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Ruthenium(II) Charge-Transfer Sensitizers Containing 4,4′-Dicarboxy-2,2′-bipyridine. Synthesis, Properties, and Bonding Mode of Coordinated Thio- and Selenocyanates

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The synthesis and properties of several complexes of Ru(II) containing 4,4′-dicarboxy-2,2′-bipyridine (dcbpyH_2), 2,6-bis(1-methylbenzimidazol-2-yl)pyridine (bmipy), or 2,6-bis(1-methylbenzimidazol-2-yl)-4-phenylpyridine (ph-bmipy), and monodentate ligands ($X^- = Cl^-, I^-, NCS^-, NCSe^-, CN^-$) are reported. The introduction of the ambident ligands $X^- = NCS^-$, $NCSe^-$, and CN^- into the coordination sphere of $[Ru(bmipy)(dcbpy)I]^-$ and *cis*-Ru(dcbpyH_2)$_2$$Cl_2$ has been studied *in situ* via ^1H and ^{13}C NMR spectroscopy using ^{13}C-enriched ligands X^-. Introduction of thiocyanate and selenocyanate initially yields the two possible linkage isomers in comparable amounts; prolonged reaction time converts the S-bound isomer and the Se-bound isomer to the N-bound isomers. The isoselenocyanate complex decomposes rapidly, yielding the cyano complex under loss of Se. The N-bound isothiocyanato complex K[Ru(bmipy)(dcbpy)(NCS)] was found to be an efficient sensitizer for nanocrystalline TiO_2; the incident monochromatic photon-to-current efficiency (IPCE) is nearly quantitative at 520 nm. Introduction of a phenyl group in the 4-position of the 2,6-bis(1-methylbenzimidazol-2-yl)pyridine ligand gives a red-shifted absorption maximum for the corresponding phenylated K[Ru(ph-bmipy)(dcbpy)(NCS)] complex with an increased molar absorption coefficient for the MLCT maximum at 508 nm. At longer wavelengths above 620 nm, phenyl substitution does not enhance the absorption coefficients of the complex. Compared to that of K[Ru(bmipy)(dcbpy)(NCS)], the performance of the phenylated complex is reduced in a solar cell due to lower IPCE values. The visible spectra of the halide complexes K[Ru(bmipy)(dcbpy)X] ($X^- = Cl^-, I^-$) show enhanced red response, but the complexes exhibit strongly reduced overall IPCE values. A comparison of the complexes to *cis*-Ru(dcbpyH_2)$_2$(NCS)$_2$ is presented. Possible strategies for the design of more efficient sensitizers are discussed.

Introduction

There has been an increasing interest in Ru(II) complexes containing 4,4′-dicarboxy-2,2′-bipyridine as an attaching group for the sensitization of nanocrystalline TiO_2.[1−11] Because of the carboxyl group, there are differences in synthesis and chemical properties between ruthenium(II) 4,4′-dicarboxy-2,2′-bipyridines and the analogous ruthenium(II) 2,2′-bipyridine complexes. It is difficult to obtain crystalline products of ruthenium(II) 4,4′-dicarboxy-2,2′-bipyridine complexes. Usually, the complexes are isolated by adding an acid to the aqueous solution of the complex anions in order to precipitate the complex at the isoelectric point. Another method is precipitation of the complex from the reaction mixture by adding a less polar solvent such as diethyl ether. NMR data or spectra are not reported.

The thiocyanate ligand in *cis*-Ru^{II}(dcbpyH_2)$_2$(NCS)$_2$ was found to be N-bound, determined by infrared spectroscopy.[8] In general, a variety of physical methods have been utilized to determine the bonding mode of coordinated thiocyanate in transition metal complexes.[12,13] Thio- and selenocyanate ligands in Ru complexes are known in the N-, S-, and Se-bound modes and as bridging ligands for dimer complexes.[14−30]

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An important goal in recent publications on Ru sensitizers has been the structural variation of the complexes in order to obtain sensitizers showing increased absorption coefficients for enhanced light harvesting. Several attempts have been made. Low π^*-level ligands[31] such as 5,5′-dicarboxy-2,2′-bipyridine (π^*-level tuning) resulted in a red-shifted spectrum and increased light absorption at longer wavelengths.[10] Unfortunately, the use of low π^*-level ligands was accompanied by strongly reduced injection yields in the conduction band of TiO_2. Polynuclear complexes exhibiting an antenna effect have been employed in order to increase absorption coefficients.[4,5,11] However, the antenna does not enhance the light response efficiently at longer wavelengths, where absorption coefficients and the IPCE of Ru charge-transfer sensitizers decrease strongly. Moreover, these bulky sensitizers require more space on the TiO_2 surface and penetrate less easily in the small cavities of the nanocrystalline TiO_2 than the mononuclear complexes. Hence, for polynuclear complexes, the increased absorption coefficients in solution do not necessarily lead to enhanced light absorption on the TiO_2 electrode because of the reduced surface concentration of the bulkier sensitizer molecules on the nanoporous TiO_2.

Phenyl groups introduced in a suitable position of a polypyridyl ligand in a Ru complex increase the absorption coefficients of the metal to ligand charge transfer (MLCT) maxima.[32−39] Visible spectra of Ru sensitizers containing the 4,4′-bis(*p*-carboxyphenyl)-2,2′-bipyridine show this effect.[37] The introduction of phenyl groups between the peripheral carboxyl group and bipyridine caused a red shift and increased absorption coefficients of the MLCT maxima. However, the sensitization of TiO_2 was found to be inefficient. In general, Ru polypyridyl sensitizers already show suitable absorption coefficients in the wavelength domain between 400 and 600 nm. In this work, we focus our attention on longer wavelengths, where insufficient light absorption of Ru sensitizers limits its performance in a solar cell.

Due to the high mass of ruthenium, its complexes exhibit significant spin−orbit coupling.[40] We attempted to enhance the red response by using the heavy iodide ligand in order to increase the spin−orbit coupling constant of the complex and the absorption coefficient of the spin-forbidden ^{3}MLCT transition.

Experimental Section

Materials. Reagents and solvents were purchased from Fluka AG and used without further purification, unless otherwise stated. ^{13}C-enriched potassium cyanide (92% ^{13}C) and ^{13}C-enriched potassium thiocyanate (99% ^{13}C) are products from The British Oxygen Co. and Glaser AG, respectively. *cis*-$Ru(dcbpyH_2)_2(NCS)_2$, nanocrystalline TiO_2 electrodes (prepared according to a sol−gel procedure described previously[7]), and electrolyte (34% *N*-methyloxazolidin-2-one, 32% acetonitrile, 34% diethyl ketone, 0.5 M 1-hexyl-3-methylimidazolium iodide, and 40 mM iodine) for solar cell measurements were obtained from Solaronix SA. ^{13}C-enriched potassium selenocyanate was synthesized according to a published procedure by using ^{13}C-enriched potassium cyanide and selenium.[41] The crude product was dissolved in methanol, the mixture was filtered, the filtrate was evaporated to dryness, and the residue was used as such. In the ^{13}C NMR spectrum of the colorless crystalline product, cyanide was not detectable. Sephadex LH-20 (Pharmacia) was used for the chromatographic purification of the Ru complexes. The ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine was obtained in two steps according to a published procedure.[42,43] 4,4′-Dicarboxy-2,2′-bipyridine[44] containing 4-carboxy-4′-methylbipyridine was purified as follows. The crude product containing 8% of the monomethyl species was dissolved in sulfuric acid (96%) and precipitated by diluting the acid carefully with water to a concentration of 20%. The product was filtered off and washed with water. Repeating this procedure three times yielded a pure product. The 4,4′-dicarboxy-2,2′-bipyridine was dissolved in diluted base, precipitated by using an excess of 20% HCl, filtered off, and dried under vaccum. *cis*-$Ru(dcbpyH_2)_2Cl_2$ was synthesized by a procedure similar to that described earlier[8] and purified on a Sephadex LH-20 column using methanol.

