$
$$ML*EE_{3}A + *S \qquad \underbrace{\frac{3k_{eq}}{2k_{eq}}}_{2k_{eq}} \qquad ML*E_{2}E_{2}A + S$$

$$ML^*E_2E_2A + *S \xrightarrow{2k_{eq}} ML^*E_3EA + S$$

$$ML^*E_3EA + *S \xrightarrow{K_{eq}} ML^*E_4A + S$$

$$d[ML*EE_{3}A] / dt = 4k_{eq}[MLE_{4}A] \cdot W - k_{eq}[ML*EE_{3}A] \cdot W - 3k_{eq}[ML*EE_{3}A] \cdot W + 2k_{eq}[ML*E_{2}E_{2}A] \cdot W$$

$$d[ML^*E_2E_2A] / dt = 3k_{eq}[ML^*EE_3A] \cdot W - 2k_{eq}[ML^*E_2E_2A] \cdot W - 2k_{eq}[ML^*E_2E_2A] \cdot W + 3k_{eq}[ML^*E_3EA] \cdot W$$

$$d[ML^*E_3EA] / dt = 2k_{eq}[ML^*E_2E_2A] \cdot W - 3k_{eq}[ML^*E_3EA] \cdot W - k_{eq}[ML^*E_3EA] \cdot W + 4k_{eq}[ML^*E_4A] \cdot W$$

$$d[ML*E_4A] / dt = k_{eq}[ML*E_3EA] \cdot W - 4k_{eq}[ML*E_4A] \cdot W$$
  
$$d[*E] / dt = d[ML*EE_3A] / dt + 2d[ML*E_2E_2A] / dt + 3d[ML*E_3EA] / dt + 4d[ML*E_4A] / dt$$

After using definition S1-S7 and the same mathematical treatment as in the axial case we obtain:

$$d[*E] / dt = -k_{eq}([*E] - 4 \cdot q \cdot [*S])$$
  

$$\Rightarrow dx_{eq} / dt = -k_{eq}(x_{eq} - 4 \cdot q \cdot x_{s})$$
(13)

The exchange in the hexa-aquacomplex is identical and has already been developed.<sup>1</sup> Using definition S7 to S10, we can write:

$$x_{\rm s} = 1 - x_{\rm ax} - x_{\rm eq} - x_{\rm hex} \tag{15}$$

## Establishment of equation 16 to 19

All the possible composition of complexes of the general formula  $[RuL(H_2^{17}O)_j(H_2O)_{5-j}]^{2+}$  are shown in Figure S1. The variation of the concentration of enriched water in the axial position

given by equation S11, where the numbers correspond to the complexes in Figure S1.

is

$$\frac{d^*A}{dt} = \frac{d(3)}{dt} + \frac{d(5)}{dt} + \frac{d(8)}{dt} + \frac{d(9)}{dt} + \frac{d(11)}{dt} + \frac{d(12)}{dt}$$
(S11)

The equivalent equation can be written for the concentration of enriched water in the equatorial position (equation S12).

$$\frac{d^{*}E}{dt} = \frac{d(2) + d(5)}{dt} + 2 \cdot \left(\frac{d(4) + d(6) + d(8) + d(9)}{dt}\right) + 3 \cdot \left(\frac{d(7) + d(11)}{dt}\right) + 4 \cdot \left(\frac{d(10) + d(12)}{dt}\right)$$
(S12)



Figure S1. All possible structures of complexes of the general formula  $[RuL(H_2^{17}O)_j(H_2O)_{5\cdot j}]^{n+}$  (O represents a water molecule enriched in oxygen-17,  $H_2^{17}O$ ; the non-enriched water molecules are not drawn).

