Coordination Chemistry Reviews, 48 (1983) 157–202
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

LIGAND-FIELD MODELS AND THE PHOTOCHEMISTRY OF COORDINATION COMPOUNDS

L. G. VANQUICKENBORNE and A. CEULEMANS

Department of Chemistry, University of Leuven, Celestijnenlaan 200 F, B-3030 Heverlee (Belgium)

(Received 16 March 1982)

CONTENTS

ABBREVIATIONS

bipy	2,2′-Bipyridyl
cyclam	1,4,8,11-Tetraazacyclotetradecane
DMF	Dimethyl formamide

0010-8545/83/$13.80

dmso	Dimethyl sulphoxide
en	Ethylene diamine
phen	1,10-Phenanthroline
py	Pyridine
2,3,2-tet	1,4,8,11-Tetraazaundecane
tren	β,β',β''-Triaminotriethylamine
trien	Triethylene tetramine

A. SCOPE AND LIMITATIONS

Knowledge of photosubstitution processes in coordination compounds is continuously growing and expanding. A comprehensive survey of the period preceding 1970 is available in the excellent monograph by Balzani and Carassiti [1]. In the past decade substantial new progress has been made, which is only partially covered in a second monograph [2]. In order to provide a more updated account of the field several reviews have very recently appeared, dealing with different actual trends [3–9].

The present paper shares this aim, by offering a discussion of theoretical contributions to inorganic photochemistry. The advent of theoretical models has profoundly influenced the orientation of experimental studies; in turn new experimental developments justify sustained theoretical interest. It should be stressed, however, that this dialogue between the two disciplines is of a limited range so far; it is virtually confined to the photochemistry of classical Werner-type coordination compounds in their visible spectrum. Disappointingly few theoretical models pay attention to photoredox processes [10] or to photocatalysis [11].

The most recent advances are to a great extent attributable to ligand-field (LF) theory, which provides a versatile model of the electronic structure in coordination compounds. The opening section therefore briefly examines the essential features of LF theory.

It can only be hoped that we are currently witnessing a prelude to a more comprehensive theory of inorganic photochemistry, but such a development would certainly imply the extension of the LF model beyond its classical limits.

B. FORMALISM AND CHEMICAL RELEVANCE OF LIGAND-FIELD THEORY

LF theory has been developed and elaborated in numerous textbooks, mainly in relation to spectroscopic applications [12–17]. Its use as a kinetic and thermodynamic theory is less well documented. Since the existing models for predicting photosubstitution reactions of coordination compounds all adopt LF theory, in one or another of its many different versions, a brief comment on the theoretical content of LF theory is in order.

Originally developed as an electrostatic field model, the point-charge aspect of the theory has gradually lost its meaning, and thus maintains only the formal characteristics of the field, i.e. the way it parametrizes the molecular geometry. The field parameters are now usually thought of as consisting of various contributions, such as covalent and ionic parts, which cannot be calculated in a simple way. The parametrization schemes that are in use, can be divided into two classes: global and local [18].

(i) Global parametrization

A global parametrization scheme has a clear phenomenological starting point. Its ultimate physical realities are observable level splittings that can be detected in d–d spectra; they are assumed to be traceable to d-orbital splittings. Since the splitting pattern is symmetry determined, the corresponding parametrization scheme will generate parameters, associated with a given symmetry. As an example, in cubic symmetry, the d orbitals transform as e_g and t_{2g} (or e and t_2) representations, and therefore separate into two subshells with only one splitting parameter, 10 Dq (see Fig. 1A). Lower symmetries, due to trigonal and tetragonal fields for instance, will cause further splitting of both subshells, requiring two additional parameters: $D\sigma$ and $D\tau$ for a trigonal field, or Ds and Dt for a tetragonal field. Although these and similar parameters resulted from the application of a localized electrostatic model, it was soon realized that their minimal empirical rele-

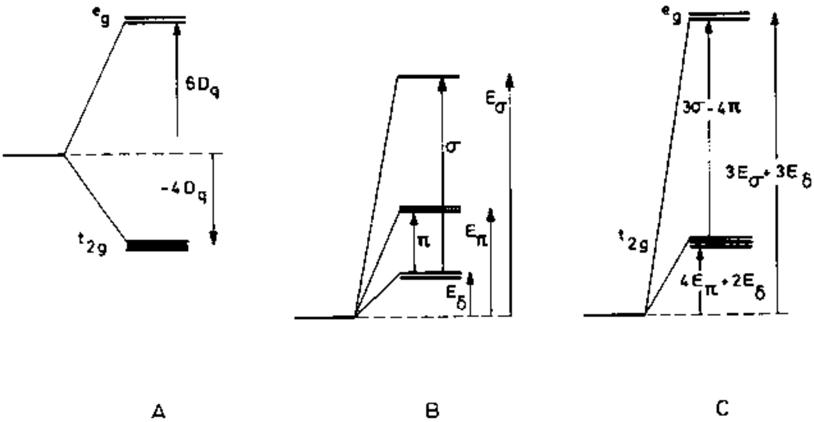


Fig. 1. Various orbital energy diagrams for the d manifold. (A) Crystal-field theory parametrization of the orbital splitting in an octahedral environment. (B) Angular overlap model description of the ligand field, exerted by one single ligand; $\sigma = E_\sigma - E_\delta$ and $\pi = E_\pi - E_\delta$. (C) The combined effect of six identical ligands in an octahedral setting, according to the angular overlap model.

vance comes from the characterization of a splitting scheme, which only depends on the global symmetry. This way of thinking has found its most rigorous expression in the Normalized Spherical Harmonic Hamiltonian (NSH) [19]. According to this method, the LF Hamiltonian is dissected into symmetry species by using projection techniques.

(ii) Local parametrization

Local parametrization schemes, as opposed to the above concepts, arise from a typical chemical way of thinking. The Angular Overlap Model (AOM) of Schäffer and Jørgensen [20,21], following earlier ideas of Yamatera [22] and McClure [23], focuses on this line of thought. Its conceptual basis is the elementary unit of a metal ion and one single ligand. This entity has a local rotational symmetry, $C_{\infty v}$, and allows for three different orbital interactions, or two different parameters, as indicated in Fig. 1B.

The resultant field in a complex is simply assumed to be the sum of all individual ligand contributors (additivity postulate).

Figure 1C illustrates the AOM result for an octahedral complex. Clearly the AOM theory is not purely descriptive. It offers an interpretative analysis of orbital splittings, beyond what is spectroscopically observable. The relevance of this analysis therefore has to be appreciated in a typical chemical context.

Indeed consider a reaction, where one ligand is replaced by another one; if the remaining (inert) part of the coordination sphere is not affected, it will still be described by the same AOM parameters (transferability postulate). Comparison of energy levels in initial and final product then exactly corresponds to an AOM operation.

The two basic concepts of additivity and transferability are not unrelated. Stricto sensu, additivity of the elementary units implies the absence of neighbouring unit effects, and hence transferability of a given unit from one complex to another one. These two postulates continue to develop interest and debate [24]. They are certainly more significant than the overlap interpretation, which was originally associated with the AOM parameters.

Of course spectroscopically obtained AOM parameters will always effectively incorporate electron donating or withdrawing effects from all other ligands. These effects fall in principle beyond the reach of any additive model. Global parametrization schemes on the other hand, are free of this problem, and therefore they are sometimes referred to as non-additive LF models [25]. In apology of the AOM scheme, an individual ligand contribution can be said to be a meaningful quantity, if its parameters are shown to perform reasonably well over a series of mixed ligand complexes.

Comparison of spectra for a series of substituted complexes lends consid-

TABLE 1

Ligand-field parameters[a] for various ligands coordinated at Cr(III)- or Co(III)-ions

	10 *Dq*	σ_L	π_L	Ref.
Cr–Br	12.02	5.34	1.00	[b]
Cr–Cl	13.07	5.56	0.90	[b]
Cr–F	15.37	7.63	1.88	[b,c]
Cr–DMF	14.87	5.81	0.64	28 [d]
Cr–H_2O	15.83	5.94	0.50	28
	(17.30	6.77	0.75)	29 [e]
Cr–OH	17.00	8.66	2.25	29
Cr–NCS	17.71	6.41	0.38	28
Cr–py	19.71	5.80	−0.58	29 [f]
Cr–NH_3	21.55	7.18	0.00	30
Cr–en	21.85	7.28	0.00	31
Cr–CN	26.50	8.48	−0.29	30
Co–Cl	14.60	6.29	1.29	35 [g]
Co–H_2O	15.47	6.60	1.08	35 [h]
Co–OH	10.67	9.61	4.54	35 [i]
Co–N_3	18.98	6.76	0.32	35 [j]
Co–NH_3	23.43	7.81	0.00	40
Co–en	23.77	7.92	0.00	40
Co–CN	34.89	12.15	0.39	35 [k]

[a] Units of 10^3 cm^{-1}. [b] Taken from [26]; see also [27]. [c] Average value for *trans*$[\text{Cr}(\text{NH}_3)_4\text{F}_2]^+$ and *trans*$[\text{Cr}(\text{en})_2\text{F}_2]^+$. [d] Oxygen-coordinating ligand. Ligand abbreviations are listed at the beginning. [e] Concurrent fit of all ten isomers of the aquo-aminechromium(III) series. [f] Non-linearly ligating ligand. [g] Determined from a comparison of five members of the chloroamine series [32–34]. [h] Determined from a comparison of five members of the aquocyanocobaltate series [36–39]. [i] Calculated on the basis of four members of the hydroxocyanocobaltate series [36–39]. [j] Estimated from the spectra of *cis*- and *trans*$[\text{Co}(\text{NH}_3)_4(\text{N}_3)_2]^+$ [40]. [k] Calculated on the basis of seven isomers of the cyanoaminecobaltate series [36,37,40,41].

erable support to the postulates of the local parametrization scheme. From these data, parameters could be obtained and Table 1 represents a collection of acceptable values for complexes of trivalent chromium and cobalt, drawn from various references [26–41].

Table 1 illustrates that well-defined "chemical" parameters can be attributed to individual ligand–metal interactions, although numerical values of the parameters are subject to rather large uncertainties and should not be overemphasized. Some irregularities are noteworthy. Co(III) values normally show a slight and uniform increase with respect to the corresponding Cr(III) values [14]. The cyanide ligand forms an exception with a marked 30% increase in going from Cr(III) to Co(III). Another exceptional case is the aquo ligand: the 10 *Dq* values characteristic of hexaaquo complexes cannot be transferred to $[Cr(NH_3)_4(H_2O)_2]^{3+}$ or $[Co(CN)_4(H_2O)_2]^-$ [29]. Interestingly the same effect has been noticed in square planar complexes of Pt(II) [42].

(iii) Many-electron LF theory

In the previous section, LF theory has been presented as a one-electron theory that provides *d*-orbital energies as a function of a limited set of parameters, more or less in the same way that Hückel theory parametrizes π orbital energies in conjugated systems. However, if there is more than one *d* electron (and less than nine), the many-electron repulsion effects have to be considered explicitly. Usually one resorts to techniques of atomic spectroscopy [43] to account for these interactions. Resulting state energies are combined expressions of LF parameters and Racah's electron repulsion parameters B and C.

