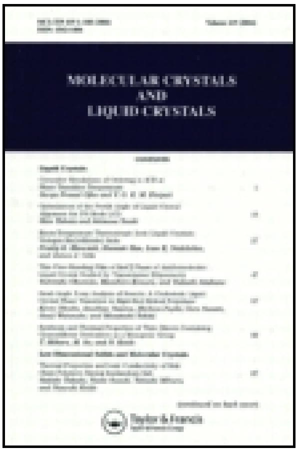

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Synthesis, Characterization, and Crystal Structure of Bis(2,2′-Dipyridyl) (Nitropyridylsulfide) Ruthenium(II) (Hexafluorophosphate)

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Synthesis, Characterization, and Crystal Structure of Bis(2,2′-Dipyridyl) (Nitropyridylsulfide) Ruthenium(II) (Hexafluorophosphate)

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The S—S bond undergoes a reductive cleavage when 2,2′-dithiobis(5-nitropyridine) is reacted with $Ru(bpy)_2Cl_2$ (bpy = 2,2′-bipyridine) and yields the monocationic species $[Ru(bpy)_2(S\text{-}Py\text{-}NO_2)]^+$. The synthesized complex $Ru(N_5S)^+$ was characterized by UV-visible (UV-Vis), cyclic voltammetry, FT-IR, ^1H-NMR, and X-ray. The ^1H-NMR spectra show a set of signals according to low complex symmetry. The electrochemistry analysis showed a quasi-reversible $Ru^{III/II}$ wave observed at 0.78 V versus Ag/AgCl. X-ray structural analysis revealed a distorted octahedral coordination sphere around the metal. The octahedral N_5S chromophore surrounding the metal ion is formed via two trans N and S atoms and four nitrogen atoms from two bis(2,2′-bipyridiyl) ligands. The distortion provoked by an N,S-schelating short-bite ligand has already been shown in similar derivatives. In the title compound, this effect is more dramatic since the four-membered ring presents more strain, and this effect is similar to the previously analyzed four-membered N,S-chelating short-bite ligand.

Keywords Crystal structure; electrochemical properties; ruthenium complex synthesis

Introduction

In the past decades, there has been considerable interest in the design and synthesis of new derivates of ruthenium(II) complexes and a promising contribution to understanding their remarkable properties [1]. The properties of a metallic ion in a complex are governed by ligand, so the properties of the complexes strongly depend on the choice of a suitable ligand [2]. Many studies have focused on heterocyclic N-atom donors since they are often good ligands for Ru(II) metal. The coordination chemistry of organosulfur compounds has also been studied extensively. The coordination chemistry of pyridine and pyrimidine thiolates has emerged as an important class of sulfur donor ligands for transition metals. There are two donor atoms in these types of ligands: the S atom, which is a soft center, and the N atom, which is considered as a hard center [3,4]. The reaction of $Ru(bpy)_2Cl_2$ with 2,2′-dithiobis-5-nitropyridine has indeed afforded a new ruthenium complex S,N-chelated by reductive cleavage of disulfide ligand, as expected.

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The bidentate N,S donor ligands form four-membered chelate rings with the metal ion. The molecular structure and the electrochemical and spectroscopic properties are described in this work. We are interested in the knowledge of new properties of thiolates ruthenium complexes and applications in interfacial electron transfer process [5], charge separation states, and dssc's for the development of an efficient dye sensitized solar cell [6,7].