Synthesis of the Ligand and Complexes. (a) $Ru(bmipy)Cl_3$. A 500 mg (1.47 mmol) sample of 2,6-bis(1-methylbenzimidazol-2-yl)-pyridine was dissolved in 200 mL of ethanol. To the stirred solution of the ligand was added an equimolar solution of ruthenium(III) chloride (352 mg, 42.34% Ru) in 30 mL of ethanol, and the mixture was refluxed in the dark under argon for 1 h. After cooling at 25 °C, the precipitate was filtered off. Washing with ethanol and drying of the product in vacuo yielded a brown product. Yield: 92%. Anal. Calcd for $Ru(bmipy)Cl_3{\cdot}2.5H_2O$: C, 42.62; H, 3.75; N, 11.83. Found: C, 42.80; H, 3.14; N, 11.83.

(b) $Ru(ph\text{-}bmipy)Cl_3$. The complex was obtained in the same way as described above by using 500 mg (1.20 mmol) of 2,6-bis(1-methylbenzimidazol-2-yl)-4-phenylpyridine instead of 2,6-bis(1-methylbenzimidazol-2-yl)pyridine and 287 mg (1.20 mmol) of ruthenium(III) chloride. Anal. Calcd for $Ru(ph\text{-}bmipy)Cl_3{\cdot}H_2O$: C, 50.60; H, 3.62; N, 10.93. Found: C, 50.63; H, 3.76; N, 10.69.

(c) Ru(bmipy)(dcbpyH)Cl. To 925 mg (1.56 mmol) of $Ru(bmipy)Cl_3{\cdot}2.5H_2O$ and 400 mg (1.64 mmol) of 4,4′-dicarboxy-2,2′-bipyridine in 250 mL of DMF was added 3 mL of triethylamine. The mixture was refluxed for 3 h in the dark under argon. During this time, the color of the solution turned violet and a solid precipitated. The solution was allowed to cool at room temperature. The precipitate was filtered off, washed with DMF and a small amount of ethanol, and dried. Yield: 83%. Anal. Calcd for $Ru(bmipy)(dcbpyH)Cl{\cdot}3H_2O$: C, 48.95; H, 3.86; N, 12.11. Found: C, 48.45; H, 4.07; N, 12.60.

(d) Ru(ph-bmipy)(dcbpyH)Cl. The complex was synthesized by reacting 400 mg (1.64 mmol) of 4,4′-dicarboxy-2,2′-bipyridine with 1.0 g (1.56 mmol) of $Ru(ph\text{-}bmipy)Cl_3{\cdot}H_2O$ as described above. Anal. Calcd for $Ru(ph\text{-}bmipy)(dcbpyH)Cl{\cdot}H_2O$: C, 57.60; H, 3.72; N, 12.06; Cl, 4.36; Ru, 12.43. Found: C, 56.74; H, 4.29; N, 12.08; Cl, 4.23; Ru, 12.28.

(e) Na[Ru(bmipy)(dcbpy)I]. A 320 mg (0.41 mmol) sample of $Ru(bmipy)(dcbpyH)Cl{\cdot}3H_2O$ was dissolved in 150 mL of methanol and 1 mL of triethylamine. A 1.8 g (120 mmol) amount of sodium iodide was added, and the mixture was refluxed for 3 h in the dark under argon. After evaporation to dryness, the solid was redissolved in a minimum amount of methanol, and the solution was added to the top of a LH-20 column (3 × 20 cm). Chromatography was carried out under reduced light by first using a solution of methanol containing 40 g/L sodium iodide. When the front of the product band passed half-way through the column, elution was continued with pure methanol.

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The product band was collected and the solvent evaporated to a volume of 30−40 mL. Diethyl ether was slowly added until the product precipitated. The solid was filtered off, washed with a small amount of a 2:1 mixture of diethyl ether/methanol, and dried in vacuo. Yield: 79%. The product contained about 3% sodium iodide. Anal. Calcd for Na[Ru(bmipy)(dcbpy)I]·$3H_2O$, containing 3.3% sodium iodide: C, 43.24; H, 3.19; N, 10.70; I, 16.61. Found: C, 43.38; H, 3.01; N, 10.65; I, 16.75.

(f) Na[Ru(ph-bmipy)(dcbpy)I]. The complex was synthesized and purified in the same way as described above by using 320 mg (0.39 mmol) of Na[Ru^{II}(ph-bmipy)(dcbpyH)Cl]·H_2O as starting material. The material contained between 3 and 5% sodium iodide. Elemental analysis gave a C:N ratio of 4.71; calcd 4.77.

(g) K[Ru(bmipy)(dcbpy)(NCS)]. A 200 mg (0.22 mmol) sample of Na[Ru(bmipy)(dcbpy)I] was dissolved in 25 mL of methanol, and 1.0 g (10.3 mmol) of potassium thiocyanate was added. The mixture was refluxed for 6 h in the dark under argon, and the solution was allowed to cool at room temperature. The N-bound K[Ru(bmipy)(dcbpy)(NCS)] complex crystallized slowly from the reaction mixture. The dark needles were filtered off, washed with a small amount of cold methanol, and dried in air. The product contained small amounts of S-bound isomer. Anal. Calcd for K[Ru(bmipy)(dcbpy)(NCS)]·$4H_2O$: C, 47.94; H, 3.67; N, 13.15; K, 4.59; S, 3.76. Found: C, 47.93; H, 3.63; N, 12.73; K, 4.89; S, 3.95.

The mother liquor was evaporated and the resulting solid redissolved in 10 mL of water. The solution was acidified dropwise with 5% HCl to precipitate the product at the isoelectric point. The precipitated solid contained a mixture of S-bound and N-bound complex. It was washed with water and dried in vacuo. Working in this manner yielded a product containing about 80% N-bound and 20% S-bound complex. Anal. Calcd for Ru(bmipy)(dcbpyH)(NCS)·$2.5H_2O$: C, 51.90; N, 14.24; H, 3.72; S, 4.07. Found: C, 52.10; N, 14.20; H, 3.35; S, 3.97.

(h) K[Ru(ph-bmipy)(dcbpy)(NCS)]. The complex was synthesized as described above by using Na[Ru(ph-bmipy)(dcbpy)I] as starting material. Dark crystals of the N-bound complex were obtained; S-bound complex was not detectable by ^1H NMR spectroscopy. The mother liquor was enriched with S-bound complex. Anal. Calcd for K[Ru(ph-bmipy)(dcbpy)(NCS)]·H_2O: C, 54.97; N, 12.82; H, 3.34; S, 3.67. Found: C, 55.11; N, 12.95; H, 3.43; S, 3.45.

(i) 2,6-Bis(1-methylbenzimidazol-2-yl)-4-phenylpyridine. The ligand was synthesized in six steps according to the preparation of a similar ligand reported in the literature.[45] The product was recrystallized from methanol. Mp: 251 °C. $C_{27}H_{21}N_5$. Anal. Calcd: C, 78.05; H, 5.09; N, 16.86 Found: C, 78.00; H, 5.08; N, 16.93. ^{13}C NMR data ($CDCl_3$): a 15-line spectrum with peaks at 150.46, 150.27, 150.01, 142.52, 137.12, 136.93, 129.53, 129.00, 127.22, 123.53, 122.92, 122.77, 120.10, 109.85, 32.48 ppm. ^1H NMR data ($CDCl_3$) (multiplicity, integral): 8.67 (s, 2), 7.93−7.83 (m, 4), 7.58−7.28 (m, 9), 4.26 ppm (s, 6).