(iv) Limitations

In summary, at this point it is preferable to conceive LF theory from two different points of view. On the one hand a symmetry analysis will reveal the minimum number of parameters that constitute a global parametrization scheme. Since a limited orbital basis is used (gerade *d* orbitals only), no full representation of the true symmetry can be achieved, and an effective holohedral symmetry will be adopted in practice. On the other hand the global parameter set can be considered as a reference set to which local parametrization schemes can be related [44].

Local parametrization schemes carry more assumptions, hence more interpretative information, but also more inherent limitations.

As will be shown in the following sections, several aspects of the photochemistry of coordination compounds have been described rather adequately in terms of global parameters. However local models are needed, whenever individual ligands are to be distinguished. In that sense the photolysis results add to the credibility of AOM ligand classification.

C. EARLY DEVELOPMENTS

A very early and capital step towards an understanding of the photochemical properties associated with the visible absorptions of coordination compounds, was the realization that these LF transitions do not change the oxidation state of the metal ion, and thus are likely to involve non-redox processes only, such as solvolysis, ligand anation, isomerization and racemization. All these processes are commonly observed in ground state reactivity as well, though at a much lower rate. Rate increases upon irradiation can be quite spectacular. Recently, laser techniques allowed direct measurement of dissociation rates in excited states, Ford and coworkers obtained a photodissociation constant for chloride in $[Rh(NH_3)_5Cl]^{2+}$ of $12.7 \cdot 10^6$ sec^{-1} in aqueous solution at room temperature, which is more than fourteen orders of magnitude faster than the analogous thermal reaction [46].

In one of the earliest reviews [47], Wehry suggested that the only function of light absorption was the enhancement of the thermal processes. Radiation energy was thought to increase ground state reactivity by adding heat to the system. At the time, the available information indeed suggested that the reaction products of the dark and light reactions were the same.

As is apparent, most photochemical studies concentrated on just a few metal ions. Table 2 collects the best known systems [48,49]. All complexes in Table 2 have one property in common: they are characterized by high ground-state stability. In fact, originally, they were studied more because of this stability, and hence availability, rather than because of any presumed photoactivity. Table 2 also illustrates some simple rules of thumb, characterizing stable ground states:

(a) Orbitals that are strongly destabilized by the ligand field, such as e_g orbitals in an octahedron, remain vacant.

(b) No orbitally degenerate ground states are present in Table 2, since Jahn–Teller effects would tend to destabilise them.

Qualitative considerations of this kind are typical thermodynamic implications of LF theory. The earliest more quantitative arguments were based on the concepts of LF activation energy (LFAE) and LF stabilization energy (LFSE) [50,51]. In practice, energy expressions were often simplified by adopting constant ratios between 10 *Dq* and the parameters needed to describe ligand fields of lower than cubic symmetry.

Schläfer has applied this formalism to excited states of d^3- and d^6-octahedral complexes [52]. His results for the lowest excited states are summarized in Table 3. The third column in Table 3 lists the difference in LFAE between ground and excited state. This difference is of course a measure for

TABLE 2

The paradigmatic systems of inorganic photochemistry

Complex	Ground state	Examples
ML_6	$d^3\ {}^4A_{2g}(t_{2g}^3)$	Cr(III)
	$d^6\ {}^1A_{1g}(t_{2g}^6)$	Co(III), Rh(III), Ir(III) [Fe(II), Ru(II), Pt(IV)…]
ML_4	$d^8\ {}^1A_{1g}(a_{1g}^2 e_g^4 b_{2g}^2)$	Pt(II)

TABLE 3

Estimate of ligand-field activation energy [a] for a dissociative (SN_1) or associative (SN_2) rate controlling step in various electronic states, according to Schläfer [52]

State	LFAE		Excited state enhancement
	SN_1	SN_2	
d^3: $^4A_{2g}(t_{2g}^3)$	$2\ Dq$	$4.26\ Dq$	
$^2E_g(t_{2g}^3)$	$2\ Dq - P$	$4.26\ Dq - P$	P
$^4T_{2g}(t_{2g}^2e_g^1)$	$-8\ Dq$	$-5.74\ Dq$	$10\ Dq$
d^6: $^1A_{1g}(t_{2g}^6)$	$4\ Dq$	$8.52\ Dq$	
$^3T_{1g}(t_{2g}^5e_g^1)$	$-6\ Dq + P$	$-1.48\ Dq + P$	$10\ Dq - P$
$^1T_{1g}(t_{2g}^5e_g^1)$	$-6\ Dq$	$-1.48\ Dq$	$10\ Dq$

[a] Given as a function of spectrochemical strength $10\ Dq$ and spinpaining energy P.

the rate enhancement of the light reaction, relative to the dark reaction. It simply corresponds to the spectroscopic energy gap, as determined from LF theory and therefore Table 3 joins the early qualitative idea that the photon energy, in its entirety, serves to lower the activation barrier.

From these results, Schläfer [52] concluded that in the case of d^3 complexes both quartet and doublet excited states should be strongly photoactive. He assigned the doublet state as the precursor of the photoreaction, since this state has a comparatively long lifetime.

It is of interest to compare Schläfer's [52] view with the ideas expressed a few years later by Wrighton et al. [53]. The starting point of their analysis was a more detailed treatment of the metal–ligand bond. Ligands were classified in three bonding types, as reflected in the AOM parameters (see Table 1): (a) σ donors capable of bonding to the metal by σ interactions only (amine ligands); (b) π donors characterized in addition by π interactions between the metal t_{2g} orbitals and the occupied ligand π orbitals (positive π parameters with respect to amines); (c) π acceptors, characterized in addition by π interactions between the metal t_{29} orbitals and vacant ligand π^* orbitals (negative π parameters in Table 1).

For all three types of ligands the e_g level (Fig. 1) is σ antibonding (and therefore vacant in the ground state). The bonding character of the t_{2g} d-electrons is variable however, being non-bonding for σ-donors, π antibonding for π donors, and π bonding for π acceptors. A $t_{2g} \rightarrow e_g$ excitation in octahedral complexes will always labilize the M–L bonds through the σ^* effect, but t_{2g} depletion can have different effects: π donors show increased π bonding, while π acceptors are destabilized. In summary the enhancement of excited state reactivity relative to the thermal behaviour is expected to increase in the order π donor $<$ σ donor $<$ π acceptor. Now this sequence parallels the spectrochemical series, based on 10 Dq; indeed as shown in Fig. 1C, the 10 Dq parameter reflects the difference between σ- and π-bonding capability. In thise sense the σ- and π-bonding analysis leads to the same conclusions as the LFAE calculations of Table 3. The difference in the paper of Wrighton et al. [53] is that these authors make "equivalent predictions for configurationally analogous pairs". The activation energy is supposed to depend only on the electron configuration (occupation of σ and π orbitals) and not on the interelectronic repulsion; the spin pairing energy P has no role in this model of photochemistry. For example, the ${}^2E_g(t_{2g}^3)$ state reactivity in the Cr(III) complexes is expected to be roughly comparable to the ground state behaviour, clearly in contrast with the predictions of Schläfer [52]: from Table 3, the reactivity of ${}^2E_g$ and ${}^4T_{2g}$ will be expected to be very similar, since P and 10 Dq are very close in magnitude.

The approach of Wrighton et al. [53] has the advantage that it recognizes explicitly, for a given state, the importance of the electronic structure, and not only of the energy. Excited states are not merely ground states with an additional energy packet, but they are chemically different species. As far as *d–d* spectra are concerned, this difference is describable by LF theory.

Much of the conceptual development that had taken place between Wehry's 1967 [47] review and the paper by Wrighton et al. [53], was related to a pioneering proposal by Adamson [54]. On the basis of a very limited amount of experimental data, Adamson introduced the notion of 'antithermal' behaviour of excited states and he formulated empirical rules for predicting the photoreactivity of mixed-ligand complexes.

D. THE LEAVING LIGAND PROBLEM

(i) Adamson's rules

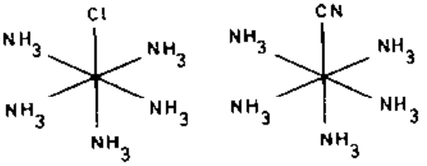
By 1967 it had become known from studies on mixed-ligand complexes that in some cases the thermal and photochemical reaction modes did not coincide. Typical examples were acidopentamine complexes of trivalent chromium such as $[Cr(NH_3)_5NCS]^{2+}$ [55]. Thermally this complex exclusively aquates thiocyanate, whereas under irradiation ammonia release is by far the dominant mode.

This type of result led Adamson to the proposal of empirical rules that would predict the photoactivity of chromium(III) complexes. The leaving ligand could be determined in two steps [54].

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

(b) If the labilized axis contains two different ligands, then the ligand of greater field strength preferentially aquates. This may be a type of *trans* effect [56]. (Rule 2).

Moreover Adamson realized that the spectrospecific photochemistry could not be explained by adopting the (otherwise attractive) hypothesis, that the photoactive state be the lowest excited doublet; he proposed that the antithermal behaviour as expressed in his rules, was characteristic of the lowest excited quartet state. The quartet hypothesis has been substantiated over the years in extensive photophysical studies. (For a detailed account see ref. 9.) Subsequent LF models have been founded on quartet excited state properties. Although the rules were intended to be empirical laws, their connection to theory is immediate because of the use of crystal field parameters.



Consider for instance monosubstituted complexes, of tetragonal symmetry such as

In these complexes, two different ammonia ligands can be distinguished: the NH_3 ligand on the unique tetragonal axis will be referred to as an axial ligand, while the ligands adjacent to the heteroligand will be designated as equatorial ligands. Following the rules, and as is indeed observed, the chloro-complex photo-aquates axial ammonia [57,58], whereas the cyano-complex must be characterized by dominant equatorial labilization.

Today after extensive examinations of more than seventy hexacoordinated complexes, it can be safely decided that the first rule is remarkably well obeyed, not only for d^3 but also for strong-field d^6 complexes. In the latter case photoreactivity is usually ascribed to the lowest excited triplet state. (For a detailed account see ref. 6). Only one manifest exception has been found so far: *trans*$[Cr(en)_2F_2]^+$ (or *trans*$[Cr(NH_3)_4F_2]^+$) photoaquates the amine ligand preferentially, although not on the weak-field axis [59,60]. The second rule is much less general. Especially in d^6 complexes weak-field acido ligands are good leaving groups, contrary to the d^3 case.

