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Syntheses of Formato-, Acetato-, Benzoato-, and Chlorosubstituted Acetatoruthenium Complexes, and Their Properties

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Complexes with the general formula of $[Ru_2(RCOO)_4X]$, where R=H, X=Cl, or Br; R=Me, X=Cl, Br, I, SCN, NO_3, or MeCOO; R=ph, X=Cl, or Br, were prepared. The magnetic properties, conductivities, polarographic behavior, and infrared spectra of these complexes were investigated. All the complexes show magnetic moments of 2.84—2.96 B.M., and their susceptibilities, at from about 300 to 100°K, can be fitted to the Curie-Weiss law with negative values of the Weiss constant ($\theta = -30 - -60$°K). These complexes seem to be isostructural. Monochloroacetato-, and trichloroacetatoruthenium complexes ($[Ru_2(CH_2ClCOO)_4Cl]\cdot 2H_2O$ and $[Ru(OH)(CCl_3COO)_2(H_2O)]$) were also prepared.

Carboxylatoruthenium complexes of the $[Ru_2(RCOO)_4Cl]$ (R=Me, Et, *n*-Pr) type have been prepared by the reaction of hydrated ruthenium trichloride with carboxylic acid-acid anhydride mixtures, and the complexes have been formulated as containing Ru(II) and Ru(III).[1] $[Ru_2(RCOO)_4Cl]$ (R=H, Me) complexes have also been obtained by the reaction of ruthenium(III and IV) chlorides with acetic or formic acid in a sealed tube.[2] An X-ray investigation of the analogue butyrato complex has recently been accomplished.[3] In this study, formato-, acetato-, and benzoatoruthenium complexes were

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prepared and their properties were investigated. Monochloroacetato- and trichloroacetatoruthenium complexes, $[Ru_2(CH_2ClCOO)_4Cl]\cdot 2H_2O$ and $[Ru(OH)(CCl_3COO)_2(H_2O)]$, were also prepared.

Experimental

Syntheses. $[Ru_2(MeCOO)_4Cl]$ (Complex [1]). A ruthenium(III, IV)-hydrochloric acid solution (Ru, 250 mg) was evaporated to dryness on a water bath. The residue was dissolved in 12N acetic acid (30 m*l*) and then gently heated for about 100 min at 110°C in a sealed, stainless-steel (SUS 32) tube. The solution thus obtained was concentrated on a water bath to prepare crystals. The crude crystals were recrystallized from a 3N acetic acid solution. Brown crystals were thus obtained; they were filtered and washed several times with ethanol and ether, and then dried *in vacuo*, to yield about 300 mg. The complex is poorly soluble both in water and in methanol.

Found: Ru, 42.23; C, 20.3; H, 2.40; Cl, 7.17%. Calcd for $Ru_2(MeCOO)_4Cl$: Ru, 42.66; C, 20.27; H, 2.53; Cl, 7.49%.

$[Ru_2(MeCOO)_4Br]$ (Complex [2]), $[Ru_2(MeCOO)_4I]$ (Complex [3]), and $[Ru_2(MeCOO)_4SCN]$ (Complex [4]) were prepared by adding large amounts of sodium bromide, sodium iodide, and potassium thiocyanate respectively to an acetic acid solution of Complex [1]. Complex [2] is poorly soluble both in water and in methanol, and Complexes [3] and [4] are insoluble in these solvents.

Complex [2]. Found: Ru, 38.54; C, 18.7; H, 2.44; Br, 15.08%. Calcd for $Ru_2(MeCOO)_4Br$: Ru, 39.00; C, 18.54; H, 2.32; Br, 15.43%.

Complex [3]. Found: Ru, 35.34; C, 17.3; H, 2.05; I, 21.30%. Calcd for $Ru_2(MeCOO)_4I$: Ru, 35.76; C, 16.99; H, 2.12; I, 22.45%.

Complex [4]. Found: C, 21.86; H, 2.12; N, 2.82%. Calcd for $Ru_2(MeCOO)_4SCN$: C, 21.77; H, 2.44; N, 2.82%.

