Supporting Information

Complexation and bonding studies on [Ru(NO)(H$_2$O)$_5$]$_3^+$ with nitrate ions by using density functional theory calculation

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### Table S1  Calculated bond lengths (Å) and bond angles (deg.) of [Ru(NO)(NO₃)x(H₂O)₅−x]^{3−x/+−}

| Complexes | x = 0 | x = 1 | x = 2 | x = 3 | x = 4 | x = 5 |
|-----------|------|------|------|------|------|------|
|           | a    | f    | ab   | ac   | af   | abc  |
| Ru-NO    | 1.768 | 1.762 | 1.785 | 1.765 | 1.761 | 1.772 |
| Ru-Oₐ     | 2.061 | 2.012 | 2.090 | 2.055 | 2.081 | 2.025 |
| Ru-Oₐ     | 2.082 | 2.056 | 2.093 | 2.010 | 2.101 | 2.087 |
| Ru-Oₖ     | 2.056 | 2.128 | 2.094 | 2.123 | 2.046 | 2.131 |
| Ru-Oₖ     | 2.080 | 2.083 | 2.091 | 2.119 | 2.083 | 2.093 |
| Ru-Oₖ     | 2.046 | 2.079 | 2.006 | 2.078 | 2.083 | 2.032 |
| N-Ru-Oₐ   | 97.73 | 96.36 | 95.44 | 91.93 | 92.02 | 96.26 |
| N-Ru-Oₐ   | 93.9 | 97.03 | 92.26 | 96.86 | 95.19 | 95.47 |
| N-Ru-Oₐ   | 96.59 | 93.49 | 92.10 | 92.88 | 98.37 | 92.62 |
| N-Ru-Oₐ   | 93.21 | 92.72 | 95.34 | 97.21 | 93.07 | 93.37 |
| Oₐ-Ru-Oₐ  | 92.49 | 95.09 | 87.95 | 100.20 | 95.87 | 95.53 |
| Oₐ-Ru-Oₐ  | 92.95 | 82.81 | 94.85 | 83.54 | 84.47 | 85.60 |
| Oₐ-Ru-Oₐ  | 82.51 | 87.54 | 88.31 | 88.91 | 85.17 | 87.70 |
| Oₐ-Ru-Oₐ  | 86.02 | 86.18 | 89.32 | 84.01 | 82.75 | 87.43 |
| Oₐ-Ru-Oₐ  | 88.29 | 82.54 | 84.00 | 82.85 | 85.12 | 81.71 |
| Oₐ-Ru-Oₐ  | 86.87 | 94.23 | 87.86 | 91.07 | 95.42 | 90.05 |
| Oₐ-Ru-Oₐ  | 83.19 | 82.61 | 83.94 | 86.29 | 84.45 | 83.61 |
| Oₐ-Ru-Oₐ  | 85.09 | 87.79 | 88.18 | 83.02 | 86.67 | 89.33 |
| N-Ru-Oₐ   | 178.29 | 176.10 | 174.61 | 179.15 | 177.18 | 175.37 |
| Oₐ-Ru-Oₐ  | 165.66 | 169.83 | 171.71 | 173.18 | 169.61 | 170.32 |
| Oₐ-Ru-Oₐ  | 170.81 | 170.20 | 171.61 | 165.31 | 171.72 | 170.91 |
| Ru-N-O    | 179.54 | 179.56 | 179.82 | 178.21 | 177.72 | 177.55 |

S2
Table S2  Calculated IR frequencies and intensities of the complexes with x = 3

