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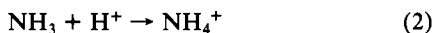
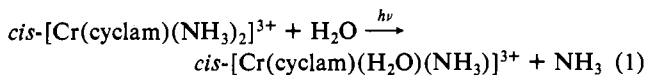
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### Occurrence of a Chemically Reactive Intermediate Formed via a Doublet-State Pathway in the Photoaquation of the *cis*-Diammine(1,4,8,11-tetraazacyclotetradecane)chromium(III) Ion

Sir:

The photosubstitutional mechanisms of octahedral chromium(III) complex ions containing ammonia and saturated organic amine ligands continue to elicit considerable debate on several key issues: the relative chemical importance of the lowest electronically excited states (spin-forbidden doublet and spin-allowed quartet states), the role of thermally activated back intersystem crossing (bisc) from the lowest doublet to a low-lying quartet state(s), and recently the suggested involvement of chemically reactive intermediates.<sup>1-6</sup> The results reported herein on the photoaquation of *cis*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>, where cyclam is the macrocyclic tetraamine 1,4,8,11-tetraazacyclotetradecane, now provide direct evidence for the occurrence of a chemically reactive intermediate. Because this system represents one of the few examples where prompt chemical reaction is not observed following laser excitation of the ligand field quartet bands, its photobehavior affords a propitious opportunity to address more directly the aforementioned issues.

An earlier study of *cis*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> has reported on its synthesis, its phosphorescence emission centered around 680 nm in aqueous solutions, and the chemical quantum yield of 0.2 (steady-state photolysis, 365 nm) for photoaquation (eq 1).<sup>7</sup> In



acidic media, protonation of free ammonia is very rapid and will lead to a change in conductivity.<sup>8</sup> In the present study, ac and dc conductivity techniques with microsecond and submicrosecond time resolutions, respectively, have been used to follow such changes and to correlate them with emission from the doublet state.<sup>9</sup> To generate this state, the first and second quartet absorption bands were irradiated by using laser lines at 530 and 347 nm, respectively, under the following conditions: deaerated so-

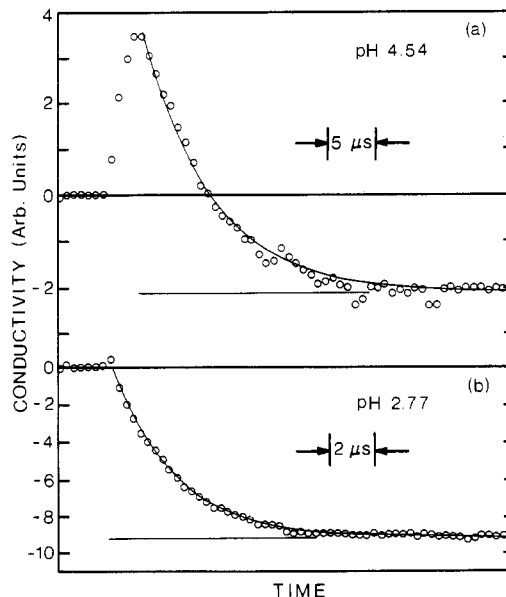


Figure 1. Conductivity changes occurring on irradiation of deaerated solutions of 2.0 mM *cis*-[Cr(cyclam)(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> for 347-nm excitation: (a) pH 4.54; (b) pH 2.77. Solid curves represent first-order kinetic fits.

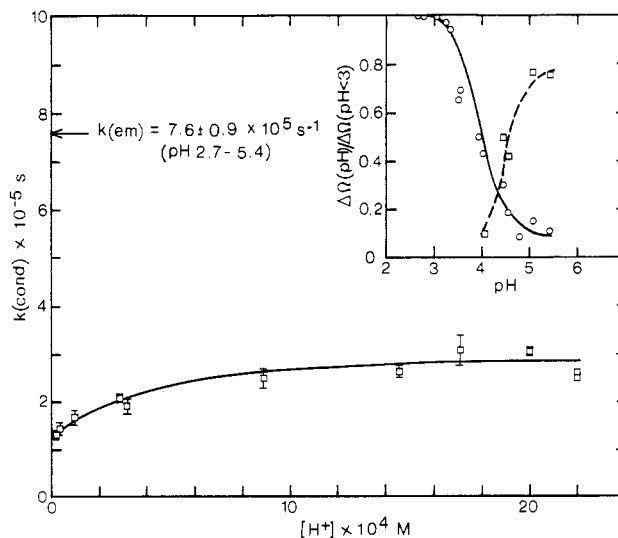


Figure 2. Plot of the observed first-order rate constant for the long-term decrease in conductivity versus the concentration of proton. The insert shows the fractional changes in conductivity relative to the net decrease in conductivity for pHs < 3 ( $\Delta\Delta(\text{pH} < 3)$ ) versus solution pH: (O)  $\Delta\Delta(\text{pH})$  represents the long-term net decrease in conductivity; (□)  $\Delta\Delta(\text{pH})$  represents the maximum net initial increase in conductivity.

