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X-ray Crystallographic Analysis

Pyridine-2-carboxylic acid (4'-bromo-phenyl)-amide (L13). Colorless prisms suitable for X-ray crystallography were obtained from a concentrated methanol solution. **L13** crystallised in a triclinic cell and structural solution was performed in the space group P $\bar{1}$ with the asymmetric unit containing one molecule. The molecular structure is shown in **Figure S1** and selected bond lengths and angles are given in **Table S1** and the X-ray crystallographic data is stated in **Table S2**. X-ray crystallographic data for ligand **L13** has been deposited in the CCDC with reference number 1449660.

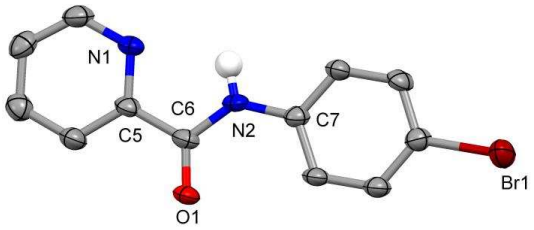


Figure S1 Molecular structure of ligand **L13**. Hydrogen atoms are omitted for clarity and displacement ellipsoids are at the 50% probability level.

Table S1 Selected bond lengths and angles for ligand **L13**, with s.u.s shown in parenthesis

Bond length (Å)	L13	Bond Angle (°)	L13
C1-N1	1.378(10)	N1-C5-C6	117.8(6)
N1-C5	1.375(9)	C5-C6-O1	121.3(6)
C5-C6	1.513(10)	O1-C6-N2	124.6(6)
C6-O1	1.257(8)	C6-N2-C7	130.3(6)
C6-N2	1.378(9)	N2-C7-C8	117.9(6)
N2-C7	1.427(9)	C9-C10-Br1	118.4(5)
C7-C8	1.392(10)		
C10-Br1	1.943(7)		

Table S2 X-ray crystallographic data for ligand **L13**, with s.u.s shown in parenthesis

Ligand	L13
formula	$C_{12}H_9BrN_2O$
formula wt	277.12
cryst syst	Triclinic
space group	P $\bar{1}$
a (Å)	6.3232(10)
b (Å)	8.2665(15)
c (Å)	11.1055(19)
α (°)	89.585(10)
β (°)	87.599(9)
γ (°)	78.366(10)
V (Å^3)	568.07(17)
Z	2
density (mg/m^3)	1.62
absorp coeff (mm^{-1})	3.597
λ[Mo−Kα] (Å)	0.71073 Å
T (K)	150(2)
reflns collected	19736
independent reflns	3323
R_1	0.0953
wR_2	0.287
Goodness of Fit	1.045

Bis(N-Ph-picolinamide) ruthenium dichloride complexes

The X-ray crystallographic data is presented in **Table S3** for complexes **1**[a-b], **3** and **5-7**[a-b] and **Table S4** for complexes **9**, **11**-**13** and **15**-**16**[a-b].

Table S3 X-ray data for bis(N-Ph-picolinamide) ruthenium dichloride complexes **1**[a-b], **3** and **5-7**[a-b], with s.u.s shown in parenthesis

Complex	**1**[a]	**1**[b]	**3**	**5**	**6**	**7**[a]	**7**[b]
formula	$C_{24}H_{19}Cl_2N_4\ O_2\ Ru{\cdot}2(CH_4O)$	$C_{24}H_{19}Cl_2N_4O_2\ Ru{\cdot}(CH_4O)$	$C_{24}H_{17}Cl_2F_2N_4O_2Ru$	$C_{24}H_{15}Cl_2F_4N_4O_2\ Ru{\cdot}(CH_4O)$	$C_{24}H_{17}Cl_4N_4O_2Ru{\cdot}\ 1.25(CH_4O)$	$C_{24}H_{17}Cl_4N_4O_2Ru$	$C_{24}H_{17}Cl_4N_4O_2\ Ru{\cdot}(CH_4O)$
formula wt	631.49	599.44	603.39	671.41	1312.62	636.29	668.33
cryst syst	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	P-1	$P2_1/c$	$P2_1/n$	P-1
a (Å)	12.4207(6)	15.7095(6)	10.1863(5)	8.5290(11)	20.4382(12)	7.9504(11)	8.5066(5)
b (Å)	14.7167(6)	8.3304(3)	12.7202(6)	8.6964(14)	15.1424(8)	16.070(2)	10.1491(6)
c (Å)	15.1423(7)	18.7473(6)	17.8694(10)	17.728(3)	19.7673(11)	24.526(3)	15.1443(9)
α (°)	90	90	90	89.6705(5)	90	90	88.281(5)
β (°)	109.149(5)	93.397(3)	95.399(5)	78.981(5)	113.339(3)	95.268(7)	86.551(5)
γ (°)	90	90	90	89.770(5)	90	90	83.546(5)
V ($Å^3$)	2449.08(15)	2449.08(15)	2305.1(2)	1290.6(3)	5617.1(5)	3120.2(7)	1296.48(13)
Z	4	4	4	2	4	4	2
density (mg/m^3)	1.604	1.626	1.739	1.728	1.552	1.354	1.712
absorp coeff (mm^{-1})	0.844	0.894	0.959	0.88	0.97	0.869	1.053
λ[Mo−Kα] (Å)	0.71073	0.7107	0.7107	0.71073	0.71073	0.71073	0.7107
T (K)	100.01(10)	100.01(10)	100.01(10)	150(2)	150.15	150(2)	100.01(10)
reflns collected	11026	28232	10765	13034	52269	9430	10188
independent reflns	5313	5118	4718	6035	11441	9430	5316
R_1	0.0458	0.0681	0.0484	0.0452	0.0535	0.0315	0.0419
wR_2	0.0882	0.1404	0.1116	0.1368	0.1524	0.084	0.0815
Goodness of Fit	1.029	1.143	1.021	1.101	1.005	1.105	1.038

TableS4 X-ray data for bis(N-Ph-picolinamide) ruthenium dichloride complexes **9**, **11**-**13** and **15**-**16**[a-b], with s.u.s shown in parenthesis

Complex	**9**	**11**	**12**	**13**	**15**	**16**[a]	**16**[b]
formula	$C_{24}H_{15}Cl_6N_4O_2Ru\cdot(CH_4O)$	$C_{24}H_{17}Br_2Cl_2N_4O_2Ru\cdot(CH4O)$	$C_{24}H_{17}Br_2Cl_2N_4O_2Ru$	$C_{24}H_{17}Br_2Cl_2N_4O_2Ru\cdot(CH_4O)$	$C_{24}H_{15}Br_4Cl_2N_4O_2Ru\cdot2(CH_4O)$	$C_{24}H_{17}Cl_2I_2N_4O_2Ru$	$C_{24}H_{17}Cl_2I_2N_4O_2Ru\cdot(CH_4O)$
formula wt	737.21	757.25	722.81	756.24	947.09	819.19	851.23
cryst syst	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
space group	*P*-1	$P2_1/c$	$P2_1/n$	*P*-1	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a (Å)	9.3548(12)	8.6661(9)	8.0068(6)	11.1486(11)	14.508(3)	12.1869(4)	8.4296(8)
b (Å)	12.7693(15)	18.3450(17)	16.0313(11)	11.3608(13)	17.366(3)	16.5955(5)	17.8286(11)
c (Å)	13.3128(15)	19.1627(18)	24.677(2)	12.3471(12)	14.786(3)	12.6582(4)	18.1388(11)
α (°)	104.592(5)	90	90	103.937(9)	90	90	90
β (°)	98.755(5)	114.132(6)	93.717(4)	108.713(9)	116.143(6)	83.836(3)	90
γ (°)	100.683(5)	90	90	103.653(9)	90	90	90
V ($Å^3$)	1478.8(3)	2780.5(5)	3160.9(4)	1351.5(2)	3344.2(11)	255.56(14)	2726.1(3)
Z	2	4	4	2	4	4	4
density (mg/m^3)	1.656	1.809	1.524	1.858	1.881	2.13	2.074
absorp coeff (mm^{-1})	1.107	3.664	3.218	3.769	5.444	3.27	24.54
λ[M−Kα] (Å)	0.71073	0.71073	0.71073 (Mo)	0.7107	0.71073	0.7107	1.5418 (Cu)
T (K)	150(2)	150(2)	150(2)	100.01(10)	150(2)	100.00(10)	100.00(10)
reflns collected	79310	106652	55509	13453	55567	11805	7629
independent reflns	14172	9463	9479	6362	9366	4510	4785
R_1	0.0394	0.0427	0.0399	0.0617	0.0392	0.0344	0.0618
wR_2	0.1036	0.111	0.1009	0.0938	0.1082	0.0679	0.1491
Goodness of Fit	1.029	1.147	1.048	1.01	1.033	1.039	1.036

Bis(N-Ph-picolinamide) ruthenium diiodide complexes

The X-ray crystallographic data is presented in **Table S5** for complexes **18**, **19**, **28** and **29**.

