BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 415—417 (1971)

# Chloropentakis(trichlorostannato)ruthenate(II)

Hisateru Okuno, Tatsujiro Ishimori, Kunihiko Mizumachi, and Haruhiko Ihochi*

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

(Received June 26, 1970)

The cesium and triethylammonium salts of chloropentakis(trichlorostannato)ruthenate(II), $Cs_4[RuCl(SnCl_3)_5]\cdot CsCl$ and $(Et_3NH)_4[RuCl(SnCl_3)_5]$, were prepared. Their IR absorption bands near 210 cm$^{-1}$ are thought to be due to the Ru–Sn stretching vibration. The electronic spectra of dilute hydrochloric acid solutions of the complex salts were the same as the spectrum of a single crystal of the cesium salt. This suggests the presence of the complex ion, $[RuCl(SnCl_3)_5]^{4-}$, in acid solutions. A hydrolysis product of the complex ion contained ruthenium, tin and chlorine in the atom ratio of 1 : 5 : [$\alpha(<1)$], and the cesium salt was yielded from a dilute hydrochloric acid solution of the hydrolysis product. The observations show the presence of the Ru–Sn bonds in the complex ion.

. Complexes of platinum metals with the coordinating $(SnCl_3)^-$ groups have recently been studied.1—7) As for the ruthenium complexes of this kind, $M^I_2[RuCl_2(SnCl_3)_2]$,3) $[Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_3(Me_2CO)_2]$, $[Ru_2Cl_3(SnCl_3)(CO)_2(PPh_3)_4]$ ($PPh_3$=triphenylphosphine)6) and $[Me_4N][RuX_2(CO)_2(SnCl_3)_2]$ (X=Cl or Br)6,7) have been reported. In the present work salts of chloropentakis(trichlorostannato)ruthenate(II), $[RuCl(SnCl_3)_5]^{4-}$ were prepared, and their chemical properties were investigated. A hydrolysis product of the complex ion was also isolated.

## Experimental

Ruthenium(III and IV) in a hydrochloric acid solution was prepared from the distillate of ruthenium(VIII) tetroxide passed into an alcoholic hydrochloric acid solution. All the other reagents were of analytical grade. IR-spectra were measured in Nujol mull over the region of 700—200 cm$^{-1}$ on JASCO IR-F.

*Preparation of* $[RuCl(SnCl_3)_5]^{4-}$ *Complex Ion.* Sufficient tin(II) chloride dihydrate (1.13 g) was added to 40 mg of ruthenium(III and IV) in 50 m*l* of 2—3 M hydrochloric acid solution, and the solution was digested in a boiling water bath for 45—60 min. The yellowish red solution obtained was passed through an anion-exchange column of Dowex 1, X-16 (20 m*l* of the chloride form), yielding a hydrochloric acid solution of the complex ion. This ion-exchange procedure is to remove tin(IV) and an excess of tin(II), and, if present, any small anionic ruthenium species

---

* Present address: Department of Chemistry, University of Arkansas, Fayetteville, Ark., U. S. A.

1) R. D. Cramer, E. L. Jenner, R. V. Lindsey, Jr., and U. G. Stolberg, *J. Amer. Chem. Soc.*, **85**, 1691 (1963).

2) A. G. Davies, G. Wilkinson, and J. F. Young, *ibid.*, **85**, 1692 (1963).

3) J. F. Young, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, **1964**, 5176.

4) R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, **87**, 658 (1965).

5) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *Inorg. Chem.*, **5**, 109 (1966).

6) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

7) J. V. Kingston and G. Wilkinson, *ibid.*, **29**, 2709 (1967).

in the reaction mixture. However, no complex ion of a large size was adsorbed appreciably by the anion-exchanger with a high crosslinkage.

