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Article

Effects of Steric Constraint on Chromium(III) Complexes of Tetraazamacrocycles. 3. Insights into the Temperature-Dependent Radiationless Deactivation of the ^2E_g (O_h) Excited State of *trans*-$[Cr(N_4)(CN)_2]^+$ Complexes

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Macrocyclic complexes of the type *trans*-$[Cr(N_4)(CN)_2]^+$, where N_4 = cyclam, 1,11-C_3-cyclam, and 1,4-C_2-cyclam demonstrate significant variation in their room-temperature excited-state behavior; namely, the lifetimes of the ^2E_g (O_h) excited states are 335, 23, and 0.24 μs, respectively. The lifetimes of these complexes have been measured in acidified H_2O/dimethyl sulfoxide over the temperature range between –30 and +95 °C. Arrhenius activation parameters were calculated from these data. There was very little variation in the values of the Arrhenius preexponential factor between these three complexes, whereas the value of E_a is 40.6 kJ/mol for the cyclam complex, 35.5 kJ/mol for the 1,11-C_3-cyclam complex, and 22.3 kJ/mol for the 1,4-C_2-cyclam complex. Thus, differences in the room-temperature excited-state lifetimes can be rationalized based on the competition between thermally independent nonradiative relaxation and a thermally activated channel. To test whether a photodissociation mechanism involving Cr–macrocyclic N bond cleavage is a plausible explanation for the thermally activated relaxation pathway, samples of the cyclam complex were photolyzed in acidified D_2O. A marked increase in the lifetime after photolysis demonstrated the occurrence of photodeuteration and thus a likely photodissociation of a macrocyclic N.

Introduction

The lowest-energy ^2E_g (O_h) excited states of many chromium(III) complexes in fluid solution exhibit two regimes with respect to their relaxation rates, namely, a strongly temperature-dependent (high-temperature) region and a weakly temperature-dependent (low-temperature) regime.[1−5] An operationally useful formalism discussed for chromium(III) complexes expresses the observed excited-state decay rate constant, k_{obs}, as the sum of temperature-dependent and -independent components (eq 1).[1b] The strongly temperature-dependent regime can be explained with classical activation energies of 25−60 kJ/mol.[1−4] Endicott has summarized possibilities for the temperature-dependent deactivation pathways for ^2E_g chromium(III) excited states (pathways b−d in Figure 1).[5,6]

$$\tau^{-1} = k_{obs} = k(T) + k^\circ \qquad (1)$$

We have recently been studying a set of *trans*-dicyanochromium(III) complexes of topologically constrained tetraazamacrocycles, namely, *trans*-$[Cr(1,11\text{-}C_3\text{-cyclam})(CN)_2]^+$ and *trans*-$[Cr(1,4\text{-}C_2\text{-cyclam})(CN)_2]^+$ (Figure 2), to determine the effect that the additional strap has on the overall chemistry and photophysics relative to the cyclam complex.[7,8]

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(1) (a) Targos, W.; Forster, L. S. *J. Chem. Phys.* **1966**, *44*, 4342−4346. (b) Forster, L. S. *Coord. Chem. Rev.* **2002**, *227*, 59−92.

(2) Pfeil, A. *J. Am. Chem. Soc.* **1971**, *93*, 5395−5398.

(3) Allsopp, S. R.; Cox, A.; Kemp, T. J.; Reed, W. J.; Sostero, S.; Traverso, O. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 162−173.

(4) Endicott, J. F.; Tamilarasan, R.; Lessard, R. B. *Chem. Phys. Lett.* **1984**, *112*, 381−386.

(5) Endicott, J. F.; Lessard, R. B.; Lei, Y.; Ryu, C. K.; Tamilarasan, R. In *Excited States and Reactive Intermediates*; Lever, A. B. P., Ed.; ACS Symposium Series 307; American Chemical Society: Washington, DC, 1986; pp 85−103.

(6) Lessard, R. B.; Heeg, M. J.; Buranda, T.; Perkovic, M. W.; Schwarz, C. L.; Rudong, Y.; Endicott, J. F. *Inorg. Chem.* **1992**, *31*, 3091−3103.

(7) Wright-Garcia, K.; Basinger, J.; Williams, S.; Hu, C.; Wagenknecht, P. S.; Nathan, L. C. *Inorg. Chem.* **2003**, *42*, 4885−4890.