| Vibration                        | abc Freq. / cm\(^{-1}\) | bc Intensity | abf Freq. / cm\(^{-1}\) | af Intensity | acf Freq. / cm\(^{-1}\) | cf Intensity |
|---------------------------------|--------------------------|--------------|--------------------------|--------------|--------------------------|--------------|
| \(\delta_{\text{sym}(\text{NO}_3)}\), Ru-H\(_2\)O rocking | 737                      | 61           | 737                      | 38           | 712                      | 60           |
|                                 | 743                      | 158          | 741                      | 36           | 733                      | 89           |
|                                 | 746                      | 152          |                          |              | 734                      | 169          |
| \(\nu_{\text{sym}(\text{NO}_3)}\) | 756                      | 30           | 756                      | 38           | 749                      | 10           |
|                                 | 767                      | 49           | 762                      | 13           | 752                      | 21           |
|                                 | 772                      | 32           | 767                      | 116          | 769                      | 18           |
|                                 | 779                      | 46           | 772                      | 133          | 770                      | 18           |
|                                 |                          |              |                          |              | 776                      | 87           |
|                                 |                          |              |                          |              | 773                      | 16           |
| \(\delta_{\text{sym}(\text{NO}_3)}\) | 883                      | 800          | 889                      | 387          | 892                      | 710          |
|                                 | 904                      | 193          | 900                      | 587          | 905                      | 154          |
|                                 | 927                      | 546          | 957                      | 486          | 950                      | 396          |
|                                 | 949                      | 229          |                          |              | 971                      | 436          |
|                                 | 977                      | 217          |                          |              |                          |              |
| \(\delta_{\text{sym}(\text{NO}_3)}, \nu_{\text{sym}(\text{NO}_3)}\) | 1236                     | 1078         | 1249                     | 902          | 1243                     | 811          |
|                                 | 1262                     | 416          | 1283                     | 278          | 1251                     | 806          |
|                                 | 1286                     | 356          | 1296                     | 730          | 1284                     | 251          |
| \(\nu_{\text{sym}(\text{H}_2\text{O})}\) | 1522                     | 209          | 1552                     | 154          | 1498                     | 403          |
|                                 | 1524                     | 501          | 1557                     | 138          | 1556                     | 634          |
| \(\nu_{\text{asym}(\text{H}_2\text{O})}\) | 1608                     | 640          | 1601                     | 649          | 1603                     | 647          |
|                                 | 1618                     | 376          | 1609                     | 879          | 1610                     | 321          |
|                                 | 1625                     | 297          | 1633                     | 219          | 1636                     | 279          |
| \(\nu(\text{NO})\)               | 1968                     | 1280         | 1954                     | 1514         | 1962                     | 1333         |
| \(\nu(\text{H}_2\text{O})\)      | 2948                     | 1169         | 2984                     | 1269         | 2826                     | 1389         |
|                                 | 3218                     | 846          |                          |              | 3114                     | 997          |
Table S3  Thermodynamic data of compounds (hartree)

| Compounds | $E_{\text{tot}}$   | $H_{\text{corr}}$ | TS  | $G_{\text{corr}}$ |
|-----------|-------------------|-------------------|-----|------------------|
| x = 0     | −5041.4060        | 0.1518            | 0.0525 | 0.0993         |
| x = 1     |                  |                   |     |                  |
| a         | −5245.5921        | 0.1432            | 0.0582 | 0.0850         |
| f         | −5245.5869        | 0.1448            | 0.0573 | 0.0875         |
| x = 2     |                  |                   |     |                  |
| ab        | −5449.7678        | 0.1345            | 0.0644 | 0.0701         |
| ac        | −5449.7685        | 0.1341            | 0.0618 | 0.0724         |
| af        | −5449.7686        | 0.1353            | 0.0617 | 0.0737         |
| x = 3     |                  |                   |     |                  |
| abc       | −5653.9417        | 0.1260            | 0.0688 | 0.0571         |
| abf       | −5653.9388        | 0.1265            | 0.0696 | 0.0569         |
| acf       | −5653.9410        | 0.1262            | 0.0685 | 0.0577         |
| x = 4     |                  |                   |     |                  |
| abcd      | −5858.1035        | 0.1187            | 0.0750 | 0.0436         |
| abcf      | −5858.1051        | 0.1186            | 0.0743 | 0.0444         |
| x = 5     | −6062.2608        | 0.1115            | 0.0816 | 0.0300         |
| H$_2$O    | −76.4900          | 0.0236            | 0.0215 | 0.0021         |
| NO$_3^-$  | −280.6445         | 0.0170            | 0.0286 | −0.0116        |

