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Polynuclear chain complexes of ruthenium(II, III) pivalate dimers linked by 2,5-dimethyl-*N,N′*-dicyanobenzoquinonediimine, 1,4-benzoquinone and 1,4-naphthoquinone[*]

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Reactions of the ruthenium(II, III) pivalate dimer with 2,5-dimethyl-*N,N′*-dicyanobenzoquinonediimine (2,5-dmdcnqi), 1,4-benzoquinone (1,4-bq), and 1,4-naphthoquinone (1,4-nq) produce polynuclear chain complexes ($[Ru_2(O_2CCMe_3)_4(L)]_nX_n$, where L = 2,5-dmdcnqi, 1,4-bq, or 1,4-nq, and X = BF_4^- or PF_6^-). It has been shown that weak antiferromagnetic interaction ($J = -0.15$ cm^{-1}) operates between Ru(II, III) dimers in the 2,5-dmdcnqui complex.

Key words: *Ru(II, III) dimer; dicyanobenzoquinonediimine; p-quinones ; polymer complexes*

1. Introduction

In metal carboxylate dimers ($[Ru_2(O_2CR)_4]^{m+}$, $m = 0$–2) with a lantern-like structure ruthenium(II, II or II, III) dimers are quite unique, because they are paramagnetic with two or three unpaired electrons accommodated in their degenerated π^* and δ^* orbitals based on the metal-metal bond ($\sigma^2\pi^4\delta^2(\pi^*\delta^*)^4$ for Ru(II, II) or $\sigma^2\pi^4\delta^2(\pi^*\delta^*)^3$ for Ru(II, III) electronic configurations), although they have a large zero-field splitting (D = ca. 300 cm^{-1} for Ru(II, II) and ca. 60 cm^{-1} for Ru(II, III) [1–5]. Recently, there

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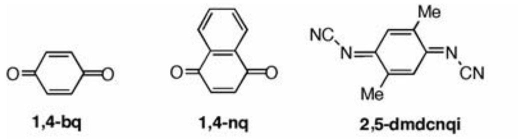
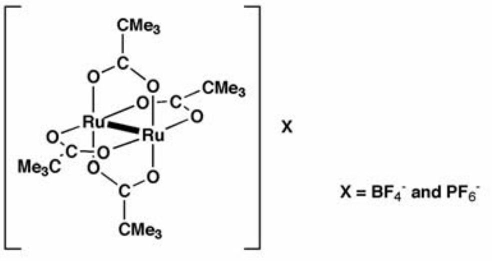
have been many efforts to use these dimers as building blocks in combination with bridging ligands to produce new magnetic materials [6–13]. We have studied polynuclear and oligonuclear compounds of ruthenium(II, II or II, III) carboxylate dimers ($[Ru_2(O_2CR)_4]^{+/0}$), linked by nitronylnitroxide radicals [14–20] and *N,N'*-didentate ligands such as pyrazine and 4,4′-bipyridine [21, 22]. Beside these linkage ligands, the electron acceptors 7,7,8,8-tetracyanoquinodimethane (tcnq) and 9,10-anthraquinone (9,10-aq) have also been employed in combination with ruthenium(II, III) pivalate dimers to produce the tetranuclear complexes $[\{Ru_2(O_2CCMe_3)_4(H_2O)\}_2(L)](BF_4)_2$ (**1**: L = tcnq, and **2**: L = 9,10-aq) [23, 24], of which the "dimer-of-dimers" structures were crystallographically determined for **1**. It has also been confirmed that tcnq and 9,10-aq work as neutral linkage ligands and mediate weak magnetic interactions between dimetal units in the tetranuclear complexes **1** and **2**.

In this study, we used 2,5-dimethyl-*N,N'*-dicyanobenzoquinonediimine (2,5-dmdcnqi), 1,4-benzoquinone (1,4-bq), and 1,4-naphthoquinone (1,4-nq) (Scheme 1a) for the reaction with the ruthenium(II, III) pivalate dimer (Scheme 1b) in benzene. The obtained compounds were found to be polynuclear chain complexes, described as $[Ru_2(O_2CCMe_3)_4(L)]_nX_n$, where L = 2,5-dmdcnqi, 1,4-bq, or 1,4-nq, and X = BF_4^- or PF_6^- .



a) employed linkage ligands



b) ruthenium(II,III) pivalate dimers

Scheme 1

2. Experimental

Preparations. The tetrafluoroborate and hexafluorophosphate salts, $[Ru_2(O_2CCMe_3)_4(H_2O)_2]X$ (X = BF_4^- or PF_6^-) and 2,5-dmdcnqi were prepared according to methods reported in literature [25, 26]. The *p*-quinones 1,4-bq and 1,4-nq were used as supplied by Wako Chemicals.

