A neutral paddlewheel-type diruthenium(III) complex with benzamidinato ligands: Synthesis, crystal structure, magnetism, and electrochemical and absorption properties

Yusuke Kataoka [a,*], Saki Mikami [a], Hiroshi Sakiyama [b], Minoru Mitsumi [c], Tatsuya Kawamoto [d], Makoto Handa [a,*]

[a] Department of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue, Shimane 690-8504, Japan
[b] Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, Kojirakawa, Yamagata 990-8560, Japan
[c] Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Kita-ku, Okayama 700-005, Japan
[d] Department of Chemistry, Faculty of Science, Kanagawa University, 2946 Tsuchiya, Hiratsuka, Kanagawa 259-1293, Japan

A B S T R A C T

A new neutral diruthenium(III) complex coordinated with benzamidinato (bam) ligands, $[Ru_2(bam)_4Cl_2]\cdot H_2O$ (**1**), was synthesized and characterized, and its electronic structure was closely investigated via magnetic susceptibility, absorption spectrum, cyclic voltammetry, and density functional theory (DFT) calculations. Single crystal X-ray diffraction analysis revealed that complex **1** has a typical paddlewheel-type structure with a Ru—Ru bond (bond length: 2.342(1) Å), in which the diruthenium (Ru_2) core is coordinated by four equatorially μ-bridging bam ligands and two axial Cl^- ions. The magnetic study and DFT calculations proved that complex **1** has a triplet spin state ($S = 1$) and a unique electronic structure ($\pi^4\delta^2\pi^{*2}\sigma^2$). Absorption spectral feature and electrochemical property of complex **1** were also carefully investigated both experimentally and theoretically in this study.

1. Introduction

In the past few decades, the paddlewheel-type diruthenium (Ru_2) complexes have become one of the most extensively investigated families of dinuclear complexes with multiple metal–metal bonding [1–10]. This type of Ru_2 complexes generally show unique electronic structures with degenerate molecular orbitals (MOs) [11,12] and display unique redox [13,14], spectroscopic [15], magnetic [16,17], and catalytic characteristics [18,19]. Recently, the paddlewheel-type Ru_2 units have also been employed as robust paramagnetic building blocks for the supramolecular complexes [20,21], coordination polymers [22,23], and porous metal-organic frameworks [24,25]. It is well known that the paddlewheel-type Ru_2 complexes typically take three different paramagnetic oxidation states: Ru(II)–Ru(II), Ru(II)–Ru(III), and Ru(III)–Ru(III). However, the most reported species is the mixed-valent Ru(II)–Ru(III) oxidation state with a spin state (S) of 3/2, because it is thermodynamically preferred and highly stable in air when normally used bidentate ligands such as carboxylate ions bridge the Ru metals.

The electronic structure and magnetic and redox properties of Ru_2 complexes with Ru(II)–Ru(III) oxidation state have been well investigated so far and already reviewed in the literatures by few groups [1,26–28]. In addition, study of Ru_2 complexes with the Ru(II)–Ru(II) oxidation state has also progressed well recently because of their strong electron-donating properties, oxidation reactivity, and interesting magnetic properties [29–31]. In contrast, the electronic structure and chemical and physical properties of Ru_2 complexes with the Ru(III)–Ru(III) oxidation state [1,32–34], which are still a rare species, are not yet sufficiently understood and established.

Among the various types of bridging organic ligands already utilized for the synthesis of paddlewheel-type Ru_2 complexes, amidinate is considered to be a suitable ligand because of the formation of a robust Ru_2 complex due to the strong Ru-N bond. However, the oxidation states and electronic structures of the Ru_2 complex with amidinate ligands are not sufficiently clear yet; they easily change depending on the Ph- and H-substituted positions in the amidinate ligands, as depicted in Fig. 1. In concrete terms, it is known that the Ru_2 complex coordinated with *N,N*-diphenylformamidinate (dpf), $[Ru_2(dpf)_4Cl]$, has the Ru(II)–Ru(III) oxidation state with $S = 3/2$ [35], while the Ru_2 complex coordinated with *N,N*-dimethylbenzamidinate (dmba), $[Ru_2(dmba)_4Cl_2]$, has the Ru

