

# Articles

## Synthesis and Photoproperties of a Quencher, Na[Cr(1,3-diaminopropane)(CN)<sub>4</sub>], and Reinvestigation of Cr(1,3-diaminopropane)<sub>3</sub><sup>3+</sup> Photoproduct Quenching

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The photochemical, photophysical, and general properties of the compound Na[Cr(tn)(CN)<sub>4</sub>] (tn = 1,3-diaminopropane) suggest that it has considerable potential as a new and useful quencher. It does not absorb over most of the visible spectrum, and it is reasonably stable both to thermo- and photosubstitution processes. Only at a pH of 2 or less does acid-catalyzed loss of cyanide become significant; the first-order rate constant at pH 2 and 20 °C was  $4 \times 10^{-5} \text{ s}^{-1}$ , for a half-life of 5 h. There was a quantum yield of  $0.040 \pm 0.006$  for photoaquation on irradiation at 406 nm. In dmsO or dmf room-temperature solutions, the compound emits at 748 nm; in these solvents this emission can be used as a probe for energy transfer to the quencher. At the same time, its low charge reduces the danger of precipitation of quenching partner cations as double salts or the formation of ion pairs. The efficiency of this quencher was explored through a comparison of its quenching of Cr(tn)<sub>3</sub><sup>3+</sup> with that by hydroxide; the quenching rate constants at 20 °C were  $(6 \pm 2) \times 10^8$  and  $6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , respectively. This quenching study confirmed an earlier report of different photoproduct isomer ratios for the quenched and unquenched photochemistry of Cr(tn)<sub>3</sub><sup>3+</sup> but did not show the wavelength effect reported earlier.

### Introduction

The use of quenchers, and to a lesser extent sensitizers, has long been one of the standard means<sup>1–5</sup> of exploring the excited state participation in photochemistry generally and in coordination compounds in particular. Several coordination complexes have been extensively used as quenchers, as has the hydroxide ion. Most of the complexes used have been less than ideal. The ideal quencher should be thermally and photochemically stable, should have a high quenching efficiency, should be freely soluble in a range of aqueous and nonaqueous media, should not interfere with the complex studied or its products, as for example by precipitation, etc., should not interfere with standard analysis techniques, and should not absorb at the wavelengths of excitation. Very few meet all these criteria and compromises are usually required.

Hydroxide meets most of these criteria better than the coordination compounds. It is, nevertheless, always suspect when used as a quencher because it has been reported<sup>6</sup> to lead to reactive quenching and also because the mechanism of quenching is not well understood. Most metal complexes that have been used in the past, such as Cr(CN)<sub>6</sub><sup>3–</sup> and Cr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub><sup>3–</sup>, can be photochemically active, can have interfering absorptions, and are also usually highly charged. The last is a serious

disadvantage, as many of the molecules to be quenched have been triple cations such as Cr(tn)<sub>3</sub><sup>3+</sup>, so that precipitation of double salts in aqueous media and ion pair formation in nonaqueous media become serious problems. There is therefore always room for new potential quenchers that may improve on the current systems.

In the course of our photochemical studies of some mixed Cr(III) diaminopropane cyano complexes,<sup>7</sup> we have prepared the molecule Na[Cr(tn)(CN)<sub>4</sub>] and have studied its photochemistry and photophysics. These, and its general properties, led us to try this molecule as a quencher for a typical triply charged cationic complex, Cr(tn)<sub>3</sub><sup>3+</sup> (tn = 1,3-diaminopropane), which has been previously studied<sup>8</sup> using hydroxide as a quencher. The purpose was severalfold: to establish that, as claimed earlier, hydroxide was an innocent quencher in this system and then to confirm our earlier findings on the wavelength dependence of the photoproduct isomer ratios and their difference for the two pathways of photoreaction. We report on all these aspects here.