$[Ru_2(O_2CCMe_3)_4(2,5\text{-dmdcnqi})]_n(BF_4)_n \cdot 2.5nH_2O$ (3). 50 mg (0.069 mmol) of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ was put into a Schlenk tube and heated to 60 °C under vacuum for one hour in order to remove the axial water molecules, and then dissolved in benzene (5 cm^3) under argon. A benzene solution (10 cm^3) of 2,5-dmdcnqi (25 mg, 0.136 mmol) was subsequently added to the tube and stirred overnight with the water-removed tetrafluoroborate salt at room temperature under argon. The resultant precipitate was collected by filtration, washed with benzene, and dried under vacuum to give a brown powder. The yield was 42 mg (67% based on $[Ru_2(O_2CCMe_3)_4(H_2O)]BF_4$). Anal. Found C, 38.83; H, 5.01; N, 6.39. Calcd. for $C_{30}H_{49}BF_4N_4O_{10.5}Ru_2$: C, 39.05; H, 5.35; N, 6.07. IR (KBr) ν(CN) 2174, 2110, $\nu_{as}(CO_2)$ 1481, $\nu_s(CO_2)$ 1419, $\nu(BF_4^-)$ 1080 cm^{-1}.

$[Ru_2(O_2CCMe_3)_4(1,4\text{-bq})]_n(PF_6)_n$ (4). This compound was obtained as a brown powder from a reaction of the anhydrous hexafluorophosphate salt, which was obtained by heating $[Ru_2(O_2CCMe_3)_4(H_2O)_2]PF_4$ (30 mg, 0.038 mmol) to 120 °C under vacuum, with 1,4-bq (4.5 mg, 0.042 mmol) in benzene using the same method as for **3**. The yield was 19 mg (58% based on $[Ru_2(O_2CCMe_3)_4(H_2O)_2]PF_6$). Anal. Found C, 36.20; H, 4.51. Calcd. for $C_{26}H_{40}F_6O_{10}PRu_2$: C, 36.33; H, 4.69. IR (KBr) ν(CO) 1657, 1600, $\nu_{as}(CO_2)$ 1485, $\nu_s(CO_2)$ 1420, $\nu(PF_6^-)$ 844 cm^{-1}.

$[Ru_2(O_2CCMe_3)_4(1,4\text{-nq})]_n(PF_6)_n \cdot 3nH_2O$ (5). This compound was obtained as a reddish-brown powder by treating $[Ru_2(O_2CCMe_3)_4(H_2O)_2]PF_6$ (30 mg, 0.038 mmol) with 1,4-nq (7 mg, 0.044 mmol) in the same way as **4**. The yield was 17 mg (46% based on $[Ru_2(O_2CCMe_3)_4(H_2O)_2]PF_6$). Anal. Found C, 37.09; H, 4.64. Calcd. for $C_{30}H_{48}F_6O_{13}PRu_2$: C, 37.39; H, 5.02. IR (KBr) ν(CO) 1662, 1642, $\nu_{as}(CO_2)$ 1484, $\nu_s(CO_2)$ 1420, $\nu(PF_6^-)$ 850 cm^{-1}.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Perkin-Elmer Series II, CHN/O Analyzer. Infrared spectra (KBr pellets) and electronic spectra were measured with JASCO IR-700 and Shimadzu UV-3100 spectrometers, respectively. Magnetic susceptibilities were measured on a Quantum Design MPMS-5S SQUID susceptometer, operating at a magnetic field of 0.5T over the temperature range of 4.5−300 K. Susceptibilities were corrected for the diamagnetism of constituent atoms using Pascal's constant [27]. Effective magnetic moments were calculated from the equation: $\mu_{eff} = 2.828(\chi T)^{1/2}$, where χ is the magnetic susceptibility per Ru(II, III) dimer unit.