(ii) Theoretical foundations

Specific site labilization immediately suggests a connection between the photochemical process and the angular properties of the *d* orbitals. For instance in a tetragonal complex, occupation of the d_{z^2} orbital (main density along the tetragonal axis), can be expected to labilize the axial sites preferentially through σ antibonding; similarly occupation of $d_{x^2-y^2}$ would affect the equatorial sites. This possible correlation was first noted by Balzani and Carassiti [1] but rejected for the following reason: whereas the relative energy of the antibonding orbitals $d_{x^2-y^2}$ and d_{z^2} depends only on the σ-bonding abilities of the different ligands, the relative position of each ligand in the spectrochemical series (i.e. the 10 *Dq*-criterion, required by Adamson's rules) is the result of both σ and π effects. Hence orbital considerations do not automatically lead to a simple understanding of the empirical generalizations.

Zink has been the first to undertake a more systematic theoretical analysis of the electronic structure of the relevant excited states in view of their photoactivity [61]. He developed a model which was originally based on crystal-field theory [61–64] but later on resorted to MOT calculations [65,66] where bond strengths were estimated from overlap populations in the excited state (see also [67]). (This idea is currently reactivated, using more sophisticated ab initio calculations [68]). Zink has advanced several premises, which set the foundation for later theoretical developments.

(a) It is assumed that the lowest excited energy level of a given multiplicity will be the dominant photoactive level of that multiplicity (Kasha's photochemical rule). The identity of this lowest state can be determined from spectral analysis or by theoretical methods [61].

(b) No detailed photomechanism is proposed except that a primary dissociative event is considered essential in the foundation of Adamson's rules [61].

(c) Orbital arguments can only be made if the detailed configurational composition of the photoactive state is considered. Hence an adequate treatment of excited states requires the use of many-electron wavefunctions [65]. This point had already been stressed by Whitesides [69] and is also one of the central themes of the present review.

The explicit use of state functions can result in counter-intuitive effects, since orbital sequences, as obtained in a one-electron model, are not necessarily simply reflected in state sequences. This was precisely the difficulty encountered by Balzani and Carassiti [1], when they compared orbital model predictions with the photolysis rules.

Consider the specific example of $[Cr(NH_3)_5F]^{2+}$, where fluoride is a stronger σ donor than amine, but has a weaker overall field (10 *Dq* in Table 1). Because of the relative value of the σ parameters, $d_{x^2-y^2}$ is lower than d_{z^2}. If the photoactive state corresponds to the population of this lowest excited $d_{x^2-y^2}$ orbital, one would expect equatorial labilization [59,70]. Yet, both from experiment [71,72] and from Adamson's rules, the leaving ligand is found to be the axial amine ligand.

The problem disappears if one realizes that the photoactive first excited state does not simply correspond to the population of $d_{x^2-y^2}$ [73]. Indeed, consider the $t^3 \rightarrow t^2e^1$ excitation in the parent octahedral $[Cr(NH_3)_6]^{3+}$ molecule. Although the σ orbitals d_{z^2} and $d_{x^2-y^2}$ are degenerate in this case, the orbital excitations $(xy \rightarrow x^2-y^2)$ and $(xy \rightarrow z^2)$ are definitely not degenerate. In fact, the excitation $(xy \rightarrow x^2-y^2)$ is one of the components of ${}^4T_{2g}$, whereas the excitation $(xy \rightarrow z^2)$ is one of the components of ${}^4T_{1g}$. Both quartets correspond to the same t^2e^1-configuration, but ligand-field theory predicts

$$E({}^4T_{1g}) - E({}^4T_{2g}) = 12\,B \tag{1}$$

where B is the Racah repulsion parameter; therefore ${}^4T_{1g}$ is some 8000 cm^{-1} higher in energy than ${}^4T_{2g}$, and need not be considered from our qualitative point of view.

To first order in perturbation theory, the photoactive state will correspond to one of the ${}^4T_{2g}$ components. Figure 2 shows the splitting of the ${}^4T_{2g}$ state into ${}^4B_{2g}$ and ${}^4E_g$. The magnitude of this splitting is described by Dt in classical crystal field theory [13,74] and by DT in the NSH approach [19,75]. The orbital composition [73] is given by eqn. (2)

$${}^4B_{2g}\colon xy \rightarrow x^2 - y^2 \tag{2a}$$

$${}^4E_g\colon \begin{cases} xz \rightarrow x^2 - z^2 \\ yz \rightarrow y^2 - z^2 \end{cases} \tag{2b}$$

Clearly, both states are characterized by oppositely polarized labilization properties: ${}^4B_{2g}$ labilizes the equatorial ligands, and hence, ${}^4E_g$ must preferentially weaken the axial bonds (since the parent T_{2g} state is of course

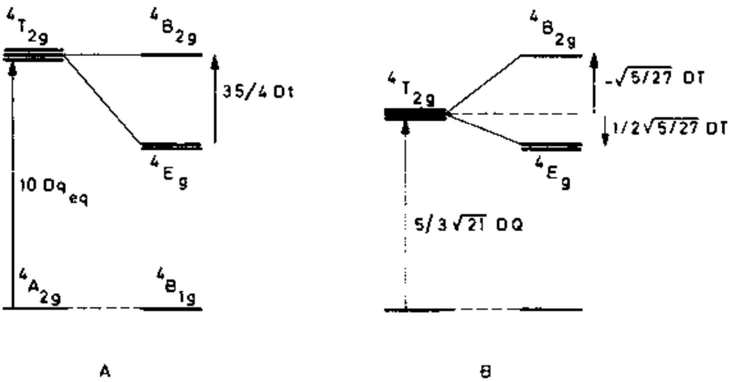


Fig. 2. Schematic state energy level diagram for the lowest quartet states in d^3 complexes of tetragonal symmetry. Octahedral parentage according to either (A) crystal-field theory or (B) normalized spherical harmonic hamiltonian approach.

isotropic). This result somewhat resembles the formulation of electronic selection rules that describe the polarization of electronic transitions. From crystal-field theory the tetragonal splitting is given by

$$E(^4B_{2g}) - E(^4E_g) = \tfrac{35}{4}Dt = \tfrac{1}{2}(10\,\overline{Dq}_{\mathrm{eq}} - 10\,\overline{Dq}_{\mathrm{ax}}) \tag{3}$$

where $\overline{Dq}_{\mathrm{eq}}$ and $\overline{Dq}_{\mathrm{ax}}$ correspond to the average equatorial and axial field strengths respectively [76]. Therefore, if the z axis has the weakest overall field strength, the ^4E_g state is lowest and predominant axial labilization can be expected; if the equatorial axes are weaker, equatorial labilization can be expected; a conclusion which is in agreement with Adamson's first rule. The same conclusions prevail for d^6 excited states [76].

(iii) Expectation values for bonding in LF-states

In the the preceding paragraph global parametrization schemes were used to reveal the symmetry foundations of Adamson's first rule. The simple qualitative arguments that were used there are not suited to handle more detailed questions, such as the prediction of the actual leaving ligand on the labilized site, or the effect of configuration interaction, etc. In order to answer these questions, the I^* model has been developed [76,77], on the basis of the AOM parametrization scheme, and guided by the particularly simple view of the coordination bond, that is present in the work of McClure [23], Kettle [78], Burdett [79–81] and others.

In this view it is assumed that a coordination bond is formed because occupied ligand orbitals interact with unoccupied d orbitals; the stabilization of the bonding combination is assumed to outweigh exactly the destabilization of the antibonding combination. (For π-acceptor ligands, the d orbitals are dative and form the bonding part of the diagram.)

This mirror-image model offers a simple way to estimate individual bond indices. In what follows, the bond index idea will be elaborated on the example of complexes, characterized by O_h and D_{4h} holohedral symmetry. These cases cover most practical applications. For lower (orthorhombic) symmetry, an extension of the present ideas has been given elsewhere [77]. First consider the total bonding energy, I, corresponding to a given orbital configuration

$$I = \sum_i h_i \epsilon_i \tag{4}$$

where the summation runs over the five d orbitals, h_i being the number of holes in the i^{th} d orbital, and $\epsilon_i = \langle d_i | V | d_i \rangle$ the d orbital destabilization energy, under a LF potential V. Because of the additivity postulate of AOM, this quantity can be partitioned in individual ligand contributions

$$I(\mathrm{M{-}L}) = \sum_i h_i \langle d_i | V_L | d_i \rangle \tag{5}$$

where V_L is the individual ligand contribution to the LF potential. The states of interest in octahedral d^3 or d^6 complexes offer simple applications, because most of them can be described as one-configuration states e.g. for the ${}^4A_{2g}$ (t_{2g}^3) ground state of CrA_6 complexes one finds

$$\begin{aligned} I &= 4\epsilon(e_g) + 3\epsilon(t_{2g}) = 12\sigma + 12\pi \\ I(\mathrm{M{-}L}) &= 2\sigma + 2\pi \end{aligned} \tag{6}$$

and for both the ${}^4T_{2g}(t_{2g}^2e_g)$ and ${}^4T_{1g}(t_{2g}^2e_g)$ excited states

$$\begin{aligned} I^* &= 3\epsilon(e_g) + 4\epsilon(t_{2g}) = 9\sigma + 16\pi \\ I^*(\mathrm{M{-}L}) &= \tfrac{3}{2}\sigma + \tfrac{8}{3}\pi \end{aligned} \tag{7}$$

These equations simply reflect the more qualitative considerations of the previous section: the σ bonding decreases, while π bonding increases upon excitation.

For both transitions, the net bond weakening upon excitation is easily determined

$$I(\mathrm{M{-}L}) - I^*(\mathrm{M{-}L}) = \tfrac{1}{2}\sigma - \tfrac{2}{3}\pi = \tfrac{1}{6}(10\,Dq) \tag{8}$$

The total labilization $(I - I^*)$ then equals 10 Dq whereas the transition energy is 10 Dq for ${}^4A_{2g} \rightarrow {}^4T_{2g}$, but 10 $Dq + 12\ B$ for ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (see previous paragraph). So far the model is consistent with the conclusions of Wrighton et al. [53] (section C). The photon energy has thus been divided into a metal-centered electron repulsion contribution and an orbital part, that describes the weakening of the bond with the ligand sphere. In turn, the latter energy is further partitioned over the individual ligands, leading to relative bond strength estimates.

If one applies the same ideas to a lower symmetry tetragonal complex, where the photoactive state is either ${}^4B_{2g}$ or ${}^4E_g$ (Fig. 2 and eqn. 2), one obtains

$$\begin{aligned} I({}^4B_{2g}) &= \epsilon(xz) + \epsilon(yz) + 2\epsilon(xy) + \epsilon(x^2-y^2) + 2\epsilon(z^2) \\ &= 4\bar{\sigma}_{ax} + 4\bar{\pi}_{ax} + 5\bar{\sigma}_{eq} + 12\bar{\pi}_{eq} \end{aligned} \tag{9}$$

The bar refers to average values of the site in subscript (axis or plane). This result is obtained from the usual AOM expressions for tetragonal complexes $\epsilon(z^2) = 2\bar{\sigma}_{ax} + \bar{\sigma}_{eq}$, $\epsilon(x^2-y^2) = 3\bar{\sigma}_{eq}$, $\epsilon(xy) = 4\bar{\pi}_e$, $\epsilon(xz) = \epsilon(yz) = 2\bar{\pi}_{ax} + 2\bar{\pi}_{eq}$.

