WHITHER INORGANIC PHOTOCHEMISTRY? A PAROCHIAL VIEW

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Abstract - The main streams of development of the photochemistry of coordination compounds are summarized and related to current areas of major activity. Several are illustrated in terms of work in progress in the author's laboratory. The d^3 system of Cr(III) complexes has become the paradigm one for the field, and detailed studies of emission lifetimes and of rates of primary photoproduct formation clarify the chemistry of the first doublet and quartet thermally equilibrated excited (thexi) states. New rules governing emission lifetimes are presented. Excited state absorption spectra and possible resonance Raman spectroscopy of thexi states are described for Rh(III) complexes. Results on the photochemistry of Co(III) ammines having a Co-S bond are given, and on the chemistry and photophysics of aqueous polymers of $Pt(CN)_4{}^{2-}$. Likely directions of development in the next decade are discussed. Existing and new model systems will be explored in increasing depth; there will be major advances in elucidating the reaction mechanisms of thexi states and on their spectroscopy and thermodynamics. Studies on solar energy conversion systems will continue, with some laboratory but no economic success.

INTRODUCTION

The field of inorganic photochemistry has become a large and diverse one; the overlook presented here emphasizes those aspects that seem to augur important developments to come. The approach is parochial in that illustrations are mainly in terms of current work in this laboratory.

First, some historical perspective is needed in order to give direction to current and likely future progress (see Refs. 1 and 2 for general earlier reviews). Before about 1955, inorganic photochemical studies consisted mainly of investigations on isolated cases. Examples include the uranyl, Co(III), and Fe(III) oxalate systems, ferrocyanide ion and certain Co(III) ammines. There was little attempt to explain results in terms of specific excited state behavior and essentially no inter-relating of photochemical and photophysical processes. Many photochemical observations were purely qualitative, although sometimes of synthetic importance.

The next period, extending to the middle 1960's, saw increasingly systematic studies of Werner-type complexes, and the emergence of the rule that irradiation in the wave length region of a ligand field (LF) absorption band leads to substitution or isomerization reaction, while irradiation of a charge transfer (CT) band leads to redox decomposition. In fact, the nature of the photochemistry was useful in characterizing the transition. Thus if photoreduction of the central metal ion occurred, the transition was considered to be charge transfer to metal (CTTM) in nature, while if a ligand was reduced or if solvated electron production occurred, the excitation was taken to be charge transfer to ligand (CTTL) or to solvent (CTTS). In the case of Co(III) ammines, both ligand substitution and redox decomposition were found to occur on irradiation of a CTTM band, and an early and still important mechanistic scheme accounted for this behavior in terms of homolytic bond fission as the primary photoprocess, followed by alternative cage reactions (see Refs. 1, 2, 3c).

It became evident that photoreactions did not necessarily amount to a photocatalysis of some characteristic thermal reaction. In the case of Cr(III) ammines, for example, while the photochemistry that occurs on irradiation of a LF band is primarily one of ligand substitution, the ligand involved is often not the thermally labile one. Such photoreactions are called antithermal. Thus aqueous $Cr(NH_3)_5Cl^{2+}$ aquates thermally to give

$Cr(NH_3)_5(H_2O)^{3+}$ but the predominate photoreaction is that of ammonia loss (3d). Empirical rules (4) allowed the prediction of whether the photochemistry of a given complex would be thermal or antithermal in type:

> Rule 1: Consider the six ligands to lie in pairs at the ends of three mutually perpendicular axis. That axis having the weakest average crystal field will be the one labilized, and the total quantum yield will be about that for an O_h complex of the same average field.

> Rule 2: If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates.

The relative crystal field "strength" of a ligand is determined by its position in the spectrochemical series, in turn given (in the d^3 system) by the energy of the first spin allowed LF transition, that is, by the L_1 band maximum (3a). Thus $CN > bipyr > en > NH_3 > NCS > F$ (bipyr = 2,2'-bipyridine, en = ethylenediamine).

The publication of these rules stimulated their testing and, more recently, their theoretical explanation in terms of the bonding changes expected, following excitation (3d,5-7). The theoretical treatments followed the implication inherent in the formulation of the rules that the chemically active state is the first quartet excited state. It was possible, as an additional success, to account for the anomalous behavior of trans-$Cr(en)_2F_2^+$, which photoaquates ethylenediamine (8).

During this same period, however, came the realization that excitation at a wave length around an absorption band maximum leads in fact to a vibrationally excited state--a Franck-Condon (FC) state. Relaxation of the set of molecules to an ensemble in Boltzmann equilibrium with the medium (with respect to vibration, rotation, and translation) then follows. Such thermally equilibrated excited states have been called thexi states (9). The rules and their theoretical rationalizations should actually relate to the chemistry and bonding of ligand field thexi states. Traditional ligand field theory deals with energies at band maxima and treats the corresponding FC state as a free ion state perturbed by a set of ligands fixed in their ground state geometry (and also allows the inter-electronic repulsion parameters to become variables). Such theory cannot be applied rigorously to thexi states because these may be significantly different in energy and in geometry from the parent FC state. Direct evidence for energy distortion is the large Stokes' shift for fluorescence from $Q_1°$, the first thexi quartet state (10), which amounts to 4000 cm^{-1} in the case of $Cr(urea)_6^{3+}$. A chemical indication of geometric distortion is that a ligand photosubstitution reaction may be differently stereospecific than the thermal reaction. Thus the photolysis product of aqueous $Cr(NH_3)_5Cl^{2+}$ is cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$ although it is the trans ammonia that is released (3d). By contrast, the thermal reaction is the stereorententive aquation of the labilized ligand, in this case Cl^-. The stereochemical contrast exists even in cases where the photochemically and thermally labilized ligand is the same. Photolysis of trans-$Cr(en)_2Cl_2^+$ yields cis-$Cr(en)_2(H_2O)Cl^{2+}$, while the thermal reaction gives the trans isomer (3d).
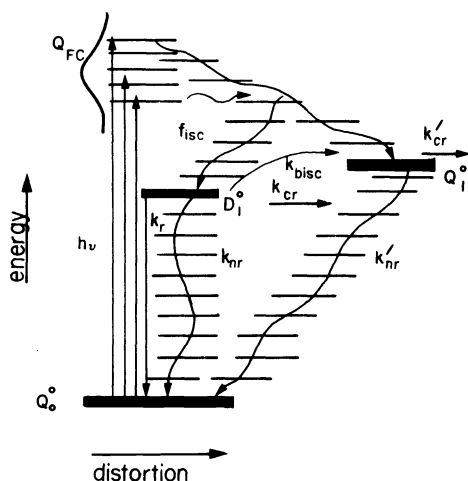
Q_{FC}: collection of Franck-Condon states reached on absorption corresponding to the first ligand field band, f_{isc}: efficiency of prompt ISC. k_r: rate constant for radiative deactivation from $D_1°$. k_{nr}, k'_{nr}: rate constants for non-radiative deactivation from $D_1°$ and $Q_1°$ k_{cr}, k'_{cr}: rate constants for chemical reaction from $D_1°$ and $Q_1°$. k_{bisc}: rate constant for back ISC.

