Inorg. Chem. **1985**, *24*, 3106-3110

on the Cr ion, lies about 2 eV below the singly occupied Cr 3d orbitals and may be responsible for the poor results.

Quantitative errors in spin densities at the nuclei do occur in systems such as the M(II) porphines, but these errors are apparently small compared to what happens in *trans*-$[Cr(ox)_2(py)_2]^-$. Mechanisms that disperse spin into the ligand by a qualitatively incorrect mechanism are forbidden in Cu(II) and Ag(II) porphines because of the orbital occupations and in Fe(II) porphine by symmetry. This conjecture is further supported by a calculation in which the d_{z^2} partial wave on the Cr atom was removed from the wave function. This calculation could only be converged to 10^{-3} in the potential, but the spin populations of the hydrogen atoms show the same trend in chemical shifts as is observed experimentally. Since 93–95% of the total spin populations on the hydrogen atoms is contributed by the σ orbitals, it is believed that the low metal d-orbital energies are the principal cause of the problem.

Calculations using larger empirical metal sphere radii tend to have metal d-orbital energies about 1 eV higher than in calculations using Norman radii.[6] How this affects magnetic properties, however, has not been described. It would be interesting to compare our results by the Norman procedure with new calculations using the empirical radii. This choice of radii will undoubtedly raise the Cr(III) d-orbital energies, but it may not be sufficient to improve the magnetic properties to an extent that is useful for chemical applications to low-symmetry Cr(III) complexes.

Conclusions

The Xα–SW method is a valuable tool for describing the electronic and magnetic properties of Cr(III) compounds. However, serious errors should be expected when ligand to metal (and metal to ligand) charge-transfer transitions are described, as is the case with other first-row transition metals. The anomalously low energies of the metal d orbitals tend to match the formally unoccupied metal d orbitals with ligand MOs. In transition-metal complexes of low symmetry where singly occupied and empty metal d orbitals belong to the same irreducible representation, large errors can be expected for hyperfine interactions. The mixing of singly occupied and empty metal orbitals along with the energy match of the ligand MOs with the metal d orbitals allows spin into the ligand through channels that would normally not be available.

Acknowledgment. We gratefully acknowledge Dr. D. A. Case for helpful discussions, Dr. J. G. Norman for instruction on using the Xα programs, J. I. Legg (thesis advisor to W.D.W.), and both the National Institutes of Health (Contract No. GM23081-06) and the U.S. Department of Agriculture (Contract No. 82-CRCR-1-1005) for partial support of this work.

Registry No. *trans*-$[Cr(ox)_2(py)_2]^-$, 36444-16-3; ^{53}Cr, 13981-78-7.

Contribution from the Institute of Inorganic Chemistry,
University of Cologne, D-5000 Köln 41, West Germany

Joint Bond Breaking in the Photolysis of the Tris(1,3-diaminopropane)chromium(III) Ion

E. GOWIN and F. WASGESTIAN*

Received May 30, 1984

The photoaquation of $[Cr(tn)_3]^{3+}$ (tn = 1,3-diaminopropane) was studied in acid and alkaline solution by means of absorption spectroscopy, ion-exchange chromatography, pH measurements, acid–base titrations, phosphorescence intensity studies, and determination of free tn. The data indicate two parallel photochemical reaction paths leading to $[Cr(tn)_2(H_2O)(tnH)]^{4+}$ and $[Cr(tn)_2(H_2O)_2]^{3+}$ with quantum yields of 0.14 and 0.04, respectively.

Introduction

To substitute a bidentate ligand, two coordination sites have to be replaced. For many compounds the final detachment of the ligand is much faster than the breaking of the first bond. Therefore, one-ended species often escape detection. As far as the thermal aquation of chromium(III) diamine complexes is concerned, several studies[1-5] succeeded in identifying one-ended species. Especially in the well-studied $[Cr(en)_3]^{3+}$ system (en = 1,2-diaminoethane) the $[Cr(en)_2(enH)(H_2O)]^{4+}$ ion had been found to be the thermal[2] as well as the photochemical[5] reaction product.

Complexes with 1,3-diaminopropane (tn) are kinetically more stable than en complexes.[6-8] This property contradicts expectations, which considered five-membered chelate rings to be more stable than six-membered ones.[9]

The importance of the ring size in photochemical reactions of chromium(III) chelate complexes has not been given much thought, yet.[10] $[Cr(tn)_3]^{3+}$ provides an appropriate object for the purpose of studying the influence of ring size, because the spectral characteristics of $[Cr(tn)_3]^{3+}$ are very similar to those of $[Cr(en)_3]^{3+}$ and other CrN_6 systems. Hence, in solution any difference in photochemical reactivity have to be attributed to steric effects.

