

ORIGINAL PAPER

Synthesis, crystal structure, and ¹H NMR spectra of a chloride-bridged chain complex of dinuclear ruthenium(II,III) 3,4,5-tri(ethoxy- d_5)benzoate

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Received 28 May 2010; Revised 27 July 2010; Accepted 3 August 2010

Deuterated dinuclear ruthenium(II,III) 3,4,5-tri(ethoxy- d_5)benzoate, [Ru₂{3,4,5-(C₂D₅O)₃C₆H₂-COO}₄Cl]_n, was synthesized by a reaction of [Ru₂(C₂H₅COO)₄Cl]_n and 3,4,5-tri(ethoxy- d_5)benzoic acid and characterized by single-crystal X-ray analysis as well as IR, UV-VIS, and ¹H NMR spectra, and compared with those of the undeuterated complex [Ru₂{3,4,5-(C₂H₅O)₃C₆H₂COO}₄Cl]_n. Single-crystal X-ray analysis showed that chloride ligands bridge the dinuclear ruthenium(II,III) units at the axial positions to form a zigzag chain molecule with the Ru¹—Cl—Ru² angle of 123.82(4)°. ¹H NMR spectra in CD₂Cl₂ displayed a broad signal attributable to *o*-H atoms on the phenyl rings of the benzoate ligands from approximately $\delta = 23$ to $\delta = 32$ at 25°C and several signals from approximately $\delta = -50$ to $\delta = 50$ at -80°C. These spectra show the preservation of the polymeric or oligomeric chain structure in dichloromethane, which is supported by the solution behavior confirmed by the UV-VIS spectra and electronic conductance. © 2010 Institute of Chemistry, Slovak Academy of Sciences

Keywords: dinuclear ruthenium(II,III) carboxylate, benzoate complex, chlorido bridging, crystal structure, ¹H NMR spectra, UV-VIS spectra

Introduction

Dinuclear ruthenium(II,III) carboxylates have attracted much attention in recent years because of their intriguing paddlewheel structure and potential applications in metal-assembled complexes. These carboxylates are paramagnetic with three unpaired electrons in the degenerated $\pi^{*2}\delta^{*1}$ orbitals in metal-metal bonds and can be used as building blocks for polymeric metal-assembly (Aquino, 1998, 2004; Mikuriya et al., 2006). Such metal-assembled complexes are unique due to the metal-metal bonding (Ishida et al., 2007, 2009a, 2009b). Recently, a chain complex of dinuclear ruthenium(II,III) 3,4,5-tri(ethoxy)benzoate, [Ru₂{3,4,5-(C₂H₅O)₃C₆H₂COO}₄Cl]_n · 1.2nC₂H₅OH (*I*), has been prepared (Ishida et al., 2009b). X-ray crystal structure analysis of *I* shows that dinuclear ruthenium(II,III) units are bridged by chloride ligands to form a zigzag chain complex with alternating arrangement of Ru₂{3,4,5-(C₂H₅O)₃C₆H₂COO}⁺₄ and Cl⁻. This complex dissolves in CH₂Cl₂ in spite of its polymeric structure. UV-VIS spectrum of *I* in CH₂Cl₂ exhibits absorption characteristics of dinuclear ruthenium(II,III) core. This fact shows that the paddlewheel dinuclear structure is maintained in the solution although it is unclear whether the polymer structure is preserved or not. ¹H NMR spectra should be useful in the study of the solution behavior of this

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Fig. 1. Structure of $[Ru_2\{3,4,5-(C_2D_5O)_3C_6H_2COO\}_4Cl]_n$ (II).

complex. However, ¹H NMR spectra are complicated due to the existence of many proton atoms attached to the ethoxy and benzoato groups. In this study, all ethoxy groups of *I* were deuterated to simplify the spectra (Fig. 1). Accordingly, hydrogen atoms exist in only ortho positions of the benzoato groups in the deuterated chain complex, which should enable simple interpretation of the spectra. Herein, we report on the synthesis, crystal structure of the deuterated complex [Ru₂{3,4,5-(C₂D₅O)₃C₆H₂COO}₄Cl]_n · $2nC_2H_5OH (II \cdot 2nC_2H_5OH)$, and solution studies of *I* and *II* in CH₂Cl₂ by electronic conductivity, UV-VIS spectral and ¹H NMR spectral measurements.

