

Fig. S1 Aromatic region of the ^1H NMR spectra of $\alpha\text{-[Ru(azpy)}_2\text{(NO}_3)_2\text{]}$ in acetone- d_6 at 25 $^\circ\text{C}$ (proton numbering as in Fig. 7)

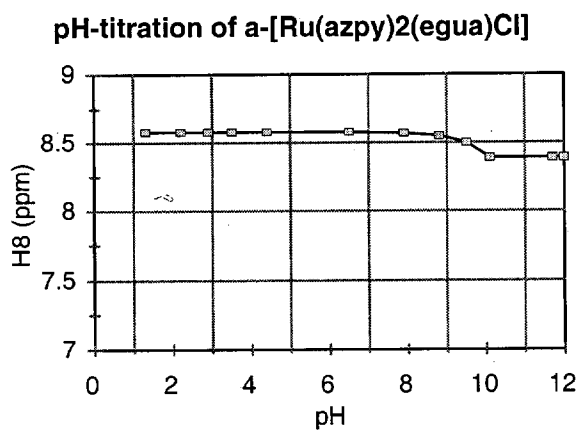


Fig. S2: pH dependence of the ¹H NMR chemical shifts of the H8 signal of α -[Ru(azpy)₂(9egua)Cl]PF₆

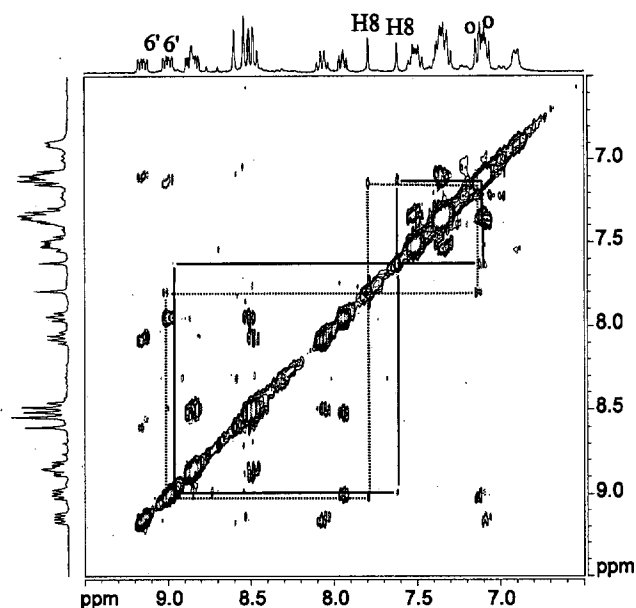


Fig. S3: 2D ^1H - ^1H NOESY spectrum of the aromatic region of α -[Ru(azpy) $_2$ (guo)(H $_2$ O)](PF $_6$) $_2$ (proton numbering as in Fig. 7) acetone- d_6 at 25 °C. The H8- o and H8-H6' NOEs of one diastereoisomer are indicated by dotted lines. The H8- o and H8-H6' NOEs of the other diastereoisomer are indicated by solid lines.