(8) Wagenknecht, P. S.; Hu, C.; Ferguson, D.; Wright-Garcia, K.; Nathan, L. C.; Hancock, R. D.; Whitehead, J. M.; Vagnini, M. T. *Inorg. Chem.* **2005**, *44*, 9518−9526.

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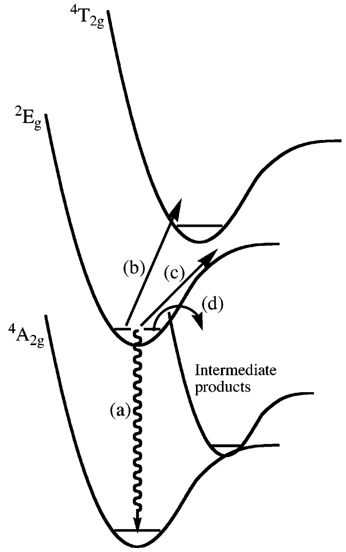

Figure 1. Qualitative potential energy well diagram for chromium(III) complexes. Radiationless ^2E_g deactivation pathways include (a) direct deactivation to the ground state, (b) back intersystem crossing, (c) direct doublet reactivity, or (d) crossing to an intermediate in a ground-state electronic configuration.

Differences in thermal reactivity, UV−vis absorption spectra, and low-temperature photophysics can be explained on the basis of steric arguments, symmetry arguments, and differences in the number of N−H oscillators in the molecule. However, differences in the room-temperature photobehavior of these complexes have eluded explanation. For example, the 1,11-C_3-cyclam and 1,4-C_2-cyclam complexes have room-temperature ^2E_g excited-state lifetimes that are 1−3 orders of magnitude lower, respectively, than the corresponding cyclam complex.[7,8] In addition, although the excited-state lifetime of the cyclam complex is nearly temperature-independent at room temperature,[9] the lifetimes for the complexes of the topologically constrained ligands are strongly temperature-dependent near room temperature in an acidified aqueous solution and the Arrhenius plots are linear.[8] We have attempted to elucidate the cause of these differences.[8] As is typically the case for cyanoam(m)ines, back intersystem crossing (Figure 1b) as the mechanism for the thermally activated relaxation is inconsistent with our experimental results.[8] Productive photoreaction has also been ruled out. Several nonproductive photoreactions have also been investigated: Molecular mechanics studies suggest that neither solvent association nor symmetry-destroying molecular “twists” are likely causes for the temperature-dependent regime. However, one possibility that was *not* excluded in these investigations was macrocyclic amine dissociation followed by rapid recoordination.[8] In an attempt to more thoroughly understand the temperature-dependent behavior, we have performed a thorough investigation of the temperature dependence of the emission lifetimes of the complexes shown in Figure 2, employing a much broader temperature range than that in prior studies.[8] The results of these investigations are reported herein, along with photodeuteration studies, which provide support for the hypothesis that thermal deactivation may be due to Cr−macrocyclic N bond dissociation.

Experimental Section

Materials and Methods. Reagent-grade dimethyl sulfoxide (DMSO), D_2O, and HCl(aq) were used without further purification. The complexes *trans*-[Cr(1,4-C_2-cyclam)$(CN)_2$]PF_6,[7] *trans*-[Cr(1,11-C_3-cyclam)$(CN)_2$]PF_6,[8] and *trans*-[Cr(cyclam)$(CN)_2$]ClO_4[9] were prepared according to literature procedures. All measurements were performed under an air atmosphere. UV−vis absorption spectra were recorded using an HP-8452 spectrophotometer. Emission lifetimes were measured using as the excitation source a Photon Technology International (PTI) GL-3300 pulsed-nitrogen laser fed into a PTI GL-302 dye laser. The dye laser was operated at 440 nm, corresponding to $^4A_{2g} \rightarrow {}^4T_{2g}$ (O_h) excitation of the *trans*-$[Cr(N_4)(CN)_2]^+$ complexes. A TLC 50 temperature-controlled fluorescence cuvette holder from Quantum Northwest housed the sample, and emission was monitored at right angles through a Corning CS 2-64 cutoff filter using a Hamamatsu R928 photomultiplier tube. The signal from the photomultiplier was fed into a LeCroy 9350A digital oscilloscope and stored for further analysis. Exponential fits typically exceeded $r = 0.9999$.

