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Interaction of I^- and I_3^- with a Redox-Stable Cr(III)-Based Structural Surrogate for Photo-Oxidized "N3 Dye"

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A series of $[Cr (L)_2(NCS)_2]X$ complexes, where L = 2,2′-bipyridine (bpy) or 4,4′-dimethyl-2,2′-bipyridine (dmb) and X^- is I^-, I_3^-, or NO_3^-, have been prepared for study as redox-inactive surrogates for diisothiocyanatobis-(2,2′-bipyridine-4,4′-dicarboxylic acid)ruthenium(III) ("$N3^+$"). Dilute solution spectra in dichloromethane or acetonitrile of the I^- and NO_3^- salts are the same, but the I^- salts show clear evidence of a charge-transfer interaction between the cation and anion in the solid state and in concentrated I^- solutions in acetonitrile. X-ray structural determination of the dmb complex shows that this interaction is between the I^- and one of the dmb ligands. X-ray structural determination of the bpy complex as the I_3^- salt indicates a similar interaction between one of the bpy ligands and one of the terminal iodine atoms of the anion. These results have potential implications in the reduction mechanism of photo-oxidized N3 dye used as a sensitizer in nanocrystalline TiO_2-based photogalvanic cells.

Introduction

Photogalvanic cells consisting of nanocrystalline TiO_2 sensitized with transition metal complex dyes, sometimes called Grätzel cells,[1] have become a topic of considerable recent interest. This interest has focused heavily on the process of charge injection from the photoexcited dye into the TiO_2 electrode. Corollary efforts to develop better dyes have also received much attention.[2] At present, the "industry standard" against which all new dyes are compared is *cis*-diisothiocyanatobis(2,2′-bipyridine-4,4′-dicarboxylic acid)ruthenium(II), $[Ru(NCS)_2(Bp\text{-}COOH)_2]$, also called "N3 dye"[3]. Considerably less attention, however, has been given to the other redox component in this cell, the I^-/I_3^- couple.[4−6]

This redox couple plays several special roles in the cell's operation that are equal in importance to the fast injection of electrons into the TiO_2 from the photoexcited dye. First, the iodide functions to reduce the oxidized dye after charge injection and then it transports the hole to the cathode. To do this efficiently, I^- must reduce the Ru(III) before it can recombine with the photoinjected electron and then not react, itself, with the injected electron. Under the conditions of cell operation, the product of I^- oxidation is I_3^-. Despite the I^-/I_3^- couple's important role in the operation of a Grätzel cell, its functional mechanism is not well understood. Attempts to replace I^-/I_3^- with other redox couples have resulted in cells with lower efficiencies.[4] The photophysics of the N3 dye and its interaction with the semiconductor have been well studied. The uncertainty about its reduction by I^- is due in part to the inherent difficulty of studying interactions between the oxidized dye ($N3^+$) and I^- prior to the electron-transfer event that occurs rapidly. Furthermore, the rate of this redox reaction is influenced by many factors.[5−8] The net reaction at the photoanode is:

$$^{3}/_{2}I^- \rightarrow {}^{1}/_{2}I_3^- + e^- \qquad (1)$$

Mechanism I, below, was suggested by Grätzel et al. to be the prevailing route for dye reduction[9] and is supported by spectral evidence for $I_2^{\bullet-}$ in transient laser spectroscopy.[5,7] One important thing to notice about this mechanism is that in reaction 2 there is a termolecular event. At the concentrations used in the typical cell, the likelihood of a three-body encounter is quite low. Consequently, for this reaction to proceed at the rates observed, some preassociation between two of the three reacting species is necessary—either an (I^-,I^-) pair or (I^-,$N3^+$) pair.[9]

Mechanism I

$$N3^+ + 2I^- \rightarrow N3 + I_2^{\bullet-} \qquad (2)$$

$$2I_2^{\bullet-} \rightarrow I^- + I_3^- \qquad (3)$$

Grätzel et al. have shown that there are two kinetic regimes in the reduction of $N3^+$ that depend greatly on the nature and amounts of cations in the cell.[9] When using electrolytes with large cations, such as tetrabutylammonium, the surface of the TiO_2 electrode is negatively charged. With the addition of enough Li^+ or Mg^{2+} cations, this surface charge changes from negative to positive. A sharp increase in the reduction rate of $N3^+$ coincides with this change. This suggests that I^- anions are adsorbing on the now-positive surface of the electrode, enhancing the possibility of (I^-,I^-) or (I^-,$N3^+$) pairing.

