**Supplementary material**

# Coordination chemistry of pyrazine derivatives analogues of *PZA*: design, synthesis, characterization and biological activity.

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**Keywords:** Ru(III) complexes; Pyrazine derivatives; Spectrophotometric titration; Cyclic voltammetry; Biological assay

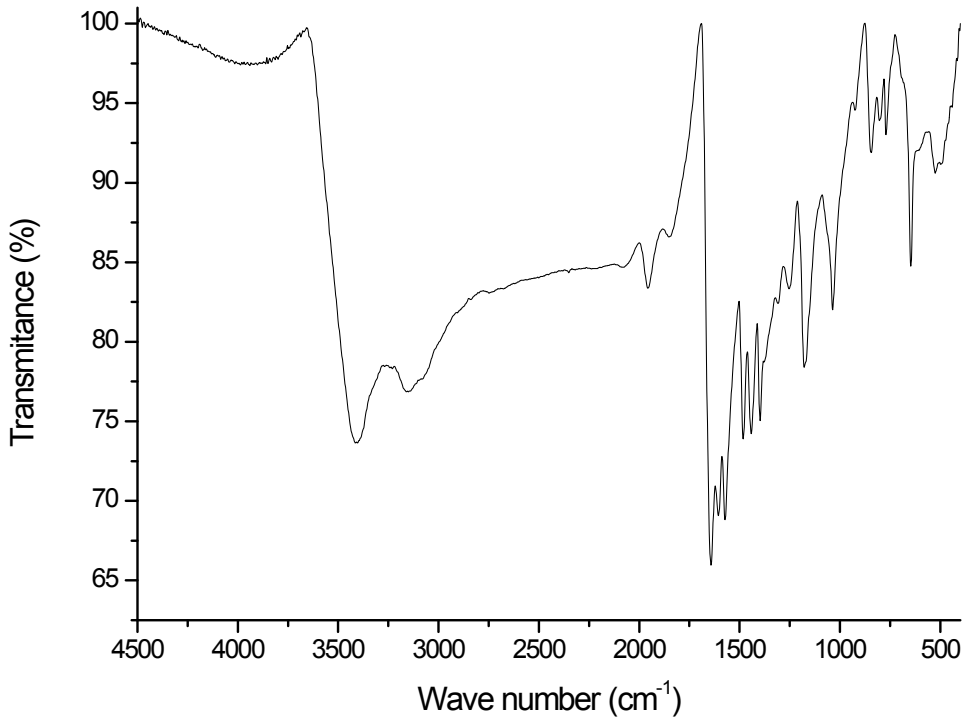


**Fig.S1**. FT-IR spectrum of [RuCl(*PAOX*)$_2$(OH$_2$)]Cl$_2$.

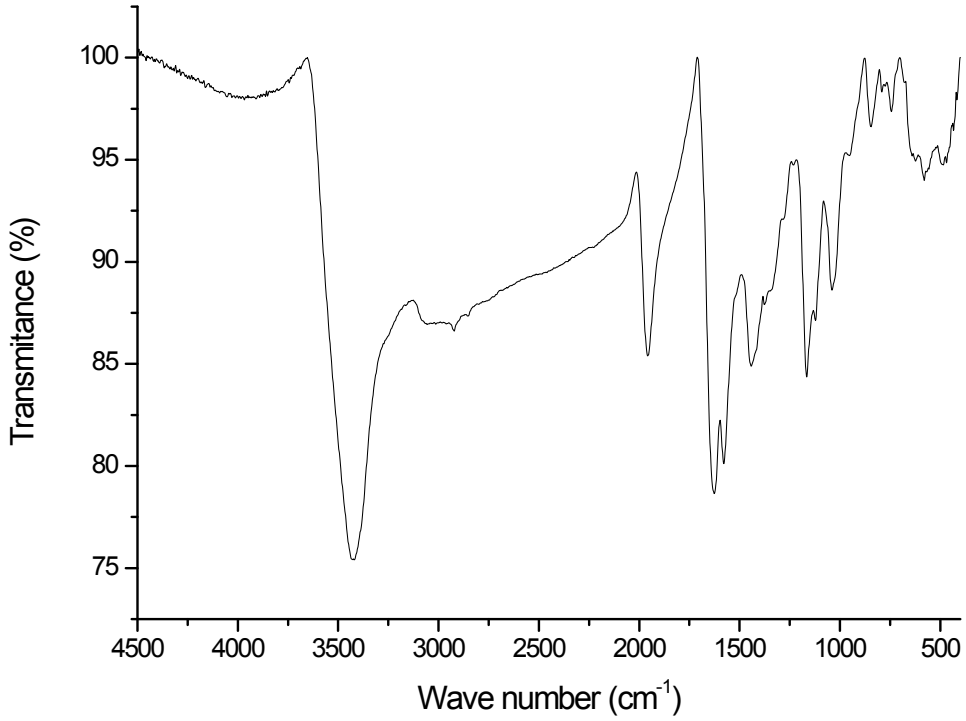


**Fig. S2**. FT-IR spectrum of [RuCl(*PTCA*)$_2$($OH_2$)]$Cl_2$.

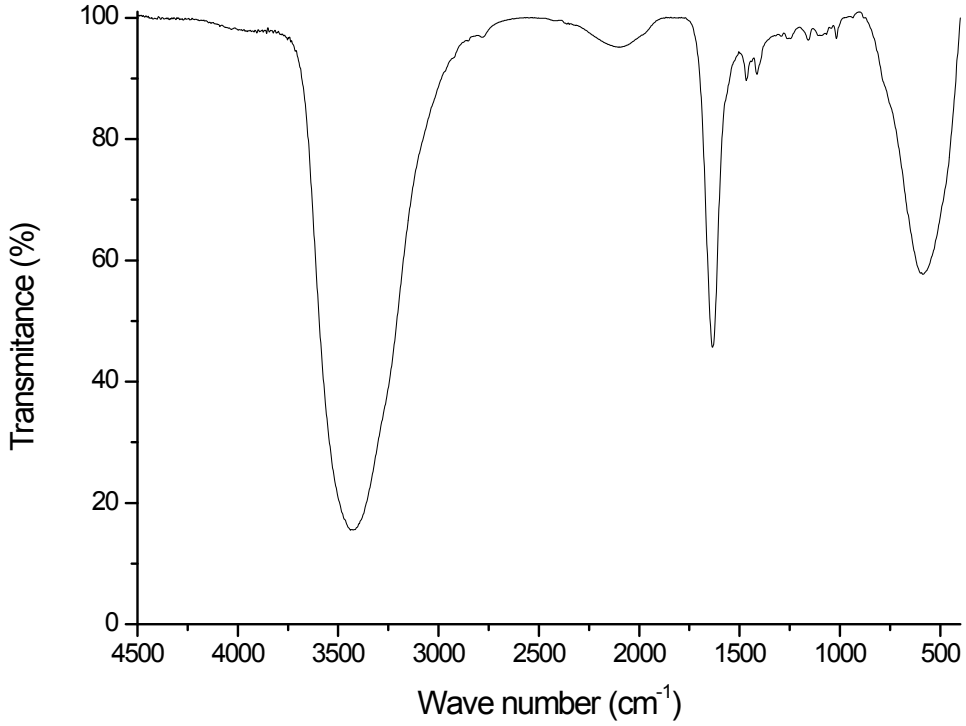


