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Electronic Structures of *cis* and *trans* Tetraammineruthenium(III) Complexes

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Introduction

The stereochemical isomers of the complexes $RuCl_2(NH_3)_4^+$[A] and $RuCl(OH_2)(NH_3)_4^{2+}$[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].

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*-$RuCl_2(NH_3)_4^+$, and I (–2241.34 eV), II (–2241.32 eV) for *trans*-$RuCl(OH_2)(NH_3)^{2+}$. The reason for stabilizing this configuration is attributable to the d_π–p_π bonding interactions between the Ru half-occupied d_π-orbital and the Cl p_π-orbital in the configuration I. Calculated results are shown in Table I.

Suggested electronic stability by the total energy is *cis*-$RuCl_2(NH_3)_4^+$ < *trans*-$RuCl_2(NH_3)_4^+$, and *trans*-$RuCl(OH_2)(NH_3)_4^{2+}$ < *cis*-$RuCl(OH_2)(NH_3)_4^{2+}$. 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_3 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_{Ru-NH_3}). The Ru–OH_2 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 $Ru(OH_2)(NH_3)_5^{3+}$ [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 Ru^{III}/Ru^{II} couple (*vs.* SCE) observed is –0.274 V for *cis*-$RuCl_2(NH_3)_4^+$ and –0.380 V for *trans*-$RuCl_2(NH_3)_4^+$ [1]. The calculated SOMO energy level is *trans* (–6.75 eV) < *cis* (–5.81 eV), which implies that *trans*-$RuCl_2(NH_3)_4^+$ is less easily reduced than is the *cis*. The electrochemical stability of two isomers is consequently supported as *cis*-complex < *trans*-complex.

The kinetic studies have showed that the anation reaction proceeds only in *trans*-$RuCl(OH_2)(NH_3)_4^{2+}$

TABLE 1. Electronic Structures of $RuCl_2(NH_3)_4^+$[A] and $RuCl(OH_2)(NH_3)_4^{2+}$[B].

	Cis-isomer		*Trans*-isomer	
Complex	[A][a]	[B]	[A]	[B]
E_{AB}[b] (eV)				
cis-Ru–NH_3	–10.34	–10.98	–10.44	–10.58
trans-Ru–NH_3	–10.33	–10.78		
Ru–Cl	–14.75	–15.28	–14.43	–15.47
Ru–OH_2		–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

[a] From Ref. 3. [b] A large value of E_{AB} indicates a strong interaction between atoms A and B.

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

trans-$RuCl(OH_2)(NH_3)_4{}^{2+}$[B] $\xrightarrow{Cl^-}$ *trans*-$RuCl_2(NH_3)_4{}^+$[A] + H_2O. 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]:

cis or *trans*-$RuCl_2(NH_3)_4{}^+$[A] $\xrightarrow{H_2O}$ *cis* or *trans* $RuCl(OH_2)(NH_3)_4{}^{2+}$[B] + 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 $\Delta H^{\neq}$) of *cis*-[A] through an S_N2 reaction path may be elucidated with this LUMO level, because there is no remarkable repulsion between coordinated ligand and introduced ligand.

The thermal stability of $[RuCl_2(NH_3)_4]Cl$[A] is investigated in the solid state. In this complex, the deammonation-anation reaction takes place:

cis- or *trans*-$[RuCl_2(NH_3)_4]Cl$ (s) $\xrightarrow{\Delta}$ *mer*-$[RuCl_3(NH_3)_3]$ (s) + NH_3(g). The initiation temperature for the deammonation is 200 and 227 °C for *cis*-[A] and *trans*-[A] respectively, on a TG-curve with a heating rate of 10°C min^{-1}. The heat for the above deammonation step, estimated from DTA-curve, is *ca.* 11 kJ mol^{-1} for *cis*[A] and *ca.* 60 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_3 bond strength indicated by the $E_{Ru\text{-}NH_3}$ value; *cis*-[A] (–10.33 eV for *trans*-Ru–NH_3) < *trans*-[A] (–10.44 eV for *cis*-Ru–NH_3).

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

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