Experimental

Synthesis of I was performed according to the method described in our previous paper (Ishida et al., 2009b). The chloride-bridged complex of dinuclear ruthenium(II,III) propionate $[\operatorname{Ru}_2(\operatorname{C}_2\operatorname{H}_5\operatorname{COO})_4\operatorname{Cl}]_n$ was prepared by the method described in literature (Stephenson & Wilkinson, 1966). Other reagents and solvents were obtained from commercial sources and were used without further purification.

3,4,5-tri(ethoxy- d_5)benzoic acid

A mixture of methyl 3,4,5-trihydroxybenzoate (408 mg, 2.22 mmol), bromoethane- d_5 (1.00 g, 8.77 mmol), K_2CO_3 (2.20 g, 15.9 mmol), and KI (10 mg, 0.06 mmol) was stirred in dimethylformamide (5 mL) at 80 °C for 24 h under nitrogen atmosphere to yield methyl 3,4,5-tri(ethoxy- d_5)benzoate. The colorless oil was refluxed in ethanol (15 mL) for 4 h with aqueous solution (2 mL) of KOH (654 mg, 11.6 mmol). The solution was adjusted to pH 1 by adding 35 %HCl. The resulting white precipitate was filtered, washed with water, and dried under vacuum over $CaCl_2$ yielding 439 mg (1.58 mmol, 71 % based on $3,4,5-(C_2D_5O)_3C_6H_2COOH)$ of the product. IR (KBr, ν/cm^{-1}): $\nu(\text{ArH})$ 3077br, $\nu(\text{CD})$ 2230, 2216, 2148, 2096, 2073, voCOO) 1684. ¹H NMR (CDCl₃): 7.31 (s, 2H). ¹³CNMR (CDCl₃): 171.4 (s, COOH), 152.7 (s, m-C), 142.8 (s, p-C), 123.6 (s, ipso-C), 108.5 (d, o-C), 63.9 (q, CD₂), 13.7 (m, CD₃).

Formula	C56H20ClD60O22B112
Formula mass	1403.15
T/K	90
Crystal dimensions/mm	0.48 imes 0.07 imes 0.07
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	13.1717(10)
b/Å	14.4535(11)
$c/\text{\AA}$	15.9807(12)
$\alpha/^{\circ}$	86.292(1)
$\beta/^{\circ}$	88.593(1)
$\gamma/^{\circ}$	79.095(1)
$V/Å^3$	2980.9(4)
Ζ	2
$D_{\rm calcd.}/({\rm g~cm^{-3}})$	1.563
μ/mm^{-1}	0.628
F(000)	1394
No. of reflections collected	18351
No. of independent reflections	12617
$\theta \text{ range}/^{\circ}$	1.44 to 27.10
Data / Restraints / Parameters	12617 / 0 / 730
Goodness-of-fit on F^2	1.057
$R_1, wR_2 [I > 2\sigma(I)]^a$	0.0551, 0.1492
R_1, wR_2 (all data)	0.0658, 0.1591
$(\Delta/\sigma)_{ m max}$	0.001
$(\Delta \rho)_{\rm max} / ({\rm e}{\rm \AA}^{-3})$	1.378
$(\Delta \rho)_{\rm min} / ({\rm e}{\rm \AA}^{-3})$	-0.787
CCDC deposition number	724314

Table 1. Crystal and experimental data for $II \cdot 2nC_2H_5OH$

a) $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|;$ $wR_2 = [\sum \omega (F_o^2 - F_c^2)^2 / \sum \omega (F_o^2)^2]^{1/2}.$

$Ru_2(3,4,5-(C_2D_5O)_3C_6H_2COO)_4Cl]_n$ (II)

