Magnetic and Gas-Occlusion Properties and Catalytic Activity of Microporous Materials: Dinuclear Ruthenium(II,II) Dicarboxylates

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A new series of dinuclear ruthenium(II,II) dicarboxylates, but not dinuclear ruthenium(II,III) dicarboxylates, have been prepared. Dinuclear ruthenium(II,II) dicarboxylates, which have a regular two- or three-dimensional network structure, occlude large amounts of gas. The maximum amount of N_2 gas that can be occluded by these complexes is 1.0–1.7 moles per mole of ruthenium atoms, indicating the presence of a large number of micropores. These complexes exhibited pore volume-dependent catalytic activity for the hydrogenation of ethylene.

In recent years, metal-organic frameworks have received considerable attention as new and attractive materials in the areas of gas storage, ion exchange, and potential catalysis. Previously, we reported that copper(II) dicarboxylates,[1] molybdenum(II) dicarboxylates,[2] and ruthenium(II,III) dicarboxylates[3] reversibly occluded large amounts of gas such as N_2, Ar, O_2, CH_4, and Xe. The uniform linear micropores of these adsorbents were assumed as having been constructed by the stacking or bonding of two-dimensional lattices of dinuclear transition-metal dicarboxylates. Also, we reported the first example of two-dimensional microporous coordination polymers of rhodium(II) dicarboxylates, which exhibited a high degree of catalytic activity for the dissociation of hydrogen molecules as well as for hydrogen exchange and the hydrogenation of olefins such as ethylene, propene, and butene at 200 K.[4] Many excellent studies of adsorbent porous complexes have also been reported by Yaghi,[5] Kitagawa,[6] Williams,[7] and Fujita.[8]

In the present work, we have succeeded in synthesizing novel dicarboxylate-bridged dinuclear ruthenium(II,II) complexes, $[Ru_2(\mu\text{-}O_2C\text{–}C_6H_4\text{–}CO_2)_2]$ **1**, $[Ru_2(\mu\text{-}O_2C\text{–}C_6H_4\text{–}C_6H_4\text{–}CO_2)_2]$ **2**, $[Ru_2(\mu\text{-}O_2C\text{–}C_6H_4\text{–}CO_2)_2(DABCO)]$ **3**, and $[Ru_2(\mu\text{-}O_2C\text{–}C_6H_4\text{–}C_6H_4\text{-}CO_2)_2(DABCO)]$ **4**, where DABCO is 1,4-diazabicyclo[2,2,2]octane, which also exhibit the gas-occlusion capability and catalytic activity similar to that of rhodium(II) dicarboxylates.[4] Here, we report on the synthesis of these complexes and their gas-occlusion properties, magnetic behavior, and pore volume and/or BET surface area dependent catalytic activity.

The starting material, $[Ru_2^{II,III}(\mu\text{-}O_2C\text{–}Me)_4(THF)_2]BF_4$, was synthesized by a procedure similar to that described in the literature.[9] Dark brown, plate-like crystals[10] dried under a vacuum at room temperature for 6 h, yielded a soluble dark-brown powder. $[Ru_2(\mu\text{-}O_2C\text{–}Me)_4(H_2O)_2]BF_4$ **5** Anal. Found: C, 17.12; H, 2.83%. Calcd for $C_8H_{16}BF_4O_{10}Ru_2$: C, 17.12; H, 2.87%. Complexes **1** and **2**, capable of occluding gas, were synthesized by using a carboxylate-exchange procedure under reaction conditions similar to those employed in the preparation of ruthenium(II,III) dicarboxylates[3] but without the presence of lithium chloride, which caused a one-electron reduction. An insoluble black powder was obtained. **1** · $3.5H_2O$ Anal. Found: C, 32.16; H, 2.25%. Calcd for $C_{16}H_{15}O_{11.5}Ru_2$: C, 32.38; H, 2.55%. **2** · $3H_2O$ Anal. Found: C, 45.49; H, 2.72%. Calcd for $C_{28}H_{22}O_{11}Ru_2$: C, 45.66; H, 3.01%. Complex **3**, capable of occluding gas, was synthesized as follows. To a methanol solution (100.0 mL) of DABCO (211.5 mg, 1.885 mmol) was added **1** (100.0 mg, 0.1885 mmol), and then the mixture was refluxed overnight at 100 °C. An insoluble black powder was obtained. **3** · $6H_2O$ Anal. Found: C, 35.20; H, 3.45; N, 3.55%. Calcd for $C_{22}H_{32}N_2O_{14}Ru_2$: C, 35.20; H, 4.30; N, 3.73%. Complex **4**, capable of occluding gas, was synthesized in the same manner as **3**. An insoluble dark brown powder was obtained. **4** · $6.5H_2O$ Anal. Found: C, 44.52; H, 3.51; N, 2.02%. Calcd for $C_{34}H_{41}N_2O_{14.5}Ru_2$: C, 44.79; H, 4.53; N, 3.07%.