Table S5 X-ray data for bis(N-Ph-picolinamide) ruthenium diiodide complexes **18**, **19**, **28** and **29**, with s.u.s shown in parenthesis

Complex	**18**	**19**	**28**	**29**
formula	$C_{24}H_{16}F_2I_2N_4O_2Ru$	$C_{24}H_{17}F_2I_2N_4O_2Ru$	$C_{27}H_{24}Br_2I_2N_5O_3Ru$	$C_{27}H_{24}Br_2I_2N_5O_3Ru$
formula wt	785.28	786.29	981.2	981.2
cryst syst	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
space group	*P*na2$_1$	*P*na2$_1$	*C*c	*P*2$_1$/*n*
a (Å)	19.4788(15)	19.483(2)	15.7434(14)	11.5135(11)
b (Å)	10.3583(11)	10.2433(9)	9.3052(9)	18.5582(18)
c (Å)	12.0324(12)	12.4461(11)	21.721(2)	14.3455(12)
α (°)	90	90	90	90
β (°)	90	90	95.791(4)	99.770(4)
γ (°)	90	90	90	90
V (Å^3)	2427.7(4)	2483.9(4)	3165.7(5)	3020.7(5)
Z	4	4	4	4
density (mg/m^3)	2.148	2.103	2.059	2.158
absorp coeff (mm^{-1})	3.235	3.162	5.006	5.247
λ[M−Kα] (Å)	0.71073	0.71073	0.71073	0.71073
T (K)	100.01(10)	100.01(10)	120(2)	100.01(10)
reflns collected	6768	27470	26603	20606
independent reflns	3133	7404	5403	6131
R_1	0.0624	0.0519	0.0174	0.0554
wR_2	0.1652	0.1523	0.0496	0.1118
Goodness of Fit	1.029	1.066	1.123	0.96

NMR Spectroscopy

^{1}H NMR spectra was obtained for compound **4** and shows resonance peaks in the paramagnetic region, however, attempts to assign the data have proven unsuccessful (**Figure S2**). ^{1}H NMR was also obtained for compound **8** between +100→-100 ppm, and broad peaks were observed in the diamagnetic region, which could not be assigned to free ligand (**Figures S3 and S4**). Paramagnetic resonances were not observed in compound **8**, and the broad nature of the peaks in the diamagnetic region could be due to picolinamide ligand exchange in solution, and this could correlate to the mixture of different $RuCl_2L_2$ isomers which are obtained.

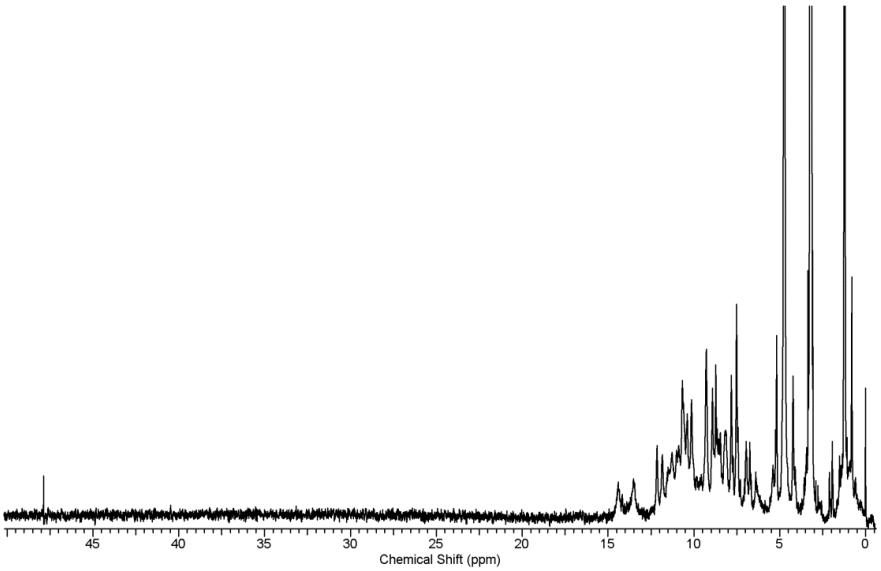


Figure S2 Paramagnetic ^{1}H NMR of compound **4** (d_4-methanol, 500 MHz, 300 K)

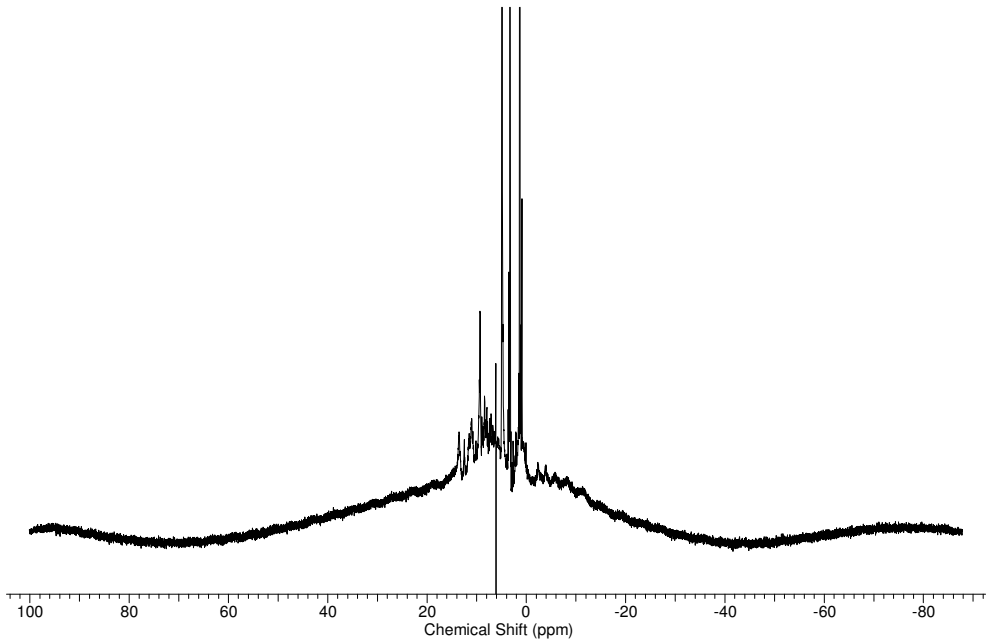


Figure S3 Paramagnetic ^{1}H NMR of compound **8** (d_4-methanol, 400 MHz, 300 K)

