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# Carboxylato-Modified New Oxo-Centred Triruthenium Cluster Compounds with CO and Solvent Ligands: The X-ray Structure of $[Ru_3O(C_2H_5CO_2)_6(CO)(THF)_2]$

**Atsushi Inatomi,[a] Masaaki Abe,*[a] and Yoshio Hisaeda*[a]**

**Keywords:** Ruthenium / Cluster compounds / Carboxylato ligands / Cyclic voltammetry / Substituent effects

New synthetic precursors for CO-coordinated, oxo-centred triruthenium(II,III,III) complexes with varied carboxylato groups $[Ru_3O(RCO_2)_6(CO)(solvent)_2]$ where R = $C_2H_5$, $CH_3$ and $C_6H_5$ have been prepared and characterised. Among the series, the propionato-bridged complex $[Ru_3O(C_2H_5CO_2)_6(CO)(THF)_2]$ (**1**) was structurally determined by single-crystal X-ray crystallography. Cyclic voltammetry revealed that the benzoato-bridged complex $[Ru_3O(C_6H_5CO_2)_6(CO)(C_2H_5OH)_2]$ in 0.1 mol dm$^{-3}$ $n$Bu$_4$NPF$_6$/DMF undergoes two consecutive one-electron processes assignable to the redox of the $Ru_3(\mu_3\text{-}O)$ core, the redox potentials of which are highly dependent on the electron-donating/accepting nature of the carboxylato groups. UV-light excitation of the compounds in $CH_3CN$ resulted in the dissociation of CO to form the tris($CH_3CN$) compounds $[Ru_3O(RCO_2)_6(CH_3CN)_3]$ (R = $C_2H_5$, $CH_3$ and $C_6H_5$). These compounds are highly useful as synthetic precursors to a wide range of $\mu_3$-oxo-triruthenium derivatives with well-defined redox responses.

## Introduction

A well-defined family of oxo-centred, acetato-bridged trinuclear ruthenium compounds of the type $[Ru_3O(CH_3CO_2)_6L_3]^{n+}$, in which L represents a monodentate ligand,[1–5] have been of considerable interest due to their versatility including their redox chemistry,[6–10] intramolecular electron-transfer on the IR timescale,[11] photoinduced electron transfer,[12] ligand substitution[13–16] and catalytic properties.[17] They are also used as molecular components for a wide range of discrete oligomers[18–20] and for building 2D and 3D architectures on electrode surfaces.[21,22] In addition, many useful applications have been developed including logic gates, electrochromic materials, sensing materials, patterned surfaces and heat shielding materials.[23–27]

Among the derivatives, mixed-valent triruthenium compounds containing one CO and two solvent ligands in terminal positions, i.e. $[Ru_3O(CH_3CO_2)_6(CO)(solvent)_2]$ where solvent is $CH_3OH$[4,6] and THF,[5] are key synthetic precursors for preparing versatile derivatives of the triruthenium compounds and their supramolecular assemblies. For instance, facile substitution of a stronger base such as pyridine (py) for weakly-coordinated solvent ligands in $[Ru_3O(CH_3CO_2)_6(CO)(solvent)_2]$ allows complexes of the type $[Ru_3O(CH_3CO_2)_6(CO)(py)_2]$ to be isolated.[4] When bidentate ligands such as pyrazine (pz) and 4,4′-bipyridine (bpy) are employed as spacers, the synthesis of ligand-bridged discrete compounds such as dimers, trimers, linear and branched tetramers and higher oligomers can be achieved.[1,6,8–11,18–20] In $[Ru_3O(CH_3CO_2)_6(CO)L_2]$, the CO ligand stabilises the +II valency on one of three Ru centres so that the compounds contain valence-localised (mixed valent) states which are best described as $\{Ru^{II}\text{–}CO\}\{Ru^{III}\text{–}L\}_2$.[28–30] The CO ligand is subsequently released by conducting one-electron chemical oxidation[4,5] or UV irradiation[14] in solution to form $[Ru_3O(CH_3CO_2)_6(solvent)L_2]$ and $[Ru_3O(CH_3CO_2)_6L'L_2]$ when L′ is present.[4] The majority of synthetic studies on the $\mu_3$-oxo-triruthenium compounds stem from utilisation of the "acetato"-bridged precursors $[Ru_3O(CH_3CO_2)_6(solvent)_3]$ and $[Ru_3O(CH_3CO_2)_6(CO)(solvent)_2]$ and the derivatives that involve other carboxylato groups or different types of bridging ligands have rarely been examined to date.[3a,31,32] This is in remarkable contrast to the situation of analogous $\mu_3$-oxo-trimetal compounds where a wide range of carboxylato units or related ligands have been introduced, allowing structural/electronic tuning through the synthetic modifications to be achieved.[33–35]

Herein we describe the synthesis, characterisation, redox chemistry and photoinduced CO ligand dissociation reactions of a novel series of CO-coordinated $\mu_3$-oxo-triruthenium compounds, **1**–**3**, with varied carboxylato bridges as illustrated in Scheme 1. Due to the presence of weakly-coordinated solvent ligands in terminal sites and carboxylato-dependent well-defined redox features, these compounds should be useful as synthetic precursors for electronically designed cluster compounds. The molecular structure of **1**

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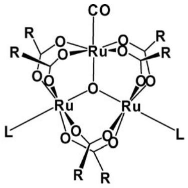
[a] Department of Applied Chemistry, Graduate School of Engineering, Kyushu University,
Nishi-ku, Fukuoka 819-0395, Japan
Fax: +81-92-802-2828
E-mail: mabe@mail.cstm.kyushu-u.ac.jp
yhisatcm@mail.cstm.kyushu-u.ac.jp

is also described in this paper as the first example of a structurally characterised $\mu_3$-oxo-triruthenium compound that contains a mixed terminal ligand composition: "(CO)(solvent)$_2$".



| R | L | |
|---|---|---|
| $C_2H_5$ | THF | **1** |
| $CH_3$ | THF | **2** |
| $C_6H_5$ | $C_2H_5OH$ | **3** |

Scheme 1.

