BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (2), 619—620 (1979)

# Preparation of Potassium Glycinatotrihydroxonitrosylruthenate(II)

Toshio Ishiyama* and Takashi Matsumura
*Radiation Center of Osaka Prefecture, Shinke-cho, Sakai, Osaka 593*

(Received March 3, 1978)

**Synopsis.** A new mono-glycinato complex of hydroxonitrosylruthenium(II), K[Ru(gly)$(OH)_3NO$] was isolated by use of ion exchange resin from the product formed by the reaction of $[RuCl_3(H_2O)_2NO]$ with glycine. The complex was characterized by means of infrared, visible, and ultraviolet absorption spectra, capillary type isotachophoresis, magnetic moment and molar conductivity.

The hydroxonitrosylruthenium(II) complex with amino acid is not known. Belot and Pignon[1] studied the behavior of nitrosylruthenium in the presence of potentially complexing organic compounds. They reported that the mercapto carboxylic acids were the best complexing agents and that the complex formation of nitrosylruthenium(II) hydroxide with mercaptoacetic acid could evidenced by measuring the relative amount of dissolved species with ultra-filtration or gel chromatography. In the present paper we report on potassium glycinatotrihydroxonitrosylruthenate(II).

## Experimental

*Materials.* Commercial ruthenium(III) chloride monohydrate (Mitsuwa Chemicals and Co.) and glycine (extra pure grade, Kishida Chemicals and Co., Ltd.) were used. Commercial Dowex 1×4 sieved to a fraction of 100—200 mesh was used as anion exchange resin. The resin was converted into the Cl-form by treatment with 2 M NaOH and 2 M NaCl in a beaker. The resin was washed with distilled water until the chloride ion was no longer detected in the washing. The Cl-form resin was dried at 60 °C for 48 h and then stored in a desiccator.

*Preparation.* *Diaquatrichloronitrosylruthenium(II),* $[RuCl_3(H_2O)_2NO]$: The complex was prepared by a modification of the method of Fletcher *et al.*[2] After the solution of nitrosyl derivative formed by the reaction of ruthenium(III) chloride with sodium nitrite has been adjusted to pH 6.4 with 2 M sodium hydroxide, the solution was evaporated to dryness and extracted with ethanol. The crystals formed by the removal of ethanol by distillation were dried *in vacuo.* (Found: Ru, 36.05; H, 1.74; N, 5.26; Cl, 39.36%. Calcd for $[RuCl_3(H_2O)_2NO]$: Ru, 36.95; H, 1.46; N, 5.12; Cl, 38.92%).

*Potassium Glycinatotrihydroxonitrosylruthenate(II),* K[Ru(gly)$(OH)_3NO$]: Diaquatrichloronitrosylruthenium(II) (3 g) was dissolved in 20 ml of distilled water. To this was added a solution obtained by dissolving 1.2 g of glycine in a small amount of distilled water. The resulting solution was refluxed on a hot-water bath for 3 h. This was concentrated and then cooled in a refrigerator for several days. The crystals formed were filtered and dissolved in 5 ml of distilled water. The solution was passed through a column (diam. 11 mm, height 245 mm) filled with Cl-form anion exchange resin. The adsorbed complex was eluted with 2 M KCl. After the eluent had been concentrated, potassium chloride deposited was filtered off. The crystals formed were filtered, recrystallized from water and dried *in vacuo.* The complex is insoluble in organic solvents. Found: K, 13.76; Ru, 33.80; C, 8.19; H, 2.60; N, 9.89; yield 36.84%. Calcd for $K[Ru(H_2N\text{-}CH_2\text{-}COO)(OH)_3NO]$: K, 13.24; Ru, 34.23; C, 8.13; H, 2.39; N, 9.49%.