Table S4  Calculated values of $G_{\text{form}}$, $\Delta G_{\text{form}}$

| Reaction | $G_{\text{form}}$(A···B) / kJ mol$^{-1}$ | $\Delta G_{\text{form}}$(A···B) / kJ mol$^{-1}$ |
|----------|------------------------------------------|-----------------------------------------------|
|          | Initial | Final |            |                |
| x = 1 (x = 0 → a) | −48.1  | 7.0   | 55.1        |
| x = 2 (a → ab)    | −23.6  | 21.6  | 45.2        |
| x = 3 (ab → abc)  | 3.8    | 46.5  | 42.7        |
| x = 4 (abc → abcd)| 21.5   | 53.9  | 32.4        |
| x = 5 (abcd → x = 5)| 13.7  | 43.8  | 30.2        |
| MO number | PDOS of Ru(d) (%) | BODOS (%) | Ru(d)-All | Ru(d)-N\textsubscript{nitrosyl} |
|-----------|-------------------|-----------|-----------|-----------------|
|           | a                 | f         | a         | f               | a             | f               |
| 36        | 7.92              | 8.16      | 3.85      | 4.07            | 3.77          | 3.86            |
| 37        | 3.18              | 3.31      | 1.58      | 1.54            | 0.02          | −0.36           |
| 38        | 8.66              | 5.30      | 2.69      | 1.64            | 2.10          | 1.18            |
| 39        | 3.52              | 4.88      | 1.47      | 1.81            | 0.00          | 1.11            |
| 40        | 4.38              | 4.35      | 1.79      | 1.77            | 0.56          | 0.67            |
| 41        | 4.45              | 2.05      | 1.71      | 0.82            | 0.93          | 0.20            |
| 42        | 1.09              | 0.88      | 0.43      | 0.31            | 0.13          | 0.35            |
| 43        | 2.35              | 1.52      | 0.78      | 0.53            | 0.94          | 0.70            |
| 44        | 0.80              | 0.30      | 0.25      | 0.09            | 0.35          | 0.16            |
| 45        | 0.48              | 0.30      | 0.19      | 0.14            | −0.07         | −0.11           |
| 46        | 0.65              | 0.07      | 0.24      | 0.02            | 0.01          | 0.00            |
| 47        | 0.50              | 0.20      | 0.17      | 0.06            | 0.00          | −0.02           |
| 48        | 17.20             | 9.43      | 5.49      | 2.91            | 0.01          | −0.15           |
| 49        | 3.70              | 25.03     | 1.12      | 8.37            | −1.16         | −0.02           |
| 50        | 10.93             | 6.20      | 3.09      | 1.84            | −0.70         | −0.02           |
| 51        | 3.53              | 1.45      | 0.90      | 0.38            | 0.02          | 0.01            |
| 52        | 21.03             | 17.46     | 4.00      | 3.32            | −0.10         | 0.27            |
| 53        | 18.91             | 9.76      | 3.37      | 1.97            | −0.20         | 0.06            |
| 54        | 12.12             | 16.83     | 1.69      | 2.01            | 0.18          | −1.22           |
| 55        | 1.64              | 3.82      | 0.17      | 0.22            | −0.03         | −0.64           |
| 56        | 5.98              | 5.47      | 0.62      | 0.52            | 0.11          | 0.02            |
| 57        | 19.30             | 18.97     | 1.05      | 1.31            | 0.51          | 0.73            |
| 58        | 9.34              | 10.45     | 0.51      | 0.50            | 0.14          | 0.14            |
| 59        | 6.36              | 0.40      | −0.30     | −0.02           | 0.46          | 0.03            |
| 60        | 45.43             | 50.05     | −1.75     | −0.85           | 3.01          | 3.08            |
| 61        | 36.95             | 32.88     | −2.34     | −1.77           | 2.00          | 2.69            |
| 62        | 17.68             | 2.88      | −0.46     | −0.59           | −0.03         | −0.82           |
| 63(HOMO)  | 51.75             | 79.26     | −5.10     | −6.87           | 0.37          | 0.02            |
| Sum       | 319.81            | 321.66    | 27.21     | 26.05           | 13.34         | 11.94           |
Table S6  Stepwise complexation formation constants \((K_x)\) for fitting models 1 and 2

| \(\log_{10} K_x\) | Model 1 | Model 2 |
|-------------------|---------|---------|
| \(x = 1\)         | 2.31    | 2.20    |
| \(x = 2\)         | 1.64    | 1.64    |
| \(x = 3\)         | 1.15    | 1.21    |
| \(x = 4\)         | 0.94    | 1.00    |

