Supporting Information
for the
Article entitled

Metalloligand-based Coordination Polymer Embedding the Nitrosyl Ruthenium Complex for Photoactive Materials with Bounded Nitric Oxide

authored by

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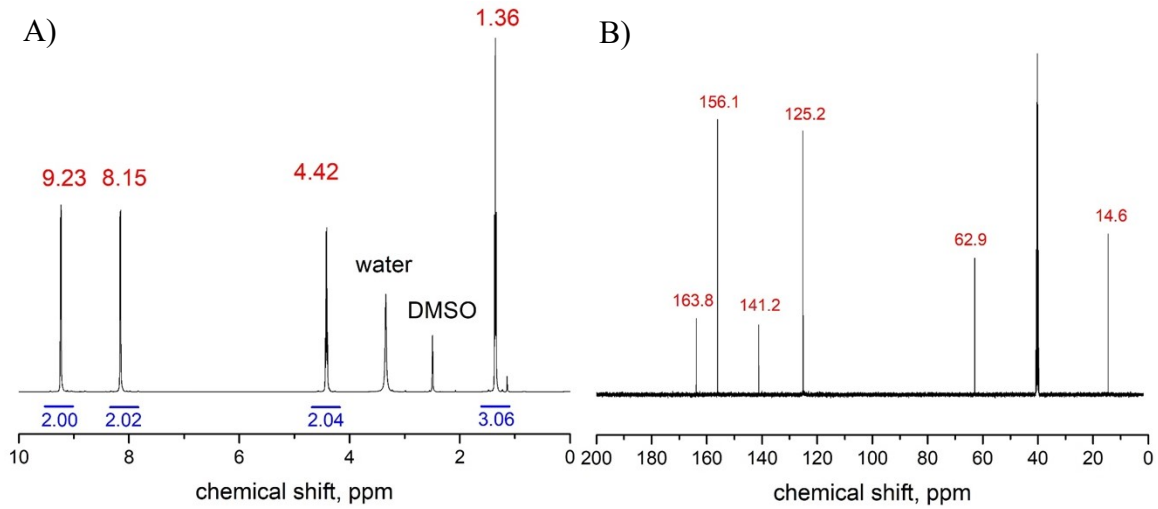


Figure S1. a) ^{1}H-NMR and b) ^{13}C-NMR spectra of insoluble product after reaction between $[RuNO(inicEt)_2Cl_3]$ with HNO_3 dissolved in DMSO.

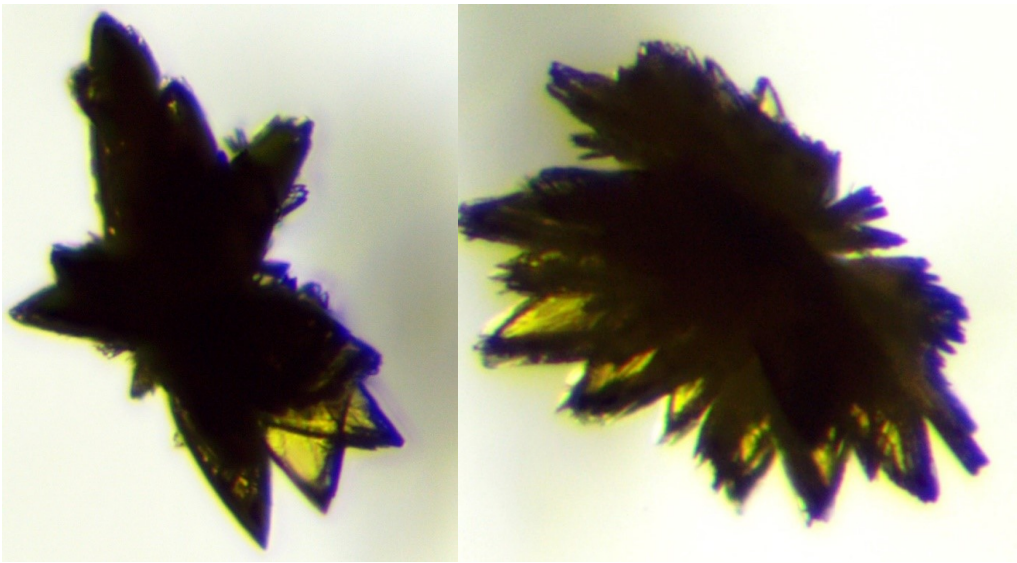
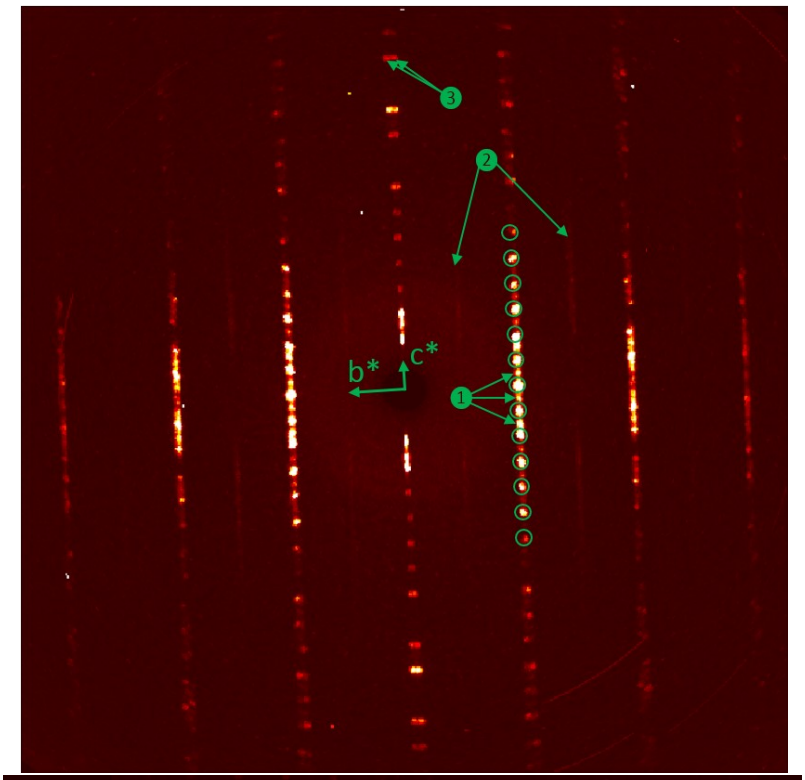
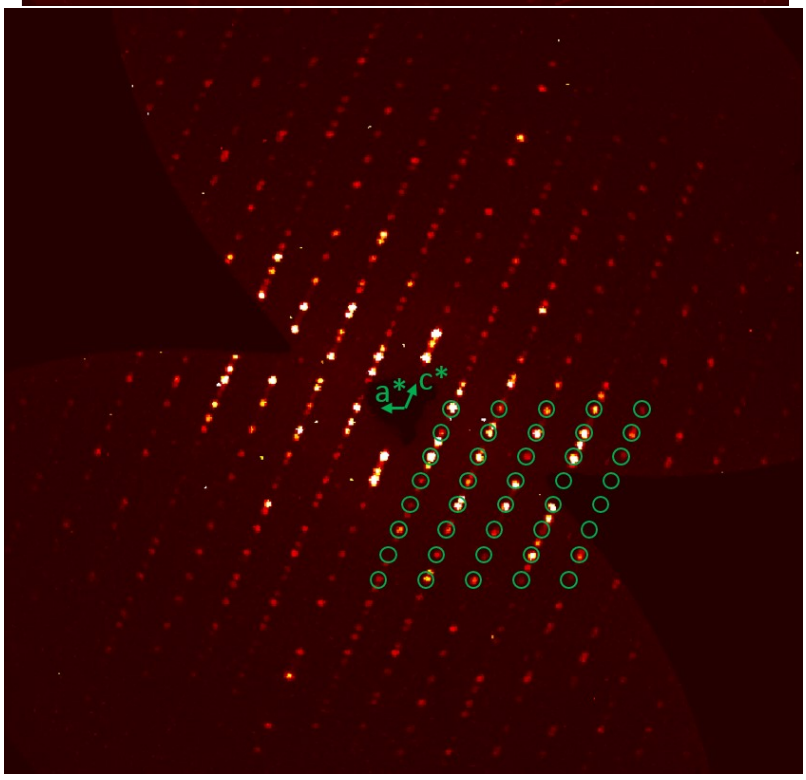


Figure S2. The typical view of the crystal aggregates for $[RuNO(H_2O)_2(inic)_2(OH)]*xH_2O$. The largest aggregate size in both cases is equal 0.25 mm.


3
2
b*
c*
1


a*
c*

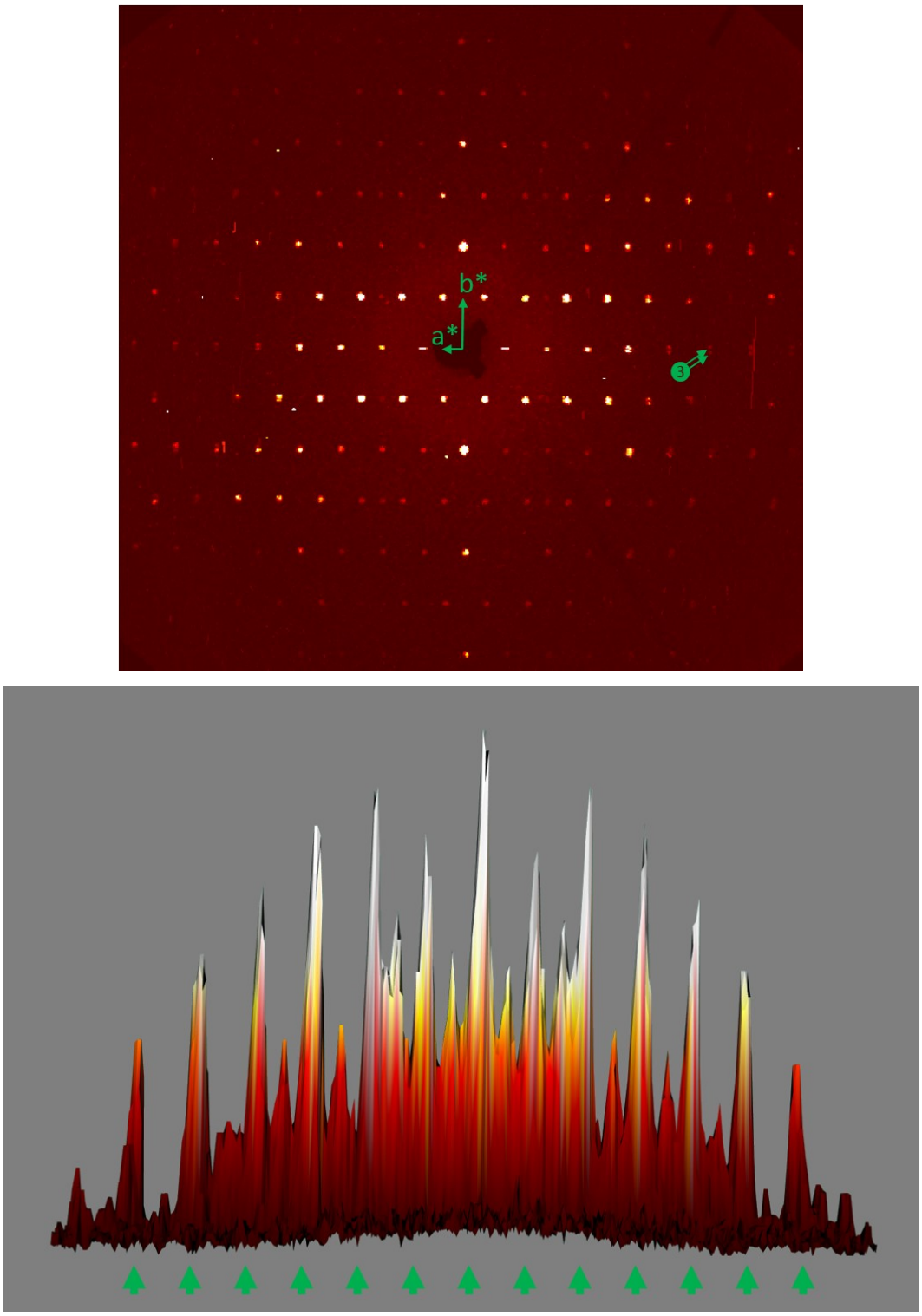


Figure S3. Flat (0*kl*, *h*0*l*, *hk*0) and linear (02*l*) reconstructions of the intensity distribution in reciprocal space. The open circles mark the positions of the selected reflections of the monoclinic *C* lattice. ❶ - sharp peaks outside the lattice; ❷ - diffuse

intensity; ❸ - splitting of high-angle peaks. The intensity distribution on the 02*l* reconstruction (logarithmic intensity scale) has a complex character.

