

MIXED-METAL COMPLEXES OF RUTHENIUM(II,III) CARBOXYLATE AND TETRACYANIDOPLATINATE(II)

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Abstract. Mixed-metal complexes constructed from dinuclear ruthenium(II,III) carboxylates and tetracyanidoplatinate(II), $[\{\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\}_2\text{Pt}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (**1**) and $[\{\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4\}_2\text{Pt}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (**2**), were synthesized and characterized by elemental analysis and IR and UV-vis spectroscopies. These data are in accordance with the formulation of the PtRu_4 complexes with two lantern-type dinuclear Ru_2 and $\text{Pt}(\text{CN})_4$ units. A broad band at near-IR and a distinctive band at visible region (1088 and 443 nm for **1** and 1090 and 446 nm for **2**), which can be ascribed to a $\delta(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$ and a $\pi(\text{RuO}, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$ transitions, respectively, were observed in the diffused reflectance spectra. Temperature-dependence of magnetic susceptibilities (4.5–300 K) showed that antiferromagnetic interaction between the two $3/2$ spins of the Ru_2 units through tetracyanidoplatinate(II) is weak ($zJ = -0.1 \text{ cm}^{-1}$) with zero-field-splitting values of 45 and 65 cm^{-1} for **1** and **2**, respectively.

Keywords: dinuclear ruthenium(II,III) carboxylate, magnetic property, mixed-metal complex, tetracyanidoplatinate(II).

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Introduction

Dinuclear metal carboxylates with a lantern-type (or paddlewheel-type) dinuclear core are interesting compounds and have attracted much attention over the past five decades because of the unique dinuclear core [1-5]. It is known that most of these compounds have metal-metal bonds between the two metal atoms, giving diamagnetic property for these systems. In this context, dinuclear ruthenium carboxylates are unique compounds, showing paramagnetic properties irrespective of the lantern-type (or paddlewheel-type) dinuclear core with metal-metal bonding. Especially, interesting features are that mixed-valent ruthenium(II,III) carboxylates $[\text{Ru}_2(\text{O}_2\text{CR})_4]^+$ have three unpaired electrons on the $\pi^*2\delta^*$ orbitals in the metal-metal bonds and show various functional properties such as liquid crystalline properties as well as magnetic properties [3-42]. These ruthenium carboxylates are useful as building block for constructing magnetic materials. We reported on some metal-assembled complexes such as one-dimensional chain compounds prepared by application of bidentate linking ligands to dinuclear ruthenium carboxylates. Most of these compounds are antiferromagnetic between the dinuclear ruthenium units through the linking ligands and the strength of the magnetic interaction depends on the linking ligands [17-32]. Dinuclear ruthenium carboxylates form polymeric mixed-metal complexes by reaction with octacyanidometalate $[\text{M}(\text{CN})_8]^{4-}$ ($\text{M} = \text{W}$), hexacyanidometalate ion $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Fe}$, Co , and so on) and some of them show an antiferromagnetic interaction between the dinuclear ruthenium units through the diamagnetic cyanidometalate ion and a ferrimagnetic interaction among the hetero metal ions [33-42].

Recently, our continuing study on these systems led us to obtain mixed-metal complexes with dicyanoargentate(I) and tetracyanidonickelate(II) ions [41,42]. In these mixed-metal systems, it was difficult to obtain single crystals to elucidate the polymeric structures. In this study, we extended these systems to mixed-metal complexes with tetracyanidoplatinate(II) ion $[\text{Pt}(\text{CN})_4]^{2-}$ in the hope of obtaining new mixed-metal systems of ruthenium(II,III) carboxylates. The isolated complexes were characterized based on elemental analysis, infrared and UV-vis spectra, and temperature dependence of magnetic susceptibilities (4.5–300 K).

Experimental

Synthesis: Unless otherwise specified, commercial chemicals were used as supplied. Tetrafluoroborate salts of dinuclear ruthenium(II,III) acetate and pivalate, $[\text{Ru}_2\{\text{O}_2\text{CCH}_3\}_4(\text{H}_2\text{O})_2]\text{BF}_4$ and $[\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4(\text{H}_2\text{O})_2]\text{BF}_4$, were synthesized according to the literature methods [6,7].



