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Dynamics in N_2 Uptake by New Ruthenium(II) Tertiary Polyamine Complexes in Aqueous Solution

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When Ti(III)Cl_3 was injected to aqueous 1 mM HCl solutions of *trans*-[Ru(III)Cl_2L_1]$^+$ (L_1 = 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane) under N_2, almost quantitative N_2 uptake by the reduced ruthenium(II) complex was observed. The first order initial rate constant $2.6 \pm 0.3 \times 10^{-4}$ s^{-1} was obtained which is the highest value among those so far reported. Much lower rate constants and absorption ratios were observed for homologous ruthenium tertiary polyamine complexes.

In the previous paper,[1)] we have reported the tertiary polyamine ruthenium(III) complex *trans*-[$RuCl_2(L_1)$]$^+$ (L_1 = 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane) (**1**) that reacts with magnesium metal and an atmospheric nitrogen gas in aqueous solution at room temperature to form selectively mononuclear ruthenium(II) dinitrogen complex (Scheme 1). This reaction was the first preparative method to obtain mononuclear dinitrogen complex from an atmospheric N_2 gas in aqueous solution.

Our recent observation of the redox potential of **1** ($E_{1/2}(3+/2+) = +147$mV *vs.* NHE, 25 °C) have shown that titanium(III) trichloride ($E_{1/2}$ ($TiO^{2+} + e^- + 2H^+ / Ti^{3+} + H_2O$) = 100 - 108 × p*H* mV) [2)] can reduce **1** completely (> 99%) even in acidic (p*H* > 1) conditions. This new reductant enabled us to investigate the N_2 uptake reaction progress by following the gas volume decrease.

$$\underset{\mathbf{1}}{trans\text{-}[Ru^{III}Cl_2(L_1)]^+} \xrightarrow[\substack{\text{or Ti(III)}\\ (\text{ this work })}]{Mg} \left[\ \underset{\mathbf{1^*}}{trans\text{-}[Ru^{II}Cl_2(L_1)]}\ \right] \xrightarrow{N_2} \underset{\mathbf{2}}{trans\text{-}[Ru^{II}Cl(L_1)(N_2)]^+} \xrightarrow{OH^-}$$

$$\underset{\mathbf{3}}{trans\text{-}[Ru^{II}(OH)(L_1)(N_2)]^+} \underset{H^-}{\overset{H^+}{\rightleftarrows}} \underset{\mathbf{4}}{trans\text{-}[Ru^{II}(L_1)(N_2)(H_2O)]^+}$$

Scheme 1.

Since each of the active species (**1*** in Scheme 1 is under axial ligand exchange equilibrium) [3)] and the resulting N_2-complexes in the present system is not a single species, [1)] it is almost impossible to determine all the accurate kinetical and thermodynamical parameters. To avoid this complexity in the data elucidation, we herein have analyzed the system by two parameters, one is the first order initial rate constant (k_i / s^{-1})) and the other is the final gas absorption ratio ($c = V_\infty$ (final gas volume absorbed) / V_{Ru} (maximum gas absorption volume for 1:1 complex formation to Ru)), as to represent the efficiency and the capacity of each complex as an N_2 absorber respectively. The parameters obtained here might be closely related to the first order reaction rate coefficient and the equilibrium constant in each reaction. The unprecedently fast N_2 uptake rate was discovered with **1**, which is reported herein.

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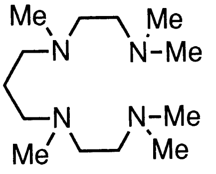
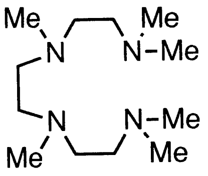
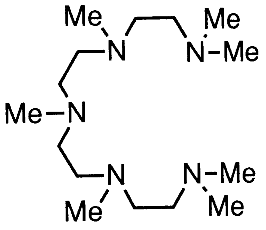
As the precursors, we here have used *trans*-[RuCl$_2$(L$_1$)]Cl (**1**•Cl), *cis*-[RuCl$_2$(L$_2$)](ClO$_4$) (**5**•ClO$_4$) 4) (L$_2$ = 2,5,8,11-tetramethyl-2,5,8,11-tetraazadodecane) and [RuCl(L$_3$)]Cl$_2$ (**6**•Cl$_2$) 5) (L$_3$ = 2,5,8,11,14-pentamethyl-2,5,8,11,14-pentaazapentadecane). 6) We also have investigated [RuCl(NH$_3$)$_5$]Cl (**7**•Cl) (Aldrich) for comparison wth the literature data.



