May, 1986] © *1986 The Chemical Society of Japan* **NOTES** *Bull. Chem. Soc. Jpn., 59, 1597—1598 (1986)* 1597

Silver *cis*-Tetrachlorohydroxonitrosylruthenate (2–)

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(Received January 13, 1986)

Synopsis. A new chloronitrosylruthenate ion was separated from the hydrolysis mixture of $[RuCl_5(NO)]^{2-}$ by the anion-exchange method, and it formed $Ag_2[RuCl_4(OH)(NO)]$ on the addition of silver nitrate. The anion of the silver salt was found to have the cis form on the basis of its IR spectrum.

Silver and ammonium salts of $[RuCl_4(OH)(NO)]^{2-}$ were prepared from the hydrolysis mixture of $[RuCl_5(NO)]^{2-}$ by Mercer et al.[1–3] The anion of these salts and its protonated aqua complex have been considered to have the trans form.[1–3] Separation of the possible isomers of $[RuCl_4(H_2O)(NO)]^-$ was reported without identification of the isomers.[4] The authors isolated *cis*-$Ag_2[RuCl_4(OH)(NO)]$ from a component of the hydrolysis mixture of $[RuCl_5(NO)]^{2-}$.

Experimental

$(NH_4)_2[RuCl_5(NO)]$ was prepared by Fletcher's method.[5] Electronic spectra of complexes in aqueous solutions were recorded on a Hitachi 340 spectrophotometer, and IR spectra of the isolated complexes on JASCO A-202 and IR-F spectrometers.

Preparation of *cis*-$Ag_2[RuCl_4(OH)(NO)]$. A solution of $(NH_4)_2[RuCl_5(NO)]$ (2.4 g) in 0.01 mol dm^{-3} $HClO_4$ (40 cm^3) was heated at 50 °C for 6 h, and stored at 5 °C overnight. The species in the solution were separated with a QAE Sephadex A-25 column (the nitrate form, ϕ 4 cm×40 cm) at below 10 °C. After $[RuCl_2(H_2O)_3(NO)]^+$ and $[RuCl_3(H_2O)_2(NO)]$ had been eluted out of the column with 0.05 mol dm^{-3} HNO_3, the elution was continued until three separate adsorption bands appeared. Since $[RuCl_5(NO)]^{2-}$ was strongly adsorbed on the uppermost part of the column, the uppermost part was taken out of the column by using a suction pump. *trans*-$[RuCl_4(H_2O)(NO)]^-$ in the lower adsorption band of the remaining bands was eluted out with 0.1 mol dm^{-3} HNO_3. The species in the final adsorption band was eluted with 1 mol dm^{-3} $HClO_4$. The effluent was collected under cooling with ice-water and it gave a silver salt on the addition of 5 wt% $AgNO_3$ solution. The silver salt was filtered off, washed with dilute HNO_3 containing a small amount of $AgNO_3$ and dilute HNO_3 successively, and then dried in a vacuum desiccator with $CaCl_2$ and NaOH. Yield, 80 mg. Found: Ru, 20.1; Cl, 28.35; N, 2.85%. Calcd for $Ag_2[RuCl_4(OH)(NO)]$: Ru, 19.99; Cl, 28.10; N, 2.77%.

Electronic spectra of $[RuCl_2(H_2O)_3(NO)]^+$, $[RuCl_3(H_2O)_2(NO)]$, and *trans*-$[RuCl_4(H_2O)(NO)]^-$ in the effluents were the same as those reported by Mercer et al.[1] *trans*-$Ag_2[RuCl_4(OH)(NO)]$ was prepared according to Ref. 1 by the addition of 5 wt% $AgNO_3$ solution to the *trans*-$[RuCl_4(H_2O)(NO)]^-$ solution separated.

