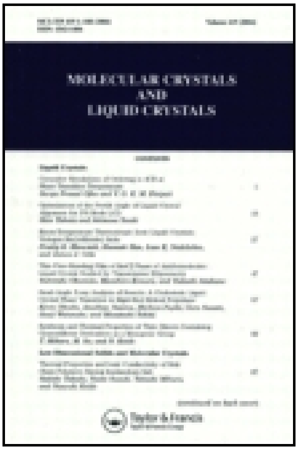


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Gas-Occlusion Properties of Ruthenium(II,III) Dicarboxylates (Fumarate, trans-trans-Muconate and Terephthalate) Bridged by Halogen Atoms

Satoshi Takamizawa [a] [b] , Tetsushi Ohmura [a] , Kizashi Yamaguchi [b] & Wasuke Mori [a]

[a] Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa, 259-1293, Japan

[b] Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560-0043, Japan

Version of record first published: 24 Sep 2006

To cite this article: Satoshi Takamizawa, Tetsushi Ohmura, Kizashi Yamaguchi & Wasuke Mori (2000): Synthesis and Gas-Occlusion Properties of Ruthenium(II,III) Dicarboxylates (Fumarate, trans-trans-Muconate and Terephthalate) Bridged by Halogen Atoms, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 342:1, 199-204

To link to this article: http://dx.doi.org/10.1080/10587250008038265

Mol. Cryst. Liq. Cryst., 2000, Vol. 342, pp. 199-204
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Synthesis and Gas-Occlusion Properties of Ruthenium(II,III) Dicarboxylates (Fumarate, *trans-trans*-Muconate and Terephthalate) Bridged by Halogen Atoms

SATOSHI TAKAMIZAWA[ab], TETSUSHI OHMURA[a],
KIZASHI YAMAGUCHI[b] and WASUKE MORI[a]

[a]*Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259–1293, Japan and* [b]*Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560–0043, Japan*

The bis-μ-dicarboxylate ruthenium (II,III) complexes, Ru $(II,III)_2L_2Br$ (L=*trans*-O_2C-CH=CH-CO_2 (**1**), *trans-trans*-O_2C-CH=CH-CH=CH-CO_2 (**2**), and p-O_2C-C_6H_4-CO_2 (**3**)), were prepared and their gas-occlusion properties were measured. The effective magnetic moments at room temperature are in the range 3.76 and 4.02 BM per dinuclear, consistent with the values of Ru(II)-Ru(III) compounds. All these complexes are capable of occluding a large amount of gas. The maximum amounts of occluded nitrogen for **1–3** are 0.6, 0.9, and 1.4 moles per one mole of ruthenium atoms, respectively. These amounts are almost the same as those of the correspondent chloride complexes. This suggests that bromide complexes **1–3** would form a highly similar capillary structure to that of ruthenium (II,III) dicarboxylate bridged by chloride atoms.

Keywords: mixed-valence ruthenium carboxylate; dicarboxylate complex; microporous substance; gas adsorbent; magnetic moment

INTRODUCTION

Previously, we reported on the following new absorbents, copper(II),[1] molybdenum(II),[2] and Ruthenium(II,III)[3] dicarboxylates, which have the same dinuclear structure as that of copper(II) acetate monohydrate. Dicarboxylate bridges make up a two-dimensional network with homogeneous micropores in the solid state. These are known as useful adsorbents for storing CH_4 under low pressure.[4] In 1995, after we had applied to patent the microporous complexes, Kitagawa,[5] Yaghi,[6] and Williams[7] reported the gas-adsorption phenomena of similar porous complexes.

Since the discovery of binuclear tetra-μ-carboxylates of ruthenium(II,III) $Ru_2(O_2CR)_4Cl$, various studies have aroused much interest in ruthenium(II,III) acetate derivatives in the field of solid-state physics and chemistry[8] because of their halogen-bridged -Ru-Ru-X- mixed-valence structure and the +2.5 oxidation state of the ruthenium atom with a $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$ configuration per dinuclear.[9] We have focussed on ruthenium (II, III) dicarboxylate derivatives, which will make up a rigid network structure, assisted by the axial-halogen bridge, rather than those of copper(II) dicarboxylates and molybdenum(II) dicarboxylates. In the present work, we synthesized ruthenium (II,III) dicarboxylates bridged by bromides and investigated the gas-occlusion behavior of these complexes.

