**Figure 2.** Illustration of the near-linear dependence of log $k_{Co}$ on the position of the lowest energy d–d band for all the Co(III) amine complexes except Co(sep)$^{3+}$ (9) and Co(chxn)$_3{}^{3+}$ (not shown). The numbering scheme is the same as in Table I.
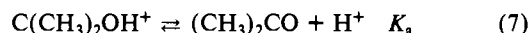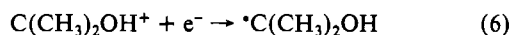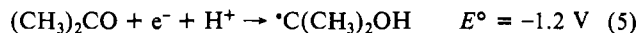
A readily available parameter that should be related to the oxidizing power is the energy of the lowest excited state of these complexes.[15] A plot depicting the relationship between the kinetics of the reduction of the Co(III) amines by ·C(CH$_3$)$_2$OH and the position of the first d–d band for the Co(III) complexes is shown in Figure 2. If we ignore for the moment the point for Co(sep)$^{3+}$, the plot indicates a good correlation between the two parameters for Co(NH$_3$)$_6{}^{3+}$ and all the complexes with the bidentate amines except Co(chxn)$_3{}^{3+}$. Since the self-exchange rate constants and the reduction potentials are unknown for most of the complexes, it is difficult to analyze the data in much more detail. We would like to point out, however, that two of the complexes for which the data are available, namely Co(NH$_3$)$_6{}^{3+}$ and Co(en)$_3{}^{3+}$, differ substantially in their reduction potentials and self-exchange rate constants,[16–18] yet both complexes fit the correlation in Figure 2 quite well. The position of a complex in the plot thus seems to be determined by its overall kinetic reducibility and not the reduction potential alone, at least for this series of closely related complexes of monodentate and bidentate amines.

Co(sep)$^{3+}$ reacts by over 1 order of magnitude more rapidly than predicted on the basis of its visible spectrum. This seems to be the result of the exceptionally high self-exchange rate constant, which generally causes the redox reactivity of Co(sep)$^{3+}$ to exceed significantly[19] that of Co(en)$_3{}^{3+}$, despite the close similarity in the visible spectra of the two complexes.

The "normal" behavior of Co(sep)$^{3+}$ in terms of its redox reactivity toward ·C(CH$_3$)$_2$OH strongly suggests that this is a purely outer-sphere reaction and that there are no special requirements as to the site of the radical attack at the complex as compared to the case for other reductants. This being true for this encapsulated complex, we infer that the reduction of other Co(III) amine complexes by carbon-centered radicals should also be free of any special steric or geometric requirements. Indeed, the rate constant for the reduction of Co(NH$_3$)$_6{}^{3+}$, Co(en)$_3{}^{3+}$ and Co(tn)$_3{}^{3+}$ by ·C(CH$_3$)$_2$OH follows the same reactivity pattern as the reduction by an outer-sphere transition-metal reductant, Cr(bpy)$_3{}^{2+}$.[5a] Thus, the attack of the radical at a trigonal face of the Co(III) complexes seems to be ruled out by the high reactivity of Co(sep)$^{3+}$ (trigonal faces blocked) relative to that of the other Co(III) amines (trigonal

faces accessible). Similarly, the extremely low reactivity of Co(chxn)$_3{}^{3+}$ toward ·C(CH$_3$)$_2$OH cannot be explained by the inability of Co(chxn)$_3{}^{3+}$ to undergo conformational changes, since the rigid and bulky Co(sep)$^{3+}$ reacts readily. At the present time we are unable to offer a good explanation for the low reactivity of Co(chxn)$_3{}^{3+}$.

