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Co(tacn)(NCS)$_3$ Synthesis and Thiocyanate Photosubstitution. Yield Enhancement by Added Thiocyanate

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The complex Co(tacn)(NCS)$_3$ (tacn = 1,4,7-triazacyclononane) has been prepared and characterized by elemental analysis, NMR, IR, and UV−vis spectroscopy, and conductivity measurements. It is thermally stable in dmso and aqueous/dmso solution but, on irradiation of the latter solutions at 360 nm, undergoes parallel photosubstitution processes to form dmso- and aqua-substituted products with a quantum yield of 0.012 ± 0.005. Under these conditions, no photoredox reaction was detected. On addition of thiocyanate ion to the solutions, the product yields were increased in an almost linear fashion. For 1 M thiocyanate solution, the quantum yield for disappearance of the starting complex rose to 0.022 ± 0.002 and a small redox yield of 0.0008 ± 0.0003 was found. Under these same conditions, nanosecond laser flash photolysis at 355 nm revealed a transient absorption owing to (NCS)$_2^{-\bullet}$, which was produced with an estimated quantum yield of 0.036. These results were interpreted in terms of scavenging of radical pair species by thiocyanate ion followed by back electron transfer to give photosubstituted product. Comparison with results for other ammine thiocyanate systems shows that the distribution of redox versus substitution products depends on the rate of loss of the strong field ligands from the Co(II) fragment of the radical pair. A radical pair yield of 0.29 and lifetime of 12 ps was derived from a kinetic model of the scavenging by thiocyanate. The final recombination step between the Co(II) fragment and (NCS)$_2^{-\bullet}$ was shown to be second-order and, hence, that it was a bulk recombination process with $k = 6 \times 10^9$ M^{-1} s^{-1}.

Introduction

It is well-known that cobalt(III) acido am(m)ine complexes undergo photoredox reaction on irradiation in their charge transfer bands, and the quantum yield for redox decomposition is high relative to that for photosubstitution.[1−3] The accepted mechanism via a radical-pair species was postulated by Adamson[4,5] and was supported by wavelength and viscosity dependence studies.[3,6,7] Attempts to obtain direct spectroscopic evidence for a putative radical pair species in photoredox of some thiocyanato−cobalt(III) cations were not successful,[8,9] however.

It was found[9] that on irradiation near the threshold wavelength for redox reaction of dithiocyanatotetram(m)inecobalt(III) complexes in the presence of thiocyanate, a significant increase in photoredox yields occurs. This raised questions regarding the role of inner- and outer-sphere electron transfer in the primary process and the mechanism of scavenging by thiocyanate ion in these systems. It was found possible to model those results equally well in terms of thiocyanate ion scavenging of the thiocyanate radical from an initial caged radical pair having a lifetime of tens of picoseconds, the kinetic model, or in terms of photolysis of a thiocyanate/cobalt complex ion pair, the ion pair model. There was no good basis on which to distinguish the two.

The present work reports an approach to settling this issue. A zero-charged complex should be susceptible to thiocyanate enhancement of redox yields by any scavenging mechanism but would not form ion pairs, thus turning off any ion-pair outer-sphere electron transfer mechanism. We therefore sought a thermally stable triam(m)inetrithiocyanatocobalt(III) complex. We were concerned that the goal might be difficult as increasing the number of weak field ligands destabilizes Co(III) complexes. Few such compounds appear to be known, and the closest described[10] is Co(dan)(SCN)$_3$, where dan = 1,4,7-triazaheptane. This compound was reported to be prone to thermal solvolysis. We therefore chose as a more promising target Co(tacn)(NCS)$_3$ (where tacn = 1,4,7-triazacyclononane) on the basis of the probable stability of the Co(tacn) moiety. This complex was synthesized and characterized, and its more than adequate thermal stability was established. These results and its photochemical behavior are reported in this paper.

Experimental Section

Synthesis of Co(tacn)(NCS)$_3$. tacn·3HCl, 0.80 g (3.3 mmol), was mixed with a stoichiometric amount of freshly prepared sodium ethoxide in ethanol. The resulting sodium chloride was filtered off, leaving the free amine in ethanol. CoCl$_2$, 0.65 g (5 mmol), and 1.5 g of KNCS (15 mmol) were then added to this solution and air bubbled through the mixture until the color turned from blue to brownish (ca. 12 h). After removal of the excess reactants by extraction with 0.1 M aqueous hydrochloric acid, a tan compound was obtained. This was dissolved into the minimum amount of dmso, and the filtered solution was then added dropwise into a 100-fold volume of water. The

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orange powder that formed was washed with water, ethanol, and ether and was dried under vacuum. The total yield was 0.62 g (52%). The compound was soluble in dmso, dmf, and pyridine but insoluble in nonpolar solvents as well as in ethanol, thf, acetonitrile, ethyl acetate, formamide, and water. It was stable in air and in dmso or aqueous/dmso solutions.

