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Synthesis and characterization of *trans*-$[Ru(NO)Cl(L)_4](PF_6)_2$ (L = isonicotinamide; 4-acetylpyridine) and related species

Ivy Calandreli [a], Fabiana de Souza Oliveira [a], Guogang Liang [b], Zênis Novais da Rocha [c], Elia Tfouni [a,*]

[a] Departamento de Química da Faculdade de Filosofia Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Av. dos Bandeirantes 3900, 14040-901 Ribeirão Preto, SP, Brazil
[b] Institute of Chinese Materia Medica, Academy of Chinese Medical Science, Beijing 100700, China
[c] Instituto de Química, Universidade Federal da Bahia, Rua Barão de Geremoabo, 147, 40170-290 Salvador, Bahia, Brazil

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ABSTRACT

The *trans*-$[RuCl_2(L)_4]$, *trans*-$[Ru(NO)Cl(L)_4](PF_6)_2$ (L = isonicotinamide and 4-acetylpyridine) and *trans*-$[Ru(NO)(OH)(py)_4]Cl_2$ (py = pyridine) complexes have been prepared and characterized by elemental analysis, UV–visible, infrared, and ^1H NMR spectroscopies, and cyclic voltammetry. The MLCT band energies of *trans*-$[RuCl_2(L)_4]$ increase in the order 4-acpy < isn < py. The reduction potentials of *trans*-$[RuCl_2(L)_4]$ and *trans*-$[Ru(NO)Cl(L)_4]^{2+}$ increase in the order py < isn < 4-acpy. The stretching band frequency, ν_{NO}, of the nitrosyl complexes ranges from 1913 to 1852 cm^{-1} indicating a nitrosonium character for the NO ligand. Due to the large π-acceptor ability of the equatorial ligands, the coordinated water is much more acidic in the water soluble *trans*-$[Ru(NO)(H_2O)(py)_4]^{3+}$ than in *trans*-$[Ru(NO)(H_2O)(NH_3)_4]^{3+}$.

The discovery that nitric oxide (NO) is involved in several physiological processes and pathologies [1] launched large investigations on nitrosyl metal complexes ranging from fundamental to biological aspects [2]. In this context, the chemical and photochemical reactivities and NO donor properties of Ru complexes, such as *trans*-$[Ru(NO)(NH_3)_4(L)]^{n+}$ (L = NH_3, OH^-, Cl^-, H_2O, triethylphosphite (P(OEt)3), isonicotinamide (isn), nicotinamide (nic), 4-picoline (4-pic), pyridine (py), 4-chloropyridine (4-Clpy), pyrazine (pz), 4-acetylpyridine (4-acpy), N-bound imidazole (imN), C-bound imidazole (imC) and L-histidine (L-hist)) [3], *trans*-$[Ru(NO)Cl(cyclam)]^{2+}$ [4], *trans*-$[Ru(NO)Cl(1\text{-}(3\text{-propylammonium})cyclam)]^{3+}$ [4], *cis*-$[Ru(NO)(cyclen)(H_2O)]^{+}$ [4], *cis*-$[Ru(NO)(H_2O)(imcyclen)]^{+}$ [4] have been investigated in solution and also in materials [5]. These complexes release NO upon irradiation with light and/or by reduction, and their reduction potentials, which can be tuned by the choice of the ligands, lie in the −0.3 to +0.13 V *vs.* NHE range [3,4], which is biologically available. The properties of other Ru nitrosyl complexes, such as *trans*-$[Ru(NO)Cl(py)_4](PF_6)_2$ [6], *trans*-$[Ru(NO)Cl(bpy)_2]^{2+}$ (bpy = 2,2′-bipyridine) [7], and *cis*-$[Ru(NO)L(bpy)_2]^{n+}$ (L = Cl^-, py, 4-pic, 4-acpy) [8] were also reported. All these complexes can also undergo a second reduction at lower potentials, the result of which is claimed to be either coordinated HNO (or NO^-) or NH_3. The tetrakispyridine nitrosyl complex is a stable compound and its electrochemical studies showed reduction potentials higher potentials than the analogous tetraamine [3], cyclam [4] and cyclen [4]. In view of that, it would be interesting to extend the studies of *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ to include other pyridine-like L ligands to investigate the effect of the π-acceptor ability of the equatorial plane on the complexes properties. Nitrosyl complexes with high reduction potentials may be important biologically; they can make, for instance, the second reduction available. This paper reports the new ruthenium nitrosyl complexes *trans*-$[Ru(NO)ClL_4](PF_6)_2$ (isn; 4-acpy) and their precursors *trans*-$[RuCl_2(L)_4]$, along with other related complexes. The acidity of the coordinated water in *trans*-$[Ru(NO)(H_2O)(py)_4]^{3+}$ is also discussed.