Figure 1. Excited state scheme for a d^3 system.

Figure 1 shows a partial energy level scheme for a d^3 system, drawn in a way that emphasizes excited state distortion. Note, however, that the first doublet thexi state, D_1°, is shown as only slightly distorted from the ground state, Q_0°, geometry, as evidenced by the small Stokes' shift for phosphorescence (3b,10). Note also that the possibility of prompt intersystem crossing, ISC, is indicated. The importance of prompt ISC has been inferred from temperature dependence studies (4) and is supported by more recent work (11).

Although the Cr(III) family of complexes is still the best studied with respect to photosubstitution reactions, there is now a considerable body of data on complexes of Co(III), Rh(III), and Ru(II), as well as of metal carbonyls and related complexes, including ones with metal-metal bonds (3def, 12-16).

A major new channel of experimentation was opened by the observation of sensitization of and by coordination compounds (see Note a). The first observations were of sensitized redox decompositions of Co(III) ammines and of substitution reactions of Cr(III) ammines by organic donors (see Refs. 3cd). The next development was the finding that a coordination compound, $Ru(bipyr)_3^{2+}$, could act as a sensitizer for both types of reaction (17, 18). The sensitized redox decomposition of Co(III) ammines was explained on the basis that excited state $Ru(bipyr)_3^{2+}$ acts as a one electron reducing agent. The proposal, controversial at the time, was soon confirmed in other laboratories (see Ref. 19).

During the present decade, there has been a rapidly expanding interest in excited state redox reactions (see Ref. 19). There is now a considerable body of kinetic studies on bimolecular reactions involving an excited state coordination compound (see Ref. 20). Thexi state $Ru(bipyr)_3^{2+}$ has become perhaps the most widely studied complex of all time, capable of both excited state reduction and oxidation reactions. Elaborate kinetic studies now provide probably accurate standard half-cell potentials for the excited state, which is thus acquiring thermodynamic status (see Refs. 21, 22 as recent examples of studies on excited state $Ru(bipyr)_3^{2+}$).

An important application of excited state redox chemistry currently is to the development of reaction systems, the net effect of which is the photochemical decomposition of water (see Ref. 3g). Such efforts have been partially successful (23, 24, 25).

Reversible sensitization has also been reported (26), that is, the reversible process

$$A^* + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A + B^* \tag{1}$$

A point of potential importance in suggesting future directions is that in the case of $A = \underline{trans}\text{-}Cr(en)_2(NCS)_2^+$ and $B = Cr(CN)_6^{3-}$, the activation energies for both k_1 and k_{-1} were determined. Their difference gives ΔH, the enthalpy difference between the two D_1° states involved. Again, a thermodynamic quantity previously accessible only through spectroscopic estimates has been obtained by kinetic measurements.

The above example is one facet of a rapidly developing general field, that of the kinetic study of the various first order processes that occur following excitation. The d^3, Cr(III), system has become the paradigm one. This is partly because of the wealth of prior photochemical information, but, in addition, major impetus was given by the finding that emission from D_1° is often observable under ordinary photochemical conditions (27), so that emission and photochemistry can be studied concurrently. D_1° emission had previously been studied in low temperature, rigid matrices, under which condition lifetimes, τ, are typically of the order of msec (3b). Lifetimes in room temperature, fluid media are of the order of μsec or less, however, and an important question has become that of whether k_{nr}, k_{bisc}, or k_{cr} are the rate setting processes for the disappearance of D_1° (see Fig. 1).

In one important type of study, quenching experiments have shown that some but not all of the photoreaction is quenched on complete quenching of the emission from D_1° (Ref. 28 and citations therein). The conclusion is that part of the photosubstitution yield, ϕ, occurs with the intermediacy of D_1°, and that the non-quenchable portion, ϕ_0, occurs from Q_1° directly. Thus in the case of $Cr(en)_3^{3+}$, 50-60% of the primary photoreaction,

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Note a. We will define sensitization phenomenologically, that is, as chemical reaction or emission by compound B, following excitation of donor compound A, with no net concomitant change in A. We thus include cases where excited state A, A*, undergoes chemical reaction with B, but with regeneration of A in one or more subsequent reaction.

$$Cr(en)_3^{3+} \quad \xrightarrow[H_2O]{hv} \quad Cr(en)_2(enH)(H_2O)^{4+} \qquad (2)$$
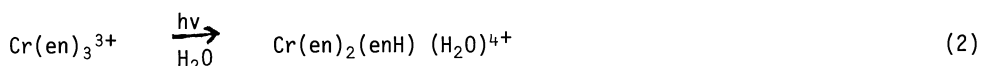
was found to be quenched on complete quenching of the phosphorescence (29,30). The proposed explanation was that prompt ISC to D_1° occurs, followed by back ISC to Q_1°, which then reacts. It was thus possible to retain the supposition that only from the Q_1° state does significant chemistry occur. The same mechanistic explanation could be applied to the similar quenching results for trans-$Cr(NH_3)_2(NCS)_4^-$ (R^-) ion (31), and has been applied in the cases of $Cr(CN)_6^{3-}$ and trans-$Cr(en)_2(NCS)_2^+$ (19, 28). In the case of $Cr(bipyr)_3^{3+}$, however, the quenchable part of the photoreaction (97%) was proposed to be due to direct reaction from D_1° (32).

We have been inclined to question the back ISC mechanism more generally. In a recent paper (33) on the temperature and solvent dependence of D_1° emission from R^- ion, we suggested that τ is more likely controlled by k_{cr} than by k_{bisc}.

An important, relatively recent development has been the observation of excited state absorption, ESA, an important example being that of R^- ion (33-35). The absorption occurs within short psec of forming the Q_1 FC state (36). ESA has been reported for other thiocyanate complexes of Cr(III) (36) and for $Cr(bipyr)_3^{3+}$ (33). Spectroscopic assignments are as yet speculative.

The above summarizes the main streams of development in the field, as we see them, although some important contributions are omitted for lack of space. Others are noted in the sections that follow as having special relevence to our own current work or to likely future developments. We turn, in the next section, to the results of some current investigations in this Laboratory.

RESULTS AND DISCUSSION

The paradigm system.
As noted in the Introduction, so detailed and so many types of investigations have been made on Cr(III) complexes that this d^3 case has become the model one for intensive photochemical and photophysical studies. As also noted, there is current and very active interest in the relative importance of the Q_1° and D_1° states in the excited state reactions of this family of coordination compounds. We report here some of our current results and conclusions on this question.

