



CHEMISTRY JOURNAL OF MOLDOVA.
General, Industrial and Ecological Chemistry

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TETRACYANIDOAUATE TO
TETRAKIS(μ -BUTANOATO)DIRUTHENIUM**

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Accepted version posted online: 10 April 2023

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To cite this article: M. Mikuriya, S. Kawauchi, R. Mitsuhashi, M. Tsuboi, M. Handa. Geometrical Isomerism in Ru₂Au Heterometal Assembly: *cis*-Linking of Tetracyanidoaurate to Tetrakis(μ -butanoato)diruthenium. *Chemistry Journal of Moldova*, 2023, DOI: doi.org/10.19261/cjm.2023.1059

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GEOMETRICAL ISOMERISM IN Ru₂Au HETEROMETAL ASSEMBLY: CIS-LINKING OF TETRACYANIDOAUROATE TO TETRAKIS(μ -BUTANOATO)DIRUTHENIUM

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Abstract. A heterometal assembled complex of tetrakis(μ -butanoato)diruthenium(II,III) and tetracyanidoaurate(III) [Ru^{II}Ru^{III}(n -C₃H₇COO)₄Au^{III}(CN)₄]_n was synthesized and characterized by the elemental analysis and infrared spectroscopy. The single-crystal X-ray structure analysis revealed that the complex consists of zigzag chain molecules of alternating arrangement of the Ru₂(n -C₃H₇COO)₄⁺ and Au(CN)₄⁻ units with *cis*-bridging mode of the Au(CN)₄⁻ units. The temperature dependence of the magnetic susceptibility data (4.5–300 K) showed that the magnetic interaction between the dinuclear Ru^{II}Ru^{III} units ($S = 3/2$) is negligibly small with a zero-field splitting parameter D value of 60 cm⁻¹.

Keywords: dinuclear ruthenium carboxylate, tetracyanidoaurate, heterometal complex, X-ray crystallography, magnetic property.

Received: 23 February 2023/ Revised final: 31 March 2023/ Accepted: 04 April 2023

Introduction

Dinuclear metal carboxylates have attracted much attention from many researchers because of their lantern- or paddlewheel-shaped clusters [1-7]. Axial and equatorial sites of the dinuclear clusters are available for coordination of linker ligands to construct coordination polymers and metal-organic frameworks, respectively, giving interesting gas-adsorption [3] and charge transfer [4] phenomena. In these dinuclear clusters, mixed-valent diruthenium(II,III) carboxylates are paramagnetic and promising to make magnetic materials because they can be used as building blocks with three unpaired electrons within the dinuclear clusters [5-7]. Some crystal structures and magnetic properties were investigated for metal-assembled complexes of dinuclear ruthenium carboxylates with linker ligands such as *N,N'*-bidentate ligands, *p*-quinones, and organic and inorganic cyano groups to construct one-, two- and three-dimensional assemblies [7]. Antiferromagnetic, ferrimagnetic, and ferromagnetic interactions were found in these metal-assembled systems. An attempt to add more functionality such as liquid crystalline properties to these systems by introducing long alkyl chains to

the carboxylate ligand moieties was made and a molecular fastener effect in magnetic interactions [8] and liquid crystalline properties [9] were found.

Metal cyanides can be used as linker ligands with triple CN bonds, which may be expected to communicate electrons between the adjacent metal atoms and provide an opportunity to construct heterometal systems. The synthesis of heterometal assemblies of diruthenium(II,III) carboxylates as well as dirhodium(II) carboxylates was accomplished by the use of dicyanidoargentate(I) [10,11], dicyanidoaurate(I) [12-14], tetracyanidonickelate(II) [15-17], tetracyanidopalladate(II) [17-19], tetracyanidoplatinate(II) [17,20,21], teracyanidoaurate(III) [22], hexacyanidochromate(III) [23-27], hexacyanidoferrate(III) [23-25,28,29], hexacyanidocobaltate(III) [22-24,27,28,30,31] and octacyanidotungstate(V) [32-35]. Tetracyanidometalates are unique linker ligands, showing geometric isomerism, that is, *trans*- and *cis*-orientations to the two linked dimetal carboxylate units [15-22]. In the case of dirhodium(II) acetate, an almost linear chain structure with a *trans*-bridging