A F analysis was conducted using a RIGAKU 3370 wavelength dispersive X-ray fluorescence spectrometer. The results of the X-ray fluorescence (XRF) analysis indicated the existence of the F atom in **5** but not in **1** and **2** (Figure 1). This result was helpful for structural analysis.

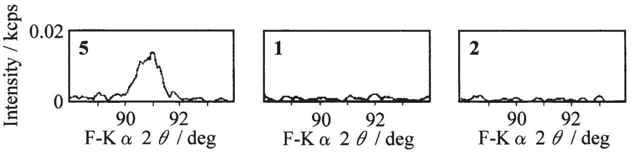

Figure 1. Qualitative analysis of X-ray fluorescence for **5**, **1**, and **2**.

The temperature dependence of the magnetic susceptibilities was measured by a SQUID magnetometer (Quantum Design, MPMS-5S) in a temperature range of 2–300 K (Figure 2). The temperature dependence of the effective magnetic moments (μ_{eff}) was calculated from the magnetic susceptibility, which was also observed in any of the ruthenium(II,II) complexes forming the same dinuclear structure as the lantern-like structure (Figure 3A). These complexes are species containing two unpaired electrons per dinuclear ruthenium with the ground electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*\delta^*)^4$.[11] It is reasonable to assume that **1**–**4** has the same configuration as the homovalent ruthenium(II,II) complexes so that, considering the linear structure of dicarboxylic acid, a two-dimensional lattice structure is proposed for **1** and **2** (Figure 3B). In view of their similarity to metal (copper(II)[12] and rhodium(II)[13]) carboxylates bridged by pyrazine derivatives as a pillar ligand, it is most likely that the DABCO in **3** and **4** links the two ruthenium ions to construct three-dimensional networks

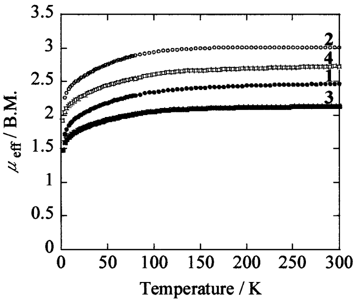

Figure 2. Temperature dependence of the effective magnetic moments for **1**(●), **2**(○), **3**(■), and **4**(□).

Table 1. BET surface area, micropore volume, pore diameter, TOF, and maximum amount of occluded N_2 gas

Complex	BET surface area ($\times 10^{-3}$ m^2/mol of Ru)	micropore volume (cm^3/mol of Ru)	pore diameter (Å)	TOF after 5 min (mol of ethane/s·atom of Ru)[a]	Maximum amount of occluded N_2 gas (mol/mol of Ru atom)
1	167.2 (315.2 m^2/g)	62.4 (0.1176 cm^3/g)	8.4	2.1×10^{-6}	1.0
2	205.9 (301.7 m^2/g)	77.3 (0.1133 cm^3/g)	8.5	3.2×10^{-6}	1.3
3	243.5 (378.9 m^2/g)	90.8 (0.1413 cm^3/g)	8.6	3.9×10^{-6}	1.4
4	281.4 (354.0 m^2/g)	104.6 (0.1316 cm^3/g)	8.4	6.6×10^{-6}	1.7
5	—	—	—	9.3×10^{-9b}	0.0
6	148.7 (240.9 m^2/g)	55.4 (0.0897 cm^3/g)	9.1	4.0×10^{-8b}	0.9

[a] with 100% selectivity of ethane
[b] initial rate after 60 min

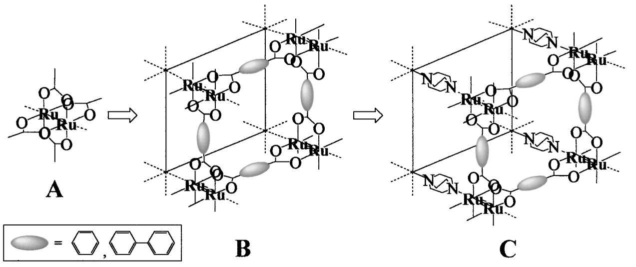

Figure 3. Lantern-like structure of dinuclear ruthenium complex (A), deduced two-dimensional lattice structure of ruthenium(II,II) dicarboxylates (B), and proposed three-dimensional structure of ruthenium(II,II) dicarboxylates bridged by DABCO (C).

