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LETTER

The binding of dinitrogen to ruthenium(II) in aqueous solution

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The first dinitrogen complex to be characterized, $[Ru(NH_3)_5N_2]^{2+}$, was prepared by Allan and Senoff [1]; it is now evident that dinitrogen forms complexes with all transition elements [2]. In 1971 Creutz and Taube [3], searching for evidence of reduction of bound dinitrogen, prepared the fully aquated dinitrogen ruthenium(II) dimer $[(H_2O)_5RuN_2Ru(H_2O)_5]^{4+}$. The recent availability of solid salts of hexaaquaruthenium(II) [4] opens new and efficient synthetic routes to a remarkable variety of new compounds [5], including novel routes in aqueous organometallic catalysis [6]. In this context it was decided to try to prepare the first fully aquated monomeric dinitrogen complex $[Ru(H_2O)_5N_2](tos)_2$ (Htos = *para*-toluenesulfonic acid) according to eqn. (1). This complex should be a potentially new starting reagent and catalyst, as well as a particularly simple model compound for aqueous nitrogen fixation.

$$[Ru(H_2O)_6]^{2+} + N_2 \longrightarrow [Ru(H_2O)_5N_2]^{2+} + H_2O \qquad (1)$$

Reaction (1) was performed in a sapphire NMR tube supporting pressure up to 100 bar [7], and was followed by ^{17}O and ^{15}N NMR. $[Ru(H_2O)_6](tos)_2$ [4] was first enriched with 10% ^{17}O water (Yeda, Israel) at ambient temperature and pressure under inert atmosphere. Under these conditions the half-life of the water exchange is less than one minute ($k_{ex}^{H_2O} = 0.018\ s^{-1}$ at 298 K) [8]. The ^{17}O NMR spectrum of this solution shows the free water signal (chemical shift reference) and the characteristic signal of $[Ru(H_2O)_6]^{2+}$ at −192 ppm. The sample was then pressurized with 99% ^{15}N enriched dinitrogen (Cambridge Isotope Laboratories, USA) up to 3.7 bar and finally with normal dinitrogen at 50 bar, and mixed for one day on a shaker. As a function of time we observe for this 0.03 m (mol kg^{-1} solvent) Ru^{2+} solution the almost total disappearance of the ^{17}O signal of the hexaaquaruthenium(II) ion and the appearance of two new resonances at −165.2 and −86.2 ppm corresponding to the equatorial and axial water oxygens of $[Ru(H_2O)_5N_2]^{2+}$, respectively (Fig. 1(a)). The ratio of observed integrals is 3.8 in good agreement with the theoretical value of 4. During the same time the ^{15}N spectrum (Fig. 2(a)) shows the growth of two doublets of equal intensities on each side of the signal due to free N_2 in solution at −71.5 ppm (chemical shift reference: external

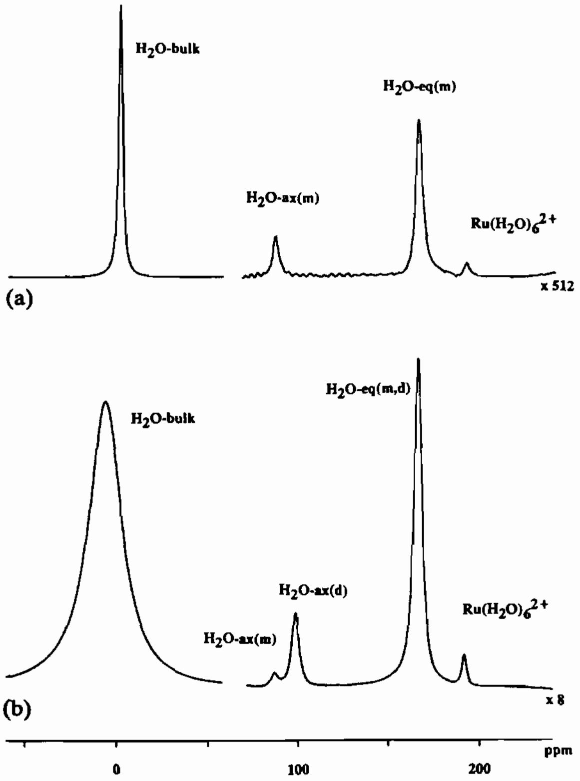

Fig. 1. 54.24 MHz ^{17}O NMR spectra of 10% ^{17}O enriched aqueous solutions, at 298 K, of: (a) $[Ru(H_2O)_5N_2]^{2+}$ 0.029 m and $[Ru(H_2O)_6]^{2+}$ 0.001 m under 50 bar pressure of dinitrogen (7.4% $^{15}N_2$) ($[N_2]_{free}$ in solution = 0.044 m); (b) $[\{Ru(H_2O)_5\}_2N_2]^{4+}$ 0.207 m, $[Ru(H_2O)_5N_2]^{2+}$ 0.066 m and $[Ru(H_2O)_6]^{2+}$ 0.020 m under 25 bar pressure of dinitrogen (11.2% $^{15}N_2$) ($[N_2]_{free}$ in solution = 0.008 m). m = monomer and d = dimer.

