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Preparation, Separation, and Characterization of Ruthenium(II) Thiocyanate Linkage Isomers

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The reaction of [(*p*-cym)Ru(bpy)Cl]$^+$ (*p*-cym = η^6-*p*-cymene; bpy = 2,2′-bipyridine) with SCN$^-$ gives a mixture of the linkage isomers [(*p*-cym)Ru(bpy)(SCN)]$^+$ and [(*p*-cym)Ru(bpy)(NCS)]$^+$. The linkage isomers were efficiently separated by column chromatography on $Hg(NO_3)_2$-coated Al_2O_3. Both isomers were fully characterized by elemental analysis, ^{1}H NMR and IR spectroscopy, and X-ray crystallography. The equilibrium constant for the conversion of the S-bound to the N-bound isomer was determined to be 0.29(4) in methanol-d_4 and 0.74(7) in acetone-d_6, respectively, at 50 °C. Kinetic data for the linkage isomerization reaction are also reported.

Ruthenium complexes of a variety of ambidentate ligands have been of significant interest for a number of years. Linkage isomers of ruthenium complexes containing ligands such as 2-mercaptopyridine,[1] sulfoxides,[2−4] nitrosyl,[5] α-cyanocarbanions,[6] alizarin,[7,8] carboxamides,[9,10] sulfur dioxide,[11] 1,2-hydroxyanthoquinonato,[12] unsymmetrical diimines,[13,14] nitrite,[15−18] nitrosyl,[19,20] urea,[21] acetone,[22] and 1,5-dithiacyclooctane 1-oxide[23] have all been studied. Surprisingly, little work has been reported on ruthenium thiocyanate linkage isomers, in spite of thiocyanate being a prototypical ambidentate ligand and the importance of ruthenium thiocyanate complexes as sensitizers for nanocrystalline TiO_2 solar cells.[24−29] There are three studies where ruthenium thiocyanate linkage isomers have been isolated,[30−32] but the separation methods are tedious, no X-ray structures are reported, and no kinetic or thermodynamic data for linkage isomerization reactions are given. These data are important in designing sensitizers for nanocrystalline TiO_2 solar cells because the linkage isomers can be used to tune the spectral properties of the sensitizers.[30,33−35] Herein we report the synthesis, a novel separation technique, and crystal structures for [(*p*-cym)Ru(bpy)(SCN)]PF_6 and [(*p*-cym)Ru(bpy)(NCS)]PF_6. We also report kinetic and thermodynamic data for linkage isomerization.

The reaction of [(*p*-cym)Ru(bpy)Cl]PF_6[36−39] with excess SCN$^-$ in refluxing methanol gives a mixture of two compounds (designated as **1** and **2**) as determined by ^{1}H

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NMR. The ratio of compounds **1** to **2** changes from 1:1 (2 h reflux) to 3:2 (4 h reflux). Longer reaction times do not affect the ratio. Attempts at separating the compounds on silica, alumina, and ion-exchange resins were unsuccessful. Separation was achieved on neutral alumina coated with $Hg(NO_3)_2$ (ca. 5% by weight). Eluting the mixture of **1** and **2** through a column of Hg/Al_2O_3 with acetonitrile gave a clear separation between a faster-moving dark yellow/orange band and a slower-moving light-yellow band. An orange product (**1**) was isolated from the faster-moving band, and a light-yellow product (**2**) was isolated from the trailing band. The two compounds were characterized by ^1H NMR and IR spectroscopy, elemental analysis, and X-ray crystallography.[40] As will be shown, **1** and **2** are [(*p*-cym)Ru(bpy)(SCN)]PF_6 and [(*p*-cym)Ru(bpy)(NCS)]PF_6, respectively. The Hg/Al_2O_3 column presumably discriminates between the linkage isomers based on differing affinities for the $Hg^{2+}$of the nonligated end of the thiocyanate. As expected, the N-bound isomer has a greater retention time because of the stronger affinity of the "soft" nonligated sulfur for the "soft" Hg^{2+}.[41] We are currently investigating whether this technique can be used to separate other thiocyanate linkage isomer mixtures and whether other, less toxic, metal cations will also be effective.

