The Photochemistry of Transition-metal Co-ordination Compounds — A Survey

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1 Introduction

In recent years, there has been a rapid and expanding interest in the photo-chemistry of transition-metal co-ordination compounds. This has been due not only to the resurgent interest in the chemistry of these systems, but also to the extensive progress that has been made both in the interpretation of their electronic spectra and in the photochemistry of organic systems. The purpose of this article is to present a systematic survey of the diverse behaviour manifested by co-ordination complexes upon exposure to visible and near-u.v. light. The material has been chosen to indicate areas of active interest and to illustrate the interdisciplinary dependence between this and related fields such as absorption and emission spectroscopy. This aim has necessitated a rather restricted choice of citations; however, a number of recent and comprehensive review articles on the photochemistry[1-5] and the photoluminescence[6] of transition-metal complexes as well as an excellent monograph[7] are available.

2 Nature of the Excited State

The absorption of electromagnetic radiation is a quantized phenomenon, and for radiation in the visible and u.v. regions sufficient energy is available to bring about change in the electronic state of a system as well as changes in its vibrational and rotational motion. The relationship between this energy of transition, E, and the frequency of the exciting radiation is given by equation 1 and thus

[1] E. L. Wehry, *Quart. Rev.*, 1967, **21**, 213.
[2] (a) V. Balzani, L. Moggi, F. Scandola, and V. Carassiti, *Inorg. Chim. Acta, Rev.*, 1967, **1**, 7; (b) V. Balzani, L. Moggi, and V. Carassiti, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 288; (c) L. Moggi, V. Balzani, and V. Carassiti, *ibid.*, p. 293.
[3] D. H. Valentine, jun., *Adv. Photochem.*, 1968, **6**, 124; *Ann. Survey Photochem.*, 1969, **1**, 457; *ibid.*, 1970, **2**, 341.
[4] (a) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 1968, **68**, 541; (b) A. W. Adamson, *Co-ordination Chem. Rev.*, 1968, **3**, 169; (c) A. W. Adamson, *Rec. Chem. Progr.*, 1968, **29**, 191; (d) A. W. Adamson, *Pure Appl. Chem.*, 1969, **20**, 25.
[5] J. F. Endicott, *Israel J. Chem.*, 1970, **8**, 209.
[6] (a) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, 1970, **70**, 199; (b) F. E. Lytle, *Appl. Spectroscopy*, 1970, **24**, 319.
[7] V. Balzani and V. Carassiti, 'Photochemistry of Co-ordination Compounds', Academic Press, London, 1970.

$$E = Nh\nu = Nhc/\lambda = (2\cdot859 \times 10^4)/\lambda \text{ kcal mol}^{-1} \tag{1}$$

where N = Avogadro's number

h = Planck's constant

ν = frequency of the radiation

λ = wavelength of absorbed radiation in nanometres

c = velocity of light

the energy which is available for photochemical processes. For the regions of interest, 200—800 nm, this represents energies between values of *ca.* 143 and 36 kcal mol^{-1} respectively. For co-ordination compounds, sufficient energy is available to cause homolytic and heterolytic bond cleavage and in some instances photoionization.

It is important to realize that chemical reaction by an energetically enriched system represents only one of several potential modes of energy dissipation available to the system. In general, the energy dissipation scheme can be quite complex, as shown in Figure 1. The energy level diagram is representative of
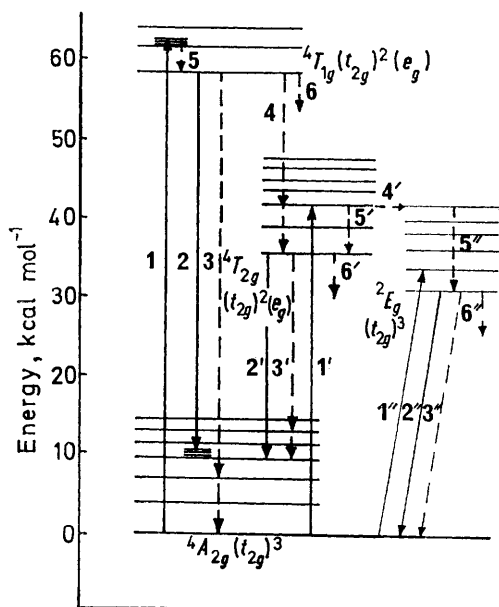

Figure 1 *Energy level diagram for* Cr^{III} *complexes in octahedral symmetry, O$_h$. (a) Transitions:* **1, 1', 1''**: *absorption.* **2, 2', 2''**: *emission—***2** *and* **2'**, *fluorescence;* **2''**, *phosphorescence.* **3, 3', 3''**: *non-radiative deactivation.* **4, 4'**: *non-radiative crossing—***4** *(and also* **3, 3'**), *internal conversion;* **4'** *(and* **3''**), *intersystem crossing.* **5, 5', 5''**: *thermal equilibration of vibrational and rotational levels.* **6, 6', 6''**: *chemical reaction. (b) Capital letters designate the terms or energy states, and the superscripts indicate the spin multiplicities of the states. (c) Lower-case letters symbolize electronic configurations in the strong-field approximation of ligand-field theory, and from these configurations arise the various energy states. (d) In some instances, the* $^4T_{2g}$ *level may be below that of the* ^2E_g *state. (e) After A. W. Adamson,* J. Phys. Chem., *1967,* **71**, *798.*

Cr^{III} complexes of octahedral microsymmetry (O_h symmetry). The overall symmetry of the complex will generally be lower than octahedral, but in the first approximation, the six identical atoms bonded directly to the Cr^{III} centre and octahedrally situated about it determine the form of the energy-level diagram for the ligand-field states of Figure 1. For the sake of clarity, only the lower excited energy states ($^4T_{1g}$, $^4T_{2g}$, and ^2E_g) and the ground state ($^4A_{2g}$) are shown. Other states higher in energy exist and may be of importance to the photo-processes of Cr^{III} systems.[6,8] In connection with Figure 1, several general points warrant particular attention.

The absorption of light (transitions **1, 1′**, and **1″**) leads to electronically excited states that are generally vibrationally and rotationally excited by virtue of the Franck–Condon Principle. The latter modes equilibrate rapidly with their surroundings (transitions **5, 5′**, and **5″**) to give a vibrationally and rotationally equilibrated system, but the system is still in an electronically excited state from which both radiative and non-radiative processes may occur as well as chemical ones. The radiative and non-radiative processes can be classified on the basis of whether the transitions occur between states having the *same* spin multiplicity, such as the quartet states, or between states having *different* spin multiplicities, such as quartet–doublet crossings.† A radiative transition between states of the same spin multiplicity (**2** and **2′** of Figure 1) is termed fluorescence whereas a non-radiative one (**3, 3′**, and **4**) is called internal conversion. Likewise, between states differing in their spin multiplicities, the radiative and non-radiative crossings are referred to as phosphorescence (**2″**) and intersystem crossing (**3″** and **4′**) respectively.