Methods. ^1H- and proton-decoupled ^{13}C NMR spectra were recorded with a Bruker AC-P 200 spectrometer. Chemical shifts are given in ppm, relative to TMS. The substitution reaction of Na[Ru(bmipy)(dcbpy)I] and *cis*-Ru($dcbpyH_2)_2Cl_2$ with nucleophilic agents (potassium salts of CN^-, NCS^-, and $NCSe^-$) were followed by reacting a few milligrams of the precursor complex with about 8 mg of the potassium salt of the pseudohalide in methanol-d_4 solution in an NMR tube. The reaction was carried out by heating the NMR tube in an oil bath in the dark; the bath temperature was between 50 and 75 °C. NMR spectra were recorded after cooling the NMR tube to room temperature. Ligand exchange is slow at room temperature; the substitution reaction can be stopped when desired. Repeated heating, cooling, and recording of the NMR spectra resulted in the presented figures. Exact conditions (reaction time, temperature, and concentration) are reported under Results and Discussion. All thermal reactions and measurements were carried out under exclusion of light. Pulse repetition time for the ^{13}C NMR measurements was 3 s.

Infrared spectra were obtained from KBr pellets with a Perkin-Elmer Paragon 1000 spectrophotometer. Electronic spectra in the UV−vis range were measured in methanol solution with a Hewlett Packard 8452A diode array spectrophotometer at room temperature using quartz cells of 1 cm path length. Cyclic voltammetry was performed with an EG&G 273A potentiostat in electrochemical cells with a volume of 5 mL. A three-electrode setup was composed of a glassy carbon working electrode (surface 0.07 cm^2, embedded in Teflon), a glassy carbon counter electrode separated from the working electrode compartment by a bridge containing the same electrolyte as the test solution, and a silver/silver chloride wire as a quasi reference electrode. The quasi reference electrode was calibrated with a Ag/AgCl/saturated KCl electrode. If not stated otherwise, all potentials were measured in 1-methyl-2-pyrrolidone (Fluka) dried over molecular sieves. In all experiments, 0.1 M tetrabutylammonium trifluoromethanesulfonate (Fluka) was used as electrolyte. Scan rates were between 100 and 300 mV/s. Action spectra were measured according to a procedure described elsewhere.[8] The IPCE values reported are overall yields which are uncorrected for losses due to light absorption and reflection by the conducting glass support. Coating of electrodes was carried out by soaking the TiO_2 films in a solution of the Ru complex in ethanol until the layer was intensely colored. After adsorption of the complexes, the layers were treated for a few seconds with acetic acid in order to control the degree of protonation on the TiO_2 surface. The treatment with acetic acid resulted in increased IPCE values and a good reproducibility of the measurements.

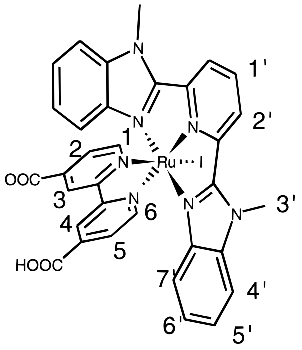

Figure 1. Structure of Ru(bmipy)(dcbpyH)I.

Results and Discussion

The nucleophilic substitution of coordinated iodide in $[Ru(bmipy)(dcbpy)I]^-$ by $X^- = CN^-, NCS^-$, and $NCSe^-$ and of the chloride in *cis*-Ru($dcbpyH_2)_2Cl_2$ by NCS^- was studied in methanol-d_4 by ^1H and ^{13}C NMR spectroscopy using ^{13}C-enriched ligands X^-:

$$[Ru(bmipy)(dcbpy)I]^- + X^- \rightarrow [Ru(bmipy)(dcbpy)X]^- + I^- \quad (1)$$

$$cis\text{-}Ru(dcbpyH_2)_2Cl_2 + 2NCS^- \rightarrow cis\text{-}Ru(dcbpyH_2)_2(NCS)_2 + 2Cl^- \quad (2)$$

Na[Ru(bmipy)(dcbpy)I] was a suitable precursor for these studies. Chromatography yielded a product that was pure by NMR criteria. It showed a sufficient solubility in methanol-d_4, which was found to be a useful solvent for studying the substitution reactions. Figure 1 shows the structure of the Ru(bmipy)(dcbpyH)I complex.

Spectra a−d of Figure 2 monitor portions of the ^1H NMR spectra recorded during the reaction of the iodo complex with cyanide. Only the signal of the 6H doublet of the complex is shown. The chemical shift of the 6H doublet is strongly influenced when the iodide ligand is replaced by other nucleophiles; other signals superpose more or less. Spectrum a of Figure 2 corresponds to a solution of Na[Ru(bmipy)(dcbpy)I] and ^{13}C-enriched potassium cyanide in methanol-d_4. When the mixture was heated, the iodo complex disappeared quickly and two new doublets appeared. In the ^{13}C NMR spectrum, apart

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Table 1. ^{1}H NMR Data (in Methanol-d_4)

complex	1′	2′	3′	4′	5′	6′	7′	*o*	*m*/*p*
Li[Ru(bmipy)(dcbpy)Cl]	8.26 t	8.74 d	4.54 s	7.71 d	7.42 ddd	7.10 ddd	6.28 d		
Na[Ru(bmipy)(dcbpy)I]	8.27 t	8.75 d	4.53 s	7.70 d	7.42 ddd	7.10 ddd	6.33 d		
K[Ru(bmipy)(dcbpy)(NCS)]	8.34 t	8.78 d	4.57 s	7.74 d	7.45 ddd	7.14 ddd	6.25 d		
Na[Ru(ph-bmipy)(dcbpy)I]		8.84 s	4.62 s	7.70−7.80 m	7.43 ddd	7.13 ddd	6.36 d	8.23 d	7.70−7.80 m
K[Ru(ph-bmipy)(dcbpy)(NCS)]		8.87 s	4.64 s	7.75 d	7.46 ddd	7.15 ddd	6.28 d	8.26 d	7.70−7.80 m

complex	1	2	3	4	5	6
Li[Ru(bmipy)(dcbpy)Cl]	7.50 d	7.35 dd	8.78 d	9.26 d	8.50 dd	10.72 d
Na[Ru(bmipy)(dcbpy)I]	7.35−7.40 m	7.35−7.40 m	8.74 d	9.23 d	8.41 dd	11.27 d
K[Ru(bmipy)(dcbpy)(NCS)]	7.47 d	7.39 dd	8.80 d	9.26 d	8.53 dd	10.23 d
Na[Ru(ph-bmipy)(dcbpy)I]	7.45 m	7.40−7.45 m	8.76 d	9.24 d	8.42 dd	11.29 d
K[Ru(ph-bmipy)(dcbpy)(NCS)]	7.56 d	7.41 dd	8.87 d	9.27 d	8.55 dd	10.25 d

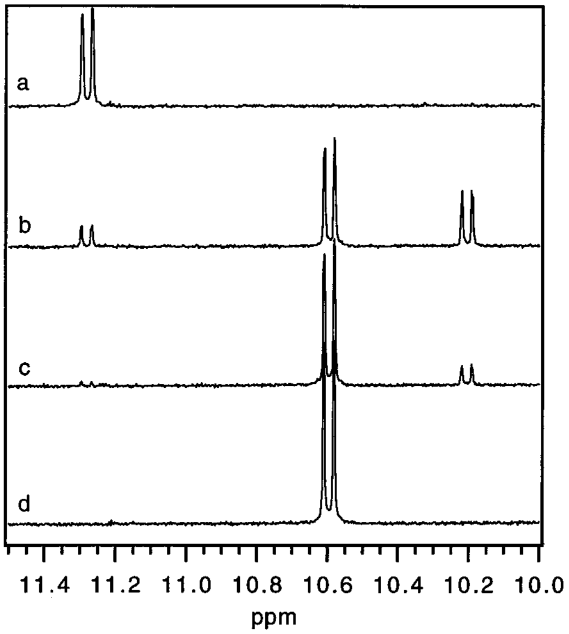

Figure 2. Substitution reaction of 3 mg of Na[Ru(bmipy)(dcbpy)I] with 10 mg of KCN in 0.6 mL of methanol-d_4 followed by ^{1}H NMR spectroscopy: (a) before heating; (b) +1 h at 70 °C; (c) +1 h at 70 °C; (d) +10 h at 70 °C.

