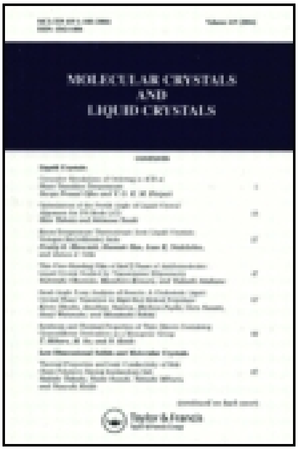

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Synthesis and Gas Occlusion of Rhodium(II) Benzoate Bridged by Pyrazine Derivatives

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Synthesis and Gas Occlusion of Rhodium(II) Benzoate Bridged by Pyrazine Derivatives

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Rhodium(II) benzoate bridged by pyrazine derivatives occlude a large amount of N_2 gas, reversibly. The maximum amounts of the occluded N_2 were 1.8, 1.7, 0.5, 0.1, 1.3, and 1.3 mol per one mole of rhodium(II) salt with 2-methylpyrazine, 2,3-dimethylpyrazine, quinoxaline, 1,5-naphthyrizine, and triethylenediamine, respectively, indicating the presence of a large number of micropores in these rhodium(II) carboxylates. The porous structure which is formed by the self-assembly of linear rhodium(II) benzoate-pyrazine derivatives was deduced by analogy to the structure of rhodium(II) benzoate-pyradine reported previously.

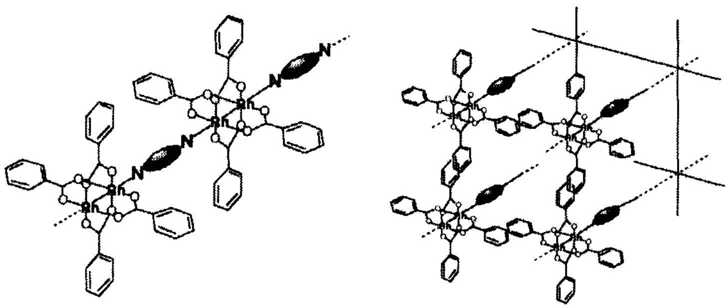
Keywords: rhodium(II) carboxylate; gas occlusion; linear structure; self-assembly; micropore; pyrazine derivatives

INTRODUCTION

Previously, we reported that copper(II) dicarboxylates,[1] molybdenum(II) dicarboxylates,[2] and ruthenium(II,III) dicarboxylates[3] occlude a large amount of gases such as N_2, O_2, Ar, and Xe. These are known as useful adsorbents for storing CH_4 under low pressure.[4]

Recently, we have found that one-dimensional rhodium(II) benzoate–pyrazine[5] and copper(II) benzoate—pyrazine[6] also occlude a large amount of gas. The three-dimensional structure, which has a large number of micropores, is shown in Figure 1. The van der Waals interaction between phenyl moieties of ligands, the so-called π-π stack, may acts as driving force for the self-assembly of one-dimensional metal carboxylates–pyrazine to form three-dimensional microporous solids.

Here, we report the synthesis and gas occlusion of rhodium(II) benzoate bridged by pyrazine derivatives.



(a) (b)

FIGURE 1. Linear structure of complexes (a) and proposed porous strucure (b).

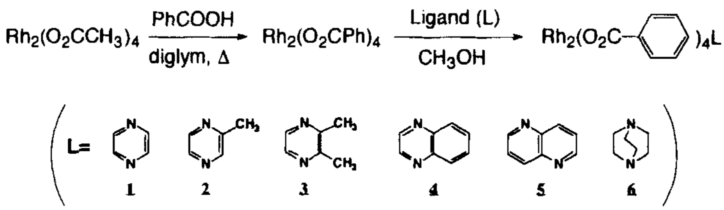
EXPERIMENTAL

The temperature dependence of the amount of occluded N_2 gas was determined by a Cahn (Cahn 1000 model) electric balance at 20 Torr in a temperature range of 77-250 K. Magnetic moments (μ_{eff}) were measured by the Gouy method at room temperature.

