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Photoaquation of *trans*-[Cr(en)$_2$NCSF]$^+$

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On photolysis in aqueous solution in the wavelength range 366–578 nm and temperatures of 10 and 20 °C, *trans*-[Cr(en)$_2$NCSF]$^{2+}$ aquates mainly thiocyanate (ϕ = 0.22–0.28) with a small yield of ethylenediamine (ϕ = 0.05–0.11). No observable aquation of fluoride occurs ($\phi < 0.005$). The ratio of the two modes of photoreaction varies with wavelength, particularly at 10 °C, at wavelengths longer than 436 nm. These results support reaction via at least two excited states which are not in thermal equilibrium. The various models of chromium(III) photochemistry are considered briefly and the results shown to agree best with a recent semiempirical molecular orbital theory. The wavelength and temperature-dependence data, the theory, and general considerations are suggestive that both ^4E and $^4B_2$ states may be photoreactive in complexes of this type.

Introduction

In the last decade a number of models, empirical and theoretical, for chromium(III) photochemistry have appeared,[1-7] the most recent being a semiempirical molecular orbital approach.[8,9] This study of *trans*-[Cr(en)$_2$NCSF]$^+$ was undertaken to compare its behavior with the reported photochemistry of *trans*-[Cr(en)$_2$F$_2$]$^{+}$[2] and *trans*-[Cr(en)$_2$(NCS)$_2$]$^{+}$[10] and to provide a further test of the models then existing. In particular we anticipated from the σ-donor model[2] that the ratio of ethylenediamine to thiocyanate or fluoride aquation should be intermediate to the values of >5 for [Cr(en)$_2$F$_2$]$^+$ and ~0.5 for [Cr(en)$_2$(NCS)$_2$]$^+$.

The molecule was also of interest as it emits phosphorescence at 719 nm from room-temperature aqueous solution and can be quenched by [Cr(ox)$_3$]$^{3-}$ and [Cr(CN)$_6$]$^{3-}$. It therefore represented an opportunity to study both the quenching of emission and multiple reaction modes under identical conditions. The investigation of this aspect of the photochemistry has been rendered difficult by analytical problems and by the high absorbance of the available quenchers and is therefore not reported here.

Experimental Section

trans-[Cr(en)$_2$NCSF]ClO$_4$ was prepared as previously described.[11] The purity of the compound was confirmed by analysis[11] and by ion-exchange chromatography[12] and was at least 99% pure with respect to elutable complexes including *cis*-[Cr(en)$_2$NCSF]$^+$.

The UV/visible spectrum of the compound is shown in Figure 1.

Photolysis was carried out in the apparatus previously described.[12] Proton uptake measurements[13] were used to determine amounts of ethylenediamine released. These measurements were performed at pH 3 so that about 50% of any released fluoride would also have been included in the measurement. Fluoride was not measured directly; instead ion-exchange chromatography to detect *cis*-[Cr(en)$_2$H$_2$ONCS]$^{2+}$ was used to determine the extent of fluoride loss. Thiocyanate was measured by the method of Wegner and Adamson.[14]

Table I. Apparent Quantum Yield for *trans*-[Cr(NH$_3$)$_2$(NCS)$_4$]$^-$ at Various Wavelengths and Temperatures

wavelength, nm	temp, °C					
	30	23	15	10	5	1
578		0.269	0.244	0.220	0.205	0.195
546	0.311	0.281	0.256	0.228	0.219	
436		0.310	0.276		0.239	

Ion-exchange chromatography was carried out on a 20 cm long, 8 mm diameter column of either Baker Analyzed CGC 241 or Hamilton HC8X cation-exchange resin, eluted with gradients (0.2–1.0 M) of ammonium sulfate solution. A modified Technicon AutoAnalyser was used to react the eluted complexes with 1 M sodium hydroxide and 0.5% (w/v) hydrogen peroxide. By monitoring the chromate absorbance at 370 nm a complete chromatogram[12] could be recorded.

