Polynuclear Chain Compound of Tetrakis(μ -*n*-butyrato-*O,O'*)diruthenium Bromide

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The title compound of $[\text{Ru}_2(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_3)_4\text{Br}]_n$ was prepared and the crystal structure was determined by the single-crystal X-ray diffraction method at 90 K. It crystallizes in the tetragonal space group $\bar{I}4_2d$ with $a = 13.2222(10)\text{\AA}$, $c = 24.0779(18)\text{\AA}$, $V = 4209.5(7)\text{\AA}^3$, $D_x = 1.990\text{ g/cm}^3$, and $Z = 8$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0310 and 0.0572, respectively, for all 2430 independent reflections. The two ruthenium atoms are bridged by four *n*-butyrato ligands in the *syn-syn* mode with the Ru-Ru distance of $2.2897(9)\text{\AA}$. Both of the axial sites of the dinuclear ruthenium units are bridged by bromido ligands with the Ru-Br distance of $2.7078(7)\text{\AA}$ to form an alternated zig-zag chain molecule with Ru-Ru-Br and Ru-Br-Ru angles of $172.68(2)$ and $117.21(3)^\circ$, respectively. The temperature-dependent profile of the magnetic moment was simulated with $g = 2.14$, $D = 67\text{ cm}^{-1}$, $zJ = 0.38\text{ cm}^{-1}$ values. The g and D values are similar to those of other tetracarboxylato Ru_2^{5+} complexes.

(Received September 7, 2021; Accepted October 2, 2021; Published on web February 10, 2022)

Much interest has been directed to lantern-type dinuclear metal carboxylates with a metal-metal bond due to their unique properties based on the metal-metal bond.¹ In the case of diruthenium(II,III) carboxylates, which have a valence-averaged Ru_2^{5+} core, three unpaired electrons exist in the dinuclear core with the $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ electronic configuration, and the Ru_2^{5+} unit can be used as building blocks by using axial linking ligand for chain compounds with extended magnetic systems.¹⁻³ The first structurally characterized chain compound based on the Ru_2^{5+} unit was tetrakis(μ -*n*-butyrato-*O,O'*)diruthenium chloride $[\text{Ru}_2(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_3)_4\text{Cl}]_n$.⁴ Since then, many chlorido-bridged chain compounds of Ru_2^{5+} unit have been reported.^{1,2} The axial coordination effects on the structures and magnetic properties should be important for constructing magnetic materials based on the Ru_2^{5+} units. The bromido ligand is also known to work as a linkage ligand for Ru_2^{5+} units and some crystal structures have been reported.^{1,2} To our knowledge, the crystal structure of the title complex has not been reported so far, although crystal data were only examined.⁵ In this study, we prepared a chain compound of tetrakis(μ -*n*-butyrato-*O,O'*)diruthenium bromide $[\text{Ru}_2(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_3)_4\text{Br}]_n$ (**1**), and determined the crystal structure of this compound (Fig. 1).

The starting material, $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4]\text{BF}_4$, was prepared according to a method similar to that described in the literature.⁶ The precursor complex, $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Br}]$, was prepared as follows: 157.4 mg (0.3 mmol) of $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4]\text{BF}_4$ and 107.6 mg (0.9 mmol) of KBr were dissolved in 10 mL of water and the mixed solution was stirred at room temperature for 24 h. The

resulting brown precipitate was filtered, washed by water, and dried under a vacuum at 353 K for 3 h. The yield was 95.8 mg (61.7% based on $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4]\text{BF}_4$). *Anal.* Found: C, 18.50; H, 2.43%. Calcd for $\text{C}_8\text{H}_{12}\text{BrO}_8\text{Ru}_2$: C, 18.54; H, 2.33%. Then, 218.2 mg (0.42 mmol) of $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Br}]$ and 30 mL of *n*-butyric acid were dissolved in 10 mL of methanol and the

Fig. 1 Chemical structure of the title compound **1**.

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Table 1 Crystal and experimental data