First, the temperature and solvent dependence studies on R^- ion (33) have been extended to other Cr(III) complexes (37). The principal data are summarized in Table 1; apparent activation energies for the τ's, not included, range from 4 to 12 kcal mole^{-1} and obey the previously noted Barclay-Butler plot(33). The most important outcome of the data of Table 1 is perhaps that a new set of rules emerges, this time for the τ's of Cr(III) complexes under photochemical conditions. These rules are:

> Rule 1: For complexes with six equivalent Cr-L bonds, the emission lifetime in room temperature fluid solution decreases with decreasing field strength.

> Rule 2: If two different kinds of ligands are coordinated, τ will be relatively short if that ligand which is preferentially substituted in the thermal reaction lies on the weak field axis.

(L denotes ligand).

The order of τ's in Table 1 is indeed that of the spectrochemical series. The case of L = CN also obeys rule 1 if results in non-aqueous solvents are used (see Note b). The

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Note b. Cyanide lies high in the spectrochemical series, and τ for $Cr(CN)_6^{3-}$ is indeed quite large in non-aqueous solvents (490 μsec (26) to 540 μsec (38) in DMF, 116 μsec in DMSO (26) and about 600 μsec in AN (33 and unpublished data). In water, however, τ is 0.1-0.2 μsec, depending on excitation wave length (39). Some special explanation clearly is required for this extremely large specific solvent effect; there may be important oxygen or other impurity quenching.

Table 1. Phosphorescence Lifetimes for Cr(III) Complexes.
(20°C; τ, μsec)

Complex	Solvent[a]					
	H_2O	D_2O	AN	DMF	DMSO	Sulfolane[b]
$Cr(bipyr)_3^{3+}$[c]	53[d]		38			
$Cr(en)_3^{3+}$	1.85	2.27	1.23	1.61	1.64	2.00
<u>trans</u>-$Cr(en)_2(NCS)_2^+$	6.0[e]	7.8	6.3	4.75	3.6	6.5
<u>cis</u>-$Cr(en)_2(NCS)_2^+$	0.52	0.56	0.15	0.37	0.50	0.40
$Cr(en)(NCS)_4^-$	0.040[f]					
$Cr(NH_3)_6^{3+}$	2.2	3.6	1.5[g]	3.0	4.2	3.0
$Cr(ND_3)_6^{3+}$	3.0	3.8				
$Cr(NH_3)_5(NCS)^{2+}$	0.26	0.30	h	0.51	0.92	h
<u>trans</u>-$Cr(NH_3)_4(NCS)_2^+$	0.56	0.53	h	0.85	0.44	h
<u>trans</u>-$Cr(NH_3)_2(NCS)_4^-$	0.005[i]	0.005[i]	0.12	0.080	0.090	0.25
$Cr(NH_3)_5(H_2O)^{3+}$	<0.005					
$Cr(NH_3)_5(D_2O)^{3+}$		<0.005				
$Cr(NH_3)_5Cl^{2+}$	<0.005					
<u>trans</u>-$Cr(NH_3)_4Cl_2^+$	<0.005				<0.005	
<u>trans</u>-$Cr(NH_3)_4(H_2O)Cl^{2+}$	<0.005				<0.005	
$Cr(NCS)_6^{3-}$	0.005[j]		0.03	0.12	0.10	0.14

(a) AN = acetonitrile, DMF = dimethyl sulfoxide, DMSO = dimethyl sulfox-
ide. (b) glass. (c) Pyridine: 14 μsec. (d) Literature value: 51
μsec at 22°C (32). (e) Literature value: 10.5 μsec at 15°C. (28)
(f) Maximum value because of possible impurities. (g) solubilized as
the CCl_3COO^- salt. (h) Not sufficiently soluble. (i) Extrapolated from
lower temperatures. These values for R^- agree within experimental error
with those previously reported (33). (j) Rise in $D_1°$ absorption (36).

applicability of rule 2 is illustrated by the contrast between both <u>cis</u>-$Cr(en)_2(NCS)_2^+$ and
<u>trans</u>-$Cr(NH_3)_4(NCS)_2^+$ and <u>trans</u>-$Cr(en)_2(NCS)_2^+$, three complexes for which rule 2 points to
thiocyanate. In the first two cases, the thermally labile ligand is also thiocyanate, and
τ is small, while in the last case, the thermal reaction is one of ethylenediamine aquation
(40), and τ is now relatively large.

A mechanistic explanation of these rules is that the bonding in $D_1°$ facilitates substitution
by essentially the same mechanism as for that of the thermal reaction (note Ref. 32 for
similar suggestion), and that this facilitation is greatest for the weak field ligand on the
weak field axis. Reaction from $D_1°$ will then be especially fast (and τ short) if that ligand
is also the thermally labile one.

The emerging overall picture is that stereochemically antithermal type photosubstitution
occurs from $Q_1°$ and that thermal type photosubstitution occurs from $D_1°$ and also controls τ.
This conclusion regarding $Q_1°$ and $D_1°$ reactivities is supported, in the case of $Cr(NH_3)_5$~
$(NCS)^{2+}$, by studies on the wave length dependence of the photochemistry and by sensitization
results (40).

The second approach that we currently are making to the question of $Q_1°$ vs. $D_1°$ reactivity
is to determine the actual rate of appearance of primary photoproduct (42). The experiment
consists of doing the photochemistry by means of a single, high energy 530 nm, 20 nsec pulse
from an amplified, frequency doubled Nd laser,and observing the transient change in optical
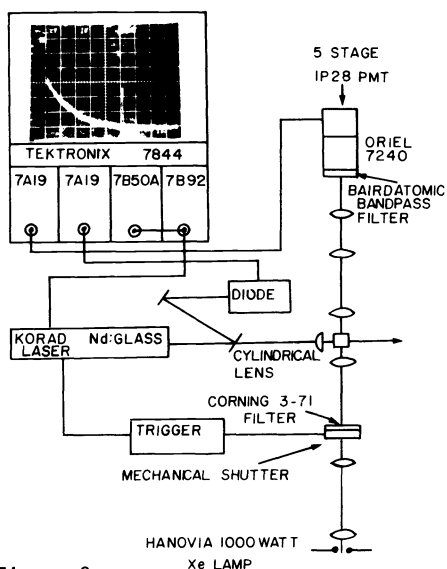density by means of a monitoring beam.

Figure 2.

Block diagram for the Nd laser and detection equipment. Inset: typical oscilloscope trace for the case of aqueous $Cr(en)_3^{3+}$. The upper trace (10 mV/div, 2 μsec/div) shows the transmitted monitoring beam intensity. The lower trace (100 nsec/div) shows the photodiode response to the laser pulse.

A typical oscilloscope trace, in the case of $Cr(en)_3^{3+}$, and the apparatus lay-out is shown in Figure 2. A prompt increase in absorbance is seen, followed by a measurably slow one. This delayed absorbance grows in with the emission lifetime (and with its temperature dependence) and clearly represents reaction from or through $D_1°$. We assign the prompt (<10 nsec) increase to reaction from directly formed $Q_1°$. The alternative assignment would be to reaction from a FC state (a "hot" excited state reaction) and this seems unlikely because reaction would then probably have to occur within a few psec of excitation in order to compete with ISC (assuming that the results with thiocyanate complexes (36) are of general validity). Such very fast chemical reaction should not be as ligand and stereochemically selective as is characteristic of Cr(III) photochemistry.

