

MIXED-METAL COMPLEXES OF MIXED-VALENT DINUCLEAR RUTHENIUM(II,III) CARBOXYLATE AND TETRACYANIDONICKELATE(II)

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Abstract. Mixed-metal chain complexes constructed from lantern-type dinuclear ruthenium(II,III) carboxylate unit and tetracyanonickelate(II), $(\text{PPh}_4)_n[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Ni}(\text{CN})_4]_n \cdot n\text{H}_2\text{O}$ (**1**) and $(\text{PPh}_4)_n[\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4]_n[\text{Ni}(\text{CN})_4]_{2n} \cdot 2n\text{H}_2\text{O}$ (**2**), were synthesized and characterized by elemental analysis, IR, and UV-vis spectroscopies. These data are in accordance with the formation of the chain complex with an alternative arrangement of the dinuclear Ru_2 unit and tetracyanonickelate(II). A broad band at near-IR and a band at visible region (1058 and 452 nm for **1** and 1082 and 454 nm for **2**) were observed in the diffused reflectance spectra and 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. Temperature-dependence of magnetic susceptibility (4.5–300 K) showed that the antiferromagnetic interaction between the dinuclear units is weak ($zJ = -0.2 \text{ cm}^{-1}$) with D value of 75 cm^{-1} for both complexes.

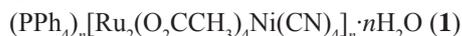
Keywords: dinuclear ruthenium(II,III) carboxylate, magnetic property, mixed-metal complex, tetracyanidonickelate(II).

Introduction

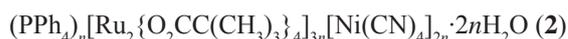
The chemistry of dinuclear metal carboxylates has attracted much attention over the past five decades because of the unique lantern-type (or paddlewheel-type) dinuclear core [1-5]. Among the dinuclear metal carboxylates, mixed-valent ruthenium(II,III) carboxylates $[\text{Ru}_2(\text{O}_2\text{CR})_4]^+$ are interesting, because these dinuclear systems are paramagnetic with three unpaired electrons on the $\pi^* \delta^*$ orbitals in the metal–metal bonds and with large zero-field splitting (ZFS) [3–37]. The dinuclear ruthenium carboxylates show various interesting features such as liquid crystalline properties [25] as well as the paramagnetic properties. We prepared many metal-assembled complexes from dinuclear species to one-dimensional chain compounds by application of linking ligands to dinuclear ruthenium carboxylates and found that most of them are antiferromagnetic between the dinuclear ruthenium units and the strength of the antiferromagnetic interaction depends on the linking ligands [16-29]. About ten years ago, we and Miller's group reported that the dinuclear ruthenium carboxylates form polymeric mixed-metal complexes with hexacyanometalate ion $[\text{M}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Fe}, \text{Co}$, and so on) and found some of them show an antiferromagnetic interaction between the dinuclear ruthenium units through the diamagnetic hexacyanometalate ion and a ferrimagnetic interaction among the hetero metal ions [30-35]. Recently, our continuing study on these systems led us to mixed-metal complexes with octacyanometalate ions $[\text{M}(\text{CN})_8]^{4-}$ ($\text{M} = \text{W}$) [36,37]. In these mixed-metal systems, a ferrimagnetic interaction between the dinuclear Ru_2 spins and octacyanometalate spins was observed for $[\{\text{Ru}_2(\text{O}_2\text{CC}(\text{CH}_3)_3)_4\}_3(\text{H}_2\text{O})\text{W}(\text{CN})_8]_n$ [37]. Therefore, it is important to develop these mixed-metal systems to find interesting molecular magnetic compounds. In this study, we extended these systems to mixed-metal complexes with tetracyanonickelate ion by using tetracyanonickelate(II) ion $[\text{Ni}(\text{CN})_4]^{2-}$ in order to obtain new metal-assembled complexes of ruthenium(II,III) carboxylate. The isolated complexes were characterized by elemental analysis, IR, UV-vis spectra, and temperature dependence of magnetic susceptibilities (4.5–300 K). Here, we report on the preparation and structural characterization of these new systems.