### Experimental Section

**Synthesis of Na[Cr(tn)(CN)<sub>4</sub>].** Finely ground NaCN (3.2 g, 65 mmol, vacuum-dried) was dissolved in 40 mL of DMSO (dried over 4A molecular sieves) by heating to 78–80 °C in a RB flask. Then 1.2 g (2.7 mmol) of *trans*-Cr[(tn)<sub>2</sub>Br<sub>2</sub>]Br (green), prepared from *trans*-Cr[(tn)<sub>2</sub>F<sub>2</sub>]Cl by methods analogous to those reported for the ethanediamine analogues,<sup>9</sup> was added to the solution, which immediately turned dark red. As a precaution, the neck of the flask was kept closed whenever possible to minimize exposure to atmospheric moisture. On heating at 78–80 °C with magnetic stirring for 2 h, the solution gradually turned yellow and the UV/vis spectrum shifted to the blue. Heating was continued until the two ligand field band maxima of this

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solution were close to the wavelengths expected for the desired product using the known ligand field strengths. The solution was allowed to cool, and excess NaCN was filtered off through a sintered-glass funnel.

The filtrate was diluted to 1.6 L with distilled water and placed on a  $16 \times 3$  (i.d.) cm Sephadex-QAE A-25 anion exchange resin column, giving a yellow band, about 3 cm wide. At flow rates of about  $10 \text{ mL min}^{-1}$ , the column was washed with 200 mL of distilled water and then eluted with 0.02 M aqueous  $\text{NaClO}_4$ . Two distinct yellow bands were separated. Passing 1 L of eluent moved the fast moving band to the bottom of the column. The following 350 mL fraction containing this first band was collected and rotary evaporated to dryness at 50–55 °C. Then about 15–20 mL of dry ethanol was added, and the mixture was stirred thoroughly and allowed to stand on ice for 30 min. The bright yellow product was filtered off, washed with 20 mL portions of dry ethanol and acetone, and vacuum dried; yield 400 mg (60%).

The material is readily soluble in water ( $>50 \text{ mg mL}^{-1}$ ), dmsO, and dmF, moderately so in pyridine and methanol, but insoluble in ethanol, acetone, ether, ethyl acetate, acetonitrile, and methylene chloride.

The compound contained residual sodium perchlorate and a small amount of free cyanide, which was estimated to be less than 1%, on the basis of pH measurements in aqueous solutions. Therefore, when the compound was used in experiments where exact pH of the solution was important, it was adjusted to the desired value with a few microliters of 1 M  $\text{HClO}_4$ . The spectral and kinetic data reported have been corrected to reflect the roughly 80% purity of the various samples used, and the uncertainties, enlarged as necessary.

**Other Materials.** The slow moving band was eluted with 0.4 M aqueous  $\text{NaClO}_4$  and found to be  $\text{Na}_3[\text{Cr}(\text{CN})_6]$ .

The quenching studies were carried out using a sample of  $\text{Cr}(\text{tn})_3\text{Cl}_3$  available from the earlier<sup>8</sup> study. It was recrystallized from slightly acidic aqueous solution prior to use.

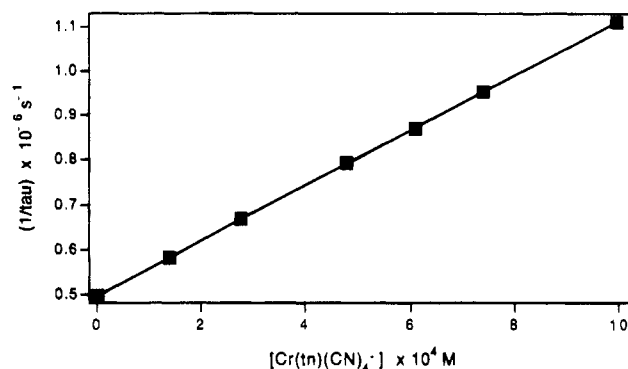
**HPLC Analysis, Spectroscopy, Photochemistry, and Photophysics.** The techniques and equipment used for the above measurements were recently described<sup>10</sup> in detail.

