

## Electronic Structures of *cis* and *trans* Tetraammine-ruthenium(III) Complexes

SUSUMU KOHATA

Yatsushiro College of Technology, Hirayamachinmachi, Yatsushiro 866, Japan

and AKIRA OHYOSHI\*

Faculty of Engineering, University of Kumamoto, Kumamoto 860, Japan

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### Introduction

The stereochemical isomers of the complexes  $\text{RuCl}_2(\text{NH}_3)_4^+[\text{A}]$  and  $\text{RuCl}(\text{OH}_2)(\text{NH}_3)_4^{2+}[\text{B}]$  reveal a different profile in chemical behavior: (i) the redox potential of the *trans*-[a] is more negative than that of the *cis*-[A] [1], (ii) the *cis*-[A] gives more increased rate constant for the aquation reaction than does the *trans*-[A], while (iii) the anation reaction proceeds only in the *trans*-[B], and (iv) the thermal stability in a solid state is enhanced in the *trans*-[A] rather than in the *cis*-[A]. In order to elucidate these behavior, electronic structures have been examined for stability or reactivity of two stereochemical isomers of tetraammineruthenium(III) complexes.

### Method

The method used for MO calculation is the INDO-type Unrestricted Hartree Fock (UHF) method, which has been described in detail elsewhere [2]. All of the parameters used here are the same one as presented previously [3].

\*To whom correspondence should be addressed.

TABLE I. Electronic Structures of  $\text{RuCl}_2(\text{NH}_3)_4^+[\text{A}]$  and  $\text{RuCl}(\text{OH}_2)(\text{NH}_3)_4^{2+}[\text{B}]$ .

Complex	Cis-isomer		Trans-isomer	
	[A] <sup>a</sup>	[B]	[A]	[B]
$E_{\text{AB}}^{\text{b}}$ (eV)				
<i>cis</i> -Ru–NH <sub>3</sub>	–10.34	–10.98	–10.44	–10.58
<i>trans</i> -Ru–NH <sub>3</sub>	–10.33	–10.78		
Ru–Cl	–14.75	–15.28	–14.43	–15.47
Ru–OH <sub>2</sub>		–4.70		–4.36
SOMO energy (eV)	–5.81	–10.10	–6.75	–10.18
LUMO energy (eV)	–4.53	–9.07	–4.66	–99.14
Total nergy (eV)	–2202.97	–2241.59	–2203.21	–2241.34

<sup>a</sup>From Ref. 3. <sup>b</sup>A large value of  $E_{\text{AB}}$  indicates a strong interaction between atoms A and B.

### Results and Discussion

The  $d^5$  electron-configurations of Ru(III) have investigated for two cases of I  $[(d_{xy}^2)/(d_{xz}^2, d_{yz}^1)]$  and II  $[(d_{xz}^2, d_{yz}^2)/(d_{xy}^1)]$ . From the total energies the configuration I is taken as a ground state; those are I (–2203.21 eV), II (–2202.84 eV) for *trans*- $\text{RuCl}_2(\text{NH}_3)_4^+$ , and I (–2241.34 eV), II (–2241.32 eV) for *trans*- $\text{RuCl}(\text{OH}_2)(\text{NH}_3)^{2+}$ . The reason for stabilizing this configuration is attributable to the  $d_{\pi}$ – $p_{\pi}$  bonding interactions between the Ru half-occupied  $d_{\pi}$ -orbital and the Cl  $p_{\pi}$ -orbital in the configuration I. Calculated results are shown in Table I.

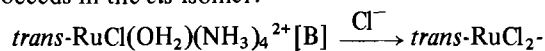
Suggested electronic stability by the total energy is *cis*- $\text{RuCl}_2(\text{NH}_3)_4^+ < \text{trans}$ - $\text{RuCl}_2(\text{NH}_3)_4^+$ , and *trans*- $\text{RuCl}(\text{OH}_2)(\text{NH}_3)_4^{2+} < \text{cis}$ - $\text{RuCl}(\text{OH}_2)(\text{NH}_3)_4^{2+}$ . The stability then may not necessarily depend on the stereochemical configuration with respect to these four complexes.

Both in [A] and [B] complexes, the Ru–NH<sub>3</sub> bond is slightly stronger in the *trans*-isomer than in the *cis*-isomer of *ca.* 0.1–0.4 eV (see the value of  $E_{\text{Ru–NH}_3}$ ). The Ru–OH<sub>2</sub> bond strength of the complex [B] is weakened *ca.* 1.0 eV for *cis*-[B] and *ca.* 1.4 eV for *trans*-[B] relative to  $\text{Ru}(\text{OH}_2)(\text{NH}_3)_5^{3+}$  [3]. The chloride ligand then reveals a *trans* or *cis* influence on the water molecule, with the influence of the former being greater than that of the latter.