The precursor complex $[\text{Ru}_2(\text{C}_2\text{H}_5\text{COO})_4\text{Cl}]_n$ (47 mg, 0.090 mmol) and 3,4,5-tri(ethoxy- d_5)benzoic acid (204 mg, 0.757 mmol) were refluxed for 24 h in 5 mL of ethanol. A crystalline product was obtained by leaving the solution at room temperature for one day. Recrystallization from CHCl₃ layered with hexane afforded red-brown crystals of $II \cdot 2n\text{C}_2\text{H}_5\text{OH}$, which were collected and dried under vacuum over CaCl₂ yielding 93 mg (0.071 mmol, 78 % based on $[\text{Ru}_2(3,4,5-(\text{C}_2\text{D}_5\text{O})_3\text{C}_6\text{H}_2\text{COO})_4\text{Cl}]_n$) of II. IR (KBr, ν/cm^{-1}): ν (OH) 3650, ν (ArH) 3101br, ν (CH) 2800br, ν (CD) 2233, 2147, 2114, 2098, 2073, ν (Ar) 1497w, 1584, $\nu_{\rm as}$ oCOO) 1455, $\nu_{\rm s}$ oCOO) 1397.

Infrared spectra were recorded on a JASCO MFT-2000 (Japan) spectrophotometer as KBr pellets. UV-VIS spectra were measured using a Shimadzu UV-VIS-NIR Recording Spectrophotometer (Model UV-3100, Japan). Electronic conductivities were obtained on a TOA conductivity meter CM-5S (Japan). ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM-AL 400 (Japan) operating at 400 MHz for ¹H. Chemical shifts were referenced to the residual peaks of deuterated solvents; CD₂Cl₂ ($\delta = 5.32$ for ¹H) and CDCl₃ ($\delta = 7.24$ for ¹H and $\delta = 77.0$ for ¹³C).

A preliminary examination of $H \cdot 2nC_2H_5OH$, was



Fig. 2. Infrared spectrum of $II \cdot 2nC_2H_5OH$.

Table 2. Selected bond lengths and angles of $II \cdot 2nC_2H_5OH$

Bond	Bond length/Å	Bond geometry	$Angle/^{\circ}$
$\begin{array}{c} {\rm Ru}^{1} {\rm - Ru}^{1,i} \\ {\rm Ru}^{1} {\rm - Cl} \\ {\rm Ru}^{1} {\rm - O}^{1} \\ {\rm Ru}^{1} {\rm - O}^{2,i} \\ {\rm Ru}^{1} {\rm - O}^{6,i} \\ {\rm Ru}^{2} {\rm - Ru}^{2,ii} \\ {\rm Ru}^{2} {\rm - Ru}^{2,ii} \\ {\rm Ru}^{2} {\rm - Cl} \\ {\rm Ru}^{2} {\rm - O}^{11} \\ {\rm Ru}^{2} {\rm - O}^{12,ii} \\ {\rm Ru}^{2} {\rm - O}^{16} \\ {\rm Ru}^{2} {\rm - O}^{17,ii} \end{array}$	2.2749(7) 2.5404(11) 2.022(3) 2.028(3) 2.017(3) 2.023(3) 2.2767(7) 2.5603(11) 2.035(3) 2.005(3) 2.026(3) 2.019(3)	$\begin{array}{l} {\rm Ru}^{1,i}{\longrightarrow} {\rm Ru}^{1}{\longrightarrow} {\rm Cl} \\ {\rm Ru}^{1,i}{\longrightarrow} {\rm Ru}^{1}{\longrightarrow} {\rm O}^{1} \\ {\rm Ru}^{1,i}{\longrightarrow} {\rm Ru}^{1}{\longrightarrow} {\rm O}^{2,i} \\ {\rm Ru}^{1,i}{\longrightarrow} {\rm Ru}^{1}{\longrightarrow} {\rm O}^{6} \\ {\rm Ru}^{1,i}{\longrightarrow} {\rm Ru}^{1}{\longrightarrow} {\rm O}^{7,i} \\ {\rm Ru}^{2,ii}{\longrightarrow} {\rm Ru}^{2}{\longrightarrow} {\rm Cl} \\ {\rm Ru}^{2,ii}{\longrightarrow} {\rm Ru}^{2}{\longrightarrow} {\rm Cl} \\ {\rm Ru}^{2,ii}{\longrightarrow} {\rm Ru}^{2}{\longrightarrow} {\rm O}^{11} \\ {\rm Ru}^{2,ii}{\longrightarrow} {\rm Ru}^{2}{\longrightarrow} {\rm O}^{12,ii} \\ {\rm Ru}^{2,ii}{\longrightarrow} {\rm Ru}^{2}{\longrightarrow} {\rm O}^{16} \\ {\rm Ru}^{2,ii}{\longrightarrow} {\rm Ru}^{2}{\longrightarrow} {\rm O}^{17,ii} \end{array}$	175.44(3) $89.85(9)$ $89.00(9)$ $89.71(9)$ $89.44(9)$ $123.82(4)$ $170.37(3)$ $90.50(9)$ $88.39(9)$ $88.56(9)$ $90.45(9)$

Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) 2 - x, 2 - y, 1 - z.

made and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX, USA) using graphitemonochromated Mo- K_{α} radiation. Crystal data and details concerning data collection are given in Table 1. The structure was solved by direct methods using the program SHELXS-97 (Sheldrick, 1997a) and refined by the full-matrix least-squares method on F^2 using SHELXL-97 (Sheldrick, 1997b). Hydrogen and deuterium atoms were inserted at their ideal positions except for the hydroxyl hydrogen atoms of ethanol molecules which were located by the D-Fourier synthesis and fixed there. Crystallographic data were deposited at the Cambridge Crystallographic Data Centre as a supplementary publication (CCDC 724314) and can be obtained free of charge on application to CCDC, 12 union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and discussion

The deuterated compound, 3,4,5-tri(ethoxy- d_5) benzoic acid, was synthesized by a hydrolysis reaction of methyl 3,4,5-tri(ethoxy- d_5)benzoate. The deuterated complex II was prepared by a substitution reaction of the precursor complex $[\operatorname{Ru}_2(\operatorname{C_2H}_5\operatorname{COO})_4\operatorname{Cl}]_n$ with 3,4,5-tri(ethoxy- d_5)benzoic acid and isolated as $[\operatorname{Ru}_2{3,4,5-(C_2D_5O)_3C_6H_2COO}_4Cl]_n \cdot 2nC_2H_5OH.$

IR spectrum of $H \cdot 2nC_2H_5OH$ showed weak absorption bands due to CH stretchings of benzoate phenyl rings and ethanol molecules between 2800 cm^{-1} and 3200 cm^{-1} (Fig. 2). Several absorption bands appeared between 2073 $\rm cm^{-1}$ and 2233 $\rm cm^{-1}$ which can be attributed to the CD stretching bands of the deuterated ethoxy groups. Asymmetric and symmetric stretching bands of the carboxyl groups can be clearly seen at 1455 cm^{-1} and 1397 cm^{-1} , respectively, because of the absence of CH₂ and CH₃ bending modes due to the deuteration of the ethoxy groups. A set of weak and strong bands at 1497 cm^{-1} and 1584 $\rm cm^{-1}$ can be assigned to vibration bands of the benzoate phenyl rings. Weak absorptions at 3650 cm^{-1} and 1624 cm^{-1} correspond to stretching and bending bands of hydroxy groups of ethanol molecules contained in the crystals, respectively.

Crystal structure of $II \cdot 2nC_2H_5OH$, was determined by single-crystal X-ray crystallography. OR-TEP diagram of $II \cdot 2nC_2H_5OH$, is shown in Fig. 3 and the selected bond lengths and angles are given in Table 2. Four 3,4,5-tri(ethoxy- d_5)benzoate ligands bridge two ruthenium atoms to form a paddlewheel-



Fig. 3. ORTEP diagram of $H \cdot 2nC_2H_5$ OH, showing 50 % probability ellipsoids. H and D atoms, and ethanol molecules are omitted for clarity. Symmetry codes: prime: 1 - x, 2 - y, 1 - z; double prime: 2 - x, 2 - y, 1 - z.