Experimental

Synthesis: $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]\text{BF}_4$ 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 by literature methods [6,7]. Other reagents and solvents were purchased from commercial sources and were used without further purification.



Tetraphenylphosphonium chloride (6.7 mg, 0.018 mmol) and potassium tetracyanonickelate(II) (2.3 mg, 0.0088 mmol) were dissolved in 4 mL of H_2O , respectively. To an aqueous solution (2 mL) of $[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]\text{BF}_4$ (10.0 mg, 0.0178 mmol) were added these solutions, stirred for 1 min. The resulting precipitate was filtered, washed with 9 mL of water, and dried *in vacuo*. Yield: 5.4 mg (62%). Anal. Found: C, 45.15; H, 3.44; N, 5.87%. Calcd. for $\text{C}_{36}\text{H}_{34}\text{N}_4\text{NiO}_9\text{PRu}_2$: C, 45.11; H, 3.58; N, 5.85%. IR (KBr): $\nu(\text{Ar-H})$ 3060, 3100, $\nu(\text{CN})$ 2130, $\nu_{\text{as}}(\text{CO}_2^-)$ 1442, $\nu_{\text{s}}(\text{CO}_2^-)$ 1403. Diffuse reflectance spectrum: λ_{max} 338, 452, 1058, 1670 nm.



Tetraphenylphosphonium chloride (5.1 mg, 0.014 mmol) and potassium tetracyanonickelate(II) (1.8 mg, 0.0070 mmol) were dissolved in 5 mL of H_2O , respectively. To an aqueous solution (5 mL) of $[\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4(\text{H}_2\text{O})_2]\text{BF}_4$ (10.0 mg, 0.0137 mmol) were added these solutions, stirred for 1 hr. The resulting precipitate was filtered, washed with 9 mL of water, and dried *in vacuo*. Yield: 6.5 mg (77%). Anal. Found: C, 43.70; H, 5.29; N, 4.46%. Calcd. for $\text{C}_{92}\text{H}_{132}\text{N}_8\text{Ni}_2\text{O}_{26}\text{PRu}_6$: C, 43.83; H, 5.28; N, 4.45%. IR (KBr): $\nu(\text{Ar-H})$ 3061, 3085, $\nu(\text{CN})$ 2128, $\nu_{\text{as}}(\text{CO}_2^-)$ 1487, $\nu_{\text{s}}(\text{CO}_2^-)$ 1421. Diffuse reflectance spectrum: λ_{max} 346, 454, 1082, 1676 nm.

Measurements: Elemental analyses for carbon, hydrogen, and nitrogen were done 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 tetracyanonickelate(II) ion in the presence of tetraphenylphosphonium ion gave orange and brown precipitates, respectively. The formulation of the mixed-metal systems of dinuclear ruthenium(II,III) carboxylate with tetracyanonickelate(II), $(\text{PPh}_4)_n[\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Ni}(\text{CN})_4]_n \cdot n\text{H}_2\text{O}$ (**1**) and $(\text{PPh}_4)_n[\text{Ru}_2\{\text{O}_2\text{CC}(\text{CH}_3)_3\}_4]_{3n}[\text{Ni}(\text{CN})_4]_{2n} \cdot 2n\text{H}_2\text{O}$ (**2**), was confirmed by the elemental analyses, infrared and electronic spectra, and temperature dependence of magnetic susceptibility data (4.5–300 K).

In the infrared spectra, two strong bands were observed at 1442 and 1403 cm^{-1} assignable to asymmetric and symmetric stretching vibrations of the *syn-syn* acetate bridges, respectively, for **1**, whereas two strong bands observed at 1487 and 1421 cm^{-1} assignable to asymmetric and symmetric stretching vibrations of the *syn-syn* pivalate bridges, respectively, for **2** (Figure 1). The sharp bands at 2130 cm^{-1} in **1** and 2128 cm^{-1} in **2** may be attributed to $\nu(\text{CN})$ stretching band of the tetracyanonickelate(II) ion. These bands appeared at a little higher energy region compared with that of $\text{K}_2[\text{Ni}(\text{CN})_4]$ ($\nu(\text{CN})$: 2125 cm^{-1}), suggesting the bridging of the tetracyanonickelate(II) to the dinuclear ruthenium carboxylate unit [38,39]. The C-H stretching vibrations of aromatic rings were observed at 3100 and 3060 cm^{-1} for **1** and at 3085 and 3061 cm^{-1} for **2**, respectively, in agreement with the presence of the tetraphenylphosphonium ions.