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(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737−740.
(2) Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, *33*, 269−277.
(3) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphrybaker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382−6390.
(4) Gregg, B. A.; Pichot, F.; Ferrere, S.; Fields, C. L. *J. Phys. Chem. B* **2001**, *105*, 1422−1429. Thompson, D. W.; Kelly, C. A.; Farzad, F.; Meyer, G. J. *Langmuir* **1999**, *15*, 650−653.
(5) Nasr, C.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem. B* **1998**, *102*, 4944−4951.
(6) Alebbi, M.; Bignozzi, C. A.; Heimer, T. A.; Hasselmann, G. M.; Meyer, G. J. *J. Phys. Chem. B* **1998**, *102*, 7577−7581.
(7) Fitzmaurice, D. J.; Frei, H. *Langmuir* **1991**, *7*, 1129−1137.
(8) Myung, N.; Licht, S. *J. Electrochem. Soc.* **1995**, *142*, L129-L132.
(9) Pelet, S.; Moser, J. E.; Grätzel, M. *J. Phys. Chem. B* **2000**, *104*, 1791−1795.

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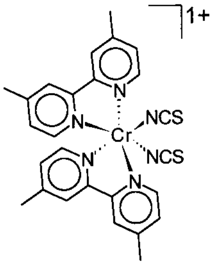
There is previous evidence suggesting that an (I^-,$N3^+$) association would be possible. Fitzmaurice and Frei find transient spectral evidence for a $Ru^{II}L_3I_2^-$ charge-transfer complex.[7] Hagfeldt and Grätzel theorize that an I^- interaction with the sulfur atom of an isothiocyanate ligand might facilitate reduction of the $N3^+$ dye.[2] The isothiocyanate ligands are ostensibly situated relative to the TiO_2 surface such that they point toward the solution and away from the electrode; therefore, the sulfur termini will be far enough from the surface charge that an (I^-,$N3^+$) pair involving the sulfur should be possible regardless of the surface charge. However, because the sharp increase in dye reduction rate accompanies the change in surface charge,[9] the possibility of this specific type of (I^-,$N3^+$) interaction was dismissed by Grätzel et al. What was not considered was the possibility of an (I^-,$N3^+$) pairing where the I^- interaction is with the bipyridine ligands on the $N3^+$. Such an interaction would place the I^- close to the surface where it could be affected by the surface charge.

In an effort to evaluate how an I^- might interact with $N3^+$, we have prepared a surrogate for the $N3^+$ dye—one with the same charge and very similar structure but without the redox chemistry. Chromium(III) will react with certain diimine ligands to yield *cis*-diisothiocyanato-bis(2,2′-diimine)chromium(III) ion, $[Cr(L)_2(NCS)_2]^+$. When L is 2,2′-bipyridine (bpy) or 4,4′-dimethyl-2,2′-bipyridine (dmb), the reaction goes in good yield. Numerous attempts at making $[Cr(Bp\text{-}COOH)_2(NCS)_2]^+$, however, were not successful, nor were attempts using the ester-substituted bipyridine in place of the carboxylic acid.