*Measurements.* Potassium in the complex was determined as follows. Potassium was precipitated with 2% sodium tetraphenylborate solution. After being filtered and washed, the precipitate was dissolved in acetone. To this solution was added excess mercury(II)–EDTA, and the EDTA liberated was back-titrated with a standard zinc solution using a PAN indicator.[3] Ruthenium in the complex was determined spectrophotometerically by measuring the absorbance at 465 nm after thermal decomposition of the complex at 320 °C followed by alkali fusion.[4] Infrared absorption spectra were measured in KBr disks on a JASCO Model IR-S infrared spectrophotometer. Magnetic susceptibility was measured by the Faraday method[5] at 20 °C with a Cahn R. G. electrobalance. Molar conductivity was measured at 20 °C with Yanagimoto Model MY-7 conductivity outfit. Isotachophoresis was measured with a Shimadzu Model IP-1B capillary tube isotachophoretic analyzer as described below. 1.8 mg of potassium glycinatotrihydroxonitrosylruthenate(II) was dissolved in 500 μl of distilled water. A 10 μl portion of the aqueous solution of the sample was poured into a capillary tube, length 20 cm, inner diam. 0.57 mm. An aqueous mixture solution of 0.01 M ammediol–HCl adjusted to pH 8.8 was used as the leading electrolyte, and an aqueous mixture solution of 0.01 M $\beta$-alanine–$Ba(OH)_2$ adjusted to pH 10.9 as the terminal electrolyte. The electrophoreogram was recorded with migration current and migration time 100 μA and 20 min, respectively.

## Results and Discussion

It was found from the electrophoreogram shown in Fig. 1 that the complex behaves like an anionic species in electrophoretic migration. A potential gradient inversely proportional to the mobility was obtained, the potential unit value (*PU* value) of the sample being calculated from the relative ratio of the potential gradient of leading electrolyte and the sample zone by means of the following equation:[6]

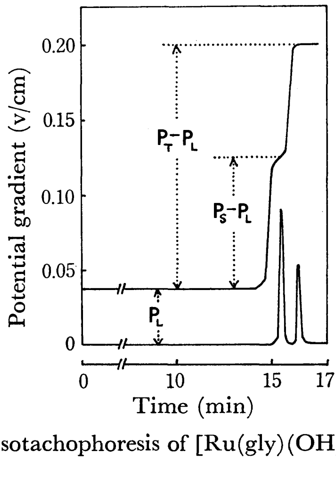

Fig. 1. Isotachophoresis of $[Ru(gly)(OH)_3NO]^-$.

$$PU \text{ value} = \frac{P_S - P_L}{P_T - P_L} = 0.531,$$

where $P_S$: potential gradient of the sample,

$P_L$: potential gradient of leading electrolyte,

$P_T$: potential gradient of terminating electrolyte.

The leading electrolyte has a mobility larger than that of the sample and the terminating electrolyte a smaller mobility. The $PU$ value 0.531 indicates that the mobility of the complex anion is nearly intermediate between that of 0.01 M ammediol–HCl at pH 8.8 and 0.01 M $\beta$-alanine–$Ba(OH)_2$ at pH 10.9, assuming the formation of mono-glycinato complex anion of hydroxonitrosylruthenium(II) in weak alkali solution.

From the results of elemental analysis, the ratio of potassium, ruthenium, carbon, hydrogen and nitrogen of the complex was found to be 1: 1: 2: 7: 2. The molar conductivity of aqueous solution of the complex was 143.6 $\Omega^{-1}$ cm$^2$ mol$^{-1}$, showing that the complex is a 1: 1 type electrolyte.

TABLE 1. THE CHARACTERISTIC INFRARED ABSORPTION BANDS OF THE PRESENT Ru(II) COMPLEX (cm$^{-1}$)

| Assignment | Glycine | $K[Ru(gly)(OH)_3NO]$ |
|---|---|---|
| $\nu$(N–H) | 3480 | 3400 |
| $\nu$(O–H) | | 3060 |
| $\nu$(O–D) | | 2140 |
| $\nu$(N–O) | | 1865s—1825br |
| Antisymmetric $\nu$(COO) | 1595 | 1603 |
| Symmetric $\nu$(COO) | 1399 | 1395 |
| $\nu$(C–N) | 1034 | 1030sh |

s=strong, br=broad, sh=shoulder.