In his thesis Cimolino[6] reported some experiments on the thermal and photochemical reactivity of $[Cr(tn)_3]^{3+}$ as a supplement to his study of the stereophotochemistry of $[Cr(en)_3]^{3+}$. Our study gives further information about the $[Cr(tn)_3]^{3+}$ system concerning the mechanism of the detachment of a bidentate ligand.

Experimental Section

$[Cr(tn)_3]Cl_3$ was prepared according to Pedersen.[11] It was transformed to the perchlorate salt by repeated precipitation (three times) from aqueous solution. *cis*-$[Cr(tn)_2(H_2O)_2](NO_3)_3{\cdot}H_2O$ was obtained by the method of Nakano and Kawaguchi.[12] Purity was checked by visible spectra, IR spectra, and elemental analysis (C, H, N, Cr).

All visible spectra were recorded with a Cary Model 14 instrument. Additional spectroscopic measurements were accomplished on a Zeiss PMQ II. Absorbed quanta were recorded by a thermostated bolometer apparatus described elsewhere.[13] pH changes were determined with a

---

(1) Childers, R. F.; Vander Zyl, K. G.; House, D. A.; Hughes, R. G.; Garner, C. S. *Inorg. Chem.* **1968**, *7*, 749.

(2) Mønsted, L.; Mønsted, O. *Acta Chem. Scand., Ser. A* **1975**, *A29*, 29.

(3) Mønsted, L. *Acta Chem. Scand., Ser. A* **1976**, *A30*, 599.

(4) Fukuda, R.; Walters, R. T.; Mäcke, H.; Adamson, A. W. *J. Phys. Chem.* **1979**, *83*, 2097.

(5) Cimolino, M. C.; Linck, R. G. *Inorg. Chem.* **1981**, *20*, 3499.

(6) Cimolino, M. C. Thesis, University of California at San Diego, 1982.

(7) DeJovine, J. D.; Mason, W. R.; Vaughn, J. W. *Inorg. Chem.* **1974**, *13*, 66.

(8) Couldwell, M. C.; House, D. A. *Inorg. Chem.* **1972**, *11*, 2024.

(9) Basolo, F.; Pearson, R. G. "Mechanismen in der anorganischen Chemie"; Georg Thieme Verlag: Stuttgart, West Germany 1973; p 186.

(10) Zinato, E. "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975.

(11) Pedersen, E. *Acta Chem. Scand.* **1970**, *24*, 3362.

(12) Nakano, M.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3563.

0020-1669/85/1324-3106$01.50/0

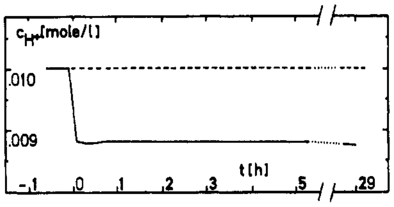


Figure 1. Postirradiation effect—H^+ consumption vs. time, typical sample with 0.01 M complex/0.01 M $HClO_4$ (λ_{irr} = 366 nm, T_{irr} = 20 ± 0.1 °C, t_{irr} = 7 min, V = 10 mL): (dashed line) nonirradiated sample.

Schott N 59 micro glass electrode in connection with a Knick 641 digital pH meter (reproducibility: ΔpH ± 0.001). Solutions were irradiated with light from a high-pressure mercury lamp (Osram HBO 100 W/2) passing a 250-mm Bausch and Lomb grating monochromator.

Luminescence studies were performed with use of a right-angle device consisting of an Osram HBO 100 W/2 lamp stabilized by a PRA TX-5 optical feedback system, a GCA/McPherson EUE-700/2 grating monochromator, and an RCA 3104 photomultiplier in a Peltier PFR TE 104 cooled socket housing. An interference filter was used to isolate the 436-nm line for excitation. Spectra were recorded with a Kipp & Zonen BD 8 x-t recorder and integrated by a Kipp & Zonen BC 1 integrator. Low-temperature measurements were done in a liquid-nitrogen-cooled optical Dewar.

All samples were thermostated to 20 ± 0.1 °C and contained 0.01 M complex–0.01 M $HClO_4$, if not noted differently.

Potentiometric acid–base titrations were performed with a Schott N 61 micro glass electrode, a Knick 641 digital pH meter, and a Ströhlein Type 3250 microburet. Defined volumes were titrated at room temperature with 0.1 N NaOH.

Ion-exchange chromatographic separations were done with Lewatit S 100 resins on thermostated columns (1 cm × 3 cm; 1 °C). For elution in acidic media[8] we used HNO_3 and in alkaline solution KOH (flow rate ≃ 1 mL/min). Sample volumes were limited to 3 mL in order not to overload the resin. Fractions were monitored spectroscopically with use of a flow cell.