L$_1$



L$_2$



L$_3$

In a two necked round bottomed flask (25 - 30 ml) with one inlet serum capped, and the other connected to a gas buret (20 ml) with a reservoir filled with liquid paraffin that can balance the inner pressure to the outer one (commonly used as a monitoring apparatus for hydrogenation reaction), 1 mM (1 M = 1 mol dm^{-3}) HCl aqueous solution (5 - 20 ml) of ruthenium complex was bubbled with N$_2$ gas for 20 min with continuous stirring and at the same time the gas phase within the apparatus were substituted by water saturated nitrogen gas, then all the stopcocks of the apparatus were closed and the solution was kept stirring for 20 min to allow the whole apparatus to be isothermal.

The gas volume measurement was started on the injection of 1 mM HCl solution of Ti(III)Cl$_3$ (Kanto Chemical Co. Inc., Japan) which was pre-saturated with N$_2$ gas. On injection, the color of the solutions was immediately (< 1 sec) changed from yellow to light orange, showing that the reduction of Ru(III) to Ru(II) was completely finished.

In most of the experiments, the amount of Ti(III)Cl$_3$ injected was 1.33 equivalent to Ru to ensure the reduction of Ru(III) to Ru(II). The mechanical condition was of importance for complex **1**, because the N$_2$ uptake rate was fast enough to compete with the diffusion rate. With other compounds, this mechanical factor affected little (see run 6).

Typical time courses of the reaction progress are illustrated in Fig. 1a. The N$_2$ gas absorption were observed for all the complexes investigated here. In every run except for the run 7, the gas absorption completely finished within 24 h (48 h for run 7). The N$_2$ gas absorption ratio c of each complex was calculated by averaging data around at 24 h (48 h for run 7). The initial rate constant k_i for each run is calculated by least square analyses on a plot of t to log (1 - V_t / V_{Ru}) (Fig. 1b). In this fitting procedure, all the sequential data at least for 1h were used. These results for each run are summarized in Table 1.

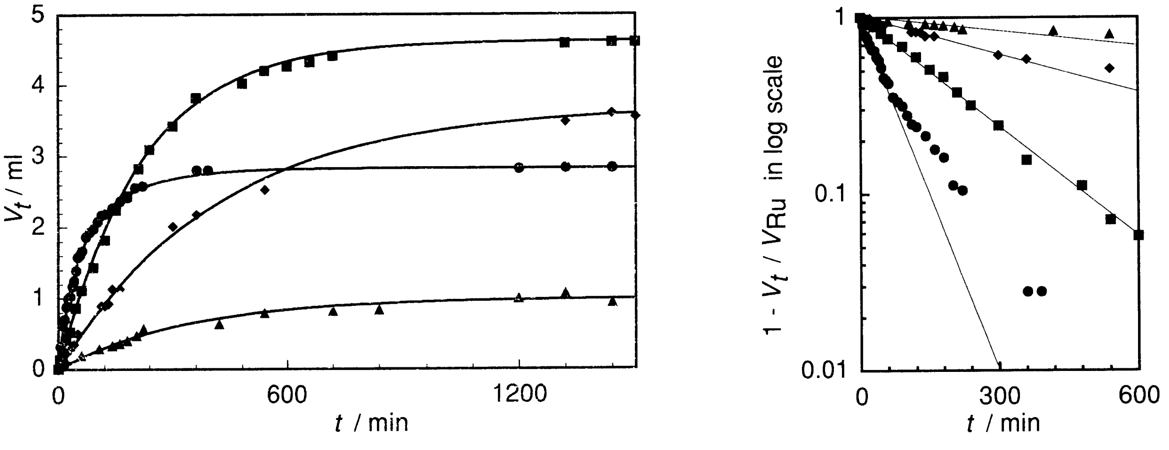


Fig. 1. (a, left) Typical time courses of N$_2$ absorption. Vt: gas volume (ml) absorbed as function of t. t: time (min). (b, right) t to log(1- V_t / V_{Ru}) plot of (a). ■: run 2, ●: run 3, ▲: run 5, ◆: run 7.

The error factors involved in these gas volume measurements mainly come from the dead volume of the apparatus (typically about 70 ml) and the fluctuation of the outer atmospheric pressure and the temparature. The other error factors (weighing error, injection volume error, gas solubility change in the solution) are less than the major error in the present experimental condition. The standard error of the observed volume fluctuation was about ± 0.1 ml in every experimental runs. The error range listed in Table 1 are calculated as the sum of the total volume error and the standard deviation in the line fitting procedures.

