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ARTICLE TYPE

How the total charge and the isomerism influence the Ru-NO ammine complexes?

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Supplementary Material

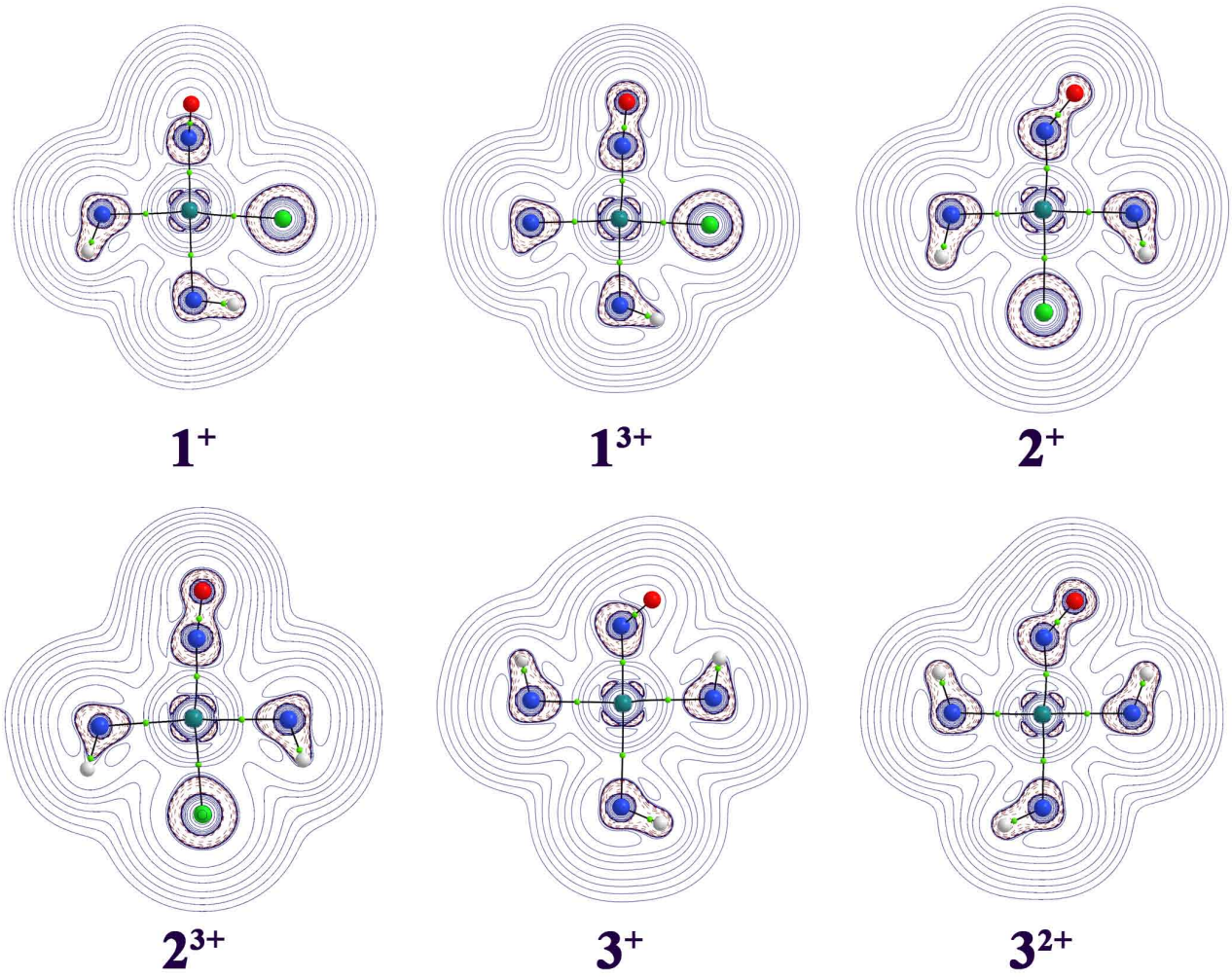

Fig. S1 Electron density Laplacian contour line maps to the structures, **1**$^{+}$, **1**$^{3+}$, **2**$^{+}$, **2**$^{3+}$, **3**$^{+}$ and **3**$^{2+}$ from of the planes in Fig. 3. The red dashed lines indicate charge concentration ($\nabla^2\rho(r) < 0$); the blue solid lines show charge depletion ($\nabla^2\rho(r) > 0$).