In solutions at room temperature, most transition-metal complexes do not luminesce but in the solid state and in low-temperature media, luminescence (usually phosphorescence) is more prevalent.[6,9] The non-radiative transitions are not observed directly, but their relative importance is inferred from the absence or presence of luminescence and/or photochemical reaction. From luminescence and photochemical studies of transition-metal complexes (and also those of organic systems), it is generally inferred that the non-radiative transitions between excited states of a given spin multiplicity, *e.g.* $^4T_{1g} \longrightarrow ^4T_{2g}$ of Figure 1, are very fast, with first-order rate constants of the order of 10^{11} s^{-1}. Similarly, intersystem crossings between excited states, such as $^4T_{2g} \longrightarrow ^2E_g$, appear to be fast even though they are formally spin-forbidden owing to the change in spin multiplicities accompanying such crossings.[6-9] Luminescence from higher excited states of transition-metal complexes apparently has not been observed; this implies that the non-radiative processes are favoured over the radiative ones. In contrast, both the radiative and non-radiative transitions from the lowest excited states of a given spin multiplicity to the ground state appear to be relatively slow. For Cr^{III} complexes, the first-order rate constants for transitions from the lowest quartet and doublet states to the ground state

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† Spin multiplicity $= 2S + 1$, where S is the spin quantum number.

[8] L. S. Forster, *Transition Metal Chem.*, 1969, **5**, 1.
[9] J. N. Demas and G. A. Crosby, *J. Amer. Chem. Soc.*, 1970, **92**, 7262.

appear to be in the range of 10^4—10^9 s^{-1} and of 10^1—10^5 s^{-1} respectively.[6-10]

Although information on photophysical events is still quite meagre, several general conclusions can be drawn in regard to the effects of these photophysical processes on the photochemical ones. Owing to the relative time scales involved, it is more probable that photochemical reactions will occur from the lowest excited state of a given spin multiplicity. Since the lowest excited state differing in spin multiplicity from that of the ground state is generally expected to have a longer lifetime than that of the lowest excited state having the same spin multiplicity as that of the ground state, photochemical reaction from the former may be more probable than from the latter one. There is, however, mounting theoretical[11] and experimental evidence (see Section 3A) that, at least for Cr^{III} systems, both of the low-lying states ($^4T_{2g}$ and ^2E_g) can be photochemically active, and indeed can show a difference in their photochemical behaviour. In any event, for photochemical reactions to be competitive with the relatively fast photophysical ones, the activation energies for the former must be small ($\leqslant ca.$ 10 kcal mol^{-1}) in comparison to the activation energies encountered in the thermal chemistry of transition-metal complexes. Crystal-field calculations suggest activation energies of the order of zero for photosubstitutional reactions in Cr^{III} complexes occurring from either ^2E_g or $^4T_{2g}$; the situation for Co^{III} complexes appears to be less favourable.[12]

In addition to characterizing photoevents in terms of the associated rate constants, it is more common to describe the efficiency of such events relative to the amount of absorbed light because these are usually more readily obtainable experimentally. The efficiency for a particular photochemical or physical process such as those shown in Figure 1 is expressed in terms of the quantum yield, ϕ, (equation 2).

$$\phi = \frac{\text{rate of change of the process of interest}}{\text{rate of absorption of light quanta of a specified wavelength}} \qquad (2)$$

The totality of all such events, excluding possible secondary thermal ones, must be unity. Thus a chemical quantum yield less than one indicates the occurrence of other competing processes.

An energy level diagram, such as Figure 1, provides a convenient representation of possible excited-state events, but does not adequately convey one very important point; that is, the change in electron density upon excitation. Such change is not only the source of the non-equilibrium condition of the excited state but also determines the nature of the excited state and thus has a strong bearing on the subsequent course of events. This change in electron density on excitation is better portrayed by a molecular orbital energy diagram, such as that for ferrocyanide, Fe(CN)$_6^{4-}$, shown in Figure 2, where the relative positions

[10] Schoen-nan Chen and G. B. Porter, *J. Amer. Chem. Soc.*, 1970, **92**, 2189.

[11] A. W. Adamson, *J. Phys. Chem.*, 1967, **71**, 798.

[12] H. L. Schlaefer, *J. Phys. Chem.*, 1965, **69**, 2201; *Z. Chem.*, 1970, **10**, 9 (*Chem. Abs.*, 1970, **72**, 72 639z).

of the metal and ligand orbitals contributing to a given molecular energy configuration provide a measure of the electron distribution.
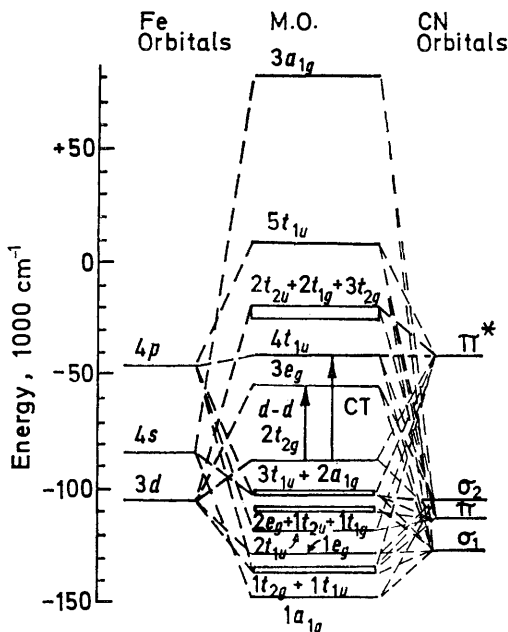

Figure 2 *Molecular orbital energy diagram for ferrocyanide ion. (a) Electrons fill the levels completely up to and including the $2t_{2g}$ level. (b) The d–d or ligand-field excitations correlate with the $2t_{2g}$ to $3e_g$ transition whereas a charge-transfer band, CT, arises from the $2t_{2g}$ to $4t_{1u}$ transition. (c) After J. J. Alexander and H. B. Gray, J. Amer. Chem. Soc., 1968, **90**, 4260.*

From such quantum mechanical descriptions and from the spectral properties of absorption and emission bands, there has arisen an oversimplified, but useful, classification of electronic transitions as *d–d* or charge-transfer, CT.[7,13,14] Transitions of the *d–d* or ligand-field type are essentially localized on the central metal and represent an angular redistribution of electronic charge. Since these absorption transitions occur from bonding or non-bonding orbitals to antibonding orbitals, they are generally characterized by weakening of the metal-ligand bonds. They frequently fall into the category of symmetry-forbidden transitions (Laporte forbidden) for centrosymmetric complexes such as octahedral ones. This results in low values for the molar extinction coefficients, typically 1—150 l mol^{-1} cm^{-1} for octahedral complexes and smaller if the transitions are also spin-forbidden, *e.g.* $^2E_g \leftarrow {}^4A_{2g}$, Figure 1. These restrictions are

[8] J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, 1968, **90**, 4260.
[14] See for example, T. M. Dunn, in 'Modern Co-ordination Chemistry', ed. J. Lewis and R. G. Wilkins, Interscience Publishers Inc., New York, 1960, Chapter 4.

also applicable to the radiative transitions. Although the spin rule is also valid for non-radiative processes, these processes are now symmetry-allowed ones (see ref. 7).

In contrast to the ligand-field case, CT transitions are generally symmetry-allowed, and consequently the extinction coefficients are frequently much larger in magnitude, *ca.* $10^4 \, \mathrm{l \, mol^{-1} \, cm^{-1}}$. They represent a much more extensive redistribution of electron density and one of a more radial nature. In a limiting sense, they can represent changes in the formal oxidation numbers of the atoms involved. In addition, they are generally observed at higher energies (but not always) than those for *d–d* transitions, and in fact may mask the higher-energy, ligand-field ones. Within the CT classification, one can further subdivide the transitions into ones involving movement of charge from the metal to the ligand(s) (CTTL) or to the solvent (CTTS), from the ligand(s) to the metal (CTTM), or from one ligand-centred orbital to another one (L–L).