* Corresponding authors.
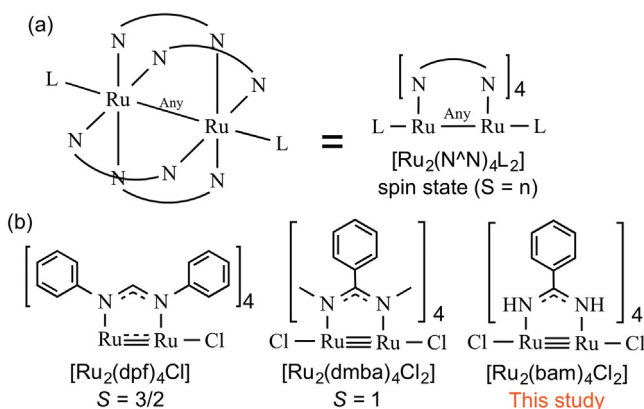*E-mail addresses:* kataoka@riko.shimane-u.ac.jp (Y. Kataoka), handam@riko.shimane-u.ac.jp (M. Handa).

Fig. 1. Schematic representation for (a) simplified molecular geometry of diruthenium complex, [Ru$_2$(N^N)$_4$L$_2$], where N^N and L are bridging amidinate and axial halogen ions, respectively and (b) simplified molecular geometries and their thermodynamically preferred spin state (S) of [Ru$_2$(dpf)$_4$Cl], [Ru$_2$(dmba)$_4$Cl$_2$], and [Ru$_2$(bam)$_4$Cl$_2$] (complex **1**).

(III)–Ru(III) oxidation state with $S = 1$ [36]. For a deeper understanding of the relationship between the substitution position in amidinate ligands and the oxidation state (electronic structure) of the Ru$_2$ complexes with amidinate ligands, the study of the electronic structure and oxidation state of the Ru$_2$ complex coordinated with benzamidinate (bam) is indispensable.

Herein, we describe the detailed synthesis and characterization of the paddlewheel-type Ru$_2$ complex with bam ligands, [Ru$_2$(bam)$_4$Cl$_2$]·H$_2$O (**1**). To determine the oxidation state and electronic structure of complex **1**, variable-temperature magnetic susceptibility measurement study and density functional theory (DFT) calculations were performed. In addition, the redox and spectroscopic properties of complex **1** were carefully investigated, both experimentally and theoretically, in this study.

2. Experimental

2.1. Materials and instruments

All the chemicals and reagents were purchased from commercial sources and used without further purification. [Ru$_2$(O$_2$CCH$_3$)$_4$Cl] was prepared according to a previously reported method with slight modifications [2]. Elemental analyses for carbon, hydrogen, and nitrogen were conducted using a Yanaco CHN CORDER MT-6 installed at Shimane University, Japan. The fourier transform infrared (FT-IR) spectrum was measured using a JASCO FT-IR 660-plus spectrometer in KBr disks at room temperature. Electrospray ionization mass spectrometry (ESI-MS) was conducted using a Bruker micro-TOF analyzer. Variable-temperature magnetic susceptibility measurement was carried out using a superconducting quantum interference device (SQUID) MPMS XL-5 from Quantum Design installed at Okayama University of Science, Japan. UV–Vis absorption spectrum was measured in CHCl$_3$ using a JASCO V-670 spectrometer. Cyclic voltammetry (CV) was measured in dried CHCl$_3$ containing tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$) as an electrolyte using BAS ALS-DY 2325 Electrochemical Analyzer. A glassy carbon disk (1.5 mm radius), Pt wire, and saturated calomel electrode (SCE) were used as the working, counter, and reference electrodes, respectively.