Photodeuteration Studies. Extended photolyses were performed on absorbance-matched solutions (~1 mM) in a 1-cm glass emission cell using a Rayonet photochemical reactor (RPR-100) operating at 350 nm, corresponding to $^4A_{2g} \rightarrow {}^4T_{1g}$ (O_h) excitation of *trans*-$[Cr(N_4)(CN)_2]^+$. The photon flux on a 3-mL sample was measured as 5×10^{16} photons/s using potassium ferrioxalate actinometry.[10] For temperature control, the cuvette was placed in a water bath on a small hot plate placed into the photochemical reactor.

Results and Discussion

Temperature Dependence of the Excited-State Lifetimes. Significant differences in room-temperature excited-state lifetimes between complexes have been related to thermally activated behavior. Thus, factors that influence the room-temperature lifetimes include the activation barrier, the Arrhenius preexponential factor, and the temperature at which the transition occurs from the weakly temperature-dependent regime to the thermally activated regime.[1,4,5] To determine the role of such factors for the complexes shown in Figure 2, we have performed an investigation of the $^2E_g \rightarrow {}^4A_{2g}$ (O_h) emission lifetimes of these complexes over the temperature range of −31 to +95 °C (the operational range of our thermostated cuvette holder). A broad temperature range has been chosen so as to alleviate some concerns about the reliability of thermal activation parameters obtained from statistical fits of the data.[1b] We have chosen a 1:1 DMSO/H_2O solvent system for two reasons, namely, (1) a large liquid operational range and (2) straightforward comparison with 77 K data typically performed in a DMSO/H_2O glass. The solutions were also made 0.01 M in HCl (using concentrated HCl) to avoid the known base-quenching mechanism for the cyclam complex.[5,9] It is also worth noting that there are at most only moderate differences in the room-

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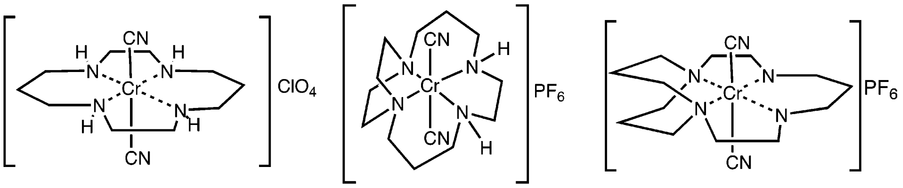
(9) (a) Kane-Maguire, N. A. P.; Bennett, J. A.; Miller, P. K. *Inorg. Chim. Acta* **1983**, *76*, L123−L125. (b) Kane-Maguire, N. A. P.; Crippen, W. S.; Miller, P. K. *Inorg. Chem.* **1983**, *22*, 696−698.

(10) (a) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518−536. (b) Bowman, W. D.; Demas, J. N. *J. Phys. Chem.* **1976**, *80*, 2434−2435. (c) Kirk, A. D.; Namasivayam, C. *Anal. Chem.* **1983**, *55*, 2428−2429.



[Cr(cyclam)(CN)$_2$]ClO$_4$ [Cr(1,4-C$_2$-cyclam)(CN)$_2$]PF$_6$ [Cr(1,11-C$_3$-cyclam)(CN)$_2$]PF$_6$

Figure 2. *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ complexes discussed in this paper.

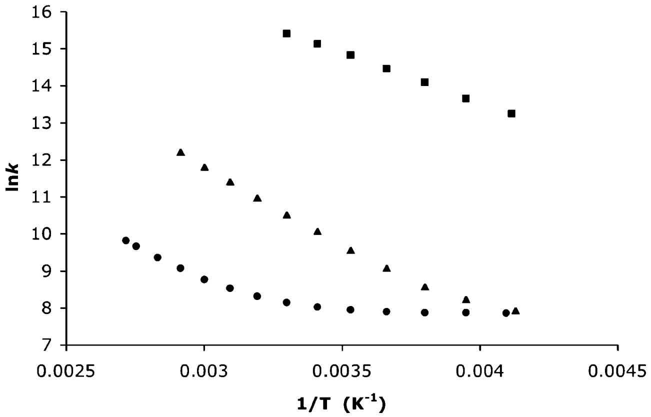


Figure 3. Temperature dependence of the ^2E_g excited-state lifetimes of *trans*-[Cr(cyclam)(CN)$_2$]$^+$ (●), *trans*-[Cr(1,11-C$_3$-cyclam)(CN)$_2$]$^+$ (▲), and *trans*-[Cr(1,4-C$_2$-cyclam)(CN)$_2$]$^+$ (■) in 1:1 DMSO/H$_2$O (0.01 M HCl).