**Fig. S3**. FT-IR spectrum of $[RuCl(DPP)(OH_2)_3]Cl_2$.

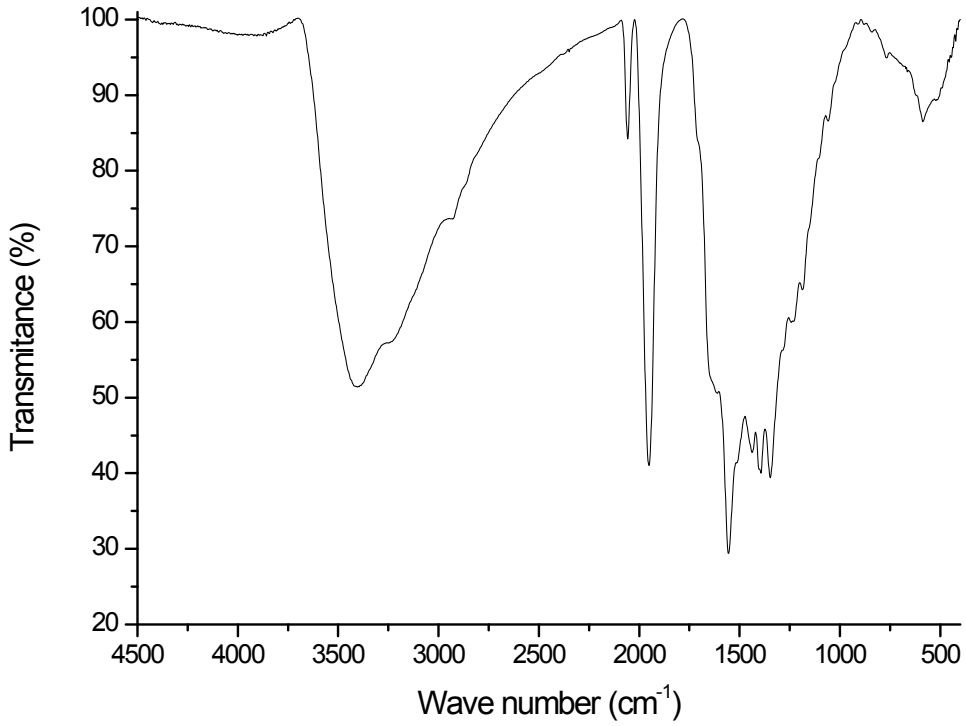


**Fig. S4**. FT-IR spectrum of $[RuCl_2(ABMAP)_2]Cl$.

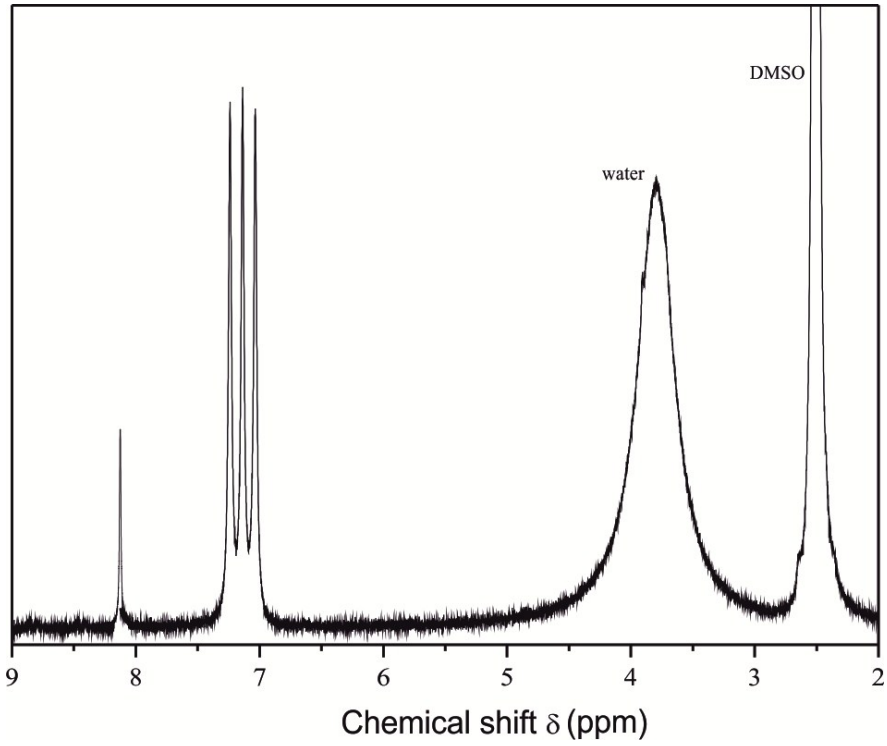


**Fig. S5.** $^{1}$H NMR spectrum of [RuCl(*PTCA*)$_2$(OH$_2$)]Cl$_2$ in DMSO-d$_6$ at 500 MHz.

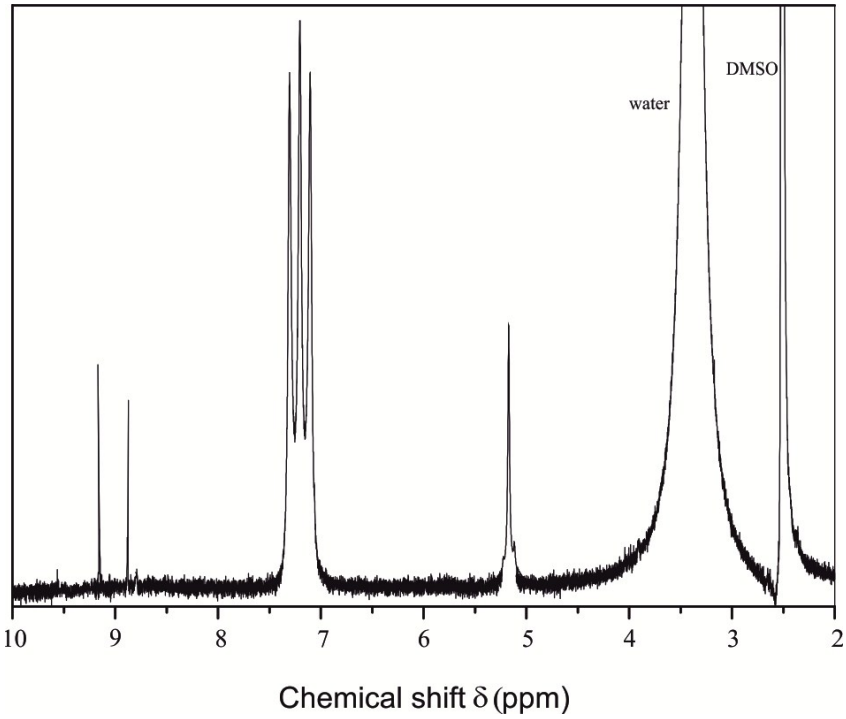


**Fig. S6.** $^{1}$H NMR spectrum of [RuCl(*PAOX*)$_2$(OH$_2$)]Cl$_2$ in DMSO-d$_6$ at 500 MHz.

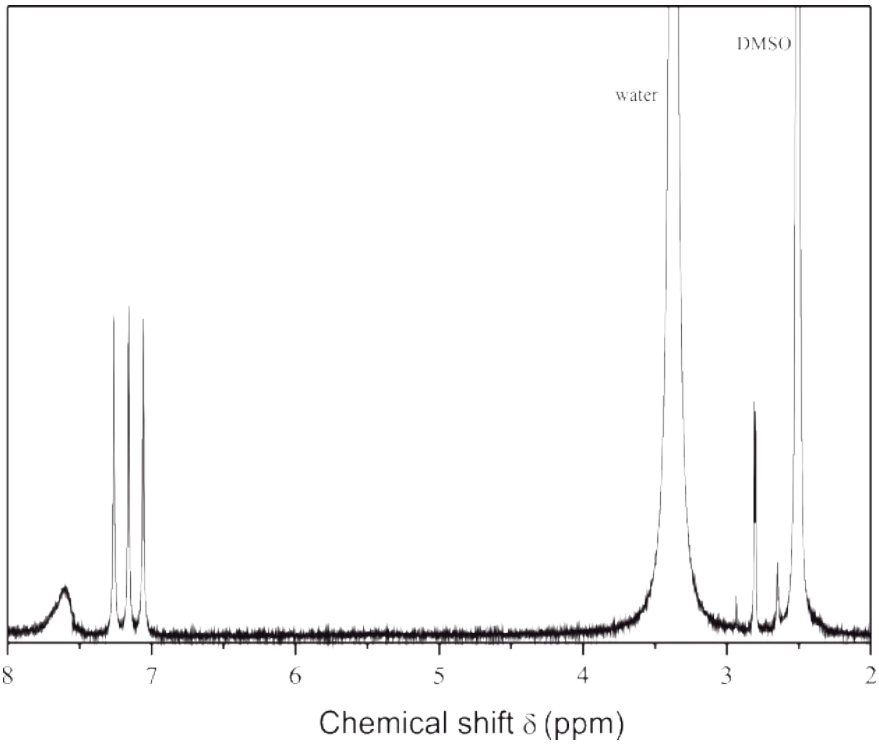


**Fig. S7.** $^{1}$H NMR spectrum of $[RuCl_2(ABMAP)_2]Cl$ in DMSO-$d_6$ at 500 MHz.

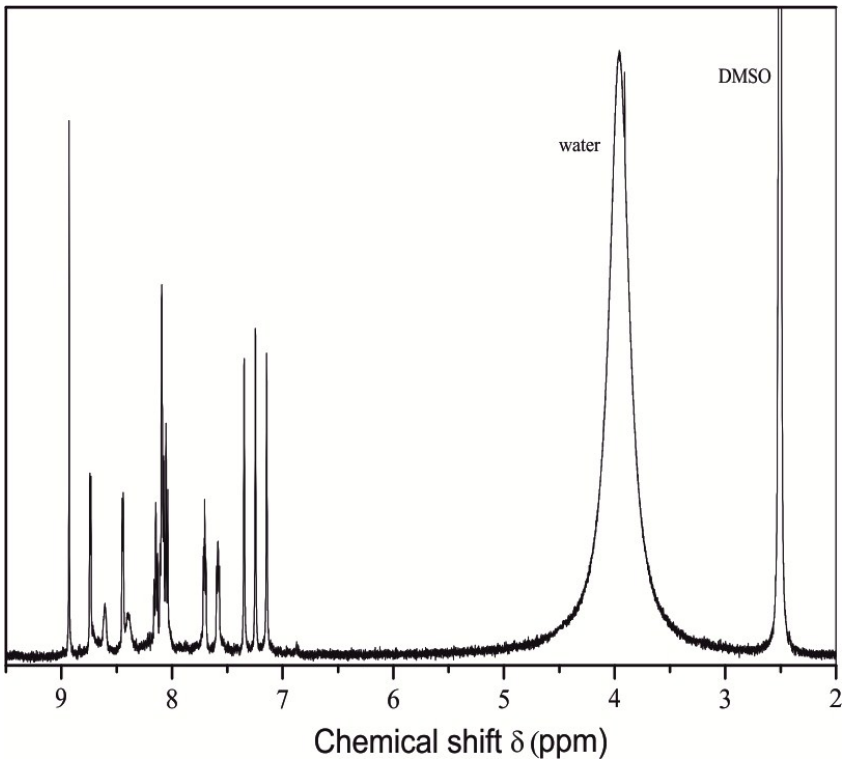


