

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

An Unprecedented Up-Field Shift in ^{13}C NMR Spectrum for Carboxyl Carbon of Lantern-Type Dinuclear Complex $\text{TBA}[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2]$ (TBA^+ = Tetra(*n*-butyl)ammonium Cation)

Received 00th May 2015,
Accepted 00th May 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yuya Hiraoka,^a Takahisa Ikeue,^{*a} Hiroshi Sakiyama,^b Frédéric Guegan,^c Dominique Luneau,^c Béatrice Gillon,^d Ichiro Hiromitsu,^e Daisuke Yoshioka,^f Masahiro Mikuriya,^{*f} Yusuke Kataoka^a and Makoto Handa^{*a}

A large up-field shift (-763 ppm) has been observed for carboxyl carbon of a dichlorido complex $\text{TBA}[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2]$ (TBA^+ = tetra(*n*-butyl)ammonium cation) in the ^{13}C NMR spectrum (CD_2Cl_2 at 25°C). DFT calculation showed the spin delocalization from the paramagnetic Ru_2^{5+} core to ligands, in agreement with the large up-field shift.

Because of the unique physicochemical properties of the lantern (or paddlewheel)-type (Ru_2^{5+}) dinuclear cores with the direct metal-metal bond, of which crystal structure was first reported for $[\text{Ru}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CH}_3)_4\text{Cl}]$ by Cotton et al. in 1969,¹ there have been many reports on the valent-averaged diruthenium(II,III) complexes.^{2–4} It is well known that the ($\text{Ru}_2^{5+}\text{Cl}$) dinuclear units are polymerized to be expressed as $(\text{Ru}_2^{5+}\text{Cl})_n$ in the solid state.^{1–6} In such case, the magnetic interaction can be operative through Cl^- ion between the dinuclear Ru_2^{5+} cores with three unpaired electrons, where the electronic configuration has been described as $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$.^{2–4} Fruitful results have been also presented as building blocks to produce magnetic materials in combination with paramagnetic linkers such as hexacyanidoferrate $[\text{Fe}(\text{CN})_6]^{3-}$, octacyanidotungstate $[\text{W}(\text{CN})_8]^{3-}$ and nitroxide radicals instead of the axial chlorido ligand.^{6–9} The Ru_2^{5+} dinuclear complexes have a

large zero-filed splitting ($D = 60 - 70 \text{ cm}^{-1}$), which is also one of the characteristic feature promoting its use as a building block.^{2–4} The diruthenium complexes have sharp enough NMR signals for the surrounding ligands to be analysed.^{10–12} Because the paramagnetic shifts of the signals should be related to the spin delocalization from the dinuclear core to surrounding ligands, the NMR spectroscopy can give the useful magnetic information. The information obtained by looking into the ligands could give the new important angle to develop the chemistry and physics of lantern-type diruthenium(II,III) complexes as the building block for the magnetic materials. However, paramagnetic NMR has not been used for the diruthenium(II,III) complexes from such a point of view. This may come from the fact that they are poorly soluble in less solvating organic solvents such as dichloromethane, due to their polymerizing nature based on the axial halogen bridges of $[\text{Ru}_2(\text{O}_2\text{CR})_4\text{X}]_n$. In 1996, Chisholm et al. reported the ^1H NMR spectra of $[\text{Ru}_2\{\text{O}_2\text{C}(\text{CH}_2)_6(\text{CH}_3)_4\}\text{BF}_4]$ in the rather solvating THF-*d*₈ solution.¹¹ The crystal structure of $\text{Cs}[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2]$ had been determined,¹³ while $\text{Q}[\text{Ru}_2(\text{O}_2\text{C}-\text{CH}_3)_4\text{X}_2]$ ($\text{Q} = \text{N}(\text{C}_2\text{H}_5)_4$ and PPh_4 ; $\text{X} = \text{Cl}^-$, Br^- , and I^-) were reported to be soluble in dichloromethane.¹⁴ In the present study, $\text{TBA}[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2]_4$ (**1**) (TBA^+ = tetra(*n*-butyl)ammonium cation) was newly prepared and the crystal structure was determined by X-ray diffraction method. ^1H and ^{13}C NMR spectra could be measured in CD_2Cl_2 at 25°C as the result of the increased solubility by the help of the bulky counter cation TBA^+ , showing a considerably large up-field shift of the carboxyl carbon of the acetato ligand ($\delta = -763 \text{ ppm}$ in ^{13}C NMR spectrum). Variable-temperature (2 – 300 K) magnetic moment, EPR and absorption and diffuse reflectance spectra and cyclic voltammograms are also given with DFT calculation results in this report.