2.2. Synthesis of [Ru$_2$(bam)$_4$Cl$_2$]·H$_2$O (**1**)

A 20.0 mL aqueous solution of [Ru$_2$(O$_2$CCH$_3$)$_4$Cl] (0.50 mmol, 236.7 mg) was mixed with a 30.0 mL aqueous solution containing benzamidine hydrochloride (Hbam·HCl: 25.0 mmol, 200.6 mg) and NaOH (5.0 mmol, 3915.2 mg) at room temperature, and the resulting solution was refluxed at 373 K under N$_2$ atmosphere for 2 days. The precipitated green crude solid was collected by filtration and dried under vacuum at 343 K. The dried crude powder was then purified by column chromatography on silica gel (Wako gel, Wako Pure Chemical Industries Ltd.) with CH$_3$Cl-CH$_3$OH (19:1) as an eluent. The reddish-brown band was collected and evaporated to dryness. The resulting residue was collected on a membrane filter, washed with diethylether, and dried at 343 K for 6 h to give a black powder of complex **1**. The obtained yield was 83.4 mg (21.7%). *Anal.* Calc. for Ru$_2$H$_{30}$C$_{28}$N$_8$Cl$_2$O: C, 43.81; H, 3.94; N, 14.60. Found: C, 43.80; H, 3.93; N, 14.46%. IR (KBr pellet, cm^{-1}): 3447 (m), 3365 (s), 3278 (m), 2925 (vw), 1636 (vw), 1513 (vs), 1470 (vs), 1290 (w), 1259 (m), 1029 (vw), 785 (vw), 699 (s), 676 (s), 530 (m). ESI-MS: Calcd. for [M−Cl]$^+$ 715.0207 m/z; found 715.0212 m/z.

2.3. Single crystal X-ray diffraction analyses

X-ray diffraction date of complex **1** was collected at 150 K on a RIGAKU Saturn 724 CCD system equipped with Mo rotating-anode X-ray generator with Monochromated Mo Kα radiation ($\lambda = 0.71075$ Å) installed in Kanagawa university and were processed with using CrystalClear program (RIGAKU). The structure of complex **1** was solvated by direct method (SIR-2004) and refined using the full-matrix least-squares technique F^2 with SHELXL2014 equipped in the CrystalStructure 4.2.1 software (RIGAKU). Non-hydrogen atoms were refined with anisotropic displacement and almost all of hydrogen atoms were located at the calculated positions and refined as riding models. The residual electron density in the void spaces of final refined structure of complex **1** was evaluated using PALTON SQUEEZE program. Crystal data as well as the details of data collection and refinement for complex **1** is summarized in Table 1 and is obtained as CIF file from Cambridge Crystallographic Data Center (CCDC). Deposition numbers of complex **1** is CCDC-1523719.

2.4. Details of DFT calculations

All the DFT calculations were performed using the GAUSSIAN 09 C.01 program package [37]. The hybrid DFT functional method, B3LYP, with the Los Alamos effective core potential (ECP) basis set, LANL2DZ, for Ru atoms and the double zeta polarized basis set, 6-31G*, for the other atoms. In this study, we used the unrestricted broken-symmetry approach for determining the

Table 1
Crystallographic data for complex **1**.

Crystal size (mm^3)	$0.05 \times 0.05 \times 0.02$
Chemical formula	C$_{28}$H$_{28}$Cl$_2$N$_8$Ru$_2$
T (K)	150
Formula weight (g/mol)	749.63
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.476(3)
b (Å)	10.600(3)
c (Å)	10.735(4)
α (°)	74.805(13)
β (°)	81.287(15)
γ (°)	70.549(15)
V (Å^3)	875.4(5)
Z	1
D_{calc}(g cm^{-3})	1.422
$F(000)$	374
Final R_1 indices [$I > 2\sigma(I)$]	$R_1 = 0.0232$, $wR_2 = 0.0616$
R indices (all data)	$R_1 = 0.0266$, $wR_2 = 0.0631$
Goodness of fit (GOF) on F^2	1.115