Experimental

All chemicals used in this work were analytical reagent grade and employed as supplied, without further purification, except for acetonitrile, which was dried and stored over 4 Å molecular sieves for the electrochemical measurements. *cis*-$Ru(bpy)_2Cl_2$ was synthesized by reported procedures [8]. For the synthesis of the bis(2,2′-dipyridyl) (nitropyridylsulfide) ruthenium(II) (hexafluorophosphate), 200 mg (0.0398 mmol) of *cis*-$Ru(bpy)_2Cl_2$ was dissolved in 30 mL of methanol mixture to which 160 mg (0.0500 mmol) of 2,2′-ditiobis(5-nitropyridine) was dissolved in 20 mL of CH_2Cl_2. The mixture was refluxed and stirred for 24 h. The solution was cooled to room temperature, followed by the addition of an NH_4PF_6 aqueous solution. The corresponding solids thus obtained were filtered and washed. The resulting crude product was purified by column chromatography on an alumina column using $CHCl_3$/EtOH (2:1) as eluent. The solvent was removed under vacuum (yield of 43%). Single crystals were grown by direct diffusion of n-hexane into a dilute dichloromethane solution of the complex. Fourier transform infrared spectroscopy (FT-IR) (KBr pellet) ν/cm^{-1}: 1331, 1093,761, 557, 842. ^{1}H-NMR (400 MHz, acetone-d_6, δ): 9.75 (1H, d); 8.78 (2H, d); 8.70 (1H, d); 8.65 (2H, m); 8.24 (2H, t); 8.08 (3H, m); 7.96 (3H, m); 7.88 (1H, t); 7.72 (1H, t); 7.44 (1H, t); 7.34 (1H, t); 7.01 (1H, d). UV-visible (UV-Vis) (CH_3CN) λ_{max}: 492 nm. Diffraction data were collected at room temperature using a Bruker-Nonius KappaCCD diffractometer with graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å). Frames were collected with the COLLECT program [9], indexed, and processed using Denzo SMN, and the files scaled together using the HKL2000 program [10]. Relevant crystal data, experimental conditions, and the final refined parameters are listed in Table 1. The absorption correlation was applied using a semi-empirical method based on multiple scanned reflections on PLATON [11] program. The structure solution and refinement process were made using the SIR95 [12] and SHELXL-97 [13] programs, respectively. All nonhydrogen atoms were refined with anisotropic thermal parameters using full-matrix least squares procedures on F^2. Hydrogen atoms were located geometrically and refined allowing to ride on their parent atoms with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. ^{1}H-NMR spectra were obtained with a Bruker AVANCE 400 spectrometer, the spectra being referred to tetramethylsilane as an internal standard. UV-Vis absorption spectra were recorded on a Shimadzu UV-Vis-NIR 3101 PC160 instrument, using 1-cm quartz cells. Infrared spectra were obtained as KBr pellets with a Bruker VECTOR 22 FT-IR spectrometer. Electrochemistry experiments were carried out with a BAS CV-50 W cyclic voltammetry equipment, using an H-type cell, with a conventional three-electrode array consisting of a platinum working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl (3 M KCl) or saturated calomel electrode (SCE) as the reference electrode. All solutions were prepared in acetonitrile, with 0.1 M $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) as the supporting electrolyte, and thoroughly degassed with N_2, prior to each experiment. Working and auxiliary electrodes

Table 1. Structure determination summary for $C_{25}H_{19}RuF_6N_6O_2PS$

Empirical formula	$C_{25}H_{19}RuF_6N_6O_2PS$
Formula weight	713.56
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 9.2040(18)$ Å, $\alpha = 104.52(3)^\circ$ $b = 13.314(3)$ Å, $\beta = 90.61(3)^\circ$ $c = 13.495(3)$ Å $\gamma = 106.04(3)^\circ$
Exptl. crystal description	Prism
Exptl. crystal color	Red
Volume	1532.9(7) $Å^3$
Z	2
Density (calculated)	$1.546\ \mathrm{Mg} \cdot \mathrm{m}^{-3}$
Absorption coefficient	$0.701\ \mathrm{mm}^{-1}$
F(000)	712
Crystal size	0.55 × 0.20 × 0.6 mm
Theta range for data collection	5.85°–27.48°
Index ranges	$-11 < = \mathrm{h} < = 11$; $-14 < = \mathrm{k} < = 17$; $-17 < = \mathrm{l} < = 17$
Different measurement device type	Nonius KappaCCD area-detector diffractometer
Different measurement method	$\omega/2\theta$
Reflections collected	14827
Independent reflections	6857 [R(int) = 0.0848]
Reflections observed (>2 sigma)	3821
Data completeness	0.975
Absorption correction type	Multiscan [14]
Exptl. absorpt._correction_*T*min	0.775
Exptl._absorpt._correction_*T*max	0.880
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6857/28/376
Goodness-of-fit on F^2	1.218
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0925$, $wR_2 = 0.1441$
R indices (all data)	$R_1 = 0.1885$, $wR_2 = 0.1704$
Largest diff. peak and hole	0.888 and −0.698 e. $Å^{-3}$
Computing structure solution	SIR95 [12]
Computing structure refinement	SHELXL-97 [13]
Refine ls. hydrogen treatment	Treated by constrained refinement

