Formation and *in situ* characterization of the first dihydrogen aqua complex: [Ru(H$_2$O)$_5$(H$_2$)]$^{2+}$

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The product of the reaction between [Ru(H$_2$O)$_6$]$^{2+}$ and pressurized H$_2$ in water is [Ru(H$_2$O)$_5$(H$_2$)]$^{2+}$ whose nature was unambiguously demonstrated by ^{1}H and ^{17}O NMR and which is the first characterized dihydrogen aqua complex.
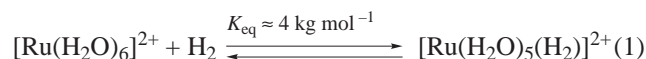
[Ru(H$_2$O)$_6$]$^{2+}$ **1** is an ideal starting material for the preparation of a great variety of new Ru(II) aqua complexes. For example, the easy reaction of **1** with dissolved gases (CO,[1] N$_2$[2] and C$_2$H$_4$[3]) to form the corresponding [Ru(H$_2$O)$_5$L]$^{2+}$ complex is of particular interest for its simplicity and its cleanliness. More interestingly, the dimerization of ethylene catalyzed by **1** in water and under very soft conditions was described.[3] The products of the reaction were identified as different butene isomers, but no indication about the mechanism was given. The existence of a hydride complex may be an intermediate in the reaction pathway. However, no ruthenium(II) aquacomplex containing either a hydride or a dihydrogen ligand has ever been described.

Morris *et al.* proposed a way to predict the stability of a H$_2$ complex.[4] If a N$_2$ complex exhibits a stretching frequency, ν_{NN}, in the range 2060–2150 cm^{-1}, the corresponding H$_2$ complex will be stable *vs.* thermally unstable complexes for $\nu > 2150$ cm^{-1} and hydrides for $\nu < 2060$ cm^{-1}. In the case of [Ru(H$_2$O)$_5$(N$_2$)]$^{2+}$, a ν_{NN} of 2156 cm^{-1} was reported for the solid compound (Nujol mull), and of 2141 cm^{-1} in aqueous solution.[2] These values indicate thus that a dihydrogen complex of limited stability could be prepared but not the hydride complex.

To a 0.1 mol kg^{-1} aqueous solution of [Ru(H$_2$O)$_6$]$^{2+}$, prepared in a home-made 10 mm sapphire tube,[5] we applied 4.0 MPa of dihydrogen pressure.† The appearance of only one new peak at −7.68 ppm (beside the peaks of the starting materials) was detected in the ^{1}H NMR spectra. After 1.5 h, Ru(0) started to deposit on the wall of the tube, probably due to the reduction of the metal by dihydrogen. A new solution was prepared containing [Ru(H$_2$O)$_6$]$^{2+}$ (0.110 mol kg^{-1}), toluene-*p*-sulfonic acid (Htos, 0.130 mol kg^{-1}) in 99.95 % D$_2$O. Subsequently, 3.9 MPa of dihydrogen was applied. After 20 min, beside the signals of the solvent and of the tosylate anion, two singlets at −7.65 and at 4.62 ppm (bound and free dihydrogen) could be observed in the ^{1}H NMR spectrum. The solution was kept under H$_2$ pressure for 19 h and shaken from time to time. Then, two 1 : 1 : 1 triplets could be observed [Fig. 1(a)] in addition to the previously mentioned singlets. The first triplet at 4.59 ppm exhibits a coupling constant, $^1J_{HD}$, of 42.8 Hz and is typical of free HD dissolved in bulk water. The second triplet at −7.68 ppm exhibits a $^1J_{HD}$ value of 31.2 Hz and an isotopic shift, δ_{HH} − δ_{HD}, of +0.023 ppm compared to the signal of bound H–H. The chemical shift as well as the coupling constant of this latter signal are characteristic of a dihydrogen ligand bound to a metal center.[6] No reduction was observed after keeping the solution for three days under H$_2$ pressure, showing the increased stability of the complex in more acidic medium.

