An MO-theoretical Approach to the Aquation Mechanism of Carboxylatopentaammineruthenium(III) Complexes in Acid Solutions

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The aquation mechanism of carboxylatopentaammineruthenium(III) complexes, $(NH_3)_5RuO_2CR^{2+}$, where R=H, CH_3, C_2H_5, $(CH_3)_2CH$, and CH_2OH, has been investigated with the Wolfsberg-Helmholz-LCAO-MO extended Hückel method augmented by metal d-orbitals. The very weak Ru–O coordination linkage (bond population=0.085—0.092) formed mainly by the antibonding $d_{z^2}p_z$-σ and p_zp_z-σ orbitals facilitates the heterolytic bond-breaking of the Ru–O (dissociation energy=4.61—9.22 kcal/mol), and the order of the bond populations of the Ru–O is well reflected in that of the overall aquation rates. The preferable structure of the protonated complex is $(NH_3)_5RuOHC(=O)R^{2+}$, produced by the interaction between the H^+ catalyst and the non-bonding lonepair orbital of the neighboring oxygen atom attached to the metal. The H_2O solvent was found to play an important role in the bond dissociation of the metal-oxygen linkage from a linear dependence between the reactivity index $(1/2N^{LU}_{z^2})$ of the protonated complex to such nucleophiles as H_2O and the activation energy for the S_N2 aquation reaction. The proposed tetragonal pyramidal intermediate of $(NH_3)_5Ru^{3+}$ combines easily the Ru–O through the lowest unoccupied d_{z^2} Ru-orbital, forming an aquo-complex with the binding energy of with H_2O linkage, 30.25 kcal/mol.

The aquation of carboxylatopentaammineruthenium(III) complexes (referred to as $(NH_3)_5RuO_2CR^{2+}$, where R=H, CH_3, C_2H_5, $(CH_3)_2CH$, and CH_2OH) has proved to be accelerated by an acid catalyst (H^+), in accordance with:1)

$$(NH_3)_5RuO_2CR^{2+} + H_2O \xrightleftharpoons[E_a=18.58-25.43\ \mathrm{kcal/mol}]{H^+} (NH_3)_5RuH_2O^{3+} + RCO_2^- \quad (1)$$

where E_a denotes the activation energy. A simulation analysis of the above aquation reaction has led to the proposing of the following reaction sequences of an S_N1 mechanism combined with an S_N2 one:2)

$$(NH_3)_5RuO_2CR^{2+} \xrightarrow[E_a=18.12-22.22\ \mathrm{kcal/mol}]{H^+} (NH_3)_5Ru^{3+} + RCO_2^- \quad (2a)$$

$$(NH_3)_5RuO_2CR^{2+} \xrightarrow[E_a=21.82-30.29\ \mathrm{kcal/mol}]{} (NH_3)_5Ru^{3+} + RCO_2^- \quad (2b)$$

$$(NH_3)_5Ru^{3+} + H_2O \xrightleftharpoons[E_a=6.869\ \mathrm{kcal/mol}]{E_a=2.094\ \mathrm{kcal/mol}} (NH_3)_5RuH_2O^{3+} \quad (2c)$$

where $(NH_3)_5Ru^{3+}$ stands for a momentarily living five-coordinated intermediate (tetragonal pyramidal structure). The five-coordinated intermediate has also proved to be plausible in an anation study3) of aquopentaammineruthenium(III) complexes.

In the aquation mechanism of carboxylatopentaammine complexes of Co(III),4-6) Rh(III),6) or Ir(III),6) however, there remain some obscurities in terms of the structure of the protonated complex, $(NH_3)_5MO_2CR^{n+}$—H^+ (M=central metal), the position of the bond-breaking of the complex (metal-oxygen or acyl-oxygen bond), and the reaction sequences (S_N1, S_N2, *etc.*).

Since the aquation mechanism is still open to question on a molecular level, it seems of interest and significant to reinvestigate the mechanism in connection with the electronic properties of the reactant, the intermediate, and the product in Reactions (2a—c).

Some extended-Hückel-MO-base SCF methods7) have been used to investigate the electronic structures of metal complexes. However, the reliability of such self-consistent charge and configuration-MO calculation depends directly on the parameters for the diagonal and off-diagonal Hamiltonian matrix elements. In this respect, the EHMO (without SCF) method seems to be useful so long as the parameters are suitably selected to explain such experimental results as d-orbital splittings, electron-excitation energies, *etc.* In our previous EHMO treatment of the pentacyanocobaltate(II) complex,8) it was found that the EHMO-method produced sufficient calculation results for the electronic property of the metal complex to be discussed qualitatively or quantitatively.