In run 2, which differs only in concentration from run 1, is demonstrated a good reproducibility of the experimental data. In spite of the complexity of these reaction systems, each absorption curve except for run 3 is traced on almost a single exponential curve. In case of run 3, the curve in Fig. 1 was fitted by a double exponential expression : $2.8 \text{ ml} \times (1 - 0.50 \exp (-2.8 \times 10^{-2} t) - 0.50 \exp (-7.5 \times 10^{-3} t))$.

Complex **1** shows the highest performance in both k_i and c , which are largest among the four complexes investigated here. On the other hand, the values obtained for **5** and **6** are low (run 4 - 6). The k_i in run 7 is in good agreement to the reported value of k_1 (Table 1), though the dimerization reaction in scheme 2 is not taken into account here, and both the concentration of the starting complex and the ionic strength are different from the literature conditions. 7) The first order reaction coefficients of some ruthenium amine complexes have been reported with the highest k_1 to be 8.5×10^{-5} s^{-1} for *cis*-$[Ru(trien)(H_2O)_2]^{2+}$ (trien = *N,N'*-bis(2-aminoethyl)-ethylenediamine) at 25 °C.8) Though the reaction temperature differs, the observed efficiency with **1** is 3 times larger than with the trien complex.

$$[Ru(NH_3)_5(H_2O)]^{2+} + N_2 \overset{k_1}{\rightleftharpoons} [Ru(NH_3)_5(N_2)]^{2+} + H_2O \qquad K_1$$

$$[Ru(NH_3)_5(H_2O)]^{2+} + [Ru(NH_3)_5(N_2)]^{2+} \rightleftharpoons [Ru(NH_3)_5(N_2)Ru(NH_3)_5]^{4+} + H_2O \qquad K_2$$

Scheme 2.

The final gas volume absorbed (24 h) reached about 98% of the starting Ru complex in run 1 to 3. These data indicate that the product binding with N_2 is in 1:1 molar ratio. When the final reaction solution of **1** was treated with NaOHaq (at p*H* 13 for 12 h) then precipitated solid was removed and was added solid KPF_6, *trans*-$[Ru(OH)(L)(N_2)]PF_6{\bullet}H_2O$ (**4**$\bullet PF_6$) was separated in a good yield (70%) which had completely

Table 1. Initial rate constants and absorption ratios in N_2 uptake reaction by ruthenium complexes a)

Run	Precursor complex	Ru / mmol	[Ti(III)] / [Ru]	[Ru] / mM	Initial rate const. $k_i \times 10^5$ / s^{-1}	Absorption ratio $c = V_\infty / V_{Ru}$
1	*trans*-$[RuCl_2L_1]^+$	0.192	1.33	16.7	7.8 ± 0.5	0.98 ± 0.02
2	*trans*-$[RuCl_2L_1]^+$	0.186	1.33	29.5	7.8 ± 0.5	0.98 ± 0.02
3	*trans*-$[RuCl_2L_1]^{+}$ b)	0.119	1.33	5.5	26 ± 3	0.99 ± 0.03
4	*cis*-$[RuCl_2L_2]^+$	0.189	1.33	29.6	2.2 ± 0.4	0.19 ± 0.02
5	$[RuClL_3]^{2+}$	0.213	1.33	33.1	1.4 ± 0.4	0.22 ± 0.02
6	$[RuClL_3]^{2+}$ b)	0.125	1.33	5.5	1.6 ± 0.4	0.21 ± 0.03
7	$[Ru(NH_3)_5Cl]^{2+}$ c)	0.214	1.10 d)	19.0	2.8 ± 0.5	0.72 ± 0.02
Ref.	$[Ru(NH_3)_5Cl]^{2+}$ (20.1°C) e)			2.5	2.83	0.52 (calculated) f)

a) In normal conditions, $p_{N_2} = 1.013 \times 10^5$ Pa, 21.0 ± 0.2 °C, [HCl] = 1 mM, normal stirring condition (< 300 rpm with 8 mm stirrer bar and with little fluctuation of the surface of the gas-liquid interface). b) Vigorous stirring condition (1400 rpm with a 3 cm stirring bar) . c) Initially, the solution was not homogeneous. d) 1.33 equivalent of Ti(III) caused Ru metal deposition. e) Ref. 7a. f) Though this value was not directly denoted in the paper, we could calculate this by the specified value of K_1 and K_2 (Scheme 2) at 25 °C in Ref. 7a.

identical data (UV, IR, NMR, elemental analysis) to the complex prepared by the previous method using Mg. This new preparative procedure for **3** is superior to the previous one in yield.1)

Run 4 - 6 show that complex **5** and **6** are less effective in the N_2 absorption capacity. As to **5**, the reaction rate was faster but the capacity was less than that of **6**.

