isolated by Michaelis[11,12] and further investigated by Velbel and co-workers[13] before the structural confirmation by Søtofte.

Only four examples of *syn*-bimanes, *syn*-(benzo)(CH₃,H)B, *syn*-(benzo)(CH₃,Br)B, *syn*-(benzo)(CH₃,CH₃CH₂)B, and *syn*-(benzo)(C₆H₅,H)B, have previously appeared in the literature. The first two were characterized by Michaelis[14,15] and the latter two by Velbel and Lillelund.[16] The intense fluorescence was noted,[14-16] but the syntheses were rather limited in applicability. The only chemical reactions mentioned were bromination, converting the first *syn*-bimane mentioned above to the second, and treatment with 0.1 N NaOH which caused ring opening to the 1-(2-carboxyphenyl)pyrazol-3-ones.[16] The idea that a new and useful class of compounds was under study was not advanced and, indeed, became plausible only with our discovery of a reasonably general synthesis, illustrated as follows.

syn-(CH₃,CH₃)B is prepared by mixing 3,4-dimethyl-4-chloro-2-pyrazolin-5-one (0.48 mol) in CH₂Cl₂ (500 mL) with K₂CO₃·½H₂O (1 mol) and K₂CO₃ (0.36 mol) at 0 °C (1 h), stirring at room temperature for 18 h, filtering through Celite, evaporation with solvent, and crystallization from boiling CH₃CN (150 mL). Essentially pure syn isomer separates in 60% yield. Evaporation of filtrate and chromatography on alumina with CH₂Cl₂ yields *anti*-(CH₃,CH₃)B (~4.6% yield) and additional syn isomer (~9%). *syn*-(CH₃,CH₃)B: yellow–white crystals; mp 211–212 °C; UV λ_max (dioxane) 359 nm (ε_max 6500), 255 (sh, 5200), 235 (14 600); IR ν_max (KBr) 2890, 1745, 1670, 1610, 1400, 1030 cm⁻¹; NMR (CDCl₃) δ 1.85 (s), 2.28 (s); ¹³C NMR δ 160.5, 146.1, 111.8, 11.9, 6.7; mass spectrum 192 (parent peak). *anti*-(CH₃,CH₃)B: white needles; mp 174 °C (EtOAc); UV λ_max (dioxane) 322 nm ε (15 100); IR (KBr) ν_max 2930, 1750 (sh), 1695, 1630, 1415, 1275, 1170 cm⁻¹; NMR (CDCl₃) δ 1.80 (s), 2.40 (s); Anal. (C₁₀H₁₂N₂O₂, both isomers) C, H, N.

Among the bimanes which have been synthesized and characterized are *syn*-(CH₃,Cl)B, mp 253 °C; *syn*-(C₆H₅,CH₃)B, mp 308–310 °C dec; *syn*-(C₆H₅,C₆H₅)B, mp 312 °C; *syn*-(CH₃,C₆H₅)B, mp 284 °C; *anti*-(CH₃,Cl)B, mp 196–197 °C; *anti*-(C₆H₅,Cl)B, mp 236–237 °C; *anti*-(CH₃,C₆H₅)B, mp 265 °C.

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Picosecond Studies of Excited-State Decay Kinetics in Chromium(III): *trans*-Diisothiocyanato-bis(ethylenediamine)chromium(III), Reinecke's Salt, and Hexaisothiocyanatochromium(III) in H₂O and D₂O at Room Temperature

Sir:

The interest in excited-state relaxation in Cr(III) complexes stems from the debate over the identity of the photoactive state in Cr(III) photochemistry. Early work by Plane and Hunt[1] and Schläfer[2] suggested that the lowest doublet state was the primary intermediate responsible for photochemistry. Subsequently, Chen and Porter[3] established that at least some of the photoproduct in the photoaquation of *trans*-Cr(NH₃)₂(NCS)₄⁻ must derive from sources other than the doublet. They suggested that the lowest quartet excited state was responsible. In addition, the lack of direct evidence for doublet photochemistry led them to suggest that all other photoproduct could be a consequence of thermally activated back intersystem

