

Synthesis and characterization of a novel (μ_3 -oxo)tetraruthenium cluster

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Abstract

A novel (μ_3 -oxo)tetraruthenium cluster (**2**) was synthesized in an isolated yield of 73% by the reaction of a zerovalent ruthenium complex, $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ (**1**) [cot = 1,3,5-cyclooctatriene, dmfm = dimethyl fumarate], with water under reflux in 1,4-dioxane for 6 h. The structure and the X-ray characterization of this novel complex **2** as well as a possible formation mechanism of **2** are disclosed.

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1. Introduction

It is generally known that the majority of organometallic compounds are stable only in the absence of water, and many of them can be synthesized only under rigorously dry conditions. Although in most cases water acts destructively on organometallics, in some cases the organometallic compounds resist water [1]. If the control of the reaction of organometallic compounds with water is easily accessed, a novel method for the use of water as a raw material in homogeneously catalyzed organic reactions can be developed, which is quite attractive from recent environmental, sustainable, and atom-economy perspectives [2]. The first step in the reaction of organometallic compounds with water should be the coordination of water to the metal center to give the corresponding aqua complexes [3]. The coordinated water then oxidatively adds to the low-valent

transition metal center to give (hydrido)(hydroxo)metal complexes [4].

Among various metals, we focused our attention on the reactivity of ruthenium complexes, since ruthenium complexes often show interesting and unique reactivity as well as catalytic activity, which are quite different from those of palladium and other transition metal complexes [5]. For example, we recently succeeded in synthesizing the first stable and isolable ruthenium(0) aqua complex, $\text{Ru}(\text{dppe})(\eta^2\text{-dmfm})_2(\text{H}_2\text{O})$ [dppe = 1,2-bis(diphenylphosphino)ethane] [6]. The further detailed study realized optical resolution of this chiral complex, and the nonequivalent geminal protons of the coordinated water in solution were successfully observed [7].

Thus the reactivity of the coordinated water in $\text{Ru}(\text{dppe})(\eta^2\text{-dmfm})_2(\text{H}_2\text{O})$ is quite attractive, however, when we initially examined the thermal reaction of $\text{Ru}(\text{dppe})(\eta^2\text{-dmfm})_2(\text{H}_2\text{O})$, no oxidative addition of water to ruthenium was observed. We next investigated the reaction of $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ (**1**) [5c,5e,8], a starting material for the synthesis of $\text{Ru}(\text{dppe})(\eta^2\text{-dmfm})_2(\text{H}_2\text{O})$ [6], with

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water in the absence of phosphorus ligands under various reaction conditions, since we considered that the high coordination ability of phosphorus ligands such as dppe may prevent the coordination and oxidative addition of water to ruthenium(0). After many trials, we found that water can react with a low-valent ruthenium complex such as $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ to give a novel $(\mu_3\text{-oxo})$ -tetraruthenium cluster (**2**). Here, we report the synthesis and the X-ray characterization of this novel complex **2** as well as consideration of a possible formation mechanism of **2**.

2. Results and discussion

As shown in Scheme 1, a mixture of 0.50 mmol of $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ (**1**) and 5.0 mmol of water was refluxed in 1,4-dioxane for 6 h under an argon atmosphere. After the solvent was evaporated under vacuum, purification of the residue by column chromatography (aluminum oxide,

eluent: diethyl ether/ethyl acetate = 1/1) and recrystallization from CH_2Cl_2 /pentane under an argon atmosphere gave green microcrystals of a novel $(\mu_3\text{-oxo})$ -tetraruthenium cluster (**2**) in an isolated yield of 73%.

