

Synthesis, Characterization, Spectral Properties and Electrochemical of Compounds *trans*-[Ru(NH₃)L(bpa)]²⁺

Wagner Batista dos Santos^{1*}, Marcio Adriano Sousa Chagas¹, Katia Meirelles Duarte de Sousa¹, Daniel Tizo Costa², Luiz Alfredo Pavanin³

¹Institute of Exact and Earth Sciences, Federal University of Mato Grosso, Cuiabá, Brazil ²FESURV, University of Rio Verde, Rio Verde, Brazil ³Chemical Institute, Federal University of Uberlândia, Uberlandia, Brazil Email: ^{*}wbsantos@ufmt.br

Received 23 December 2016; accepted 26 April 2016; published 29 April 2016

Copyright © 2016 by authors and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY). http://creativecommons.org/licenses/by/4.0/

Abstract

In this work, we present synthesis of the compounds *trans*-[Ru(NH₃)₄L(bpa)]²⁺ where L is pyridine ligands: pyridine (py), isonicotinamide (isn), 4-acetylpyridine (4-acpy) and 4-picoline (4-pic) and 1,2-bis (4-pyridyl) ethane (bpa), their characterization by UV-visible spectroscopy and electrochemical properties. This series shows intense bands in the region between 400 and 515 nm, allocated bands charge transfer (MLCT), the influence of substituents on the pyridine ring (4-acpy and isn), and the interaction between the ligand and the metal, causing a second MLCT band, which is lighter and has more energy. The compound is characterized by spectroscopy by Fourier transform infrared spectroscopy (FTIR). The displacement observed in the symmetrical stretching of v_s (CCN) group in the complex compared with the v_s (CCN) group in the free ligand is indicative of coordination of the pyridine group to the Ruthenium (II) metallic center. The electrochemical data (cyclic voltammetry) show that reversibility criteria are well defined and formal E_f potential, indicating the influence of the pyridine ring substituent.

Keywords

Ruthenium, Pyridine Ligands, MLCT Bands

1. Introduction

In recent years, work with the amines ruthenium (II) and (III) has been further developed in different areas, such

*Corresponding author.

as anti-tumor treatment [1]-[3], antibacterial agents [4], and photochemical properties [5], among others. Transtetra ammine ruthenium (II) shows intense band charge transfer (MLCT) and an intimate dependency on the position of the band with the ligand [6]-[11]. In previous studies with complexes obtained with ruthenium coordinated to heterocyclic nitrogenous ligands [6]-[9], an effective capacity load back donation between the metal and the binder is shown, opening up the possibility of using of these systems in several processes induced by light [12]-[15]. However for use of these properties induced by lighting the knowledge of the electrochemical properties of the compounds especially redoxes are necessary. Studies conducted by Lim et al. [16] and Matsubara et al. [17] with amines of ruthenium have shown that the change of a molecule of ammonia in $[Ru(NH_3)_6]^{+3/+2}$ or water in $[Ru(NH_3)_5H_2O]^{+3/+2}$, by an unsaturated ligand L, such as pyridines caused an increase in the value of the formal potential (E_f), for the compound. This increase is attributed to the π and σ interactions of ligand L with metal; thus, for ruthenium, unsaturated ligands stabilize the lowest oxidation state. Chatt et al. [18] observe the effect of the ligands on the metal atom, similar to that observed for aromatic compounds using cyclic voltammetry. These studies show that the higher the reception capability of electrons π is allied to the smaller capacity σ of ligand L, the greater the value of the formal charge E_f will be. This work presents the synthesis, and spectroscopic and electrochemical properties, highlighting the influence of the substituent on the pyridine ring binder, in the charge transfer bands, and in the formal potential and reversibility criteria presented by the synthesized compounds.

2. Experimental

Synthesis: The synthesis of the isomers *trans*-[Ru(NH₃)₄L L']²⁺ where $L \neq L'$ (L' = bpa; L = 4-acpy, py, isn and 4-pic) was adapted from previously reports [6]-[8] [19].

