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TRICHLORO- AND TRIBROMOTRIS{TRICHLOROSTANNATO(II)}RHODATES(III)

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Tetramethylammonium salt of trichlorotris{trichlorostannato(II)}-rhodate(III), $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$ was prepared by treating rhodium trichloride with tin(II) chloride in hydrochloric acid solution. The complex rapidly changed to $[RhBr_3(SnCl_3)_3]^{3-}$ in the presence of Br^- in hydrochloric acid solution. Both these complexes are new six-coordinate rhodium(III) complexes which can be considered to be facial.

It has been reported that salts of $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ 1) and $[Rh(SnCl_3)_4]^{3-}$ 2) were obtained by reaction of rhodium trichloride with tin(II) in hydrochloric acid solution. A number of trichlorostannato-organo-rhodium(I) complexes have also been studied.1), 3) Most of these complexes were four-coordinate rhodium(I) complexes. However, $[RhCl(SnCl_3)_2py_3]$,3) $[RhCl_2(SnCl_3)(\text{norbornadiene})_2]$,2) and $[RhCl_2(SnCl_3)(PhMe_2As)_3]$ 2) have been reported to be presumably six-coordinate complexes. These can be thought to be rhodium(III) complexes containing trichlorostannato groups.

In the present work, while the Rh(III)-Sn(II) system in hydrochloric acid solution was being studied, new six-coordinate rhodium(III) complexes with trichlorostannato(II) ligands were obtained.

EXPERIMENTAL

Preparation of $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$: $RhCl_3\cdot 3H_2O$(150 mg, 0.57 mmol) in 3 M hydrochloric acid solution was treated with $SnCl_2\cdot 2H_2O$(386 mg, 1.71 mmol) for 70 min in a boiling water bath. Initial concentration of tin(II) was 0.05 M. After the resulting dark red solution had been kept at below -5 °C for 20 hr, addition of $(CH_3)_4NCl$ yielded an orange-yellow salt(complex-1) which was filtered and washed with 3 M hydrochloric acid solution containing a small amount of $(CH_3)_4NCl$ and then with 3 M hydrochloric acid, successively, and dried in vacuo. (Yield, 50%).

Preparation of $[(CH_3)_4N]_3[RhBr_3(SnCl_3)_3]$: $RhCl_3 \cdot 3H_2O$ was treated with tin(II) in the same way as in the preparation of $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$. To the dark red solution kept at below -5 °C, hydrobromic acid was added to give 0.2 M bromide concentration. The solution turned bright red. Addition of $(CH_3)_4NCl$ yielded an orange-red salt(complex-2) which was filtered and washed with 0.2 M hydrobromic-3 M hydrochloric acid solution containing a small amount of $(CH_3)_4NCl$ and then with 0.2 M hydrobromic-3 M hydrochloric acid solution, successively, and dried in vacuo. (Yield, 60%). Triethylammonium salts of the complexes were obtained when $(C_2H_5)_3NHCl$ was used as a precipitating reagent.

Determination of reduction equivalent of complex-1: Complex-1 and a large excess of $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ were added to a mixed solution of 40 ml of 3 M hydrochloric acid and 10 ml of 0.5 M sulfric acid and the solution was heated for 6 hr in a boiling water bath under deoxygenated nitrogen. The amount of Fe(II) formed by the reaction of Fe(III) with complex-1 was determined by potentiometric titration with 0.05 N standard dichromate solution using glass and platinum electrodes as reference and indicator electrodes, respectively.

Measurements: The infrared spectra were recorded as Nujol mulls using a JASCO model IR-F spectrophotometer over the range of 700∿200 cm^{-1}. The electronic spectra were measured with HITACHI-181 and -124 spectrophotometers at 10 °C.

RESULTS AND DISCUSSION

Table 1. Elemental analyses of complex-1 and -2.

	(%)	Rh	Sn	Cl	Br	C	H	N
complex-1	Found	9.33	32.0	38.62	---	12.89	3.16	3.70
$[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$	Calcd	9.30	32.17	38.43	---	13.02	3.28	3.80
$[(CH_3)_4N]_3[RhCl(SnCl_3)_3]$	Calcd	9.93	34.37	34.22	---	13.91	3.51	4.06
complex-2	Found	8.17	28.7	25.6	19.6			
$[(CH_3)_4N]_3[RhBr_3(SnCl_3)_3]$	Calcd	8.30	28.71	25.72	19.33			
$[(CH_3)_4N]_3[RhBr(SnCl_3)_3]$	Calcd	9.53	32.96	29.53	7.40			

The complexes were analyzed carefully and repeatedly. The data in Table 1 indicate that the complexes obtained in this work are six-coordinate rhodium(III) complexes rather than four-coordinate rhodium(I) complexes.

One mole of complex-1 corresponded to 5.96 equivalent weight in the oxidation reduction reaction with Fe(III)/Fe(II). This value together with the data in Table 1 suggests that complex-1 is not the salt of $[Rh^{I}Cl(Sn^{II}Cl_3)_3]^{3-}$ but that of $[Rh^{III}Cl_3(Sn^{II}Cl_3)_3]^{3-}$. It can be seen from the table that three chloro ligands of complex-1 were substituted by bromide ions to give complex-2.