$\text{TBA}[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2]$ (**1**) was prepared by the reactions of the parent dinuclear complexes of $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}]$ with excess amount of tetra(*n*-butyl)ammonium chloride ($\text{TBA}(\text{Cl})$) in dichloromethane at room temperature (ESI^+). Crystals suitable for X-ray crystal structures were obtained as $\mathbf{1} \cdot 2\text{CH}_2\text{Cl}_2$ by the recrystallization from dichloromethane–benzene. Crystal data and details concerning data collection are given in Table S1 (ESI^+). Selected bond distances

^a Department of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan
E-mail: handam@riko.shimane-u.ac.jp

^b Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12 Kojirakawa, Yamagata 990-8560, Japan

^c Laboratoire des Multimatiériaux et Interfaces (UMR 5615), Université Claude Beernard Lyon 1, Campus de La Doua, 69622 Villeurbanne Cedex, France

^d Laboratoire Léon Brillouin CEA/CNRS, UMR0012, Centre d'Etudes de Saclay, 91191, Gif sur Yvette, France

^e Department of Physics and Materials Science, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504

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

[†] Electronic Supplementary Information (ESI) available: Synthetic details, crystal data and details concerning data collection, selected bond distances and angles, crystal structures, packing diagram, reflectance and NMR spectra. CCDC 998328. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x.

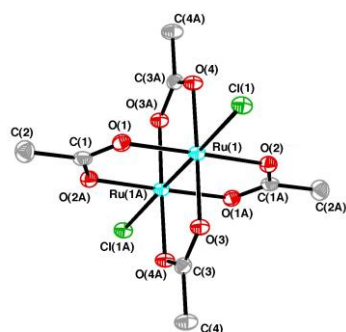


Fig. 1 ORTEP drawing of the Ru1-Ru1A anionic unit of **1**•2CH₂Cl₂, thermal ellipsoids shown at 25% probability level. Hydrogen atoms are omitted for clarity.

and angles are given in Table S2 (ESI[†]). There are two crystallographically independent dinuclear anionic units of [Ru₂(O₂CCH₃)₄Cl₂]⁻ in the crystal of **1**•2CH₂Cl₂.

In Fig. 1, the ORTEP drawing is shown for the one of the dinuclear units, where the dinuclear centre is designated by Ru1-Ru1A. The other dinuclear unit, of which the central dinuclear unit is designated as Ru2-Ru2A, is shown in Fig. S1 (ESI[†]). Each dinuclear unit has a crystallographic inversion centre. Both of the axial sites of the dinuclear units are occupied by Cl⁻ anions. The Ru-Ru and Ru-Cl^{ax} distances are similar to those reported for Cs[Ru₂(O₂CCH₃)₄Cl₂], N(C₂H₅)₄[Ru₂(O₂CCH₃)₄Cl₂], and PPh₄[Ru₂(O₂CCH₃)₄Cl₂].^{13,14} In Fig. S2 (ESI[†]), packing diagram is given for **1**•2CH₂Cl₂. The anionic dinuclear units [Ru₂(O₂CCH₃)₄Cl₂]⁻ and the counter cations TBA⁺ are isolated and no important contacts are observed among them.