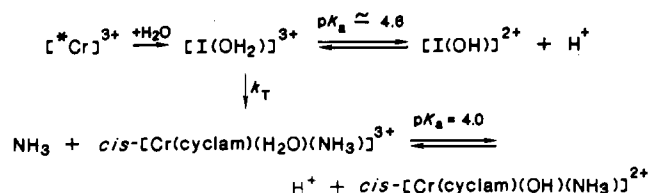
lutions of 0.6–3.0 mM complex; pH 2.65–5.4; 22–27 °C.

For these conditions, the emission lifetime remains constant at  $1.3 \pm 0.2 \mu\text{s}$  whereas the nature of the conductivity changes depends upon the pH as exemplified in Figure 1. Between pH 4.0 and 5.4 (and concomitant with the decay of emission), a net increase in conductivity occurs relative to that of the unirradiated solution. Its subsequent decay gives rise to an overall net decrease in conductivity. At pHs below 4, only this latter change is observed (Figure 1b), and in general, no further alteration occurs over our longest period of observation (1 s).

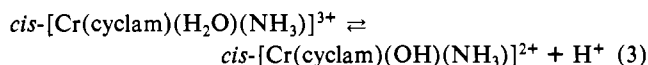
The development of this net decrease in conductivity obeys a first-order rate law over the entire range of pHs used, but as shown in Figure 2, the value of the rate constant initially increases with increasing acid concentration until a plateau region is reached at  $\text{pH} \approx 3$ ; this position also corresponds to the maximum extent of the decrease in the conductivity level. The plot of the fractional change in conductivity versus pH (insert of Figure 2; open circles) indicates that the final product exhibits an acid-base process with a  $\text{p}K_a$  of 4.0. This value is typical of those found for a water

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Scheme I



coordinated to a chromium(III) center<sup>10</sup> and thus indicative of the reaction



Below pH 3, the equilibrium will lie to the left side so that now the net decrease in conductivity will *only* reflect the reaction of proton with released ammonia (eq 2). By comparison of the signal levels here with those arising from the photorelease of ammonia from  $[Cr(NH_3)_6]^{3+}$  ( $\phi = 0.45$ ),<sup>11</sup> the quantum yields for ammonia formation on irradiation of the first and second quartet bands are found to be  $0.16 \pm 0.04$  (3) and  $0.14 \pm 0.02$  (3), respectively, in agreement with the value 0.2, measured under steady-state photolytic conditions.<sup>7</sup> These features substantiate that the formations of  $cis-[Cr(cyclam)(H_2O)(NH_3)]^{3+}$  and free ammonia are being observed here.

Because none of the conductivity changes occur with rates exceeding that for decay of the doublet state, one can conclude that the nascently populated quartet states are chemically unreactive; i.e., greater than 90% of the formation of ammonia arises in association with the decay of the emitting doublet level. This state's central role is further shown by results obtained in quenching experiments with  $K_3[Cr(CN)_6]$ : this compound does not absorb significantly at the excitation wavelength of 530 nm, and its lowest doublet level, which is chemically unreactive, lies below that for the cyclam complex.<sup>12</sup> The quenching of the latter's emission under steady-state irradiation is well described by a Stern-Volmer plot having a slope of  $(9.2 \pm 0.3) \times 10^3 M^{-1}$ . Under conditions where 48% of the emission is quenched, a corresponding decrease in the net conductivity level of  $49 \pm 4\%$  occurs at pH 2.8. The quenching is a dynamical process as shown by the fact that the associated rate constants are the same for emission and conductivity:  $(7.0 \pm 0.8) \times 10^9$  and  $(6.4 \pm 0.9) \times 10^9 M^{-1} s^{-1}$ , respectively.