3 Photochemical Reaction Modes

Three fundamental types of photochemical reaction are known for co-ordination compounds: substitution, rearrangement, and redox reactions.[1-5,7] In a number of instances more than one mode is observed for a given system.

A. Photosubstitution.—A large number of metal complexes undergo photo-substitution, involving solvation, anation, or ligand (solvent) exchange. Of the systems studied, those of chromium(III) complexes have provided the greatest amount of information on this type of reaction, generally one of photoaquation. For complexes possessing octahedral microsymmetry, *e.g.* $\mathrm{Cr^{III}L_6}$, photo-substitution, shown as photoaquation in equation 3, occurs on irradiation of the

$$\mathrm{Cr^{III}L_6} + \mathrm{H_2O} \xrightarrow{h\nu} \mathrm{Cr^{III}L_5(H_2O)} + \mathrm{L} \qquad (3)$$
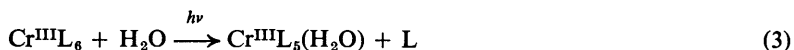
quartet and doublet *d–d* bands (see Figure 1), and the reaction is believed to involve heterolytic cleavage of the Cr–L bond. The quantum yields range from *ca.* 0·01—*ca.* 0·5, and the values are nearly independent of the particular *d–d* band irradiated.[1,3,4,7] A similar situation is encountered for non-O_h systems, *i.e.* those with mixed ligands; however, there is now a greater variation in the quantum yields with wavelengths, and several aquation modes are possible (see below).* There is also some evidence that u.v. irradiation of the CT bands may give rise to redox processes.[4,7,15,16]

For O_h systems, the constancy of the photochemical quantum yield whether the quartet bands or doublet band were irradiated led to the early proposal that the lowest energy doublet state, ^2E_g, is responsible for chemical reaction.[12,17]

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* The term system shown in Figure 1 is not strictly applicable to non-O_h complexes although the designation of a state as a doublet or quartet remains valid.

[15] (a) P. Riccieri and H. L. Schläfer, *Inorg. Chem.*, 1970, 9, 727; (b) H. F. Wasgestian and H. L. Schläfer, *Z. phys. Chem. (Frankfurt)*, 1968, 62, 127.
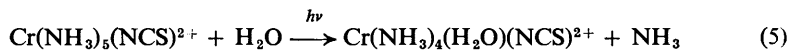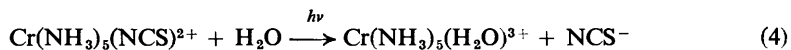[16] P. D. Fleischauer, Ph.D. Thesis, University of Southern California, 1968.
[17] (a) M. R. Edelson and R. A. Plane, *Inorg. Chem.*, 1964, 3, 231; (b) R. A. Plane and J. P. Hunt, *J. Amer. Chem. Soc.*, 1957, 79, 3343.

Support for this proposal comes from the relatively long lifetime of this state as determined by emission studies, where lifetimes in the range 10^{-5}—10^{-1} s are observed, usually in low-temperature media or in the solid state (see also ref. 18).

Of recent interest is the possible photochemical activity of the quartet states and the lowest energy one in particular (see Figure 1). Central to this issue are the lifetimes of the quartet states, especially the $^4T_{2g}$ state, and certain photophysical features germane to this point warrant mentioning. Where fluorescence is observed from the lowest quartet level, it is found at considerably lower energies than that for absorption,[6,8] suggesting considerable distortion of this level relative to the ground state, and as such the quartet's lifetime may be longer than otherwise expected. This interpretation finds support from recent low-temperature measurements of fluorescence and phosphorescence lifetimes for several Cr[III] complexes where the ratio of the ^2E_g lifetime to that of $^4T_{2g}$ varied from *ca.* 10:1 to *ca.* 500:1.[10] An allied point is that in their pure electronic states (zeroth vibrational levels), the ^2E_g and $^4T_{2g}$ may in a number of systems be close in energy, with the latter possibly being below the doublet one where fluorescence is observed. When the two levels are energetically reasonably close, thermal repopulation of the $^4T_{2g}$ from the ^2E_g (the reverse of processes **5″** and **4′** of Figure 1) can be significant in the energy degradation scheme.[4,6-8,10,17a,19-21] Other aspects of this subject have also been discussed.[11,22-24]

Photochemical studies of non-O_h Cr[III] complexes that can exhibit two different photoaquation modes have helped to clarify the photochemical role of the quartet state(s). A number of such studies have been carried out.[4,7,15,24-26] The extensive investigations of $Cr(NH_3)_5(NCS)^{2+}$ in aqueous 0·1N-H_2SO_4 by Adamson and co-workers[24] will be discussed in some detail as the results illustrate some features of general occurrence. For this complex, two aquation modes occur, equations 4 and 5. Both aquation reactions occur upon irradiation

$$Cr(NH_3)_5(NCS)^{2+} + H_2O \xrightarrow{h\nu} Cr(NH_3)_5(H_2O)^{3+} + NCS^- \qquad (4)$$

$$Cr(NH_3)_5(NCS)^{2+} + H_2O \xrightarrow{h\nu} Cr(NH_3)_4(H_2O)(NCS)^{2+} + NH_3 \qquad (5)$$

of the quartet and doublet bands and the quantum yields progressively decrease with increasing wavelength of radiation. However, if the doublet state is *not*

[18] T. Ohno and S. Kato, *Bull. Chem. Soc. Japan*, 1970, **43**, 8.

[19] (*a*) G. B. Porter, Schoen-nan Chen, H. L. Schläfer, and H. Gausmann, *Theor. Chim. Acta*, 1971, **20**, 81; (*b*) Schoen-nan Chen and G. B. Porter, *J. Amer. Chem. Soc.*, 1970, **92**, 3196.

[20] F. D. Camassei and L. S. Forster, *J. Chem. Phys.*, 1969, **50**, 2603.

[21] J. L. Laver and P. W. Smith, *Chem. Comm.*, 1970, 1497.

[22] V. Balzani, R. Ballardini, M. T. Gandolfi, and L. Moggi, *J. Amer. Chem. Soc.*, 1971, **93**, 339.

[23] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Canad. J. Chem.*, 1971, **49**, 375.

[24] (*a*) J. E. Martin and A. W. Adamson, *Theor. Chim. Acta*, 1971, **20**, 119; (*b*) A. W. Adamson, J. E. Martin, and F. D. Camessei, *J. Amer. Chem. Soc.*, 1969, **91**, 7530; (*c*) E. Zinato, R. D. Lindholm, and A. W Adamson, *ibid.*, 1969, **91**, 1076.

[25] M. F. Manfrin, L. Moggi, and V. Balzani, *Inorg. Chem.*, 1971, **10**, 207.

[26] A. D. Kirk, *J. Amer. Chem. Soc.*, 1971, **93**, 283.