mode was observed in heterometal complexes with tetracyanidometalate(II) $(\text{PPh}_4)_2n[\{\text{Rh}_2(\text{CH}_3\text{COO})_4\}\{\text{M}(\text{CN})_4\}]_n$ (M= Ni, Pd, Pt) [17]. On the other hand, such geometric isomerism was observed in heterometal complexes of diruthenium(II,III) carboxylates $\text{Ru}_2(\text{RCOO})_4^+$ (R= CH_3 , C_2H_5 , $i\text{-C}_3\text{H}_7$, and $t\text{-C}_4\text{H}_9$) with tetracyanidoaurate(III) [22]. The X-ray crystal structure analysis revealed that the Ru_2Au complex of acetate (R= CH_3) and 2,2-dimethylpropanoate (R= $t\text{-C}_4\text{H}_9$) are wave-like chain molecules with *trans*-bridging mode of the tetracyanidoaurate(III) linkers, while the Ru_2Au complex of propanoate (R= C_2H_5) and 2-methylpropanoate ($i\text{-C}_3\text{H}_7$) are zigzag chain molecules with *cis*-bridging mode of the $\text{Au}(\text{CN})_4^-$ linkers [22].

The aim of this study was to examine the geometric isomerism in tetracyanidoaurate(III) for the metal assembly of tetrakis(μ -butanoato)diruthenium(II,III) (R= $n\text{-C}_3\text{H}_7$), because the assembled compound may be regarded as a test case to develop liquid-crystalline materials based on heterometal complexes of diruthenium(II,III) carboxylates with long alkyl chains [36,37]. Hence a new heterometal complex, *catena*-(bis(μ -cyanido)-tetrakis(μ -butanoato)-dicyanido-gold-diruthenium), $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}^{\text{III}}(\text{CN})_4]_n$ was synthesized and the crystal structure was determined by the single-crystal X-ray diffraction method to disclose the orientation of the linking ligands. Magnetic susceptibility data were also measured.

Experimental

Materials

Unless otherwise stated, the reagents and solvents were obtained from commercial sources and used without further purification. The starting complex $[\text{Ru}_2\text{Cl}(\text{CH}_3\text{COO})_4]$ was synthesized by the modified method to the procedure described by Wilkinson, G. *et al.* [38].

Synthesis of $[\text{Ru}_2\text{Cl}(\text{CH}_3\text{COO})_4]$

A quantity of $\text{RuCl}_3 \cdot 6\text{H}_2\text{O}$ (1.517 g, 7.31 mmol) and LiCl (1.511 g, 35.6 mmol) was dissolved in a mixture of acetic acid and acetic anhydride (V/V= 52.5 mL/10.5 mL) and refluxed in a stream of dried air overnight. The resulting reddish-brown precipitate was collected by filtration, washed with methanol and diethyl ether, and dried in vacuo over P_2O_5 . Yield: 1.525 g, 88.0%. Found C 20.14, H 2.29%. Calcd. for $\text{C}_8\text{H}_{12}\text{ClO}_8\text{Ru}_2$: C 20.28, H 2.55%.

The precursor complexes, $[\text{Ru}_2\text{Cl}(n\text{-C}_3\text{H}_7\text{COO})_4]$ and $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4(\text{H}_2\text{O})_2]\text{BF}_4$ were synthesized in an inert atmosphere, using

standard Schlenk techniques according to the literature procedures [39].

Synthesis of $[\text{Ru}_2\text{Cl}(n\text{-C}_3\text{H}_7\text{COO})_4]$

To $[\text{Ru}_2\text{Cl}(\text{CH}_3\text{COO})_4]$ (0.303 g, 0.639 mmol) was added an excess amount of butanoic acid (2.79 mL, 30.4 mmol). The reaction mixture was heated under reflux for 4.5 h under argon, to give a brown precipitate. The precipitate was collected by filtration, washed with small amounts of water and diethyl ether, and dried in vacuo over P_2O_5 . Yield: 240 mg, 64.1%. Found C 32.53, H 5.08%. Calcd. for $\text{C}_{20}\text{H}_{36}\text{ClO}_8\text{Ru}_2$: C 32.80, H 4.82%.

