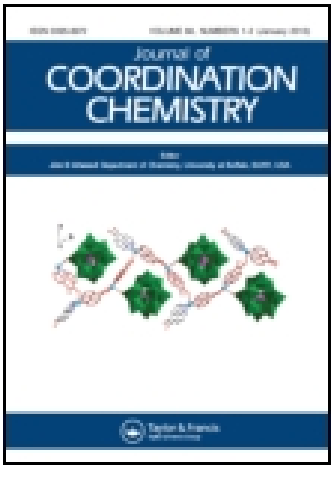

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Thiocyanate linkage isomerism in the isobutyl ester form of the ruthenium dye known as N3

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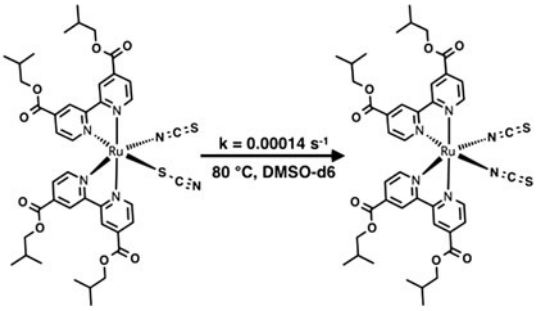

Using a modification of a recently reported convenient synthesis of the isobutyl ester form of the bis (isothiocyanato) ruthenium dye (N3), we report the isolation and spectroscopic characterization of the minor isomer in which one NCS^- is N-bound and the other is S-bound. The synthesis involves the reaction of $Ru(^iBu_2dcbpy)_2Cl_2$, where $^iBu_2dcbpy$ is the diisobutyl ester of 4,4′-dicarboxy-2, 2′-bipyridine, with a source of thiocyanate. The impact of the isocyanate salt, solvent, and temperature on the yield of the linkage isomers is presented. In addition to the two linkage isomers **1** and **2**, the partially substituted chloroisothiocyanato complex **3**, $Ru(^iBu_2dcbpy)_2Cl(NCS)$, was also isolated. Selective removal of the chloride using silver triflate provided a path to $[Ru(^iBu_2dcbpy)_2(pyridine)(NCS)]OTf$, **4**, in high yield. The complexes were characterized by ^1H and ^{13}C NMR, IR, and electronic absorption spectroscopies and mass spectrometry. At 80 °C in DMSO-d_6, the isomerization of **2** to **1** is complete and exhibits first-order kinetics with a rate constant of 0.00014 s^{-1}. Room temperature hydrolysis of the isobutyl ester groups of **2** using $[^nBu_4N]OH$ in acetonitrile produced a mixture of the two linkage isomers.

Keywords: N3; Ruthenium; Isocyanate; Linkage isomerism; Bipyridine

1. Introduction

During the past two decades, dye-sensitized solar cells (DSSC) utilizing titanium dioxide and ruthenium complexes have emerged as promising options for solar energy conversion due to low costs and increasing efficiencies [1, 2]. The diisothiocyanato ruthenium complexes

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known as N3 and N719 (figure 1) produce dye cells with high efficiencies (11.2%), making them the standard for comparison for all new sensitizers [3]. Thiocyanate is an ambidentate ligand that can bind to the metal center through the nitrogen (isothiocyanate) or the sulfur (thiocyanate). In the synthesis of the doubly N-bound diisothiocyanato complex N3 (abbreviated NN), there is also the possibility of producing the NS and SS linkage isomers. While the SS isomer has not been reported, the NS isomer is believed to be present in small amounts (less than 4%) based on observation of a small fraction that was separated from the NN isomer using high-pressure liquid chromatography [4, 5]. Unfortunately, the NS isomer of N3 has not been isolated in pure form. Several reports, however, have noted that when mixtures of the NN and NS isomers are used in DSSCs, their cell efficiencies are reduced relative to devices prepared using only the NN isomer [6].

The study of inorganic linkage isomerism dates back to the early 1900s [7], with the first well-characterized thiocyanate linkage isomers reported in 1963 by Basolo, Burmeister, and Poe. Since the first report, Burmeister has studied how ancillary ligands [8–10], solvents [11, 12], and synthetic conditions [13] have an impact on the binding mode of the thiocyanate. In dithiocyanato complexes, steric and electronic factors of the other ligands