A form of rhodium(II) benzoate—pyrazine derivatives, capable of occluding gases was synthesized as follows. (Scheme 1)

Rh(II)(PhCOO)$_2$ (100 mg, 1.4 x10^{-4} mol) and pyrazine derivatives (2.9 x10^{-4} mol) were dissolved in acetone (40 ml) and stirred overnight. The brown precipitates were collected, washed by acetone, dried in a vacuum at 40 °C for two hours, giving brown crystalline powder with a high yield.

Scheme 1



RESULT AND DISCUSSION

The yields, analytical data, maximum amount of occluded nitrogen, and magnetic moments are summarized in Table I and Table II.

The effective magnetic moments (μ_{eff}) which were calculated from the magnetic susceptibilities, are small and almost the diamagnetism. These small μ_{eff} values are inconsistent with those of dinuclear rhodium(II) carboxylates such as dinuclear rhodium(II) acetate.[7,8] Judging from the results of elemental analyses and magnetic measurements, all complexes **2-6** appear to have a one-dimensional chain of dinuclear rhodium(II) bridged by linking ligands.

The complexes obtained in this study occlude a large amount of gas in their micropores, with the exception of complex **4**. The maximum amounts of occluded nitrogen for the complexes bridged by **1–6** are 1.8,[5] 1.7, 0.5, 0.1, 1.3, and 1.3 moles per one mole of rhodium atoms, respectively. The temperature dependence of the amount of occluded gas of complexes **2–6** is very similar to that of complex **1** reported before.[5] The similarity indicates that complexes **2–6** form a similar microporous structure to that of complex **1**. (See Figure 1.) The microporous structure constructed by the self-assembly of one-dimensional complexes is strongly influenced by the structure of the bridging ligands.

TABLE I. Yields and analytical data.

Compound	Formula	Yield	Analysis[a] C/%	H/%	N/%
1[b]	$Rh_2(O_2CC_6H_5)_4(C_4H_4N_2)$	91%	50.11	3.11	3.64
			(49.89)	(3.14)	(3.64)
2	$Rh_2(O_2CC_6H_5)_4(C_5H_6N_2)$	97%	50.25	2.90	3.34
			(50.53)	(3.34)	(3.57)
3	$Rh_2(O_2CC_6H_5)_4(C_6H_8N_2)$	98%	50.68	3.26	3.40
			(51.15)	(3.53)	(3.51)
4	$Rh_2(O_2CC_6H_5)_4(C_8H_6N_2)$	90%	50.25	3.01	3.23
			(52.70)	(3.19)	(3.41)
5	$Rh_2(O_2CC_6H_5)_4(C_8H_6N_2)$	85%	51.39	2.88	3.31
			(50.70)	(3.19)	(3.41)
6	$Rh_2(O_2CC_6H_5)_4(C_6H_6N_2)$	91%	49.22	3.84	3.84
			(50.89)	(4.02)	(3.49)

[a] Calculated values are in parentheses, [b]Ref. 5.

TABLE II. Maximum amount of occluded nitrogen, and magnetic moments.

Compound	Amount of occluded nitrogen (mol / mol of rhodium atom)	Magnetic moment μ_{eff} [a] (BM (r.t.))
1[b]	1.8	0.38
2	1.7	~ 0
3	0.5	0.09
4	0.1	0.08
5	1.3	0.39
6	1.3	~ 0

[a] Gouy method, [b] Ref. 5.

In conclusion, the microporous complexes of the linear rhodium(II) carboxylate are formed by the replacement of pyrazine by pyrazine derivatives. This method can produce microporous substances with various range of pore sizes and pysicochemical properties. The investigation of physicochemical and thermal properties are underway in our laboratory.

In 1995, after we had applied to patent the microporous complexes, Kitagawa[9], Yaghi[10], and Williams[11] reported the gas-adsorption phenomena of similar porous complexes.

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