Table 3.	Hydrogen	bond	geometry	of	$\mathit{II} \cdot \mathit{n}\mathrm{C}_{2}\mathrm{H}_{5}\mathrm{OH}$

D—H···A	D—H/Å	$\mathrm{H}{\cdots}\mathrm{A}/\mathrm{\mathring{A}}$	$D{\cdots}A/{\rm \AA}$	$\mathrm{D}\!\!-\!\!\mathrm{H}\!\cdots\!\mathrm{A}/^{\circ}$	
$C^{10,i}$ — $D^{10}B^i \cdots \pi^a$	0.99	2.65	3.402	133	
$\mathbf{C}^{35,ii}$ — $\mathbf{D}^{10}\mathbf{B}^{ii}\cdots\mathbf{O}^{4}$	0.98	2.47	3.435(7)	169	
C^{20} — $\mathrm{H}^{20}\mathrm{A}\cdots\mathrm{O}^{1}\mathrm{S}^{ii}$	0.95	2.45	3.401(7)	177	
C^{25} — $D^{25}B$ ··· O^1S^{ii}	0.99	2.60	3.244(6)	123	
C^2S^{iii} — H^2SB^{iii} ···· O^9	0.98	2.69	3.535(7)	144	
\mathbf{C}^{12} — $\mathbf{D}^{12}\mathbf{B}\cdots\mathbf{O}^{2}\mathbf{S}^{ii}$	0.99	2.54	3.325(9)	136	
O^1S^{iv} — H^1SC^{iv} ···Cl	0.84	2.49	3.250(3)	151	
O^2S^{iv} — H^2SD^{iv} ····Cl	0.84	2.51	3.182(4)	138	

a) Centroid of phenyl ring with C², C³, C⁴, C⁵, C⁶, and C⁷. Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) x, 1 + y, z; (iii) 1 - x, 1 - y, -z; (iv) 1 - x, 1 - y, 1 - z.

type dinuclear unit with a ruthenium(II,III) mixedvalence state. There are two crystallographically independent halves of each dinuclear unit which are bridged by chloride ligands to give a zigzag chain molecule in the crystal. The Ru—Ru bond lengths of 2.2749(7) Å and 2.2767(7) Å are a little shorter than those of the undeuterated complex *I* (2.291(1) Å and 2.292(1) Å) and the related complex [Ru₂{(3,4,5-C₄H₉O)₃C₆H₂COO}₄Cl]_n $\cdot n$ H₂O (*III*) (2.290(1) Å and 2.292(1) Å) (Ishida et al., 2009a) and they are in the range of those of ruthenium(II,III) carboxylates reported so far (Aquino, 1998; Mikuriya et al., 2006). The Ru¹— Cl—Ru² angle is 123.82(4)°, similar to those of the related complexes (120.38(7)° for *I*, 122.52(9)° for *III*, 118.8(1)° for [Ru₂(μ -C₆H₅COO)₄Cl] (Abe et al., 1992), 117.8(1)° and 124.2(1)° for [Ru₂Cl(*p*-MeOC₆H₄COO)₄](H₂O)_{0.25} (Das et al., 1991)). The Ru¹—Cl and Ru²—Cl bond lengths (2.540(1) Å and 2.560(1) Å, respectively) are comparable to those of *I* (2.558(2) Å and 2.575(2) Å), *III* (2.560(2) Å and 2.566(2) Å), and other chloridebridged chain complexes of ruthenium(II,III) carboxylates (2.564(1)–2.587(5) Å) (Aquino, 1998; Abe et al., 1992; Das & Chakravarty, 1991; Mikuriya et al., 2006). The least-squares planes of phenyl rings of the



Fig. 4. Packing diagram of $II \cdot 2nC_2H_5OH$, showing the hydrogen bonding. H and D atoms are omitted for clarity.



Fig. 5. UV-VIS spectra of I (a) and II (b) in CH₂Cl₂ during addition of TBAC.

benzoate ligands are twisted with torsion angles of $3.4(5)-13.0(7)^{\circ}$ with respect to those of the carboxylato groups suggesting flexible rotation of the phenyl rings. A packing diagram viewed along the *a*-axis is shown in Fig. 4. The chain molecules are parallel with the *a*-axis and they are in contact with each other by C—D···O and C—D··· π interactions and by C— D···O, C—H···O and O—H···Cl interactions involving ethanol molecules (Table 3).