It is very tedious to write all the possible reactions for all the complexes shown in Figure S1. We will only take the complex labelled (9) as an example. In Figure S2 are shown all the reactions that can consume or produce (9). All the chemical reactions shown in Figure S2



Figure S2. Complex formation and complex dissociation reactions where complex (9) of Figure S1 is involved.

can be summarized as in equation S13. The factors appearing in front of the different

$$\frac{d(9)}{dt} = \frac{3}{5} [Ru(H_2^{17}O)_3(H_2O)_3] \cdot \frac{1}{6} \cdot k_f + \frac{1}{5} [Ru(H_2^{17}O)_4(H_2O)_2] \cdot \frac{2}{3} \cdot k_f - k_d \cdot (9)$$
(S13)

concentrations can be explained as follows: (3/5) represents the probability that a complex of the general formula  $[M(H_2^{17}O)_3(H_2O)_3]^{2+}$  has a structure "*mer*" as in the structure on the right in Figure S2. The second order rate constant,  $k_f$ , represents the rate constant for the substitution of any of the six water molecules in the hexa-aquacomplex. In Figure S2, only the substitution of one water molecule (the one towards the top of the page) can give the complex (9). This is the origin of the factor 1/6 in equation S13. The other factors can be explained the same way. If we explain the same procedure for all the complexes in Figure S2, and using equations S11 and S12, we can express the variation of the concentration of enriched coordinated water in axial and equatorial positions by equations S14 and S15 respectively, where [L] is the concentration of free ligand.

$$\frac{d[*A]}{dt} = \frac{1}{6} \cdot k_{f} \cdot [*H] \cdot [L] - k_{d} \cdot [*A]$$
(S14)

$$\frac{d[*E]}{dt} = \frac{2}{3} \cdot k_{f} \cdot [*H] \cdot [L] - k_{d} \cdot [*E]$$
(S15)

Equations S14 and S15 can be understood intuitively without needing a complete and rigorous mathematical treatment. If there is one water molecule, enriched in oxygen-17, present in the hexa-aquacomplex, there is one chance in six that this water be coordinated in the axial position after the formation of the complex  $[Ru(H_2O)_5L]^{2+}$ . This explains the factor 1/6 in equation S14 (identical for equation S15 where the probability is now 2/3).

The concentration of enriched water in the hexa-aquacomplex is modified by three different reactions: the water exchange with the bulk, the formation and the dissociation of the monocomplex. The first process has already been developed<sup>1</sup> and gives the two first terms of equation S17. The other terms of equation S17 can be obtained in the same way as for equations S14 and S15. Applying equation S16 for all types of hexa-aquacomplexes gives equation S17.

$$\frac{d[*H]}{dt} = \sum_{j=1}^{6} j \cdot [Ru(H_2^{17}O)_j(H_2O)_{6-j}]$$
(S16)

$$\frac{d[^{*}H]}{dt} = \begin{cases} k_{ex} \cdot ^{*}W \cdot [H] - k_{ex} \cdot W \cdot [^{*}H] - k_{f} \cdot [L] \cdot [^{*}H] \\ + k_{d} \cdot ^{*}W \cdot [RuL] + k_{d} \cdot ([^{*}E] + [^{*}A]) \end{cases}$$
(S17)

Using  $6*C_{hex} = [H] + [*H]$ , eqs S3 and S5 we obtain equation S18.

$$\frac{d[*H]}{dt} = k_d([*E] + [*A] + q \cdot [*S]) - k_f[*H] \cdot [L] + 6 \cdot k_{ex} C_{hex} \cdot *W - k_{ex}[*H]$$
(S18)

Regardless of the exchange reactions, the variation of the concentration of hexa-aquacomplex in solution is given by equation S19, which is zero if the only reaction that takes place in the solution is the exchange of water.

$$\frac{d[Ru(H_2O)_6]^{2+}}{dt} = k_d[Ru(H_2O)_5L]^{2+} - k_f[Ru(H_2O)_6^{2+}][L] = 0$$
(S19)

Using S4, S9, S18 and S19 gives equation 18 in the publication.

**Caption** for **Figure S3.** Evolution of the mole fractions of enriched water coordinated in the hexa-aquacomplex  $[Ru(H_2O)_6]^{2+}$  (**I**), in the monocomplex  $[Ru(H_2O)_5MeCN]^{2+}$  at the axial ( $\blacktriangle$ ) and equatorial (**•**) positions as a function of time at 297.8 K;  $[Ru(H_2O)_6^{2+}] = 0.031 \text{ mol kg}^{-1}$ ;  $[Ru(H_2O)_5MeCN^{2+}] = 0.038 \text{ mol kg}^{-1}$ ;  $[Htos] = 0.083 \text{ mol kg}^{-1}$ .

<sup>(1)</sup> Helm, L.; Elding, L.; Merbach, A. E. Inorg. Chem. 1985, 24, 1719.



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