leads to more rapid metalation reactions with porphyrins having negatively charged substituent groups, with the largest rate enhancements found for the most highly charged substrate. Thus, Uro-I has k_{Zn} = 75 M^{-1} s^{-1} at I = 1.0, 2000 M^{-1} s^{-1} at I = 0.1, and 36 000 M^{-1}/s^{-1} at I = 0. The formally dinegative Deutero-IX varies only from 60 M^{-1} s^{-1} at I = 0 to 25 M^{-1} s^{-1} at I = 1.0. At high ionic strengths, the observed Zn^{2+} rates approach one another, and such ionic leveling effects must be taken into account before porphyrin structure reactivity data can be developed. Such effects perhaps account for the observation that six porphyrins of varying basicity[20,21] exhibit similar incorporation rates toward $Zn(OH)_3^-$ at high ionic strengths.[8]

At I = 0, the formally octa-, tetra-, and dinegative porphyrins react with Zn^{2+} in the order 36 000:1600:60, in the ratio 600:25:1, and a similar order (380:27:1) was found for the same porphyrin charge types by Kassner and Wang[22] for Fe(II) incorporation in a buffered water/pyridine mixture. They demonstrated that the activation energy was constant, and the activation entropy term was responsible for the variation of rate with porphyrin charge, at constant ionic strength. If "A" in eq 6 can be considered equal to Z_aZ_b, the formally 8− porphyrin acts an an effective 2.7− charged ion, the 4− porphyrin as 1.7−, and the 2− derivative as a 0.4− species. Similar lowered effective charge behavior is also found for positively charged porphyrins.[7]

In summary, we report the first full pH and ionic strength profile of a metal–porphyrin incorporation reaction in aqueous solution. Such a rate profile can be explained in terms of the free-base form of the porphyrin reacting with zinc in the order $Zn^{2+} > Zn(OH)_3^- >> Zn(OH)_4^{2-}$. This order may in part reflect electrostatic stabilization of metal–negatively charged porphyrin outer-sphere and activated complexes. In contrast to the case for negative porphyrins, positive porphyrins show incorporation rate increases with increases in ionic strength.[5] However, possible specific-anion catalysis associated with the porphyrin[4] or metal[1] or both complicate interpretations. With uncharged porphyrins in DMF, the metalation rates are fairly independent of ionic strength[1] and show isokinetic behavior,[2] and the overall porphyrin structure becomes influential. For Cu^{2+} in DMF, $k_{Cu} \approx 3 \times 10^2$ M^{-1} s^{-1} for *N*-methylporphyrins, ca. 10^{-2} M^{-1} s^{-1} for tetraphenylporphyrin,[1] ca. 10^{-4} M^{-1} s^{-1} for the "picket fence" porphyrin,[23] and ca. 10^{-5} M^{-1} s^{-1} for the "capped" porphyrin, a factor of over 10^7 at 25 °C. The rate-determining step in such reactions has been postulated to involve a deformed porphyrin with simultaneous loss of the central proton from the porphyrin and solvent from the metal ion.[14]

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Registry No. Zn, 7440-66-6; URO, 607-14-7; COPRO, 14643-66-4; DEUTERO, 448-65-7.

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[20] Worthington, P.; Hambright, P.; Williams, R. F. X.; Feldman, M. R.; Smith, K. M.; Langry, K. C. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 441.

[21] Valiotti, A.; Adeyemo, A.; Williams, R. F. X.; Ricks, L.; North, J.; Hambright, P. *J. Inorg. Nucl. Chem.* **1981**, *43*, 265.

[22] Kassner, R.; Wang, J. *J. Am. Chem. Soc.* **1966**, *88*, 5170.

[23] Turay, J.; Hambright, P. *Inorg. Nucl. Chem. Lett.* **1979**, *35*, L319.

[24] Shamin, A.; Worthington, P.; Hambright, P. *J. Chem. Soc. Pak.* **1981**, *3*, 1.

Communications

Unusual Photobehavior of *trans*-Dicyano(1,4,8,11-tetraazacyclotetradecane)chromium(III) Perchlorate[1]

Sir:

We report here the results of a photostudy of the Cr(III) complex *trans*-$[Cr(cyclam)(CN)_2]ClO_4$, where cyclam is the macrocyclic tetradentate amine ligand 1,4,8,11-tetraazacyclotetradecane. The photobehavior observed in room-temperature solution is in marked contrast to that normally displayed by Cr(III) complexes. The compound shows no discernible photochemical reactivity and exhibits an intense, long-lived (335-μs) $^2E_g \rightarrow {}^4B_{1g}$ phosphorescence. Furthermore, deuteration of the cyclam N–H protons results in a marked increase in the intensity and lifetime of the emission. This *solution* behavior is reminescent of that observed for most Cr(III) complexes at liquid-N_2 temperature[2,3] and for several *solid-state* Cr(III) systems at room temperature.[4] The details and possible significance of these observations are discussed below.