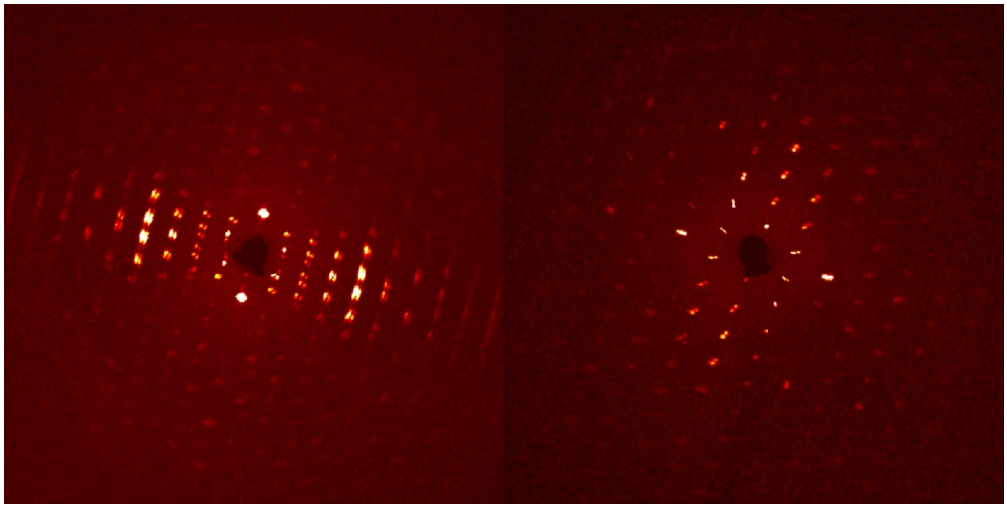


Figure S4. Reconstructions of the diffraction intensity distribution from a crystal aged under the mother liquor drawn through planes equivalent to *h*0*l* and *hk*0 of a freshly fallen crystal (compare with Fig. S3). The diffraction was collected at 170 K.

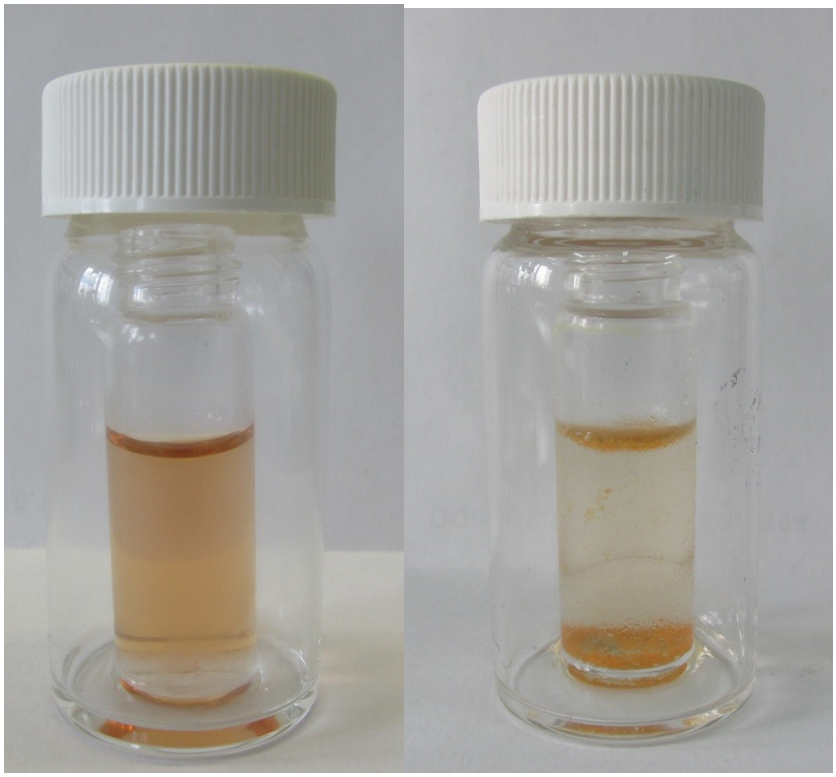


Figure S5. The vial with alkaline solution of $[RuNO(inicEt)_2Cl_3]$ and $Zn(CH_3COO)_2$ before (left) and after (right) saturation with acetic acid.

Table S1. Crystal data and geometry parameters for $[Zn\{RuNO(H_2O)(inic)_2(OH)_2\}_2]\cdot 12H_2O$

Crystal data and structure refinement for complex.

Identification code	$[Zn\{RuNO(H_2O)(inic)_2(OH)_2\}_2]\cdot 12H_2O$
Empirical formula	$C_{24}H_{40}N_6O_{28}Ru_2Zn$
Formula weight	1128.13
Temperature/K	150(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.0341(19)
b/Å	9.664(2)
c/Å	12.968(3)
α/°	71.157(7)
β/°	72.824(6)
γ/°	73.170(7)
Volume/Å^3	999.9(4)
Z	1
ρ_{calc}g/cm^3	1.874
μ/mm^{-1}	1.447
F(000)	568.0
Crystal size/mm^3	0.538 × 0.515 × 0.278
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.404 to 57.9
Index ranges	$-12 \le h \le 12$, $-13 \le k \le 8$, $-17 \le l \le 17$
Reflections collected	15540
Independent reflections	5208 [R_{int} = 0.0781, R_{sigma} = 0.0978]
Data/restraints/parameters	5208/0/277
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0630, wR_2 = 0.1528
Final R indexes [all data]	R_1 = 0.0874, wR_2 = 0.1658
Largest diff. peak/hole / e Å^{-3}	3.36/-2.25

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	O2	2.018(4)	O12	C16	1.265(7)
Ru1	O1	1.946(4)	N2	C21	1.346(7)
Ru1	O4	2.109(4)	N2	C25	1.354(7)
Ru1	N2	2.103(5)	N1	C11	1.355(7)

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	N1	2.065(5)	N1	C15	1.347(7)
Ru1	N3	1.759(5)	O3	N3	1.132(6)
Zn1	O2[1]	2.150(4)	C12	C11	1.375(8)
Zn1	O2	2.150(4)	C12	C13	1.402(8)
Zn1	O1[1]	2.097(4)	C23	C24	1.393(8)
Zn1	O1	2.097(4)	C23	C26	1.524(8)
Zn1	O11[2]	2.122(4)	C23	C22	1.388(8)
Zn1	O11[3]	2.122(4)	C24	C25	1.381(8)
O11	Zn1[4]	2.122(4)	C21	C22	1.381(8)
O11	C16	1.253(7)	C14	C15	1.386(8)
O22	C26	1.251(7)	C14	C13	1.380(8)
O21	C26	1.254(7)	C13	C16	1.510(8)

[1]1-X,1-Y,2-Z; [2]1-X,-Y,2-Z; [3]+X,1+Y,+Z; [4]+X,-1+Y,+Z

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Ru1	O4	169.40(15)	Ru1	O2	Zn1	99.20(15)
O2	Ru1	N2	93.38(17)	Ru1	O1	Zn1	103.42(17)
O2	Ru1	N1	85.79(18)	C16	O11	Zn1[4]	124.0(4)
O1	Ru1	O2	81.93(15)	C21	N2	Ru1	121.2(4)
O1	Ru1	O4	87.82(16)	C21	N2	C25	118.3(5)
O1	Ru1	N2	87.54(17)	C25	N2	Ru1	120.5(4)
O1	Ru1	N1	90.01(17)	C11	N1	Ru1	123.4(4)
N2	Ru1	O4	88.84(16)	C15	N1	Ru1	118.6(4)
N1	Ru1	O4	91.55(16)	C15	N1	C11	118.0(5)
N1	Ru1	N2	177.50(18)	O3	N3	Ru1	173.8(5)
N3	Ru1	O2	97.78(18)	C11	C12	C13	119.5(5)
N3	Ru1	O1	178.4(2)	C24	C23	C26	120.7(5)
N3	Ru1	O4	92.39(18)	C22	C23	C24	118.1(5)
N3	Ru1	N2	94.0(2)	C22	C23	C26	121.3(5)
N3	Ru1	N1	88.4(2)	C25	C24	C23	119.2(5)
O2	Zn1	O2[1]	180.0(2)	N2	C21	C22	122.1(5)
O1	Zn1	O2[1]	104.54(14)	N1	C11	C12	122.3(5)
O1	Zn1	O2	75.46(14)	O22	C26	O21	125.5(6)
O1[1]	Zn1	O2	104.54(14)	O22	C26	C23	117.0(5)
O1[1]	Zn1	O2[1]	75.46(14)	O21	C26	C23	117.4(5)
O1	Zn1	O1[1]	180.0	C21	C22	C23	119.9(5)
O1[1]	Zn1	O11[2]	90.07(15)	C13	C14	C15	119.7(5)
O1	Zn1	O11[3]	90.07(15)	N2	C25	C24	122.4(5)

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1[1]	Zn1	O11[3]	89.93(15)	N1	C15	C14	122.4(5)
O1	Zn1	O11[2]	89.93(15)	C12	C13	C16	121.6(5)
O11[2]	Zn1	O2[1]	90.54(16)	C14	C13	C12	118.0(5)
O11[3]	Zn1	O2	90.54(16)	C14	C13	C16	120.5(5)
O11[2]	Zn1	O2	89.46(16)	O11	C16	O12	126.8(5)
O11[3]	Zn1	O2[1]	89.46(16)	O11	C16	C13	116.7(5)
O11[2]	Zn1	O11[3]	180.0	O12	C16	C13	116.4(5)

[1]1-X,1-Y,2-Z; [2]1-X,-Y,2-Z; [3]+X,1+Y,+Z; [4]+X,-1+Y,+Z

TGA studies of $[Zn\{RuNO(H_2O)(inic)_2(OH)_2\}_2]\cdot 12H_2O$

At least three overlapped stages can be detected on TG(DTG) and DTA curves for Zn-Ru complex (Fig. S3).

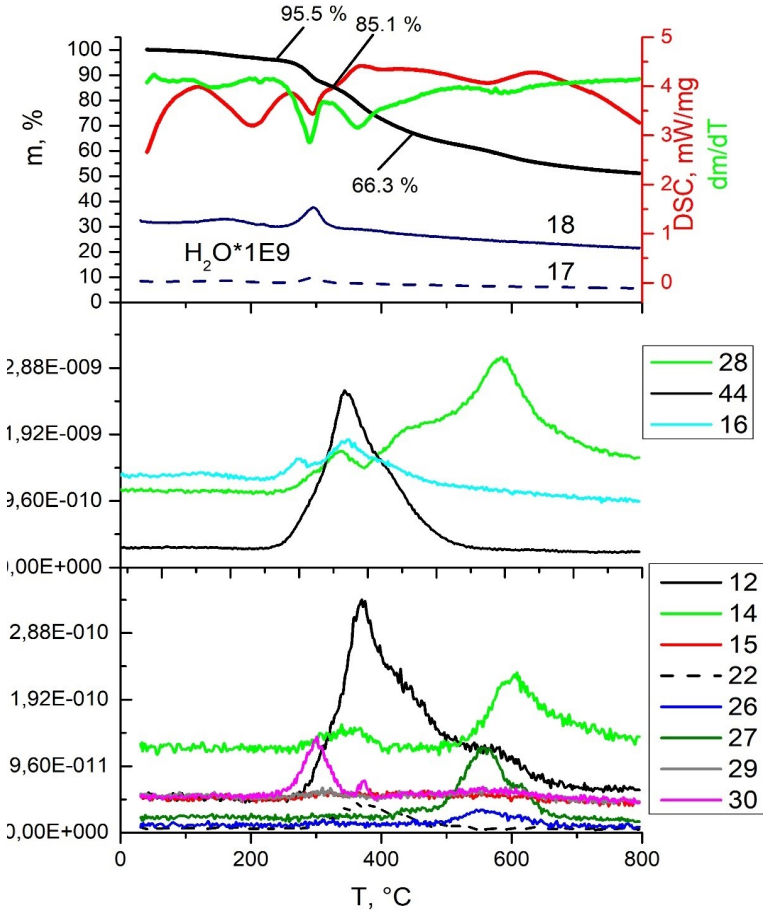


Figure S6. Synchronous TG – MS data for $[Zn\{RuNO(H_2O)(inic)_2(OH)_2\}_2]\cdot 12H_2O$ in Ar atmosphere with 10K/min heating rate.

Guest water molecules are gradually released upon heating of the sample up to 200-250°C. The mass loss at 250°C (4.5 %) approximately corresponds to 4-5 H_2O molecules. The main water release takes place at the temperatures 250-320°C and associated with sharp increase of the ion current with m/z ratio of 18. At 320°C the mass loss (15 %, 9-10 H_2O molecules) well corresponds to the elemental analysis for the fresh crystals and the water content derived from single crystal XRD studies. The destruction of Ru-NO fragment also begins at that stage (ion current m/z = 30).