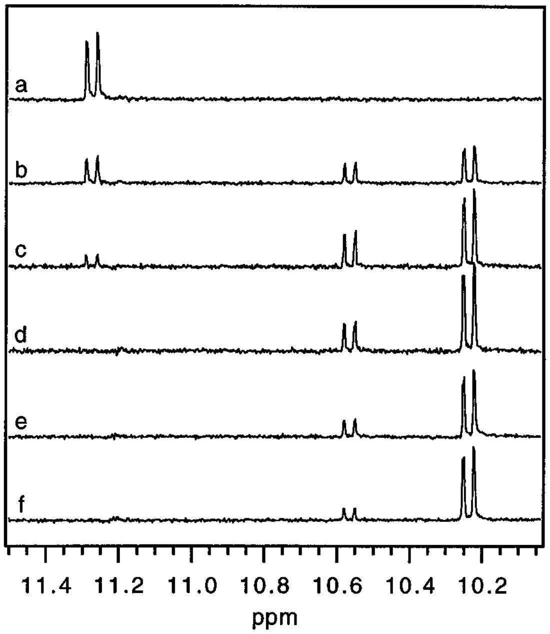

Figure 3. Portions of the ^{1}H NMR spectra for the reaction of ^{13}C-enriched potassium thiocyanate (7 mg) with Na[Ru(bmipy)(dcbpy)I] (2 mg) in 0.6 mL of methanol-d_4: (a) before heating; (b) +30 min at 70 °C; (c) +30 min at 70 °C; (d) +1 h at 70 °C; (e) +2 h at 70 °C; (f) +24 h at 70 °C.

from the signal at 163.5 ppm (free cyanide), only one intense peak at 154.4 ppm showing coordinated cyanide was detectable. The second species appearing as an intermediate product in spectrum b of Figure 2 at 10.20 ppm corresponds to the hydroxo complex. Iodide is easily substituted by water, yielding an aquo complex. The neutral aquo complex is not soluble in methanol and hence escapes detection by NMR. Cyanide acts as a base and deprotonates the aquo complex, forming the hydroxo complex. In spectrum d of Figure 2, the iodo and the hydroxo complex have completely reacted with the strong nucleophile cyanide, yielding the C-bound cyano complex (doublet at 10.60 ppm).[46,47]

The substitution of iodide by thiocyanate gave a different result. Figures 3 and 4 illustrate the reaction followed by ^{1}H (6H doublet) and ^{13}C NMR spectroscopy, respectively. Spectrum a of Figure 3 presents the reaction mixture before the tube was heated. After 30 min of heating, two new doublets indicated two products (spectrum b). The corresponding ^{13}C NMR spectra (Figure 4) exhibited two new signals which are attributed to two differently coordinated thiocyanates. The signal of ionic thiocyanate was found at 133.6 ppm, that of the N-bound at 134.4 ppm, and that of the S-bound at 123.4 ppm. Weaker signals appearing in the ^{13}C NMR spectrum corresponded to the carbon atoms of the organic complex ligands. The weak downfield shift of 0.8 ppm for the N-bound isomer and the relatively strong upfield shift of the S-bound isomer compared to free thiocyanate are in agreement with literature data for transition metal complexes of thiocyanate.[12,13] After 1 h of heating, the N-:S-bound ratio in the reaction mixture was 2:1; prolonged heating for 24 h converted most of the S-bound isomer to the N-bound. In Figure 3, the doublet at 10.24 ppm is attributed to the N-bound isomer and the doublet

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(46) Pesek, J. J.; Mason, W. R. *Inorg. Chem.* **1979**, *18*, 924.
(47) Jackson, W. G.; Rahman, A. F. M. M. *Inorg. Chem.* **1990**, *29*, 3247 and references cited therein.

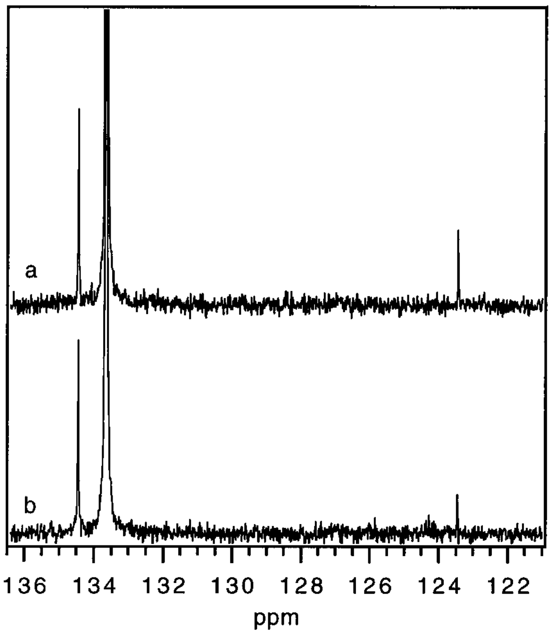

Figure 4. ^{13}C NMR spectra corresponding to the ^{1}H NMR spectra presented in Figure 3: (a) spectrum c of Figure 3; (b) spectrum e of Figure 3.

at 10.56 ppm to the S-bound isomer. Conversion of the S-bound to the thermodynamically more stable N-bound isomer was not complete even after 24 h of reflux (spectrum f), and about 5% S-bound isomer remained. The binding constants of the N- and S-bound thiocyanates appear to be similar. The proportion of the isomers was determined by integrating the NMR signals of the 6H doublets.

Illuminating an NMR tube containing the iodo complex and potassium thiocyanate in methanol-d_4 for 1 h at room temperature by a xenon lamp equipped with a 420 nm cutoff UV filter gave the same result of a 2:1 ratio of the linkage isomers. The N-bound isothiocyanato complex was found to be quite insoluble in methanol and crystallized slowly (concentration of the precursor complex should be about 4−8 mg/mL of methanol) from the supersaturated reaction mixture. Form and size of the crystals depended on the excess of potassium thiocyanate used in the reaction mixture. The reaction with sodium thiocyanate instead of potassium thiocyanate also yielded crystals. After crystallization, the mother liquor was enriched with the S-bound isomer. We could not observe the formation of a dimeric species containing bridging thiocyanate when the iodo complex was reacted with an equimolar amount of isothiocyanato complex in methanol-d_4 without potassium thiocyanate. The reaction did not yield any NMR-detectable product.

Our results on the linkage isomers are supported by infrared spectroscopy. Figure 5 shows a portion of the IR spectrum of the crystalline isothiocyanato complex and a sample containing both isomers with an N:S ratio of 79%:21%, determined by ^{1}H NMR spectroscopy. In agreement with the literature,[16] the ν_{CN} band of the S-bound isomer is shifted to lower energies, relative to those of the N-bound species. The band of a dimer Ru complex containing a bridged thiocyanate should be shifted to higher energies.[27] The value of the S-bound complex ν_{CN} band is within the region commonly associated with ionic thiocyanate. The use of ^{13}C NMR chemical shifts of coordinated pseudohalides was demonstrated to be a powerful diagnostic tool for bonding mode determination of these groups.[12,13] The NMR results clearly point out the advantage of ^{13}C NMR measurements. The ^{13}C NMR chemical shift reveals that the ion is coordinated and S-bound.[12,13]

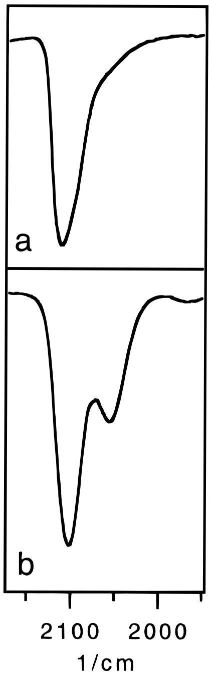

Figure 5. Portion of the IR spectrum in KBr of (a) N-bound K[Ru(bmipy)(dcbpy)(NCS)], (ν_{CN} = 2110 cm^{-1}) and (b) a sample containing 21% S- and 79% N-bound forms of the same complex (S-bound complex: ν_{CN} = 2056 cm^{-1}).