Depending on the wavelength of interest, both ferrioxalate[15] and reineckate[14] actinometry were employed for measurement of the incident light flux. The latter actinometer exhibited temperature dependence of its photolysis yield. Consequently calibration was required. For this purpose the light flux was monitored continuously by a Phillips 150 CV phototube observing 8% of the incident beam and the relative yield of thiocyanate measured for various temperatures and wavelengths. The temperature dependence of photolysis yield observed could be due partly to a change in solution absorbance with

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Table II. Spectral Data for *trans*-$[Cr(en)_2NCSF]^+$, Its Thermal and Photoreaction Products, and Relevant Complexes

complex	λ_{max}[a] (ϵ_{max})	λ_{min} (ϵ_{min})	λ_{max} (ϵ_{max})	ref
trans-$[Cr(en)_2NCSF]^+$	375 (33.9)	422 (20.8)	502 (41.2)	*a*
cis-$[Cr(en)_2NCSF]^+$	375 (52)		500 (85)	28
trans-$[Cr(en)_2H_2OF]^{2+}$	369 (29.9)	457[b] (23.9)	519 (23.1)	28
	368 (29.7)	455[b] (23.9)	519 (22.3)	*a*
cis-$[Cr(en)_2H_2OF]^{2+}$	373 (31.5)		503 (72.5)	18
	369 (33.0)	428 (15.5)	503 (69.0)	*a*
trans-$[Cr(en)_2H_2ONCS]^{2+}$	365 (49.6)		501 (52.4)	29
cis-$[Cr(en)_2H_2ONCS]^{2+}$	371 (58.0)	418 (25.3)	480 (102)	29
complex 1[c] fraction A	381 (23)	440 (8)	514 (36)	
fraction B	381 (29)	437 (10.5)	513 (38)	
fraction C	380 (26)	437 (9)	514 (38)	
complex 2[d] fraction A	379 (22)	434 (11)	514 (31)	
fraction B	380 (24)	435 (11)	514 (35)	
fraction C	377 (25)	433 (10)	511 (38)	

[a] This work. λ_{max} in nm, ϵ_{max} in L mol^{-1} cm^{-1}. [b] This is an absorption maximum. The two absorption minima for this complex are found at 417 (18.2) and 492 (21.0). [c] Spectra of successive cuts of the eluted product of thermal ethylenediamine aquation. [d] Spectra of successive cuts of the eluted product of photochemical ethylenediamine aquation.

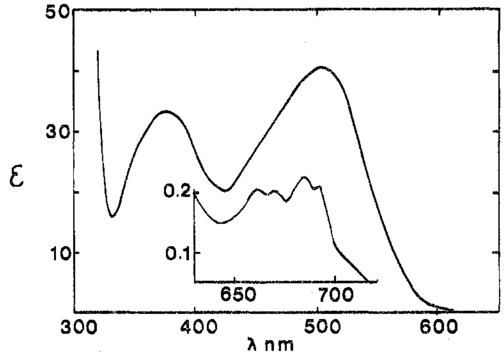

Figure 1. Ultraviolet/visible absorption spectrum of *trans*-$[Cr(en)_2NCS F]^+$. The inset shows the weak doublet absorption. Please note the different wavelength scale for this part of the spectrum.

temperature, but the data in Table I were calculated on the assumption of constant absorbance. The apparent activation energy for all three wavelengths is the same, about 10 kJ mol^{-1}.

Further details of the above procedures have been published.[16]

Results

Thermal Aquation of *trans*-$[Cr(en)_2NCSF]^+$. The complex was found to aquate thermally with proton uptake and release of thiocyanate ion. The rate constant for the first-order (to 10% decomposition) proton uptake in the pH range 2.7–3.4 and ionic strength 0.04 (potassium perchlorate) was found to be 4.2×10^{-6} s^{-1} at 20 °C, 1.5×10^{-5} s^{-1} at 30 °C and 5.4×10^{-5} s^{-1} at 40 °C; these values yield an activation energy of 97 kJ mol^{-1}. The first-order (to 16% overall decomposition) rate constant for thiocyanate loss was roughly $(4 \pm 1) \times 10^{-7}$ s^{-1} at 30 °C and $(10 \pm 2) \times 10^{-7}$ s^{-1} at 40 °C. These values parallel the published rate constant[16] for $[Cr(NH_3)_5NCS]^{2+}$ of 2×10^{-7} s^{-1} at 30 °C.

