RECENT ADVANCES IN THE PHOTOCHEMISTRY OF COORDINATION COMPOUNDS

ARTHUR W. ADAMSON

Department of Chemistry,
University of Southern California,
Los Angeles, California 90007

ABSTRACT

Some recent developments in the photochemistry of Co(III), Cr(III), and Pt(II) complexes are described. Interest with respect to the first group is centring on photosensitization results and on the emerging importance of triplet excited states. In the case of Cr(III) compounds, the results of both direct and sensitized photolyses, as well as of emission studies, are leading to a distinction between the first ligand field quartet excited state, $^4L_1$, and the thermally equilibrated one, $^4L_1^0$. There are indications that much of Cr(III) photochemistry derives from this second state and that its geometry and energy are quite different from those of $^4L_1$. An empirical procedure is given for estimating $^4L_1^0$ energies. Although Pt(II) complexes are less well studied than those of the other two groups, the situation may be similar to that with Cr(III) complexes in that the photochemistry appears to proceed from thermally equilibrated excited states of geometry different from the ground state. A call is made for a new ligand field theory—one that deals with thermally equilibrated or true excited states.

1. INTRODUCTION

The photochemistry of coordination compounds has become a field of study to which new investigators are being drawn at a noticeably accelerating rate. The general subject has been reviewed in varying detail[1–5], and the purpose of this paper is rather to point out certain recent results that appear to open doors to extensive new areas of study, and to emphasize explicitly some of the tensions with established theory that these results are creating. The material is restricted to primary photochemical reactions (and immediately following cage processes) and to their relationship both to excited states and to ordinary or thermal reactions. In brief, the emphasis of the paper is on the physical chemistry of the excited states of certain families of coordination compounds.

The general molecular orbital diagram for an octahedral complex is shown in *Figure 1.* The figure illustrates that ligand field transitions generally place an electron in a σ antibonding orbital, and are parity forbidden. Ligand field absorption bands will be designated as L_1, L_2, etc., in order of decreasing wavelength. Transitions to higher, *ungerade* states are parity allowed and are usually of much higher intensity than ligand field ones; they are generally called charge transfer (CT) absorptions—charge transfer to metal (CTTM) if from a ligand localized orbital and terminating on a metal localized one and charge transfer to ligand (CTTL) if from a metal localized orbital and terminating on a π^* ligand one.

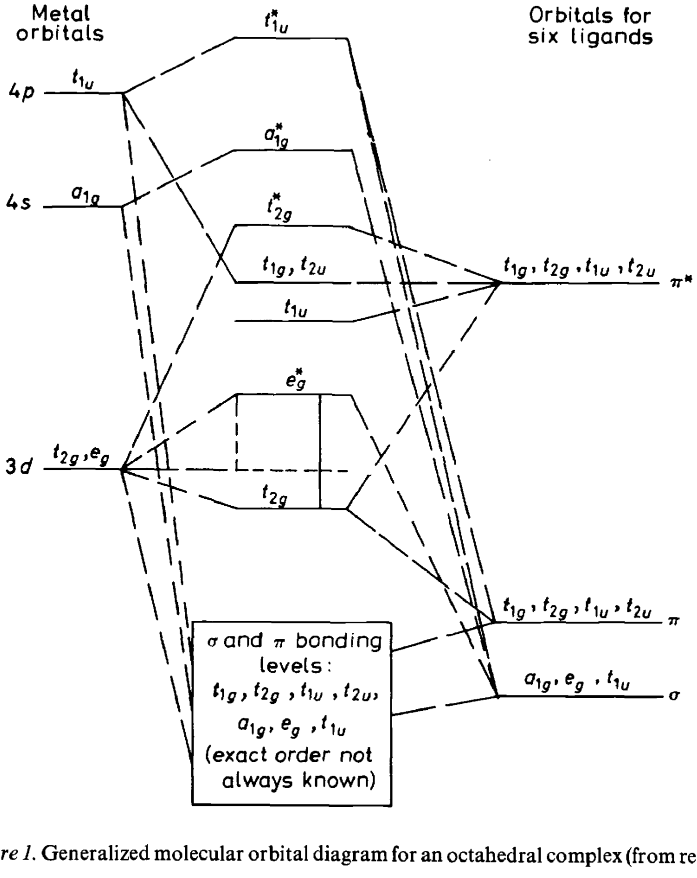

Figure 1. Generalized molecular orbital diagram for an octahedral complex (from ref. 1).

Photochemical reactions that have been observed include redox decomposition in which the central metal ion is reduced, electron production, ligand replacement by solvent (aquation if it is water), and isomerization or racemization. This paper will be limited to some considerations of the excited state processes leading to redox decomposition of Co(III) complexes, and to those leading to aquation and isomerization in Cr(III) and Pt(II) ones. A great deal of other work is in the recent literature, but limitations of space require that only these three families of coordination compounds be mentioned. They are the best studied ones, however, and it is with them that the more probing experiments have been made.

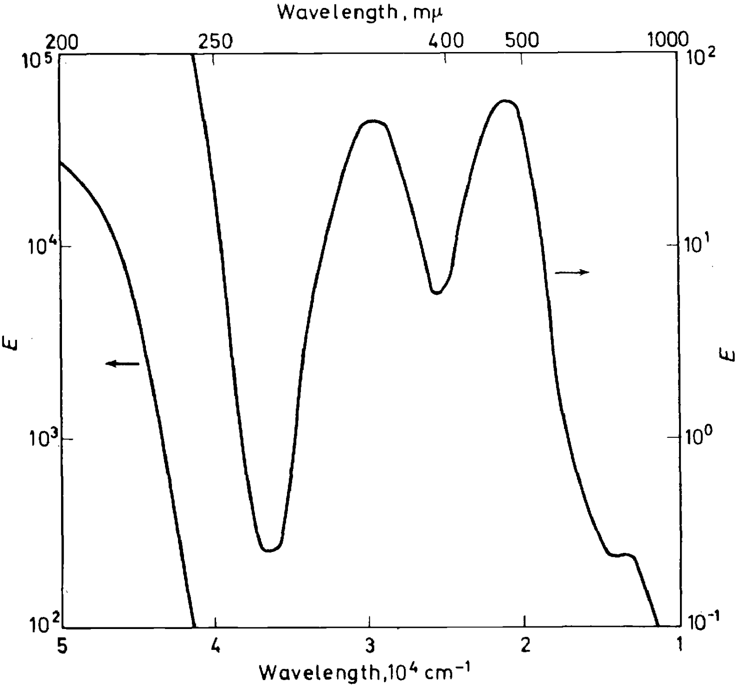

Figure 2. Absorption spectrum for $Co(NH_3)_6^{3+}$.

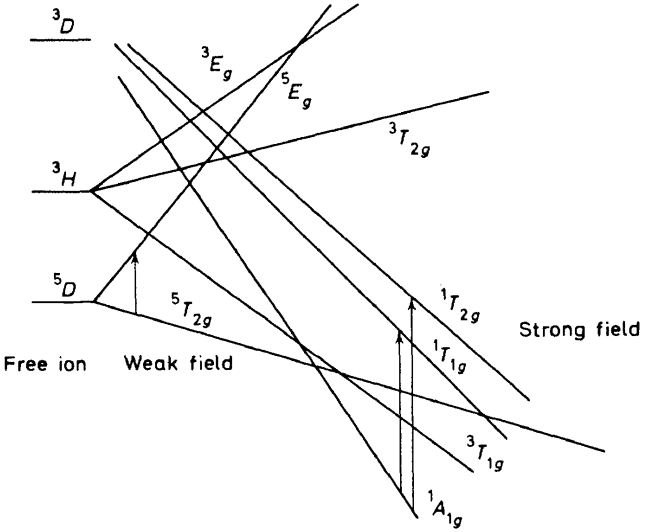

Figure 3. Ligand field term system for Co(III) complexes in O_h symmetry.

2. COBALT (III) COMPLEXES

A typical absorption spectrum for a Co(III) ammine is shown in *Figure 2*, for $Co(NH_3)_6^{3+}$, and the corresponding standard ligand field term system, in *Figure 3*. As the figures show, one finds two ligand field bands, L_1 and L_2, corresponding to the transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, and a first intense CT band in the ultra-violet, considered on qualitative theoretical grounds to be CTTM. With complexes of the type $Co(NH_3)_5X^{2+}$, where X is a halogen or pseudo-halogen, the CTTM band moves towards the visible as the ionization potential of X decreases—as illustrated in *Figure 4*.