Complex **2** was exclusively formed in 1,4-dioxane. No isolable complex was obtained in other solvents such as MeOH, THF, diglyme, CH_2Cl_2 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, benzene, or *n*-octane, which suggests that only 1,4-dioxane could operate as a suitable ligand to stabilize the coordinatively unsaturated ruthenium intermediates (vide infra). The structure of complex **2** was first deduced based on ^1H , ^{13}C NMR, and FAB-MS spectra. In the ^1H and ^{13}C NMR, two cyclooctadienyl and one cyclooctatrienyl ligands together with two nonequivalent dmfm ligands were identified. In particular, FAB-MS of **2** showed a molecular ion peak at $m/z = 1061$, in agreement with a tetranuclear structure. Finally, the molecular structure of **2** was eventually determined by a low-temperature X-ray crystallography (Fig. 1).

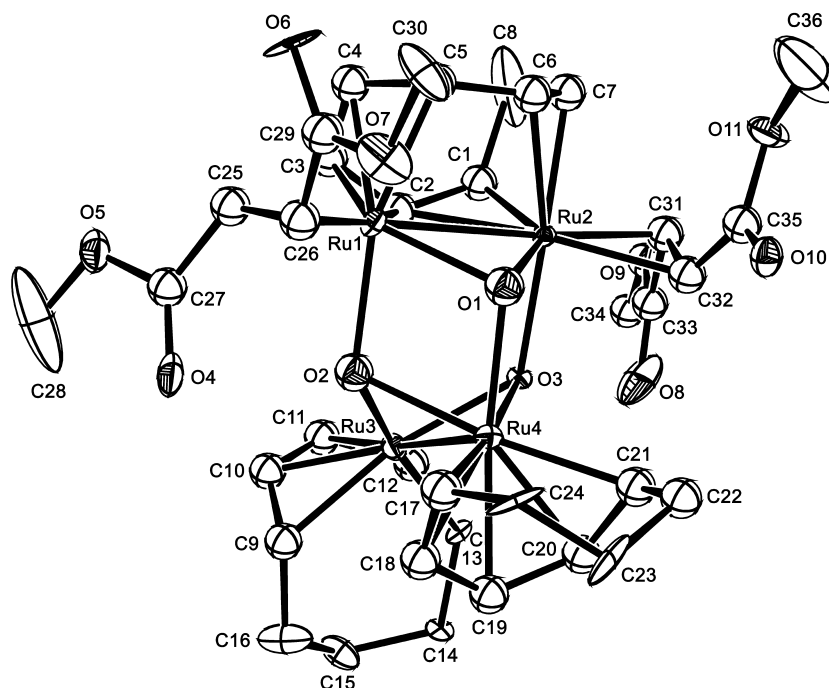
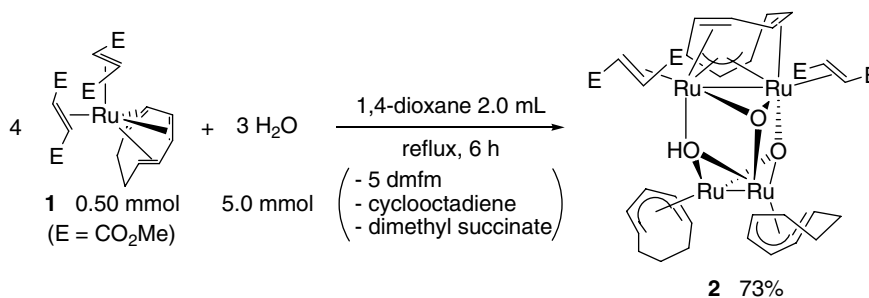


Fig. 1. Molecular structure of **2**.