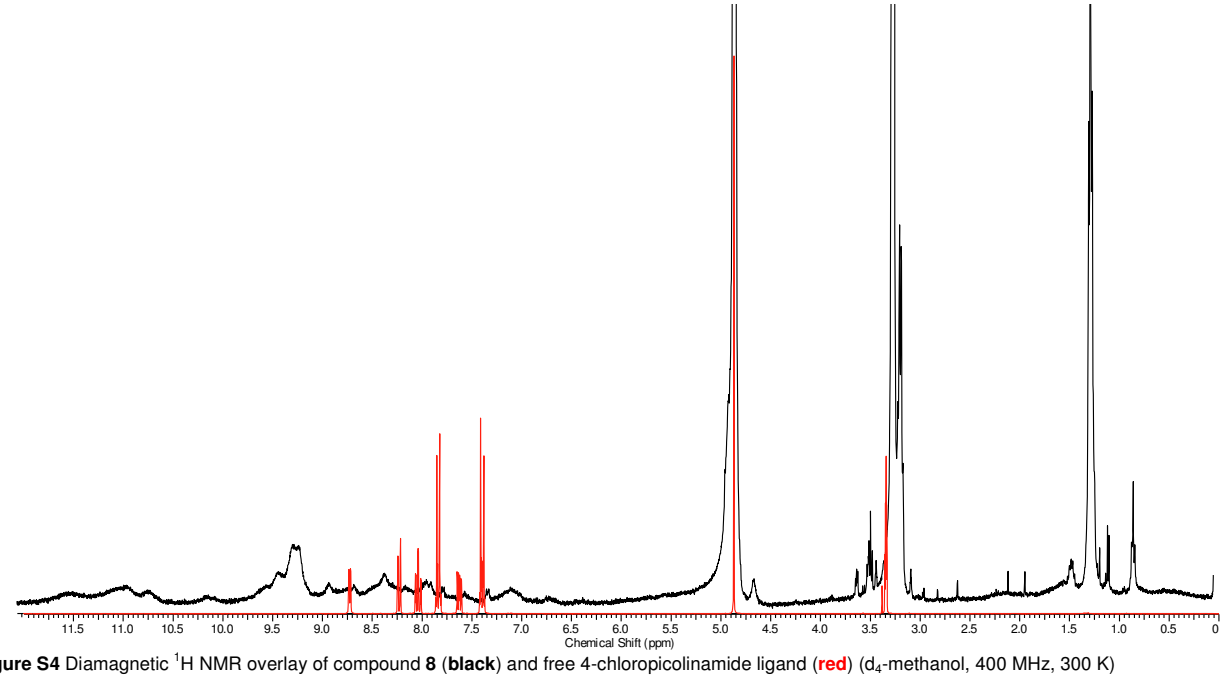
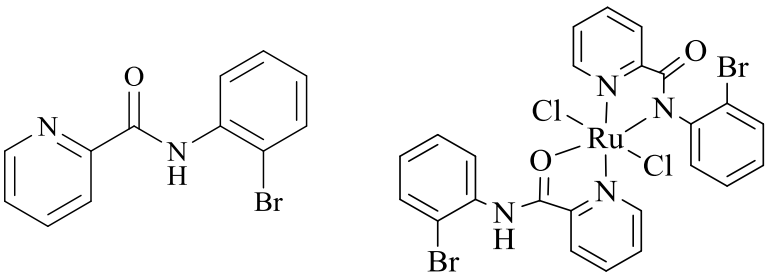


Figure S4 Diamagnetic ^{1}H NMR overlay of compound **8** (**black**) and free 4-chloropicolinamide ligand (**red**) (d_4-methanol, 400 MHz, 300 K)

IR data

IR data for the bis(N-Ph-picolinamide) ruthenium dichloride complex 11

The IR data was analysed for ligand **L11** and complex **11** and the spectra between 4000-450 cm^{-1} is shown in **Figure S5**. In the spectrum of the uncoordinated ligand, a strong CO stretch is observed at 1691 cm^{-1}, and is shifted to 1590 cm^{-1} showing a weak split of the stretch into two bands. The aromatic CH stretching is seen at 3105 cm^{-1} for the ligand, which is shifted to 3065 cm^{-1}, and an NH stretching is at 3281 cm^{-1} seen shifted to 3202 cm^{-1} for the complex. This pattern is consistent for all of the *bis*-picolinamide ruthenium dichloride complexes reported.



Ligand **L11** (black) Complex **11** (blue)

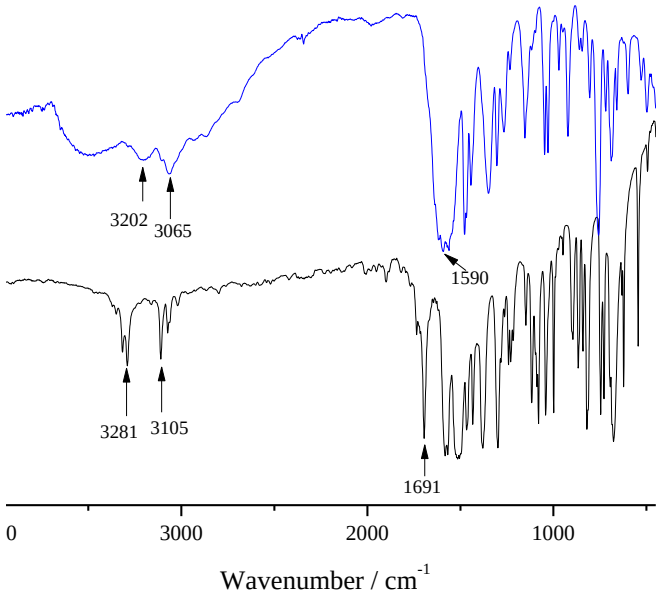
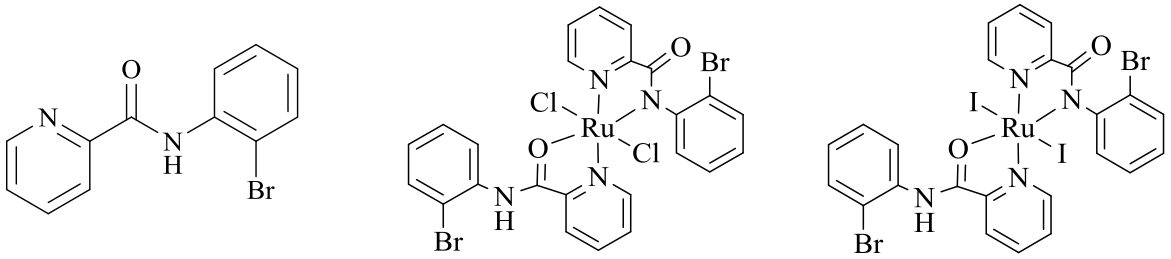


Figure S5 IR spectra of ligand **L11** (**black**) and complex **11** (**blue**)

IR data for the bis(N-Ph-picolinamide) ruthenium diiodide complex 27

The IR spectra of ligand **L11** and complexes **11** and **27** are shown in **Figure S6**. In the spectrum of the uncoordinated ligand, the strong CO stretch is observed at 1691 cm^{-1} which is shifted to 1590 cm^{-1} in complex **11** and to 1563 cm^{-1} in complex **27**, and splits into two bands. The two NH stretches seen in the region 3000-3300 cm^{-1} are shifted from 3290 cm^{-1} and 3108 cm^{-1} in ligand **L11**, to 3209 cm^{-1} and 3062 cm^{-1} in complex **11** and to 3172 cm^{-1} and 3054 cm^{-1} in complex **27**.



Ligand **L11** (black) Complex **11** (green) Complex **27** (pink)

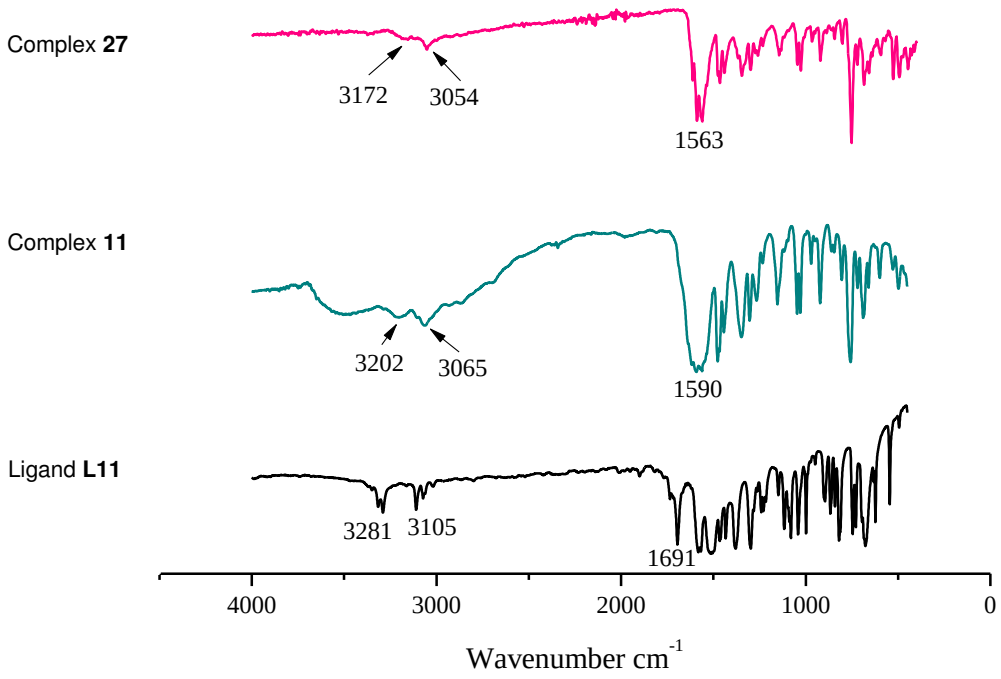


Figure S6 IR spectra of ligand **L11** (**black**) and complexes **11** (**green**) and **27** (**pink**)

Isomerisation studies

Bis(N-Ph-picolinamide) ruthenium (III) dichloride complexes.