Ion-exchange chromatography of an aquated acidic solution (1 h at 35 °C) gave a main product peak which followed *trans*-$[Cr(en)_2NCSF]^+$ closely off the column consistent with a dipositive ion with aquo ligands. The product was collected and spectrally examined, Table II, and the spectrum and elution behavior are consistent for $[Cr(en)(enH)H_2O(NCS)F]^{2+}$; the configuration is likely to be that resulting from stereoretentive aquation of one end of an ethylenediamine ligand. It was noted that different cuts of the eluted band gave slightly different molar absorptivities but the same maximum values suggesting some mixture of isomers might be present but this is uncertain. No *cis*-$[Cr(en)_2H_2ONCS]^{2+}$ was observed.

In summary, the thermal decomposition of the compound leads to proton uptake with $k = 4.2 \times 10^{-6}$ s^{-1} at 20 °C and a small thiocyanate and negligible fluoride loss.

Photolysis Products and Quantum Yields. Photolysis of *trans*-$[Cr(en)_2NCSF]^+$ in aqueous solution at pH 3 leads to an increase in the pH of the solution and the initially orange solution becomes red. Analysis shows that thiocyanate is released; at pH 3 this ion is unprotonated.[17] Proton uptake could be due to both ethylenediamine and fluoride aquation since the latter would be about 50% protonated at pH 3.

Ion-exchange chromatography of a photolyzed solution yielded three main bands. Band I was identified as *trans*-$[Cr(en)_2NCSF]^+$ and band III as *cis*-$[Cr(en)_2H_2OF]^{2+}$, both by elution time on the column and by collection of the eluted fraction and determination of the UV/vis spectrum including analysis for chromium(III) to obtain the molar absorptivities of the spectral peaks. Band II was collected and examined spectrally in the same way, but it was noted that different cuts of the eluent gave slightly different spectra. The relevant spectral data are all presented in Table II.

Band II did not correspond in elution behavior with *cis*- or *trans*-$[Cr(en)_2H_2ONCS]^{2+}$ and did not correspond in spectrum to *cis*-$[Cr(en)_2NCSF]^+$ or *trans*-$[Cr(en)_2H_2OF]^{2+}$. The spectral data, the elution characteristics, the inseparability of this photoproduct from the thermal product of thermal aquation of ethylenediamine, and the observation that proton uptake does occur upon photolysis all support assignment of band II to (an) isomer(s) of $[Cr(en)(enH)H_2O(F)NCS]^{2+}$. Considerable evidence has now been accumulated by photolysis of various ethylenediaminechromium(III) complexes to support the existence of this type of metastable protonated monodentate ethylenediamine complex. Much time and effort were devoted to using longer columns of different selective ion-exchange resins in an attempt to resolve these isomers which has been unsuccessful to date. This failure unfortunately greatly increased the uncertainties in the study of relative quenching of photolysis modes and prevented completion of this aspect of the work at this time.

No *cis*-$[Cr(en)_2H_2ONCS]^{2+}$ was observed, even for 25% decomposition of the starting complex. The compound elutes later than any of the other products in a clear region of the chromatogram where the baseline is excellent and the bandwidth reasonably narrow. Assuming this would be the major product of fluoride aquation (experience suggests it would be the exclusive product) the results show this cannot be a significant photoreaction. For equal chromatographic sensitivities[16] for *cis*-$[Cr(en)_2H_2OF]^{2+}$ and *cis*-$[Cr(en)_2H_2ONCS]^{2+}$ the data yield an upper limit quantum yield for fluoride of 0.005, a figure which includes a safety margin of five above the detectability limit to allow for the uncertainties. The determination was carried out with 436-nm light for which all modes would be expected to occur and where secondary photolysis effects would be small.