Table S7  Thermodynamic data of transition state models (hartree)

| Compounds       | \(E_{\text{tot}}\) | \(H_{\text{corr}}\) | \(TS\)  | \(G_{\text{corr}}\) |
|-----------------|-------------------|-----------------|--------|-------------------|
| \(S_N1\)       |                   |                 |        |                   |
| \(a\rightarrow ab\) | \(-5169.0452\)    | 0.1147          | 0.0549 | 0.0598            |
| \(a\rightarrow ac\) | \(-5169.0543\)    | 0.1143          | 0.0549 | 0.0593            |
| Intermediate    |                   |                 |        |                   |
| \(a\rightarrow ab\) | \(-5526.2157\)    | 0.1618          | 0.0694 | 0.0924            |
| \(a\rightarrow ac\) | \(-5526.2199\)    | 0.1616          | 0.0692 | 0.0924            |
| Intermediate    |                   |                 |        |                   |
| \(a\rightarrow ab\) | \(-5526.2106\)    | 0.1629          | 0.0687 | 0.0942            |
| \(a\rightarrow ac\) | \(-5526.2218\)    | 0.1621          | 0.0691 | 0.0930            |

Intermediate up-side entry

Intermediate down-side entry
Figure S1  Dependences of $a_{\text{NO}_3^-}$ and $a_{\text{H}_2\text{O}}$ on $C_{\text{HNO}_3^{\text{tot}}}$.

Figure S2  Fitting of speciation of Ru species on total HNO$_3$ concentration, in which the plot was obtained by Ref. 6.
Figure S3  Transition states search in intermediate model between $S_{N1}$ and $S_{N2}$ mechanisms by relaxed surface scanning.
**Supplementary Methods**

**Gibbs energy calculation**

Standard Gibbs energy, $G$, can be described as sum of total energy, $E_{\text{tot}}$, and thermal correction to the Gibbs energy term, $G_{\text{corr}}(T)$ (eq. S1). The $G_{\text{corr}}(T)$ can be divided into thermal correction to enthalpy term, $H_{\text{corr}}(T)$, and entropy term, $S(T)$ (eq. S2). The $H_{\text{corr}}(T)$ can be divided into zero-point energy, $E_{\text{ZPE}}$, the contributions of vibration, $E_{\text{vibration}}(T)$, rotation, $E_{\text{rotation}}(T)$, translation, $E_{\text{translation}}(T)$, and Boltzmann thermal distribution, $k_B T$ ($k_B$ denotes Boltzmann constant), as shown in eq. S3. The $S(T)$ can be divided into the contributions of electron, $S_{\text{electron}}$, vibration, $S_{\text{vibration}}(T)$, $S_{\text{rotation}}(T)$, translation, $S_{\text{translation}}(T)$ (eq. S4). The contributions of vibration and rotation to enthalpy and entropy are formulated based on harmonic oscillator and rigid rotator approximations, respectively. Quasi-harmonic approximation, which was the well-known breakdown of the harmonic oscillator model for Gibbs energies of low-frequency vibrational modes, was introduced in analyzing the vibrational enthalpy and entropy terms by raising the vibrational frequencies, which are less than 60 cm$^{-1}$ [1,2]. The derivation of formulas was referred to “Thermochemistry in Gaussian” by Ochterski [3].

\[
G = E_{\text{tot}} + G_{\text{corr}}(T) \quad (S1)
\]

\[
G_{\text{corr}}(T) = H_{\text{corr}}(T) - TS(T) \quad (S2)
\]

\[
H_{\text{corr}}(T) = E_{\text{ZPE}} + E_{\text{vibration}}(T) + E_{\text{rotation}}(T) + E_{\text{translation}}(T) + k_B T \quad (S3)
\]

\[
S(T) = S_{\text{electron}} + S_{\text{vibration}}(T) + S_{\text{rotation}}(T) + S_{\text{translation}}(T) \quad (S4)
\]