Table 1
Crystal data and structure refinement data for complex **2**

| | |
|--|---|
| Empirical formula | C ₃₆ H ₄₈ O ₁₁ Ru ₄ |
| Formula weight | 1061.05 |
| Crystal color | Green |
| Habit | Platelet |
| Crystal size (mm) | 0.02 × 0.10 × 0.05 |
| Crystal system | Orthorhombic |
| Space group | <i>Pca</i> 2 ₁ |
| <i>a</i> (Å) | 17.964(8) |
| <i>b</i> (Å) | 30.833(12) |
| <i>c</i> (Å) | 13.503(5) |
| β (°) | 90 |
| <i>V</i> (Å ³) | 7478.9(53) |
| <i>Z</i> | 4 |
| <i>D</i> _{calc} (g cm ⁻³) | 0.942 |
| μ(Mo Kα) (cm ⁻¹) | 8.22 |
| λ (Å) | 0.71070 |
| <i>T</i> (K) | 173 |
| Scan mode | ω-2θ |
| Scan width (°) | -70.0 to 110.0 |
| 2θ _{max} (°) | 55.0 |
| Reflections collected | 60695 |
| Reflections unique [<i>R</i> _{int}] | 8589 |
| Final <i>R</i> indices [<i>I</i> > 3σ(<i>I</i>)] ^a | <i>R</i> ₁ = 0.096, <i>wR</i> ₂ = 0.112 |
| Goodness-of-fit | 1.929 |

$$^a R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|, wR_2 = [\sum w(|F_o| - |F_c|)^2] / \sum wF_o^2]^{1/2}.$$

Complex **2** crystallizes with at least two molecules of water, judging from the result of an elemental analysis. Uncertainty regarding both the number and position of the solvents of crystallization (H₂O and CH₂Cl₂) leads to a complicated full X-ray crystallographic analysis of **2**, however, the *R* value reaches 9%, and a (μ₃-oxo)tetraruthenium framework of **2** could be established. Crystal data and the details of the data collection are given in Table 1, while lists of selected bond lengths and angles are provided in Table 2.