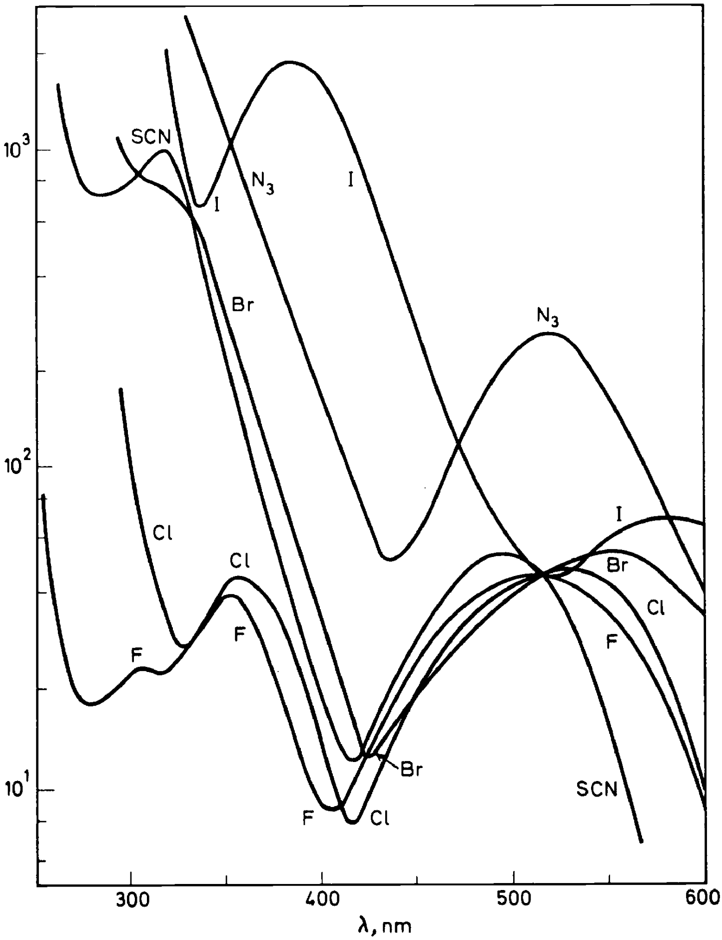

Figure 4. Absorption spectra for $Co(NH_3)_5X^{2+}$ complexes (from ref. 1).

The general observation is that irradiation of a CTTM band leads to Co(II) production and oxidation of a ligand, while that of an *L* band results in aquation[4,6], thus qualitatively confirming the CTTM and ligand field assignments. A complication is that aquation may also be an important consequence of irradiation of the first CTTM band[4,7,8], or, as an interesting alternative, linkage isomerization in the case[9] of $Co(NH_3)_5(NO_2)^{2+}$. An important question has been whether the redox and substitutional reaction modes represent alternative chemistries of the CTTM excited state or whether some intersystem crossing to a ligand field state has occurred. The relatively high aquation quantum yields that may be observed, as with $Co(NH_3)_5Br^{2+}$, contrast with the generally very low yields found on irradiation of L_1 or L_2 bands (of normal intensity). Moreover, studies[10] with *trans*-$Co(en)_2(NCS)(Cl)^+$ showed that the ratio of chloride to thiocyanate aquation varies over the CTTM to L_1 wavelength region. It seems, therefore, that the aquation mode of reaction stems from at least two different excited states. An early mechanism[6,7] which still appears adequate treats the primary reaction from the CTTM state as a homolytic bond fission, with net redox decomposition and aquation alternative consequences of subsequent cage reactions.

In the case of the ammine complexes, a series of investigations is unravelling the details of how the nature of the oxidation products depends on that of the ammine ligand and on medium conditions, such as pH[11], following irradiation of a CTTM band. For example, the redox photolysis of $Co(NH_3)_5(H_2O)^{3+}$ leads to nitrogen production, while that of $Co(en)_3^{3+}$, to ammonia and formaldehyde.

An interesting observation has been that of the production of coordinatively unsaturated Co(III) intermediates. Irradiation of the peroxo complex, $(H_3N)_5Co(O_2)Co(NH_3)_5^{5+}$ apparently leads to oxygen (ground state) and $Co(NH_3)_5^{3+}$, the latter then scavenging solvent or X^- ions present in the solution[12]. Irradiation of $Co(CN)_6^{3-}$ in the region of the first ligand field band [probably a d–π^*(CN) transition[13]] yields $Co(CN)_5^{2-}$, which again scavenges solvent or available X^- ions[14].

With the above as relatively current background, a potentially valuable development has been the finding that Co(III) complexes may be photosensitized. Such complexes have been known to quench organic triplet excited states[15–17], and the observation that organic sensitizers, such as benzophenone, benzil, *trans*-stilbene-4-carboxylate ion, and biacetyl can induce photoredox decomposition[18] of $Co(NH_3)_6^{3+}$ and $Co(NH_3)_5(H_2O^{3+})$ is perhaps not surprising. Two different mechanisms may be operative, however. Triplet benzophenone may abstract a hydrogen atom from the solvent (water–acetone in this case), to produce ketyl radical[19]; the observed formation of Co(II), for which the limiting quantum yield, at high complex concentration, is unity, may therefore have occurred through a chemical mechanism. This is unlikely in the case of the other sensitizers used, and for these excitation energy transfer appears to have taken place. The same conclusion applies to the biacetyl sensitized aquation[20] of $Co(CN)_6^{3-}$.

The interesting point that emerges, however, is that illustrated in *Figure 5*. The triplet energies of these sensitizers lie well below those of the CTTM bands of the complexes used and, in fact, are such as to most easily populate the first ligand field excited state. This state is photochemically very inert, however; direct irradiation of the L_1 band leads to aquation but in very low quantum yield. The photosensitized reaction mode, namely redox decomposition, suggests that a CTTM state is involved, and the suggestion is that the active state may be a lower lying triplet, ^{3}CT. A ^{3}CT (or ^{3}CTTM) state is expected to exist with Co(III) complexes, but has not been detected spectrophotometrically. Similarly, the photosensitized aquation of $Co(CN)_6^{3-}$ was suggested to involve the $^3T_{1g}$ state[20]. Sensitization experiments thus appear to provide access to non-spectroscopic excited states—that is, to ones not populated directly on absorption.

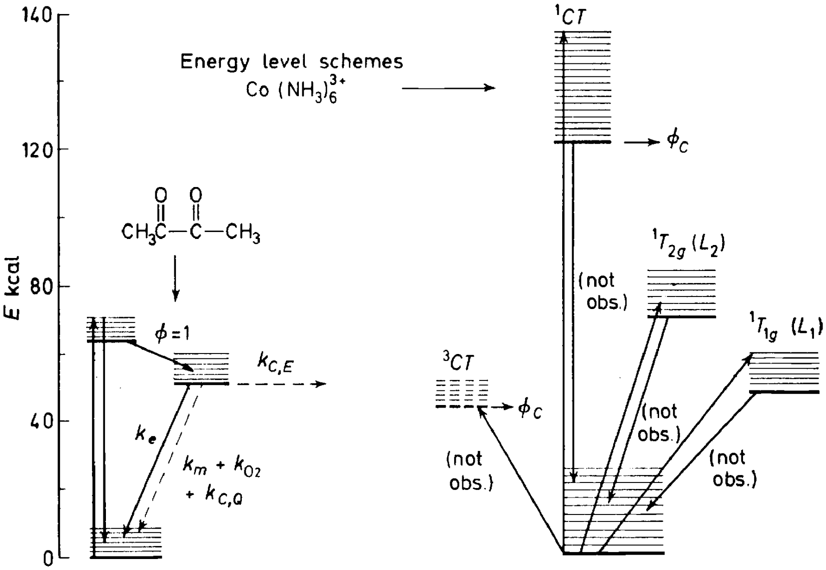

Figure 5. Energy level schemes for biacetyl and $Co(NH_3)_6^{3+}$.

Clearly, many additional investigations of the above type are needed. A current one is on the photosensitized decomposition[21] of $Co(NH_3)_5Br^{2+}$, to determine if the same or some different ratio of redox to aquation reaction modes occurs, relative to that found on direct photolysis. The result may serve to characterize further the chemistry of the ^{3}CTTM state which is assumed to be involved.

Another point is that of the applicability of spin conservation rules. In the case of Co(III) systems, one expects triplet (singlet) excited states to be produced by triplet (singlet) state donors. One exception has already appeared. If *trans*-stilbene-4-carboxylate ion, TSC, is coordinated in the complex $Co(NH_3)_5(TSC)^{2+}$, irradiation of the virtually unaltered singlet–singlet absorption band of the TSC ligand leads to redox decomposition of the complex, plus some aquation, but without any isomerization either of the released or of the still coordinated TSC ligand[22]. The isomerization normally proceeds via the TSC triplet state and one implication is that this state is never reached. Furthermore, the normal fluorescence of TSC is entirely quenched on being coordinated. It thus appears that the intramolecular energy transfer occurs from the TSC first excited singlet state. Yet the same energy problem as before suggests that it is a ^{3}CT state of the cobalt centre that has been populated, in violation of spin conservation. Such violation occurs generally, of course, in intersystem crossing, and it may be that hindrances called for by the spin rule will prove to be unimportant in the case of coordination compounds (see also ref. 23).

An experimental limitation in the case of Co(III) complexes is that emission is rarely observed, $Co(CN)_6^{3-}$ being the principal exception [24, 25]. As a consequence it has not been possible to characterize Co(III) excited states in terms of their emission properties.

To summarize, current investigations with Co(III) complexes have involved the further detailing of the nature of ammine oxidation products in redox photolyses, and the use of sensitized reactions as a means of learning more about the excited state precursors to chemical reaction. At the moment it appears that irradiation of the first CTTM band may be followed by intersystem crossing to a lower lying ^{3}CTTM state, which then undergoes homolytic bond fission. As yet, rather little is known about the photochemistry of essentially pure L_1 or L_2 absorption bands other than the fact that substitution reactions occur in low quantum yield. Sensitization of such reactions has not so far been reported.