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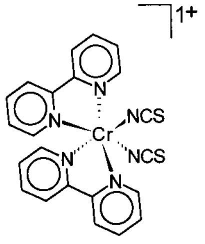

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Herein, we report our studies of these Cr(III)-based surrogates as their I^- and I_3^- salts. For the dmb complex, we were successful in growing crystals with each anion that were nominally of diffraction quality; however, with the I_3^- salt, there was significant disorder of the anions (which constitute a large fraction of the total electron density). The I^- salt of this complex, on the other hand, produced good quality crystals. Good diffraction quality crystals were obtained from the analogous bpy complex of the I_3^- salt. Below we consider these structural results along with spectral information, as it relates to potential I^-/$N3^+$ interaction.

Experimental Section

Synthesis. 2,2′-Bipyridine (Aldrich) and 4,4′-dimethyl-2,2′-bipyridine (Reilly Tar and Chemical) were both recrystallized from ethyl acetate before use. Silica gel (Aldrich) was of flash quality, 200−400 mesh, and used as received.

$[Cr(dmb)_2(NCS)_2]NO_3$. A modification of a previously reported preparation[10] was used resulting in a “one-pot” synthesis of the complex cation. 4,4′-Dimethyl-2,2′-bipyridine (3.00 g,16.3 mmol) and KSCN (15.82 g, 160.3 mmol) were added to 100 mL of ethanol and degassed with nitrogen. The reaction was then kept under a nitrogen atmosphere from this point until completion. The KSCN was nearly, but not entirely, dissolved. $CrCl_3{\cdot}6H_2O$ (2.17 g, 8.14 mmol) was added over 5 min, forming a dark green solution (anhydrous $CrCl_3$ can also used with similar results). A few grains of zinc metal were added, and after 5 min of stirring, the reaction had become dark brown in color. At this point, the reaction was heated to reflux for 30 min. The solution color first became a lighter yellow brown and then a reddish brown at completion. The reaction vessel was cooled in a freezer, and a brown-orange precipitate formed that was filtered. The dark purple solution was discarded. The precipitate was washed generously with water, ethanol, and finally ether. The precipitate was dissolved in about 1 L of hot acetone and filtered through a frit leaving behind a purple-gray residue. The filtrate was rotary evaporated to a small volume and the crude product precipitated by the addition of cold ether and collected on a frit. TLC (silica) in acetone showed two compounds—a fast-moving red-pink band and a yellow-orange band that remained near the origin. The crude product was dissolved in acetone, loaded onto a silica column, and eluted with acetone until the pink band had been completely removed from the column. The orange product was then eluted with 50% acetonitrile/49% water/1% aqueous saturated potassium nitrate. The orange fraction was collected and rotary evaporated until the acetonitrile was removed, at which point the product, $[Cr(dmb)_2(NCS)_2]NO_3$, precipitates. The precipitate was collected on a frit, washed with water, ethanol and ether and then vacuum-dried, yield 63%.

$[Cr(bpy)_2(NCS)_2]NO_3$. The 2,2′-bipyridine complex was prepared under identical conditions as the dmb analogue substituting bpy (2.54 g, 16.3 mmol) for dmb.

$[Cr(Bp\text{-}COOH)_2(NCS)_2]NO_3$. Attempts at making the 2,2′-bipyridine-4,4′-dicarboxylic acid complex were unsuccessful. In all cases, the stoichiometry in the reaction was kept the same as in the preparation of the dmb derivative, i.e., 1 mol of chromium to 2 mol of Bp-COOH to 10 mol of KSCN. Both $CrCl_3{\cdot}6H_2O$ and anhydrous $CrCl_3$ were used as chromium sources, and the solvent was varied from ethanol to dimethylformamide to ethylene glycol. Soluble products that were obtained appeared not to be charged as they moved on silica TLC plates with acetone and dichloromethane eluents. Attempts to protonate the complex (in case it was the singly deprotonated neutral complex) had no effect on the chromatography. Last, none of these reactions yielded any products with spectroscopy that corresponded to that of the dmb or bpy analogues described above.

$[CrL_2(NCS)_2]I$ (L = dmb or bpy). The nitrate salt was first dissolved in acetonitrile and a 10-fold excess of NaI in methanol was added. This solution was stirred for 10 min and then rotary evaporated to dryness. The residue was washed generously with water to remove KNO_3 and excess NaI followed with methanol and ether. The product was vacuum-dried.