Potassium tetracyanidoplatinate(II) (30 mg, 0.080 mmol) was dissolved in 5 mL of H_2O . To an aqueous solution (5 mL) of $[\text{Ru}_2\{\text{O}_2\text{CCH}_3\}_4(\text{H}_2\text{O})_2]\text{BF}_4$ (50 mg, 0.089 mmol) was added this solution, stirred overnight. The resulting precipitate was filtered, washed with small amount of water, and dried *in vacuo*. Yield: 34 mg (35%). Anal. Found: C, 20.12; H,

2.34; N, 4.73%. Calcd. for $C_{20}H_{28}N_4O_{18}PtRu_4$: C, 19.82; H, 2.33; N, 4.62%. IR (KBr): $\nu(\text{CH})$ 2934; $\nu(\text{CN})$ 2150, 2138; $\nu_{\text{as}}(\text{CO}_2^-)$ 1443; $\nu_{\text{s}}(\text{CO}_2^-)$ 1401 cm^{-1} . Diffuse reflectance spectrum: λ_{max} 250, 290sh, 443, 1088 nm.

$[\{\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4\}_2\text{Pt}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (2)

Potassium tetracyanidoplatinate(II) (14 mg, 0.037 mmol) was dissolved in 5 mL of H_2O . To an aqueous solution (5 mL) of $[\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4(\text{H}_2\text{O})_2]\text{BF}_4$ (28 mg, 0.038 mmol) was added this solution, stirred overnight. The resulting precipitate was filtered, washed with small amount of water, and dried *in vacuo*. Yield: 24 mg (42%). Anal. Found: C, 34.35; H, 4.75; N, 3.73%. Calcd. for $C_{44}H_{80}N_4O_{17}PtRu_4$: C, 34.39; H, 5.25; N, 3.65%. IR (KBr): $\nu(\text{CH})$ 2967, 2936, 2910, 2876; $\nu(\text{CN})$ 2137; $\nu_{\text{as}}(\text{CO}_2^-)$ 1488; $\nu_{\text{s}}(\text{CO}_2^-)$ 1421 cm^{-1} . Diffuse reflectance spectrum: λ_{max} 262, 304, 446, 1090 nm.

Measurements: Elemental analyses for carbon, hydrogen, and nitrogen were conducted using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000—600 cm^{-1} region. Electronic spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer (Model UV-3100). Magnetic susceptibilities were measured with 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 susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants. 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 dinuclear ruthenium(II,III) unit.

Results and discussion

Reaction of the mixed-valent dinuclear ruthenium(II,III) acetate and ruthenium(II,III) pivalate with tetracyanidoplatinate(II) ion gave orange and brown precipitates, respectively. Formulation of the mixed-metal systems of two dinuclear ruthenium(II,III) carboxylate units with one tetracyanidoplatinate(II) unit, $[\{\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\}_2\text{Pt}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (**1**) and $[\{\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4\}_2\text{Pt}(\text{CN})_4]\cdot 2\text{H}_2\text{O}$ (**2**), was confirmed by the elemental analyses, infrared and electronic spectra, and temperature dependence of magnetic susceptibility data (4.5—300 K).

The infrared spectra of the present complexes are shown in Figure 1. In the infrared spectra, C-H stretching vibrations were observed at 2934 cm^{-1} for **1** and at 2967, 2936, 2910, and 2876 cm^{-1} for **2**, respectively, in agreement with the presence of the methyl or *t*-butyl groups. Distinctive sharp bands were observed at 2150 and 2138 cm^{-1} in **1** and 2137 cm^{-1} in **2**. These bands may be assigned to $\nu(\text{CN})$ stretching band of tetracyanidoplatinate(II) ion. These bands appeared at a little higher energy region compared with that of $\text{K}_2[\text{Pt}(\text{CN})_4]$ ($\nu(\text{CN})$: 2134 and 2121 cm^{-1}), suggesting the bridging of the tetracyanidoplatinate(II) to the dinuclear ruthenium carboxylate units [43–45]. Two strong bands were observed at 1443 and 1401 cm^{-1} assignable to asymmetrical and symmetrical stretching vibrations of the *syn-syn* acetate bridges, respectively, for **1**, where as two strong bands observed at 1488 and 1421 cm^{-1} assignable to asymmetrical and symmetrical stretching vibrations of the *syn-syn* pivalate bridges, respectively, for **2**.