Variable Temperature (VT) magnetic moment[‡] $\mu_{eff} = (3k\chi T/N\mu_B^2)^{1/2}$ is shown in Fig. S3(a) (ESI[†]). The effective magnetic moment is 3.91 μ_B at 300 K, which is consistent with the existence of three unpaired electrons in the Ru₂⁵⁺ core. This moment decreases with lowering the temperature due to the large zero-field splitting (*D*). The magnetic behaviour of **1** was fully simulated with the parameter values $g_{//} = 1.96$, $g_{\perp} = 2.07$ ($g_{average} = 2.03$) and $D = 75.5 \text{ cm}^{-1}$ without taking the inter-dimer interaction into account (Fig. S3 (ESI[†])).⁴ The EPR spectrum (in solid at 4 K) measured for the simulation of VT magnetic moment showed the signals at $g_{//}^e (\approx g_{//}) = 1.96$ and $g_{\perp}^e (\approx 2g_{\perp}) = 4.14$, where g^e means the effective *g* value ($g^e = h\nu/(\mu_B H)$) (Fig. S4 (ESI[†])).¹⁵ The EPR simulation was performed using the software "GeeStrain-5".¹⁶

Absorption and diffuse reflectance spectra (Fig. S5 (ESI[†])) were measured for **1**, both showing the absorption bands at 1120 and 465 nm. The similarity in the spectral feature in solution (CH₂Cl₂) and solid indicates that the anionic (Ru₂⁵⁺Cl₂)⁻ core structure shown in the X-ray crystal structure should be maintained in CH₂Cl₂. ¹H NMR spectrum of **1** was measured in CD₂Cl₂ at 25°C. In the spectrum (Fig. S6, ESI[†]), the signal for methyl protons was observed at -42.6 ppm. Chisholm et al. reported that the methylene protons closest to the carboxylato bridging of [Ru₂(O₂C(CH₂)₆(CH₃))]BF₄

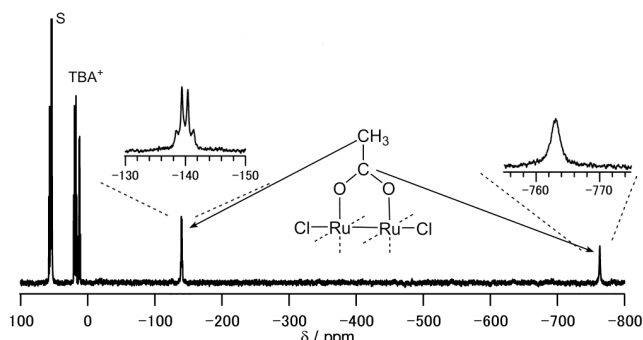


Fig. 2 ¹³C NMR spectrum of **1** measured in CD₂Cl₂ at 25°C.

appeared at -42.4 ppm in THF-*d*₈.¹¹ We also reported that methyl protons of [Ru₂(O₂CCH₃)₄Cl] appeared at -44.8 ppm in DMSO-*d*₆ at 25°C.^{10a} The signal position (-42.6 ppm) of **1** was not shifted when the excess (ca. 10-fold) molar amount of TBA(Cl) to (Ru₂⁵⁺Cl₂)⁻ was added to the CD₂Cl₂ solution of **1**. This result means that the dichlorido adduct (Ru₂⁵⁺Cl₂)⁻ species is exclusively present in the measured solution; the equilibrium shown by (Ru₂⁵⁺Cl₂)⁻ ↔ (Ru₂⁵⁺Cl) + Cl⁻ ↔ (Ru₂⁵⁺) + 2(Cl⁻) may not be significant. The exclusive existence of the bis-adduct (Ru₂⁵⁺Cl₂)⁻ species in CH₂Cl₂ was also confirmed by cyclic voltammogram (CV) (see below).