Attempts have been made to separate the different $RuCl_2L_2$ species, using; fractional sublimation, column chromatography, solubility differences and preparing the compounds *via* a different synthetic procedures. Complex **7** crystallised with two different structural isomers and the bulk material was analysed by UV-Vis spectrophotometry as a function of time and temperature. **Figure S7 a)** shows the time-dependent UV-Vis spectrum of compound **7** in dry MeOH between 0-24 h, with changes observed at 298 nm, which decreases in intensity after 48 h. The graph shows an isosbestic point at 275 nm, which could indicate equilibrium between different $RuCl_2L_2$ species, suggesting the possibility of picolinamide ligand exchange (see previous NMR). **Figure S7 b)** shows the UV-Vis spectrum of complex **7** in dry methanol upon decreasing the temperature from 331-283 K. An increase in intensity of the peak at 298 nm can be seen as the temperature decreases; however, no new peaks appeared over these temperatures, indicating minimal structural changes.

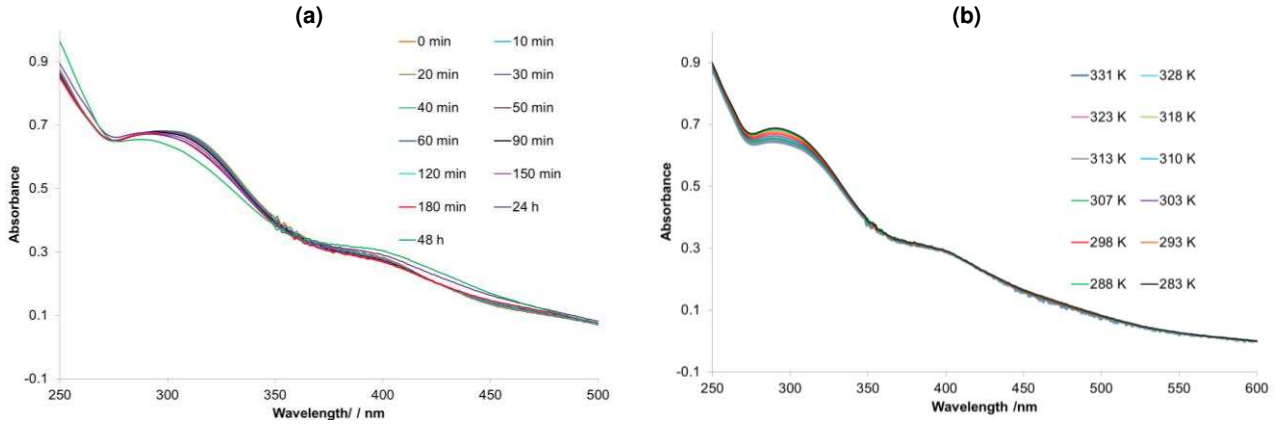


Figure S7 a) Time-dependent, and **b)** Temperature-dependent UV-Vis solution studies in dry MeOH for complex **7** (30 µM)

Bis(N-Ph-picolinamide) ruthenium (III) diiodide complexes.

In order to assess the potential isomerisation of the RuI_2L_2 compounds, UV-Vis spectra was obtained for compound **29** in a solution of DMF. **Figure S8 a)** shows the UV-Vis spectrum of complex **29** at Day 0 and Day 5 and **Figure S8 b)** shows the UV-Vis spectrum from 373-273 K. Using PXRD only one structural *trans* isomer is observed for the RuI_2L_2 compounds, and with no changes observed in the UV-Vis spectra over time or temperature, it is suggested the RuI_2L_2 compounds only form the *trans* structural geometry and no picolinamide ligand exchange occurs in solution.

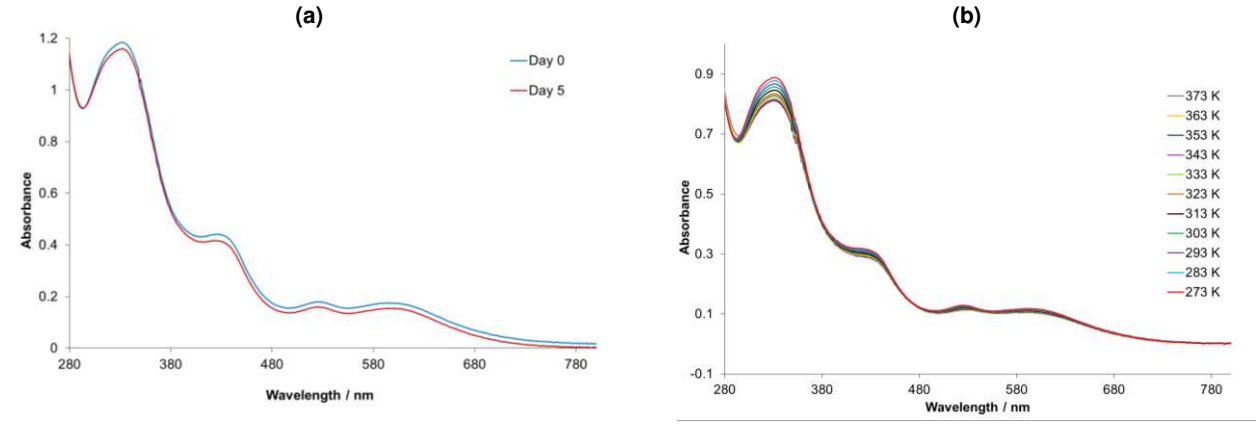


Figure S8 a) Time-dependent and **b)** Temperature-dependent UV-Vis solution studies in DMF for complex **29** (30 µM)

Hydrophobicity Studies (Partition Coefficient)

A calibration curve was prepared for each complex by dissolving the complexes in octanol, and diluting with deionised water to obtain the concentrations of 100, 80, 60, 40 and 20 µM. The maximum absorbance (λ_{max}) was taken to plot the calibration curve of concentration against absorbance. Equal amounts of octanol and deionised water (containing 300 mM NaCl to prevent complexes from undergoing hydrolysis) were stirred overnight for saturation and separated to obtain water-saturated octanol and octanol-saturated water solutions. Approximately 1 mg of complexes **2**, **3**, **5**, **7**, **10**, **11**, **12**, **13** and **14** were dissolved in 25 mL of water-saturated octanol, and sonicated for complete dissolution. Six independent samples were prepared for each complex by adding 2 mL of octanol-saturated water, followed by 2 mL of the stock solution containing ruthenium complexes in each labelled 15 mL Falcon tubes. The samples were then shaken using the IKA Vibrax VXC basic shaker at 500 g/min for 4 hours. Organic (octanol) layer of the stock solution and from the six independent samples were taken for analysis on UV-Vis spectrophotometry. The concentration of each complex was determined using its individual calibration curve. The following equations (**Equation S1** and **S2**) are used to calculate the partition coefficient of the complexes (Log P) and the Log P values stated in **Table S6**.

$$\mathbf{Log\ P} = \mathbf{Log}\ \frac{[\mathbf{C}]_{\mathbf{org}}}{[\mathbf{C}]_{\mathbf{aq}}} \qquad \textbf{(S1)}$$

$$[C]_{aq} = [C]_{org}\,\mathbf{stock} - [C]_{org}\mathbf{final} \qquad \textbf{(S2)}$$

Table S6 Log P values for complexes **2**, **3**, **5**, **7**, **8** and **10**-**14**