Referring to individual axial or equatorial ligands

$$\begin{aligned} I^*(\mathrm{ML}_{ax};\, {}^4B_{2g}) &= 2\sigma_{ax} + 2\pi_{ax} \\ I^*(\mathrm{ML}_{eq};\, {}^4B_{2g}) &= \tfrac{5}{4}\sigma_{eq} + 3\pi_{eq} \end{aligned} \tag{10}$$

This equation offers a semi-empirical assessment of the equatorial polarization of the $^4B_{2g}$ state. The labilization takes a particularly simple form

$$\begin{aligned} I(\mathrm{ML_{eq}}) - I^*(\mathrm{ML_{eq}}; {}^4B_{2g}) &= +\tfrac{5}{2} Dq_{\mathrm{eq}} \\ I(\mathrm{ML_{ax}}) - I^*(\mathrm{ML_{ax}}; {}^4B_{2g}) &= 0 \end{aligned} \tag{11}$$

The ^4E_g state can be treated in a similar way. The weighted average of both tetragonal components ^4E and $^4B_2$ must converge to the octahedral results of eqn. (7), as long as the analysis is based on the same wavefunctions. Therefore

$$\begin{aligned} \tfrac{1}{3} I^*(\mathrm{ML_{eq}}; {}^4B_{2g}) + \tfrac{2}{3} I^*(\mathrm{ML_{eq}}; {}^4E_g) &= \tfrac{3}{2}\, \sigma_{\mathrm{eq}} + 3\, \pi_{\mathrm{eq}} \\ \tfrac{1}{3} I^*(\mathrm{ML_{ax}}; {}^4B_{2g}) + \tfrac{2}{3} I^*(\mathrm{ML_{ax}}; {}^4E_g) &= \tfrac{3}{2}\, \sigma_{\mathrm{ax}} + 3\pi_{\mathrm{ax}} \end{aligned} \tag{12}$$

Specifically for the ^4E_g state one obtains

$$\begin{aligned} I^*(\mathrm{ML_{ax}}; {}^4E_g) &= \tfrac{5}{4}\sigma_{\mathrm{ax}} + 3\, \pi_{\mathrm{ax}} \\ I^*(\mathrm{ML_{eq}}; {}^4E_g) &= \tfrac{13}{8}\sigma_{\mathrm{eq}} + \tfrac{5}{2}\, \pi_{\mathrm{eq}} \end{aligned} \tag{13}$$

For the labilization one finds

$$\begin{aligned} I(\mathrm{ML_{ax}}) - I^*(\mathrm{ML_{ax}}; {}^4E_g) &= \tfrac{5}{2}\, Dq \\ I(\mathrm{ML_{eq}}) - I^*(\mathrm{ML_{eq}}; {}^4E_g) &= \tfrac{5}{4}\, Dq \end{aligned} \tag{14}$$

Exactly the same equations are obtained for the ^3E and $^3A_2$ states of the d^6 case. Thus for the E states under consideration, and for a given 10 Dq value, an axial bond absorbs twice as much excitation energy as an equatorial bond, and it is justified to characterize an E state as being oppositely polarized to an A or a B state. Moreover it is evident from eqns. (11) and (14) that each M–L bond on the labilized site, absorbs a fraction of the photon-energy, which is proportional to its spectrochemical strength. In this sense some light is thrown on the foundation of the second rule, since stronger ligands are seen to be more labilized.

As a matter of fact, at the present level of approximation Adamson's two photolysis rules are strictly reducible to one single rule: "The leaving ligand is the ligand characterized by the largest labilization energy $I - I^*$".

A priori, it appears more reasonable that the leaving ligand be characterized, not so much by the largest value of $I - I^*$, but rather by the smallest value of I^*. This is the essence of a proposal we made a few years ago [76]. Obviously, a small labilization energy will contribute to a large excited state bond index I^*, but the prediction of the two models may be quite different if the ground state bond indices I vary significantly from one ligand to another.

TABLE 4

I^* (M–L) values for the separate ^4E_g components, quantized along the z-axis

	$\|E\eta\rangle$	$\|E\xi\rangle$
I^* (M–L$_z$)	$3\pi_{ax}+(2-\sin^2\theta)\sigma_{ax}$	$3\pi_{ax}+(2-\sin^2\theta)\sigma_{ax}$
I^* (M–L$_x$)	$3\pi_{eq}+(2-\sin^2(\theta+\pi/3))\sigma_{eq}$	$2\pi_{eq}+(2-\sin^2(\theta-\pi/3))\sigma_{eq}$
I^* (M–L$_y$)	$2\pi_{eq}+(2-\sin^2(\theta-\pi/3))\sigma_{eq}$	$3\pi_{eq}+(2-\sin^2(\theta+\pi/3))\sigma_{eq}$

Before a detailed comparison can be made between these models and experiment, the effect of configuration interaction in the E states needs to be taken into account. Indeed in D_{4h} the states corresponding to the excitations $xz \to x^2-z^2$ and $xz \to y^2$ (and similarly for $yz \to y^2-z^2$ and $yz \to x^2$) have the same symmetry and will interact [63]. The lower E state excitations (valid for d^3 and d^6) can be rewritten in a more convenient form, using an alternative tetragonal basis set [77]

$$|E\eta> \,:\, xz \to \sin(\theta)d_{z^2}-\cos(\theta)\,d_{x^2-y^2}$$

$$|E\xi> \,:\, yz \to \sin(-\theta)\,d_{z^2}-\cos(-\theta)\,d_{x^2-y^2} \tag{15}$$

where θ is a function of the ligand field parameters and the Racah repulsion parameters [76,77] ($\pi/2<2\theta<3\pi/2$).

The zeroth-order wavefunctions, on which the preliminary analysis was based, have $\theta=\pi/3$, which simplified the calculation of I*. Table 4 lists the relevant expressions for variable θ values, Since the E state is described to an equal extent by the functions $|E\eta\rangle$ and $|E\xi\rangle$, the results of Table 4 have to be averaged. Introducing $x=\sin^2\theta$, to denote the fraction of d_{z^2} in the E state (in zeroth order $x=3/4$) we obtain

$$\begin{aligned}
I^*(\mathrm{ML}_{ax}) &= 3\pi_{ax}+(2-x)\sigma_{ax}\\
&= x(3\pi_{ax}+\sigma_{ax})+(1-x)(3\pi_{ax}+2\sigma_{ax})\\
&= xI^*(\mathrm{ML}_{ax};\, xz\to z^2)+(1-x)I^*(\mathrm{ML}_{ax};xz\to x^2-y^2)\\
I^*(\mathrm{ML}_{eq}) &= \frac{5}{2}\,\pi_{eq}+\left[2-\frac{1}{2}\,\sin^2\!\left(\theta+\frac{\pi}{3}\right)-\frac{1}{2}\,\sin^2\!\left(\theta-\frac{\pi}{3}\right)\right]\sigma_{eq}\\
&= \frac{5}{2}\,\pi_{eq}+\left(2-\frac{3}{4}+\frac{x}{2}\right)\sigma_{eq}\\
&= x\left(\frac{5}{2}\pi_{eq}+\frac{7}{4}\sigma_{eq}\right)+(1-x)\left(\frac{5}{2}\pi_{eq}+\frac{5}{4}\sigma_{eq}\right)\\
&= xI^*(\mathrm{ML}_{eq};\, xz\to z^2)+(1-x)I^*(\mathrm{ML}_{eq};\, xz\to x^2-y^2)
\end{aligned} \tag{16}$$

For $x = \frac{3}{4}$, eqn. (16) reduces to eqn. (13). The derivation proves that the bonding properties of the E state can be analyzed as a fractional sum of two single configurations in the one-electron scheme of the tetragonal orbitals. Weak axial σ donors will increase x [76] so that axial labilization is even more pronounced. Recently Zinato et al. [82] have remarked that this type of σ effect can indeed be observed in a series of complexes, but always as a minor correction to the 10 Dq based selectivity, established on the zeroth-order basis functions.

(iv) Comparison with experiment

Table 5 offers a broad spectrum of photolysis data [1,9,48,83–105] on Cr(III)- and Co(III)-complexes. In all cases the leaving ligand is compared with predictions of the I^* model. Calculated values refer to the lowest component of the excited quartet states (d^3) or triplet states (d^6). For the E states, configuration interaction is taken into account, and the fraction of d_{z^2} is explicitly given in the Table. Expressions for d^3 systems follow eqns. (10) and (16). The d^6 analogs of these equations are simply obtained from the d^3 expressions by subtracting $2\pi_{ax}$ or $2\pi_{eq}$. (π acceptors have different π contributions, as elaborated in ref. 76.)

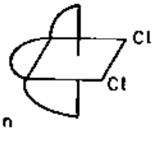
Table 5 shows a remarkable agreement between the model and experiment. Notwithstanding, thermodynamic implications of the I^* values should not be believed beyond reason. The I^* model is designed as a consistent bond-order model for coordination compounds within the framework of LF theory. Probably the relevant empirical essence of Table 5 is that a thrustworthy interpolation from one complex to another is possible, adequately embodied in the I^* indices.

Some interesting trends will now be noted.

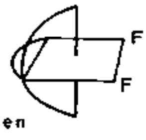
(a) Site discrimination in the I^* model is usually so large that violation of Adamson's first photolysis rule is very unlikely. An apparent exception is the *trans*$[Cr(en)_2F_2]^+$ case. Obviously the very large π bonding of the fluoro ligand is responsible for the unusual behaviour of this complex [73]. Poor polarization is also observed for *trans*$[Cr(en)_2(NH_3)NCS]^{2+}$ [97].

(b) Several complexes disobey Adamson's second photolysis rule while virtually none of them disobey the I^* rule. Weak-field acidoligands are usually good leaving groups, if coordinated at a Co(III) ion, because of decreased π bonding, compared to Cr(III).