Synthesis of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4(\text{H}_2\text{O})_2]\text{BF}_4$

A suspension of $[\text{Ru}_2\text{Cl}(n\text{-C}_3\text{H}_7\text{COO})_4]$ (107 mg, 0.18 mmol) in tetrahydrofuran (15 mL) was treated with AgBF_4 (34 mg, 0.17 mmol) in tetrahydrofuran (15 mL). The mixture was stirred for 24 h, and then the precipitate of AgCl was removed by filtration over celite. The filtrate was concentrated by a rotary evaporator to cca. 5 mL, and n -hexane was added to give a brown precipitate. The precipitate was collected by filtration and washed with diethyl ether. Yield: 101 mg, 88.3%. Found C 28.21, H 4.46%. Calcd. for $\text{C}_{16}\text{H}_{32}\text{BF}_4\text{O}_{10}\text{Ru}_2$: C 28.54, H 4.79%.

Synthesis of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$

To an aqueous solution (5 cm^3) of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4(\text{H}_2\text{O})_2]\text{BF}_4$ (50.5 mg, 0.075 mmol), an aqueous solution (5 cm^3) of $\text{K}[\text{Au}(\text{CN})_4]$ (24.3 mg, 0.071 mmol) was added. The solution was stirred for a while. The resulting yellow-brown precipitate was filtered off, washed with water, and desiccated in vacuo over P_2O_5 . Yield: 40.6 mg, 63.6%. Found C 27.86, H 3.24, N 6.05%. Calcd. for $\text{C}_{20}\text{H}_{28}\text{AuN}_4\text{O}_8\text{Ru}_2$: C 28.21, H 3.31, N 6.58%. IR (KBr, cm^{-1}): $\nu(\text{CN})$ 2211, $\nu_{\text{as}}(\text{COO})$ 1451, $\nu_{\text{s}}(\text{COO})$ 1427.

Physical measurements

Elemental analyses for carbon, hydrogen, and nitrogen were performed using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer.

Infrared spectra were recorded on a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm^{-1} region using a KBr disc.

The *variable-temperature magnetic susceptibility* data were measured on a Quantum Design MPMS-XL7 SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5–300 K. The susceptibility data were corrected for the diamagnetism of the constituent atoms using Pascal's constants [40]. The effective magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.828\sqrt{\chi_{\text{M}}T}$, where χ_{M} is the molar magnetic susceptibility per mole of

[Ru₂(*n*-C₃H₇COO)₄Au(CN)₄] unit. The magnetic data were analyzed by the use of Eq.(1-4) described below for the *S*= 3/2 system with the zero-field splitting parameter *D* and the magnetic interaction between the Ru₂(*n*-C₃H₇COO)₄⁺ units being taken into account by the mean-field approximation [7,22,41-43]:

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

where, *zJ* is the exchange energy multiplied by the number (*z*) of interacting neighbors;
 χ is the magnetic susceptibility.

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

where, χ_{\parallel} and χ_{\perp} are magnetic susceptibility terms defined as follows:

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

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

Single-crystal X-ray diffraction

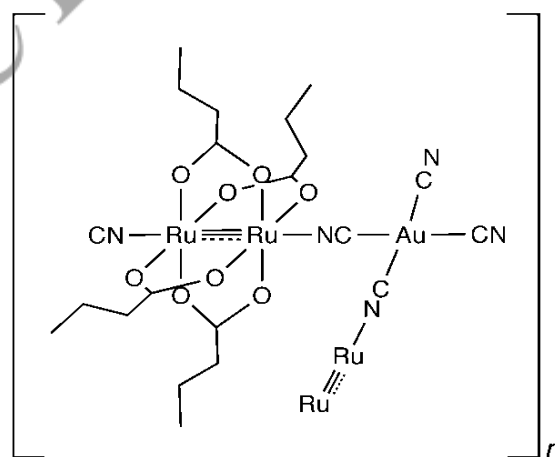
Crystals suitable for X-ray diffraction work were grown by reaction with a slow diffusion technique using an H-shaped tube at room temperature. Single-crystal diffraction data were measured on a Bruker Smart APEX CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by intrinsic phasing methods, and refined by full-matrix least-squares methods. The carbon atoms C15 and C16 were found to be disordered and divided into two positions (A and B). The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out utilizing the SHELXTL software package [44]. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit numbers CCDC-1846173. Copies of the data can be obtained free of charge via