**Fig. S8.** $^{1}$H NMR spectrum of [RuCl(*DPP*)$(OH_2)_3$]$Cl_2$ in DMSO-$d_6$ at 500 MHz.

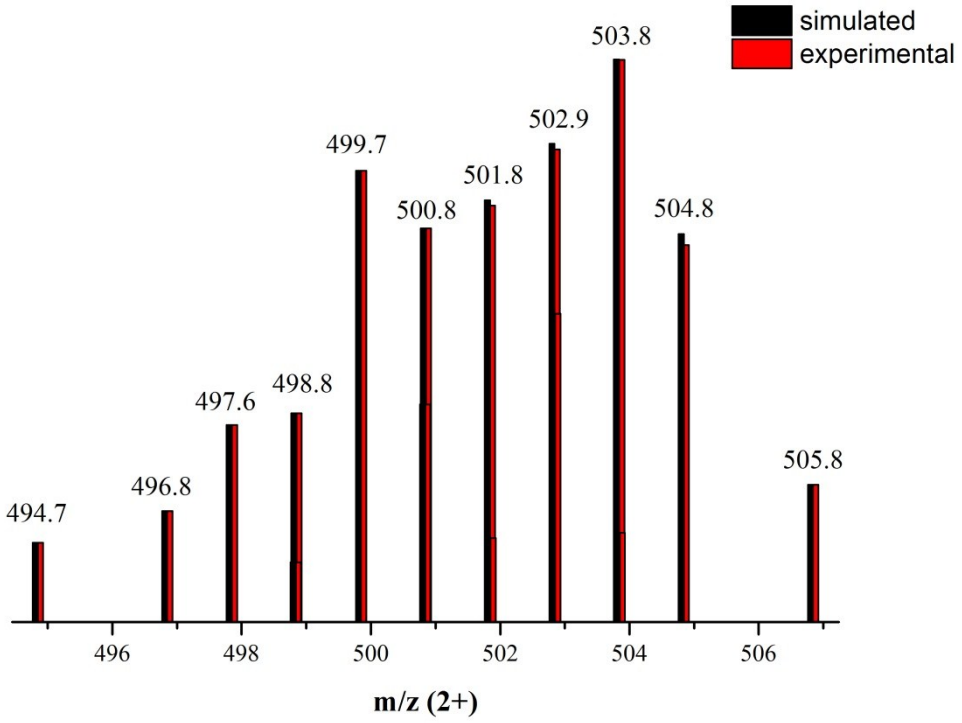


**Fig. S9.** ESI/MS of [RuCl(*PTCA*)$_2$(OH$_2$)]Cl$_2$ showing the m/z$^{2+}$ for the experimental (red columns) and simulated (black columns) spectra.

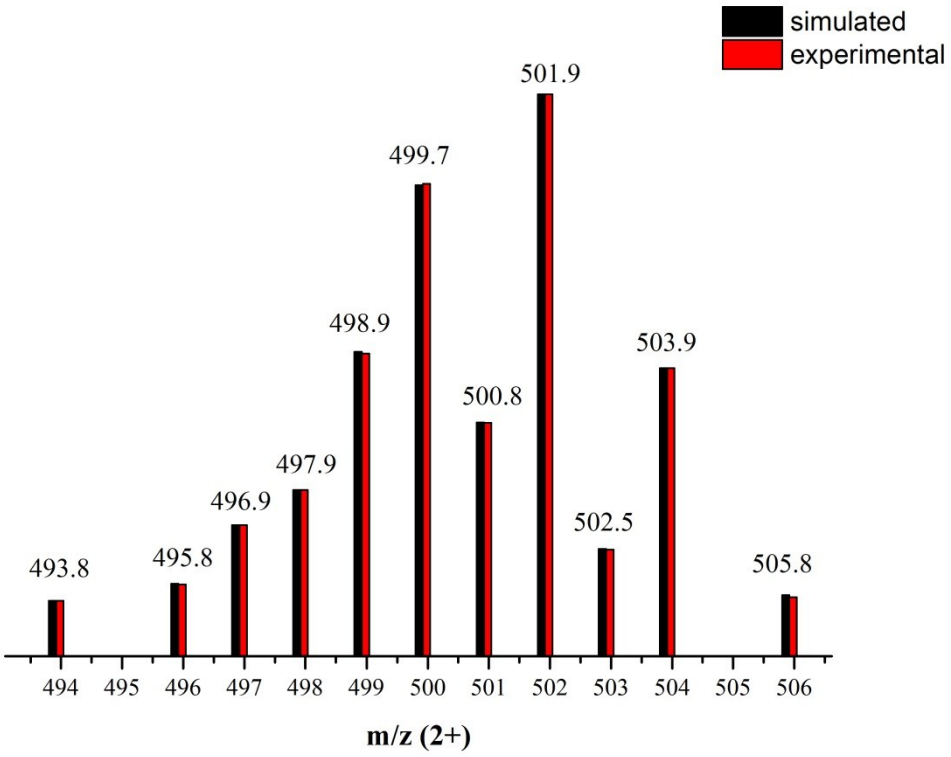


**Fig. S10.** ESI/MS of $[RuCl(PAOX)_2(OH_2)]Cl_2$ showing the $m/z^{2+}$ for the experimental (red columns) and simulated (black columns) spectra.

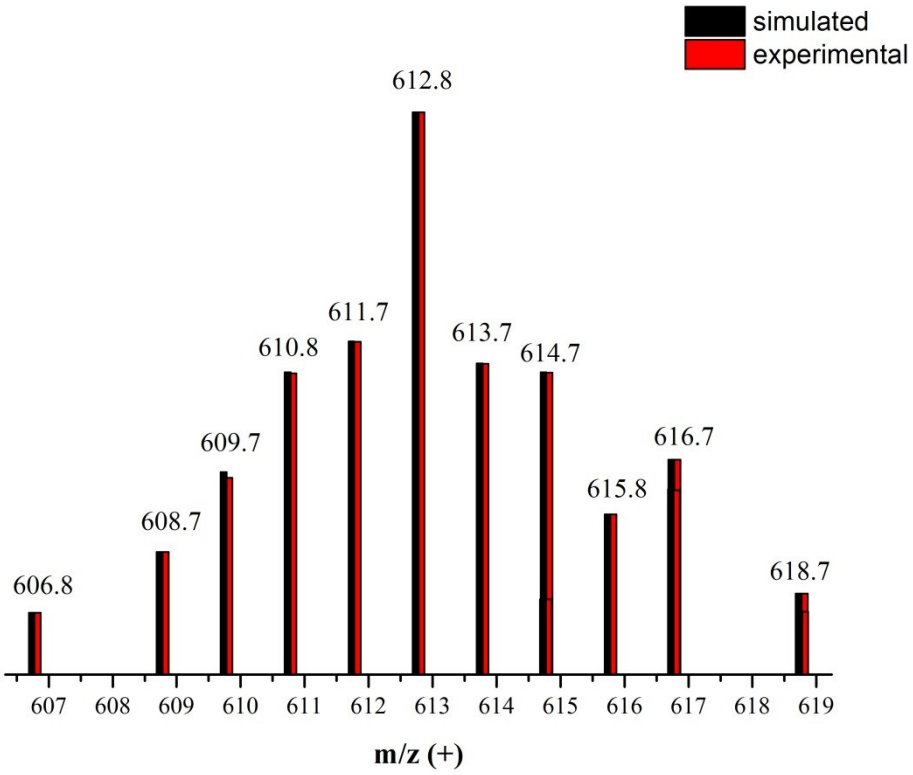


**Fig. S11.** ESI/MS of $[RuCl_2(ABMAP)_2]Cl$ showing the $m/z^{2+}$ for the experimental (red columns) and simulated (black columns) spectra.