(c) Nothing prevents the use of the I^* methodology to examine the reactivity



α-trien



tren

TABLE 5

Predicted and observed leaving ligand in tetragonal complexes

Complex	I^* (M–L) [a]			x	Leaving L predicted	Dominant leaving L observed	Ref.
ML_5X	I^* (M–X)	I^* (M–L_{ax})	I^* (M–L_{eq})				
$Cr(H_2O)_5NCS^{2+}$	13.58	12.88	8.93	0.000	$(H_2O)_{eq}$	(H_2O)	1 [b]
$Cr(NH_3)_5CN^{2+}$	18.12	14.36	8.98	0.000	$(NH_3)_{eq}$	NH_3	83
$Cr(NH_3)_5F^{2+}$	15.33	9.12	11.60	0.730	$(NH_3)_{ax}$	$(NH_3)_{ax}$	71–73, 84
$Cr(NH_3)_5NCS^{2+}$	8.94	8.74	11.79	0.783	$(NH_3)_{ax}$	NH_3	55
$Cr(NH_3)_5H_2O^{3+}$	8.61	8.59	11.86	0.803	NH_3, H_2O	NH_3	48 [c]
$Cr(NH_3)_5DMF^{3+}$	8.85	8.55	11.88	0.808	$(NH_3)_{ax}$	NH_3 > DMF	85
$Cr(NH_3)_5Cl^{2+}$	9.27	8.48	11.91	0.818	$(NH_3)_{ax}$	$(NH_3)_{ax}$	58, 86
$Cr(NH_3)_5Br^{2+}$	9.26	8.42	11.94	0.827	$(NH_3)_{ax}$	NH_3	48
$Co(NH_3)_5H_2O^{3+}$	8.75	9.07	13.03	0.838	H_2O	(H_2O)	87 [b]
$Co(NH_3)_5Cl^{2+}$	8.48	8.93	13.11	0.857	Cl^-	$NH_3 > Cl^-$	87 [d]
$Co(CN)_5OH^{3-}$	14.98	13.58	20.94	0.914	$(CN^-)_{ax}$	CN^-	89
$Co(CN)_5(NH_3)^{2-}$	7.98	12.81	21.32	0.978	NH_3	NH_3	48
$Co(CN)_5(N_3)^{3-}$	7.11	12.60	21.43	0.995	N_3^-	N_3^-	90
$Co(CN)_5(H_2O)^{2-}$	7.71	12.59	21.43	0.996	H_2O	(H_2O)	91, 92
$Co(CN)_5Cl^{3-}$	6.82	12.55	21.45	0.999	Cl	Cl^-	48
trans-ML_4XY	I^* (M–X)	I^* (M–Y)	I^* (M–L)				
trans-$Cr(NCS)_4(NH_3)_2^-$	14.36		9.15	0.000	NCS^-	NCS^-	1, 93
trans-$Cr(NH_3)_4(CN)_2^+$	17.54		8.98	0.000	NH_3	NH_3	82
trans-$Cr(NH_3)_4F_2^+$	15.49		11.52	0.709	NH_3	NH_3	60
trans-$Cr(NH_3)_4(H_2O)NCS^{2+}$	8.43	8.62	11.96	0.833	H_2O	(H_2O)	9, 94 [e]
trans-$Cr(NH_3)_4(NCS)Cl^+$	8.52	9.11	12.02	0.848	NCS^-	$NCS^- > Cl^-$	9, 94
trans-$Cr(NH_3)_4(H_2O)_2^{3+}$	8.32		12.03	0.851	H_2O	(H_2O)	9, 94 [e]
trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$	8.24	9.02	12.08	0.864	H_2O	(H_2O)	9, 94 [e]
trans-$Cr(NH_3)_4(DMF)Cl^{2+}$	8.49	8.99	12.09	0.869	DMF	DMF > Cl^-	85
trans-$Cr(NH_3)_4Cl_2^+$	8.94		12.12	0.877	Cl^-	Cl^-	9, 94
trans-$Cr(en)_2(CN)_2^+$	17.54		9.10	0.000	en	en	95

trans-$Cr(en)_2F_2^+$	15.42		11.71	0.718	en	en	59
trans-$Cr(en)_2(NH_3)F^{2+}$	9.05	15.26	11.79	0.739	NH_3	NH_3	71
trans-$Cr(en)_2(NCS)F^+$	9.01	15.00	11.91	0.773	NCS^-	NCS^-	9, 96
trans-$Cr(en)_2(NH_3)NCS^{2+}$	8.67	8.88	11.98	0.792	NH_3	NH_3, en	97
trans-$Cr(en)_2FCl^+$	14.73	9.33	12.04	0.808	Cl^-	Cl^-	70, 71
trans-$Cr(en)_2(NCS)_2^+$	8.68		12.09	0.823	NCS^-	NCS^-	9
trans-$Cr(en)_2(NH_3)Cl^{2+}$	8.43	9.23	12.11	0.826	NH_3	NH_3	57
trans-$Cr(en)_2(NCS)Cl^+$	8.48	9.06	12.21	0.855	NCS^-	$NCS^- > Cl^-$	98
trans-$Cr(en)_2Cl_2^+$	8.90		12.32	0.884	Cl^-	Cl^-	99,100
trans-$Cr(en)_2Br_2^+$	8.89		12.37	0.897	Br^-	Br^-	99
trans-$Co(en)_2(CN)Cl^+$	18.24	10.53	12.00	0.531	Cl^-	Cl^-	101
trans-$Co(en)_2(NH_3)Cl^{2+}$	8.82	8.39	13.35	0.871	Cl^-	$NH_3 > Cl^-$	102
trans-$Co(en)_2(H_2O)Cl^{2+}$	8.13	8.01	13.59	0.932	Cl^-, H_2O	(H_2O)	103 [b]
trans-$Co(en)_2Cl_2^+$	7.93		13.64	0.945	Cl^-	Cl^-	87
trans-$Co(CN)_4(OH)_2^{3-}$	14.24		21.40	0.991	OH^-	(OH^-)	39
trans-$Co(CN)_4(H_2O)_2^-$	7.68		21.41	1.000	H_2O	(H_2O)	39 [b,f]
cis-ML_4X_2	I^* (M–X)	I^* (M–L_{eq})	I^* (M–L_{ax})				
cis-$Cr(NH_3)_4(CN)_2^+$	14.45	11.87	8.57	0.806	$(NH_3)_{ax}$	NH_3	104
cis-$Cr(NH_3)_4F_2^+$	15.18	9.98	14.36	0.000	$(NH_3)_{eq}$	NH_3	60
cis-$Cr(NH_3)_4Cl_2^+$	9.65	8.98	14.36	0.000	$(NH_3)_{eq}$	$NH_3 > Cl^-$	105
cis-$Cr(en)_2(CN)_2^+$	14.42	12.01	8.73	0.801	$(en)_{ax}$	en	95
cis-$Cr(en)_2(H_2O)_2^{3+}$	10.13	9.10	14.56	0.000	$(en)_{eq}$	en > H_2O	1
cis-$Cr(en)_2Cl_2^+$	9.65	9.10	14.56	0.000	$(en)_{eq}$	en	100
cis-$Co(CN)_4(OH)_2^{3-}$	16.55	15.58	24.30	0.000	$(CN^-)_{eq}$	CN^-	38
cis-$Co(CN)_4(H_2O)_2^-$	9.33	15.58	24.30	0.000	H_2O	(H_2O)	39 [e]
cis-$Co(en)_2Cl_2^+$	9.15	9.90	15.84	0.000	Cl^-	Cl^-	103

---

[a] In 10^3 cm^{-1}; x is the fraction of d_{z^2}, calculated according to [76], using AOM parameters of Table 1. CN^- is treated as a π-donor in Co(III) complexes. [b] Unusual photoinertness is taken as an indicator of H_2O exchange. [c] H_2O photolysis is not unlikely, given a rather low quantum yield for NH_3 aquation and the behaviour of the comparable $Cr(NH_3)_5DMF^{2+}$ [85]. [d] See however ref. 88. [e] Efficient photoisomerization points to H_2O loss. [f] Configuration interaction is so large, that the approximate method to estimate x is no longer valid.

of other excited states. Indeed wavelength dependence studies indicate that direct excitation in the high-energy tail of the first LF band can promote side reactions, that are of opposite labilization to the dominant photochemistry. This effect has been observed in several cases, e.g. *trans*$[Cr(en)_2(NH_3)Cl]^{2+}$ [57] and *trans*$[Cr(en)_2(NCS)Cl]^+$ [98].

(d) LF arguments cannot be supposed to incorporate steric factors. Blocking a good leaving ligand through steric hindrance can reverse the leaving ligand order. This seems to be the case in *cis*-$\alpha[Cr(trien)Cl_2]^+$ where Cl^- is a good leaving ligand [105] as opposed to other *cis*-dichloro amines (Table 5). Sheridan and co-workers [106] have also studied the somewhat similar *cis*$[Cr(tren)F_2]^+$. In solutions of fairly high acidity, this complex efficiently releases F^-, in contrast to predictions in Table 5. However in this case only one of the labilized Cr–N bonds is susceptible to the 'anchoring effect'. The authors [106] have suggested that this complex should be treated with the orthorhombic formalism. One could indeed anticipate [77] F^- labilization if the tertiary amine is a weaker σ-donor than the primary amine.

(e) Many more examples are available in Rh(III)- and Ir(III)-photochemistry [49]. Again in these cases Adamson's first photolysis rule appears to be quite well obeyed. A correct prediction of the leaving ligand order is difficult since no reliable two-dimensional spectrochemical series has been resolved. Some specific features have to be noted though. The efficiency of halo ligand labilization decreases sharply from Cl^- to I^-, in contrast to first row (hard Lewis acid) metal ions [53,62,107]. The Rh(III)–en bond is remarkably photoinert [108]. This is especially puzzling since in the case of Cr(III) complexes en is even more photolabile than NH_3 [9].

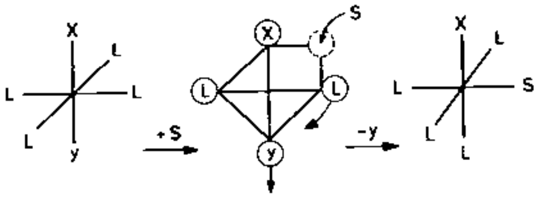
In summary the leaving ligand in the photo exchange of coordination complexes appears to be quite well describable by a LF analysis. Apparently different types of thermodynamic 'influences' [109] that are so often invoked to explain thermal behaviour, are of minor importance here.

E. PHOTOSTEREOCHEMISTRY

(i) Kirk's rule and the first generalizations

Soon after the formulation of the photolysis rules the question arose whether these rules had any stereochemical implications or not [86,110,111]. Clearly Adamson's original formulation observes a strict reticence regarding positional preferences of the entering solvent molecule. The first stereochemical studies on Cr(III) compounds came as a great surprise, since it turned out that the photosubstitution reactions are extremely stereospecific; moreover, they are stereospecific in a counterintuitive way, at least if the ubiquitous [112] stereoretention of the ground state is considered normative.

These observations led Kirk to the formulation of the following stereo-



chemical rule [113]: "The entering ligand will stereospecifically occupy a position corresponding to entry into the coordination sphere *trans* to the leaving ligand". Strictly speaking, this rule is not an empirical proposition, since it is biased towards a specific substitution mechanism, the edge displacement. As an example, consider an axially labilized *trans* complex, where Y is the leaving ligand upon *trans* entry of a solvent molecule S (see eqn. 17). A *cis* solvento complex results, and the reaction is 100% stereomobile.

Stereochemical aspects of photosubstitutions in strong field d^6 complexes have only been studied much more recently. In 1977 Strauss and Ford [114] reported the first clearcut example of a concomitant substitution and isomerization in a d^6 complex, thus proving that ligand exchange reactions of d^6 complexes could be completely stereomobile.