3. CHROMIUM(III) COMPLEXES

General observations

Some rather interesting developments have occurred with Cr(III) systems. First, a typical absorption spectrum, that of $Cr(NH_3)_5(NCS)^{2+}$, is shown in *Figure 6*; the corresponding excited state scheme, labelled for O_h symmetry, is given in *Figure 7*. The two figures illustrate the spin forbidden or doublet transition which generally occurs at around 650 nm, corresponding to $^4A_{2g} \rightarrow {}^2E_g$ (in O_h), the first and second ligand field transitions, L_1 and L_2 ($^4A_{2g} \rightarrow {}^2T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$, again in O_h), a thiocyanate intra-ligand excitation at 300 nm, and a first CT band (presumably CTTM) appearing near 200 nm†.

The photochemistry of Cr(III) complexes, using visible and near ultraviolet light, has so far consisted entirely of substitution type reactions. With O_h complexes, such as $Cr(NH_3)_6^{3+}$, only one such reaction is possible, solvation, and the photochemistry appears as a photocatalysis of the thermal reaction; quantum yields are essentially wavelength independent. It therefore appeared at first to be quite possible that all reaction was taking place from the first excited doublet (D) state, reached by intersystem crossing[26] from $^4L_1$.

The behaviour of non-O_h compounds is more complicated. A set of photolysis rules allows a prediction of which ligand should be lost in the photoaquation reaction[27]. The complex, whether O_h or not, is regarded as having three mutually perpendicular axes, each of an average ligand field strength determined from the positions of the ligands in the spectrochemical series. The

---

† The symmetry based designations for the terms of a Cr(III) complex depend on its point group symmetry and, for simplicity, the practice will be adopted here of describing the state or states giving rise to the first and second ligand field bands as $^4L_1$ and $^4L_2$, respectively, and that corresponding to the first doublet band, as ^2D. This terminology also avoids very likely unwarranted assumptions as to the equilibrium geometry of the quartet excited states—see further below.

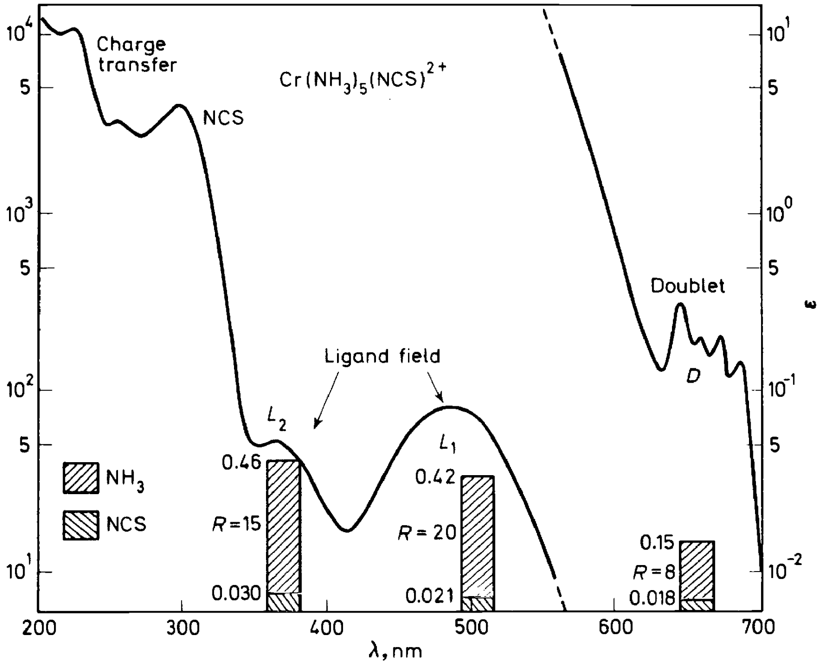

Figure 6. Absorption spectrum and photolysis quantum yields for $Cr(NH_3)_5(NCS)^{2+}$ (0.1 N H_2SO_4). (Ref. 28).

weak field axis is the one labilized, and if this axis contains two different ligands, then it is the stronger ligand field one of the two that is replaced. Thus in the case of $Cr(NH_3)_5(NCS)^{2+}$ the prediction, confirmed by experiment[28], is that photoaquation of ammonia should predominate, in contrast to the thermal reaction which gives thiocyanate aquation only. Analogous behaviour occurs with $Cr(NH_3)_5Cl^{2+}$ [29, 30] and $Cr(NH_3)_5Br^{2+}$ [31, 32]. These rules are best understood, however, if reaction is occurring from the first

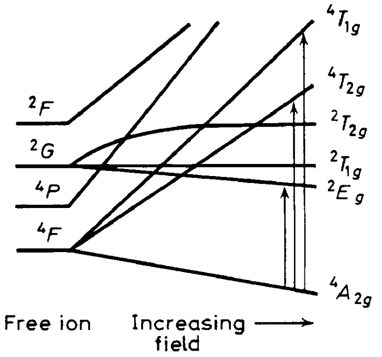

Figure 7. Ligand field term system for Cr(III) complexes in O_h symmetry.

excited quartet rather than from the ^2D state, since the latter is relatively unaffected by the spectrochemical position of the ligands. The matter is discussed further in the next section.

Continuing with the above examples, some aquation of the X^- group does occur as well, the ratio† of quantum yields, Φ_{NH_3}/Φ_X, being about 20:1 for X = NCS^- (see *Figure 6*), and about 35:1 for X = Cl^- or Br^-. In the case of X = NCS^-, moreover, direct irradiation of the *D* band gives a ratio[28] of only 8:1; this observation was taken as a strong indication that ammonia and thiocyanate aquation are associated with different excited state precursors, and it was suggested that the $^4L_1$ state leads to the former mode of reaction only and the ^2D state, only to the latter one.

Sensitization experiments

Several observations have made it clear that excitation energy transfer can occur to a Cr(III) complex. Schläfer and co-workers reported that on irradiation at 77°K of salts of the type $[Cr(urea)_6]\,[Cr(CN)_6]$, absorption in the *L* bands of the cation may lead to phosphorescence emission[33] from the $Cr(CN)_6^{3-}$, although a later paper tends to retract this conclusion[34]. Similar excitation energy transfer at 77°K has been reported for the $Ru(bipyr)_3^{2+}$ (bipyr = 2,2′-bipyridine) salt[35] of $Cr(C_2O_4)_3^{3-}$, and we find the fluorescence emission of aqueous $Ru(bipyr)_3^{2+}$ to be quenched by various anionic complexes, including[36] $Cr(C_2O_4)^{3-}$, $Cr(NCS)^{3-}$, and $PtCl_4^{2-}$. Finally, light absorption by benzil sensitizes phosphorescence emission by $Cr(NCS)_6^{3-}$, in low temperature but liquid solution[37], and Reinecke's salt, *trans*-$Cr(NH_3)_2(NCS)_4^-$, acts as a donor to excite the phosphorescence of $Cr(CN)_6^{3-}$, also in low temperature liquid media[38]. A recent observation is that biacetyl, acridinium ion, Michler's ketone, and methylene blue sensitize the aquation of complexes such as $Cr(NH_3)_5(NCS)^{2+}$ and Reinecke's salt[39].

Some further results are the following[40]. It is found that acridinium ion fluorescence is quenched by aqueous $Cr(NH_3)_5(NCS)^{2+}$ and that both ammonia and thiocyanate aquation are sensitized, in about 25:1 ratio, depending on the complex concentration, as shown in *Figures 8* and *9*. The figures further show that the sensitized ammonia aquation is unaffected by dissolved oxygen while that of thiocyanate is inhibited.

Experimental

The solutions were 4.6×10^{-4} M in acridine, of the indicated concentrations in complex, and 0.1 M in sulphuric acid. Acridine is not soluble in neutral solution, and 0.1 M sulphuric acid was chosen as the medium so as to be able to tie the results to the earlier direct photolysis studies[28].

Irradiation was at 410 ± 10 nm or in the region of the first singlet–singlet transition of acridinium ion; direct absorption by the complex was less than two per cent. It was necessary, however, to correct for photolysis by the fluorescence emission of the sensitizer. Light intensities were determined

---

† The ratio is in all cases somewhat dependent on whether the L_1 or the L_2 band is irradiated. In addition Φ_{Br^-} shows a rise in the region of the tail of the first CT band[32], possibly due to the onset of a new mode of photolysis.