Table S1 Absolute (r/Å or </°), and relative errors (%) between the calculated, and (experimental) bond lengths (r/Å), and angles (</°) of the compounds $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$, and $\mathbf{3}^{3+}$

Geometric parameter	$\mathbf{1}^{2+}$	$\mathbf{2}^{2+}$	$\mathbf{3}^{3+}$	Absolute error[a]	Absolute relative error[b]
r(Ru-NO)	1.750 (1.773)	1.771 (1.799)	1.772 (1.771)	$\mathbf{1}^{2+}$ (0.02) $\mathbf{2}^{2+}$ (0.03) $\mathbf{3}^{3+}$ (0.00)	$\mathbf{1}^{2+}$ (1.27) $\mathbf{2}^{2+}$ (1.56) $\mathbf{3}^{3+}$ (0.01)
r(N-O)	-	1.129 (1.026)	1.116 (1.172)	$\mathbf{2}^{2+}$ (0.10) $\mathbf{3}^{3+}$ (0.06)	$\mathbf{2}^{2+}$ (10.04)[c] $\mathbf{3}^{3+}$ (4.78)
<(Ru-N-O)	176.3 (175.2)	180.0 (176.6)	179.3 (172.9)	$\mathbf{1}^{2+}$ (0.08) $\mathbf{2}^{2+}$ (3.40) $\mathbf{3}^{3+}$ (6.40)	$\mathbf{1}^{2+}$ (3.88) $\mathbf{2}^{2+}$ (1.93) $\mathbf{3}^{3+}$ (3.70)
r(Ru-Cl)	-	2.310 (2.376)	-	0.07	2.79
r̄(Ru-NH_3)	2.184 (2.103)	2.166 (2.100)	2.186 (2.077)	$\mathbf{1}^{2+}$ (1.06) $\mathbf{2}^{2+}$ (0.07) $\mathbf{3}^{3+}$ (0.11)	$\mathbf{1}^{2+}$ (0.60) $\mathbf{2}^{2+}$ (3.14) $\mathbf{3}^{3+}$ (5.25)
r[Ru-N(1)]	-	2.166 (2.113)	2.186 (2.133)	$\mathbf{2}^{2+}$ (0.05) $\mathbf{3}^{3+}$ (0.05)	$\mathbf{2}^{2+}$ (2.51) $\mathbf{3}^{3+}$ (2.48)
r[Ru-N(2)]	-	2.165 (2.094)	2.186 (2.094)	$\mathbf{2}^{2+}$ (0.07) $\mathbf{3}^{3+}$ (0.09)	$\mathbf{2}^{2+}$ (3.39) $\mathbf{3}^{3+}$ (4.39)
r[Ru-N(3)]	-	2.166 (2.039)	2.185 (2.042)	$\mathbf{2}^{2+}$ (0.13) $\mathbf{3}^{3+}$ (0.14)	$\mathbf{2}^{2+}$ (6.23) $\mathbf{3}^{3+}$ (7.00)
r[Ru-N(4)]	-	2.166 (2.152)	2.186 (2.101)	$\mathbf{2}^{2+}$ (0.01) $\mathbf{3}^{3+}$ (0.09)	$\mathbf{2}^{2+}$ (0.65) $\mathbf{3}^{3+}$ (4.05)
r(Ru-N_{trans})	-	-	2.186 (2.017)	0.17	8.38