The compound was characterized using the elemental analysis, NMR, IR, UV−vis, and conductivity data that follow. Anal. Found (calcd) for $CoC_9H_{15}N_6S_3$: C, 29.88 (29.83); H, 4.07 (4.17); N, 22.65 (23.19); S, 27.06 (26.54). ^{1}H-NMR (dmso-d_6): δ 2.59 (6.6H, CH_2), 2.98 (5.4H, CH_2), 7.94 (2.8H, NH). (Compare tacn·3HCl in dmso-d_6, δ 3.4 (12.0H, CH_2), 4.3 (6.6 H, br, NH + HCl); or in D_2O, δ 3.4 (12.0H, CH_2).) ^{13}C-NMR (dmso-d_6): δ 51.2 (CH$_2$), 139.1 (NCS). (Compare tacn·3HCl in D_2O, δ 42.1 (CH$_2$).) ^{14}N-NMR (D_2O) for tacn·3HCl: δ −340.5 (standard reference CH$_3$$NO_2$). IR, cm^{-1}: 3440 (s, br) and 3100 (s, br), ν(NH); 2100 (s), ν(CN); 1620(w) and 1340 (w), δ(NH); 815, ν(CS); 485, δ(NCS). UV−vis in v/v = 1/1.5 acidic H_2O/dmso [λ_{max}, nm (ϵ)]: 507 (5.10×10^2), 342 (3.85×10^3); $\epsilon_{L2}/\epsilon_{L1} = 7.55$. Conductivity μS/cm: 2.6; compare to NaCl, 31.1, and $CaCl_2$, 39.6 (all corrected for solvent).

Red crystals were obtained by dissolving the above tan powder into dmso and evaporating in a stream of air overnight. After careful washing with cold dmso and drying under vacuum, these monoclinic crystals were found by elemental analysis to be $Co(tacn)(NCS)_3 \cdot 3dmso$. Anal. Found (calcd) for $CoC_{15}H_{33}N_6S_6O_3$: C, 30.13 (30.19); H, 5.49 (5.57); N, 14.25 (14.08); S, 30.87 (32.32).

Synthesis of $Co(Me_3tacn)(NCS)_3$. An analogous preparation starting with *N,N',N''*-trimethyltriazacyclononane, a yellowish oil prepared by the reaction of free tacn with excess HCOOH/HCHO,[11] gave a crude tan product of which the solubility in all solvents tried was not improved compared with $Co(tacn)(NCS)_3$. It was therefore not explored further.

Analysis and Spectroscopy. C, H, N, and S analyses were performed by Canadian Microanalytical Service Ltd. (Delta, British Columbia, Canada). Cobaltous ion Co^{2+} was determined according to a literature procedure[12] by forming the blue complex ion $Co(NCS)_4{}^{2-}$ in a water−dmso−acetone solution and measuring the absorbance at 625 nm in a 10 cm glass cell (calibration data $A = (2.02 \pm 0.02) \times 10^4[Co^{2+}] - (0.001 \pm 0.004)$ with correlation coefficent $R = 0.9999$). Infrared spectra were obtained in KBr pellets by using a Bruker IFS-25 FTIR spectrophotometer coupled with an IBM PS/2 Model 50-Z computer. UV−vis spectra were run on a Philips PU 8740 UV/vis spectrophotometer or Cary 5 UV−vis−near-IR spectrophotometer using 1 cm quartz cells. Conductivity measurements were carried out by using a CDM 83 conductivity meter with 1.0×10^{-3} M solutions. ^{1}H-NMR, ^{13}C-NMR, and ^{14}N-NMR were run on a Bruker AMX 360 MHz NMR spectrometer. The chemical shifts (δ, ppm) were reported relative to tetramethylsilane (TMS) unless otherwise specified. Solution pH values were determined with a Fischer "Accumet" 910 digital pH meter and Ingold electrode calibrated with appropriate buffers.

Chromatography. A Varian 5000 liquid chromatograph was used with a 25 × 0.46 cm Chromatographic Sciences ODS2 10 μm C18 column. The eluents used were 25 mM in sodium hexanesulfonate (Aldrich, 98%) as ion interaction reagent and 20 mM in triethylamine hydrochloride (Aldrich, 98%) as competing ion, dissolved in organo-pure water (SYBRON/Barnstead Nanopure-A system) and in 95% HPLC grade methanol. The pH of the eluent was adjusted to 3.5 (unless otherwise specified). The best separations were obtained by using a 30% isocratic combination of these two eluents with a flow rate of 2 mL·min^{-1}. Peaks were detected by a Varichrom variable-wavelength detector at 310 nm (unless otherwise specified), which is close to the band maximum of most of the reactants and products. This technique gave rapid and good separation of all the peaks of interest. Quantitative analyses were based on peak areas determined by cutting and weighing of photocopies combined with calibration with pure starting complex and consideration of molar absorptivity ratios from difference spectroscopy for product peaks, discussed later.

Photochemical Procedures. An Osram HBO 100 W mercury lamp was used as a light source for steady-state measurements of quantum yields. The light was filtered through a Corning CS 7-60 filter and a monochromator set at 360 nm, with 5 cm of water as an infrared absorber. The lamp intensity was measured by ferrioxalate actinometry to be in the range of 1 to 4×10^{-8} einstein·s^{-1},[13,14] and as a check, the light intensity was continuously monitored with an Alphametrics Model P111OS silicon diode detector and Model 1020 meter. Solutions were irradiated with magnetic stirring in 1 cm rectangular glass cells thermostated at 20.0 ± 0.1 °C. The solvent used was 1/1.5 v/v 2×10^{-3} M aqueous perchloric acid/dmso solution, and the concentration of complex was typically 5.30×10^{-4} M. The solutions were photolyzed to conversions less than 15% (unless otherwise specified) to minimize secondary photolysis.