Results and Discussion

The silver salt newly prepared had the formula, $Ag_2[RuCl_4(OH)(NO)]$, and was isomeric with *trans*-$Ag_2[RuCl_4(OH)(NO)]$ prepared by Mercer et al.[1]

The IR data of the new salt are shown in Table 1, together with those of *trans*-$Ag_2[RuCl_4(OH)(NO)]$ prepared. The IR bands were assigned by referring to Refs. 2, 6, and 7. The spectra of the trans salt were the same as those reported by Mercer et al.[2] The IR spectrum of the new salt in the Ru–Cl stretching region was clearly different from that of the trans salt. The trans salt gave two bands assigned to a doubly degenerate Ru–Cl stretching vibration and a totally symmetric Ru–Cl stretching vibration. The new salt gave three bands due to nondegenerate Ru–Cl stretching vibrations. *cis*-$[PtCl_4(NH_3)_2]$[8] and *cis*-$[SnCl_4(bpy)]$[9] gave typically four bands due to the metal–Cl stretching vibtations. However, it has been also observed that the number of the Sn–X stretching bands for *cis*-$[SnX_4(L–L)]$(X=Cl, Br, or I; L–L=phen, 1,2-bis(methylthio)ethane, or 1,2-bis(diphenylphosphino)ethane) ranges from two to four.[9] The three bands observed for the new salt strongly indicate that the new salt is the silver salt of *cis*-$[RuCl_4(OH)(NO)]^{2-}$.

The N–O stretching frequencies of the two salts show that the anions of both salts are of the linear

Table 1. Wavenumbers/cm^{-1} and Assignments of IR Bands for *trans*- and the New $Ag_2[RuCl_4(OH)(NO)]$

Assignment	O-H str	N-O str	O-H bend	a)	Ru-OH str	Ru-Cl str
Trans salt	3545 m	1888 vs	916 m, br	610 sh	519 s, br	327 vs
				597 m		297 vw
New salt	3500 m	1908 vs	810 m, br	585 sh	503 s, br	332 vs
				577 m		301 s
						275 m

a) Skeletal vibrations between Ru and NO. Abbreviations: str=stretching, bend=bending, vs=very strong, s=strong, m=medium, vw=very weak, sh=shoulder, br=broad.

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{RuNO}^{6} type.[10] Both OH^- and Cl^- are largely σ-bonding ligands, while π-donor ability of OH^- is greater than that of Cl^-. The NO in trans salt's anion is considered to withdraw more π electron density from the Ru than the NO in new salt's anion of the cis form. This can explain the results that the N–O stretching frequency of the trans salt was smaller than that of the new salt and the frequencies of the skeletal vibrations due to the RuNO group of the trans salt were greater than those of the new salt. The same results were observed for *trans*-$[RuL(NH_3)_4(NO)]^{2+}$(L=OH, or Cl)[11]; the N–O stretching frequency for the chloro complex (1880 cm^{-1}) was greater than that for the hydroxo complex (1841 cm^{-1}) and the frequencies of the skeletal vibrations due to the RuNO group for the chloro complex (562 and 603 cm^{-1}) were smaller than those for the hydroxo complex (589 and 630 cm^{-1}).

In complexes of the linear {RuNO}^{6} type, the NO is such a good π-acceptor and poor σ-donor that rather than a competition between the NO and the *trans*-L ligand for the same orbitals, there is mutual reinforcement in both Ru–NO and Ru–L bonds when L is a good σ-donor and poor π-acceptor, e.g. Cl^- or OH^-.[12] Therefore, the OH^- trans to the NO is considered to bind to the Ru more strongly than the OH^- cis to the NO. This can explain the results that each frequency of ν_{O-H}, δ_{O-H}, and ν_{Ru-OH} of the new salt was smaller than that of the trans salt.

On the basis of the IR data discussed above, the anion of the new salt can be assigned to the cis form.

In $[RuCl_5(NO)]^{2-}$, the Ru–Cl bonds cis to the NO were found to be longer than that trans to the NO[13] and were also indicated to be weaker than that trans to the NO.[14] Hydrolysis of the Cl ligand in *cis*-$[RuCl(NH_3)_4(NO)]^{2+}$ was found to be faster than the corresponding hydrolysis in *trans*-$[RuCl(NH_3)_4(NO)]^{2+}$.[15] Consequently, the formation of *cis*-$[RuCl_4(H_2O)(NO)]^-$ can be expected in the first step of the hydrolysis of $[RuCl_5(NO)]^{2-}$ in an acid solution. For the process of the preparation of the new salt, it can be also considered that the *cis*-$[RuCl_4(H_2O)(NO)]^-$ is separated from the hydrolysis mixture and it forms *cis*-$Ag_2[RuCl_4(OH)(NO)]$ on the addition of silver nitrate.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 58470038 from the Ministry of Education, Science and Culture.

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