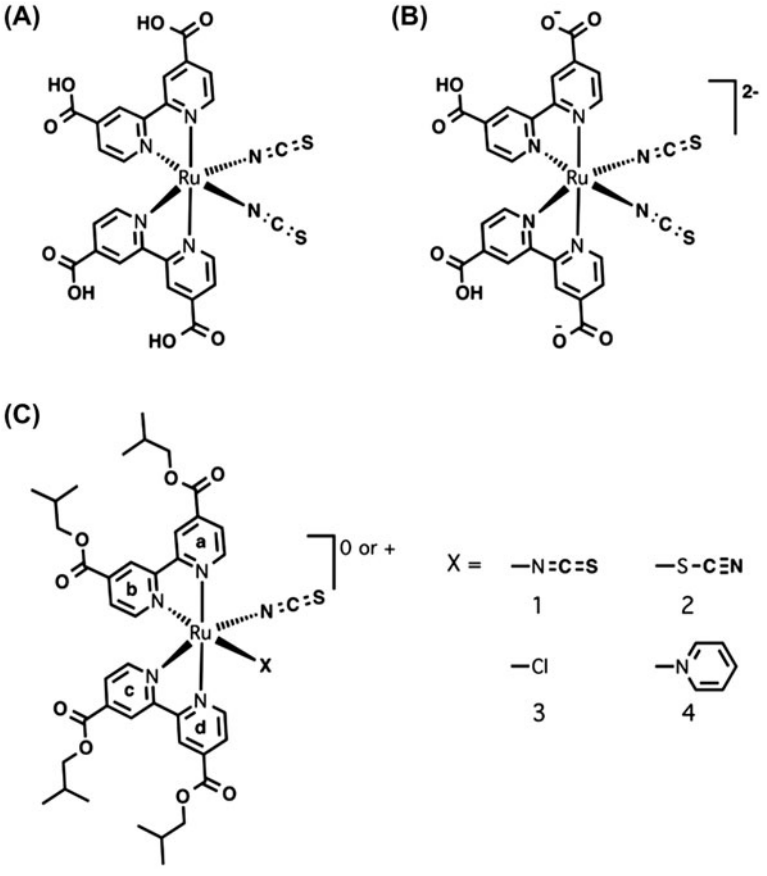

Figure 1. Structure of metal complexes A: N3, B: N719, C: **1–4**.

tend to dictate the bonding mode of the thiocyanate ligand, often leading to either doubly N or S-bonded products [7, 9]. By using bidentate ligands (such as bipyridine), however, mixed bonding of the thiocyanate ligand has been observed in square planar Pd(II) complexes [14, 15].

More recently, thiocyanate linkage isomerism has been observed in several ruthenium complexes. Grätzel and co-workers distinguished thiocyanate linkage isomers by NMR and IR of two anionic ruthenium benzimidazol (bmipy) complexes, $[Ru(bmipy)(dcbpy)SCN]^-$ and $[Ru(ph\text{-}bmipy)SCN]^-$ [16]. Freedman and co-workers were able to synthesize and isolate both linkage isomers of $[Ru(\textit{para}\text{-cymene})(bpy)SCN]^+$ and characterize each by crystallography [17]. The most recent example of thiocyanate linkage isomerism was reported by Brewster *et al.*, in which both linkage isomers of $[Ru(terpyridine)(^tBubpy)SCN]^+$ were isolated and characterized by NMR, IR, and crystallography [18]. While linkage isomerism has been well studied in mono-thiocyanate ruthenium complexes, a mixed isomer complex that exhibits both an N-bound and S-bound thiocyanate has yet to be isolated in pure form.

We have adapted the procedure described by Rawling *et al.* [19] that makes use of isobutyl ester groups at the 4- and 4′-bipyridine positions to synthesize and isolate the doubly N-bound, the N- and S-bound, and a mono-substituted NCS^- ester analog to N3. The isobutyl esters make purification on a silica gel column straightforward. By modifying the synthesis conditions, particularly the choice of solvent and thiocyanate salt, it is possible to control the amount of each isomer formed.

2. Experimental

2.1. *Materials*

Ruthenium(III) chloride trihydrate ($RuCl_3 \cdot 3H_2O$) was purchased from Pressure Chemical Company and used as received. Spectroscopic grade methanol, 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine, isobutanol, ammonium thiocyanate, and silver thiocyanate were purchased from Sigma Aldrich and used as received. Deuterated solvents were used as received. The following solvents were dried by the listed reagents and distilled prior to use: acetonitrile (CaH_2), ethanol (Mg), and tetrahydrofuran (sodium and benzophenone). Solvents were deoxygenated prior to use and all procedures were performed using standard Schlenk techniques. 4,4′-Dicarboxylic acid-bipyridine (dcbpy) and bis(2-methylpropyl)-2,2′-bipyridine-4,4′-dicarboxylate ($^iBu_2$dcbpy) were synthesized according to literature methods [19, 20].

2.2. *Methods*

NMR spectra were taken on a Varian Inova 300 or 500 MHz spectrometer and chemical shifts were referenced to the residual solvent peak. Mass spectral data were taken on a Bruker BioTOF II operating in the ESI-TOF mode. Electronic absorption spectra were collected on an Ocean Optics DH-2000-BAL spectrometer using quartz cuvettes with a 3 mm path length. The IR spectra of ruthenium complexes were recorded on a Nicolet MAGNA-IR 560 spectrometer. Cyclic voltammograms were obtained on a BAS-100B electrochemical analyzer using methods previously described [21]. All solutions were prepared in acetonitrile or dimethylformamide with 0.1 M tetra-n-butylammonium

hexafluorophosphate, $[N(C_4H_9)_4][PF_6]$, as the supporting electrolyte and degassed with argon. Potentials were referenced to a Ag/AgCl electrode and are reported *versus* NHE. The elemental analysis was performed by Columbia Analytical Services, Tucson, AZ.