## Results and Discussion

### Syntheses

Two new CO-coordinated $\mu_3$-oxo-triruthenium cluster compounds, **1** and **3**, modified with varied carboxylato groups have been synthesised and characterised. One-electron reduction of the cationic $Ru_3^{III}$ precursors $[Ru_3O(RCO_2)_6(C_2H_5OH)_3]^+$ (R = $C_2H_5$, $CH_3$ and $C_6H_5$) with Zn/Hg in $C_2H_5OH$ under an $N_2$ atmosphere led to the formation of mixed-valent neutral compounds in the $Ru_3^{II,III,III}$ states, i.e. $[Ru_3O(RCO_2)_6(C_2H_5OH)_3]$. These compounds were formed in situ and were not isolated in this study. After filtering off the Zn/Hg, carbon monoxide gas was vigorously passed through the solution with stirring to form the CO-coordinated compounds, $[Ru_3O(RCO_2)_6(CO)(C_2H_5OH)_2]$. Purification of the products was accomplished by chromatography on a silica gel column. The crystalline materials **1** and **3** were successfully obtained by recrystallisation from two-component, mixed solvent systems of THF/*n*-hexane and $C_2H_5OH$/*n*-hexane, respectively. Compound **1** was found to show enhanced solubility in common organic solvents over the acetato analogue **2**, especially in halogenated solvents such as dichloromethane. This indicates the remarkable utility of **1** as a precursor material for $\mu_3$-oxo-triruthenium cluster derivatives.

ESI mass spectrometry of **1** and **3** dissolved in $CH_3OH$ showed parent peaks at $m/z$ = 851.2 and 1139.5, respectively, which are in accord with the calculated molecular weights of $[Ru_3O(RCO_2)_6(CO)(CH_3OH)_2]$ (R = $C_2H_5$ and $C_6H_5$) where the two solvent ligands in **1** and **3** are replaced by $CH_3OH$ upon dissolution. Observed isotopic patterns of the mass envelopes are consistent with the respective calculated patterns.

### Crystal Structure

The molecular structure of **1** was unambiguously determined by X-ray crystallography. An ORTEP drawing of **1** is presented in Figure 1 and selected interatomic lengths and angles are summarised in Table 1. It should be noted that X-ray structures available to date for triruthenium compounds containing carboxylato functions other than acetato are scarce and the examples include $[Ru_3O(C_6H_5CO_2)_6(py)_3]^+$,[36] $[Ru_3O(HCO_2)_6(H_2O)_3]^+$,[37] $[Ru_3O(C_2H_5CO_2)_6(py)_3]^+$[38] and $[Ru_3O(CF_3CO_2)_6(acetone)_3]^+$[39] where three terminal ligands are identical. The present X-ray structure analysis of **1** can thus be regarded as the first example of a molecular structure of mixed-terminal-ligand derivatives containing non-acetato bridges.

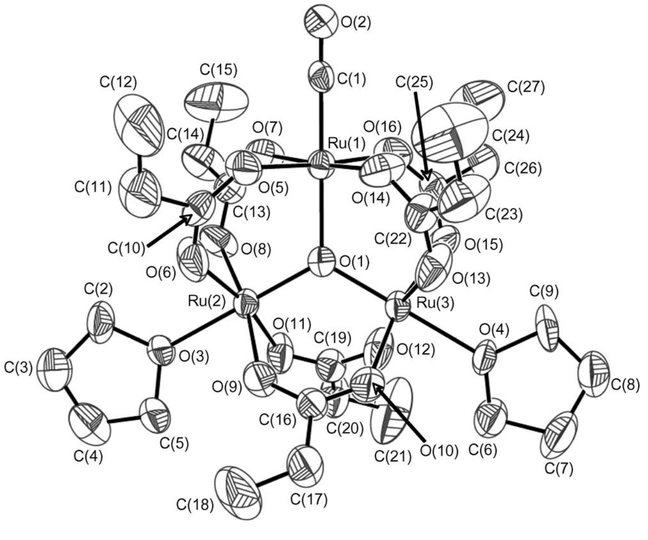


Figure 1. An ORTEP drawing of **1** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **1**.

| | | | |
|---|---|---|---|
| Ru(1)–O(1) | 2.067(7) | Ru(3)–O(4) | 2.139(7) |
| Ru(2)–O(1) | 1.885(8) | C(1)–O(2) | 1.129(13) |
| Ru(3)–O(1) | 1.881(8) | Ru(1)···Ru(2) | 3.4196(13) |
| Ru(1)–C(1) | 1.852(13) | Ru(1)···Ru(3) | 3.4190(13) |
| Ru(2)–O(3) | 2.153(8) | Ru(2)···Ru(3) | 3.2665(12) |
| Ru(1)–O(1)–Ru(2) | 119.7(4) | O(3)–Ru(2)–O(9) | 84.6(4) |
| Ru(1)–O(1)–Ru(3) | 119.9 (4) | C(2)–O(3)–C(5) | 109.7(11) |
| Ru(2)–O(1)–Ru(3) | 120.3(4) | Ru(2)–O(3)–C(5) | 124.0(8) |
| C(1)–Ru(1)–O(5) | 87.7(4) | Ru(2)–O(3)–C(2) | 124.2(8) |
| C(1)–Ru(1)–O(1) | 179.8(5) | C(3)–C(2)–O(3) | 109.6(14) |
| O(1)–Ru(2)–O(3) | 179.9(3) | O(5)–C(10)–O(6) | 128.2(12) |
| O(3)–Ru(2)–O(6) | 84.6(4) | C(11)–C(10)–O(6) | 114.7(14) |
| O(3)–Ru(2)–O(11) | 83.9(4) | Ru(1)–C(1)–O(2) | 179.8(12) |
| O(3)–Ru(2)–O(8) | 84.9(3) | C(4)–C(5)–O(3) | 104.1(13) |