Free tn was extracted with *n*-butyl alcohol from solutions made alkaline after exposure. Determinations were done spectrophotometrically with ninhydrin.[14] As the color and the absorbance of the probes sometimes differed from one run to the other, we analyzed reference samples containing known amounts of tn and $[Cr(tn)_3]^{3+}$ parallel to photolyzed samples.

Results

1. Qualitative Observations. Irradiation of an acid solution of $[Cr(tn)_3]^{3+}$ into the ligand field bands shifted the absorption maxima to the red and produced an increase in pH. When the light was shut off, the pH and the spectral features remained constant for at least 5 h (20 °C) or 30 min (50 °C); see Figure 1. Therefore, stable products were formed. Possible products are the one-ended species $[Cr(tn)_2(tnH)(H_2O)]^{4+}$ and the diaquo complex $[Cr(tn)_2(H_2O)_2]^{3+}$, each one in a cis and/or a trans form. The diaquo complex could have been formed in a fast secondary thermal reaction from the photochemical primary product:

$$[Cr(tn)_3]^{3+} \xrightarrow[H^+/H_2O]{h\nu} [Cr(tn)_2(tnH)(H_2O)]^{4+} \xrightarrow[H^+/H_2O]{kT} [Cr(tn)_2(H_2O)_2]^{3+} + tnH_2{}^{2+}$$

However, direct photochemical production of the diaquo complex cannot be excluded a priori.

Absorption spectra and difference spectra (irradiated vs. nonirradiated samples) showed three isosbstic points at 362, 414, and 487 nm up to 30% conversion, determined from pH change. That means either one product was formed or more products were produced at a constant ratio.

Table I. Spectral Data of the Alkaline Chromatographic Product Fraction

	λ_{max}, nm (ϵ, mol/(L cm))	
$[Cr(tn)_3]^{3+}$	351 (61)	457 (76)
cis-$[Cr(tn)_2(OH)_2]^+$	382 (53)	521 (51)
product fraction[a]	391 (71)	518 (71)
	388 (71)	514 (67)

[a] Typical data of two different runs, corrected for a reference sample; extinction coefficients were estimated from the chromium content of the fractions.

Table II. H^+ Consumption vs. Conversion Determined from Alkaline Chromatography[a]

t_{irr}, min	$\Delta c_{photo}/c_0$	$\Delta c_{dark}/c_0$	$\Delta c_{H^+}/c_0$	$\Delta c_{IEC}/\Delta c_{H^+}$
3	0.15*	0.12*	0.07	0.43*
10	0.09*	0.02*	0.20	0.35*
20	0.17	0.03	0.40	0.35
20	0.23	0.05	0.40	0.48
27	0.32	0.09	0.50	0.46

[a] Legend: conversions determined by alkaline ion-exchange chromatography (chromium content of fractions eluted with ≤0.5 M KOH); Δc_{H^+}, conversion calculated from H^+ consumption; c_0, starting concentration of $[Cr(tn)_3]^{3+}$ ($c_0 \simeq 0.01$ M); $\Delta C_{IEC} = \Delta C_{photo} - \Delta C_{dark}$. Acid samples were loaded on the columns (asterisks indicate alkaline loading): λ_{irr} = 366 nm; T_{irr} = 20.0 ± 0.1 °C; T_{IEC} = 1.0 ± 0.1 °C.

Irradiated alkaline samples showed an analogous behavior: the absorption maxima were shifted to the red, and three isosbestic points were observed (361, 427, and 485 nm). Irradiated solutions were stable for at least 30 min at room temperature. Samples acidified after irradiation showed the same spectral shifts as samples photolyzed in acid medium. The same spectral changes were found in acid samples made alkaline as in samples irradiated in alkaline solution. We therefore conclude that apart from acid–base equilibria of the produced aquo complexes the same products were formed in alkaline and acid solutions. However, the photochemical conversion in alkaline solution was quenched to one-third of that of acid samples (determined spectrophotometrically from acidified solutions).

2. Chromatographic Experiments. Separation of the reaction products in acid medium on strong-acid ion-exchange resins turned out to be problematic for two reasons: (i) a possible diaquo product would have the same charge as the starting material; (ii) $[Cr(tn)_3]^{3+}$ could not be eluted completely so that pure fractions of the one-ended product could not be obtained.

In alkaline solution the aquation products dissociate to the hydroxo complexes $[Cr(tn)_2(tn^*)(OH)]^{2+}$ and $[Cr(tn)_2(OH)_2]^+$, which differ in charge from the starting material. Therefore, we tried to separate the photolysis products in alkaline solution by cation-exchange chromatography. Although we took precautions to work at low temperatures (1 °C), some secondary reactions might have been catalyzed at the column.[2,5] Nevertheless, we feel it necessary to report our results, for the data were reproducible and provide additional evidence.

KOH at 0.5 N concentration eluted the reaction products almost exclusively, whereas with 1 N KOH the $[Cr(tn)_3]^{3+}$ ion appeared. Because all fractions of nonirradiated solutions contained the starting material, we corrected the values of each run for the amount of $[Cr(tn)_3]^{3+}$, as obtained from the dark sample.