Elemental analyses of both compounds are identical within experimental error and consistent with the formula of [(*p*-cym)Ru(bpy)(thiocyanate)]PF_6. The ^1H NMR spectra for **1** and **2**are nearly identical except that the peaks for the *p*-cymene aromatic protons and the bipyridine $H^{2,2'}$ signals are shifted slightly downfield in **2** relative to **1**. The IR spectra of **1** and **2** show strong peaks at 2109 and 2099 cm^{-1}, respectively, consistent with the ν_{SC-N} bands of the thiocyanate ligand. Typically, the frequency of the CN stretch is higher in the S-bound isomer, but that is not universally true.[42,43]

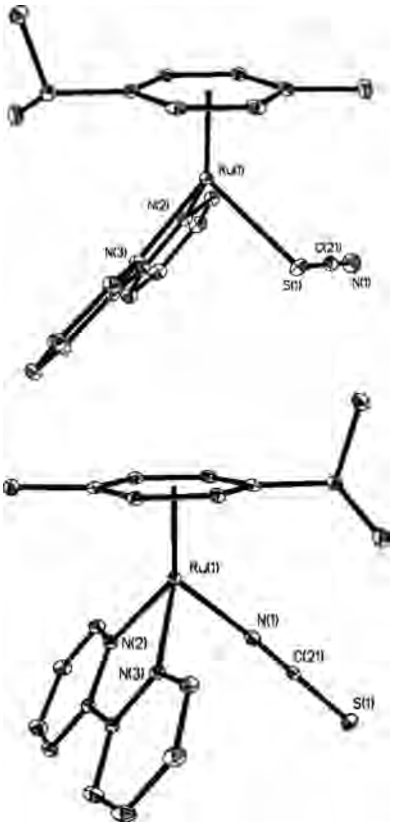

Figure 1. Molecular structures of **1** (top) and **2** (bottom). Selected bond distances (Å) and angles (deg). **1**: Ru−S(1) 2.4193(4), Ru−N(2) 2.080(1), Ru−N(3) 2.072(1), S(1)−C(21) 1.677(2), C(21)−N(1) 1.156(2), N(1)−C(21)−S(1) 178.0(2), C(21)−S(1)−Ru 104.35(6), S(1)−Ru−N(2) 87.58(3), S(1)−Ru−N(3) 84.61(3), N(2)−Ru−N(3) 77.34(5). **2**: Ru−N(1) 2.048(2), Ru−N(2) 2.084(1), Ru−N(3) 2.085(1), N(1)−C(21) 1.156(2), C(21)−S(1) 1.637(2), N(1)−C(21)−S(1) 178.8(2), C(21)−N(1)−Ru(1) 175.9(1), N(1)−Ru−N(2) 82.86(6), N(1)−Ru−N(3) 85.07(6), N(2)−Ru−N(3) 77.04(5).

X-ray structure determinations were carried out on both **1** and **2** (Figure 1), showing that **1** is the S-bound isomer and **2** is the N-bound isomer of $[(p\text{-cym})Ru(bpy)(thiocyanate)]^+$. For **1**, the Ru−S−C(21) angle is 104.35(6)°, similar to values reported in the literature for other S-bound ruthenium thiocyanate complexes.[42,44] For **2**, the thiocyanate binds close to linear, with the Ru−N(1)−C(21) angle being 175.9(1)°, which is at the upper end of the range observed for M−NCS complexes.[45] Interestingly, the Ru−NCS distance in **2** [2.048(2) Å] is very similar to the Ru−NCS distances in $[Ru(bpy)_2(NCS)_2]$ [2.055(5) Å][46] and [Ru(4,4′-CO_2Et-2,2′-