3. Results and discussion

Elemental analyses of the complexes obtained showed the stoichiometry of $[Ru_2(O_2CCMe_3)_4]^+$:L = 1:1, which is consistent with that for the polynuclear chain structure of $[Ru_2(O_2CCMe_3)_4(L)]_nX_n$ (L = 2,5-dmdcnqi and X = BF_4^- for complex **3**; L = 1,4-bq and X = PF_6^- for complex **4**; L = 1,4-nq and X = PF_6^- for complex **5**). These complexes are not stable in air because they easily replace their axial ligands with atmospheric water molecules, although **3** is relatively stable compared to **4** and **5**. It is noteworthy that the complex formation did not occur for the reactions of the tetrafluoroborate salt $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ with 1,4-bq and 1,4-nq. It is unclear why the complex formation occurred in the case of 9,10-aq and gave the tetranuclear complex $[\{Ru_2(O_2CCMe_3)_4(H_2O)\}_2(9,10\text{-aq})](BF_4)_2$ (**2**).

In the IR spectra of the powder samples (KBr pellets) of complexes **3–5** there are two strong bands for each complex: at 1419 and 1481 cm^{-1} for **3**, 1420 and 1485 cm^{-1} for **4**, and 1420 and 1484 cm^{-1} for **5**. They are assigned to carbonyl stretching modes of the carboxylato group in the Ru(II, III) dimeric core, because the parent dimer complexes $[Ru_2(O_2CCMe_3)_4(H_2O)_2]X$ (X = BF_4^- or PF_6^-) show bands at 1420 and 1490 cm^{-1} [18, 22, 24]. The other carbonyl stretching bands, observed at 1600 and 1657 cm^{-1} for **4,** and at 1642 and 1662 cm^{-1} for **5,** originate from the linkage *p*-quinones 1,4-bq and 1,4-nq [28]. The bands based on the CN group of 2,5-dmdcnqi appear at 2216 and 2104 cm^{-1} for **3** [29, 30]. The bands at 1080 for **3**, 844 for **4**, and 850 cm^{-1} for **5** are due to the counter ions BF_4^- and PF_6^- [31]. These IR-spectral results strongly support the formation of the polynuclear chain complexes $[Ru_2(O_2CCMe_3)_4(L)]X$, where L = 2,5-dmdcnqi, 1,4-bq, or 1,4-nq, and X = BF_4^- or PF_6^- .

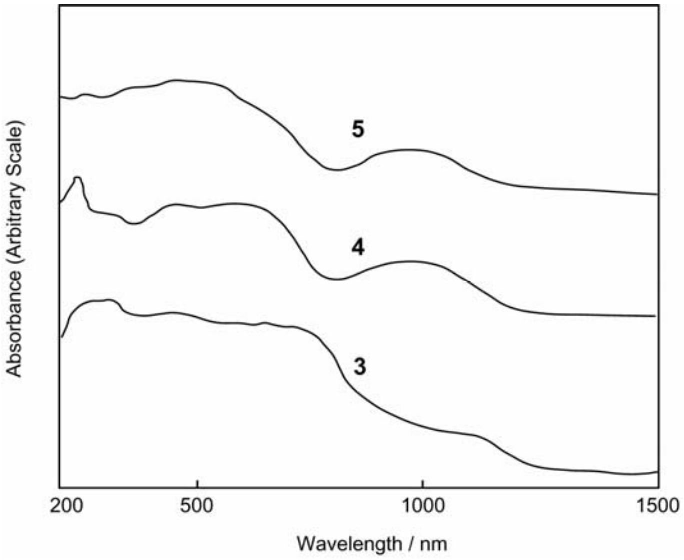


Fig. 1. Reflectance spectra of **3**, **4** and **5**

Diffuse reflectance spectra of **3–5** are displayed in Fig. 1. All of the complexes have absorption bands ascribed as the $\delta(Ru_2)\rightarrow\delta^*(Ru_2)$ transition within the Ru(II, III) dimeric core around 1000 nm, though the band of **3** appears as a shoulder, due to the intensive band in the visible region (below 800 nm) assigned to the $\delta^*/\pi^*(Ru_2)\rightarrow\sigma^*(Ru\text{–}O)$ transition and considered to be red-shifted to this region by the stronger σ-donation of 2,5-dmdcnqi [22]; the parent complex, $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$, shows a corresponding band at 545 nm in addition to the $\delta(Ru_2)\rightarrow\delta^*(Ru_2)$ transition band at 990 nm [22].