2.1. Synthesis of trans-[Ru(NH₃)₄SO₄L']²⁺

Here, 600 mg of *trans*-[Ru(NH₃)₄SO₂Cl]Cl (synthesized as previously described in the literature [6]-[8] [19]) was suspended in 11 ml of water, followed by the slow addition of 347 mg of sodium bicarbonate. Then, the ligand (L = 4-acpy, py, ISN, 4-pic) was added in excess. The final solution was filtered and about 5 mL of concentrated HCl was added to the filtrate. The mixture was placed in an ice bath to precipitate and the solid obtained was filtered, rinsed with ethanol and ether and air dried (brown solid in all ligands). The brown solid obtained was dissolved in approximately 50 ml of a solution of 0.1 mol·L⁻¹ HCl, followed by the addition of a few drops of H₂O₂, until the color changed (pale yellow to brown). Then, 500 ml of acetone was added, resulting in the precipitation of a light yellow solid. After cooling, the solid was collected by filtration, washed with ethanol and ether and air dried. The medium yield was 60%.

2.2. Synthesis of trans-[Ru(NH₃)₄LL']²⁺

Here, 180 mg *trans*-[Ru(NH₃)₄SO₄L]Cl (L = isn, 4-pic, 4-acpy and py) was dissolved in 2.0 ml of previously distilled and deaerated water. Argon was bubbled for 15 minutes in this yellow solution and then zinc amalgam was added. This solution remained under an inert atmosphere for about 20 minutes. During the reaction, the solution turned to an orange-red color. In parallel, 440 mg of the ligand 1,2-bis (4-pyridyl) ethane (BPA) was dissolved in the lowest portion of distilled and deaerated water possible, by addition to the initial solution. The resulting mixture was left under constant argon bubbling for 2 hours, protected from light. After this period, the resulting solution was filtered over a freshly prepared saturated solution of NaBF₄ and filtered on a 1:1 basis (NaBF₄ 1 g/1 ml of water), and then taken to a refrigerator to crystallize. The resulting mixture was filtered and the crystals washed with ethanol, ether and dried in a vacuum. The medium yield was 50%.

2.3. Elemental Analysis

Elemental analysis of carbon, nitrogen and hydrogen was performed at the Chemistry Institute of the University of São Paulo. *Trans*-[Ru(NH₃)₄(py)(bpa)](BF₄)₂·NaBF₄·5H₂O: calcd.: C, 25.29; N, 12.15; H, 4.83. found.: C, 24.96; N, 13.21; H, 4.17. *Trans*-[Ru(NH₃)₄(isn)(bpa)](BF₄)₂·NaBF₄·3H₂O: calcd.: C, 26.56; N, 13.77; H, 4.42. found.: C, 26.73; N, 13.40; H, 4.14. *Trans*-[Ru(NH₃)₄(4-pic)(bpa)](BF₄)₂·2NaBF₄. H₂O: calcd.: C, 25.20; N, 11.43; H, 3.88. found.: C, 25.12; N, 12.00; H, 4.12. *Trans*-[Ru(NH₃)₄(4-acpy)(bpa)](BF₄)₂·NaBF₄.: calcd.: C, 30.11; N, 12.94; H, 4.12. found.: C, 30.80; N, 13.92; H, 4.50.

3. Results and Discussion

3.1. Absorption Spectra (UV-Vis)

The spectroscopic monitoring for the compounds obtained is shown in **Figures 1-4**. We observed the formation of charge-transfer bands (MLCT-1) as well as the appearance of a second charge transfer band for the compounds *trans*-[Ru(NH₃)₄(isn)(bpa)]²⁺ and *trans*-[Ru(NH₃)₄(4-acpy)(bpa)]²⁺. Due to the structural similarity of py and 4-pic binders, it is possible to observe the initial existence of 4 well-defined peaks, where the first band observed between 200 and 300 nm is attributed to internal transitions of the ligand (IL) $\pi - \pi^*$ in analogy to other ruthenium amines [6] [19] [20]. The energies and intensity observed are similar to those of the free ligands, but shifted to higher energies. With the development of the reaction (**Figure 1**), the decrease in intensity of this band is observed (IL) indicating the greater interaction of ligands with the metal [6] [19] [20]. It can be observed that the bands at 319 nm, 424 nm and 520 nm are characteristic of the compound *trans*-[Ru(NH₃)₄SO₂L']²⁺, where L = py



Figure 1. Qualitative spectrum monitoring the synthesis of the compound *trans*-[Ru $(NH_3)_4(py)(bpa)]^{+2}$.



Figure 2. Qualitative spectrum monitoring the synthesis of compound *trans*-[Ru $(NH_3)_4(4\text{-pic})(bpa)$]⁺².



