

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

Tetsuro Kizaki,¹ Takeru Abe,¹ Takahiro Matsumoto,^{1,2} and Seiji Ogo^{*1,2}¹Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Moto-oka, Nishi-ku, Fukuoka 819-0395²Core 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 N₂ sensor, we report an adaptation that allows for reversible data storage. The N₂ complex can be “fixed” and made stable across a range of pHs by the substitution of OH⁻ with F⁻ to form [Ru^{II}(F)(TMC)(N₂)]⁺ (**1**, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). The addition of Ca²⁺ and irradiation with light at high pH removes the F⁻, thereby regenerating the sensor in its reversible configuration.

In a recent publication, we reported a Ru-based complex [Ru^{II}(OH)₂(TMC)] (**C**, TMC = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) that is capable of colorimetrically sensing N₂ dissolved in aqueous solutions at N₂ partial pressures as low as 0.01 MPa.¹ This complex was based on a Ru^{II} 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^{II}(OH)(H₂O)(TMC)](PF₆) {**[B]**(PF₆)}, and [Ru^{II}(H₂O)₂(TMC)](PF₆)₂ {**[A]**(PF₆)₂}.¹ Such protonation destabilized the N₂ complex, essentially “switching off” the sensor. It should be noted that the dihydroxo complex **C** was so sensitive to N₂ that it could be only observed under an Ar atmosphere.¹

In an effort to stabilize the sensor across all pHs, we substituted one of the OH⁻ ligands with a F⁻ ligand. We considered that hard ligand capable of strong π donation would produce a complex with chemical behavior similar to that of [Ru^{II}(OH)(TMC)(N₂)](PF₆) {**[D]**(PF₆)},¹ without being liable to deactivation by protonation.

Hereafter, we report the characterization and synthesis of the water-soluble, Ru-based, N₂ complex, [Ru^{II}(F)(TMC)(N₂)](PF₆) {**[1]**(PF₆)}, with a F⁻ ligand coordinated to the Ru^{II} center. We also describe its ability to reversibly store N₂ concentration data.

A single crystal of **[1]**(BF₄)·H₂O suitable for X-ray analysis was obtained by the addition of NaBF₄ to an aqueous solution of **[1]**(PF₆).² The structure of **[1]**⁺ is shown in Figure 1. The Ru^{II} center adopts a distorted octahedral coordination surrounded by one TMC, one F⁻, and one N₂ 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 N₂ (1.098 Å),³ which is consistent with back-donation of electron density from the t_{2g} orbital of Ru^{II} to the π* anti-bonding orbital of N₂. The N–N bond length in **1** is comparable to that in the N₂ complex **D** {1.128(6) Å} and longer than those in most Ru^{II}N₂ complexes. This is the first example of a water-soluble, F⁻-coordinated, N₂ complex.

The IR spectrum of **[1]**(PF₆) in the solid state shows a sharp band at 2064 cm⁻¹ typical of ν(N≡N)^{4–8} in an end-on fashion