In Fig. 2, ¹³C NMR spectrum (measured in CD₂Cl₂ at 25°C without decoupling of the proton region) is given with the assignment. While the methyl carbon (-140 ppm) was observed as a quartet signal due to the coupling with its protons ($J_{C-H} = 126 \text{ Hz}$), the carboxyl carbon (-763 ppm) was observed as a singlet signal. We further measured ¹³C NMR spectrum of [Ru₂{O₂¹³C(CH₂)₂CH₃}₄Cl₂]⁻ in CD₂Cl₂ at 25°C (Fig. S7(a), ESI[†]) to consolidate the assignment for the carboxyl carbon. The spectrum only shows the intense signal at -729 ppm for the ¹³C-enriched carboxyl carbon other than that for the solvent, because the concentration was not high enough to observe the signals for the carbons on the propyl group (Fig. S7, ESI[†]). We could manage to measure the ¹³C NMR spectrum of [Ru₂{O₂C(CH₂)₂CH₃}₄]BF₄ in CD₂Cl₂ at 25°C (Fig. S8, ESI[†]) and the signal for the carboxyl carbon appeared at -820 ppm. This result means that the large up-field shift for the carboxyl carbon is not due to the axial coordination of the chloride ions. The observed chemical shifts ($\delta_{observed}$) were used to estimate the net paramagnetic nature ($\delta_{isotropic}$) by the equation $\delta_{observed} = \delta_{diamagnetic} + \delta_{isotropic}$.¹¹ The estimated $\delta_{isotropic}$ values are -953 ppm for the carboxyl carbon and -163 ppm for the methyl carbon of **1**.¹⁷ To our knowledge, such a large up-field shift for the carboxyl carbon ($\delta_{isotropic} = -953 \text{ ppm}$) has not been reported before for the lantern-type dinuclear complexes.

Fig. 3 shows the cyclic voltammogram (CV) of **1**, which was measured in CH₂Cl₂ with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the electrolyte. Redox couples were observed at $E_{1/2} (E_{pa} + E_{pc}) = -0.34$ and 1.33 V (vs. SCE), in the reduction and oxidation sides, respectively. It has been reported that

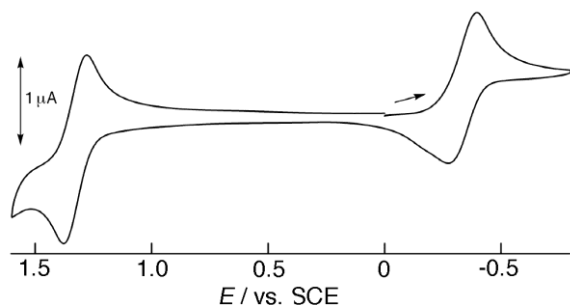


Fig. 3 Cyclic voltammogram of complex **1** in dichloromethane; scan rate = 50 mV s⁻¹, [complex] = 1 × 10⁻³ M, [TBAP] = 0.1 M. Glassy carbon and Pt wire were used as working and counter electrodes, respectively.