Table I shows that the absorption maxima of the first fractions of irradiated samples differ slightly from those of the *cis*-$[Cr(tn)_2(OH)_2]^+$ ion. Table II compares the chromatographic results with those obtained from the pH change.

3. Acid–Base Titrations. In principle the two possible products may be distinguished by potentiometric acid–base titrations; if the diaquo complex is produced, four acid–base equilibria should occur

$$[Cr(tn)_2(H_2O)_2]^{3+} \overset{K_1}{\rightleftharpoons} [Cr(tn)_2(H_2O)(OH)]^{2+} + H^+$$

$$[Cr(tn)_2(H_2O)(OH)]^{2+} \overset{K_2}{\rightleftharpoons} [Cr(tn)_2(OH)_2]^+ + H^+$$

$$tnH_2{}^+ \overset{K_3}{\rightleftharpoons} tnH^+ + H^+$$

$$tnH^+ \overset{K_4}{\rightleftharpoons} tn + H^+$$

with pK_1(trans) = 4.15, pK_2(trans) = 7.64, pK_1(cis) = 4.68

---

(13) Wasgestian, F.; Schläfer, H. L. *Z. Phys. Chem.* (*Munich*) **1966**, *51*, 208.

(14) Häntzsch, S.; Prescher, K. E. *Fresenius' Z. Anal. Chem.* **1965**, *213*, 408.

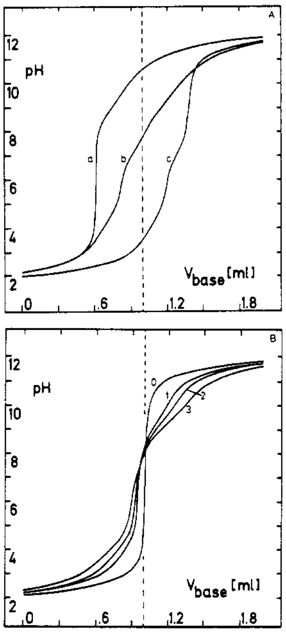


Figure 2. (A) Potentiometric titration of photolysis components with 0.1 N NaOH (0.01 M each component/0.01 M $HClO_4$, T = 22 °C, V = 10 mL): (a) tnH_2^{2+}; (b) tnH_2^{2+} + *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$; (c) *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$. (B) Potentiometric titration of photolyzed acid $[Cr(tn)_3]^{3+}$ solutions (0.01 M complex/0.01 M $HClO_4$, T = 22 °C, $\lambda_{irr} >$ 350 nm, $t_{irr}(0\text{–}3)$ = 0, 2, 3, 4 min).

(estimated), $pK_2(\text{cis})$ = 7.18 (estimated), pK_3 = 8.95, and pK_4 = 10.54. The p*K*'s for all four steps are known or can be estimated by comparison with $[Cr(en)_2(H_2O)_2]^{3+}$.[15-17]

If, on the other hand, the one-ended complex is formed, there will be only two equilibria, provided that the complex is also sufficiently stable in alkaline solution:

$$[Cr(tn)_2(tnH)(H_2O)]^{4+} \rightleftharpoons [Cr(tn)_2(tnH)(OH)]^{3+} + H^+$$

$$[Cr(tn)_2(tnH)(OH)]^{3+} \rightleftharpoons [Cr(tn)_2(tn^*)(OH)]^{2+} + H^+$$

For the first equilibrium a $pK \leq 4.5$ may be estimated, because the deprotonation should be slightly more facile than that of the diaquo species on account of the more positive charge of $[Cr(tn)_2(tnH)(H_2O)]^{4+}$. The coordinated tnH^+ should be more acidic than the free tnH^+ but less acidic than tnH_2^{2+}. Therefore, we expect a p*K* between 9 and 10.

Figure 2A shows the titration curves of the *cis*-diaquo complex, free tn, and their mixture, all dissolved in 0.01 M $HClO_4$. In the absence of the amine, both deprotonation steps are clearly separated, giving rise to points of inflection at pH 4.1 and 7.2 (Figure 2A, curve c). Of the two steps expected for the deprotonation of tnH_2^{2+} only the first one is seen in the titration curve by a point of inflection at pH 9.2. In the mixture, the second dissociation of the complex overlaps the deprotonation of tnH_2^{2+} so that only the first inflection point is observed.

The titration curves of the irradiated solutions of $[Cr(tn)_3]^{3+}$ are presented in Figure 2B. The first point of inflection is found at pH 3.8. A second deprotonation reaction starts above pH 6, while the dissociation of the protonated amine can be assigned to the point of inflection at pH 9.5.