The application of the Marcus cross relation to the reductions of Co(en)$_3{}^{3+}$ and Co(sep)$^{3+}$ by ·C(CH$_3$)$_2$OH may yield an estimate of the self-exchange rate constant for the couple ·C-(CH$_3$)$_2$OH/C(CH$_3$)$_2$OH$^+$. The standard reduction potential for the couple (CH$_3$)$_2$CO/·C(CH$_3$)$_2$OH (eq 5) is related to the potential of the desired couple (eq 6) by the acidity constant of protonated acetone (eq 7). Although the value of the last value

$$(CH_3)_2CO + e^- + H^+ \rightarrow \cdot C(CH_3)_2OH \qquad E^\circ = -1.2 \text{ V} \quad (5)$$

$$C(CH_3)_2OH^+ + e^- \rightarrow \cdot C(CH_3)_2OH \qquad (6)$$

$$C(CH_3)_2OH^+ \rightleftharpoons (CH_3)_2CO + H^+ \quad K_a \qquad (7)$$

is somewhat uncertain, p$K_a$ = -4 ± 1,[20] it still yields a useful estimate of $E^\circ$ for the C(CH$_3$)$_2$OH$^{+/0}$ couple, -0.97 ± 0.07 V. The use of this value in the equation for the electrostatics-corrected Marcus cross relation[13,21] yields a self-exchange rate constant for the C(CH$_3$)$_2$OH$^{+/0}$ couple of 10$^{4\pm1}$ M$^{-1}$ s$^{-1}$ from the data on Co(en)$_3{}^{3+}$ and 10$^{2\pm1}$ M$^{-1}$ s$^{-1}$ from the data on Co(sep)$^{3+}$. The agreement is almost acceptable within the framework of Marcus theory. We want to emphasize, however, that this treatment is justified only if the proton is bound in the transition state, a point that will have to be addressed independently.

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**Singlet Oxygen Production by Energy Transfer from the Chromium Complex Cr(tacn)(NCS)$_3$ (tacn = 1,4,7-Triazacyclononane)**

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Quenching of the phosphorescence of chromium(III) complexes by molecular oxygen was first reported and systematically studied by Pfeil.[1] He found that complexes with "conducting" ligands such as isothiocyanate and cyanide were subject to quenching to an extent that increased at lower temperatures as the doublet state lifetime increased. The activation energy for the quenching rate constant was about the same as that for diffusion (6 kcal mol$^{-1}$), and there was no quenching at lower temperatures where the medium was rigid. He suggested that the quenching mechanism was collisional and suggested energy transfer to produce O$_2$($^1\Delta_g$) on the basis of its energetic feasibility. In contrast to this behavior,

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Notes

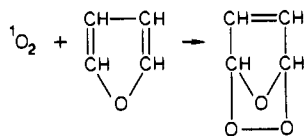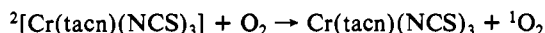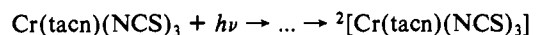he found that complexes with "insulating" ligands such as diamines were unquenched by oxygen.

A few years later, Demas and co-workers demonstrated directly[2,3] that oxygen quenching of Ru(II), Os(II), and Ir(III) polypyridyl complexes produces singlet oxygen. The evidence was detection of the final alcohol products arising from reduction of hydroperoxides derived from addition of singlet oxygen to 1,1,2-trimethylethene. Subsequently this group described[4] a method of singlet oxygen generation using an ion-exchange column with resin-bound Ru(bpy)$_3$$^{2+}$.

Brunschwig and Sutin[5] studied the relationship between the redox potential of chromium(III) polypyridyls and their oxygen quenching rate constants and found none. They concluded that the mechanism of the quenching must be energy transfer rather than electron transfer. Serpone et al.[6] reached a similar conclusion on the basis of an analogous study. In addition these workers questioned Pfeil's conclusions regarding the effects of conducting and insulating ligands.

It is important to note, however, that none of the earlier work with Cr(III) complexes presented any direct evidence for the production of singlet oxygen by energy transfer. It remains possible that the oxygen quenching of the doublet state of Cr(III) complexes leads only to ground-state species.