[Ru₂{O₂C(CH₂)₂CH₃]₄Cl] exhibits two step reductions (0.00 and -0.34 V (vs. SCE) in CH₂Cl₂ containing TBAP, although one step reduction is observed at -0.34 V (vs. SCE) when TBA(Cl) is used as the electrolyte instead of TBAP in CH₂Cl₂, which was explained by the existence of the equilibrium shown by [Ru₂{O₂C(CH₂)₂CH₃]₄⁺ + n(Cl⁻) ↔ [Ru₂{O₂C(CH₂)₂CH₃]₄Cl_n⁻.¹⁸ No important change was observed for the redox potential of **1** in the reduction side when 0.1 M TBA(Cl) was used as the electrolyte in CH₂Cl₂ (E_{1/2} = -0.32 V (vs. SCE)) (Fig. S9 ESI[†]). This may be because dichlorido adduct anion (Ru₂⁵⁺Cl₂)⁻ is predominant even when TBAP or TBA(Cl) is used as the electrolyte in CH₂Cl₂. The observed redox couples (shown in Fig. 3) are considered to be based on the reduction and oxidation of the dichlorido species (Ru₂⁵⁺Cl₂)⁻, respectively. DFT calculation^{19,20} suggests the assignment that the observed redox potentials (E_{1/2} = -0.34 and 1.33 V) correspond to the reduction and oxidation of the dichlorido species (Ru₂⁵⁺Cl₂)⁻ because the potential values could be fully reproduced by the calculations (Table S3, ESI[†]). It is noteworthy that the calculated redox values, 0.06 V (for Ru₂⁴⁺ / Ru₂⁵⁺ of [Ru₂{O₂C(CH₂)₂CH₃]₄Cl]) and -0.32 V (for Ru₂⁴⁺ / Ru₂⁵⁺ of [Ru₂{O₂C(CH₂)₂CH₃]₄Cl₂)⁻), are similar to the observed values, 0.00 V and -0.34 V, for [Ru₂{O₂C(CH₂)₂CH₃]₄Cl] in CH₂Cl₂ containing TBAP.¹⁸ The successful simulation for the observed redox potentials of **1** (E_{1/2} = -0.34 and 1.33 V) enables us to choose the correct functional methods and basis sets for the DFT calculation to estimate the spin delocalization. The DFT calculation result¹⁹ indicates that an electron is removed from the filled σ orbital on the oxidation (Ru₂⁵⁺Cl₂)⁻ → (Ru₂⁶⁺Cl₂); Fig. S10 (ESI[†]) illustrates that the axial Ru-Cl interaction energetically enhances the σ orbital in the (Ru₂⁵⁺Cl₂)⁻ core. It is known that the redox potentials are affected by the axial ligand nature.^{2,3} As shown in Fig. 4, in the case of (Ru₂⁵⁺Cl₂)⁻, spin density (ρ_s) is distributed from the dinuclear core to the surrounding ligands (ρ_s(Ru₂⁵⁺) = 2.778, ρ_s(8 × O(CO₂)) = 0.247, ρ_s(4 × C(CO₂)) = -0.085, ρ_s(4 × C(CH₃)) = 0.002, ρ_s(2 × Cl) = 0.070). The delocalized spin density onto the carboxylate COO⁻ group should contribute seriously to the large paramagnetic shifts of the carboxyl carbon (due to the Fermi contact coupling) found in the ¹³C NMR spectrum (δ_{isotropic} = -953 ppm) for **1**; the δ* unpaired electron in the Ru₂⁵⁺ core could play an important role in the large paramagnetic shift because the Ru₂⁴⁺ complex (with no δ* unpaired electron) has been reported to be δ_{isotropic} = -277 ppm measured in THF-d₈ for the corresponding carboxyl carbon of [Ru₂{O₂C(CH₂)₆(CH₃)₄]₄, although the dipolar coupling should be also taken into account (δ_{isotropic} = δ_{contact} + δ_{dipolar}).¹¹ Using the DFT calculation result, we have estimated the δ_{contact} values to be -929 (for carboxyl carbon) and

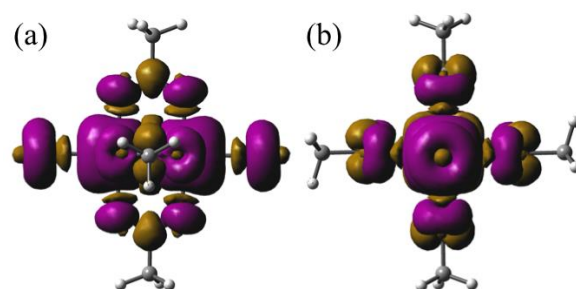


Fig. 4 Spin density map calculated from (BS)-DFT (ωB97XD) calculation for the dichlorido anion (Ru₂⁵⁺Cl₂)⁻. (a) top and (b) side views.