$[Ru_2(MeCOO)_4NO_3]$ (Complex [5]). An 1N acetic acid solution containing 500 mg of Complex [1] was passed through an anion exchange column of Dowex 1-X4 (30 m*l* of the NO_3^- form). To the effluent, a 200-mg portion of potassium nitrate was then added, and the solution was concentrated on a water bath. The brown crystals thus obtained were filtered, washed with water, methanol, and ether, and dried *in vacuo*, to yield about 350 mg. The complex is poorly soluble both in water and in methanol.

Found: C, 18.90; H, 2.48; N, 2.91%. Calcd for $Ru_2(MeCOO)_4NO_3$: C, 19.21; H, 2.42; N, 2.80%.

$[Ru_2(MeCOO)_4OCOMe]$ (Complex [6]). An 1N acetic acid solution containing 400 mg of Complex [1] was passed through an anion exchange column of Dowex 1-X4 (30 m*l* of the SO_4^{2-} form). The effluent was concentrated on a water bath. The brown crystals thus obtained were filtered, washed with water, methanol, and ether, and dried *in vacuo*, to yield about 200 mg. The complex is poorly soluble both in water and in methanol.

Found: C, 23.58; H, 3.62%. Calcd for $Ru_2(MeCOO)_4OCOMe$: C, 24.15; H, 3.04%.

$[Ru_2(HCOO)_4Cl]$ (Complex [7]). This complex was prepared by the same procedure as was Complex [1], but using formic acid, as was reported previously.[2)]

$[Ru_2(HCOO)_4Br]$ (Complex [8]). The bromo-formato complex was prepared by adding a large amount of sodium bromide to a solution of Complex [7]. The complex is poorly soluble both in water and in methanol.

Found: Ru, 43.35; C, 10.5; Br, 16.82%. Calcd for $Ru_2(HCOO)_4Br$: Ru, 43.73; C, 10.39; Br, 17.30%.

$[Ru_2(phCOO)_4Cl]$ (Complex [9]). The chloro-formato complex [7] (100 mg) was dissolved in a mixture of methanol and water (30 m*l*+30 m*l*), and then a methanol solution of benzoic acid (100 mg/10 m*l*) was added to that solution. The mixture thus obtained was kept at room temperature for a week. The brown, crystalline material thus obtained was filtered, washed with water, methanol, and ether, and dried *in vacuo*, to yield about 150 mg. The complex is insoluble in most organic solvents and in water.

Found: Ru, 28.04; C, 46.4; H, 2.61; Cl, 4.90%. Calcd for $Ru_2(phCOO)_4Cl$: Ru, 27.98; C, 46.54; H, 2.77; Cl, 4.91%.

$[Ru_2(phCOO)_4Br]$ (Complex [10]). The bromo-benzoato complex was prepared in the same way as was the chloro-benzoato complex, using the bromo-formato complex [8] as the starting material. (Yield, about 150 mg). The complex is insoluble in most organic solvents and in water.

Found: Ru, 26.51; C, 43.9; H, 2.60; Br, 9.64%. Calcd for $Ru_2(phCOO)_4Br$: Ru, 26.36; C, 43.85; H, 2.61; Br, 10.43%.

$[Ru_2(CH_2ClCOO)_4Cl]\cdot 2H_2O$ (Complex [11]). To Complex [1] (200 mg) in a mixture of methanol (50 m*l*) and water (50 m*l*), a monochloroacetic acid solution (500 mg/10 m*l* H_2O) was added. The solution was then kept at room temperature for one or two weeks. The brown crystals thus obtained were filtered, washed with methanol, and ether, and dried *in vacuo*, to give 200 mg. Recrystallization was made from a 2M monochloroacetic acid solution. The complex is slightly soluble in methanol.

Found: Ru, 31.14; C, 15.52; H, 2.40; H_2O, 5.85%. Calcd for $Ru_2(CH_2ClCOO)_4Cl\cdot 2H_2O$: Ru, 31.20; C, 14.83; H, 1.85; H_2O, 5.55%.

$[Ru(OH)(CCl_3COO)_2(H_2O)]$ (Complex [12]). To a solution of Complex [1] (500 mg) in a mixture of methanol (100 m*l*) and water (100 m*l*), trichloroacetic acid (8 g) was added. The solution was then heated about 10 min. A flaky, brown crystalline material was thus obtained; and it was filtered, washed with water, and dried in a vacuum line (10^{-3} mmHg), to give 200 mg. The complex is soluble in most organic solvents.