## Results

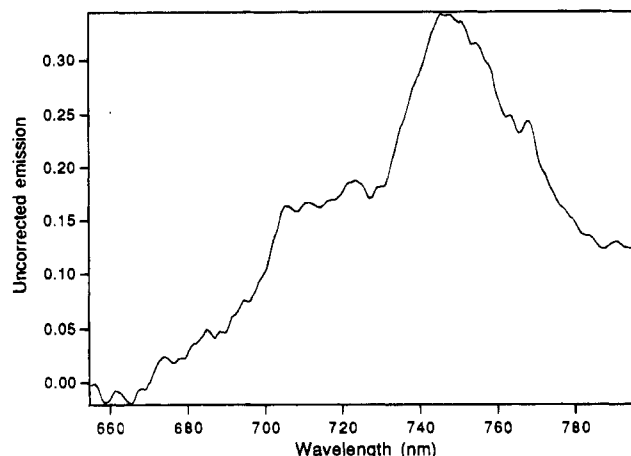
**Spectroscopic Properties of  $\text{Na}[\text{Cr}(\text{tn})(\text{CN})_4]$ .** The compound has two ligand field absorption bands at 408 and 329 nm with  $\epsilon$  values of  $70 \pm 5$  and  $45 \pm 5 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively. Like  $\text{Cr}(\text{CN})_6^{3-}$ , it does not emit perceptibly in aqueous solution<sup>11</sup> but emits in dmsO at 748 nm with a doublet lifetime at 20 °C of 4  $\mu\text{s}$  (uncertainties about 1 nm and 0.1  $\mu\text{s}$ ) while the corresponding data in dmF are 747 nm and 17  $\mu\text{s}$ . For both the absorption and emission spectra, as expected, the band maxima lie roughly equidistant in energy between those for  $\text{Cr}(\text{tn})_2(\text{CN})_2^+$  and  $\text{Cr}(\text{CN})_6^{3-}$  and the absorption spectral maxima match reasonably with those<sup>12</sup> for the analogous  $\text{Cr}(1,2\text{-diaminopropane})(\text{CN})_4^+$  of 404 and 324 nm. The lowest energy absorption band of the compound lies only 30 nm to the red of that for  $\text{Cr}(\text{CN})_6^{3-}$  and also has a significantly lower  $\epsilon$  value, so this compound has almost as large a visible window, a desirable property in a quencher.

**Thermo- and Photostability.** The pseudo-first-order rate constant for proton uptake was measured at various pH values using the pH-stat method. At pH 2 and 20 °C and in aqueous 0.1 M  $\text{KClO}_4$  medium, the rate constant for proton uptake was  $4 \times 10^{-5} \text{ s}^{-1}$ . The nature of the products was not confirmed carefully; they can safely be assumed to be the stereoretained products of cyanide loss of which two are anticipated.

The quantum yield of proton uptake was similarly measured to be  $0.040 \pm 0.006$  for irradiation at 406 nm and 21 °C in pH 3  $\text{HClO}_4/0.10 \text{ M KClO}_4$  aqueous medium. Again the photoproducts were not explored, as our concern was the photo-



**Figure 1.** Stern–Volmer quenching of  $\text{Cr}(\text{tn})_3^{3+}$  by  $\text{Na}[\text{Cr}(\text{tn})(\text{CN})_4]$ . Conditions: 21 °C, pH 3.0 aqueous solution.



**Figure 2.** Emission from  $[\text{Cr}(\text{tn})_2(\text{CN})_2][\text{Cr}(\text{tn})(\text{CN})_4]$  in dmsO solution, 23 °C. Excitation wavelength was 460 nm, 80% of the absorption being by the cation. The peak at about 745 nm is the sensitized anion emission, and the cation emission at 703 nm is strongly quenched.

stability; theory<sup>13</sup> and the behavior of other cyano am(m)ine complexes<sup>14</sup> suggest they would arise from both tn and  $\text{CN}^-$  aquation,<sup>15</sup> likely with complex stereochemical relationships.