A Spectra Physics YAG laser with GCR-12 harmonic generator/Spectra Physics Model PHS-1 wavelength separator was used for flash photolysis studies. The laser pulse characteristics were 355 nm, 7 ns half-width, and 60 mJ energy. In transient measurements at fixed wavelength of absorption, a 150 W Oriel Xe-arc lamp and a CVI Model Digikrom 240 monochromator were used together with two 435 nm cut off filters. One filter, placed between the lamp and sample, minimized photolysis of the sample, while the other, set in front of the monochromator, cut off environmental and scattered light. Solutions were adjusted to absorbance 0.3 at 355 nm in 7 × 7 mm^2 quartz cells with rubber septa and deaerated and stirred between laser shots by N_2 bubbling which was paused for data collection. The solutions were irradiated at 355 nm for 10 laser shots while the $(SCN)_2{}^{-\bullet}$ transient absorption signal was detected at 475 nm. Data were collected by a TDS 520 Tektronix oscilloscope.

Time-resolved absorption spectra were obtained using the same procedures but with detection using an intensified dual diode array system (Princeton Instruments DIDA 700/RG, detector controller ST116, ISA Spectrometer HR-320 and high-voltage gating pulse generator PG200).

A dc-conductivity quartz flow cell with three 0.5 mm diameter × 10 mm long Pt electrodes was used in a Wheatstone bridge configuration as input to a fast amplifier (×30) and the TDS 520 oscilloscope to obtain transient conductivity data after excitation with a 7 ns, 40 mJ pulse of 355 nm light during the application of a 150 V, 4 ms pulse to the Wheatstone bridge circuit.

Results

Characterization of $Co(tacn)(NCS)_3$. The elemental analysis and NMR results establish the identity of this compound and its purity, which is confirmed by chromatography (*vide*

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infra). The large positive chemical shift of N*H*, $\Delta\delta = 7.9 - 4.3 = 3.6$, in the complex indicates that coordination to the cobalt center of the tacn nitrogen reduces its electronic density and deshields its proton, shifting δ to lower field. The two CH_2 peaks found in the complex NMR compared with the one found in the free ligand reveal the magnetic inequivalency of the CH_2-CH_2 protons expected upon coordination. The very small conductivity compared to that of NaCl (1:1 electrolyte) and $CaCl_2$ (1:2 electrolyte) demonstrates that the complex synthesized is a neutral molecule in solution.

The bonding mode of the thiocyanate ligands can be decided from the IR spectrum. The bands observed at 815 (ν(CS), N-bonded) and 485 cm^{-1} (δ(NCS), N-bonded) and the absence of bands in the range 690–720 (ν(SC), S-bonded) and near 420 cm^{-1} (δ(SCN), S-bonded) show that they are N-bonded,[15] consistent with findings for other cobalt(III) thiocyanate am(m)ine complexes.[9]

The ratio of the UV–vis molar absorptivity maxima for the two ligand field bands, L_1 and L_2, in increasing energy, is 7.6 in this compound, similar to other N-bonded cobalt(III) thiocyanate am(m)ine analogues (8.2–10.5) but far smaller than is found in the S-bonded types (211).[9,16] This also supports N-bonded thiocyanate in the complex synthesized.

We were pleasantly surprised by the thermal stability of the compound in aqueous/dmso solutions. No kinetic studies of the thermal reaction were deemed necessary, as solutions were stable at room temperature over several hours, sufficient that no interference, before, during, or after irradiation occurred from thermal processes involving reactant or products.

Photoreaction. The complex underwent both photoredox and photosubstitution reactions on steady-state irradiation at 360 nm and 22 °C in 1.0 M sodium thiocyanate in a 1/1.5 v/v 2×10^{-3} M aqueous perchloric acid/dmso medium. The photoredox quantum yield, $\phi(Co^{2+})$, was found to be 0.0008 ± 0.0003 (4 determinations), much smaller than that for its analogues *cis/trans*-$Co(en)_2(NCS)_2^+$ (0.026 and 0.023, respectively) and *cis/trans*-$Co(NH_3)_4(NCS)_2^+$ (0.153 and 0.146, respectively) under similar conditions.[9] In the absence of added thiocyanate, $\phi(Co^{2+})$ was too small to be measured.

On laser flash photolysis of all solutions, the transient signal corresponding to the dithiocyanate radical ion $(NCS)_2^{-\bullet}$ ($\lambda_{max} = 475$, $\epsilon = 7.6 \times 10^3$ M^{-1} cm^{-1} [17]) was observed. The absorption was very weak in the absence of added thiocyanate ion and increased almost linearly with its addition. The transient absorption decayed by second-order kinetics, and Figure 1 shows the result obtained in 2 M $NCS^-/dmso/H^+$ solution. Figure 2 shows the estimated quantum yield of dithiocyanate radical $\phi((NCS)_2^{-\bullet})$ as a function of thiocyanate concentration. These estimates were based on the observed absorbance change at 475 nm, the laser pulse energy, the solution absorbance at 355 nm, and the geometry of the beam intersection region for the analyzing and laser beams; the concentration dependence can be relied on, but the absolute yields may be subject to systematic errors and to our assessment of a ±10% relative uncertainty. For 1 M thiocyanate ion, Figure 2 gives a $\phi((NCS)_2^{-\bullet})$ of 0.036 which is just over 50% larger than ϕ(total) for disappearance of starting material measured chromatographically of 0.022 ± 0.002(4). In the absence of thiocyanate, the corresponding yields are about 0.004 and 0.012 ± 0.005(6), respectively, so that photosubstitution has about three times the quantum yield of the photoredox intermediate $(NCS)_2^{-\bullet}$.