It is instructive to plot the differences in base consumption of irradiated and nonirradiated solutions as a function of pH. Although the ionic strength was not kept constant, it will be almost identical in different samples, if we compare points of equal pH. Figure 3 shows the base consumption relative to the photochemical conversion obtained from pH change. The diagram also contains

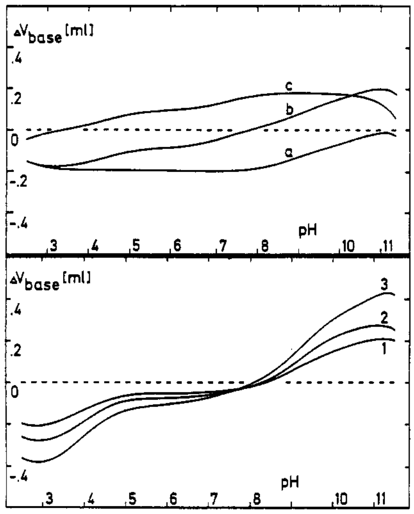


Figure 3. Differences in base consumption of irradiated and nonirradiated samples and differences between constituents and 0.01 M $HClO_4$ (for conditions see Figure 2): (a) tnH_2^{2+}; (b) tnH_2^{2+} + (c); (c) *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$; (1) t_{irr} = 2 min; (2) t_{irr} = 3 min; (3) t_{irr} = 4 min.

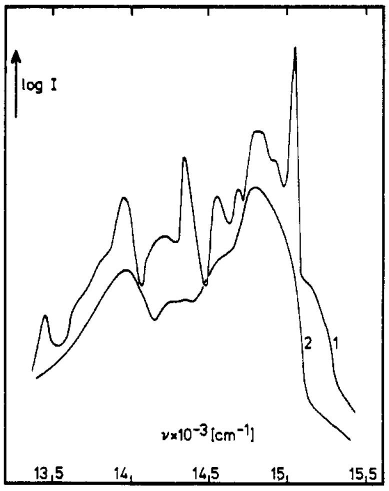


Figure 4. Low-temperature phosphorescence spectra of (1) $[Cr(tn)_3]^{3+}$ and (2) *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$ in a H_2O/dimethyl sulfoxide glass (1:1) at 77 K (λ_{exc} = 438 nm).

the differences for curves b and c of Figure 2A, in order to demonstrate the use of this method. In Figure 2B the second dissociation of the diaquo complex is obscured by the deprotonation of the amine. But the difference curve clearly shows both steps at 0.5 and 1.0 mol of OH^-/mol of complex.

At low pH the photolyzed samples show the H^+ consumption in agreement with the potentiometric determination. After 75% of the protons have been recovered by the dissociation of the aquo complex, a plateau is reached between pH 5.5 and 7. Finally, the curve comes to a maximum at pH 11. Here, one proton is produced for each dissociated Cr–N bond because the protons consumed in acid solution are all recovered and the coordinated water molecules contribute one proton per liberated ammonium ion.

4. Luminescence. We tried to identify the photoproduct by its phosphorescence. The spectra of the starting material, *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$, and irradiated samples were recorded at room temperature in solution and at low temperature (liquid nitrogen) in a dimethyl sulfoxide–H_2O glass (1:1). The $[Cr(tn)_3]^{3+}$ ion showed a structured phosphorescence at 666–735 nm, being in good agreement with literature values.[11,18,19] The diaquo complex had no measurable luminescence at room temperature.[20] In the

---

(15) "Beilsteins Handbuch der Organischen Chemie"; Luckenbach, R., Ed.; Springer Verlag: Berlin, 1979; p 1258.

(16) Couldwell, M. C.; House, D. A.; Powell, H. K. J. *Aust. J. Chem.* **1973**, *26*, 425.

(17) Woldbye, F. *Acta Chem. Scand.* **1958**, *12*, 1079.

(18) Kühn, K.; Wasgestian, F.; Kupka, H. *J. Phys. Chem.* **1981**, *85*, 665.

(19) Porter, G. B.; Schläfer, H. L. *Ber. Bunsenges. Phys. Chem.* **1964**, *68*, 316.

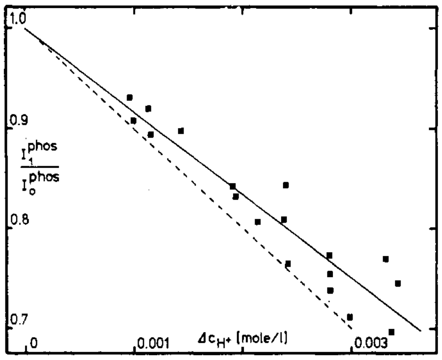


Figure 5. Phosphorescence intensity decrease of photolyzed acid $[Cr(tn)_3]^{3+}$ solutions vs. H^+ consumption (0.01 M complex/0.01 M $HClO_4$, λ_{irr} = 366 nm, T_{irr} = 20 ± 0.1 °C, λ_{exc} = 438 nm (T = 22 °C), λ_{obsd} = 665 nm): (solid line) experimental slope; (dashed line) slope for $\Delta c_{Cr} = \Delta c_{H^+}$. Δc_{H^+} was determined from the pH change; phosphorescence intensities were corrected for the inner filter effect.

low-temperature spectrum the most intense phosphorescence peak had about 40% of the intensity of that of $[Cr(tn)_3]^{3+}$ and coincided with a stronger band of the starting material (Figure 4).