Chemical formula: $C_{16}H_{28}BrO_8Ru_2$	
Formula weight = 630.43	
$T = 90$ K	
Crystal system: tetragonal	Space group: $\bar{I}42d$
$a = 13.2222(10)$ Å	
$c = 24.0779(18)$ Å	
$V = 4209.5(7)$ Å ³	$Z = 8$
$D_x = 1.990$ g/cm ³	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073$ Å)	
$\mu(\text{Mo } K\alpha) = 3.372$ mm ⁻¹	$F(0\ 0\ 0) = 2488$
Crystal size = $0.12 \times 0.10 \times 0.08$ mm ³	
No. of reflections collected = 13016	
No. of independent reflections = 2430	
θ range for data collection: 1.757 to 27.483°	
Data/Restraints/Parameters = 2430/0/125	
Goodness-of-fit on $F^2 = 0.959$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0310$, $wR2 = 0.0556$	
R indices (all data): $R1 = 0.0394$, $wR2 = 0.0572$	
$(\Delta/\sigma)_{\max} = 0.001$	
$(\Delta\rho)_{\max} = 0.932$ e Å ⁻³	$(\Delta\rho)_{\min} = -0.515$ e Å ⁻³
Measurement: Bruker Smart APEX CCD diffractometer	
Program system: SHELXTL	
Structure determination: intrinsic phasing (SHELXT-2014/4)	
Refinement: full matrix least-squares (SHELXL-2014/7)	
CCDC deposition number: 2104692

Fig. 2 ORTEP view of **1**. The thermal ellipsoids are shown at the 50% probability level. Symmetry code: (i) $(2-x, 1-y, z)$, (ii) $(3/2-x, y, 3/4-z)$.Table 2 Selected bond distances (Å) and angles ($^\circ$) of $[Ru_2(O_2CCH_2CH_2CH_3)_4Br]_n$ (**1**)

Ru1-Ru1 ⁱ	2.2897(9)	Ru1-O3	2.014(4)
Ru1-O1	2.021(4)	Ru1-O4 ⁱ	2.009(4)
Ru1-O2 ⁱ	2.030(4)	Ru1-Br1	2.7078(7)
Ru1 ⁱ -Ru1-Br1	172.68(2)	Ru1-Br1-Ru1 ⁱⁱ	117.21(3)

Symmetry code: (i) $(2-x, 1-y, z)$, (ii) $(3/2-x, y, 3/4-z)$.

mixed solution was refluxed for 24 h. The product was purified by column chromatography (silica gel, eluent ($CHCl_3$ 95%: CH_3OH 5%)). A brown solid was isolated. The yield was 162.5 mg (61.2% based on $[Ru_2(O_2CCH_3)_4Br]$). *Anal.* Found: C, 30.55; H, 4.31%. Calcd for $C_{16}H_{28}BrO_8Ru_2$: C, 30.48; H, 4.48%. IR (KBr, cm^{-1}): $\nu(CH)$ 2965, 2935, 2871; $\nu(COO^-)$ or $\delta(CH)$ 1460, 1425, 1410.

One of the crystals of **1** was mounted on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- $K\alpha$ radiation, and data were collected. Crystal data and details concerning data collection are given in Table 1. Selected bond distances and angles are listed in Table 2. The structure was solved by an intrinsic phasing method and refined by full-matrix least-squares methods.⁷ The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Windows 7 Core i5 computer utilizing the SHELXTL software package and SHELXL-2014.

The crystal structure is isomorphous with those of $[Ru_2(O_2CCH_2CH_2CH_3)_4Cl]_n$.⁴ An ORTEP drawing of **1** is given in Fig. 2. The two ruthenium atoms are bridged by four *n*-butyrato ligands in a *syn-syn* mode⁸ to form a lantern-type dinuclear core. The crystallographic C_2 axis exists at the midpoint of the dinuclear core. The Ru1 atom is related by the C_2 symmetry with the Ru1ⁱ atom with the Ru1-Ru1ⁱ distance of 2.2897(9) Å, which is in the range of the Ru-Ru bond distance observed for tetracarboxylato Ru_2^{5+} complexes (2.25 – 2.31 Å).^{1,2}

The Br1 atom is located at the crystallographical special point with the C_2 axis and coordinated to the axial site of the Ru_2^{5+} core with the Ru1-Br1 distance of 2.7078(7) Å to form an alternated zigzag chain molecule with the Ru-Ru-Br and Ru-Br-Ru angles of 172.68(2) and 117.21(3) $^\circ$, respectively, extending along the *a* axis. In the crystal, another alternated zigzag chain molecule exists, extending along the *b* axis. Therefore the crystal structure consists of two types of chain molecules perpendicularly crossing each other (Fig. 3).

The isomorphous zig-zag chain complex $[Ru_2(O_2CCH_2CH_2CH_3)_4Cl]_n$ has Ru-Ru and Ru-Cl bond distances of 2.281(4) and 2.587(5) Å and Ru-Ru-Cl and Ru-Cl-Ru bond angles of 175.1(1) $^\circ$ and 125.4 $^\circ$, respectively,⁴ where the unit-cell dimensions of $[Ru_2(O_2CCH_2CH_2CH_3)_4Cl]_n$ are $a = 13.265(5)$ Å and $c = 24.453(8)$ Å,⁴ being close to those of **1** ($a = 13.2222(10)$ Å and $c = 24.0779(18)$ Å). The difference in the axial halogen ligand (Cl^- or Br^-) does not seem to have any important effect on the chain structure, although $[Ru_2(O_2CCH_2CH_2CH_3)_4Cl]_n$ has a relatively short Ru-Cl distance (2.587(5) Å) and a rather large Ru-Cl-Ru bond angle (125.4 $^\circ$), compared with the bond distance and angle of **1** (Ru-Br = 2.7078(7) Å and $\angle Ru-Br-Ru = 117.21(3)^\circ$).