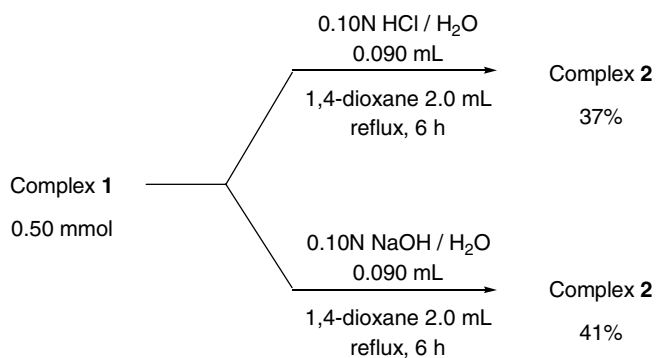
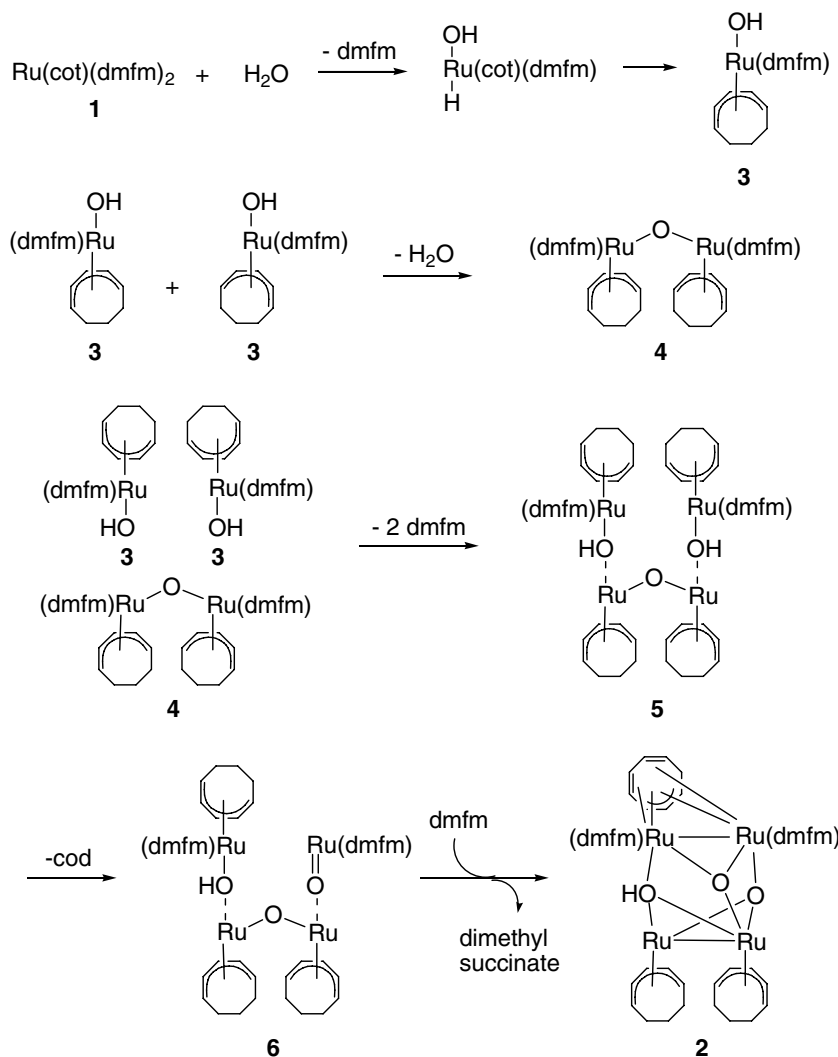
As can be readily seen from Fig. 1, one cyclooctatrienyl ligand bridges between Ru1 and Ru2 in an μ₂,η³-allyl manner, and the other two cyclooctadienyl ligands are coordinated to Ru3 and Ru4, respectively, in an η⁵ manner. All ruthenium atoms are thought to have a d⁶ configuration with 18 valence electrons, which means that this complex is coordinatively saturated, and one of the bridged oxygen, O2, should be a hydroxyl (OH) group. This OH proton was observed at δ 5.71 ppm, and disappeared upon the addition of D₂O in the ¹H NMR spectra of **2**. The bond distances of Ru1–Ru2 and Ru3–Ru4 are 2.803(4) and 2.724(5) Å, respectively. Ru–O bonds are within 2.12–2.19 Å, which means that all Ru–O bonds are single bonds by degeneracy of the first generated Ru=O double bond order.

The possible pathway for the formation of **2** from **1** is considered and illustrated in Scheme 2. First, a mononuclear (hydrido)(hydroxo)ruthenium complex would be formed via the activation (oxidative addition) of water on the zerovalent ruthenium center [4f]. Since the examples of deprotonation of an aqua ligand resulting in the formation of hydroxo- [9] and/or oxo-metal complexes [10] have

