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Syntheses of dinuclear rhodium(II) monocarboxylates with micropores

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The following three dinuclear rhodium(II) monocarboxylates were synthesized and their structures determined by single-crystal X-ray diffraction: $Rh_2(o\text{-}CH_3C_6H_5COO)_4$ (complex **1**), $Rh_2(m\text{-}CH_3C_6H_5COO)_4$ (complex **2**), $Rh_2(p\text{-}CH_3C_6H_5COO)_4$ (complex **3**). All complexes formed lantern-like structures. It was revealed that complex **1** does not consist of π-π stackings, but both complex **2** and complex **3** do consist of π-π stackings and are constructed from one-dimensional micropores when viewed from the direction of the *b* axis and *c* axis, respectively. In addition, two methanol molecules that are used as their solvents are linked to the axial sites of these complexes. The Rh-Rh distance in complex 1 was 0.2390 nm, that in complex **2** was 0.2379 nm, and that in complex **3** was 0.2388 nm.

Key-words: lantern-like structure, π-π stacking, one-dimensional micropore

1. INTRODUCTION

Zeolite and active carbon are well-known porous materials[1]. Their representative functions are adsorption and catalysis. Metal-organic complexes[2] have recently been given much attention as materials for gas storage, molecular sieves, and potential catalysts.

Various transition metal carboxylates have been synthesized for producing new porous materials[3] as building blocks(so-called lantern-like structures (Fig. 1)) since we found in 1972 that copper(II) terephthalate (of the dinuclear transition metal carboxylates) could adsorb a large amount of nitrogen gas[4].

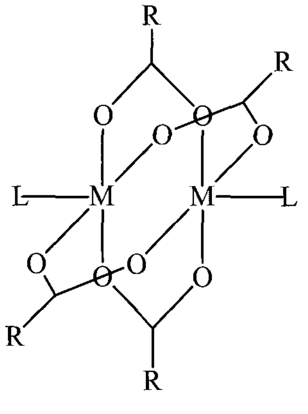

Fig.1 Lantern-like structure

Rhodium(II) complexes are suitable for forming dinuclear structures because a single bond exists between rhodium(II) ions. Compared with copper(II) complexes, rhodium(II) complexes are inert at room temperature and ligand exchange is difficult under the mild conditions. Therefore, they have fewer complexes[5] of revealed crystal structures than do other metal complexes. In this paper, we synthesized dinuclear rhodium(II) monocarboxylates that have micropores by using various ligands and clarified their crystal structures.

2. EXPERIMENTAL

Rhodium(II) acetate dihydrate, *p*-toluic acid, and dehydrated methanol(quantitative analysis grade) were purchased from Wako Pure Chemical Industries, Ltd.; *o*-toluic acid and *m*-toluic acid were purchased from Tokyo Chemical Industries, Ltd. All chemicals were used as received without further purification. Carbon, hydrogen, and nitrogen analyses were conducted using a Perkin-Elmer PE 2400 series-II CHNS/O analyzer.

2.2 Syntheses of rhodium(II) monocarboxylate complexes

2.2.1 Synthesis of $[Rh_2(o\text{-}CH_3C_6H_5COO)_4(CH_3O)_2]$ (complex 1)

Under nitrogen, rhodium(II) acetate dihydrate (150 mg, 0.314×10^{-3} mol) and *o*– toluic acid) (342 mg, 2.53×10^{-3} mol) added to dehydrated methanol (25 ml) in an autoclave were heated at 453 K for 6 h, then cooled to room temperature. The solution was filtered and allowed to stand at room temperature. Deep green block crystals formed after several days. $[Rh_2(o\text{-}CH_3C_6H_5COO)_4(CH_3O)_2]$ (complex **1**) Anal. Calcd for $C_{34}H_{34}Rh_2O_{10}$: C, 50.51; H, 4.24% Found: C, 50.35; H, 4.30%.