We denote the ratio of delayed to prompt increase in optical density by R, and analysis shows that

$$R = \frac{\phi_D(\gamma - 1) + f_{isc}(1 - \delta)}{\phi_Q(\gamma - 1) - f_{isc}(1 - \delta)} \tag{3}$$

where ϕ_D is the quantum yield for reaction by $D_1°$, $\phi_D + \phi_Q = \phi$. f_{isc} is the efficiency of prompt ISC, γ is the ratio of the extinction coefficient at the monitoring wave length of the photoproduct (Eq. 2) to that of $Cr(en)_3^{3+}$, and δ is the corresponding ratio for $D_1°$ vs. $Cr(en)_3^{3+}$ absorption.

That we are indeed observing reaction (2) is indicated by the fact that the total optical density change, following the exciting pulse, varies with monitoring wave length according to the variation of γ. Next, the variation of R with monitoring wave length is shown in Figure 3. For wave lengths between 575 and 600 nm, R is constant, consistent with the large values for γ. We conclude δ is not important, otherwise its variation would affect R. Further, R increases at wave lengths greater than 600 nm in just the manner expected because of the decrease in γ. The R(calc) line in the figure is for $f_{isc} = 0.3$ and $\phi = 0.37$, whence $\phi_D' = 0.85$ and $\phi_Q' = 0.15$, where these last denote the efficiency of direct chemical reaction from $D_1°$ and $Q_1°$, respectively ($\phi_D = f_{isc}\phi_D'$, $\phi_Q = (1 - f_{isc})\phi_Q'$).

This result allows an important conclusion. We can now rule out back ISC as the mechanism for the quenchable part of the $Cr(en)_3^{3+}$ photoaquation since $\phi_D' > \phi_Q'$. The back ISC mechanism requires $\phi_D' \lesssim \phi_Q'$. The high value of ϕ_D', moreover, confirms the conclusion from the emission rules that τ is primarily determined by chemical reaction from $D_1°$.

While excited state absorption does not appear to be important for wave lengths larger than 575 nm, the decrease in R at shorter wave lengths can best be explained by an increasing ESA. The values for δ shown in Fig. 3 are approximate, but suggest that the $D_1°$ absorption band is similar in extinction coefficient to that for the L_1 band of the ground state, but shifted to longer wave lengths. This is about what would be expected if the changes in orbital population were about the same for the $Q_0°$ and $D_1°$ spin allowed excitations.
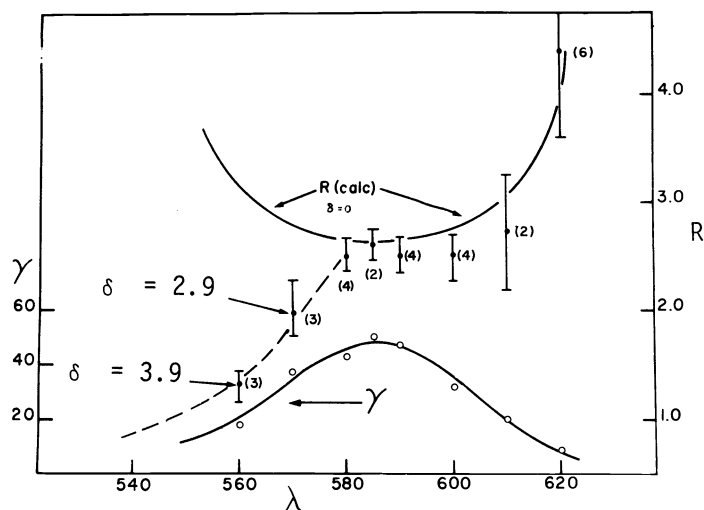
Figure 3. Primary photoproduct formation on 530 nm pulse photolysis of aqueous $Cr(en)_3^{3+}$. Dark circles: experimental R values (numbers in parentheses give the number of experiments) vs. monitoring wave length. Open Circles (with smoothing line): variation of γ with wave length. Upper full line: R calculated for $\delta = 0$.

A second complex under study is $Cr(NH_3)_5Cl^{2+}$. In this case, monitoring shows a prompt increase in optical density at 580 nm, followed by a delayed one of grow-in time about 100 nsec in neutral or alkaline buffers. The delayed component is absent, however, in acid solution. The situation is shown in Figure 4. Since the emission lifetime is less than
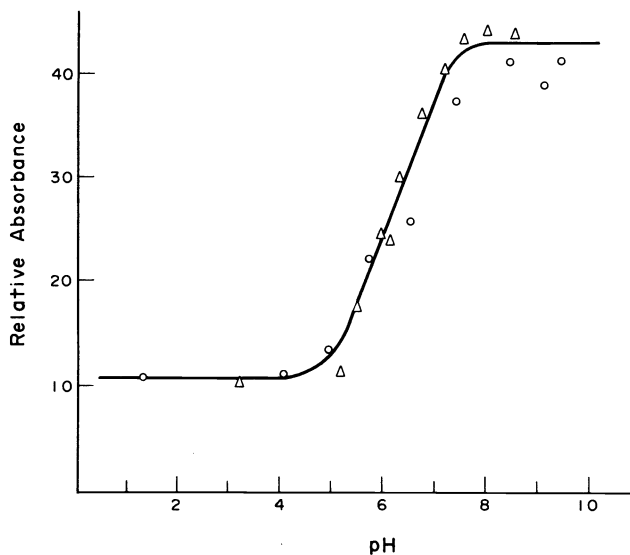

Figure 4. Absorbance increase (prompt plus delayed) on 530 nm pulse laser photolysis of aqueous $Cr(NH_3)_5Cl^{2+}$ as monitored at 580 nm. The triangles show the spectral transition from $Cr(NH_3)_4(H_2O)Cl^{2+}$ to $Cr(NH_3)_4(OH)Cl^+$.