In 1978 we summarized the then existing empirical evidence on d^3 and d^6 systems in a very concise table [115,116–118] (cf. Table 6). All data referred to solvolysis of mono- and di-substituted octahedra. In all cases effective tetragonal symmetry applied, so that Table 6 was divided into axial and equatorial labilization. An obvious lacuna had to be tolerated since all experimental tests of Kirk's rule were restricted to axial labilization. This may not be too surprising. Indeed, while *cis*- and *trans*-photoproducts are fairly easily distinguished spectroscopically, separation and determination of more complex isomers like CrL_3X_2S which are potential photoproducts of equatorial labilization, is a much more difficult task.

TABLE 6

Resumé of photostereochemistry up to 1978 [a]

	d^3: Cr(III)	d^6: Co(III), Rh(III), Ir(III)
Axial labilization	Stereomobility in all cases	Stereoretention in all cases
ML_5X *trans*-ML_4XY	*cis*-ML_4XS	*trans*-ML_4XS
Equatorial labilization		Stereomobility in most cases
cis-ML_4X_2	?-ML_3X_2S	*trans*-ML_4XS

[a] Taken from ref. 118. L is a strong σ donor, X and Y are weak-field ligands and S the incoming solvent molecule.

The table represents an obvious challenge to the development of new selection rules. Since then a general theory of photostereochemistry in d^3 and d^6 complexes has been proposed [117–119]. It will be reviewed in detail in the following paragraphs, together with a survey of experimental results; in the last three years new results have been obtained and many blanks have been filled in what is now a rich and complex pattern of reaction schemes. Still inorganic photostereochemistry is in a youthful stage [9] and many more cases, other than the ones considered in Table 6 await further exploration.

(ii) The question of the mechanism

Table 6 is of obvious simplicity. Whenever chemical reactions exhibit such a pronounced stereoregularity, one could think of two possible explanations, based on either mechanistic or electronic selectivity.

A mechanistic explanation can be invoked, whenever the mechanism leads to only one product isomer. Examples are the edge displacement mechanism in a square-planar complex, proceeding through a trigonal bipyramidal (TBP) intermediate [51,120], or the associative mechanism for thermal substitution of octahedral complexes via an octahedral wedge [121]. In both cases stereoretention is almost a trivial feature of the mechanism.

Electronic selection rules on the other hand, are likely to operate whenever a mechanism allows for several isomeric products but when actual product ratios do not obey the mechanistic statistics. Electronic selection rules have been known since the early beginnings of molecular quantum mechanics, but it cannot be denied that they have received a new impetus and a very different content since the work of Woodward and Hoffmann which has profoundly influenced modern organic chemistry [122]. In inorganic chemistry strict stereoregularity is the exception rather than the rule and the complexes of Table 6 therefore constitute a fortunate assembly; they provide a test case as to whether or not selectivity in the Woodward–Hoffmann sense can be found here too, or if a mechanistic explanation applies.

In fact, as such, both the associative and the dissociative limiting mechanisms should clearly produce statistical mixtures of isomers. In neither case, are the statistical ratios of these isomers compatible with Table 6. This is especially true for the associative mechanism, although for some reason, stereomobility was originally considered an argument in favour of that mechanism [113]; this issue has obscured the subsequent debate on the photomechanism in Cr(III) photochemistry.

No single mechanistic hypothesis by itself explains the regularities of Table 6; the question of an associative versus a dissociative transition state remains unanswered from the purely stereochemical point of view. But even more generally, experimental evidence apparently rarely offers unequivocal support for any given mechanistic proposal. Thermodynamic and kinetic studies report macroscopic variables, which are somehow related to the intimate reaction process, but the link is usually far from simple or direct.

For d^6 systems there is fairly strong evidence that the photosubstitution proceeds via a dissociative mechanism, but there are also several indications to the contrary. For instance, there is no apparent correlation between rate constants for the photosubstitution reaction and the Gutmann donor number for the entering ligand [123], a general observation pointing towards a dissociative mechanism. But on the other hand, in one case, $[Rh(NH_3)_5Cl]^{2+}$, the leaving ligand order can be reversed, depending on the solvent [6,123].

The study of solvent effects on photosubstitution reactions of Cr(III) complexes is more complex and has less diagnostic value. Krause and Wasgestian studied the competition between chloride anation and aquation of irradiated $[Cr(NH_3)_6]^{3+}$ [124]. The total quantum yield for NH_3 loss was remarkably constant over the whole range of Cl^- concentration. One might be inclined to interpret this independence of entering ligand as an indication in favour of a primary dissociative event, in agreement with Zink's interpretation of Adamson's rules. However recent pressure dependence studies on a series of $[Cr(NH_3)_5X]^{2+}$ complexes ($X = Cl^-$, Br^-, NCS^-) reported negative activation volumes. On this basis a seven-coordinated structure was postulated, although with some degree of bond weakening of the leaving ligand in the transition state [125]. A more cautious appraisal of similar experimental studies was made by Langford and Tong [126]. They pointed out that the role of an entering ligand in a photoreaction is different from its behaviour in a thermal activation process and probably more subtle than experience with thermal reactions has revealed.

Another commonly applied strategy in the experimental assessment of a mechanism is to introduce steric hindrance. Kutal and Adamson investigated the influence of the cyclam ligand, a bulky tetradentate group [127,128]. *Trans*$[Cr(cyclam)Cl_2]^+$ turned out to be one of the only exceptions to the stereomobility rule for axially labilized Cr(III) complexes (Table 6), but quite remarkably, this complex is almost photoinert and so is, to a lesser extent, *cis*$[Cr(cyclam)Cl_2]^+$. On the other hand steric hindrance has no pronounced effect on the efficiency of photoprocess in Rh(III) complexes with bulky ligands, such as cyclam, bipy or phen [129–131]; these complexes are photoactive though quite understandably they do not isomerize, also in exception to Table 6. Hence stereochemical change seems to be a condition sine qua non for d^3 but not for d^6 photochemistry.

Versus this complex experimental background, the outcome of a theoretical model represents a remarkably unified picture of both d^3 and d^6 photostereochemistry. A limiting associative mechanism could not be reconciled with the photolysis rules and failed to produce electronic selection rules

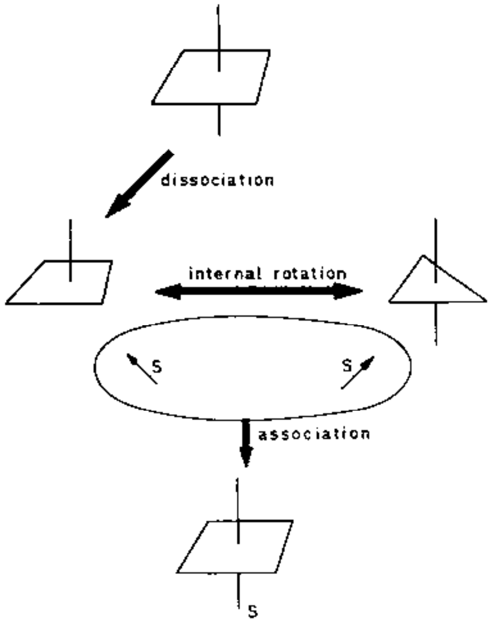


Fig. 3. General three-step mechanism of photosubstitutions in hexacoordinated complexes.

in agreement with the observed stereomobility, so that a dissociative reaction mechanism was adopted. Formally a dissociative mechanism is dissected in three steps. Upon photolysis, all cases in Table 6 give rise to one archetypal fragment, a square pyramid (SPY) ML_4X, where X is either apical (from axial labilization) or basal (from equatorial labilization). Next the internal rotation of this structure and the formation of trigonal bipyramid (TBP) structures are investigated. Finally the third step restores a hexacoordinated structure through association of a solvent molecule on TBP or SPY fragments. The overall process is schematically represented in Fig. 3. The vast majority of experimental facts can be explained by referring to orbital control in the pathways of Fig. 3. The way control is exerted depends on the number of *d* electrons and will be reviewed in subsequent paragraphs.

(iii) The Woodward–Hoffmann approach in inorganic photochemistry

The analysis of the different steps proceeded according to very simple principles, which can be looked upon as specifications of the Woodward–Hoffmann approach, and also Fukui's HOMO–LUMO concepts [132], to structural changes of the coordination sphere.

(a) An occupied *d* orbital pointing towards a ligand will tend to expel this ligand or shift its angular position.

(b) Unoccupied d orbitals attract these ligands or point in the direction of favoured nucleophilic attack from outside the first coordination sphere.

(c) Ligand motion and d orbital control are interrelated in that the changing LF potential can generate interactions between the d orbitals and a corresponding change of the orbital shape. The application of the above principles can only be realized in a state correlation diagram. Many-electron LF theory seems to be the suitable level of sophistication to construct these diagrams [117–119].

(iv) d^3 Complexes

The pathways in Fig. 3 have been extensively studied so that a reliable description of the underlying orbital rationale could be obtained [117–119]. We present here an attempt to generalize these results and to summarize them in a set of operational rules.

(a) It is remembered from eqn. (2) that the excitation to the lowest excited quartet state corresponds to an in-plane rotation of d-electron density: ($xy \rightarrow x^2 - y^2$), or alternatively ($xz \rightarrow x^2 - z^2$; $yz \rightarrow y^2 - z^2$). One consequence is the expulsion of a Y ligand but at the same time the other ligands are labilized as well and they will try to rearrange so as to match the vacant

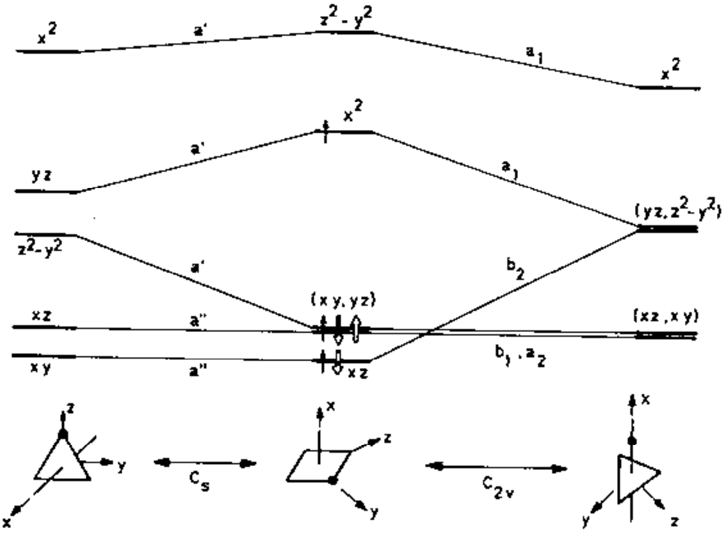
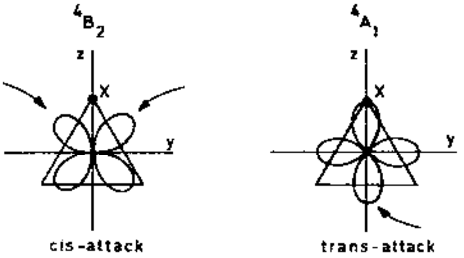


Fig. 4. Schematic d orbital correlation diagram for the two possible rearrangements of a SPY fragment, containing one basal weak-field heteroligand. Orbital occupation corresponds to the lowest excited quartet $((x^2)(xz)(yz))$ or triplet state $((x^2)(xy)(yz)^2(xz)^2)$ for a d^3 or d^6 metal ion respectively. In both cases the C_s path is orbitally allowed and the C_{2v} path is forbidden.



cis-attack trans-attack

Fig. 5. Lowest unoccupied d orbitals in the equatorial TBP plane for $^4B_2$ and $^4A_1$ states respectively. Arrows indicate directions of favorable nucleophilic attack for each state.

t_{2g} orbital. Out-of-plane rotations are orbitally forbidden since the remaining t_{2g} electrons occupy the available space. Figure 4 offers an illustration of this selectivity. The SPY fragment, formed upon dissociation of X in equatorially labilized *cis*-CrL_4X_2 (secondary reaction) can only reach a TBP with equatorial X. This is typical Woodward–Hoffmann type selectivity, comparable to well known organic cases, such as the ring opening of cyclobutenes. The concepts of allowedness and forbiddenness receive their meaning through a comparison of two alternative isomeric forms of one and the same molecular species.

