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N_2-Binding Mononuclear Ruthenium(II) Tertiary Polyamine Complex by Direct Action of Gaseous Nitrogen in Aqueous Solution

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Tertiary polyamine ruthenium(III) complex *trans*-$[RuCl_2(L)]^+$ (L = 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane) has been prepared which can react with Mg and an atmospheric N_2 gas in aqueous solution at room temperature to yield the first N_2-binding ruthenium(II) tertiary polyamine complex *trans*-$[RuCl(L)(N_2)]^+$ that is converted into *trans*-$[Ru(OH)(L)(N_2)]^+$ and *trans*-$[Ru(L)(N_2)(OH_2)]^{2+}$.

N_2 uptake reaction by metal complexes in aqueous solution has long been of intrest. Harrison and Taube first found N_2-bound ruthenium complexes **1** and **2** from $[Ru(NH_3)_5(OH_2)]^{2+}$ and an atmospheric N_2 gas in aqueous solution. 1) The mononuclear complex **1** was originally discovered by Allen and Senoff in the reaction of $RuCl_3 \cdot nH_2O$ and hydrazine hydrate. 2)

$$[Ru(NH_3)_5(OH_2)]^{2+} + N_2 \rightarrow \underset{\lambda_{max} = 221\ nm}{[Ru(NH_3)_5(N_2)]^{2+}\ (\mathbf{1})} + \underset{\lambda_{max} = 263\ nm}{[Ru(NH_3)_5N_2Ru(NH_3)_5]^{4+}\ (\mathbf{2})}$$

Since then a number of N_2 complexes have been prepared from dinitrogen in *inert organic solvents.* 3) However, N_2 uptake reaction in aqueous media has never been reported with few exceptions of several ruthenium(II) complexes with aquo, ammine (above noted), diamine and tetraamine ligands. 4) In all of these cases, the main products of N_2 uptake reaction were not mononuclear dinitrogen complexes but dinuclear dinitrogen bridged ones because the rates of the dimerization reactions (e.g. **1** + $[Ru(NH_3)_5(OH_2)]^{2+} \rightarrow$ **2**) were faster than those of the formations of the mononuclear ones under normal conditions. 5) Some interesting parts of possible aqueous chemistry of N_2 complexes might be concealed in these dimerization reactions.

Herein we report a new tertiary tetraamine ruthenium complex that binds with N_2 that stays as *mononuclear* dinitrogen complexes in aqueous solution. As a ligand we used 2,5,9,12- tetramethyl-2,5,9,12-tetraazatridecane (= L) 6) which was prepared by methylation of 2,3,2-tet (= *N,N'*-bis-(2-aminoethyl)-1,3-propanediamine) with HCHO. 7)

L was mixed with $K_2[RuCl_5(OH_2)]$ (Aldrich Chemical Co. Inc.) in ethanol by Poon-Che's method 8) to yield a *trans*-dichloro-tetraamine-ruthenium complex (*trans*-$[RuCl_2(L)]^+$ (**3**)) as a chloride salt (Yield 48%). 9)