Note: R indices: $R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = |\Sigma w(|Fo|^2 - |Fc|^2)|/\Sigma[w(F_o)^2]^{1/2}$ (based on F^2). $w = 1/[\sigma^2(Fo^2) + (0.0403^*P)^2 + 0.74^*P]$, where $P = [\max\ (F_o{}^2,0) + 2^*F_c{}^2)]/3$. Goodness-of-fit = $[\Sigma_w(|Fo|^2 - |Fc|^2)/(N_{\mathrm{obs}} - N_{\mathrm{parameters}})]^{1/2}$.

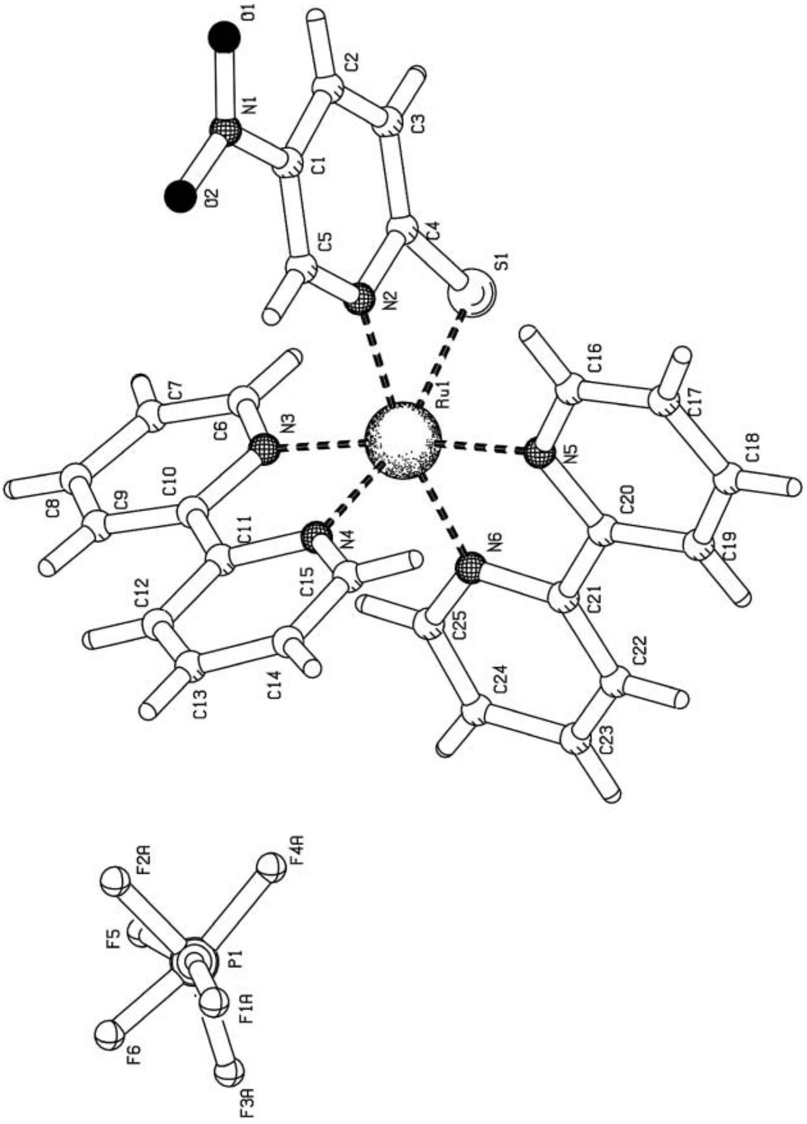

Figure 1. The structure of asymmetric unit of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

were polished with a suspension of alumina (0.05 μm) in acetonitrile. Cyclic voltammograms were run at a sweep rate of 100 mV $\cdot$ s^{-1}. The reported $E_{1/2}$ values were calculated as the semidifference between the E_p corresponding to the cathodic and anodic waves: $E_{1/2} = (E_c + E_a)/2$. The potential values reported in this work are referred versus SCE. Crystallographic data (excluding structure factors) for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication number CCDC-798270. Data copies can be obtained free of charge on application to CCDC, Cambridge, UK [fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