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(40) [(p-cym)Ru(bpy)(SCN)]PF_6 (**1**): ^1H NMR (300 MHz, acetone-d_6) 9.447 (d, bpy-$H^{6,6'}$, J = 5.76 Hz, J_2 = 1.38 Hz, J_3 = 0.83 Hz), 8.694 (d, bpy-$H^{3,3'}$, J = 7.71 Hz), 8.346 (apparent td, bpy-$H^{5,5'}$, J_1 = 7.71 Hz, J_2 = 1.38 Hz), 7.835 (ddd, bpy-$H^{4,4'}$, J_1 = 7.71 Hz, J_2 = 5.78 Hz, J_3 = 1.38 Hz), 6.328 and 6.077 (d, $CH_3C_6H_4CH(CH_3)_2$, J = 6.60 Hz), 2.806 (hept, $CH_3C_6H_4CH(CH_3)_2$, J = 6.88 Hz), 2.34 (s, $CH_3C_6H_4CH(CH_3)_2$), 1.097 (d, $CH_3C_6H_4CH(CH_3)_2$, J = 6.88 Hz); IR (ATR) ν_{SC-N} 2109 cm^{-1}. Calcd for [(p-cym)Ru(bpy)(SCN)]PF_6: C, 42.42; H, 3.68; N, 7.30. Found: C, 42.56, H, 3.88, N, 7.13. [(p-cym)Ru(bpy)(NCS)]PF_6 (**2**): ^1H NMR (300 MHz, acetone-d_6) 9.696 (d, bpy-$H^{6,6'}$, J = 5.50 Hz), 8.686 (d, bpy-$H^{3,3'}$, J= 7.98 Hz), 8.410 (apparent td, bpy-$H^{5,5'}$, J_1 = 7.98 Hz, J_2 = 1.38 Hz), 7.903 (ddd, bpy-$H^{4,4'}$, J_1 = 7.43 Hz, J_2 = 5.78 Hz, J_3 = 1.38 Hz), 6.429 and 6.217 (d, $CH_3C_6H_4CH(CH_3)_2$, J = 6.60 Hz), 2.790 (hept, $CH_3C_6H_4CH(CH_3)_2$, J = 6.88 Hz), 2.291 (s, $CH_3C_6H_4CH(CH_3)_2$), 1.120 (d, $CH_3C_6H_4CH(CH_3)_2$, J = 6.88 Hz); IR (ATR) ν_{SC-N} 2099 cm^{-1}. Calcd for [(*p*-cym)Ru(bpy)(NCS)]PF_6: C, 42.42; H, 3.68; N, 7.30. Found: C, 42.31; H, 3.73; N, 7.07.

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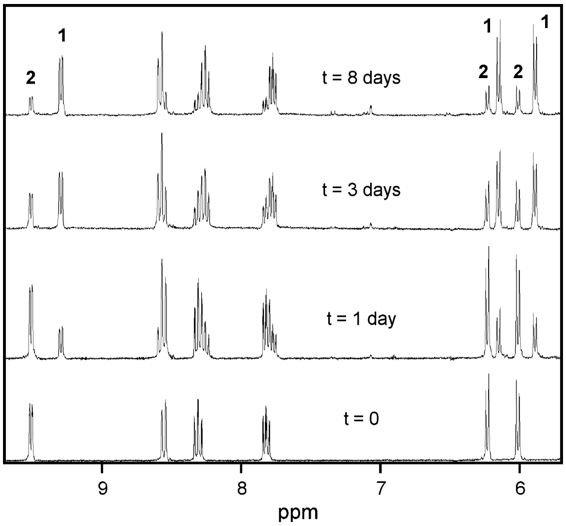

Figure 2. ^{1}H NMR spectra of **2** over 8 days in methanol-d_4 at 50 °C.

bpy)$_2$(NCS)$_2$] [2.07(2) Å],[47] which are models for [Ru(4,4′-CO$_2$H-2,2′-bpy)$_2$(NCS)$_2$], one of the most widely used nanocrystalline TiO$_2$ sensitizer.

With both linkage isomers fully characterized, we could study the linkage isomerization reaction. The reactions of **1** and **2** were followed in methanol-d_4 and acetone-d_6 at 50 °C. Figure 2 shows the NMR changes observed over 1 week at 50 °C in methanol-d_4 starting with **2**. As the ^{1}H NMR spectra illustrate, **2** cleanly converts into a mixture of **1** and **2** over 8 days. Similar results were observed starting with **1**.

