Crystal Structure and ^1H NMR Spectral Property of a Lantern-Type Diruthenium(II,III) Complex with One Formamidinato and Three Acetato Bridges

Makoto HANDA,^{*,†} Takahisa IKEUE,^{*} Masanari IIDA,^{*} Daisuke YOSHIOKA,^{**,†} and Masahiro MIKURIYA^{***†}

^{*}Department of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan

^{**}Department of Chemistry and Research Center for Coordination Molecule-based Devices, School of Science and Technology, Kwansei Gakuin University, 2-1 Gakuen, Sanda 669-1337, Japan

The title compound of a lantern-type diruthenium(II,III) complex, $[\text{Ru}_2(2,6\text{-Me}_2\text{-pf})(\text{O}_2\text{CMe})_3\text{Cl}(\text{THF})_2]\cdot 0.5\text{THF}\cdot \text{H}_2\text{O}$ (2,6-Me₂-pf = *N,N'*-bis(2,6-dimethylphenyl) formamidinato ion), was isolated, and the crystal structure was determined by the single-crystal X-ray diffraction method at 90 K. It crystallizes in the monoclinic space group *C2/c* with $a = 26.178(5)$ Å, $b = 13.567(3)$ Å, $c = 18.796(4)$ Å, $\beta = 108.168(4)^\circ$, $V = 6343(2)$ Å³, $D_x = 1.659$ g/cm³, and $Z = 8$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0294 and 0.0591, respectively, for all 7283 independent reflections. The Ru-Ru distance is 2.2931(5) Å and the axial Ru-Cl and Ru-O (THF) distances are 2.4923(9) and 2.315(2) Å, respectively. The ^1H NMR spectrum was measured in CD₂Cl₂ at 298 K, and the observed signals were assigned for the 2,6-Me₂-pf[−] and MeCO₂[−] ligands.

(Received January 27, 2014; Accepted March 17, 2014; Published on web June 10, 2014)

Much interest has been devoted to dinuclear ruthenium(II,III) complexes with a lantern-like structure because they are paramagnetic due to unpaired electrons located in the degenerated π^* and δ^* orbitals formed by a direct metal-metal interaction.¹⁻⁴ Like carboxylato ions (RCO₂[−]), *N,N'*-bis(phenyl) or substituted phenyl)formamidinato (R'-pf[−]) ions are also known to work as bridging ligands for metal ions to give dinuclear complexes.¹ The mixed-ligands dinuclear complexes $[\text{Ru}_2(\text{R}'\text{-pf})_m(\text{O}_2\text{CR})_n\text{Cl}]$ are intriguing, because their structures and properties can be systematically changed by changing m and n as well as the substituent groups R and R'.⁵⁻⁷ We have reported on the crystal structures of the dinuclear complexes *cis*- $[\text{Ru}_2^{\text{II,III}}(4\text{-Me-pf})_2(\text{O}_2\text{CMe})_2\text{Cl}]$ (1) (4-Me-pf[−] = *N,N'*-bis(4-methylphenyl)formamidinato ion) and *trans*- $[\text{Ru}_2^{\text{II,III}}(2,6\text{-Et}_2\text{-}$

pf)₂(O₂CMe)₂Cl(THF)] (2) (2,6-Et₂-pf[−] = *N,N'*-bis(2,6-diethylphenyl)formamidinato ion), where the bulky ethyl groups at the 2,6-positions on the phenyl groups of the formamidinato ligand

Table 1 Crystal and experimental data

Chemical formula: C ₂₉ H ₄₂ ClN ₂ O _{8.5} Ru ₂	
Formula weight = 792.24	
$T = 90$ K	
Crystal system: monoclinic	Space group: <i>C2/c</i>
$a = 26.178(5)$ Å	$\alpha = 90^\circ$
$b = 13.567(3)$ Å	$\beta = 108.168(4)^\circ$
$c = 18.796(4)$ Å	$\gamma = 90^\circ$
$V = 6343(2)$ Å ³	$Z = 8$
$D_x = 1.659$ g/cm ³	
Radiation: Mo K_α ($\lambda = 0.71073$ Å)	
$\mu(\text{Mo } K_\alpha) = 1.089$ mm ^{−1}	$F(0\ 0\ 0) = 3224$
Crystal size = $0.26 \times 0.22 \times 0.10$ mm ³	
No. of reflections collected = 18555	
No. of independent reflections = 7283	
θ range for data collection: 1.64 to 28.44°	
Data/Restraints/Parameters = 7283/0/383	
Goodness-of-fit on $F^2 = 0.850$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0294$, $wR2 = 0.0591$	
R indices (all data): $R1 = 0.0522$, $wR2 = 0.0622$	
$(\Delta/\sigma)_{\text{max}} = 0.001$	
$(\Delta\rho)_{\text{max}} = 1.055$ e Å ^{−3}	$(\Delta\rho)_{\text{min}} = -0.603$ e Å ^{−3}
Measurement: Bruker Smart APEX CCD diffractometer	
Program system: SHELXTL	
Structure determination: Direct methods (SHELXS-97)	
Refinement: full matrix least-squares (SHELXL-97)	
CCDC deposition number: 982673