Table 2. Ruthenium compounds with capable ligands forming four-membered ring

N,S-ligands forming 4-membered ring	Bite angle (°)	References
6-Methyl-2-thiouracil	68.6 (6)	[18]
Pyridine-2-thiolato-N,S	67.9 (4)	[15]
1,3,5-Triazine-2,4,6-trithiolato	67.4 (5)	[19]
Pyridine-2-thiolato	68.2 (4)	[19]
Methyl dithiocarbazato	65.9 (5)	[20]
(2-Pyridyl) sulfide-N,S	67.9 (6)	[21]
Pyridine-2-thiolato	68.5 (5)	[22]
4-methylpyrimidine-2-thionato	68.2 (3)	[23]
Salicylaldehyde thiosemicarbazonato	66.8 (7)	[24]
4-methylpyrimidine-2-thionato	67.0 (6)	[25]

Results and Discussion

The S—S bond undergoes a reductive cleavage when 2,2′-dithiobis(5-nitropyridine) is reacted with $Ru(bpy)_2Cl_2$, forming nitropyridylsulfide ligand, which acts as a single negative charge bidentate ligand coordinating to ruthenium vía the thiolate sulfur and the heterocyclic ring N atom resulting in the formation of four-membered chelate ring. A tentative mechanism for the cleavage of the disulfide bond in the reaction of 2,2′-dithiobis(5-nitropyridine) with $Ru(bpy)_2Cl_2$ could be similar to as proposed by Pal et al. [15]. Accordingly, the Ru atom has an irregular pseudo-octahedral N_5S donor set (see Fig. 1), with the most marked deviations from octahedral geometry being associated with the small bite angle [67.2(2)°] of the bidentate units within the four-membered chelate ring. To our knowledge, no examples could be found of nitropyridylsulfide ligands forming complexes with a four-member chelate ring. A search in the Cambridge Structural Database (version 5.31) [16] for ruthenium compound yielded 10 structures with another bidentate N,S-ligand that form a four-membered chelate ring, with bite angle ranging from 65.9(5)–68.6(6)° (see Table 2). This unusual coordination mode may relate to some extent to the central metal ruthenium, possibly due to the fact that the Ru(II) ion late transition metal provided with unfilled outer d orbital may play a key role in the formation of the unusual four-membered chelate ring.

The Ru–N(bpy) bonds are all equivalent at 2.075(5), 2.080(5), 2.072(5), 2.066(5) Å in length apart from N4, which is trans to the sulfur atom and has a significantly longer bond length at 2.084(5) Å. These values are somewhat shorter than the 2.104 Å value in $Ru(NH_3)_6{}^{3+}$ [17], indicating significant π-backbonding between t_{2g} orbital of the Ru(II) and the π^* orbitals of bpy, in agreement with the absorption band at 497 nm. In each of the bpy, the two five-membered rings are approximately coplanar, intersection angles being

Table 3. Angles (°) for $C_{25}H_{19}RuF_6N_6O_2PS$

C3—C2—C1	117.5 (6)	C2—C1—C5	122.7 (7)
C4—C3—C2	119.1 (7)	C3—C4—S1	129.1 (6)
C1—C5—N2	119.0 (6)	C3—C4—N2	121.0 (6)

Table 4. Electronic spectral data (acetone solution, 298 K)

$[Ru(bpy)_2(S\text{-}Py\text{-}NO_2)]^+$	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})
	239 (62), 289 (95), 345 (21), 442(sh) 497 (13)

