singlet oxygen generation by the complex is 77% of that of rose bengal. The latter efficiency has been measured in acetone solution by Gottschalk et al.[10] as 0.70, suggesting that we may not have been entirely successful in avoiding oxygen depletion or in quantitatively collecting and estimating the peroxo products.

For the complex, the observed yield is the product of (i) the intersystem crossing yield to the doublet, (ii) the efficiency of doublet quenching by oxygen, (iii) the fraction of such quenching events that lead to free singlet oxygen, (iv) the efficiency of formation of furan endoperoxide from singlet oxygen, and (v) the efficiency of collection and analysis of the peroxo products. These processes may, of course, have efficiencies less than 1. For example, in most similar Cr(III) complexes the intersystem crossing yield (i) is between 0.7 and 1.0. Under our experimental conditions, an estimate of 0.93 for step ii can be based on our observation that the Cr complex has lifetimes of 12 and 50 μs[11] in *aerated* (not oxygenated) and nitrogen-degassed dmso, respectively. This estimate assumes that Henry's law applies, and it ignores possible solvent effects. Recognition of such inefficiencies implies that energy transfer from the doublet state of the complex to produce the singlet state of oxygen, step iii, could have a yield much closer to one than to the measured lower limit of 0.5. This chromium complex could therefore be a useful generator of singlet oxygen.

These results for Cr(tacn)$(NCS)_3$, coupled with those of Kane-Maguire et al.[13] on diammine(cyclam)chromium(III), are consistent with Pfeil's contention[1] regarding "conducting and insulating" ligands. These complexes have dmso solution emission lifetimes of 50[11] and 138 μs at 20 °C respectively, the shorter lived being efficiently quenched by oxygen and the longer not at all. The difference can be accounted for by the presence in our complex of the "conducting" thiocyanate ligand.

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Registry No. Cr(tacn)$(NCS)_3$, 112421-68-8; O_2, 7782-44-7; O, 17778-80-2; furan, 110-00-9; furan endoperoxide, 6824-18-6.

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(11) Reference 7 reported 26 μs at 25 °C but this was low owing to quenching by impurities. Recent work[12] has shown that the lifetime is significantly concentration dependent with a limiting infinite dilution value of 50 μs at 20 °C.

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Comparison of Subnanosecond Transients from Cobalt(III) Linkage Isomers: Ligand Field Triplets versus the Radical Pair

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Cobalt(III) acido pentaammines have been known for many years to undergo efficient photoredox reaction on irradiation in the ultraviolet region.[1] These processes are accompanied by photosolvation, and, with appropriate ligands, linkage isomerization. Studies of the wavelength and viscosity dependence of these processes have lent support to extensions (see discussion in ref 1) of the original model of Adamson[2,3] and co-workers, who postulated photoreaction via a radical-pair species. This radical pair has been suggested[4] to evolve through a caged form with a "memory" of its precursor state to a solvent-separated species that has lost this memory and can recombine only to form the thermodynamically stable linkage isomer, in those cases where this can be studied.[5] It was of interest to us that this radical pair has never been observed even though it has been around for over 20 years! We report here an attempt to observe it by kinetic spectroscopy in the picosecond domain.

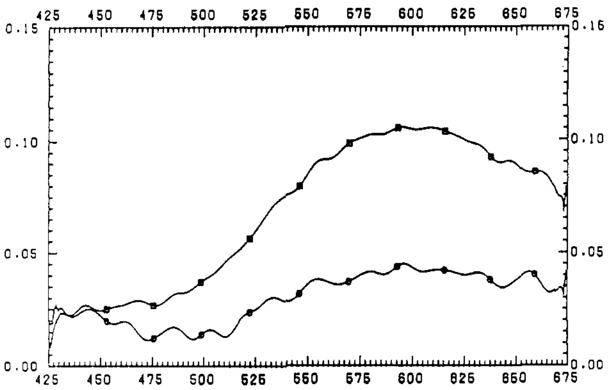

Figure 1. Transient absorption spectrum of the aqueous (isothiocyanato)pentaamminecobalt(III) cation as a function of time: squares, 50 ps after the pulse center; circles, 100 ps.