<http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

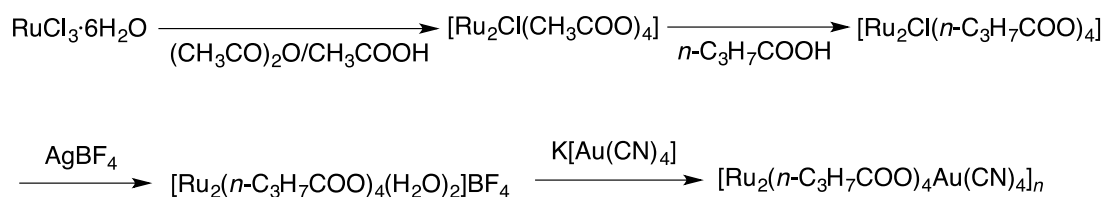
Results and discussion

Synthesis and characterization of [Ru^{II}Ru^{III}(*n*-C₃H₇COO)₄Au^{III}(CN)₄]_n

The chemical structure of the present complex, *catena*-(bis(μ -cyanido)-tetrakis(μ -butanoato)-dicyanido-gold-diruthenium), is depicted in Scheme 1. The present complex was synthesized as described in Scheme 2. The starting material, [Ru₂Cl(CH₃COO)₄], was synthesized by the reaction of RuCl₃·6H₂O and (CH₃CO)₂O/CH₃COOH under aerobic conditions. The corresponding butanoate, [Ru₂Cl(*n*-C₃H₇COO)₄], was obtained by the substitution reaction of the acetato-ligands by butanoato-ligands under anaerobic conditions. Then, the chlorido-ligand was eliminated by reaction with AgBF₄ to give [Ru₂(*n*-C₃H₇COO)₄(H₂O)₂]BF₄. The present complex was synthesized as a result of the interaction of [Ru₂(*n*-C₃H₇COO)₄(H₂O)₂]BF₄ and K[Au(CN)₄] in a 1:1 molar ratio in aqueous solution as a yellow–brown precipitate.



Scheme 1. Chemical structure of *catena*-(bis(μ -cyanido)-tetrakis(μ -butanoato)-dicyanido-gold-diruthenium).



Scheme 2. Synthetic route for the synthesis of the present complex.

Elemental analysis of the complex showed the formation of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$. The infrared spectra of the complex showed antisymmetric and symmetric stretching bands for the COO^- group at 1451 and 1427 cm^{-1} with an energy difference of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of 24 cm^{-1} , which are similar to those observed for the related Ru_2Au complexes $[\text{Ru}_2(\text{RCOO})_4\text{Au}(\text{CN})_4]_n$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7,$ and $t\text{-C}_4\text{H}_9$) ($\nu_{\text{as}}(\text{COO})$ 1437–1487 cm^{-1} and $\nu_{\text{s}}(\text{COO})$ 1400–1435 cm^{-1}) with the *syn-syn* mode of μ -carboxylato bridges [22,45] and consistent with the crystal structure. It is known that the frequency shift of $\nu(\text{CN})$ bands of metal cyanides to the higher energy side is indicative of the bridging state of the CN groups [45]. The CN stretching-vibration band of the present complex appeared at 2211 cm^{-1} , which is at the higher-energy side compared with the $\nu(\text{CN})$ band (2190 cm^{-1}) of $\text{K}[\text{Au}(\text{CN})_4]$ [22], suggesting the bridging $\nu(\text{CN})$ band of the $\text{Au}(\text{CN})_4^-$ ligand to the

diruthenium cluster. The lower-energy band ascribed to the uncoordinated CN groups is obscure in the present complex.