Found: Ru, 22.02; C, 10.58; H, 0.61%. Calcd for $Ru(OH)(CCl_3COO)_2(H_2O)$: Ru, 21.87; C, 10.39; H, 0.87%.

Apparatus and Reagents. The molar conductivity was measured with a Metrohm Konduktoskope E365, the IR spectra, with Leitz 221, JASCO DS-301, and Hitachi EPI-L IR spectrometers, and the molecular weight, with a Mecrolab Osmometer 302. The magnetic susceptibility was measured by the Gouy method.

Ruthenium (III, IV) in a hydrochloric acid solution was prepared from a distillate of ruthenium (VIII) tetroxide passed into an alcoholic acid solution. All the other reagents used were of an analytical grade.

Results and Discussion

The complexes obtained are summarized in Table 1, along with the magnetic data, the conductivity data, the molecular weights, and the absorption maxima in their visible spectra.

The chloro-acetato complex [1] and chloro-formato complex [7] were prepared by the reaction of ruthenium(III and IV) chloride with acetic and formic acid respectively in a sealed tube. Complex [1] was confirmed by X-ray fluorometry to be free from contamination by the components of the sealed, stainless-steel

Table 1. The carboxylatoruthenium complexes and their properties

Complex No.	Chemical formula	$\chi_g \cdot 10^6$ (c.g.s.)	μ_{eff}(°C) (B.M.)[a]	Visible absorption spectra[d] mμ(ε in parentheses)	Molar conductivities[c] (mho cm^{-1})	Molecular weight[d]
1	$Ru_2(MeCOO)_4Cl$	14.89	2.90 (20)	428 (793)	80	460[e]
2	$Ru_2(MeCOO)_4Br$	13.39	2.89 (23)	426—430 (787)		608[e]
3	$Ru_2(MeCOO)_4I$	12.11	2.85 (18)			
4	$Ru_2(MeCOO)_4SCN$	13.73	2.85 (19)			
5	$Ru_2(MeCOO)_4NO_3$	13.74	2.87 (19)	426—430 (798)	93	
6	$Ru_2(MeCOO)_4OCOMe$	13.54	2.84 (20)	424—428 (830)	69	
7	$Ru_2(HCOO)_4Cl$	16.96	2.92 (24)	428—430 (774)	70	423[e]
8	$Ru_2(HCOO)_4Br$	15.77	2.94 (20)	428—430 (1160)		
9	$Ru_2(phCOO)_4Cl$	10.08	2.96 (19)			
10	$Ru_2(phCOO)_4Br$	9.13	2.91 (20)			
11	$Ru_2(CH_2ClCOO)_4Cl \cdot 2H_2O$[b]	11.28	2.99 (20)	435 (816)	79	648[e]
12	$Ru(OH)(CCl_3COO)_2(H_2O)$	3.54	2.10 (20)	460 (217)	3	461[e]

a) Corrections for diamagnetism were made and effective magnetic moments in Bohr magnetons, μ_{eff}, were calculated according to the formula, $\mu_{\mathrm{eff}}=8T\chi_{\mathrm{corr}}{}^{1/2}$, where χ_{corr} is the molar susceptibility corrected for diamagnetism and T is the absolute temperature.

b) The hydrated water was determined by the weight loss at 140°C.

c) in MeOH (30°C), 10^{-3} mol/*l*.

d) in MeOH. e) The values in Table are twice the observed ones for 1:1 electrolytes.

tube.[4] The chloro-benzoato complex [9] was obtained from a mixture of the chloro-formato complex [7] and benzoic acid. The other acetato complexes [2]—[6] were obtained from solutions of the chloro-acetato complex [1] in acetic acid containing an excess of the anions. A similar derivation can also be expected for the chloro-formato complex [7]. The conversion from the chloro-acetato complex [1] to the chloro-formato complex [7], and *vice versa*, are possible. The monochloroacetato and trichloro-acetato complexes, [11] and [12], $[Ru_2(CH_2ClCOO)_4Cl] \cdot 2H_2O$ and $[Ru(OH)(CCl_3COO)_2(H_2O)]$, were obtained as reaction products of Complex [1] and the corresponding monocarboxylic acid. In Fig. 1, these conversion procedures are shown schematically.