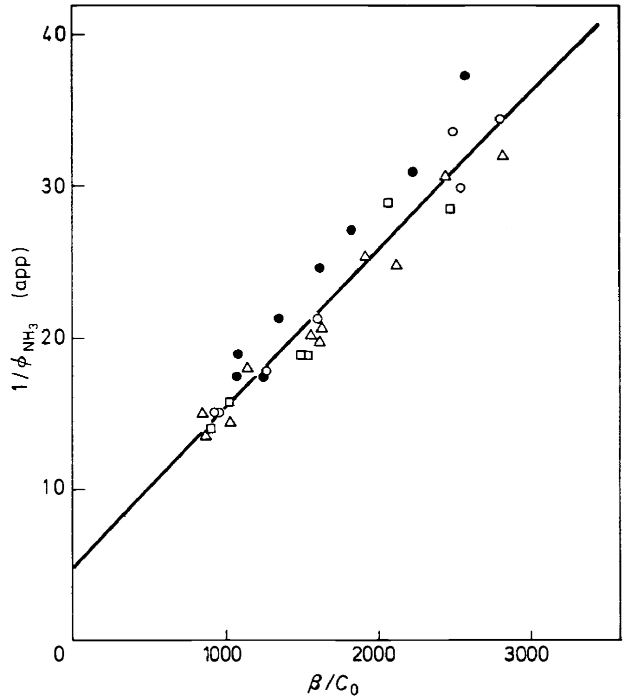

Figure 8. Acridinium ion sensitized ammonia aquation of $Cr(NH_3)_5(NCS)^{2+}$ in 0.1 N H_2SO_4. ○ Argon bubbled, 25°C, short irradiation; △ Argon bubbled, 25°C, long irradiation; □ Oxygen bubbled, 25°C, long irradiation; ● Argon bubbled, 10°C, long irradiation. (From ref. 40).

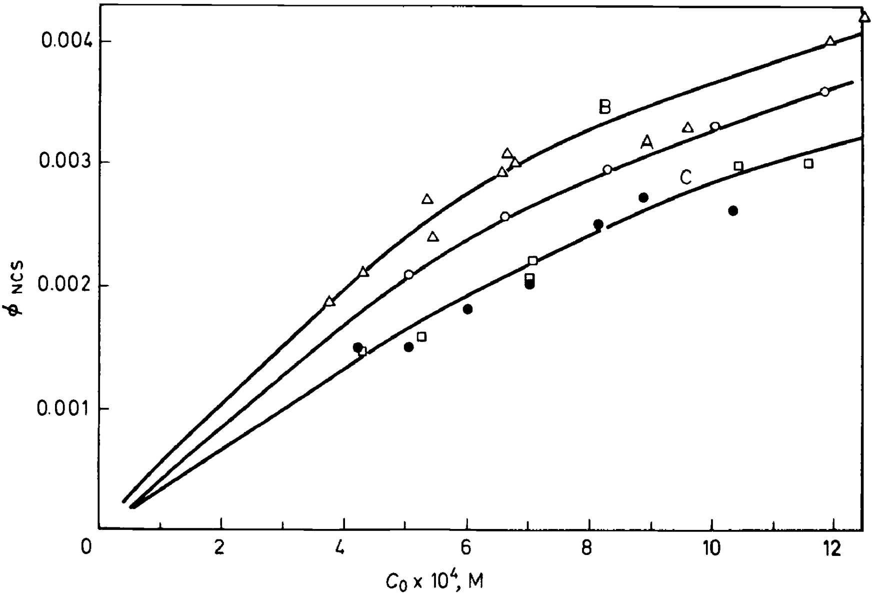

Figure 9. Acridinium ion sensitized thiocyanate aquation of $Cr(NH_3)_5(NCS)^{2+}$ 0.1 N H_2SO_4, long irradiations. △ Argon bubbled, 25°C; ○ Air bubbled, 25°C; □ Oxygen bubbled, 25°C; ● Argon bubbled, 10°C. (From ref. 40).

by ferrioxalate actinometry[41]. The photolysis train is that referred to earlier[39], as well as the equipment for emission studies.

The function β used in plotting *Figures 8* and *9* is described in a previous paper[18], and allows for the decrease in complex concentration during a sensitized photolysis; its value is close to unity. The kinetic scheme is the standard one in which energy transfer competes with other deactivating processes of the donor, and leads to the steady state equation

$$1/\Phi_C = \alpha_C + \beta_C\beta/C_0 \tag{1}$$

where Φ_C is the quantum yield for the sensitized reaction and where α_C is the yield when the complex concentration, C_0, is infinite. The slope β_C contains products and quotients of various rate constants.

The detailed analysis, which will not be given here, indicates that the acridinium ion singlet excited state populates the $^4L_1$ state of the complex, leading to a 33:1 ration of ammonia to thiocyanate aquation, and that the donor triplet state populates the ^2D state of the complex, which then undergoes only thiocyanate aquation.

Table 1. Ordinary and sensitized photochemistry of $Cr(NH_3)_5(NCS)^{2+}$ [a]

State populated[ab]	*Mechanism of population*	*Reaction*[c]
$^4L_1$	Direct irradiation at band maximum	95.5% NH_3
(58.7, *ca.* 52)	Acridinium ion singlet (62)	97% NH_3
	Biacetyl triplet (56)	100% NH_3
^2D (41.8)	Direct irradiation at band maximum	11% NCS
	Acridinium ion triplet (48)	100% NCS

[a] Numbers in parentheses give energies in kcal/mole of the various excited states or absorption band maxima.

[b] The absorption band maximum is at 58.7 kcal/mole, but the true or $^4L_1^0$ state is probably about 52 kcal/mole above the ground state.

[c] NH_3 and NCS denote ammonia and thiocyanate aquation, respectively.

Triplet state biacetyl is also a sensitizer[39,40], and yields only ammonia aquation of the complex. The general situation as it now appears to us is summarized in *Table 1*. The lower the energy of the donor state which is populating $^4L_1$, the more nearly is the sensitized reaction purely one of ammonia aquation. The doublet state gives only thiocyanate aquation, the presence of ammonia aquation on direct irradiation being entirely explainable as due to absorption in the tail of the L_1 band. These results and the more general situation with Cr(III) complexes are discussed further below.

4. CHROMIUM(III) EXCITED STATES AND THEIR KINETICS

Emission behaviour

It has been mentioned that Cr(III) complexes may emit; it is in fact common for phosphorescence to be seen at low temperatures[25,31,42,43]. In several cases both fluorescence and phosphorescence are observed, the first and now classic example being that of $Cr(urea)_6^{3+}$, shown in *Figure 10*; in a few instances only fluorescence is found. *Figure 10* also illustrates an important situation with Cr(III) complexes, namely that the fluorescence

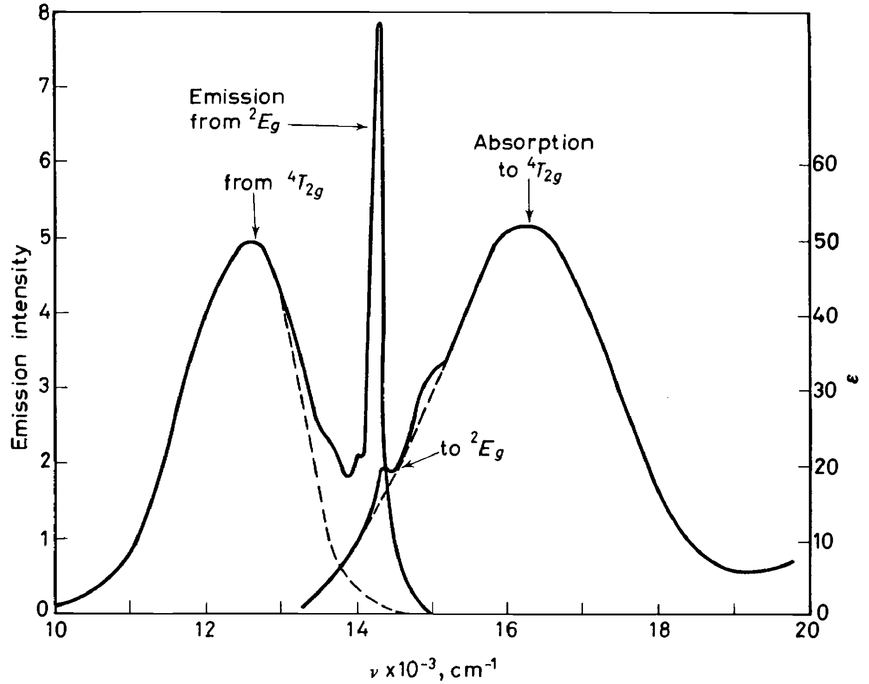

Figure 10. Absorption and emission spectra for $Cr(urea)_6^{3+}$ (from ref. 43).

maximum from the $^4L_1$ state is at a *longer* wavelength than is the phosphorescence from the ^2D state; this contrasts with the usual situation in organic photochemistry, in which the order of singlet–singlet and singlet–triplet maximum absorption energies is normally the same as that of the energies of the respective emission processes. That is, fluorescence occurs at a shorter wavelength than does phosphorescence. The generality of the reverse situation with Cr(III) complexes is illustrated by some representative data (from refs. 25 and 44) given in *Table 2.*

Table 2. Absorption, emission, and $^4L_1^0$ energies for some Cr(III) complexes[a] [25,44]

Compound	*Absorption*		$^4L_1^0$ *From crossing or calc.*[b]		*Fluorescence*[d]
	$^4L_1(\bar{\nu}_{max})$	$^2D(\bar{\nu}_{max})$		$\bar{\nu}_{0.05}$[c]	
$CrCl_3(s)$	13.70	13.15	12.6	12.4	11.5 F
$Cr(urea)_6^{3+}$	16.26		14.4	13.6[e]	12.55 F,P
$[Cr(H_2O)_6]F_3$	17.27	15.15	15.2	14.4	13.10 F,P
$Cr(H_2O)_4(NCS)_2^+$	17.50	—	15.24	14.4	(P)
$Cr(NCS)_6^{3-}$	17.7	13.01	15.8	15.0	(P)
$Cr(NH_3)_5I^{2+}$	18.36	14.5	16.7	15.9	(P)
$Cr(NH_3)_6^{3+}$	21.75	15.20	19.3	18.2	(P)

[a] Energies are given in kK. [b] From the crossing of the absorption and emission curves (normalized to the same peak heights on the comparison plot) where fluorescence is observed and otherwise from *Figure 14.* [c] Wavenumber at five per cent of maximum absorption. [d] F and P denote fluorescence and phosphorescence, respectively. [e] Corrected for ^2D absorption.