The simplest conceivable dihydrogen complex has the formula [Ru(H$_2$O)$_5$(H$_2$)]$^{2+}$. To verify the formation of such a complex, a new solution was prepared containing [Ru(H$_2$O)$_6$]$^{2+}$ (0.0994 mol kg^{-1}) and Htos (0.562 mol kg^{-1}) in 10%

oxygen−17 enriched water.‡ Then, 54.0 MPa of dihydrogen pressure was applied to this solution at 297.0 K in a home made high gas-pressure NMR microreactor which assured a constant mixing between the solution and the gas.[7] After 35 min, a singlet at −7.54 ppm was the only new peak in the ^{1}H NMR spectrum. Simultaneously, the ^{17}O NMR spectrum revealed the appearance of two new peaks at −80.4 and −177.4 ppm beside the signal of bulk water (at 0 ppm) concomitant to the decrease of the Ru(II) hexaqua complex signal at −191.0 ppm [Fig. 1(b)]. The ratio of the integral of the two new peaks is 4.1, with is in very good agreement with the theoretical value of 4 expected for a complex of the formula [Ru(H$_2$O$_{ax}$)(H$_2$O$_{eq}$)$_4$(H$_2$)]$^{2+}$. The formation reaction of the dihydrogen complex is summarized in eqn. (1), where an estimated value of the equilibrium constant, calculated from the integrals of the ^{17}O NMR signal, is also given.

$$[\text{Ru(H}_2\text{O)}_6]^{2+} + \text{H}_2 \xrightleftharpoons{K_{eq} \approx 4 \text{ kg mol}^{-1}} [\text{Ru(H}_2\text{O)}_5(\text{H}_2)]^{2+} \quad (1)$$

An empirical equation has been proposed to calculate the H–D bond distance (in Å) from the $^1J_{HD}$ coupling constant [in Hz, eqn. (2)].[8] With a $^1J_{HD}$ value of 31.2 Hz (*vide supra*), we can
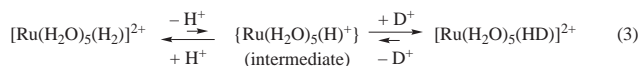
$$d_{H–D} \cong -0.0167 J_{HD} + 1.42 \quad (2)$$

calculate a H–H bond length of 0.899 Å, only slightly longer than the experimental bond length of free dihydrogen (0.740 Å). This indicates little electron back donation from the metal to the σ* antibonding orbital of the dihydrogen ligand. The main contribution to the Ru–H$_2$ bond is thus probably an electron donation from the σ orbital of H$_2$ to the metal. This should cause
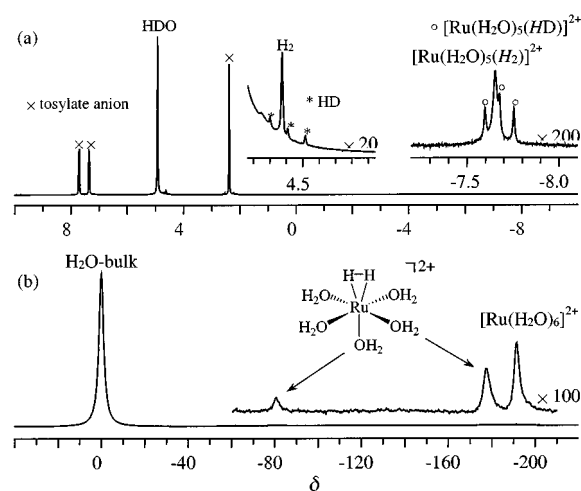
Fig. 1 (a) 400 MHz ^{1}H NMR spectrum, recorded at 298.4 K, of a solution containing initially [Ru(H$_2$O)$_6$]$^{2+}$ (0.110 mol kg^{-1}), toluene-*p*-sulfonic acid (0.130 mol kg^{-1}) in 99.95 % D$_2$O and kept for 19 h at ambient temperature and under 3.9 MPa of dihydrogen pressure in a 10 mm sapphire tube; (b) 54 MHz ^{17}O NMR spectrum, recorded at 297.0 K, of a solution containing initially [Ru(H$_2$O)$_6$]$^{2+}$ (0.099 mol kg^{-1}) and toluene-*p*-sulfonic acid (0.562 mol kg^{-1}) in 10% H$_2$^{17}O and kept for 40 min under 54.0 MPa of dihydrogen pressure at 297.0 K.

