Supporting Information for

Synthesis, Structural Characterization and Solution Chemistry of Ruthenium(III) Triazole-Thiadiazine Complexes

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Figure S1. FAR-IR spectrum of Na[RuCl₄(L₁)(dmso)] (1), CsI disk (above); calculated IR spectra b3lyp/lanl2dz(Ru)-6-31G(C H Cl N O S) (below). The discrepancy between the Ru-S stretching frequency is due to the difference between the experimental geometry (d(Ru-S)=2.310(3) Å) and the optimized geometry (d(Ru-S)=2.531 Å). According to this, in the optimized geometry the Ru-S bond is weakened with respect to the X-ray structure. The discrepancy between the calculated and experimental geometry for the other coordination distances are less than 0.15 Å.

Table S1. Observed frequencies (cm⁻¹) for the Ru-D (D = donor atom) in Ru(III) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(Ru-N)</th>
<th>ν(Ru-S)</th>
<th>ν(Ru-Cl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(DMSO)₂H][trans-RuCl₄(DMSO)]²⁺</td>
<td>415</td>
<td>345, 329</td>
<td></td>
</tr>
<tr>
<td>Na[RuCl₄(DMSO)(L₁)] (1)</td>
<td>458</td>
<td>436</td>
<td>364, 343</td>
</tr>
<tr>
<td>Na[RuCl₄(DMSO)(L₂)] (2)</td>
<td>448</td>
<td>431</td>
<td>356, 332</td>
</tr>
</tbody>
</table>

a): ref.: S2
Figure S2. Negative ESI-MS spectrum of Na\([\text{trans-RuCl}_4\text{(dms)}\text{(L1)}]\) (1) dissolved in acetonitrile.
Figure S3. Negative ESI-MS spectrum of Na[trans-RuCl₄(dmso)(L2)] (2) dissolved in acetonitrile.
Figure S4. Stack plot of the $^1$H NMR spectra of 1 in D$_2$O recorded in the 0-180 min interval. * = coordinated ligand signals. # = water and acetone.
Figure S5. Stack plot of the $^1$H NMR spectra of 1 in D$_2$O recorded in the 0-180 min interval, together with the free ligand spectrum in D$_2$O. * = coordinated ligand signals, $\S$ = free ligand signals, £ = free DMSO signal (2.71 ppm, ref. S3).
**Figure S6.** Stack plot of the $^1$H NMR spectra of 2 in D$_2$O recorded in the 0-180 min interval. * = coordinated ligand signals. # = water, acetone and 3-(trimethylsilyl)propane sulfonate as reference.
Figure S7. Stack plot of the $^1$H NMR spectra of 2 in D$_2$O recorded in the 0-180 min interval, together with the free ligand spectrum in D$_2$O. * = coordinated ligand signals, § = free ligand signals, £ = free DMSO signal (2.71 ppm, ref. S3).
**Figure S8.** Upper diagram: UV-Vis spectra of Na[RuCl₄(dmso)(L₂)] (2) in water at 7.5 min interval (0-170 min after dissolution). Lower diagram: UV-Vis spectra of 2 in water at 180 min interval (540-3000 min after dissolution).

**Figure S9.** Experimental (dots) and calculated (lines) absorbances for the hydrolytic reaction of Na[RuCl₄(dmso)(L₂)] (2) in water (0-170 min after dissolution) at 342 and 398 nm.
Figure S10. Upper diagram: UV-Vis spectra of Na[RuCl₄(dms)(L1)] (1) in buffered water (pH = 7.4) at 60 sec interval (0-30 min after dissolution). Lower diagram: UV-Vis spectra of 1 in buffered water (pH = 7.4) at 120 sec interval (32-180 min after dissolution).
Figure S11. Upper diagram: UV-Vis spectra of Na[RuCl₄(dmso)(L2)] (2) in buffered water (pH = 7.4) at 60 sec interval (0-26 min after dissolution). Lower diagram: UV-Vis spectra of 2 in buffered water (pH = 7.4) at 120 sec interval (28-180 min after dissolution).
**Figure S12.** Solvolysis of Na[RuCl₄(dmso)₂] in dmso; t = 0, 1, 3, 6, 24 h. Conc. = 2 x 10⁻⁴ M.

**Figure S13.** Solvolysis of Na[trans-RuCl₄(dmso)(L1)] (1) in dmso; t = 0, 1, 3, 6, 24 h. Conc. = 2 x 10⁻⁴ M. At t = 0, λ_max = 410 nm.
**Figure S14.** Cyclic voltammograms of a $5 \times 10^{-4}$ M solutions of 2 dissolved in water. Supporting electrolyte: KNO$_3$ 0.1 M. Scan rate: 25 mV/s. First scan (black line), second scan (gray line).
Figure S15. Dose-response plot obtained after a 48 h incubation of HT1080 and HF cells with the indicated concentrations of 1 and 2. The effect of cis-platin on both cell lines is reported for comparison.

References.