At the state level the internal rotation is exothermic and can be expected to assist ligand loss, as confirmed in the cyclam experiment. In summary, SPY structures will spontaneously stabilize to a TBP structure, according to the rule: *Consider the plane of excitation. In the lowest excited quartet, this is the plane formed by the two axes of weakest average field [77]. Upon removal of the leaving ligand from this plane, the resulting T shape structure will rearrange to an equilateral triangle. The perpendicular axis is conserved. If there are two equivalent weak-field planes, the rule yields the same result when applied to either one of them.*

(b) Next consider the electronic structure of a TBP. It has two frontier orbitals, one of which is occupied (Fig. 4; yz and z^2-y^2). In D_{3h} they are degenerate, giving rise to a $^4E'$ ground state. The interesting case occurs if the equatorial triangle has C_{2v} symmetry, i.e. if it contains two different types of ligands, two L and one X (the heteroligand). $D_{3h} \rightarrow C_{2v}$ symmetry reduction causes a splitting of the $^4E'$ into two components: $^4A_1$ and $^4B_2$. Now $^4B_2$ corresponds to the occupation of z^2-y^2, the orbital directed towards the heteroligand X, while $^4A_1$ corresponds to the occupation of yz, the orbital directed towards the two L ligands (Fig. 4). Surprisingly the splitting between $^4A_1$ and $^4B_2$ is again determined only by the difference in spectrochemical strength 10 Dq (compare also Fig. 2 and eqn. 3).

$$E(^4A_1) - E(^4B_2) = \tfrac{1}{4}(10\,Dq_{\mathrm{L}} - 10\,Dq_{\mathrm{X}}) \qquad (18)$$

Now the second rule determines which one of these two components will be reached: the result depends on the symmetry of the movement within the triangle (independent of the axial ligands).

If the rearrangement $T \rightarrow \Delta$ does not conserve symmetry elements, other than the plane in which the motion takes place, the TBP will be reached in its first excited state. If the motion has C_{2v} symmetry, a $^4B_2$ is reached. This will be the ground or excited state, depending on whether the ligand on the diagonal axis has the weaker field or not.

(c) The TBP could isomerize further to the complementary SPY ground-state but at the same time it is very susceptible to nucleophilic attack. A concerted pathway from TBP to hexacoordinated endproduct is therefore

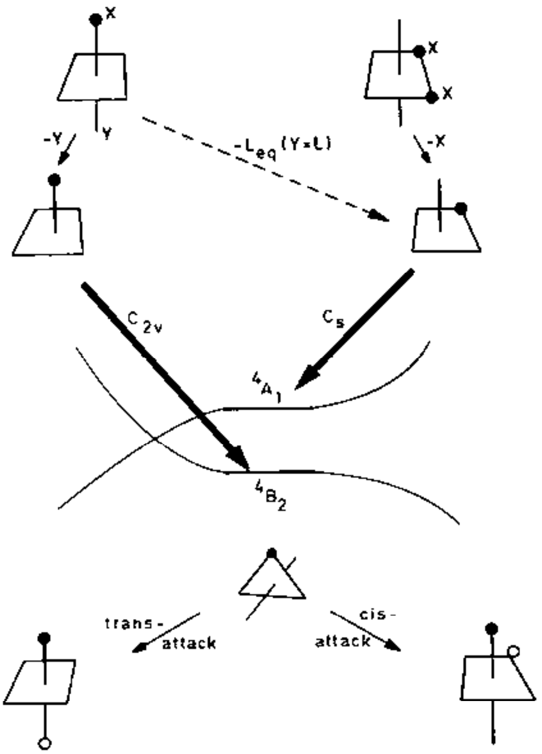


Fig. 6. Pattern of photosubstitutions in mono- and disubstituted chromium(III) complexes, as predicted from the three stereochemical rules. X is assumed to be a weak-field ligand. The relevant part of the correlation diagram for the association reactions of the TBP is included. Three possible reactions are envisaged: (i) Y loss from an axially labilized *trans*-CrL_4XY leads to a *cis*-CrL_4XS product via a C_{2v} path; (ii)X loss from equatorially labilized *cis*-CrL_4X_2 gives rise to a *trans* product via a C_s path. (iii) The dashed line represents subsidiary equatorial L loss from the predominantly axially labilized complex in its ^4E_g excited state. In case Y = L, this pathway leads to the same SPY intermediate as considered sub (ii), and ultimately to the same photoproducts.

more realistic. If the TBP structure has C_{2v} symmetry the same predictions will prevail, irrespective of the degree of concertation. Figure 5 represents the limit of pure association. This case can also be treated by using Fukui's orbital approach [117]. In the $^4A_1$ state the vacant $z^2 - y^2$ lobes preferentially attract incoming ligands in the *trans* position, whereas the $^4B_2$ state is *cis*-directing. These conclusions are summarized in a third rule: *If the TBP is in its ground state, an incoming nucleophile has preferential access* trans *to the strongest equatorial ligands. The excited state favours attack on the complementary sites.*

These rules can now be confronted with a large set of experimental data. Consider the general case, presented in Table 6 where X and Y are weak field ligands; the predicted stereochemistry is summarized in Fig. 6. From the Fig. 6 the central TBP can be seen to act as a traversing platform with two oppositely polarized reaction possibilities. One important complication arises. The process which takes place via the excited state can be expected to be subject to competing deactivation to the ground state. This branching scheme will limit the stereochemical purity of the product, and hence the predictive power of the model [119]. The most important and best docu-

TABLE 7

Photostereochemistry of axial labilization in tetragonal Cr(III) complexes

$Cr(NH_3)_5X^{n+} + S \xrightarrow{h\nu}$ *cis*-$Cr(NH_3)_4XS^{n+} + NH_3$

X:	NCS	DMF	OCOR.	F	Cl	Br
Ref:	111	85	[a] 133	71, 84	86	134

trans-$Cr(NH_3)_4XY^{n+} + S \xrightarrow{h\nu}$ *cis*-$Cr(NH_3)_4XS^{n+} + Y$

XY:	Cl–Cl	Cl–H_2O	Cl–NCS	Cl–DMF	NCS–H_2O	H_2O–H_2O
Ref:	94	94	94	85	94	94

trans-$Cr(en)_2XY^{n+} + S \xrightarrow{h\nu}$ *cis*-$Cr(en)_2XS^{n+} + Y$

XY:	F–NH_3	F–Cl	Cl–Cl	Cl–NH_3	Cl–NCS	NCS–NCS	Br–Br
Ref:	71	71	99	57	98	9, 135	99

trans-$Cr(2,3,2\text{-tet})Cl_2^+ + S \xrightarrow{h\nu}$ *cis*-$Cr(2,3,2,\text{tet})Cl(H_2O)^{2+} + Cl^-$ [128]

trans $Cr(NH_3)_5OHCr(NH_3)_4H_2O^{5+}$

$\Big\rangle \xrightarrow{h\nu}$ *cis*-$Cr(NH_3)_5OHCr(NH_3)_4H_2O^{5+}$ [b] [136]

trans-$Cr(NH_3)_5OHCr(NH_3)_4Cl^{4+}$

[a] R = CF_3, CCl_3, $CHCl_2$, CH_2Cl, CH_3. [b] Also NH_3-loss is reported but the product stereochemistry is unknown.

mented application of the previous considerations is the case of axial labilization. From Fig. 6, axially labilized complexes are not complicated by branching possibilities and should give rise to 100% *cis* products. Indeed, as expressed by Kirk's empirical rule, the experimental evidence for the almost exclusive formation of *cis* products is now overwhelming: in fact, *trans*$[Cr(cyclam)Cl_2]^+$ is the only exception [127]. A survey of the experimental data is given in Table 7 [133–136].

In contrast, the experimental study of *cis*-CrL_4X_2 meets many problems. In those cases, where subsidiary X-loss is reported, the extent of stereomobility is uncertain. For instance, for *cis*$[Cr(NH_3)_4Cl_2]^+$, production of *trans*$[Cr(NH_3)_4(H_2O)Cl]^{2+}$ has been estimated at a maximum of 8% of the total(?) photoproduct, or 25% of CrL_4XS-product [105], but on the other hand, efficient *cis* → *trans* photoisomerization was reported for *cis*$[Cr(en)_2(H_2O)_2]^{3+}$ [1,5].

The photolysis of the reineckate, *trans*$[Cr(NH_3)_2(NCS)_4]^-$, should constitute a simple test case for the first stereochemical rule, not incorporated in Table 6. The lowest excited quartet state involves excitation in the weak-field sulfocyanate plane. NCS^- is predicted to be the leaving ligand (as confirmed in Table 5) and the amine axis is expected to be conserved throughout the reaction sequence. Unfortunately the stereochemistry has never been solved; quoting from Balzani and Carassiti, "the photoaquation sometimes seemed to be different from the thermal one" [ref. 1, p. 93] an ambiguity which persists today. In recent years new information has been gathered on several complexes containing fluoro and cyano substituents. These studies constitute an impressive piece of research, mainly carried out by Kirk and Zinato, and their respective co-workers. The data do not follow the pattern in Table 6 because the unusual LF parameters of the substituents (both for F^- and CN^-, the σ-parameter is larger than for NH_3). This allows one to investigate the stereorules (a–c) in more detail.