The equilibrium constant for reaction I can then be determined by integrating the two most downfield peaks (the H$^{6,6'}$ bpy protons for the two isomers) in the final spectrum.

$$[(p\text{-cym})\mathrm{Ru(bpy)(SCN)}]^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{\mathbf{1}}{[(p\text{-cym})\mathrm{Ru(bpy)(NCS)}]^+} \qquad \text{(I)}$$

K was determined to be 0.30(3) by following the reaction of **1** and 0.27(3) starting with **2** at 50 °C in methanol-d_4. These values are identical within experimental error. In acetone-d_6, *K* was determined to be 0.74(7) at 50 °C starting with **1**. The solvent dependence of *K* is consistent with previous reports that protic solvents stabilize the S-bound isomer.[48,49]

By assuming that the reaction follows a reversible, first-order mechanism, k_f and k_r can also be determined. The integrated rate law for a reversible first-order reaction is shown in eq 1:[50]

$$\ln[f_{(\mathbf{2})t} - f_{(\mathbf{2})e}] = -(k_f + k_r)t + \ln[f_{(\mathbf{2})0} - f_{(\mathbf{2})e}] \qquad (1)$$

where $f_{(\mathbf{2})0}$, $f_{(\mathbf{2})e}$, and $f_{(\mathbf{2})t}$ refer to the initial, equilibrium, and time = *t* fractions of [(*p*-cym)Ru(bpy)(NCS)]$^+$ present. The values of $f_{(\mathbf{2})t}$ and $f_{(\mathbf{2})e}$ can be determined from integration of the H$^{6,6'}$ ^{1}H NMR peaks for **1** and **2** as a function of time. The linearity of the plot of $\ln[f_{(\mathbf{2})t} - f_{(\mathbf{2})e}]$ vs time (Figure 3) is consistent with the reversible first-order rate law. Similar data were collected for the reaction of **1** at 50 °C in methanol-d_4 and acetone-d_6. Using the experimentally determined equilibrium constants, both k_f and k_r can be determined. Starting with **2**, $k_f = 1.5(2) \times 10^{-6}$ s^{-1} and $k_r = 5.3(5) \times 10^{-6}$ s^{-1}. Starting with **1**, $k_f = 1.6(2) \times 10^{-6}$ and $k_r = 5.4(5) \times 10^{-6}$ s^{-1}. Excellent agreement is observed between the rate constants determined separately for each isomer. In acetone-d_6, the rate constants were measured at 50 °C starting with **1**, giving $k_f = 1.8(2) \times 10^{-6}$ s^{-1} and $k_r = 2.4(2) \times 10^{-6}$ s^{-1}. To our knowledge, these are the first kinetic measurements of a ruthenium(II) thiocyanate linkage isomerization reaction. These data illustrate that ruthenium(II) thiocyanate complexes can be expected to equilibrate between the linkage isomers over extended periods of time, which is of importance in the use of these types of compounds as solar cell sensitizers.

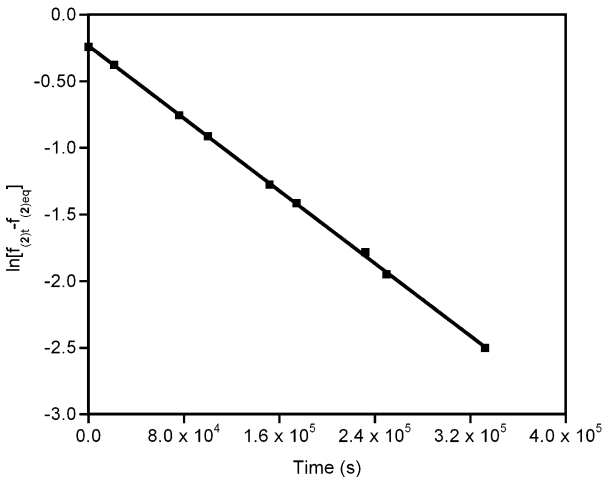

Figure 3. Plot of $\ln[f_{(\mathbf{2})t} - f_{(\mathbf{2})eq}]$ vs time for the reaction of **2** in methanol at 50 °C. Fitting parameters: slope -6.80×10^{-6} s^{-1}, intercept = 0.23.

We have demonstrated that it is possible to easily prepare and separate ruthenium thiocyanate linkage isomers and that, for this system, the linkage isomerization reaction is reversible. It is fortuitous that this should be the case for these particular ruthenium thiocyanate linkage isomers because families of [(arene)Ru(L$_2$)Cl] complexes can be readily prepared with wide variations in the arene and L$_2$ ligands. It should be possible to tune the kinetic and thermodynamic parameters for the linkage isomerization reaction by systematic variations of these ligands.

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Supporting Information Available: X-ray crystallographic files in CIF format, experimental details for synthetic procedures, kinetic measurements, and X-ray determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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