EXPERIMENTAL

Scheme 1

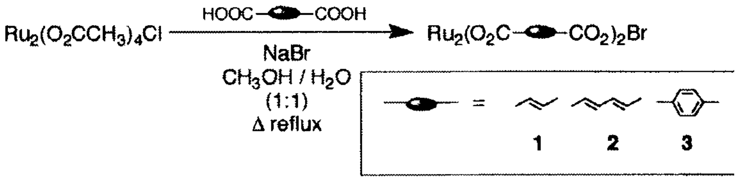


TABLE I Analytical data for complexes.

Complex	Yield / %	H_2O[a]	Found (Calcd.) / %		
			C	H	Ru
1	92	1.0	18.37(18.19)	1.40(1.15)	38.0 (38.27)
2	98	1.5	24.53(24.46)	2.16(1.88)	34.1(34.30)
3	97	0.5	30.93(31.03)	1.65(1.46)	32.6(32.64)

[a] Analytical data is calculated for complexes to which a few water molecules are added because complexes have a strong hygroscopicity.

Complexes of Ru_2(*trans*-O_2C–CH=CH–CO_2)$_2$Br (**1**), Ru_2(*trans*-*trans*-O_2C–CH=CH-CH=CH–CO_2)$_2$Br (**2**) and Ru_2(*p*-O_2C–C_6H_4–CO_2)$_2$Br (**3**) were synthesized by a ligand exchange method between $Ru_2(O_2CCH_3)_4Cl$ and appropriate dicarboxylic acids in the presence of sodium bromide (Scheme 1): $Ru_2(O_2CCH_3)_4Cl$[10] (0.211 mmol), anhydrous NaBr (2.11 mmol) and an appropriate dicarboxylic acid (0.422 mmol), dissolved in a 1:1 mixed solvent (100 ml) of water and methanol, and then the mixture was refluxed for three hours. A brown precipitate was collected, washed with methanol, and dried under a vacuum. An insoluble brown powder was obtained with a high yield. The analytical data for complexes **1**-**3** are summarized in Table I.

RESULT AND DISCUSSION

Magnetic measurements revealed that the electronic structures of **1**-**3** are very similar to that of $Ru_2(O_2CCH_3)_4Br$, as shown in Table II. The effective magnetic moments at room temperature are in the range of 3.76 to 4.02 BM per dinuclear, consistent with the values obtained previously for Ru(II)-Ru(III) compounds and species containing three unpaired electrons per dinuclear with the ground electronic configuration of

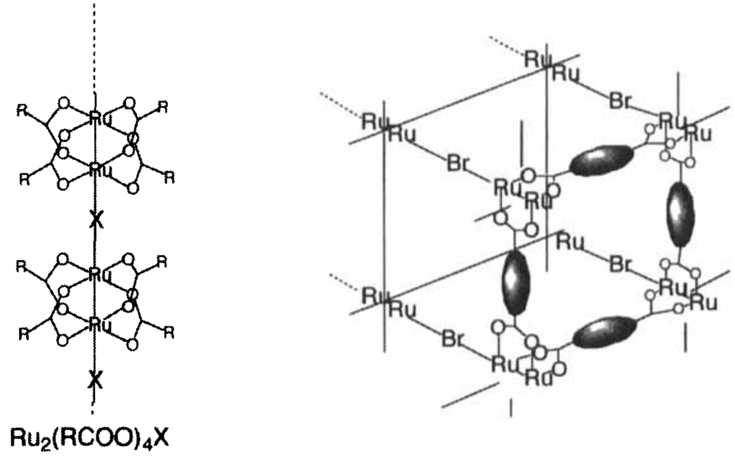
$(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^2(\delta^*)^1$.[11] In view of their similarity to mixed-valence $Ru_2(O_2CR)_4X$ derivatives, it is most likely that the chloride anions in **1-3** link two ruthenium ions to construct linear chains. (See Figure 1a.) Thus, the proposed structure, which has a three-dimensional network bridged by dicarboxylate ligands in the plane direction, and halide ions in the axial direction, is shown in Figure 1b.