Fig. 1 Chemical structure of the title compound.

[†] To whom correspondence should be addressed.
E-mail: handam@riko.shimane-u.ac.jp

Fig. 2 ORTEP view of the dinuclear molecular unit of the title compound. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level.

lead to a *trans*-(2:2) arrangement of the ligands around the $\text{Ru}_2^{\text{II,III}}$ core for **2**, although the *cis*-(2:2) arrangement is given in the case without any substituent groups at the 2,6-positions of the phenyl rings of the ligand for **1**.⁷ As for the (1:3) arrangement of the formamidinato and acetato ligands around the $\text{Ru}_2^{\text{II,III}}$ core, to our knowledge, only two crystal structures were reported by Cotton *et al.* for $[\text{Ru}_2^{\text{II,III}}(2,6\text{-Me}_2\text{-pf})(\text{O}_2\text{CMe})_3\text{Cl}(\text{THF})]\cdot 0.5\text{THF}$ (**3**) and $[\text{Ru}_2^{\text{II,III}}(2,6\text{-Me}_2\text{-pf})(\text{O}_2\text{CMe})_3\text{Cl}\{\text{H}(2,6\text{-Me}_2\text{-pf})\}]\cdot \text{toluene}$ (**4**) (2,6- $\text{Me}_2\text{-pf}^- = N,N'$ -bis(2,6-dimethylphenyl)formamidinate ion).⁵ These crystallographic measurements were performed at 213 K. In this study, we determined the crystal structure of **3** at 90 K, because confirming crystal structure at low temperature was needed in order to study the magnetic properties of **3**. We here report on the crystal structure of $[\text{Ru}_2^{\text{II,III}}(2,6\text{-Me}_2\text{-pf})(\text{O}_2\text{CMe})_3\text{Cl}(\text{THF})]\cdot 0.5\text{THF}\cdot \text{H}_2\text{O}$ (**3'**), of which the chemical structure is depicted in Fig. 1.

$[\text{Ru}_2^{\text{II,III}}(2,6\text{-Me}_2\text{-pf})(\text{O}_2\text{CMe})_3\text{Cl}]$ was obtained as a red-brown powder using almost the same method described as that by Cotton *et al.*;⁵ $[\text{Ru}_2(\text{O}_2\text{CMe})_4\text{Cl}]$ was reacted with 1.8-times greater mole amount of $\text{H}(2,6\text{-Me}_2\text{-pf})$ in a refluxed THF solution. Purification was performed chromatographically using a silica-gel column with CHCl_3 as an eluent. Crystals suitable for X-ray single crystal analysis were obtained from a THF-hexane solution in the form of **3'**.

Crystal data and details concerning data collection are given in Table 1. Disorders were found at carbon atoms C25 and C26 on the coordinated THF molecule, and hence they were divided into two positions, (C25A and C26A) and (C25B and C26B), with the occupancy factors of 0.504 and 0.496, respectively (Fig. 2). Hydrogen atoms were inserted at their calculated positions and included in the least-squares calculation using a riding-atom model.

The crystal structure drawn by the ORTEP format is shown for the dinuclear molecular unit for **3'** in Fig. 2. The selected bond distances and angles are given in Table 2S. The $\text{Ru}_2^{\text{II,III}}$ dinuclear core with the (1:3) arrangement of 2,6- $\text{Me}_2\text{-pf}^-$ and acetato bridging ligands is axially coordinated by a Cl^- ion and a THF molecule. The dinuclear structure is basically the same as that reported by Cotton *et al.*, showing only slight changes in the bond distances and angles, accompanying a decrease in the