Complex	Log P ± SD
2	0.83 ± 0.04
3	1.18 ± 0.02
5	0.67 ± 0.04
7	1.37 ± 0.03
8	1.1 ± 0.2
10	1.05 ± 0.07
11	1.16 ± 0.06
12	0.10 ± 0.04
13	1.39 ± 0.07
14	1.15 ± 0.02

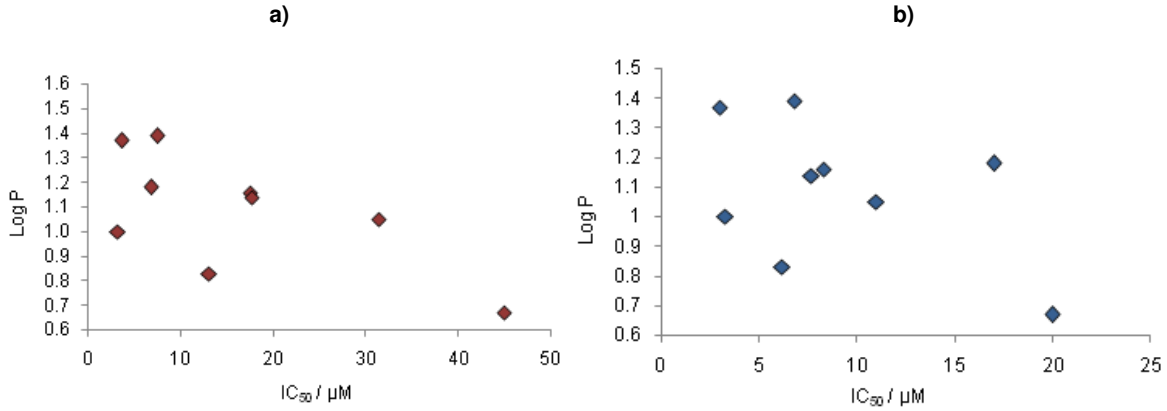


Figure S7 Scatter-grams of Log P values against cytotoxicity for **a)** A2780 ovarian cancer cell line **b)** HT-29 colon cancer cell line.

The scatter-grams in **Figure S7** show IC_{50} values for $RuCl_2L_2$ complexes **2**, **3**, **5**, **7** and RuI_2L_2 complexes **10 – 14** versus their Log P values, for cell lines **a)** A2780 and **b)** HT-29. The complexes are hydrophobic in nature, but show no significant correlations with the IC_{50} values observed. This may suggest that the cell uptake mechanism of the complexes differs from passive diffusion, potentially binding to a specific transporter on the cell membrane, in a similar fashion as KP1019.[6, 7]

Chemosensitivity Studies

In order to assess the compounds cytotoxicity in the initial stages of the drug exposure, the active compounds **25** and **30** were selected and shorter exposure times were assessed. Table S7 presents the IC_{50} values of these compounds average 1, 3, 6 and 120 hour exposure times.

Table S7 IC_{50} values of compounds **25** and **30** against HT-29 cells

Compound		**Exposure Time/ hr**			
		1	**3**	**6**	**120**
IC_{50} ± SD/µM	**25**	> 50	> 50	49 ± 2	3.4±0.3
	30	30 ± 1	26 ± 1	20 ± 1	4.3±0.2

Hydrolysis studies

Samples were prepared by dissolving $RuCl_2L_2$ compounds **3**, **5**, **7**, **10**, **12** and **14** in 10% MeOH and RuI_2L_2 compounds **23**, **26**, **27** and **28** in 10% DMF, followed by the addition of 90% deionised water to give a final concentration of 70 µM. UV-Vis spectra

were recorded every 24 hours over a period of 5 days at 293 K. The concentration of the new compounds was determined from calibration graphs, and equation **S3** was used to calculate the percentage decrease of initial concentration for each compound. UV-Vis spectra for $RuCl_2L_2$ compounds **3**, **5**, **7**, **10**, **12** and **14** are shown in **Figure S8** and the changes in maximum absorbance and relating energies (eV) are stated in **Table S8**.

$$\% \text{ new compound} = \frac{[C]_{\text{initial}} - [C]_{\text{final}}}{[C]_{\text{initial}}} \text{ x } 100 \qquad \textbf{(S3)}$$

Table S8 Change in energies (eV) for $RuCl_2L_2$ compounds **3**, **5**, **7**, **10**, **12** and **14**

Compound	**Δ*E* (eV)**
3 (at 261 nm) (at 313 nm)	138 eV 61 eV
5 (at 259 nm) (at 276 nm)	414 eV 414 eV
7 (at 298)	248 eV
10 (at 258 nm) (at 307 nm)	310 eV 65 eV
12 (at 258 nm) (at 301 nm)	207 eV 89 eV
14 (at 259)	83 eV

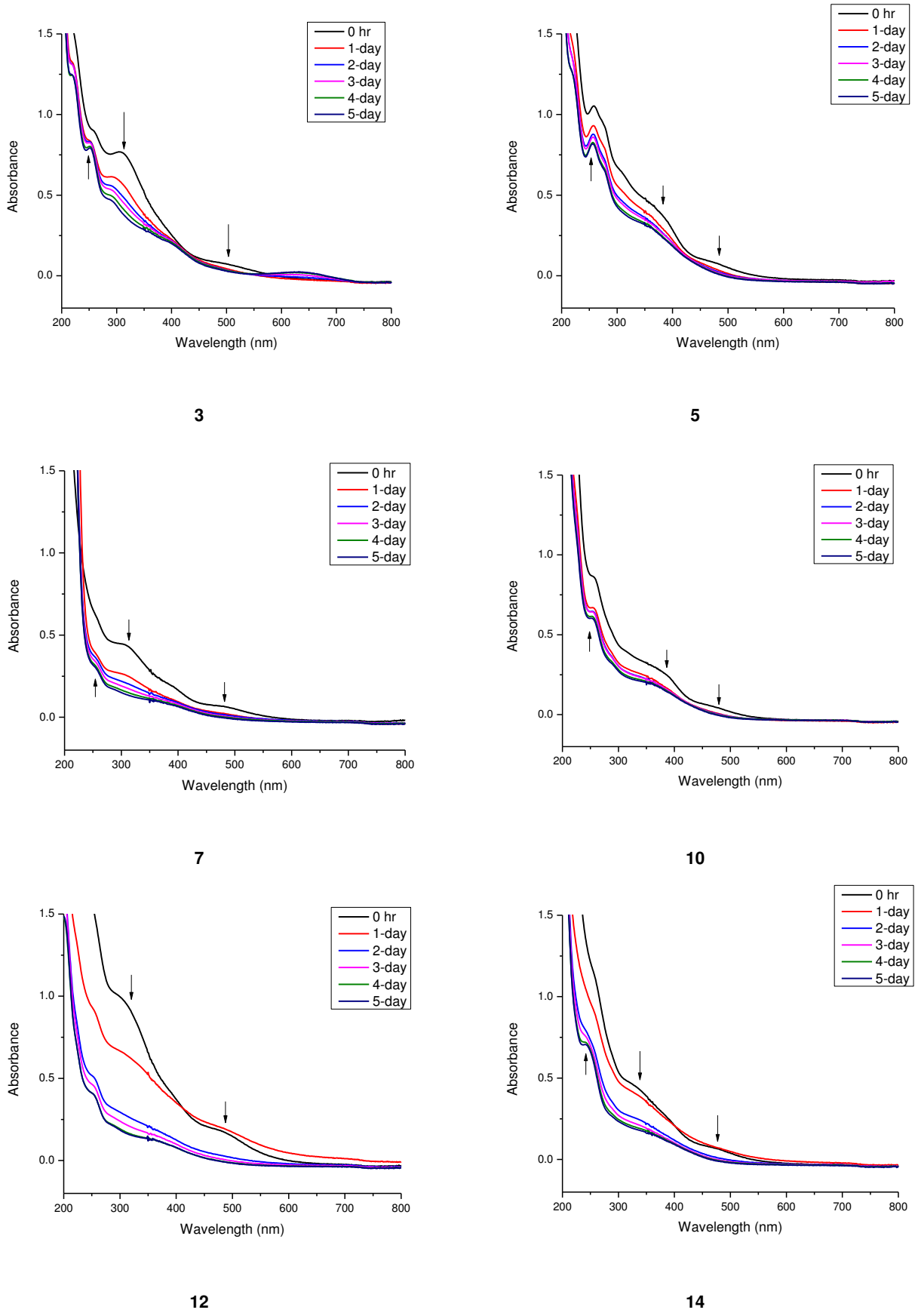


Figure S8 UV-Vis Spectra from hydrolysis studies of complexes **3**, **5**, **7**, **10**, **12** and **14** (70 μM) in 10% methanol/90% water taken every 24 hours for 5 days at 293 K

The UV-Vis spectra for RuI_2L_2 compounds **23**, **26**, **28** and **29** are shown in **Figure S9** and the corresponding changes in absorbance and energies (eV) are presented in **Table S9**.