The next stage 320-450°C is associated with de-carboxylation of isonicotinic acid residues (ion current m/z = 44) and also with the release of coordinated hydroxide and water ligands. The mass loss after 450°C is equal 34 %. And the final decomposition of pyridine rings in inert atmosphere slowly goes after 450°C.

The similar picture is observed in reductive atmosphere (Fig. S4), except of NO formation. In the reductive atmosphere nitric oxide is transformed to nitrogen (ion current m/z = 28).

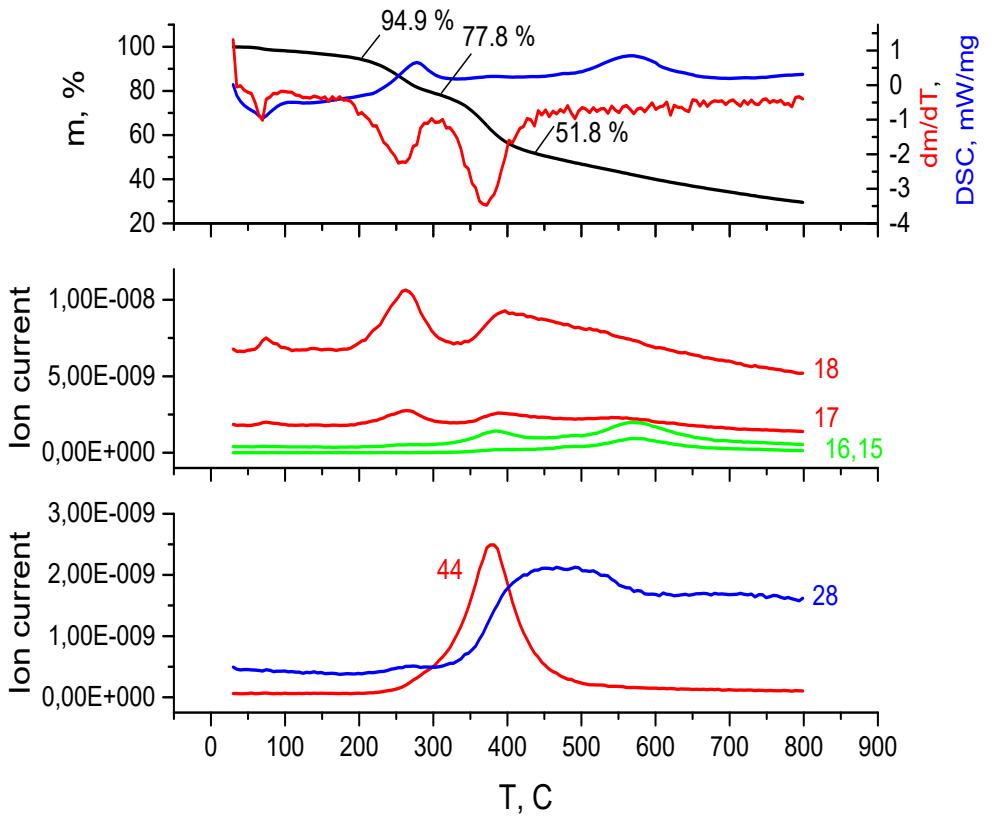


Figure S7. Synchronous TG – MS data for $[Zn\{RuNO(H_2O)(inic)_2(OH)_2\}_2]\cdot 12H_2O$ in Ar/H_2 atmosphere with 10K/min heating rate.

The TG (DTG) and DSC curves for $[RuNO(H_2O)_2(inic)_2(OH)]\cdot xH_2O$ clearly demonstrate three separated stages of decomposition: 150-230°C, 270-390°C and 430-500°C (Fig. S5). The first and second stages are slightly endothermic and the last stage is exothermic.

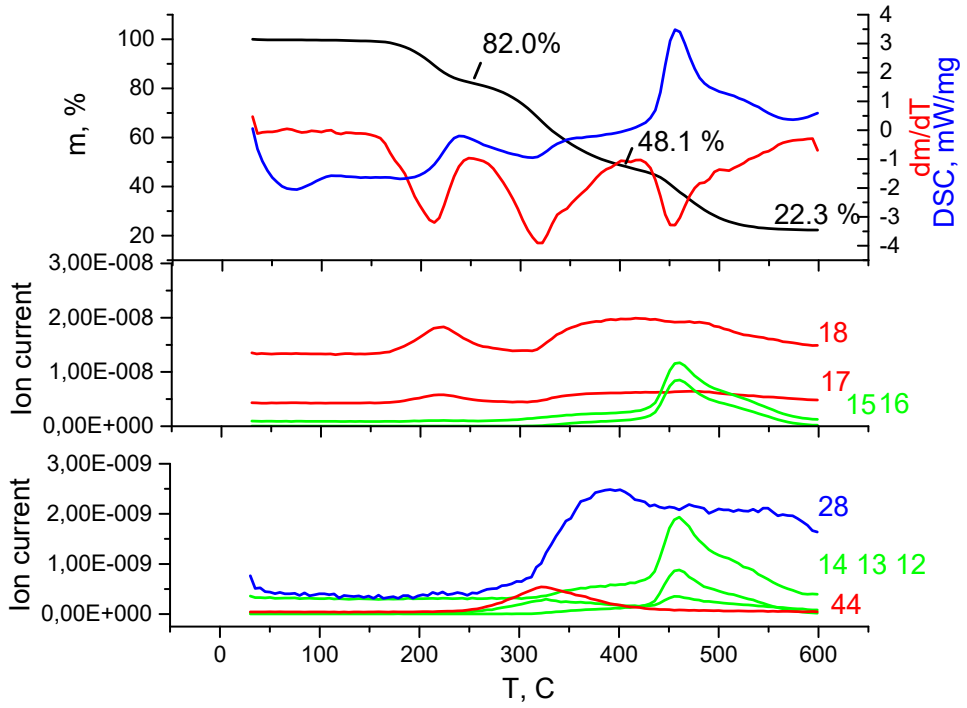


Figure S8. Synchronous TG – MS data for $[RuNO(H_2O)_2(inic)_2(OH)]\cdot xH_2O$ in Ar/H_2 atmosphere with 10 K/min heating rate.

According to mass changes and mass-spectra of gaseous phase the stages can be attributed to the following processes:

1. Complete removal of all water molecules and hydoxo-ligands. The only visible ion currents at that stage (m/z = 17 and 18) correspond to water molecules. Mass change at that stage (near 18 %) corresponds to 77-83 Da, depending on the initial formula, which is equal to 4-4.5 H_2O molecules.
2. The second stage is mainly accompanied by ion currents corresponding to CO_2 (m/z = 44), nitrogen (m/z = 28) and water (m/z = 17, 18). Thus the decarboxylation of isonicotinic acid fragments and reduction of NO group should be taken into consideration. However, the mass change (50-52 %) is larger than supposed for removal of H_2O_x + NO + $2CO_2$; thus, the beginning of pyridine rings decomposition should be considered.

3. The mass-spectra show the set of ion currents (m/z = 12-16) that is typical for decomposition of hydrocarbons in H_2 atmosphere. Thus the last stage corresponds to the removal of the pyridine residuals.

Final residue after heating up to 600°C was analyzed by powder XRD. The only product that can be determined by XRD was metallic ruthenium (Fig. S6).

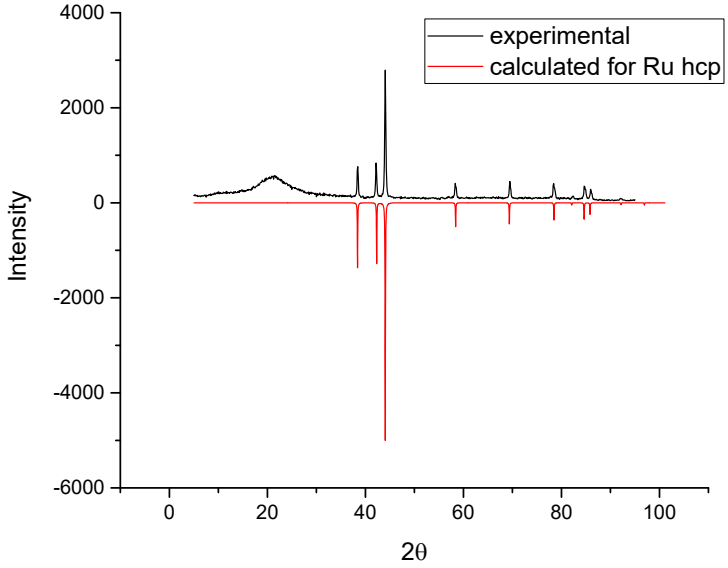


Figure S9. Experimental XRD pattern for the residue after thermal decomposition of $[RuNO(H_2O)_2(inic)_2(OH)]\cdot xH_2O$ in Ar/H_2 atmosphere (600°C) and theoretical XRD for HCP ruthenium.

Thus, the data of elemental analysis and TG-MS confirm the formula $[RuNO(H_2O)_2(inic)_2(OH)]\cdot xH_2O$, where x is in the range 1-2.

Model 1

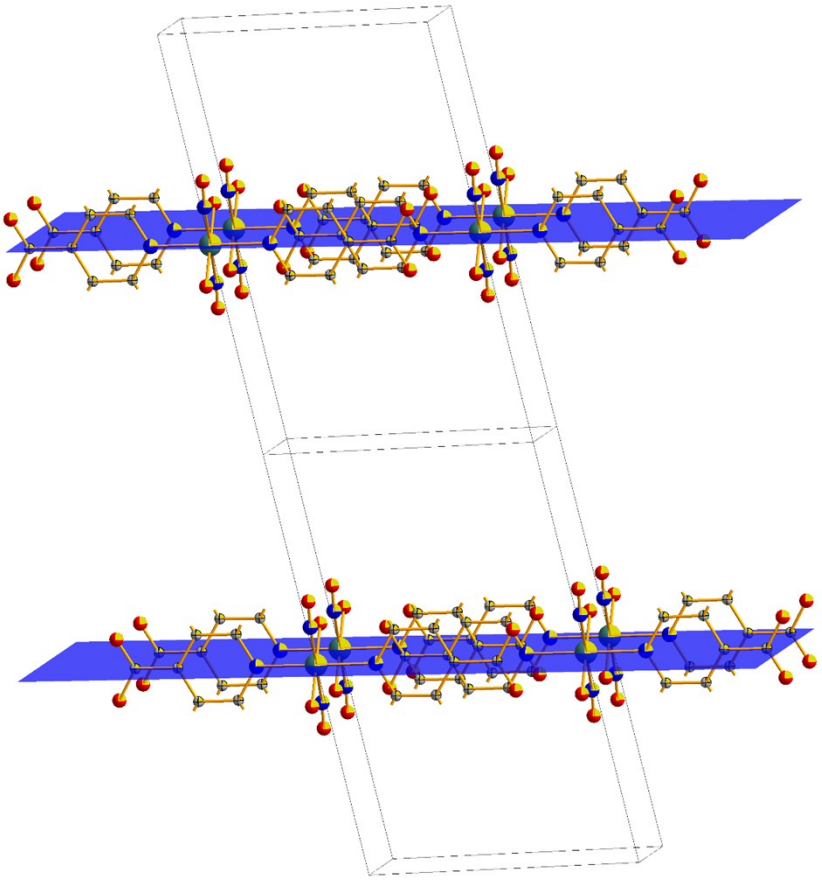


Figure S10. The crystal package in Model 1. Planes corresponding to complex layers are built as average for ruthenium atoms and nitrogen atoms of heterocycles.

The model was fitted with only one layer of complexes in the unit cell. SQUEZZE procedure of Platon determined Solvent Accessible Volume = 590 Å^3 per unit cell and electrons found in S.A.V. = 305.