A key observation in regard to the reaction mechanism is that the rate of emission decay always exceeds that for the formation of the aquochromium product: the closest approach in these rates occurs in the plateau region of Figure 2, where  $k(em)/k(cond) = (2.7 \pm 0.4)/1$ . This feature is *not* consistent with mechanisms commonly proposed to explain the photobehavior of related chromium(III) amine systems, namely, ones involving formation of the final product directly from the decay of the doublet state or from a rate-limiting bisc process to a low-lying quartet level, followed by prompt chemical reaction, because both situations require at pHs below 4, where the rate of ammonia protonation is not rate-limiting, that  $k(cond)$  should be equal to  $k(em)$ . The fact that  $k(em)$  is always greater than  $k(cond)$  indicates that there is formation of an intermediate from the decay of the doublet state and that this intermediate subsequently reacts to give the final chromium(III) aquo product of eq 1.

We propose the mechanism given by Scheme I, where the chemistry begins with the decay of the doublet state  $[^*Cr]^{3+}$ : for clarity, the reaction steps regenerating the starting material from the decay of  $[^*Cr]^{3+}$  and perhaps also from that of the intermediate are not shown.

The intermediate  $[I(OH_2)]^{3+}$  is proposed to involve the coordination of a water molecule and to exhibit its own rapidly es-

tablished acid-base reaction in order to account for the following features. A nascent increase in conductivity occurs over the pH range of 5.4 to ca. 4, and this represents an increase in proton concentration. The rate of this increase is the same as that for the decay of emission; however, the maximum level in conductivity drops on progressing from pH 5.4 to ca. 4, as shown in the insert of Figure 2 (open squares). The shape of this plot suggests that  $[I(OH_2)]^{3+}$  exhibits a  $pK_a$  around 4.6. Ammonia release is portrayed as being in association with the formation of the final chromium(III) aquo product rather than with that of  $[I(OH_2)]^{3+}$  because, if the latter situation prevailed, then at pHs  $\leq 3$  the rate of the conductivity decrease through protonation of ammonia (eq 2) would now be the same as that for the emission decay: this is not in accord with the experimental findings.

The value of the rate constant  $k_T$  for the conversion of  $[I(OH_2)]^{3+}$  into  $cis-[Cr(cyclam)(H_2O)(NH_3)]^{3+}$  will be closely approximated by the limiting value of  $k(cond)$  (Figure 2), and this implies that, at pHs below 3, the effective lifetime of  $[I(OH_2)]^{3+}$  is about  $3 \mu s$ .<sup>13</sup> Is this intermediate an excited-quartet-state species formed by a bisc process or is it a ground-state entity? In regard to the first alternative, no emission (aside from that for the doublet state) has been found up to 800 nm whereas such might be expected for a long-lived excited quartet state. Indeed, quartet states are generally perceived to be very short lived, in contrast to the intermediate's considerable longevity.<sup>1-5,14</sup> Given the facile quenching by  $[Cr(CN)_6]^{3-}$  of the doublet state, which is shorter lived than the intermediate, then the expectation from spin correlation is that  $[Cr(CN)_6]^{3-}$  should also be an effective quenching agent toward the chemical reactive intermediate if it were in an electronically excited quartet state. The consequence would be that the percentage of emission quenching should be less than that for the quenching of the chemical reaction, but this is not found here. These features militate against an excited-state description of the intermediate and perforce favor its designation as being a ground-state species.

**Acknowledgment.** We wish to express our appreciation to the Natural Sciences and Engineering Council of Canada for financial support, to Dr. F. Wasgestian for providing the  $K_3[Cr(CN)_6]$  sample used in this study, and to Dr. N. A. P. Kane-Maguire for his comments and assistance.

**Registry No.**  $cis-[Cr(cyclam)(NH_3)_2]^{3+}$ , 94536-68-2;  $cis-[Cr(cyclam)(H_2O)(NH_3)]^{3+}$ , 94536-66-0;  $NH_3$ , 7664-41-7.

- (13) Because  $cis-[Cr(cyclam)(NH_3)_2]^{3+}$  undergoes rapid thermal aquation in basic solutions, it was not experimentally possible to determine if  $[I(OH_2)]^{3+}$  undergoes direct conversion to  $cis-[Cr(cyclam)(OH)(NH_3)]^{2+}$ .
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### Electron-Transfer Rates of a Co(-I)/Co(0) Couple and Crystal Structure of the Tetrakis(trimethyl phosphite)cobaltate(-I) Ion

Sir:

The determination of self-exchange rates has been an important facet of the study of electron-transfer reactions in inorganic chemistry.<sup>1</sup> However, much of the available data is restricted

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