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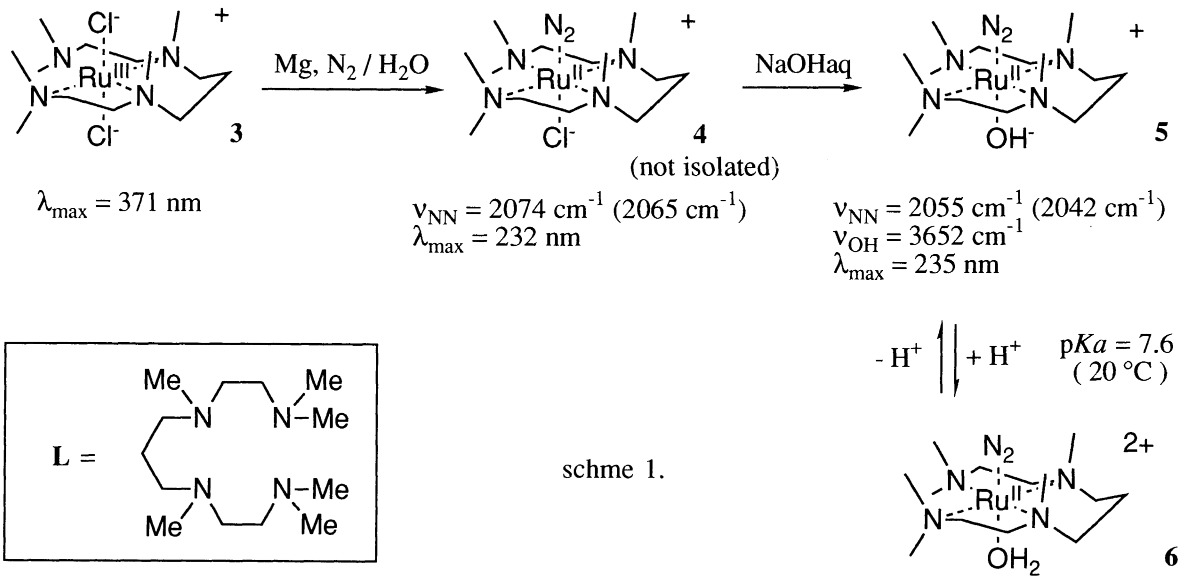

(not isolated)

λ_{max} = 371 nm

ν_{NN} = 2074 cm^{-1} (2065 cm^{-1})
λ_{max} = 232 nm

ν_{NN} = 2055 cm^{-1} (2042 cm^{-1})
ν_{OH} = 3652 cm^{-1}
λ_{max} = 235 nm

p*Ka* = 7.6 (20 °C)

schme 1.

ν_{NN} = 2113 cm^{-1} (2103 cm^{-1})
ν_{OH} = 3144 cm^{-1}
λ_{max} = 224 nm

- Configurations of unsymmetrical axial ligands have not been explicitly determined.
- Stretching frequencies in parentheses are the values for the minor species.

The aqueous solution (5 ml) of **3**•Cl (200 mg, 0.42 mmol) was put in a Schrenk flask and kept under a slow stream of nitrogen gas. To this solution was added 200 mg of magnesium turnings (Kishida Chemical Co. Ltd., Osaka, Japan) and the mixture was stirred for 24 h.[10)] The color of the solution became pale yellow, and precipitated solids together with the unreacted Mg metal were filtered off. To this filtrate, after acidified to pH 2 by CF_3SO_3H, was added concentrated aqueous solution of NH_4PF_6. Yellowish white powders of *trans*-[RuCl(L)(N_2)]PF_6 (**4**(PF_6)) precipitated, which were collected by filtration, washed with cold THF-H_2O (20:1) and ether, then dried in *vacuo* at room temperature. Yield of this crude compound was about 40-60 %. This compound showed the strong N≡N stretching bands at 2074 cm^{-1} (major) and 2065 cm^{-1} (minor) in IR spectrum and the characteristic metal to N_2 charge transfer (MLCT) band at 232 nm (ε – 10^4). Since the N_2 complex in **4** was labile and easily oxidized to Ru(III) species, it was purified as the hydroxo complex *trans*-[Ru(OH)(L)(N_2)]$^+$ (**5**) .

50 mg of **4**(PF_6) was dissolved in a 2 ml of 0.1 M (1 M = 1 mol dm^{-3}) NaOH solution and stirred under nitrogen at room temperature for 12 h. To this solution was added solid KPF_6 and stored in a refrigerator under N_2, then pale yellow needles of *trans*-[Ru(OH)(L)(N_2)]PF_6•(H_2O) (**5**(PF_6)) slowly precipitated (Yield 54%). Found: C, 28.24; H, 6.28; N, 15.22%. Calcd for $C_{13}H_{35}N_6O_2F_6PRu$: C, 28.21; H, 6.37; N, 15.18%. SIMS m/z found (calcd): **5**$^+$ 391.2 (391.2) , **5**$^+$-N_2 363.2 (363.2).