Table S2. Crystal data and structure refinement for Model 1

Empirical formula	$C_{12}H_8N_4O_7Ru$
Formula weight	421.29
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.7164(7)
b/Å	9.6430(12)
c/Å	15.5894(18)

α/°	75.772(7)
β/°	77.973(4)
γ/°	69.733(4)
Volume/Å^3	909.63(19)
Z	1
ρ_{calc}g/cm^3	0.769
μ/mm^{-1}	0.450
F(000)	208.0
Crystal size/mm^3	0.280 × 0.130 × 0.040
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.72 to 59.454
Index ranges	$-9 \le h \le 9$, $-13 \le k \le 13$, $-21 \le l \le 21$
Reflections collected	15240
Independent reflections	5118 [R_{int} = 0.0797, R_{sigma} = 0.0896]
Data/restraints/parameters	5118/6/115
Goodness-of-fit on F^2	1.152
Final R indexes [I>=2σ (I)]	R_1 = 0.0744, wR_2 = 0.1945
Final R indexes [all data]	R_1 = 0.0764, wR_2 = 0.1969
Largest diff. peak/hole / e Å^{-3}	3.10/-2.01

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru01	N1	1.923(5)	O118	C117	1.214(9)
Ru01	N1[1]	1.923(5)	N1	O2	1.027(14)
Ru01	O1	1.981(5)	C114	C113	1.334(9)
Ru01	O1[1]	1.981(5)	C114	C115	1.371(9)
Ru01	N111[1]	2.086(4)	C114	C117	1.491(8)
Ru01	N111	2.086(4)	C116	C115	1.397(7)
N111	C112	1.333(7)	C112	C113	1.401(7)
N111	C116	1.345(7)	O119	C117	1.251(9)

[1]2-X,-Y,1-Z

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	Ru01	N1[1]	180.0(4)	C112	N111	C116	118.9(4)
N1	Ru01	O1	90.7(3)	C112	N111	Ru01	120.5(4)
N1[1]	Ru01	O1	89.3(3)	C116	N111	Ru01	120.6(3)
N1	Ru01	O1[1]	89.3(3)	O2	N1	Ru01	159.8(10)
N1[1]	Ru01	O1[1]	90.7(3)	C113	C114	C115	119.1(5)

O1	Ru01	O1[1]	180.0	C113	C114	C117	120.9(6)
N1	Ru01	N111[1]	89.84(19)	C115	C114	C117	120.1(6)
N1[1]	Ru01	N111[1]	90.16(19)	N111	C116	C115	121.1(5)
O1	Ru01	N111[1]	90.66(17)	C114	C115	C116	119.3(5)
O1[1]	Ru01	N111[1]	89.34(17)	N111	C112	C113	121.0(5)
N1	Ru01	N111	90.16(19)	C114	C113	C112	120.6(6)
N1[1]	Ru01	N111	89.84(19)	O118	C117	O119	120.0(7)
O1	Ru01	N111	89.34(17)	O118	C117	C114	120.9(6)
O1[1]	Ru01	N111	90.66(17)	O119	C117	C114	119.1(6)
N111[1]	Ru01	N111	180.0				

Model 2

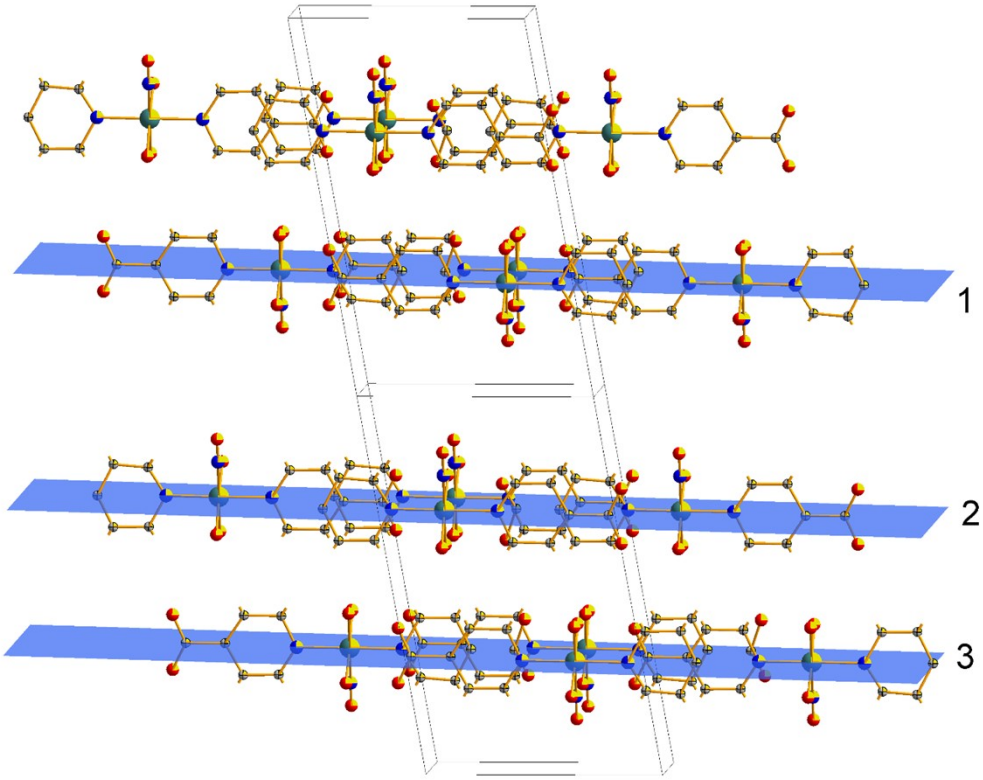


Figure S11. The crystal package in Model 2. Planes corresponding to complex layers are built as average for ruthenium atoms and nitrogen atoms of heterocycles.

The model was fitted with two layers of complexes in the unit cell. Interplane distance between planes 2 and 3 is equal to 5.706 Å, between planes 1 and 2 – 9.265 Å. SQUEZZE procedure of Platon determined Solvent Accessible Volume = 232 Å^3 electrons found in S.A.V. = 131. Solvent accessible volume is located between planes 1 and 2.

Table S3. Crystal data and structure refinement for Model 2

Identification code	Model 2
Empirical formula	$C_{12}H_8N_3O_8Ru$
Formula weight	423.28
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.7164(7)
b/Å	9.6430(12)
c/Å	15.5894(18)
α/°	75.772(7)

β/°	77.973(4)
γ/°	69.733(4)
Volume/Å^3	909.63(19)
Z	2
ρ_{calc}g/cm^3	1.545
μ/mm^{-1}	0.902
F(000)	418.0
Crystal size/mm^3	0.280 × 0.130 × 0.040
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.72 to 59.454
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21
Reflections collected	15240
Independent reflections	5118 [R_{int} = 0.0728, R_{sigma} = 0.0831]
Data/restraints/parameters	5118/0/98
Goodness-of-fit on F^2	2.116
Final R indexes [I>=2σ (I)]	R_1 = 0.1872, wR_2 = 0.4513
Final R indexes [all data]	R_1 = 0.1902, wR_2 = 0.4636
Largest diff. peak/hole / e Å^{-3}	7.92/-3.55

Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ru1	N1	1.868(12)	C212	N211	1.295(16)
Ru1	O1	1.926(12)	C212	C213	1.39(2)
Ru1	O3	2.015(11)	N111	C112	1.311(15)
Ru1	O2	2.022(13)	N111	C116	1.393(16)
Ru1	N111	2.071(11)	N211	C216	1.375(17)
Ru1	N211	2.075(12)	C216	C215	1.45(2)
C214	C215	1.349(19)	C112	C113	1.363(17)
C214	C213	1.435(18)	C113	C114	1.38(2)
C214	C217	1.54(2)	C117	O119	1.37(2)
O118	C117	1.15(2)	C117	C114	1.69(2)
O219	C217	1.209(19)	C115	C114	1.38(2)
O218	C217	1.207(19)	C115	C116	1.40(2)
O4	N1	1.066(16)			

Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

N1	Ru1	O1	177.4(4)	C116	N111	Ru1	117.7(8)
N1	Ru1	O3	90.0(5)	C212	N211	C216	121.0(12)
O1	Ru1	O3	87.4(5)	C212	N211	Ru1	122.4(9)
N1	Ru1	O2	93.7(5)	C216	N211	Ru1	116.6(9)
O1	Ru1	O2	88.9(5)	O4	N1	Ru1	170.1(12)
O3	Ru1	O2	176.1(4)	N211	C216	C215	116.4(12)
N1	Ru1	N111	91.5(5)	C212	C213	C214	118.2(13)
O1	Ru1	N111	88.6(5)	N111	C112	C113	127.0(11)
O3	Ru1	N111	89.4(4)	O218	C217	O219	128.9(16)
O2	Ru1	N111	91.8(5)	O218	C217	C214	115.3(13)
N1	Ru1	N211	90.6(5)	O219	C217	C214	115.2(13)
O1	Ru1	N211	89.1(5)	C214	C215	C216	123.4(14)
O3	Ru1	N211	87.5(4)	C112	C113	C114	112.3(12)
O2	Ru1	N211	91.2(5)	O118	C117	O119	132.9(17)
N111	Ru1	N211	176.3(3)	O118	C117	C114	118.2(15)
C215	C214	C213	116.4(12)	O119	C117	C114	108.7(13)
C215	C214	C217	123.5(12)	C114	C115	C116	116.0(12)
C213	C214	C217	120.0(11)	N111	C116	C115	119.3(11)
N211	C212	C213	124.5(12)	C113	C114	C115	126.2(15)
C112	N111	C116	118.9(11)	C113	C114	C117	116.5(13)
C112	N111	Ru1	123.2(8)	C115	C114	C117	117.1(13)

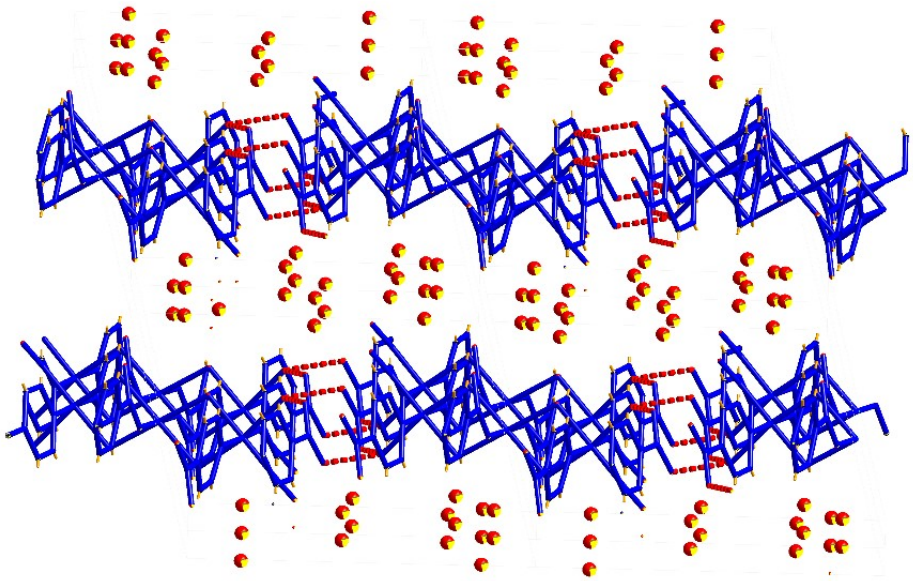


Figure S12. The view on the crystal cell of $\{Zn[RuNO(H_2O)(inic)_2(OH)_2]_2\}\cdot 12H_2O$ along b-axis.

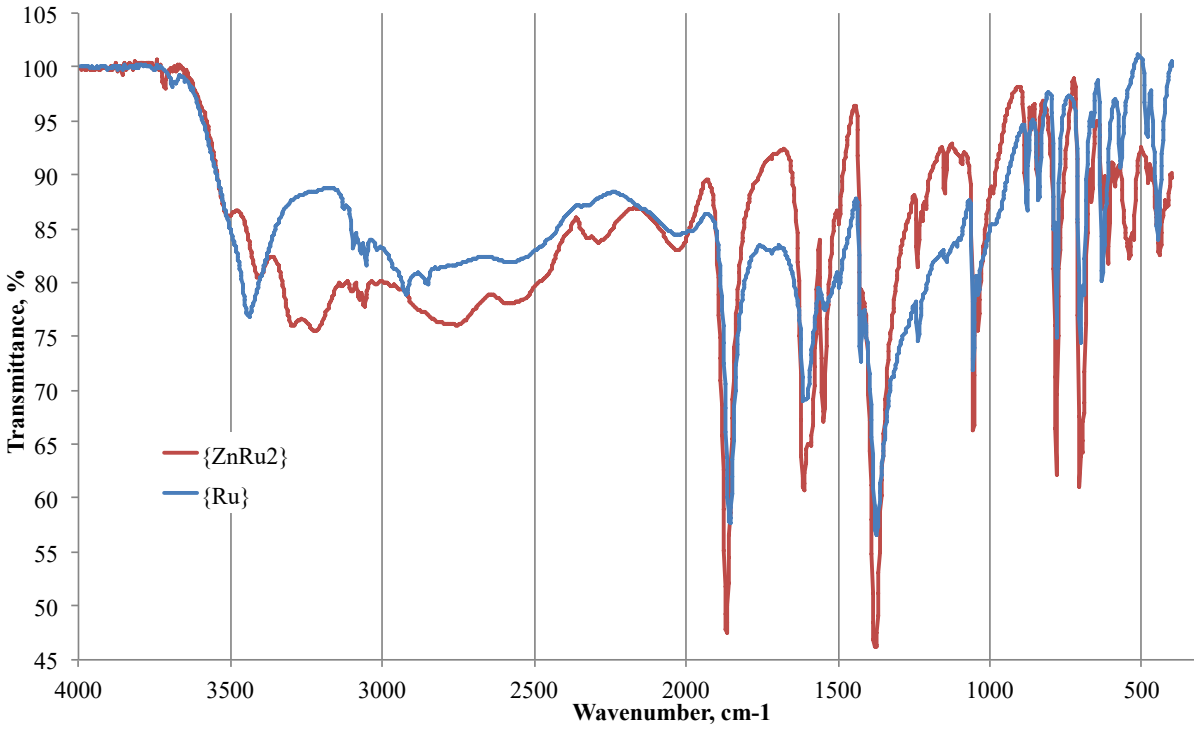


Figure S13. FTIR spectra of *trans*-{Zn[RuNO(H_2O)(inic)$_2$(OH)$_2$]$_2$}·12H_2O (red) and *trans*-[RuNO(H_2O)$_2$(inic)$_2$(OH)]·H_2O (blue) complexes.