Table S9 Change in energies (eV) for RuI_2L_2 compounds **23**, **26**, **28** and **29**

Compound	**Δ*E* (eV)**
23 (at 260 nm) (at 316 nm)	620 eV 155 eV
26 (at 261)	310 eV
28 (at 261 nm) (at 314 nm)	310 eV 260 eV
29 (at 258 nm)	413 eV

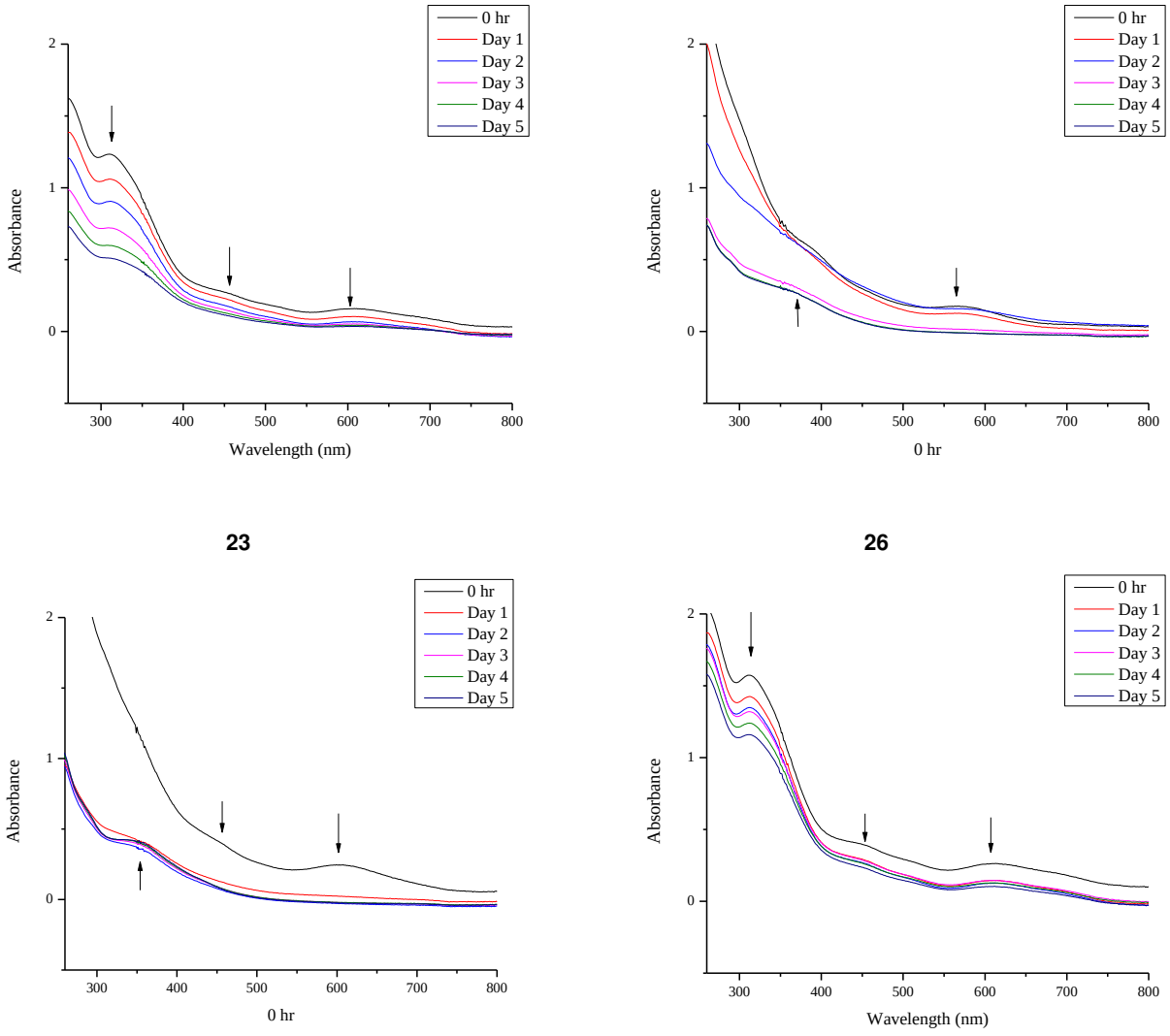


Figure S9 UV-Vis Spectra from hydrolysis studies of complexes **23**, **26**, **28** and **29** (50 μM) in 10% DMF/90% water taken every 24 hours for a period of 5 days at 293 K

In order to understand the possibility of ancillary ligand exchange, UV-Vis spectra have been recorded for the initial time points. **Figure S10** shows the UV-Vis spectra for compounds **3**, **4**, **19** and **20** at 5, 10, 20, 30, 45, 60, 90, 120 and 150 minutes and 298 K. The spectra showed only small absorbance changes in the region 500→900 nm and the main changes were observed in the region of 200→400 nm. As suggested by previous literature on Ru(III) picolinamide complexes,[1] the peaks observed have been assigned to intraligand $\pi \rightarrow \pi^*$ ligand transitions.

