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Inorganic Frameworks Made by Combining Paddle-wheel Diruthenium(II, III) Complexes and Polyoxometalate Clusters

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The reactions of a pivalate-bridged paddle-wheel diruthenium(II, III) complex, $[Ru_2^{II,III}(piv)_4(THF)_2]BF_4$, with two kinds of polyoxometalates (POMs), $(TBA)_2[Mo_6O_{19}]$ and $(TBA)_3[H_3V_{10}O_{28}]$ (TBA: tetra-*n*-butylammonium cation), led to the formation of one- and two-dimensional inorganic frameworks composed of $[–\{Ru_2\}_n–(POM)–]^-$ repeating units with $n = 1$ and 2, respectively.

Polyoxometalates (POMs) are inorganic metaloxide clusters, which provide various kinds of polygons composed of a fragment of [–(M=O)–O–] containing terminal oxo groups (i.e., M=O) and bridging oxo groups (i.e., μ-oxo groups, M–O–M). Owing to their characteristics such as structural diversity, electronic-structural diversity, high redox activity, and relatively high stability even in several oxidation states, POMs have attracted much attention in fields such as catalysis,[1–3] medicine,[4,5] and materials science.[6–10] In particular in a view of solid-state materials, POMs can be regarded as fragments of metaloxides or minerals that are often categorized as strong-correlated electronic systems. This point really motivates us because assembling of POMs is a unique method to design artificial strong-correlated electronic frameworks. Hence, our idea is to assemble such versatile POMs with paramagnetic metal ions or metal complexes to design functional inorganic frameworks in a bottom-up method. Indeed, POMs act as coordinating-donor building blocks, in which both of the terminal oxo and μ-oxo groups can catch another metal ion to assemble.[11] Meanwhile, these oxo-sites have relatively weak coordinating affinity, which are regarded as rather soft Lewis bases. Hence, few cases are known in which POMs are successfully assembled with coordinating-acceptor building blocks to form inorganic frameworks.[12]

In order to design such frameworks, it is useful to use Coulombic attraction between the precursors utilizing anionic character of typical POMs in combination with cationic metal complexes. Here, we chose carboxylate-bridged paddle-wheel diruthenium(II, III) complexes (abbreviated henceforth as $[Ru_2^{II,III}]^+$) as a cationic coordinating-acceptor. $[Ru_2^{II,III}]^+$ is a useful building block to design multidimensional frameworks assembling with coordinating-donor building blocks because of its relatively high ability to accept coordination at the axial positions resulting the construction of a paramagnetic linear edge of frameworks with $S = 3/2$.[13,14] The use of a pivalate-bridged paddle-wheel diruthenium(II, III) complex, $[Ru_2^{II,III}(piv)_4(THF)_2]BF_4$,[15] in reactions with two kinds of POMs, $(TBA)_2[Mo_6O_{19}]$[16] and $(TBA)_3[H_3V_{10}O_{28}]$[16] (TBA: tetra-*n*-butylammonium cation), led successfully to the formation of one- and two-dimensional inorganic frameworks composed of a repeat of $[–\{Ru_2\}_n–(POM)–]^-$ with $n = 1$ and 2, respectively: $(TBA)[\{Ru_2(piv)_4\}\{Mo_6O_{19}\}]\cdot x(solv)$ (**1**) and $(TBA)[\{Ru_2(piv)_4\}_2\{H_3V_{10}O_{28}\}]\cdot x(solv)$ (**2**). In this paper, structure and magnetic properties of **1** and **2** are reported.

Compounds **1** and **2** were synthesized under aerobic conditions by a slow diffusion of solutions containing the precursors, $[Ru_2]BF_4$ and POM, in a solvent set of CH_2Cl_2 (bottom) and 1,2-dichloroethane (top), respectively (see Supporting Information; SI[21]). Note that the solvents used were reagent grade and were used without any further purification (therefore, several water molecules were contained as crystallization solvents in crystals of **2**). The crystal samples are relatively stable in air; keeping their crystallinity, although the loss of several crystallization solvents is observed even at room temperature (Figure S1[21]).