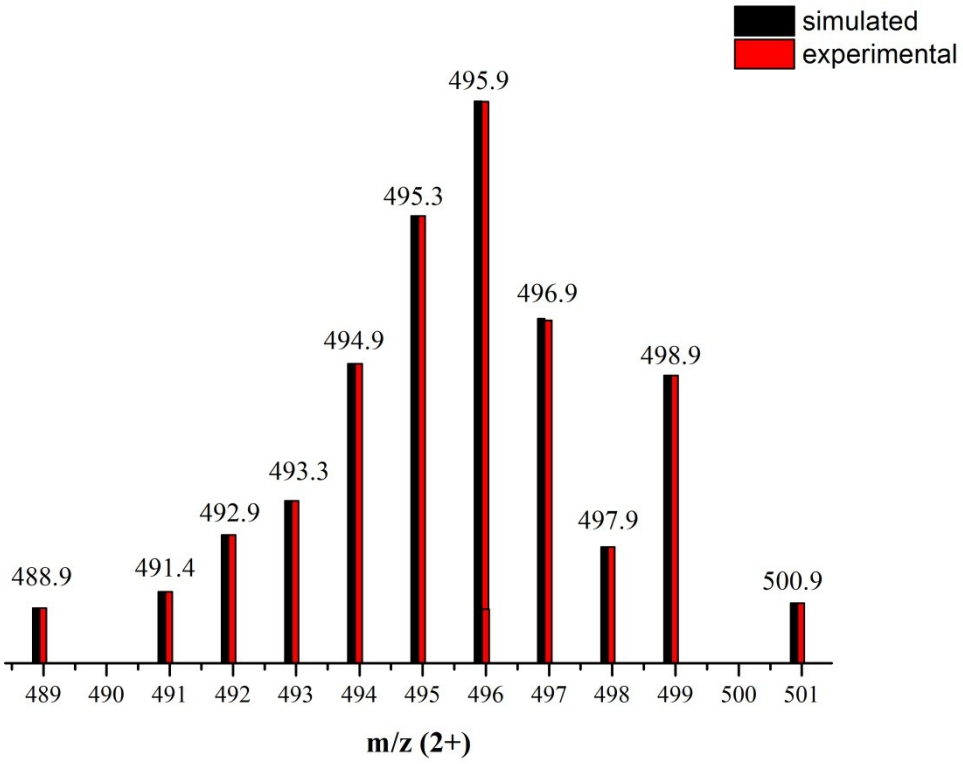


**Fig. S12.** ESI/MS of $[RuCl(DPP)(OH_2)_3]Cl_2$ showing the $m/z^{2+}$ for the experimental (red columns) and simulated (black columns) spectra.

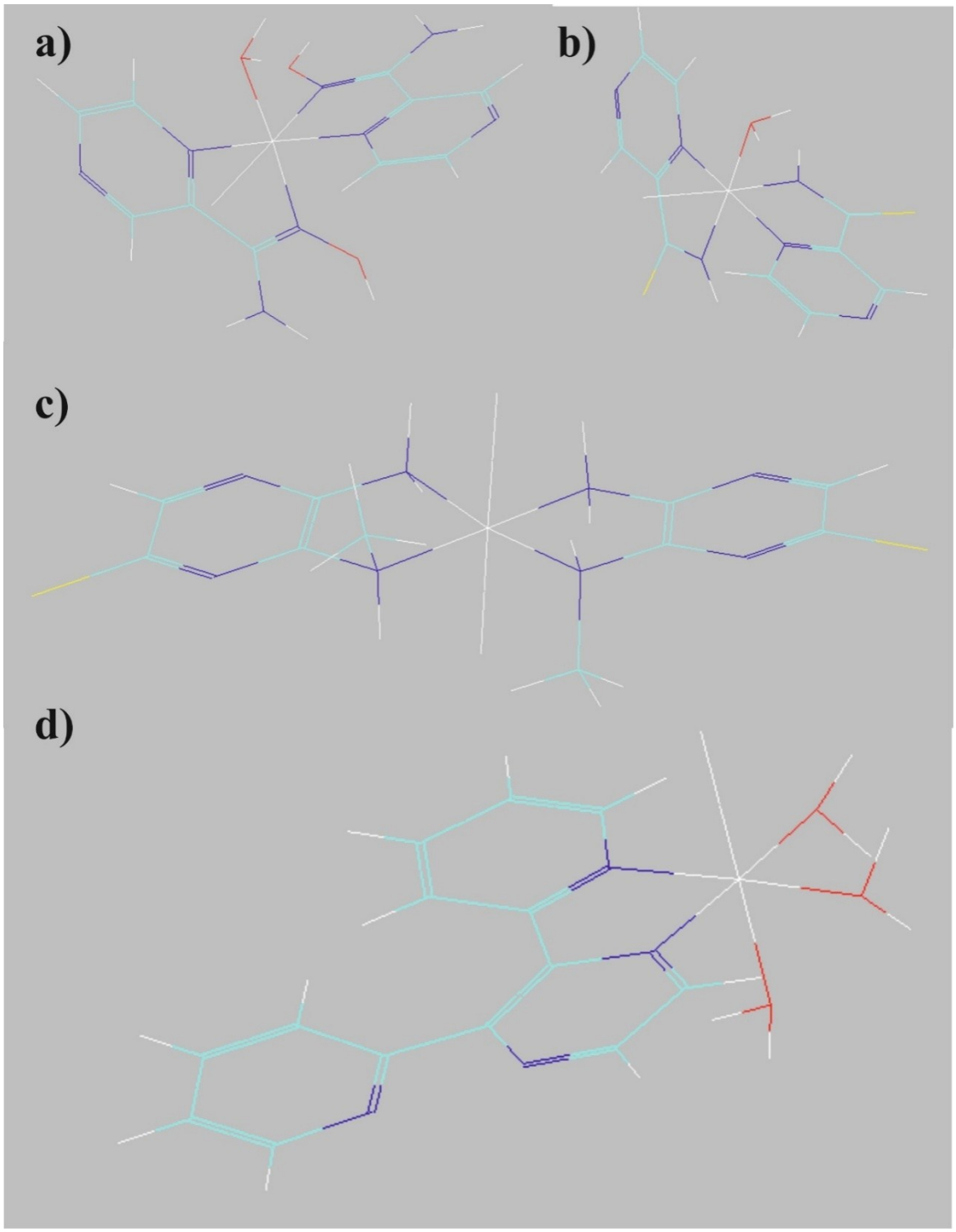


**Fig. S13.** Structure od Ru(III) complexes studied with pyrazine derivatives: **a)** pyrazine-2-amidoxime (*PAOX*); **b)** pyrazine-2-thiocarboxamide (*PTCA*); **c)** 2-amine-5-bromo-(3-methyl)-amine-pyrazine (*ABMAP*); **d)** 2,3-bis-(2-pyridyl)pyrazine (*DPP*).

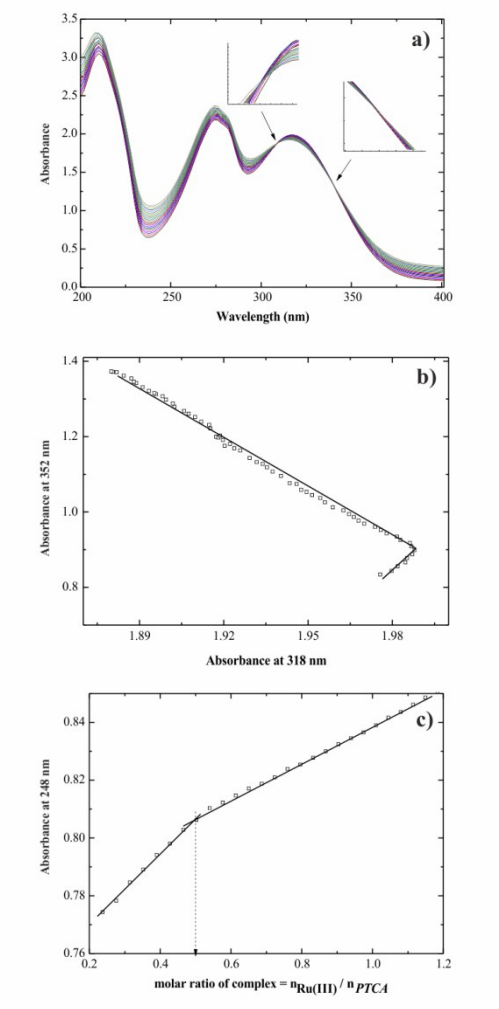


**Fig. S14. a)** Spectrophotometric titration curves of pyrazine-2-thiocarboxamide ($1.00 \cdot 10^{-4}$ mol $L^{-1}$) using a mixture of *PTCA* at the same concentration and $RuCl_3$ ($1.81 \cdot 10^{-3}$ mol $L^{-1}$). **b)** The A-diagram plot for Ru(III) ion with pyrazine-2-thiocarboxamide complexation process, major stoichiometry 1:2. **c)** Dependence of absorbance at 228 nm for *PTCA* as a function of molar ratio $n_{Ru(III)}/n_{PTCA}$.