Crystal structure of $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}^{\text{III}}(\text{CN})_4]_n$

Crystal data and details concerning data collection are given in Table 1. Selected bond lengths and angles are listed in Table 2. The butanoato complex $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$ crystallized in the monoclinic lattice.

A perspective view of the molecular structure is shown in Figure 1. The structure consists of a 1-D chain molecule with alternating arrangement of $\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4^+$ and $\text{Au}(\text{CN})_4^-$ units, where two cyanido groups of each $\text{Au}(\text{CN})_4^-$ linker are coordinated to the axial sites of two $\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4^+$ units in a *cis*-bridging mode. The Au1 atom is coordinated by C1, C2, C3, and C4 atoms, forming a square planar $\text{Au}(\text{CN})_4^-$ unit. The Au-C distances are 1.992(11)–2.020(14) Å.

Table 1

Crystallographic data of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$. ^a	
Parameter	Value
Empirical formula	$\text{C}_{20}\text{H}_{28}\text{AuN}_4\text{O}_8\text{Ru}_2$
Formula mass	851.57
Temperature	273 K
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i>	10.390(5) Å
<i>b</i>	20.297(10) Å
<i>c</i>	13.695(7) Å
β	109.394(9)°
Unit-cell volume, <i>V</i>	2724(2) Å ³
Formula per unit cell, <i>Z</i>	4
Density, <i>D</i> _{calcd}	2.076 g cm ⁻³
Crystal size	0.04×0.02×0.02 mm ³
Absorption coefficient, μ	6.515 mm ⁻¹
θ range for data collection	2.308–27.497°
Reflections collected/unique	17130/6247
R indices [<i>I</i> > 2 σ (<i>I</i>)] ^b	$R_1 = 0.0606, wR_2 = 0.1399$
Goodness-of-fit on F^2	0.875

^aStandard deviations in parentheses; ^b $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum(F_o^2)^2]^{1/2}$.

Table 2

Selected structural parameters of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$.			
Bond length	<i>d</i> , Å	Bond length	<i>d</i> , Å
Ru1-Ru2	2.2671(15)	Ru2-O6	2.018(8)
Ru1-O1	2.007(8)	Ru2-O8	2.017(7)
Ru1-O3	2.041(8)	Ru2-N2 ^b	2.273(9)
Ru1-O5	1.999(8)	Ru2 ^a -N2	2.273(9)
Ru1-O7	2.021(8)	Au1-C1	1.997(12)
Ru1-N1	2.284(9)	Au1-C2	1.992(11)
Ru2-O2	2.023(7)	Au1-C3	1.984(13)
Ru2-O4	2.025(8)	Au1-C4	2.020(14)
Bond Angle	ω, °	Bond Angle	ω, °
Ru2-Ru1-N1	173.6(3)	Ru1-Ru2-N2 ^b	177.1(2)

Symmetry codes: (a) $(-x+3/2, y-1/2, -z+3/2)$, (b) $(-x+3/2, y+1/2, -z+3/2)$.

The diruthenium cluster takes a paddlewheel-type Ru_2 core with four *syn-syn* butanoato-bridges with a Ru1-Ru2 distance of 2.2671(15) Å, Ru1-O and Ru2-O distances of 1.999(8)—2.041(8) Å, Ru1-N1 distance of 2.284(9) Å, and Ru2-N2^b distance of 2.273(9) Å, which are in the normal ranges observed in tetrakis(μ -carboxylato)diruthenium(II,III) clusters [5-7,22]. The Ru1-Ru2-N2^b and Ru2-Ru1-N1 angles are 177.1(2) and 173.6(3)°, deviating from the linear arrangement slightly. The *cis*-bridging of the $\text{Au}(\text{CN})_4^-$ linker results in the formation of zigzag chain molecules in the crystal, similar to the

