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Short Note

Cis-Bis(2,2′-Azopyridinido)dicarbonylruthenium(II)

Tsugiko Takase [1,*], Shuya Kainuma [2], Takatoshi Kanno [2] and Dai Oyama [1,*]

[1] Department of Natural Sciences and Informatics, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan
[2] Graduate School of Science and Engineering, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan; s.016.kai@gmail.com (S.K.); s1970013@ipc.fukushima-u.ac.jp (T.K.)
* Correspondence: ttakase@sss.fukushima-u.ac.jp (T.T.); daio@sss.fukushima-u.ac.jp (D.O.); Tel.: +81-24-548-8199 (D.O.)

Abstract: An $[Ru(apy)_2Cl_2]$ precursor (apy = 2,2′-azopyridine) in 2-methoxyethanol was heated under a pressurized CO atmosphere to afford a diradical complex, $[Ru(apy^{\cdot-})_2(CO)_2]$, containing one-electron-reduced azo anion radical ligands. The electronic states of the complex were characterized by spectroscopic techniques and computational studies. Magnetic measurements revealed the existence of antiferromagnetic interactions in the diradical complex.

Keywords: ruthenium; carbonyl complex; azopyridine; anion radical; electronic structure; magnetic properties

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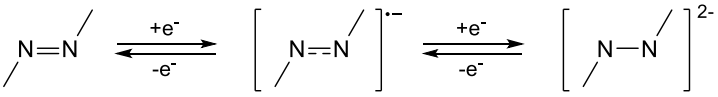
1. Introduction

The oxidation number of the central metal atom in a complex generally determines the electronic states of the complex. In a metal complex containing a redox-active non-innocent ligand, conversely, ligands as well as the metal centers can also control the electronic states of the complex. For example, azo compounds can directly accept one or two electrons because they have a low-lying azo-centered vacant π* molecular orbital (Scheme 1) [1]. Due to this property, many transition metal complexes, particularly those in groups 7 and 8, containing azopyridyl ligands, e.g., 2,2′-azopyridine (apy) and 2-phenylazopyridine (pap), (Figure 1a), have been reported [2–7]. Based on numerous studies, metal complexes containing non-innocent azo ligands are expected to be applied to multifunctional materials which surpass conventional magnetic materials, such as metal oxides [8,9].



Scheme 1. Two-step electron transfers in azo compounds.

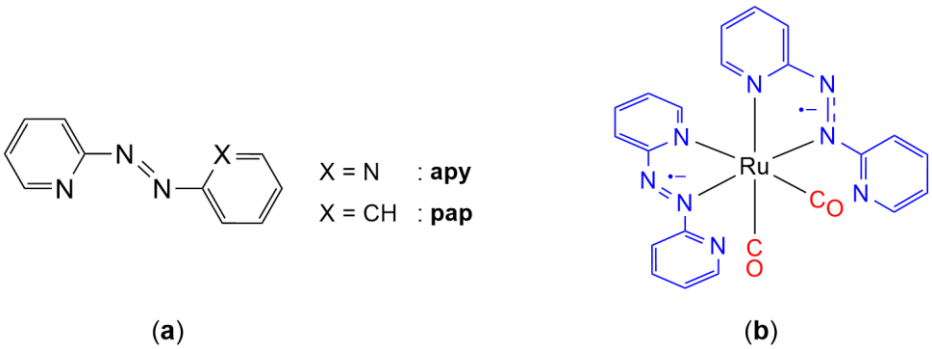


Figure 1. Chemical structures of (**a**) azopyridines; (**b**) The Ru-complex presented in this study.

We have previously reported the synthesis and properties of a monocarbonylruthenium(II) complex containing two azopyridine molecules [10]. All the azopyridyl ligands in the monocarbonyl complex were neutral (nonradical, singlet state: $S = 0$). In contrast, the newly synthesized dicarbonylruthenium(II) complex in this work (Figure 1b) experimentally and theoretically revealed that both the azopyridyl ligands are coordinated as anion radicals (triplet state: $S = 1$). Additionally, the magnetic properties of the diradical complex were examined.

2. Results and Discussion

2.1. Synthesis and Characterization of the Diradical Complex

We previously reported the detailed characterization, including X-ray crystallography, of the monocarbonyl complex ($[Ru(pap)_2(CO)Cl]^+$) [10]. In this report, we confirmed that the two azo ligands were neutral in the monocarbonyl complex. Meanwhile, two carbonyl stretching frequencies in the newly prepared dicarbonyl complex were observed at 2060 and 1995 cm^{-1} in the IR spectra (Figure S1). These values are 30–40 cm^{-1} lower than those of similar Ru complexes ($[Ru(N\text{-}N)_2(CO)_2]^{2+}$; N-N = bidentate pyridyl ligands) [11–13]. The reason is that the reduction of the azo moiety increases the electron density of the complex, resulting in a red shift of the CO bands [5]. Additionally, no peaks assignable to the present complex were observed in the mass spectra, and its ^{1}H-NMR spectrum was silent. It is, therefore, interpreted that the introduction of two CO molecules, which function as ligand and reducing agents, led to the selective formation of the diradical neutral complex, in which both the azo ligands underwent one-electron reduction (Equation (1)).