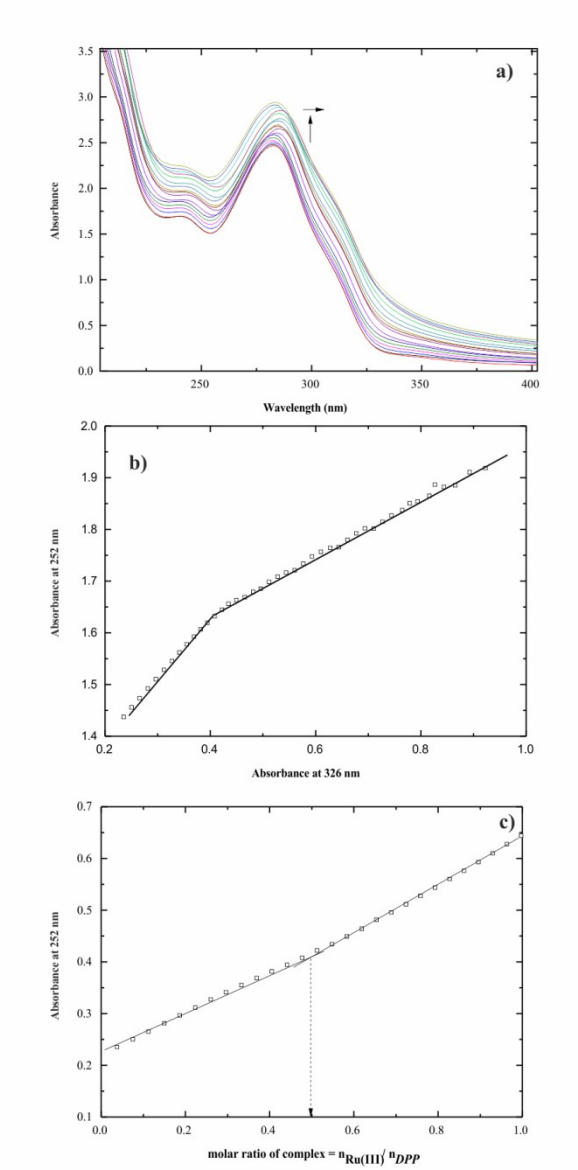


**Fig. S15**. **a)** Spectrophotometric titration curves of 2,3-bis(2-pyridyl)pyrazine ($5.15 \cdot 10^{-5}$ mol $L^{-1}$) using a mixture of *DPP* at the same concentration and $RuCl_3$ ($9.29 \cdot 10^{-4}$ mol $L^{-1}$). **b)** The A-diagram for Ru(III) ion with 2,3-bis(2-pyridyl)pyrazine for complexation process, major stoichiometry 1:2. **c)** Dependence of absorbance at 326 nm for *DPP* as a function of molar ratio $n_{Ru(III)}/n_{DPP}$.

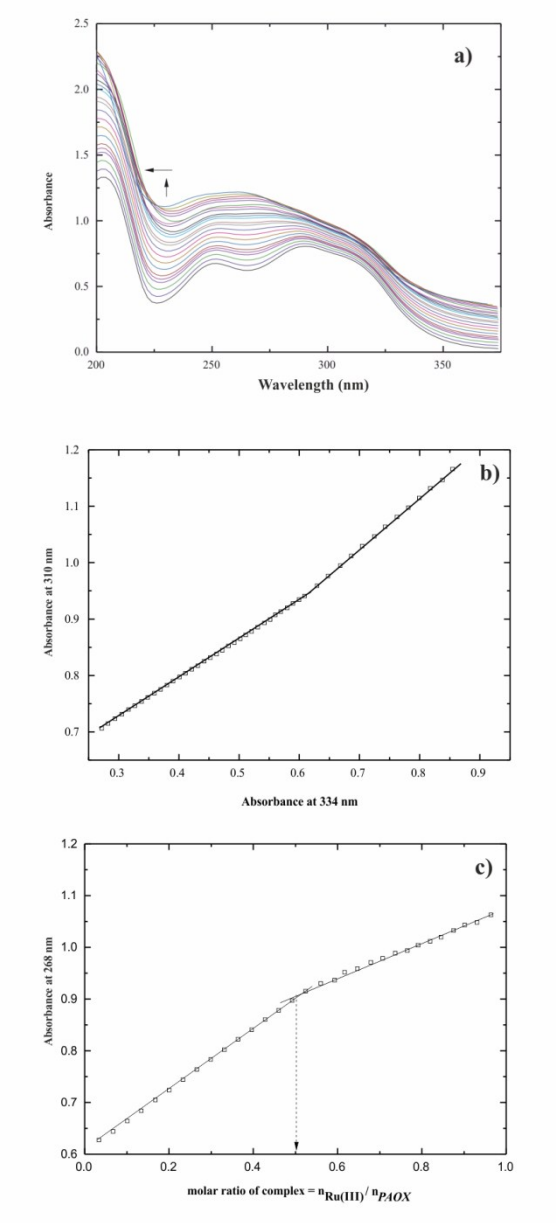


**Fig. S16. a)** Spectrophotometric titration curves of pyrazine-2-amidoxime ($1.70 \cdot 10^{-4}$ mol $L^{-1}$) using a mixture of *PAOX* at the same concentration and $RuCl_3$ ($2.76 \cdot 10^{-3}$ mol $L^{-1}$). **b)** The A-diagram for Ru(III) ion with pyrazine-2-amidoxime for complexation process, major stoichiometry 1:2. **c)** Dependence of absorbance at 268 nm for *PAOX* as a function of molar ratio $n_{Ru(III)}/n_{PAOX}$.

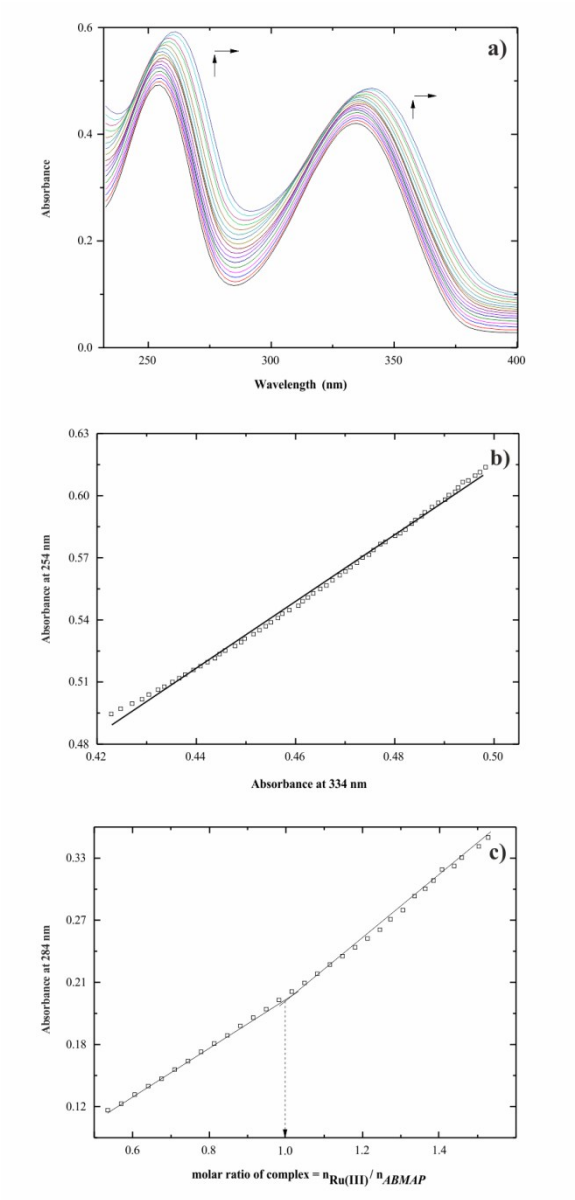


**Fig. S17. a)** Spectrophotometric titration curves of 2-amine-5-bromo(3-methylamine)-pyrazine ($5.01 \cdot 10^{-5}$ mol $L^{-1}$) using a mixture of *ABMAP* at the same concentration and $RuCl_3$ ($1.00 \cdot 10^{-3}$mol $L^{-1}$). **b)** The A-diagram plot for Ru(III) ion with 2-amine-5-bromo(3-methylamine)-pyrazine for complexation process, major stoichiometry 1:1. **c)** Dependence of absorbance at 284 nm for *ABMAP* as a function of molar ratio $n_{Ru(III)}/n_{ABMAP}$.