When this complex was acidified to pH 2 with CF_3SO_3H in an aqueous solution *trans*-[Ru(L)(H_2O)(N_2)](PF_6)$_2$•H_2O, (**6**(PF_6)$_2$) precipitated as pale yellow needles on addition of concentrated NH_4PF_6 aqueous solution (Yield 77%). Found: C, 22.50; H, 5.06; N, 11.98%. Calcd for $C_{13}H_{36}N_6O_2F_{12}P_2Ru$: C, 22.32; H, 5.19; N, 12.02%.

5 and **6** are appreciably stable in air in a solid state, showing sharp strong IR bands of $\nu_{N\equiv N}$ at 2055, 2042 cm^{-1} (**5**) and 2113, 2103 cm^{-1} (**6**) (in KBr pellet). Aqueous solution of them showed a strong absorption band at 235 nm (ε 1.04×10^4 in 0.1 M NaOH) (**5**) and 224 nm (ε 1.12×10^4, in 0.1M CF_3SO_3H) (**6**). These spectroscopic data resemble to those for $[Ru(NH_3)_5N_2]^{2+}$ ($\nu_{N\equiv N}$ = 2167 cm^{-1} for PF_6^- salt [11]) λ_{max} (MLCT) = 221 nm (ε 1.6×10^4) [5]) .

^{1}H NMR spectra of **5** and **6** [12]) clearly showed these complex structures had C_s symmetry (**4** also was C_s symmetry in NMR but the spectra could only be observed as mixtures with **5** or **6**).

Detailed observation of the NMR spectra and IR bands of $\nu_{N\equiv N}$ revealed the existence of isomers with C_s symmetry (from ^{1}H NMR) for each complex. These observed isomers may be aroused from the unsymmetric axial positions. For the most stable complex **5**, we have attempted recrystallization from 0.1 M NaOH for 3 times and reached to get the contents of the minor species about 5 to 8% which was at first 15 to 20 % (estimated by ^{1}H NMR). In addition, microanalytical and UV spectral data showed no change during this purification process. The explicit configurations of these isomers are now under investigation.

The pK_a of the axial aquo ligand was estimated by the titration using UV spectra. When the 1 mM NaOH solution of **5** (0.1 mM) was titrated by CF_3SO_3H (0.1 M), the recorded curves of UV spectra changed with an isosbestic point at 228 nm, and from this data pK_a was estimated to be 7.6 (20 °C). The observed change was reversible within normal experimental duration.

The values of $\nu_{N\equiv N}$ obtained for **4** and especially for **5** are considerably lower than that for **1** indicating greater π-back donation from Ru^{2+} to the coordinated dinitrogen. The order of the *trans*-influence observed in $\nu_{N\equiv N}$ was OH^- > Cl^- > H_2O in this complex.

Another unique observation on IR spectra was in the ν_{OH} region (Fig. 1). IR spectra of **5** showed a very sharp and strong band at 3652 cm^{-1} which was assigned to ν_{OH} of isolated (little influenced by hydrogen bond) OH group and the value being shifted to a higher frequency than that of water of crystallization or of adhesion. As to **6**, this band was shifted down to 3144 cm^{-1} (lower than ν_{OH} of water) and was broadened.

These observations suggest that the axial ligands are in a sterically protected environment. The *N*-methyl groups of L would prevent the commonly occurring aggregation of metal complexes through OH^-.

