A Novel Tetra Nuclear Ruthenium Complex Containing Deltoid Core Topology, $[Ru_4(\mu_3\text{-}O)_2]^{8+}$, Incorporating Simultaneous O,O- and γ-C Bonded Bridging Acetylacetone Units

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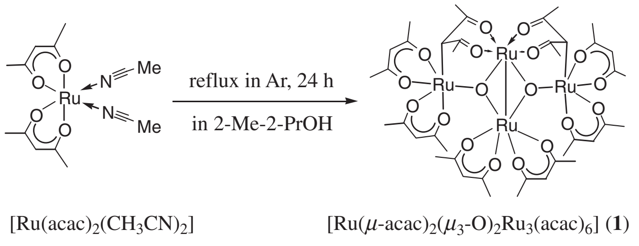
The reflux of mononuclear ruthenium precursor $[Ru^{II}(acac)_2(CH_3CN)_2]$ (acac = acetylacetonate) in 2-methyl-2-propanol formed the novel diamagnetic β-diketonato ruthenium tetranuclear complex $[Ru(\mu\text{-}acac)_2(\mu_3\text{-}O)_2Ru_3(acac)_6]$ (**1**), in which was contained the deltoid core, $[Ru_4(\mu_3\text{-}O)_2]^{8+}$, consisting of four ruthenium and two oxygen atoms. The complex **1** has been characterized on the basis of elemental analysis, ^1H NMR, structural and cyclic voltammetric analyses. The molecular structure of **1** showed that each ruthenium ion was bridged by two oxygen atoms and two ruthenium ions link to γ-carbon on acetylacetonate coordinated to another ruthenium. The cyclic voltammogram of **1** showed two reversible one-electron oxidation peaks and an one-electron reduction peak corresponding to the redox of $[Ru_4(\mu_3\text{-}O)_2]^{8+}$ core.

The complex $[Ru^{II}(\beta\text{-dik})_2(CH_3CN)_2]$[1] and $[Ru^{III}(\beta\text{-dik})_2(CH_3CN)_2]^{+}$ [2] (β-dik = β-diketonate ion) are very useful precursors for variety of novel reactions. These acetonitrile complexes have been used to prepare several mono-, di-, tri-, and tetranuclear complexes with $\{Ru(acac)_2\}$ moieties:[3,4] syntheses of binuclear complexes using the substitution reactions of coordinated acetonitriles on β-diketonato ruthenium complexes; syntheses of β-ketiminato ruthenium with the reaction in the several kinds of ketones; the reactions of the coordinated acetonitriles on β-diketonato ruthenium complexes to acetic acid. Recently, G. K. Lahiri et al. have reported interesting symmetric triangular mixed-valence triruthenium complexes containing ruthenium–γ-carbon on acetylacetonate ion bonding. In addition, several papers relating to the multinuclear complexes bridged by transition metals[5–10] (rhodium, iridium, platinum, and palladium) and γ-carbon on acetylacetonate have been reported. The tetranuclear complexes with $\{Fe_4O_2\}^{8+}$ core have been reported.[11]



$[Ru(acac)_2(CH_3CN)_2]$ $[Ru(\mu\text{-}acac)_2(\mu_3\text{-}O)_2Ru_3(acac)_6]$ (**1**)

Scheme 1. Formation of the complex **1**.

The complex **1** has been synthesized from $[Ru^{II}(acac)_2(CH_3CN)_2]$ as shown in Scheme 1. In a typical experiment, $[Ru^{II}(acac)_2(CH_3CN)_2]$ (0.40 g, 1.0 mmol) was added to the solvent (40 cm^3) and the mixture was refluxed for 24 h. During the course of the reflux, Ar was bubbled through the solution. The color of the solution turned to dark brown from yellowish orange. The solvent was then evaporated under vacuum and the residue was chromatographed on a silica gel column. The four (a green, two dark-, and a light-brown) main fractions were collected with benzene–acetonitrile (2:1 v/v). The green fraction was again chromatographed with benzene–acetonitrile (4:1 v/v). The solvent was evaporated to yield green $[Ru(\mu\text{-}acac)_2(\mu_3\text{-}O)_2Ru_3(acac)_6]$ (**1**).[12] Yield: 25 mg (8.1% based on Ru). The two dark-brown compounds (11%) were found to be the isomers of **1** and the light brown compound (20%) found to be $[Ru_3(acac)_6(\mu_3\text{-}O)]$ by FAB-mass spectrometry. The details of these compounds will be report separately.