0.9(3) and 2.4(3)°. The angle between bpy ligands are almost orthogonal [88.6(2)°]. The Ru–S distance [2.457(2) Å] is in agreement with those observed in a related complex with similar donor set [15,18–25]. The C—S distance [1.728(7) Å] is likewise somewhat less than a typical C(aromatic)–S single-bond distance, although not as much, and is actually very similar [1.733(3) Å] to those found in $Ru(bipy)_2(2pyth)]^+$ [22], where 2pyth is pyridine-2-thiol, as a representative example. The nitro group is rotated at 9.0(9)° out of the plane of the pyridine ring. Also noteworthy are the C—C—C, C—C—S, and C—C—N angles at the ipso positions (see Table 3), where the C—C—C angles, in particular, are consistent with the electron-withdrawing properties of nitro substituents [26]. The hexafluorophosphate counter-ion is disordered (see supplementary publication no. CCDC-798270). The crystal packing of (I) is mainly stabilized by dipolar interaction, Coulombic interactions further stabilizing the overall solid-state structure.

Electronic spectra were recorded in acetone solution, (data shown in Table 4). Several intense absorptions and shoulder peaks were observed, which are probably due to allowed metal-to-ligand charge-transfer (MLCT) transitions and overlap. Multiple charge-transfer transitions in such a mixed-ligand complex may arise from the lower-symmetry splitting of the metal level, the presence of different acceptor orbitals, and the mixing of singlet and triplet configurations in the excited state through spin-orbit coupling. The absorption spectra of $[Ru(bpy)_2(S\text{-}Py\text{-}NO_2)]^+$ exhibit intense ligand-centered bands in the UV region

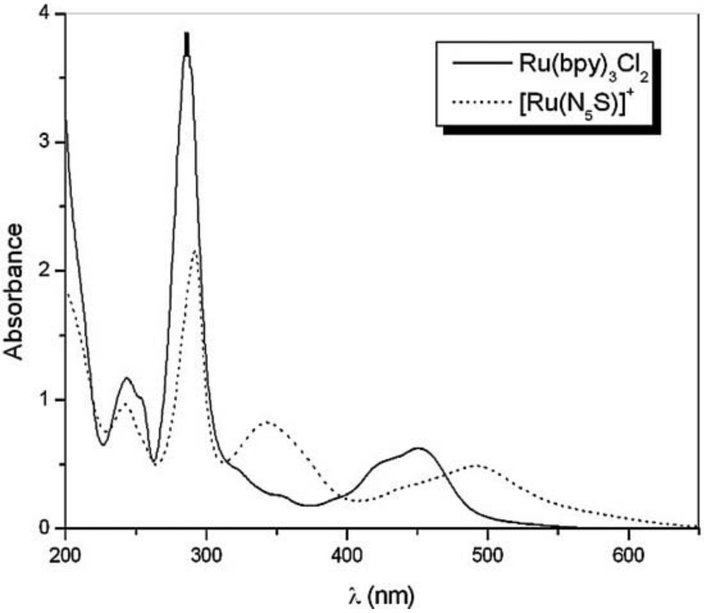

Figure 2. Electronic absorption spectrum of $[Ru(bpy)_2(S\text{-}Py\text{-}NO_2)]PF_6$ in acetonitrile measured at room temperature.

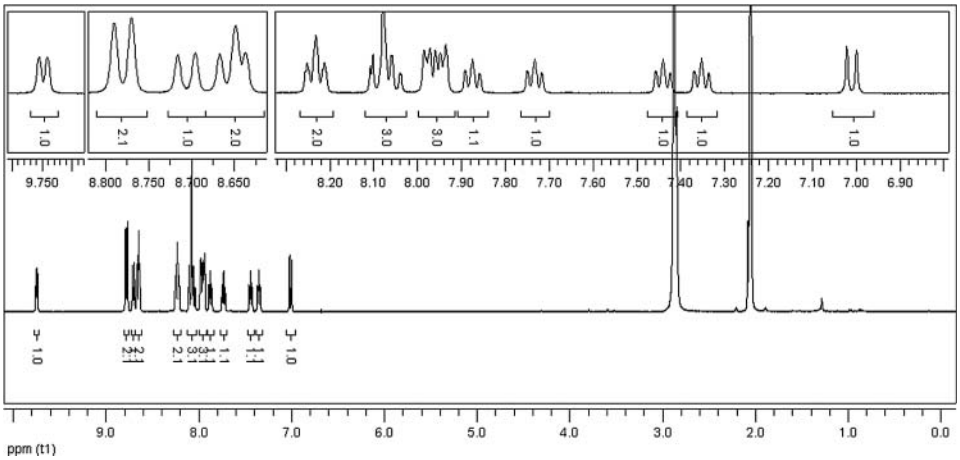

Figure 3. ^{1}H-NMR spectrum of $[Ru(bpy)_2(S\text{-}Py\text{-}NO_2)]PF_6$ measured in acetone-d_6.