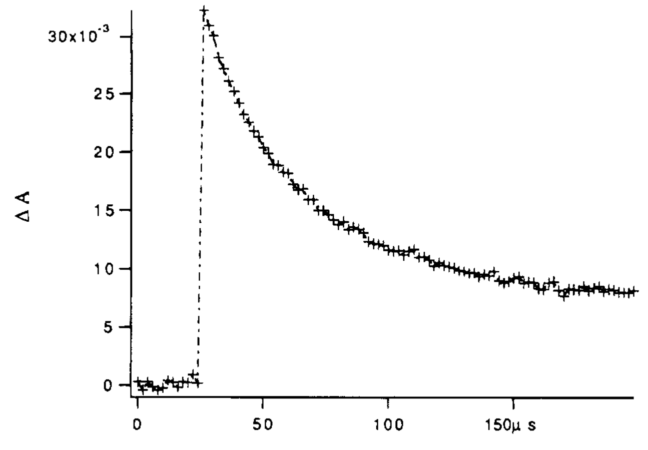

Figure 1. Decay of the $(NCS)_2^{-\bullet}$ transient absorption at 475 nm for 1.20×10^{-4} M $Co(tacn)(NCS)_3$ in 2 M $NCS^-/dmso/H^+$ solution.

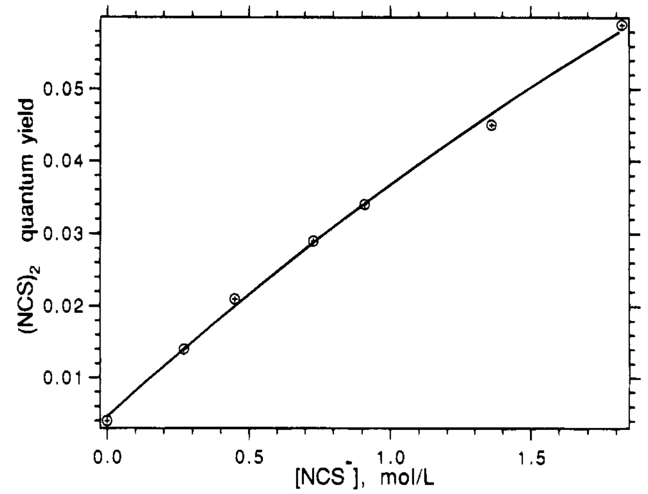

Figure 2. Quantum yield of $(NCS)_2^{-\bullet}$ from $Co(tacn)(NCS)_3$ vs $[NCS^-]$ by laser flash photolysis experiment: marker, experimental points; line, fit to the kinetic model discussed in the text.

These results indicate that pure $Co(tacn)(NCS)_3$ is rather photoredox inert but that the addition of thiocyanate can enhance its yield of photoredox intermediates, and the main concurrent photosubstitution reaction is also enhanced under these conditions. In all cases photosubstitution dominates; e.g. in 1 M NCS^- solution, about 96% photosubstitution product is found with 4% Co^{2+} photoredox product. A study of these predominant photosubstitution reactions was therefore undertaken using HPLC chromatography to analyze the photoproducts, coupled with UV–vis difference spectroscopy and some thermal kinetics experiments. Note at the outset that substitution of the tacn ligand at one or more coordination sites is quite unlikely. The thermal stability of the photoproducts commented on in the following is inconsistent with the possible formation of protonated partially coordinated tacn species analogous to those formed in photoreactions of other polyamine complexes. Linkage isomerization is another possibility to be considered; here one would expect the product $Co(tacn)(NCS)_2(SCN)$. Small amounts of this species would be hard to detect (it would likely elute with the starting material under the chosen chromatographic conditions) and could have been missed.

To explore the question, a 1.19×10^{-4} M $Co(tacn)(NCS)_3$ solution in the $dmso/HClO_4$ medium, $A_{355} = 0.39$, was flashed

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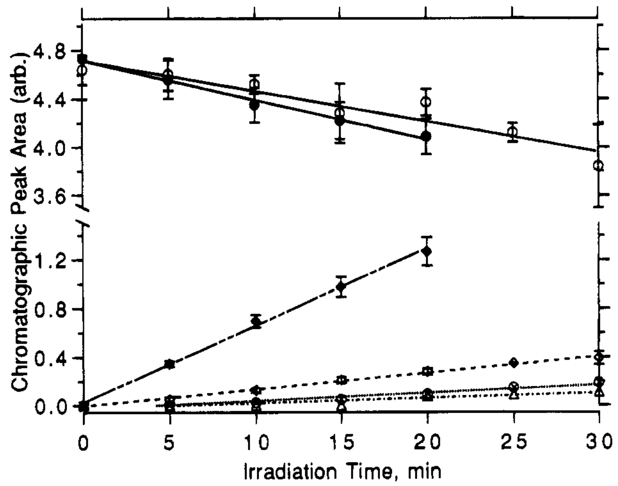

Figure 3. Experimental (markers) and theoretical fittings (lines) for HPLC results of 5.30 × 10^{-4} M Co(tacn)(NCS)$_3$ photolysis. Standard deviations are based on a norm of 5 measurements. The letter in parentheses identifies the corresponding chromatographic peak. Key: (○) Co(tacn)(NCS)$_3$ (A) in dmso/H$^+$; (◇) Co(tacn)(NCS)$_2$(dmso)$^+$ (B) in dmso/H$^+$; (⊗) Co(tacn)(NCS)(dmso)$_2^{2+}$ (C) in dmso/H$^+$; (△) Co(tacn)(NCS)$_2$(H$_2$O)$^+$ (D) in dmso/H$^+$; (●) Co(tacn)(NCS)$_3$ (A) in 1 M NCS$^-$/dmso/H$^+$ (◆) Co(tacn)(NCS)$_2$(dmso)$^+$ (B) in 1 M NCS$^-$/dmso/H$^+$.

with 40 mJ of 355 nm light and the transient conductivity change compared with the blank without the Co complex. A (noisy) conductivity increase with a rise time of tens of microseconds was observed, demonstrating the generation of ionic products by photolysis. Together with the following experimental data this supports ligand substitution as the major process.

