Synthesis and Gas Occlusion of New Micropore Substance Rhodium(II) Carboxylates Bridged by Pyrazine

Wasuke Mori,* Hiroyuki Hoshino, Yuko Nishimoto, and Satoshi Takamizawa†
Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-1293
†*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043*

(Received January 5, 1999; CL-990002)

Rhodium(II) carboxylates bridged by pyrazine occlude a large amount of N_2 gas, reversibly. The maximum amounts of the occluded N_2 gas were 1.8, 1.1, 0.8, 0.6, 0.2, 0.2, 0.5, and 0.6 mol per one mole of rhodium(II) salt with benzoate, *o*-hydroxybenzoate, *m*-hydroxybenzoate, *p*-hydroxybenzoate, *o*-toluate, *m*-toluate and *p*-toluate, respectively, indicating the presence of a large number of micropores in these rhodium(II) carboxylates.

The porous structure which is formed by self-assembly of linear rhodium(II) carboxylates−pyrazine was deduced from the magnetic susceptibilities and by analogy to the structure of copper(II) dicarboxylates which show similar gas-occlusion behavior.

Previously, we reported that the copper(II) dicarboxylates[1], molybdenum(II) dicarboxylates[2] and ruthenium(II, III) dicarboxylates[3] occluded a large amount of gases such as N_2, Ar, O_2, and Xe.

The uniform micropores of these adsorbents in which gases were occluded were concluded to be constructed by stacking or bonding of two-dimensional lattices of metal dicarboxylates.

Recently, it has been found that one-dimensional rhodium(II) carboxylates−pyrazine also occlude a large amount of gases.

In this paper, we report the synthesis and magnetic and gas occlusion properties of the rhodium(II) carboxylates−pyrazine.

A form of rhodium(II) benzoate − pyrazine, capable of occluding gases was synthesized as follows. A solution of $Rh(II)(CH_3COO)_2 \cdot H_2O$ (0.5 g, 1.04 mmol) and C_6H_5COOH (1.0 g, 8.18 mmol) in 20 ml of diethyleneglycoldimethylether was stirred for 2 h at 200 ℃. After evaporation of the solvent, recrystallization from acetone gave a yellowish-green needle crystals of $Rh(II)(C_6H_5COO)_2$. The acetone solution of $Rh(II)(C_6H_5COO)_2$ (200 mg, 2.89 mmol) and pyrazine (34 mg, 4.24 mmol) was stirred for 10 h to yield a precipitate of yellowish-brown microcrystals of $Rh(II)(C_6H_5COO)_2 \cdot 0.5C_4H_4N_2$. Heating the microcrystals for 2 h at 100 ℃ in vacuum, yellowish-brown microcrystals, which are capable of occluding gases, were obtained. The other $Rh(II)(R\text{-}COO)_2 \cdot 0.5C_4H_4N_2$ (R = *o*-$C_6H_4(OH)$, *m*-$C_6H_4(OH)$, *p*-$C_6H_4(OH)$, *o*-$C_6H_4(CH_3)$, *m*-$C_6H_4(CH_3)$, *p*-$C_6H_4(CH_3)$)

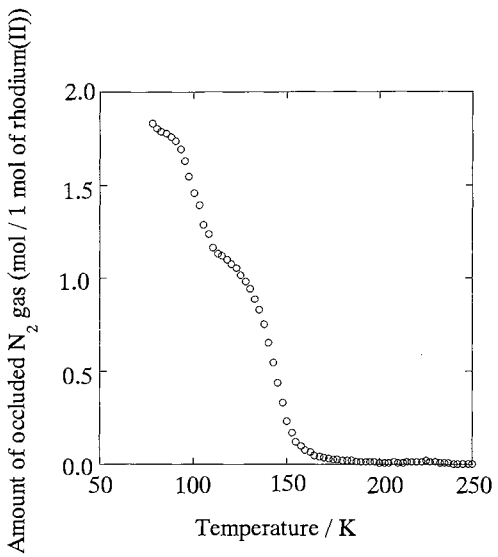

Figure 1. The temperature dependence of the amount of occluded N_2 gas in the $Rh(II)(C_6H_5CO_2)_2 \cdot 0.5C_4H_4N_2$.