UV-VIS spectrum of II was measured over the range of 300–800 nm in CH₂Cl₂. The spectrum has an absorption maximum at 459 nm similarly to that

of I (460 nm) showing that complex II maintains the paddlewheel-type dinuclear structure in CH₂Cl₂ (Ishida et al., 2009b). This absorption can be assigned to the $\pi(\text{RuO}, \text{Ru}_2) \to \pi^*(\text{Ru}_2)$ transition (Barral et al., 2005; Miskowsky et al., 1987, 1988). Molar conductivities of I and II in CH_2Cl_2 are nearly zero: $0.0045~\mu S~cm^2~mol^{-1},~and~0.0017~\mu S~cm^2~mol^{-1},$ respectively. This indicates that both complexes are nonelectrolytes in CH_2Cl_2 (Geary, 1971). Thus, these complexes can be considered to exist as neutral species such as polymers or oligomers $[Ru_2\{3,4,5 (C_2D_5O)_3C_6H_2COO_4Cl_n$ in CH_2Cl_2 . Fig. 5 shows UV-VIS spectral changes of I and II at an addition of tetrabutylammonium chloride (TBAC) to CH_2Cl_2 . Addition of an excessive amount of TBAC resulted in a slight shift of the absorption band at 460 nm to 468 nm and a decrease in the absorbance. Plots of the absorbance at 460 nm vs. the mole ratio of TBAC for I and II in CH_2Cl_2 are shown in Fig. 6. For both Iand II, the absorbance decreased with an increase in the molar ratio and reached a plateau around the 1: 1 ratio suggesting that I and II react with an equivalent ratio of TBAC for the Ru₂(II,III) unit to form monoanionic species. The reaction for II can be described by Eq. (1).:

$$[\operatorname{Ru}_{2}\{3,4,5-(\operatorname{C}_{2}\operatorname{D}_{5}\operatorname{O})_{3}\operatorname{C}_{6}\operatorname{H}_{2}\operatorname{COO}\}_{4}\operatorname{Cl}]_{n} + + n \left((\operatorname{C}_{4}\operatorname{H}_{9})_{4}\operatorname{N}^{+}\operatorname{Cl}^{-}\right) \rightleftharpoons n \left(\operatorname{C}_{4}\operatorname{H}_{9}\right)_{4}\operatorname{N}^{+} + + n \left[\operatorname{Ru}_{2}\{3,4,5-(\operatorname{C}_{2}\operatorname{D}_{5}\operatorname{O})_{3}\operatorname{C}_{6}\operatorname{H}_{2}\operatorname{COO}\}_{4}\operatorname{Cl}_{2}\right]^{-} (1)$$



Fig. 6. Plots of absorbance at 460 nm vs. mole ratio of TBAC for $I(\bullet)$ and $II(\bullet)$ in CH₂Cl₂.

The ¹H NMR spectrum of II in CD₂Cl₂ at 25 °C (Fig. 7a) displayed a broad signal from approximately $\delta = 23$ to $\delta = 32$. This signal is attributable to o-H atoms on the phenyl rings of the benzoate ligands because only these o-H atoms are undeuterated in II. The broad signal changed to a sharp signal at $\delta = 30$ at an addition of excessive amounts of TBAC, which can be interpreted by the decomposition of the chain molecules into dinuclear units (Fig. 7b) (Angaridis, 2005). This is in accordance with the results of UV-VIS spectral variation with the addition of TBAC. A similar reaction was observed in the chain complex [Ru₂{CH₃(CH₂)₇COO}₄(SCN)]_n (Handa et al., 2008). Moreover, the Ru₂(II,II) com-



Fig. 7. ¹H NMR spectra of *II* measured in CD₂Cl₂ at 25 °C (a), with excessive amounts of TBAC at 25 °C (b), at −80 °C (c), and with excessive amounts of TBAC at −80 °C (d). Asterisk indicates signals of ethanol protons and proton impurities in the solvent and ethoxy groups, and of tetrabutylammonium ions.