$[CrL_2(NCS)_2](I_3)$ (L = dmb or bpy). The nitrate salt and excess NaI were dissolved in hot 3:1 dichloromethane:methanol. Excess I_2 was added to this solution and stirred until all solids were dissolved. This mixture was left open to the air in a warm place (above a drying oven) overnight. The remaining methanol and excess I_2 were then removed by rotary evaporation. The residue was washed with water, collected on a frit and vacuum-dried.

Crystal Growth. Crystals of $[Cr(dmb)_2(NCS)_2](I_3)$ were grown by dissolving the complex in dichloromethane and adding methanol. This solution was degassed with argon in a scintillation vial and covered with the cut-off finger from a latex glove to allow the dichloromethane to slowly evaporate. Within 1 week, dark red crystals had formed.

Crystals of $[Cr(dmb)_2(NCS)_2]I$ were grown by dissolving the nitrate salt of the complex in dichloromethane and adding an ethanol solution containing a large molar excess of NaI. This solution was also degassed with argon in a scintillation vial covered with the cut-off finger of a latex glove. Within1 week, orange crystals formed. Good-quality crystals could also be grown starting with the I^- salt and adding no additional NaI. Attempts using methanol instead of ethanol yielded crystals, but they were small and of poor diffraction quality.

X-ray Crystallography of $[Cr(dmb)_2(NCS)_2]I$, $[Cr(dmb)_2(NCS)_2](I_3^-)$, and $[Cr(bpy)_2(NCS)_2](I_3^-)$. Diffraction data were collected on a Siemens SMART CCD diffractometer. Lorentz and polarization corrections were applied along with empirical absorption corrections

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(10) Ryu, C. K.; Endicott, J. F. *Inorg. Chem.* **1988**, *27*, 2203−2214. Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570−3579.

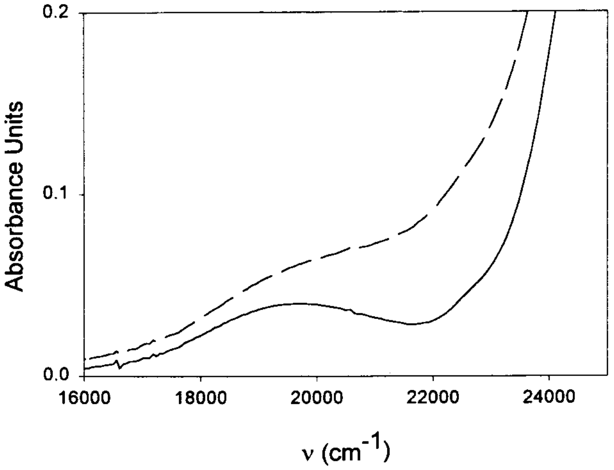

Figure 1. Solution spectra of $[Cr(dmb)_2(NCS)_2][NO_3]$ in the presence (dashed line) and absence (solid line) of ca. × 4500 molar excess NaI. Spectra were taken in acetonitrile.

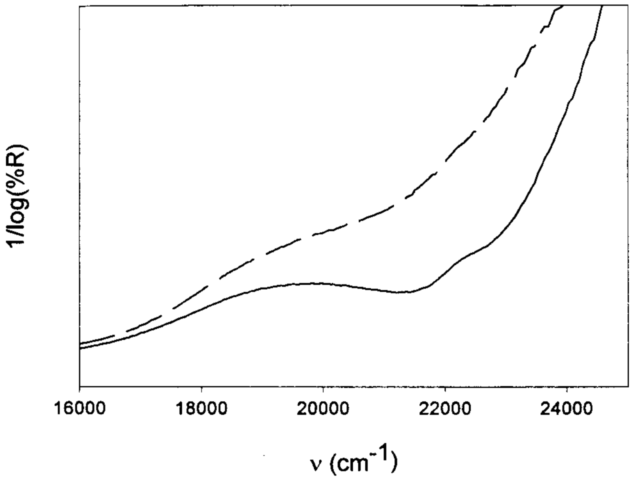

Figure 2. Solid-state reflectance spectra of $[Cr(dmb)_2(NCS)_2]^+$ as I^- (dashed line) and NO_3^- (solid line) salts. The ordinate is 1/log(%*R*) where %*R* is relative reflectance.

