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Syntheses of Trinuclear Ruthenium(III) Complexes with Dichloroacetato Ligands

Masao MUKAIDA, Mitsumasa KUSAKARI, Tadashi TOGANO, Toshihiro ISOMAE, Terunosuke NOMURA, and Tatsujiro ISHIMORI*

Department of Chemistry, Sophia University, Chiyoda, Tokyo 102

**Department of Chemistry, Rikkyo (St. Paul's) University, Ikebukuro, Tokyo 171*

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Synopsis. Trinuclear ruthenium(III) complexes were prepared by the reaction of the dinuclear ruthenium(II, III) acetato complex with dichloroacetic acid. On the basis of chemical and thermal analyses, and on the basis of observations of the magnetic properties, the conductivities, the molecular weight, the alkalimetry, the infrared spectra and the electronic spectra, the complexes prepared here were formulated as $[Ru_3O(CHCl_2COO)_6(CH_3OH)_3](CHCl_2COO)$ and $[Ru_3O(CHCl_2COO)_6(OH)(H_2O)_2]$.

Some years ago, tetra-μ-monocarboxylato-chlorodiruthenium(II, III) complexes, $[Ru_2(RCOO)_4Cl]$ (R= H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, C_6H_5), were prepared.[1,2] The structure of the butyrato complex was determined to have $[Ru_2(C_4H_9COO)]^+$ units linked into chains by Ru–Cl–Ru bridges.[3] Trinuclear acetato ruthenium(III) complexes, $[Ru_3O(CH_3COO)_6X_3]^{n+}$ (X=H_2O, py, CH_3OH, n=0 or 1), which contain an oxygen-centred structure, have recently been prepared.[4,5] Monochloro- and trichloroacetato ruthenium complexes have also been prepared.[2] However, no ruthenium complex with dichloroacetato ligands has yet been reported. This paper will describe the preparation and the properties of two dichloroacetato ruthenium complexes, $[Ru_3O(CHCl_2COO)_6(CH_3OH)_3](CHCl_2COO)$ and $[Ru_3O(CHCl_2COO)_6(OH)(H_2O)_2]$. The complexes prepared here were thought to have a skeletal structure similar to those of μ_3-oxo-trinuclear metal (Fe, Cr, Ru) acetato complexes.

Experimental

Preparation of $[Ru_3O(CHCl_2COO)_6(CH_3OH)_3](CHCl_2COO)$, *(1).* To a solution of tetra-μ-acetato-chlorodiruthenium(II, III) (1500 mg) in a mixture of CH_3OH (150 ml) and H_2O (150 ml), was added dichloroacetic acid (60 ml), after which the solution was left standing at room temperature.

After one or two weeks, the solution separated into two layers. The under layer (dark green) was transferred to a beaker, after which it was again kept standing for about a month. The dark green crystals thus obtained were filtered, washed with petroleum ether, and dried *in vacuo*, giving 350 mg. The crystals were recrystallized from CH_3OH. Found: Ru, 23.2; C, 15.34; H, 1.46%. Calcd for $[Ru_3O(CHCl_2COO)_6(CH_3OH)_3](CHCl_2COO)$: Ru, 23.1; C, 15.55; H, 1.45%.

The same complex was also obtained when tetra-μ-acetato-nitratodiruthenium(II, III) was used as the starting material in place of tetra-μ-acetato-chlorodiruthenium (II,III).

Preparation of $[Ru_3O(CHCl_2COO)_6(OH)(H_2O)_2]$, *(2).* The preparation was very similar to that described above, except that ethanol was used as the reaction solvent in place of methanol. Attempted recrystallization from methanol and ethanol were unsuccessful. Found: C, 12.54; H, 1.13; Cl, 37.12; H_2O, 3.3%. Calcd for $[Ru_3O(CHCl_2COO)_6(OH)(H_2O)_2]$: C, 12.64; H, 0.97; Cl, 37.32; H_2O, 3.16%.

The binuclear acetato ruthenium complexes used as the starting materials in these syntheses were prepared by methods described previously.[2]

Results and Discussion

The compositions were consistent with the formulae given in Table 1. The presence of two molecules of the coordinating water in **2** were determined by DTA and TG measurements. No endothermic peak due to the deaquation was found for **1**. The trimeric structure of the complexes was indicated by the molecular-weight measurement of **1** (Table 1). X-Ray single crystal photographs of **1** showed that the cell volume of the complex was about 4200×10^{-24} cm^3. The density calculated using the assumption of four molecules per cell was 2.07 g·cm^{-3} while the observed density was 2.03 g·cm^{-3} (by the flotation method in CCl_4 and CH_2I_2).

