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Mixed-Valent Diruthenium Diphosphonate with Kagomé Structure

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This paper reports the first example of diruthenium phosphonate with kagomé structure, namely, $[NH_3(CH_2)_4NH_3][Ru_2(hedpH_{0.5})_2]\cdot 2H_2O$ (hedp = 1-hydroxyethylidenediphosphonate). The compound contains kagomé layers that are linked by very strong hydrogen bonds into a nanoscale kagomé structure. Ferromagnetic interactions are mediated between the paramagnetic diruthenium units.

The kagomé lattice is a two-dimensional lattice of corner-sharing triangles. Paramagnetic compounds with kagomé structures have been of great interest because of their unusual magnetic properties such as spin frustration.[1] Investigations have been centered on the jarosite family of minerals with the general formula $AFe_3(OH)_6(SO_4)_2$ [2] and other metal sulfate compounds with related structures.[3,4] Rather few molecular kagomé lattices have been reported so far,[5−8] including a copper compound $[(Cu_2(py)_2(bdc)_2)_3]_n$ (bdc = 1,3-benzenedicarboxylate)[5] and an organic radical compound.[6] In these compounds, antiferromagnetic interactions are commonly observed between the magnetic carriers except in $NaV_3(OH)_6(SO_4)_2$, where the V^{3+} ions are ferromagnetically coupled to each other.[4]

The paramagnetic metal−metal-bonded diruthenium tetracarboxylates $Ru_2(O_2CR)_4^{n+}$, as efficient building blocks, have been used in the supramolecular assembly of a number of compounds with one-, two-, and three-dimensional structures.[8−12] Diruthenium phosphonates with extended structures are rare,[13,14] including compound $(NH_4)_3[Ru_2(hedp)_2]\cdot 2H_2O$[14] [hedp = 1-hydroxyethylidenediphosphonate, $CH_3C(OH)(PO_3)_2$] with a square-grid layer structure. In this paper, we report the first example of diruthenium phosphonate with kagomé lattice, namely, $[NH_3(CH_2)_4NH_3][Ru_2(hedpH_{0.5})_2]\cdot 2H_2O$ (**1**), which shows ferromagnetic exchange coupling between the mixed-valent diruthenium units of $Ru_2(hedpH_{0.5})_2^{2-}$.

Hydrothermal treatment of a mixture of $RuCl_3\cdot xH_2O$ (0.23 mmol), $hedpH_4\cdot H_2O$ (0.68 mmol), and H_2O (3 cm^3), adjusted by $NH_2(CH_2)_4NH_2$ to pH = 2.85, at 140 °C for 6 days resulted in brown-red hexagonal block crystals of compound **1** with a yield of 98% (based on Ru).[15] The IR spectrum

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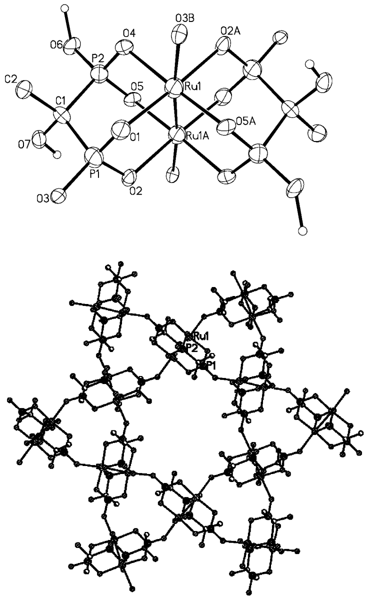

Figure 1. Building unit of structure **1** (top) and one layer of structure **1** (bottom).

