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Magnetic behavior in heterometallic one-dimensional chains or octanuclear complex regularly aligned with metal–metal bonds as –Rh–Rh–Pt–Cu–Pt

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ABSTRACT

Heterometallic one-dimensional chains, $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}]_n(PF_6)_{2n}$ (**1** and **2**, piam = pivalamidate) and $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}_2](CF_3CO_2)_2(ClO_4)_2\cdot 2H_2O$ (**3**), are paramagnetic one-dimensional chains or octanuclear complexes that are either aligned as –Rh–Rh–Pt–Cu–Pt– (**1** and **2**) or as Pt–Cu–Pt–Rh–Rh–Pt–Cu–Pt (**3**) with metal–metal bonds. Compounds **1**–**3** have rare structures, from the standpoint of that the paramagnetic species of Cu atoms are linked by direct metal–metal bonds. Magnetic susceptibility measurements for **1**–**3** performed at temperatures of 2 K –300 K indicated that the unpaired electrons localize in the Cu $3dx^2-y^2$ orbitals, where $S = 1/2$ Cu(II) atoms are weakly antiferromagnetically coupled with $J = -0.35\ cm^{-1}$ (**1**), $-0.47\ cm^{-1}$ (**2**), and $-0.45\ cm^{-1}$ (**3**).

1. Introduction

Low-dimensional polymeric coordination compounds have produced peculiar magnetic behaviors, such as single-chain magnets [1], and wide varieties of structures have been synthesized using various metals and multinuclear complexes that serve as the paramagnetic species [2–4]. A square planar Cu(II) ion has a well-defined magnetic $3dx^2-y^2$ orbital with one unpaired electron that exhibits easily interpretable magnetic behaviors. Consequently, magnetic exchange interactions in Cu(II)–linker–Cu(II) complexes have been extensively studied in relation to the mutual arrangement of magnetic orbitals [2,5,6]. Multiple networks [5–30] that contain Cu(II) ions employing bidentate organic ligands [7–21], halogen ions [22–26], or hydrogen bonds [27,28] as linkers and a few one-dimensional networks [29,30] wherein the second metal bridges the Cu(II) ions with direct metal–metal bonds have been reported. Heterometallic trinuclear complexes, such as $[Cu_2Pd(dpa)_4Cl_2]$ (dpa = dipyridylamide) and $[Cu_2Pt(dpa)_4Cl_2]$, are rare examples of antiferromagnetic coupling in a Cu–M–Cu (M = Pd and Pt) structure, where the Cu(II) ions are bridged by M with a separation of approximately 5.0 Å [29]. Although these types of metal–metal bonds can generate interesting magnetic interactions between the spin centers [31–33], there are only a few examples of the paramagnetic one-dimensional chains synthesized via direct metal–metal bonding due to the lack of appropriate synthetic methodology.

Recently, we have succeeded in obtaining paramagnetic one-dimensional chains using the HOMO–LUMO interaction at the dz^2 orbital between two complexes [34] and reported three resulting compounds (Scheme 1): $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}]_n(PF_6)_{2n}$ (**1** and **2**, piam = pivalamidate) and $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}_2](CF_3CO_2)_2(ClO_4)_2\cdot 2H_2O$ (**3**) [30]. Compounds **1**–**3** comprise two types of complex, $[Rh_2(O_2CCH_3)_4]$ and $[Pt_2Cu(piam)_4(NH_3)_4]^{2+}$, that are either aligned as infinite one-dimensional chains of –Rh–Rh–Pt–Cu–Pt– (**1** and **2**) or as the octanuclear structure of Pt–Cu–Pt–Rh–Rh–Pt–Cu–Pt (**3**) [30]. Although qualitative analyses for **1**–**3** had been carried out revealing that all metal have +2 oxidation states containing Cu $3dx^2-y^2$ unpaired spins [30], quantitative analyses have never been done due to the fact that only a small amount of these compounds could be obtained. In this report, the magnetic susceptibility measurements are performed for compounds **1**–**3**, showing the degree of magnetic interaction between Cu(II) ions through direct metal–metal bonds with a discussion based on the fitting of the magnetometry data to appropriate theoretical models.

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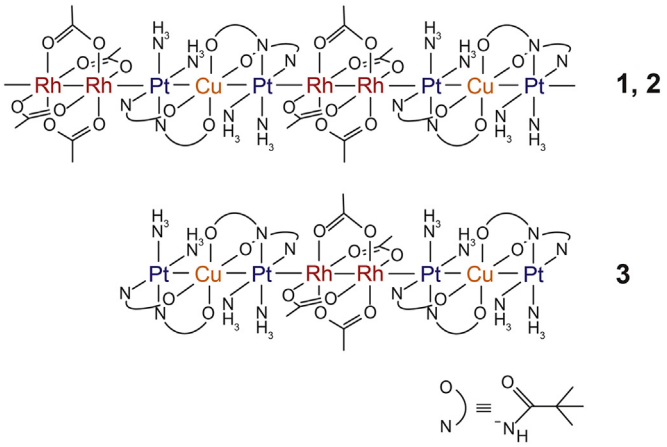

Scheme 1. Heterometallic one-dimensional chains (**1** and **2**) and octanuclear complex (**3**).

2. Experimental

2.1. Materials

Rhodium(III) chloride trihydrate and potassium tetrachloroplatinate(II) were obtained from Tanaka Kikinzoku Co. Sodium hexafluorophosphate and tetrabutylammonium perchlorate were obtained from Tokyo Chemical Industry Co. $CuCl_2 \cdot 2H_2O$ was obtained from Wako Co. $[Pt_2Cu(piam)_4(NH_3)_4](PF_6)_2$, $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}]_n(PF_6)_{2n}$ (**1** and **2**), and $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}_2](CF_3CO_2)_2(ClO_4)_2 \cdot 2H_2O$ (**3**) were synthesized according to the previous procedures [30].