Figure 3. Qualitative spectrum monitoring the synthesis of compound *trans*-[Ru(NH₃) $_4$ (isn)(bpa)^{]+2}.

 $(NH_3)_4(4-acpy)(bpa)]^{+2}$.

converged to only one band at 422 nm with the addition of bpa ligand; this may be attributed to the replacement process of bpa to the SO₂ ligand. Similar remarks can be made for the compound obtained for ligand L' = 4-pic (Figure 2). The final intense bands observed at 422 (L = py) and 424 (L = 4-pic), where ε is in the order of 10⁴ mol⁻¹·cm⁻¹ ml in the visible region, have been attributed to electronic transitions between molecular orbital centered on metal (orbital t_{2g}) and a molecular orbital centered ligand (π^* of ligand) [19] [21] (Figure 5(a)). Already for the compounds trans- $[Ru(NH_3)_4(isn)(bpa)]^{2+}$ and trans- $[Ru(NH_3)_4(4-acpy)(bpa)]^{2+}$, bands were obtained at 275, 325 and 400 nm (isn) and 285 and 340 nm (4-acpy). The spectral behavior reveals that for compound $trans-[Ru(NH_3)_4(isn)(bpa)]^{2+}$, a displacement of the bands observed at 325 and 400 nm occurs as a result of substitution of the SO₂ by bpa ligand with maintenance of the band (IL) in the region of 275 nm, which is characteristic of the ligand (isn) (Figure 3); also, there is displacement of the bands 325 nm to 366 nm and 400 nm to 474 nm, which is attributed to electronic transitions between molecular orbitals centered on metal (orbital $t_{2\alpha}$) and molecular orbital centered ligands (π^* ligand). The spectral behavior of the compound *trans*- [Ru(NH₃)₄ (4-acpy)(bpa)²⁺ (Figure 4) exhibits a shift of the band at 285 nm (IL) to 275 nm and 340 nm to 382 nm, resulting from replacement of the ligand SO₂ by bpa. It also shows the appearance of an intense band at 510 nm attributed to electronic transitions between the molecular orbital centered on the metal ($t_{2\sigma}$ orbital) and the ligand (π^* ligand). The literature shows [6] [9] [19] that the *trans*-tetra ammine of ruthenium (II) may present more than one absorption band in the visible region when $L \neq L'$, and second band MLCT is weak [20]. Comparing the ligands involved in this series of compounds, it can be observed that the pyridinic ligands, (isn and/or 4-acpy) show the pyridine ring substituent groups that change the charge density on the metal; this change is evidenced by the presence of MLCT bands with low energy (366 and 382 nm) (Figure 5(b)).

Table 1 summarizes the spectroscopic properties of the complex *trans*- $[Ru(NH_3)_4L(L')]^{+2}$ reported here.

3.2. Absorption Spectra (IR)

Electronic spectroscopy in the medium infrared region: The absorption spectrum in the infrared region was used to characterize the ligands coordinated to the metal according to the energy of their vibrations **Figure 6. Table 2** shows the values identified are highlighted to vibrational groups and their respective wave numbers of complex *trans*-[Ru(NH₃)(bpa)(L)]⁺² where L = py, isn 4-acpy and 4-pic in comparison to the experimental vibrational spectra of free ligands. The displacement observed in the symmetric stretch of the v_s (CCN) group of the complex compared to v_s (CCN) group in the free ligand is indicative of coordination of the pyridine group to the Ru²⁺ metallic centre [22]. It was also noted that there is no significant displacements at asymmetric and symmetric stretching mode of the carbonyl group of free ligand (4-acpy and isn) compared to complex. Meanwhile, the rise of a second stretching is observed in the complexes assigned to v_s (C = C) group of bpa ligand. It was not observed asymmetric and symmetric stretching displacement of v_s (C = C) group of the pyridine ring between free ligand and the complex for the obtained compounds with pyridine (py), and 4-picoline (4-pic) which shows that there was no interaction at this site. The intense band observed around 1070 cm⁻¹, and attributed to the asymmetric stretching of (bpa) group, present in all of the compounds as well as the band seen in 3400 cm⁻¹ range.