The new *trans*-$[RuCl_2(4\text{-acpy})_4]$ complex was prepared by refluxing $[RuCl_2(DMSO)_4]$ [9] in 4-acetylpyridine following the procedure described for *trans*-$[RuCl_2(py)_4]$ [10]. The new *trans*-$[RuCl_2(isn)_4]$ complex was prepared by refluxing $[RuCl_2(DMSO)_4]$ in water with isonicotinamide. All the complexes synthesized are very stable in the solid state.

The nitrosyl complexes *trans*-$[Ru(NO)Cl(L)_4](PF_6)_2$ (L = isn, 4-acpy) were prepared by a route different from that used for *trans*-$[Ru(NO)Cl(py)_4](PF_6)_2$ [6]. The py complex was prepared by reaction of *trans*-$[RuCl_2(py)_4]$ with $NaNO_2$ in pyridine, to form *trans*-$[Ru(NO_2)_2(py)_4]$, which is then reacted with concentrated HCl to result in *trans*-$[Ru(NO)Cl(py)_4]^{2+}$. We were unable to isolate the *trans*-$[Ru(NO_2)_2(L)_4]$ (L = isn, 4-acpy) complexes. Also, as reported [6] for *trans*-$[Ru(NO)Cl(py)_4](PF_6)_2$, attempts to synthesize the isn and 4-acpy complexes from *trans*-$[RuCl_2(L)_4]$ using Ag(I) to remove the chloride proved unsuccessful. The bipyridine

* Corresponding author. Tel.: +55 16 36023748; fax: +55 16 36024838.
E-mail address: eltfouni@usp.br (E. Tfouni).

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nitrosyl complexes synthetic route described by Meyer and coworker [7] showed better results in the synthesis of the isn and 4-acpy complexes. In this route, *trans*-$[RuCl_2(L)_4]$ (L = isn, 4-acpy) reacts with NO_2^- in acidic solution forming the nitrosyl complex *trans*-$[Ru(NO)Cl(L)_4]^{2+}$.

The hydroxo complex *trans*-$[Ru(NO)(OH)(py)_4](PF_6)_2$ was obtained adding *trans*-$[Ru(NO_2)_2(py)_4]$ to 1.5 mol L^{-1} trifluoroacetic acid. The compound was precipitated as a PF_6^- salt which is aqueous insoluble. Changing the PF_6^- counter-ion by Cl^- results in the aqueous soluble *trans*-$[Ru(NO)(OH)(py)_4]Cl_2$ (see detailed syntheses of all complexes described in this work in Supplementary material).

Table 1 lists ^1H NMR and electronic and vibrational infrared absorption spectral, data. The ^1H NMR spectrum of *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ in acetone-d_6 shows three signals at 7.67 (8H, t, $H^{2,4} \times 4$), 8.22 (4H, t, $H^3 \times 4$) and 8.67 (8, d, $H^{1,5} \times 4$) referring to three different kinds of aromatic ring hydrogens, as reported for *trans*-$[Ru(NO)Cl(py)_4](PF_6)_2 \cdot ½H_2O$ [10], and one hydroxyl signal at 8.28 (1H, s, $H^{OH} \times 1$). This py complex has a *trans* configuration according to X-ray diffraction studies [11]; the four equatorial pyridines form a propeller-like arrangement with an average pitch of about 46. It was suggested that rapid cogwheel rotation of the pyridine rings about the Ru–N(py) axis is occurring in solution, which would explain the three aromatic ring H's NMR signals instead of five for *trans*-$[Ru(NO)Cl(py)_4](PF_6)_2 \cdot ½H_2O$ [11]. Since, *trans*-$[Ru(NO)(OH)(py)_4]^{2+}$ has the same *trans* configuration [12], it is reasonable to expect the same NMR pattern. The spectrum obtained in D_2O presents three signals at 7.66 (8H, t, $H^{2,4} \times 4$), 8.24 (4H, t, $H^3 \times 4$), 8.41 (8H, d, $H^{1,5} \times 4$) but does not show the singlet signal due to H exchange with D. In summary, the ^1H NMR spectrum informs that the hydroxo complex is formed instead of an aquo complex, despite being synthesized at pH ~ 1.

The ^1H NMR spectra of *trans*-$[RuCl_2(4\text{-acpy})_4]$ and *trans*-$[Ru(NO)Cl(4\text{-acpy})_4](PF_6)_2$ were obtained in acetone-d_6. The same NMR pattern was observed for both the nitrosyl complex (2.64 (12H, s, $H^m \times 4$), 7.66 (8H, d, $H^{1,4} \times 4$), 8.71 (8H, d, $H^{2,3} \times 4$)) and the dichloro complex (2.72 (12H, s, $H^m \times 4$), 8.15 (8H, d, $H^{1,4} \times 4$), 9.04 (8H, d, $H^{2,3} \times 4$)). This result suggests a rapid rotation of the pyridine rings on the Ru–N(py) axis as for the tetrakis-pyridine complexes.