$$[Ru^{II}(apy)_2Cl_2] + 2CO \rightarrow [Ru^{II}(apy^{\cdot -})_2(CO)_2] + 2Cl^- \quad (1)$$

2.2. Electronic Structure Analysis

We performed quantum chemical calculations for both the diradical and the corresponding nonradical complexes to evaluate their stability (Figure S2). The adiabatic energy gap between the two complexes in methanol were calculated (1530.0478 Hartree for the nonradical state and 1530.3652 Hartree for the diradical one) [14]. The results indicate that the diradical state is 30.75 kcal/mol more stable than the nonradical one. Figure 2 shows the spin densities in the optimized structures. Since the spin densities of both azo sites in the diradical state are 0.623, the azo site is the primary spin-bearing center.

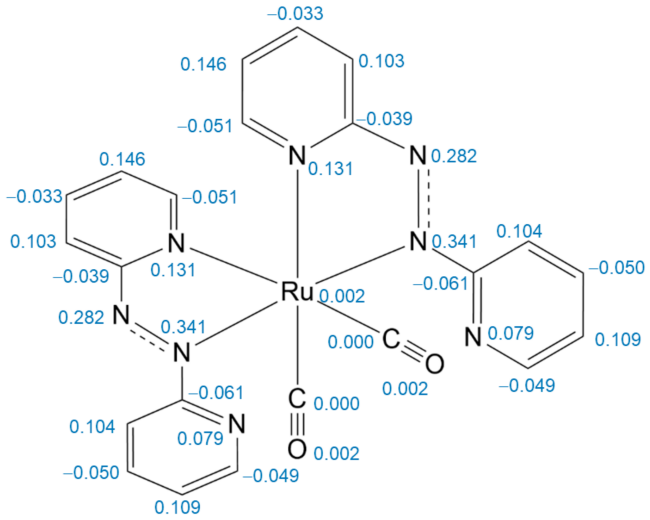


Figure 2. Spin density analyses for $[Ru(apy^{\cdot -})_2(CO)_2]$, calculated at the DFT/B3LYP/LanL2DZ/6-31G(d) level of theory.

Figure 3a shows the estimated absorption spectra of the nonradical ($S = 0$) and diradical complexes ($S = 1$) using time-dependent density functional theory (TDDFT) calculations. It is presumed that the nonradical complex exhibits absorption maximum around 400 nm, while the diradical one exhibits absorptions around 350 and 470 nm. Since the latter values are consistent with the spectral data of the prepared complex (λ_{max} = 355 and 487 nm; Figure 3b), computational results also suggested that the present complex contains two anion radical ligands (apy·$^{-}$).

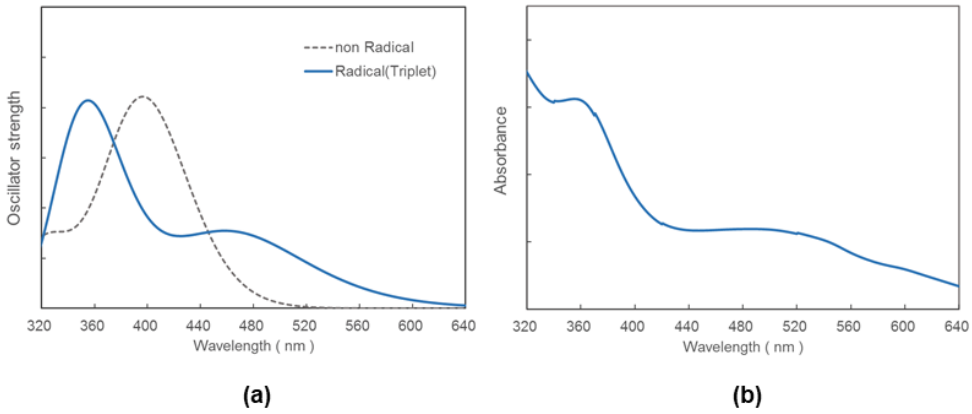


Figure 3. (**a**) The theoretical absorption spectra calculated for the singlet and triplet spin configurations of $[Ru(apy)_2(CO)_2]^{2+/0}$ at the TDDFT/B3LYP/LanL2DZ/6-31G(d) level of theory; (**b**) The absorption spectrum of $[Ru(apy^{\cdot -})_2(CO)_2]$.