The effective magnetic moment (μ_{eff} , per Ru_2^{5+} unit) of **1** is 4.04 μ_B at 300 K, which is indicative of three unpaired electrons in the dinuclear core in accordance with the electron configuration of $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$, because the value is close to the spin-only value for three unpaired electrons ($\mu_{\text{eff}} = 3.87 \mu_B$). The variable magnetic moment over the temperature range of 2 – 300 K is shown in Fig. 4. The moment value decreases with lowering the temperature to 18 K, then being followed by its increase down to 2 K. The temperature-dependent profile of μ_{eff} ($= 2.828 \sqrt{\chi T}$, where χ is the molar susceptibility per mole of Ru_2^{5+} unit) was simulated using Eqs. (1) – (4), described below for the $S = 3/2$ system with a zero-field splitting (D) of the Ru_2^{5+} species, the inter-dinuclear-units interaction being taken into account by the mean-field approximation.²

Fig. 3 Packing diagram of **1** viewed along the *b* axis. Hydrogen atoms are omitted for clarity.

Fig. 4 Temperature dependence of the effective magnetic moment (μ_{eff}) of **1**. The red solid line denotes the simulated magnetic moment with parameters of $g = 2.14$, $D = 67 \text{ cm}^{-1}$, $zJ = 0.38 \text{ cm}^{-1}$.

$$\chi' = \chi / \{1 - (2zJ/Ng^2\mu_B^2)\chi\}, \quad (1)$$

where zJ is the exchange energy multiplied by the number (z) of interacting neighbors.

$$\chi = (\chi_{\parallel} + 2\chi_{\perp})/3, \quad (2)$$

where $\chi_{\parallel}$ and $\chi_{\perp}$ are magnetic susceptibility terms defined as follows:

$$\chi_{\parallel} = (Ng^2\mu_B^2/kT)\{1 + 9\exp(-2D/kT)\}/4\{1 + \exp(-2D/kT)\}, \quad (3)$$

$$\chi_{\perp} = (Ng^2\mu_B^2/kT)[4 + (3kT/D)\{1 - \exp(-2D/kT)\}]/4\{1 + \exp(-2D/kT)\}. \quad (4)$$

The simulation result is drawn with a red solid line ($g = 2.14$, $D = 67 \text{ cm}^{-1}$, $zJ = 0.38 \text{ cm}^{-1}$) in Fig. 4. The g and D values are similar to those for the other lantern-type Ru_2^{5+} complexes.² The magnetic interaction between the Ru_2^{5+} units is small, but not negligible ($zJ = 0.38 \text{ cm}^{-1}$), suggesting a kind of ferromagnetic interaction. The Ru_2^{5+} cores are too distant from each other to be directly interacting [the closest intermolecular (interchain) Ru–Ru distance is $6.8038(10) \text{ \AA}$ of Ru1–Ru1 ($3/2 - y, -1/2 + x, 1/2 - z$), while the closest intramolecular (intrachain) Ru–Ru distance is $4.6228(10) \text{ \AA}$ of Ru1–Ru1 ($3/2 - x, y, 3/4 - z$)], as can be seen in the packing diagram of **1** (Fig. 3). Hence, the interaction may be considered to be operative through the axial bromido-bridge. No axial interaction was observed in the case of the isomorphous chain complex $[\text{Ru}_2(\text{O}_2\text{CCH}_2\text{CH}_2\text{CH}_3)_4\text{Cl}]_n$ ($zJ = 0 \text{ cm}^{-1}$).^{3,9,10} That is, this difference in the axial ligand $X = \text{Cl}^-$ or Br^- gives rise to the different magnetic behavior. To our knowledge, the axial ferromagnetic interaction, such as $zJ = 0.38 \text{ cm}^{-1}$ observed for **1**, has not been reported so far for the halogenido-bridged chain complexes $[\text{Ru}_2(\text{O}_2\text{CCR})_4\text{X}]_n$.^{1,2,10}

Acknowledgements

The present work was partially supported by the MEXT-Supported Program for the Strategic Research Foundation at Private Universities and Grants-in-Aid for Scientific Research Nos. 16K05772 and 17K05820 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

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