In this paper, we attempted to apply the Wolfsberg-Helmholz-LCAO-EHMO method9) to explain the electronic structures of ruthenium complexes, in connection with their aquation reactions.

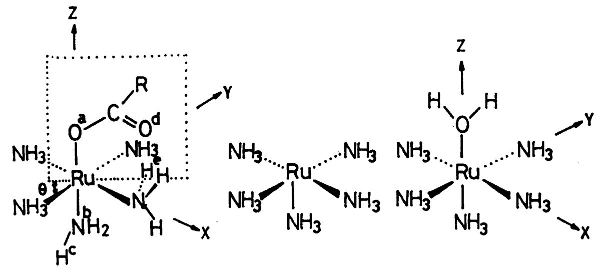
Method of Calculation

The following four systems were investigated in this work: (a) carboxylatopentaammineruthenium(III) complexes, $(NH_3)_5RuO_2CR^{2+}$ (R=H, CH_3, C_2H_5, $(CH_3)_2CH$, and CH_2OH), (b) an interacting system of $(NH_3)_5RuO_2CH^{2+}$ and the acid catalyst (H^+), (c) an intermediate, $(NH_3)_5Ru^{3+}$, and (d) an aquo-complex, $(NH_3)_5RuH_2O^{3+}$.

The diagonal terms for the central ruthenium metal orbitals, H_{ii}, are estimated from the negative of the valence-state ionization energies (VSIE) of Fe, Co, Rh, Ir, *etc.*; That is the VSIE values for the d, s, and p orbitals of Ru were, respectively, taken to be 12.0,10) 9.0,10) and 7.0 eV.10) The off-diagonal terms, H_{ij}, were evaluated by the Wolfsberg-Helmholz approximation:11)

$$H_{ij} = K(H_{ii}+H_{ij})S_{ij}/2$$

where K is a constant of 1.75 and where S_{ij} is the overlap integral between the *i*-th AO and the *j*-th AO. The orbital exponents were taken from Clementi,12)



Ru–O=2.5 Å; Ru–N=2.23 Å; N–H=1.031 Å

(NH$_3$)$_5$-RuO$_2$CR^2 (R)	C–C/Å	C–O/Å	C–O/Å	∠OCO	∠OCC or ∠OCH	∠COH
H	—	1.36	1.23	122.4°	118.8°	
CH$_3$	1.54	1.43	1.24	130°	120.5°	
C$_2$H$_5$	1.54	1.43	1.24	130°	120.5°	
(CH$_3$)$_2$CH	1.54	1.43	1.24	130°	120.5°	
CH$_2$OH	1.44	1.28	1.24	124°	120.5°	109°

Cited from L. E. Sutton, editor, "Interatomic Distances," The Chemical Society, London (1958).

Fig. 1. Geometries used for the calculation.

while the VSIE values for H, C, N, and O atoms were supplied by Hinze and Jaffe.[13]

The geometries used for the calculation are illustrated in Fig. 1; for simplicity of computation, the interatomic distances of Ru–O and Ru–N were uniformly taken to be the purely covalent bond lengths of 2.5 and 2.23 Å respectively, and the valence angle of Ru–O–C in the bond between the metal-carboxylato ligand was assumed to be 105° a value which corresponds to that of H–O–C of usual carboxylic acids (RC(=O)OH).

Calculated Results and Discussion

Electronic Property of (NH$_3$)$_5$RuO$_2$CR^{2+}. Mention should first be made of the molecular structure of (NH$_3$)$_5$RuO$_2$CR^{2+}. In the energetically stable state of (NH$_3$)$_5$RuO$_2$CR^{2+}, the RCO$_2$ ligand has a rotation angle of $\pi/4$ ($\theta=\pi/4$ in Fig. 1) in the direction of d$_{xz}$ Ru-orbital expansion; (NH$_3$)$_5$RuO$_2$CCH$_3$$^{2+}$ in the case of $\theta=\pi/4$ is, for example, energetically more stable by 18.34 kcal/mol than that in the case of $\theta=0$. In such a situation, an intramolecular hydrogen bonding can be expected between the carbonyl oxygen of the RCO$_2$ ligand and the hydrogen atom of the ammine group (see Table 1). This hydrogen bond may stabilize the complex molecule.