crystal cell volume from 6447.1(7) $\text{\AA}^3$ for **3** at 213 K to 6343(2) $\text{\AA}^3$ for **3'** at 90 K; *e.g.*, the Ru-Ru bond distances are 2.3053(3) $\text{\AA}$ for **3** and 2.2931(5) $\text{\AA}$ for **3'** (see below). The crystal packing diagram is given for **3'** in Fig. 3S, indicating the existence of crystal solvents of THF and H_2O . Complex **4** also has a similar dinuclear structure, two Ru ions being bridged by one formamidinato and three acetato bridging ion, where the axial positions are occupied by $\text{H}(2,6\text{-Me}_2\text{-pf})$ and Cl^- .⁵ As shown in Table 3S, the $\text{Ru}_2^{\text{II,III}}$ core dimensions of **3'**, **3**, and **4** are similar to each other. However, when we compared these parameters with the other systems, we found that the Ru-Ru distances of **3'** (2.2931(5) $\text{\AA}$) and **3** (2.3053(3) $\text{\AA}$) are nearly the same as that of the *cis*-(2:2) $\text{Ru}_2^{\text{II,III}}$ complex **1** (2.3090(6) $\text{\AA}$) (at 90 K), but rather shorter than those of the *trans*-(2:2) $\text{Ru}_2^{\text{II,III}}$ complex **2** (2.3247(5) $\text{\AA}$) (at 90 K), *trans*- $[\text{Ru}_2(2,6\text{-Me}_2\text{-pf})_2(\text{O}_2\text{CMe})_2\text{Cl}(\text{THF})]$ (2.3259(3) $\text{\AA}$) (at 213 K), and **4** (2.3326(8) $\text{\AA}$) (at 213 K).^{5,7} The Ru-Ru bond length is sensitive to the bridging and axial ligands, as well as their arrangement around the $\text{Ru}_2^{\text{II,III}}$ dinuclear core.

We have reported that the protons (CH) attached to linking the coordinating nitrogen atoms of the formamidinato bridging ligands of the lantern-type $\text{Ru}_2^{\text{II,III}}$ dinuclear complexes are significantly upfield-shifted to -70 – -80 ppm in the ^1H NMR spectra (measured in CD_2Cl_2 at 298 K); -84.8 ppm for *cis*- $[\text{Ru}_2^{\text{II,III}}(4\text{-Me-pf})_2(\text{O}_2\text{CMe})_2\text{Cl}]$ (**1**), -69.4 ppm for *trans*- $[\text{Ru}_2^{\text{II,III}}(2,6\text{-Et}_2\text{-pf})_2(\text{O}_2\text{CMe})_2\text{Cl}(\text{THF})]$ (**2**), and -70.5 ppm for *trans*- $[\text{Ru}_2^{\text{II,III}}(2,6\text{-Me}_2\text{-pf})_2(\text{O}_2\text{CMe})_2\text{Cl}(\text{THF})]$.⁷ The upfield shift due to the paramagnetic $\text{Ru}_2^{\text{II,III}}$ core ($S = 3/2$) was also observed for the present dimer complex $[\text{Ru}_2^{\text{II,III}}(2,6\text{-Me}_2\text{-pf})(\text{O}_2\text{CMe})_3\text{Cl}(\text{THF})]$; the spectrum (measured in CD_2Cl_2 at 298 K) shows the CH proton signal at -77.5 ppm, as can be seen in Fig. 4S.

Acknowledgements

The present work was partially supported by MEXT-Supported Program for the Strategic Research Foundation at Private Universities, and Grants-in-Aid for Scientific Research (No. 22550066) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References

1. F. A. Cotton, C. A. Murillo, and R. A. Walton, *Multiple Bonds Between Metal Atoms*, 3rd ed., Springer Science and Business Media, New York, **2005**.
2. M. A. S. Aquino, *Coord. Chem. Rev.*, **1998**, 170, 141.
3. M. A. S. Aquino, *Coord. Chem. Rev.*, **2004**, 248, 1025.
4. M. Mikuriya, D. Yoshioka, and M. Handa, *Coord. Chem. Rev.*, **2006**, 250, 2194.
5. P. Angaridis, F. A. Cotton, C. A. Murillo, D. Villagrán, X. Wang, *Inorg. Chem.*, **2004**, 43, 8290.
6. M. C. Barral, D. Casanova, S. Herrero, R. Jiménez-Aparicio, M. R. Torres, F. A. Urbanos, *Chem. Eur. J.*, **2010**, 16, 6203.
7. T. Ikeue, Y. Kimura, K. Karino, M. Iida, T. Yamaji, I. Hiromitsu, T. Sugimori, D. Yoshioka, M. Mikuriya, and M. Handa, *Inorg. Chem. Commun.*, **2013**, 33, 133.