crossing from the doublet to the quartet similar to the process of E-type delayed fluorescence. Since then, it has been demonstrated that some, if not all, of the photochemistry for several complexes derives from the lowest excited quartet state.[4] The quartet hypothesis is supported by the successful prediction of product stoichiometry by models based on the ligand field strength of the first coordination sphere. The first of the spectroscopic models was developed by Adamson.[5] Models have since been developed to rationalize Adamson's rules which use MO theory to account for changes in the σ and π character of the metal ligand bonds as a result of the change in electronic configuration in the lowest excited quartet state.[6] Even stereochemical changes have been rationalized.[7] The similarity in formal electronic configuration between the ground and doublet states (t_{2g}^3) and the negligible Stokes shift of the doublet phosphorescence has suggested that there was negligible difference in geometry between the two states and that bond rupture in the doublet was therefore no more likely than in the ground state.[8] However, this argument is weakened by the following considerations. Intensity progressions in the vibrational structure of the phosphorescence of Cr(CN)₆³⁻ have been interpreted as evidence for considerable distortion arising from compression of the metal–ligand bonds in the doublet relative to the ground state.[9] In addition, configuration interaction (t_{2g}^3–$t_{2g}^2 e_g$) could cause some increase in average bond lengths as the crystal field parameter (10 *Dq*) decreases and the excited quartet-doublet energy gap shrinks.[10] Thus, doublet reactivity cannot, at present, be completely ruled out.

Excited-state kinetic and spectroscopic studies of Cr(III) complexes under photochemical conditions may contribute to the understanding of the mechanism of the photochemical reaction. Until recently, however, studies of the photophysics of excited states in Cr(III) have been limited to studies of ruby; observations of phosphorescence of complexes at low temperature; and to data obtained indirectly through studies of photochemistry, emission quenching or sensitization. Nanosecond pulsed laser studies of the decay of emission or excited state absorbance (ESA) in acidoammine complexes of Cr(III) may be helpful in assessing the role of the doublet state in photoreaction.[11-13] However, picosecond time resolution is needed to examine the role of the excited quartet state in Cr(III) photochemistry. Earlier studies in our laboratory, of picosecond excited-state relaxation in transition metal complexes, suggested that the excited quartet lifetime in Cr(III) complexes was too short to measure (<10 ps).[14] We have extended this work. Repeated studies of *trans*-Cr(en)₂(NCS)₂⁺, *trans*-Cr(NH₃)₂(NCS)₄⁻ and Cr(NCS)₆³⁻ show that, while the rise time of transient absorbance is fast (11 ps < τ < 24 ps), it is within the time resolution of our picosecond flash system. We have also studied the influence of the medium on the rate of appearance of transient absorbance.

Excited-state spectroscopy and measurement of excited-state lifetimes were performed using the picosecond flash photolysis system described elsewhere.[15] Solutions were prepared in H₂O and D₂O at the start of each experiment. The counterions were K⁺ and NH₄⁺ in Cr(NCS)₆³⁻ and *trans*-Cr(NH₃)₂(NCS)₄⁻, respectively. The counterions were Cl⁻ and ClO₄⁻ in the case of *trans*-Cr(en)₂(NCS)₂⁺, and the rise times of transient absorbance were equivalent in both media. Solutions of Cr(III) were typically 0.1 M, and a fresh solution was used for each flash. The transient spectra were identical with those observed in the earlier picosecond work[14] as well as those reported for the excited doublet state in low temperature glassy media.[16] Similar spectra were also observed in nanosecond room-temperature kinetic spectroscopy.[12,13] We have estimated the extinction coefficients of the excited-state transitions by comparison with the excited singlet transition in Rhodamine 6-G ($\epsilon(S_1) = 4.8 \times 10^4$ M⁻¹ cm⁻¹ at 450 nm[17]). The values all lie between 10³ and 10⁴ M⁻¹ cm⁻¹ and agree

complex	$\tau \times 10^{12}$, s	
	H$_2$O	D$_2$O
trans-Cr(en)$_2$(NCS)$_2$$^+$	16 ± 3 (4)^a	24 ± 2 (2)
trans-Cr(NH$_3$)$_2$(NCS)$_4$$^-$	22 ± 2 (4)	11 ± 2 (3)
Cr(NCS)$_6$$^{3-}$	16 ± 2 (2)	12 ± 6 (2)

^{a} The value in parentheses represents the number of measurements from which the standard deviation was calculated. In cases where an average is presented for only two measurements, the uncertainty reflects arbitrarily twice the difference between the two experimental values.

reasonably well with previously reported values.[12,16b] The rise times of excited-state absorbance (ESA) were independent of probe wavelength and are listed in Table I. By measuring the rate of appearance of excited singlet absorbance (S$_1$) in Rhodamine 6-G (6 ± 2(4) ps), we established that our measured rise times of transient absorbance observed for the Cr(III) complexes were within our experimental time resolution and also provided an independent measure of the width of our picosecond pulse. Rate plots were linear for 1 to 2 lifetimes and were not corrected for the influence of the pump pulse.