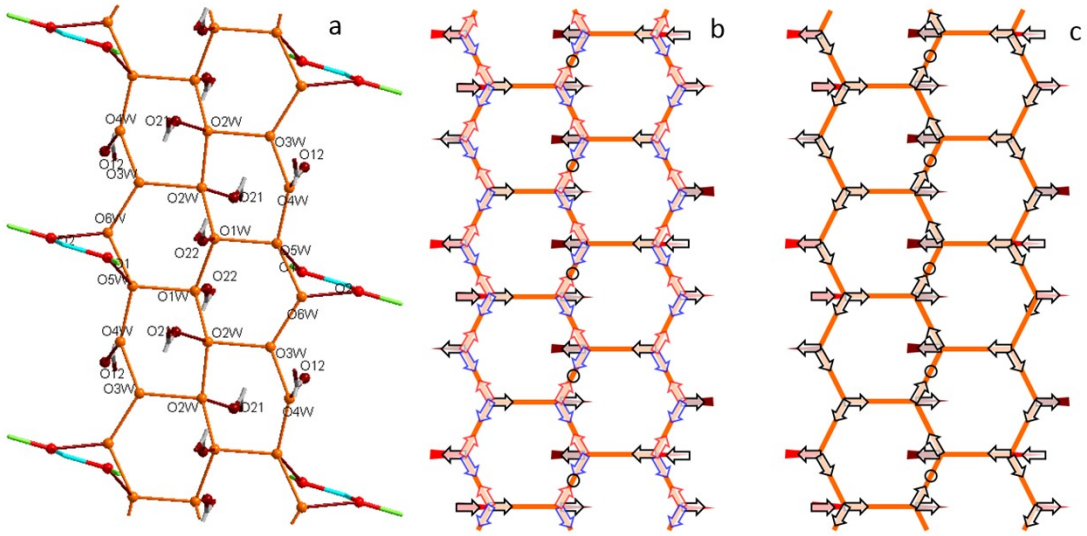
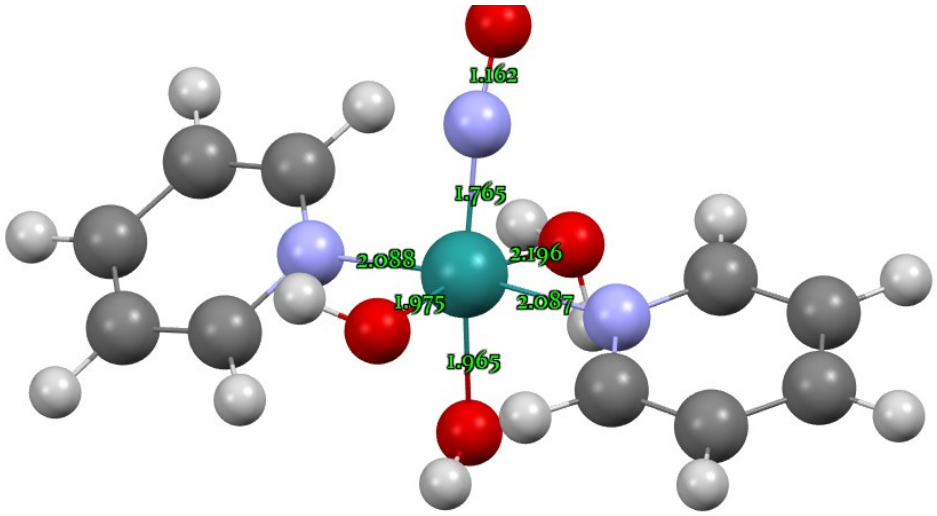


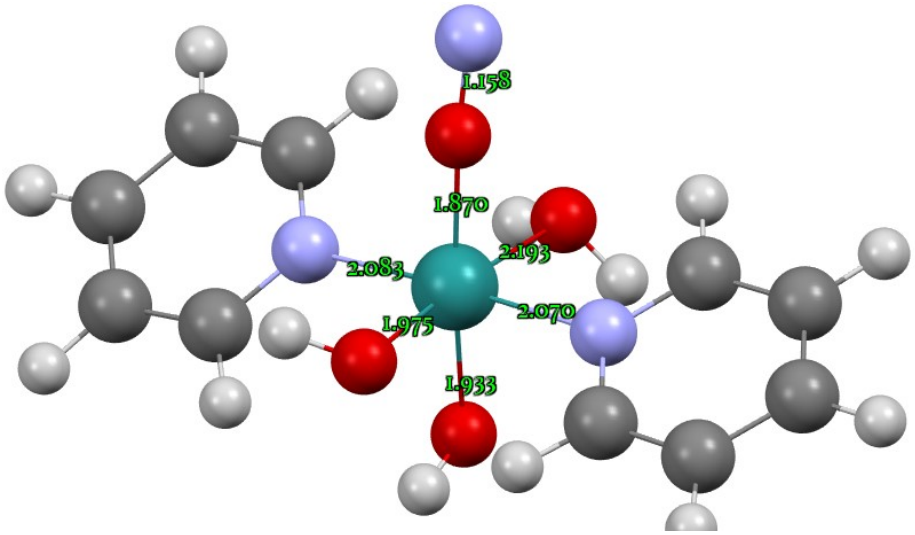
Figure S14. Explanation of hydrogen atoms distribution over the hydrogen bond networks of [Zn{RuNO(H_2O)(inic)$_2$(OH)$_2$}$_2$]·12H_2O: (a) oxygen atoms labeling (green for Ru, cyan for Zn, red for bridging hydroxyl O, brown for carboxyl O, orange for solvate water O); (b) probable averaged distribution of H atoms over the hydrogen bond

network of the water ribbons (black arrows – “ordered” H, red and blue arrows – alternative positioning of “disordered” H, black circles – inversion centers); (c) a variant of local (“ordered”) distribution of H atoms over the hydrogen bond network.

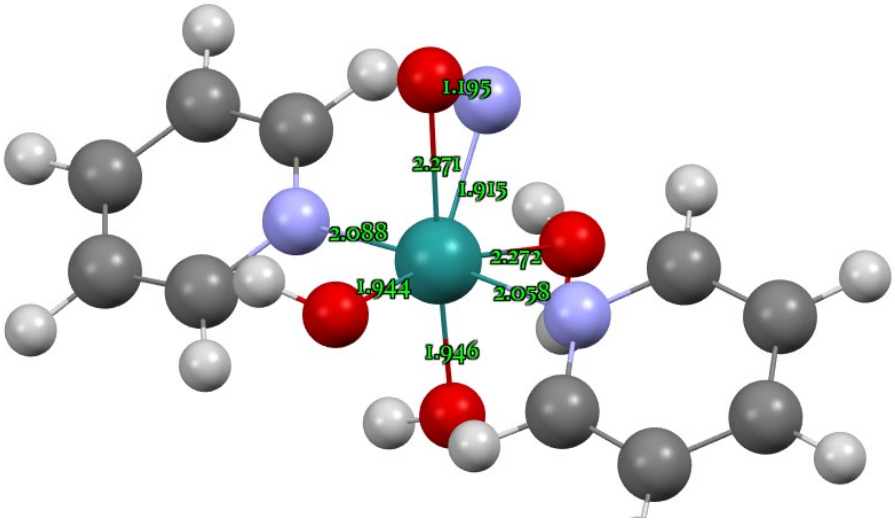
a)


1.162
1.765
2.088
2.196
1.975
2.087
1.965

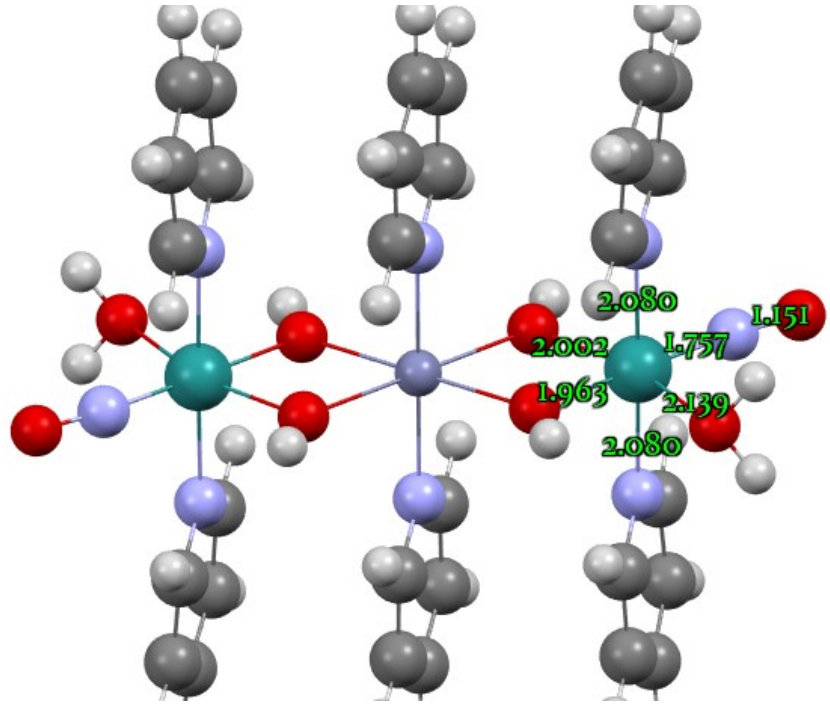
b)


1.158
1.870
2.083
2.193
1.975
2.070
1.933

c)


1.195
2.271
1.915
2.088
2.272
1.944
2.058
1.946

d)



e)