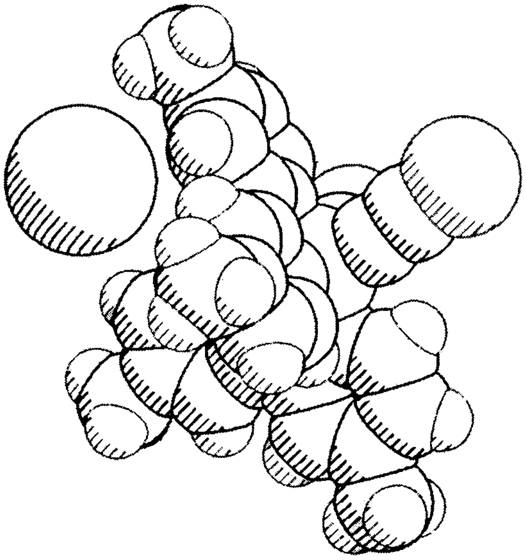

Figure 3. Space-filling view of the X-ray crystal structure of **1** as the iodide salt. A disordered solvent has been omitted for clarity.

(SADABS[11]). Each structure was solved by direct methods and refined by using the Siemens SHELXTL program library.[12]

In the case of $[Cr(dmb)_2(NCS)_2]I$, data was collected at 170 K and refinement employed full-matrix (341 parameters total, data/parameters = 21.7) weighted least-squares refinement on F^2 for all reflections. All non-hydrogen atoms except those in a disordered solvent were refined with anisotropic displacement parameters. The disordered solvent was refined with isotropic displacement factors using partial occupancy at some positions. Hydrogen atoms were included in the structure factor calculations at idealized positions. Further crystallographic information pertaining to the structure is provided in the Supporting Information.

In the case of $[Cr(bpy)_2(NCS)_2](I_3^-)$, data was collected at 173 K and refinement employed full-matrix (307 parameters total, data/parameters = 21.0) weighted lease-squares refinement on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the structure factor calculations at idealized positions. Further crystallographic information, including the structure, is provided in the Supporting Information.

UV−Vis Spectroscopy. Reflectance measurements were taken on a Varian Cary 5000 spectrometer utilizing a diffuse reflectance accessory (Praying Mantis) made by Harrick. One hundred percent reflectance was referenced to a Teflon film. Solution UV−vis spectra were made using a Hewlett-Packard 8452A spectrometer.

Results

UV−Vis Spectra. Reflectance spectra were obtained on solid samples of the I^- and NO_3^- salts of $[Cr(L)_2(NCS)_2]^+$. These solid state spectra (Figure 2) show distinct differences between the two salts. Baker and co-workers previously reported the solid-state spectra of a series of halide and pseudohalide salts of $[Cr(L)_2Cl_2]^+$.[13] They observed similar differences which they attributed to solid-state charge-transfer interactions between the complex and the anion. The energy of the spectral transition increased as $I^- < N_3^- < SCN^- < Br^- < Cl^-$. This proposed charge-transfer interaction was spectrally manifested as a broad high energy band that changed wavelength with the anion. The spectral differences evident in Figure 2 are consistent with these earlier results from Baker et al.[13]