Compound **1** contains the mixed valence II,III,III oxidation states and the +II oxidation state is localised on the Ru site coordinated by CO. The triangle thus formed by the three Ru centres is a near isosceles. For **1**, the Ru1···Ru2 and Ru1···Ru3 distances [3.4196(13) and 3.4190(13) Å, respectively] are considerably longer than the Ru2···Ru3 distance [3.2665(12) Å]. This structural feature originates from the differences in Ru–($\mu_3$-O) bonds where Ru1–O1 2.067(7), Ru2–O1 1.885(8) and Ru3–O1 1.881(8) Å. The significantly longer distance of Ru1–O1 is definitely caused by the *trans* influence of CO. According to the Cambridge Crystallographic Database, there are four crystal structures of CO-

Table 2. Structural comparison for triruthenium complexes of the type $[Ru_3O(RCO_2)_6(CO)L_2]$ and related complexes.

| Complex | Coord. atoms in L[a] | Bond lengths [Å] $Ru^{CO}$–($\mu_3$-O)[b] | $Ru^{L}$–($\mu_3$-O)[b] | $Ru^{CO}\cdots Ru^{L}$ | $Ru^{L}\cdots Ru^{L}$ | Ref. |
|---|---|---|---|---|---|---|
| $[Ru_3O(C_2H_5CO_2)_6(CO)(THF)_2]$ (**1**) | O,O | 2.067(7) | 1.885(8), 1.881(8) | 3.4196(13), 3.4190(13) | 3.2665(12) | this work |
| $[Ru_3O(CH_3CO_2)_6(CO)(mbpy^+)_2](ClO_4)_2\cdot DMF$[c] | N,N | 2.039(11) | 1.894(6) | 3.410(2) | 3.276(2) | [30] |
| $[Ru_3O(CH_3CO_2)_6(CO)(abco)_2]\cdot 2CH_2Cl_2$[d] | N,N | 2.065(3) | 1.888(3), 1.894(3) | 3.4217(5), 3.4084(6) | 3.2979(5) | [40] |
| $[\{Ru_3O(CH_3CO_2)_6(CO)(abco)\}_2(\mu\text{-pz})]\cdot 2CH_2Cl_2$[e] | N,N | 2.057(4) | 1.889(5), 1.896(3) | 3.3973(9), 3.4340(5) | 3.2892(8) | [40] |
| $[\{Ru_3O(CH_3CO_2)_6(CO)\}_2(\mu\text{-dppf})(\mu\text{-odppf})\cdot 0.5C_2H_4Cl_2$[f] | P,O | 2.071(7) | 1.882(6), 1.918(6) | 3.410, 3.442 | 3.314 | [41] |
| | P,O | 2.082(7) | 1.888(7), 1.916(7) | 3.415, 3.457 | 3.32 | |
| $[Ru_3O(CH_3CO_2)_6(CNXy)(py)_2]\cdot 2CHCl_3$[g] | N,N | 2.035(3) | 1.888(1) | 3.3909(4) | 3.2840(7) | [8] |

[a] Coordination atoms in terminal ligand L. [b] $Ru^{CO}$ and $Ru^{L}$ represent Ru atoms coordinated by CO and L, respectively. [c] $mbpy^+$ = 1-methyl-4,4′-bipyridinium ion. [d] abco = 1-azabicyclo[2,2,2]octane. [e] pz = pyrazine. [f] dppf = 1,1′-bis(diphenylphosphanyl)ferrocene; odppf = 1,1′-bis(oxodiphenylphosphoranyl)ferrocene. [g] CNXy = 2,6-dimethylphenyl isocyanide; py = pyridine.

coordinated complexes among acetato-containing triruthenium complexes[30,40,41] which are summarised in Table 2, along with a structurally related complex $[Ru_3O(CH_3CO_2)_6(CNXy)(py)_2]\cdot 2CHCl_3$ (CNXy = 2,6-dimethylphenyl isocyanide).[8] All the compounds show the isosceles structural feature for the $Ru_3$ frameworks in which the +II valency is believed to be localised on the Ru centre coordinated by CO or the isocyanide ligand. From Table 2, short distances for the $Ru^{L}$–($\mu_3$-O) bonds for **1** are notable among the series, which is a reflection of the weaker coordination of THF molecules compared with nitrogen-based ligands such as pyridine derivatives,[30] abco and pz.[40] The Ru–O(THF) bond lengths in **1** are 2.153(8) and 2.139(7) Å. The structural inequivalency again indicates that the triruthenium core in **1** is in the valence-trapped $\{Ru^{II}–CO\}Ru^{III}_2$ state. All the Ru–($\mu_3$-O)–Ru angles in **1** are close to 120°, ranging from 119.7(4) to 120.3(4)°. The average Ru–O(propionato) bond lengths of 2.070 Å for Ru1–O, 2.037 Å for Ru2–O and 2.037 Å for Ru3–O may also reflect the lower oxidation state in Ru1 and the higher oxidation states in Ru2 and Ru3.