The phenylated [Ru(ph-bmipy)(dcbpy)I]$^{-}$ complex behaved in a similar way, forming N- and S-bound linkage isomers in a 2:1 ratio, respectively. The N-bound complex also yielded dark crystals. The additional phenyl group did not affect the shift of the ^{13}C NMR peaks of the coordinated N- and S-bound thiocyanates significantly in comparison to the ^{13}C NMR spectrum of [Ru(bmipy)(dcbpy)(NCS)]$^{-}$. When the solutions of K[Ru(bmipy)(dcbpy)(NCS)] and K[Ru(ph-bmipy)(dcbpy)(NCS)] in methanol were exposed to intense visible light, we could observe decomposition and formation of the cyano complexes.

The selenocyanate anion behaved in a more complex fashion than the thiocyanate anion when introduced into the complex. Figures 6 and 7 monitor the reaction of the [Ru(bmipy)(dcbpy)I]$^{-}$ with selenocyanate, followed by ^{1}H and ^{13}C NMR spectroscopy. When the reaction mixture was heated, the isomeric N- and Se-bound complexes appeared in nearly equal amounts. First, the disappearance of the 6H doublet of the iodo complex was accompanied by the appearance of three doublets (spectrum b of Figure 6). Thereafter, in spectrum c of Figure 6, a fourth doublet was visible. ^{13}C NMR spectroscopy allowed us to assign the different species. The line at 119.8 ppm in the ^{13}C NMR spectrum is attributed to the free selenocyanate anion, and the two weaker lines at 122.5 and 117.1 ppm are assigned to free NC^{77}Se^{-}. The signal shifted 12.1 ppm upfield at 107.6 ppm represents an Se-bound ligand, while the signal downfield shifted at 121.7 ppm is attributed to N-bound selenocyanate. The line strongly downfield shifted at 154.7 ppm indicates decomposition via loss of Se from coordinated selenocyanate and the formation of the cyano complex. After a reaction time of 2 h under reflux, most of the iodo complex had been converted. Monitoring the ^{1}H NMR spectrum of the sample left at room temperature in the dark showed the instability of the isoselenocyanato complex. Spectrum e shows a decreased intensity for the doublet at 10.22 ppm (isoselenocyanato complex) and an increased intensity for the doublet at 10.58 ppm (cyano complex) after a period of 48 h at room temperature. Further heating of the NMR tube transformed the Se-bound

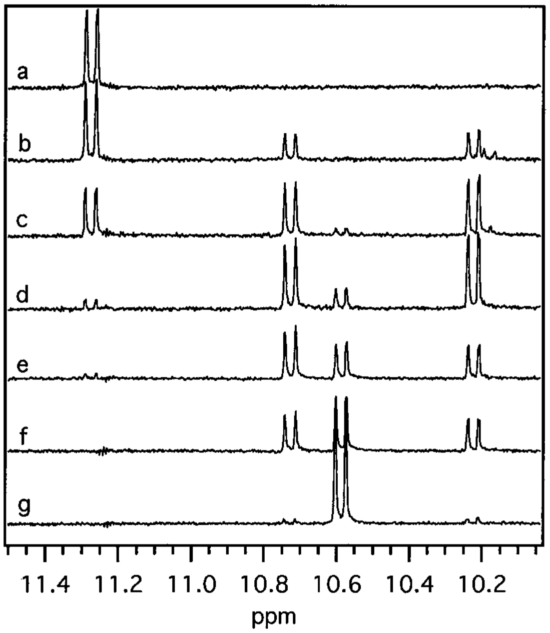

Figure 6. Reaction of 3.5 mg of Na[Ru(bmipy)(dcbpy)I] with 6 mg of $KN^{13}CSe$ in 0.6 mL of methanol-d_4 followed by ^1H NMR spectroscopy: (a) before heating; (b) +30 min at 75 °C; (c) + 30 min at 75 °C; (d) + 1 h at 75 °C; (e) +48 h at room temperature; (f) +3.5 h at 75 °C; (g) +14 h at 75 °C.

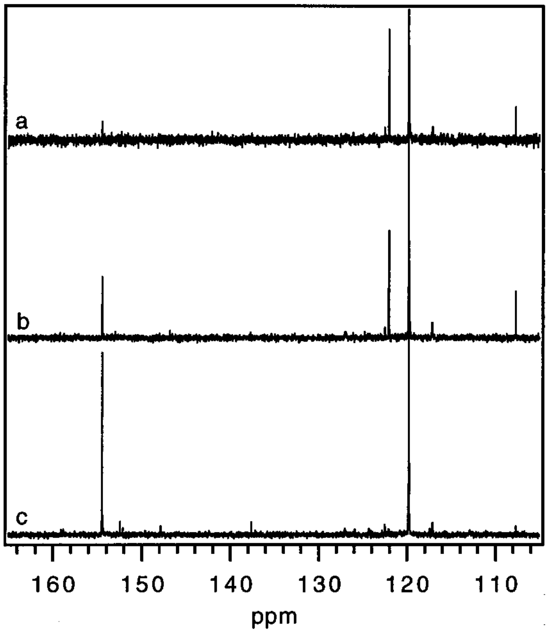

Figure 7. ^{13}C NMR spectra of the substitution reaction described in Figure 6. Corresponding spectra: (a) spectrum c of Figure 6; (b) spectrum d of Figure 6; (c) spectrum g of Figure 6.

isomer to the N-bound, and decomposition of the latter yielded cyano complex. Decomposition was nearly complete after 20 h of heating (spectrum g of Figure 6). Instability was found only for coordinated selenocyanate; free selenocyanate did not decompose to cyanide. In the ^{13}C NMR spectrum, no signal at 163.5 ppm corresponding to free cyanide was detectable. During our ^{13}C NMR measurement, we could not observe a signal for N-bound cyanide which should be formed after loss of Se. This can be explained by the low stability and the fast isomerization of the N-bound cyano complex to the C-bound species. The additional doublet visible in spectrum b of Figure 6 at 10.20 ppm arises from the hydroxo complex, indicating basic conditions in the reaction mixture.

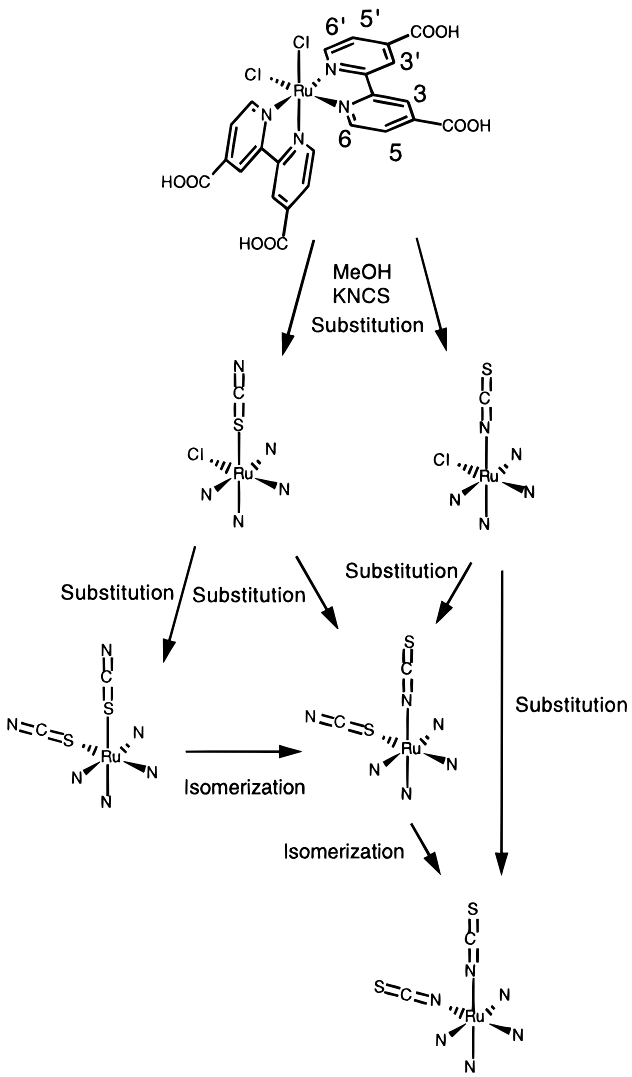

Figure 8. Reaction route to *cis*-$Ru(dcbpyH_2)_2(NCS)_2$ from *cis*-$Ru(dcbpyH_2)_2Cl_2$ and potassium thiocyanate in methanol.