an electron depletion of the H–H bond and thus gives an acidic character to the dihydrogen ligand. This may explain the enhanced stability of the dihydrogen complex with the decrease of the pH, possibly by displacing an equilibrium between dihydrogen–hydride complexes [eqn. (3)]. The increase of the

$$[Ru(H_2O)_5(H_2)]^{2+} \underset{+\,H^+}{\overset{-\,H^+}{\rightleftarrows}} \{Ru(H_2O)_5(H)^+\} \underset{-\,D^+}{\overset{+\,D^+}{\rightleftarrows}} [Ru(H_2O)_5(HD)]^{2+} \quad (3)$$
(intermediate)

acidic character of η^2-coordinated H_2 is in accord with the formation of both bound and free HD molecules observed in the ^{1}H NMR spectra, resulting from an activation of the H–H bound by the metal center.

The longitudinal relaxation time of the ^{1}H NMR signal of bound dihydrogen was also determined at different temperatures by inversion–recovery experiments.§ The T_1 values decreased as a function of the temperature, yet the minimum of the T_1 values was not reached. Nevertheless, all the measured values, < 100 ms, confirm the dihydrogen nature of the ligand. It was shown that dihydrogen ligand has T_1 values < 100 ms but for hydride ligand the value is usually > 350 ms.[6]

The $[Ru(H_2O)_5(H_2)]^{2+}$ complex is the first example of an η^2-dihydrogen complex containing only water as other ligand in the first coordination sphere. There is thus no π-acid ligands to discharge the ruthenium center from some of its electronic density. This situation is similar to the previously reported $[Os(NH_3)_5(H_2)]^{2+}$,[9] and $[Os(NH_3)_4(H_2O)(H_2)]^{2+}$,[10] complexes where, similarly, no π-acid ligands are present in the first shell. However, for these two latter examples, very long relaxation times determined at 20 °C and 400 MHz (T_1 = 345 and 346 ms, respectively) and very small coupling constants ($^1J_{HD}$ = 15.2 and 8.1 Hz, respectively) were reported, indicating long H–H distances. This is due to electron back−donation from the osmium center to the σ^* orbital of H_2 causing the elongation of the H–H bond. A similar trend was reported for the complex $[Os(en)_2(H_2)H_2O]^{2+}$, where a dissociative mechanism for the substitution of the water molecule was assigned, with a stabilization of the penta−coordinate intermediate by rearrangement to the dihydride of Os(IV) complex, $[Os(en)_2(H)_2]^{2+}$.[11] In $[Ru(H_2O)_5(H_2)]^{2+}$, the situation is completely different as short relaxation times and large coupling constants were determined. This indicates little π-back-donation to the σ^* orbital of H_2. This is a surprising result, as it is well known that Ru(II) aqua complexes bind strongly to π−acid ligands with efficient back-donation from the metal to the ligand which stabilizes the metal center towards oxidation.[12] A similar behavior was reported for $[Ru(H_2O)_5(N_2)]^{2+}$ where it was shown using density functional calculation results that there was no π back-bonding from Ru to N_2, resulting in a weak Ru–N_2 binding energy.[12]

We report here the characterization of the first dihydrogen aquacomplex containing water as the only other ligand. The dihydrogen nature of the ligand was demonstrated by the value of the ^{1}H NMR chemical shift of the bound H_2 signal, by the longitudinal relaxation time, T_1, of this signal and by the characteristic $^1J_{HD}$ value of the coordinated H–D ligand. Moreover, the $[Ru(H_2O_{ax})(H_2O_{eq})_4(H_2)]^{2+}$ structure of the complex was demonstrated by ^{17}O NMR. The activation of the H–H bond was also demonstrated by the appearance in D_2O of the ^{1}H NMR signals of coordinated and free HD molecules. These observations may be of primary importance in understanding the catalytic activity of $[Ru(H_2O)_6]^{2+}$ in the ring opening metathesis polymerisation reaction or in the dimerisation of ethylene. It may also open a new perspective in designing new H_2 activators with very simple chemical structure and efficient catalytic activity in water.

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