ORTEP drawings of anionic parts of **1** and **2** are depicted in Figures 1a and 2a, respectively. Compounds **1** and **2** crystallize in the orthorhombic space group *Pnma* (#62) and the monoclinic space group $P2/c$ (#13), respectively, where a half of the formula unit was determined as an asymmetric unit ($Z = 4$ and 2, respectively; see SI[21]).

Compound **1** contains one $[Ru_2]^+$ unit, where a mirror plane bisects $[Ru_2]^+$ and the POM units. Two μ-oxo groups, which are in a trans position of the Lindqvist $[Mo_6O_{19}]^{2-}$ POM, coordinate

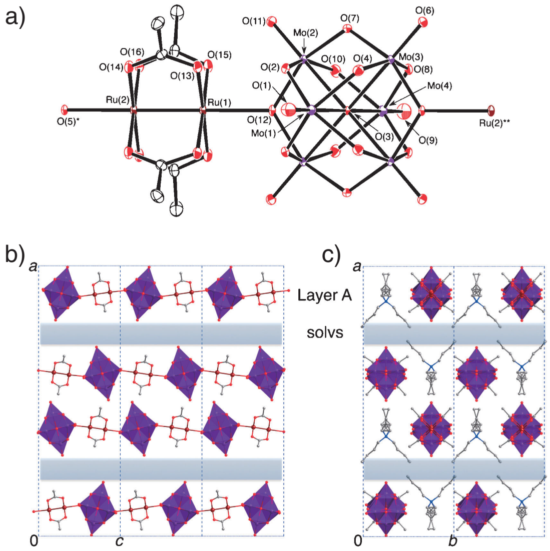

Figure 1. ORTEP drawing of the chain of **1** (30% probability ellipsoids; symmetry operation: $^*x, y, z + 1$, $^{**}x, y, z - 1$) (a) and packing diagrams projected along the *b* axis (b) and the *c* axis (c), where three methyl groups of piv⁻ were omitted for clarity, and TBA cations were omitted in (b). The crystallization solvents (solvs), are shown as gray layers in (b) and (c) to represent the solvent columns.