**Table S1.** Selected bond lenghts (Å) of [RuCl(*DPP*)$(OH_2)_3$]$Cl_2$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4c.

| Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|---|---|
| C(2)-C(1) | 1.3964 | C(7)-C(5) | 1.3905 | H(27)-C(17) | 1.1000 |
| N(3)-C(2) | 1.4014 | C(8)-C(4) | 1.3370 | H(28)-C(18) | 1.1000 |
| H(20)-C(2) | 1.1000 | Ru(29)-N(6) | 1.5061 | C(9)-C(7) | 1.4122 |
| N(6)-C(1) | 1.3899 | N(14)-C(8) | 1.3509 | N(13)-C(7) | 1.3872 |
| H(19)-C(1) | 1.1000 | C(18)-C(8) | 1.3858 | C(12)-N(13) | 1.3899 |
| C(4)-N(3) | 1.3968 | C(15)-N(14) | 1.3509 | O(32)-Ru(29) | 1.8900 |
| C(5)-N(6) | 1.3871 | C(16)-C(15) | 1.3858 | O(33)-Ru(29) | 1.8900 |
| C(17)-C(18) | 1.3910 | H(25)-C(15) | 1.1000 | O(34)-Ru(29) | 1.8900 |
| C(10)-C(9) | 1.3967 | H(26)-C(16) | 1.1000 | Cl(31)-Ru(29) | 2.2400 |
| H(22)-C(10) | 1.1130 | H(21)-C(9) | 1.1130 | C(11)-C(12) | 1.3965 |
| H(37)-O(32) | 0.9420 | H(23)-C(11) | 1.1130 | H(24)-C(12) | 1.1130 |
| H(40)-O(33) | 0.9420 | H(38)-O(32) | 0.9420 | H(39)-O(33) | 0.9420 |
| H(41)-O(34) | 0.9420 | H(42)-O(34) | 0.9420 | H(30)-C(11) | 1.1035 |

**Table S2.** Selected bond lenghts (Å) of [RuCl(*PAOX*)$_2$(OH$_2$)]Cl$_2$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4d.

| Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|---|---|
| C(2)-C(1) | 1.3445 | N(9)-C(7) | 1.2744 | N(13)-C(12) | 1.2647 |
| N(3)-C(2) | 1.2652 | N(8)-C(7) | 1.2686 | H(31)-C(12) | 1.1026 |
| H(25)-C(2) | 1.1025 | O(10)-N(9) | 1.3230 | C(14)-C(15) | 1.3480 |
| C(4)-N(3) | 1.2665 | N(16)-Ru(21) | 1.9402 | C(17)-C(15) | 1.3463 |
| C(5)-C(4) | 1.3482 | N(19)-Ru(21) | 1.9448 | N(18)-C(17) | 1.2682 |
| H(26)-C(4) | 1.1013 | O(22)-Ru(21) | 1.9392 | O(20)-N(19) | 1.3221 |
| N(6)-C(1) | 1.2712 | Cl(23)-Ru(21) | 2.2477 | H(32)-C(14) | 1.1015 |
| C(7)-C(5) | 1.3482 | C(11)-N(16) | 1.2714 | H(27)-N(8) | 1.0481 |
| Ru(21)-N(6) | 1.9401 | C(15)-N(16) | 1.2748 | H(28)-N(8) | 1.0496 |
| H(24)-C(1) | 1.1065 | C(12)-C(11) | 1.3444 | H(30)-C(11) | 1.1035 |
| H(29)-O(10) | 0.9421 | H(34)-N(18) | 1.0499 | H(36)-O(22) | 1.0497 |
| H(33)-N(18) | 1.0481 | H(35)-O(20) | 0.9421 | H(37)-O(22) | 1.0595 |

**Table S3.** Selected bond lenghts (Å) of $[RuCl_2(ABMAP)_2]Cl$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4a.

| Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|---|---|
| C(2)-C(1) | 1.3432 | H(12)-N(7) | 1.0567 | Br(29)-C(20) | 1.8901 |
| N(3)-C(2) | 1.2648 | H(32)-N(7) | 1.0507 | H(30)-C(14) | 1.1022 |
| Br(10)-C(2) | 1.8928 | H(33)-N(8) | 1.0593 | H(26)-N(13) | 1.0569 |
| C(4)-N(3) | 1.2698 | Cl(40)-Ru(37) | 2.2510 | H(38)-N(13) | 1.0506 |
| C(5)-C(4) | 1.3540 | Cl(41)-Ru(37) | 2.2504 | H(15)-C(9) | 1.1147 |
| N(8)-C(4) | 1.2813 | C(23)-N(21) | 1.2827 | H(16)-C(9) | 1.1153 |
| N(6)-C(1) | 1.2644 | C(28)-N(21) | 1.5003 | H(17)-C(9) | 1.1148 |
| N(7)-C(5) | 1.2740 | H(39)-N(21) | 1.0595 | H(34)-C(28) | 1.1150 |
| H(11)-C(1) | 1.1024 | N(22)-C(23) | 1.2748 | H(35)-C(28) | 1.1153 |
| C(9)-N(8) | 1.4987 | C(24)-N(13) | 1.2737 | H(36)-C(28) | 1.1147 |
| Ru(37)-N(8) | 1.9492 | N(25)-C(24) | 1.2673 | C(20)-N(22) | 1.2688 |
| N(13)-Ru(37) | 1.9416 | C(14)-N(25) | 1.2647 | N(21)-Ru(37) | 1.9500 |

**Table S4.** Selected bond lenghts (Å) of [RuCl(*PTCA*)$_2$(OH$_2$) ]Cl$_2$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4b.

| Bond | Length (Å) | Bond | Length (Å) | Bond | Length (Å) |
|---|---|---|---|---|---|
| C(2)-C(1) | 1.3442 | N(16)-Ru(10) | 1.9422 | H(26)-C(11) | 1.1077 |
| N(3)-C(2) | 1.2642 | N(9)-Ru(10) | 1.9312 | N(13)-C(12) | 1.2646 |
| H(23)-C(2) | 1.1023 | N(19)-Ru(10) | 1.9295 | H(27)-C(12) | 1.1023 |
| C(4)-N(3) | 1.2657 | O(21)-Ru(10) | 1.9382 | C(14)-C(15) | 1.3506 |
| C(5)-C(4) | 1.3507 | S(8)-C(7) | 1.5771 | C(17)-C(15) | 1.3592 |
| H(24)-C(4) | 1.1029 | Cl(20)-Ru(10) | 2.2457 | H(28)-C(14) | 1.1029 |
| N(6)-C(1) | 1.2726 | H(25)-N(9) | 1.0078 | S(18)-C(17) | 1.5775 |
| C(7)-C(5) | 1.3577 | C(11)-N(16) | 1.2723 | H(29)-N(19) | 1.0080 |
| Ru(10)-N(6) | 1.9426 | C(15)-N(16) | 1.2787 | H(30)-O(21) | 1.0512 |
| H(22)-C(1) | 1.1077 | C(12)-C(11) | 1.3442 | H(31)-O(21) | 1.0560 |

**Table S5.** Selected bond angles (in degrees) of [RuCl(*DPP*)$(OH_2)_3$]$Cl_2$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4c.

| **Angle** | **[Deg.]** | **Angle** | **[Deg.]** |
|---|---|---|---|
| N(3)-C(2)-C(1) | 120.5861 | C(16)-C(15)-N(14) | 123.7955 |
| H(20)-C(2)-C(1) | 119.7069 | H(25)-C(15)-N(14) | 118.1024 |
| N(6)-C(1)-C(2) | 118.6280 | C(17)-C(18)-C(8) | 118.2317 |
| H(19)-C(1)-C(2) | 120.6860 | H(26)-C(16)-C(15) | 120.8826 |
| C(4)-N(3)-C(2) | 120.2919 | H(27)-C(17)-C(16) | 120.3423 |
| C(5)-N(6)-C(1) | 121.8610 | H(28)-C(18)-C(8) | 120.8839 |
| C(7)-C(5)-C(4) | 131.2583 | C(9)-C(7)-C(5) | 131.2647 |
| C(8)-C(4)-N(3) | 120.4270 | N(13)-C(7)-C(5) | 109.2478 |
| Ru(29)-N(6)-C(1) | 127.3286 | C(12)-N(13)-C(7) | 121.8614 |
| N(14)-C(8)-C(4) | 118.0986 | O(32)-Ru(29)-N(6) | 108.5257 |
| C(18)-C(8)-C(4) | 118.0990 | O(33)-Ru(29)-N(6) | 89.9999 |
| C(15)-N(14)-C(8) | 116.6196 | O(34)-Ru(29)-N(6) | 103.4694 |
| Cl(31)-Ru(29)-N(6) | 89.9997 | H(37)-O(32)-Ru(29) | 119.9999 |
| C(10)-C(9)-C(7) | 119.1468 | H(38)-O(32)-Ru(29) | 119.9997 |
| H(21)-C(9)-C(7) | 106.9818 | H(39)-O(33)-Ru(29) | 120.0003 |
| C(11)-C(12)-N(13) | 118.6271 | H(40)-O(33)-Ru(29) | 119.9999 |
| H(22)-C(10)-C(9) | 106.6826 | H(41)-O(34)-Ru(29) | 119.9999 |
| H(23)-C(11)-C(10) | 106.6078 | H(42)-O(34)-Ru(29) | 120.0004 |
| H(24)-C(12)-C(11) | 107.1167 | | |

**Table S6.** Selected bond angles (in degrees) of $[RuCl(PAOX)_2(OH_2)]Cl_2$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4d.