Table 1. Arrhenius Parameters for Thermally Activated ^{2}E Relaxation of *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ and Room-Temperature (RT) Lifetimes for These Complexes

complex	E_a (kJ/mol)	A (s^{-1})	T_{tr} (°C)	RT lifetime (μs)
cyclam	40.6	9×10^9	30[a]	335[c]
1,11-C$_3$-cyclam	35.5	5.0×10^{10}	−25[b]	23[d]
1,4-C$_2$-cyclam	22.3	3.4×10^{10}	−110[b]	0.24[d]

[a] Determined from Figure 3. [b] Determined from the temperature at which the *y* value of the Arrhenius plot equals ln $k°$ ($k°$ is assumed to be the inverse of the 77 K lifetime; $\tau_{77\,K} = 535$ μs for 1,11-C$_3$-cyclam and 322 μs for 1,4-C$_2$-cyclam). [c] From ref 9. [d] From ref 8.

temperature lifetimes of the complexes in acidified H$_2$O versus acidified DMSO, i.e., no significant difference for the cyclam complex; 23 vs 58 μs, respectively, for the 1,11-C$_3$-cyclam complex; and 0.24 vs 0.37 μs, respectively, for the 1,4-C$_2$-cyclam complex. In the DMSO/H$_2$O solvent mixture, the room-temperature lifetimes are intermediate between the values given above. The temperature dependence is summarized as an Arrhenius plot in Figure 3.

It is noteworthy that the thermal relaxation data for the cyclam complex is fully in the temperature-independent regime at the lower temperatures measured (≤−10 °C). The data for the 1,11-C$_3$-cyclam complex, on the other hand, are just beginning to show curvature indicative of its transition into the low-temperature regime; i.e., at −31 °C, the measured lifetime is 358 μs, whereas its 77 K lifetime has been reported to be 535 μs.[8] Finally, the data for the 1,4-C$_2$-cyclam complex are linear over the entire region measured. Higher temperatures for the 1,4-C$_2$-cyclam complex are omitted because of evidence of some thermal decomposition and decreasing signal-to-noise ratios at the lower lifetimes. Activation energies and Arrhenius preexponential factors can be determined from Arrhenius plots for the 1,4-C$_2$-cyclam complex ($r^2 = 0.9993$) and for the 1,11-C$_3$-cyclam complex in its linear range (10−70 °C; $r^2 = 0.9997$). For the cyclam complex, on the other hand, the linear region is never reached. Therefore, the observed lifetime data ($\tau = 1/k$) were fit[11] to eq 2, as has been done by Allsopp et al. for a series of chromium(III) complexes.[3] Values from the three-parameter fit (A, E_a, and $k°$) for the cyclam complex agree well with linear plots obtained by plotting ln($k - k°$) vs T^{-1}.[12] Alternatively, the data could be fit by the procedure adopted by Endicott in which the temperature dependence of the Arrhenius preexponential factor is considered.[4] In light of the excellent fit of our data to eq 2 (see the Supporting Information), this alternative treatment is unlikely to significantly alter the values of the Arrhenius parameters and therefore is unlikely to significantly affect the conclusions herein.[13]

$$k = k^\circ + A\mathrm{e}^{-E_a/RT} \tag{2}$$

Arrhenius parameters from the Arrhenius plots for the 1,4-C$_2$-cyclam and 1,11-C$_3$-cyclam complexes and from the three-parameter fit of eq 2 for the cyclam complex are summarized in Table 1. The E_a values agree closely with the literature values obtained from measurements in an acidified aqueous solution for the cyclam complex[4] and the topologically constrained complexes.[8] The transition temperature, T_{tr}, from the thermally independent regime to the thermally activated regime can be determined either directly from Figure 3 or from an extrapolation of the Arrhenius plot. The importance of T_{tr} in governing room-temperature excited-state lifetimes has been discussed.[5] These values are also collected in Table 1, along with the room-temperature lifetimes for each complex for the sake of discussion.