2.3. *Synthesis of Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$*

$RuCl_3$–$3H_2O$ (1.0 g, 4 mM) was added under nitrogen to a solution of lithium chloride (0.920 g, 2.17 mM) in ethylene glycol : water (20 mL, 4 : 1) at 110 °C. After 15 min, ^{i}Bu$_2$dcbpy (2.96 g, 8.3 mM) was added under nitrogen. After an additional 15 min, glucose (0.15 g, 8 mM) was added, and then after an additional 15 min, ascorbic acid (0.373 g, 2 mM) was added and the reaction was maintained at 110 °C for 30 min. The reaction was quenched with the addition of 10 mL of a saturated NaCl solution and cooled to 0 °C for 60 min. The reaction mixture was then filtered, washed with brine, and then toluene : ether : acetone (70 : 20 : 5). Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$ was purified using a neutral alumina column with methylene chloride:ethyl acetate (50 : 50) as eluant to yield 3.5 g (82% yield) of a green solid. ^{1}H NMR (300 MHz; CD_2Cl_2): δ 10.34 (dd, J = 6.0, 0.5 Hz, 2H), 8.89 (d, J = 1.2 Hz, 2H), 8.72 (d, J = 1.3 Hz, 2H), 8.21 (dd, J = 5.9, 1.7 Hz, 2H), 7.75 (dd, J = 6.0, 0.5 Hz, 2H), 7.53 (dd, J = 6.0, 1.8 Hz, 2H), 4.29 (d, J = 6.6 Hz, 4H), 4.14 (d, J = 6.6 Hz, 4H), 2.29–2.15 (m, 2H), 2.13–2.02 (m, 2H), 1.11 (d, J = 6.7 Hz, 12H), 1.00 (d, J = 6.7 Hz, 2H).

2.4. *Synthesis of Ru(^{i}Bu$_2$dcbpy)$_2$(NCS)(X) (1–3)*

Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$ (0.20 g, 0.23 mM), either ammonium thiocyanate or silver thiocyanate (9.2 mM), and 50 mL of either tetrahydrofuran or ethanol were refluxed under nitrogen for between 3 and 32 h. Reaction times in tetrahydrofuran were 32 and 3–6 h in ethanol. Table 1 lists specific times for solvent and counterion combinations. The reaction was stopped at the disappearance of Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$ as monitored by TLC, and excess solvent was evaporated. Complexes **1** (Ru(^{i}Bu$_2$dcbpy)$_2$(NCS)$_2$), **2** (Ru(^{i}Bu$_2$dcbpy)$_2$(NCS)(SCN)), and **3** (Ru(^{i}Bu$_2$dcbpy)$_2$Cl(NCS)) were separated on a silica gel column using methylene chloride : ethyl acetate (95 : 5) as eluant. The order of elution was excess thiocyanate salt, then **1**, followed by **2**, and finally **3**. All ruthenium complexes appeared as dark purple bands on the column and were isolated as dark purple solids. Table 1 lists the yields for the individual reactions.

1: ^{1}H NMR (500 MHz; CD_2Cl_2): δ 9.71 (dd, 6ad, J = 5.8 (5ad), 0.6 (3ad) Hz, 2H), 8.91 (dd, 3ad, J = 1.8 (6ad), 0.6 (5ad) Hz, 2H), 8.75 (dd, 3bc, J = 1.8 (6bc), 0.7 (5 cd) Hz, 2H), 8.30 (dd, 5ad, J = 5.8 (6ad), 1.7 (3ad) Hz, 2H), 7.65–7.60 (m, 5bc, 6bc, 4H), 4.31 (d, J = 6.6 Hz, 4H), 4.16 (d, J = 6.6 Hz, 4H), 2.27–2.16 (m, 2H), 2.13–2.02 (m, 2H), 1.12 (d, J = 6.7 Hz, 12H), 0.99 (d, J = 6.7 Hz, 12H). HR-ESIMS *m/z* expected [M + Na^+] = 953.1916, *m/z* observed [M + Na^+] = 953.1921. ν_{NCS} (KBr) = 2099 cm^{-1}.

Table 1. Reaction conditions and yields for the ruthenium complexes.

Solvent	NCS^- reagent	Reaction time (h)	Isolated **1**	Isolated **2**	Isolated **3**
THF	NH_4NCS	32	0.076 g 30%	0.012 g 4%	0.086 g 32%
THF	AgNCS	32	0.151 g 72%	–	–
EtOH	NH_4NCS	3	0.156 g 73%	0.033 g 15%	–
EtOH	AgNCS	6	0.160 g 77%	0.007 g 3%	–

2: ^{1}H NMR (500 MHz; CD_2Cl_2): δ 10.08 (dd, 6a, J = 5.9 (5a), 0.6 (3a) Hz, 1H), 9.60 (dd, 6d, J = 5.9 (5d), 0.6 (3d) Hz, 1H), 8.90 (overlapping dd, 3ad, J = 1.7 (6ad), 0.7 (5ad) Hz, 2H), 8.76 (overlapping dd, 3bc, J = 1.5 (6bc), 0.7 (5bc) Hz, 2H), 8.26 (overlapping dd, 5ad, J = 5.9 (6ad), 1.7 (3ad) Hz, 2H), 7.69–7.63 (m, 5bc, 6bc, 4H), 4.30 (dd, J = 6.6, 2.5 Hz, 4H), 4.15 (dd, J = 11.7, 6.7 Hz, 4H), 2.30–2.15 (m, 2H), 2.15–2.01 (m, 2H), 1.12 (d, J = 6.7 Hz, 12H), 1.00 (dd, J = 6.7, 2.9 Hz, 12H). HR-ESIMS *m/z* expected $[M + Na^+]$ = 953.1916, *m/z* observed $[M + Na^+]$ = 953.1921. ν_{NCS} (KBr) = 2092 cm^{-1}.