Diffused reflectance spectra of **1** and **2** are shown in Figure 2. A weak broad absorption band, which is typical for ruthenium(II,III) carboxylate and can be attributed to a $\delta(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$ transition, was observed at around 1088 nm in solid of **1** [8]. A distinctive band at 443 nm in **1** may be due to $\pi(\text{RuO}, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$ transition [11,12]. From these spectral feature, we can consider that the lantern-type dinuclear structure of the mixed-valent dinuclear ruthenium(II,III) carboxylate is maintained in the present mixed-metal complexes, because the spectra contain the characteristic bands of dinuclear ruthenium(II,III) carboxylate. The spectra contain another feature due to the presence of tetracyanidoplatinate(II) moiety. The bands at 250 and 290 nm in **1** can be assigned to the ${}^1A_{1g} \rightarrow {}^1E_u$ and ${}^1A_{1g} \rightarrow {}^1B_{1u}$ transitions, respectively, of the tetracyanidoplatinate(II) moiety [46]. Similar spectral feature was observed for **2**: 1090 ($\delta(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$), 446 ($\pi(\text{RuO}, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$), 304 (${}^1A_{1g}(\text{Pt}) \rightarrow {}^1B_{1u}(\text{Pt})$), 262 (${}^1A_{1g}(\text{Pt}) \rightarrow {}^1E_u(\text{Pt})$) nm.

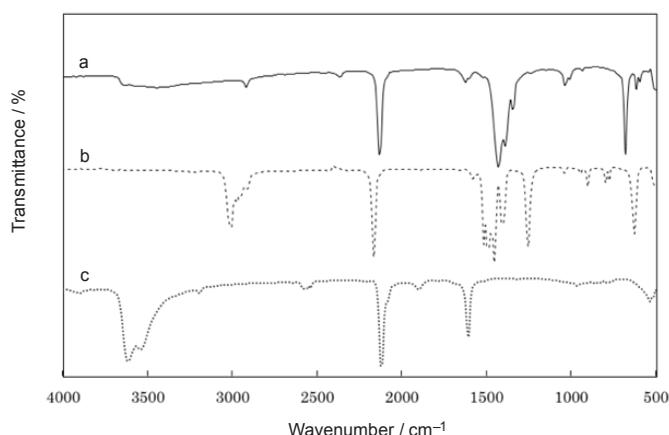


Figure 1. Infrared spectra: 1 (a), 2 (b), and $\text{K}_2\text{Pt}(\text{CN})_4$ (c).

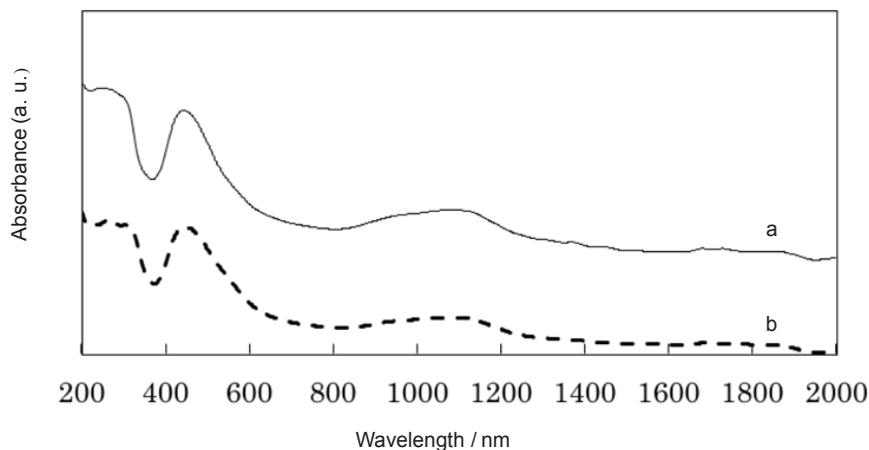


Figure 2. Diffused reflectance spectra of **1** (a) and **2** (b).