Identification of Photosubstitution Products. As shown in Figure S1, an unphotolyzed solution of starting complex gave a major peak (A) at retention time (t_R) of 3.6 min and two small impurity peaks, B and C, which corresponded to less than 4% of the total peak area. On irradiation of the complex in the absence of thiocyanate, a clear product peak, B, grew in at the expense of the starting material, which it just preceded in the elution sequence (at t_R = 2.7 min). The area of peak B increased linearly with irradiation time (Figure S1a–c and Figure 3). At somewhat higher conversions it became evident that two additional peaks, C at t_R = 8.3 min and coincident with the impurity peak mentioned above and a new peak (D), t_R = 5.4 min, were also being produced, Figure 3. No other peaks appeared for conversion less than 15%. Because of the small size of peaks C and D, it was not possible to decide from their growth kinetics alone whether they were secondary or primary photolysis products; see later. The starting complex (peak A) disappeared linearly with irradiation time as also shown in Figure 3.

In contrast, in the presence of 1 M thiocyanate, the behavior was simpler: peak B again grew linearly but at about five times the rate in the absence of added thiocyanate and peak C remained essentially constant at the impurity level while D did not appear; the reactant (peak A) decreased linearly about 30% faster (Figure S1d and Figure 3).

During these sequences of irradiations, the UV–vis spectral changes were monitored, Figure 4. Without thiocyanate, Figure 4a, reasonable isosbestic points were seen at 335, 411, 454, and 545 nm. A peak grew in at 290 nm. It should be noted that, at the irradiation wavelength of 360 nm, Δ*A* was negative, showing that products were less strongly absorbing than the starting complex. This bears later on the question of secondary photolysis. With 1 M thiocyanate, similar isosbestic points were seen at 365, 383, 460, and 537 nm, and a similar peak grew in at 290 nm with much greater absorbance. For both sets of conditions, the ligand field band of the product was red shifted relative to the starting material, consistent with replacement by solvent of the stronger field thiocyanate ligand. The band developed at 290 nm is consistent with a charge transfer transition from dmso/H$_2$O to cobalt(III). These difference absorption spectra were combined with the percent conversion data for the starting complex measured chromatographically to obtain calculated absorption spectra for the photoproduct mixtures obtained in the two sets of experiments. These are shown in Figure S2a,b, displayed in terms of apparent molar absorptivity to emphasize that they correspond to some undetermined mixture of product absorption spectra, not to a single compound.

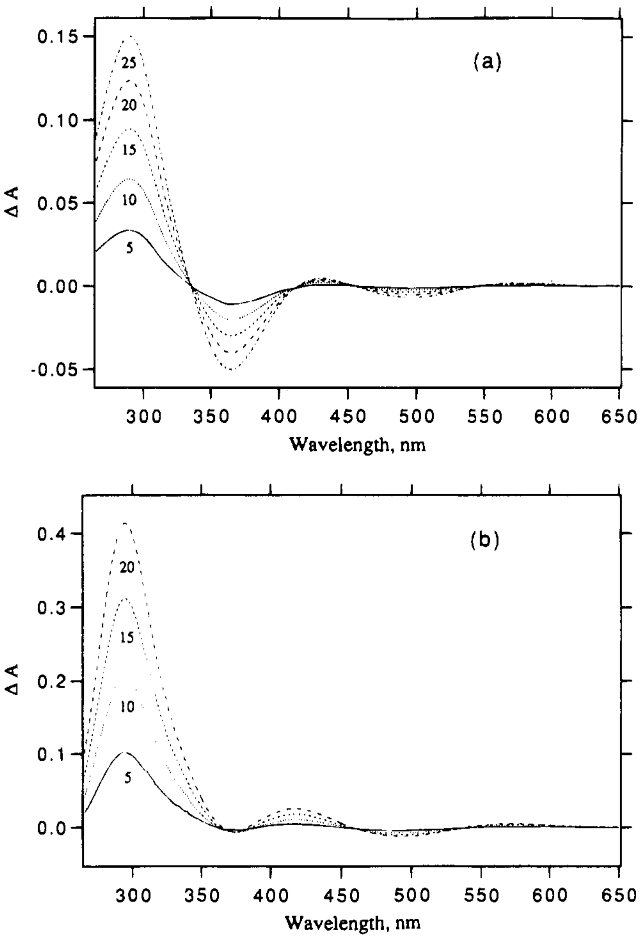

Figure 4. Difference absorption spectra changes for photolysis of 5.30 × 10^{-4} M Co(tacn)(NCS)$_3$ measured against an unphotolyzed aliquot for different irradiation times (minutes) as shown in the figure: (a) in dmso/H$^+$ solution; (b) in 1 M NCS$^-$/dmso/H$^+$ solution.