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solely responsible for photoaquation, the ratio of ϕ_{NH_3} : ϕ_{NCS^-} should be *dependent* upon wavelength. Indeed, this ratio varies with wavelength, being 15·3 : 1 (373 nm radiation; quartet band), 22·1 : 1 (492 nm; quartet band), and 8·2 : 1 (652 nm; doublet band). This lends strong support to the idea that both the lowest quartet state and the doublet one can be involved in chemical reaction. Furthermore, the preferred mode of photoaquation (ammonia release) differs from the thermal one, where thiocyanate release predominates. This illustrates the important point that the photosubstitution mode need not necessarily be an acceleration of the thermal process. Another generally encountered feature exhibited by $Cr(NH_3)_5(NCS)^{2+}$ is that the apparent activation energies for both photoreactions are small, being about 1—2 kcal mol^{-1}, compared to that for the thermal release of thiocyanate (*ca.* 25 kcal mol^{-1}).

For the product of reaction (5), $Cr(NH_3)_4(H_2O)(NCS)^{2+}$, both *cis-* and *trans-* isomers could occur. Evidence has been presented that suggests the photo-product is the *trans-*isomer: this is in accord with the empirical rules proposed by Adamson for predicting the photochemical product(s) of non-O_h chromium(III) complexes.[11] The general validity of these rules has recently been challenged principally upon the grounds that the stereochemical products arising from $Cr(NH_3)_5(Cl)^{2+}$ or (Br) and *trans-*dichlorobis(ethylenediamine)-chromium(III) are in the *cis-* rather than the expected *trans-*configurations.[7,15,25,26] However, as Kirk[26] has suggested, these discrepancies may be a manifestation of the stereomobility in the photosubstitutional reactions of chromium(III), and if this proves to be general, it would be somewhat in contrast to the thermal behaviour of these systems.[27]

A final point concerns the interaction of Cr^{III} systems with electronically excited organic or inorganic species. The effect of complex ions in quenching triplet states of organic compounds is well known,[28] and recently such studies have been extended to inorganic systems, such as Cr^{III} complexes, both in solution and in the solid state.[6,7,18,19,22,24,28-33] The results, while so far limited to a few systems, do indicate that the interaction involves collisional processes accompanied at least in part by intermolecular energy transfer. There is, however, some evidence that other processes, such as quenching without energy transfer, may also be important,[18,22,29,30] and more detailed discussions of energy transfer mechanisms can be found elsewhere.[7,34]

[27] R. D. Archer, *Co-ordination Chem. Rev.*, 1969, **4**, 243.

[28] (a) J. G. Calvert and J. N. Pitts, jun., 'Photochemistry', John Wiley and Sons, Inc., New York, 1966, Chapter 4; (b) H. F. Wasgestian and G. S. Hammond, *Theor. Chim. Acta*, 1971, **20**, 186.

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

[30] (a) H. Gausmann and H. L. Schläfer, *J. Chem. Phys.*, 1968, **48**, 4056; (b) A. D. Kirk, A. Ludi, and H. L. Schläfer, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 669; (c) H. L. Schläfer, H. Gausmann, and C. H. Möbius, *Inorg. Chem.*, 1969, **8**, 1137.

[31] G. B. Porter, *J. Amer. Chem. Soc.*, 1969, **91**, 3980.

[32] (a) V. S. Shastri and C. H. Langford, *J. Amer. Chem. Soc.*, 1969, **91**, 7533; (b) J. N. Demas and A. W. Adamson, *ibid.*, 1971, **93**, 1800.

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

[34] F. Wilkinson, *Adv. Photochem.*, 1964, **3**, 241.

The methodology of such studies has in general been to observe the quenching of emission from the energy-donor by the Cr^{III} energy-acceptor, and the subsequent sensitization of phosphorescence and/or photoaquation from the Cr^{III} entity. The intermolecular energy transfer reactions between $Cr(NH_3)_5(NCS)^{2+}$ and excited biacetyl molecules or acridinium ions in aqueous $0.1N-H_2SO_4$ exemplify this technique.[24] In the presence of $Cr(NH_3)_5(NCS)^{2+}$, the phosphorescence from the lowest triplet state of biacetyl is quenched, whereas the fluorescence from the lowest singlet state is not affected. That energy transfer has occurred from the biacetyl triplet level is shown by the release of ammonia, with no apparent chemical degradation of the biacetyl. When acridinium ion is the sensitizer, the quenching of the acridinium ion's fluorescence is accompanied by release of both ammonia and thiocyanate, with the former predominating. Although the phosphorescence of acridinium ion is not observed, the quantum yield of thiocyanate release decreases in the presence of oxygen. This suggests that the triplet state of acridinium ion may be sensitizing the release of thiocyanate. For both sensitizers, the ϕ_{NH_3} is about half of the value resulting from direct excitation of the lowest quartet band. Of particular importance is the comparison of the ratio $\phi_{NH_3}:\phi_{NCS^-}$ for the sensitized reactions and those for direct photolysis of the lowest quartet and doublet states, these being $> 100:1$ (biacetyl), $33.3:1$ (acridinium ion), $22.2:1$ (quartet), and $8.2:1$ (doublet). This comparison strongly suggests that ammonia release occurs primarily from the lowest quartet level whereas thiocyanate loss originates within the doublet level. Furthermore, from considerations of the variations in the quantum yields themselves as well as those of the ratios, it has been postulated that the method of population of a given excited state (direct excitation *versus* sensitization) may be vital to the subsequent course of excited-state events (see also ref. 22). This powerful tool of photosensitization has also been applied to the substitution reactions of $Co(CN)_6^{3-}$ (ref. 31) and $PtCl_4^{2-}$ (ref. 32), as well as to the photoredox decomposition of cobalt(III) acido-ammines (see Section 3C).

B. Photorearrangements.—Within this classification occur geometrical isomerization, racemization, linkage isomerization, and ligand rearrangement. Square-planar complexes of platinum(II) afford examples of geometrical photoisomerization, *i.e. cis–trans* isomerization.[4,7,35] The *cis*-bis(glycinato)platinum(II), upon irradiation of the *d–d* type bands in the near-u.v., rearranges to the *trans*-isomer with a value of ϕ_{isom} of *ca.* 0.13.[35] The reverse reaction, that is *trans* to *cis* isomerization, does not occur, although prolonged irradiation of the CT band (254 nm) for the *trans*-isomer leads to decomposition. In contrast to thermal isomerization, where the presence of unco-ordinated glycine is required, photoisomerization does not lead to incorporation of free, radioactive glycine into either isomer. These features suggest that the photoprocess involves an intramolecular twist mechanism (one without bond cleavage) whereas the thermal

[35] (a) V. Balzani and V. Carassiti, *J. Phys. Chem.*, 1968, **72**, 383; (b) F. Scandola, O. Traverso, V. Balzani, G. L. Zucchini, and V. Carassiti, *Inorg. Chim. Acta*, 1967, **1**, 76; (c) V. Balzani, V. Carassiti, L. Moggi, and F. Scandola, *Inorg. Chem.*, 1965, **4**, 1243.