TABLE II Effective magnetic moments (μ_{eff}) and amounts of occluded nitrogen gas of complexes.

Complex	μ_{eff}[a)] / BM (at r.t.)	Maximum amount of occluded N_2 (mol/mol of Ru atom)
$Ru_2(O_2CCH_3)_4Br$	3.97[b)]	—
1	3.76	0.6
2	3.83	0.9
3	4.02	1.4

[a)] Gouy method
[b)] Measured by carrying magnetometer for complexes.

Complexes **1-3** have displayed the ability to occlude a large amount of gas. The gas-occlusion behaviors of the present bromide complexes are highly similar to those of the chloride complexes reported previously.[3] This suggests that complexes **1-3** would form a similar capillary structure to that of ruthenium(II,III) dicarboxylate bridged by chloride atoms. The maximum amounts of occluded nitrogen are summarized in Table II. The maximum amount increases in the following order: **1<2<3**. The gas occlusion properties depend upon the diameter of the capillary, which is controlled by the size and structure of the dicarboxylate ligands, as was also recognized in previous studies of copper(II) and molybdenum(II) dicarboxylates.[1,2]



(a) (b)

FIGURE 1. Linear structure of mixed valence $Ru_2(O_2CR)_4X$ (a) and porous structure of complexes **1-3**.

In conclusion, we succeeded in synthesizing the microporous complex of mixed-valence ruthenium(II,III) dicarboxylates bridged by bromide atoms. The electronic properties of a mixed-valence -Ru-Ru-X- system are strongly influenced by the replacement of bridging halogen atoms. The cooperative character derived from the porosity and electronic properties is expected for the present microporous complex system. Further investigation is underway in our laboratory.

ACKNOWLEDGEMENTS

This work was partially supported by Grant-in-Aids for Scientific Research Nos. 10149253, 10149105, and 10554041 from the Ministry of Education, Science and Culture, Japan.

References

[1] W. Mori, F. Inoue, K. Yoshida, H. Nakayama, S. Takamizawa, and M. Kishita, *Chem. Lett.*, (1997) 1219; W. Mori and S. Takamizawa, *Kagaku to Kogyo*, **51**, 210 (1998). (Japanese).

[2] S. Takamizawa, W. Mori, M. Furihata, S. Takeda, and K. Yamaguchi, *Inorg. Chim. Acta*, **283**, 268 (1998).

[3] S. Takamizawa, K. Yamaguchi, and W. Mori, *Inorg. Chem. Commun.*, **1**, 177 (1998).

[4] W. Mori, S. Takamizawa, M. Fujiwara, K. Seki, Patent Nos. JP 09132580 (1995) and EP 0727608 (1996).

[5] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, and S. Kitagawa, Angew. *Chem. Int. Ed. Engl.*, **36**(16), 1725(1997).

[6] H. Li, M. Eddaoudi, T. L. Groy, and O. M. Yaghi, *J. Am. Chem. Soc.*, **120**, 8571 (1998).

[7] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, *Science*, **283**, 148 (1999).

[8] M. Yamashita, K. Inoue, T. Ohishi, T. Takeuchi, T. Yoshida, and W. Mori, *Mol. Cryst. Liq. Cryst.*, **274**, 25 (1995).

[9] J. G Norman, G. E. Renzoni, and D. A Case, *J. Am. Chem. Soc.*, **101**, 5256 (1979).

[10] R. W. Mitchell, A. Spencer, and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, **846** (1973).

[11] F. A. Cotton and R. A. Walton, *"Multiple Bonds between Metal Atoms"*, 2nd ed, Oxford Univ. Press, New York (1993).