3.3. Cyclic Voltammetry

From the cyclic voltammograms obtained, the parameters are: i_{pa} , i_{pc} , E_{pa} , E_{pc} , $E_{1/2a}$, and $E_{1/2c}$; these are listed in

Figure 5. Quantitative electronic spectra of the compounds *trans*- $[\operatorname{Ru}(\operatorname{NH}_3)_4\operatorname{L}(\operatorname{bpa})]^{+2}$ where (a) L = py and 4-pic and (b) L = isn and 4-acpy, in water concentration of $4.84 \times 10^{-5} \operatorname{mol} \cdot \operatorname{L}^{-1}$.

Table 1. spectroscopic properties of the compounds *trans*- $[Ru(NH_3)_4L(bpa)]^{+2}$ and analogues *trans*- $[Ru(NH_3)_4LL']^{+2}$ and $[Ru(NH_3)_5L]^{+2}$ in aqueous solution.

TIPO	Ľ'	L	MLCT-1 (nm)/log ε	MLCT-2 (nm)/log ε	Ref.
trans	*bpa	py^*	422 (4.31)		
trans	*bpa	4-pic*	422 (4.32)		
trans	*bpa	Isn*	474 (4.23)	366 (3.61)	
trans	*bpa	4 -acpy *	510 (4.22)	382 (3.67)	
trans	4-pic	4-pic	417 (4.26)		[19]
trans	4-pic	ру	420 (4.21)		[19]
trans	4-pic	isn	474 (4.21)	355 (3.51)	[19]
trans	4-pic	4-acpy	513 (4.17)	358 (3.54)	[19]
trans	Ру	ру	422 (4.24)		[19]
trans	Ру	isn	470 (4.22)	363 (3.45)	[19]
trans	Ру	4-acpy	507 (4.11)	369 (3.52)	[19]
trans	Isn	4-acpy	514 (4.28)	378 (3.25)	[19]
trans	4-acpy	4-acpy	532 (4.32)	383 (3.87)	[19]

*This work.

W. B. dos Santos et al.

Figure 6. Spectrum in the infrared region for the complex trans- $[Ru(NH_3)_4(L)(bpa)]^{+2}$ in KBr.

Table 3. The results obtained for the potential has an uncertainty of the order of 10 mV, and for all compounds studied here, generally fit the criteria of reversibility [25]-[29]. The potential anodic and cathodic peaks for compounds are within the experimental error and are independent of the potential sweep speed. Comparing the spectral data with voltammetry, as shown in **Table 4**, there is a decrease in the formal potential (E_f), similar to the decreased energy observed in the electronic spectra of the monomers. This decrease can be attributed to an increase in the electron captor capacity of the substituent groups on the aromatic rings of ligands that occurs in

Table 2. FTIR experimental for free ligand and complex <i>trans</i> - $[Ru(NH_3)(bpa)(L)]^{+2}$.									
Band (cm ⁻¹) assignments									
Compound	v _s (CO)	$v_{s}(C=C)$	$v_{\rm s}({\rm CCN})$	(NH ₃)					
$bpa_{(\rm free)}{}^a$	-	1600	1200						
$py_{(\mathrm{free})}^{\mathrm{b}}$	-	1586	1218						
4-pic _(free) ^b	-	1632	1230						
4-acpy _(free) ^b	1726		1262						
isn _(free) ^b	1655	1622	1219						
<i>trans</i> -[Ru(NH ₃)(bpa)(py)] ⁺²	-	1630	1274	3446					
trans-[Ru(NH ₃)(bpa)(4-pic)] ⁺²	-	1632	1276	3424					
<i>trans</i> -[Ru(NH ₃)(bpa)(4-acpy)] ⁺²	1686	1606	1276	3434					
trans-[Ru(NH ₃)(bpa)(isn)] ⁺²	1672	1618	1348	3432					

^arefer [23]; ^bfree gas-phase [24].