Table 1. Color, analytical data, magnetic moments, and maxmum amount of gas occluded

Compund (Color/Yield)	Aanalysis[a] H/%	C/%	N/%	μ_{eff}/BM	Amount of gas occluded (mol /1 mol of rhodium atom)
$Rh(II)(C_6H_5CO_2)_2 \cdot 0.5C_4H_4N_2$ (Yellowish-brown/91%)	3.11 (3.14)	50.11 (49.89)	3.64 (3.64)	0.38	1.8
$Rh(II)(o\text{-}(OH)C_6H_4CO_2)_2 \cdot 0.5C_4H_4N_2$ (Yellowish-brown/70%)	2.64 (2.90)	45.41 (46.07)	3.06 (3.36)	0.27	1.1
$Rh(II)(m\text{-}(OH)C_6H_4CO_2)_2 \cdot 0.5C_4H_4N_2$ (Yellowish-brown/80%)	3.17 (2.90)	45.53 (46.07)	3.14 (3.36)	0.21	0.8
$Rh(II)(p\text{-}(OH)C_6H_4CO_2)_2 \cdot 0.5C_4H_4N_2$ (Yellowish-brown/77%)	2.94 (2.90)	44.10 (46.07)	3.80 (3.36)	0.30	0.6
$Rh(II)(o\text{-}(CH_3)C_6H_4CO_2)_2 \cdot 0.5C_4H_4N_2$ (Brown/75%)	3.60 (3.90)	52.96 (52.32)	3.25 (3.39)	0.25	0.2
$Rh(II)(m\text{-}(CH_3)C_6H_4CO_2)_2 \cdot 0.5C_4H_4N_2$ (Brown/85%)	3.66 (3.90)	53.06 (52.32)	3.30 (3.39)	0.33	0.5
$Rh(II)(p\text{-}(CH_3)C_6H_4CO_2)_2 \cdot 0.5C_4H_4N_2$ (Brown/93%)	3.62 (3.90)	53.24 (52.32)	3.28 (3.39)	0.19	0.6

[a]Calculated values are in parentheses.

were synthesized by similar methods to that for Rh(II)$(C_6H_5COO)_2 \cdot 0.5C_4H_4N_2$ The color and analytical data of the Rh(II)$(R\text{-}COO)_2 \cdot 0.5C_4H_4N_2$ are shown in Table 1.

The temperature dependence of the amount of occluded N_2 gas was determined by a Cahn (model Cahn-1000) electric balance at 20 torr in the temperature range of 77-250 K. The occlusion of N_2 gas by Rh(II)$(C_6H_5COO)_2 \cdot 0.5C_4H_4N_2$ occurs at temperatures below 200 K, and the amount of occluded N_2 gas almost reached saturation at 77 K (Figure 1). The maximum amounts of occluded N_2 gas for the Rh(II) complexes are summarized in Table 1. The maximum amount of the occluded gas for Rh(II) $(C_6H_5COO)_2 \cdot 0.5C_4H_4N_2$ is almost equal to that for Cu(II)(*p*-OOC-C_6H_4-COO)[1].

The magnetic susceptibilities were measured by the Gouy method at room temperature. The effective magnetic moments (μ_{eff}) which were calculated from the magnetic susceptibilities, are almost

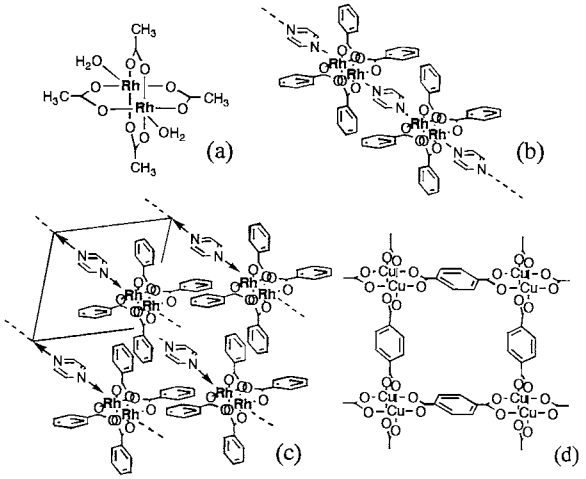

Figure 2. The molecular structure of dinuclear rhodium(II) acetate hydrate (a), the deduced one-dimensional structure of Rh(II)$(C_6H_5CO_2)_2 \cdot 0.5C_4H_4N_2$ (b), the deduced three-dimensional structure of Rh(II)$(C_6H_5CO_2)_2 \cdot 0.5C_4H_4N_2$ (c), the two-dimensional structure of copper(II) terephthalate (d).