and a broad band centered at 497 nm in the visible region assigned to MLCT transitions (see Fig. 2 and Table 4). This bathocromic displacement of the MLCT band in comparison to $[Ru(bpy)_3]^{2+}$ and the metal oxidation potentials become less positive with regard to $[Ru(bpy)_3]^{2+}$ (which has a MLCT band centered at 454 nm) [27] and can be attributable to the electronic influence of the S donor in the thiolate ligand. The electrochemistry analysis showed a quasi-reversible $Ru^{III/II}$ wave, $E^{\circ}(Ru^{III/II}) = 0.78$ V versus Ag/AgCl in 0.1 M $TBAPF_6$ in acetonitrile. The increase of electronic density around the metal center is reflected in the displacement of the MLCT bands towards lower energies in comparison to $[Ru(bpy)_3]^{2+}$ and a shift of the reduction potential in comparison to $[Ru(bpy)_3]^{2+}$ which has a reduction potential $Ru^{III/II}$ at 1.26 V, in CH_3CN, [27].

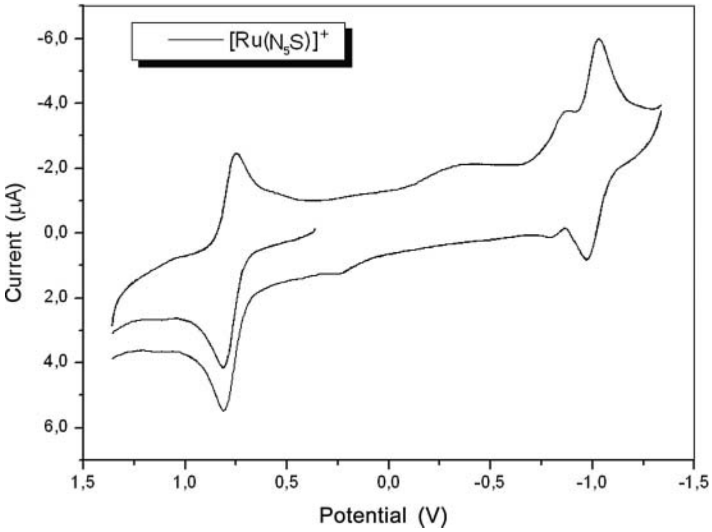

Figure 4. Cyclic voltammogram of $[Ru(bpy)_2(S\text{-}Py\text{-}NO_2)]PF_6$ in acetonitrile.

The ^{1}H-NMR spectra of the monocationic complex in acetone-d_6 show the set of signals as a consequence of the low-symmetric structure. The complex contains 19 nonequivalent pyridyl protons of the five aromatic rings in the region $\delta = 9.8$–7.0 ppm (see Fig. 3). We have assigned the signal at 9.75 ppm at the more deprotection proton H11 of the pyridyl thiolate neighboring at nitro group.

The electrochemical properties of $[Ru(bpy)_2(S\text{-}Py\text{-}NO_2)]^+$ were studied in acetonitrile solution (0.1 M $TBAPF_6$) by cyclic voltammetry. The thiolate ruthenium complex shows a quasi-reversible $Ru^{III/II}$ process (see Fig. 4). The electrochemistry is classified as quasi-reversible because the anodic and cathodic currents were equal and the peak-to-peak separation was greater than 60 mV. The ruthenium (III)–ruthenium(II) couple of the $[RuN_5S]^+$ complex appears at 0.78 V. This effect is similar to others Ru-S thiolate compounds [19], where the substitution of one π-acidic group by a σ-donating thiolate decreases the $Ru^{III/II}$ potential.

Acknowledgments

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