In either acetonitrile or dichloromethane there are essentially no experimentally significant differences in the visible spectra of the I^- and NO_3^- salts of $[Cr(L)_2(NCS)_2]^+$. Crude titrations were also conducted where I^- was incrementally added to solutions of $[Cr(L)_2(NCS)_2]NO_3$ (ca. 4×10^{-4} M, L = bpy or dmb). Again, no evidence of a change in the spectrum (in either dichloromethane or acetonitrile) was detected up to the point where a ca. ×3 molar excess of I^- had been added. However, in concentrated NaI solutions in acetonitrile (0.667 M) spectral changes similar to those observed for the solid I^- salt were evident for $[Cr(dmb)_2(NCS)_2]^+$ (see Figure 1). From these spectra we can estimate a lower limit for the formation constant for the charge-transfer complex under these conditions to be $K_{CT} > 1.5\ M^{-1}$.

X-ray Crystal Structure. Figure 3 shows a space-filling view of the structure of $[Cr(dmb)_2(NCS)_2]I$ determined by X-ray diffraction. The I^- anion sits near and above the plane of one of the dmb ligands. Comparing these results with structural data from several other systems which have been demonstrated to exhibit strong charge-transfer donation by I^-,[14] this structure gives clear indication of a significant charge donation from the I^- into the nearest dmb ligand to it. The closest carbon atom of

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(11) Sheldick, G. M. SADABS, University of Göttingen, Germany, 1997.

(12) Bruker AXS, I. SHELXTL 5.1, Madison, WI, 1998.

(13) Baker, W. A.; Phillips, M. G. *Inorg. Chem.* **1965**, *4*, 915−917.

(14) Bockman, T. M.; Chang, H. R.; Drickamer, H. G.; Kochi, J. K. *J. Phys. Chem.* **1990**, *94*, 8483−8493.

the bipyridine ring sits 3.607 Å from the iodide. It is noteworthy that the I^- seems to be in no way associated with the isothiocyanate ligands.

Attempts to look at possible interactions between I_3^- and the $[Cr(dmb)_2(NCS)_2]^+$ cation were only partially successful. The crystals grown yielded a structure with a largely disordered I_3^- anion, although the cation itself appeared free of disorder. Because the anion constitutes 36% of the electron density in the molecule, refinement was poor (R1 = 0.19). On the other hand, we were able to obtain diffraction quality crystals of $[Cr(bpy)_2(NCS)_2]^+$ cation as the I_3^- salt which refined well (R1 = 0.0453). Again the closest non-hydrogen contact between the ions is between one of the terminal iodine atoms and a carbon of one of the bipyridine ligands (3.711 Å). For other structural examples in which there is evidence for a I_3^-/cation charge-transfer interaction, the reported interaction distances are between 3.70 and 4.11 Å.[15] The relative positioning and separation of the I_3^- and bpy ligand strongly suggest a solid-state charge-transfer interaction in $[Cr(bpy)_2(NCS)_2]I_3$ similar to that for I^- in $[Cr(dmb)_2(NCS)_2]I$. Unfortunately, because of the interference from the strong, broad I_3^- spectral band we were not able to obtain the same sort of corroborating spectral data with I_3^- as was possible for I^-.

Discussion

It is unfortunate that all attempts to prepare $[Cr(Bp\text{-}COOH)_2(NCS)_2]^+$ were unsuccessful. Nevertheless, the information obtained from $[Cr(L)_2(NCS)_2]^+$ with L = bpy and dmb could in some respects be more useful. There are indisputable structural differences between these complexes and an $N3^+$ dye adsorbed on a TiO_2 surface. However, Cr(III) complexes incorporating more electron-rich ligands such as dmb and bpy are in some regards a more stringent test of the potential relevance of a $N3^+-I^-$ charge-transfer interaction (than would be the complex with the more electron deficient Bp-COOH ligand).