The immediate and apparently necessary interpretation is that with Cr(III) compounds, the ${}^4L_1$ state is populated at a high vibrational level in direct absorption, with emission occurring after thermal equilibration and to a high vibrational level of the ground state, as shown in *Figure 11*[1]. The phosphorescence emission is essentially unshifted from the D absorption band maximum, as also indicated in the figure. The further conclusion is that the true or non-vibrationally excited first quartet state, designated here as ${}^4L_1^0$, lies close to the ${}^2D$ state in energy, judging from the point of crossing of the absorption and emission bands. The long wavelength tail of the L_1 band has some anti-Stokes component since sharpening does occur in low temperature absorption spectra, but the error introduced by using room temperature spectra in determining crossing is not large.

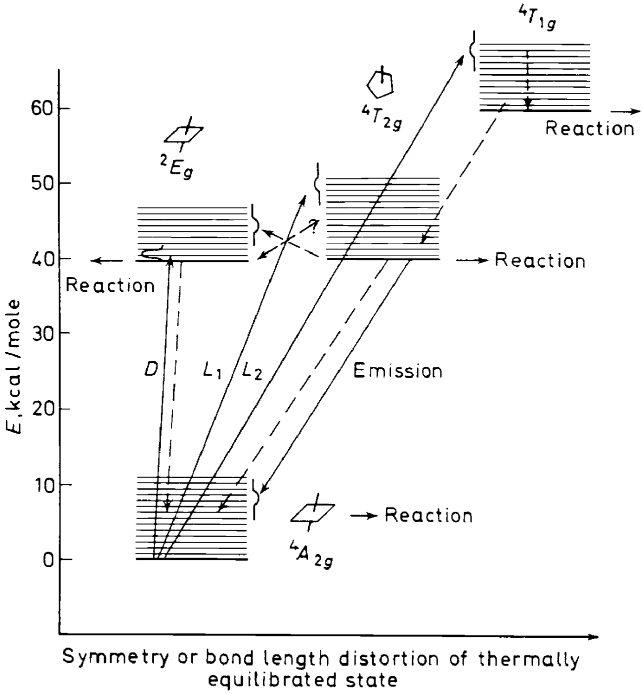

Figure 11. Processes that may occur following excitation of a Cr(III) complex. Dashed lines indicate radiationless processes. The octahedral figures are inserted to indicate that little change in geometry occurs on excitation to the ${}^2E_g$ state, and the pentagonal pyramidal one, to suggest that a major change in geometry could occur in the thermally equilibrated ${}^4T$ states. The term symbols are for O_h symmetry, but the diagram is intended to serve as a generalized one for any Cr(III) complex.

The late Professor Schläfer and his co-workers noted these implications and proposed that the type of emission observed depended on the relative positions of the ${}^4L_1^0$ and ${}^2D$ states and that these could be judged by the amount of the (${}^4L_1$–${}^2D$) separation, that is, by the separation between the two absorption band maxima. If this separation is small, ${}^4L_1^0$ should lie below ${}^2D$ and only fluorescence should occur; if it is large, the reverse should be true, and only phosphorescence should be found. In other words, internal conversion or intersystem crossing processes should terminate at the lower lying of the two states, which would then be the emitting one. This analysis certainly appears to be correct in low temperature, rigid media; in fact, at intermediate but still low temperatures a thermal re-population of $^4L_1$ from ^2D has been observed[45].

Most Cr(III) complexes show only phosphorescence, and the above picture supports the earlier hypothesis that photochemical reaction occurs from ^2D in such cases. The conclusion appears not to be generally correct, however. For example, it has been concluded that Reinecke's salt undergoes photoaquation largely from the $^4L_1^0$ state, as evidenced first by the results of comparative studies of the temperature dependence of the aquation quantum yield and that of phosphorescence emission (see ref. 27). The specific conclusion was that the radiationless deactivation process which reduces the emission yield with increasing temperature *leads* to the photochemically active state; the process was therefore identified with the rate of thermal equilibration of $^4L_1$ (see further below). More recently it has been reported[46] that while the phosphorescence emission of Reinecke's salt in low temperature but fluid solution is completely quenched by a sufficiently high concentration of $Cr(CN)_6^{3-}$, the photoaquation yield of the former drops not to zero but to a limiting value of about half of that in the absence of the quencher. The conclusion reached was that at least half of the photoaquation does not proceed through the ^2D state and must presumably occur from $^4L_1^0$.

As a second example, the results with $Cr(NH_3)_5(NCS)^{2+}$ cited in the preceding section indicate that ammonia aquation proceeds from the $^4L_1^0$ state. Yet here again the complex shows only phosphorescence, indicating the ^2D state to be the lower lying. Finally, the photolysis rules mentioned earlier also suggest the $^4L_1$ state to be dominant in the photochemistry of Cr(III) complexes.

The writer believes that the ^2D state may be photochemically important with certain O_h complexes, notably $Cr(NH_3)_6^{3+}$ (for which the photoaquation quantum yield is essentially the same for the L_2, L_1 and D bands[47]), but that the $^4L_1$ state is of greater importance with non-O_h complexes. Some further aspects are discussed below in connection with excited state distortion.

Excited state distortion

The unusually large red shift of the fluorescence emission relative to the corresponding absorption band, such as illustrated in *Figure 10* and *Table 2*, makes it necessary to take rather explicit account of the matter of excited state distortion. The point is emphasized in *Figure 11* by sketching the geometry of the $^4L_1^0$ state as having C_{5v} or D_{5h} symmetry. That is, distortion in a hexacoordinated complex may involve angular as well as radial displacements.

Bond angle changes in the excited states of organic molecules are known—for example the $^2A_1$ state of NO_2 is considered to be linear[48].

As a simple, although at best only mildly persuasive, argument, the crystal field stabilization of a Cr(III) complex is 12 Dq in the ground state and 2 Dq in the first quartet excited state, assuming retention of O_h symmetry. However, the crystal field parameters for D_{5h} give a stabilization[49] of 7.74 Dq, or *more* than that of the first O_h excited state. The $^4L_1^0$ excited state should therefore have D_{5h} symmetry (assuming Dq has not changed and making some implicit assumptions as the Racah interelectronic repulsion parameters). Such symmetry would be approximated if a seventh group, water, were coordinated.

The explanation of the Cr(III) photolysis rules noted earlier may then be that the original weak field axis becomes the D_{5h} one, along which solvent and one of the original ligands are coordinated. Collapse of this structure, with expulsion of the ligand, could then lead to the predicted photolysis behaviour. This picture helps to explain why the rules appear not to apply in a stereospecific sense. That is, while the photoaquation product[28] of $Cr(NH_3)_5(NCS)^{2+}$ is *trans*-$Cr(NH_3)_4(H_2O)(NCS)^{2+}$, it appears that the corresponding *cis* product is formed in the cases of $Cr(NH_3)_5Cl^{2+}$ [29] and $Cr(NH_3)_5Br^{2+}$ [32]. The literal application of the rules in a retained O_h reference would predict that only *trans* product should form. If the actual reaction proceeds from a pentagonal bipyramidal geometry, no simple prediction as to isomer seems possible.

Several important implications may be drawn if such a drastic change in geometry actually occurs. First, the usual Lewis–Kasha formula[50] ceases to be valid as a means of predicting natural emission lifetimes from integrating absorption bands. This is so not only on the general ground that the treatment of Einstein coefficients assumes absorption and emission to be reversible while in the actual situation the irreversible step of thermal equilibration is present ($^4L_1 \rightarrow {}^4L_1^0$), but also on the specific basis that the matrix elements governing emission and absorption probabilities may be quite different if the geometries of the two states are not the same[27]. It must be remembered that the processes are orbitally forbidden (and parity forbidden in the case of centrosymmetric molecules) and have non-zero probabilities only by virtue of vibronic coupling with higher excited states[51].

Returning to the crystal field analysis, a yet more sobering point is that the spin pairing energy for Cr(III) complexes (essentially that for $^4A_{2g} \rightarrow {}^2D$) is small enough that a D_{5h} excited state might be *spin paired*, that is, be $^2L_1^0$ rather than $^4L_1^0$. As an example, in the case of $Cr(en)_3^{3+}$ the crystal field energies relative to the ground state are 21.9 kK for $^4L_1$, 9.3 kK for $^4L_1^0$ (in D_{5h}), and only 6.6 kK for $^2L_1^0$ (in D_{5h}).