The chemical shift of **1** in ^1H NMR was in the range from 5.30–1.85 ppm. This means that **1** is diamagnetic and that electrons around ruthenium atoms in the $[Ru_4(\mu_3\text{-}O)_2]^{8+}$ core are delocalized.

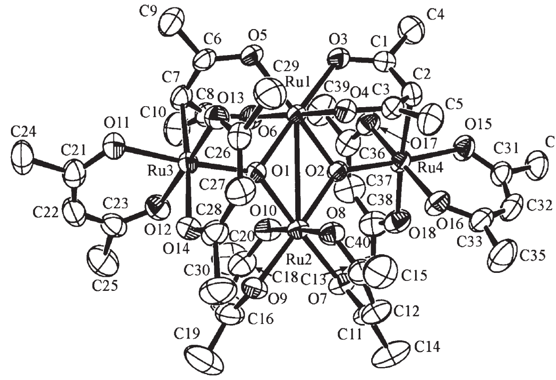


Figure 1. Molecular structure of $[Ru(\mu\text{-}acac)_2(\mu_3\text{-}O)_2Ru_3(acac)_6]$ (**1**). Selected bond lengths (Å) and angles (°): Ru1–Ru2 = 3.0805(4), Ru1–Ru3 = 3.3668(3), Ru1–Ru4 = 3.3692(3), Ru2–Ru3 = 3.6089(3), Ru2–Ru4 = 3.5891(4), Ru1–O1 = 1.973(2), Ru1–O2 = 1.968(2), Ru2–O1 = 1.973(2), Ru2–O2 = 1.973(2), Ru3–O1 = 1.911(2), Ru4–O2 = 1.903(2), Ru4–C2 = 2.270(4), Ru3–C7 = 2.271(3), Ru3–Ru1–Ru4 = 135.36(1), Ru3–Ru2–Ru4 = 119.93(1), Ru1–Ru3–Ru2 = 52.27(1), Ru1–Ru4–Ru2 = 52.44(1).

The structure of **1** has been determined by single crystal X-ray diffraction. The molecular structure and the important bond lengths and bond angles are given in Figure 1.[13] The $[Ru_4(\mu_3\text{-}O)_2]^{8+}$ core has C_2 symmetry for Ru1–Ru2 bond axis. The four ruthenium atoms in the core lie at the corners of a "deltoid" (kite shape), therefore Ru1–Ru3 and Ru1–Ru4 lengths are nearly the same. The lengths of Ru2–Ru3 and Ru2–Ru4 are also the same. The sum of the four angles in the ruthenium deltoid core is 360.00°. The fact means that the four ruthenium atoms are in the same plane. Furthermore, the sum of the three Ru–O–Ru angles around the μ_3-oxo atom is 359.49° for O1, and 359.59° for O2. Therefore the two μ_3-oxo atoms lie on the same plane of the deltoid consisting of the four ruthenium atoms. Two acac ions, coordinated to Ru1 with two oxygen atoms, simultaneously link to Ru3 and Ru4 atoms with γ-C on each acac, whereas γ-C on acac ions coordinated to Ru2 does not link Ru3 or Ru4 atom. It is clear that the acac ions coordinating Ru1 are diketonic in form, in which the γ-C center should exhibit sp^3 hybridization. Therefore the acac ions bridged with γ-C take boat conformation. The acac ions coordinated with Ru2, Ru3, and Ru4 are normal enolic form and take planer conformation.

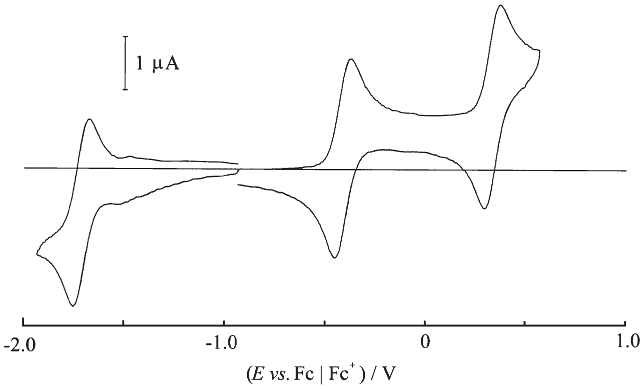


Figure 2. Cyclic voltammograms of complex **1** in dichloromethane solution containing 0.1 mol dm^{-3} tetrabuthylammonium perchlorate at 25 °C. The test electrode is a stationary platinum disk ($\phi = 1.6$ mm). The potentials are measured against Ag|AgCl (3 mol dm^{-3} NaCl aq. solution). The concentrations of complex **1** are 0.5 mmol dm^{-3} and the potential scan rate is 0.1 V s^{-1}.