3: ^{1}H NMR (500 MHz; CD_2Cl_2): δ 10.29 (dd, 6a, J = 5.9 (5a), 0.6 (3a) Hz, 1H), 9.73 (dd, 6d, J = 5.9 (5d), 0.6 (3d) Hz, 1H), 8.88 (overlapping dd, 3ad, J = 1.5 (6ad), 0.6 (5ad) Hz, 2H), 8.72 (overlapping dd, 3bc, J = 1.7 (6ad), 0.6 (5ad) Hz, 2H), 8.30 (dd, 5a, J = 5.9 (6a), 1.7 (3a) Hz, 1H), 8.28 (dd, 5d, J = 5.8 (6d), 1.7 (3d) Hz, 1H), 7.74 (dd, 6b, J = 6.0 (5b), 0.6 (3b) Hz, 1H), 7.64 (dd, 6c, J = 6.0 (5c), 0.6 (3c) Hz, 1H), 7.55 (dd, 5b, J = 6.0 (6b), 1.7 (3b) Hz, 1H), 7.53 (dd, 5c, J = 5.9 (6c), 1.7 (3c) Hz, 1H), 4.30 (dd, J = 6.6, 2.6 Hz, 4H), 4.15 (dd, J = 6.6, 3.1 Hz, 4H), 2.29–2.16 (m, 2H), 2.15–2.01 (m, 2H), 1.11 (dd, J = 6.7, 1.1 Hz, 12H), 0.99 (dd, J = 6.7, 3.5 Hz, 12H). HR-ESIMS *m/z* expected $[M + Na^+]$ = 930.1853, *m/z* observed $[M + Na^+]$ = 930.1855. ν_{NCS} (KBr) = 2099 cm^{-1}. Anal. Calcd C, 54.27; H, 5.33; N, 7.27. Found: C, 53.99; H, 5.45; N, 7.61.

2.5. *Synthesis of [Ru(^{i}Bu$_2$dcbpy)$_2$(NCS)(pyridine)]OTf (4)*

A solution of **3** (0.060 g, 0.065 mM) and silver trifluoromethanesulfonate (AgOTf, 0.051 g, 0.20 mM) in acetonitrile (15 mL) was heated at 60 °C for 12 h giving the mono-solvento species (confirmed through ESI MS). Pyridine (1.0 mL, 12 mM) was injected and the reaction refluxed for an additional 12 h. The reaction was cooled to room temperature, excess solvent was evaporated, and **4** was purified on a silica gel column with methylene chloride : acetonitrile (90 : 10) as eluent to yield 0.060 g (80%) of a dark red solid. ^{1}H NMR (300 MHz; CD_2Cl_2): δ 9.70 (d, J = 5.9 Hz, 1H), 9.01 (d, J = 1.4 Hz, 1H), 8.87 (dd, J = 5.6, 1.4 Hz, 2H), 8.79 (d, J = 1.5 Hz, 1H), 8.59 (d, J = 5.9 Hz, 1H), 8.33 (dd, J = 5.8, 1.7 Hz, 2H), 8.21 (dd, J = 5.9, 1.7 Hz, 2H), 8.05 (d, J = 5.9 Hz, 1H), 7.90 (dd, J = 5.9, 1.7 Hz, 1H), 7.83 (tt, J = 7.6, 1.4 Hz, 1H), 7.73 (dd, J = 5.9, 1.7 Hz, 1H), 7.66 (d, J = 5.9 Hz, 1H), 7.39 (t, J = 6.9 Hz, 2H), 4.29 (dd, J = 6.6, 3.9 Hz, 4H), 4.18 (dd, J = 6.7, 4.7 Hz, 4H), 2.15 (ddtd, J = 29.9, 13.4, 6.7, 3.2 Hz, 4H), 1.09 (dd, J = 6.7, 1.3 Hz, 12H), 1.00 (dd, J = 6.7, 4.2 Hz, 12H). HR-ESIMS *m/z* expected $[M^+]$ = 951.0940, *m/z* observed $[M^+]$ = 950.9939. ν_{NCS} (KBr) = 2090 cm^{-1}.

2.6. *Kinetic determination of the isomerization of 2 to 1*

Complex **2** (0.0005 g, 5.4×10^{-4} mM) was dissolved in 500 μL of DMSO-d_6 and placed in a Varian Inova 300 MHz spectrometer preheated to 80(1) °C. The sample was allowed to equilibrate for 5 min at which point an initial spectrum was acquired. From that point, a spectrum consisting of 32 scans was taken every 5 min for 900 min. Upon completion, the sample was cooled to room temperature, allowed to equilibrate for an hour, and a final spectrum was acquired.