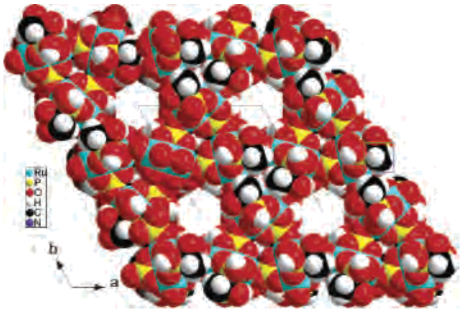

Figure 2. Space-filling diagram of structure **1** viewed along the *c* axis. The lattice water molecules and the protonated 1,4-butanediamine are omitted for clarity.

shows a series of strong bands between 1000 and 1200 cm^{-1}, characteristic of the stretching vibration of the phosphonate PO_3 groups. Bands between 1300 and 1620 cm^{-1} correspond to the C−H and N−H bending vibrations. The diffuse reflectance spectrum gives a major band at ca. 500 nm and a weak band at ca. 980 nm, which are assigned to the $\pi(\mathrm{Ru{-}O,Ru_2}) \rightarrow \pi^*(\mathrm{Ru_2})$ and $\delta(\mathrm{Ru_2}) \rightarrow \delta^*(\mathrm{Ru_2})$ transitions, respectively,[16] in agreement with the mixed-valent nature of the compound.

Single-crystal X-ray diffraction studies[17] reveal that compound **1** crystallizes in a highly symmetrical trigonal space group $P\bar{3}1c$. It has a layered structure made up from the paddlewheel diruthenium building blocks of $\mathrm{Ru_2(hedpH_{0.5})_2}^{2-}$ similar to the diruthenium tetracarboxylates (Figure 1). In this building block, the two equivalent $\mathrm{hedpH_{0.5}}^{3.5-}$ ligands chelate and bridge the two equivalent Ru atoms into a dimer. Therefore, the equatorial positions of each Ru octahedron are occupied by the phosphonate oxygens O1, O2, O4, and O5, while the axial positions are occupied by an equivalent Ru atom and a phosphonate oxygen atom O3 from the adjacent dimer units. The Ru−O bond lengths [2.018(3)−2.237(3) Å] and the Ru−Ru distance [2.351(1) Å] in **1** are comparable to those in $\mathrm{(NH_4)_3[Ru_2(hedp)_2]\cdot 2H_2O}$ [2.023(4)−2.283(4) and 2.354(1) Å].[14] Unlike $\mathrm{(NH_4)_3[Ru_2(hedp)_2]\cdot 2H_2O}$, where the $\mathrm{Ru_2(hedp)_2}^{3-}$ units are linked into a square-grid layer, however, the neighboring $\mathrm{Ru_2(hedpH_{0.5})_2}^{2-}$ units in **1** are connected by the phosphonate oxygen O3, forming a typical kagomé lattice containing trigonal and hexagonal rings (Figure 1, bottom). The hydroxy groups of $\mathrm{hedpH_{0.5}}^{3.5-}$ all point toward the middle of the hexagonal rings with the opposite O7···O7 distance of 9.822 Å. The phosphonate oxygen atom O6 forms the links that connect neighboring layers together and is hydrogen bonded to its own symmetry relative across the inversion center. The O6···O6^{i} distance is 2.384(4) Å (symmetry code: i, $-x + y$, y, $^3/_2 - z$). The O6−H6···O6^{i} moiety necessarily consists of one hydrogen for two oxygens, resulting in a 50% crystallographic occupancy for H6. An extremely strong hydrogen bond has also been observed in $\mathrm{CsMnHP_3O_{10}}$ [O···O distance of 2.372(12) Å].[18] A three-dimensional nanoscale kagomé structure is thus constructed, with trigonal and hexagonal channels generated along the *c* axis (Figure 2). The lattice water molecules are disordered and reside inside these channels. The protonated 1,4-butanediamine are locked on the sidewalls of the hexagonal channels through hydrogen bonds [N1···O7^{ii} = 2.936 Å, N1···O2w = 2.861 Å, N1···O4^{iii} = 2.952 Å; symmetry codes: ii, $-x + y + 1$, $-x + 1$, z; iii, $-y + 2$, $x - y + 1$, z]. A similar nanoscale kagomé structure was observed only in compound $\mathrm{[(Cu_2(py)_2(bdc)_2)_3]}_n$.[5]

Thermal analysis shows a weight loss (4.82%) in the temperature range of 20−120 °C corresponding to the removal of two water molecules (4.91%), followed by a plateau up to ca. 260 °C. The X-ray powder diffraction patterns confirm that the lattice water in compound **1** can be removed and readsorbed without the collapse of the nanoscale kagomé structure. The weight losses above 270 °C could be due to the decomposition of the organic components. The final product was not characterized.