equal to those of dinuclear rhodium(II) carboxylates such as rhodium(II) acetate (Figure 2a),[4,5] indicating the existence of same dinuclear structure in the present rhodium(II) carboxylates which have bridges by pyrazine, forming the one-dimensional structure as shown in Figure 2b. The one-dimensional polymer complex is elementary component to construct the micropore in which a large amount of gases can be occluded.

The three-dimensional structure which, has a large number of micropoers as shown in Figure 2c, is reasonably proposed for our rhodium(II) carboxylates – pyrazine by analogy the structure of copper(II) terephthalate (Figure 2d) which shows similar occlusion behavior to the rhodium(II) salt.

The van der Waals interaction between phenyl groups of ligands, so called π-π stack,[6] may act as driving force for the self-assembly[7]

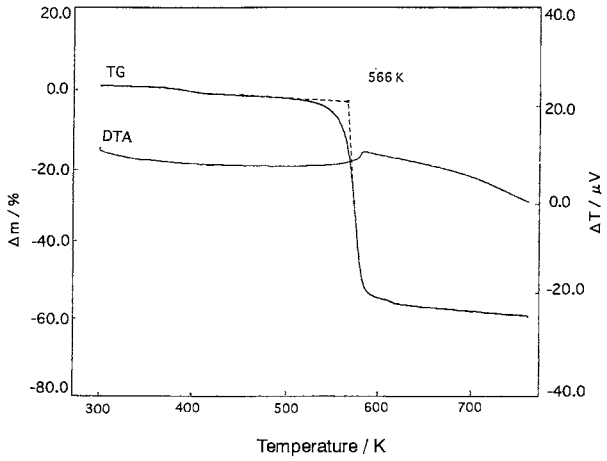

Figure 3. TG-DTA curves of Rh(II)$(C_6H_6CO_2)_2 \cdot 0.5C_4H_4N_2$. Sample of 1.75 mg, heating in an aluminum pan at 5 K/min in nitrogen flow at 200 ml/min.

of one-dimensional rhodium(II) carboxylates – pyrazine to form three-dimensional solids.

The thermogravimetic differential-thermal analysis was carried out using S I I Exstar 6000 TG-DTA 300 with an aluminum pan in a N_2 gas flow.

Figure 3 shows the TG-DTA curves of Rh(II)$(C_6H_5CO_2)_2 \cdot 0.5C_4H_4N_2$, which have no endo- or exo-thermic peak and no remarkable weight loss at the temperature below 520 K (thermal decomposition temperature: 540-600 K). It is noteworthy that the micropores of the rhodium(II) carboxylates – pyrazine are surprisimgly thermally stable, although the micropores are formed from one-dimensional polymer complexes with weak van der Waals force between phenyl groups.

This work was supported by Grant-In-Aids for Scientific Research No.10149253 and 10554041 from Ministry of Education, Science, Sports and Culture, Japan.

References

1 W. Mori, F. Inoue, K. Yoshida, H. Nakayama, S. Takamizawa, and M. Kishita, *Chem. Lett.*, **1997**, 1219.
2 S. Takamizawa, W. Mori, M. Furihata, S. Takeda, K. Yamaguchi, *Inorg. Chem. Acta*, **283**, 268 (1998).
3 S. Takamizawa, K. Yamaguchi, W. Mori, *Inorg. Chim. Comm.*, **1**, 177, (1998).
4 F. A. Cotton and R. A. Walton, "Multiple Bonds Between Metal Atoms 2ed, " Oxford, New York (1993).
5 "Theory and Applications of Molecular Paramagnetism," ed by E. A. Boudreaux and L. N. Mulay, John Winley Sons, New York (1976).
6 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, **112**, 5525 (1990).
7 M. W. Hosseini and A. D. Cian, *Chem. Commun.*, **1998**, 727.