The formation of S-bound isomers was also detected with *cis*-$Ru(dcbpyH_2)_2(NCS)_2$ synthesized as previously described.[8] The ^1H NMR spectrum of the product always indicated the presence of byproducts. These weak additional NMR signals were assigned to the mixed N-/S-bound *cis*-$Ru(dcbpyH_2)_2$-(NCS)(SCN) complex. For a complex containing two ligand sites for substitution, several isomeric species are possible. During the reaction of the precursor complex *cis*-$Ru(dcbpyH_2)_2$-Cl_2 with thiocyanate, all possible isomers, *cis*-$Ru(dcbpyH_2)_2$-$(NCS)_2$, *cis*-$Ru(dcbpyH_2)_2$(NCS)(SCN), and *cis*-$Ru(dcbpyH_2)_2$-$(SCN)_2$, as well the two monochloro intermediate species *cis*-$Ru(dcbpyH_2)_2$Cl(NCS) and *cis*-$Ru(dcbpyH_2)_2$Cl(SCN), were identified on the basis of *in situ* ^1H and ^{13}C NMR data and the trends observed for the reaction of K[Ru(bmipy)(dcbpy)I] with potassium thiocyanate. Simultaneously measuring ^1H and ^{13}C NMR spectra during reaction with ^{13}C-enriched thiocyanate, monitoring the appearance and disappearance of the signals, and comparing the intensities allowed us to correlate the signals. Figure 8 illustrates the reaction route in detail. Figure 9 shows the change in the ^1H NMR spectrum of the 6H protons of the two 4,4′-dicarboxy-2,2′-bipyridine ligands during the reaction of *cis*-$Ru(dcbpyH_2)_2Cl_2$ with thiocyanate; Figure 10, the change in the ^{13}C NMR spectrum. In the ^1H NMR spectrum, a complex containing two different types of monodentate ligands gives two doublets of the same intensity for the 6H protons, while for a complex containing two identical ligands, only one doublet is

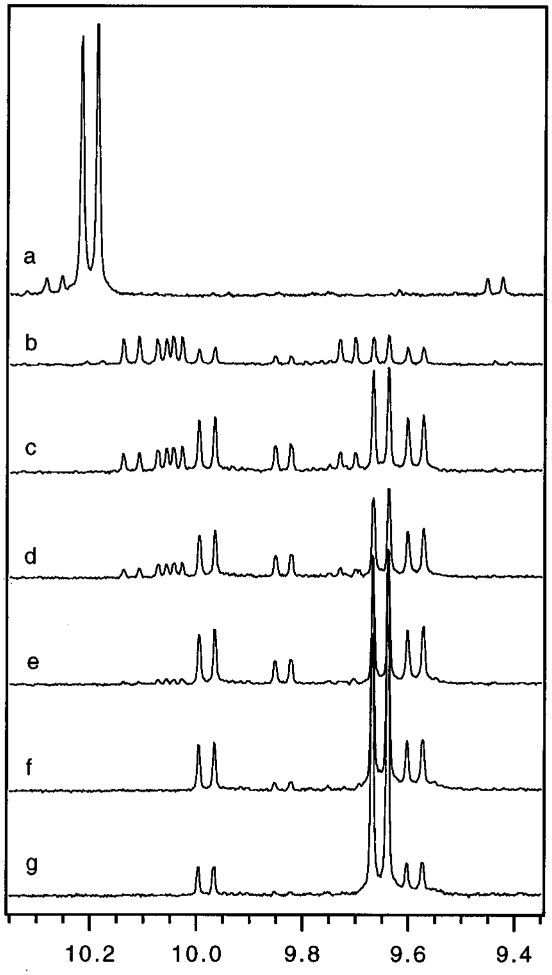

Figure 9. Reaction of *cis*-Ru(dcbpyH$_2$)$_2$Cl$_2$ with ^{13}C-enriched thiocyanate followed by ^{1}H NMR: (a) before heating; (b) +1 h at 55 °C; (c) +1 h at 55 °C; (d) +12 h at room temperature; (e) +2 h at 55 °C; (f) +2 h at 55 °C; (g) +16 h at 75 °C. Figure 10 shows the corresponding ^{13}C NMR spectra.

obtained. As expected, the five intermediate and final species shown in Figure 8 gave eight new doublets for the 6H protons in ^{1}H NMR spectra b and c of Figure 9. According to Figure 8, three different complexes containing S-bound thiocyanate were visible in the domain between 124 and 125 ppm of the corresponding ^{13}C NMR spectrum, spectrum a of Figure 10. Spectrum a of Figure 9 corresponds to the dichloro complex (doublet at 10.20 ppm), contaminated with small amounts of the mixed aquo/chloro complex (doublets at 10.27 and 9.44 ppm). The chloro ligand reacted easily with water in methanol solution; substitution of chloride by traces of water occurred slowly in the dark even at room temperature. Spectra f and g of Figure 9 represent the final products: the bis(isothiocyanato) complex (doublet at 9.65 ppm) and the mixed N-/S-bound complex (two smaller doublets of the same intensity at 9.98 and 9.59 ppm). The corresponding ^{13}C NMR spectrum, spectrum c of Figure 10, shows four signals: a broad signal at 133.6 (free thiocyanate), a strong signal at 135.4 (bis(isothiocyanato) complex), and two weaker ones at 136.0 and 124.2 ppm (mixed N-/S-bound complex). The additional doublet in spectrum e of Figure 9 at 9.84 ppm corresponds to the bisthiocyanato complex, containing two S-bound ligands. The corresponding ^{13}C NMR spectrum, spectrum b of Figure 10, shows a further peak at 124.1 ppm, indicating S-bound thiocyanate. Spectra b−d of Figure 9 show four additional doublets, corresponding to the mixed chloro/isothiocyanato complex and the mixed chloro/thiocyanato complex. The ^{13}C NMR spectrum shows an additional signal at 125.0 ppm for the S-bound thiocyanate; the signal of the chloro/isothiocyanato complex could be covered by the signal of the bis(isothiocyanato) complex. The signals of the monochloro complexes disappeared quickly due to the fast exchange of chloride by thiocyanate. Spectrum g of Figure 9 represents the final state of the reaction after additional refluxing for 16 h. It should be noted that most of the reaction time for the synthesis of *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ is required for the isomerization of S-bound thiocyanate, the chloro ligand being substituted within a period of 1 h by thiocyanate under reflux in higher boiling point solvents. We could not obtain *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ completely free of the mixed N-/S-bound complex even by using higher boiling point solvents such as DMF/water mixtures. Nevertheless, it was possible to reduce the amount of the mixed N-/S-bound isomer to about 2% in higher boiling solvents under prolonged refluxing.