The possibility that 'fluorescence' emission from the supposedly $^4L_1^0$ state is actually from $^2L_1^0$ and therefore spin forbidden seems not to have been considered before. An important recent paper gives some 'fluorescence' lifetimes for Cr(III) complexes[52]; for example, that for $Cr(en)_3^{3+}$ is 1.1×10^{-5} sec, as compared to 1×10^{-4} sec for emission from the ^2D state. The two values are close enough to suggest that since the one emission does involve a spin forbidden process, the other might likewise.

The above thought is highly speculative, and for the moment we will continue to assume $^4L_1^0$ and proceed to consider in more detail the possible nature of the thermal equilibration process. It may firstly be inferred that unstable geometries can persist in low temperature, rigid media. Thus photolysis of $Cr(CO)_6$ produces $Cr(CO)_5$, a moderately stable yellow intermediate.

If produced in a low temperature rigid hydrocarbon matrix, its infra-red spectrum corresponds to C_{4v} geometry; on warming to around the glass point, the splitting of the lines now corresponds[53] to D_{3h}. It is, of course, possible that the equilibrium geometry changes on warming, but the alternative explanation which seems reasonable is that the unstable D_{4v} form persists at low temperatures because of the rigidity of its environment. We suppose, therefore, that the thermal equilibrium process may also be medium dependent in its rate.

The following picture, while speculative, does serve to tie otherwise loose ends. We assume that thermal equilibration proceeds in two somewhat distinct stages. The first is a vibrational relaxation around essentially O_h geometry to an intermediate state, ${}^4L_1'$, and the second is a slower relaxation to the non-O_h structure of ${}^4L_1^0$—slower because of the confining effect of the solvent cage. The first stage, but not the second, is taken to be rapid in low temperature, rigid media, and our suggestion is that the ${}^4L_1'$ state may participate in radiationless deactivation to the ground state and in efficient intersystem crossing to ${}^2D$ (efficient because the geometry of ${}^4L_1'$ is close to the equilibrium geometry of ${}^2D$). In fluid solution, however, the above processes are now in competition with the second stage of thermal equilibration, ${}^4L_1' \rightarrow {}^4L_1^0$, the efficiency of ${}^2D$ production is reduced, and much of the photochemistry proceeds through ${}^4L_1^0$ instead. A specific expectation is that fluorescence could have a different spectrum in fluid solution versus a rigid medium. This is borne out to some extent by results[54] for $Cr(urea)_6^{3+}$ and $Cr(antp)^{3+}$ (antp = antipyrene).

Some support for the above mechanism comes from the temperature dependence studies on the phosphorescence and aquation yields for Reinecke's salt, mentioned earlier. Also, the data of *Table 1*, for $Cr(NH_3)_5(NCS)^{2+}$, suggest that the greater the donor energy and hence supposedly the higher the ${}^4L_1$ state is populated in its vibrational manifold, the smaller the chance of its reaching ${}^4L_1^0$ and showing the characteristic photoreaction of that state. A very interesting observation is that phosphorescence emission from $Cr(CN)_6^{3-}$ in the solid salt $[Cr(antp)_6]\,[Cr(CN)_6]$ at 77°K goes through a minimum in intensity when the stimulating radiation is at the wavelength of the minimum in the cation absorption band[34]. The authors interpreted the observation as reflecting an 'inner filter' effect and therefore as evidence that the emission was entirely due to direct absorption by the anion. We would raise the possibility that the probability of excitation energy transfer was larger for cation molecules produced around the ${}^4L_1$ state than for those produced around ${}^4L_1^0$. The additional observation that irradiation in the region around the L_2–L_1 bands of the cation ceased to produce phosphorescence at room temperature would be in line with this alternative interpretation.

A schematic showing of the general picture envisaged is given in ***Figure 12***. The various rays of vibrational states represent different types of modes. This graphical technique allows the use of a general distortion scale and yet shows as vertical the most probable transitions involving radiation.

Use of true ligand field excited states

A minimum conclusion from the above analyses would seem to be that the

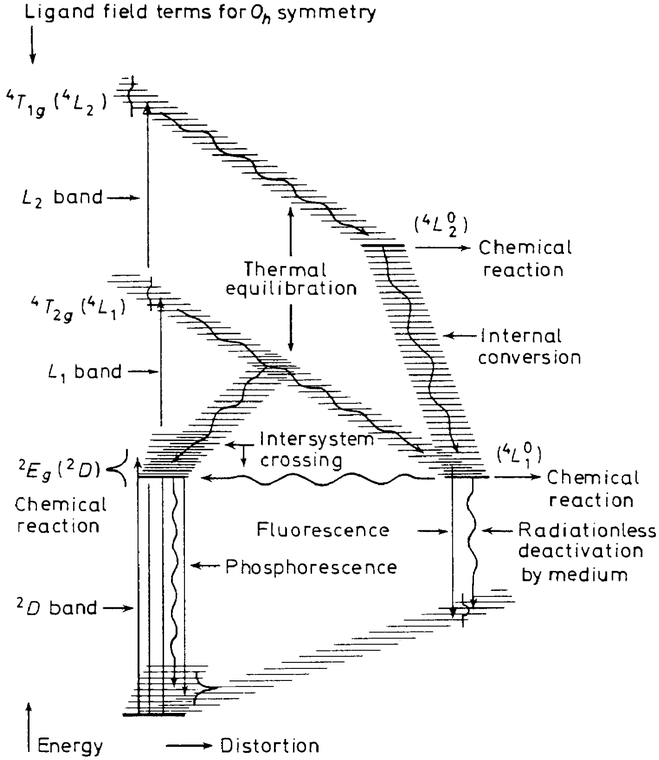

Figure 12. Excited state processes for a Cr(III) complex. The various rays of vibrational levels indicate various vibrational modes.

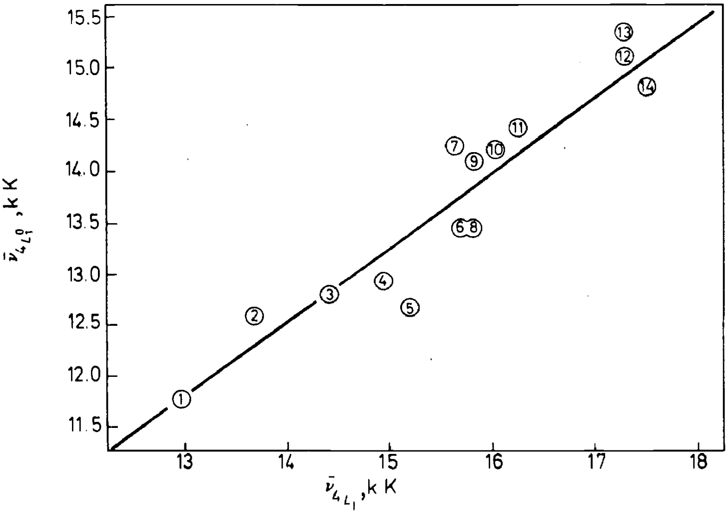

Figure 13. Plot of $^4L_1^0$ versus $^4L_1$ energies for Cr(III) complexes. The former are estimated from the crossing point of the absorption and fluorescence emission curves, the two being normalized as to peak height on the common graph (from ref. 44).

energy as well as the geometry of the $^4L_1^0$ state may be significantly different from those of the species produced following absorption at the L_1 band maximum. Further, it is the $^4L_1^0$ state which is relevant to photochemistry and may be so to emission. The situation is thus the unhappy one that conventional ligand field theory deals with and undertakes to explain the wrong energy and the wrong geometry.

It has been supposed that L_1 band maxima or 10Dq values should at least be proportional to the $^4L_1^0$ energy, or may be taken to be the average of $\bar{\nu}$ at the absorption and fluorescence emission maxima[55]. If this latter can be estimated as given by the crossing of absorption and fluorescence curves, the correlation with the former is actually not very good[44], as illustrated in *Figure 13*. Also, several inversions occur in the 'spectrochemical' series in $^4L_1^0$ relative to the usual one. Thus from the absorption band maxima,

$$\mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{dsc} < \mathrm{sexant} < \mathrm{dtc} < \mathrm{F^-} < \mathrm{tgl} < \mathrm{antip} < \mathrm{imid} < \mathrm{urea}$$

and from the $^4L_1^0$ energies,

$$\mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{sexant} < \mathrm{dsc} < \mathrm{tgl} < \mathrm{dtc} < \mathrm{antip} < \mathrm{imid} < \mathrm{F^-} < \mathrm{urea}$$

where dsc = diseleno carbamate, sexant = diseleno xanthate, tgl = thioglycollic acid, dtc = dithiocarbamate, antip = antipyrene, and imid = imidazolidone (data referenced in ref. 25). It seems desirable, therefore, to use $^4L_1^0$ energy values for Cr(III) complexes as appropriate to emission and photochemical work, retaining the conventional ligand field energies as relevant to absorption spectroscopy.