Two THF ligands are nearly parallel to the triangular plane of the three Ru atoms. It is also of note that four ethyl groups of the propionato anions bridging $Ru^{II}\cdots Ru^{III}$ (e.g., Ru1···Ru2 and Ru1···Ru3) stand upward while those of the remaining two propionato anions bridging $Ru^{III}\cdots Ru^{III}$ (e.g., Ru2···Ru3) point in the opposite directions to each other. The orientation for the latter can be ascribed to intermolecular short contacts between methylene carbons in ethyl groups and oxygens in the CO ligands of the neighbouring molecules in which C···O distances of 2.635 and 2.697 Å can be observed.

## Spectroscopic Characterisation

In the IR spectra (KBr pellet), compounds **1** and **3** show intense absorption peaks at 1958 and 1955 $cm^{-1}$, respectively, which can be ascribed to the ν(CO) mode of the terminal carbonyl ligands.[28,30] Two resolved bands ascribed to the asymmetric stretching mode of the carboxylato bridges, $\nu_{asym}$(COO) are observable at ca. 1610 and 1570 $cm^{-1}$, and the symmetric stretching band $\nu_{sym}$(COO), which is stronger in intensity than $\nu_{asym}$(COO), can be observed at ca. 1420 $cm^{-1}$.[30,42] The principal feature in the IR spectra of **1** and **3** is thus very similar to that for the acetato analogue **2**.[30]

All the compounds are diamagnetic and have been well characterised by $^1H$ NMR spectroscopy. The inequivalent ligand environment for the bridging carboxylato units in **1** and **3**, based on the mixed valency of the triangle framework as discussed above, is also evident from $^1H$ NMR spectroscopy. Compound **1** in $CD_3OD$ shows two inequivalent bridging propionato units in the 2:1 ratio. This feature is also observed for the bridging benzoato groups in **3**. Due to a fast exchange of two solvent ligands at the $Ru^{III}$ centres in a room-temperature solution, the coordinated ligands in **1** and **3** were not recognised.

UV/Vis absorption data for **1**–**3** in $CH_3CN$ are provided in Table 3. The compounds show three intense absorption bands in the UV/visible region. The band maxima for **1** and **3** are 581 ($\varepsilon$ = 3600 $mol^{-1} dm^3 cm^{-1}$) and 594 nm ($\varepsilon$ = 2900 $mol^{-1} dm^3 cm^{-1}$) in $CH_3CN$, respectively, which can both be assigned to "intracluster charge-transfer (ICCT)" transitions.[1b,8] The spectroscopic patterns for **1**–**3** are similar to each other but the peak positions are sensitively affected by the nature of the bridging carboxylato units (Table 3). It can be observed that the peak position shifts to a longer wavelength region in the order $\mathbf{1} \approx \mathbf{2} < \mathbf{3}$, indicating that the HOMO–LUMO gap in energy levels of the $Ru_3(\mu_3\text{-O})$ framework is decreased by the introduction of electron-withdrawing groups on the carboxylato groups.

Table 3. UV/Vis absorption spectroscopic data of **1**–**3** in $CH_3CN$.[a]

| Complex | $\lambda_{max}$ [nm] ($\varepsilon$ [$mol^{-1} dm^3 cm^{-1}$]) |
|---|---|
| **1** | 581 (3600), 370 sh |
| **2** | 582 (3200), 380 sh |
| **3** | 594 (2900), 400 sh |

[a] sh = shoulder.

## Redox Chemistry

Carboxylato substituent effects in **1**–**3** are most clearly observed in the redox potential shift. Figure 2 presents cyclic voltammograms (CVs) of those compounds dissolved in 0.1 $mol\,dm^{-3}$ $nBu_4NPF_6$/DMF at 298 K. The redox potentials are summarised in Table 4.

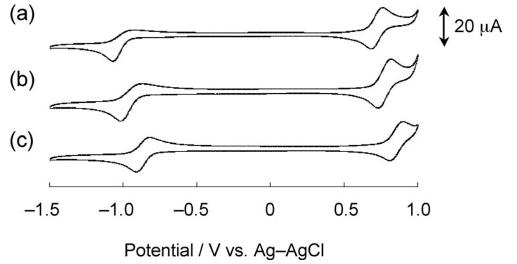


Figure 2. Cyclic voltammograms of (a) **1**, (b) **2** and (c) **3** in 0.1 mol dm$^{-3}$ $n$Bu$_4$NPF$_6$/DMF at 298 K. Scan rate: 0.1 V s$^{-1}$. [complex] = 1.0 mmol dm$^{-3}$.

Table 4. Cyclic voltammetric data of **1**–**3** in 0.1 mol dm$^{-3}$ $n$Bu$_4$NPF$_6$/DMF at 298 K.[a]

| Complex | $E_{1/2}$[b] [V] vs. Ag/AgCl ($\Delta E_p$[c] [mV]) | |
|---|---|---|
| | $\{Ru^{II}–CO\}Ru_2^{III,III}/$<br>$\{Ru^{II}–CO\}Ru_2^{II,III}$ | $\{Ru^{II}–CO\}Ru_2^{III,III}/$<br>$\{Ru^{III}–CO\}Ru_2^{III,III}$ |
| **1** | –1.07[d] | 0.72 (78) |
| **2** | –1.02[d] | 0.77 (86) |
| **3** | –0.86 (90) | 0.86 (89) |

[a] Working electrode, counter electrode and reference electrode are glassy carbon, platinum wire and Ag/AgCl, respectively. Scan rate: 0.1 V s$^{-1}$. [b] Half-wave potential, $E_{1/2} = (E_{pa} + E_{pc})/2$, where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials, respectively. [c] Peak-to-peak separation, $\Delta E_p = E_{pa} - E_{pc}$ (in mV). [d] Reduction peak potential for irreversible process.