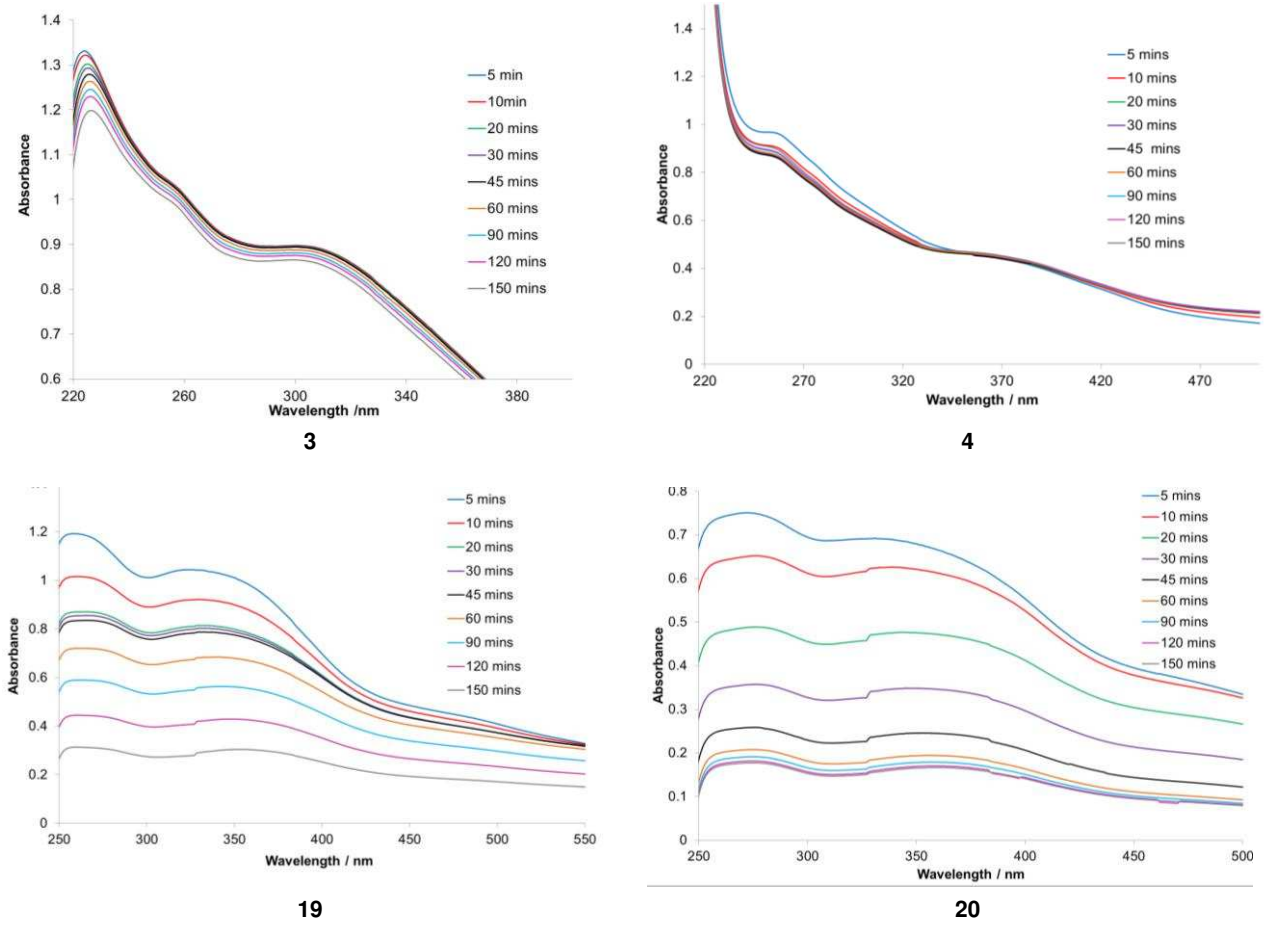
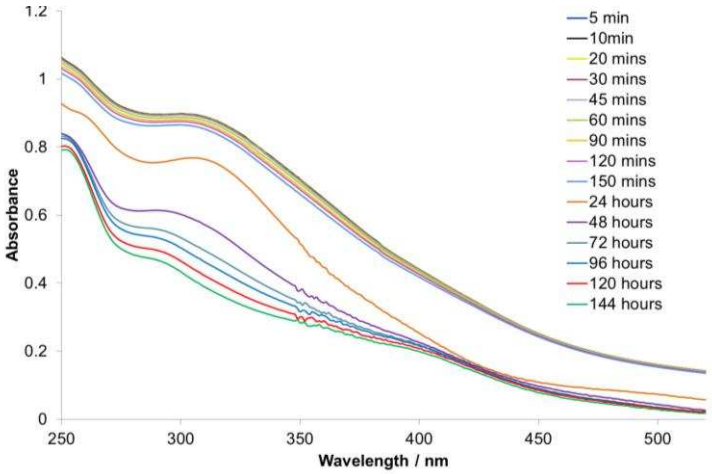


Figure S10 Time-dependent UV-Vis spectra of $RuCl_2L_2$ compounds **3** and **4** (70 μM), and RuI_2L_2 compounds **19** and **20** (70 μM) in 10% MeOH/90% H_2O and 10% DMF/90% H_2O respectively.

UV-Vis spectra was obtained for compound **3** across all time points from 5 minutes to 144 hours (**Figure S11**) and the spectrum shows only a small change in A_{max} between 5–150 minutes. The largest changes in A_{max} are seen over the 5 day period, showing a hypsochromic shift at 313 nm. Over the shorter time points compound **4** showed isosbestic points (**Figure S12**), suggesting the $RuCl_2L_2$ compounds are in equilibrium with another species, this is possibility due to picolinamide ligand exchange of the $RuCl_2L_2$ compounds.



3

Figure S11 UV-Vis spectra of compound 3 over different time points from 5 minutes to 5 days

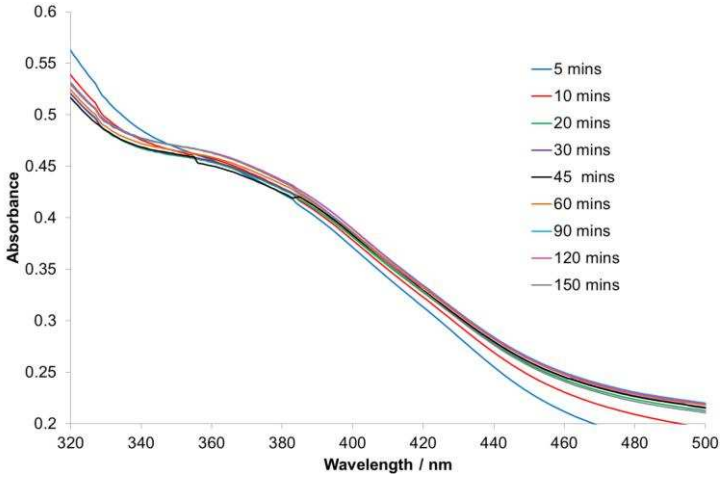


Figure S12 UV-Vis spectra of compound **4** showing the isosbestic points and the compounds in equilibrium

Complex **3**, unlike all the other ruthenium complexes, has the appearance of additional absorption bands at 223, 403 and 627 nm, and an intense color change was observed after 5 days, from orange to blue. In accordance with literature,[2,3] it is possible the complex forms a dimeric species with an oxygen bridging two ruthenium metal centers. **Figure S13** shows the possible structure of the hydrated blue *bis*-picolinamide ruthenium dimer complex. ES-MS analysis of this compound gave an m/z ratio of 1221.9 [M+Na^+] which satisfy the mass of the complex shown in **Figure S13**. Attempts to isolate or synthesise the product *via* a different method have been unsuccessful. Attempts have been made to isolate other hydrated species and characterise the discrete structure by X-ray crystallography analysis. To date we have only confirmed the compound $[Ru[C_{24}H_{17}Br_2N_4O_2)(H_2O)_2][SbF_6]_2$ (**Figure S14**) by mass spectrometry, IR and elemental analysis.

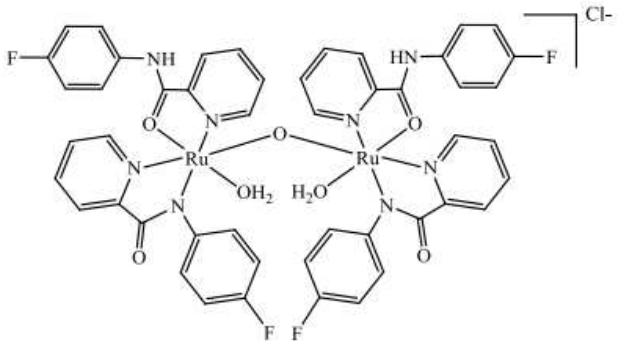


Figure S12 Possible structure of blue *bis*-picolinamide ruthenium aqua dimer complex

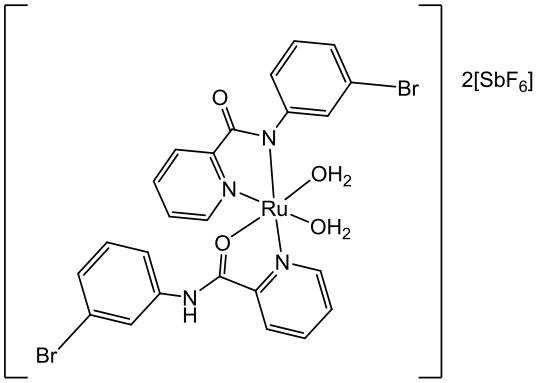


Figure S14 Attempted isolation of the hydrated compound **12** with the large cation [SbF_6]

Yield: 0.098 g, 0.08 mmol, 60%. ES+MS (CH_3OH, m/z): 689.8 [M+H+]. **Analysis found:** C 24.6; H 1.9; N 4.2%. **Analysis Calculated:** C 24.8; H 1.8; N 4.8%. **IR (cm^{-1}):** 3284 (w), 3073 (w), 2950 (w), 1557 (s), 1467 (m), 1427 (w), 1338 (w), 1263 (w), 1229 (w), 1153 (w), 1120 (w), 1065 (w), 1030 (w), 976 (w), 765 (s), 669 (m), 593 (m), 430 (m)

After 5 days, the compounds in aqueous solutions were measured by ES-MS (+), and the spectra for $RuCl_2L_2$ compounds **12** and **14**, and RuI_2L_2 compounds **26** and **27** are shown in **Figure S15** and **Figure S16** respectively. Peaks are observed which can tentatively be assigned to the mono-hydrated and di-hydrated species in the aqueous solutions. Additional ES-MS (+) have been measured for compound **3** (**Figure S17**) in **(a)** 10% MeOH/ 90% H_2O and **(b)** 10% MeOH/ 90% D_2O. The H_2O spectra shows a m/z 509.1 which has been assigned to the di-hydrated species $[RuL_2(H_2O_2)]^{2+}$ and the D_2O spectra shows the corresponding peak at an m/z 511.1 due to the heavier deuterium.