| **Angle** | **[Deg.]** | **Angle** | **[Deg.]** |
|---|---|---|---|
| N(3)-C(2)-C(1) | 122.1158 | C(11)-N(16)-Ru(21) | 120.2191 |
| H(25)-C(2)-C(1) | 120.8925 | C(15)-N(16)-C(11) | 117.0381 |
| C(4)-N(3)-C(2) | 116.4129 | C(12)-C(11)-N(16) | 121.3299 |
| C(5)-C(4)-N(3) | 122.6950 | H(30)-C(11)-C(12) | 117.3928 |
| H(26)-C(4)-N(3) | 114.9263 | N(13)-C(12)-C(11) | 122.2155 |
| N(6)-C(1)-C(2) | 120.7375 | H(31)-C(12)-C(11) | 120.8558 |
| C(7)-C(5)-C(4) | 126.7921 | C(14)-C(15)-N(16) | 120.6255 |
| Ru(21)-N(6)-C(1) | 120.9908 | C(17)-C(15)-C(14) | 125.5614 |
| H(24)-C(1)-C(2) | 117.9977 | N(18)-C(17)-C(15) | 122.2790 |
| N(9)-C(7)-C(5) | 113.2311 | O(20)-N(19)-C(17) | 116.1785 |
| N(8)-C(7)-C(5) | 121.0709 | H(32)-C(14)-N(13) | 114.9634 |
| O(10)-N(9)-C(7) | 115.4612 | H(27)-N(8)-C(7) | 121.6432 |
| N(16)-Ru(21)-N(6) | 110.7465 | H(28)-N(8)-C(7) | 119.4669 |
| N(19)-Ru(21)-N(6) | 161.7345 | H(29)-O(10)-N(9) | 111.1263 |
| O(22)-Ru(21)-N(6) | 92.0746 | H(33)-N(18)-C(17) | 121.8395 |
| Cl(23)-Ru(21)-N(6) | 89.0088 | H(34)-N(18)-C(17) | 118.8826 |
| H(35)-O(20)-N(19) | 110.8119 | H(37)-O(22)-Ru(21) | 106.1700 |
| H(36)-O(22)-Ru(21) | 105.3142 | | |

**Table S7.** Selected bond angles (in degrees) of $[RuCl_2(ABMAP)_2]Cl$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4a.

| **Angle** | **[Deg.]** | **Angle** | **[Deg.]** |
|---|---|---|---|
| N(3)-C(2)-C(1) | 119.7568 | C(28)-N(21)-C(23) | 112.3373 |
| Br(10)-C(2)-C(1) | 120.2487 | H(39)-N(21)-C(23) | 107.7352 |
| C(4)-N(3)-C(2) | 119.5023 | N(22)-C(23)-N(21) | 126.2549 |
| C(5)-C(4)-N(3) | 119.6111 | C(24)-N(13)-Ru(37) | 103.2801 |
| N(8)-C(4)-N(3) | 128.8825 | N(25)-C(24)-N(13) | 125.8472 |
| N(6)-C(1)-C(2) | 122.0601 | C(14)-N(25)-C(24) | 115.7610 |
| N(7)-C(5)-C(4) | 112.2941 | C(20)-N(22)-C(23) | 111.8045 |
| H(11)-C(1)-C(2) | 121.7740 | Br(29)-C(20)-C(14) | 119.8779 |
| C(9)-N(8)-C(4) | 112.3896 | H(30)-C(14)-C(20) | 122.4016 |
| Ru(37)-N(8)-C(4) | 102.9789 | H(26)-N(13)-C(24) | 108.4755 |
| N(13)-Ru(37)-N(7) | 90.1454 | H(38)-N(13)-C(24) | 115.0964 |
| N(21)-Ru(37)-N(7) | 160.9081 | H(15)-C(9)-N(8) | 110.7970 |
| H(12)-N(7)-C(5) | 109.3388 | H(16)-C(9)-N(8) | 113.7069 |
| H(32)-N(7)-C(5) | 114.9945 | H(17)-C(9)-N(8) | 110.4408 |
| H(33)-N(8)-C(4) | 108.4065 | H(34)-C(28)-N(21) | 110.4075 |
| Cl(40)-Ru(37)-N(7) | 104.2654 | H(35)-C(28)-N(21) | 113.7423 |
| Cl(41)-Ru(37)-N(7) | 84.6328 | H(36)-C(28)-N(21) | 110.8934 |
| C(23)-N(21)-Ru(37) | 104.1034 | | |

**Table S8.** Selected bond angles (in degrees) of $[RuCl(PTCA)_2(OH_2)]Cl_2$ in gaseous phase from PM3 calculations. Atom labels as in Figure 4b.

| Angle | Degree (°) | Angle | Degree (°) |
|---|---|---|---|
| N(3)-C(2)-C(1) | 121.6435 | H(25)-N(9)-C(7) | 122.2726 |
| H(23)-C(2)-C(1) | 121.2212 | C(11)-N(16)-Ru(10) | 116.2602 |
| C(4)-N(3)-C(2) | 115.7469 | C(15)-N(16)-Ru(10) | 103.9610 |
| C(5)-C(4)-N(3) | 123.1702 | C(12)-C(11)-N(16) | 122.2288 |
| H(24)-C(4)-N(3) | 114.8885 | H(26)-C(11)-C(12) | 117.8395 |
| N(6)-C(1)-C(2) | 122.7640 | N(13)-C(12)-C(11) | 121.6544 |
| C(7)-C(5)-C(4) | 119.9335 | H(27)-C(12)-C(11) | 121.1570 |
| Ru(10)-N(6)-C(1) | 116.3274 | C(14)-C(15)-N(16) | 120.2453 |
| H(22)-C(1)-C(2) | 117.7442 | C(17)-C(15)-C(14) | 120.3962 |
| N(16)-Ru(10)-N(6) | 106.1515 | H(28)-C(14)-N(13) | 114.8301 |
| N(9)-Ru(10)-N(6) | 77.0872 | S(18)-C(17)-C(15) | 127.7193 |
| N(19)-Ru(10)-N(6) | 165.3079 | H(29)-N(19)-Ru(10) | 123.2818 |
| O(21)-Ru(10)-N(6) | 91.4324 | H(30)-O(21)-Ru(10) | 106.0504 |
| S(8)-C(7)-C(5) | 127.7973 | H(31)-O(21)-Ru(10) | 101.5025 |
| Cl(20)-Ru(10)-N(6) | 100.1856 | | |

**Table S9.** Optimized structures of the favorable conformation of ruthenium(III) complexes with pyrazine derivatives: *PAOX*, *DPP*, *ABMAP* and *PTCA*, total energies (E in kcal/mol), and atom Cartesian (X,Y,Z) coordinates (Å). The data were obtained at the PM3 calculations.

| **Complex** | **Total energy and atom coordinates** | | | |
|---|---|---|---|---|
| | E = 262 | | | |
| | **Atoms** | **X** | **Y** | **Z** |
| | C(1) | 2.641049 | -1.681573 | -0.840185 |
| | C(2) | 3.631160 | -1.755560 | -1.747350 |
| | N(3) | 3.968254 | -0.612462 | -2.511264 |
| | C(4) | 3.339951 | 0.503806 | -2.356231 |
| | C(5) | 2.255031 | 0.585205 | -1.365930 |
| | N(6) | 1.950426 | -0.457307 | -0.669318 |
| | C(7) | 1.447639 | 1.779223 | -1.080414 |
| | N(8) | 0.555291 | 1.590150 | -0.162870 |
| | N(9) | 1.647822 | 3.007996 | -1.753569 |
| | O(10) | -0.277791 | 2.488224 | 0.277099 |
| | C(11) | -1.165968 | 0.662371 | 2.913894 |
| | C(12) | -2.347357 | 0.901145 | 3.510834 |
| | N(13) | -3.550001 | 0.658378 | 2.805902 |
| | C(14) | -3.535212 | 0.211726 | 1.595851 |
| | C(15) | -2.243342 | -0.048380 | 0.942219 |
| | N(16) | -1.146967 | 0.170881 | 1.585939 |
| | C(17) | -2.069577 | -0.553380 | -0.425138 |
| | N(18) | -0.830307 | -0.702163 | -0.763814 |
| | N(19) | -3.166949 | -0.850147 | -1.268416 |
| [RuCl(*PAOX*)$_2$(OH$_2$)]Cl$_2$ | O(20) | -0.413646 | -1.146512 | -1.914282 |
| see **Fig. S5a** | Ru(21) | 0.489097 | -0.211516 | 0.597606 |
| | Cl(22) | 2.072353 | 0.362661 | 2.107750 |
| | O(23) | 0.540522 | -1.992125 | 1.336475 |
| | H(24) | 2.385446 | -2.524401 | -0.270139 |
| | H(25) | 4.153992 | -2.655191 | -1.891296 |
| | H(26) | 3.611459 | 1.335057 | -2.935928 |
| | H(27) | 1.051328 | 3.786622 | -1.589521 |
| | H(28) | 2.380167 | 3.106192 | -2.419420 |
| | H(29) | -0.307513 | 3.368907 | -0.044050 |
| | H(30) | -0.272239 | 0.841513 | 3.432636 |
| | H(31) | -2.380965 | 1.265833 | 4.495499 |
| | H(32) | -4.442110 | 0.040136 | 1.097163 |
| | H(33) | -3.027991 | -1.203454 | -2.187405 |
| | H(34) | -4.099336 | -0.698929 | -0.957171 |
| | H(35) | -0.988134 | -1.397975 | -2.611712 |
| | H(36) | 0.245249 | -1.903905 | 2.266064 |
| | H(47) | -0.179730 | -2.487644 | 0.896394 |
| | E = 203 | | | |
| | **Atoms** | **X** | **Y** | **Z** |
| | C(1) | -0.878892 | -1.390374 | -2.277264 |
| | C(2) | -1.987850 | -2.178895 | -1.734610 |
| | N(3) | -2.197560 | -2.179982 | -0.463625 |
| | C(4) | -1.366290 | -1.461940 | 0.435556 |