In a recent study[7] of the photophysical and photochemical properties of Cr(tacn)(NCS)$_3$ (tacn = 1,4,7-triazacyclononane) in a variety of nonaqueous solvents, we observed unusually intense phosphorescence that was strongly quenched by an equilibrium concentration of oxygen in a room-temperature aerated solution. In addition, in dmso and only in dmso, oxygen was scavenged on irradiation, leading to an unusual *increase* in the emission intensity as the solution was photolyzed. We hypothesized that this was a result of energy transfer to produce singlet oxygen, followed by its scavenging by dimethyl sulfide impurity in the dmso.

In this communication evidence is presented that oxygen quenching of the phosphorescent state of this complex indeed produces singlet oxygen, which can be trapped as furan endoperoxide, and that the efficiency of this process is high. The work employed the following scheme:

$$Cr(tacn)(NCS)_3 + h\nu \rightarrow ... \rightarrow {}^2[Cr(tacn)(NCS)_3]$$

$$^2[Cr(tacn)(NCS)_3] + O_2 \rightarrow Cr(tacn)(NCS)_3 + {}^1O_2$$



In the first experiment, two solutions were prepared in dry(molecular sieves) acetone (chosen because of its volatility to avoid interference from the large solvent peak in the subsequent GC/MS analysis). Solution 1 contained complex at $1.3 \times 10^{-3}$ M with $1.2 \times 10^{-2}$ M furan; solution 2 contained the same concentration of furan plus $5.3 \times 10^{-5}$ M rose bengal. Aliquots of these two solutions were irradiated for 30 min by 150 mW of 514-nm radiation from a Spectrophysics argon ion laser, fitted with a beam expander to give an 8-mm beam diameter. Solutions were stirred and oxygen provided by bubbling solvent/furan-saturated oxygen at 1 atm through the solutions.

At the end of these irradiations both the rose bengal and the chromium complex remained intact as evidenced by the unchanged spectrum for the visible absorption bands. Part of solution 2 was

not irradiated, although it was not kept completely dark, and this was used as a blank.

The volatile components of the irradiated solutions were removed by evaporation under vacuum at room temperature and analyzed by capillary column/quadrupole mass spectrometry (Finnegan 3300) with methane chemical ionization. The large acetone and furan peaks eluted early, and the detector was not switched on until after these had eluted. Both irradiated solutions showed a late-eluting peak that was larger for the rose bengal case, the mass spectrum of which was dominated by an M + 1 peak at 101 mass units. The peaks for the two solutions showed the same retention times and mass spectra. (The M + 1 101 peak was absent from the furan/acetone solvent mixture.) A small peak was found in the rose bengal unirradiated "blank"; this we attribute to stray room light from which this solution was not completely shielded. In separate experiments, rose bengal and the complex were each irradiated in oxygenated furan-free acetone and the 101 mass unit chromatographic peak was absent from both.

In a second experiment, $1.8 \times 10^{-3}$ M complex was irradiated in $1.5 \times 10^{-2}$ M furan in dry acetone for 0, 15, 30, and 60 min under the conditions described above. The GC/MS results for the volatile components of these solutions confirmed that the 101 M + 1 GC peak was absent from the unirradiated solution and present in the irradiated solution in an amount that increased with increasing photolysis time. The electron-impact mass spectrum for the photoproduct was obtained but was uninformative because it was necessary to work at maximum sensitivity where carbon dioxide was the major peak present. No evidence for an M − 32 peak was seen.

The efficiency of singlet oxygen generation was estimated as follows. In a 9.6 mL, 3.5 cm diameter, 1 cm path length cylindrical cell, solutions were irradiated with 40 mW of beam-expanded (2.5-cm) 514-nm argon ion radiation. The large beam diameter was required because initial experiments showed that otherwise oxygen depletion occurred in the irradiated path, leading to serious errors. The light intensity was measured by reineckate actinometry, keeping conversions below 3%. Oxygen saturation was maintained in the irradiated solutions by continuously bubbling pure oxygen. Separate solutions of complex and rose bengal in 0.1 M furan/acetone medium having known absorbances near 0.15 were exposed for 30 min.