Table 3. Electrochemical parameters and observed relationships for compounds *trans*- $[Ru(NH_3)_4(L)(bpa)]^{2+}$ to 0.5 mmol/L NH₄PF₆, T = 25°C and potential (±10 mV).

trans-[Ru(NH ₃) ₄ (4-acpy)(bpa)] ⁺²										
Solvent	V (mV/s)	$I_{pa}\left(\mu A\right)$	$I_{pc}\left(\mu A\right)$	$E_{pa}\left(V ight)$	$E_{pc}\left(V ight)$	$E_{1/2a}\left(V\right)$	$E_{1/2c}\left(V\right)$	$i_{\rm pa}/i_{\rm pc}$	$\Delta E(V)$	$E_{f}\left(V\right)$
	50	2.21	1.97	0.588	0.515	0.501	0.551	1.12	0.073	0.551
Acotono	100	3.21	2.86	0.588	0.520	0.501	0.564	1.12	0.068	0.554
Acetone	200	4.41	4.16	0.586	0.520	0.494	0.572	1.06	0.066	0.553
	300	5.30	4.90	0.588	0.520	0.485	0.580	1.08	0.068	0.554
	50	2.86	2.28	0.625	0.552	0.542	0.583	1.25	0.073	0.589
Acatonitrila	100	3.86	3.41	0.625	0.554	0.540	0.592	1.13	0.071	0.590
Acetomitrie	200	5.28	4.22	0.627	0.557	0.531	0.609	1.25	0.070	0.592
	300	6.54	5.13	0.627	0.552	0.528	0.615	1.27	0.075	0.590
	50	0.70	0.78	0.369	0.293	0.277	0.369	0.90	0.076	0.331
Dimethal wilford	100	1.26	1.27	0.371	0.295	0.290	0.373	0.99	0.076	0.333
Dimetnyi sulloxide	200	1.98	2.24	0.374	0.298	0.296	0.371	0.88	0.076	0.336
	300	2.00	2.96	0.374	0.293	0.280	0.375	0.68	0.081	0.334
			trans-[]	Ru(NH ₃) ₄ (4	l-pic)(bpa)] ⁺²				
	50	2.75	2.73	0.488	0.413	0.422	0.454	1.01	0.075	0.451
Acotono	100	3.50	3.74	0.491	0.417	0.415	0.462	0.94	0.074	0.454
Acetone	200	4.83	5.26	0.488	0.413	0.418	0.469	0.92	0.075	0.451
	300	5.93	6.03	0.491	0.413	0.419	0.477	0.98	0.078	0.452
	50	2.69	2.69	0.517	0.452	0.452	0.485	1.00	0.065	0.485
Acatonitrila	100	3.71	3.61	0.518	0.452	0.449	0.500	1.03	0.066	0.485
Acetomitrie	200	4.78	4.99	0.520	0.447	0.439	0.507	0.96	0.073	0.484
	300	5.80	6.21	0.522	0.449	0.436	0.509	0.93	0.073	0.486
	50	0.55	0.72	0.276	0.200	0.202	0.282	0.77	0.076	0.238
Dimethrul1f1	100	0.80	1.04	0.273	0.200	0.200	0.292	0.77	0.073	0.237
Dimethyl sulfoxide	200	1.26	1.67	0.276	0.200	0.200	0.298	0.75	0.076	0.238
	300	2.11	3.13	0.281	0.200	0.209	0.283	0.67	0.081	0.241

Continued										
<i>trans</i> -[Ru(NH ₃) ₄ (isn)(bpa)] ⁺²										
	50	1.80	1.72	0.566	0.491	0.477	0.540	1.04	0.075	0.528
Apatona	100	2.49	2.36	0.569	0.493	0.469	0.552	1.06	0.076	0.531
Acetone	200	3.58	3.14	0.566	0.493	0.464	0.567	1.14	0.073	0.529
	300	4.24	3.80	0.569	0.493	0.454	0.576	1.12	0.076	0.531
	50	2.11	1.49	0.608	0.527	0.504	0.565	1.42	0.081	0.568
Acatonituila	100	2.57	2.04	0.605	0.525	0.477	0.583	1.26	0.080	0.565
Acetonitrite	200	3.70	2.82	0.605	0.525	0.465	0.597	1.31	0.080	0.565
	300	4.69	3.73	0.610	0.522	0.451	0.601	1.26	0.088	0.566
	50	0.63	0.77	0.342	0.276	0.250	0.357	0.81	0.066	0.309
Dimothyl sulfoyido	100	0.93	1.23	0.342	0.271	0.248	0.364	0.76	0.071	0.306
Dimetriyi sunoxide	200	1.19	1.89	0.344	0.266	0.233	0.379	0.63	0.078	0.305
	300	1.05	2.43	0.347	0.264	0.163	0.401	0.43	0.083	0.305
trans-[$\mathbf{Ru}(\mathbf{NH}_3)_4(\mathbf{py})(\mathbf{bpa})$] ⁺²										
	50	3.09	3.04	0.515	0.447	0.456	0.483	1.02	0.068	0.481
Acetone	100	4.42	4.46	0.515	0.447	0.457	0.489	0.99	0.068	0.481
Acetolie	200	6.27	6.18	0.515	0.449	0.458	0.495	1.01	0.066	0.482
	300	7.69	7.71	0.513	0.452	0.463	0.493	1.00	0.061	0.483
	50	3.53	3.27	0.549	0.479	0.483	0.515	1.08	0.070	0.514
Acetonitrile	100	5.06	4.88	0.552	0.479	0.483	0.520	1.04	0.073	0.516
Accionitine	200	6.85	6.83	0.554	0.483	0.478	0.527	1.00	0.071	0.518
	300	8.59	8.63	0.554	0.479	0.478	0.530	1.00	0.075	0.516
	50	0.70	0.86	0.298	0.225	0.221	0.311	0.82	0.073	0.262
Dimethyl sulfoyide	100	1.09	1.33	0.298	0.227	0.221	0.316	0.82	0.071	0.263
Dimentyl sunoxide	200	1.63	2.09	0.300	0.227	0.222	0.325	0.78	0.073	0.264
	300	2.11	3.00	0.303	0.225	0.222	0.323	0.70	0.078	0.264