Ru_2Au complexes of the propanoate ($\text{R} = \text{C}_2\text{H}_5$) and 2-methylpropanoate (*i*- C_3H_7) [22]. In the crystal, the zigzag chain molecules are extended along the *b*-axis, as shown in Figure 2. There are no auophilic interactions between the chain molecules, as found in the related Ru_2Au complexes, diruthenium(II,III) carboxylates $\text{Ru}_2(\text{RCOO})_4^+$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7,$ and *t*- C_4H_9) with tetracyanoaurate(III) [22]. This is in contrast with the case for the heterometallic complex of dirhodium carboxylate and dicyanoaurate, $\text{K}_n[\text{Rh}_2(\text{C}_2\text{H}_5\text{COO})_4\text{Au}(\text{CN})_2]_n$ [14]. There are no voids in the crystal structure.

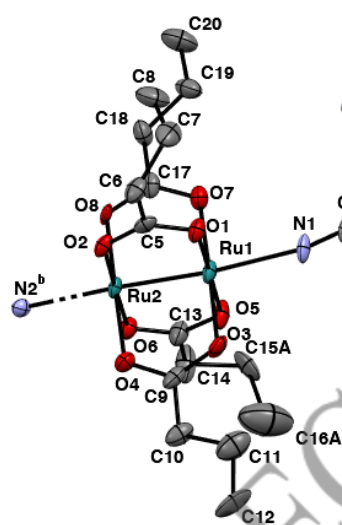


Figure 1. The ORTEP view of molecular structure of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$, showing thermal ellipsoids at the 50% probability level. The disordered carbon atoms (C15B and C16B) and hydrogen atoms are omitted for clarity.

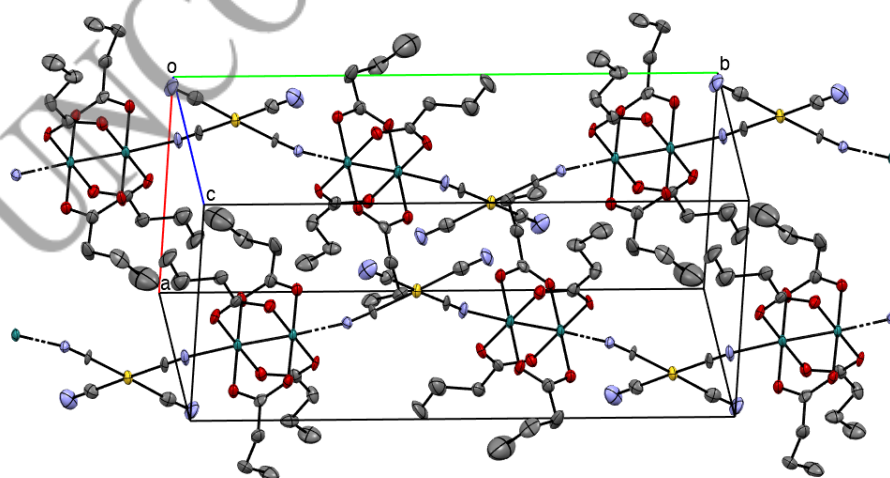


Figure 2. Packing diagram of $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$. The disordered carbon atoms (C15B and C16B) and hydrogen atoms are omitted for clarity.

Magnetic property of $[\text{Ru}^{\text{II}}\text{Ru}^{\text{III}}(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}^{\text{III}}(\text{CN})_4]_n$

The magnetic property of the present complex was studied by measuring the temperature dependence of magnetic susceptibility and the result is illustrated in Figure 3. The magnetic moment per $\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}$ unit is $4.05 \mu_{\text{B}}$ at 300 K, which is in accordance with the existence of three unpaired electrons per $\text{Ru}^{\text{II}}\text{-Ru}^{\text{III}}$ unit with an $S=3/2$ state. The magnetic moment decreases gradually with decreasing temperature until 80 K and then decreases steeply close to 4.5 K, which may be due to the zero-field splitting (D) within the $\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4^+$ unit and the antiferromagnetic interaction between the $\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4^+$ units through the axial $\text{Au}(\text{CN})_4^-$ linker.