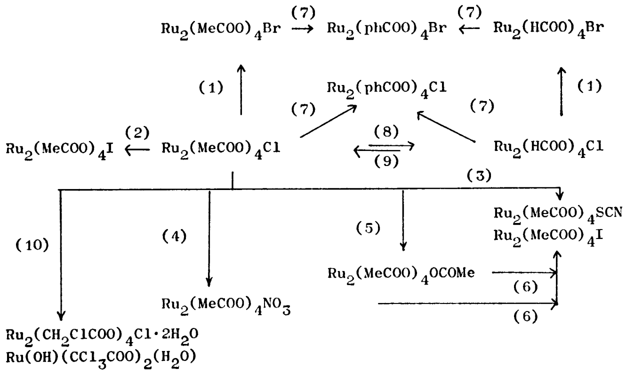

Fig. 1. Preparative conversion procedure of carboxylatoruthenium complexes.
1—3), 6): addition of the anions.
4,5): addition of the anions (after complex [1], chloroacetato complex, was passed through an anion exchanger column).
7): crystallized from a mixture solution of complex [1], $[Ru_2(MeCOO)_4Cl]$, or complex [7], $[Ru_2(HCOO)_4Cl]$, and benzoic acid.
8,9): interconversion of acetato and formato complexes.
10): crystallized from a mixture solution of complex [1], $[Ru_2(MeCOO)_4Cl]$, and monochloroacetic acid or trichloroacetic acid.

As has been described above, several monocarboxylatoruthenium complexes, $[Ru_2(RCOO)_4Cl]$ (R= Me, Et, *n*-Pr), have been reported.[1] An X-ray diffraction study of the analogous butyratoruthenium complex has indicated that the complex contains binuclear units consisting of two ruthenium atoms bridged by four *n*-butyrato groups, and that these binuclear units are linked by bridging chlorine atoms into infinite zigzag chains.[3] The complexes of the $[Ru_2(RCOO)_4X]$ type prepared in this study are thought to be analogous to those reported in Refs. 1 and 3.

Conductivities and Molecular Weight. The molar conductivities for Complexes [1], [5], [6], [7], and [11] are within 70 to 90 mho cm^{-1}, indicating that these complexes are 1: 1-type electrolytes. The small conductivity for Complex [12] suggests that the complex is non-electrolyte. The chloride ion of Complex [1] in an acetic acid solution was adsorbed quantitatively by the NO_3^--form ion exchanger (Dowex 1-X4). These facts suggest that the formato and acetato complexes can dissociate into $Ru_2(RCOO)_4(solvent)^+$ and X^-, and that the cation formed is present without decomposition.

The molecular weights measured for Complexes [1], [2], [7], [11], and [12] support the formulae expected for these complexes.

Polarographic Measurement. The polarographic behavior of the $[Ru_2(OAc)_4]^+$ cation has very recently been described.[5] The acetato complex [1] gave two polarographic waves when acetic acid was used as the supporting electrolyte (Fig. 2). One of them is the oxidation wave of mercury in the presence of the chloride ion; this supports the idea that the complex

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4) The authors wish to thank Mr. Tadao Ooizumi of the Rigaku Denki Co., Ltd., for this data.

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TABLE 2. THE MAGNETIC SUSCEPTIBILITY AND EFFECTIVE MAGNETIC MOMENT PER RUTHENIUM ATOM OF THE CARBOXYLATORUTHENIUM COMPLEXES AT VARIOUS TEMPERATURES

$[Ru_2(MeCOO)_4Cl]$ M.W: 473.5; Diamagnetic correction: 135×10^{-6};									
Temp. (K)···	277.6	262.5	227.9	227.6	202.8	168.2	129.8	98.6	
$10^6\chi_a$ ········	3496.5	3666.9	4152.9	4147.0	4578.5	5440.2	6484.6	7991.3	
μ_{eff} ···········	2.79	2.77	2.75	2.75	2.73	2.71	2.59	2.51	
$[Ru_2(HCOO)_4Cl]$ M.W.: 417.5; Diamagnetic correction: 88×10^{-6};									
Temp. (K)···	268.6	257.6	232.8	220.1	198.1	174.3	150.5	129.0	89.0
$10^6\chi_a$ ········	3616.7	3705.5	4016.5	4187.3	4554.4	5040.7	5583.3	6195.9	7683.2
μ_{eff} ···········	2.79	2.76	2.74	2.72	2.69	2.65	2.59	2.53	2.34
$[Ru_2(C_6H_5COO)_4Cl]$ M.W: 721.9; Diamagnetic correction: 244×10^{-6};									
Temp. (K)···	269.8	256.8	235.1	211.9	173.6	149.7	125.8	103.8	
$10_6\chi_a$ ········	3815.7	3996.9	4295.7	4669.1	5490.9	6044.6	6831.1	7714.4	
μ_{eff} ···········	2.87	2.87	2.84	2.81	2.76	2.69	2.62	2.53	