<[N(1)-Ru-N(2)]	-	89.7 (86.6)	89.6 (90.7)	$\mathbf{2}^{2+}$ (3.10) $\mathbf{3}^{3+}$ (1.10)	$\mathbf{2}^{2+}$ (3.58) $\mathbf{3}^{3+}$ (1.21)
<[N(1)-Ru-N(3)]	-	171.6 (174.6)	174.7 (179.0)	$\mathbf{2}^{2+}$ (3.00) $\mathbf{3}^{3+}$ (4.30)	$\mathbf{2}^{2+}$ (1.72) $\mathbf{3}^{3+}$ (2.40)
<[N(1)-Ru-N(4)]	-	89.7 (93.0)	89.2 (86.8)	$\mathbf{2}^{2+}$ (3.30) $\mathbf{3}^{3+}$ (2.40)	$\mathbf{2}^{2+}$ (3.55) $\mathbf{3}^{3+}$ (2.76)
<[N(1)-Ru-NO]	-	94.2 (91.2)	93.2 (87.3)	$\mathbf{2}^{2+}$ (3.00) $\mathbf{3}^{3+}$ (5.90)	$\mathbf{2}^{2+}$ (3.29) $\mathbf{3}^{3+}$ (6.33)
<[N(1)-Ru-Cl]	-	85.8 (88.6)	-	2.80	3.16
<[N(2)-Ru-N(3)]	-	89.7 (89.2)	89.8 (90.2)	$\mathbf{2}^{2+}$ (0.50) $\mathbf{3}^{3+}$ (0.40)	$\mathbf{2}^{2+}$ (0.56) $\mathbf{3}^{3+}$ (0.44)
<[N(2)-Ru-N(4)]	-	171.6 (175.5)	176.0 (176.5)	$\mathbf{2}^{2+}$ (3.90) $\mathbf{3}^{3+}$ (0.50)	$\mathbf{2}^{2+}$ (2.22) $\mathbf{3}^{3+}$ (0.28)
<[N(2)-Ru-NO]	-	94.2 (92.4)	92.3 (93.3)	$\mathbf{2}^{2+}$ (1.80) $\mathbf{3}^{3+}$ (1.00)	$\mathbf{2}^{2+}$ (0.02) $\mathbf{3}^{3+}$ (1.07)
<[N(2)-Ru-Cl]	-	85.8 (87.9)	-	2.10	2.39
<[N(3)-Ru-N(4)]	-	89.7 (91.1)	91.1 (92.7)	$\mathbf{2}^{2+}$ (1.40) $\mathbf{3}^{3+}$ (1.60)	$\mathbf{2}^{2+}$ (1.54) $\mathbf{3}^{3+}$ (1.73)
<[N(3)-Ru-NO]	-	94.2 (88.8)	92.1 (93.3)	$\mathbf{2}^{2+}$ (5.40) $\mathbf{3}^{3+}$ (1.20)	$\mathbf{2}^{2+}$ (6.08) $\mathbf{3}^{3+}$ (1.29)
<[N(3)-Ru-Cl]	-	85.8 (89.2)	-	3.40	3.81
<[N(4)-Ru-NO]	-	94.2 (95.7)	91.6 (89.2)	$\mathbf{2}^{2+}$ (1.50) $\mathbf{3}^{3+}$ (2.40)	$\mathbf{2}^{2+}$ (1.57) $\mathbf{3}^{3+}$ (0.03)
<[N(4)-Ru-Cl]	-	85.8 (86.5)	-	0.70	0.81
<[Cl-Ru-NO]	-	180.0 (177.9)	-	2.10	1.18
<[N_{trans}-Ru-N(1)]	-	-	87.9 (88.2)	0.30	0.34
<[N_{trans}-Ru-N(2)]	-	-	88.1 (86.4)	1.70	1.97
<[N_{trans}-Ru-N(3)]	-	-	86.8 (91.2)	4.40	4.82
<[N_{trans}-Ru-N(4)]	-	-	88.0 (91.3)	3.30	3.61
<[N_{trans}-Ru-NO]	-	-	178.9 (175.4)	3.50	2.00