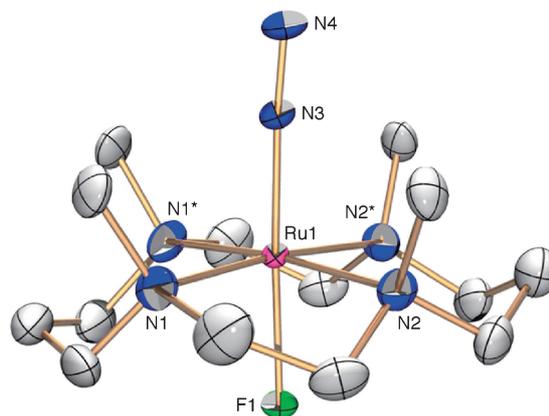


Figure 1. An ORTEP drawing of **[1]**⁺ with ellipsoids at 30% probability. The counter anion (BF₄⁻), the solvent (H₂O), and the hydrogen atoms are omitted for clarity. Selected interatomic distances (*l*/Å) and angles (*φ*/degree): N3–N4 = 1.144(8), Ru1–N1 = 2.126(4), Ru1–N3 = 1.847(5), Ru1–F1 = 2.015(3), 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).⁹ The lowering of the ν(N≡N) relative to that of free N₂ (2331 cm⁻¹)¹⁰ is in agreement with a weakening of the N–N bond in comparison to the free N₂ molecule. The ν(N≡N) in **1** is comparable to that in **D** (2050 cm⁻¹),¹ which indicates the axial F⁻ ligand is not different from the OH⁻ ligand with respect to the electronic effect on the stretching vibration of N₂. However, the behavior of **1** toward the change of pH is quite different from **D**. The IR spectra of aqueous solutions of **[1]**(PF₆) show a sharp band at 2069 cm⁻¹, 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 N₂ complex **D** releases N₂ at pH 2.0–10.0 although the structure is stable at pH 10.0–14.0.¹

Complex **1** with Ca²⁺ 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 N₂ atmosphere to give **D** and CaF₂ (Figure S2 in Supporting Information).^{9,11} 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]**⁺ (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]**⁺ (Figure S2f). At

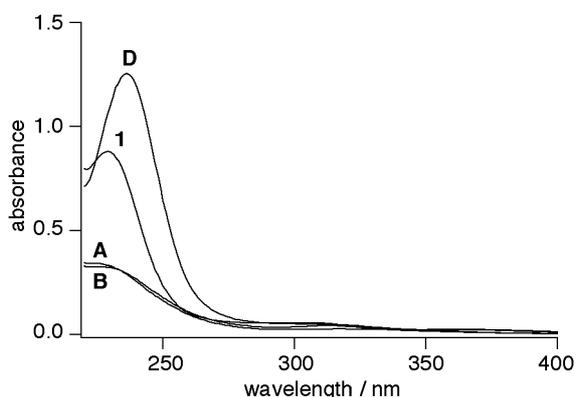


Figure 2. UV-vis spectra of the aqueous solutions of **A** at pH 2.0, **B** at pH 7.0, **D** at pH 12.0, and **1** at pH 12.0 under a N_2 atmosphere.

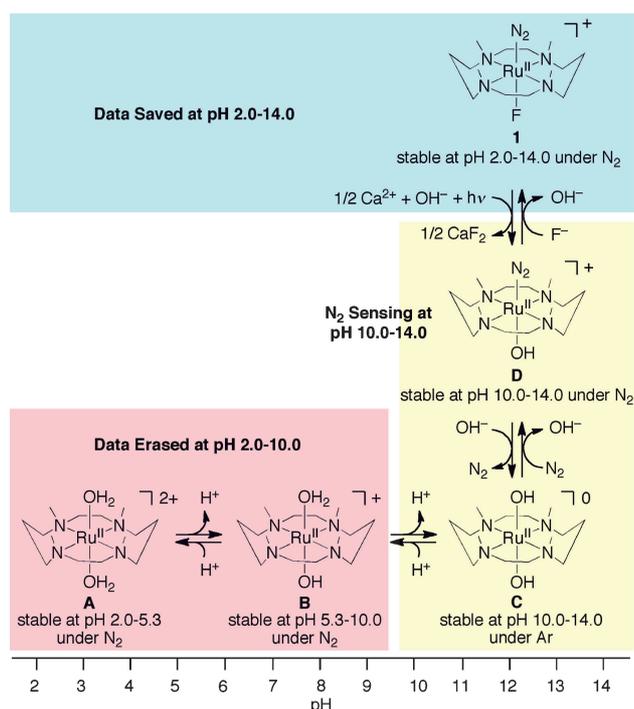


Figure 3. pH-dependent properties of all five Ru^{II} complexes. Interconversion of **1** to **D** proceeds in the reaction of $[1](PF_6)$ (100 μM) with $CaSO_4$ (3.0 mM) in water in the range of pH 10.0–14.0 with halogen light at 25 $^{\circ}C$ for 6 h under a N_2 atmosphere. Interconversion of **D** to **1** proceeds in the reaction of $[D](PF_6)$ (100 μM) 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.¹

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,^{4,7} and the shoulders around 310 nm, assigned to d-d transition.¹²

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.