Spectra of photolyzed samples showed no extra emission bands either at room temperature or at low temperature; only the $[Cr(tn)_3]^{3+}$ emission intensity decreased. Excitation of photolyzed samples at the wavelength of the isosbestic point renders the relative decrease in phosphorescence intensity equal to the photochemical conversion, if quenching or sensitation processes are absent. Using 436-nm light, we had to correct our data for the inner filter effect (Figure 5):

$$\frac{I_1^{phos}}{I_0^{phos}} = F\left(1 - \frac{\Delta c}{c_0}\right) \qquad (1)$$

$$F = \frac{E_0}{E_0 + \Delta E}\,\frac{1 - 10^{-(E_0 + \Delta E)}}{1 - 10^{-E_0}}$$

with I_0^{phos} = phosphorescence intensity, c_0 = starting concentration of $[Cr(tn)_3]^{3+}$, Δc = photochemical conversion, E_0 = absorbance of nonirradiated solution at 436 nm, and ΔE = change in absorbance caused by photolysis (436 nm). Due to the short phosphorescence lifetime of about 1 μs and the low concentrations of the photoproducts energy-transfer processes were negligible. Hence, we could obtain the photochemical conversion from the decrease in phosphorescence intensity. Tests with *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$ reproduced the concentrations within 10% accuracy.

Comparing the data obtained from phosphorescence intensity decrease with that from H^+ consumption, we found that proton uptake was larger by a factor of 1.25. The ratio did not depend on the degree of photochemical conversion.

5. Quantum Yields. From the pH increase in weakly acid solutions, the quantum yields for proton uptake can be obtained. Besides, in 0.01 N $HClO_4$ the spectral changes could be correlated with the acid consumption. Thus photochemical conversion could also be determined under conditions where proton uptake was not measurable (pH 0, 1, 3, 13).

The results are shown in Table III. In acid solution the quantum yield was independent of H^+ concentration but dropped to one-third of this value in alkaline solution. Within experimental error the temperature had no influence on the photochemical conversion (5–35 °C; Table III). Secondary photolysis did not interfere in acid solutions at conversions below 30%. In alkaline solutions we observed a slight decrease in the photolysis rate at longer exposure times. These values were extrapolated to zero conversion (cf. Table III).

Table III. pH and Temperature Dependence of Acid $[Cr(tn)_3]^{3+}$ Photolysis on Irradiation at 366 nm

pH	T_{rk}, °C	ϕ_{pH},[a] mol/einstein	ϕ_{LRA},[a] mol/einstein	n
0	20		0.20	4
1			0.22	4
2		0.21	0.21	4/3
		0.22		20
3		0.22	0.21	4/3
13			0.07[c]	15
			0.06[b]	4
2	5	0.21		2
	15	0.21		3
	20	0.21[b]		27
	25	0.22		2
	35	0.21		3

[a] Standard deviations of the quantum yields did not exceed ±0.01. [b] Irradiation with 436-nm light. [c] Extrapolated for $\Delta c/c_0 \rightarrow 0$. [d] All samples used for pH-dependence measurements contained 0.01 M complex/1 M ClO_4^- ($NaClO_4$), except for pH 13 with 0.01 M complex/0.1 M NaOH; the temperature dependence was measured with samples containing 0.01 M complex/0.01 M $HClO_4$. Legend: ϕ_{pH}, conversion determined from H^+ consumption; ϕ_{LRA}, conversion determined from spectral changes (irradiated vs. dark sample); n, number of independent runs.

Table IV. Diamine Release vs. H^+ Consumption in the Photolysis of $[Cr(tn)_3]^{3+}$ (λ_{irr} = 366 nm)

exposure time 6 min		exposure time 9 min	
$\Delta c_{H^+}/c_0$	$\Delta c_{tn}/c_0$	$\Delta c_{H^+}/c_0$	$\Delta c_{tn}/c_0$
0.24	0.024	0.36	0.058
0.26	0.034	0.40	0.056
0.26	0.046	0.36	0.060
0.28	0.040	0.45	0.065
0.27	0.043	0.37	0.048
0.24	0.054	0.37	0.056
0.26 ± 0.02	0.040 ± 0.010	0.39 ± 0.04	0.057 ± 0.005

The spectrophotometric determination of free 1,3-diaminopropane provided evidence for the detachment of the coordinated tn ligand. Table IV compares the amount of liberated tn with the conversion obtained from pH measurements. Fifteen percent of the tn was set free relative to H^+ consumption; i.e., 30% of the $[H^+]$ change was caused by protonation of free tn.