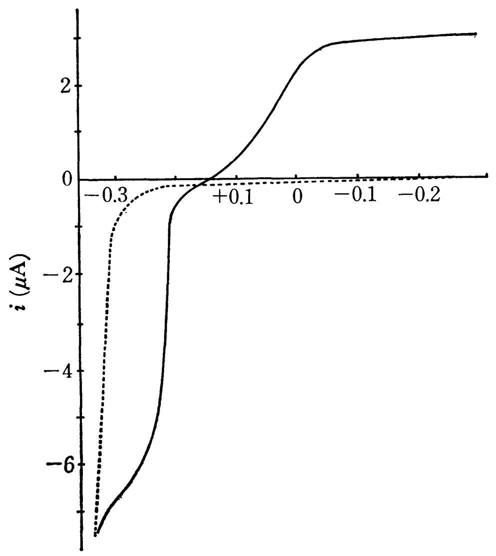

Fig. 2. D.C. polarogram of $[Ru_2(MeCOO)_4Cl]$, [1].
concentration=1 mM complex [1]. supporting electrolyte= 0.5M acetato buffer+0.5M KNO_3+0.005% gelatin. pH=5.0, 25°C.
Dotted line indicates the curve for the supporting electrolyte only.

in an aqueous solution dissociates to give the chloride ion. The other wave ($E_{1/2}$=+0.06 V vs S.C.E.) results from the reduction of the complex. The nitrato-acetato complex [5] also gave the same polarographic wave as that of Complex [1] except for the oxidation wave due to the chloride ion. The reversibilities of the second step were confirmed by the measurement of the A. C. polarogram. The log-plot analysis of the reduction wave gave linear relations, with a reciprocal slope following into 63 mV. These facts indicate that the electrode reduction of the complex solutions proceeds reversibly in the usual polarographic sense; the reduction is thought to be a one-electron one on the basis of the diffusion current.

Magnetic Property and Visible Absorption Spectra. As is shown in Table 1, Complexes [1]—[10] have effective magnetic moments of 2.84—2.96 B.M. at room temperature. The values are significantly higher than the spin-only moment for a binuclear ruthenium-(II, III) complex with a single unpaired electron. The temperature variation in the experimental atomic susceptibilities and effective magnetic moments of Complexes [1]—[3] and [7]—[10] were also examined. The data for Complexes [1], [7], and [9] are given in Table 2. The reciprocal susceptibilities varied linearly with the temperature and obeyed the Curie-Weiss law with θ over the range of −30——60°K. These results are similar to those obtained by Stephenson *et al.*[1] Bennett, Caulton, and Cotton have explained the effective magnetic moments of $[Ru_2(RCOO)_4Cl]$ complexes by saying that the paramagnetism indicates three unpaired electrons per pair of metal atoms. They also suggested that the two ruthenium atoms in the complexes exist in the same nonintegral oxidation state of +2.5.[3]

TABLE 3. INFRARED ABSORPTION BANDS (cm^{-1}) IN CARBOXYL STRETCHING FREQUENCY REGION OF $[Ru_2(HCOO)_4Cl]$, [7], $[Ru_2(MeCOO)_4Cl]$, [1], $[Ru_2(CH_2ClCOO)_4Cl]$, [11],[a] AND $[Ru(OH)(CCl_3COO)_2(H_2O)]$,[12]. (KBr disk).

Complex [1]	Complex [11][a]	Complex [7]	Complex [12]	Tentative assignments
1643 w	1618 m	1580 vw	1670 sh	ν_{anti}COO (?)
		1498 sh 1480 s	1608 s 1598 sp	ν_{anti}COO
1470 sh 1444 s 1420 sh 1402 sp	1488 sh 1427 s 1397 sh 1350 sh			ν_{anti}COO and ν_{sym}COO
		1336 vs	1380 s	ν_{sym}COO

a) dehydrated complex.