A difficulty is that relatively few Cr(III) species fluoresce, and the crossing point method is therefore only occasionally available. An empirical alternative is the following. For most Cr(III) complexes, the crossing occurs around

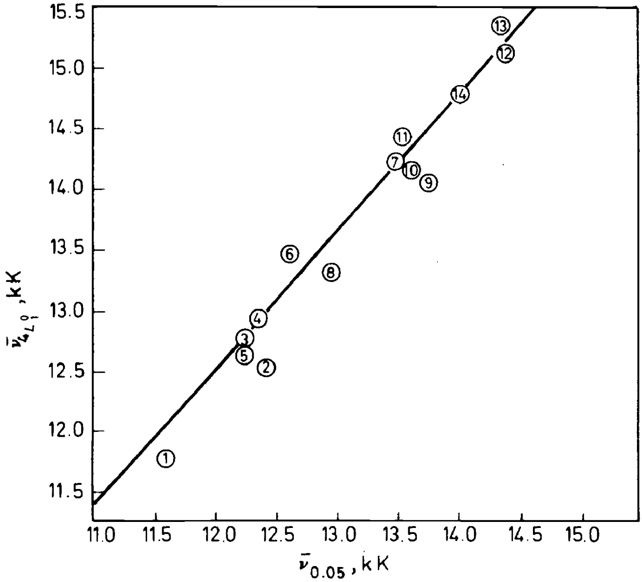

Figure 14. Plot of $^4L_1^0$ energy versus $\bar{\nu}_{0.05}$ for Cr(III) complexes (from ref. 44).

the wavenumber at which the intensity of the absorption band has dropped to five per cent of its maximum value. Thus, as shown in *Figure 14*, there is a fairly good correlation between the five per cent value, $\bar{\nu}_{0.05}$ and ${}^4L_1^0$, leading to the relationship

$$\bar{\nu}_{{}^4L_1^0} = 1.11\,\bar{\nu}_{0.05} - 0.88 \quad \text{(in kK)} \tag{2}$$

Some values of $\bar{\nu}_{0.05}$ and of ${}^4L_1^0$ energies estimated by means of equation 2 are included in *Table 2*. We suggest that in the future published papers either show complete absorption spectra or at least include $\bar{\nu}_{0.05}$ as well as $\bar{\nu}_{\text{max.}}$.

5. PLATINUM (II) COMPLEXES

A brief discussion of the photochemistry of square planar Pt(II) complexes seems relevant. The spectra of complexes, such as $Pt(CN)_4^{2-}$, $PtCl_4^{2-}$, and $Pt(NH_3)_a(Cl)_b^{2-b}$, have been interpreted in a general way[56–60]; a complication is that the expected stronger spin orbit coupling for third row transition metal complexes makes spin allowed and spin forbidden transitions of comparable intensity. Interestingly, single crystal spectra of $Ni(CN)_4^{2-}$, whose electronic structure is probably similar to that of $Pt(CN)_4^{2-}$, have been interpreted as indicating that one of the singlet–singlet transitions may terminate on a state having D_{2d} (or approximately tetrahedral) geometry[61].

The photochemistry of Pt(II) complexes such as the above is generally one of photocatalysis of the thermal reaction, namely aquation (see ref. 1 for details). However, a particularly interesting study is that of *cis*-Pt(glycine)$_2$ which undergoes photoisomerization without exchange with free ligand[62]; it was postulated that a tetrahedral excited state geometry was reached.

As with Cr(III) complexes, those of Pt(II) often show emission (see ref. 25 for details). For example, in the case of $Pt(CN)_4^{2-}$ absorption and emission are in the region of 28 kK and 22 kK, respectively, and for $PtCl_4^{2-}$, the corresponding values are about 20 kK and 12 kK. If the interpretation is correct, there is thus a large red shift between absorption and emission, itself an indication that the equilibrium geometry of one or more of the excited states differs significantly from that of the ground state. One case of photosensitization has been reported—that of the aquation of $PtCl_4^{2-}$ by biacetyl[63].

A somewhat different pattern of behaviour is shown by Zeise's salt, $PtCl_3(C_2H_4)^-$. The ion provides a classic example of the *trans* effect in that the thermal reaction in aqueous solution is one of immediate aquation of the chloride ion *trans* to the ethylene. We find that absorption of light leads to to aquation of the ethylene[64]; the absorption spectrum of the complex is shown in *Figure 15*, along with a bar diagram giving the observed quantum yields for the indicated wavelength regions.

Experimental

The irradiation arrangement was essentially that previously described[39]; ferrioxalate actinometry was used. Solutions were generally 2.5×10^{-3} M in complex and 0.1 M in hydrochloric acid (to reduce the equilibrium amount of *trans*-chloride aquation to a few per cent) and were irradiated in a thermostatically controlled cell. Ethylene production was determined both by chemical analysis of the released gas and by the fact that the product,

$PtCl_3(H_2O)^-$, is anated in 0.1N hydrochloric acid to $PtCl_4^{2-}$, which in turn is easily measured spectrophotometrically. *Cis*-chloride photoaquation was determined by passing the photolysed solution through an anion exchange column, which did not retain *cis*-$Pt(C_2H_4)(H_2O)Cl_2$. Treatment of the effluent solution with hydrochloric acid regenerated Zeise's salt, which was then determined spectrophotometrically.

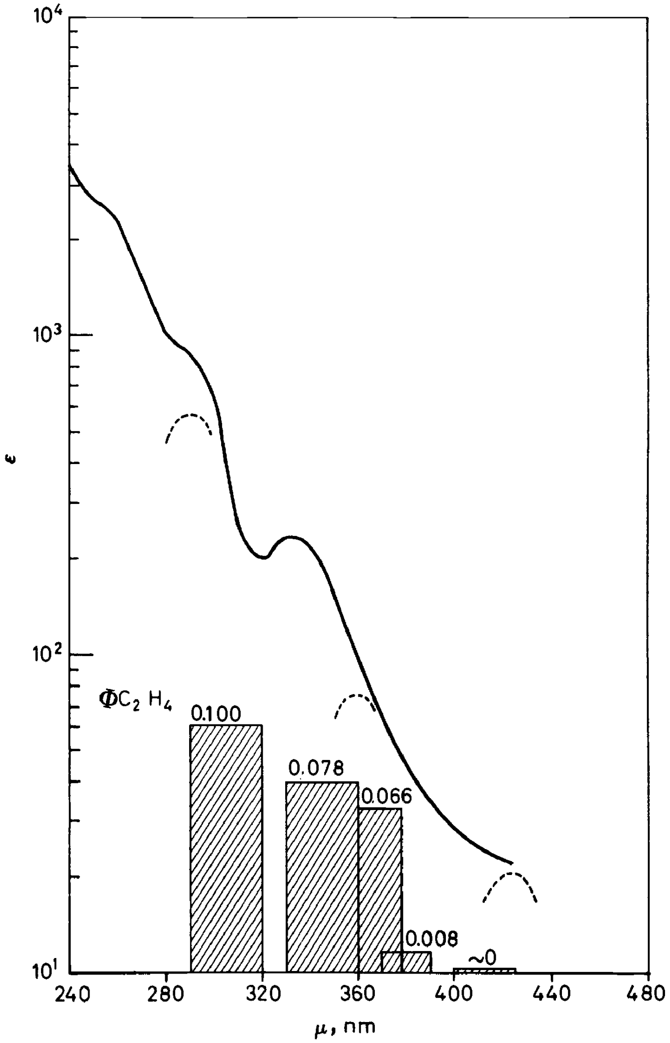

Figure 15. Absorption spectrum and photolysis quantum yields for Zeise's salt. 0.1 M HCl at 25°C.

A point of significance is that ethylene aquation, the *anti*-thermal reaction, is an important photolysis mode. A possible explanation is the following. The wavelength dependence of the quantum yield suggests that the transition at 330 nm (assigned as $^1A_1 \rightarrow {}^1A_2^{65}$) is responsible for the photoreaction.

If the thermally equilibrated excited state is highly distorted and perhaps nearly tetrahedral in configuration, then the ethylene–Pt π bonding should be much weakened. It will be recalled that in the ground state the ethylene axis is perpendicular to the square plane, and the bonding is thought to involve d_{xz} or d_{yx} Pt orbitals and the ethylene π bond. The available d_{z^2} and $d_{x^2-y^2}$ Pt orbitals in tetrahedral geometry would be unsuited for such bonding. The observation of ethylene release thus provides indirect support for strong excited state distortion of certain of the excited states of Zeise's salt.

Photoaquation of *cis*-chloride also occurred (any *trans*-chloride release would have gone undetected because of the speed of the back thermal anation reaction), and the ratio $\Phi_{Cl^-}/\Phi_{C_2H_4}$ is 2.0 at 355 nm and 1.5 at 305 nm, or apparently rising with decreasing wavelength. Current sensitization studies may help to determine whether the two photolysis modes derive from the same or different excited states.

In summary, while the photochemistry of Pt(II) complexes has not been studied in the same detail as has that of Cr(III) ones, it appears that a similar pattern of behaviour exists. As the field develops, it should similarly become important to assign energies and eventually definite geometries to the thermally equilibrated excited states.

6. CONCLUSIONS

Most of the conclusions have been stated in the context of their supporting evidence. In the case of Co(III) complexes, the importance of ^{3}CTTM and other triplet states needs much more substantiation, presumably through further sensitization studies. The full explanation of why the L_1 and L_2 bands are generally photoinert in the case of the ammines is not yet known—it may be simply that radiationless deactivation processes are too rapid, although such an explanation begs the question. Also not well understood is the contrasting behaviour of $Co(CN)_6^{3-}$ whose first *d–d* bands are strongly photoactive towards aquation of a cyanide, and similarly towards the X group in $Co(CN)_5X^{3-}$. It is curious also that Co(III) glyoxime type complexes may be strongly photoactive towards aquation of axial ligands[66], while the corresponding positions in vitamin B_{12} coenzyme complexes are sensitive towards redox photolysis[67, 68].