[a] Absolute error = |Experimental − Calculated| (S1). [b] Absolute relative error = |Experimental - Calculated|\(Experimental) x 100 % (S2). [c] Similar experimental result is used in the reference 51, and it was considered not reliable due disorder problems.

Table S2 Nucleophilic Fukui function (f^+/a.u.) for all atoms of the compounds $\mathbf{1}^{2+}$, $\mathbf{2}^{2+}$ and $\mathbf{3}^{3+}$

Atom	f_2^+	f_5^+	f_9^+
Ru	0.125	0.103	0.132
N(NO)	0.263	0.241	0.280
O	0.202	0.199	0.210
Cl	0.126	0.189	-
N(1)	-	0.001	0.001
N(2)	0.003	0.004	0.003
N(3)	-0.011	0.001	0.002
N(4)	0.003	0.004	0.002
N_{trans}	0.008	-	0.007
H	0.030-0.019	0.024-0.019	0.029-0.018

Table S3 Ru-Cl parameters in compounds **1** and **2**: bond length (r/Å), Wiberg bond index (WBI/a.u.), stretching wave numbers ($\bar{\nu}$/cm^{-1}), electron density (ρ(r)/a.u.), Laplacian of ρ(r) ($\nabla^2\rho$(r)/a.u.), total energy density (H(r)/a.u.), total interaction energy (E_{int}^{AB}), classical interaction energy (V_{cl}^{AB}), exchange and correlation energy (V_{xc}^{AB})

Parameter	$\mathbf{1}^{+}$	$\mathbf{1}^{2+}$	$\mathbf{1}^{3+}$	$\mathbf{2}^{+}$	$\mathbf{2}^{2+}$	$\mathbf{2}^{3+}$
r(Ru-Cl)	2.374	2.337	2.257	2.425	2.310	2.254
$\bar{\nu}$(Ru-Cl)[a]	325	342	380	283	349	353
WBI(Ru-Cl)	1.197	1.283	1.704	1.075	1.231	1.666
ρ(r)(Ru-Cl)	0.079	0.091	0.106	0.069	0.094	0.108
$\nabla^2\rho$(r)(Ru-Cl)	0.214	0.184	0.238	0.209	0.210	0.230
H(r)(Ru-Cl)	-0.018	-0.025	-0.035	-0.014	-0.028	-0.036
E_{int}^{RuCl}	-0.299	-0.304	-0.270	-0.297	-0.331	-0.285
V_{cl}^{RuCl}	-0.148	-0.133	-0.037	-0.171	-0.169	-0.061
V_{xc}^{RuCl}	-0.151	-0.171	-0.233	-0.126	-0.162	-0.224

[a] Coupled with other vibrational modes, such as, angular deformation of N-H, and bond stretching of Ru-NH_3.

Table S4 Ru-N(1) parameters in compounds **2** and **3**: bond length (r/Å), Wiberg bond index (WBI/a.u.), electron density (ρ(r)/a.u.), Laplacian of ρ(r) ($\nabla^2\rho$(r)/a.u.), total energy density (H(r)/a.u.), total interaction energy ($E_{\mathrm{int}}^{\mathrm{AB}}$), classical interaction energy ($V_{\mathrm{cl}}^{\mathrm{AB}}$), exchange and correlation energy ($V_{\mathrm{xc}}^{\mathrm{AB}}$)

Parameter	$\mathbf{2}^{+}$	$\mathbf{2}^{2+}$	$\mathbf{2}^{3+}$	$\mathbf{3}^{+}$	$\mathbf{3}^{2+}$	$\mathbf{3}^{3+}$
r[Ru-N(1)]	2.167	2.166	2.188	2.178	2.187	2.186
WBI[Ru-N(1)]	0.696	0.723	0.739	0.685	0.702	0.733
ρ(r)[Ru-N(1)]	0.080	0.086	0.087	0.074	0.076	0.082
$\nabla^2\rho$(r)[Ru-N(1)]	0.327	0.290	0.232	0.354	0.319	0.275
H(r)[Ru-N(1)]	-0.014	-0.018	-0.019	-0.011	-0.012	-0.016
$E_{\mathrm{int}}^{\mathrm{RuN(1)}}$	-0.443	-0.503	-0.522	-0.390	-0.437	-0.501
$V_{\mathrm{cl}}^{\mathrm{RuN(1)}}$	-0.311	-0.365	-0.383	-0.260	-0.306	-0.362
$V_{\mathrm{xc}}^{\mathrm{RuN(1)}}$	-0.132	-0.139	-0.139	-0.130	-0.131	-0.138