reaction proceeds *via* an intermolecular path. The constancy of ϕ_{isom}, the intramolecular character of the photoreaction, and the spectroscopic-theoretical evidence for excited triplet states of tetrahedral conformation for square-planar $PtCl_4^{2-}$,[36] have led to the suggestion that the reactive intermediate is a triplet state of pseudo-tetrahedral geometry, as shown in equation 6, where N⌢O designates the glycinato ligand.[35] Further support for a tetrahedral intermediate

| *cis*, singlet ground state | tetrahedral intermediate, triplet state | *trans*, singlet ground state | (6) |
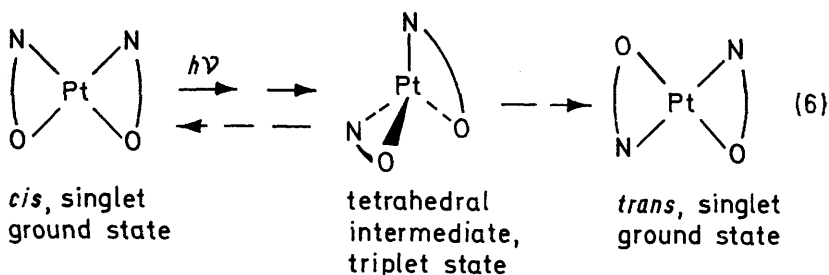
comes from symmetry considerations where the square-planar–tetrahedral interconversion is photochemically allowed but thermally disallowed, and from a recent semi-quantitative theoretical study.[37] A tetrahedral intermediate has also been postulated in an attempt to explain the photoisomerization of $Pt(Et_3P)_2Cl_2$ in organic solvents, where both *cis* to *trans* and *trans* to *cis* reactions occur and a photostationary equilibrium, different from the thermal equilibrium, is encountered.[38]

A number of metal systems have been reported to photoracemize, with that of aqueous tris(oxalato)chromium(III), $Cr(C_2O_4)_3^{3-}$, having been studied in detail.[1,4,7,39,40] The photoracemization mechanism appears to be an intramolecular one involving cleavage of a Cr—O bond in the primary step, as shown in equation 7, followed by the reaction leading to inversion, equation 8.[39]
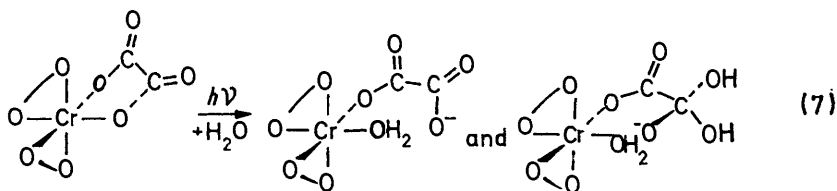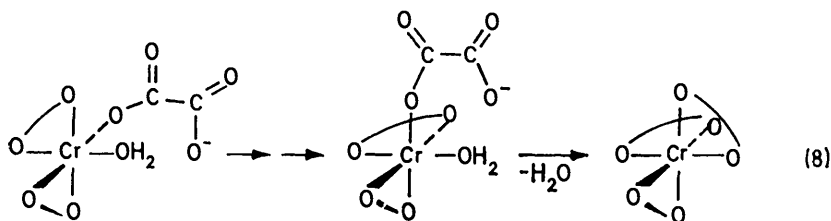
[36] D. S. Martin, jun., M. A. Tucker, and A. J. Kassman, *Inorg. Chem.*, 1965, 4, 1682.
[37] (a) T. H. Whitesides, *J. Amer. Chem. Soc.*, 1969, 91, 2395; (b) D. R. Eaton, *J. Amer. Chem. Soc.*, 1968, 90, 4272; (c) F. S. Richardson, D. D. Shillady, and A. Waldrop, *Inorg. Chim. Acta.*, 1971, 5, 279.
[38] P. Haake and T. A. Hylton, *J. Amer. Chem. Soc.*, 1962, 84, 3774.
[39] S. T. Spees and A. W. Adamson, *Inorg. Chem.*, 1962, 1, 531.
[40] V. S. Sastri and C. H. Langford, *J. Phys. Chem.*, 1970, 74, 3945.

$$(8)$$

The incorporation of water into the free carboxy-group at least some of the time (equation 7) is shown by the fact that photoexchange of solvent oxygen accompanies the racemization reaction to some extent. The ϕ_{racem} of *ca.* 0·1 is essentially independent of the nature of the *d–d* bands irradiated (Figure 1) and of temperature, but sensitive to the composition of the solvent: D_2O or aqueous acetone, alcohols, and dimethyl sulphoxide mixtures depress ϕ_{racem}.[39,40] The photoreaction is reported to be sensitive to acidity in 0·2 M dimethyl sulphoxide[40] but not so in water.[39] The solvent sensitivity of the photoreaction may well be a reflection of the extent to which hydrogen-bonding to water favours distortion of the excited state and thus to the bond cleavage reaction.[40] Solvent effects are also observed in the thermal racemization and aquation reactions of $Cr(C_2O_4)_3^{3-}$, and these reactions appear to be mechanistically similar to the photoreaction.[41] An interesting observation about a racemic mixture of $Cr(C_2O_4)_3^{3-}$ is that preferential racemization of one enantiomer can be induced using circularly polarized light ($\lambda > 500$ nm).[42] Finally, u.v. photolysis of the CT band leads to photoredox decomposition similar to that observed for other metal(III) oxalates such as ferrioxalate.[1,4,7]

For linkage photoisomerization, the isomerization of the nitro-group (—NO_2) to the nitrito-form (—ONO) is representative, the case of $Co(NH_3)_5(NO_2)^{2+}$ being well documented.[2,4,5,7,43–45] While the photochemistry of $Co(NH_3)_5(NO_2)^{2+}$ appears to be complex (redox decomposition, aquation, and linkage isomerization being reported under various conditions), the results obtained by Balzani and co-workers provide a reasonably coherent picture of the photolytic behaviour of this system.[43] This complex exhibits CT bands of CTTM character at 239 and 325 nm and a ligand-field band at 458 nm. Upon irradiation of the CT and *d–d* bands, aqueous 0·1N-$HClO_4$ solutions of $Co(NH_3)_5(NO_2)^{2+}$ exhibit, as the primary photoprocesses, both redox decomposition (the major process) and nitro to nitrito isomerization. The quantum yields decrease significantly with increasing wavelengths of radiation; however, the ratio of ϕ_{redox} : ϕ_{isom} changes only slightly, being 3·9 : 1 (254 nm radiation; CT band), 3·7 : 1 (313 nm; CT), 5·6 : 1 (365 nm; between CT and *d–d*), and 3·4 : 1 (442 nm; *d–d*).[43] These features suggest that both photoreactions may originate from the same

[41] K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, 1961, **61**, 213.
[42] B. Nordén, *Acta Chem. Scand.*, 1970, **24**, 349.
[43] V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 1968, **7**, 1398.
[44] B. Adell, *Z. anorg. Chem.*, 1955, **279**, 219.
[45] W. W. Wendlandt and J. H. Woodlock, *J. Inorg. Nuclear Chem.*, 1965, **27**, 259.