Table III. Corrected Quantum Yields for *trans*-$[Cr(en)_2NCSF]^+$

λ, nm	T, °C	$\phi_{H^+}{}^a$	$\phi_{NCS^-}{}^a$	$\phi_{H^+} \times 100 / \phi_{total}$
578	10	0.050 (2)	0.222 (3)	18
546	10	0.049 (2)	0.241 (3)	17
	20	0.069 (4)	0.273 (4)	20
436	10	0.113 (3)	0.253 (4)	31
	20	0.109 (3)	0.269 (4)	29
404	10	0.100 (3)	0.263 (4)	28
	20	0.114 (2)	0.277 (2)	29
366	10	0.098 (3)	0.256 (2)	28
	20	0.105 (2)	0.277 (2)	27

[a] Quantum yields for proton uptake and thiocyanate release, respectively. 1.0×10^{-2} M solutions of complex in 10^{-3} M $HClO_4$/0.01 M $KClO_4$ were used except for 578 nm where 2.0×10^{-2} M complex was used. The data have been given to three significant figures; the values in parentheses are the numbers of determinations. The variability of measurements was quite small and appeared randomly distributed. Calculation of the standard deviation of the pooled data set yields the value 0.003 indicating the magnitude of the random errors. The 99% confidence levels on the individual results are then theoretically $\pm 0.008/N^{1/2}$ where N is the number of determinations.

In summary, thiocyanate and ethylenediamine aquation are the only significant reaction modes observed. Quantum yields were measured, on the basis of spectrophotometric thiocyanate analysis[14] with Fe^{3+} and proton uptake for ethylenediamine, at 10 and 20 °C and 578-, 546-, 436-, 404-, and 366-nm excitation. These data, corrected for thermal reaction and for secondary photolysis, are presented in Table III. The secondary photolysis correction procedure has been described earlier.[18,19] The parameters used are given in Table IV; a few of these are estimates. In all quantum yield determinations, however, the total percentage conversion was maintained in the range 3–8% so the correction was never greater than 8% of the observed quantum yield. Hence the parameter uncertainties do not cause serious error.

The data show that at all wavelengths and temperatures thiocyanate is the predominant reaction mode. At a wavelength of 436 nm or shorter, the ratio $\phi(en)/\phi(NCS^-)$ and the absolute values of the quantum yields become fairly temperature independent, with about 30% ethylenediamine aquation.

At longer wavelengths the ethylenediamine mode falls to under 20% and at 546 nm shows a much larger temperature coefficient. The apparent activation energies, quite uncertain, are about 0.3–8 kJ mol^{-1} for thiocyanate at all wavelengths and ethylenediamine at 366, 404, and 436 nm. For ethylenediamine at 546 nm a value of 25 kJ mol^{-1} was found. Similar behavior was observed[19] for *trans*-$[Cr(en)_2NH_3F]^{2+}$.

Discussion

Comparison with Theory. Since this work was undertaken, a new theory of chromium(III) photochemistry has been published[8,9] by Vanquickenborne and Ceulemans (VC). It incorporates the earlier ideas of preferential labilization of axes,[1,2] and the separation of σ and π contributions[2,3,5,6] to labilization of axes and to (Cr–ligand) bond strength changes for various excited states. The main new contributions lie in providing a simple means for estimation of excited-state bond strengths based on spectroscopic parameters and in the demonstration that excited-state bond strengths, not the extent of labilization, should be used to determine which ligands are preferentially lost. In view of the obvious success of the theory in rationalizing the existing data on Cr(III) and Co(III) photochemistry, the fact that it incorporates the important features of the earlier models, and the way it illuminates the important factors leading to prediction of a particular reaction mode, the theory will be used as the basis of this discussion.