As shown in Figure 2, the compounds display two redox processes in the potential region between +1.00 and –1.50 V vs. Ag/AgCl. For example, compound **1** (Figure 2, a) displays a reversible one-electron redox couple at $E_{1/2}$ = +0.72 V and an irreversible reduction peak at –1.07 V at a scan rate of 0.1 V s$^{-1}$ and these can be ascribed to $\{Ru^{II}–CO\}Ru_2^{III,III}/\{Ru^{III}–CO\}Ru_2^{III,III}$ and $\{Ru^{II}–CO\}Ru_2^{II,III}/\{Ru^{II}–CO\}Ru_2^{III,III}$, respectively.[28] The latter process is also irreversible for the acetato analogue **2** (Figure 2, b) but becomes reversible for the benzoato analogue **3** (Figure 2, c). The redox potentials are shifted to the positive direction from **1** to **2** and to **3** by 140 mV for the reversible redox process. This potential shift can be readily ascribed to substituent effects of the carboxylato units. As more electron-withdrawing carboxylato groups are incorporated, the $Ru_3(\mu_3\text{-}O)$ centre is reduced more easily and oxidised with more difficulty. The p$K_a$ values of the protonated form of the carboxylato anions are 4.62 for propionic acid, 4.57 for acetic acid and 4.00 for benzoic acid.[43]

The carboxylato substituent effects on the redox potentials of "basic carboxylate"-type complexes have been so far reported in a limited number of cases. A series of triiron compounds of the type $[Fe_3O(RCO_2)_6L_3]^{n+}$ (where $RCO_2^-$ stands for carboxylato or deprotonated amino acids; L = $H_2O$, pyridine or imidazole)[33,34] is the most thoroughly studied and it was shown that redox potentials of reversible waves ascribed to $Fe_3^{II,III,III}/Fe_3^{III,III,III}$ are shifted in a positive direction as more electron-withdrawing substituents are introduced on the carboxylato frame with a slope of 251 mV/p$K_a$.[33] For triruthenium compounds, only two examples[36] are available for direct comparison of carboxylato substituent effects on metal-based redox potentials. A tris(pyridine)benzoato complex $[Ru_3O(C_6H_5CO_2)_6(py)_3]^+$ in 0.1 mol dm$^{-3}$ $n$Bu$_4$NPF$_6$/CH$_3$CN shows $E_{1/2}$ values of +1.58, +0.71, –0.26 and –1.54 V vs. Ag/AgCl and the corresponding values for the acetato analogue $[Ru_3O(CH_3CO_2)_6(py)_3]^+$ are +1.60, +0.63, –0.42 and –1.70 V vs. Ag/AgCl under the same conditions.[36] It is thus apparent that on going from the acetato to the benzoato complexes, the corresponding $E_{1/2}$ values are shifted in a positive direction and differences between the corresponding $E_{1/2}$ values increase as the oxidation numbers decrease. These trends reported in different systems are consistent with our triruthenium compounds **1**–**3** and indicate that the electron density of the $Ru_3(\mu_3\text{-}O)$ framework is tuned as a function of the electron push/pull effect of the bridging carboxylato groups. The linear correlation of redox potentials and p$K_a$ values of the bridging carboxylato units has also been described by Neubold et al.[44] for a series of (μ-oxo)bis(μ-carboxylato)diruthenium(III,III) complexes $[L_2Ru_2(\mu\text{-}O)(\mu\text{-}RCO_2)_2](PF_6)_2$ (L = 1,4,7-triazacyclononane; R = $CH_3$, $CF_3$, H, $C_6H_5$, $CCl_3$ and $CH_2Cl$) in 0.1 mol dm$^{-3}$ $n$Bu$_4$NPF$_6$/CH$_3$CN. It is of note that the extent of the substituent effect of six carboxylato groups is much larger than the substituent effect of three terminal ligands. Toma et al. have previously reported[45] that for a series of triruthenium complexes $[Ru_3O(CH_3CO_2)_6(N\text{-}Het)_3]^{0/+}$ (N-Het = N-heterocyclic ligands such as py and pz derivatives), $E_{1/2}$ values are linearly shifted as a function of the p$K_a$ values of the terminal N-Het ligands with slopes of 74, 39, 29 and 23 mV/p$K_a$ for four successive redox processes.

## Photoreactivity

The photosubstitution behaviour for **1**–**3** in CH$_3$CN has been studied by UV/Vis/NIR spectroscopy. As proposed in our earlier study,[14] the UV irradiation to **2** in CH$_3$CN gives rise to the dissociation of CO to form a tri(CH$_3$CN) complex $[Ru_3O(CH_3CO_2)_6(CH_3CN)_3]$. The photoactive band in the reaction is localised in the wavelength region less than 400 nm and can be tentatively assigned to a "cluster-to-CO" charge-transfer transition.[14,15]