Discussion

The reaction mixture of photolyzed acid $[Cr(tn)_3]^{3+}$ solutions might have contained up to five different chromium(III) complexes, including the starting material. $[Cr(tn)_2(tnH)(H_2O)]^{4+}$ and $[Cr(tn)_2(H_2O)_2]^{3+}$ could have been produced as the cis and the trans isomers. On account of the low conversions ($\Delta c_{H^+}/c_0$ < 0.3) and the great stability of irradiated samples we exclude the presence of a $[Cr(tn)(tnH)_2(H_2O)_2]^{5+}$ ion that would have been formed in a secondary photolysis or a thermal aquation of $[Cr(tn)_2(tnH)(H_2O)]^{4+}$. trans-$[Cr(tn)_2(H_2O)_2]^{3+}$ can be ruled out on spectroscopic reasons, for we did not find absorption at wavelengths longer than 600 nm in irradiated solutions ($\Delta c/c_0$ ≤ 0.05). As aquopentaamine complexes, *cis*- and *trans*-$[Cr(tn)_2(tnH)(H_2O)]^{4+}$ may be expected to have rather similar properties. The corresponding en complexes only differ in the intensity of the absorption bands, significantly.[5] In his ion-exchange experiments Cimolino[6] could not separate two different fractions of the tetrapositive band as he was able to do with photolyzed $[Cr(en)_3]^{3+}$ solutions. In our experiments the spectral features did not depend on the reaction conditions (apart from acid dissociation of the aquo complexes). We therefore assume all reaction products to be formed at a constant ratio. In this case, we can analyze the data on the basis of the average properties of the constituents.

At first sight the ion-exchange results seemed to provide evidence for the sole formation of the diaquo complex: the number of protons consumed during photolysis was twice the number of chromium ions eluted. However, the absorption spectra of the

---

(20) The luminescence of the *cis*-diaquo complex is too weak to interfere with the luminescence of $[Cr(tn)_3]^{3+}$, because in the aquo complex the nonradiative deactivation is faster by a factor of 1000. Phosphorescence decay times at room temperature are 3.1 μs and 3.5 ns for $[Cr(tn)_3]^{3+}$ [26] and *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$,[21] respectively.

(21) Linck, N. J.; Berens, S. J.; Magde, D.; Linck, R. G. *J. Phys. Chem.* **1983**, *87*, 1733.

fractions had the maxima at wavelengths shorter than that of *cis*-$[Cr(tn)_2(OH)_2]^+$. If, on the other hand, only the monodentate species were formed, half of those had to rechelate at the resin, irrespective of the elution conditions. The latter aspect being unlikely, we conclude that both, the *cis*-diaquo and the monoaquo complexes, were present in the reaction mixture.

The same conclusion emerges from the acid–base titrations and the phosphorescence studies. Figure 3 shows that at the plateau (pH 6.5) one-fourth of the protons that had been consumed during photolysis had not been regained by acid dissociation of the aquo complexes. The first dissociation step would be completed at that pH value, as is evidenced in the titration curve of *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$ (Figure 2A). That means the missing protons must still be attached to the coordinated water molecules. This will be the case, if diaquo complexes are formed, where the second deprotonation step takes place at pH 7. Therefore, the 25% of the protons not regained at pH 6 correspond to the concentration of $[Cr(tn)_2(H_2O)_2]^{3+}$.

The luminescence studies lead to the same conclusion. The photochemical conversion obtained from the proton uptake is 1.25 times larger than that determined from the phosphorescence decrease

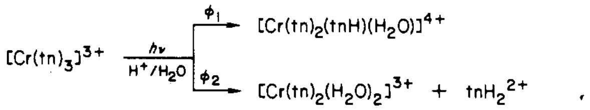
$$\frac{\Delta c_{H^+}}{\Delta c_{phos}} = \frac{c_1 + 2c_2}{c_1 + c_2} = 2 - x_1 \qquad (2)$$

with c_1 and c_2 being the concentrations of the mono- and diaquo complexes, respectively, and x_1 the fraction of the monoaquo complex.

About 20% of the photolyzed $[Cr(tn)_3]^{3+}$ ions have caused the uptake of two protons by the liberation of 1,3-diaminopropane, in agreement with the spectrophotometric determination of free tn.