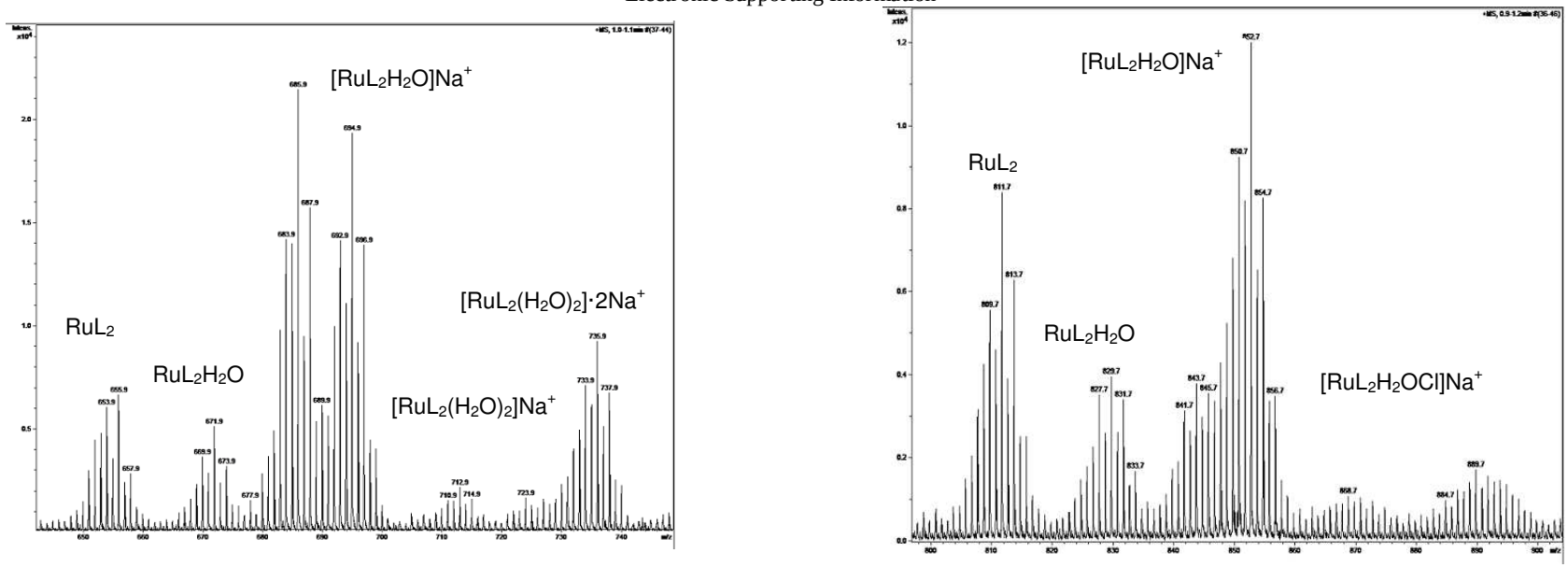


Figure S15 ES-MS (+) spectra of compounds **12** and **14** in a deionised water solution

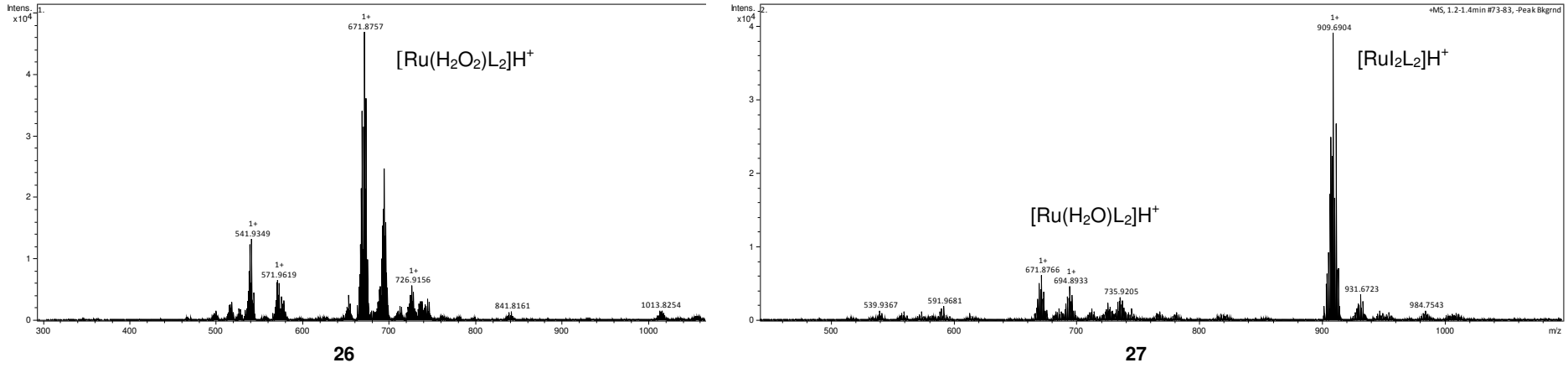


Figure S16 ES+MS spectra for complexes **26** and **27** in a deionised water solution

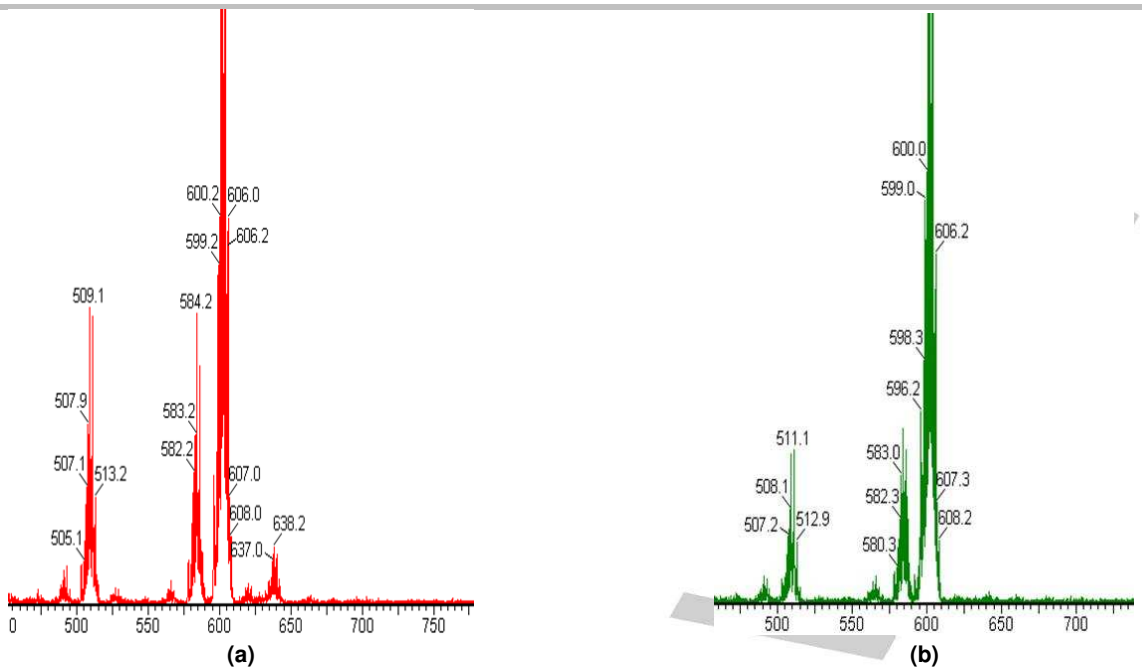


Figure S17 ES+MS spectra for compound **3** in **(a)** 10% MeOH/ 90% H_2O and **(b)** 10% MeOH/ 90% D_2O

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