The UV/Vis/NIR spectra that monitor the photoreaction of **1** in CH$_3$CN are provided in Figure 3 as a typical example. Upon UV irradiation (a band pass filter at 365 nm was employed), the absorption spectrum of **1** gradually changed. The intensity of the peak at 591 nm decreased and new bands at 893 nm increased with isosbestic points at 685 and 467 nm, showing a two-component feature. Similar to the photoreaction of **2**,[14] we propose that a $[Ru_3O(C_2H_5CO_2)_6(CO)(CH_3CN)_2]$ complex, which is formed upon dissolution of **1** in CH$_3$CN, is transformed to a tris(CH$_3$CN) complex $[Ru_3O(C_2H_5CO_2)_6(CH_3CN)_3]$ during the photolysis. For **3**, isosbestic points at 697, 478 and 316 nm were observed during the photoreaction. Spectroscopic features seen in the photoproducts, as summarised in Table 5, are typical for those of valence-averaged $Ru_3^{II,III,III}$ complexes $[Ru_3O(RCO_2)_6L_3]$ which are free from CO.[14]

The photodissociation of CO from **1**–**3** was well described by first-order kinetics and rate constants of $8.3 \times 10^{-5}$, $1.1 \times 10^{-4}$ and $8.6 \times 10^{-5}$ $s^{-1}$ (298 K) were obtained for **1**, **2** and **3**, respectively. The small difference in the rate constants for **1**–**3** may support a previous claim[14] that the photoactive band for the CO dissociation is associated with a "$Ru_3(\mu_3\text{-}O)$ cluster-to-CO" charge-transfer band which may be less influenced by the nature of bridging carboxylato groups.

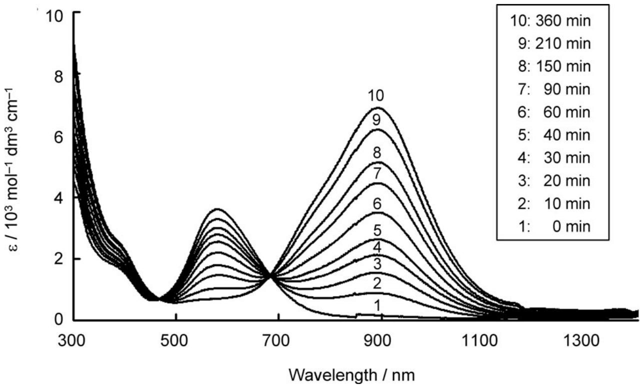


Figure 3. UV/Vis/NIR spectra that monitor photoinduced CO dissociation reactions of **1** (0.052 mmol dm$^{-3}$) in $CH_3CN$. The inset shows the time of UV irradiation.

Table 5. UV/Vis/NIR absorption spectroscopic data for photoproducts obtained from **1**–**3** in $CH_3CN$.[a]

| Complex | $\lambda_{max}$ [nm] ($\varepsilon$ [mol$^{-1}$ dm$^3$ cm$^{-1}$]) |
|---|---|
| $[Ru_3O(C_2H_5CO)_6(CH_3CN)_3]$ | 893 (6800), 750 sh, 380 sh |
| $[Ru_3O(CH_3CO)_6(CH_3CN)_3]$ | 895 (6300), 750 sh, 370 sh |
| $[Ru_3O(C_6H_5CO)_6(CH_3CN)_3]$ | 896 (4500), 750 sh, 332 (13000) |

[a] sh = shoulder.

## Conclusions

We described herein the synthesis, characterisation and photoreactivity of two new oxo-centred trinuclear ruthenium compounds coordinated by CO which incorporate six propionato (**1**) or benzoato (**3**) groups as bridging ligands. The substituent effects of carboxylato groups can be observed in the redox potentials that are negatively shifted at 140 mV on going from the electron-withdrawing phenyl group to the electron-donating ethyl group on the six carboxylato groups. Introduction of the propionato bridges onto the $Ru_3(\mu_3\text{-}O)$ framework results in considerable enhancement of solubility compared with the acetato analogue. From a synthetic viewpoint, this feature indicates that compound **1** is promising as a useful synthon for yielding more versatile, soluble discrete assemblies containing $\mu_3$-oxo-triruthenium cluster motifs, especially in the development of higher molecular weight oligomeric clusters. Research in this direction is in progress.

## Experimental Section

**Materials:** All solvents and reagents were purchased from commercial sources and used without further purification unless otherwise stated. Compound **2** was prepared according to an earlier report.[5]

**Physical Measurements:** UV/Vis/NIR absorption spectra were recorded with a JASCO V-670KS spectrophotometer (300–1400 nm). Infrared spectra were obtained from KBr pellets with a JASCO FTIR 460 Plus spectrometer (4000–400 cm$^{-1}$). NMR spectra were recorded at 500 MHz, by using, respectively, $CD_3OD$ and $C_2D_5OD$ as the solvent with a Bruker AVANCE 500 FT NMR spectrometer. TMS was used as an internal standard for chemical shifts. Electrospray ionisation (ESI) mass spectrometry was performed with a JEOL JMS-T100CS instrument. Elemental analyses were carried out at the Service Centre of Elementary Analysis of Organic Compounds at Kyushu University.

**Electrochemical Measurements:** Cyclic voltammograms (CVs) and differential-pulse voltammograms (DPVs) were measured in a three electrode cell using a 3.0 mm diameter glassy carbon or platinum disk working electrode, a platinum auxiliary electrode and a Ag/AgCl reference electrode. Measurements were carried out at room temperature using an ALS 630c instrument (Bioanalytical Systems). Deaeration of the solution was accomplished by passing a stream of nitrogen through the solution for 15 minuets prior to the measurement and then maintaining a blanket atmosphere of nitrogen over the solution during the measurement. The cyclic voltammograms were recorded in 0.1 mol dm$^{-3}$ $n\mathrm{Bu_4NPF_6}$/DMF at a scan rate of 0.1 V s$^{-1}$. Under the present experimental conditions, the half-wave potential ($E_{1/2}$) of ferrocene was observed at +0.48 V vs. Ag/AgCl.