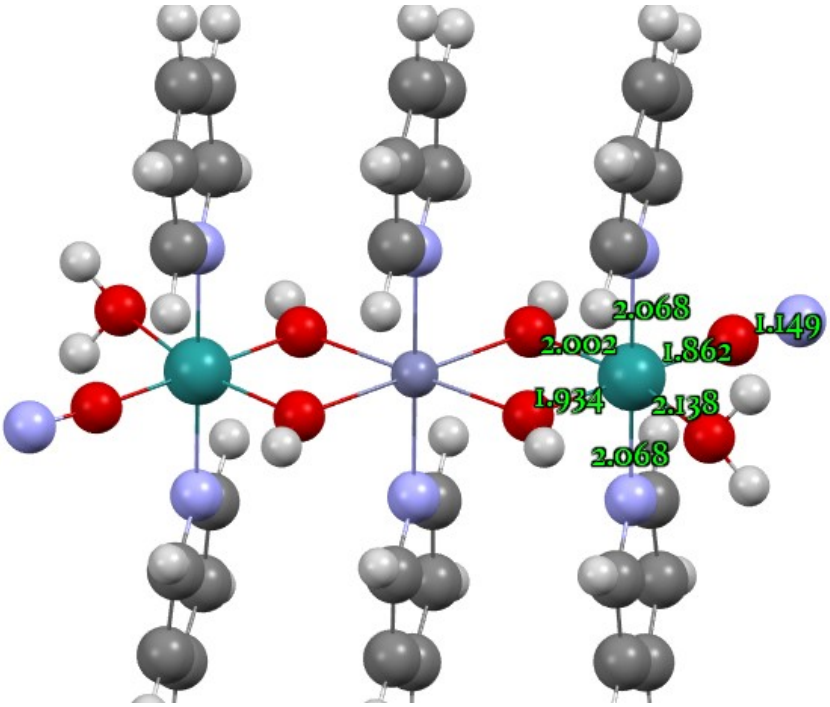
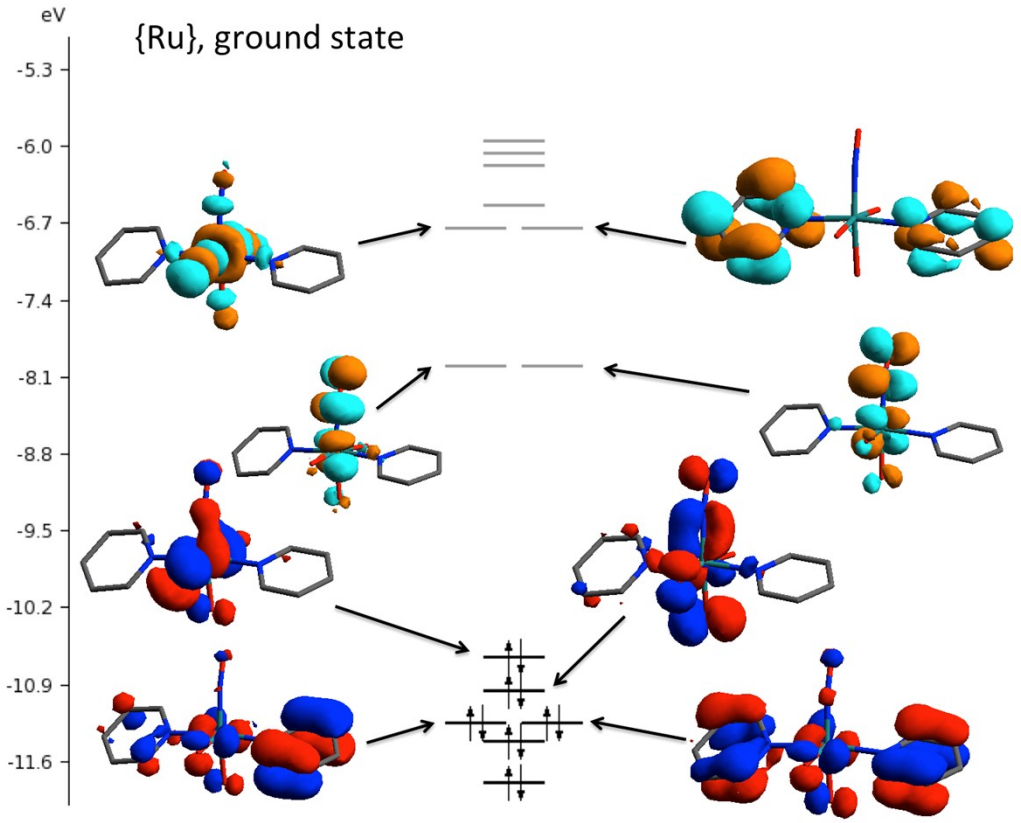
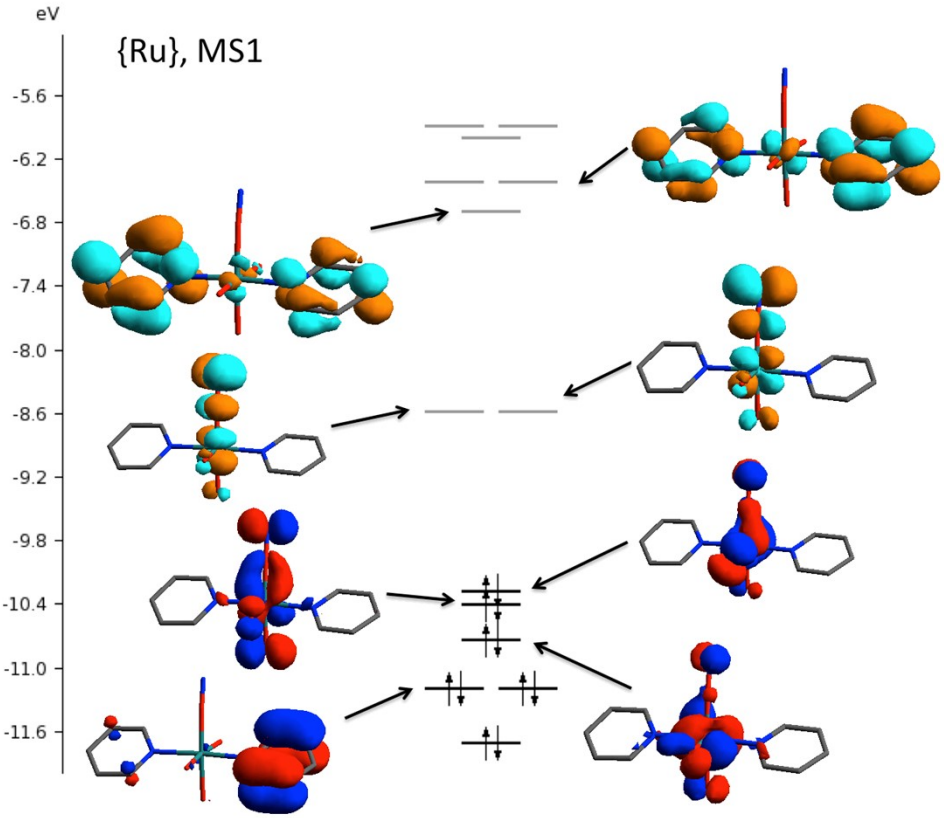


Figure S15. The DFT optimized structures (OPBE/TZP/COSMO) of the model compounds *trans*-$[RuNO(Py)_2(OH)_2(H_2O)]^+$ with the a) *N*-, b) *O*-, c) side-coordinated nitrosyl group and *trans*-$\{Zn(Py)_2[RuNO(Py)_2(OH)_2(H_2O)]_2\}^{4+}$ with d) *N*- or e) *O*-coordinated nitrosyl groups.

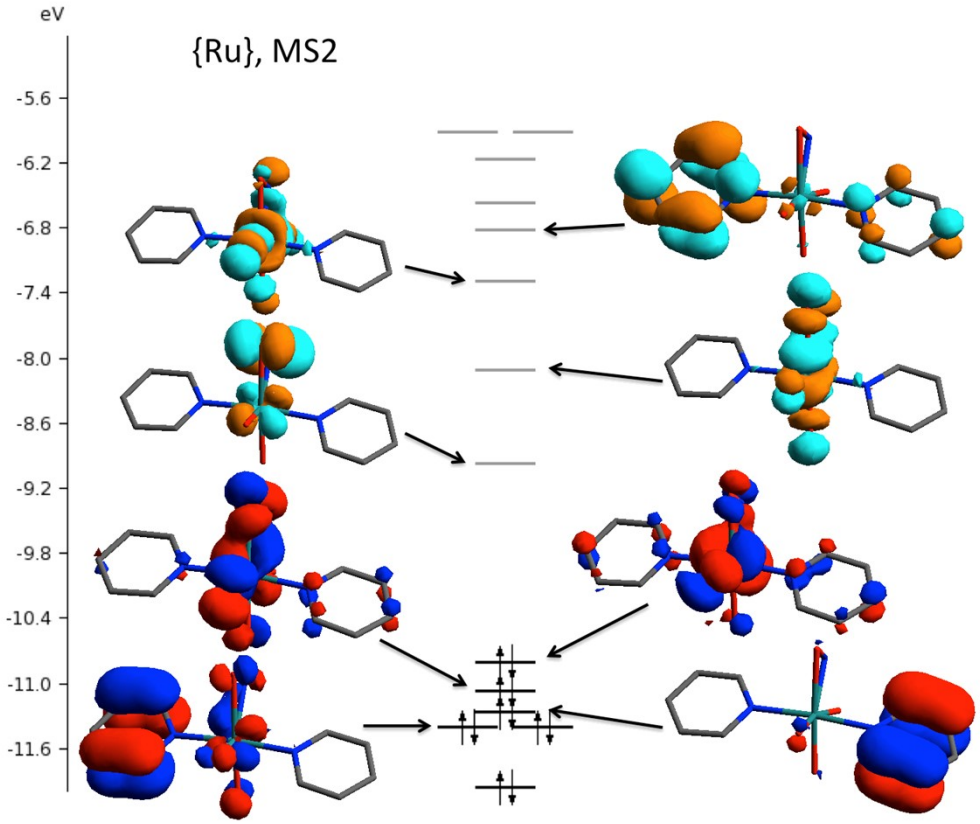
a)


eV
{Ru}, ground state
-5.3
-6.0
-6.7
-7.4
-8.1
-8.8
-9.5
-10.2
-10.9
-11.6

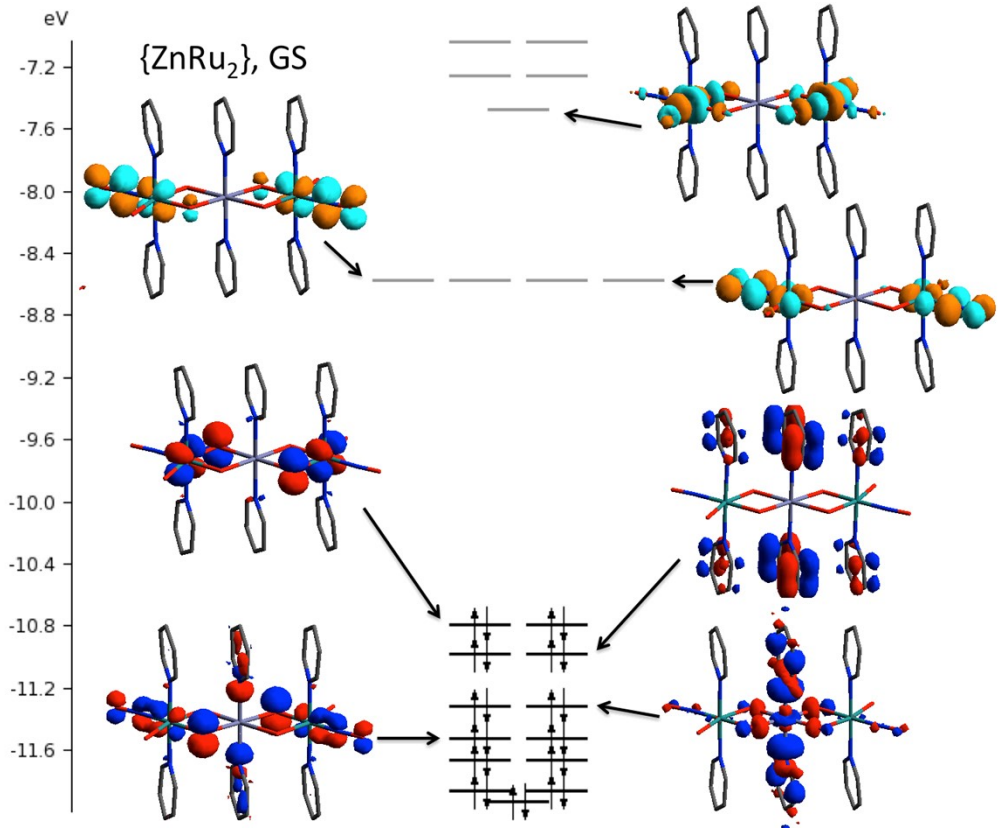
b)


eV
{Ru}, MS1
-5.6
-6.2
-6.8
-7.4
-8.0
-8.6
-9.2
-9.8
-10.4
-11.0
-11.6

c)


eV
{Ru}, MS2
-5.6
-6.2
-6.8
-7.4
-8.0
-8.6
-9.2
-9.8
-10.4
-11.0
-11.6

d)