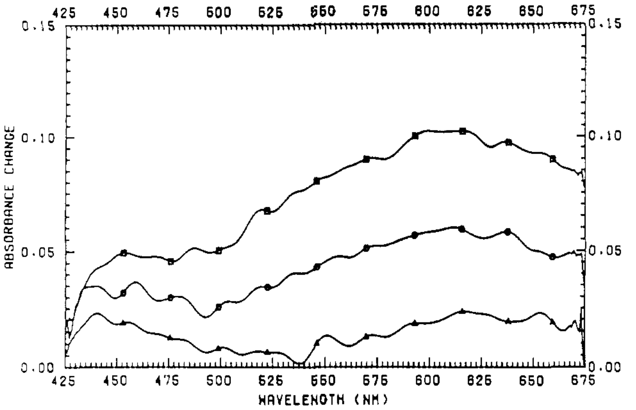

Figure 2. Transient absorption spectrum of the aqueous (thiocyanato)pentaamminecobalt(III) cation as a function of time: squares, 20 ps after the pulse center; circles, 50 ps; triangles, 100 ps.

The isothiocyanato/thiocyanato–pentaammine system was chosen because its photochemistry has been reported in some detail[4,6,7] and in addition both linkage isomers meet the criteria necessary for successful picosecond work, namely a strong absorption band at the best excitation wavelength of 355 nm for both isomers and reasonable yields of photoredox reaction at this wavelength. The interesting nitro/nitrito isomers cannot be properly studied at this wavelength.

Experimental Section

The compounds (isothiocyanato)pentaamminecobalt(III) perchlorate, $[Co(NH_3)_5NCS](ClO_4)_2$ and (thiocyanato)pentaamminecobalt(III)

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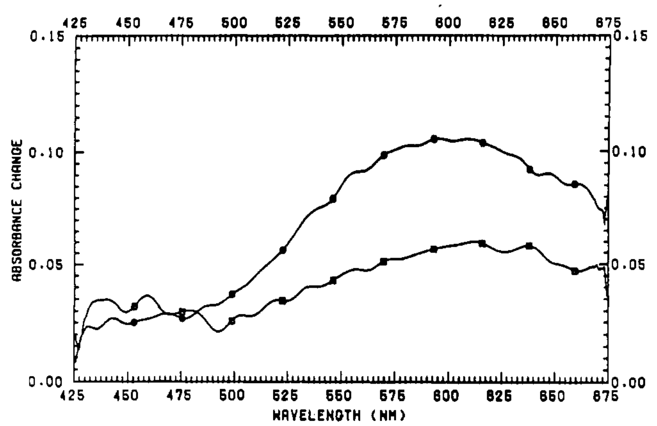

Figure 3. Comparison of the isothiocyanato and thiocyanato transients at 50 ps: circles, isothiocyanato; squares, thiocyanato.

chloride, $[Co(NH_3)_5SCN]Cl_2 \cdot {}^3/_2H_2O$, were prepared by established methods[8] and characterized by elemental analysis and UV-visible spectra. The latter were in agreement with the literature.[4,8] Aqueous solutions, having an absorbance of 0.6 in a 2-mm path length (and therefore concentrations of about 5 mM for the N-bonded and 10 mM for the S-bonded isomer), were excited by the 30-ps, 2.5-mJ, 355-nm pulse from the Nd/Yag laser of the Canadian Centre for Picosecond Spectroscopy.[9] Transient absorption was probed by means of a double-beam OMA system employing a 30-ps probe pulse of wavelength range 400–700 nm with an optical delay line to alter the time interval between the arrival at the sample of the excitation and probe pulses over the range 20 ps–10 ns.

Results and Discussion

The results for the two complexes at time intervals of 20, 50, and 100 ps are shown in Figures 1 and 2. Figure 3 shows a comparison of the 20-ps transients of the linkage isomers on the same scale. Each curve shown is based on averages of eight flashes and eight base-line pulses. The standard deviations on the absorbance values are in the range 0.01–0.02 AU, the larger values occurring at the wavelength extremes, where the continuum is not so bright.