The $E_{\text{ZPE}}$, $E_{\text{vibration}}(T)$, and $S_{\text{vibration}}(T)$ in eqs. S3 and S4 are described in eqs. S5–S7, where $\Theta_v(i) = h\nu_i/k_B$ ($h$ and $\nu_i$ denote Planck constant and frequency of $i$th normal vibrational mode) denotes characteristic vibrational temperature of $i$th normal vibrational frequency. The $E_{\text{rotation}}(T)$ of nonlinear molecules and $E_{\text{translation}}(T)$ equal to (3/2)$k_B T$. The $S_{\text{electron}}$ is considered to correspond to spin entropy of electrons generated from spin multiplet, $2s + 1$ ($s$ denotes spin quantum number), and equals to $k_B \{\ln(2s + 1)\}$. The $S_{\text{rotation}}(T)$ is described in eq. S8, where $\Theta_r(t)$ and $\sigma_t$ denote characteristic rotational temperature of $t = x, y, z$ rotational axes and rotational symmetry number, respectively. The $S_{\text{translation}}(T)$ is described in eq. S9, where $m$ and $P$ denote molecular weight and pressure, respectively.

\[
E_{\text{ZPE}} = k_B \Sigma_i (\Theta_v(i)/2) \quad (S5)
\]

\[
E_{\text{vibration}}(T) = k_B \Sigma_i \{\exp(\Theta_v(i)/T) - 1\}^{-1} \quad (S6)
\]

\[
S_{\text{vibration}}(T) = k_B \Sigma_i \{\Theta_v(i)/T\} \{\exp(\Theta_v(i)/T) - 1\}^{-1} - \ln\{1 - \exp(-\Theta_v(i)/T)\} \quad (S7)
\]

\[
S_{\text{rotation}}(T) = k_B \ln(\pi^{1/2}\sigma_t)^{3/2}\{(\Theta_r(x)\Theta_r(y)\Theta_r(z))^{-1/2}\} + 3/2 \quad (S8)
\]

\[
S_{\text{translation}}(T) = k_B \{\ln(2\pi mk_B T/h^2)^{3/2}(k_B T/P) + 5/2\} \quad (S9)
\]
Density of states analysis
We show the analytical method of density of states (DOS) for partial DOS (PDOS) of Ru d-orbital and bond overlap DOS (BODOS) between Ru d-orbital and atomic orbitals of the donor atoms of ligands for \([\text{Ru(NO)(NO}_3\text{)(H}_2\text{O)}_4]^{2+}\) whose values were employed in Figure 3. This method is based on Mulliken population analysis [4]. The DOS values of the \(i^{th}\) MO, \(N(i)\), is calculated by eq. S19, where \(P_{\mu \nu}\) and \(S_{\mu \nu}\) denote the density matrix and the overlap matrix between basis functions \(\psi_\mu\) and \(\psi_\nu\), respectively.

\[
N(i) = \sum_\mu \sum_\nu P_{\mu \nu}(i) S_{\mu \nu} \quad (S19)
\]

PDOS of Ru d-orbital corresponds to values when the both \(\psi_\mu\) and \(\psi_\nu\) functions belong to Ru d-orbitals. BODOS corresponds to values when the \(\psi_\mu\) and \(\psi_\nu\) functions belong to Ru d-orbitals and atomic orbitals of the donor atoms of the ligands, respectively. The values of PDOS and BODOS are summarized in Table S5.

Fitting methods of Ru fraction
We show two fitting models to simulate the dependency of the Ru fraction on total HNO\(_3\) concentration by using the calculated \(\Delta G^x_{\text{stepwise}}\) and \(\Delta G^x_{\text{stepwise}^+}\) values for eqs. 10 and 11 in manuscript. Fitting model 1 is using the activities of H\(_2\)O and NO\(_3^-\), denoted as \(a_{\text{H}_2\text{O}}\) and \(a_{\text{NO}_3^-}\), respectively, based on the experimentally reported data [5]. We estimated the \(a_{\text{H}_2\text{O}}\) values by multiplying 55.39 mol L\(^{-1}\) (concentration of pure H\(_2\)O) with values of “Rational H\(_2\)O activity” in Table 4 of Ref. 5 for 0–12 mol L\(^{-1}\) of total HNO\(_3\) concentration \((C_{\text{HNO}_3\text{tot}})\). The \(a_{\text{HNO}_3}\) values were estimated by using the values of “Degree of dissociation” (\(\alpha\)) and “Hypothetical activity coefficient” (\(y_h\)), which means activity coefficients of fully ionized nitric acid, in Table 4 of Ref. 5 for 0–12 mol L\(^{-2}\) of \(C_{\text{HNO}_3\text{tot}}\) to give eq. S10.