A very tentative rule is that if a complex can show luminescence, the L_1 band will be photoactive towards substitution while the first CT band will be photoinert; conversely, if there is no luminescence even at low temperature, the L_1 band will be photoinert and the CT band, photoactive.

A definite problem with conventional ligand field theory has emerged in the case of Cr(III) complexes [and very likely also with Pt(II) ones] in that we cannot predict theoretically the energy and geometry of the thermally equilibrated states. For the present, emission and photochemistry are providing some indirect evidence as to their physical chemistry. However, it is much to be hoped that some useful modification of ligand field theory will be developed.

A concluding thought is that the photoactive states which have been postulated for Cr(III) and Pt(II) complexes are not, after all, very different from the transition states and even reaction intermediates that have been proposed for the corresponding thermal reactions. Specific solvent participation in solvation reactions of Cr(III) complexes seem likely[69, 70], and square planar-tetrahedral interconversions probably do occur with Ni(II) complexes[48] and may be thermally accessible to Pt(II) ones. The photochemist and the kineticist may thus come to find themselves examining the same transient species. We close with a question of semantics: in such a case should the species be called an excited state or a new chemical state?

ACKNOWLEDGEMENTS

The unpublished investigations reported here have been supported by the U.S. Army Research Office (Durham) and the U.S. Atomic Energy Commission.

REFERENCES

[1] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer and R. D. Lindholm, *Chem. Rev.* **68**, 541 (1968).

[2] E. L. Wehry, *Quart. Rev. (London)*, **21**, 213 (1967).

[3] J. Szychlinsky, *Wiadomosci Chemi.* **16**, 607 (1962).

[4] V. Balzani, L. Moggi, F. Scandola and V. Carassiti, *Inorg. Chim. Acta Rev.* **1**, 7 (1967).

[5] D. Valentine Jr, *Advances in Photochemistry*, Vol. VI. G. S. Hammond, W. A. Noyes Jr and J. N. Pitts (Eds). Interscience: New York (1968).

[6] A. W. Adamson and A. Sporer, *J. Am. Chem. Soc.* **80**, 3865 (1958).

[7] A. W. Adamson, *Disc. Faraday Soc.* **29**, 163 (1960).

[8] J. F. Endicott and M. Z. Hoffman, *J. Am. Chem. Soc.* **90**, 4740 (1968).

[9] V. Balzani, R. Ballardine, N. Sabbatini and L. Moggi, *Inorg. Chem.* **7**, 1398 (1968).

[10] A. Vogler and A. W. Adamson, *J. Phys. Chem.* **74**, 67 (1970).

[11] J. F. Endicott and M. Z. Hoffman, *J. Am. Chem. Soc.* **87**, 3348 (1965);
E. R. Kantrowitz, J. F. Endicott and M. Z. Hoffman, *J. Am. Chem. Soc.* **92**, 1776 (1970).

[12] D. Valentine and J. Valentine, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla, 10–14 April 1967.

[13] J. J. Alexander and H. B. Gray, *Coord. Chem. Rev.* **2**, 29 (1967).

[14] A. W. Adamson, A. Chiang and E. Zinato, *J. Am. Chem. Soc.* **91**, 5467 (1969).

[15] A. J. Fry, R. S. H. Liux and G. S. Hammond, *J. Am. Chem. Soc.* **88**, 4781 (1966).

[16] L. Lindquist, *Acta Chem. Scand.* **20**, 2067 (1966).

[17] H. Linschitz and L. Pekkarinen, *J. Am. Chem. Soc.* **82**, 2411 (1960).

[18] A. Vogler and A. W. Adamson, *J. Am. Chem. Soc.* **90**, 5943 (1968).

[19] J. G. Calvert and J. N. Pitts Jr, *Photochemistry*. Wiley: New York (1966).

[20] G. B. Porter, *J. Am. Chem. Soc.* **91**, 3980 (1969).

[21] With D. Cram of this Laboratory.

[22] A. W. Adamson, A. Vogler and I. Lantzke, *J. Phys. Chem.* **73**, 4183 (1969).

[23] J. N. Demas, *Dissertation*, Washington State University (1970).

[24] M. Mingardi and G. B. Porter, *J. Chem. Phys.* **44**, 4354 (1966).

[25] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.* **70**, 199 (1970).

[26] H. L. Schläfer, *Z. Phys. Chem. (Frankfurt)*, **11**, 65 (1957);
R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.* **79**, 3343 (1957).

[27] A. W. Adamson, *J. Phys. Chem.* **71**, 798 (1967).

[28] E. Zinato, R. D. Lindholm and A. W. Adamson, *J. Am. Chem. Soc.* **91**, 1076 (1969).

[29] H. F. Wasgestian and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt)*, **57**, 282 (1968).

[30] L. Moggi, F. Bolletta and V. Balzani, *Ric. Sci.* **36**, 1228 (1966).

[31] H. L. Schläfer, *Z. Chem.* **10**, 9 (1970).

[32] P. Ricciero and H. L. Schläfer, *Inorg. Chem.* **9**, 727 (1970).

[33] H. Gausmann and H. L. Schläfer, *J. Chem. Phys.* **48**, 4056 (1968).

[34] A. D. Kirk and H. L. Schläfer, *J. Chem. Phys.* **52**, 2411 (1970).

[35] I. Fujita and H. Kobayashi, *J. Chem. Phys.* **52**, 4904 (1970).

[36] Unpublished results of J. Demas.

[37] D. J. Binet, E. L. Goldberg and L. S. Forster, *J. Phys. Chem.* **72**, 3017 (1968).

[38] S. Chen and G. B. Porter, *J. Am. Chem. Soc.* **92**, 3196 (1970).

[39] A. W. Adamson, J. E. Martin and F. Diomedi Camassei, *J. Am. Chem. Soc.* **91**, 7530 (1969).

[40] J. E. Martin and A. W. Adamson, to be published.

[41] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*. **A235**, 518 (1956).

[42] K. DeArmond and L. S. Forster, *Spectrochim. Acta,* **19**, 1687 (1963).

[43] G. B. Porter and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt)*, **37**, 109 (1963).

[44] Current work with P. D. Fleischauer.

[45] F. Diomedi Camassei and L. S. Forster, *J. Chem. Phys.* **50**, 2603 (1969).

[46] S. Chen and G. B. Porter, private communication.

[47] E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.* **88**, 394 (1966).

[48] M. Green and J. W. Linnett, *Trans. Faraday Soc.* **57**, 1 (1961).

[49] F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions*, 2nd ed., Wiley: New York (1967).

[50] G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.* **67**, 994 (1945).

[51] A. D. Liehr and C. J. Ballhausen, *Phys. Rev.* **106**, 1161 (1957).

[52] S. Chen and G. B. Porter, *J. Am. Chem. Soc.* **92**, 2189 (1970).

[53] I. W. Stoltz, G. R. Dobson and R. K. Sheline, *J. Am. Chem. Soc.* **85**, 1013 (1963).

[54] D. M. Klassen and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.* **72**, 663 (1968).

[55] J. C. Hempel and F. A. Matsen, *J. Phys. Chem.* **73**, 2502 (1969).

[56] H. Basch and H. B. Gray, *Inorg. Chem.* **6**, 365 (1967).

[57] J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.* 386 (1958).

[58] (a) V. Balzani, V. Carassiti, L. Moggi and F. Scandola, *Inorg. Chem.* **4**, 1243 (1965); (b) F. Scandola, O. Traverso, V. Balzani, G. L. Zucchini and V. Carassiti, *Inorg. Chim. Acta,* **1**, 76 (1967).

[59] J. R. Perumareddi and A. W. Adamson, *J. Phys. Chem.* **72**, 414 (1968).

[60] E. König and H. Schläfer, *Z. Phys. Chem. (Frankfurt)*, **26**, 371 (1960).

[61] C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks and C. R. Hare, *Inorg. Chem.* **4**, 514 (1965).

[62] V. Balzani and V. Carassiti, *J. Phys. Chem.* **72**, 383 (1968).

[63] V. S. Sastri and C. H. Langford, *J. Am. Chem. Soc.* **91**, 7533 (1969).

[64] P. Natarajan and A. W. Adamson, unpublished work.

[65] J. W. Moore, *Acta Chem. Scand.* **20**, 1154 (1966).

[66] Unpublished observation by F. Diomedi Camassei in this Laboratory.

[67] E. Ochiai, K. M. Long, C. R. Sperati and D. H. Busch, *J. Am. Chem. Soc.* **91**, 3201 (1969).

[68] G. N. Schrauzer, L. P. Lee and J. W. Sibert, *J. Am. Chem. Soc.* **92**, 2997 (1970).

[69] A. W. Adamson, *J. Am. Chem. Soc.* **80**, 3183 (1958).

[70] C. H. Langford and J. F. White, *Canad. J. Chem.* **45**, 3049 (1967).