Table S5 Ru-N(2) parameters in compounds **1**-**3**: bond length (r/Å), Wiberg bond index (WBI/a.u.), electron density (ρ(r)/a.u.), Laplacian of ρ(r) ($\nabla^2\rho$(r)/a.u.), total energy density (H(r)/a.u.), total interaction energy ($E_{\mathrm{int}}^{\mathrm{AB}}$), classical interaction energy ($V_{\mathrm{cl}}^{\mathrm{AB}}$), exchange and correlation energy ($V_{\mathrm{xc}}^{\mathrm{AB}}$)

Parameter	$\mathbf{1}^{+}$	$\mathbf{1}^{2+}$	$\mathbf{1}^{3+}$	$\mathbf{2}^{+}$	$\mathbf{2}^{2+}$	$\mathbf{2}^{3+}$	$\mathbf{3}^{+}$	$\mathbf{3}^{2+}$	$\mathbf{3}^{3+}$
r[Ru-N(2)]	2.154	2.164	2.185	2.155	2.166	2.173	2.177	2.175	2.186
WBI[Ru-N(2)]	0.716	0.726	0.742	0.710	0.723	0.753	0.686	0.715	0.733
ρ(r)[Ru-N(2)]	0.082	0.086	0.087	0.082	0.086	0.090	0.075	0.078	0.082
$\nabla^2\rho$(r)[Ru-N(2)]	0.346	0.291	0.235	0.354	0.290	0.241	0.355	0.341	0.273
H(r)[Ru-N(2)]	-0.015	-0.018	-0.019	-0.014	-0.018	-0.021	-0.011	-0.013	-0.016
$E_{\mathrm{int}}^{\mathrm{RuN(2)}}$	-0.441	-0.496	-0.526	-0.443	-0.502	-0.530	-0.390	-0.438	-0.501
$V_{\mathrm{cl}}^{\mathrm{RuN(2)}}$	-0.304	-0.357	-0.386	-0.307	-0.364	-0.388	-0.260	-0.302	-0.363
$V_{\mathrm{xc}}^{\mathrm{RuN(2)}}$	-0.138	-0.139	-0.140	-0.136	-0.139	-0.142	-0.130	-0.135	-0.138

Table S6 Ru-N(3) parameters in compounds **1**-**3**: bond length (r/Å), Wiberg bond index (WBI/a.u.), electron density (ρ(r)/a.u.), Laplacian of ρ(r) ($\nabla^2\rho$(r)/a.u.), total energy density (H(r)/a.u.), total interaction energy ($E_{\mathrm{int}}^{\mathrm{AB}}$), classical interaction energy ($V_{\mathrm{cl}}^{\mathrm{AB}}$), exchange and correlation energy ($V_{\mathrm{xc}}^{\mathrm{AB}}$)

Parameter	$\mathbf{1}^{+}$	$\mathbf{1}^{2+}$	$\mathbf{1}^{3+}$	$\mathbf{2}^{+}$	$\mathbf{2}^{2+}$	$\mathbf{2}^{3+}$	$\mathbf{3}^{+}$	$\mathbf{3}^{2+}$	$\mathbf{3}^{3+}$
r[Ru-N(3)]	2.212	2.224	2.213	2.160	2.165	2.173	2.208	2.188	2.186
WBI[Ru-N(3)]	0.652	0.659	0.691	0.705	0.723	0.751	0.649	0.701	0.733
ρ(r)[Ru-N(3)]	0.071	0.075	0.081	0.082	0.086	0.089	0.069	0.076	0.082
$\nabla^2\rho$(r)[Ru-N(3)]	0.305	0.265	0.230	0.336	0.290	0.242	0.336	0.318	0.275
H(r)[Ru-N(3)]	-0.010	-0.013	-0.017	-0.014	-0.018	-0.021	-0.008	-0.012	-0.016
$E_{\mathrm{int}}^{\mathrm{RuN(3)}}$	-0.417	-0.471	-0.517	-0.445	-0.503	-0.531	-0.376	-0.438	-0.501
$V_{\mathrm{cl}}^{\mathrm{RuN(3)}}$	-0.296	-0.347	-0.389	-0.311	-0.365	-0.389	-0.256	-0.307	-0.363
$V_{\mathrm{xc}}^{\mathrm{RuN(3)}}$	-0.122	-0.123	-0.128	-0.134	-0.139	-0.142	-0.121	-0.131	-0.138