The required spectroscopic parameters given[8] are the following: for ethylenediamine $\epsilon_\sigma = 7183$, $\epsilon_\pi = 0$; fluoride $\epsilon_\sigma = 7633$, $\epsilon_\pi = 1700$; isothiocyanate $\epsilon_\sigma = 6413$, $\epsilon_\pi = 380$; all in cm^{-1}. For the latter two species the uncertainties, reflected in the disagreement between published values,[20–25] are quite large, several hundred cm^{-1} in some cases. Also note that even for ethylenediamine the values obtained for ϵ_σ vary[21] from 6600 to 7600 cm^{-1} for various *trans*-$[Cr(en)_2X_2]^+$ compounds. One must conclude that ligand field parameterization is at present an uncertain affair.

Generally for *trans*-$[Cr(en)_2XY]^+$ quadrate complexes the ^4E state lies below the $^4B_2$ and is assumed in the theory to be the main reactive state. For the ^4E state of *trans*-$[Cr(en)_2F_2]^+$, ethylenediamine aquation is predicted while for *trans*-$[Cr(en)_2(NCS)_2]^+$ thiocyanate aquation is predicted.[5,8] In both compounds the calculated bond strength difference for the two different bonds in the ^4E state is about 40 kJ mol^{-1}. Thus the theory predicts successfully the major modes observed[2,10] for these two compounds.

For *trans*-$[Cr(en)_2NCSF]^+$ the lowest quartet state is again ^4E, our calculation of the $^4B_2/^4E$ spacing yielding 2300 cm^{-1} (28 kJ mol^{-1}). The percentage d_{z^2} character in the ^4E state is found to be 76.4% and this reflects the pseudooctahedral nature of the molecule. From eq 5 of ref 8, then

$$I^*(\text{Cr–NCS}) = (2 - 0.764)\epsilon_\sigma(\text{NCS}) + 3\epsilon_\pi(\text{NCS}) = 9100 \text{ cm}^{-1}$$

$$I^*(\text{Cr–en}) = \left(\frac{(2 \times 0.764) + 5}{4}\right)\epsilon_\sigma(\text{en}) = 11700 \text{ cm}^{-1}$$

$$I^*(\text{Cr–F}) = (2 - 0.764)\epsilon_\sigma(\text{F}) + 3\epsilon_\pi(\text{F}) = 14500 \text{ cm}^{-1}$$

Hence this state is correctly predicted to favor aquation of thiocyanate.

These calculations also reveal that the main factor favoring thiocyanate loss over fluoride loss is the π bonding of fluoride in the excited-state ^4E. The main factor determining labilization on the z axis is the unfavorable σ-antibonding interaction on this axis, but the $^4B_2/^4E$ spacing of 2300 cm^{-1} arises mainly from the π interactions. *trans*-$[Cr(en)_2NCSF]^+$ is therefore interesting in that the nature of the lowest lying state and the nature of the ligand preferentially aquated are largely determined by the π-bonding interactions in the excited state.

For comparison, Adamson's original rule[1] predicts preferential thiocyanate aquation but cannot rationalize the inertness of fluoride and the significant loss of ethylenediamine. The σ-donor model[2] together with earlier ideas[3,5] would predict mainly loss of ethylenediamine. This prediction springs from recognition of the almost octahedral character of the compound, the statistical preponderance of ethylenediamine, and

Table IV. Parameters Used in the Secondary Photolysis Corrections

	ϵ_{366}	ϵ_{404}	ϵ_{436}	ϵ_{546}	ϵ_{578}	ϕ_{H^+}	ϕ_{NCS^-}
trans-$[(Cr(en)_2NCSF]^{2+}$	32.2	25.6	22.9	20.5	4.3	*a*	*a*
cis-$[Cr(en)_2H_2OF]^{2+}$	30.0	21.0	16.0	37.3	10.5	0.2^b	0
$[Cr(en)(enH)H_2ONCSF]^{2+}$	22.0	17.6	10.0	24.8	9.6	0.1^b	0.1^b

[a] The uncorrected measured quantum yield (λ, *t*) was used. [b] These are estimates based on analogy to other complexes and on theoretical estimates. The corrections were generally in the range 0–2% except for the correction to ϕ_{H^+} at 546 and 578 nm, where the corrections were 6–8%.

the anticipated π-bonding stabilization of thiocyanate and fluoride in the excited state.