The relatively close agreement of the Arrhenius preexponential factors among this set of complexes indicates that it is the activation barriers that dominate the transition temperature and thus the room-temperature behavior. Consequently, the difference in transition temperatures is best

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[11] Fitting was performed using: *IGOR Pro*, version 5.02; WaveMetrics, Inc.: Lake Oswego, OR, 2004.

[12] The data for the cyclam complex were also fit by constructing an Arrhenius plot by assuming that the −30 °C datum represents $k°$ and plotting ln($k - k°$) vs 1/T. A plot using the eight data points from 30 to 95 °C yielded a straight line ($r^2 = 0.9999$). Arrhenius parameters obtained using this method were $E_a = 41.3$ kJ/mol and $A = 1.1 \times 10^{10}$, in good agreement with the three-parameter fit.

[13] In ref 4, the thermal relaxation data are fit to the equation $k_{nr} = k° + C(k_BT^*)^{1/2}\exp(-E_a/k_BT^*)$, where $k_BT^* = {}^1/_2 h\omega_{ave} \coth(h\omega_{ave}/2k_BT)$ and C is a collection of constants. Using the value of 440 cm^{-1} for $h\omega_{ave}$ given in ref 4 for the cyclam complex, the preexponential factor would vary by only about 3% over the temperature range considered for that complex herein.

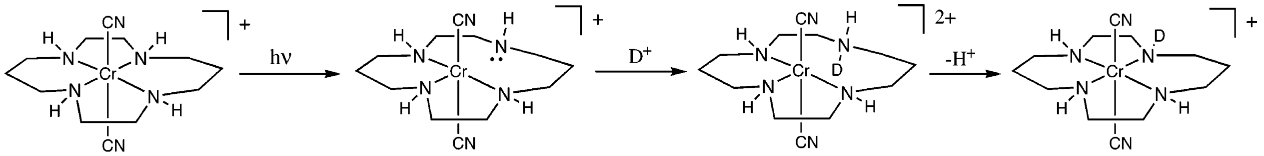

Figure 4. Possible mechanism for macrocyclic N−H deuteration in an acidified solution.

Table 2. Change of Room-Temperature Lifetimes (μs) of *trans*-[Cr(cyclam)(CN)$_2$]$^+$ Samples upon Various Conditions[a]

upon 75 °C, 3 h of photolysis in acidified (0.01 M HCl) D_2O	upon 75 °C, 3 h in the dark in acidified (0.01 M HCl) D_2O	upon 33 °C, 3 h of photolysis in acidified (0.01 M HCl) D_2O	upon 75 °C, 3 h of photolysis in acidified (0.01 M HCl) H_2O
389[b] to 972	390 to 489	378 to 448	374 to 298

[a] Irradiation at 350 nm. [b] There is a slight solvent deuterium isotope effect on the lifetime.

explained in terms of a competition between direct deactivation (pathway a in Figure 1) and the thermally activated pathways (b−d in Figure 1). As expected in this circumstance, the complex with the lowest activation barrier for thermally activated relaxation (1,4-C$_2$-cyclam) is able to access this deactivation channel at a lower temperature so that at room temperature it has the shortest room-temperature excited-state lifetime. The complex with the highest activation barrier (cyclam) can only access this relaxation channel at higher temperatures and thus has the longest room-temperature excited-state lifetime. We therefore come to the conclusion that the excited-state decay pathways for the topologically constrained complexes may not intrinsically be different from those of the parent cyclam complex. It is entirely possible that the thermal deactivation processes may be very similar for each, just with a different barrier height.

Investigations into the Mechanism of Thermally Activated Relaxation. As mentioned in the Introduction, we have previously investigated possible mechanisms for this thermally activated relaxation pathway and determined that back intersystem crossing, productive photoreaction, solvent association, and certain skeletal vibrations that are important in other systems are unlikely reasons for the differences in lifetimes observed here.[8] In that paper, the only mechanism that was not ruled out was the photodissociation of a macrocyclic N−Cr bond followed by rapid recoordination. The feasibility of this mechanism is supported by the fact that nonmacrocyclic *trans*-[Cr(N$_4$)(CN)$_2$]$^+$ complexes undergo substantial loss of the amine ligands upon photolysis.[14−17] In fact, this in-plane amine ligand loss is the predominant pathway for the photodecomposition of these complexes. If such N labilization occurs with the macrocyclic ligands, the most likely result would be rapid recoordination due to the macrocyclic effect. However, if this does occur, it could be a relaxation pathway for the excited state. Ligand dissociation return was hypothesized as a possible mechanism by Allsopp et al.[3] in their investigations of a number of chromium(III) complexes. In addition, Endicott's investigations into the thermal behavior of *trans*-[Cr(cyclam)(CN)$_2$]$^+$ in an aqueous solution suggested that the thermally activated relaxation mechanism involved high-energy deformations of the macrocyclic ring. The vibrational modes implicated in his investigation are consistent with Cr−N skeletal vibrations.[4]

