

## A pH-stable Ruthenium(II)-based Sensing System for Dissolved Dinitrogen

Tetsuro Kizaki,<sup>1</sup> Takeru Abe,<sup>1</sup> Takahiro Matsumoto,<sup>1,2</sup> and Seiji Ogo<sup>\*1,2</sup><sup>1</sup>Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395<sup>2</sup>Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency (JST), Kawaguchi Center Building, 4-1-8 Honcho, Kawaguchi 332-0012

(Received November 17, 2009; CL-091015; E-mail: ogotcm@mail.cstm.kyushu-u.ac.jp)

Building on a previous design for a Ru-based dissolved N<sub>2</sub> sensor, we report an adaptation that allows for reversible data storage. The N<sub>2</sub> complex can be “fixed” and made stable across a range of pHs by the substitution of OH<sup>-</sup> with F<sup>-</sup> to form [Ru<sup>II</sup>(F)(TMC)(N<sub>2</sub>)]<sup>+</sup> (**1**, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The addition of Ca<sup>2+</sup> and irradiation with light at high pH removes the F<sup>-</sup>, thereby regenerating the sensor in its reversible configuration.

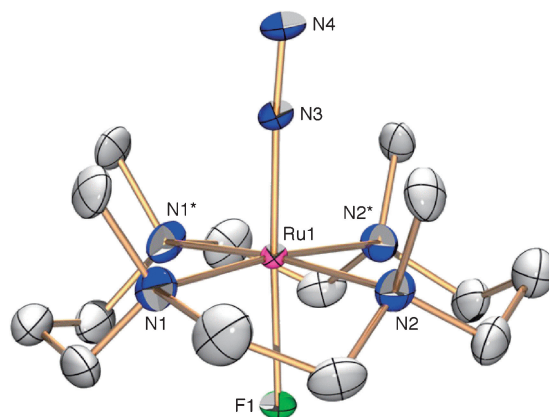
In a recent publication, we reported a Ru-based complex [Ru<sup>II</sup>(OH)<sub>2</sub>(TMC)] (**C**, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) that is capable of colorimetrically sensing N<sub>2</sub> dissolved in aqueous solutions at N<sub>2</sub> partial pressures as low as 0.01 MPa.<sup>1</sup> This complex was based on a Ru<sup>II</sup> center coordinated to a TMC macrocycle, with the crucial feature of two hydroxo ligands in the axial positions. These hydroxo ligands could be sequentially protonated at successively lower pHs to form the corresponding complexes with aqua ligands [Ru<sup>II</sup>(OH)(H<sub>2</sub>O)(TMC)](PF<sub>6</sub>) {**[B]**(PF<sub>6</sub>)}, and [Ru<sup>II</sup>(H<sub>2</sub>O)<sub>2</sub>(TMC)](PF<sub>6</sub>)<sub>2</sub> {**[A]**(PF<sub>6</sub>)<sub>2</sub>}.<sup>1</sup> Such protonation destabilized the N<sub>2</sub> complex, essentially “switching off” the sensor. It should be noted that the dihydroxo complex **C** was so sensitive to N<sub>2</sub> that it could be only observed under an Ar atmosphere.<sup>1</sup>

In an effort to stabilize the sensor across all pHs, we substituted one of the OH<sup>-</sup> ligands with a F<sup>-</sup> ligand. We considered that hard ligand capable of strong π donation would produce a complex with chemical behavior similar to that of [Ru<sup>II</sup>(OH)(TMC)(N<sub>2</sub>)](PF<sub>6</sub>) {**[D]**(PF<sub>6</sub>)},<sup>1</sup> without being liable to deactivation by protonation.

Hereafter, we report the characterization and synthesis of the water-soluble, Ru-based, N<sub>2</sub> complex, [Ru<sup>II</sup>(F)(TMC)(N<sub>2</sub>)](PF<sub>6</sub>) {**[1]**(PF<sub>6</sub>)}, with a F<sup>-</sup> ligand coordinated to the Ru<sup>II</sup> center. We also describe its ability to reversibly store N<sub>2</sub> concentration data.