The main infrared absorption bands of the present complex are given in Table 1, together with those of the pure ligand. The absorption band at 1850 cm$^{-1}$ was assigned to the $NO^+$ stretching vibration of nitrosyl group. The band shifted to the lower frequency side than that of the original complex, $[RuCl_3(H_2O)_2NO]$ by the chelation of glycine. A similar observation has been reported for $[RuCl_3(phen)NO]$ by Lewis *et al.*7) The absorption band at 3400 cm$^{-1}$ was assigned to N–H stretching vibration of the $NH_2$ group by comparison with the peak at 3480 cm$^{-1}$ of glycine. The absorption band at 1030 cm$^{-1}$ was assigned to C–N stretching vibration arising from skeleton stretching of glycine. The band at 3060 cm$^{-1}$, assigned to the OH stretching frequency, shifted after deuteration to 2140 cm$^{-1}$. The new glycinatohydroxonitrosylruthenate(II) complex was identified from the IR-data.

The electronic absorption spectrum of the complex, $K[Ru(gly)(OH)_3NO]$ was measured in aqueous solution (pH=6.15), and compared with that of the starting complex, $[RuCl_3(H_2O)_2NO]$ reported by Mercer *et al.*8) The spectrum is shown in Fig 2.. Potassium glycinatotrihydroxonitrosylruthenate(II), $K[Ru(gly)(OH)_3NO]$ has three shoulders and a peak at 540, 390, 335, and 265 nm, respectively. The 540 nm shoulder may be assigned to the d-d transition. In spite of no appearance of an absorption band of $[RuCl_3(H_2O)_2NO]$ in the ultraviolet region, the appearance of the characteristic peak of $K[Ru(gly)(OH)_3NO]$ at 265 nm may be attributed to the ligation of glycine.

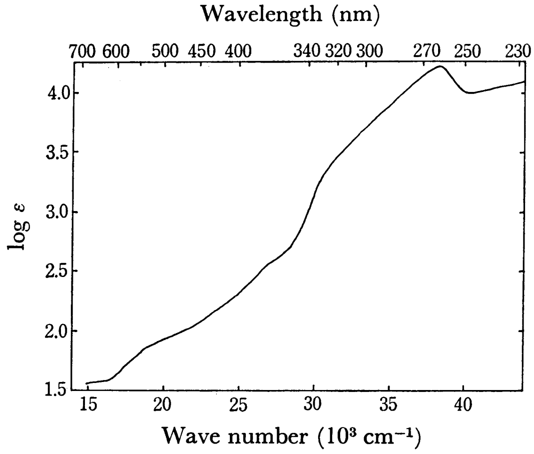

Fig. 2. Electronic spectrum of $K[Ru(gly)(OH)_3NO]$ in $H_2O$ (pH=6.15).

The observed diamagnetism of $K[Ru(gly)(OH)_3NO]$ indicates that the ruthenium atom has spin-paired $d^6$ configuration, suggesting that the complex can be formulated by the donation from $NO^+$ ion. The stereochemical configuration of $K[Ru(gly)(OH)_3NO]$ is not clear, but a facial or meridional formula can be proposed.

The authors wish to express their thanks to Prof. Masayasu Mori and Dr. Shigeichi Kubo, Osaka City University, for their guidance in the measurement of magnetic susceptibility. Thanks are also due to Dr. Yasuyo Shiogai, Shimadzu Seisakusho Ltd. for carrying out the isotachophoretic analysis.

## References

1) Y. Belot and N. Pignon, *Health Phys.*, **15**, 443 (1968).

2) J. M. Fletcher, I. L. Jenkins, F. M. Lever, A. R. Martin, A. R. Powell, and R. Todd, *J. Inorg. Nucl. Chem.*, **1**, 378 (1955).

3) H. Flaschka and F. S. Sadek, *Chem. Anal. (Warsaw)*, **47**, 30 (1958).

4) E. D. Marshall and R. R. Rickard, *Anal. Chem.*, **22**, 795 (1950).

5) L. N. Mulay, "Magnetic Susceptibility," Wiley, New York, Sydney (1963), p. 1836.

6) J. Akiyama, T. Mizuno, and Y. Shiogai, *Shimadzu Review*, **34**, 111 (1977).

7) J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

8) E. E. Mercer, W. M. Campbell, and R. M. Wallace, *Inorg. Chem.*, **3**, 1018 (1964).