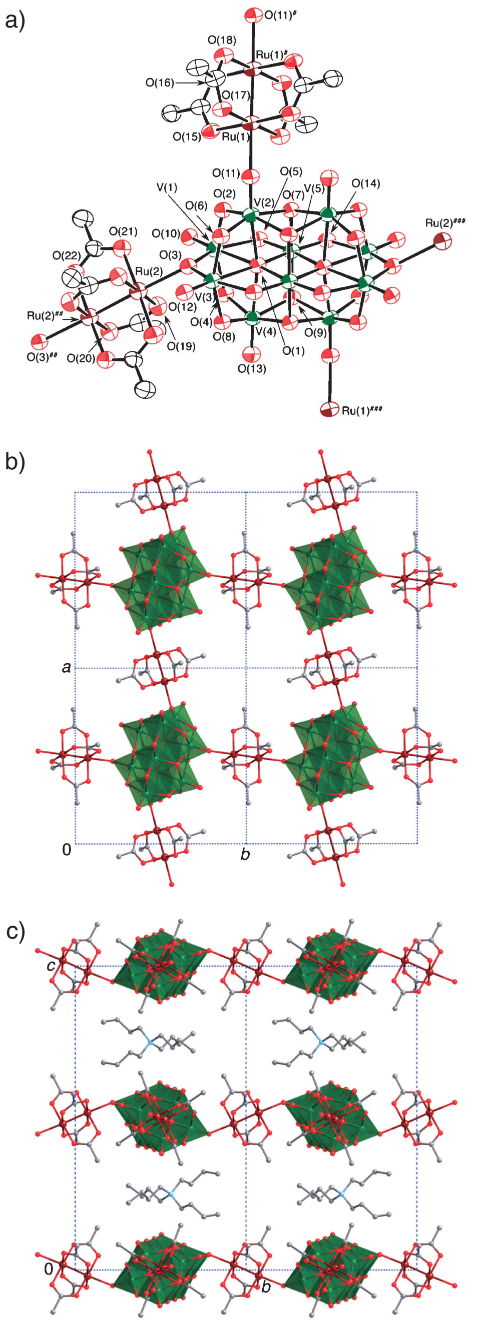

Figure 2. ORTEP drawing of the framework of **2** (30% probability ellipsoids; symmetry operation: $^{\#}-x+1$, $-y+2$, $-z+1$, $^{\#\#}-x+2$, $-y+1$, $-z+1$, $^{\#\#\#}-x+1$, $-y+1$, $-z+1$) (a) and packing diagrams projected along the *c* axis (b) and the *a* axis (c), where three methyl groups of piv$^-$ were omitted for clarity, TBA cations were omitted in (b), and the crystallization solvents (solvs) were omitted in (b) and (c).

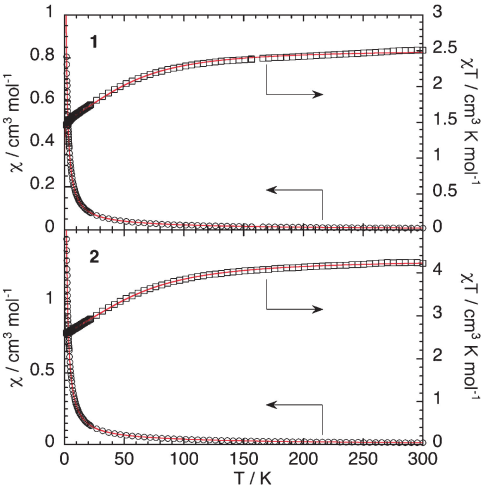

Figure 3. Temperature dependence of χ and χT of **1** (top) and **2** (bottom). The solid red lines represent the best fits using a Curie paramagnetic model of $S = 3/2$ taking into account zero-field splitting (D), temperature-independent paramagnetism (χ_{TIP}), and intermolecular interactions (zJ); see the text.

to the axial position of $[\mathrm{Ru_2}]^+$ with a bond distance and an angle of Ru(1)–O(12) = 2.269(5) Å and Mo(2)–O(12)–Ru(1) = 121.87(13)°, forming a quasi-linear-type chain of $[-\{\mathrm{Ru_2}\}-\mathrm{POM}-]_\infty$, where O(12) consequently makes a μ_3-oxo bridging motif (Figures 1a and 1b). For the $[\mathrm{Ru_2}]$ unit, the Ru–Ru bond distance is 2.2652(7) Å, and the average Ru–O$_{\mathrm{eq}}$ (O$_{\mathrm{eq}}$: carboxylate oxygen) bond distance is 2.012 Å, typical for $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ complexes.[13,14,17] The chains run along the *c* axis of the unit cell, which are alternately packed with TBA cations as if making a layer along the *b* axis (noted as layer A in Figure 1c). This virtual layer A is aligned as [···A···A···(solvs)···] along the *a* axis, where "solvs" stands for another virtual layer made from crystallization solvents of $\mathrm{CH_2Cl_2}$ and 1,2-dichloroethane (Figure 1c). The nearest interchain $[\mathrm{Ru_2}]$ units are found in a distance of 11.75 Å.

Meanwhile, **2** consists of two $[\mathrm{Ru_2}]^+$ units, one $[\mathrm{H_3V_{10}O_{28}}]^{3-}$ POM, and one TBA cation. Each of the $[\mathrm{Ru_2}]^+$ and $[\mathrm{H_3V_{10}O_{28}}]^{3-}$ units is related by the inversion centers; thus the halves of those units are considered asymmetric units (Figure 2a). The C_2 axis was involved for TBA. One of $[\mathrm{Ru_2}]^+$ units is coordinated with $[\mathrm{H_3V_{10}O_{28}}]^{3-}$ at the terminal oxo group on V(2) ions with Ru(1)–O(11) = 2.228(5) Å and Ru(1)–O(11)–V(2) = 143.1(3)°, and another unit is, similarly to **1**, bonded at the μ-oxo group between V(1) and V(3) ions with Ru(2)–O(3) = 2.283(4) Å, Ru(2)–O(3)–V(1) = 120.41(19)°, and Ru(2)–O(3)–V(3) = 119.7(2)° (where O(3) is acting as a μ_3-oxo group), forming a rhombus-grid two-dimensional (2D) framework on a (001) plane (Figure 2b). The Ru–Ru bond distances are 2.2752(6) and 2.2789(6) Å for $[\mathrm{Ru(1)_2}]$ and $[\mathrm{Ru(2)_2}]$, respectively, and the average Ru–O$_{\mathrm{eq}}$ distance is 2.017(5) Å, in agreement with a case of $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ as well as the case in **1**. Considering the charge balance of this compound, the POM unit should be a trianion with triprotonated form as $[\mathrm{H_3V_{10}O_{28}}]^{3-}$,[18] although three protons have not been assigned by X-ray crystallography. As well as **1**, **2** has a TBA cation, which is located between the layers (Figure 2c). The nearest $[\mathrm{Ru(1)_2}]$···$[\mathrm{Ru(2)_2}]$ distance is 10.09 Å (based on the midpoint of Ru–Ru).