Temperature dependence of effective magnetic moments is shown in Figure 3. The magnetic moments per dinuclear ruthenium(II,III) unit of **1** and **2** are 4.30 and 4.41 μ_B , respectively, at 300 K. These values are a little higher than the spin-only value of $S=3/2$ ($3.87 \mu_B$). The magnetic moments gradually decrease with lowering of temperature and reach the minimum values, 3.20 and 3.28 μ_B , respectively, at 4.5 K. These magnetic behaviors are typical for dinuclear ruthenium(II,III) carboxylates having a large zero-field-splitting (ZFS) with a weak antiferromagnetic interaction [3-5]. The magnetic data were analyzed by a molecular field approximation [47] considering the ZFS effect to estimate the magnitude of the antiferromagnetic interaction [9, 10], using the following equations:

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

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

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

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

where zJ - is the exchange integral multiplied by the number of interacting neighbors,
 χ - is the magnetic susceptibility of the individual dinuclear unit,
 D - is the ZFS parameter.

The g value was treated isotropic. Best fitting curve was obtained with the parameters: $zJ = -0.10 \text{ cm}^{-1}$, $g = 2.10$, $D = 45 \text{ cm}^{-1}$ for **1**. The similar parameter values $zJ = -0.10 \text{ cm}^{-1}$, $g = 2.10$, $D = 60 \text{ cm}^{-1}$ were obtained for **2**. These results show that a weak antiferromagnetic interaction is operating between the two dinuclear ruthenium 3/2 spins through the diamagnetic tetracyanidoplatinate(II) bridge, being consistent with a long separation of the Ru_2 units through the $\text{Pt}(\text{CN})_4$ bridge for the present complexes.

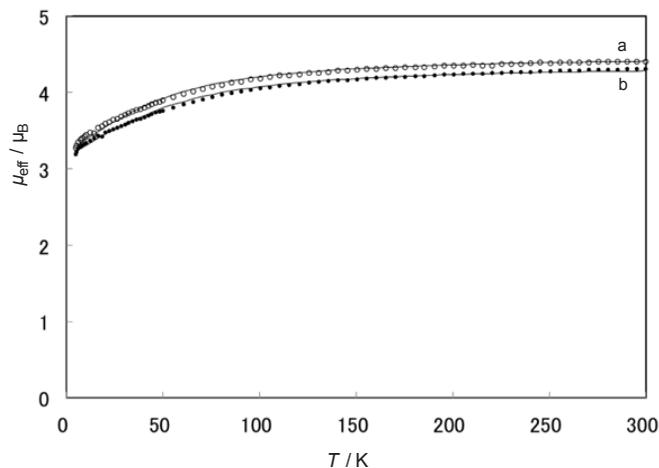


Figure 3. Temperature dependence of the magnetic moments of **1** (a) and **2** (b).

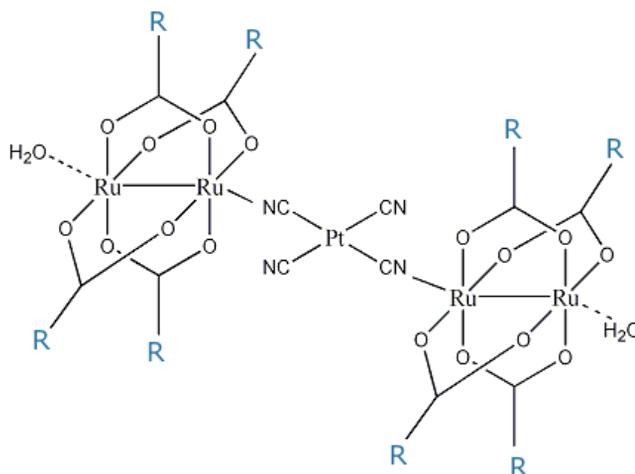


Figure 4. Proposed structure for the present complexes.

From the above results, we can assume a pentanuclear structure with a linear arrangement of two dinuclear ruthenium units and one tetracyanidoplatinate(II) ion shown in Figure 4 for **1** and **2**.

Conclusions

By using tetracyanidoplatinate(II), the preparation of the mixed-metal complexes of dinuclear ruthenium(II,III) carboxylate, $[\{\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\}_2\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\{\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_2\}_2\text{Pt}(\text{CN})_4] \cdot 2\text{H}_2\text{O}$ (**2**), was achieved. The elemental analysis, infrared spectra, UV-vis-NIR spectra, and temperature dependence of magnetic susceptibilities are consistent with pentanuclear structures composed of two dinuclear ruthenium units bridged by one tetracyanidoplatinate(II) ion. In accordance with the structural feature, a weak antiferromagnetic interaction through the tetracyanidoplatinate(II) ion was observed for the present complexes.

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