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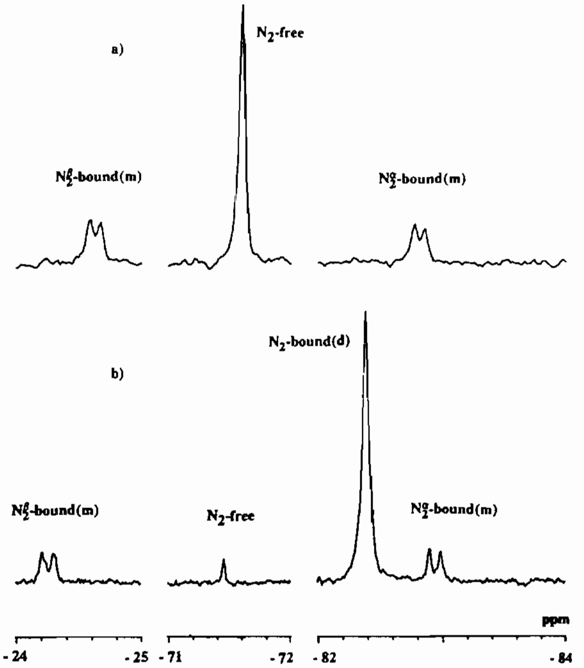

Fig. 2. 40.56 MHz ^{15}N NMR spectra of solutions (a) and (b) (see caption Fig. 1).

neat nitromethane). The two doublets are assigned to the terminally coordinated dinitrogen: the N_α atom adjacent to the metal at -82.9 ppm and the N_β distal nitrogen at -24.3 ppm. These ^{15}N chemical shift assignments are based on those made by Richards and coworkers [9] for $[Ru(NH_3)_5N_2]^{2+}$ (N_α: -81.3 ppm; N_β: -43.8 ppm) and for other terminal dinitrogen complexes. The observed $^1J(^{15}N^{15}N)$ coupling constant of 3.4 Hz is small, close to those observed previously in other metal complexes (4–7 Hz) [9]. The ambient pressure FT-IR spectrum of this yellow–brown solution shows the characteristic stretching frequency of terminally coordinated N_2 at 2141 cm^{-1}. After evaporation of the solvent water this absorption is observed at 2156 cm^{-1} in the residual solid (Nujol mull). For comparison $\nu(N_2)$ of free dinitrogen occurs at 2330 cm^{-1}, and in the analog $[Ru(NH_3)_5N_2]^{2+}$ it has been reported at 2117–2120 cm^{-1} [10]. $[Ru(H_2O)_5N_2]^{2+}$ is also less sensitive to oxidation than the hexaaqua ion.

In a second experiment we modified the experimental conditions in order to favor the formation, in a second step (eqn. (2)), of the dimer $[\{Ru(H_2O)_5\}_2N_2]^{4+}$. To reach this goal the $[Ru(H_2O)_6]^{2+}$ concentration was higher, 0.50 m instead

$$[Ru(H_2O)_5N_2]^{2+} + [Ru(H_2O)_6]^{2+} \longrightarrow [(H_2O)_5RuN_2Ru(H_2O)_5]^{4+} + H_2O \qquad (2)$$

of 0.03 m, and the nitrogen pressure was lower, 25 bar (2.8 bar 99% ^{15}N completed to 25 bar with normal N_2) instead of 50 bar. The solution was then mixed for 15 h on a shaker. The ^{17}O NMR spectrum (Fig. 1(b)) shows now, besides the decrease of the -192 ppm signal and the increase of the -165.2 and -86.2 ppm signals, the appearance of a new signal at -98.4 ppm which can be assigned to the axial water oxygen of the dimeric species. The signal of the equatorial water oxygens of the dimer has accidentally the same chemical shift as the equatorial water oxygens of the monomer. This assignment is confirmed by the 1:4 intensity ratio observed for the sum of the axial signals versus the equatorial signal. In this experiment performed at higher concentration the bulk water signal is broadened and slightly shifted by the presence of manganese(II) as trace impurity in ruthenium(II) [8]. The ^{15}N NMR (Fig. 2(b)) shows also, beside the signals observed previously, a new intense resonance at -82.4 ppm. This singlet corresponds to the two equivalent nitrogen atoms of the bridging dinitrogen in the dimer. For both experiments it has not been attempted to reach chemical equilibrium. It should also be noted that the reverse reactions are slow which is not surprising considering the behaviour of the analog pentaaminoruthenium(II) compounds [11].

In a final experiment we prepared $[Ru(H_2O)_5N_2](tos)_2$. 35 ml of a 0.05 m $[Ru(H_2O)_6](tos)_2$ (0.964 g) in 1% ^{17}O enriched water, contained in a glass vessel, was pressurised at 200 bar in a 50 ml high pressure reactor. The solution was stirred at ambient temperature with a teflon magnetic bar externally driven for 48 h. It was then opened and the reaction checked for completeness by ^{17}O NMR (absence of $[Ru(H_2O)_6]^{2+}$ and no dimer signal). The water was evaporated under vacuum and the yellow–brown solid (0.95 g) was analyzed (Analytische Laboratorien, Professor Dr H. Malissa and G. Reuter GmbH, Gummersbach, FRG). *Anal.* Calc. for $[Ru(H_2O)_5N_2](tos)_2$: Ru, 18.0; N, 4.99; S, 11.4; C, 30.0; H, 4.31. Found: Ru, 17.9; N, 4.81; S, 11.3; C, 30.0; H, 4.14%.

In conclusion, we have shown by using multinuclear NMR, that high pressure conditions allow the preparation of the first fully aquated dinitrogen monomeric ruthenium(II) complex. This will stimulate the research for similar reactions with other small molecules or metal ions.

Acknowledgements

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