2.7. *Ester hydrolysis of 1 and 2*

Complex **1** or **2** (0.015 g, 0.016 mM) was dissolved in acetonitrile (15 mL), and 0.16 mL of a 1 M tetra-n-butylammonium hydroxide (0.16 mM) solution was added. The resulting

solution was protected from light and stirred at room temperature. The reaction was stopped after 40 min at the disappearance of the starting ester as monitored by TLC. The solvent was removed at room temperature and the resulting residue was dissolved in 5 mL of water, and the pH adjusted to 3.5 using 0.1 M nitric acid, at which point the mixture became cloudy. The suspension was stored in the freezer overnight and the resulting precipitate was filtered and washed with pH 3.5 water.

Hydrolysis product of 1: ^{1}H NMR (300 MHz; CD_3OD): δ 9.60 (d, J = 5.8 Hz, 2H), 9.08 (d, J = 1.0 Hz, 2H), 8.92 (d, J = 1.1 Hz, 2H), 8.33 (dd, J = 5.8, 1.6 Hz, 2H), 7.80 (d, J = 5.9 Hz, 2H), 7.66 (dd, J = 5.9, 1.7 Hz, 2H).

Hydrolysis product of 2: ^{1}H NMR (300 MHz; CD_3OD): δ 9.92 (d, J = 5.8 Hz, 1H), 9.60 (d, J = 5.8 Hz, 1H), 9.53 (d, J = 5.8 Hz, 1H), 9.07 (s, 2H), 8.92 (d, J = 7.4 Hz, 2H), 8.30 (q, J = 5.8 Hz, 2H), 7.88–7.75 (m, 2H), 7.75–7.60 (m, 2H).

3. Results and discussion

3.1. *Synthesis*

N3-like ruthenium complexes with isobutyl ester groups in place of the acid functionality were synthesized from a two-step reaction based on the report of Rawling *et al.* [19]. Isobutyl protecting groups allowed the use of column chromatography to purify the products. To synthesize the intermediate *cis*-Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$, the glucose reaction [22] was used as opposed to the widely used DMF method [23, 24]. As glucose and ascorbic acid are the reducing agents, the reaction can be done in a range of aqueous organic solvent mixtures opening up the possibility to use a wider range of substituted bipyridines.

In the chloride substitution step to produce the thiocyanato complexes, one to three unique ruthenium complexes were isolated and characterized depending on the NCS^- salt and solvent (table 1). On the basis of the evidence discussed below, the three complexes were identified as the two linkage isomers of the NCS^- ligands (doubly N-bound **1** and N- and S-bound **2**) and a chlorothiocyanate complex **3** (figure 1). When a polar solvent like ethanol was used, the reaction times were significantly decreased compared to the less polar tetrahydrofuran (THF). Using ethanol and ammonium thiocyanate, appreciable amounts of the linkage isomer **2** can be isolated. However, using the more polar ethanol, the mono-substituted complex **3** is not observed in quantities sufficient for isolation. In either solvent when AgNCS was used, no **3** was observed and the yield of **1** increased.

The isolation of the mono-substitued thiocyanate complex **3** provides a synthetic path to more structurally diverse ruthenium complexes. To gage its potential use as a reactive intermediate, **3** was treated with silver triflate in acetonitrile to form the solvento complex. Addition of pyridine to the mixture gave isocyanato pyridine complex **4**. Further investigation of **3** as a useful synthon may be anticipated.

3.2. *Spectroscopic characterization*

Rawling *et al.* fully characterized the isobutyl ester derivative of N3 and established that it could be hydrolyzed to N3 or the doubly deprotonated complex N719 [19]. Purification using a silica gel column led to elution of **1** followed by smaller fractions attributed to **2** then **3** (if present). Our samples of **1**, isolated in 72% yield based on Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$,

were spectroscopically identical to those reported by Rawling *et al.* [19]. The assignment of the second band as **2** was based on the high-resolution mass spectrum, which was identical to that observed for **1**. The following spectroscopic results confirm this assignment.

Figure 2 shows the ^{1}H NMR spectra of Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$, **1**, **2**, and **3**. The spectra of **2** and **3** are more complex than the spectrum of Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$ and **1** due to the loss of the C_2 symmetry axis. The assignments listed in the experimental section for **1** are from the literature [19] and those for Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$, **2**, and **3** are based on chemical shift similarities to **1**. The letters identifying the pyridyl rings are shown in figure 1(c), and the numbers correspond to the standard nomenclature. Of particular note are the differences associated with 6a and 6d. In **1**, these are equivalent and appear as a doublet of doublets at 9.71 ppm with total integration intensity of 2H. The lowered symmetry of **2** further splits these into two doublets of doublets at 10.08 and 9.60 ppm. In this case, one of the hydrogens is above an N-bound isothiocyanate and one is above an S-bound thiocyanate. Based on chemical shift similarity to the 9.71 ppm resonance in **1**, the 9.60 ppm resonance of **2** is assigned to 6d. Based on related compounds, the downfield shift of the resonance for 6a is expected [16]. The assignments for the analogous protons 6a and 6d of **3** are based on the close correlation with the related protons on Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$ and **1**.