 Table 4. Comparison of the formal potential and band metal ligand charge transfer complexes of ruthenium *trans*tetrammines with "donor number" in various solvents.

Trans-[Ru(NH ₃) ₄ (L)(bpa)] ²⁺ Dimethyl sulfoxide		Water		Acetone		Acetonitrile		
т	DN = 29.8		DN = 17.1		DN = 17.0		DN = 14.1	
L	$E_{f}\left(mV\right)$	λ (nm)	$E_{f}\left(mV\right)$	λ_{\max} (nm)	$E_{f}\left(mV\right)$	λ_{\max} (nm)	$E_{f}\left(mV\right)$	λ_{\max} (nm)
4-acpy	533	547	594	510	752	506	789	503
Isn	505	499	470	474	729	471	765	474
Ру	462	456	449	426	681	431	715	428
4-pic	438	451	413	422	651	428	684	428

solvents (Donor Number), leading to an increase in the formal potential. Already in dimethylsulfoxide solvent, systems have shown evidence of electrochemical reactions, which can be attributed to the basicity of the solvent employed (high Gutmann donor number [30]), making it possible to replace the pyridinic ligands.

4. Conclusion

The spectroscopic characterizations using UV-vis characterization reveal the presence of band charge transfer

(MLCT) with ε values in the order of $10^4 \text{ mol}^{-1} \text{ L} \cdot \text{cm}^{-1}$, which is a very important characteristic for cases in which light is a fundamental role. The infrared analysis (**Table 2**) shows that the CCN symmetric stretching of pyridine ring is shifted to lower frequency band at 1274 cm⁻¹, 1276 cm⁻¹, 1276 cm⁻¹ and 1348 cm⁻¹ due to the coordination of the nitrogen with the metal. The analysis carried out by cyclic voltammetry reveals the system's reversibility, accrediting the compounds studied here to the dyes used in photoregenerative cells.

Acknowledgements

The authors thank the Brazilian agencies CAPES and FAPEMAT, for the material and financial support.