In a recent report Zinato and co-workers[5] described the photochemical behavior of *trans*-$[Cr(NH_3)_4(CN)_2]ClO_4$. This complex differs from most Cr(III) amine systems in that the axial cyanide ligands have stronger ligand field (LF) strengths than the in-plane NH_3 ligands. As a result, for the first spin-allowed quartet excited state the $^4B_{2g}$ component lies substantially lower in energy (~2500 cm^{-1}) than the ^4E_g component.[5,6] An important consequence of this energy ordering is the expectation[5,7] that photolabilization should be essentially restricted to the in-plane NH_3 positions—a prediction experimentally confirmed by Zinato and co-workers[5] (for example, on 440-nm excitation, ϕ_{NH_3} = 0.24 and ϕ_{CN^-} < 0.005). A more limited photochemical investigation by Kirk and Porter[8] of the analogous ethylenediamine system, *trans*-$[Cr(en)_2(CN)_2]ClO_4$, provides further experimental confirmation of this theoretical prediction for species with the $^4B_{2g}$ excited-state component lying lowest in energy. Thus, for such complexes, if amine ligand loss could also be prevented without significant alteration of the overall electronic properties, then photoreactivity might be effectively eliminated altogether.

With this latter objective in mind, we have synthesized and characterized the complex *trans*-$[Cr(cyclam)(CN)_2]ClO_4$.[9] We were hopeful that the presence of the macrocyclic ring would seriously restrict cleavage of an individual Cr–amine bond and render complete cyclam ligand loss highly improbable. LF photolysis (436 nm) was carried out on 0.001 M

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[1] Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982.

[2] G. B. Porter, "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Eds., Wiley, New York, 1975, Chapter 2.

[3] C. D. Flint, *Chem. Br.*, **14**, 223 (1978), and references therein.

[4] N. A. P. Kane-Maguire, G. M. Clonts, and R. C. Kerr, *Inorg. Chim. Acta*, **44**, L157 (1980).

[5] E. Zinato, P. Riccieri, and M. Prelanti, *Inorg. Chem.*, **20**, 1432 (1981).

[6] P. Riccieri and E. Zinato, *Inorg. Chem.*, **20**, 3722 (1981).

[7] L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **99**, 2208 (1977), and references therein.

[8] A. D. Kirk and G. B. Porter, *Inorg. Chem.*, **19**, 445 (1980).

[9] N. A. P. Kane-Maguire, J. A. Bennett, and P. K. Miller, *Inorg. Chim. Acta*, in press. Absorption maxima in aqueous solution are at 414 and 328 nm with molar absorptivities of 63 and 62, respectively.

0020-1669/83/1322-0696$01.50/0

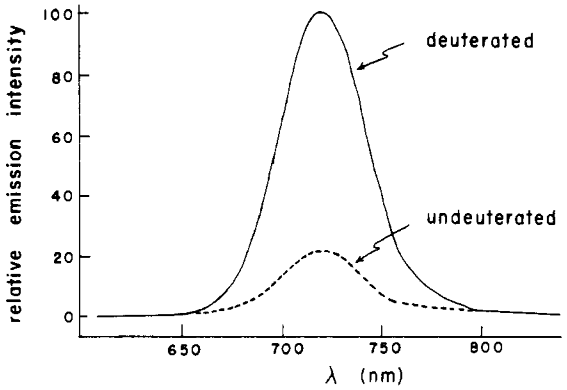

Figure 1. Emission spectra of absorbance-matched deuterated (—) and undeuterated (- - -) *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ in 0.005 M HNO$_3$ aqueous solution at 22 °C on 436-nm excitation.