2.2.2 Synthesis of $[Rh_2(m\text{-}CH_3C_6H_5COO)_4(CH_3O)_2]$ (complex 2)

Under nitrogen, rhodium(II) acetate dihydrate (150 mg, 0.314×10^{-3} mol) and *m*– toluic acid) (342 mg, 2.53×10^{-3} mol) added to dehydrated methanol (25 ml) in an autoclave were heated at 453 K for 9 h, then cooled to room temperature. The solution was filtered and allowed to stand at room temperature. Deep green block crystals formed after several days. $[Rh_2(m\text{-}CH_3C_6H_5COO)_4(CH_3O)_2]$ (complex **2**) Anal. Calcd for $C_{34}H_{34}Rh_2O_{10}$: C, 50.51; H, 4.24% Found: C, 50.40; H, 4.10%.

2.2.3 Synthesis of [$Rh_2(m\text{-}CH_3C_6H_5COO)_4(CH_3O)_2$] (complex **3**)

Under nitrogen, rhodium(II) acetate dihydrate (150 mg, 0.314×10^{-3} mol) and *p*– toluic acid) (342 mg, 2.53×10^{-3} mol) added to dehydrated methanol (25 ml) in an autoclave were heated at 453 K for 6 h, then cooled to room temperature. The solution was filtered and allowed to stand at room temperature. Deep green block crystals formed after several days. [$Rh_2(p\text{-}CH_3C_6H_5COO)_4(CH_3O)_2$] (complex **3**) Anal. Calcd for $C_{34}H_{34}Rh_2O_{10}$: C, 50.51; H, 4.24% Found: C, 50.32; H, 4.14%.

2.3 X-ray crystal structure determinations

The crystal structures of all complexes were determined by X-ray diffraction using a Rigaku R-AXIS rapid diffractometer with graphite-monochromated Mo Kα radiation. The temperature was controlled with a temperature control unit.

3. RESULTS AND DISCUSSION

The crystal structures of complexes **1**-**3** are shown in Figs. **2**-**4**, respectively. Tables **I**-**III** list the crystallographic data. All complexes have lantern-like structures and are linked with the solvent molecules (methanol) toward the axial sites. The Rh-Rh distance in complex **1** is 0.2390 nm, that in complex **2** is 0.2379 nm, and that in complex **3** is 0.2388 nm. The values are similar to the Rh-Rh distance(0.23855 nm) of rhodium(II) acetate dihydrate used as a starting material. The microporous structures are exhibited in Figs. **5** and **6**. Complex **2** and Complex **3** have a one-dimensional micropore because these complexes are constructed by π-π stacking of two benzene rings.

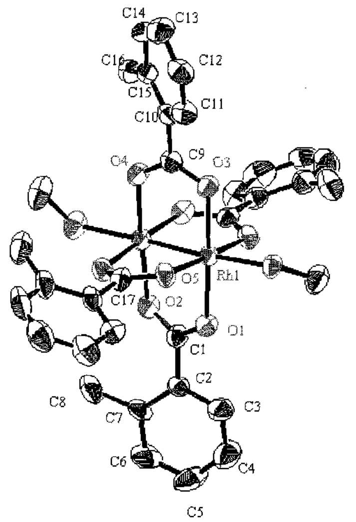

Fig.2 ORTEP view of complex 1
The hydrogen atoms and the solvent molecules(methanol) have been omitted.

Table I Crystallographic Data for complex 1

Complex	rhodium(II) *o*-toluate
Chemical formula	$Rh_2C_{32}H_{28}O_8$
Formula mass,Da	746.38
Space group	*P*-1
a,Å	10.71
b,Å	12.27
c,Å	14.30
α ,deg	112.59
β ,deg	92.91
γ ,deg	91.80
V,Å^3	1729
T,K	293
R_1	0.064
*R*w	0.152
Z value	2

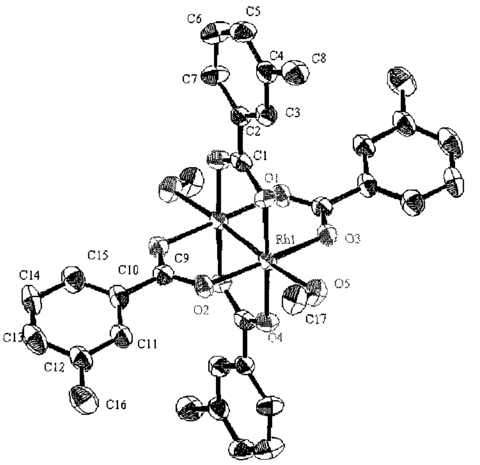

Fig. 3 ORTEP view of complex 2
The hydrogen atoms and the solvent molecules(methanol) have been omitted.