In addition to the resonances due to the aromatic carbons, the ^{13}C NMR spectra in the range from 115 to 145 ppm (Supplementary material, see online supplemental material at http://dx.doi.org/10.1080/00958972.2013.87998) of **1–4** exhibit resonances that can be assigned to the NCS$^-$ ligands. When the NCS$^-$ ligand is bound to a metal through sulfur, the ^{13}C resonance appears upfield (120–125 ppm) compared to the N-bound NCS$^-$ carbon (135–140 ppm) [4, 5, 25]. The ^{13}C NMR spectrum of **2** shows a peak at 120.6 ppm, which we assign to the carbon of an S-bound thiocyanate. The N-bound NCS$^-$ resonance of **2** is obscured by overlap with one of the resonances of the aromatic carbons. The ^{13}C NMR spectra of **1**, **3,** and **4** do not show peaks around 120 ppm, but they do exhibit resonances at 136.5, 136.1, and 137.4 ppm, respectively, which are assigned to the N-bound isothiocyanate carbons.

Figure 3 shows the infrared spectra of the NCS$^-$ region for **1–3**. Both **1** and **3** exhibit sharp CN stretches at 2099 cm^{-1}, while **2** has a broader CN stretch centered at 2092 cm^{-1}. The C–N stretch is expected to appear at slightly higher frequency for an S-bound NCS$^-$ compared to the N-bound NCS$^-$ [17, 18]. Even though **2** has both an N- and S-bound NCS$^-$, it is not possible to resolve the individual peaks [18]. The NCS$^-$ vibration for **4** appears at 2090 cm^{-1}.

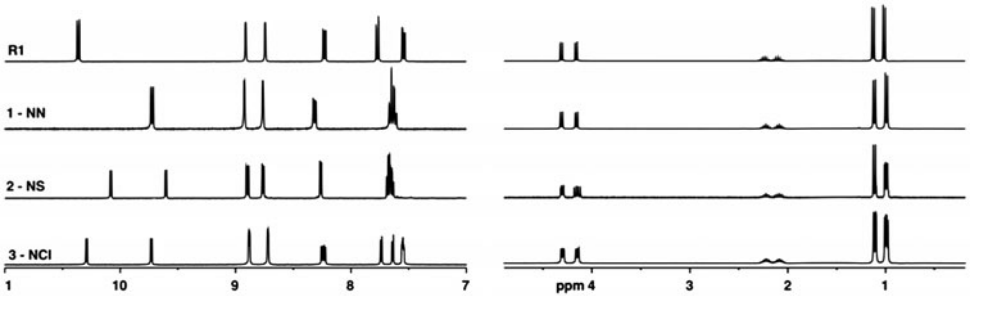

Figure 2. Five hundred megahertz ^{1}H NMR spectra of Ru(^{i}Bu$_2$dcbpy)$_2$Cl$_2$ (labeled **R1**), and **1–3** in CD_2Cl_2. Note: The intensity of the aromatic region is scaled upward by a factor of 7 compared to the intensity of the alkyl region to better show the peaks. The singlet at 1.5 ppm is due to water from the solvent.

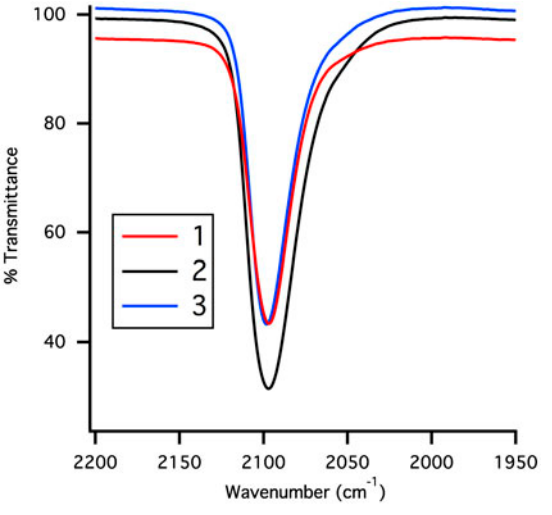

Figure 3. IR spectra (KBr) of **1–3** in the C–N stretching region.

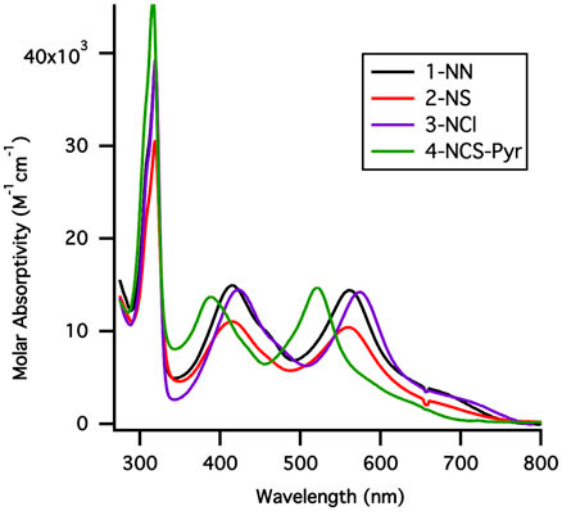

Figure 4. Molar absorptivity of the metal complexes in CH_2Cl_2.