The redox potential for  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  couple (*vs.* SCE) observed is –0.274 V for *cis*- $\text{RuCl}_2(\text{NH}_3)_4^+$  and –0.380 V for *trans*- $\text{RuCl}_2(\text{NH}_3)_4^+$  [1]. The calculated SOMO energy level is *trans* (–6.75 eV)  $< \text{cis}$  (–5.81 eV), which implies that *trans*- $\text{RuCl}_2(\text{NH}_3)_4^+$  is less easily reduced than is the *cis*. The electrochemical stability of two isomers is consequently supported as *cis*-complex  $< \text{trans}$ -complex.

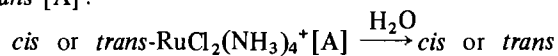
The kinetic studies have showed that the anation reaction proceeds only in *trans*- $\text{RuCl}(\text{OH}_2)(\text{NH}_3)_4^{2+}$

through an  $S_N2$  type mechanism\*, but it scarcely proceeds in the *cis*-isomer:



$(\text{NH}_3)_4^+[\text{A}] + \text{H}_2\text{O}$ . The difference of the total energy between [B] and [A] is minor when *trans*- ( $\Delta E = 38.13$  eV) rather than *cis*-configurations ( $\Delta E = 38.63$  eV) are taken. This difference suggests that the *trans*-[B] may be favorable to the above anation reaction. The proposed reaction path might be an  $S_N2$  type mechanism: the LUMO energy level is  $-9.07$  and  $-9.14$  eV for *cis*-[B] and *trans*-[B] respectively, suggesting less advantage of *trans*-[B] for this associative mechanism. The electronic repulsion between two halogens concerning the anation product [A] is enhanced when they are at the *cis*-position (1.258 eV) rather than being at the *trans*-position (0.684 eV). This remarkable repulsion in *cis*-configuration should make it too difficult for the chloride ion to migrate from the outer-sphere to the coordination sphere.

The aquation reaction proceeds in both isomers of [A] through an  $S_N2$  type mechanism\*\*, but the rate constant of *cis*-[A] is 2.5-fold larger than that of *trans*-[A]:



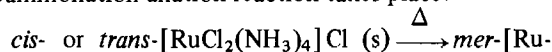
$\text{RuCl(OH}_2\text{)(NH}_3\text{)}_4^{2+}[\text{B}] + \text{Cl}^-$ . The difference of the total energy between [A] and [B] again suggests that the *trans* isomer may have a preference for the aquation reaction. The LUMO energy levels, however, are  $-4.53$  and  $-4.66$  eV for *cis*-[A] and *trans*-[A], respectively. The larger rate constant (or small value of  $\Delta H^\ddagger$ ) of *cis*-[A] through an  $S_N2$  reaction path

\*Kinetic parameters for *trans*-[B];  $k = 1.42 \times 10^{-4} \text{ M}^{-1} \cdot \text{S}^{-1}$  ( $54.7^\circ\text{C}$ ,  $\mu = 0.1$ ),  $\Delta H^\ddagger = 89.5 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -25 \text{ JK}^{-1} \text{ mol}^{-1}$ . For *cis*-[B],  $k$  is significantly small.

\*\*Kinetic parameters for *cis*-[A];  $k = 7.55 \times 10^{-4}$  ( $75.0^\circ\text{C}$ ,  $\mu = 0.1$ ),  $H = 77.0$ ,  $\Delta H^\ddagger = 77.0$ ,  $\Delta S^\ddagger = -79$ . For *trans*-[A];  $k = 3.02 \times 10^{-4}$  ( $75.0^\circ\text{C}$ ,  $\mu = 0.1$ ),  $\Delta H^\ddagger = 92.9$ ,  $\Delta S^\ddagger = -46$ .

may be elucidated with this LUMO level, because there is no remarkable repulsion between coordinated ligand and introduced ligand.

The thermal stability of  $[\text{RuCl}_2(\text{NH}_3)_4]\text{Cl}[\text{A}]$  is investigated in the solid state. In this complex, the deammonation-anation reaction takes place:



$\text{Cl}_3(\text{NH}_3)_3]$  (s) +  $\text{NH}_3(\text{g})$ . The initiation temperature for the deammonation is  $200$  and  $227^\circ\text{C}$  for *cis*-[A] and *trans*-[A] respectively, on a TG-curve with a heating rate of  $10^\circ\text{C min}^{-1}$ . The heat for the above deammonation step, estimated from DTA-curve, is *ca.*  $11 \text{ kJ mol}^{-1}$  for *cis*[A] and *ca.*  $60 \text{ kJ mol}^{-1}$  for *trans*-[A]. Thermal analysis data lead to a consideration that the order of thermal stability is *cis*-[A] < *trans*[A], consistent with the presumption from the calculated total energy. The order of deammonation also corresponds to that of the Ru-NH<sub>3</sub> bond strength indicated by the  $E_{\text{Ru-NH}_3}$  value; *cis*-[A] ( $-10.33$  eV for *trans*-Ru-NH<sub>3</sub>) < *trans*-[A] ( $-10.44$  eV for *cis*-Ru-NH<sub>3</sub>).

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