Table 2
Selected bond lengths (Å) and angles (°) for **2**

| Bond lengths (Å) | | Bond angles (°) | |
|------------------|----------|------------------|----------|
| Ru(1)–Ru(2) | 2.803(4) | Ru(1)–O(1)–Ru(2) | 81.6(4) |
| Ru(1)–O(1) | 2.13(1) | Ru(1)–O(1)–Ru(4) | 107.7(5) |
| Ru(1)–O(2) | 2.15(1) | Ru(1)–O(2)–Ru(3) | 127.4(6) |
| Ru(1)–C(2) | 2.50(2) | Ru(1)–O(2)–Ru(4) | 104.1(6) |
| Ru(1)–C(3) | 2.15(2) | Ru(2)–O(1)–Ru(4) | 106.2(5) |
| Ru(1)–C(4) | 2.17(2) | Ru(2)–O(3)–Ru(3) | 129.3(7) |
| Ru(1)–C(5) | 2.16(2) | Ru(2)–O(3)–Ru(4) | 105.1(5) |
| Ru(1)–C(25) | 2.15(2) | Ru(3)–O(2)–Ru(4) | 78.4(5) |
| Ru(1)–C(26) | 2.13(2) | Ru(3)–O(3)–Ru(4) | 77.8(4) |
| Ru(2)–O(1) | 2.16(1) | Ru(1)–Ru(2)–O(1) | 48.6(3) |
| Ru(2)–O(3) | 2.13(1) | Ru(1)–Ru(2)–O(3) | 88.5(4) |
| Ru(2)–C(1) | 2.14(2) | Ru(2)–Ru(1)–O(1) | 49.7(3) |
| Ru(2)–C(2) | 2.45(2) | Ru(2)–Ru(1)–O(2) | 89.8(4) |
| Ru(2)–C(6) | 2.23(2) | Ru(3)–Ru(4)–O(3) | 50.6(4) |
| Ru(2)–C(7) | 2.12(2) | Ru(3)–Ru(4)–O(2) | 49.7(4) |
| Ru(2)–C(31) | 2.20(2) | Ru(3)–Ru(4)–O(1) | 103.9(4) |
| Ru(2)–C(32) | 2.15(2) | Ru(4)–Ru(3)–O(2) | 51.9(4) |
| Ru(3)–Ru(4) | 2.724(5) | Ru(4)–Ru(3)–O(3) | 51.6(4) |
| Ru(3)–O(2) | 2.12(1) | O(1)–Ru(1)–O(2) | 74.4(5) |
| Ru(3)–O(3) | 2.15(1) | O(1)–Ru(2)–O(3) | 74.4(5) |
| Ru(3)–C(9) | 2.15(2) | O(1)–Ru(4)–O(2) | 73.8(5) |
| Ru(3)–C(10) | 2.06(2) | O(1)–Ru(4)–O(3) | 74.1(5) |
| Ru(3)–C(11) | 2.16(2) | O(2)–Ru(3)–O(3) | 79.7(5) |
| Ru(3)–C(12) | 2.09(2) | O(2)–Ru(4)–O(3) | 77.6(5) |
| Ru(3)–C(13) | 2.15(2) | | |
| Ru(4)–O(1) | 2.12(1) | | |
| Ru(4)–O(2) | 2.19(1) | | |
| Ru(4)–O(3) | 2.18(1) | | |
| Ru(4)–C(17) | 2.12(2) | | |
| Ru(4)–C(18) | 2.12(2) | | |
| Ru(4)–C(19) | 2.18(2) | | |
| Ru(4)–C(20) | 2.11(2) | | |
| Ru(4)–C(21) | 2.20(2) | | |

been reported, the synthesis of **2** from **1** was carried out under acidic (0.10 N HCl/H₂O) or basic (0.10 N NaOH/H₂O) reaction condition. However, the yields of **2** considerably decreased in both reactions (Scheme 3), which suggests that protonation and/or deprotonation mechanism are not operative in the formation of **2** from **1** [11]. Thus, the following hydrogen transfer and dehydration processes on the ruthenium could be considered. Insertion of a 1,3,5-cyclooctatriene ligand into a hydrido-ruthenium bond would give an intermediate **3**. Intermolecular dehydration of **3** occurs to form a dinuclear (μ₂-oxo)ruthenium complex **4**. Dissociation of a dmfm ligand from **4** and the assembling of **3** with **4** simultaneously proceed to give **5**. Further dehydrogenative condensation via **6** proceeds to give the final complex **2**. Careful GC analysis showed the liberation of six equivalents of dimethyl fumarate, one of which was hydrogenated to dimethyl succinate in the last step for the formation of **2** from **6** in Scheme 2, as well as the formation of an equimolar amount of cyclooctadiene. This result supports the mechanism depicted in Scheme 2 [12]. The marked solvent effect may be explained by assuming that only 1,4-dioxane could operate as a suitable ligand to stabilize the coordinatively unsaturated ruthenium species **3–6** [13].