10 nsec for this complex, the prompt absorbance could be due to reaction from either Q_1° or D_1°, although we assign it to Q_1°. We attribute the delayed increase in absorbance to the secondary reaction

$$Cr(NH_3)_4(H_2O)Cl^{2+} \ + \ B \ = \ Cr(NH_3)_4(OH)Cl^+ \ + \ HB^+ \tag{4}$$
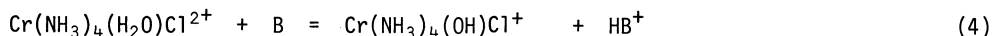
where B denotes the buffer base. The relevent absorption spectra are given in Figure 5; the pK_a for $Cr(NH_3)_4(H_2O)Cl^{2+}$ is about 6.3 from the pH dependence of the absorption spectrum, and this is essentially the inflection pH for the appearance of the delayed component (Fig. 4). Also, the ratio of delayed to prompt optical density change in alkaline solution at various monitoring wave lengths is that expected from Fig. 5. This analysis is consistent with the excited state reaction being very fast since the first product involves the substitution of coordinated ammonia by <u>neutral</u> water even though the hydroxy form may be the more stable one.
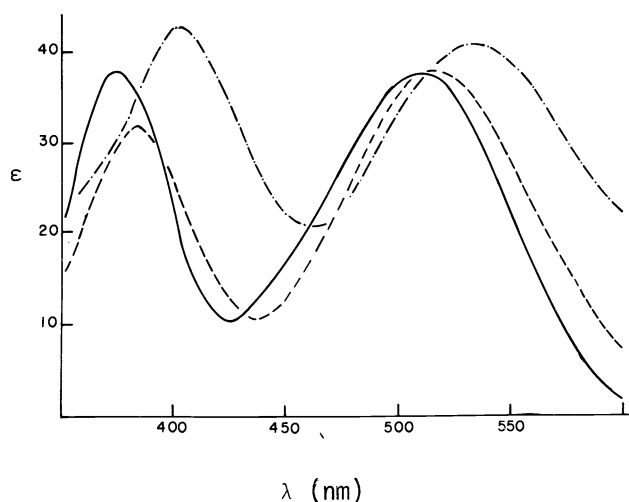
Figure 5. Absorption spectra for $Cr(NH_3)_5Cl^{2+}$ and photolysis products. ——————, $Cr(NH_3)_5Cl^{2+}$; -----, cis-$Cr(NH_3)_4(H_2O)Cl^{2+}$; —·—·—·—, $\underline{cis}$-$Cr(NH_3)_4(OH)Cl^+$.

λ (nm)

Spectroscopy of thexi states

Current studies in this laboratory using the previously mentioned Nd laser equipment, but with a third harmonic generator (giving 353 nm pulses) are extending monitoring experiments to second and third row transition metal complexes. Figure 6 shows the ESA spectrum
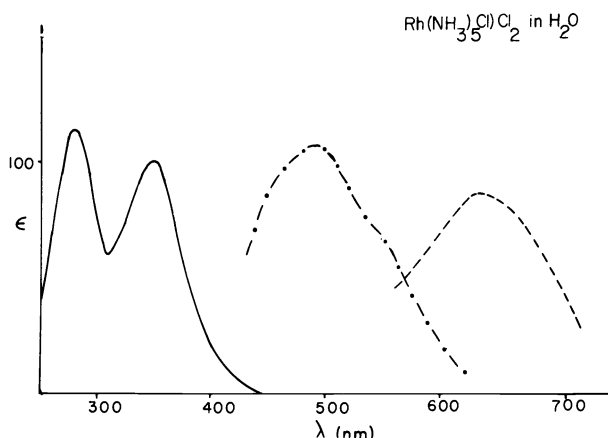

$Rh(NH_3)_5Cl)Cl_2$ in H_2O

Figure 6. Aqueous $Rh(NH_3)_5Cl^{2+}$. —————— absorption spectrum. —·—·—·— excited state absorption (minimum ϵ_{max}. ca. 100 $M^{-1}cm^{-1}$). -----emission spectrum (uncorrected for variation in vidicon sensitivity with wave length; correction will shift the maximum somewhat to longer wavelengths).

λ (nm)

of $Rh(NH_3)_5Cl^{2+}$, as one result (43). The extinction coefficient at the ESA maximum is about 100 M^{-1} cm^{-1}, as estimated from the laser pulse energy calculated to be absorbed in the monitoring zone; this is a minimum value since unit efficiency of excited state formation is assumed. The state is probably a first excited triplet thexi state, T_1°; it emits, and the ESA decays with about the same lifetime as that observed for the emission, 20 nsec (44).

The emission spectrum is included in Fig. 6; it is very similar to that reported for a low temperature matrix (45). While the position of the ground state, S_0°, to T_1 absorption band maximum is not known, the Stokes' shift relative to the L_1 band is quite large.

New photochemical systems

As noted in the Introduction, there is now fairly extensive photochemistry known for several families of complexes. A current interest in this Laboratory is in the photochemistry of the metal-sulfur bond--a topic about which little has so far been reported. Summarized here are some results on the series $Co(en)_2L^{n+}$ (46), the ligands L being identified in Fig. 7. As typical examples, the absorption spectra of $Co(en)_2(SN)^{2+}$ and $Co(en)_2(MeSN)^{3+}$
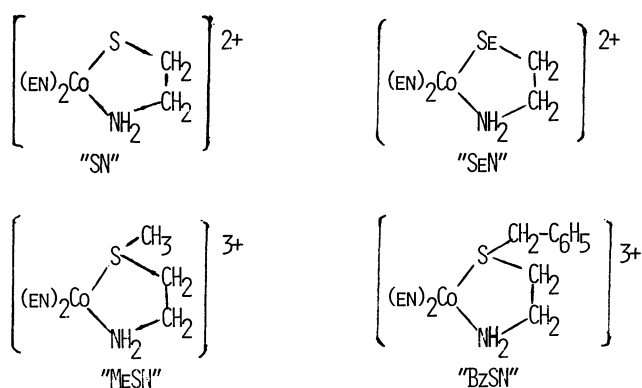
Figure 7. Structure and designations of ligands L in $Co(en)_2L^{n+}$.

are compared with that for $Co(en)_3^{3+}$ in Figure 8. The new band at 280 nm is assigned as

Figure 8. Absorption b spectra for $Co(en)_2L^{n+}$ complexes.
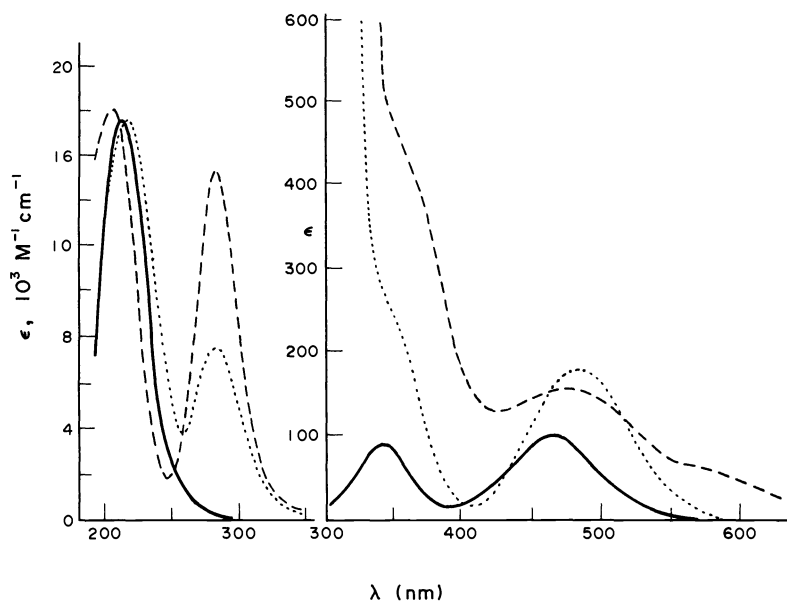———, $Co(en)_3^{3+}$.
----, $Co(en)_2$ $(SN)^{2+}$. ....,
$Co(en)_2(MeSN)^{3+}$.