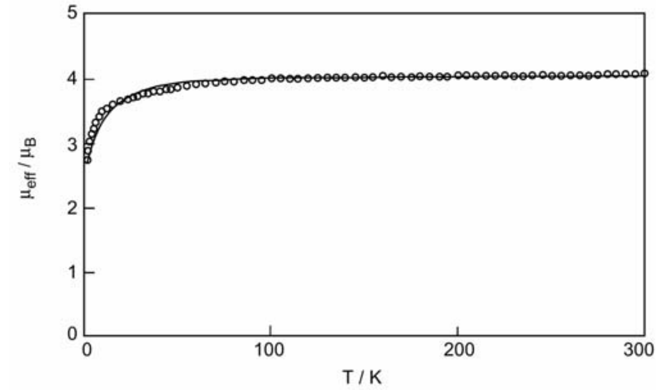
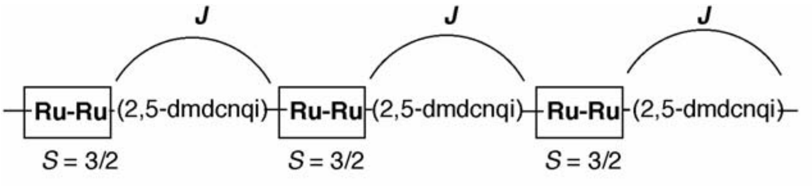


Fig. 2. Temperature dependence of the effective magnetic moment of **3**. The solid line was calculated for the parameters described in the text

Magnetic-susceptibility data could be obtained only for complex **3,** because of the relative instability of complexes **4** and **5**, which decomposed before being measured. The temperature dependence of the magnetic moment of **3** is displayed in Fig. 2. The moment at room temperature (300 K) is $4.10\mu_B$, which is slightly larger than the spin-only value calculated for the three unpaired electrons within the Ru(II, III) dimeric core ($3.87\mu_B$) and slightly lower than that of the parent complex $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ ($4.31\mu_B$ at 300 K) [18]. The moment decreases slowly when temperature falls from 300 K to 10 K, and then drops relatively rapidly until 4.5 K (the lower end of the measured temperatures). This behaviour is considered to originate from the antiferromagnetic interaction between Ru(II, III) dimers, as well as from the zero-field splitting within the dimeric core; no drop in the low temperature range (below ca. 10 K) was found for $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$ [32]. The model illustrated in Scheme 2 was applied in order to analyze the magnetic behaviour, using a molecular-field approximation for the interaction between Ru(II, III) dimers (z, the number of neighboring spin centers, is set to 2 in approximation) [3,18,22,27,33]. As shown by the solid line in Fig. 2, the temperature-dependent profile could be roughly reproduced with $J = -0.15 cm^{-1}$, $D = 20$ cm^{-1} (the parameter for zero-field splitting), and $g = 2.1$ (the g factor). The calculated line somewhat disagrees with the experimental values at low temperatures (T below ca. 50 K), implying that an improved model that includes parameters for interactions other than those in Scheme 2 may be needed to complete the analysis, which may be possible when the crystal structure is given for **3**. It is obvious that a weak antiferromagnetic interaction exists between the Ru(II, III) dimmers, because the drop in the moment below 10 K cannot be reproduced without the J value (-0.15 cm^{-1}). The value of J for **3** is the same as that for the tcnq-bridged



Scheme 2

tetranuclear complex **1** ($J = -0.15$ cm^{-1}) [23]. The value of D for **3** (20 cm^{-1}) is relatively small, but considered not to be unusual – similarly small values have been observed for complexes of ruthenium(II, III) carboxylate dimers [20, 34].

4. Conclusions

Polynuclear chain complexes $[Ru_2(O_2CCMe_3)_4(L)]X$ (L = 2,5-dmdcnqi, 1,4-bq, or 1,4-nq; X = BF_4^- or PF_6^-) were obtained by reactions in benzene between ruthenium (II, III) pivalate dimers and the corresponding linkage ligands with an electron-accepting nature. Complexes with 1,4-bq and 1,4-nq were unstable in air, but the complex with 2,5-dmdcnqi was stable enough to be employed in magnetic measurement. It was found that the magnetic interaction between Ru(II, III) dimers through the linkage ligands is weakly antiferromagnetic ($J = -0.15$ cm^{-1}).

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