Now, let us examine the d-orbital splittings and electron-excitation energies of (NH$_3$)$_5$RuO$_2$CR^{2+} in order to check the reliability of the calculation results. The d-orbital separation of (NH$_3$)$_5$RuO$_2$CR^{2+} is very similar to that of usual octahedral metal complexes such as M(NH$_3$)$_6$$^{3+}$, and M(NH$_3$)$_5H_2$O^{3+}; that is, the separation is shown by triply-degenerate d$_{xy}$, d$_{yz}$, and d$_{xz}$ (at about −11.95 eV) and by doubly-degenerate d$_{z^2}$ and d$_{x^2-y^2}$ (at about −11.1 eV[14]).

The 10 Dq value for (NH$_3$)$_5$RuO$_2$CR^{2+} is, then, estimated to be 5.36—5.45 kK from the energy difference between the t$_{2g}$ and e$_g$ orbitals.

The 10 Dq value for such octahedral ruthenium complexes as Ru(NH$_3$)$_5$H$_2$O^{3+} and Ru(NH$_3$)$_6$$^{3+}$ has been reported to be 1.14 Dq[15] on the basis of the crystal-field theory. Taking into consideration the fact that the Dq for the second transition series is some 50% greater than the first series (Dq=2.10 kK[16]), the value of 1.14 Dq corresponds almost exactly to 3.59 kK, which is approximately in agreement with the above 10 Dq value for (NH$_3$)$_5$RuO$_2$CR^{2+}.

In regard to the electron-excitation energies for the CT transition from the central Ru metal to the carboxylato ligand, the CT transition of (NH$_3$)$_5$RuO$_2$CR^{2+} was found from the UV absorption spectra of [(NH$_3$)$_5$-RuO$_2$CR](ClO$_4$)$_2$ in water to occur in the range of 24.9—34.1 kK. The electron-excitation energy calculated from the d$_{xz}$ (or d$_{yz}$) orbital to the oxygen p$_x$ (or p$_y$) orbital falls in the range of 27.5—36.0 kK, which is in good accordance with the above experimental results. The present calculation results, thus, seem to be useful for a qualitative or quantitative discussion of electronic property of the ruthenium(III) complex.

Next, let us discuss the charges (of (NH$_3$)$_5$RuO$_2$CR^{2+}) calculated by means of Mulliken's electron population analysis.[17]

According to the electronic charge (Q_A) in Table 1, the electron distribution in the complex seems to be somewhat characteristic; the central trivalent ruthenium is negatively charged, as are the neighboring O and N atoms attached to the metal, while the charges of the H atoms in the NH$_3$ ligands are markedly positive (+0.365). The negativeness of the Ru(III)-charge may be due to the electron-inflowing from the NH$_3$ ligand through the σ-bond, because the electron-inflowing of the ligand electrons from the NH$_3$ to the Ru metal cannot be expected through the d-π delocalization. Concerning the Ru–O coordination linkage, the negative charges localized on the neighboring O and N atoms may make the Ru–O bond very weak; in this respect, the weakness of the Ru–O bond is reflected in the very small bond population (M_{AB}) of the Ru–O bond and the small heterolytic bond dissociation energies of 4.61—9.22 kcal/mol.[18] It is of interest here that the order of the M_{Ru-O} values except for that of the glycolato-complex is in satisfactory accordance with that of the E_a values for Reaction (1) (and also with that of the overall aquation rates: formato>acetato>propionate>isobutylato>glycolato) This may suggest qualitatively that the aquation of (NH$_3$)$_5$RuO$_2$CR^{2+} proceeds *via* the S_N1 mechanism in which the bond breaking of the Ru–O linkage is more important than the bond making between the Ru metal and H$_2$O. It is also noticeable in respect to the Ru–O linkage that the antibonding d$_{z^2}$p$_z$-σ and p$_z$p$_z$-σ orbitals predominantly favor the formation of the Ru–O coordination bond. This implies the nucleophilic attack of such a third body as an electron-releasing solvent or base catalyst on the above antibonding nature of the Ru–O linkage so as to break the bond. In this respect, the order of the AO bond population (N_{Ru-O}) is also in harmony with that of the aquation rates mentioned above.