**Efficiency as a Quencher.** A Stern–Volmer plot of reciprocal lifetime of  $\text{Cr}(\text{tn})_3^{3+}$  against  $\text{Cr}(\text{tn})(\text{CN})_4^-$  concentration (Figure 1) is linear with slope  $(6 \pm 2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C in  $1 \times 10^{-3} \text{ M HClO}_4$  aqueous solution. Typical  $k_q$  values<sup>1</sup> for emission quenching in other transition metal complex systems lie in the range  $1 \times 10^6$  to  $1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , so this value is in the midrange and is therefore practical for efficient quenching. For instance,  $\text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ , for which  $k_q = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C, was successfully used in a quenching study<sup>16</sup> of *trans*- $\text{Cr}(\text{NH}_3)_4(\text{CN})(\text{NCS})^+$ . The system  $\text{Cr}(\text{tn})(\text{CN})_4^-/\text{Cr}(\text{tn})_3^{3+}$  has the same charge product, and  $\text{Cr}(\text{tn})(\text{CN})_4^-$  is therefore equally or more efficient as a quencher.

In an emission spectrum obtained for a solution of the double salt  $[\text{Cr}(\text{tn})_2(\text{CN})_2][\text{Cr}(\text{tn})(\text{CN})_4]$  in dmsO shown in Figure 2, excitation 80% into the cation at 460 nm led predominantly to emission from the anion, indicating that doublet energy transfer was occurring.

**Quenched and Unquenched Photoproduct Isomer Ratios for  $\text{Cr}(\text{tn})_3^{3+}$ .** Using both hydroxide ion and the new quencher, measurements were made of the photoproduct isomer ratio in the photolysis of  $\text{Cr}(\text{tn})_3^{3+}$ . While the results were in general

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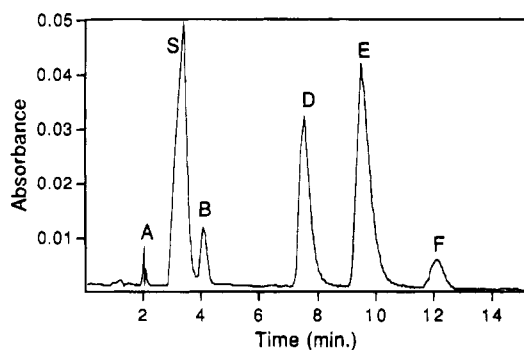
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**Figure 3.** Reversed-phase HPLC of Cr(tn)<sub>3</sub><sup>3+</sup> photoproducts. Eluent: 25 mM sodium butanesulfonate/25 mM triethylamine hydrochloride in 18% methanol/water. Column: 30 cm C18. Flow rate 2 mL min<sup>-1</sup>. Detection wavelength: 228 nm. Temperature: 23 °C. Key: S = Cr(tn)<sub>3</sub><sup>3+</sup>; D = *cis*-Cr(tn)<sub>2</sub>(tnH)(H<sub>2</sub>O)<sup>4+</sup>; E = *trans*-Cr(tn)<sub>2</sub>(tnH)(H<sub>2</sub>O)<sup>4+</sup>; F = Cr(tn)(tnH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>5+</sup>; B = unidentified secondary product; A is an artifact peak.

agreement with our earlier data,<sup>8</sup> some differences were found, the most notable being the absence of any change in the photoproduct ratio on irradiation into the red edge of the quartet absorption band. We therefore explored the behavior in greater detail. Figure 3 shows the sharp, baseline separated peaks for the *cis* and *trans* photoproduct isomers, Cr(tn)<sub>2</sub>(tnH)(H<sub>2</sub>O)<sup>4+</sup>, D and E, respectively, obtained from photolysis of Cr(tn)<sub>3</sub><sup>3+</sup>, using the earlier reversed phase HPLC method, but with the modified conditions given in the figure caption. With the increased resolution in these chromatograms, additional peaks for secondary photoproducts were observed even at low extents of photolysis but are shown here at 20% for emphasis. For example peak F, which amounts to about 6% of D and E combined, can be assigned to the secondary photoproduct Cr(tn)(tnH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>5+</sup>; it becomes observable at only 3% photo-conversion.