The identification of the main product chromatography peak B was as follows. It was likely to correspond to the product seen spectroscopically, Figure 4, with UV–vis $\lambda_{max} \approx 290$ nm, or to the photoredox product Co(NCS)$_4^{2-}$, which has λ_{max} at 320 nm and apparent ϵ_{320} = 7.68, 9.08, or 11.4 × 10^3 M^{-1} cm^{-1} in 0.5, 1.0, or 2.0 M NCS$^-$ solution. Note that these spectral data do not exhibit the very high molar absorptivity ratio for the second to first ligand field bands expected for the linkage isomer. Several pieces of evidence support the first assignment. Table S1 (nos. 1–3) shows that the peak height observed for B was reduced as the HPLC detection wavelength was changed from 300 to 310 to 320 nm, as would be expected for the product with $\lambda_{max} \approx 290$ nm. Next, injection of authentic Co(NCS)$_4^{2-}$ did not give any peak in the chromatogram, presumably because of its lability and interactions with the components of the eluent. When chloride anion was added into the photolyzed solution, no change in peak height of B was observed (Table S1, nos. 4 and 6). The significance of this is that chloride competes effectively with thiocyanate in the equilibrium

$$Co(NCS)_4^{2-} + 4Cl^- \rightleftharpoons CoCl_4^{2-} + 4NCS^- \qquad (1)$$

for which K is calculated to be 195 (in dmso) from literature data[18] to produce a species with ϵ_{310} almost zero. Last, in the absence of thiocyanate, the photoredox of the complex was barely detectable, but the major product (peak B) still appeared under these conditions. These observations rule out the redox product $Co(NCS)_4^{2-}$ and point to a photosolvation product, $Co(tacn)(NCS)_2S^+$, where S could be either water or dmso.

The choice of S was explored by irradiation in dry dmso solution. Peak B behaved almost in the same manner no matter whether there was water in the solvent or not (Figure S1e). As additional evidence, no band shift occurred in the UV−vis spectrum of a photolyzed solution on addition of ammonia. Aquo−Co(III) complexes show a red shift under these conditions owing to equilibria like

$$Co(tacn)(NCS)_2(H_2O)^+ \underset{+H^+}{\overset{+OH^-}{\rightleftharpoons}} Co(tacn)(NCS)_2(OH) \qquad (2)$$

These results show that peak B is the dmso-substituted product, $Co(tacn)(NCS)_2(dmso)^+$. Notice that the calculated total product spectra of Figure S2 have the same $\lambda_{max} \approx 300$ nm and two shoulders at ca. 320 nm and 335 nm, indicating the formation of the same major species in the absence and presence of added thiocyanate. The apparent molar absorptivity is much higher at λ_{max} in the presence of thiocyanate than in its absence. The peak at 300 nm apparently corresponds to an overlap of $Co(tacn)(NCS)_2(dmso)^+$ with the the more strongly absorbing ion pair $\{Co(tacn)(NCS)_2(dmso)^+,NCS^-\}$. The shoulder at 320 nm can arise from the small amounts of Co^{2+}.

The identities of the minor products (C and D) were explored by a series of reaction studies. They have to be photoproducts because their peak height did not increase on standing at room temperature in the dark up to 1.5 h. On heating of a photolyzed thiocyanate-containing dmso/H^+ solution at 80 °C for 30 min, the height of peak B decreased, while peaks A (starting material) and C both increased (Table S1, compare no. 4 with no. 5 and no. 6 with no. 7). This experiment was consistent with expectations for the thermal reaction of peak B, which can reanate to starting material on heating with thiocyanate or can solvate a further thiocyanate ligand, consistent with C as the $(dmso)_2$ product. The t_R of 8.4 min is about the value to be expected for a 2+ ion of type $Co(tacn)(NCS)(dmso)_2^{2+}$, and this same peak was also developed in the solution when no water was present in the solvent. The remaining product is peak D at a retention time of 5.4 min. This peak did not appear in the chromatography when pure dmso was used as solvent (Figure S1e). The retention time of 5.4 min suggests a singly charged cation, and an obvious candidate is $Co(tacn)(NCS)_2(H_2O)^+$. To explore for an aquo ligand, the eluent pH was changed from 3.5 to 9.0; peak D then disappeared, while a new peak, E, appeared at $t_R = 2.4$ min, prior to $Co(tacn)(NCS)_2(dmso)^+$ (Figure S1f). This is consistent with the formation of a zero-charged complex $Co(tacn)(NCS)_2(OH)$ in the basic solution, according to

$$Co(tacn)(NCS)_2(H_2O)^+ \xrightarrow{+OH^-} Co(tacn)(NCS)_2(OH) \qquad (3)$$

An alternate possibility that $D = Co(tacn)(NCS)(dmso)(H_2O)^{2+}$ is less likely since this doubly-charged cation and its conjugate base form should have longer retention times than observed. We conclude that peak D is the aquation product $Co(tacn)(NCS)_2(H_2O)^+$.

The elution order for the photoproduct peaks implied by these results is reasonable. Peaks generally elute in order of increasing charge and greater ligand hydrophobicity. The only exception observed is for the starting complex, which has zero charge and could be expected to be the first peak eluted. But it is hard to compare an elution time for a neutral hydrophobic species on a C18 phase with those resulting from the interactions of charged ions also possessing hydrophobic ligands with an ion-interaction reagent, a competing ion, and the electrical double layer associated with the C18 phase. Complicated elution sequences were also discovered in other tacn/thiocyanate complexes and were similarly attributed to the importance of hydrophobicity in the interactions involved.[19]

Primary vs Secondary Photolysis. Reaction Stoichiometry. Are C and D primary photoproducts or do they result from secondary photolysis of B? Figure 4a,b shows definitively that, at the irradiation wavelength of 360 nm, the products absorb less strongly than the reactant. Significant secondary photolysis under these circumstances would be most unusual, and calculations based on a simple theory[20,21] show it could occur only if B had a much larger photoreaction quantum yield than A. Given the similarity of these complexes, this is most unlikely to be true. This and the linear time dependence of these product peaks, Figure 3, indicate that they are primary products and suggest that the photochemistry in the absence of thiocyanate follows a number of parallel paths involving substitution of one or more ligands.