excited state, probably the lowest energy CT one, although in light of recent studies for cobalt(III) systems (see Section 3C), the participation of states that are lower in energy and that differ from the nascent excited state in their spin multiplicities cannot be discounted. While the absorption maximum of this CT state lies at a higher energy than that of the ligand-field one, the order of the pure electronic states could be reversed owing to distortion in the CT state, as portrayed in Figure 3. Thus, excitation of the *d–d* band could populate the CT
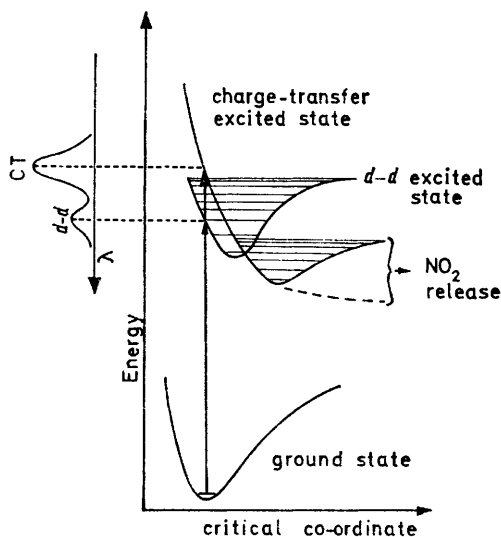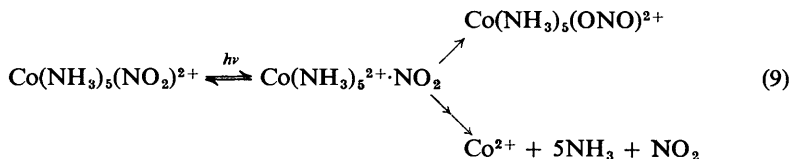

Figure 3 *Schematic representation of a possible relation of CT and d–d excited states for* $Co(NH_3)_5(NO_2)^{2+}$. *(a) Order of excited states: energy of absorption maximum, CT > d–d; pure electronic energy, d–d > CT. (b) After* V. Balzani, R. Ballardini, N. Sabbatini, and L. Moggi, *Inorg. Chem.*, 1968, **7**, 1398.

state *via* a subsequent non-radiative transition. In any event, the reaction mechanism appears to involve the homolytic bond cleavage of the Co–NO$_2$ bond, giving rise to a radical–ion pair intermediate as depicted in equation 9. Subsequent separation of NO$_2$ from the cobalt(II) entity by thermal diffusion from

$$Co(NH_3)_5(NO_2)^{2+} \overset{h\nu}{\rightleftharpoons} Co(NH_3)_5{}^{2+}\cdot NO_2 \nearrow Co(NH_3)_5(ONO)^{2+} \searrow Co^{2+} + 5NH_3 + NO_2 \tag{9}$$

the solvent cage leads to the redox products. In competition with this are the cage recombination reactions leading to formation of the original starting

material and of the nitrito-product, which itself rearranges to the thermally more stable nitro-form. In contrast to its solution behaviour, irradiation in the solid state results primarily in linkage isomerism.[43–45]

An interesting example of ligand photorearrangement occurs in the photochromism of primary metal dithizonates.[46] With radiation above *ca.* 400 nm, non-aqueous solutions of these compounds undergo striking colour changes, ranging from yellow, orange, or green to blue or violet. The transitions responsible for these changes appear to be of an intraligand character (L–L type): the nature of the metal centre does not greatly affect the colour changes. The thermal return reactions involved in the photochromic effect are fast; however, the rates are very sensitive to the nature of the metal atom, to the presence of acids and bases, and to the polarity of the solvent. These features plus the absence of free radicals and of net photochemical reaction lend support to an overall photomechanism involving a *cis–trans* isomerization of an azomethine group coupled with a proton shift, as shown in equation 10 for the square-


(10)

orange   blue
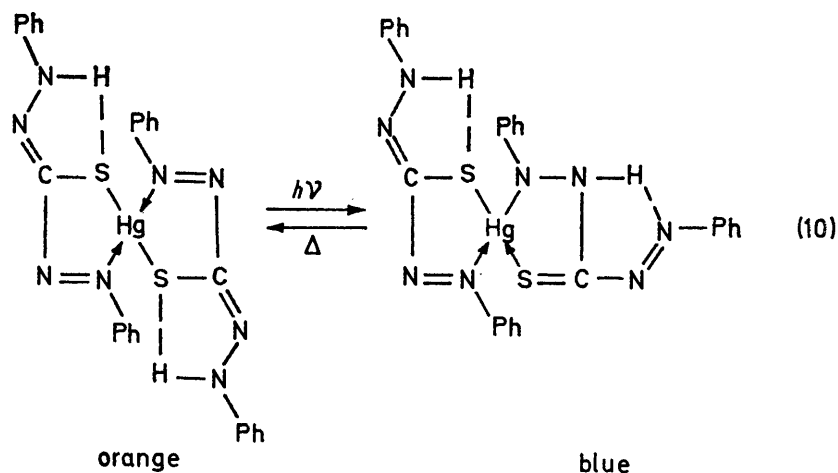
planar mercury compound. The rate-determining step in the thermal return appears to involve the proton shift. Owing to their ease of preparation, metal dithizonates readily lend themselves to a series of interesting laboratory experiments based on their photochromic behaviour.[47] It should not be concluded from this example that irradiation of L–L bands necessarily leads to ligand rearrangement, as other systems are known to exhibit different types of photochemical processes such as photoredox decomposition (see below).

[46] (*a*) L. S. Meriwether, E. C. Breitner, and C. L. Sloan, *J. Amer. Chem. Soc.*, 1965, **87**, 4441; (*b*) L. S. Meriwether, E. C. Breitner, and N. B. Colthup, *ibid.*, 1965, **87**, 4448; (*c*) W. H. Foster, jun., J. M. Dowd, jun., and R. A. Coleman, U.S.P. 3 475 339/1969 (*Chem. Abs.*, 1970, **72**, 56 633*n*).
[47] A. W. Adamson, personal communication.

C. Photo-oxidation–Reduction.—These processes can involve either intra- or inter-molecular transfer of electronic charge, and can be further distinguished on the basis of whether the central metal undergoes oxidation or reduction. Considering intramolecular ones first, few examples involving the oxidation of the central metal atom are known;[7] however, numerous examples of photo-reduction of the metal and oxidation of the ligand(s) can be cited, with the photochemistry of cobalt(III) complexes being noteworthy. The general photo-lytic features of acidic aqueous solutions of cobalt(III) acido-ammines of the type $Co^{III}(NH_3)_5X$, where X can be H_2O, NH_3, halide (and pseudohalide), NO_2^-, carboxylato, or $-O_2Co^{III}(NH_3)_5$, will be discussed;[48–54] their behaviour is somewhat representative of other cobalt(III) systems.[1–5,7] The spectra of acido-ammines consist of one or two *d–d* bands in the visible—near-u.v. regions, with the lower energy one sometimes split into two bands.[4,7,55] The higher energy band is obscured in some cases by the first of generally two CT bands at shorter wavelengths of CTTM (or L–L) character. Irradiation of the CT bands leads to the formation of Co^{II} with quantum yields ranging from *ca.* 0.1 upwards of 1, and exceeding one for X = I⁻. When the first CT band is energetically close to the *d–d* bands, as for the easily oxidized X groups, *e.g.* I⁻ and Br⁻, ligand-field excitation also leads to cobalt(II) production but in lesser amounts. The CT situation is frequently complicated by the simultaneous occurrence of photo-aquation [or linkage isomerism as for $Co(NH_3)_5(NO_2)^{2+}$]. The redox process involves the homolytic fission of the Co–X bond (or Co–N in some cases), as shown in equation 11. The overall fate of X depends upon its chemical nature.

$$(H_3N)_5Co^{III} - X \xrightarrow[H^+]{h\nu} Co^{II} + 5NH_4^+ + X \tag{11}$$
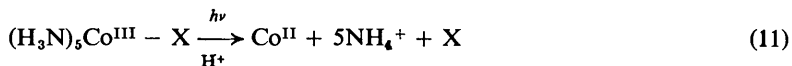
Halogen transients have been observed in flash photolysis studies for X = I⁻ or Br⁻,[48b] whereas for X = Cl⁻, nitrogeneous radicals appear to predominate.[50a] The presence of X has been inferred by scavenging techniques in other cases,[50,52] and the free-radical character of the reactions has been used to initiate poly-merization of vinyl materials.[56]

[48] (a) A. W. Adamson, A. Vogler, and I. Lantzke, *J. Phys. Chem.*, 1969, **73**, 4183; (b) S. A. Penkett and A. W. Adamson, *J. Amer. Chem. Soc.*, 1965, **87**, 2514; (c) A. W. Adamson, *Discuss. Faraday Soc.*, 1960, No. 29, p. 163; (d) A. W. Adamson and A. H. Sporer, *J. Amer. Chem. Soc.*, 1958, **80**, 3865.