λ (nm)

CTTM involving the Co-S bond. The complexity in the region of the L_1 band of $Co(en)_2(SN)^{2+}$ is made additionally evident by the magnetic circular dichroism, MCD, spectrum, as shown in Figure 9 (47). The presence of an A-type MCD feature (48) suggests the energy level diagram shown in Figure 10, corresponding to the gaussian components indicated in Fig. 9. Returning to Fig. 8, note that the long wave length shoulder to the first ligand field band is not present for L = MeSN, and we suggest that its presence in the case of L = SN⁻ as due to the removal of the ^1E degeneracy when a lone pair of electrons is present on the sulfur atom.

One sequence of spectral changes on irradiation is shown in Figure 11, and the quantum yields for the disappearance of the Co-S CT and for Co(II) production on 313 nm irradiation are given in Table 2 for several complexes. Somewhat similar results are found for the other members of the series.

Table 2.   Photolysis of $Co(en)_2L^{n+}$ complexes having a Co-S bond

Complex	Disappearance yield for Co-S CT Band		Co(II) yield (313 nm)
	313 nm	515 nm	313 nm
$Co(en)_2(SN)^{2+}$	1.77×10^{-3}	2.93×10^{-4}	$1.77 \times 10^{-3} \pm 0.2$ (3)
$Co(en)_2(MeSN)^{3+}$	8.8×10^{-3}	10^{-5}	$1.82 \times 10^{-3} \pm 0.1$ (3)
$Co(en)_2(BzSN)^{3+}$	1.1×10^{-3}		ca. 10^{-4}
$Co(NH_3)_5(SCN)^{2+}$[a]	0.59 (333 nm)	1.4×10^{-2} (510 nm)[b]	0.39 (333 nm)

(a) Ref. 50.   (b) 3.3° C.
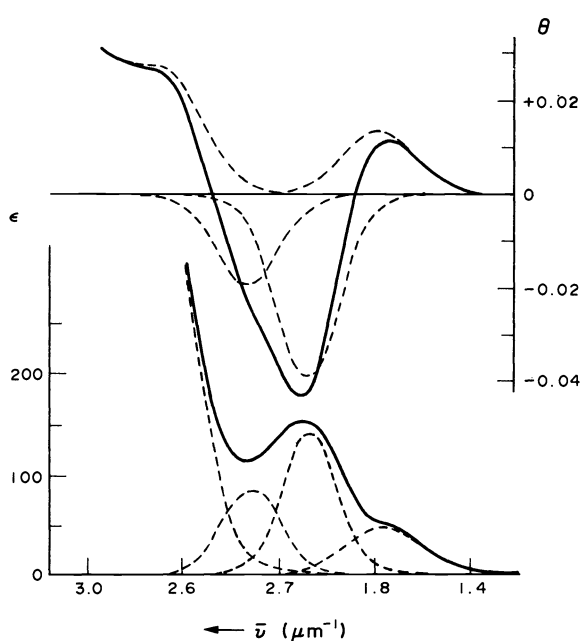
Figure 9. Upper solid line: MCD spectrum of $Co(en)_2(SN)^{2+}$ with probable components shown as dashed lines. Lower solid line: absorption spectrum with probable components shown as dashed lines.
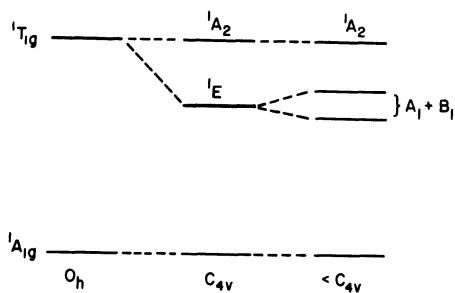
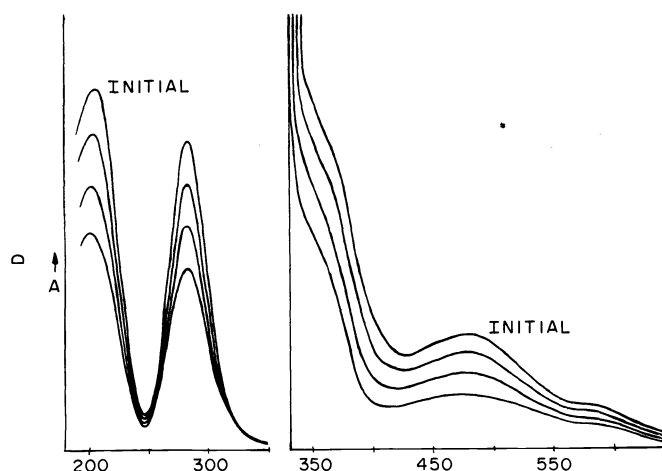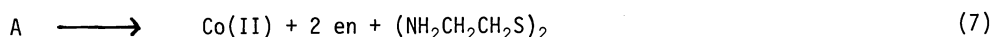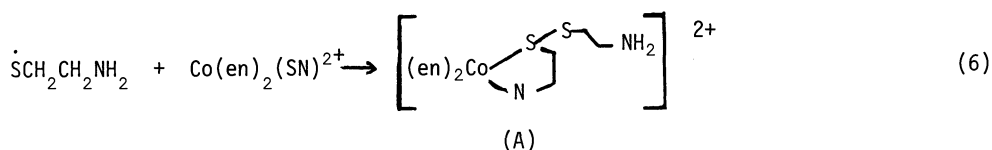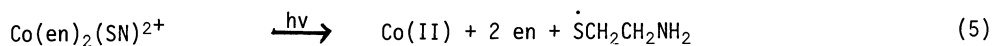Figure 10. Splitting of the $^1T_{1g}$ state in d^6 by reduction of symmetry.

Figure 11. Spectral changes on 313 nm irradiation of $Co(en)_2(SN)^{2+}$ at pH 7.06. Initial spectrum: upper curves.

The following mechanism suggests itself, in the case of $Co(en)_2(SN)^{2+}$.

$$Co(en)_2(SN)^{2+} \xrightarrow{hv} Co(II) + 2 \ en + \dot{S}CH_2CH_2NH_2 \qquad (5)$$

$$\dot{S}CH_2CH_2NH_2 + Co(en)_2(SN)^{2+} \longrightarrow \left[(en)_2Co \begin{smallmatrix} S \diagup S \diagdown NH_2 \\ \diagdown N \end{smallmatrix} \right]^{2+} \qquad (6)$$

(A)

$$A \longrightarrow Co(II) + 2 \ en + (NH_2CH_2CH_2S)_2 \qquad (7)$$

The disappearance yield of the 280 nm peak and the Co(II) yield are predicted to be the same, as observed. The complex corresponding to A^+, that is, with L = $(NH_2CH_2CH_2S)_2$ is stable (49) but it seems reasonable that the complex denoted by A would be unstable towards reaction (7). Disulfide is indeed a photoproduct and we discount its formation by direct radical-radical combination because of the low concentrations in our systems.