Extensive studies of the thermal reactions occurring in photolyzed and unphotolyzed solutions were also carried out. These showed that heating Cr(tn)<sub>3</sub><sup>3+</sup> at 60 °C for 30 min produced mainly D with traces of B and E but no F, that peaks D, E, and F were formed photochemically at 10 °C, and that, on heating a photolyzed solution at 60 °C, the D/E ratio increased. This last result can be readily understood as D, but not E, is produced thermally from Cr(tn)<sub>3</sub><sup>3+</sup> simultaneously with the removal of D and E by further aquation. No change in photoproduct peak heights occurred in a photolyzed solution over 30 min at 10 °C, however.

Consequently, a temperature of 10 °C and low photochemical conversions were adopted for all the subsequent quantitative measurements of product isomer ratios. Measurements at a number of irradiation wavelengths of the primary photoproduct ratios for the unquenched photochemistry and for the photo-aquation unquenchable by high concentrations of Cr(tn)(CN)<sub>4</sub><sup>-</sup> are compared with the old and new data for hydroxide quenching in Table 1.

## Discussion

### Comparison of Na[Cr(tn)(CN)<sub>4</sub>] and OH<sup>-</sup> as Quenchers.

The new molecule Na[Cr(tn)(CN)<sub>4</sub>] has been shown to be an effective quencher with a number of advantages. It does not significantly absorb over the wavelength range 450–735 nm, leaving a generous absorption window for partner species. It has a very low lying doublet state, almost as ideal as Cr(CN)<sub>6</sub><sup>3-</sup>, and, in nonaqueous solvents, the emission of this doublet can be followed in room temperature solutions. This is illustrated by the emission spectrum of the double salt in Figure 2.

**Table 1.** Percentage *Cis* Product in Quenched and Unquenched Photoaquation of Cr(tn)<sub>3</sub><sup>3+</sup>

quencher	% quenching	% <i>cis</i> product <sup>b</sup> at λ		
		436 nm	488 nm	514 nm
Cr(tn)(CN) <sub>4</sub> <sup>-</sup>	0	38 ± 1 (5)	38 ± 1 (4)	39 ± 1 (4)
	40 ± 3 <sup>a</sup>		40 ± 3 <sup>a</sup>	
	97	45 ± 1 (3)	<i>c</i>	<i>c</i>
	90	43 ± 1 (3)	43 ± 1 (7)	<i>c</i>
OH <sup>-</sup>	100	48 ± 2 (8)	48 ± 2 (10)	48 ± 2 (7)
	100	62 ± 2 <sup>a</sup>		73 ± 2 <sup>a</sup>
	99	48 ± 1 (4)	<i>c</i>	<i>c</i>

<sup>a</sup> Results from ref 8. <sup>b</sup> Number of experiments given in parentheses. <sup>c</sup> Entries not completed because of laser failure.

Because of its single negative charge, Cr(tn)(CN)<sub>4</sub><sup>-</sup> is much less prone to formation of precipitates or ion pairs with cationic complexes than the triply negative complexes often used. We note here that we have investigated<sup>17</sup> the obvious extension; the neutral molecules Cr(tacn)(CN)<sub>3</sub> and Cr(tacn)(NCS)<sub>3</sub> have many desirable properties but are unfortunately insoluble or sparingly soluble materials and therefore unsuitable for general use as quencher species.

The data in Table 1 show that Cr(tn)(CN)<sub>4</sub><sup>-</sup> and OH<sup>-</sup> give indistinguishable results for the photoproduct isomer ratio in quenching of Cr(tn)<sub>3</sub><sup>3+</sup>. This gives us confidence in both sets of data. In particular, and in agreement with our<sup>8</sup> and other studies in the literature,<sup>18,19</sup> it establishes the innocence of hydroxide in the quenching of am(m)ine complexes of this type. However hydroxide still suffers from the major disadvantages that it negates the possibility of pH control and exposes all the species in solution to very high pH values. This often leads to problems owing to decomposition or reactions such as oleation which complicate studies even if they remain possible. The molecule Na[Cr(tn)(CN)<sub>4</sub>] can be used at any pH in the range 2–10 or higher, and this must be viewed as a useful feature. The molecule does have some characteristics which are less than perfect; some light absorption, some acid-catalyzed thermal aquation, and some photodecomposition, but none of these is severe enough to discourage its use for a number of potential studies, and in this work it has yielded clear, unambiguous results. The excellent linearity of the Stern–Volmer quenching plot (Figure 1) testifies to the absence of complications in its use.