There is also stoichiometric evidence for such complexity. Figure 3 shows chromatographic peak area versus photolysis time curves. To calibrate these data one would ideally use isolated authentic samples of each product, but these were not available. Peak area is proportional to ϵ at 310 nm, the HPLC detector wavelength, and this is shown calculated for the photoproduct mix in Figure S2. Figure S2a indicates that $\epsilon_B/\epsilon_A = 1.4$, while Figure S2b gives 2.3 for the same ratio in 1 M thiocyanate. The first figure is likely too low because the photoproduct mix known to occur probably has lower absorbance than pure B due to the presence of C and D, while the second figure is likely too high because of intensity enhancement owing to ion-pair formation.[9] In 1 M thiocyanate, only one product, B, is formed to any significant extent, and from Figure 3, the rate of decrease in the complex, A, should match the rate of increase in the product, B; this will occur if $\epsilon_B/\epsilon_A = 2.0$. It seems reasonable to accept this value as a calibration factor consistent with the spectral data and to use it to convert the Figure 3 areas into molar quantities together with the assumption that $\epsilon_B = \epsilon_C = \epsilon_D$ at 310 nm. On summing of B, C, and D for the photolysis in the absence of thiocyanate, it becomes clear that about 40% of the complex has simply disappeared without leading to observed products. This could occur if triply charged products, which would not elute under these HPLC conditions, were being formed. We conclude that the course of the photoreaction is complex in the absence of added thiocyanate and leads to a multitude of products formed in parallel, while the addition of thiocyanate removes this complexity, moving

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the system closer to a simple A → B behavior. In the discussion we will argue that the reason is thiocyanate scavenging of highly reactive radical pair species to produce $(NCS)_2^{-\bullet}$ which results in a simplification of the products found.

Discussion

Mechanism of Photosubstitution. Photosubstitution is clearly the main photoreaction pathway of Co(tacn)(NCS)$_3$ for irradiation at 360 nm, and photoredox reaction is relatively minor. Both pathways are more efficient and the photochemistry less complex in the presence of added thiocyanate. The accepted models for cobalt(III) photochemistry recognize the possibility of formation of both redox and substitution products by a radical pair mechanism,[4,5] together with photosubstitution occurring via internal conversion to low-lying ligand field states, triplet and/or quintet in nature. Such metastable states have been observed by picosecond transient absorption spectroscopy[22] but have not yet been directly shown to lead to substitution.

The question immediately arises as to whether the observed redox and substitution modes occur in parallel or consecutively. For the reaction in the absence of added thiocyanate this is not obvious; the photosubstitution yield is higher than the yield of $(NCS)_2^{-\bullet}$, but this is misleading as the initial radical pair species does not give an observable transient absorption. The photosubstitution observed is complex, involving more than one ligand loss, and this is quite unlike the usual photoreaction from ligand field excited states. This leads one to suspect that a complex redox mechanism is operating.

In contrast, the reaction in thiocyanate looks like a clean consecutive process and we propose it occurs also through the radical pair mechanism, supplemented with a thiocyanate scavenging step. This can be represented in a simplified manner as

$$\mathrm{Co(tacn)(NCS)_3} \xrightarrow{\phi_{\mathrm{RP}}} \{\mathrm{Co^{II}},{}^{\bullet}\mathrm{NCS}\} \quad \text{(radical pair (RP) formation)} \quad (4)$$

$$\{\mathrm{Co^{II}},{}^{\bullet}\mathrm{NCS}\} \rightarrow \mathrm{Co(tacn)(NCS)_3} \quad \text{(RP recombination + linkage isomer?)} \quad (5)$$

$$\{\mathrm{Co^{II}},{}^{\bullet}\mathrm{NCS}\} \rightarrow \mathrm{Co^{II}} + (\mathrm{NCS})_2^{-\bullet}$$

$$\text{(capture of NCS}^{-}\text{ from a Co(II) fragment with separation of }(\mathrm{NCS})_2^{-\bullet}\text{ from the cage)} \quad (6)$$

$$\{\mathrm{Co^{II}},{}^{\bullet}\mathrm{NCS}\} + \mathrm{NCS^-} \rightarrow \mathrm{Co^{II}} + (\mathrm{NCS})_2^{-\bullet} \quad \text{(scavenging by NCS}^{-}\text{)} \quad (7)$$

$$\mathrm{Co^{II}} + (\mathrm{NCS})_2^{-\bullet} \rightarrow \text{substitution products} \quad (8)$$

$$\mathrm{Co^{II}} \rightarrow \mathrm{Co^{2+}} \text{ and other redox products} \quad (9)$$

To reduce their complexity, Co^{II} has been used in these equations to represent the reduced cobalt complex in its various possible solvated forms. It therefore represents a distribution of species that may vary with time and origin; for example Co^{II} will likely not be the same on the product sides of eqs 6 and 7. Reaction 7, scavenging of NCS$^\bullet$ from the RP by NCS$^-$, has been added to account for the product yield enhancement caused by thiocyanate ion. The back electron transfer reaction 8 that leads to substitution products has been represented as occurring in the bulk to be consistent with our observation that the decay of $(NCS)_2^{-\bullet}$ occurs with second-order kinetics. From the half-life for this decay and the quantum yield estimated for the production of the transient, the rate constant for reaction 8 can be estimated to be 6×10^9 M^{-1} s^{-1}. This is suffcently fast that the bulk reaction of two $(NCS)_2^{-\bullet}$ radicals to thiocyanogen would compete poorly, as it has rate constant $k = 1.2 \times 10^9$ M^{-1} s^{-1} under similar conditions.[23] This partly explains the low overall redox yield and the finding of photosubstitution via a redox intermediate in this system.