There are two notable features apparent in the data in Table I. First, there is very little change in the transient rise time from one complex to another. The transient has been assigned as the lowest doublet excited state on the basis of the close similarity in the lifetimes for the decay of ESA and the decay of phosphorescence intensity in *trans*-Cr(NH$_3$)$_2$(NCS)$_4$$^-$ at low temperature.[16b] If the rise in ESA reflects intersystem crossing (ISC) from the vibrationally equilibrated first excited quartet state to the doublet state, the lifetime might be expected to be dependent on the energy gap between the minima in the doublet and the excited quartet potential energy surfaces. The data show little or no dependence on 10 *Dq*, the value of which should reflect that gap. An alternative interpretation is consistent with evidence reported by Kane-Maguire et al.[18] that intersystem crossing may compete with vibrational equilibration in Cr(III) complexes. Since the energy of the lowest doublet is relatively insensitive to 10 *Dq*, the rise time may reflect a combination of intersystem crossing from the initially formed quartet state to the doublet state and relaxation within the doublet manifold from the vibrational level isoenergetic with the Franck–Condon state produced in the excited quartet at the energy of the laser pulse (1.88 μm^{-1} or 530 nm). The energy separation between the initially attained vibrational level in the doublet and the zeroth vibrational level would then be relatively independent of the nature of the complex. Consequently, the observed lifetime might not be sensitive to changes in 10 *Dq* if intersystem crossing were comparable with or faster than vibrational decay. A similar explanation was used recently to explain excited-state relaxation in *trans*-Cr(NH$_3$)$_2$(NCS)$_4$$^-$.[13] If this is the correct model, the observed lifetime might depend on the energy of the Franck–Condon state in the excited quartet manifold. Picosecond studies as a function of excitation wavelength would be helpful in examining this possibility.

Second, there is a modest but definite isotope effect. The expected effect of D$_2$O on the rate constant (a reduction) is observed, however, only in the case of *trans*-Cr(en)$_2$(NCS)$_2$$^+$. The reverse effect is observed in *trans*-Cr(NH$_3$)$_2$(NCS)$_4$$^-$ and perhaps in Cr(NCS)$_6$$^{3-}$, the rates in these cases being accelerated. Isotope exchange for coordinated ammine protons may be responsible for changes in the measured lifetimes, but still would be expected to lengthen quartet lifetimes in each complex regardless of whether the perturbarion was inner or outer sphere. However, the opposite effects on doublet risetimes may reflect a charge dependence similar to that reported in the photochemistry of *trans*-Cr(en)$_2$NCSF$^+$ and *trans*-

Cr(NH$_3$)$_2$(NCS)$_4$$^-$,[19] and in photophysical studies of ESA decay on the nanosecond time scale for Cr(NH$_3$)$_5$NCS$^+$, *trans*-Cr(NH$_3$)$_2$(NCS)$_4$$^-$, and Cr(NCS)$_6$$^{3-}$.[12] Additional studies of the medium dependence of excited-state decay in Cr(III) complexes are underway.

In conclusion, we have shown that the rise time of excited-state absorbance is measurable and longer than the earlier estimate of <10 ps. We believe that the available evidence favors the doublet-state assignment for the observed ESA. However, the precise details of the relaxation mechanism from the initially excited quartet state to the doublet manifold remain to be unraveled.

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Intramolecular Diels–Alder Reactions.
A New Entry into Bridgehead Bicyclo[3.*n*.1]alkenes

Sir:

Intramolecular Diels–Alder reactions have proven to be of considerable value in the synthesis of complex polycyclic molecules.[1] When the diene and dienophile are joined at the 2 position of the diene, the reaction can result in formation of a bridgehead alkene[2] (eq 1). We are not aware of any examples