[49] (a) M. F. Manfrin, G. Varani, L. Moggi, and V. Balzani, *Mol. Photochem.*, 1969, **1**, 387; (b) L. Moggi, N. Sabbatini, and V. Balzani, *Gazzetta*, 1967, **97**, 980.

[50] (a) G. Caspari, R. G. Hughes, J. F. Endicott, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1970, **92**, 6801; (b) E. R. Kantrowitz, J. F. Endicott, and M. Z. Hoffman, *ibid.*, p. 1776; (c) J. F. Endicott, M. Z. Hoffman and L. S. Beres, *J. Phys. Chem.*, 1970, **74**, 1021; (d) J. F. Endicott and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1965, **87**, 3348.

[51] H. Way and N. Filipescu, *Inorg. Chem.*, 1969, **8**, 1609.

[52] J. E. Barnes, J. Barrett, R. W. Brett, and J. Brown, *J. Inorg. Nuclear Chem.*, 1967, **30**, 2207.

[53] J. S. Valentine and D. Valentine, jun., *J. Amer. Chem. Soc.*, 1971, **93**, 1111.

[54] N. Shinozuka and S. Kikuchi, *Nippon Kagaku Zasshi*, 1966, **87**, 97; 1966, **87**, 1413.

[55] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 1965, **4**, 709.

[56] (a) L. V. Natarajan and M. Santappa, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 3245; (b) G. A. Delzenne, *J. Polymer Sci., Part C, Polymer Symposia*, 1967, **16**, 1027; (c) Gevaert Photo-Production N.V., Belg. P. 647 442/1964 (*Chem. Abs.*, 1965, **62**, 2400b).

The overall sequence of events leading to the final products is not completely understood. The situation is complicated by the simultaneous occurrence of photosubstitutional processes, by secondary thermal and photochemical reactions, and by the participation of excited states lower in energy than those populated directly by absorption of light (see below). An early mechanism proposed by Adamson and co-workers focused on the formation and subsequent reactions of a radical–ion pair intermediate [similar to that in equation 9] to account for the occurrence of both photoredox and photoaquation reactions.[4,48] Others have stressed the importance and possible natures of the excited states involved, and discussed various alternative mechanisms.[1–3,5,7,43,49,50,53,57] Emission studies have not helped in these investigations as cobalt(III) complexes have generally not been found to luminesce. Recent photosensitization studies do indicate, however, that not only can the nascent singlet states be photochemically active but so also can non-spectroscopic, lower energy triplet states, probably of CT character.[48a,58,59] The occurrence of excited species differing from the nascent ones has also been inferred from scavenging experiments with alcohols.[5,50] The photochemistry of the longer-wavelength, ligand-field bands is primarily one of substitutional reactions. The quantum yields, in contrast to those of the CT bands, are invariably small, *e.g. ca.* 10^{-3}, and the mechanism may now be one of heterolytic bond cleavage.[2,4,7,60] Finally, a set of empirical rules has been given that summarizes many of the features of the photochemistry of these and other cobalt(III) complexes.[60]

The fairly recent recognition of photoelectron production for transition-metal complexes serves to illustrate intermolecular photoredox, where the central metal (or more appropriately the complex) undergoes oxidation. Studies of photoelectron production have centred on aqueous solutions of cyanide complexes, in particular ferrocyanide, $Fe(CN)_6^{4-}$, for which the overall reaction is that shown in equation 12, where e_{aq}^- represents the solvated electron. Identi-

$$Fe(CN)_6^{4-} \xrightarrow{h\nu} Fe(CN)_6^{3-} + e_{aq}^- \qquad (12)$$

fication of the electron has been accomplished directly by flash photolysis[61–64] and by electron spin resonance measurements on low-temperature alkali glass,[65]

[57] Z. Simon, *Canad. J. Chem.*, 1960, **38**, 2373.
[58] (a) M. A. Scandola and F. Scandola, *J. Amer. Chem. Soc.*, 1970, **92**, 7278; (b) M. A. Scandola, F. Scandola, and V. Carassiti, *Mol. Photochem.*, 1969, **1**, 403.
[59] A. Vogler and A. W. Adamson, *J. Amer. Chem. Soc.*, 1968, **90**, 5933.
[60] A. Vogler and A. W. Adamson, *J. Phys. Chem.*, 1970, **74**, 67.
[61] M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, 1963, **67**, 2613.
[62] (a) M. Ottolenghi and J. Rabani, *J. Phys. Chem.*, 1968, **72**, 593; (b) G. Czapski and M. Ottolenghi, *Israel J. Chem.*, 1968, **6**, 75.
[63] (a) W. L. Waltz and A. W. Adamson, *J. Phys. Chem.*, 1969, **73**, 4250; (b) W. L. Waltz, A. W. Adamson, and P. D. Fleischauer, *J. Amer. Chem. Soc.*, 1967, **89**, 3923.
[64] R. Devonshire and J. J. Weiss, *J. Phys. Chem.*, 1968, **72**, 3815.
[65] P. B. Ayscough, R. G. Collins, and F. S. Dainton, *Nature*, 1965, **205**, 965.

and indirectly but quantitatively by chemical scavenging techniques.[63,66-68]

The spectrum of ferrocyanide consists of *d–d* bands in the blue and near-u.v. regions and CT bands in the u.v. The ligand-field bands arise from the $3e_g \leftarrow 2t_{2g}$ transition (see Figure 2), and their photochemistry is one of aquation rather than electron production.[4,7,67-69] Electron production originates upon irradiation of the CT bands,[63,66-68] and appears to be accompanied to a lesser extent by photoaquation.[67-69] Some dispute exists as to the assignment of the CT state involved in electron production. Ohno[67] has assigned this to one arising from a CTTL transition, in agreement with the molecular orbital interpretation[13] (see Figure 2). Others contend that the photoactive state correlates with a CTTS band.[66,68] Both interpretations nevertheless involve movement of electron density from the metal centre to the periphery of the complex, followed by solvation of the electron.

The quantum yields for both photoionization and photoaquation tend to be higher than those normally found for transition-metal compounds, ranging from *ca.* 0·1—*ca.* 0·9; however, they appear to be sensitive to experimental conditions such as pH.[4,7,63,66-69] At low pH's, the photoreactions are now probably those of $HFe(CN)_6^{3-}$, a weak acid.[66-68] Although photoelectron production has been observed for only a few systems,[4,7,63,66,70] it may prove to be a fairly widespread reaction mode for transition-metal compounds.