eV
{ZnRu2}, GS
-7.2
-7.6
-8.0
-8.4
-8.8
-9.2
-9.6
-10.0
-10.4
-10.8
-11.2
-11.6

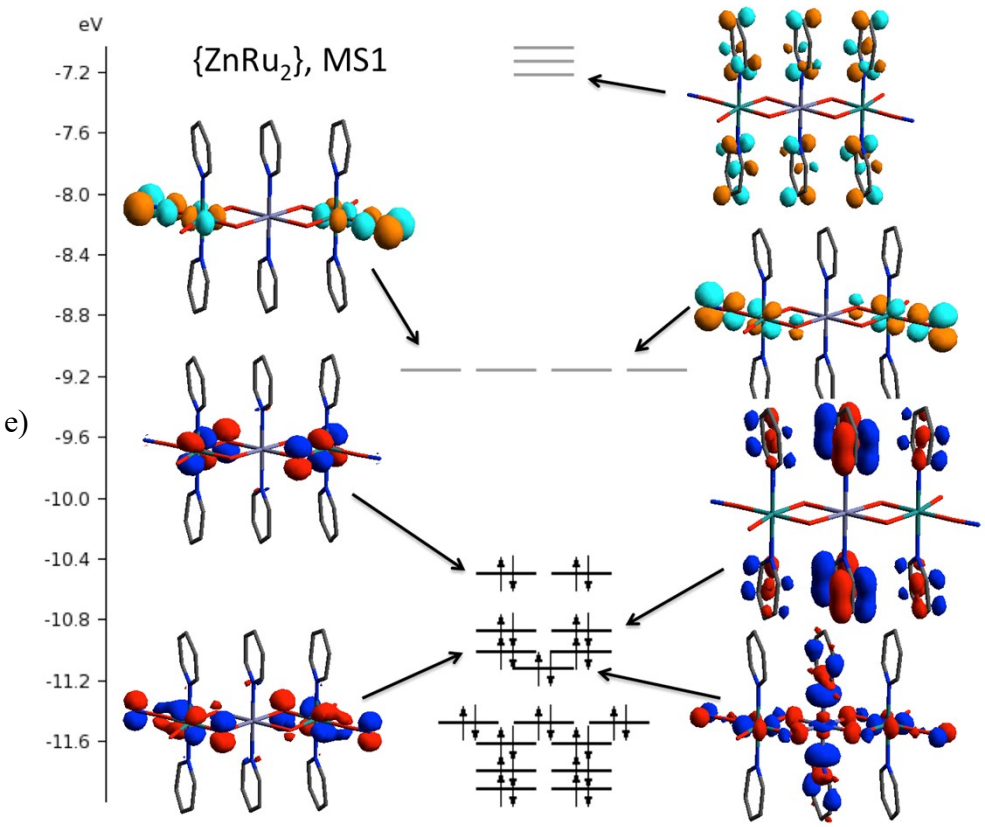
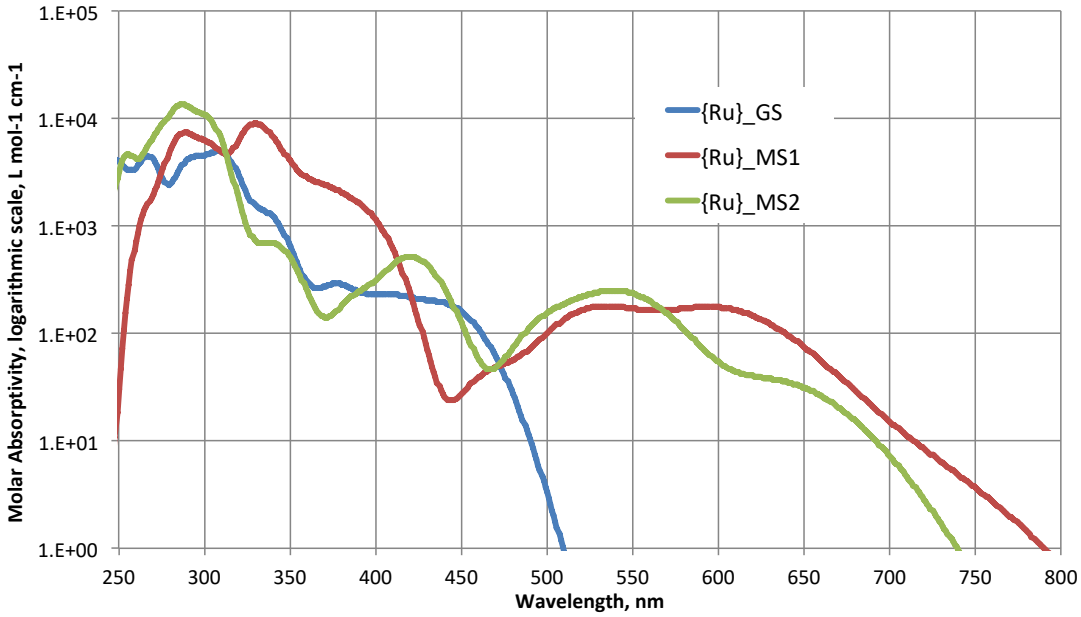


Figure S16. The DFT molecular orbitals (SAOP/TZP/COSMO) of the model compounds *trans*-$[RuNO(Py)_2(OH)_2(H_2O)]^+$ with the a) *N*-, b) *O*-, c) side-coordinated nitrosyl group and *trans*-$\{Zn(Py)_2[RuNO(Py)_2(OH)_2(H_2O)]_2\}^{4+}$ with d) *N*- or e) *O*-coordinated NO.

Table S4. The computed nitrosyl valence vibration modes (OPBE/TZP/COSMO) in the model compounds *trans*-$[RuNO(Py)_2(OH)_2(H_2O)]^+$, denoted as {Ru}, and *trans*-$\{Zn(Py)_2[RuNO(Py)_2(OH)_2(H_2O)]_2\}^{4+}$, denoted as $\{ZnRu_2\}$.

Model compound	Nitrosyl coordination	ν(NO), cm^{-1}	Exp. data, cm^{-1}
{Ru}	*N*-coordinated	1847	1865
	O-coordinated	1801	1720
	side-coordinated	1596	
$\{ZnRu_2\}$	*N*-coordinated	1909	1873
	O-coordinated	1848	1720

a)



b)

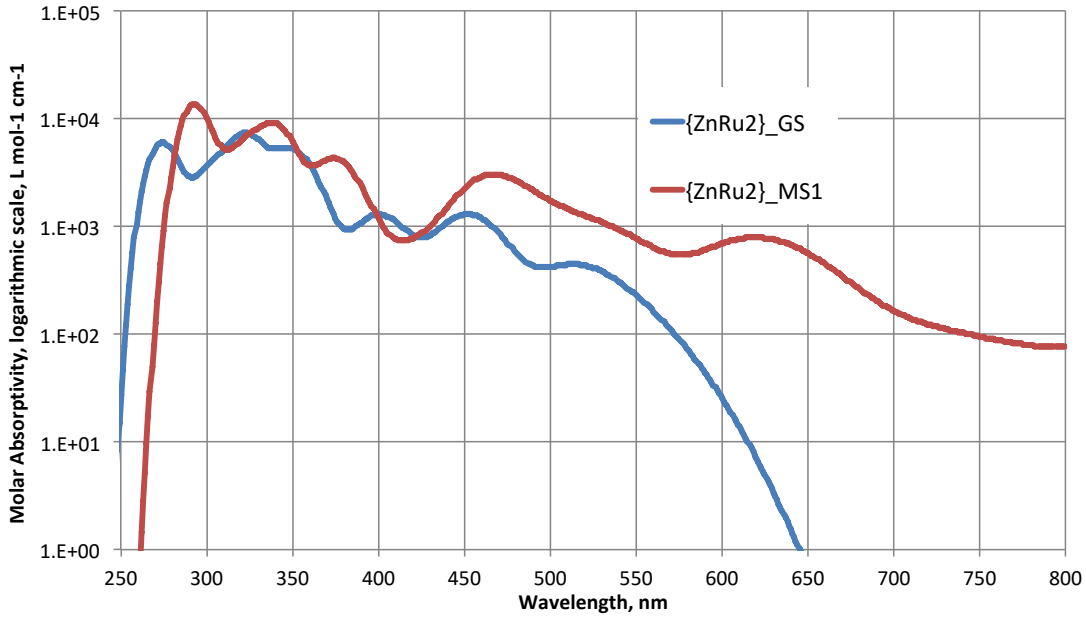


Figure S17. The simulated absorption spectra (SAOP/TZP/COSMO) of the model compounds a) *trans*-$[RuNO(Py)_2(OH)_2(H_2O)]^+$ with the *N*-, *O*-, or side-coordinated nitrosyl group in GS, MS1, or MS2 states, respectively, and b) *trans*-$\{Zn(Py)_2[RuNO(Py)_2(OH)_2(H_2O)]_2\}^{4+}$ with *N*- or *O*-coordinated NO in GS or MS1 states, respectively. The absorption lines were broadened in the energy scale with the gaussian peaks with 0.25 eV FWHM.

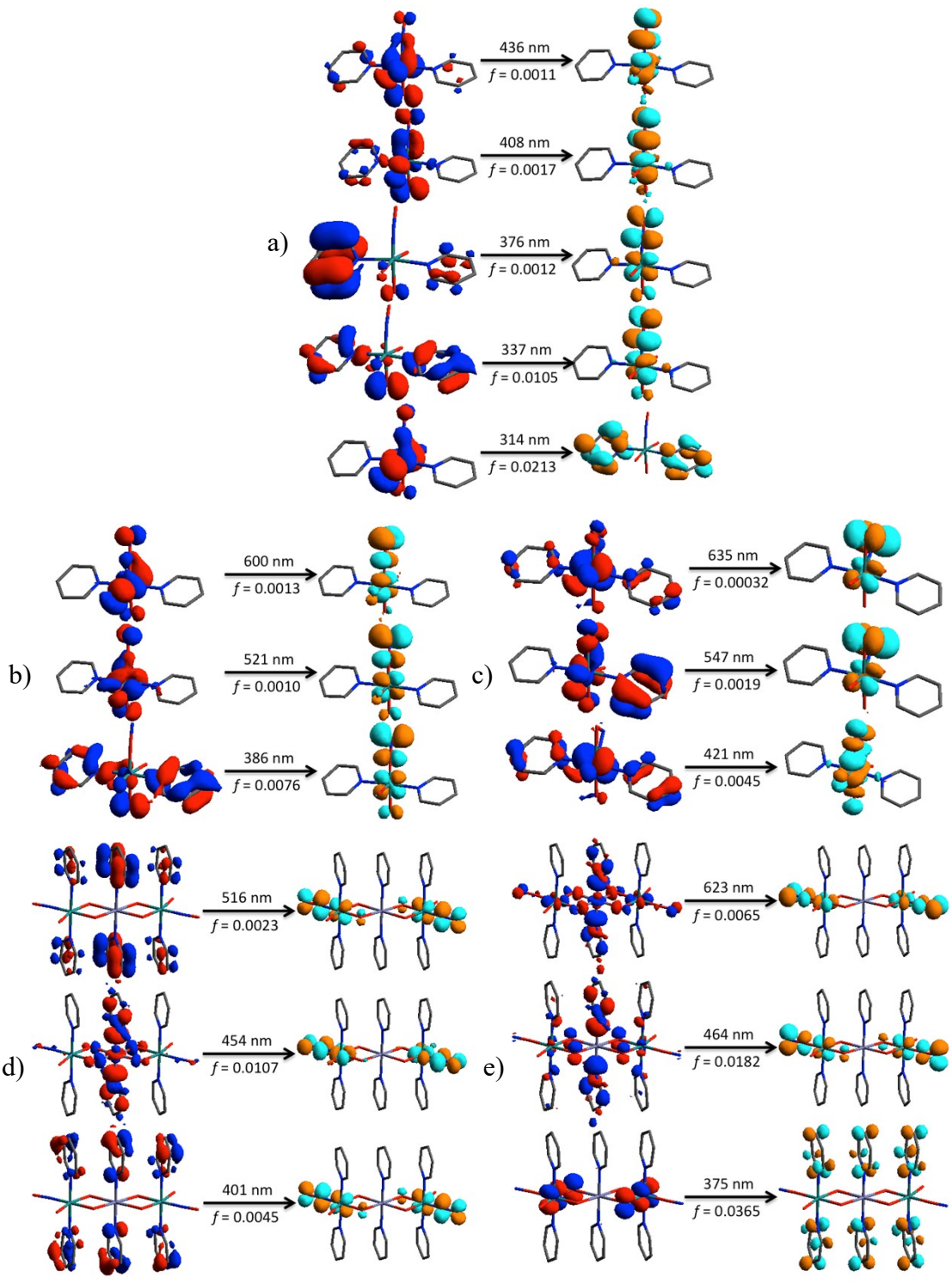


Figure S18. The intense computed transitions (SAOP/TZP/COSMO) of the models *trans*-$[RuNO(Py)_2(OH)_2(H_2O)]^+$ with the a) *N*-, b) *O*-, c) side-coordinated NO and *trans*-$\{Zn(Py)_2[RuNO(Py)_2(OH)_2(H_2O)]_2\}^{4+}$ with d) *N*- or e) *O*-coordinated NO.