*Preparation of* $Cs_4[RuCl(SnCl_3)_5]\cdot CsCl$ *and* $[(C_2H_5)_3NH]_4[RuCl(SnCl_3)_5]$. Addition of acid cesium chloride solution to the complex ion in 2—3 M hydrochloric acid solution yielded a yellow salt, which was washed with a mixture of ethanol and hydrochloric acid (5 : 1). Crystals 0.5 to 1.5 mm in length were prepared by introducing 0.2 M cesium chloride solution slowly from a capillary into a 2—3 M hydrochloric acid solution of the complex ion; the solution was covered with ligroin during the addition of cesium chloride and the formation of the crystals.

Found: Ru, 5.0; Sn, 30.4; Cs, 33.8; Cl, 30.7%. Calcd for $Cs_5RuSn_5Cl_{17}$: Ru, 5.15; Sn, 30.25; Cs, 33.87; Cl, 30.72%.

Addition of a large excess of a concentrated acid triethylammonium chloride solution yielded an orange salt. The salt was washed with an acid triethylammonium chloride solution and then with the mixture of ethanol and hydrochloric acid (5 : 1). The triethylammonium salt was much more soluble in dilute hydrochloric acid than the cesium salt.

Found: Ru, 5.94; Sn, 35.2; Cl, 33.0; N, 3.46; C, 17.82%. Calcd for $[(C_2H_5)_3NH]_4[RuCl(SnCl_3)_5]$: Ru, 6.05; Sn, 35.52; Cl, 33.96; N, 3.35; C, 17.26%.

The tetramethylammonium salt was prepared in a similar way. It was less soluble in dilute hydrochloric acid than the triethylammonium salt.

*Preparation of Hydrolysis Product of the Complex.* When a 2—3 M hydrochloric acid solution of the complex ion was diluted 40-fold with water, a yellow hydrolysis product was obtained. This product was washed with water several times by centrifuging or by decantation; the chloride ion was gradually removed from the hydrolysis product by successive washings. The product turned brown when it was washed with ethanol and then ether or when it was dried over tetraphosphorus decaoxide. The brown product contained 10.6% Ru, 61.5% Sn and 0.4—3.1% Cl; the chloride content varied with the extent of the washing.

## Results and Discussion

*Complex Salts.* The compositions of the cesium and triethylammonium salts were consistent with $Cs_5RuSn_5Cl_{17}$ and $(Et_3NH)_4RuSn_5Cl_{16}$, respectively. These compounds were diamagnetic. They are thought to be complex salts of ruthenium(II). Six-coordination is a very strong inherent tendency of ruthenium(II) complexes, and the only exceptions may be some complexes[6,8] with triphenylphosphine or triphenylstibine such as $RuCl_2(PPh_3)_3$. However, X-ray study on $RuCl_2(PPh_3)_3$[9] has shown that the complex is quasi-octahedral. From geometrical consideration, it is seen that covalent radii of ruthenium(II), tin(II), and Cl(-I) make an octahedral arrangement as $[RuCl(SnCl_3)_5]^{4-}$ possible for the complex ion presented here, and its complex salt can be represented as $Cs_4[RuCl(SnCl_3)_5]\cdot CsCl$ or $(Et_3NH)_4[RuCl(SnCl_3)_5]$. The equivalent conductivity, $\Lambda_e$, of the tetramethylammonium salt in nitromethane was 102.9, 104.1, and 106.1 ohm$^{-1}$cm$^2$ at $6.03\times10^{-5}$, $4.06\times10^{-5}$, and $2.05\times10^{-5}$ eq/*l*, respectively, at 25°C. The data were compared with those of (3 : 1), (2 : 1) and (1 : 1) electrolytes by the method of Feltham and Hyter.[10] The value of $(\Lambda_0-\Lambda_e)/\sqrt{c}$, where $\Lambda_0$ is $\Lambda_e$ at infinite dilution and $c$ equivalent concentration, was $1.66\times10^3$, while the values for $Na[BPh_4]$, $[Ni(phenan)_3](ClO_4)_2$, and $[Co(bipy)_3](ClO_4)_3$ have been reported to be 216, 465, and 1020 respectively. The results of the comparison indicate that the tetramethylammonium salt is an electrolyte of the (4 : 1) type. The electronic absorption spectra of the tetramethylammonium and triethylammonium salts in nitromethane were the same as those of the salts in a dilute hydrochloric acid solution, which in turn are the same as the spectrum of the cesium salt single crystal. Thus, both cesium and triethylammoniun salts contain an identical complex anion, $[RuCl(SnCl_3)_5]^{4-}$.