Table 1. Photoredox Yields and $(NCS)_2^{-\bullet}$ Transient Decay Kinetics for Co(III)−Am(m)ine−Thiocyanato Complexes

complexes	$\phi(\mathrm{Co^{2+}})^a$	$\phi((\mathrm{NCS})_2^{-\bullet})^a$	$\phi((\mathrm{NCS})_2^{-\bullet})/\phi(\mathrm{Co^{2+}})$	$\tau_{1/2}$ (μs)^b
cis-Co(NH$_3$)$_4$(NCS)$_2^+$	0.153^c	0.32	2.1	10
cis-Co(en)$_2$(NCS)$_2^+$	0.026^c	0.067	2.6	19
Co(tacn)(NCS)$_3$	0.0008	0.036	39	46

^{a} In 1 M NCS$^-$/dmso/H$^+$ solution. ^{b} $\tau_{1/2}$ is for the first half-life of a second-order decay in 2 M NCS$^-$/dmso/H$^+$ solution. ^{c} No dmso.

The other part of the explanation is suggested by a comparison of the redox vs substitution yields and recombination rates for the series of complexes shown in Table 1. As the amine ligand becomes more robust to substitution, the redox efficiency goes down, the substitution efficiency goes up, and the lifetime of the thiocyanate transient in the bulk increases. This suggests to us that the factor determining the partition of the radical species to redox or substitution products, either in the caged pair or in the bulk, is the rate of substitution of the strongest field ligands in the Co(II) fragment. The more rapidly they are solvated, the more back electron transfer is disfavored and overall redox dominates over photosubstitution.

Radical Pair Scavenging by Thiocyanate. The data allow us to make a clear distinction between the earlier kinetic and ion pair models of the photochemistry. For this system, no ion pair will form for the neutral starting complex. Although the primary photoproduct B does form an ion pair, secondary photolysis does not occur, and the redox and substitution yields can be attributed to the mechanism given above. That is, the increase in yield with thiocyanate concentration arises because of kinetic scavenging by the thiocyanate of the radical pair intermediates, reaction 7. We note here that these intermediates may be considerably more complex than implied by reaction 4. We have drawn attention to the complexity of the photochemistry with no added thiocyanate, and literature reports consistently refer to complicated stoichiometry, often indicative of oxidation of the ammine ligands, etc., in these systems.[9,24] These radical pair species, represented as {Co^{II},$^\bullet$NCS}, may therefore involve oxidized ligands other than thiocyanate and perhaps even solvent. We believe the thiocyanate simplifies matters by acting as electron donor to the various oxidizing species to form the less reactive $(NCS)_2^{-\bullet}$, thus reducing the photoredox complexity.

The above kinetic scheme allows an estimate of the radical pair yield and lifetime, for, applying a steady-state analysis to the radical pair species yields

$$\phi((\mathrm{NCS})_2^{-\bullet}) = a_0(a_1 + [\mathrm{NCS^-}])/(a_2 + [\mathrm{NCS^-}])$$

where $a_0 = \phi_{\mathrm{RP}}$, $a_1 = k_6/k_7$, and $a_2 = (k_5 + k_6)/k_7$.

Fitting the data of Figure 2 to this equation gave a radical pair yield at infinite thiocyanate concentration of 0.29 ± 0.10,

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of similar magnitude as reported earlier for the tetraammine and bis(ethylenediamine) thiocyanato systems[9] and a reasssuringly reasonable value. The rate constant ratios were $k_6/k_7 = 0.12 \pm 0.03$ and $(k_5 + k_6)/k_7 = 8.0 \pm 3.3$. If k_7 is about 10^{10} M^{-1} s^{-1}, about diffusion controlled, then a radical pair lifetime $1/(k_5 + k_6)$ of about 12 ps is obtained, again in good agreement with the values estimated similarly for the other systems.[9] The value assumed for k_7 is supported by our earlier estimate for k_8.

The similarity in behavior, Table 1, for the charged and uncharged systems implies that thiocyanate scavenging processes are likely to be important in both. However, for the charged complexes, the ambiguities that prompted the present study must partially remain.

Summary

The photochemistry of $Co(tacn)(NCS)_3$ consists largely of photosubstitution processes with barely detectable redox reaction. The reactions proceed via radical pair species and give rise to a complex mixture of products that results from complex secondary redox and solvolysis reactions which are not well understood. On addition of thiocyanate, matters are simplified. Thiocyanate scavenges radical pair species to form $(NCS)_2^{-\bullet}$ which then accepts back an electron from the solvolyzed cobalt(II) fragment at close to diffusion-controlled rates to cleanly give about 96% photosubstitution product. Modeling of this process leads to a lifetime estimate for the radical pair species of about 12 ps. These and our earlier results show that thiocyanate can scavenge $NCS^\bullet$ from the radical pair species, leading to an enhancement of both redox and substitution products. Rapid loss of the strong field ligands from the Co(II) fragment tends to favor redox reaction.

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Supporting Information Available: Table S1, listing details of chromatographic product distributions under different conditions, Figure S1, showing chromatograms of starting materials and products, and Figure S2, showing calculated photoproduct spectra with and without added thiocyanate (4 pages). Ordering information is given on any current masthead page.

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