A New family of Ru(II) complexes with a tridentate pyridine Schiff-base ligand and bidentate co-ligands. Synthesis, characterization, structure and *in vitro* cytotoxicity studies.

Ariadna Garza-Ortiz,^{a,b} Palanisamy Uma Maheswari,^{a,c} Maxime Siegler,^d Anthony L. Spek^d and Jan Reedijk.^{a*}

a) Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands. E-mail: reedijk@chem.leidenuniv.nl; Fax: +31 71 527 4671; Tel: +31 71 527 4459.

b) Current address: Departamento de Sistemas Biológicos, Universidad Autónoma Metropolitana-Unidad Xochimilco, Calzada de Hueso 1100, colonia Villa Quietud, 04960, Coyoacán, México.

c) Current address: Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, Tamilnadu, India

d) Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH, Utrecht, The Netherlands.

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- 1. Table S1 and discussion on IR spectra of the Ru(II) complexes.

The coordination sphere on all Ru(II)-compounds has been analyzed by means of FT-IR. The binding mode of the tridentate Schiff base and bidentate moieties to metal in the complexes have been studied by comparison of IR spectra of precursors. From IR studies, several changes were observed in the spectra of the six Ru(II) compounds when comparing with the corresponding spectra obtained from the starting reagent, [RuCl₃(L1)](H₂O). Table S1 summarizes the most important IR peaks, the corresponding assignment and frequencies in the mid-IR region, confirming the presence of the bis-(arylimino)pyridine ligand, the bidentate ligand (azpy, bpy, 3mazpy, phen, pic and tazpy) and the chloride ligand all coordinated to Ru(II).

Table S1. IR assignment of the Ru(II)-complexes spectra. Selected peaks only.											
Frequencies (cm ⁻	ν (HC=N)	ν (C=N)pyr	v Ru-Npy	Peaks v Ru-Nimin	vRu-Cl	vOCO _{as}	vClO ₄	vClO4 ⁻			

¹)							-	
[RuCl ₃ (L1)](H ₂ O) ⁶	1595.5	1540	374.3	607-586	325		-	-
RuL1-azpy	1599	1500-1450	388	590-544	318		1090	622
RuL1-bpy	1600	1505-1418	384	594	324		1090	622
RuL1-3mazpy	1650	1650-1558	376	-	326		1082	622
RuL1-phen	1599	1599-1506	382	524-470	328		1080	622
RuL1-pic	1602	-	334	601-590	324	1635	-	-
RuL1-tazpy	1599	1520	388	-	328		1081	622

A sharp vibration peak assigned to the v(Ru-Cl) stretching mode was observed around 320 cm⁻¹ in all cases and the values are in accordance with the proposed structures.^{1, 2, 3} The HC=N(imino)bond stretching vibrations of the tridentate ligand are present and the shift is associated to metal coordination. The strong band around 1595 cm⁻¹ in the Ru(III) starting material, is shifted to higher frequency in the analogues Ru(II) complexes, with the biggest shifts for RuL1-3mazpy. This shift support the participation of the imino nitrogen in binding to the metal ion.^{4, 5} The weak bands between 3200 and 2800 cm⁻¹ are related to (C-H) modes of vibration. Also, some weak bands located between 2000-1750 cm⁻¹ can be assigned to overtones of the aromatic rings. The band appearing at 374.3 for $[RuCl_3(L1)](H_2O)^6$ can be attributed to the v(M-N) bond vibration of the pyridine nitrogen. For the Ru(II) compounds, this vibration peaks present blue shifts and they are consistent with the proposed changes in the structures. The v(M-N) bond vibration of the imino nitrogen atoms around 600 cm⁻¹ for $[RuCl_3(L1)](H_2O)$, in the Ru(II) compounds, presents a red shift. Finally the strong peak around 325 cm⁻¹ is attributed to the Ru-CI stretching bond vibration.^{1, 7} Two intense vibrations observed around 1090 and 622 cm^{-1} are attributed to the presence of the ClO₄⁻ anion. As expected they are not present in RuL1-pic.

The N=N stretching frequency of the coordinated 2-(arylazo)pyridine ligands is lowered (around 1320 cm⁻¹) compared to that of the free ligand (around 1420 nm). The strong band in the region of 1650-1620 cm⁻¹ is assigned to the coordinated carboxylate group in the 2-picolinate ligand⁸⁻¹⁰ in case of RuL1-pic. In 2-picolinic acid, this vibration is observe around 1700 cm⁻¹, and then the decrease in frequency is due to coordination.¹¹

2. ESI-MS analysis.

The mass spectra were measured in the positive mode and in the range of m/z=200-1200. Ions containing ruthenium presents a clearly visible metal isotope pattern arising from the distribution, ⁹⁶Ru 5.52, ⁹⁸Ru 1.88, ⁹⁹Ru 12.7, ¹⁰⁰Ru 12.6, ¹⁰¹Ru 17, ¹⁰²Ru 31.6 and ¹⁰⁴Ru 18.7%. For all the perchlorate salts of the Ru(II) compounds studied, the loss of the perchlorate is the dominant ionization process observed, this generates a singly charged Ru(II) ion. The positive ion spectra of the compounds show mainly one major ion. In some cases an ion, which could be explained as the association of water to the positively charged complex, is also observed in the spectra. This fragmentation pattern in the ESI mass spectra of each complex strongly supports the proposed formulation of the complexes. For RuL1-pic the ion observed corresponds to the addition of one proton and the peaks exhibit the correct isotopomer distribution. The mass spectra of RuL1-phen is shown in figures S1.



Figure S1. ESI-MS positive ion spectrum of RuL1-phen (m/z in Da). See experimental section for calculated data. In the inset: The calculated spectrum for the cation of RuL1-phen (m/z in Da).

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