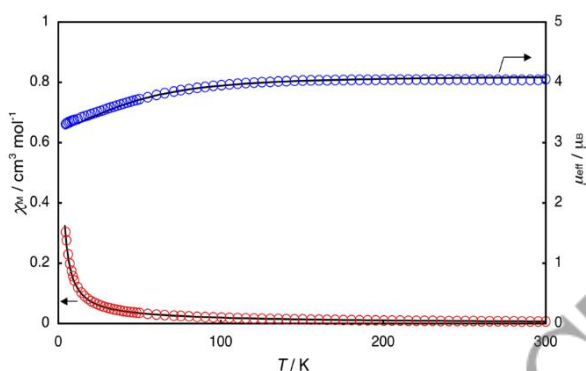


Figure 3. Temperature dependence of magnetic moment μ_{eff} and magnetic susceptibility χ_{M} for $[\text{Ru}_2(n\text{-C}_3\text{H}_7\text{COO})_4\text{Au}(\text{CN})_4]_n$. The solid black line was calculated and drawn with the parameter values described in the text.

The magnetic analysis gave the following parameter values for the present complex: $g=2.12$, $D=60 \text{ cm}^{-1}$, and $zJ=0 \text{ cm}^{-1}$. The obtained D value is normal for tetrakis(μ -carboxylato)diruthenium(II,III) cores [7,22]. The zJ value of 0 cm^{-1} means that the magnetic interaction is negligibly small in the present complex, being slightly different from those of mixed-metal complexes of diruthenium carboxylates $\text{Ru}_2(\text{RCOO})_4^+$ ($\text{R}=\text{CH}_3$, C_2H_5 , $i\text{-C}_3\text{H}_7$, and $t\text{-C}_4\text{H}_9$) with tetracyanoaurate(III) ($zJ=-0.10$ — -0.15 cm^{-1}) [22]. In these Ru_2Au complexes, dinuclear ruthenium units are well separated, the closest intermolecular $\text{Ru}\cdots\text{Ru}$ distances being 6.442 \AA ($\text{R}=\text{CH}_3$), 7.319 \AA ($\text{R}=\text{C}_2\text{H}_5$), 7.470 \AA ($\text{R}=\text{n-C}_3\text{H}_7$), 7.458 \AA ($i\text{-C}_3\text{H}_7$), and 8.183 \AA ($t\text{-C}_4\text{H}_9$). Therefore, it is difficult to evaluate the zJ values in relation to the crystal structures. Similar weak interactions were observed in the related heterometallic complexes of ruthenium(II,III) carboxylate with

dicyanidoargentate(I) ($zJ=-0.10$, -0.50 cm^{-1}) [10], tetracyanonickelate(II) ($zJ=-0.20 \text{ cm}^{-1}$) [16], tetracyanidopalladate(II) ($zJ=-0.10 \text{ cm}^{-1}$) [19], tetracyanidoplatinate(II) ($zJ=-0.10 \text{ cm}^{-1}$) [20,21].

Conclusions

In this study, a new heterometallic Ru_2Au complex was synthesized by the reaction of tetrakis(μ -butanoato)diruthenium(II,III) with tetracyanoaurate(III). The X-ray crystal structure analysis revealed that the present complex consists of zigzag chain molecules with the *cis*-bridging mode of the $\text{Au}(\text{CN})_4^-$ linkers. Compared with the previous study, it can be concluded that the different bridging modes of the $\text{Au}(\text{CN})_4^-$ linkers may come from the different steric hindrance of the substituent R groups of the carboxylato-bridges of the $\text{Ru}_2(\text{RCOO})_4^+$ core.

It may be considered that spherical CH_3 - and $t\text{-C}_4\text{H}_9$ - groups cannot allow steric hindrance between the alkyl groups for the *cis*-bridging mode, while the C_2H_5 -, $n\text{-C}_3\text{H}_7$ -, and $i\text{-C}_3\text{H}_7$ - groups can accommodate the *cis*-bridging mode because of the nonspherical alkyl groups.

The *cis*-type of bridging mode seems to be ubiquitous for heterometal complexes of dimetal carboxylates with *n*-alkyl groups and tetracyanidometalates.

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