TABLE 1. ELECTRONIC PROPERTY OF $(NH_3)_5RuO_2CR^{2+}$

$(NH_3)_5RuO_2CR^{2+}$ (R)		$Q_A$$^{a)}$			M_{AB}		
	Ru	O^a	N^b	H^c	Ru–O^a	Ru–O^b	O^d–H^e
H (I)	−0.808	−1.167	−0.918	+0.356	0.0854	0.1049	0.0204
CH_3 (II)	−0.817	−1.238	−0.918	+0.356	0.0907	0.1051	0.0172
C_2H_5 (III)	−0.822	−1.236	−0.919	+0.356	0.0912	0.1049	0.0172
$(CH_3)_2CH$ (IV)	−0.829	−1.220	−0.920	+0.356	0.0915	0.1057	0.0171
CH_2OH (V)	−0.845	−1.107	−0.920	+0.356	0.0851	0.1043	0.0165

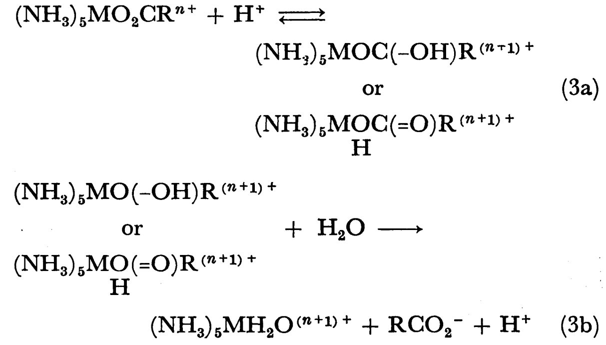
$(NH_3)_5RuO_2CR^{2+}$ (R)	Electron densities				N_{Ru-O}		
	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	d_{z^2}	d_{z^2}-p_z	p_z-p_z
H (I)	1.998	1.993	1.013	0.356	0.294	0.0159	0.0408
CH_3 (II)	1.998	1.990	1.017	0.356	0.296	0.0163	0.0410
C_2H_5 (III)	1.997	1.998	1.021	0.356	0.302	0.0167	0.0411
$(CH_3)_2CH$ (IV)	1.996	1.987	1.022	0.356	0.308	0.0169	0.0417
CH_2OH (V)	1.998	1.992	1.015	0.356	0.325	0.0185	0.0442

As to the superscripts of a—e, see Fig. 1.

a) The Q_A values for Ru were evaluated on the basis of the trivalent state of Ru (outer-shell electrons=5).

We will now, then, examine whether the above-mentioned antibonding dp-σ or pp-σ orbital plays an important role in the Ru–O bond-breaking in Reaction (2b). In view of the fact that the lowest unoccupied MO (LUMO) of the complexes is predominantly localized by the d_{z^2} Ru-orbital, the net orbital population of the d_{z^2}-orbital at the LUMO (abbreviated by $1/2N_{z^2}^{LU}$) can be taken as the reactivity index to such nucleophiles as H_2O, which is a stronger base than CH_3CO_2H. If H_2O takes part in the bond breaking of the Ru–O through its nucleophilic attack on the LU d_{z^2} Ru-orbital, there should exist a correlation between the $1/2N_{z^2}^{LU}$ values and such kinetic parameters as the E_a values for Reaction (2b). However, there was no parallelism between them. Therefore, the bond-breaking of the Ru–O linkage in Reaction (2b) may easily occur without the direct effect of H_2O on the bond dissociation of the Ru–O linkage, in view of the fairly small heterolytic dissociation energy of the metal-oxygen bond (the E_a values for Reaction (2b) are also small).

Role of the Acid Catalyst in the Dissociation of Metal-Oxygen Bond in $(NH_3)_5RuO_2CR^{2+}$. Up to now, the H^+ catalyst has been considered to participate in the protonated complex formation[19] as follows:



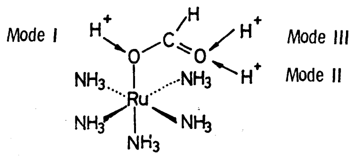
$$(NH_3)_5MO_2CR^{n+} + H^+ \rightleftharpoons (NH_3)_5MOC(-OH)R^{(n+1)+} \text{ or } (NH_3)_5M\underset{H}{O}C(=O)R^{(n+1)+} \qquad (3a)$$

$$(NH_3)_5MO(-OH)R^{(n+1)+} \text{ or } (NH_3)_5M\underset{H}{O}(=O)R^{(n+1)+} + H_2O \longrightarrow (NH_3)_5MH_2O^{(n+1)+} + RCO_2^- + H^+ \qquad (3b)$$

where M means such central metals as Co(III), Rh(III), and Ir(III); the protonated complexes of $(NH_3)_5$-$MOC(-OH)R^{(n+1)+}$ and $(NH_3)_5MOHC(=O)R^{(n+1)+}$ have been supported by Kuroda[5] (and/or Saito *et al.*[20,21]) and Basolo *et al.*[6] respectively.