The above mechanistic sequence is traditional in that a Co-S CT absorption band is irradiated and homolytic fission of the Co-S bond is therefor not unexpected. What is of more interest is that the <u>same</u> spectral sequence and therefor the <u>same</u> photoreaction occurs on irradiation of the L_1 absorption band. We have thus a case where irradiation of a normal appearing L_1 band leads exclusively to redox decomposition. A possible explanation is that the sulfur lone pair does indeed "see" metal d-orbitals, so that electron transfer to the metal might be facilitated in the LF excited state.

As suggested by the data of Table 2, the photochemistry of $Co(en)_2(MeSN)^{3+}$ is more complicated. The 285 nm disappearance yield is five times that for Co(II) and, moreover, a Co(III) photoproduct is present, which appears to be <u>trans</u>-$Co(en)_2(H_2O)_2{}^{3+}$. Part of the photochemistry is evidently substitutional, and from the behavior of Co(III) acidoammines (12) the photosubstitution product is predicted to be
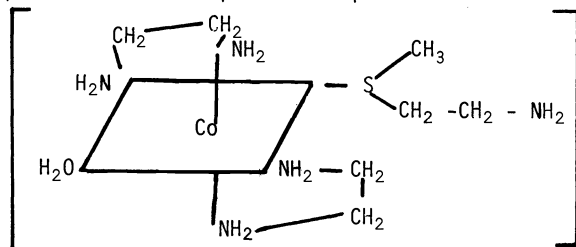
This primary product is likely unstable because of the weak Co-S linkage, and aquation to trans-Co(en)$_2$(H$_2$O)$_2$$^{3+}$ should be rapid. We attribute this change in photoreaction pattern to the lack of a sulfur lone pair so that the redox reaction is less facile and must now compete with substitution.

A rather different system under current study is that of aqueous Pt(CN)$_4$$^{2-}$. Crystalline salts of this complex have long been known to show emission, and a recent series of investigations (51) show separate parallel and perpendicular polarized emission spectra, both rather unstructured. The peak maxima are highly sensitive in wave length to the Pt-Pt distance in the Pt(CN)$_4$$^{2-}$ stacks that are present (52); this distance may be altered either by changing the cation or by application of high mechanical pressure.

We were interested in whether stacking type association occurs in solution; if so, we would be able to study the photochemical and photophysical behavior of a metal-metal interacting system very different from that of the metal carbonyls (53). Such association clearly occurs. Solutions deviate dramatically from Beer's law, as shown in Figure 12. The
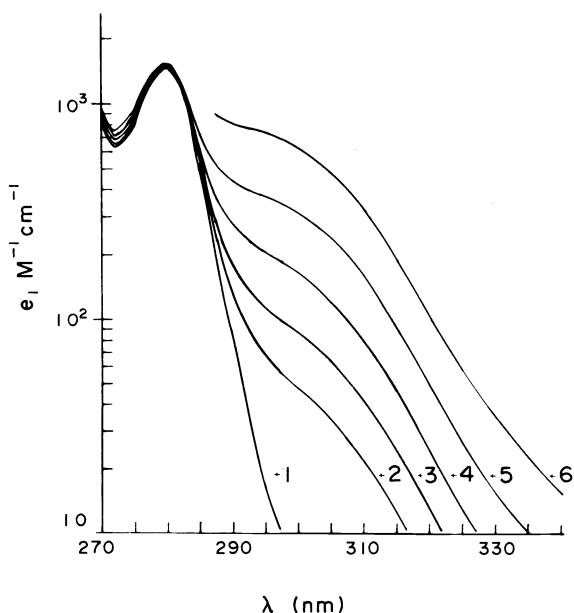
Figure 12. Apparent molar extinction coefficients for various concentrations of aqueous K$_2$Pt(CN)$_4$. Concentrations: 1, 8.96 x 10^{-3} M; 2, 0.15 M; 3, 0.218 M; 4, 0.311 M; 5, 0.445 M; 6, 0.635 M.

apparent extinction coefficient in the 300 nm region increases with concentration squared, suggesting trimer formation, but ionic strength effects are large and difficult to allow for, so we make at present no definite estimate of the association number.

The solutions emit at room temperature; a typical pair of spectra are shown in Figure 13.
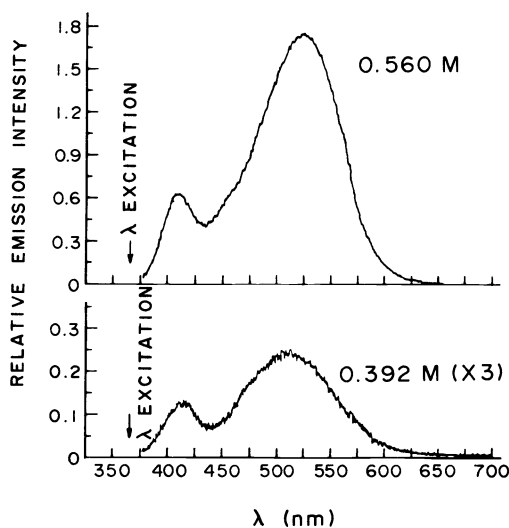
Figure 13. Spectrofluorimetric emission spectra for two concentrations of aqueous K$_2$Pt(CN)$_4$. Excitation at 366 nm. Upper curve: 0.560 M; lower curve: 0.392 M (3x).

The emission yield is small or zero at low concentration, and increases essentially linear-
ly with apparent extinction coefficient as concentration is increased. The emission
clearly is associated with the polymers present. Moreover, the two emission peaks occur in
the same wave length region as do those for the crystalline salts and probably therefor
represent emission from the same type of delocalized A_{2u}' and E_u' states postulated to be
involved for the latter (51). We conclude that the solution polymers also have a stacked
structure.