-197 ppm (for methyl carbon) for **1** (ESI[†]).^{21,22} Because the experimental δ_{isotropic} and DFT calculated δ_{contact} values of respective carbons are close to each other, it may be reasonable that the large paramagnetic shift found for the carboxyl carbon mainly comes from the contact coupling. We may say that the dipolar contribution is smaller, considering the fact that g_{||} (= 1.96) and g_⊥ (= 2.07) are not significantly different in **1**. However, more careful investigation should be made comparing the experimental and theoretical results for the dinuclear system with more carbon (and hydrogen) atoms to analyse totally their δ_{isotropic} values around the paramagnetic dinuclear core with the large D value (60 – 70 cm⁻¹); the present Ru₂(II,III) system has simply carboxyl and methyl groups on the acetato bridge, although this was important for the assignment of the carboxyl carbon in the ¹³C NMR spectrum. Recently, a detailed NMR investigation on the terbium(III)-phthalocyaninato single molecule magnets (SMMs) has been reported, referring to residual dipolar couplings and pseudocontact shifts.²³ Although such NMR studies are now still limited, they will be considered to become more important when the paramagnetic NMR data are accumulated. We here propose that the paramagnetic NMR spectroscopy in combination with DFT calculation should work effectively for the molecule-based magnetic studies.

Conclusions

TBA[Ru₂(O₂CCH₃)₄Cl₂] (**1**) (TBA = tetra(*n*-butyl)ammonium chloride) was prepared and the dichlorido adduct structure was confirmed by the X-ray crystal structure. The NMR and UV-vis spectra as well as CV showed that the bischlorido species Ru₂⁵⁺(Cl)₂⁻ is predominant in the measured dichloromethane solution. The ¹H and ¹³C NMR spectra (in CD₂Cl₂) showed the paramagnetic shifts of their proton and carbon signals. The large up-field shift (Δ_{isotropic} = -953 ppm), which was observed for the carboxyl carbon, was considered to be due to the spin delocalization from Ru₂⁵⁺ core onto the carboxylate COO⁻ group, in agreement with the DFT calculation results.

The present work was partially supported by Grants-in-Aid for Scientific Research Nos. 24560012 and 26410080 from the Ministry of Education, Culture, Sports, Science and Technology and the Support Project to Assist Private Universities in Developing Bases for Research, Japan. The authors are grateful to Ms. Michiko Egawa (Shimane University) for her measurements of elemental analysis,

Mr. Yuma Ito (Shimane University) for synthesis of $[\text{Ru}_2(\text{O}_2^{13}\text{C}(\text{CH}_2)_2\text{CH}_3)_4\text{Cl}]$, Dr. Ryoji Mitsuhashi (Kwansei Gakuin University) for his help in the X-ray crystal structure analysis, and Prof. Masahiko Hada (Tokyo Metropolitan University) for his indispensable suggestion to estimate the δ_{contact} values in the DFT calculation.

Notes and references

χ magnetic susceptibility, T temperature, k Boltzmann constant, N Avogadro number, μ_{B} Bohr magneton.