Even at the longest wavelength of irradiation and at 10 °C, some ethylenediamine is aquated. The question arises whether this comes from reaction of the ^4E state, reacting in an "impure" way, or from thermal or optical excitation to a higher Born–Oppenheimer state, such as $^4B_2$. Note that the calculated separation of the states corresponds at room temperature to a factor of 10^{-5} in population at equilibrium. The $^4B_2$ state certainly is predicted to react in the correct manner.

$$I^*(\mathrm{Cr{-}NCS}) = 2\epsilon_\sigma(\mathrm{NCS}) + 2\epsilon_\pi(\mathrm{NCS}) = 13600\ \mathrm{cm}^{-1}$$

$$I^*(\mathrm{Cr{-}en}) = 5/4\epsilon_\sigma(\mathrm{en}) = 8900\ \mathrm{cm}^{-1}$$

$$I^*(\mathrm{Cr{-}F}) = 2\epsilon_\sigma(\mathrm{F}) + 2\epsilon_\pi(\mathrm{F}) = 18700\ \mathrm{cm}^{-1}$$

The bond strength differences for thiocyanate and ethylenediamine for the ^4E and $^4B_2$ states would imply factors of 10^{-6} and 10^{-10}, respectively, for reactivity preferences at room temperature if they resulted in activation energy differences of equal magnitudes. However, given the approximations of the theory and the uncertainty of the input parameters and recognizing the importance in the photophysics of relaxation processes, solvent effects, the unknown energy differences between the Born–Oppenheimer states and those which actually undergo reaction, and many other complexities, including the uncertainties of excited state reaction mechanisms, these calculations are a poor basis on which to claim exclusive reaction modes for the two excited states.

Wavelength and Temperature Dependence of Quantum Yields. There is in the wavelength and temperature-dependence data for this and similar compounds[19] some evidence for high selectivity in reactivity of the lowest quartet and of a second state.

It is obvious from the long wavelength temperature dependence of the ethylenediamine mode that more than one excited state reacts. The data of Table III show that for thiocyanate at all wavelengths and for ethylenediamine aquation at 366, 404, and 436 nm, only very small apparent activation energies are observed, in the range 0.5–8 kJ mol^{-1}. In contrast, for ethylenediamine at 546 nm, a value of about 25 kJ mol^{-1} is observed. Although these values cannot be very certain because of the very small temperature interval, the difference is significant. Such behavior could be anticipated if two states leading predominantly to ethylenediamine and thiocyanate aquation, respectively, are populated in a wavelength-independent manner at 436 nm or shorter wavelength, but at 546 nm or longer mainly the lower lying state is populated and the second state may be reached only by thermal activation. It is a moot point whether the activation occurs in the ground-state absorption process or through the excited states. The observed activation energy of 25 kJ mol^{-1} for this activation is of the order of the calculated $^4B_2/^4E$ spacing of 28 kJ mol^{-1}. This, coupled with the theoretical expectations for the $^4B_2$ and ^4E states, is supportive of such a $^4B_2$, ^4E reactivity model.

Similar wavelength and temperature dependencies for *trans*-$[\mathrm{Cr(en)_2NH_3F}]^{2+}$ were observed and discussed in a previous paper[19] and a more detailed argument was presented there in favor of the two quartet state model together with arguments against the doublet state as the second participant in reaction.

No direct proof for such a model is currently available but, in addition to the molecular orbital theory support, there is the following circumstantial evidence. (1) There is a reasonably good relationship between the proportion of equatorial labilization observed for *trans*-$[\mathrm{Cr(en)_2XY}]^+$ complexes and the calculated $^4B_2/^4E$ spacing, Table V. (2) In complexes where the $^4B_2/^4E$ spacing is zero, namely, octahedral complexes, no wavelength dependence of quantum yield is observed.