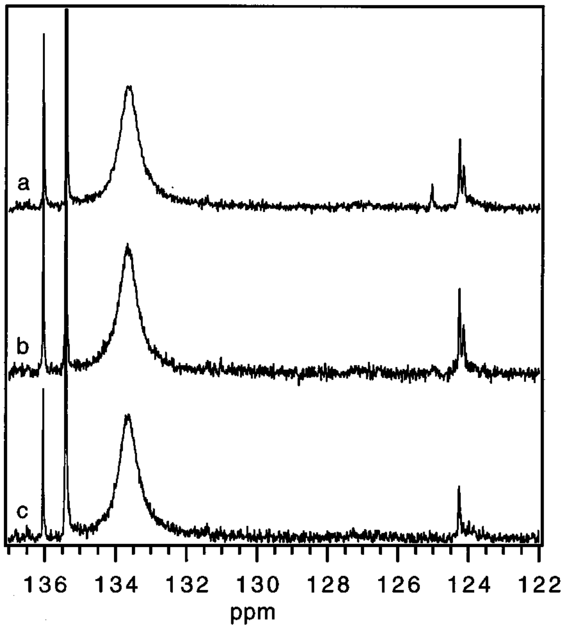

Figure 10. ^{13}C NMR spectra of the substitution reaction described in Figure 9. Corresponding spectra: (a) spectrum c of Figure 9; (b) spectrum e of Figure 9; (c) spectrum f of Figure 9.

In general, the relation between the mode of binding in mixed-ligand ruthenium thiocyanate complexes and the role of the coligands is still not very clear. Electronic, steric, and solvent factors largely influence the bonding mode of pseudohalides. In the case of bipyridine as a coligand, the S-bound mode has been ruled out by earlier workers.[14,20,28] The appearance of small amounts of S- and Se-bound linkage isomers as byproducts was observed for the complexes Ru(bipy)$_2$ClY (Y = NCS$^-$, NCSe$^-$; bipy = bipyridine).[26,27] In contrast to the behavior of *cis*-Ru(bipy)$_2$(NCS)$_2$ reported in the literature,[14,20,28] we have evidence for isomers containing S-bound thiocyanate in the case of the carboxylated complex.

Our findings on the ^{13}C chemical shifts of the N-, S-, and Se-bound isomers are in good agreement with literature.[12,13] N-bound thio- and selenocyanates are weakly shifted downfield and S- and Se-bound upfield, compared to ionic thio/selenocyanates. For the mixed complex *cis*-Na$_4$[Ru(dcbpy)$_2$(NCS)(SCN)] in D$_2$O/NaOD solution, we could observe a weakly upfield shifted signal at 132.8 ppm for N-bound thiocyanate (ionic: 134.2 ppm) and a signal at 126.8 ppm for the S-bound thiocyanate. *cis*-Na$_4$[Ru(dcbpy)$_2$(NCS)$_2$]: ^{1}H NMR data (D$_2$O/0.05 M NaOD) 9.50 (d, 6H, 6 Hz), 8.89 (d, 3H, 1.5 Hz), 8.72 (d, 3′H, 1.5 Hz), 8.16 (dd, 5H, 6 Hz, 1.5 Hz), 7.77 (d, 6′H, 6

Table 2. Electrochemical and Absorption Data

complex	E^a/V oxidn	E^a/V redn	abs max^b/nm (ϵ/10^3 M^{-1} cm^{-1})			
K[Ru(bmipy(dcbpy)(NCS)]	0.83	−1.25	308 (45.8)	346 (30.8)	360 (40.0)	500 (14.0)
K[Ru(ph-bmipy)(dcbpy)(NCS)]	0.99^d	−1.16	308 (62.4)	348 (30.7)	364 (38.1)	508 (18.0)
Li[Ru(bmipy)(dcbpy)Cl]	0.69^c	−1.28^c	310 (42.7)	344 (29.2)	360 (38.8)	512 (14.0)
Na[Ru(bmipy)(dcbpy)I]	0.70	−1.35	310 (48.6)	346 (31.6)	362 (33.4)	514 (14.0)
Na[Ru(ph-bmipy)(dcbpy)I]	0.79	−1.20	310 (59.5)	350 (30.3)	362 (31.3)	522 (17.5)

^{a} Potentials versus Ag/AgCl/satd KCl. ^{b} Measured in methanol. ^{c} Measured in DMSO. ^{d} Irreversible.

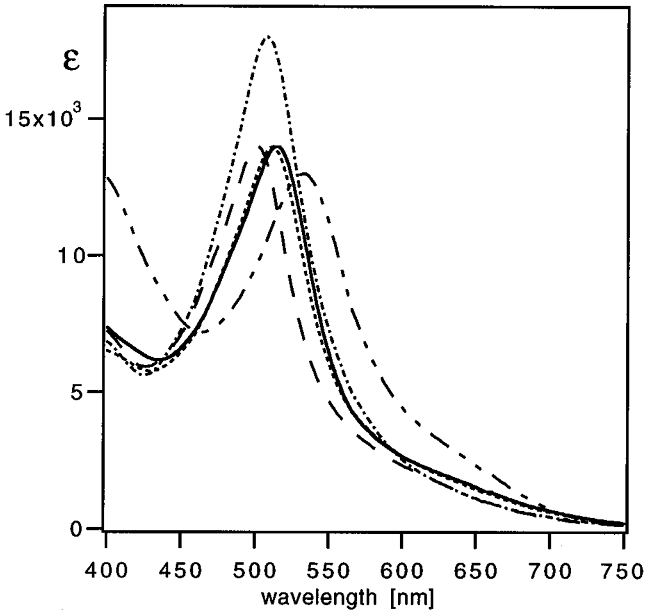

Figure 11. Visible spectra of Na[Ru(bmipy)(dcbpy)I] (—), Li[Ru(bmipy)(dcbpy)Cl] (- - -), K[Ru(bmipy)(dcbpy)(NCS)] (— — —), K[Ru(ph-bmipy)(dcbpy)(NCS)] (-•-•-), and *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ (— - - —) in methanol.

Hz), 7.47 ppm (dd, 5′H, 6 Hz, 1.5 Hz); ^{13}C NMR data (D$_2$O/0.05 M NaOD) 172.6 and 172.2 (carboxyl carbons), 159.7 and 156.6 (2, 2′), 154.1 and 153.2 (6, 6′), 145.4 and 144.8 (4, 4′), 132.8 (coord. NCS$^-$), 126.5 and 125.4 (5, 5′), 123.0 and 122.7 ppm (3, 3′). The 6H doublets of *cis*-Na$_4$[Ru(dcbpy)$_2$(NCS)(SCN)] in D$_2$O/0.05 M NaOD were detected at 9.68 (d, 6 Hz) and 9.48 ppm (d, 6 Hz). Other signals are more or less covered by the signals of *cis*-Na$_4$[Ru(dcbpy)$_2$(NCS)$_2$].

Figure 11 and Table 2 report the visible absorption features of Li[Ru(bmipy)(dcbpy)Cl], Na[Ru(bmipy)(dcbpy)I], K[Ru(bmipy)(dcbpy)(NCS)], K[Ru(ph-bmipy)(dcbpy)(NCS)], and *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ in methanol. The chloro and the iodo complexes show very similar spectra. The maximum of the iodo complex is slightly red-shifted; both spectra nearly superpose at longer wavelengths. We could not observe a significantly stronger ^{3}MLCT transition in the visible spectrum for the iodo complex due to a possible heavy-atom effect of the iodide ligand; the effect is too small. The weaker donor strength of the thiocyanate results in a blue shift of the spectrum, compared to those of the halide complexes. The MLCT maximum of the phenylated K[Ru(ph-bmipy)(dcbpy)(NCS)] exhibits a red shift and a higher molar absorption coefficient when compared to that of the unsubstituted isothiocyanato complex. Unfortunately, the phenylation does not enhance light absorption at longer wavelengths in the domain between 620 and 750 nm. The spectrum of *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ exhibits a strong red shift and a second MLCT maximum in the near-UV which is advantageous for efficient light harvesting.