One test for the macrocyclic N dissociation mechanism involves analyzing for macrocyclic N−H deuteration upon photolysis of the complexes in acidified D$_2$O. In an acidified solution, the only possible mechanism for N−H deuteration involves protonation of a lone pair on a dissociated N (Figure 4). Thus, photodeuteration would offer compelling evidence for the photodissociation of a macrocyclic N. Deuteration of *trans*-[Cr(cyclam)(CN)$_2$]$^+$ is easily detectable because of the large deuterium isotope effect on its excited-state lifetime; namely, the room-temperature lifetime in an acidified aqueous solution is 335 μs for *trans*-[Cr(cyclam)(CN)$_2$]$^+$ and 1600 μs for *trans*-[Cr(cyclam-d_4)(CN)$_2$]$^+$.[9] If photodeuteration occurs in an acidified D$_2$O solution, then this should be evident by an increased lifetime. Table 2 summarizes our experiments.

Upon photolysis in D$_2$O for 3 h at 75 °C, there is an increase in the lifetime from 389 to 972 μs. The UV−vis spectrum also showed evidence of some decomposition of the complex under these conditions. As a control, an absorbance-matched sample in D$_2$O was kept at the same temperature in the dark for 3 h and its lifetime increased to only 489 μs. Though this indicates some degree of thermal deuteration, the presence of a photodeuteration component is clearly evident. In addition, a similar photolysis experiment was performed at 35 °C, and the lifetime increased to only 448 μs. By comparison with the 75 °C experiment, this indicates that the photodeuteration process is thermally activated. Finally, as shown in the final entry of Table 2, a sample was photolyzed at 75 °C in acidified H$_2$O instead of D$_2$O in order to isolate the effect of decomposition on the lifetime. In that case, the lifetime decreased from 374 to 298 μs, demonstrating that decomposition products from photolysis quench the excited state. Such quenching by photoproducts is not unprecedented[15] and indicates that the lifetime increase observed in column 1 would likely be even larger in the absence of this photodecomposition.

Ideally, the activation barrier for photodeuteration of the cyclam complex could be calculated from the above data and compared to the activation barrier for relaxation. There are two impediments to this treatment. First, there is rapid energy-transfer self-exchange between deuterated and undeuterated *trans*-[Cr(cyclam)(CN)$_2$]$^+$. This accounts for lifetime traces exhibiting single-exponential behavior but also

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(14) Kirk, A. D.; Porter, G. B. *Inorg. Chem.* **1980**, *19*, 445−447.
(15) Kirk, A. D.; Fernando, S. R. L. *Inorg. Chem.* **1992**, *31*, 656−661.
(16) Kirk, A. D.; Fernando, S. R. L. *Inorg. Chem.* **1994**, *33*, 4041−4047.
(17) Zinato, E. *Coord. Chem. Rev.* **1994**, *129*, 195−245.

results in a nonlinear relationship between the lifetime and percent deuteration.[18] Though it would be possible to mathematically treat this behavior, such a model would require knowledge of the lifetimes of mono-, di-, and tri-N-deuterio complexes in addition to the already known per-N-protio and per-N-deuterio complexes. Second, because the observed decomposition results in photoquenching of the lifetime, it is impossible to extract the increase in magnitude of the lifetime due only to photodeuteration.