Figure 4 shows the electronic absorption spectra of **1–4** dissolved in CH_2Cl_2 and table 2 lists specific data. Each complex has an intense absorption around 315 nm corresponding to the bipyridine π–π* transition. In the visible region, all complexes have two metal-to-ligand charge-transfer (MLCT) absorptions between 400 and 600 nm. Complex **4** has a similar absorption spectrum, although it is shifted to higher energy by about 40 nm as a result of its cationic nature. While the energies of the MLCT transitions are almost identical for **1–3**, the molar extinction coefficients for **2** are ~30% smaller than those of **1**. For comparison, N719 has absorptions at 535 and 395 nm with molar absorptivities of 14,700 and 14,300 M^{-1} cm^{-1},

Table 2. Spectroscopic and electrochemical data for the metal complexes.

Sample	λ_{abs} (nm) (ε) (10^3 M^{-1} cm^{-1})			E^0Ru^{III}/Ru^{II} (V/NHE)	$E^0{}_{Red}RuL_3{}^{2+}/RuL_3{}^{1+}$ (V/NHE)	$E^0{}_{Red}RuL_3{}^{1+}/RuL_3{}^{0}$ (V/NHE)
1	318 (38.7)	415 (15.0)	565 (14.40)	0.90	−1.05	−1.28
2	315 (30.6)	413 (11.0)	560 (10.2)	0.86	−1.05	−1.26
3	318 (39.3)	422 (14.5)	574 (14.2)	0.77	−1.11	−1.39
4	316 (46.1)	388 (13.7)	520 (14.7)	0.85	−1.06	−1.41

respectively, which are similar to the values reported for **1**. In their study of a related ruthenium complex, Kohle *et al.* observed [16] that DSSC prepared with a mixture of the N-bound and S-bound NCS^- ligand exhibited reduced incident photon to current efficiencies compared to cells having only the N-bound NCS^-. The difference in extinction coefficients observed for the two linkage isomers of the N3 isobutyl esters suggests a possible explanation for this interesting observation.

Cyclic voltammetry data, shown in table 2, were used to analyze the redox processes in the complexes. In their as-synthesized forms, **1–4** show quasireversible Ru^{II}/Ru^{III} oxidations between 0.77 and 0.90 V/NHE and two quasireversible bipyridine reductions. The first reduction is between −1.05 and −1.11 V and the second reduction is between −1.26 and −1.41 V. Compounds **1** and **2** have very similar electrochemical properties, with **1** being harder to oxidize by 0.04 V.

3.3. *NS to NN isomerization*

Deuterated methanol or dichloromethane solutions of **2** were stable at room temperature for at least 12 days in laboratory light. At 80 °C in DMSO-d_6, **2** isomerized completely to **1** as monitored by ^1H NMR spectroscopy [figure 5(a)]. The process was complete in 200 min and the spectrum remained constant for an additional 700 min. The complete disappearance of the ^1H NMR resonances from **2** at 9.85 and 9.45 ppm (the entire spectrum is available in the Supplementary material) indicates that if the equilibrium between the two isomers exists, the value of K_{eq} for the reaction **2** ⇌ **1** would be approximately equal to or greater than 10^2. In the study of a thiocyanate terpyridine-bipyridine ruthenium complex, Brewster *et al.* measured the equilibrium between the S- and N-bound isomers. At 25 °C in DMSO-d_6, K_{eq} was 67 favoring the N-bound NCS^- ligand [18].

Figure 5(b) shows a graph of the natural logarithm of the integrated signal intensity of the 9.85 ppm resonance *versus* time. Linear behavior over 3.5 half-lives is consistent with an irreversible first-order process having a rate constant of 0.00014 s^{-1}. In the absence of more extensive kinetic studies (unfortunately precluded due to the small quantity of isolated **2** available), it is not possible to differentiate among several possible isomerization mechanisms – complete NCS^- dissociation, solvent assisted dissociation, or a process in which the NCS^- isomerizes within the primary coordination sphere of the ruthenium. With the aid of computational studies, Brewster *et al.* concluded [18] that the mechanism for their mono-thiocyanato complex involved complete dissociation of NCS^-, possibly with the aid of the DMSO solvent. The current results are consistent with this interpretation.