The temperature dependence of the molar magnetic susceptibilities of **1** was investigated in the range of 1.8−300 K at 2 kOe. At room temperature, the $\chi_M T$ value is 2.32 cm^3 K mol^{-1} (4.31 μ_B per dimer) corresponding to three unpaired electrons. Upon cooling, $\chi_M T$ decreases smoothly to a minimum of 1.57 cm^3 K mol^{-1} (3.54 μ_B) at 12 K, below which the $\chi_M T$ value increases rapidly and reaches to a value of 2.04 cm^3 K mol^{-1} (4.04 μ_B) at 1.8 K. This behavior is attributed to a large zero-field splitting (D) coupled with

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(15) Elem anal (%). Calcd for **1**: C, 13.10; H, 3.71; N, 3.82. Found: C, 12.71; H, 3.76; N, 3.91. IR (KBr, cm^{-1}): 3484(m), 3408(br, s), 3157(s), 3093(s), 3014(m), 2936(m), 1637(m), 1618(s), 1542(m), 1510(m), 1476(m), 1459(w), 1371(m), 1147(vs), 1124(vs), 1072(s), 971(vs), 938(vs), 902(s), 798(s), 737(w), 587(vs), 536(s), 480(s).

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(17) Crystal data for **1**: $\mathrm{C_{24}H_{81}N_6O_{48}P_{12}Ru_6}$, M_r = 2200.01, red-brown block, trigonal, space group $P\bar{3}1c$, a = 14.3827(19) Å, c = 19.992(4) Å, V = 3581.5(10) $Å^3$, Z = 2, ρ_{calcd} = 2.040 g cm^{-3}, μ(Mo Kα) = 1.606 mm^{-1}. A single crystal of dimensions 0.20 × 0.20 × 0.10 mm^3 for **1** was selected for indexing and intensity data collection on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) at room temperature. Numbers of collected and observed independent [$I > 2\sigma(I)$] reflections are 18 726 and 2365 (R_{int} = 0.0648). Full matrix least-squares refinements were based on F^2 and converged at R1 = 0.0450 and wR2 = 0.0752.

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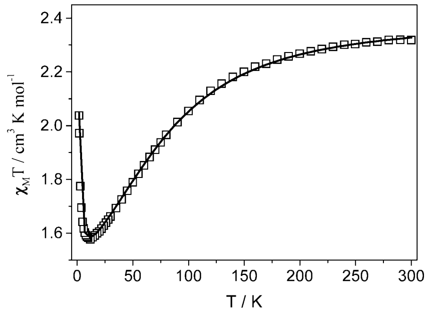

Figure 3. $\chi_M T$ vs T plot for compound **1**.

interdimer ferromagnetic interactions. The susceptibility data can be analyzed by the following equation:[12b]

$$\chi_{\mathrm{Ru}_2} = \frac{Ng^2\beta^2}{k(T-\theta)}\left[\frac{1}{3}\,\frac{1+9\mathrm{e}^{-2D/kT}}{4(1+\mathrm{e}^{-2D/kT})} + \frac{2}{3}\,\frac{1+(3kT/4D)(1-\mathrm{e}^{-2D/kT})}{1+\mathrm{e}^{-2D/kT}}\right] + \mathrm{TIP}$$

where the Weiss constant θ accounts for the magnetic interactions between the paramagnetic centers. The best fit, shown as the solid line in Figure 3, gives parameters $g = 2.25$, $D = 94.9$ cm^{-1}, $\theta = 0.53$ K, and TIP $= 1.98 \times 10^{-5}$ cm^3 mol^{-1}. The positive θ value confirms the presence of weak ferromagnetic interdimer interactions. The magnetization measurement suggests no long-range ordering down to 1.8 K.

In conclusion, this paper reports the first example of a diruthenium phosphonate showing kagomé structure. The paramagnetic diruthenium units are interacted ferromagnetically. Further work is in progress to explore materials with novel topologies and properties based on the $\mathrm{Ru_2(hedpH}_n)_2{}^{(3-2n)-}$ units using different organic templates.

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Supporting Information Available: A crystallographic file in CIF format and the experimental procedure and five figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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