Table V. Calculated $^4B_2/^4E$ Spacing and Percentage Equatorial Ligand Loss for Irradiation at Energies Higher Than the Lowest Quartet State

trans-$[\mathrm{Cr(en)_2XY}]^+$ X	Y	$(^4B_2 - {}^4E)$, cm^{-1} [a]	% eq ligand loss	ref
NH_3	NCS	958	60	30
NH_3	F	1380	35	19
NCS	NCS	1915	30–60[b]	10
NH_3	Cl	2100	15–25[b]	12
NCS	Cl	3058	15–20	31
F	Cl	3463	~20	18
Cl	Cl	4200	<1	32

[a] Calculated using the procedure and spectral parameters of ref 8. [b] The range given covers the reported variation with wavelength.

Finally, comparing the proportion of ethylenediamine aquated in the series *trans*-$[\mathrm{Cr(en)_2F_2}]^+$,[2,26] *trans*-$[\mathrm{Cr(en)_2NCSF}]^+$, and *trans*-$[\mathrm{Cr(en)_2(NCS)_2}]^+$[9] reveals that they are not in sequence, namely, ~90, 20, and 30%, respectively. For all three complexes ^4E is the lowest state and this state is predicted to lose ethylenediamine, thiocyanate, and thiocyanate, respectively; the calculated $^4B_2/^4E$ spacings are 2700, 2300, and 1900 cm^{-1}. The enhanced ethylenediamine loss observed for $[\mathrm{Cr(en)_2NCS)_2}]^+$ would be consistent with the closer proximity of its $^4B_2$ state.

This two-state model is consistent with much of the data; what is needed is direct evidence and quantitative testing. An investigation of the photochemistry of *trans*-$[\mathrm{Cr(en)_2NCSF}]^+$ and similar complexes over a wider temperature range and a search for preferential reaction quenching[27] may provide further evidence and work is currently underway toward this goal.

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Photochemistry of Azidopentacarbonyltungstate(0)[1]

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Three photoreactions are observed when the lowest energy excited state (436 nm) of the $W(CO)_5N_3^-$ anion is irradiated. For the PPN salt, coordinated nitrene formation leads to the production of $W(CO)_5NCO^-$ in the presence of added CO ($\Phi = 0.06$). For the $AsPh_4$ salt, a complex series of secondary thermal reactions leads to a noncarbonyl product ($\Phi = 0.07$). The stereochemistry of the CO substitution is investigated with labeling experiments. The photoactive excited state is assigned to an admixture of both azide to metal charge transfer and ligand field character on the basis of electronic, magnetic circular dichroism, vibrational, and emission spectra. The photochemistry is interpreted in terms of the charge transfer and ligand field character of this state, and a model of the excited-state potential surface is proposed.

The coordinated azide ligand has been the subject of many photochemical investigations.[4-10] Three modes of photodecomposition of the N_3 moiety have been observed. Azide complexes of Pt(II),[4] Au(III),[5] and $Co^{III}(NH_3)_5N_3^{2+}$ [6] exhibited photoredox chemistry resulting in the production of azide radicals. For the series of azidopentaammines of Co(III),[6] Rh(III),[7] and Ir(III),[7] photoredox in Co(III) was replaced by coordinated nitrene formation as the dominant mode of azide photodecomposition in Rh(III) and Ir(III). Although $Cr^{III}(NH_3)_5N_3^{2+}$ was initially believed to demonstrate predominantly photoredox chemistry,[8] recent work indicated that nitrene formation is dominant.[9] In contrast to the ammine complexes, the azidopentacyanides of Rh(III) and Ir(III)[10] photoaquated, eliminating azide as the anion, N_3^-.

We have introduced a model based on relative bonding changes in the coordinated azide ligand in the excited state as assessed by EHMO–SCC calculations which accounts for the observed trend from photoredox to nitrene formation in the Co, Rh, Ir triad.[11] For charge-transfer and ligand-localized excited states, these calculations predicted large changes in the internal azide nitrogen–nitrogen bond orders. These changes were a function of the overlap between the metal and the azide nitrogen atom. Ligand to metal charge transfer (LTMCT) and ligand localized (LL) states produced destabilization of the bond between the metal-bound nitrogen and the terminal N_2 which maximized for large metal–azide overlap. It is in these cases, such as third-row transition-metal–azide complexes, where coordinated nitrene photointermediates are anticipated.