It can be ruled out that the diaquo species is formed by thermal aquation of the monodentate complex, because this reaction is too slow to account for one-fifth of the photolyzed complexes. The rate constant can be estimated to $k \leqslant 3 \times 10^{-5}\ s^{-1}$ at pH 2 and 50 °C. Besides, we did not find any indication of a thermal postirradiation effect. The reaction is completed within less than 10 μs after irradiation.[22]

These facts force us to consider two photochemical reaction paths, the first leading to the one-ended species and the second including a simultaneous breaking of two coordination bonds:



In this case, the quantum yield for proton uptake is composed of the quantum yields of both reactions:

$$\Phi_{H^+} = \phi_1 + 2\phi_2 = 0.22 \qquad (3)$$

The plateaus in the titration curves and the phosphorescence measurements lead to the total quantum yield

$$\Phi_0 = \phi_1 + \phi_2 = 0.18 \qquad (4)$$

From this the quantum yield for the production of the one-ended species $\phi_1 = 0.14$ and the diaquo complex $\phi_2 = 0.04$ is calculated. Thus $\phi_2/\phi_{H^+} = 0.18$ is in good agreement with the value of 0.15 obtained from spectrophotometric determination of free tn and in reasonable agreement with the value of 0.25 from potentiometric titration. ϕ_1 agrees with the value of 0.12 that Cimolino[6] obtained by ion-exchange chromatography in acid solution, where he did not separate the triply charged $[Cr(tn)_2(H_2O)_2]^{3+}$ from $[Cr(tn)_3]^{3+}$.

The Jahn–Teller theorem requires tetragonal distortion of the photoactive $^4T_{2g}$ (assuming octahedral microsymmetry). Wilson and Solomon[23] reported the equilibrium geometry of $[Cr(NH_3)_6]^{3+}$ in its $^4T_{2g}$ state. They obtained equatorial expansion and axial contraction with respect to the ground-state geometry. From this, the photoactive state should be equatorially labilized. One tetragonal plane in $[Cr(tn)_3]^{3+}$ contains one chelate ring and two nitrogen atoms linked to the axial position. In the latter chelate rings only one coordinative bond will be expanded whereas in the equatorial ring both bonds might break simultaneously.

Another way to explain the formation of two reaction products may be found in the stereochemistry of $[Cr(tn)_3]^{3+}$. According to Jurnak and Raymond,[24] two tn ligands have the chair conformation and one is twisted (skew boat). In the latter both Cr–N bonds may be split jointly.

A second unexpected result is represented by the low total quantum yield of $\Phi_0 = 0.18$, which is about half of that of $[Cr(en)_3]^{3+}$ ($\Phi_0 = 0.37$[5]). The difference might be caused by the higher ring strain in $[Cr(en)_3]^{3+}$. The unstrained ions $[Cr(NH_3)_6]^{3+}$ and $[Cr(NH_2CH_3)_6]^{3+}$, however, have quantum yields of 0.42[25] and 0.47,[26] respectively, still larger than in the $[Cr(en)_3]^{3+}$ system.

It also might be possible that a fast rechelation reduces the quantum yield. This reaction should compete with the protonation of the detached ligand, because after protonation the coordination site is blocked. Increasing the H^+ concentration should enhance the protonation and increase the quantum yield. But the quantum yield was found independent of the acid concentration. If there is any rechelation reaction, it must be faster than the protonation. We therefore have to assume that all relevant processes occur within the time scale of the decaying photoactive quartet state.

Studies of medium effects[27] and high-pressure photolysis[28] indicate an appreciable degree of associative behavior in cationic amine complexes. Therefore, the importance of the incoming ligand must not be neglected. We explain the lower quantum yield of $[Cr(tn)_3]^{3+}$ by blocking some of the sites for the entry of the new ligand (the central methylene groups occupy three of the eight triangular faces of the octahedron).

We thank the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie for financial assistance.

Registry No. $[Cr(tn)_3]^{3+}$, 15276-12-7; *cis*-$[Cr(tn)_2(tnH)(H_2O)]^{4+}$, 97570-19-9; *cis*-$[Cr(tn)_2(H_2O)_2]^{3+}$, 38985-25-0; *trans*-$[Cr(tn)_2(tnH)(H_2O)]^{4+}$, 97643-03-3; *trans*-$[Cr(tn)_2(H_2O)_2]^{3+}$, 38985-24-9; tn, 109-76-2.

---

(22) Value obtained from flash conductivity measurements: Waltz, W., private communication.

(23) Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1978**, *17*, 17.

(24) Jurnak, F. A.; Raymond, K. N. *Inorg. Chem.* **1974**, *13*, 2387.

(25) Krause, H. H.; Wasgestian, F. *Inorg. Chim. Acta* **1978**, *29*, 231.

(26) Unpublished results of this laboratory.

(27) Cusumano, M.; Langford, C. H. *Inorg. Chem.* **1978**, *17*, 2222.

(28) Angermann, K.; van Eldik, R.; Kelm, H.; Wasgestian, F. *Inorg. Chem.* **1981**, *20*, 955.