Table S7 Ru-N(4) parameters in compounds **1**-**3**: bond length (r/Å), Wiberg bond index (WBI/a.u.), Laplacian of ρ(r) ($\nabla^2\rho$(r)/a.u.), total energy density (H(r)/a.u.), total interaction energy ($E_{\mathrm{int}}^{\mathrm{AB}}$), classical interaction energy ($V_{\mathrm{cl}}^{\mathrm{AB}}$), exchange and correlation energy ($V_{\mathrm{xc}}^{\mathrm{AB}}$)

Parameter	$\mathbf{1}^{+}$	$\mathbf{1}^{2+}$	$\mathbf{1}^{3+}$	$\mathbf{2}^{+}$	$\mathbf{2}^{2+}$	$\mathbf{2}^{3+}$	$\mathbf{3}^{+}$	$\mathbf{3}^{2+}$	$\mathbf{3}^{3+}$
r[Ru-N(4)]	2.175	2.164	2.185	2.170	2.166	2.186	2.208	2.195	2.185
WBI[Ru-N(4)]	0.688	0.726	0.742	0.692	0.723	0.744	0.649	0.692	0.733
ρ(r)[Ru-N(4)]	0.078	0.086	0.087	0.079	0.086	0.087	0.069	0.074	0.083
$\nabla^2\rho$(r)[Ru-N(4)]	0.330	0.291	0.234	0.337	0.290	0.232	0.337	0.327	0.274
H(r)[Ru-N(4)]	-0.013	-0.018	-0.019	-0.013	-0.018	-0.020	-0.008	-0.011	-0.017
$E_{\mathrm{int}}^{\mathrm{RuN(4)}}$	-0.436	-0.496	-0.525	-0.441	-0.503	-0.523	-0.376	-0.435	-0.501
$V_{\mathrm{cl}}^{\mathrm{RuN(4)}}$	-0.305	-0.357	-0.385	-0.309	-0.365	-0.383	-0.256	-0.305	-0.362
$V_{\mathrm{xc}}^{\mathrm{RuN(4)}}$	-0.131	-0.139	-0.139	-0.132	-0.139	-0.140	-0.121	-0.130	-0.138

Table S8 Ru-N_{trans} parameters in compounds **1** and **3**: bond length (r/Å), Wiberg bond index (WBI/a.u.), electron density (ρ(r)/a.u.), Laplacian of ρ(r) ($\nabla^2\rho$(r)/a.u.), total energy density (H(r)/a.u.), total interaction energy ($E_{\mathrm{int}}^{\mathrm{AB}}$), classical interaction energy ($V_{\mathrm{cl}}^{\mathrm{AB}}$), exchange and correlation energy ($V_{\mathrm{xc}}^{\mathrm{AB}}$)

Parameter	$\mathbf{1}^{+}$	$\mathbf{1}^{2+}$	$\mathbf{1}^{3+}$	$\mathbf{3}^{+}$	$\mathbf{3}^{2+}$	$\mathbf{3}^{3+}$
r(Ru-N_{trans})	2.273	2.184	2.160	2.493	2.275	2.186
WBI(Ru-N_{trans})	0.574	0.666	0.737	0.418	0.598	0.695
ρ(r)(Ru-N_{trans})	0.063	0.082	0.090	0.039	0.063	0.082
$\nabla^2\rho$(r)(Ru-N_{trans})	0.254	0.265	0.256	0.158	0.255	0.262
H(r)(Ru-N_{trans})	-0.008	-0.017	-0.022	-0.003	-0.008	-0.017
$E_{\mathrm{int}}^{\mathrm{RuN_{trans}}}$	-0.410	-0.509	-0.543	-0.289	-0.411	-0.520
$V_{\mathrm{cl}}^{\mathrm{RuN_{trans}}}$	-0.311	-0.389	-0.405	-0.223	-0.308	-0.396
$V_{\mathrm{xc}}^{\mathrm{RuN_{trans}}}$	-0.099	-0.119	-0.138	-0.067	-0.104	-0.124