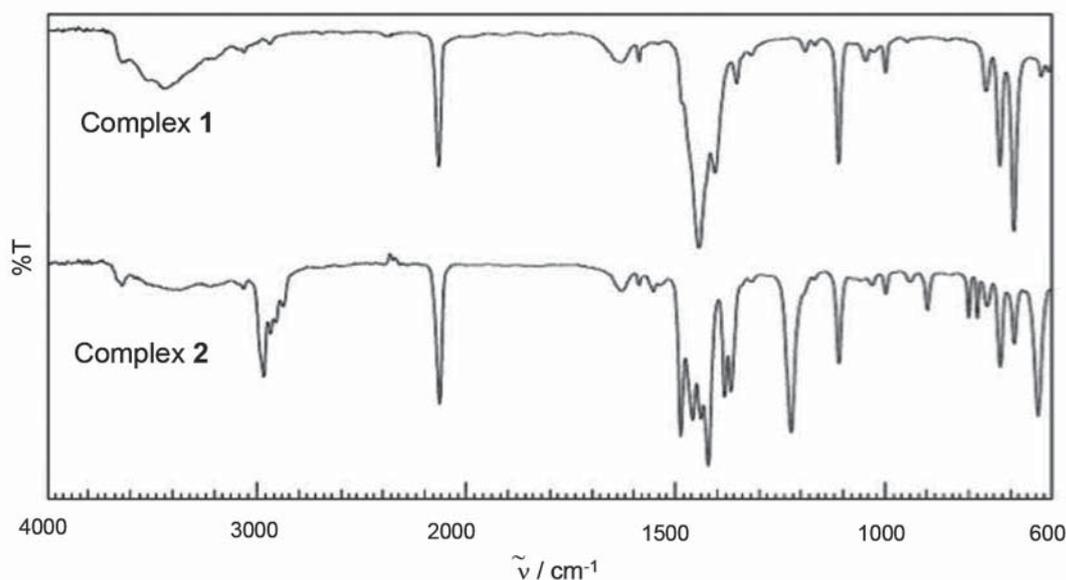


Figure 1. Infrared spectra of **1** and **2**.