Nonetheless, the present photodeuteration results offer strong evidence for macrocyclic N photodissociation for the cyclam complex, in agreement with the aforementioned mechanism proposed by Allsopp et al.[3] and with Endicott's data[4] implicating involvement of a Cr−N stretch in thermally activated relaxation. If this is also the dominant mechanism for thermally activated relaxation of the ^2E_g excited state, it might explain why the activation barrier is higher for the cyclam complex than for the corresponding topologically constrained complexes in Figure 2. Poorer overlap between the Cr d orbitals and the topologically constrained ligands versus cyclam has been demonstrated by both X-ray crystallography and UV−vis spectroscopy; i.e., the cyclam complex is the closest to octahedral geometry, and the 1,4-C_2-cyclam complex has the greatest degree of distortion.[8] This distortion may, in turn, weaken the Cr−N bonds so that macrocyclic N dissociation is more facile for the more distorted complexes.

The same photodeuteration experiment with *trans*-[Cr(1,11-C_3-cyclam)$(CN)_2]^+$, which would presumably undergo photodeuteration at lower temperatures because of the lower activation barrier, is thus of significant interest. Though this complex shows no room-temperature deuterium isotope effect, it does have a significant isotope effect at lower temperatures.[8] For example, at −27 °C, in acidified (0.01 M HCl) 1:1 D_2O/DMSO, the lifetime of *trans*-[Cr(1,11-C_3-cyclam-d_2)$(CN)_2]^+$ is 531 μs, compared with 338 μs for the protio species. Thus, the experimental procedure involved photolysis at 35 °C under the same conditions as those for photodeuteration of the cyclam complex (acidified D_2O). To monitor if photodeuteration was occurring, the sample was then diluted 1:1 with DMSO and the lifetime measured at −27 °C. In this case, there was no evidence for photodeuteration; i.e., we observed no increase in the lifetime after photolysis.[19] A likely explanation for this lack of photodeuteration is that the complex *does* undergo macrocyclic N dissociation upon photolysis but preferentially at the tertiary nitrogens. However, two alternate explanations cannot be ruled out: (1) The complex *does not* undergo macrocyclic N dissociation upon photolysis, and thus this cannot be the mechanism for the temperature-dependent deactivation. (2) This complex undergoes macrocyclic N dissociation but closes more rapidly than the corresponding cyclam complex.

Conclusions

Though the room-temperature ^2E_g excited-state lifetimes of the complexes discussed herein vary by over 3 orders of magnitude, this may not indicate significantly different mechanisms for excited-state deactivation. Temperature-dependent studies demonstrate that the room-temperature lifetimes can be simply explained by the difference in the activation barriers for thermally activated relaxation and the resulting effect on T_{tr}. Experimental evidence reported herein suggests a possible role for photodissociation of a macrocyclic N in thermally activated relaxation and is thus in agreement with implications by Allsopp et al.[3] and Endicott et al.[4]

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Note Added in Proof: To test the possibility that the observed photodeuteration might be due to N−H deprotonation out of the excited state, we attempted the photodeuteration experiment at both 0.01 and 0.002 M acid concentration. A lower lifetime for the less acidic solution following photolysis would be in agreement with the mechanism suggested in Figure 4, with protonation being rate limiting. No difference in the lifetimes between the two samples would also be consistent with our mechanism and would imply that Cr−N bond dissociation is rate limiting. After 3 h of photolysis, there was no significant difference in the lifetimes between the two samples; i.e., both samples showed increases in agreement with the data in Table 2. As expected, slightly more acid hydrolysis[20] is observed in the 0.01 M acid solution, and this may have artificially suppressed its lifetime relative to the 0.002 M acid solution. Though this experiment is not conclusive, we favor the mechanism presented herein. In part, this is because the ^2E_g excited state has the same orbital occupation as the $^4A_{2g}$ ground state, and thus a decrease of the pK_a of the excited state relative to the ground state is not expected.

Supporting Information Available: Tables of lifetime vs temperature in acidified DMSO/H_2O for the three complexes studied and a figure of the three-parameter fit of the data for *trans*-[Cr(cyclam)$(CN)_2]^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Wagenknecht, P. S.; Kane-Maguire, N. A. P.; Speece, D. G.; Helwic, N. *Inorg. Chem.* **2002**, *41*, 1229−1235.

(19) Though some photodecomposition was observed by UV−vis as in the case for the cyclam complex, no significant excited-state quenching by the photoproducts was detected in a control photolysis done in H_2O instead of D_2O. We attribute this to performing the lifetime measurements at −27 °C, where bimolecular quenching is likely slower.

(20) Heatherington, A.; Oon, S. M.; Vargas, R.; Kane-Maguire, N. A. P. *Inorg. Chim. Acta* **1980**, *44*, L279−L282.