The objectives of this investigation are to determine the modes and efficiency of the photochemical reactions of $W(CO)_5N_3^-$ from its lowest energy excited state and to describe the nature of this state through spectroscopic analysis. This is the first quantitative study of the photochemistry of a zerovalent, third-row azidometal carbonyl, a type of complex from which metal–nitrene intermediates are expected to result from a LTMCT state.[11] From the photochemical results, a model of the excited state is developed which is compared with other metal azides and the well-developed photochemistry of $W(CO)_5L$ complexes.[12-14]

Results

Spectroscopy. 1. UV–Visible and Magnetic Circular Dichroism Spectra. Both the electronic absorption and magnetic circular dichroism (MCD) spectra of $[AsPh_4][W(CO)_5N_3]$ are shown in Figure 1. The low-energy region of the absorption spectrum is dominated by an intense peak at 2.45 μm^{-1} (408.5 nm, ϵ 2900 M^{-1} cm^{-1}) with a red shoulder at approximately 2.19 μm^{-1} (457.3 nm) and is remarkably similar to the previously reported spectrum of $[NEt_4][W(CO)_5Br]$[14] where the major band is at 2.44 μm^{-1} (ϵ 2500 M^{-1} cm^{-1}) with a shoulder at 2.21 μm^{-1}. These absorption features in both complexes are red shifted relative to similar bands in $W(CO)_5$(ammine) compounds where the peaks occur at 2.53 and 2.31 μm^{-1}.[14] For $[AsPh_4][W(CO)_5N_3]$ there is no hypsochromic shift of the major band at 2.45 μm^{-1} upon changing the solvent from $CHCl_3$ to either MeOH, EPA, or propylene carbonate, nor is this band very cation dependent: Li salt, $E_{max} = 2.45$ μm^{-1}; Na salt, $E_{max} = 2.43$ μm^{-1}; $AsPh_4$ salt, $E_{max} = 2.45$ μm^{-1}; PPN (=μ-nitrido-bis(triphenylphosphorus) cation) salt, $E_{max} = 2.45$ μm^{-1}. In the 77 K absorption spectrum, a new feature is resolved at approximately 2.33 μm^{-1} (430 nm) which also appears in the low-temperature spectrum of $W(CO)_5I^-$ and $W(CO)_5Br^-$ but is not evident for any $W(CO)_5$(ammine) complexes.

The MCD spectrum of $W(CO)_5N_3^-$ (Figure 1) has a well-resolved s-shaped feature associated with the 2.45 μm^{-1} band of the electronic spectrum. As the energy of the null of the MCD corresponds to the maximum of the electronic feature, this MCD band is assigned as an *A* term of positive sign. Again there is a striking similarity between this MCD spectrum and preliminary MCD results for $W(CO)_5X$ (X = halides and ammines).[15]

2. Emission Spectra. Low-temperature (77 K) emission spectra were obtained for the $AsPh_4$ and PPN salts of $W(CO)_5N_3^-$ in the solid state, in suspensions in 2-MeTHF glasses, and in 4/1 v/v EtOH/MeOH glasses. Identical spectra were obtained under all conditions with the emission maximum at 1.945 μm^{-1} (514 nm) when excited at 2.50 μm^{-1} (400 nm). The maxima are slightly blue-shifted from those previously reported for $W(CO)_5L$ (L = ammines and phosphines) which all emit at 1.88 μm^{-1} (530 nm).[13,14,16] The observed lifetime of $[PPN][W(CO)_5N_3]$ is 10.6 ± 1 μs in a 4/1 EtOH/MeOH glass at 77 K, intermediate between the lifetimes of substituted pyridine derivatives of $W(CO)_6$ ($\tau \simeq 30$ μs)[13] and ammine and phosphine derivatives ($\tau \simeq 1$–5 μs).[16]

3. Vibrational Spectra. The proposed assignments of the carbonyl region infrared absorption bands of $W(CO)_5N_3^-$ in

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