The infrared spectroscopy is an useful technique to identify and characterize nitrosyl complexes. IR spectra of $\{RuNO\}^6$ species show a strong absorption of the NO stretching frequencies (ν_{NO}) in the 1800–2000 cm^{-1} range which are usually associated with

Table 1
Electronic absorption, and ^1H NMR spectral data and ν_{NO} values for some *trans*-Ru complexes.

	ν_{NO} (cm^{-1})	λ_{max} (nm) (ε, mol^{-1} L cm^{-1})[a,b]	δ (ppm)[b,c,d]
$[RuCl_2(py)_4]$		206 (2.9×10^{-4})	7.58 (7.0[e]) (8H, t, $H^{2,4} \times 4$)
		252 (2.2×10^4)	8.44 (7.5[e]) (4H, t, $H^3 \times 4$)
		305 (3.5×10^3)	8.53 (8.5[e]) (8H, d, $H^{1,5} \times 4$)
		398 (3.5×10^4)	
		456sh (8.7×10^3)	
$[RuCl_2(isn)_4]$		204 (2.6×10^4)	
		262 (1.2×10^2)	
		422 (1.3×10^4)	
$[RuCl_2(4\text{-acpy})_4]$		212 (3.4×10^4)	2.72 (12H, s, $H^{methyl} \times 4$)
		226sh (2.7×10^4)	8.15 (8H, d, $H^{1,4} \times 4$)
		274 (1.4×10^4)	9.04 (8H, d, $H^{2,3} \times 4$)
		480 (2.3×10^4)	
$[Ru(NO)Cl(py)_4](PF_6)_2 \cdot ½H_2O$	1911[b,f,g]	232 (1.9 (2.0)[g] $\times 10^4$)	7.83 (7.7[e]) (8H, t, $H^{2,4} \times 4$)
	1908[a,b]	258 (1.6 (1.5)[g] $\times 10^4$)	8.40 (8.3[e]) (4H, t, $H^3 \times 4$)
		450 (1.6 (1.5)[g] $\times 10^2$)	8.78 (8.6[e]) (8H, d, $H^{1,5} \times 4$)
$[Ru(NO)(OH)(py)_4](PF_6)_2$	1868[b,f,h]	376 (1.4×10^4)	7.67 (8H, t, $H^{2,4} \times 4$)
	1866[a,b]	297 (2.7×10^3)	8.22 (4H, t, $H^3 \times 4$)
		376 (2.8×10^2)	8.67 (8, d, $H^{1,5} \times 4$)
		420 (2.3×10^2)	8.28 (1H, s, $H^{OH} \times 1$)
$[Ru(NO)(OH)(py)_4]Cl_2$	1852[b,f]	242 (7.5×10^4)	7.66 (8H, t, $H^{2,4} \times 4$)
	1877[b,i]	374 (2.3×10^2)	8.24 (4H, t, $H^3 \times 4$)
		414 (2.1×10^2)	8.41 (8H, d, $H^{1,5} \times 4$)
$[Ru(NO)Cl(isn)_4](PF_6)_2$	1907[b,f]	224 (3.1×10^4)	
		260 (1.4×10^4)	
		436 (6.7×10^2)	
$[Ru(NO)Cl(4\text{-acpy})_4](PF_6)_2$	1905[b,f]	228 (3.8×10^4)	2.64 (12H, s, $H^{methyl} \times 4$)
	1913[a,b]	258 (1.7×10^4)	7.66 (8H, d, $H^{1,4} \times 4$)
		440 (4.4×10^2)	8.71 (8H, d, $H^{2,3} \times 4$)
$[Ru(NO)Cl(bpy)_2]^{2+}$	1912[f,h]		
$[Ru(NO)(OH)(bpy)_2]^{2+}$	1890[f,h]		
$[Ru(NO)Cl(NH_3)_4](BF_4)_2$	1888[f,j]		
$[Ru(NO)(H_2O)(NH_3)_4](BF_4)_3$	1912[f,j]		
$[Ru(NO)(OH)(NH_3)_4]Cl_2$	1845[k,l]		
$[Ru(NO)Cl(cyclam)_4](PF_6)_2$	1875[f,j]		

[a] Acetonitrile.
[b] This work.
[c] Dichloro complexes and PF_6^- salts were obtained in acetone-d_6.
[d] Chloride salts were obtained in D_2O.
[e] Ref. [11].
[f] KBr pellets.
[g] Ref.[6].
[h] Ref. [19].
[i] Water.
[j] Ref. [3].
[k] Ref. [23].
[l] Nujol mull.