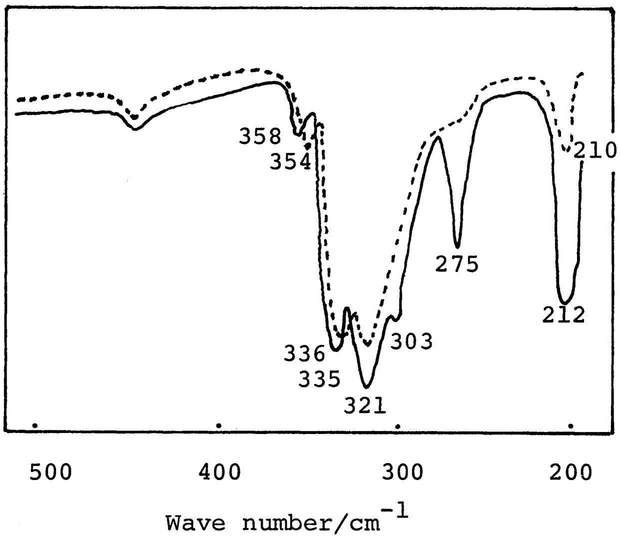

Figure 1. IR spectra of complex-1 and-2.
—— complex-1, $[(CH_3)_4N]_3[RhCl_3(SnCl_3)_3]$
······ complex-2, $[(CH_3)_4N]_3[RhBr_3(SnCl_3)_3]$

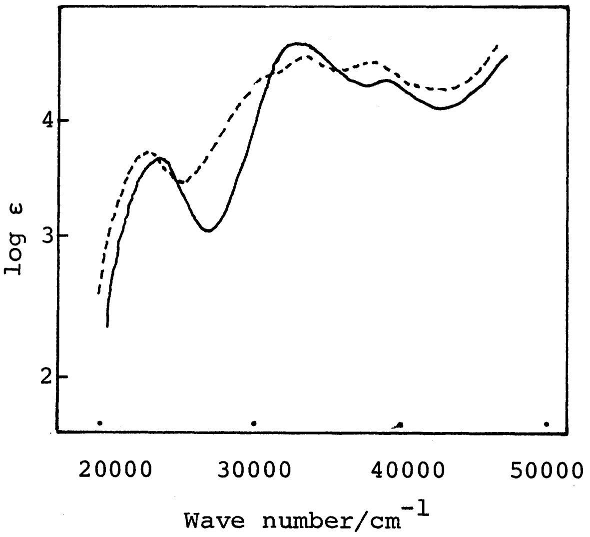

Figure 2. Electronic spectra of complex -1 and -2. —— complex-1, ---- complex-2.

Figure 1 shows the infrared spectra of complex-1 and -2. The bands in the region 370∿270 cm^{-1} and about 210 cm^{-1} can be assigned to the stretching vibrations of metal-chloride and rhodium-tin, respectively, in accordance with the assignments on similar complexes.1), 3), 4) The 303 and 275 cm^{-1} bands in complex-1 could not be observed in complex-2. These bands can be assigned to the Rh-Cl stretching vibrations and the Rh-Br stretching vibrations in complex-2 can be expected to be observed below 200 cm^{-1}.

Figure 2 shows the electronic spectra of complex-1 and -2 [$\bar{\nu}_{max}$/cm^{-1}(logε): 23400 (3.64), 33100(4.47), 38900(4.19) for complex-1; 22800(3.70), 33600(4.37), 37300(4.27) for complex-2]. The absorption maximum in the visible region shifted to the lower wave number side and the intensity of the peak increased by the substitution of chloro ligands with bromide ions. The spectrum of complex-1 in 3 M hydrochloric acid solution and that of complex-2 in 0.2 M hydrobromic-3 M hydrochloric acid solution did not change for at least 60 min. When complex-1 was dissolved in 0.2 M hydrobromic-

3 M hydrochloric acid solution, the electronic spectrum of the solution was identical with that of complex-2 in 0.2 M hydrobromic-3 M hydrochloric acid solution. Further, addition of $(CH_3)_4NCl$ to the solution gave an orange-red product which was identified as complex-2 on the basis of the IR spectra of the two. These findings can be explained in terms of rapid substitution of three chloro ligands in complex-1 with bromide ions. Also, the measurements of electronic and IR spectra showed that complex-2 dissolved in 3 M hydrochloric acid solution rapidly changed to $[RhCl_3(SnCl_3)_3]^{3-}$.

These observations show that the three halogeno ligands coordinate directly to rhodium(III) and they are substituted rapidly and reversibly. Furthermore, the 303 and 275 cm^{-1} bands assigned to the Rh-Cl stretching vibrations for complex-1 are observed in a lower region than those for the corresponding Rh-Cl stretching vibrations for six-coordinate rhodium(III) complexes 5) which do not contain strongly trans-activating ligands 6) such as $SnCl_3^-$.

The fact that the three halogeno ligands are substituted rapidly and that the Rh-Cl stretching vibrations are observed in a lower region can be explained in terms of the strong trans effect and the π-acceptor ability 7) of an $SnCl_3$ group. Complex-1 and -2 can be considered to be fac-isomers rather than mer-isomers. The fac-isomer is thought to be more thermodynamically stable than the mer-isomer according to the π-acceptor ability of the $SnCl_3$ groups. 1), 7)

Thus, in conclusion, it can be said that the complexes prepared in this work are new six-coordinate rhodium(III) complexes containing trichlorostannato(II) groups and their structure is probably facial.

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