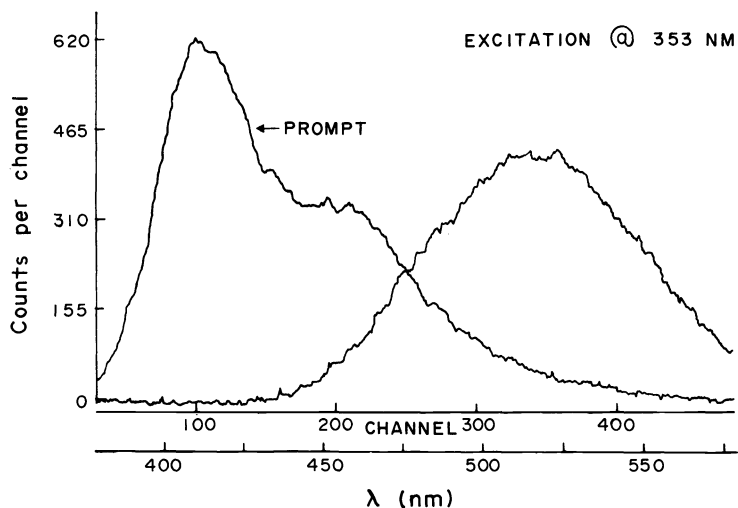Time resolved emission spectra are shown in Fig. 14 One spectrum appears and decays with

Figure 14.
Time resolved
emission spec-
tra for 0.4 M
aqueous
$K_2Pt(CN)_4$.
The prompt
spectrum (left)
follows the
20 nsec excit-
ing pulse; the
right hand
spectrum shows
a 500 nsec
decay (and is
oxygen
quenched).

the exciting pulse, and corresponds to the short wave length region of the spectra of
Fig. 13. A second emission spectrum remains after the exciting pulse, corresponding to the
long wave length feature of Fig. 13; this emission decays with a 500 nsec lifetime. These
findings differ in detail but are generally similar to those reported for $Ba[Pt(CN)_4].4H_2O$
(54) and we tentatively assign our time resolved spectra to the parallel and perpendicular
polarized emissions from the solution polymers.

There is, in addition, transient absorption in the 680-800 nm region which shows a composite
decay of 500 nsec and   several μsec. The former and the 510 nm emission both are
quenched by oxygen; neither excited state absorption is sensitive to N_2O so that solvated
electron production seems not to be involved. There appears also to be some photoproduct
formation, so that the photochemistry as well as the photophysics of these solutions is
of potential interest.

FUTURE DIRECTIONS

Model systems
In depth studies of Cr(III) complexes will continue for some time. The question of $D_1°$ vs.
$Q_1°$ reactivity is still controversial. Determinations of $Q_1°$ lifetimes are badly needed,
and may come through monitoring of the rate of product formation using a psec photolyzing
pulse. The detailed mechanism of antithermal reactions is far from understood. Use of
a related series of ligands, such as substituted amines, may reveal helpful electronic
and steric effects; stereophotochemistry, using optically active complexes, is beginning
to be explored (55).

The study of the Rh(III) family may come to rival that of the Cr(III) one in depth since
here again the presence of measurable excited state emission under photochemical conditions
gives the needed leverage. Excited state processes in a d^6 system may follow a different
pattern from those in the d^3 cases, so there is much incentive for such investigation.

An important development to be hoped for is that of the ligand field analysis of thexi
states. This may come through the use of CNDO type calculations where geometry is allowed
to become a variable (note Ref. 7).

We can expect continued investigation of the mechanism, including the role of solvent, of thermal equilibration and of ISC, both prompt and between thexi states.

Spectroscopy and structure of thexi states
We are just beginning to see reports of excited state absorption spectra. As more and better resolved spectra are obtained, a new set of ligand field analyses should become possible, perhaps in conjunction with a ligand field theory for thexi states. It may, for example, be possible to develop spectrochemical series for such states, and to obtain interelectronic repulsion parameters for them.

Raman spectroscopy of excited states should be possible. An experiment now in progress provides an illustration. We find an ESA peak for $Rh(NH_3)_5Cl^{2+}$ at 500 nm, following excitation by a 353 nm pulse, and may be producing transient concentrations as high as 10^{-3} M in the T_1° state. Since the second harmonic of the Nd laser may be permitted also to be present, it may be possible to obtain an excited state resonance Raman spectrum. That is, excited states are produced by the 353 nm pulse, and the 530 nm component also present is used for the resonance Raman effect. That it is possible to obtain a resonance Raman spectrum of a ground state by means of a single Nd laser pulse has already been demonstrated (56). Success in experiments of this type should yield information about the molecular geometry and bond force constants of thexi states.

Photochemistry and photophysics at interfaces
Many instances of emission from surface adsorbed molecules are known in the earlier literature (57) and interesting current work with monolayer assemblies is providing important information on photophysical processes (58). Examples involving coordination compounds have been found (23, 59). There is much current interest in the use of micellar emulsions to provide physical separation between donor and acceptor molecules (60).

We can certainly expect the study of the photochemistry and photophysics of coordination compounds adsorbed at interfaces to become an important activity in the next decade. As a possible novel experiment, the enhancement of the Raman effect at a reflecting surface may provide thexi state vibrational spectroscopic information. Apart from the drive for new fundamental information, a strong incentive will be in the potential usefulness of interfacial systems for solar energy conversion processes.

Bimolecular reactions of thexi states
The interest in excitation energy transfer reactions will continue unabated, but for the next few years it appears that excited state redox chemistry will be a major center of interest. Such studies will increasingly establish thermodynamic quantities for thexi states, to the point where tables of enthalpies and entropies of formation will become available.

The current preoccupation with solar energy conversion has a strong political driving force, and will no doubt continue for some years. We can expect various model systems involving coordination compounds to make their appearance. This will be in spite of the small likelihood that any such process can make an important contribution to general energy needs. The energy density of sunlight is low and the large collection area required (see Note c) would not only be costly but the environmental impact would be catastropic. It is worth pointing out that government subsidy of an uneconomic process does not provide net energy. The cost of any installation is also in the energy required for its fabrication, both in materials and in the energy consumption in the daily living of the workers. If an installation is uneconomic, it is almost certain that its creation and operation will consume more energy than that produced, so that the net effect will be one of overall energy depletion.

New Classes of compounds
The "second chemistry" will steadily make its way through all of inorganic chemistry. Enormous areas of exploration are open in the field of metalorganic and metalloprotein compounds. The variety of ligands used in the case of the conventional Werner-type complexes has so far been limited. We can expect to see more photochemistry involving sulfur, selenium, phosphorous, arsenic, etc. containing ligands.

Note c. The energy density of visible sunlight in the Los Angeles area is about 200 W m^{-2} and the annual electrical energy consumption of the city is about 17×10^9 kilowatt hour per year. Assuming eight hours of full sunlight every day, a collection system 3% efficient at converting all visible sunlight to electrical energy would require about 1000 km^2 of collection area.

Non-actinic means of excited state production

Chemiluminescent reactions have not yet become of major interest with respect to coordination compounds, but the field is likely to develop during the next few years. The outstanding current example is that of the strongly chemiluminescent reduction of $Ru(bipy)_3^{3+}$ by reducing agents such as sodium borohydride. Also, however, acidic aqueous solutions of this complex are weakly chemiluminescent even though solvent is the only reducing agent ostensibly present. Such weak chemiluminescence may be much more common as a phenomenon than now suspected.

Mention should also be made that the mechanical or electrical shock from an impinging laser pulse will induce triboluminescent emission. This has now been demonstrated for a number of crystals (62). An advantage over the conventional methods of crystal grinding and of thermal shocking is that the instant of stress is defined, so that emission lifetimes and time-dependent emission spectra can be obtained.

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