The monochloroacetato complex [11], $[Ru_2(CH_2ClCOO)_4Cl]\cdot 2H_2O$, shows a magnetic moment close to that of the acetato complex, suggesting a similar dimeric structure. On the other hand, the magnetic moment of the trichloroacetato complex [12], $[Ru(OH)(CCl_3COO)_2(H_2O)]$, is reasonable compared with the values reported for Ru(III) complexes.[6]

The visible absorption spectra of the complexes of the $[Ru_2(RCOO)_4X]$ type in a methanolic solution were almost the same. Such data for analogous complexes have also been reported.[1] The band has been assigned to the $b_{2g}-a_{1g}$ and/or $b_{2g}-a_{2u}$ transitions using a molecular orbital diagram for an M_2X_8 species.[3] The absorption spectra of the trichloroacetato complex [12], $[Ru(OH)(CCl_3COO)_2(H_2O)]$, was quite different from those of other monocarboxylato complexes, indicating that Complex [12] is different from the other monocarboxylato complexes.

Infrared Spectra. The infrared spectra of the complexes were measured over the range of 4000—200 cm^{-1}. The general features of the spectra of the chloro-monocarboxylato complexes were very similar to those of the corresponding bromo- and iodo-monocarboxylato complexes. No absorption bands due to OH and H_2O groups were found in Complexes [1]—[10]. The infrared absorption bands in the carboxyl stretching frequency region are shown in Table 3, along with their tentative assignments.

The chloro-formato complex [7] displays two strong absorption bands at 1480 and 1336 cm^{-1} in the carboxyl-stretching frequency region. These bands can be assigned to the antisymmetric and the symmetric COO-stretching vibrations respectively. The separation ($\Delta = 144$ cm^{-1}) between the two absorption bands may indicate the symmetrical coordination of the carboxyl groups.[7]

The chloro-acetato complex [1], however, shows a strong band with several shoulders near 1444 cm^{-1} in this region; the band is very different in shape from that in the chloro-formato complex. This carboxyl band has been explained by assuming an overlapping of the antisymmetric and symmetric COO-stretching vibrations of a bridged carboxyl group.[1] Since the antisymmetric COO-stretching frequency is known to be sensitive to the electronic environment of a carboxylato ion,[8] the observed different features in the carboxyl region between the formato and the acetato complexes are probably due to the difference in the character of the coordinating carboxyl bands.

The monochloroacetato complex [11], $[Ru_2(CH_2ClCOO)_4Cl]\cdot 2H_2O$, showed a carboxyl band similar to that of the acetato complex. On the other hand, the trichloroacetato complex [12], $[Ru(OH)(CCl_3COO)_2(H_2O)]$, exhibited two characteristic peaks in this region. These bands are thought to be due to the antisymmetric and symmetric stretching vibrations of the bidentate carboxyl groups respectively. The separation between the two absorption bands for the trichloroacetato complex [12], $[Ru(OH)(CCl_3COO)_2(H_2O)]$, is appreciably larger than those of known binuclear acetato metal complexes.[9] The increase in the separation may reflect the considerable influence of the halogens on the carboxyl vibrations of trichloroacetato groups.[10]

It is possible to distinguish the complex type between $[Ru_2(MeCOO)_4X]$ and $[Ru_2(MeCOO)_4]X$ on the basis of the infrared spectra of the nitrato-caetato complex [5]. Complex [5] shows N–O stretching bands of the nitrato group at 1388, 1288, and 809 cm^{-1}. The observation of three absorption bands indicates that the nitrato group in Complex [5] is present as a coordinate ligand, according to the Gatehouse *et al.* interpretation.[11]

With respect to the properties observed, a series of complexes of the $[Ru_2(RCOO)_4X]$ type were very similar. No remarkable substitution effect of R groups or X groups was observed. This might be understood on the basis of the structure for the butyrato complex.[3]

The trichloroacetato complex [12], $[Ru(OH)(CCl_3COO)_2(H_2O)]$, was thought to be monomeric. Since the ruthenium(III) complexes prefer a six-coordinated structure, the octahedral arrangement appears probable.

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