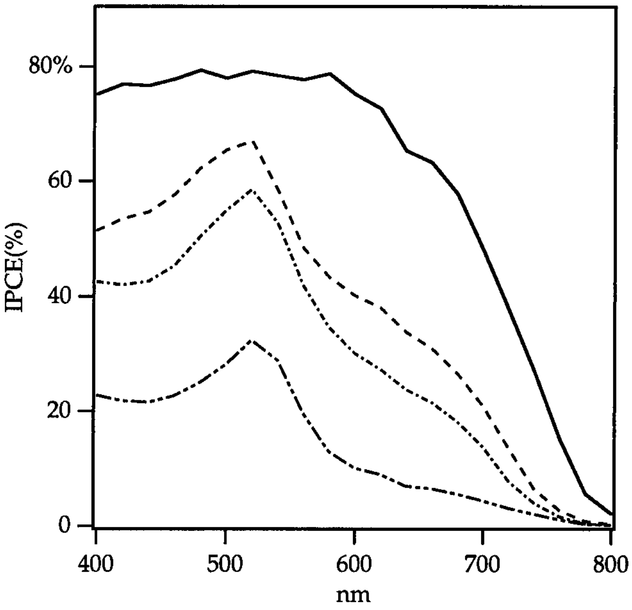

Figure 12. Photoaction spectra of Na[Ru(bmipy)(dcbpy)I] (— - - —), K[Ru(bmipy)(dcbpy)(NCS)] (- - -), K[Ru(ph-bmipy)(dcbpy)(NCS)] (-•-•-), and *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ (—). Spectra are not corrected for losses of light due to the conductive glass support.

Figure 12 shows a comparison of action spectra. The incident monochromatic photon-to-current conversion efficiency (IPCE) is defined by eq I.[8] The IPCE values for *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ of nearly 80% in the wavelength range between 400 and 600 nm are impressive. Taking into account the losses due to the conducting glass support, the conversion of the photon flux into electrical current in the external circuit is practically quantitative in this wavelength domain. Reduced IPCE values in the wavelength domain beetween 400 and 520 nm reported in the literature[8,10] are due to the light absorption by the triiodide anion. Reduced absorption coefficients of the Ru complex limit light absorption at longer wavelengths above 600 nm; the IPCE values depend on the thickness of the TiO$_2$ layer. A 8 μm thick layer gave an IPCE value at 700 nm between 45% and 50%. For the Ru(bmipy)(dcbpyH)(NCS) sensitizer, we could obtain an IPCE of about 70% at 520 nm, in agreement with earlier preliminary investigations.[48] In particular, the IPCE values are reduced at longer and at shorter wavelengths compared to those of *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$ which can be explained by a decreased packing density on the TiO$_2$ surface and by the absorption spectrum. It is blue-shifted and shows reduced absorption coefficients at shorter (400−450 nm) and longer wavelengths above 530 nm. As a consequence, the sensitizer is not as performant as *cis*-Ru(dcbpyH$_2$)$_2$(NCS)$_2$, but for

$$\text{IPCE (\%)} = \frac{(1.25 \times 10^3) \times \text{photocurrent density } (\mu\text{A/cm}^2)}{\text{wavelength (nm)} \times \text{photon flux (W/cm}^2)} \times 100\% \quad \text{(I)}$$

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[48] Müller, E.; Nazeeruddin, M. K.; Kohle, O.; Grätzel, M. Unpublished work.

regenerative cells under simulated AM 1.5 solar light, we could obtain impressive currents of 12 mA/cm^2 and a solar to electric energy conversion efficiency exceeding 6%.

The iodo and chloro complexes Na[Ru(bmipy)(dcbpy)X] ($X^- = Cl^-, I^-$) showed strongly reduced overall injection efficiencies. Compared to that of the thiocyanate ligand, the stronger electron donating effect of the halide ligands causes an increased energetic destabilization of the Ru(t_{2g}) level.[21] Shifting the Ru(t_{2g}) level too strongly may lead to problems with regeneration of the complex by iodide after electron injection into TiO_2 due to an insufficient driving force for the redox reaction.[7,8] However, the difference in the oxidation potentials (Table 2) of the isothiocyanato and the iodo complex is too small to explain the strongly decreased IPCE values of the halide complexes. The halide ligands are very labile and easily replaced by water. When heating the dye solution or exposing it to light during absorption on the TiO_2 layers, we observed increased IPCE values due to the formation of aquo complex. The aquo complex injects electrons more efficiently into TiO_2 than the halide complexes.

The phenylated complex Ru(ph-bmipy)(dcbpyH)(NCS) exhibits an IPCE value of 60% at 520 nm. Injection into TiO_2 is slightly reduced due to the phenylation but still quite efficient. The phenyl group does not influence electron injection as strongly as was observed for the Ru−4,4′-bis(*p*-carboxyphenyl)-2,2′-bipyridine complexes.[37] This confirms that the phenyl group acted as an insulating barrier (distance effect) for the excited electron when introduced between the bipyridine and the carboxyl group.

Ru(bmipy)(dcbpyH)(NCS) containing 20% S-bound complex gave about 10−20% lower IPCE values than the pure N-bound complex. Apparently, electron injection is influenced by the bonding mode of thiocyanate.

There are several reasons for the still unmatched performance of *cis*-$Ru(dcbpyH_2)_2(NCS)_2$ as a sensitizer for solar cells. The π^*-level system allows quantitative charge injection into TiO_2. Two thiocyanate ligands shift the absorption spectrum strongly to longer wavelengths, without shifting the Ru(t_{2g}) level too strongly for iodide regeneration. A better tuning of the Ru(t_{2g}) level and the π^* level appears very difficult. N-bound thiocyanate as a ligand supports quantitative charge injection; replacing thiocyanate in a Ru sensitizer by stronger donor ligands such as iodide or chloride influences electron injection negatively. The absorption spectrum exhibits two maxima for light absorption in the visible domain; absorption coefficients are relatively high due to the two bipyridines carrying four carboxyl groups. The molecule is relatively small and adsorbs efficiently on TiO_2, favoring a dense loading on the surface of porous TiO_2 and efficient light absorption of the TiO_2/dye electrode.

Conclusions

The introduction of thiocyanate and selenocyanate into Ru(II) complexes containing 4,4′-dicarboxy-2,2′-bipyridine resulted in the formation of linkage isomers in ratios of 2:1 (N:S) and 1:1 (N:Se), respectively. The S- and the Se-bound isomers were transformed to the N-bound isomers upon heating. In methanol solution, the isoselenocyanato complex decomposed readily under loss of Se. ^{13}C NMR spectroscopy is an excellent method for determining the bonding mode of ambidentate ligands such as thiocyanate and selenocyanate in Ru polypyridyl complexes. In particular, by using ^{13}C-enriched ligands, even barely soluble complexes can be studied. Reacting the precursor complex with a ligand in an NMR tube and combining ^{13}C with ^1H NMR spectroscopy give more detailed information: Thermodynamically unstable side products, in the case of the Ru complexes of the S- and Se-bound isomers, can be detected and identified.

The variation of the structure of the model sensitizer K[Ru(bmipy)(dcbpy)(NCS)] by introducing a phenyl group or replacing the thiocyanate by iodide resulted in a less performant sensitizer. The bis(isothiocyanato) complex *cis*-$Ru(dcbpyH_2)_2(NCS)_2$ is an impressively powerful sensitizer for nanocrystalline TiO_2 solar cells. As discussed in the present paper, it appears very difficult to obtain a more performant Ru sensitizer. The synthesis of organic sensitizers is more promising. Absorption coefficients increased by an order of magnitude and reduced losses by singlet−triplet relaxation compared to those of Ru sensitizers promise a further quantum step in developing a more performant dye solar cell.

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