**Photochemical Measurements and Kinetics:** All photochemical reactions were performed with a specially designed optical cell (1 cm) with a vacuum-cocked reservoir. A $CH_3CN$ solution containing either **1**, **2** or **3** was prepared and deaerated by the vacuum-pump-thaw method. The photo-irradiation apparatus was a JASCO HM-25 (Special) with a 150-W Xenon lamp, monochromater SO-X150LC and S1337–1010BQ photon quantity measurement unit. To obtain rate constants, UV/Vis/NIR spectra were recorded during the photolysis at constant time intervals (5–10 min) and the peak intensity at 893 nm ($A_t^{893}$) for **1** and 896 nm ($A_t^{896}$) for **3** was used for the kinetic analysis.

**X-ray Crystallography:** Single crystals of **1** suitable for X-ray analysis were obtained by dissolving $[Ru_3O(C_2H_5CO_2)_6(CO)(C_2H_5OH)_2]$ in THF and layering the solution with $n$-hexane at room temperature. Upon dissolution in THF, the terminal $C_2H_5OH$ ligands in $[Ru_3O(C_2H_5CO_2)_6(CO)(C_2H_5OH)_2]$ become substituted by THF molecules to yield **1**. A crystal with the approximate dimensions of $0.25 \times 0.08 \times 0.06$ mm was protected with araldite, attached to a glass fibre and mounted on a goniometer head. The measurements were carried out at 223 K using a Bruker SMART APEX CCD detector with graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and a 2 kW rotating anode generator. The data were collected at 223 K to a maximum $2\theta$ value of 28.28° in 0.30° oscillations with a 12.0 s exposure time. The crystal-to-detector distance was 50 mm and the detector swing angle was 28°. A total of 14411 reflections were collected of which 5403 were unique ($R_{int}$ = 0.1185). The data frames were integrated using SAINT (Version 6.45) and merged to give a unique data set for the structure determination. Empirical absorption corrections by SADABS[46] were carried out. The structure was solved by a direct method and refined by a full-matrix least-squares technique on all $F^2$ data using the SHELX suite of programs.[47] Non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were displaced at calculated positions and included in the structure factor calculation but they were not refined. The crystal data and details in the structure refinement are summarised in Table 6. Some unassigned atoms, due probably to a severely disordered hexane molecule, were observed in the Fourier map but they were not included in the structure refinement. CCDC-724927 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 6. Crystal and refinement data for **1**.

| Formula | $C_{27}H_{46}O_{16}Ru_3$ |
|---|---|
| Formula weight | 929.85 |
| Crystal system | trigonal |
| Space group (no.) | *P*3(2) |
| *a* [Å] | 18.063(2) |
| *b* [Å] | 18.063(2) |
| *c* [Å] | 10.1136(18) |
| *V* [Å$^3$] | 2857.7(7) |
| *Z* | 3 |
| *T* [K] | 223(2) |
| $\rho_{\text{calcd.}}$ [g cm$^{-3}$] | 1.621 |
| $\mu$ [mm$^{-1}$] | 1.237 |
| *F*(000) | 1404 |
| Reflections measured | 14411 |
| Independent reflections | 5403 [*R*(int) = 0.1185] |
| *R* indices [$I > 2\sigma(I)$] | $R_1$ = 0.0601, $wR2$ = 0.1513 |
| *R* indices (all data) | $R_1$ = 0.0654, $wR_2$ = 0.1601 |
| Goodness-of-fit on $F^2$ | 1.004 |

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(|F_o|^2)^2]\}^{1/2}$. $w = \{\sigma^2(F_o)^2 + [0.05(\max(F_o{}^2,0) + 2F_c{}^2)/3]^2\}^{-1}$

**$[Ru_3O(C_2H_5CO_2)_6$(2-propanol)$_3]C_2H_5CO_2$:** To a $C_2H_5OH$ solution (75 cm$^3$) of propionic acid (75 cm$^3$) in a 500 cm$^3$ round-bottom flask was added sodium propionate (2.0 g, 20.8 mmol) and the mixture was stirred for 0.5 h. A $C_2H_5OH$ solution (10 cm$^3$) of $RuCl_3{\cdot}xH_2O$ (1.0 g) was added and the solution was heated to reflux for 5 h. After cooling, the solution was evaporated to dryness. Recrystallisation of the solid residue from 2-propanol/*n*-hexane (1:10, v/v) afforded a green microcrystalline solid which was collected by filtration, washed with *n*-hexane and dried in vacuo; yield 1.50 g (92%).