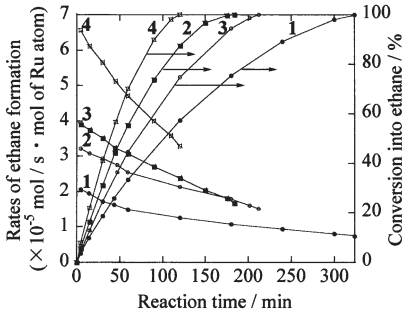

Figure 4. Rates of the hydrogenation of ethylene and the conversions into ethane over **1**(●), **2**(○), **3**(■), and **4**(□).

bridged by the dicarboxylate ligands in the plane and the pillar ligands in the axial direction, as is shown in Figure 3C.

Uniform capillary structures were elucidated by argon adsorption measurement. High-resolution adsorption isotherms of Ar gas at 87.3 K were measured in a relative pressure (P/P_0, P_0 = saturation vapor pressure) range from 10^{-6} to 10^{-1} using an ASAP 2010 volumetric adsorption equipment from Micromeritics. From the resulting data, the BET surface area, micropore volume, and pore diameter (using the Horvath–Kawazoe (HK) method[14]) were derived to characterize the porosity of the ruthenium complexes (Table 1).

The temperature dependence of the amounts of occluded N_2 gas for all complexes was determined by a Cahn 1000 electric balance at 20 Torr, where 1 Torr = (101325/760) Pa. The complexes obtained in this study occlude large amounts of gas in their micropores except **5**. The maximum amount of occluded N_2 gas was summarized in Table 1. The differences in the gas-occlusion properties are explained by the differences in the way the two-dimensional layer is stacked.[12b] These results suggest that **1**–**4** form very similar capillary structures to that of the first dinuclear absorbent, copper(II) terephthalate, as reported previously.[1]

The first example of microporous coordination polymers of rhodium(II) fumarate (5.5×10^{-5} mol/g·s) and rhodium(II) terephthalate (9.7×10^{-5} mol/g·s), which exhibited a high degree of catalytic activity for the hydrogenation over 100 mg of samples.[4] Hydrogenation of ethylene catalyzed by all complexes was conducted at 50 °C. All complexes (100 mg) were put into a reaction vessel, which was connected to a conventional closed gas circulation system (155.7 cm^3). The sample was pretreated at 50 °C in 120 Torr H_2 for 1 h. After evacuation at room temperature, the reaction gas consisting of 30 Torr ethylene, 60 Torr H_2, and 1.4 Torr He was introduced. Product analysis was performed by a gas chromatograph equipped with a thermal conductivity detector (TCD, Porapak Q). The product was ethane and no induction period was observed. The conversion reached 100% after 120–324 min. Table 1 summarizes the turnover frequency (TOF) of **1**–**5** and $[Ru_2^{II,III}(\mu\text{-}O_2C\text{–}C_6H_4\text{–}CO_2)_2]BF_4$ **6**. The TOF for **1**–**4** was on a higher order than that of **5** under the same reaction conditions. Also, the catalytic activity such as hydrogenation for the ruthenium(II,II) complexes **1**–**4** is of greater advantage than that of the ruthenium(II,III) complex **6**. Figure 4 summarizes the results of both the TOF and the conversion into ethane, estimated from the ratios of ethane to (ethane + ethylene). Consequently, larger pore volumes and/or surface areas exhibited higher activities for hydrogenation, indicating that these reactions occur primarily inside the micropores of the polymer complexes. Further study for measuring the hydrogenation reaction is needed to prove the proposed mechanism of hydrogen formation.

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10 The crystal structure was determined by X-ray diffraction using a Rigaku R-AXIS RAPID diffractometer with graphite-monochromated Mo Kα radiation. The structure was solved by the direct method using program SIR-92 and was refined by full-matrix least-squares iterations. Crystal data: triclinic, *P*-1, $a = 10.0581(1)$, $b = 11.5203(4)$, $c = 17.4353(7)$ Å, $\alpha = 83.311(4)$, $\beta = 79.927(2)$, $\gamma = 71.151(3)^\circ$, $Z = 2.0$, $R1 = 0.065$, $Rw = 0.240$.
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