To confirm the valence distribution of entities in **1** and **2**, magnetic susceptibilities were measured as a function of temperature, as shown in Figure 3. The temperature dependence of χ and χT is very similar between **1** and **2**; the χT values of 2.51 cm^3 K mol^{-1} for **1** and 4.22 cm^3 K mol^{-1} for **2** at 300 K continuously decreased to 1.47 and 2.60 cm^3 K mol^{-1} at 1.8 K, respectively, where the value of **2** is almost twice of that of **1** but should be attributed to identical paramagnetic species. Since the POM units used in this study are expected to be diamagnetic, the main contribution to the paramagnetic behavior is thus attributed to $[\mathrm{Ru_2(piv)_4}]^+$ with $S = 3/2$. The χ and χT values were simulated in the entire temperature range by using a Curie paramagnetic model with $S = 3/2$ involving zero-field splitting (D), temperature-independent paramagnetism (χ_{TIP}), and intermolecular interactions (zJ) commonly used for magnetically isolated or weakly interacting $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ complexes.[14,17] zJ was introduced in the framework of the mean-field approximation (z: number of adjacent magnetic centers). The best parameters were: $g = 2.312(4)$, $D/k_\mathrm{B} = 92(2)\,\mathrm{K}$, $zJ/k_\mathrm{B} = -0.041(7)\,\mathrm{K}$, and $\chi_{\mathrm{TIP}} = 12(48) \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ for **1** with $R = 0.99952$ and $g = 2.1338(7)$, $D/k_\mathrm{B} = 103.2(5)\,\mathrm{K}$, $zJ/k_\mathrm{B} = 0$ (fix), and $\chi_{\mathrm{TIP}} = 49(9) \times 10^{-6}\,\mathrm{cm^3\,mol^{-1}}$ for **2** with $R = 0.99989$, where $R = 1 - \Sigma(\chi T_{\mathrm{calc}} - \chi T_{\mathrm{obs}})^2/\Sigma(\chi T_{\mathrm{obs}})^2$ (fitted curves are displayed as red lines in Figure 3). The obtained values of g, which are larger than 2.00, and D are typical for $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$.[14,17] These magnetic data concluded that the components of $[\mathrm{Ru_2}]^+$ and POM are assembled without virtual charge transfer between them and are essentially isolated as the respective precursor units in a point of charge distribution. The reflection spectra support this conclusion; no unique charge-transfer band was observed in **1** and **2** (Figure S2[21]).

In conclusion, inorganic 1D and 2D frameworks composed of POMs linked with paddle-wheel $[\mathrm{Ru_2}^{\mathrm{II,III}}]^+$ units were synthesized based on $[\mathrm{Mo_6O_{19}}]^{2-}$ and $[\mathrm{H_3V_{10}O_{28}}]^{3-}$, respectively, where the POMs act as good coordinating-donor building blocks using both terminal oxo and μ-oxo groups. POM-based polymers are potentially the next targets for functional materials; it would be desired that POM subunits are electronically activated in frameworks, as well as found in the family of $[\mathrm{Ru_2}^{\mathrm{II,II}}]$/organic acceptors.[19,20] The present materials are literally topological candidates for such materials.

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