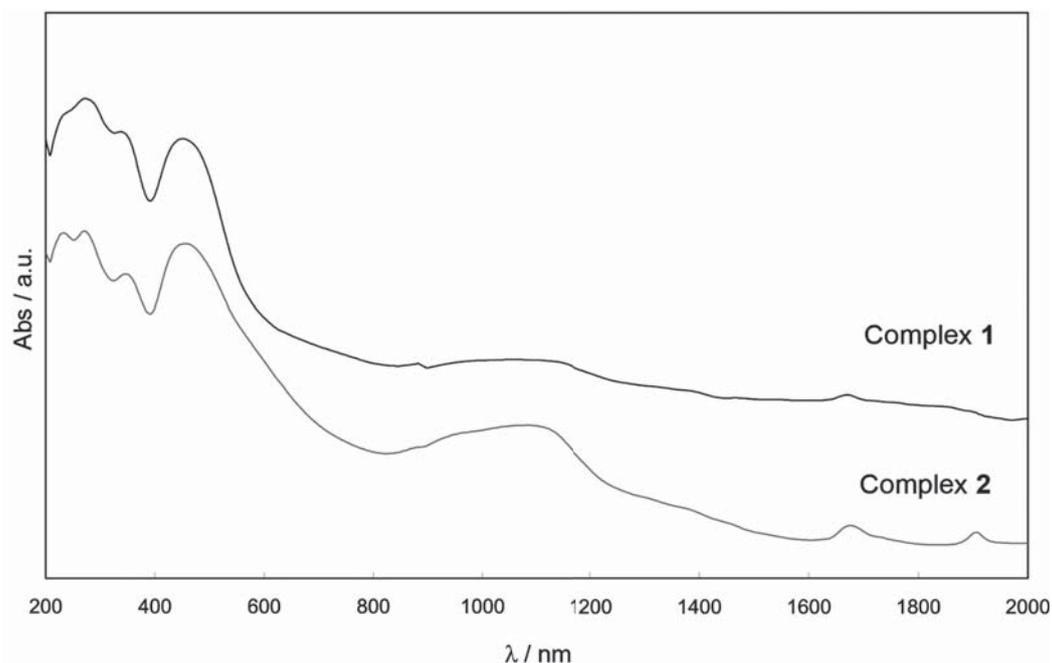


Figure 2. Diffused reflectance spectra of 1 and 2.

The diffused reflectance spectra of **1** and **2** are shown in Figure 2. The paddlewheel-type dinuclear structure of the mixed-valent dinuclear ruthenium(II,III) carboxylate can be considered to be maintained in these mixed-metal complexes, because the spectra contain the characteristic bands of dinuclear ruthenium(II,III) carboxylate. A weak broad absorption band around 1058 and 1670 nm in solid is typical for ruthenium(II,III) carboxylates and can be attributed to a $\delta(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$ and $\pi^*(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$ transitions, respectively, within ruthenium(II,III) dinuclear core [8]. A medium band at 452 nm may be due to $\pi(\text{RuO}, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$ transition [11,12]. The spectra contain another feature due to the presence of tetracyanonickelate(II) moiety. The bands at 338 and 452 nm can be assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transitions, respectively, of the tetracyanonickelate(II) moiety [38,39]. Similar spectral feature was observed for **2**: 1082 ($\delta(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$), 1676 ($\pi^*(\text{Ru}_2) \rightarrow \delta^*(\text{Ru}_2)$), 454 ($\pi(\text{RuO}, \text{Ru}_2) \rightarrow \pi^*(\text{Ru}_2)$), ${}^1A_{1g}(\text{Ni}) \rightarrow {}^1A_{2g}(\text{Ni})$, 346 (${}^1A_{1g}(\text{Ni}) \rightarrow {}^1B_{2g}(\text{Ni})$) nm.

Temperature dependence of effective magnetic moments is shown in Figure 3.

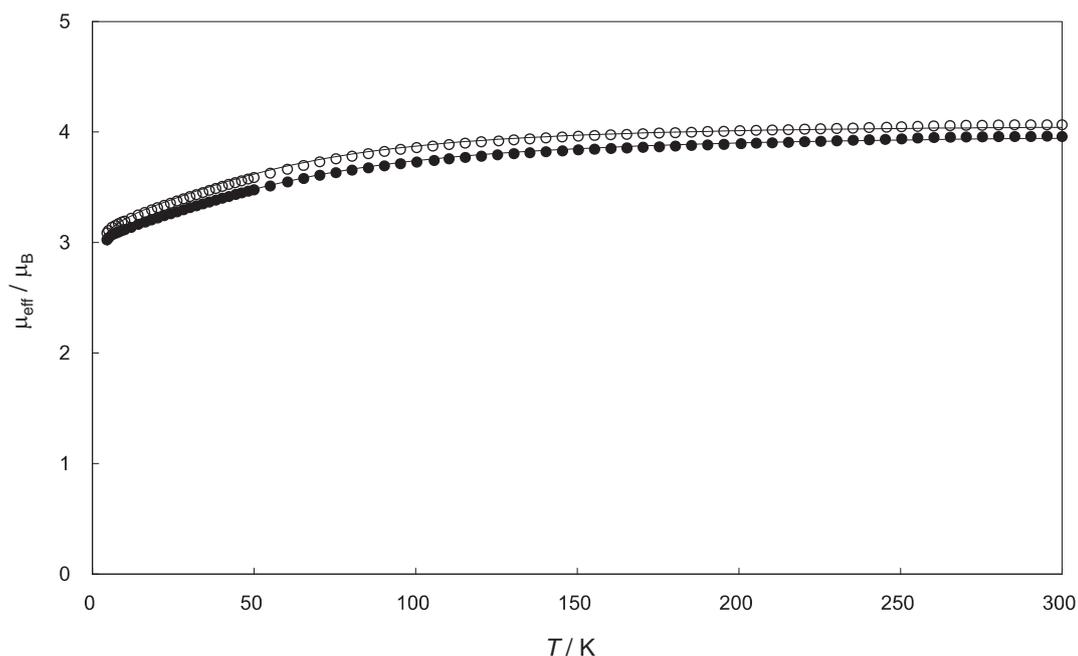


Figure 3. Temperature dependence of the magnetic moments of 1 (●) and 2 (○).