Table II Crystallographic Data for complex 2

Complex	rhodium(II) *m*-toluate
Chemical formula	$Rh_2C_{32}H_{28}O_8$
Formula mass,Da	746.38
Space group	*P*-1
a,Å	11.17
b,Å	14.12
c,Å	14.63
α ,deg	68.21
β ,deg	72.36
γ ,deg	71.79
V,Å^3	1989
T,K	296
R_1	0.066
*R*w	0.126
Z value	2

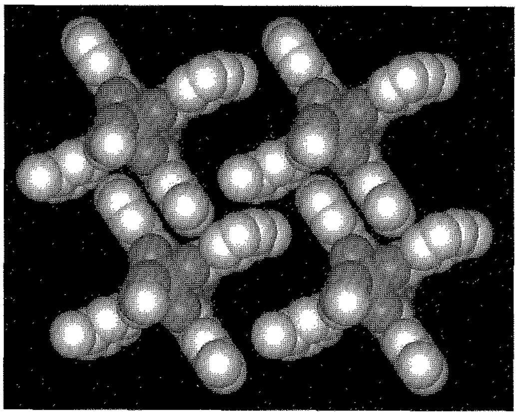

Fig. 5 View of crystal Structure of complex 2 from *c* axis.The hydrogen atoms and the solvent molecules(methanol) have been omitted.

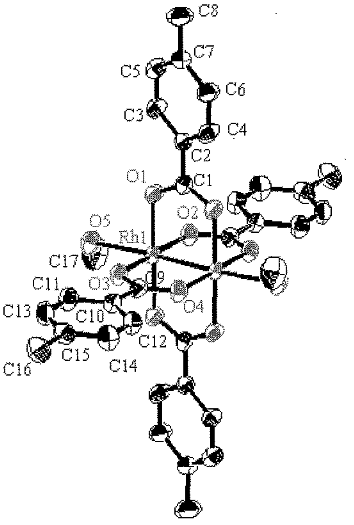

Fig. 5 ORTEP view of complex 3
The hydrogen atoms and the solvent molecules(methanol) have been omitted.

Table III Crystallographic Data for complex 3

Complex	rhodium(II) *p*-toluate
Chemical formula	$Rh_2C_{32}H_{28}O_8$
Formula mass,Da	746.38
Space group	*P*-1
a ,Å	12.40
b ,Å	19.29
c ,Å	11.82
α ,deg	90.00
β ,deg	47.65
γ ,deg	90.00
V ,Å^3	2091
T,K	326
R_1	0.053
*R*w	0.087
Z value	2

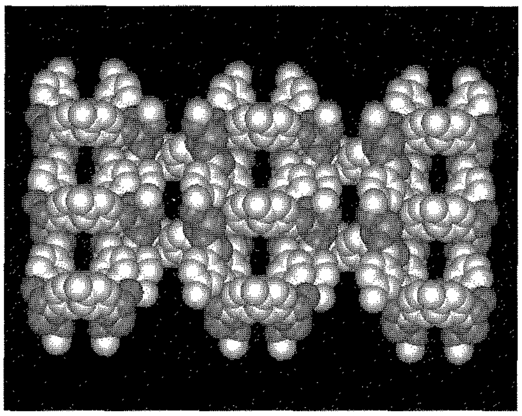

Fig. 6 View of crystal Structure of complex 3 from *c* axis.The hydrogen atoms and the solvent molecules(methanol) have been omitted.

4. CONCLUSION

By X-ray crystallography, we determined the structures of rhodium(II) *o*-toluates, *m*-toluates, and *p*–toluates that consisted of lantern-like structures. Because of the forming of π-π stackings of two benzene rings, it was revealed that rhodium(II) *m*- and *p*-toluates construct a one-dimensional micropore when viewed from the direction of the *b* axis and *c* axis, respectively.

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