HNO$_3$ solutions of the title compound with use of an Oriel 1-kW Hg–Xe arc lamp, the output of which was passed through a J-Y Optics H-10 V monochromator (band-pass 16 nm). Cyclam release was monitored via solution pH changes, while a CN$^-$-selective electrode (Sensorex 521 CN) was used for CN$^-$ loss measurements. Even following extended photolysis (28 h) no substitution photochemistry was detected: $\phi_{\text{cyclam}} \le 10^{-5}$ and $\phi_{\text{CN}^-} \le 10^{-5}$.[10]

Steady-state emission near room temperature were obtained with an Aminco-Bowman spectrofluorimeter (Model 48203-D) equipped with a red-sensitive Hamamatsu 666 photomultiplier tube. The spectra were displayed on a Houston 2000 X-Y recorder. Intense $^2E_g \rightarrow {}^4B_{1g}$ phosphorescence centered at 720 nm was observed on 436-nm excitation of an air-saturated 0.005 M HNO$_3$ solution. The signal intensity at 22 °C was greater than 2 times that of a 436 nm absorbance matched, air-saturated, aqueous solution of [Cr(bpy)$_3$](ClO$_4$)$_3$ (where bpy is 2,2′-bipyridine).[11] Only a minor decrease in phosphorescence intensity (23%) occurred on raising the solution temperature to 65 °C. In accord with prior observations on Cr(III) amine systems containing N–H protons,[12,13] emission is totally quenched in basic solution and regenerated on reacidification. Complete deuteration of the cyclam N–H protons was achieved after four cycles of heating a suspension of *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ in 99.8% D$_2$O (Aldrich) at 45 °C for several hours and precipitating with anhydrous LiClO$_4$.[14] The steady-state emission spectra of the deuterated and undeuterated title compound in 0.005 M HNO$_3$ are compared in Figure 1; an approximate fivefold increase in phosphorescence intensity is apparent on deuteration.

Emission lifetimes at room temperature and 77 K were determined with use of a 250-kW N$_2$ laser (Molectron UV-12) via procedures described earlier.[4] The decay signals were recorded on a Tektronix 5441 or 5115 storage oscilloscope and permanently recorded with a Tektronix C-5C camera loaded with Polaroid 667 film. In all cases the emission exhibited single-exponential decay, which on analysis yielded the lifetime data presented in Table I. The corresponding data for some similar ethylenediamine systems are also included for comparison purposes. The ^2E_g excited-state lifetimes for *trans*-[Cr(cyclam)(CN)$_2$]ClO$_4$ in room-temperature solution are among the longest reported for a Cr(III) species. Furthermore, these lifetimes display several unique characteristics—they are essentially temperature independent between room and liquid-N$_2$ temperature, decrease only 22% between 22 and 65 °C, and increase markedly (approximately fivefold) on deuteration. Lifetimes return to undeuterated values when the deuterated sample is placed in basic solution for 1 min and then acidified, consistent with base-catalyzed N–H proton exchange. In surprising contrast to the cases of Cr(CN)$_6^{3-}$ and Cr(phen)$_3^{3+}$ (phen is 1,10-phenanthroline), where long ^2E_g lifetimes are also reported,[11,15] the solution lifetimes of the title compound are virtually unaffected by the presence of dissolved oxygen.

Table I. Phosphorescence Lifetimes (τ) for Various Deuterated and Undeuterated Cr(III) Complexes[a,b]

compd	temp, K	τ_{H_2O}	τ_{D_2O}	τ_{Me_2SO}
trans-[Cr(cyclam)(CN)$_2$]ClO$_4$	338	260		
	295	335	357	330
	77			355
trans-[Cr(cyclam)(CN)$_2$]ClO$_4$	295	1500		1650
(deuterated)	77			3060
trans-[Cr(en)$_2$(CN)$_2$]PF$_6$	295	1		1
	77			210
cis-[Cr(en)$_2$(CN)$_2$]ClO$_4$	295	2		9
	77			200
cis-[Cr(en)$_2$(CN)$_2$]ClO$_4$	295			11
(deuterated)	77			3000

[a] Lifetimes are in μs. All solutions are 0.005 M in nitric acid.
[b] The lifetimes show no discernible dependence on complex concentration.

For Cr(III) complexes the ^2E_g lifetime may be represented as $\tau = 1/(k_r + k)$, where k_r is the radiative rate constant and k is the summed rate constant for all nonradiative processes involving the ^2E_g level;[16] i.e.

$$k = k_{cr} + k_{bisc} + k_{nr} \tag{1}$$

where (with use of O_h notation) k_{cr}, k_{bisc}, and k_{nr} are the rate constants for direct chemical reaction from ^2E_g, back intersystem crossing $^2E_g \rightsquigarrow {}^4T_{2g}$, and $^2E_g \rightsquigarrow {}^4A_{2g}$ radiationless deactivation, respectively. According to the terminology employed by Porter[2]

$$k_{bisc} = (1 - \phi_{isc})k_{-4} \tag{2}$$

where k_{-4} is the *intrinsic* rate constant and k_{bisc} the *effective* rate constant for back-ISC.[17] Since $k >> k_r$ for all Cr(III) complexes (including the title compound), the lifetimes are determined by the nonradiative rate constants. For all prior amine systems investigated, room-temperature solution lifetimes show a weak deuterium isotope effect (characteristic of strong coupling between the initial and final states)[18-20] and strong temperature dependencies. These findings are consistent with ^2E_g decay proceeding via *either* back-ISC or direct ^2E_g reaction, and definitive experimental distinctions between these two alternative modes have been difficult to devise.[4,16,19-23]