The optimized geometries of the model compounds

trans-[RuNO(Py)$_2$(OH)$_2$(H$_2$O)]$^+$, GS *N*-coordinated NO

32

Ru	5.108121	1.058205	3.353199
O	5.388632	0.307102	1.559655
O	7.001968	0.743955	3.819180
N	5.717853	2.890368	2.561867
C	7.011239	3.098020	2.282275
C	6.520384	5.241443	1.351674
H	6.835698	6.163349	0.869744
C	4.817778	3.835283	2.258311
C	5.182782	5.018893	1.645571
C	5.440021	-1.882307	3.657471
N	4.581532	-0.883713	3.911404
C	7.447448	4.265311	1.684362
C	5.134087	-3.201505	3.938635
C	2.996381	-2.474575	4.711677
C	3.381864	-1.175858	4.436165
O	3.133097	1.396205	2.453833
O	3.913697	2.308811	5.692643
N	4.516369	1.792032	4.844790
C	3.889420	-3.508320	4.466894
H	3.617346	-4.538826	4.683204
H	5.871399	-3.972875	3.733779
H	6.387542	-1.600918	3.213690
H	2.005430	-2.662036	5.115078
H	2.716502	-0.344084	4.642757
H	7.694486	2.305377	2.561947
H	8.507802	4.392859	1.485543
H	3.784083	3.625147	2.505318
H	4.415412	5.748150	1.402683
H	7.009850	0.045700	4.491517
H	6.351443	0.245885	1.457109
H	2.558439	0.629032	2.609367
H	3.377684	1.288982	1.516494

trans-[RuNO(Py)$_2$(OH)$_2$(H$_2$O)]$^+$, MS1 *O*-coordinated NO

32

Ru	5.030902	1.032624	3.194303
O	6.578093	0.222693	2.365241
O	6.089932	1.452677	4.807098
N	5.627255	2.868749	2.448470
C	4.901541	3.497331	1.512637
C	6.450747	5.309415	1.442333
H	6.775305	6.268302	1.046454
C	6.756743	3.437073	2.892543
C	7.191409	4.660315	2.418953
C	5.410904	-1.559944	4.630587

N	4.525352	-0.858944	3.905619
C	5.287514	4.711675	0.979348
C	5.136056	-2.831166	5.101291
C	3.010506	-2.700400	4.023878
C	3.341276	-1.422001	3.614173
O	4.030559	0.585571	1.295159
N	2.340815	2.153919	3.983229
O	3.407619	1.753670	3.779336
C	3.919692	-3.419419	4.786929
H	3.683424	-4.424293	5.129072
H	5.878815	-3.348249	5.702479
H	6.361818	-1.078472	4.827798
H	2.048474	-3.118345	3.740897
H	2.640966	-0.829431	3.034917
H	3.988507	3.010905	1.188073
H	4.673803	5.172367	0.210854
H	7.298085	2.892297	3.656131
H	8.104248	5.089766	2.822522
H	5.784863	0.850815	5.502993
H	7.289748	0.344419	3.015961
H	3.971547	-0.379378	1.201134
H	4.668092	0.821718	0.601368

trans-$[RuNO(Py)_2(OH)_2(H_2O)]^+$, MS2 side-coordinated NO

32

Ru	5.282088	1.021388	3.313707
O	4.941725	0.658670	1.432633
O	7.144069	0.473920	3.201687
N	5.862564	2.868682	2.616493
C	6.858126	2.905128	1.719695
C	6.467575	5.222709	1.306907
H	6.697095	6.146344	0.781881
C	5.167224	3.984126	2.879304
C	5.441431	5.177388	2.240111
C	5.308524	-1.965307	3.275597
N	4.689329	-0.911226	3.836973
C	7.192099	4.067393	1.052730
C	4.959359	-3.271913	3.566250
C	3.266236	-2.427010	5.016736
C	3.677366	-1.148825	4.690862
O	3.168522	1.744796	2.897056
O	5.664144	1.540031	5.491475
N	4.602641	1.707149	4.968004
C	3.921866	-3.513118	4.453703
H	3.625127	-4.529923	4.700569
H	5.503958	-4.084506	3.093774
H	6.105993	-1.741118	2.574122
H	2.439354	-2.557575	5.709321
H	3.186640	-0.285347	5.126792
H	7.376496	1.970280	1.543725
H	8.007372	4.049036	0.335220
H	4.364390	3.900746	3.602479
H	4.840923	6.052142	2.472253

H	7.233715	-0.349731	3.706686
H	4.664456	-0.270951	1.372391
H	2.509954	1.112121	3.225525
H	3.300839	1.472179	1.962324

$\{Zn[RuNO(Py)_2(OH)_2(H_2O)]\}^{4+}$, GS *N*-coordinated NO

87

Zn	0.000000	0.000000	0.000000
O	2.050172	-0.216817	0.000000
H	-0.896689	-1.955096	-4.648897
O	0.414176	-2.127432	0.000000
H	-0.003698	-2.995459	0.000000
H	2.820101	0.364650	0.000000
Ru	2.415938	-2.145543	0.000000
N	2.790349	-3.861705	0.000000
O	3.168005	-4.949300	0.000000
O	4.447612	-1.475338	0.000000
H	4.940288	-1.814410	0.765082
O	-3.168005	4.949300	0.000000
H	-4.940288	1.814410	0.765082
H	4.940288	-1.814410	-0.765082
H	-4.940288	1.814410	-0.765082
O	-4.447612	1.475338	0.000000
N	-2.790349	3.861705	0.000000
H	-2.638238	2.295385	5.918046
H	0.003698	2.995459	0.000000
O	-0.414176	2.127432	0.000000
O	-2.050172	0.216817	0.000000
H	0.000000	0.000000	-5.930702
H	-2.820101	-0.364650	0.000000
Ru	-2.415938	2.145543	0.000000
N	-2.404217	2.132046	2.079700
C	-2.945227	1.119449	2.766916
C	-1.912616	3.187909	2.745772
C	-3.038404	1.142713	4.144289
C	-1.984361	3.282499	4.119452
C	-2.564414	2.246469	4.834686
H	-3.301710	0.275419	2.191045
H	-1.444454	3.966632	2.156791
H	-1.579265	4.161325	4.612314
H	-3.486255	0.297973	4.657925
H	-3.486255	0.297973	-4.657925
H	3.486255	-0.297973	4.657925
H	3.486255	-0.297973	-4.657925
H	-1.579265	4.161325	-4.612314
H	1.579265	-4.161325	4.612314
H	1.579265	-4.161325	-4.612314
H	-1.444454	3.966632	-2.156791
H	1.444454	-3.966632	2.156791
H	1.444454	-3.966632	-2.156791
H	-3.301710	0.275419	-2.191045
H	3.301710	-0.275419	2.191045
H	3.301710	-0.275419	-2.191045

H	-2.638238	2.295385	-5.918046
H	2.638238	-2.295385	5.918046
H	2.638238	-2.295385	-5.918046
N	-2.404217	2.132046	-2.079700
N	2.404217	-2.132046	2.079700
N	2.404217	-2.132046	-2.079700
C	-2.564414	2.246469	-4.834686
C	2.564414	-2.246469	4.834686
C	2.564414	-2.246469	-4.834686
C	-1.984361	3.282499	-4.119452
C	1.984361	-3.282499	4.119452
C	1.984361	-3.282499	-4.119452
C	-3.038404	1.142713	-4.144289
C	3.038404	-1.142713	4.144289
C	3.038404	-1.142713	-4.144289
C	-1.912616	3.187909	-2.745772
C	1.912616	-3.187909	2.745772
C	1.912616	-3.187909	-2.745772
C	-2.945227	1.119449	-2.766916
C	2.945227	-1.119449	2.766916
C	2.945227	-1.119449	-2.766916
N	0.000000	0.000000	-2.078023
C	-0.481520	-1.042249	-2.759871
C	0.481520	1.042249	-2.759871
C	-0.496096	-1.084454	-4.139386
C	0.496096	1.084454	-4.139386
C	0.000000	0.000000	-4.843434
H	-0.858749	-1.866876	-2.165423
H	0.858749	1.866876	-2.165423
H	0.896689	1.955096	-4.648897
H	0.896689	1.955096	4.648897
H	-0.896689	-1.955096	4.648897
H	0.858749	1.866876	2.165423
H	-0.858749	-1.866876	2.165423
H	0.000000	0.000000	5.930702
N	0.000000	0.000000	2.078023
C	0.000000	0.000000	4.843434
C	0.496096	1.084454	4.139386
C	-0.496096	-1.084454	4.139386
C	0.481520	1.042249	2.759871
C	-0.481520	-1.042249	2.759871

$\{Zn[RuNO(Py)_2(OH)_2(H_2O)]\}^{4+}$, MS1 *O*-coordinated NO

87

Zn	0.000000	0.000000	0.000000
O	2.071279	-0.153935	0.000000
H	-0.959669	-1.925617	-4.631214
O	0.429936	-2.087249	0.000000
H	0.017296	-2.957369	0.000000
H	2.863990	0.398431	0.000000
Ru	2.431293	-2.054241	0.000000
O	2.815227	-3.875799	0.000000
N	3.162633	-4.971210	0.000000

O	4.477189	-1.434964	0.000000
H	4.972436	-1.768047	0.765556
N	-3.162633	4.971210	0.000000
H	-4.972436	1.768047	0.765556
H	4.972436	-1.768047	-0.765556
H	-4.972436	1.768047	-0.765556
O	-4.477189	1.434964	0.000000
O	-2.815227	3.875799	0.000000
H	-2.630649	2.350581	5.903048
H	-0.017296	2.957369	0.000000
O	-0.429936	2.087249	0.000000
O	-2.071279	0.153935	0.000000
H	0.000000	0.000000	-5.912635
H	-2.863990	-0.398431	0.000000
Ru	-2.431293	2.054241	0.000000
N	-2.418197	2.074483	2.068244
C	-2.983143	1.096697	2.786489
C	-1.891981	3.132205	2.705169
C	-3.068590	1.160012	4.163104
C	-1.957991	3.269599	4.075679
C	-2.563761	2.270435	4.821035
H	-3.366730	0.247657	2.234535
H	-1.396543	3.877702	2.095533
H	-1.522894	4.148233	4.542989
H	-3.534450	0.341518	4.702761
H	-3.534450	0.341518	-4.702761
H	3.534450	-0.341518	4.702761
H	3.534450	-0.341518	-4.702761
H	-1.522894	4.148233	-4.542989
H	1.522894	-4.148233	4.542989
H	1.522894	-4.148233	-4.542989
H	-1.396543	3.877702	-2.095533
H	1.396543	-3.877702	2.095533
H	1.396543	-3.877702	-2.095533
H	-3.366730	0.247657	-2.234535
H	3.366730	-0.247657	2.234535
H	3.366730	-0.247657	-2.234535
H	-2.630649	2.350581	-5.903048
H	2.630649	-2.350581	5.903048
H	2.630649	-2.350581	-5.903048
N	-2.418197	2.074483	-2.068244
N	2.418197	-2.074483	2.068244
N	2.418197	-2.074483	-2.068244
C	-2.563761	2.270435	-4.821035
C	2.563761	-2.270435	4.821035
C	2.563761	-2.270435	-4.821035
C	-1.957991	3.269599	-4.075679
C	1.957991	-3.269599	4.075679
C	1.957991	-3.269599	-4.075679
C	-3.068590	1.160012	-4.163104
C	3.068590	-1.160012	4.163104
C	3.068590	-1.160012	-4.163104
C	-1.891981	3.132205	-2.705169
C	1.891981	-3.132205	2.705169
C	1.891981	-3.132205	-2.705169
C	-2.983143	1.096697	-2.786489

```
C        2.983143   -1.096697    2.786489
C        2.983143   -1.096697   -2.786489
N        0.000000    0.000000   -2.062293
C       -0.514501   -1.026767   -2.742421
C        0.514501    1.026767   -2.742421
C       -0.530786   -1.068373   -4.121678
C        0.530786    1.068373   -4.121678
C        0.000000    0.000000   -4.825352
H       -0.917265   -1.838346   -2.146437
H        0.917265    1.838346   -2.146437
H        0.959669    1.925617   -4.631214
H        0.959669    1.925617    4.631214
H       -0.959669   -1.925617    4.631214
H        0.917265    1.838346    2.146437
H       -0.917265   -1.838346    2.146437
H        0.000000    0.000000    5.912635
N        0.000000    0.000000    2.062293
C        0.000000    0.000000    4.825352
C        0.530786    1.068373    4.121678
C       -0.530786   -1.068373    4.121678
C        0.514501    1.026767    2.742421
C       -0.514501   -1.026767    2.742421
```

Input files for ADF geometry optimization and frequencies calculations:

```
Atoms
INLINE geom.xyz
End

Geometry
 Step TrustRadius=0.1
End

Charge 1

Basis
 Type TZP
 Core None
End

AnalyticalFreq
End

XC
 GGA OPBE
 Dispersion Grimme4
End

SOLVATION
 Solv Name=Water
 SCF VAR ALL
END

eor
```

Input files for ADF TD-DFT calculations:

```
Atoms
INLINE geom.xyz
End

Dependency
End

EXACTDENSITY

charge 1

Basis
 Type TZP
 Core None
END

XC
 model saop
End

Excitations
 lowest 40
 NTO
 Allowed
End

SOLVATION
 Solv Name=Water Neql=1.79
 SCF VAR ALL
 NOCSMRSP
End

End input
eor
```