\[
a_{\text{NO}_3^-}^{m1} = y_h C_{\text{NO}_3^-} = \alpha y_h C_{\text{HNO}_3\text{tot}} \quad (S10)
\]

For simplicity fitting model 2 is using the activities assuming the activity coefficients of H\(_2\)O and NO\(_3^-\) as 1. We limit to the solution condition that total Ru concentration is smaller than \(C_{\text{HNO}_3\text{tot}}\) and \(C_{\text{H}_2\text{O}\text{tot}}\) enough to be ignored (such as the experimental condition of Ref. 6 as well as HLLW solution) to give eqs. S11–S13. By combining eqs. S11–S13, acid dissociation constant of HNO\(_3\) \((K_a)\), and percentage by mass of HNO\(_3\) in \(C_{\text{HNO}_3\text{tot}}\) \((W_{\text{HNO}_3})\), we obtained the activities of NO\(_3^-\) and H\(_2\)O as eqs. S17 and S18, respectively. Figure S1 shows the dependences of the activities of NO\(_3^-\) and H\(_2\)O on \(C_{\text{HNO}_3\text{tot}}\) for the two fitting models.
\[ C_{\text{HNO}}^{\text{tot}} \approx C_{\text{HNO}} + C_{\text{NO}}^- \quad (\text{S11}) \]
\[ C_{\text{H}_2\text{O}}^{\text{tot}} \approx C_{\text{H}_2\text{O}} + C_{\text{H}_3\text{O}^+} \quad (\text{S12}) \]
\[ C_{\text{NO}}^- \approx C_{\text{H}_3\text{O}^+} \quad (\text{S13}) \]
\[ a_{\text{NO}}^{\text{m2}} \approx C_{\text{NO}}^- = (1/2)\left\{(K_a^2 + 4K_aC_{\text{HNO}}^{\text{tot}})^{1/2} - K_a\right\} \quad (\text{S17}) \]
\[ a_{\text{H}_2\text{O}}^{\text{m2}} \approx C_{\text{H}_2\text{O}} = (9.97/18)(100 - W_{\text{HNO}}) - C_{\text{NO}}^- \quad (\text{S18}) \]

Based on the fraction of \([\text{Ru(NO)}(\text{NO}_3)_x(\text{H}_2\text{O})_{5-x}]\) (x = 1–4) for six experimental concentrations of \(C_{\text{HNO}}\) [6], we obtained the \(K_x\) values that minimize the root mean square deviations of fraction of Ru species (%) between calculation and experiment. Table S6 and Figure S2 show the \(K_x\) values and the simulation based on the \(K_x\) values for fitting models 1 and 2. For the both fitting models, the calculated fractions of all the Ru species reproduced within ~2 % of RMSD values.

**Transition states searching by relaxed surface scan**

We modeled the transition state structures by using constrained geometrical optimization. Octahedral wedge geometries in which the distances between Ru atom and the leaving \(\text{H}_2\text{O}\)/entering \(\text{NO}_3^-\) were fixed to 2.5 Å were created by using the equilibrium structures of the complex a. We considered the start geometries with up-side and down-side entries of \(\text{NO}_3^-\) ligand. Based on the octahedral wedge structures obtained by the constrained optimization, we scanned the potential surface of the distance between the Ru atom and the leaving \(\text{H}_2\text{O}\) from 2.0 Å to 3.0 Å by intervals of 0.1 Å with structural relaxation in which the sum of the distances between Ru atom and the leaving \(\text{H}_2\text{O}\) and between Ru atom and the entering \(\text{NO}_3^-\) were fixed to 5.0 Å. The structural relaxations were performed by the same method to the geometry optimization method in this study. The relaxed surface scanning based on the total energies by the single-point energy calculations are shown in Figure S3. The local maxima were obtained at 2.5 Å for the up-side entry and 2.6 Å for the down-side entry.

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