The cyclic voltammogram of **1** shown in Figure 2 showed two oxidation peaks ($E_{1/2}$: -0.42 and 0.34 V) and one reduction ($E_{1/2}$: -1.72 V) peak. All peaks are corresponding to reversible one-electron transfer processes. These electrode processes are attributable to the redox of the ruthenium ions in the $[Ru_4(\mu_3\text{-}O)_2]^{8+}$ core. The oxidation number of the four ruthenium ions in the core formally could be represented as Ru(III), however, because of higher electron density of ruthenium in the core, the $E_{1/2}$ of oxidation and reduction states are much shifted to negative potential comparing with that of $[Ru(acac)_3]$ (oxidation: 0.60 V, reduction: -1.16 V).[3] The large separation in potential (0.76 V) between the first and second oxidation processes is indicative of the strong electronic coupling between the ruthenium ions in $[Ru_4(\mu_3\text{-}O)_2]^{9+}$ state through the bridging function.

For the delocalization of electrons in the core, ruthenium ion corresponding to the oxidation and reduction could not be decided. Consequently, the observed peaks are assigned to stepwise electron-transfer processes involving the overall $[Ru_4(\mu_3\text{-}O)_2]^{8+}$ core. Lahiri et al. have also reported $[Ru_3(\mu_3\text{-}S)]^{6+}$ core in which the ruthenium centers are strongly coupled in the mixed-valence states.[6] The diamagnetic properties of **1** can be explained as shown in electronic state for $[Ru_3(\mu_3\text{-}S)]^{6+}$.

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12 FAB-Mass: $m^+/z = 1230$ (M^+), 1130 ($M^+ -$ acac), 1030 ($M^+ -$ 2acac). Anal. Found; C, 39.78; H, 4.79%. Calcd. for $C_{40}H_{56}O_{18}Ru_4$ (1229.15): C, 39.09; H, 4.59%. ^1H NMR (500 MHz, $CDCl_3$) $\delta = 2.82$, 2.22 (each s, 6H, Ru1-acac's β-CH_3), $\delta = 2.60$ (broad), 2.15 (each s, 6H, Ru2-acac's β-CH_3), $\delta = 2.60$, 2.04, 2.03 (broad), 1.85 (each s, 6H, Ru3, and Ru4-acac's β-CH_3), $\delta = 4.97$ (broad) (s, 2H, Ru1-acac's γ-CH), $\delta = 5.20$ (s, 2H, Ru2-acac's γ-CH), $\delta = 5.30$, 2.55 (broad) (each s, 2H, Ru3, and Ru4-acac's γ-CH). Electronic spectra: λ/nm ($\log_{10}(\varepsilon/\text{mol}^{-1}\,\text{dm}^3\,\text{cm}^{-1})$) = 228 (4.59), 273 (4.49), 372 (4.21), 753 (4.14).

13 Crystal and analytical data for $[Ru(\mu\text{-acac})_2(\mu_3\text{-}O)_2Ru_3(acac)_6]$, $C_{40}H_{56}O_{18}Ru_4$; fw = 1229.15; Triclinic, $P\bar{1}$ (#2), $Z = 2$, $a = 10.850(1)$ Å, $b = 11.221(1)$ Å, $c = 22.736(1)$ Å, $\alpha = 99.409(1)°$, $\beta = 95.465(1)°$, $\gamma = 114.988(1)°$, $V = 2433.0(2)$ Å^3, $D_{\text{calcd}} = 1.678$ g cm^{-3}, μ(Mo Kα) = 12.86 cm^{-1}, Final $R = 0.039$ ($R_W = 0.093$) for 38088 observed reflections. Measurements for diffraction data were carried out on a Rigaku AFC8R–Mercury CCD diffractometer. The structures were solved direct methods and refined by a full-matrix least-squares treatment. The data of **1** has been deposited to the CCDC (Supplementary No. CCDC-244790).

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