Beside the existence of isomers on axial ligands,1) the lability of Cl^- ligand on Ru(II) polyamine complex 3) makes the precise determination of the equilibrium constants very complicated. Though the present experimental condition lacks in the accuracy, we have calculated an apparent binding constants defined by expression , $K = [Ru\text{-}N_2] / ([Ru]\ [N_2]) = c / \{ (1-c)\ [N_2] \}$, ($[Ru\text{-}N_2]$: the concentration of absorbed dinitrogen molecule by ruthenium, [Ru] : the concentration of ruthenium with no N_2) for each complex. A literature value for $[N_2]$ (6.6×10^{-4} M at 21 °C) 9) was used here.

K for **1**, **5**, **6** and **7** were calculated to be $> 5 \times 10^4$, $3.5 \pm 1.0 \times 10^2$, $4.5 \pm 1.0 \times 10^2$, $3.9 \pm 1.0 \times 10^3$ M^{-1}, respectively. The last data is very different from the reported K_1 (4.9×10^4 M^{-1} at 20 °C), 7a) because the dimerization reaction again was not accounted here. Thus the value of K for the complexes which are subject to dimerization becomes lower than the intrinsic equilibrium constant in the present estimation.

We have calculated the theoretical value of c using the reported K_1 and K_2 (3.3×10^3 M^{-1} at 25 °C) 7a) under the same complex concentration to run 7. The resulted value was 0.52 (25 °C) in which almost all the ruthenium ion would exist as the N_2 bridged dimer (see Scheme 2), although the experimental value in run 7 was 0.72. The UV spectra of the reaction solution showed existence of large amount of N_2-bridged dimer (λ_{max} = 263 nm) and little amount of monomer (λ_{max} = 221 nm). At present, we are not sure in this discrepancy. The possibility of formation of the N_2 bridged heteronuclear complex (e.g. $Ru\text{-}N_2\text{-}Ti$) can not be negated. However, no further investigation on this subject have been done by now.

In conclusion, we have found that a Ru(III) tertiary polyamine complex **1** can work as an excellent precursor of an efficient N_2 absorber in aqueous solution at room temperature.

References

1) T. Takahashi, K. Hiratani, and E. Kimura, *Chem. Lett.*, **1993**, 1329.
2) M. Pourbaix, "Atlas of Electrochemical Equilibrium in Aqueous Solutions," Pergamon Press (1966).
3) Unpublished result. See H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972).
4) C.-M. Che, W.-T. Tang, and M. H.-W. Lam, *J. Chem. Soc., Dalton Trans.*,**1988**, 2885.
5) $[RuCl(L3)]Cl_2 \cdot KCl \cdot 4H_2O$: Found: C, 27.83; H, 6.84; N, 10.60%. Calcd for $C_{15}H_{45}N_5O_4KRuCl_4$, C, 28.08; H, 7.07; N, 10.92%. λ_{max} (in 1 M HCl aq) = 370 nm (ε 2300). The complex was prepared by a similar method as to C.-M. Che, S.-S. Kwong, and C.-K. Poon, *Inorg. Chem.*, **24**, 1691 (1985).
6) L3: ^1H NMR (δ in $CDCl_3$), 2.24 (s, 12H, $N(CH_3)_2$), 2.26 (s, 9H, $N(CH_3)$), 2.37 - 2.51 (m, 8H, $NCH_2CH_2N(CH_3)_2$), 2.51 (s, 8H, NCH_2CH_2N). $L3 \cdot 5HCl \cdot H_2O$: Found C, 37.17; H, 9.29; N, 14.27 %. Calcd for $C_{15}H_{44}N_5OCl_5$, C, 36.93; H; 9.09; N, 14.36%. The ligand synthesis was done by a similar method as to A. G. M. Barret, C. R. A. Godfrey, D. M. Hollinshead, P. A. Prokopiou, D. H. R. Barton, R. B. Boar, L. Joukhadar, J. F. McGhie, and S. C. Misra, *J. Chem. Soc., Perkin Trans. I*, **1981**, 1501.
7) a) J. N. Armor, and H. Taube, *J. Am. Chem. Soc.*, **92**, 6170 (1970). The equilibrium constants appeared in this paper had no dimension, however the same values can be interpreted in M^{-1} ; I. J. Itzkovitch and J. A. Page, *Can. J. Chem.*, **46**, 2743, (1968); C. Elson, I.J.Itzkovitch, and J. A. Page, *ibid.*, **48**, 1639 (1970).
8) L. A. P. Kane-Maguire, *J. Inorg. Nucl. Chem.*, **33**, 3964 (1971).
9) Calcurated from the data in H. Stephen, T. Stephen, "Solubilities of Inorganic and Organic Compounds," Vol. 1, Pergamon Press (1963) ; see Ref. 7a.

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