| | | | | |
|---|---|---|---|---|
| | C(5) | -0.302382 | -0.792353 | -0.061147 |
| | N(6) | -0.116096 | -0.739700 | -1.465481 |
| | C(7) | 0.749478 | -0.049507 | 0.656941 |
| | C(8) | -1.760662 | -1.493077 | 1.847679 |
| | C(9) | 0.975354 | -0.074659 | 2.115404 |
| | C(10) | 1.990780 | 0.629914 | 2.641751 |
| | C(11) | 2.867858 | 1.393965 | 1.752823 |
| | C(12) | 2.653052 | 1.350934 | 0.426965 |
| | N(13) | 1.573986 | 0.596219 | -0.108977 |
| | N(14) | -2.142593 | -0.403712 | 2.428838 |
| | C(15) | -2.561256 | -0.377779 | 3.781385 |
| | C(16) | -2.589098 | -1.512470 | 4.502680 |
| | C(17) | -2.185503 | -2.774267 | 3.869622 |
| | C(18) | -1.786618 | -2.767137 | 2.586153 |
| [RuCl(*DPP*)$(OH_2)_3$]$Cl_2$ | H(19) | -0.739496 | -1.335102 | -3.314801 |
| see **Fig. S5d** | H(20) | -2.621000 | -2.718344 | -2.375581 |
| | H(21) | 0.386219 | -0.660390 | 2.752256 |
| | H(22) | 2.171014 | 0.611606 | 3.676613 |
| | H(23) | 3.666566 | 1.951848 | 2.146197 |
| | H(24) | 3.291994 | 1.886054 | -0.209841 |
| | H(25) | -2.848325 | 0.533315 | 4.219175 |
| | H(26) | -2.897490 | -1.498425 | 5.506849 |
| | H(27) | -2.210154 | -3.672077 | 4.414868 |
| | H(28) | -1.493756 | -3.661134 | 2.117889 |
| | Ru(29) | 1.311513 | 0.454771 | -2.047598 |
| | Cl(31) | 2.735921 | -1.302222 | -2.033068 |
| | O(32) | 2.722697 | 1.693577 | -2.495282 |
| | O(33) | 0.104381 | 1.962417 | -2.048797 |
| | O(34) | 0.947073 | 0.221666 | -3.929769 |
| | H(37) | 2.309123 | 2.401313 | -3.030661 |
| | H(38) | 3.311334 | 1.222873 | -3.119955 |
| | H(39) | -0.777228 | 1.600379 | -2.273531 |
| | H(40) | 0.024087 | 2.248433 | -1.116431 |
| | H(41) | 1.786432 | -0.074436 | -4.337370 |
| | H(42) | 0.798087 | 1.118598 | -4.293157 |
| | E = 185 | | | |
| | **Atoms** | **X** | **Y** | **Z** |
| | C(1) | 1.177651 | -2.568560 | -1.125722 |
| | C(2) | 1.016449 | -3.736468 | -1.773587 |
| | N(3) | -0.186685 | -3.990720 | -2.475665 |
| | C(4) | -1.136900 | -3.118769 | -2.506557 |
| | C(5) | -0.959130 | -1.842990 | -1.798353 |
| | N(6) | 0.137942 | -1.607028 | -1.156038 |
| | C(7) | -1.949194 | -0.767198 | -1.747683 |
| | S(8) | -3.504220 | -0.857705 | -2.404037 |
| | N(9) | -1.499697 | 0.343540 | -1.015371 |
| | Ru(10) | 0.269187 | 0.112825 | -0.230858 |
| | C(11) | 0.285915 | 3.003588 | 0.455171 |
| | C(12) | 0.034398 | 4.046440 | 1.267118 |
| [RuCl(*PTCA*)$_2(OH_2)$]$Cl_2$ | N(13) | -0.565638 | 3.826006 | 2.529901 |

| | | | | |
|---|---|---|---|---|
| see **Fig. S5b** | C(14) | -0.879007 | 2.636756 | 2.918402 |
| | C(15) | -0.603903 | 1.498236 | 2.030097 |
| | N(16) | -0.053244 | 1.693860 | 0.876804 |
| | C(17) | -0.907028 | 0.102488 | 2.342481 |
| | S(18) | -1.605451 | -0.436596 | 3.784025 |
| | N(19) | -0.535013 | -0.770898 | 1.309558 |
| | Cl(20) | 1.192883 | 0.963983 | -2.110563 |
| | O(21) | 2.060595 | -0.073612 | 0.455783 |
| | H(22) | 2.067030 | -2.375265 | -0.603257 |
| | H(23) | 1.778097 | -4.459980 | -1.761079 |
| | H(25) | -2.020875 | -3.327195 | -3.033255 |
| | H(26) | 0.729014 | 3.164930 | -0.481741 |
| | H(27) | 0.280591 | 5.023007 | 0.968256 |
| | H(28) | -1.323524 | 2.494845 | 3.858890 |
| | H(29) | -2.090962 | 1.106941 | -0.779499 |
| | H(30) | 2.389389 | 0.838908 | 0.592065 |
| | H(31) | 1.964300 | -0.436812 | 1.359692 |
| | H(34) | -0.534870 | -1.759057 | 1.416922 |
| | E = 163 | | | |
| | **Atoms** | **X** | **Y** | **Z** |
| | C(1) | -4.624497 | 2.255132 | -0.510529 |
| | C(2) | -4.380343 | 1.790804 | -1.884141 |
| | N(3) | -3.306349 | 1.128015 | -2.151691 |
| | C(4) | -2.359830 | 0.838003 | -1.137901 |
| | C(5) | -2.584097 | 1.267744 | 0.114934 |
| | N(6) | -3.761037 | 1.995701 | 0.411555 |
| | N(7) | -1.600567 | 0.995299 | 1.114209 |
| | N(8) | -1.144381 | 0.121032 | -1.411508 |
| | C(9) | -1.441780 | -1.227223 | -1.945848 |
| | Br(10) | -5.611803 | 2.156513 | -3.243052 |
| | H(11) | -5.493245 | 2.797860 | -0.278646 |
| | H(12) | -1.310921 | 1.868677 | 1.553192 |
| | N(13) | 0.924399 | 0.346507 | 1.954452 |
| | C(14) | 4.062837 | -1.253871 | 2.935266 |
| | H(15) | -0.523792 | -1.805980 | -2.037711 |
| | H(16) | -2.135876 | -1.757748 | -1.293396 |
| | H(17) | -1.893799 | -1.144194 | -2.936826 |
| $[RuCl_2(ABMAP)_2]Cl$ | C(20) | 4.401950 | -1.928574 | 1.673750 |
| see **Fig. S5c** | N(21) | 1.549318 | -0.873366 | -0.382357 |
| | N(22) | 3.623557 | -1.801299 | 0.653018 |
| | C(23) | 2.445982 | -1.017300 | 0.731418 |
| | C(24) | 2.135642 | -0.407622 | 1.887423 |
| | N(25) | 2.988131 | -0.544462 | 3.008382 |
| | H(26) | 0.357892 | 0.009996 | 2.732509 |
| | C(28) | 2.240818 | -0.242441 | -1.529580 |
| | Br(29) | 5.951235 | -2.966918 | 1.539354 |
| | H(30) | 4.687450 | -1.348263 | 3.774221 |
| | H(32) | -2.003960 | 0.390859 | 1.828243 |
| | H(33) | -0.636961 | 0.635752 | -2.133061 |
| | H(34) | 2.990326 | -0.926388 | -1.934326 |

| | | | | |
|---|---|---|---|---|
| | H(35) | 2.741739 | 0.675998 | -1.221400 |
| | H(36) | 1.526380 | -0.012741 | -2.318939 |
| | Ru(37) | -0.051772 | 0.117746 | 0.246112 |
| | H(38) | 1.147348 | 1.327619 | 2.114368 |
| | H(39) | 1.259019 | -1.809290 | -0.670109 |
| | Cl(40) | -0.820361 | -1.849996 | 1.082133 |
| | Cl(41) | 0.651649 | 2.198719 | -0.333521 |