The magnetic moments of **1** and **2** are 3.98 and 4.07 μ_B , respectively, at 300 K per dinuclear ruthenium(II,III) unit, which are slightly higher than the spin-only value of $S = 3/2$ (3.87 μ_B). The magnetic moments gradually decrease with lowering of temperature until reaching 3.02 and 3.09 μ_B , respectively, at 4.5 K, being typical of dinuclear ruthenium(II,III) carboxylates [3-5].

The magnetic data were analyzed by a molecular field approximation [40] considering the ZFS effect to estimate the magnitude of the antiferromagnetic interaction [9,10]. This approximation has been commonly applied for dinuclear ruthenium(II,III) carboxylates using the following equations:

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

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

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

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

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

The D parameter was fixed at 75 cm^{-1} which is a normal value for dinuclear ruthenium(II,III) carboxylates [3]. The g value was treated as isotropic. Best fitting curve was obtained with the parameters; $zJ = -0.20 \text{ cm}^{-1}$, $g = 2.06$ for **1**. The similar parameters $zJ = -0.20 \text{ cm}^{-1}$, $g = 2.09$ were obtained for **2**. These results show that a weak antiferromagnetic interaction is operating between the dinuclear ruthenium units, being consistent with a long separation of the dinuclear ruthenium units through the tetracyanidonickelate(II) bridge for the present complexes.

From the above results, we can assume a chain structure with an alternated arrangement of dinuclear ruthenium units and tetracyanidonickelate(II) ions shown in Figure 4 (a) for **1**, whereas one- or two-dimensional array of dinuclear ruthenium units and tetracyanidonickelate(II) ions such as Figures 4 (b) and 4 (c) for **2**. There are two types of CN groups for the tetracyanidonickelate(II) moieties: bridging and non-coordinating. We can see the overlapping of these CN stretching bands in the infrared spectra as shown in Figure 5.