- 1 M. J. Bennett, K. G. Caulton and F. A. Cotton, *Inorg. Chem.*, 1969, **8**, 1-6.
- 2 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.
- 3 M. A. S. Aquino, *Coord. Chem. Rev.*, 1998, **170**, 141-202.; M. A. S. Aquino, *Coord. Chem. Rev.*, 2004, **248**, 1025-1045.
- 4 M. Mikuriya, D. Yoshioka and M. Handa, *Coord. Chem. Rev.*, 2006, **250**, 2194-2211.
- 5 T. Togano, M. Mukaida and T. Nomura, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 2085-2086.
- 6 D. Yoshioka, M. Mikuriya and M. Handa, *Chem. Lett.*, 2002, 1044-1045.
- 7 Y. Liao, W. W. Shum and J. S. Miller, *J. Am. Chem. Soc.*, 2002, **124**, 9336-9337; T. E. Vos, Y. Liao, W. W. Shum, J.-H. Her, P. W. Stephens, W. M. Reiff and J. S. Miller, *J. Am. Chem. Soc.*, 2004, **126**, 11630-11639; T. E. Vos and J. S. Miller, *Angew. Chem., Int. Ed.*, 2005, **44**, 2416-2419; B. S. Kennon, K. H. Stone, P. W. Stephens and J. S. Miller, *Inorg. Chim. Acta*, 2010, **363**, 2137-2143.
- 8 D. Matoga, M. Mikuriya, M. Handa and J. Szklarzewicz, *Chem. Lett.*, 2005, **34**, 1550-1551; M. Mikuriya, D. Yoshioka, A. Borta, D. Luneau, D. Matoga, J. Szklarzewicz and M. Handa, *New. J. Chem.*, 2011, **35**, 1226-1233.
- 9 M. Handa, Y. Sayama, M. Mikuriya, R. Nukada, I. Hiromitsu and K. Kasuga, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 119-125; Y. Sayama, M. Handa, M. Mikuriya, I. Hiromitsu and K. Kasuga, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 769-779.
- 10 (a) 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**, 133-137; (b) Y. Harada, T. Ikeue, Y. Ide, Y. Kimura, I. Hiromitsu, D. Yoshioka, M. Mikuriya, Y. Kataoka and M. Handa, *Inorg. Chim. Acta*, 2015, **424**, 186-193.
- 11 M. H. Chisholm, G. Christou, K. Folting, J. C. Huffman, C. A. James, J. A. Samuels, J. L. Wesemann and W. H. Woodruff, *Inorg. Chem.*, 1996, **35**, 3643-3658.
- 12 S. Furukawa and S. Kitagawa, *Inorg. Chem.*, 2004, **43**, 6464-6472.
- 13 A. Bino, F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1979, **18**, 2599-2604.
- 14 M. C. Barral, R. González-Prieto, S. Herrero, R. Jiménez-Aparicio, J. L. Priego, M. R. Torres and F. A. Urbanos, *Polyhedron*, 2005, **24**, 239-247.
- 15 J. Telser and R. S. Drago, *Inorg. Chem.*, 1984, **23**, 3114-3120; J. Telser and R. S. Drago, *Inorg. Chem.*, 1985, **24**, 4765.
- 16 W. R. Hagen, *Biomolecular EPR Spectroscopy*, CRC Press, Boca Raton, FL, USA, 2009.
- 17 Chemical shifts (^{13}C NMR spectrum measured in THF- d_6) of carboxyl and methyl carbons of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4]$ were used as $\delta_{\text{diamagnetic}}$ values for the corresponding carbons of **1**.
- 18 F. A. Cotton and E. Pedersen, *Inorg. Chem.*, 1975, **14**, 388-391.
- 19 Density functional theory (DFT) calculations were performed using the Gaussian 09 C.01 Program package. The long-range correlated broken-symmetry (BS)-DFT functional ωB97XD was used with the effective core potential LANL08(f) for the Ru atom and Pople basis set (6-311+G*) for the other atoms. The solvent effect of the CH_2Cl_2 was considered by the polarizable continuum model (PCM). Spin density and redox potentials of the **1** were estimated by the Mulliken's and Noodleman's methods, respectively.
- 20 Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 21 J. Mao, Y. Zahng, and E. Oldfield, *J. Am. Chem. Soc.*, 2002, **124**, 13912-13920.
- 22 M. Hada, *J. Am. Chem. Soc.*, 2004, **126**, 486-487.
- 23 M. Damjanovic, K. Katoh, M. Yamashita and M. Enders, *J. Am. Chem. Soc.*, 2013, **135**, 14349-14358.