Fig. 8. ¹H NMR spectra of I in CD₂Cl₂ at 25 °C (a), at -80 °C (b), and with excessive amounts of TBAC at -80 °C (c).

plex $[Ru_2(CH_3(CH_2)_6COO)_4]$, which has two unpaired electrons, exists as a piece of the chain structure in noncoordinating solvents and the ¹H NMR signals are somewhat broad (Chisholm et al., 1996). Thus, the broad signal of *II* may be due to the polymeric or oligomeric chain formation, and various species with different chain lengths may exist.

At low temperatures, the broad signal of II splits into several peaks in a wider range. Fig. 7c displays a spectrum at -80 °C in which more than ten peaks are observed from approximately $\delta = -50$ to $\delta = 50$. This may be due to the fact that rotation of the benzoate phenyl ring affects the π -electron densities of

Table 4. ¹H NMR chemical shift values of I in CD₂Cl₂ at 25 °C (a), and with excessive amounts of TBAC (b).

()	a	b	
Group	δ		
<i>о</i> -Н	22–29	29.8	
m-CH ₂	7.1	6.6	
m-CH ₃	6.3	2.4	
p-CH ₂	2.8	7.2	
p-CH ₃	0.4	3.4	

the carbon atoms attached to the o-protons of the phenyl group (Nakamura et al., 1996). The rotation may be fixed in different orientations at low temperatures because of crowding of the phenyl rings in the chain molecules, which results in the observation of many proton signals at a wide range of magnetic fields. However, there is another explanation of the broad signal splitting. If various species with different chain lengths exist in CD_2Cl_2 , chemical shifts of the *o*-H signals outside the chain should differ from those inside resulting in multiple splitting. Interestingly, only one signal was observed at $\delta = 45$ at an addition of excessive amounts of TBAC for II in CD_2Cl_2 even at low temperatures $(-80 \,^{\circ}\text{C})$ (Fig. 7d). This may be explained by the existence of dinuclear units $[Ru_2\{3,4,5 (C_2D_5O)_3C_6H_2COO_4Cl_2$ as the main species causing rapid rotation of the phenyl rings free from the crowding and thus, one proton signal appears at $\delta =$ 45 as the result of the average effect of the rotation in the NMR time scale.

The ¹H NMR behavior of the undeuterated complex *I* is similar to that of *II* except for the complicated spectra in the region of $\delta = 0-20$ (Fig. 8). Assignment of ¹H NMR is shown in Fig. 9 and Table 4.



Fig. 9. ¹H NMR spectra of *I* with excessive amounts of TBAC in CD₂Cl₂ at 25 °C showing the assignments of signals of the o-H(\bullet), m-CH₂(\blacksquare), m-CH₃(\blacktriangle), p-CH₂(\square), p-CH₃(\triangle), and TBAC(+).



Fig. 10. Temperature dependences of ¹H NMR chemical shifts of o-H(●), m-CH₂(■), m-CH₃(▲), p-CH₂(□), and p-CH₃(△) hydrogen atoms for I in the presence of five fold amount of tetrabutylammonium chloride in CD₂Cl₂.

Signals of the ethoxy groups changed in a similar way; one broad signal at 25 °C splitted into several peaks at -80 °C, and became one sharp signal when adding TBAC. Temperature dependence of the ¹H NMR signals of *I* with excessive amounts of TBAC in CD₂Cl₂ is shown in Fig. 10. Chemical shifts of all protons in *I* (o-H, *m*-CH₂, *m*-CH₃, *p*-CH₂, and *p*-CH₃) are proportional to the 1/T values. This behavior is typical of a paramagnetic compound (Chisholm et al., 1996; Furukawa & Kitagawa, 2004). Thus, the spin state of the dinuclear ruthenium(II,III) core may not change in the measured temperature range.

Acknowledgements. The authors thank Dr. Kenji Yoza of Bruker AXS K. K. for his assistance in the X-ray crystal structure analysis. The present work was partially supported by the Support Project to Assist Private Universities in Developing Bases for Research and Grants in Aid for Scientific Research Nos. 22550066 and 20550066 from the Ministry of Education, Culture, Sports, Science and Technology.

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