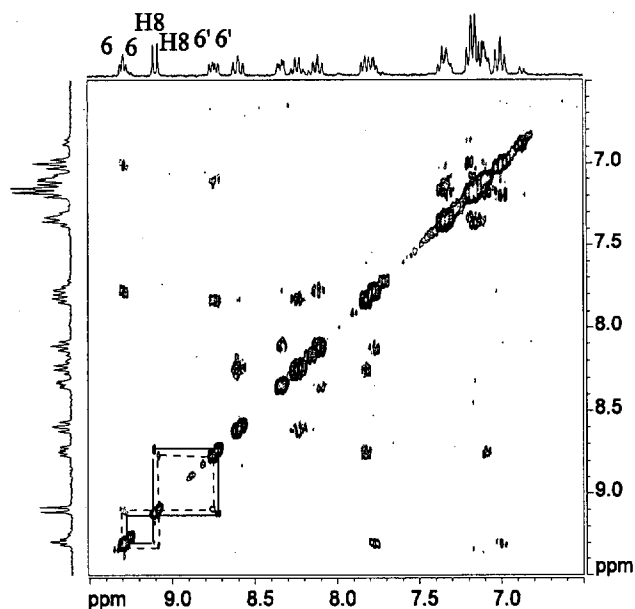


Fig. S4:2D ^1H - ^1H NOESY spectrum of the aromatic region of α -[Ru(azpy) $_2$ (guo)Cl]Cl (proton numbering as in Fig. 7) methanol- d_4 at 25 °C. The H8-H6 and H8-H6' NOEs of one diastereoisomer are indicated by dotted lines. The H8-H6 and H8-H6' NOEs of the other diastereoisomer are indicated by solid lines.

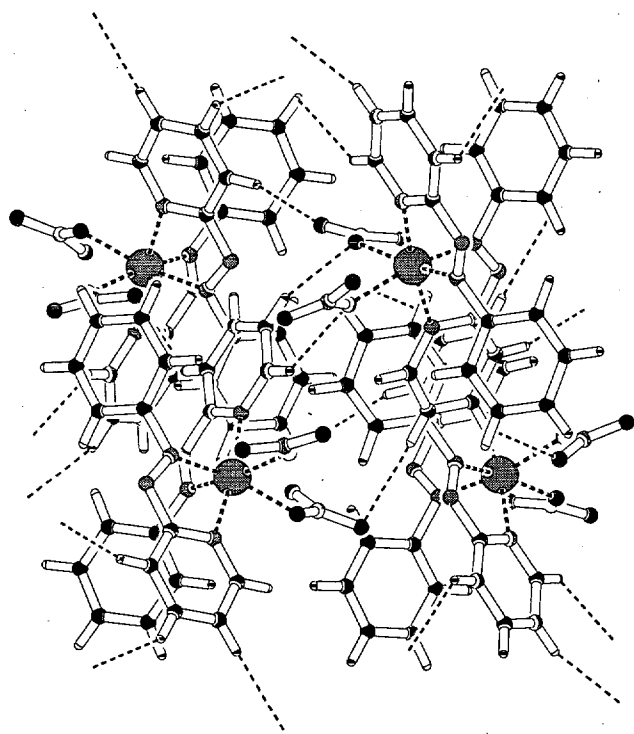


Fig. S5: Crystal lattice of **1** showing relevant hydrogen bonds.

Table SI: Relevant hydrogen bonds in the crystal lattice of **1**

| Donor...Acceptor (Å) H...Acceptor (Å) | Donor-H...Acceptor (°) |
|---|---|
| C(5A)...O(1C ⁱ) 3.305(7) H(5A)...O(1C ⁱ) 2.38(1) | C(5A)-H(5A)..O(1C ⁱ) 161(1) |
| C(3A)...O(3C ⁱⁱ) 3.135(7) H(3A)...O(3C ⁱⁱ) 2.51(1) | C(3A)-H(3A)..O(3C ⁱⁱ) 123(1) |
| C(5B)...O(3D ⁱⁱⁱ) 3.549(8) H(5B)...O(3D ⁱⁱⁱ) 2.59(1) | C(5B)-H(5B)..O(3D ⁱⁱⁱ) 178(1) |
| C(4B)..O(1D ^{iv}) 3.445(8) H(4B)..O(1D ^{iv}) 2.59(1) | C(4B)-H(4B)..O(1D ^{iv}) 148(1) |
| C(3B)...O(2C ^v) 3.460(7) H(3B)..O(2C ^v) 2.52(1) | C(3B)-H(3B)..O(2C ^v) 165(1) |

(i) $3/2-x, 1-y, 1/2+z$ (ii) $-1/2+x, 1/2-y, 1-z$ (iii) $3/2-x, 1-y, -1/2+z$ (iv) $1/2+x, 1/2-y, -z$ (v) $2-x, -1/2+y, 1/2-z$