A second point for consideration is the choice of metal center in these surrogates. Cr(III) and Ru(III) have the same charge, which is surely an important factor in any charge-transfer interactions involving I^- (vide infra). The major difference in the $N3^+$ and the surrogates, however, is their redox chemistry—the respective M(II/III) potentials differ by considerably more than 1.0 V.[16] As a result, the Ru(III) complex readily oxidizes I^- whereas the Cr(III) complex does not. Given this difference in $E°$'s, it is reasonable to ask how the proposed charge-transfer interaction might be affected by these differences in metal redox chemistry. From the relative positions of the I^- and the $[Cr(dmb)_2(NCS)_2]^+$ cation in the solid-state structure, the charge-transfer process must involve the donation of electron density from I^- into the π^* orbital of the bipyridine ligand and not directly into the metal (the Cr−I distance is 7.253 Å). Therefore, the relevant issue is how the central metal influences the acceptor ability of the bipyridine. To a good approximation, the answer to that question would be given if the reduction potential of the bipyridine ligands in each respective complex were available. Unfortunately, that information is not directly obtainable because the Ru(III) reduces more easily than the bound bipyridine and the first reduction of $[Cr(dmb)_2(NCS)_2]^+$ is chemically irreversible. However, some useful insights can be gained by considering the ligand-based reduction processes for some related complexes.

First, consider the reduction of RuL_3^{2+} and ZnL_3^{2+} where L is any of several diimine ligands including bpy, dmb and phenanthroline. Despite the fact that Ru(II) and Zn(II) have dramatically different redox chemistry, the first ligand-based reduction potentials are essentially identical.[17] Moreover, this situation extends to FeL_3^{2+} and OsL_3^{2+} as well. In contrast, for the 3+ charged AlL_3^{3+} complexes, the first ligand-based reduction occurs at a potential approximately 400 mV more positive than for each of the 2+ charged analogues.[17] These results suggest that, to a good first approximation, the donor ability of a diimine-type ligand in a metal complex should be sensitive to the charge on the metal but not to its identity or redox chemistry. Consequently, we conclude that the Cr(III) complexes under consideration here should be reasonably similar to their Ru(III) counterparts insofar as I^-/bipyridine and I_3^-/bipyridine charge-transfer interactions are concerned. Finally, even if there were a fallacy in this argument as it applies to $[M(L)_2(NCS)_2]^+$ compounds, any difference would be expected to favor the donor ability of the bipyridines in Ru(III) complexes.

Grätzel et al. dismissed the possibility of (I^-,$N3^+$) pair formation because they speculated the interactions would have to include the sulfur of the isothiocyanate ligands.[9] Under those circumstances, the surface charge on the TiO_2 electrode should have minimal influence on any (I^-,$N3^+$) interaction. An interaction between I^- and Bp-COOH ligands, on the other hand, would place the I^- close to the semiconductor surface. There the interaction would be subject to a much greater influence of the charge-state of the TiO_2 surface.

Conclusion

In almost every respect, the $[Cr(L)_2(NCS)_2]^+$ complexes chosen for this study should be poorer electron acceptors than $N3^+$. Therefore, we contend that the demonstration of a charge-transfer interaction between the diimine ligands and I^- in these complexes argues strongly that a similar interaction between I^- and $N3^+$ in the operating Grätzel cell cannot be dismissed as a possibility. Furthermore, such an interaction potentially could be involved in the unique function of the I^-/I_3^- couple in this cell.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Zurcher, S.; Petrig, J.; Gramlich, V.; Worle, M.; Mensing, C.; von Arx, D.; Togni, A. *Organometallics* **1999**, *18*, 3679−3689.

[16] The $[Cr(dmb)_2(NCS)_2]^+$ complex undergoes a chemically irreversible reduction with an E_p of −0.82 V vs SCE in acetonitrile. Moreover, it is likely that this reduction might be ligand-based.

[17] Hershenhart, E. J. Ph.D. Dissertation, *Part I. An Electrochemical Comparison of the Cobaloxime and $Co[C_2(DO)(DOH)_{pn}]$ Model Complexes to Coenzyme B_{12}. Part II. Electrochemical and Spectral Investigations of Ring-Substituted Bipyridines and Their Complexes with Ruthenium*, University of Vermont, Burlington, VT, 1983.