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

Masahiro Mikuriya*, Kenta Ono†, Shun Kawauchi‡, Daisuke Yoshioka*, Ryoji Mitsuhashi*, Makoto Handa†

*Department of Applied Chemistry for Environment and Research Center for Coordination Molecule-based Devices, School of Science and Technology, Kwansei Gakuen University, 2-1 Gakuen, Sanda 669-1337, Japan
‡Department of Chemistry, Interdisciplinary Graduate School of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan
*E-mail: junpei@kwansei.ac.jp; phone: (+81 79) 565 8365; fax: (+81 79) 565 9729

Abstract. Mixed-metal complexes constructed from dinuclear ruthenium(II,III) carboxylate and tetracyanidoplatinate(II), \([\{\text{Ru}_2(O_2CCH_3)_4\}_{l=2}\text{Pt(CN)}_4\}_{l=2}\text{H}_2\text{O} \) (1) and \([\{\text{Ru}_2(O_2CC(CH_3)_3)_4\}_{l=2}\text{Pt(CN)}_4\}_{l=2}\text{H}_2\text{O} \) (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 complexes with two lantern-type dinuclear Ru$_2$ and Pt(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 \(\delta(Ru_2)\)→\(\pi^*(Ru_2)\) and a \(\pi(Ru_2)\)→\(\pi^*(Ru_2)\) transitions, respectively, were observed in the diffuse 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 (\(J = -0.1 \text{ cm}^{-1}\)) 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).

Received: October 2015/ Revised final: October 2015/ Accepted: October 2015

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 carboxylate is 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 [Ru$_2$(O$_2$CR)$_4$]$^+$ have three unpaired electrons on 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 [Ru$_2$(O$_2$CR)$_4$]$^+$ have three unpaired electrons on 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 [Ru$_2$(O$_2$CR)$_4$]$^+$ have three unpaired electrons on 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 [Ru$_2$(O$_2$CR)$_4$]$^+$ have three unpaired electrons on properties irrespective of the lantern-type (or paddlewheel-type) dinuclear core with metal-metal bonding.

Recently, our continuing study on these systems led us to obtain mixed-metal complexes with dicyanidoargentate(I) and tetracyanidoargentate(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 [Pt(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, [Ru$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$]BF$_4$ and [Ru$_2$(O$_2$CC(CH$_3$)$_3$)$_4$(H$_2$O)$_2$]BF$_4$, were synthesized according to the literature methods [6,7].

\[
[\{\text{Ru}_2(O_2CCH_3)_4\}_{l=2}\text{Pt(CN)}_4\}_{l=2}\text{H}_2\text{O} \text{ (1)}
\]

Potassium tetracyanidoplatinate(II) (30 mg, 0.080 mmol) was dissolved in 5 mL of H$_2$O. To an aqueous solution (5 mL) of [Ru$_2$(O$_2$CCH$_3$)$_4$(H$_2$O)$_2$]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,
Potassium tetracyanidoplatinate(II) (14 mg, 0.037 mmol) was dissolved in 5 mL of H2O. To an aqueous solution (5 mL) of [Ru2(O2CC(CH3)3)4(H2O)2]BF4 (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 C44H80N4O17PtRu4: C; 34.39; H; 5.25; N; 3.65%. IR (KBr): ν(CN) 2134, 2121 cm⁻¹, suggesting the characteristic bands of dinuclear ruthenium(II,III) carboxylate. The spectra contain another feature due to the presence of the tetracyanidoplatinate(II) moiety. The bands at 250 and 290 nm in [Ru2(O2CC(CH3)3)4(H2O)2]BF4 (1A1g(Pt)), 262 (1A1g(Pt)), 304 (1A1g(Pt) → 1B1g(Pt)) nm.

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, [{Ru2(O2CC(CH3)3)4}2Pt(CN)4]·2H2O (1) and [{Ru1O2CC(CH3)3}4Pt(CN)4]·2H2O (2), was confirmed by the elemental analyses, infrared and electronic spectra, and temperature dependence of magnetic susceptibility data (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 μ_eff = 2.828√χ_m T, where χ_m is the molar magnetic susceptibility per mole of dinuclear ruthenium(II,III) unit.

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 ν(CN) stretching band of tetracyanidoplatinate(II) ion. These bands appeared at a little higher energy region compared with that of K2[Pt(CN)4] (ν(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 δ(Ru−)→δ(Ru−) transition, was observed at around 1088 nm in solid of 1 [8]. A distinctive band at 443 nm in 1 may be due to π(RuO, Ru~)→π(Ru~) transition [11,12]. From these spectral feature, we can consider that the lanturn-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 1A1g → 1Eg and 1A1g → 1B1g transitions, respectively, of the tetracyanidoplatinate(II) moiety [46]. Similar spectral feature was observed for 2: 1090 (δ(Ru−)→δ(Ru−)), 446 (π(RuO, Ru~)→π(Ru~)), 304 (1A1g(Pt) → 1B1g(Pt)), 262 (1A1g(Pt) → 1Eg(Pt)) nm.

Figure 1. Infrared spectra: 1 (a), 2 (b), and K2Pt(CN)4 (c).
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 \( \mu_B \), 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 \( \mu_B \), 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:

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

where \( zJ \) - is the exchange integral multiplied by the number of interacting neighbors, \( \chi \) - 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 Pt(CN)\(_4\) bridge for the present complexes.

![Figure 2. Diffused reflectance spectra of 1 (a) and 2 (b).](image)

![Figure 3. Temperature dependence of the magnetic moments of 1 (a) and 2 (b).](image)
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, [\{Ru₂(O₂CCH₃)₄\}₂Pt(CN)₄·2H₂O (1) and [\{Ru₂{O₂CC(CH₃)₃}₄\}₂Pt(CN)₄·2H₂O (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.

Acknowledgements

The present work was partially supported by Grant-in-Aid for Scientific Research No. 26410080 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT, Japan) and the MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2010—2014.

References


22. Sayama, Y.; Handa, M.; Mikuriya, M.; Hiromitsu, I.; Kasuga, K. Synthesis and magnetic properties of ruthenium(II,III) pivalate dimers axially coordinated by nitronyl nitroxide radicals [Ru\textsubscript{2}(O\textsubscript{2}CCMe\textsubscript{3})\textsubscript{4}(L)\textsubscript{2}]BF\textsubscript{4} and [\{Ru\textsubscript{2}(O\textsubscript{2}CCMe\textsubscript{3})\textsubscript{4}(H\textsubscript{2}O)\textsubscript{2}\}\textsubscript{2+}, L = 2,4,4,5,5-pentamethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-N-oxide and 2-ethyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxyl-3-N-oxide. Bulletin of the Chemical Society of Japan, 2003, 76, pp. 769-779.


29. Ishida, H.; Handa, M.; Hiromitsu, I.; Mikuriya, M. Synthesis, magnetic and spectral properties, and crystal structure of mixed-valence ruthenium(II,III) 3,4,5-tributanoxybenzoate. Insights into Coordination, Bioinorganic