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(10) After 28-h irradiation, minor spectral changes occurred below 300 nm, which may be associated with trans → cis isomerization.
(11) N. Serpone, M. A. Jamieson, R. Sriram, and M. Z. Hoffman, *Inorg. Chem.*, **20**, 3983 (1981).
(12) C. H. Langford and L. Tipping, *Can. J. Chem.*, **50**, 887 (1972).
(13) N. A. P. Kane-Maguire, J. E. Phifer, and C. G. Toney, *Inorg. Chem.*, **15**, 593 (1976).
(14) The extent of deuteration (>98%) was determined via IR spectroscopy by monitoring the relative areas of the absorptions in the N–H and N–D stretching regions.
(15) H. F. Wasgestian, *J. Phys. Chem.*, **76**, 1947 (1972).
(16) A. R. Gutierrez and A. W. Adamson, *J. Phys. Chem.*, **82**, 902 (1978).
(17) A good discussion bearing on the relationship between k_{bisc} and k_{-4} is found in ref 21, p 2401.
(18) D. J. Robbins and A. J. Thompson, *Philos. Mag.*, **36**, 999 (1977), and references therein.
(19) N. A. P. Kane-Maguire, R. C. Kerr and J. R. Walters, *Inorg. Chim. Acta*, **33**, L163 (1979).
(20) R. T. Walters and A. W. Adamson, *Acta Chem. Scand.*, **A33**, 53 (1979).
(21) L. S. Forster, J. V. Rund, F. Castelli, and P. Adams, *J. Phys. Chem.*, **86**, 2395 (1982).
(22) M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. Z. Hoffman, *J. Am. Chem. Soc.*, **100**, 2694 (1978).
(23) A. D. Kirk, *Coord. Chem. Rev.*, 225 (1981).

However, at liquid-N_2 temperature lifetimes show a strong deuterium isotope effect characteristic of a dominant weak-coupled deactivation mode, in accord with ${}^2E_g \rightsquigarrow {}^4A_{2g}$ relaxation.[3]

To our knowledge *trans*-Cr(cyclam)$(CN)_2^+$ is the first Cr(III) complex to display strong *intramolecular* deuterium isotope effects in room-temperature solution. The ISC efficiency (ϕ_{isc}) of $Cr(bpy)_3^{3+}$ has been recently shown to exhibit a marked deuterium isotope effect;[24] however, this is a *solvent* isotope effect (H_2O vs. D_2O) and in addition ${}^2E_g$ lifetimes were unaffected.[25] From our observation that the emission intensity and lifetime of *trans*-Cr(cyclam)$(CN)_2^+$ show almost identical enhancements on N-H deuteration, we conclude that ϕ_{isc} remains essentially constant and the increase in emission intensity results primarily from a decrease in the nonradiative rate constants k from the ${}^2E_g$ level. In particular, these observations eliminate back-ISC and direct chemical reaction as important ${}^2E_g$ relaxation modes in room-temperature solution. This conclusion is supported by the very small temperature dependence observed for the emission intensity and lifetime. For one other Cr(III) complex, $Cr(CN)_6^{3-}$, there is excellent evidence for the absence of back-ISC and direct ${}^2E_g$ reaction as important deactivation pathways for the ${}^2E_g$ state.[15] However, for $Cr(CN)_6^{3-}$ the rate constant for ${}^2E_g \rightsquigarrow {}^4A_{2g}$ radiationless deactivation displays a significant temperature dependence; in dimethylformamide solution the emission lifetime shows an apparent activation energy of 9 kcal mol^{-1}.[26] These temperature differences for $Cr(CN)_6^{3-}$ and *trans*-Cr(cyclam)$(CN)_2^+$ may be associated in part with the utilization of a lower frequency vibrational mode for ${}^2E_g \rightsquigarrow$ ground state radiationless decay in the former case ($C\equiv N$) compared with N—H). Some support for this view may be found in the greater lifetime variation with temperature (295–77 K) of *trans*-Cr(cyclam)$(CN)_2^+$ upon deuteration (Table I).

The lifetime data for *trans*-Cr(cyclam)$(CN)_2^+$ also provide an interesting contrast with those for *trans*- and *cis*-Cr$(en)_2(CN)_2^+$ (Table I). In keeping with the case for other Cr(III) amines, the lifetimes of both ethylenediamine complexes increase dramatically on lowering the temperature to 77 K, accompanied in the case of the cis species by a switch from a weak to a strong deuterium isotope effect.[27] Several alternative rationalizations for these differences warrant consideration.