Figures 1 and 2 show that both complexes give rise to a respectable absorption band that is fully developed immediately after the laser pulse and decays rapidly over a period of 100 ps. The data are insufficient to give precise lifetimes for these decays, but they are approximately equal at about 50 ps. A lower limit for the molar absorbance of these transients of about 4×10^3 L mol^{-1} cm^{-1} can be calculated by assuming unit efficiency for their generation. These results and lifetimes are very similar to spectra reported previously and attributed to charge-transfer absorption by triplet states of other cobalt(III) complexes.[10]

The more important observation in the present context is that the spectra for the isomeric compounds are different (Figure 3). The band maximum differs by about 20 nm (600 nm for the isothiocyanate and 620 nm for the thiocyanate), and the band shapes are different. It is also important to note that in both sets of spectra, Figures 1 and 2, there is an additional small absorption feature in the region 425–475 nm, which, although barely above the experimental uncertainties, appears to be the same for both complexes. This weak feature decays more slowly than the main band and is proportionately more intense in the thiocyanato compound.

In earlier work,[10] the absorption, which decayed with a lifetime of about 50 ps, was ascribed to the ligand field triplet state on the basis that its energy changed with a change in the ligand field strength of the ligands in the complex and that the band could be fitted as a metal to ligand π^* charge-transfer transition consistent with the UV spectra of the complexes. The relationship to ligand field strength seems to hold here. The lifetimes of the transients are of the same order as observed earlier, and Figure 3 shows that the absorption energy is lower for the thiocyanato species. We therefore believe that these signals are again due to absorption by the ligand field triplet states of the complex. We would not expect the radical pair to retain any "memory" (rotational or otherwise) for times as long as 50 ps.

The observation of ligand field triplets arising from charge-transfer excitation demonstrates the importance of relaxation processes that take CT excited states into ligand field states.[1] Variations with excitation energy of the efficiency of these processes probably contribute significantly to the wavelength dependence observed for redox and aquation quantum yields from cobalt complexes.

The question now arises, Where is the radical pair? It is known that the thiocyanate complex has a quantum yield for photoredox reaction of 0.32, while that for the isothiocyanate is 0.03. If the radicals are not being seen in this work, this could only be because of a very low molar absorptivity, a lifetime less than 20 ps, or absorption energies outside the range of observation. We are inclined to favor the last explanation. Given the efficiency of charge-transfer absorption of analogous outer-sphere ion pairs,[11] it seems unlikely that the radical pair would have a very small molar absorptivity unless the separation distance between the partners is large enough that electron transfer is precluded. Were this to be the case it would lead to difficulties for the standard model that must allow for efficient recombination of the original partners to account for the wavelength and medium dependence of the yields. The same observations argue against an extremely short lifetime for the radical pair. We are left with the last possibility, examination of which presents the difficult problem of predicting the charge-transfer spectrum of the putative radical pair.

In the earlier work,[10] the published optical electronegativities of Co(III) and Co(II) were taken as suggesting a similarity between the LMCT absorption of the starting complex and charge transfer from thiocyanate in the radical pair. Nevertheless, the model allows for a sizable red shift from the charge-transfer absorption of the parent complex (here at about 35×10^3 cm^{-1}) and does not exclude the tail of such an absorption band of the radical pair falling in the blue where we observe the minor signal. There is also the likelihood of Co^{II} to NCS charge transfer in the radical pair; the 30×10^3 cm^{-1} absorption energy[13] of the free NCS radical leads us to expect it at low energy, and since it is not observed, it must be weak or lie to the red of our window of observation. This suggests the further possibility that the minor band seen arises from charge transfer from Co^{II} to a higher molecular orbital in the thiocyanate radical.

In support of the assignment of the minor absorption to the radical pair is that this signal is stronger in the thiocyanato compound, consistent with the higher redox yield at 355 nm from this isomer. As well, the signal persists after the decay of the LF triplet. Satisfactory confirmation of this assignment will have to await development of experiments in which the absorption spectra of the system outside the presently accessible window can be recorded. In addition, a theoretical prediction of the spectrum to be expected for such a radical pair would be very helpful. Such predictions would have to recognize the possibility of changes in spin state in the Co^{II} fragment.

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