3. Conclusion

In conclusion, we have succeeded in the synthesis and the X-ray characterization of a novel (μ_3 -oxo)tetraruthenium cluster (**2**) which was obtained in high yield by the reaction of $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ (**1**) with water. This process would involve the activation of water by a low-valent

ruthenium complex. Investigation of the reactivity of **2** is highly desirable, since the present study would give an opportunity for developing novel catalytic reactions using water as a raw material [14].

4. Experimental

All manipulations were carried out using standard Schlenk techniques under an argon atmosphere or in a glove box under a nitrogen atmosphere. The reagents used in this study were dried, purified, and degassed prior to use by standard procedures. GLC analyses were carried out on Shimadzu GC-14B and GC-17A gas chromatographs equipped with a glass column (3.0 mm i.d. \times 3 m) packed with Silicone OV-17 (2% on Chromosorb W(AW-DMCS), 60–80 mesh) and a capillary column [Shimadzu capillary column HiCap-CBP10-M25-025 (polarity similar to OV-1701): 0.22 mm i.d. \times 25 m], respectively. The ^1H NMR spectra were recorded at 500 MHz and/or 400 MHz, and ^{13}C NMR spectra were recorded at 125 MHz and/or 100 MHz with JEOL EX 500 and EX 400 spectrometers.

Samples were analyzed in CD_2Cl_2 , and the chemical shift values are expressed relative to Me_4Si as an internal standard. Elemental analyses were performed at Microanalytical Center of Kyoto University. $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ was prepared as described in the literature [8].

4.1. Synthesis of $(\mu_3\text{-oxo})\text{tetraruthenium cluster (2)}$

A mixture of $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$ (**1**) (247.8 mg, 0.50 mmol), water (5.0 mmol, 0.090 mL, 10 equiv.) and 1,4-dioxane (2.0 mL) was placed in a two-necked 20 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under an argon atmosphere. The mixture was stirred under reflux for 6 h. After cooling, the reaction mixture was dried under vacuum, and then chromatographed on neutral aluminum oxide (Merck, standardized, #1.01097) under an argon atmosphere. Elution with diethyl ether/ethyl acetate (=1/1) gave a green solution, from which the solvent was evaporated. The green residue was recrystallized from CH_2Cl_2 /pentane to give **2** · 2H₂O (100 mg, 73% yield).