Scheme 1. Direct reaction out of the ${}^2E_g$ level is primarily responsible for the short ${}^2E_g$ lifetime of *trans*- and *cis*-Cr$(en)_2(CN)_2^+$ in room-temperature solution. Back-ISC is inefficient in both the en and cyclam complexes. Since the cyclam species is photoinert, the ${}^2E_g$ lifetime is therefore greatly lengthened.

Scheme 2. Back-ISC is primarily responsible for the short ${}^2E_g$ lifetime of *trans*- and *cis*-Cr$(en)_2(CN)_2^+$ in room-temperature solution. The ${}^2E_g$ level is inert toward direct chemical reaction. Since back-ISC is between states with different equilibrium geometries, some structural rearrangement accompanies the process. The steric constraints imposed by the macrocyclic ring may therefore render back-ISC inefficient for *trans*-Cr(cyclam)$(CN)_2^+$, leading to a long ${}^2E_g$ lifetime.[28-30]

Scheme 3. The rate constant for back-ISC, k_{-4} (eq 2), is much greater than k_{cr} and k_{nr} (eq 1) for both the en and cyclam complexes. However, the quantum yield for forward-ISC, ϕ_{isc}, is essentially unity for *trans*-Cr(cyclam)$(CN)_2^+$ due to elimination of the reaction pathway out of the ${}^4B_{2g}$ excited state. Thus, the effective rate constant for back-ISC, k_{bisc}, is small in the cyclam case; back-ISC therefore is an inefficient ${}^2E_g$ decay pathway, and the lifetime increases.[17]

No clearcut choice between these three schemes lifetime[32] of at present. However, scheme 1 receives some support from the unusually large energy gap between the lowest excited quartet and the lowest doublet indicated from absorption and emission data for these three cyanide-containing complexes.[8,9,31] The gap is larger than that for $Cr(bpy)_3^{3+}$, where back-ISC is considered highly improbable.[22,23] Finally, we note that the long ${}^2E_g$ lifetime[32] of *trans*-Cr(cyclam)$(CN)_2^+$ coupled with its strong luminescence and photoinertness make it an attractive candidate for future energy-transfer and electron-transfer studies with a variety of substrate molecules.

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Registry No. *trans*-[Cr(cyclam)$(CN)_2$]ClO_4, 84277-87-2; *trans*-[Cr$(en)_2(CN)_2$]PF_6, 84237-84-3; *cis*-[Cr$(en)_2(CN)_2$]ClO_4, 56848-41-0; deuterium, 7782-39-0.

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(24) R. Sriram, M. Z. Hoffman, and N. Serpone, *J. Am. Chem. Soc.*, **103**, 997 (1981).

(25) A small increase in emission intensity occurs for *trans*-Cr(cyclam)$(CN)_2^+$ on changing from acidified H_2O to acidified D_2O as solvent. However, this increase is accompanied by a comparable increase in emission lifetime (Table I), indicating ϕ_{isc} is independent of *solvent* deuteration.

(26) R. Dannohl-Fickler, H. Kelm, and F. Wasgestian, *J. Lumin.*, **10**, 103 (1975).

(27) Deuteration studies on *trans*-Cr$(en)_2(CN)_2^+$ were precluded by the lack of sufficient material. Kirk and Porter[8] have also noted synthetic problems associated with this compound.

(28) We thank Mark S. Wrighton for valuable comments on this point.

(29) Kutal and Adamson[30] have clearly demonstrated the importance of cyclam steric restraints on the photoreaction quantum yield for *trans*-Cr(cyclam)Cl_2^+. This compound differs importantly from *trans*-Cr(cyclam)$(CN)_2^+$ in that the lowest lying quartet excited-state component is ${}^4E_g$, for which *z*-axis photolabilization (i.e., Cl^- release) is anticipated.

(30) C. Kutal and A. W. Adamson, *Inorg. Chem.*, **12**, 1990 (1973).

(31) A. P. Sattleberger, D. D. Darsow, and W. B. Schapp, *Inorg. Chem.*, **15**, 1412 (1976).

(32) For convenience we have employed throughout the symmetry label ${}^2E_g$ to denote the lowest lying doublet excited state, although this label applies only for systems with strict O_h symmetry.

Department of Chemistry **N. A. P. Kane-Maguire***
Furman University **W. S. Crippen**
Greenville, South Carolina 29613 **P. K. Miller**

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