2.3. Magnetic Properties

To experimentally confirm that the present complex is a radical complex with unpaired spins, we carried out measurements of the dependence of the magnetic moment on the external magnetic field (*M*-*H* properties). Since $M = \chi H$ (M: magnetic moment, H: external applied magnetic field, χ: magnetic molar susceptibility) is satisfied within the temperature range measured, the complex is the radical complex, which displays paramagnetic properties. Additionally, the Curie–Weiss law defined by Equation (2) (C: Curie constant, T: absolute temperature, θ: Weiss constant) is satisfied in the low-temperature region bearing on the temperature dependence of the magnetic susceptibility (the applied magnetic field of 10000 Oe) as shown in Figure 4; the Weiss constant is negative ($\theta = -10.7$ K), suggesting that antiferromagnetic interactions exist between the spins in each radical [5].

$$\chi = C/(T - \theta) \quad (2)$$

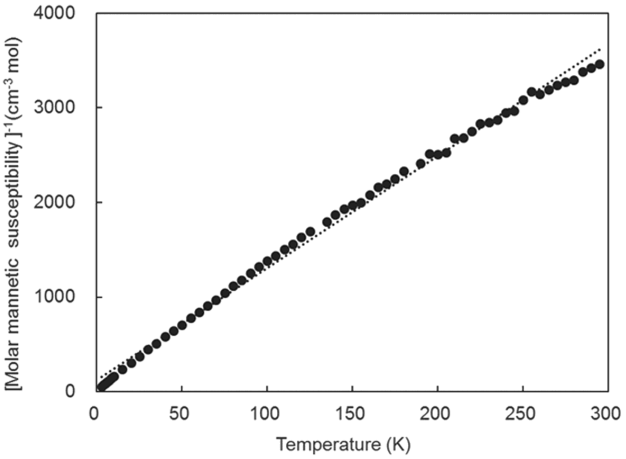


Figure 4. Temperature dependence of the inverse molar magnetic susceptibility for $[Ru(apy^{\cdot -})_2(CO)_2]$.

In summary, we have found that the electronic state of an azo ligand can be controlled by the number of coordinated carbonyls, i.e., the monocarbonyl complex has neutral azo ligands, whereas the corresponding dicarbonyl one led to anion radicals. The latter complex exhibited paramagnetic and antiferromagnetic interactions between the spins in each radical. Further studies using analogous compounds are underway, directed toward the development of multifunctional materials in detail.

3. Materials and Methods

3.1. Measurements

The infrared (IR) spectra were obtained using a JASCO FT-IR 4100 spectrometer (JASCO Corporation, Hachioji, Japan). The elemental analysis data were obtained on a Perkin-Elmer 2400II series CHN analyzer (Perkin-Elmer, Inc., Waltham, MA, USA). The absorption spectra were obtained on a JASCO V-560 spectrophotometer (JASCO Corporation, Hachioji, Japan). The magnetic susceptibilities of the complex were recorded on a SQUID magnetometer (MPMS, Quantum Design, Inc., San Diego, CA, USA) in the temperature range of 5–300 K. DFT and TDDFT calculations were performed using the quantum chemical program, Gaussian 16 [15]. The geometries of the complex in its singlet (S = 0) or triplet (S = 1) states were fully optimized by restricted (singlet) or unrestricted (triplet) DFT methods employing the B3LYP function [16,17], with a 6-31G(d) basis set for the light elements [18,19] and a LanL2DZ basis set [20] for the Ru atom. The solvent effect of methanol was evaluated using an implicit solvent model, and a conductor-like polarizable continuum model (CPCM). Vibrational analyses were performed at the same calculation level employed for geometry optimization. The spin density analyses were also calculated at the optimized geometry. Excited-state calculations based on the B3LYP-optimized geometries were conducted for the TDDFT formalism in methanol using the CPCM.

3.2. Synthesis of the Complex

The compound, 2,2′-azopyridine (apy), and the starting material ($[Ru(apy)_2Cl_2]$) were prepared according to known procedures or through modification of published methods [21,22].

A solution of $[Ru(apy)_2Cl_2]$ (38 mg, 0.071 mmol) in 2-methoxyethanol (40 mL) was heated to 100 °C under an atmosphere of CO (2 MPa) for 72 h. The volume was reduced to 5 mL using a rotary evaporator, and a black precipitate was formed by the addition of diethyl ether. The product was collected by filtration, washed with diethyl ether, and dried in vacuo. The crude product was recrystallized from dichloromethane and diethyl ether. Yield: 33 mg (88%). Anal. Calc. for $C_{22}H_{16}N_8O_2Ru{\cdot}2.5CH_2Cl_2$: C, 39.88; H, 2.87; N, 15.19. Found: C, 39.82; H, 2.89; N, 15.28%. IR (KBr): ν = 2060 and 1995 cm^{-1} (C≡O). UV-vis (dimethyl sulfoxide): λ_{max}/nm (ε/M^{-1} cm^{-1}) 355 (6800) and 487 (2900).

Supplementary Materials: The following are available online, Figure S1: The IR spectrum of $[Ru(apy^{\cdot-})_2(CO)_2]$ (KBr method), Figure S2: Optimized structures of $[Ru(apy^{\cdot-})_2(CO)_2]$ and $[Ru(apy)_2(CO)_2]^{2+}$ (in MeOH).

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Data Availability Statement: The data presented in this study are available in this article and supporting supplementary material.

Conflicts of Interest: The authors declare no conflict of interest.

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