A single crystal of **[1]**(BF<sub>4</sub>)·H<sub>2</sub>O suitable for X-ray analysis was obtained by the addition of NaBF<sub>4</sub> to an aqueous solution of **[1]**(PF<sub>6</sub>).<sup>2</sup> The structure of **[1]**<sup>+</sup> is shown in Figure 1. The Ru<sup>II</sup> center adopts a distorted octahedral coordination surrounded by one TMC, one F<sup>-</sup>, and one N<sub>2</sub> ligand with a Ru1–N3 length of 1.847(5) Å, a Ru1–F1 length of 2.015(3) Å, and a Ru1–N3–N4 angle of 176.3(5)°. The N3–N4 length of 1.144(8) Å in **1** is slightly longer than that of free N<sub>2</sub> (1.098 Å),<sup>3</sup> which is consistent with back-donation of electron density from the t<sub>2g</sub> orbital of Ru<sup>II</sup> to the π\* anti-bonding orbital of N<sub>2</sub>. The N–N bond length in **1** is comparable to that in the N<sub>2</sub> complex **D** {1.128(6) Å} and longer than those in most Ru<sup>II</sup>N<sub>2</sub> complexes. This is the first example of a water-soluble, F<sup>-</sup>-coordinated, N<sub>2</sub> complex.

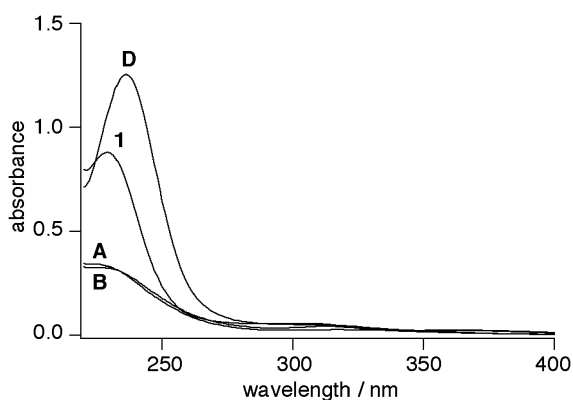
The IR spectrum of **[1]**(PF<sub>6</sub>) in the solid state shows a sharp band at 2064 cm<sup>-1</sup> typical of ν(N≡N)<sup>4–8</sup> in an end-on fashion



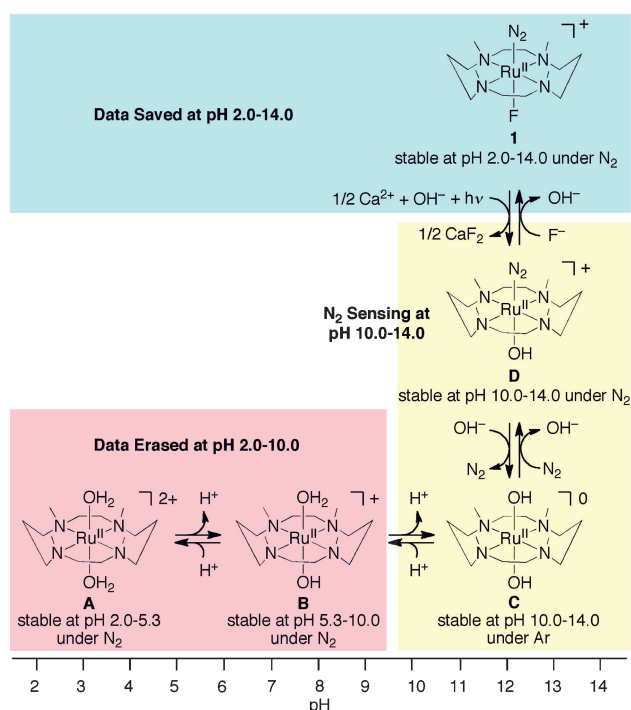
**Figure 1.** An ORTEP drawing of **[1]**<sup>+</sup> with ellipsoids at 30% probability. The counter anion (BF<sub>4</sub><sup>-</sup>), the solvent (H<sub>2</sub>O), and the hydrogen atoms are omitted for clarity. Selected interatomic distances (l/Å) and angles (ϕ/degree): N3–N4 = 1.144(8), Ru1–N1 = 2.126(4), Ru1–N3 = 1.847(5), Ru1–F1 = 2.015(3), Ru1–N3–N4 = 176.3(5), F1–Ru1–N3 = 177.6(2), N1–Ru1–N2 = 85.99(17), N1–Ru1–N1\* = 93.61(17), N2–Ru1–N2\* = 93.71(16).