**$[Ru_3O(C_2H_5CO_2)_6(CO)(THF)_2]$ (1):** $[Ru_3O(C_2H_5CO_2)_6$(2-propanol)$_3]C_2H_5CO_2$ (1.0 g, 0.99 mmol) was dissolved in 80 cm$^3$ of $C_2H_5OH$. The solution was stirred with 8.0 g of Zn/Hg amalgam for 2 h under $N_2$. The solution was filtered under $N_2$ and the carbon monoxide gas was passed vigorously, during which time the yellow-green solution became purple. CO gas was then passed through the solution for 3 h. The solution was evaporated to dryness and the resultant solid was purified by chromatography on a silica gel column (Wakogel C-300HG). A purple species was separated by elution with 5% $C_2H_5OH/CH_2Cl_2$ and solvent was removed by evaporation. Recrystallisation of the solid residue from THF/*n*-hexane (1:5, v/v) afforded a violet microcrystalline solid which was collected by filtration, washed with *n*-hexane and dried in vacuo; yield 0.13 g (14%). $C_{27}H_{46}O_{16}Ru_3{\cdot}0.25C_6H_{14}$ (951.90): calcd. C 35.98, H 5.24; found C 35.85, H 5.24. IR (KBr pellet): $\tilde{\nu}$ = 1958 [s, ν(CO)], 1610 [m, $\nu_{as}$(COO)], 1564 [m, $\nu_{as}$(COO)], 1420 [m, $\nu_s$(COO)] cm$^{-1}$. $^1$H NMR (500 MHz, $CD_3OD$, 298 K): $\delta$ = 2.20 (m, 8 H, propionato ethyl), 2.07 (q, *J* = 7.6 Hz, 4 H, propionato ethyl), 0.79 (t, *J* = 7.3 Hz, 12 H, propionato ethyl), 0.74 (t, *J* = 7.6 Hz, 6 H, propionato ethyl) ppm. ESI-MS ($CH_3OH$): *m*/*z* = 851.2 ($[Ru_3O(C_2H_5CO_2)_6(CO)(CH_3OH)_2]^+$).

**$[Ru_3O(C_6H_5CO_2)_6(C_2H_5OH)_3]PF_6$:** This complex was prepared as follows by a slight modification of the published procedure.[36] To a $C_2H_5OH$ solution (15 cm$^3$) of benzoic acid (5.0 g, 40.9 mmol) in a 100 cm$^3$ round-bottom flask was added sodium hydroxide (0.5 g, 12.5 mmol) and the mixture was stirred for 0.5 h. A $C_2H_5OH$ solution (10 cm$^3$) of $RuCl_3{\cdot}xH_2O$ (0.5 g) was added and the solution was heated to reflux for 5 h. After cooling, the solution was evaporated to dryness. The solid residue was extracted with $H_2O/CH_2Cl_2$ three times to remove water-soluble species including unreacted sodium benzoate. The organic phase was evaporated and the resultant solid was purified by chromatography on a silica gel column. A yellow species was first separated by elution with $CH_2Cl_2$. A yellow-green species was then eluted with 5% $C_2H_5OH/CH_2Cl_2$. Finally, elution with 10% $C_2H_5OH/CH_2Cl_2$ containing $NH_4PF_6$ (ca. 5 mmol dm$^{-3}$) afforded a green band which was collected and solvent was removed. Recrystallisation of the solid residue from $C_2H_5OH$/*n*-hexane (1:10, v/v) afforded a green microcrystalline solid which was collected by filtration, washed with *n*-hexane and dried in vacuo; yield 0.32 g (30%). $C_{48}H_{48}F_6O_{16}PRu_3{\cdot}0.4NH_4PF_6$ (1394.26): calcd. C 41.35, H 3.59, N 0.40; found C 41.31, H 3.39, N 0.15. IR (KBr pellet): $\tilde{\nu}$ = 1600 [s, $\nu_{as}$(COO)] and 1532 [m, $\nu_{as}$(COO)], 1401 [vs, $\nu_s$(COO)] cm$^{-1}$. $^1$H NMR (500 MHz, $C_2D_5OD$, 298 K): $\delta$ = 8.40 (d, *J* = 6.3 Hz, 12 H, benzoato phenyl 2,6-H), 7.71 (t, *J* = 6.9 Hz, 6 H, benzoato phenyl 4-H), 7.12 (t, *J* = 7.3 Hz, 12 H, benzoato phenyl 3,5-H) ppm.

**$[Ru_3O(C_6H_5CO_2)_6(CO)(C_2H_5OH)_2]$ (3):** $[Ru_3O(C_6H_5CO_2)_6(C_2H_5OH)_3]PF_6$ (0.5 g, 0.38 mmol) was dissolved in $C_2H_5OH$ (80 cm$^3$). The solution was stirred with Zn/Hg amalgam (8.0 g) for 2 h under $N_2$ and the solution was filtered to remove Zn/Hg. The carbon monoxide gas was then passed through the solution for 3 h during which time the yellow-green solution became purple. The solution was evaporated to dryness and resultant solid was purified by chromatography on a silica gel column. A purple species was separated by elution with 5% $C_2H_5OH/CH_2Cl_2$ and the solvent was removed by evaporation. Recrystallisation of the solid residue from $C_2H_5OH$/*n*-hexane (1:10, v/v) afforded a violet microcrystalline solid which was collected by filtration, washed with *n*-hexane and dried in vacuo; yield 0.29 g (67%). $C_{47}H_{42}O_{16}Ru_3{\cdot}H_2O$ (1184.05): calcd. C 47.68, H 3.75; found C 47.44, H 3.60. IR (KBr pellet): $\tilde{\nu}$ = 1955 [s, ν(CO)], 1607 [s, $\nu_{as}$(COO)], 1571 [m, $\nu_{as}$(COO)], 1398 [vs, $\nu_s$(COO)] cm$^{-1}$. $^1$H NMR (500 MHz, $C_2D_5OD$, 298 K): $\delta$ = 7.73 (d, *J* = 6.5 Hz, 12 H, benzoato phenyl 2,6-H), 7.69 (d, *J* = 7.5 Hz, 6 H, benzoato phenyl 2,6-H), 7.25–7.15 (m, a total of 18 H, overlapping benzoato phenyl 4-H and 3,5-H) ppm. ESI-MS ($CH_3OH$): *m*/*z* = 1139.5 ($[Ru_3O(C_6H_5CO_2)_6(CO)(CH_3OH)_2]^+$).

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