The properties of the cesium salt were as follows: yellow for fine crystals and orange for crystals of length of the order of millimeters, insoluble in ethanol and ether; cubic system with the well developed (1, 1, 1) plane; lattice constant, $a=15.66\pm0.22$ Å; number of chemical units in an unit cell, $Z=4$; density=3.37 g/cm$^3$ at 25°C; refractive indices, $n_{700\mathrm{m}\mu}=1.758\pm0.005$, $n_{589\mathrm{m}\mu}=1.765\pm0.004$ at 23°C.

The electronic absorption spectrum of the crystal shown in Fig. 1 was measured by a photoelectric spectrometer equipped with a special microphotometric attachment.[11,12] Since the crystal used did not have completely planar surfaces, its thickness was not measured. A decrease in absorption was observed on irradiation with ultraviolet rays. This seems to be caused by a partial decomposition of the complex salt during the course of irradiation.

The infrared spectrum of the cesium salt has absorption bands at 324, 288(shoulder), 211, and 205 (shoulder) cm$^{-1}$ as shown in Fig. 2. The spectrum of

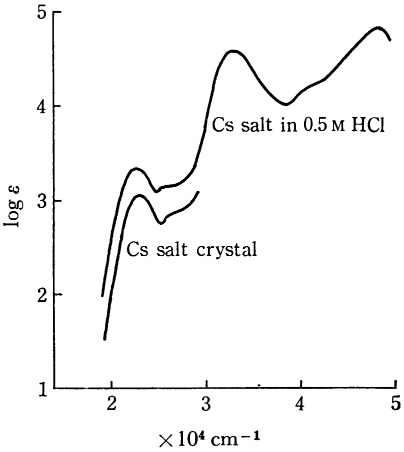

Fig. 1. Electronic Spectra of $Cs_4[RuCl(SnCl_3)_5]\cdot CsCl$. The ordinate is not to scale for the spectrum of the crystal.

---

[8] D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature*, **208**, 1203 (1965).

[9] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

[10] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, **1964**, 4588.

[11] The crystal absorption spectum was kindly measured by Professor Y. Kondo of Rikkyo University.

[12] Y. Kondo, *Science of Light*, **11**, 76 (1962).

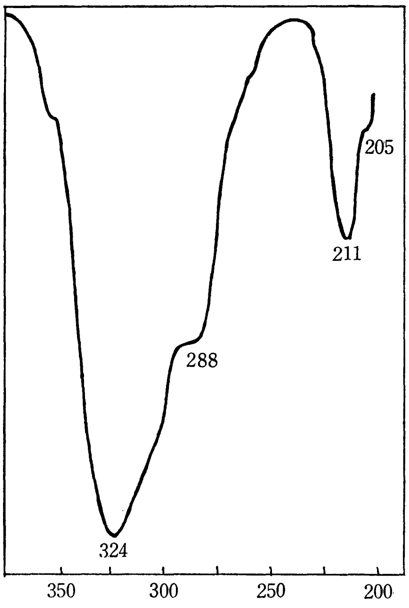

Fig. 2. Infrared spectrum of $Cs_4[RuCl(SnCl_3)_5]\cdot CsCl$ in Nujol mull.

the triethylammonium salt was the same as that of the cesium salt: the absorptions were at 318, 294(shoulder), 212, and 205(shoulder) $cm^{-1}$. The absorption bands in the region 350—275 $cm^{-1}$, including unresolved shoulders, are thought to be due to the stretching vibrations of Sn–Cl and Ru–Cl. Infrared absorptions[13] due to the platinum metal-tin bonds have been found near 200 $cm^{-1}$ for $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ and $[Pt(SnCl_3)_5]^{3-}$. The absorption bands at 210 $cm^{-1}$ observed here can be assigned to the Ru–Sn stretching vibration.