Complex 2: Green solid, m.p. 208.7 °C (dec.), ¹H NMR (CD_2Cl_2 , 500 MHz): δ -0.98 to -0.90 (q, 1H, CHH of cyclooctadienyl, $J = 13.4$ Hz), -0.25 to -0.16 (m, 1H, CHH of cyclooctadienyl), 0.82 (d, 1H, CHH of cyclooctadienyl, $J = 13.7$ Hz), 0.93 (dd, 1H, CH of cyclooctadienyl, $J = 6.1, 2.1$ Hz), 0.99–1.08 (m, 2H, CH₂ of cyclooctadienyl), 1.18–1.24 (m, 4H, CH₂, CHH, and CH of cyclooctadienyl), 1.60 (dd, 1H, CH of cyclooctadienyl, $J = 6.0, 1.2$ Hz), 1.74 (d, 2H, CH₂ of cyclooctatrienyl, $J = 15.9$ Hz), 1.95–2.06 (m, 3H, CH₂ and CHH of cyclooctatrienyl), 2.21 (t, 1H, CH of cyclooctatrienyl, $J = 6.3$ Hz), 2.55–2.58 (m, 1H, CH of cyclooctadienyl), 2.71 (dt, 1H, CHH of cyclooctadienyl, $J = 8.2, 4.7, 3.7$ Hz), 2.89–2.92 (m, 1H, CH of cyclooctadienyl), 2.96–2.99 (m, 1H, CH of cyclooctadienyl), 2.97 (d, 1H, CH of CH=CH of dmfm, $J = 8.5$ Hz), 3.11–3.16 (m, 2H, CH of cyclooctadienyl), 3.21–3.24 (m, 1H, CH of cyclooctadienyl), 3.55–3.60 (m, 2H, CH of cyclooctatrienyl), 3.62 (s, 3H, OMe), 3.65 (s, 3H, OMe), 3.68 (s, 3H, OMe), 3.69 (s, 3H, OMe), 3.93–4.00 (m, 2H, CH of cyclooctatrienyl), 4.58 (dd, 2H, CH of dmfm, $J = 8.9, 22.6$ Hz), 4.70 (d, 1H, CH=CH of dmfm, $J = 8.5$ Hz), 5.66 (t, 2H, CH of cyclooctadienyl, $J = 5.6$ Hz), 5.71 (s, 1H, OH), 6.55 (t, 1H, CH of cyclooctadienyl, $J = 6.1$ Hz); ¹³C NMR (CD_2Cl_2 , 125 MHz): δ 12.71, 19.65 (CH₂), 20.62 (CH₂), 26.80 (CH₂), 29.32 (CH₂), 29.38 (CH₂), 29.52 (CH₂), 29.54 (CH₂), 45.75, 45.99, 46.11, 47.78, 48.40, 48.50, 50.07, 50.55, 51.14, 51.18 (OCH₃), 52.13 (OCH₃), 52.25 (OCH₃), 52.50 (OCH₃), 52.55, 57.63, 60.30, 70.55, 72.27, 72.82, 74.69, 76.63, 81.88, 90.72, 94.72, 133.63, 176.18 (C=O), 176.26 (C=O), 179.45 (C=O), 179.52 (C=O); FAB-MASS m/z 1061 (M^+). Anal. Calc. for $\text{C}_{36}\text{H}_{48}\text{O}_{11}\text{Ru}_4 \cdot 2\text{H}_2\text{O}$: C, 39.41; H, 4.78. Found: C, 39.71; H, 4.60%.

4.2. X-ray crystal structure determination

Crystals suitable for X-ray diffraction measurements were obtained from recrystallization in CH_2Cl_2 /pentane

were mounted on glass fibers. X-ray data showed that the crystal is orthorhombic and the space group is $Pca2_1$ from the systematic absences of $0kl$ for l odd and $h0l$ for h odd. The lattice parameters are $a = 17.964(8)$, $b = 30.833(12)$, $c = 13.503(5)$ Å, $V = 7479$ Å³, and $Z = 4$. The diffraction data were collected on a Rigaku/MS Mercury CCD using graphite monochromated Mo K α radiation at 173 K. Crystal data and experimental details are summarized in Table 1. The structure was solved by a combination of direct method and Fourier techniques, and all the non-hydrogen atoms were anisotropically refined by full-matrix least-squares calculations. The hydrogen atoms were not included for further refinement, although the numbers of reflection data were enough to refine all the parameters of the hydrogen atoms.

In addition, complex **2** and the solvents of crystallization (H₂O and CH₂Cl₂) formed the layers alternately on the ac planes of the unit cell, which were piled up in the direction of b axis. It was very difficult to assign the atoms of solvent molecules because of their keen disorders, although we tried to assign them as much as possible. We carried out the crystal structure analyses for many crystals, but the crystal obtained here is the best one. The positions of all the atoms of complex **2** did not move greatly during refinements, although their temperature factors were changed delicately. Therefore, the $(\mu_3\text{-oxo})\text{tetranuclear}$ structure of complex **2** was confirmed, although the atomic parameters are not good for the strict and detailed discussion for bond lengths and angles. The final R and wR_2 values are 0.096 and 0.112, respectively. Absorption correction was applied empirically. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography IV [15]. All calculations were carried out on a DELL computer using the Rigaku CrystalStructure [16,17] crystallographic software package.

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Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with Cambridge Crystallographic Data Centre, CCDC No. 263410

for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www:<http://www.ccdc.cam.ac.uk>).

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