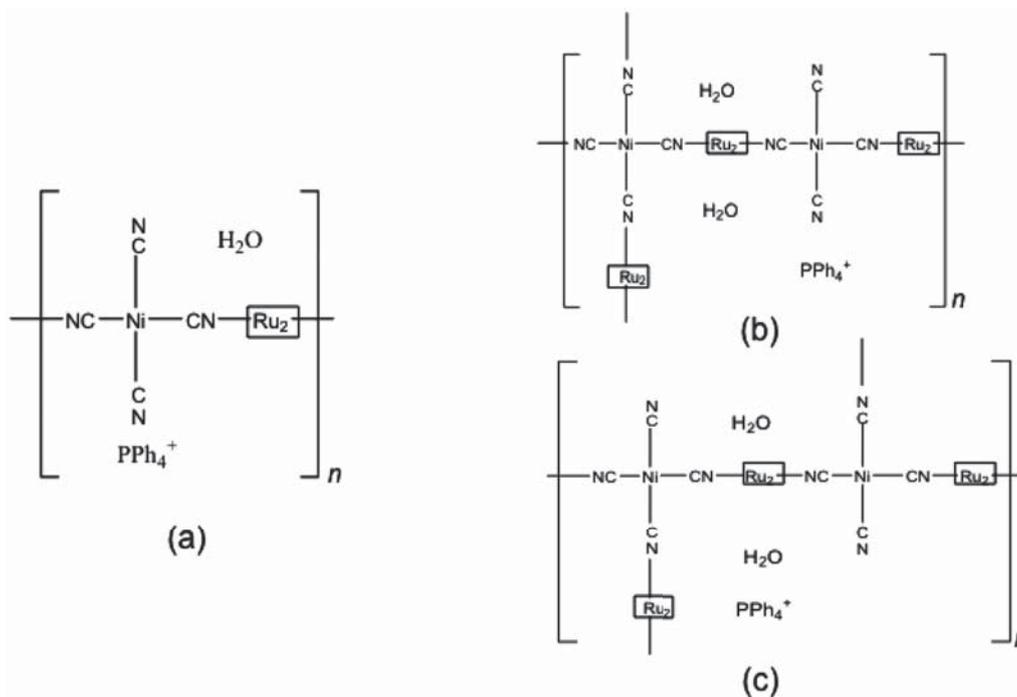


Figure 4. Proposed structures (a) for **1** and (b) and (c) for **2**, respectively. The Ru₂ unit denotes the dinuclear ruthenium carboxylate.

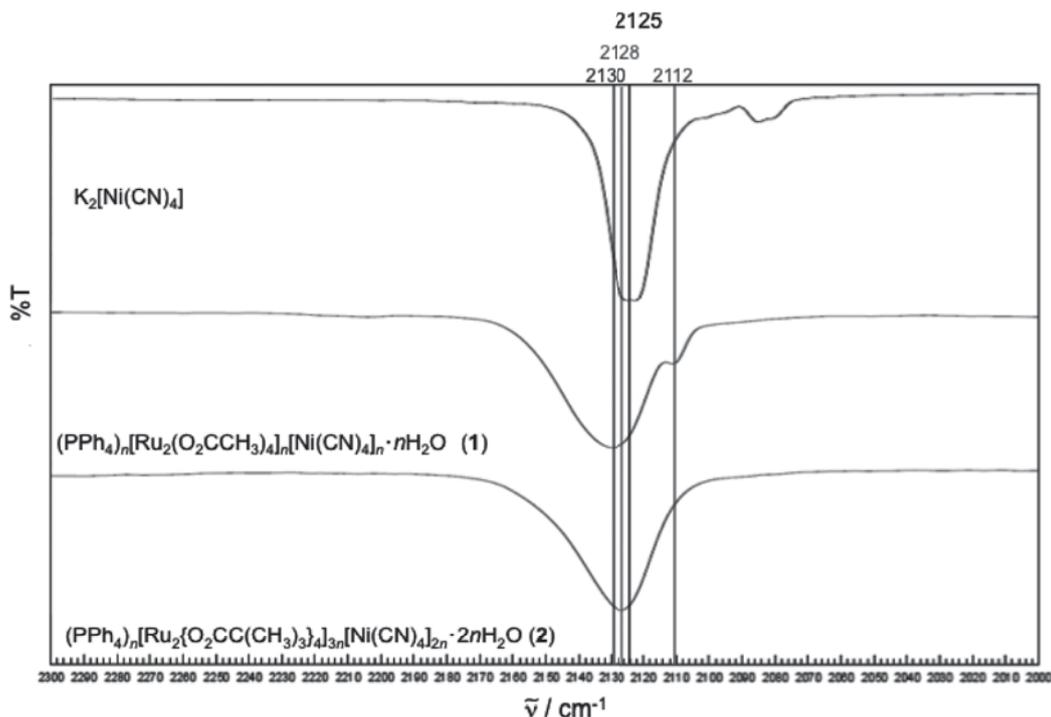


Figure 5. Infrared spectra of $K_2[Ni(CN)_4]$ and the present complexes in the CN stretching band region.

Conclusions

By using tetracyanonickelate(II), the preparation of the mixed-metal chain complexes of dinuclear ruthenium(II,III) carboxylate, $(PPh_4)_n[Ru_2(O_2CCH_3)_4]_n[Ni(CN)_4]_n \cdot nH_2O$ (**1**) and $(PPh_4)_n[Ru_2(O_2CC(CH_3)_3)_4]_{3n}[Ni(CN)_4]_{2n} \cdot 2nH_2O$ (**2**), was achieved successfully. The analytical data, infrared spectra, UV-vis-NIR spectra, and temperature dependence of magnetic susceptibilities are consistent with one- or two-dimensional chain structures with an alternated arrangement of dinuclear ruthenium units and tetracyanonickelate(II) ions. In accordance with the structural feature, a weak antiferromagnetic interaction through the tetracyanonickelate(II) ion was observed for the present complexes.

Acknowledgements

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