(Figure S1 in Supporting Information).<sup>9</sup> The lowering of the ν(N≡N) relative to that of free N<sub>2</sub> (2331 cm<sup>-1</sup>)<sup>10</sup> is in agreement with a weakening of the N–N bond in comparison to the free N<sub>2</sub> molecule. The ν(N≡N) in **1** is comparable to that in **D** (2050 cm<sup>-1</sup>),<sup>1</sup> which indicates the axial F<sup>-</sup> ligand is not different from the OH<sup>-</sup> ligand with respect to the electronic effect on the stretching vibration of N<sub>2</sub>. However, the behavior of **1** toward the change of pH is quite different from **D**. The IR spectra of aqueous solutions of **[1]**(PF<sub>6</sub>) show a sharp band at 2069 cm<sup>-1</sup>, responsible for the ν(N≡N), and is observed at pH 2.0–14.0. This result demonstrates that the structure of **1** remains over a wide pH range. Conversely, the N<sub>2</sub> complex **D** releases N<sub>2</sub> at pH 2.0–10.0 although the structure is stable at pH 10.0–14.0.<sup>1</sup>

Complex **1** with Ca<sup>2+</sup> was irradiated with halogen light (YAMAZEN YHL-500S without any filter, 500 W) in water at pH 11.0 at 25 °C for 6 h under a N<sub>2</sub> atmosphere to give **D** and CaF<sub>2</sub> (Figure S2 in Supporting Information).<sup>9,11</sup> Figure S2a shows the positive-ion electrospray ionization (ESI) mass spectrum of **1** in water at pH 11.0 before irradiation. The prominent signal at m/z 405.3 {relative intensity (I) = 100% in the range of m/z 100–2000} has a characteristic isotopic distribution (Figure S2b) that matches well with the calculated isotopic distribution for **[1]**<sup>+</sup> (Figure S2c). After irradiation, the prominent signal at m/z 405.3 was shifted to the prominent signal at m/z 403.3 (Figure S2d), which has a characteristic isotopic distribution (Figure S2e) that matches well with the calculated isotopic distribution for **[D]**<sup>+</sup> (Figure S2f). At



**Figure 2.** UV-vis spectra of the aqueous solutions of **A** at pH 2.0, **B** at pH 7.0, **D** at pH 12.0, and **1** at pH 12.0 under a  $N_2$  atmosphere.



**Figure 3.** pH-dependent properties of all five  $Ru^{II}$  complexes. Interconversion of **1** to **D** proceeds in the reaction of  $[1](PF_6)$  (100  $\mu M$ ) with  $CaSO_4$  (3.0 mM) in water in the range of pH 10.0–14.0 with halogen light at 25  $^\circ C$  for 6 h under a  $N_2$  atmosphere. Interconversion of **D** to **1** proceeds in the reaction of  $[D](PF_6)$  (100  $\mu M$ ) with NaF (100 mM) in water in the range of pH 10.0–14.0 at 25  $^\circ C$  under a  $N_2$  atmosphere for 18 h in the dark. Reversible interconversion between **A** and **D** via **B** and **C** has been previously reported.<sup>1</sup>

pH 10.0–14.0, the irradiation of the aqueous solution of **1** and  $Ca^{2+}$  with halogen light gave **D**. Complex **D** reacted with  $F^-$  in water at pH 10.0–14.0 to form **1**.

Figure 2 shows UV-vis spectra of the aqueous solutions of **A** at pH 2.0, **B** at pH 7.0, **D** at pH 12.0, and **1** at pH 12.0, respectively. The UV-vis spectra of **D** and **1** exhibit intense bands at 235 and 228 nm, respectively, assigned to the  $Ru^{II}-N_2$  metal-to-ligand charge-transfer (MLCT) transition,<sup>4,7</sup> and the shoulders around 310 nm, assigned to d-d transition.<sup>12</sup>

Complex **D** is stable in water at pH 10.0–14.0, however, **D**

releases  $N_2$  to give **A** via **B** and **C** by decreasing pH from 10.0 to 2.0. In contrast to **D**, **1** is stable in water over a wide range of pH.