References

- Silveira-Lacerda, E.P., Pavanin, L.A., Santos, W.B., Nomizo, A., *et al.* (2010) The Ruthenium Complex Cis-(Dichloro) Tetraammineruthenium (III) Chloride Presents Immune Stimulatory Activity on Human Peripheral Blood Mononuclear Cells. *Biological Trace Element Research*, **133**, 270-283. <u>http://dx.doi.org/10.1007/s12011-009-8440-8</u>
- [2] Silveira-Lacerda, E.P., Pavanin, L.A., Santos, W.B., Nomizo, A., *et al.* (2010) The Ruthenium Complex Cis-(Dichloro) Tetraammineruthenium (III) Chloride Presents Selective Cytotoxicity against Murine B Cell Lymphoma (A-20), Murine Ascitic Sarcoma 180 (S-180), Human Breast Adenocarcinoma (SK-BR-3), and Human T Cell Leukemia (Jurkat) Tumor Cell Lines. *Biological Trace Element Research*, **135**, 98-111. <u>http://dx.doi.org/10.1007/s12011-009-8498-3</u>
- [3] Silveira-Lacerda, E.P. (2003) Evaluation of the Antitumor Activity of Cis-[RuCl₂(NH₃)₄]Cl over the Human Tumor Cell Lines and Mice. Doctoral Thesis, UFU-Uberlandia, Minas Gerais.
- [4] Lemes, G.D.F. (2004) Utilization of Ruthenium Coordination Compounds (II) and (III) as Bactericides. Masters Dissertation, UFU-Uberlandia, Minas Gerais.
- [5] Tfouni, E. (2000) Photochemical Reactions of Ammineruthenium (II) Complexes. *Coordination Chemistry Reviews*, 196, 281-305. <u>http://dx.doi.org/10.1016/S0010-8545(99)00200-3</u>
- [6] Pavanin, L.A., Giesbrecht, E. and Tfouni, E. (1985) Synthesis and Properties of the Ruthenium (II) Complexes Cis-Ru (NH₃)₄(isn)L²⁺. Spectra and Reduction Potentials. *Inorganic Chemistry*, **24**, 4444-4446. <u>http://dx.doi.org/10.1021/ic00219a055</u>
- [7] Santos, W.B. (2001) Synthesis, Characterization, Chemical and Photochemical Studies of Supramolecular Systems. Masters Dissertation, UFU-Uberlandia, Minas Gerais.
- [8] Tizo, D.T. (2004) Synthesis, Characterization, Chemical and Photochemical Studies of Supramolecular Systems with Monomers Trans-Ru (II) with Ligands Pyridine Masters Dissertation, UFU-Uberlandia, Minas Gerais.
- [9] Tfouni, E. and Ford, P.C. (1980) Thermal and Photochemical Properties of Some Trans-Disubstituted Tetraammineruthenium (II) Complexes of Aromatic Nitrogen Heterocycles, Trans-Ru(NH₃)₄LL^{'n+}. *Inorganic Chemistry*, **19**, 72-76. <u>http://dx.doi.org/10.1021/ic50203a016</u>
- [10] Baba, A.I., Shaw, J.R., Simon, J.A., Thummel, R.P. and Schmehl, R.H. (1998) Thermal and Photochemical Properties of Some Trans-Disubstituted Tetraammineruthenium (II) Complexes of Aromatic Nitrogen Heterocycles, Trans-Ru(NH₃)₄LL^{'n+}. *Coordination Chemistry Reviews*, **171**, 43-59. <u>http://dx.doi.org/10.1016/S0010-8545(98)90009-1</u>
- [11] Endicott, J.F. and Chen, Y.-J. (2007) Observations Concerning Light Promoted Electronic Delocalization in Covalently Linked Transition Metal Complexes. *Inorganica Chimica Acta*, 360, 913-922. <u>http://dx.doi.org/10.1016/j.ica.2006.06.024</u>
- [12] Cummins, D., Boschloo, G., Ryan, M., Corr, D., Rao, S.N. and Fitzmaurice, D. (2000) Ultrafast Electrochromic Windows Based on Redox-Chromophore Modified Nanostructured Semiconducting and Conducting Films. *Journal of Physical Chemistry B*, **104**, 11449-11459. <u>http://dx.doi.org/10.1021/jp001763b</u>
- [13] Kalyanasundaram, K. and Gratzel, M. (1997) Photovoltaic Performance of Injection Solar-Cells and Other Applications of Nanocrystalline Oxide Layers. *Proceedings of the Indian Academy of Sciences-Chemical Sciences*, 109, 447-469. <u>http://dx.doi.org/10.1007/BF02869206</u>
- [14] Bonhote, P., Gogniat, E., Gratzel, M. and Ashrit, P.V. (1999) Novel Electrochromic Devices Based on Complementary Nanocrystalline TiO₂ and WO₃ Thin Films. *Thin Solid Films*, **350**, 269-275. http://dx.doi.org/10.1016/S0040-6090(99)00229-1
- [15] Campus, F., Bonhote, P., Gratzelm, M., Heinen, S. and Andwalder, L. (1999) Electrochromic Devices Based on Surface-Modified Nanocrystalline TiO₂ Thin-Film Electrodes. *Solar Energy Materials and Solar Cells*, 56, 281-297. http://dx.doi.org/10.1016/S0927-0248(98)00138-X
- [16] Lim, H.S., Barclay, D.J. and Anson, F.C. (1972) Formal Potentials and Cyclic Voltammetry of Some Ruthenium-Ammine Complexes. *Inorganic Chemistry*, 11, 1460-1466. <u>http://dx.doi.org/10.1021/ic50113a003</u>