**Secondary Photolysis in Cr(tn)<sub>3</sub><sup>3+</sup>.** The complex Cr(tn)<sub>3</sub><sup>3+</sup> seems to be abnormally prone to secondary photolysis, and this is worthy of comment. It has been reported earlier that tn is a poor leaving ligand,<sup>20</sup> and this appears to be the main factor that leads to the low quantum yield<sup>20,21</sup> of 0.14 for this complex, less than half that for its analogues. The degree of secondary photolysis in a system depends<sup>22</sup> on the ratio ε<sub>p</sub>Φ<sub>p</sub>/ε<sub>s</sub>Φ<sub>s</sub> for the primary photoproduct over the starting complex. For this system, at our irradiation wavelengths, the ε ratio is 1 or somewhat less, but we believe that this is more than offset by a large Φ ratio. By analogy to other monodentate amine complexes, one could anticipate a quantum yield of photoaquation as high as 0.5 for *trans*-Cr(tn)<sub>2</sub>(tn-H)(H<sub>2</sub>O)<sup>4+</sup>, which has a monodentate ligand, and coupled with the low yield from the starting complex, this could lead to the abnormal sensitivity to secondary photolysis found here.

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**Wavelength Dependence of Photoproduct Ratios.** Table 1 confirms the earlier finding that the fully quenched photoaquation of  $\text{Cr}(\text{tn})_3^{3+}$  leads to a higher yield of *cis* isomer than the unquenched reaction. When one allows for the small variations in the extent of quenching for the various experiments summarized, the data are fit best for 35% *cis* product from the reaction via the doublet and 47% *cis* from that via the quartet. This differs from the earlier data<sup>8</sup> in showing a somewhat smaller difference in the ratio for the two reaction pathways but one that is real and is in the same direction. A more important revision is that the earlier work reported a significant increase in the percent *cis* isomer on irradiation in the red edge of the quartet absorption band, an effect which is entirely absent from the data in Table 1. Since we believe the new data are more reliable, we have to attribute the earlier observation to an artifact. One possibility is that, since in the earlier work the LC peaks were not baseline resolved, errors in the peak area measurement biased the results. More likely, however, is distortion of the results owing to concurrent thermal reactions during photolysis. We have shown in this work that thermal reactions at temperatures above 10 °C tend to increase the *cis/trans* ratio. In the wavelength studies, it is necessary to significantly increase the concentration of complex along with the irradiation time as one moves to the red in irradiation wavelength. This very much increases the potential for artifacts arising from thermal reaction to and by products. Although in the earlier work, which was conducted at 20 °C, precautions

were taken to avoid such data distortion, comparison of the two sets of experiments strongly suggests that the earlier observed red edge increase in percentage *cis* isomer was just such an artifact.

These new findings need not alter the essential conclusions of the earlier study,<sup>8</sup> but they certainly weaken the arguments presented there. The red-edge effect was used to argue that  $\text{Cr}(\text{tn})_3^{3+}$  prompt photochemistry was competitive with vibrational relaxation of the quartet state, rather than being a reflection of solvation shell relaxation. This may still be true but is no longer required by the data.

**Summary.**  $\text{Na}[\text{Cr}(\text{tn})(\text{CN})_4]$  has been shown to be an effective quencher, useful in studies of reaction pathways in other transition metal complexes. Its application to the system  $\text{Cr}(\text{tn})_3^{3+}$  has shown that hydroxide is an innocent quencher in this system and confirms that the quenched and unquenched photochemistries lead to somewhat different photoproduct ratios. The red-edge effect previously observed for this ratio has not been replicated and is ascribed to inadequate correction for thermal reactions in the earlier results.

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