Let us now discuss the structure and reactivity of the protonated complex. In regard to the interacting system between the complex and the H^+ catalyst, there exist three representative modes of interaction (Modes I, II, and III in Table 2). As may be seen from Table 2, the positive stabilization energy (ΔE_s) favors the formation of the protonated complex, in particular that *via* Mode I. In view of the weakening

TABLE. 2. ELECTRONIC PROPERTY OF THE PROTONATED COMPLEX.



Mode	ΔM_{Ru-O}	HO	LU	½N^{HO}	½N^{LU}	ΔE_s/eV$^{a)}$	LUMO energy/eV
I	0.012	d_{xy}	d_{z^2}	0.986	0.848	4.46	−11.28
II	0.000	d_{yz} (d_{xz})	d_{xy}	0.827	0.959	2.34	−11.28
III	−0.003	d_{xy}	d_{z^2}	0.985	0.849	3.00	−11.28

a) Stabilization energy was estimated from $E_{EH}((NH_3)_5RuO_2CR^{2+})+E_{EH}(H^+)-E_{EH}((NH_3)_5RuO_2CR^{2+}-H^+)$ where R=H.

of the Ru–O linkage by the protonation (reflected by the decrease in the $M_{\text{Ru–O}}$, $\Delta M_{\text{Ru–O}}$), the protonation probably occurs through Mode I, in which the H^+ reacts with the nonbonding lone-pair oxygen 2p-orbital of the oxygen atom attached to the metal. It is worthy to emphasize that the bond-weakening of the acyl-oxygen linkage by the protonation cannot be expected through Modes I, II, and III. This means that the dissociation of the acyl-oxygen bond would not be promoted by the acid catalyst. It is also of interest to consider the effect of the H_2O solvent on the dissociation of the Ru metal-oxygen bond. In connection with the plausibility of Mode I, there is a noticeable correlation between the reactivity of the protonated complex formed by Mode I and the E_a value for Reaction (2a), in which the direct effect of H_2O on the Ru–O bond dissociation is not emphasized. The reactivity of $(NH_3)_5RuOHC(=O)R^{3+}$ toward such nucleophiles as H_2O can be mainly discussed by taking notice of the interaction between the LU d_{z^2} Ru-orbital of the former and the lone-pair orbitals of the latter.

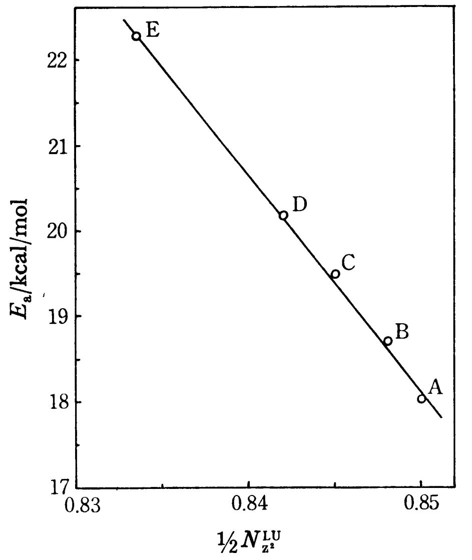


Fig. 2. Plots of E_a values for Reaction (2a) *vs.* $\frac{1}{2}N^{\text{LU}}_{z^2}$ values for $(NH_3)_5RuOHC(=O)R^{3+}$.
R: A=H, B=CH_3, C=C_2H_5, D=$(CH_3)_2CH$, E=CH_2OH

Figure 2 shows that there is a linear dependence between the $1/2N^{\text{LU}}_{z^2}$ values of $(NH_3)_5RuOHC(=O)R^{3+}$ and the E_a values. It may be deduced, therefore, that the H_2O solvent may promote the bond-dissociation of the Ru–O linkage and that Reaction (2a) can be divided into following steps:

$$(NH_3)_5RuO_2CR^{2+} + H^+ \overset{\text{fast}}{\rightleftharpoons} (NH_3)_5RuOHC(=O)R^{3+}$$
$$\xrightarrow{H_2O} (NH_3)_5Ru^{3+} + RCO_2^- + H^+ \quad (4)$$

Reaction (4) would then be followed by:

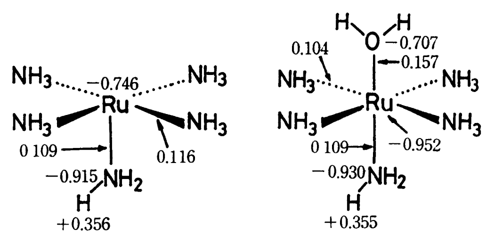
$$(NH_3)_5Ru^{3+} + H_2O \longrightarrow (NH_3)_5RuH_2O^{3+} \quad (5)$$

Reaction (4) proceeds more easily than Reaction (2b), with a lower activation barrier. However, there is, even now, an ambiguity with regard to the presence of $(NH_3)_5Ru^{3+}$, although we can cast doubt on the acyl-oxygen bond-breaking mechanism[22] from the MO-theoretical point of view; that is, there is a possibility of the direct formation of the aquo-complex through the proposed S_N2 mechnism:[4–6,20,21]

$$(NH_3)_5RuO_2CR^{2+} + H^+ \overset{\text{fast}}{\rightleftharpoons} (NH_3)_5Ru\underset{\displaystyle H}{O}C(=O)R^{3+}$$
$$\xrightarrow{H_2O} (NH_3)_5RuH_2O^{3+} \quad (6)$$

Bearing in mind that, in the aquation of Co(III) complexes in an acid solution, the complexes possessing the NH_3 (or NO_2^-) ligand at the *cis* or *trans* position toward the releasing ligand (in the present case, the RCO_2 ligand) react with a retention of configuration,[23] the five-coordinated tetragonal pyramidal intermediate is selectively formed so long as the bond breaking of the metal-releasing ligand occurs first. Moreover, the seven-coordinated octahedral wedge-type intermediate cannot be excepted so long as the aquation proceeds through the d_{z^2} metal-orbital. Therefore, the nonbonding lone-pair 2p O-orbital of H_2O would start to make a tight bond with the d_{z^2} Ru-orbital of $(NH_3)_5Ru^{3+}$ (LUMO=d_{z^2}) after the releasing of the RCO_2 ligand from the metal, because there is a large steric hindrance to the reaction of H_2O with $(NH_3)_5RuOC(=O)R^{3+}$ before the releasing of the RCO_2 ligand (the orbital overlapping between the above-mentioned orbitals is also small). Taking account of the above discussion, the five-coordination of $(NH_3)_5Ru^{3+}$ seems to be present and seems to be the plausible intermediate, mainly made from Reaction (4) in the aquation mechanism; in the experimental analysis, the concentration of the intermediate was very low (by a factor of approximately $1/10^3$), as compared with that of $(NH_3)_5RuH_2O^{3+}$ under the conditions shown in Refs. 1 and 2.

Electronic Property of $(NH_3)_5Ru^{3+}$ and $(NH_3)_5RuH_2O^{3+}$. From the electronic structure of $(NH_3)_5Ru^{3+}$ shown briefly in Fig. 3, it may be seen that the intermediate does not differ extremely from the parent carboxylato-complexes in terms of the Q_A and M_{AB} values and the frontier orbitals. This is in harmony with the fact that the coordination of RCO_2^- to $(NH_3)_5Ru^{3+}$ with a small binding energy (4.61—9.22 kcal/mol) has no



Frontier orbitals	LUMO	d_{z^2}	$d_{x^2-y^2}$
	HOMO	d_{xy}	d_{xy} or d_{xy}
Electron densities	d_{xz}	2.000	1.509
	d_{yz}	1.004	1.524
	d_{xy}	1.010	2.000
	$d_{x^2-y^2}$	0.356	0.356
	d_{z^2}	0.225	0.415

Fig. 3. Electronic structures of $(NH_3)_5Ru^{3+}$ and $(NH_3)_5RuH_2O^{3+}$.

marked effect on the d Ru-orbital separation of $(NH_3)_5$-RuO_2CR^{2+} (only the d_{z^2}-orbital energy was elevated slightly).

The intermediate of $(NH_3)_5Ru^{3+}$ once formed can easily be reconciled with the nucleophilic attack of the H_2O solvent on its d_{z^2}-orbital so as to form the aquo-complex. The coordination of H_2O to the Ru metal is relatively strong as compared with that of RCO_2^- to the metal, in view of the relatively large binding energy of 32.25 kcal/mol. This is reflected in such an electronic structure of $(NH_3)_5RuH_2O^{3+}$ as its Ru–O bond population (0.157).

The calculations were carried out on a FACOM 230-60 computer at the Data Processing Center of Kyushu University.

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