- [17] Matsubara, T. and Ford, P.C. (1976) Some Applications of Cyclic Voltammetry to the Reactions and Properties of Ruthenium Ammine Complexes. Reduction Potentials and Rate Studies. *Inorganic Chemistry*, **15**, 1107-1110. <u>http://dx.doi.org/10.1021/ic50159a025</u>
- [18] Chatt, J., Kan, C.T., Leigh, G.J., Pickett, C.J. and Stanley, D.R. (1980) Transition-Metal Binding Sites and Ligand Parameters. *Journal Chemical Society. Dalton Transition*, 10, 2032-2038. <u>http://dx.doi.org/10.1039/dt9800002032</u>
- [19] Bento, M.L. and Tfouni, E. (1988) Spectra, Reduction Potentials, and Coordinated Pyrazine Basicities in the Ruthenium (II) Complexes *trans*-Ru(NH₃)₄LL^{'n+1}. *Inorganic Chemistry*, 27, 3410-3413. <u>http://dx.doi.org/10.1021/ic00292a028</u>
- [20] Bento, M.L. (1993) Structural Properties of Some Amines Ruthenium (II) with Azines and Pyrazines. Doctoral Thesis, UNESP-Araraquara, São Paulo.
- [21] Ford, P., Rudd, D.F.P., Gaunder, R. and Taube, H. (1968) Synthesis and Properties of Pentaamminepyridineruthenium(II) and Related Pentaammineruthenium Complexes of Aromatic Nitrogen Heterocycles. *The Journal of the American Chemical Society*, 90, 1187-1194. <u>http://dx.doi.org/10.1021/ja01007a015</u>
- [22] Xue, J., Hua, X., Yang, L., Li, W., Xu, Y., Zhao, G., Zhang, G., Liu, L., Liu, K., Chen, J. and Wu, J. (2014) Cobalt(II) and Strontium(II) Complexes of Three Isomers, Nicotinamide, Isonicotinamide and Picolinamide. *Journal of Molecular Structure*, **1059**, 108-117. <u>http://dx.doi.org/10.1016/j.molstruc.2013.11.001</u>
- [23] Kurt, M. and Yurdakul, S. (2003) Molecular Structure and Vibrational Spectra of 1,2-bis(4-pyridyl) Ethane by Density Functional Theory and *Ab initio* Hartree-Fock Calculations. *Journal of Molecular Structure*, **654**, 1-9. http://dx.doi.org/10.1016/S0022-2860(03)00185-6
- [24] BIORAD: Infrared Spectral Data from the Bio-Rad/Sadtler IR Data Collection Was Obtained from Bio-Rad Laboratories, Philadelphia, PA (US).
- [25] Brown, E.R. and Large, R.F. (1971) Cyclic Voltammetry, A.C. Polarography and Related Techniques of Chemistry. In: Brown, E.R. and Large, R.F., Eds., *Physical Methods of Chemistry—Electrochemical Methods*, Vol. I, II-A, Wiley Interscience, New York, 423.
- [26] Nicholson, R.S. and Shain, I. (1964) Theory of Stationary Electrode Polarography. Single Scan and Cyclic Methods Applied to Reversible, Irreversible, and Kinetic Systems. *Analytical Chemistry*, 36, 706-723. <u>http://dx.doi.org/10.1021/ac60210a007</u>
- [27] Gosser, D.K. (1994) Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms. VCH Publishers, New York, 31-33.
- [28] Reichardt, R. (1990) Solvents and Solvent Effects in Organic Chemistry. VCH Publishers, New York.
- [29] Gosser, D.K. (1994) Cyclic Voltammetry: Simulation and Analysis of Reaction Mechanisms. VCH Publishers, New York, 6.
- [30] Gutmann, V. (1976) Solvent Effects on the Reactivities of Organometallic Compounds. *Coordination Chemistry Reviews*, 18, 225-255. <u>http://dx.doi.org/10.1016/S0010-8545(00)82045-7</u>