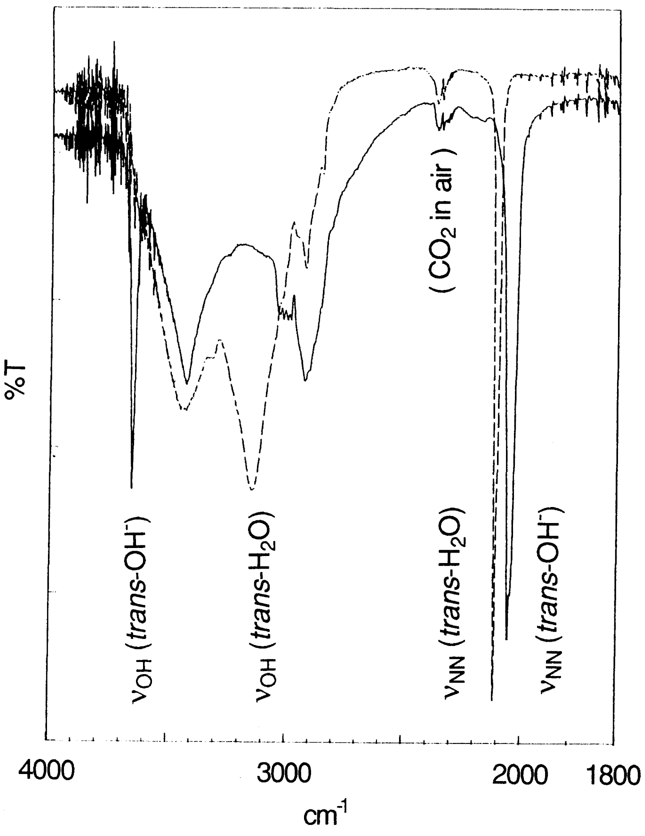

Fig. 1. IR spectra (4000 - 1800 cm^{-1}) of N_2 complexes (in KBr). —— : $5(PF_6)\cdot H_2O$, ---- : $6(PF_6)_2\cdot H_2O$.

The anticipated dimerization reaction through N_2 could also be prevented by the same effect. Through all of our experiments, N_2 bridged dimers have not been detected by UV spectra in which characteristic strong band should be observed at around 260 nm.[1,4,5] Thus the protection effect by the ligand might have resulted in the stable mononuclear N_2 complexes in which observation of pK_a or ν_{OH} was enabled.

At first, we have attempted to get the target N_2 complex by the Harrison-Taube's method using amalgamated zinc.[1] However, only trace amount of the N_2 complex formation was detected by UV spectra. The reason why the original method was not available for the present case is now under investigation.

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6) L: ^{1}H NMR: δ ($CDCl_3$) 1.65 (quintet, 2 H, J = 7.6 Hz, CH_2-CH_2-CH_2), 2.20 (s, 12 H, N-CH_3), 2.25 (s, 6 H, N-CH_3), 2.36 (t, 4 H, J = 7.6 Hz, N-CH_2-CH_2), 2.44-2.56 (m, 8H, N-CH_2CH_2-N). L•4HCl: Found C, 39.73; H, 9.28; N, 14.36%. Calcd. for $C_{13}H_{36}N_4Cl_4$. C, 40.04; H, 9.30; N, 14.36%.

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9) $[RuCl_2(L)]Cl\cdot 1.5H_2O$ (**3**•Cl), Found: C, 32.67; H, 7.17; N, 11.62%. Calcd for $C_{13}H_{35}N_4O_{1.5}Cl_3$ C, 32.61; H, 7.37; N, 11.70%. λ_{max} (in 1 M HCl) = 371 nm (ε 2.8×10^3).

10) Several reports in Ref. 3a) had utilized Mg as a reducing agent in organic solvent.

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12) ^{1}H NMR: δ (from DSS) **5** (in 0.1 M NaOD / D_2O): 1.71 (m, 1 H, CH_2-CH*H*-CH_2), 2.1–2.3 (m , 3 H, N-CH*H*-CH*H*), 2.33 (m, 4 H, N-CH*H*-CH*H*-N), 2.45, 2.65, 2.77 (s, 18 H, N-CH_3), 2.94 (m, 4 H, N-CH*H*-CH*H*-N), 3.42 (m, 2 H, N-CH*H*-CH_2). **6** (in 0.1 M CF_3SO_3H / D_2O): 1.90 (m, 1H CH_2-CH*H*-CH_2), 2.3–2.6 (m 3 H, N-CH*H*-CH*H*), 2.62 (m, 4 H, N-CH*H*-CH*H*-N), 2.51, 2.77, 2.87 (s, 18H, N-CH_3), 2.94 (m, 2 H, N-CH*H*-CH_2), 3.42 (m, 4 H, N-CH*H*-CH*H*-N).

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