3.4. *Ester hydrolysis forms N3*

The ability to cleave the isobutyl esters is an important aspect of the N3 synthesis using the method of McDonagh *et al.* [19]. Hydrolyses of the ester groups of **1** and **2** at room

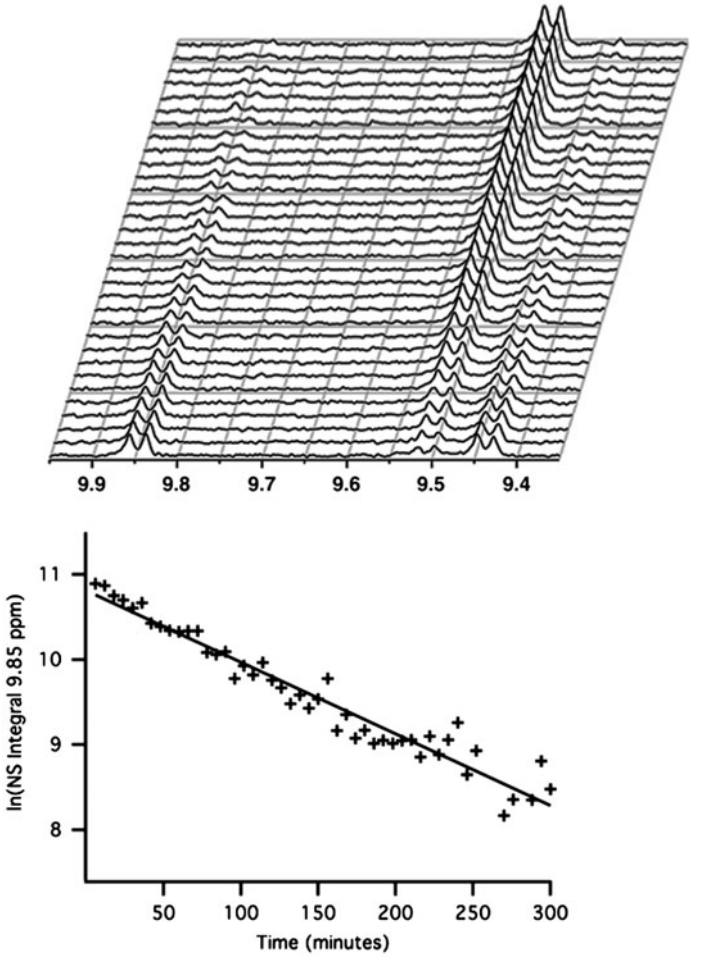

Figure 5. Top: ^{1}H NMR spectrum in DMSO-d_6 of the downfield peaks during kinetic isomerization of **2** at 80 °C over the first 200 min. The initial spectrum is on the bottom. Bottom: First-order kinetic plot of ln[**2**] *vs.* time over 3.6 half-lives, where [**2**] is determined by the integration of the peak at 9.85 ppm. The rate constant was found to be 0.00014 s^{-1}.

temperature were successful using acetonitrile solutions of [$^{n}Bu_4N$][OH], followed by acidification. Based on a comparison of our ^{1}H NMR spectra to the results of Grätzel and co-workers (who obtained their isomer mixture from the reaction of $Ru(dcbyp)_2Cl_2$ with NCS^{-}) [4], the hydrolysis product of **1** (figure 6) is mainly the doubly N-bound form of N3 (doublet at 9.65 ppm) with 4% of the N-, S-bound isomer of N3 (doublets at 9.95 and 9.53 ppm). The spectrum of hydrolyzed **2** confirms the formation of both the NS and NN isomer of N3. Integration indicates that 40% of the product isomerized. Clearly, isomerization is faster for **2** (or its hydrolyzed products) in the presence of [$^{n}Bu_4N$][OH] and CH_3CN. Determining which one of these factors is responsible for the acceleration of isomerization compared to the esters (**1** and **2**) in DMSO is beyond the scope of this report. While we cannot unambiguously state that we have measured the value of K_{eq} for the linkage isomerization,

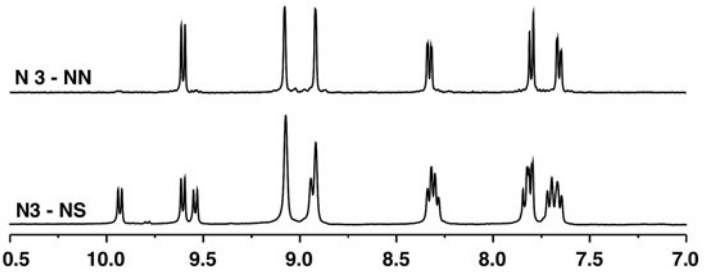

Figure 6. ^{1}H NMR spectra in the aromatic region in CD_3OD of the products resulting from the hydrolysis of **1** (upper) and **2** (lower).

the maximum value of 10^2 is consistent with the work of Brewster *et al.* on a related mono-thiocyanato ruthenium complex [18].

4. Conclusion

While there have been numerous reports of the linkage isomers of the well-known compound, *cis*-diisothiocyanatobis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II) (N3), this report includes the first extensive spectroscopic characterization of the minor isomer, **2**, in which the carboxylic acid groups have been converted into isobutyl esters. Compound **2** has one N-bound and one S-bound thiocyanate and was best prepared from the corresponding dichlorocomplex using ammonium thiocyanate in ethanol. At 80 °C, it quantitatively isomerized to the more stable, major isomer bearing two N-bound NCS^- ligands, **1**, in 200 min and was partially isomerized during the room temperature hydrolysis of the isobutyl esters using $[^nBu_4N][OH]$.

Supplementary material

Parent ion mass spectra of **1** and **2**, ^{13}C NMR spectra from 115 to 145 ppm and cyclic voltammetry results are available as Supplementary material.

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