Immediately after photolysis, furan endoperoxide was removed along with the solvent by vacuum distillation. Reaction of the furan endoperoxide with iodide under nitrogen in glacial acetic acid/2-propanol/acetone (3:40:57 v/v) medium[8] then formed triiodide ion. The triiodide ion produced was estimated colorimetrically at 360 nm by using our measured molar absorptivity of $1.362 \times 10^4$ M$^{-1}$ cm$^{-1}$ in this medium. After allowance for the fraction of light absorbed by each solution, quantum efficiencies of 0.48 and 0.62 were found for peroxide formation for complex and rose bengal respectively.

These results confirm directly that energy transfer from the doublet state of this chromium complex leads to singlet oxygen, which, like that formed by oxygen quenching of rose bengal, adds to furan to produce its endoperoxide. The endoperoxide has a molecular mass of 100 and obviously is stable enough in the absence of protic solvents to be volatilized, collected, and analyzed by GC/MS. We have no idea of the efficiency of this step, however, and in the GC/MS work we may be observing only a small fraction of the initial product. These results are similar to some reported[9] for the endoperoxide of 2,5-dimethylfuran, generated and analyzed entirely in the gas phase and giving the analogous parent ion at mass 128.

The iodometric determination can be expected to be nearly quantitative, however, and this is supported by the high efficiencies we observe. We chose also to compare the complex against rose bengal under the same conditions so that any errors in the estimation would be revealed. The overall quantum efficiency of

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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 $\mu s$[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 $\mu s$ 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.

**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.

(10) Gottschalk, P.; Paczkowski, J.; Neckers, D. C. *J. Photochem.* 1986, 35, 277.
(11) Reference 7 reported 26 $\mu s$ 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 $\mu s$ at 20 °C.
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**Comparison of Subnanosecond Transients from Cobalt(III) Linkage Isomers: Ligand Field Triplets versus the Radical Pair**

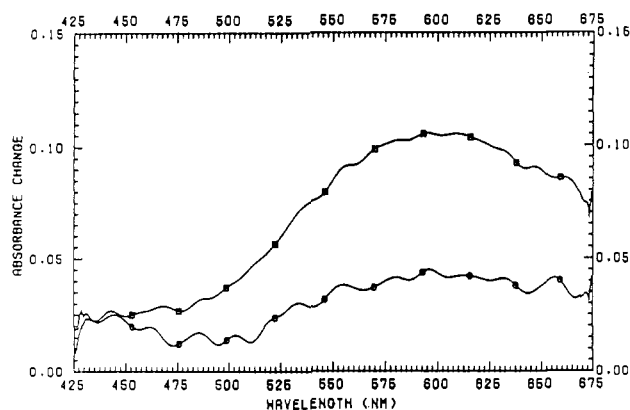A. D. Kirk,*,† C. H. Langford,‡ and D. K. Sharma‡

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
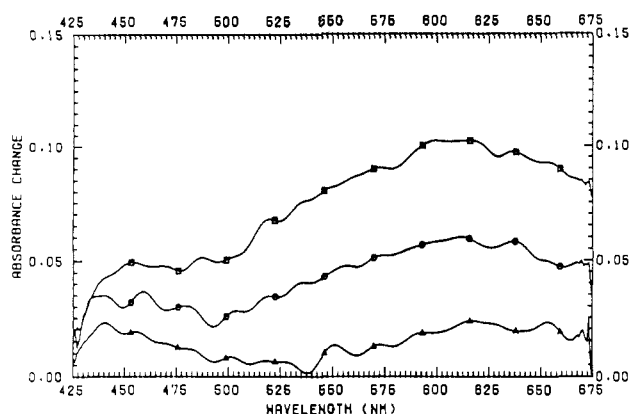
* To whom correspondence should be addressed.
† University of Victoria.
‡ Concordia University.



**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.

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.

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$_3$)$_5$NCS](ClO$_4$)$_2$ and (thiocyanato)pentaamminecobalt(III)

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