Examples of photo-oxidation–reduction reactions of an intermolecular type involving *reduction* of the metal centre appear to be relatively scarce.[2,4,5,7] Ion-pair complexes of the type $Co(NH_3)_6^{3+} \cdot X^-$, where X^- is I^- or Cl^-, which exist at high concentrations of aqueous $Co(NH_3)_6^{3+}$ and X^-, can be considered in this category.[48d,49a,50a,50d,58b] The near-u.v. spectra[71] of the ion-pairs differ from that of the sum of the components, $Co(NH_3)_6^{3+}$ and X^-: the difference is generally one of higher level of absorption and, for $X = I^-$, the partial masking of the higher energy *d–d* band of $Co(NH_3)_6^{3+}$. Irradiation at 254 nm of the chloride ion-pair leads to yields of cobalt(II) in the range *ca.* 0·3—*ca.* 0·8.[49a,50d,58b] Formation of chlorine as a product does not occur;[50d] however, a transient, presumably Cl_2^-, has been reported in flash photolysis studies.[50a] The photosensitization of what could be the ion-pair by naphthalene in a 50% water-ethanol mixture gives rise to a higher cobalt(II) yield than does direct photolysis.[58b] Exposure of the iodide ion-pair to 370 nm light gives rise to iodine ($\phi_{I_2} = 0.77$) and presumably cobalt(II), although it was not reported as such.[48d] The general reaction mechanism appears to be that of equation 13, which bears

[66] P. D. Airey and F. S. Dainton, *Proc. Roy. Soc.*, 1966, A291, 340, 479.

[67] S. Ohno, *Bull. Chem. Soc. Japan*, 1967, **40**, 1765, 1770, 1776, 1779.

[68] (*a*) G. Stein, *Israel J. Chem.*, 1970, **8**, 691; (*b*) M. Shirom and G. Stein, *ibid.*, 1969, **7**, 405; (*c*) G. Stein, in 'Solvated Electron', ed. R. F. Gould, American Chemical Society, Washington, D.C., 1965, pp. 230–241; (*d*) M. Shirom and G. Stein, *Nature*, 1964, **204**, 778; (*e*) M. Shirom and G. Stein, *J. Chem. Phys.*, 1971, **55**, 3372, 3379.

[69] G. Emschwiller and J. Legros, *Compt. rend.*, 1965, **261**, 1535.

[70] G. V. Buxton, F. S. Dainton, and J. Kalencinski, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 87.

[71] (*a*) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, 1953, **49**, 363; (*b*) N. Tanaka, Y. Kobayashi. and M. Kamada. *Bull. Chem. Soc. Japan*, 1967, **40**, 2839.

$$Co(NH_3)_6^{3+} \cdot X^- \xrightarrow[H^+]{h\nu} Co^{2+} + 6NH_4^+ + X \qquad (13)$$
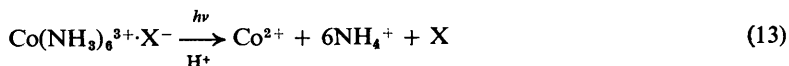
a formal resemblance to that for the cobalt(III) acido-ammines (equation 11). An additional feature concerns the irradiation of the lower-energy ligand-field band of $Co(NH_3)_6^{3+}$ (peak at 475 nm) in the presence of I^-. While the spectral characteristics of this band are not affected by ion-pair formation, irradiation of this band, that is photochemically inactive[48d] in the absence of I^-, leads to formation of iodine from the ion-pair. This feature suggests the possibility that the excited $Co(NH_3)_6^{3+}$ entity may be a stronger oxidizing agent than the ground-state species. Such photoredox reactions of ion-pairs may prove to be a fairly common reaction mode for transition-metal complex ions in the presence of easily oxidized counter-ions and in solvents where the ion-pair formation constants are considerably greater than those found in aqueous media.

4 Discussion
For a number of these photoreactions, there are similar thermal processes. It is apparent, however, that the chemistry of the excited state does represent a situation different from that of the thermal one and not merely an acceleration of thermal reactions. In this regard, the inclusion into the photochemistry of these systems of vibrationally excited ground-state species does not at this time appear to be necessary, although the occurrence of such reactions remains a distinct possibility.

In general, the quantum yields for photochemical reactions of transition-metal complexes are less than unity and in many instances much less. This indicates that to understand the chemistry of the excited states not only must the photochemical aspects be investigated but also the competing photophysical ones. While the general absence of luminescence for these systems in solution at room temperatures has hindered such studies, the recent introduction of the technique of photosensitization into this field has contributed substantially to the understanding of photo-processes, and particularly to the recognition of the importance of various excited states, both spectroscopic and non-spectroscopic ones, to the course of excited-state events.

In a number of cases, some correlation appears to exist between the nature of the band irradiated and the mode of the resulting photochemical reaction. Thus, irradiation of ligand-field bands frequently results in substitutional or related processes whereas irradiation of CT bands gives rise to oxidation–reduction modes. This generalization can be a useful one, but it presupposes, aside from the restricted nomenclature of designating transitions as *d–d* or CT, certain conditions that may not always be met in practice. It suggests a certain level of incommutability between *d–d* and CT states, and such a condition may not always exist; such may be the case with some cobalt(III) acido-ammines. The participation of states lower in energy than those populated directly by light absorption, and particularly those differing in their spin multiplicities, may complicate the situation. This may not always involve a change in the type of

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photochemical reaction, but rather a change in the pathway of reaction as exemplified by $Cr(NH_3)_5(NCS)^{2+}$. The extent to which this type of generalization is fulfilled and the possible development of other relationships requires further detailed investigations.

Finally, since sustained interest in a field can result from both its fundamental and applied importance, it is well to inquire briefly into some of the applications of the photochemistry of transition-metal co-ordination compounds (see also refs. 4a and 7). Substantial use is made of these types of compounds in the imaging industry, *e.g.* iron cyanides in the blueprinting field.[72] Systems such as ferrioxalate and Reinecke's salt find widespread use as u.v.–visible chemical actinometers.[4a,7] The employment of the photochemistry of transition-metal complexes occurs in other areas such as polymerization,[56] generation of reagents in analytical chemistry,[73] and synthetic inorganic chemistry.[74] Although attention in this article has been confined mostly to the liquid phase, the photochemical and photophysical processes of transition-metal systems in the solid state are receiving increased attention.[7,75] Such great diversity in the photobehaviour of transition-metal co-ordination compounds suggests a continuing and expanding interest in these systems both from applied and fundamental viewpoints.

[72] J. Kosar, 'Light-Sensitive Systems', John Wiley and Sons, Inc., New York, 1965.
[73] See for example (a) C. E. Bricker and S. S. Schonberg, *Analyt. Chem.*, 1958, **30**, 922; (b) A. A. Nemodruk and E. V. Bezrogova, *J. Analyt. Chem. (U.S.S.R.)*, 1969, **24**, 239.
[74] (a) R. A. Bauer and F. Basolo, *J. Amer. Chem. Soc.*, 1968, **90**, 2437; (b) J. A. Broomhead and W. Crumley, *Chem. Comm.*, 1968, 1211; (c) L. H. Berka and G. E. Philippon, *J. Inorg. Nuclear Chem.*, 1970, **32**, 3355; (d) S. H. Mastin and P. Haake, *Chem. Comm.*, 1970, 202; (e) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, 1967, **6**, 1943.
[75] E. L. Simmons and W. W. Wendlandt, *Co-ordination Chem. Rev.*, 1971, **7**, 11.