Figure 3 summarizes the pH-dependent properties of all five  $Ru^{II}$  complexes. The structure of **A** is changed to **B** by raising the pH. Complex **B**, via a short-lived dihydroxo complex **C**, can coordinate to  $N_2$  at pHs above 10 at 25  $^\circ C$  for 1 min to form complex **D**. Adding  $F^-$  to **D** forms complex **1** which is stable over a wide range of pH. Complex **1** can then be reverted to **D** by the simple application of  $Ca^{2+}$  ions and light.

This behavior could potentially be used for reversible data storage of dissolved  $N_2$  sensor information. As a first step, complex **C** would behave as a  $N_2$  sensor at pH 10.0–14.0. Adding  $F^-$  would then lock this data and protect it against erasure by protonation. To unlock the data,  $Ca^{2+}$  ions and light would be applied at high pH and the data could then be erased by lowering the pH. All of the chemical processes described above have been performed in the laboratory and so relatively little work is required to develop this system for data recording. We expect the principles at work here will allow a wide variety of new applications.

This work was supported by Grants-in-Aid: Nos. 17350027, 17655027, 18033041, and 18065017 (Chemistry of Concerto Catalysis), the Global COE Program, “Science for Future Molecular Systems” from the Ministry of Education, Culture, Sports, Science and Technology, Japan and the Basic Research Programs CREST Type, “Development of the Foundation for Nano-Interface Technology” from JST, Japan.

#### References and Notes

- 1 T. Kizaki, T. Matsumoto, S. Ogo, *Dalton Trans.* **2010**, in press. doi:10.1039/b918940h
- 2 The crystal data for  $[1](BF_4)\cdot H_2O$  have been deposited with Cambridge Crystallographic Data Center as a supplementary publication No. CCDC-753963.
- 3 a) P. G. Wilkinson, N. B. Houk, *J. Chem. Phys.* **1956**, *24*, 528. b) P. G. Wilkinson, *Can. J. Phys.* **1956**, *34*, 250.
- 4 a) A. D. Allen, C. V. Senoff, *Chem. Commun.* **1965**, 621. b) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, C. V. Senoff, *J. Am. Chem. Soc.* **1967**, *89*, 5595. c) A. D. Allen, F. Bottomley, *Acc. Chem. Res.* **1968**, *1*, 360.
- 5 a) D. E. Harrison, H. Taube, *J. Am. Chem. Soc.* **1967**, *89*, 5706. b) D. F. Harrison, E. Weissberger, H. Taube, *Science* **1968**, *159*, 320. c) H. A. Scheidegger, J. N. Armor, H. Taube, *J. Am. Chem. Soc.* **1968**, *90*, 3263. d) C. Creutz, H. Taube, *Inorg. Chem.* **1971**, *10*, 2664. e) I. M. Treitel, M. T. Flood, R. E. Marsh, H. B. Gray, *J. Am. Chem. Soc.* **1969**, *91*, 6512.
- 6 a) L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, R. G. Pearson, *J. Am. Chem. Soc.* **1968**, *90*, 5295. b) L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, R. G. Pearson, *J. Am. Chem. Soc.* **1970**, *92*, 5865.
- 7 a) T. Takahashi, K. Hiratani, E. Kimura, *Chem. Lett.* **1993**, 1329. b) T. Takahashi, K. Hiratani, K. Kasuga, E. Kimura, *Chem. Lett.* **1993**, 1761. c) K. Okamoto, T. Takahashi, K. Kohdate, H. Kondoh, T. Yokoyama, T. Ohta, *J. Synchrotron Rad.* **2001**, *8*, 689.
- 8 a) J. P. Collman, P. S. Wagenknecht, J. E. Hutchison, *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1537. b) M. Hidai, Y. Mizobe, *Chem. Rev.* **1995**, *95*, 1115. c) S. C. Lee, R. H. Holm, *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 3595. d) M. D. Fryzuk, S. A. Johnson, *Coord. Chem. Rev.* **2000**, *200–202*, 379.
- 9 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.
- 10 H. P. Wang, J. T. Yates, Jr., *J. Phys. Chem.* **1984**, *88*, 852.
- 11 W. Weber, P. C. Ford, *Inorg. Chem.* **1986**, *25*, 1088.
- 12 a) V. I. Baranovskii, N. V. Ivanova, A. B. Nikol'skii, *J. Struct. Chem.* **1973**, *14*, 115. b) C.-M. Che, K.-Y. Wong, C.-K. Poon, *Inorg. Chem.* **1986**, *25*, 1809.