*Complex Ion in a Hydrochloric Acid Solution.* The solution of the complex ion was prepared by use of an anion exchange column, and the Ru : Sn ratio in the solution was 1 : 5. When tin(II) chloride was added to this complex ion solution and the mixture again treated with the anion exchange column, the Ru : Sn ratio in the effluent was still 1 : 5. The results suggest that the complex ion in a dilute hydrochloric acid solution contains ruthenium and tin in the ratio of 1 : 5, and further that the coordinating $(SnCl_3)^-$ groups do not greatly dissociate and the rate of dissociation is not fast. The electronic absorption spectrum of the cesium salt in 0.5 M hydrochloric acid is shown in Fig. 1 ($\log \varepsilon=3.34$, 4.58, and 4.83 at 22520, 32890, and 48540 $cm^{-1}$ respectively). It is the same as that of the crystals of the cesium salt in the region $1.9\times10^4$—$2.9\times10^4$ $cm^{-1}$. The spectrum of the complex ion prepared as a dilute hydrochloric acid solution was also identical with that of the cesium salt solution. Thus, the complex ion, $[RuCl(SnCl_3)_5]^{4-}$, is thought to be present in a dilute hydrochloric acid solution. However, the complex ion in an acid solution slowly fades.

*Hydrolysis Product.* The Ru : Sn : Cl ratio in the hydrolysis product was 1 : 5 : $[\alpha(<1)]$. The infrared absorption bands due to the Ru–Sn stretching vibrations were observed for the complex salts, but the corresponding bands were not found for the hydrolysis product. This is probably due to a polymer structure of the hydrolysis product. However, when the hydrolysis product was dissolved in 1 M hydrochloric acid, the electronic absorption spectrum of the solution was the same as that of the cesium salt in a hydrochloric acid solution ($\log \varepsilon=3.0$ and 4.5 at 22520 and 34130 $cm^{-1}$). The slight differences in $\log \varepsilon$ and the wave numbers at the maximum absorptions are thought to be caused by the decomposition of a small part of the hydrolysis product. The cesium salt was prepared from a dilute hydrochloric acid solution of the hydrolysis product in a reasonable yield; decomposition products in the hydrolysis product, if any, were previously removed from the solution by the anion exchange technique. The cesium salt prepared was identified by means of electronic and infrared spectra. Thus, the skeleton of "$RuSn_5$" remains in the hydrolysis product, and the presence of direct metal-metal bonds in the complex ion is shown in terms of chemical reactions, the formation of the hydrolysis product from the complex ion and the reformation of the complex ion from the hydrolysis product. Incidentally, any hydrolysis product with metal-metal bonds other than that described above has not been reported yet.

Young *et al.*[3] have reported the preparation of $(Me_4N)_2[RuCl_2(SnCl_3)_2]$, and we tried to prepare this complex salt following their directions. However, the Ru : Sn ratio in the product was 1 : 5, not 1 : 2. The infrared spectrum was the same as that of $(Et_3NH)_4[RuCl(SnCl_3)_5]$.

The authors wish to express their appreciation to Professors Yukio Kondo and Masayoshi Nakahara of Rikkyo University for many helpful discussions, and to Miss Noriko Okazaki for her technical assistance. This work was made possible by the support of the Scientific Research Fund of the Ministry of Education.

---

[13] D. M. Adams and P. J. Chander, *Chem. Ind.* (London), **1965**, 269.