The unipositive cation assumed for **1** was supported by the absorbing behavior toward cation-exchange resin(Dowex 50W-X 8) in a methanolic solution, although the molar conductivities observed were quite small compared to those found for ordinary complexes of 1:1-type electrolytes. In the titration of a methanolic solution of **1** with a sodium hydroxide solution, two infliction points were observed, as is shown in Fig. 1. This is probably due to the ligand substitution between the coordinated methanol in **1** and the hydroxide ion.

Table 1. CHEMICAL FORMULAE AND THEIR PROPERTIES

	Complex	Λ_M in 10^{-3} M S cm^2	M.W.[c]	μ_{eff}[d] (B.M.)	λ nm[a] (ε)
1,	$[Ru_3O(CHCl_2COO)_6(CH_3OH)_3](CHCl_2COO)$	16[a]	1455[a]	2.16 (293 K)	715—690 (*ca.* 1570) 610—600 sh —420 sh
		12[b]	1366[b]		
2,	$[Ru_3O(CHCl_2COO)_6(OH)(H_2O)_2]$	20[a]		2.04 (298 K)	730—700 (*ca.* 2950) 630—600 sh —420 sh

a) in CH_3OH. b) in DMF. c) by vaper pressure osmometry. d) by Gouy method.

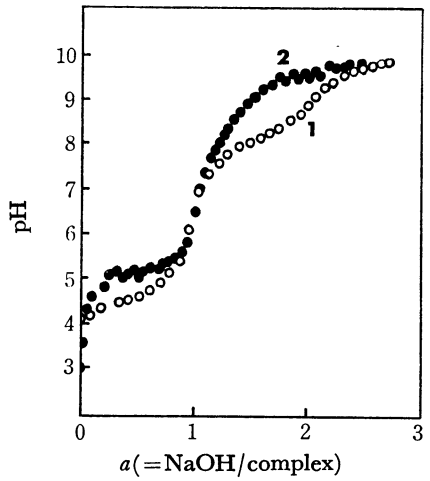

Fig. 1. pH titration curves for **1** and **2** in methanolic solution.
Complexes: 3×10^{-4} M.

On the other hand, **2** in a methanolic solution was absorbed by anion-exchange resin(Dowex 1-X 4), and only one infliction point was observed in its pH titration curve. This behavior seem to be evidence for the proton-dissociation of the aqua ligand in **2**:

$$[Ru_3O(CHCl_2COO)_6(OH)(H_2O)_2] \text{ (in solid)} \longrightarrow$$
$$[Ru_3O(CHCl_2COO)_6(OH)_2(H_2O)]^- + H^+ \text{ (in } CH_3OH)$$

The presence of methanol in **1** was ascertained by infrared spectroscopy. The IR spectra of the two complexes were almost identical except for the bands in the 1000 cm^{-1} region. In this region, two absorption bands at 996 and 968 cm^{-1} were observed for **1**, while only one absorption band, at 967 cm^{-1}, was found for **2**. The band at 996 cm^{-1} in **1** can be assigned to the methyl rocking vibration.

It has been reported that the observations of the electronic absorption spectra can serve as a guide for the characterization of μ_3-oxo-trinuclear acetato ruthenium complexes.[5] The electronic absorption spectra and the effective magnetic moments of **1** and **2** were similar to those of the complexes mentioned above.[5] The observed magnetic moments may also suggest an oxygen-centred structure in which marked spin-spin interaction occurs *via* the central oxygen atom in the Ru_3O unit.[6]

In the present study, **1** and **2** were obtained under the same reaction conditions. It is interesting to note that the formation of these species depends on the kind of alcohol used as a solvent in the syntheses. As has been noted in the Experimental section, attempts to recrystallize **2** from ethanol were unsuccessful. However, when **2** was treated by a mixture of methanol and water containing dichloroacetic acid, a crystalline material, which is thought to be $[Ru_3O(CHCl_2COO)_6(H_2O)(CH_3OH)_2](CHCl_2COO)$ on the basis of its composition and infrared spectrum, was obtained. This finding indicates a fairly strong coordinating nature of methanol in the complexes.

References

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