2.2. Physical measurements

X-ray powder diffraction (XRPD) data were collected on a Rigaku MiniFlex diffractometer with CuKα radiation. Magnetic data were obtained in the 2–300 K range using a Quantum Design MPMS superconducting SQUID susceptometer working at a 1-T field strength. Crude data were corrected for the contribution of a sample holder and diamagnetism of constituent atoms.

3. Results and discussion

3.1. XRPD and one-dimensional structures of *1*–*3*

Fig. 1 shows XRPD patterns for crystalline powder samples for **1**–**3** with the simulation based on the results of single-crystal X-ray analyses. In all three compounds, the positions and relative intensities of diffraction peaks coincide with simulated ones, indicating that powder samples have similar polycrystalline structures. However, in **2**, some peaks labelled with asterisk, which are absent in the simulated diffractogram, are observed. Those may be attributed to the crystal structure of **1**, because both **1** and **2** have same formulae and similar crystal structures, but slightly different molecular packing [30]. Considering the density based on the crystal structures at 123 K [30], 2.093 g cm^{-3} (**1**) and 2.158 g cm^{-3} (**2**), compound **2** is more thermodynamically stable than **1**, where some portion of kinetically stable **1** contaminated the sample of compound **2**. The curve fitting of XRPD patterns for **2** in the range of $2\theta = 8.0–10.5°$ shows that the amount fraction for **1** is about 30% (Fig. S1). Although the contamination ratio is not low, this crystalline powder sample was used for the magnetic susceptibility measurement for **2**, taking into account that both compounds have

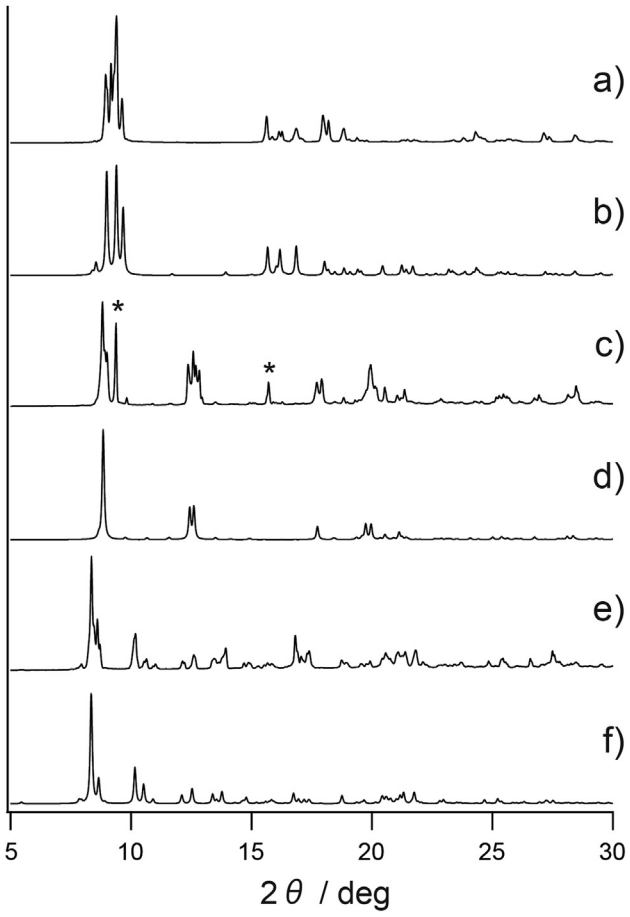

Fig. 1. XRPD for (a) observed $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}]_n(PF_6)_{2n}$ (**1**), (b) simulated **1**, (c) observed $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}]_n(PF_6)_{2n}$ (**2**), (d) simulated **2**, (e) observed $[\{Rh_2(O_2CCH_3)_4\}\{Pt_2Cu(piam)_4(NH_3)_4\}_2](CF_3CO_2)_2(ClO_4)_2 \cdot 2H_2O$ (**3**), and (f) simulated **3**.

similar chain structures. As a result, there is no significant difference in magnetic behaviors between **1** and **2** (vide infra).

Fig. 2 shows the sequence of metal alignments for compounds **1**–**3**. Both **1** and **2** have a similar metal alignment of –Rh–Rh–Pt–Cu–Pt–, where the distances between the paramagnetic Cu(II) ions are 13.060(4) Å and 13.1305(16) Å, respectively [30]. All one-dimensional chains in the crystals are parallel (Fig. 1a and b), where Cu–Cu interchain distances are approximately 11 Å. The significant difference between **1** and **2** is the angle of the Rh–Pt–Cu bonds, 155.010(19)° (**1**) and 164.340(7)° (**2**), which induces a difference in the atomic Pt–Cu distances of 2.7034(9) Å (**1**) and 2.6716(3) Å (**2**) (Figs. S2 and S3). However, in compound **3**, two trinuclear Pt–Cu–Pt complexes are bridged by a dinuclear rhodium complex to form an octanuclear structure, such as Pt–Cu–Pt–Rh–Rh–Pt–Cu–Pt, with a separation of Cu–Cu = 13.3535(13) Å. As shown in Fig. 2c, octanuclear complexes are perpendicular to each other throughout the crystal. In compound **3**, the closest distance in the Cu–Cu is 10.2 Å, which is between neighboring octanuclear units that are oriented perpendicular to each other (Fig. S4).

3.2. Magnetic susceptibility measurements for *1*–*3*

Variable-temperature magnetic susceptibility measurements for the original compound $[Pt_2Cu(piam)_4(NH_3)_4](PF_6)_2$ and complexes **1**–**3** were performed on polycrystalline samples in the range