First consider the monofluoropentamine-complex [71–73,84]. Dominant axial NH_3 loss leads to a *cis* product, as already tabulated in Table 7. Interestingly, equatorial amine loss may occur as a minor product of the same ^4E_g excited state. Unfortunately no separate identification of the isomer ratio in the product of the equatorial mode is possible, unless radioisotopes are used. Assuming that the axial mode is 100% stereo mobile, and furthermore that the ratio ϕ_{ax}/ϕ_{eq} is comparable (see however ref. 72) to ϕ_{NH_3}/ϕ_{en} in *trans*$[Cr(en)_2(NH_3)F]^{2+}$ ($\phi_{NH3} = 0.254$, $\phi_{eq} = 0.07$) one has for irradiation with 546 nm light at 10°C [71]

$$Cr(NH_3)_5F^{2+} \overset{h\nu}{\rightarrow} 85\%\, \mathit{trans}\, Cr(NH_3)_4F(H_2O)^{2+} + 15\%\, \mathit{cis}\, Cr(NH_3)_4F(H_2O)^{2+}$$

$$\begin{array}{lll} \mathrm{Cr(NH_3)_5F^{2+}} & \xrightarrow{78.4\%} & cis\,\mathrm{Cr(NH_3)_4F(H_2O)^{2+}} + (\mathrm{NH_3})_{ax} \\ & \searrow^{21.6\%} & \\ & & 30\%\ cis\,\mathrm{Cr(NH_3)_4F(H_2O)^{2+}} + \\ & & 70\%\ trans\,\mathrm{Cr(NH_3)_4F(H_2O)^{2+}} + (\mathrm{NH_3})_{eq} \end{array} \tag{19}$$

The possibility of an equatorial mode in ^4E_g is indicated by a dotted line in Fig. 6. In contrast to the axial mode, a C_s-symmetry path now leads to the excited TBP state [119]. Hence the third stereo rule predicts a *trans* product, in agreement with experiment, although no strict stereoregularity is required, because of the branching process discussed earlier. Prompt photoreaction

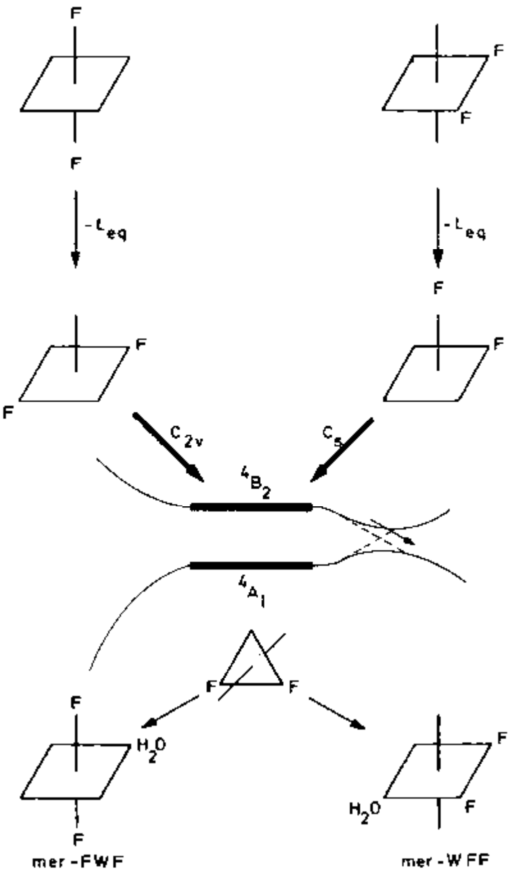


Fig. 7. Stereochemistry of amine photosubstitution in *trans*- and *cis*-difluoro tetramine chromium(III) complexes. In both cases application of the second stereo rule predicts formation of the $^4B_2$ state. From this state the *mer* WFF isomer is reached preferentially. No *fac* isomer can be formed.

from the higher excited $^4B_{2g}(xy \rightarrow x^2 - y^2)$ state would produce *cis* product as well. Parenthetically, we note that F^- loss from *cis*$[Cr(NH_3)_4F_2]^+$ would lead to the same photoproducts, since the same SPY fragment is involved. A photolyzed solution of *cis*$[Cr(NH_3)_4F_2]^+$ indeed contains small fractions of *cis*- and *trans*$[Cr(NH_3)_4(H_2O)F]^{2+}$, but since the dominant mode is NH_3 loss, accurate determination of the fluoro–aquo products is virtually impossible [60]. Subsequent to less conclusive studies [137,138] on *trans*$[Cr(en)_2F_2]^+$, Kirk and Frederick [60] demonstrated that for both difluoro complexes, amine photolysis (at 577 nm) leads almost exclusively to meridional isomers [60].

$$\textit{trans}\text{-}Cr(NH_3)_4F_2^+ \xrightarrow{h\nu} 30\%\ \textit{mer}\text{-FWF} + 70\%\ \textit{mer}\text{-WFF} + \ldots$$

$$\textit{cis}\text{-}Cr(NH_3)_4F_2^+ \xrightarrow{h\nu} 45\%\ \textit{mer}\text{-FWF} + 55\%\ \textit{mer}\text{-WFF} + \ldots \qquad (20)$$

In eqn. (20) *mer*-FWF stands for 1,6-difluoro-2-aquotriamine chromium(III) and *mer*-WFF for 1,2-difluoro-6-aquotriamine chromium(III). Kirk has applied the methodology developed here to this system; his findings are in agreement with the reaction pattern in Fig. 7. No facial isomer is formed, since the precursor of such an isomer would be TBP with one axial and one equatorial F^- substituent, which is strongly disallowed by the first stereo rule. According to Kirk [9], the correct application of his original edge-displacement proposal (see section E (i)) would predict a predominancy of the *fac* isomer, clearly in contrast to the observations. The provenance of the small amount of *fac* isomer, present in a photolyzed solution of *cis*$[Cr(NH_3)_4F_2]^+$, could well be the higher excited ^4E_g state, as suggested by wavelength dependence studies [60].

From Fig. 7, it is not surprising that the meridional products, that are actually formed, show a somewhat random distribution, with a preference for 1,2-difluoro-6-aquotriamine. A possible criticism of the model argues that both *cis* and *trans* complexes are predicted to give rise to the same product ratios, since the same precursor state intervenes. However, one should note that this precursor state is attained via two different pathways, of C_{2v} and C_s symmetry for the parent *trans* and *cis* compounds respectively.

The C_s path is characterized by an avoided crossing; the C_{2v} path is not. The dynamics of excited state deactivation along these potential curves are far outside the range of this simple model, but it is not an unreasonable conjecture to suppose that the TBP ground state plays a more significant role in photochemistry of the *cis* complex, because of the intended state correlation. This would be in line with the reported stereochemistry.

The photochemistry of the analogous *cyano*-complexes is somewhat complementary to the fluorosystem [82,83,104]

$$\mathrm{Cr(NH_3)_5(CN)^{2+}} \xrightarrow{h\nu} 66\%\ cis\text{-}\mathrm{Cr(NH_3)_4(CN)(H_2O)^{2+}}$$

$$+\,34\%\ trans\text{-}\mathrm{Cr(NH_3)_4(CN)(H_2O)^{2+}}$$

$$trans\text{-}\mathrm{Cr(NH_3)_4(CN)_2^{+}} \xrightarrow{h\nu} 70\%\ mer\text{-}\mathrm{CN,W,CN} + 30\%\ mer\text{-}\mathrm{W,CN,CN}$$

$$cis\text{-}\mathrm{Cr(NH_3)_4(CN)_2^{+}} \xrightarrow{h\nu} 70\%\ fac\text{-}\mathrm{CN,W,CN} + 30\%\ mer\text{-}\mathrm{W,CN,CN} \qquad (21)$$

(The convention of eqn. 20 is used and *fac*-CN,W,CN stands for 1,2-dicyano-3-aquotriamine chromium(III).)

The mono-cyano and *trans*-dicyano complexes should exhibit a simple photochemistry. According to the first stereo rule the lower excited state ($^4B_{2g}$) involves excitation in the NH_3 plane, leading to *cis*[$\mathrm{Cr(NH_3)_4(H_2O)CN}$]$^{2+}$ and *mer*-1,6-dicyano-2-aquotriamine chromium(III) respectively. These are indeed predominant products, but in both cases another isomer is observed as well. ^4E_g-photochemistry would

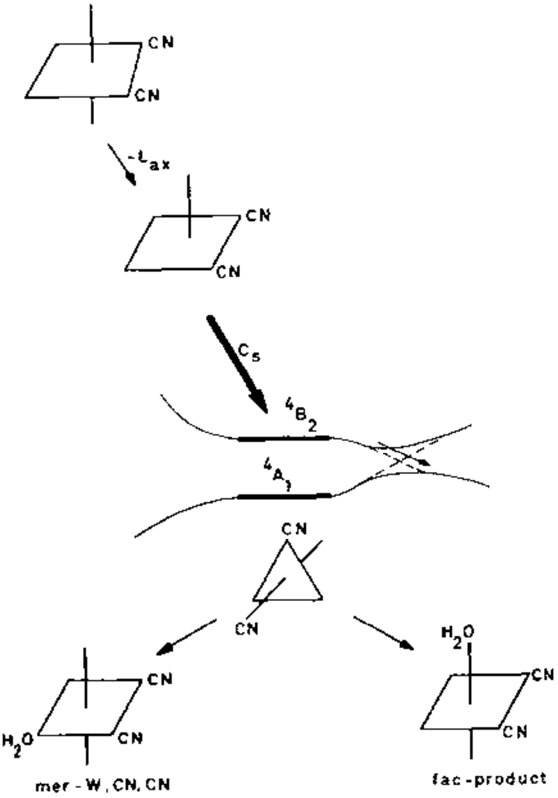
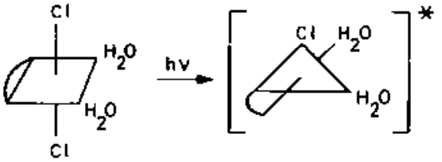


Fig. 8. Photostereochemistry of axial amine loss in *cis*-dicyanotetramine chromium(III). The *fac* isomer is predicted to be the predominant product.

lead to a mixture of *cis* and *trans* products in the case of the mono-cyano compound and uniquely to the alternative *mer* isomer in the case of the *trans*-dicyano complex. In this latter case the second stereo rule predicts correlation to a TBP ground state, and hence high stereo selectivity can be expected. No spectrospecificity of the isomer yields is observed, but the first LF band is broad and structureless; the $^4B_{2g}$ and ^4E_g components cannot be resolved [82,83]. The small amount of photolyzed cyanide in the case of *trans*$[Cr(en_2)(CN)_2]^+$ might indicate that the ^4E_g-state indeed participates in the photochemistry [95]. In this respect, photolysis of *trans*$[Cr(en)_2(NH_3)CN]^{2+}$ might be instructive, since axial amine loss acts as an indicator for ^4E_g reactivity.

Finally the *cis*-dicyano complex is expected to react via its ^4E_g state. Now indeed the *fac* isomer is observed and correctly predicted, together with a smaller amount of only one meridional isomer, as indicated in Fig. 8.

So far the stereo rules have been applied to a TBP intermediate with "in



(22)

plane" C_{2v} symmetry. One isolated observation urges us to examine a less symmetric TBP intermediate. Walters and Linck investigated the photolysis of 1,6-dichloro$[Cr(en)(H_2O)_2Cl_2]^+$ [139]. In spite of its low microsymmetry this complex still has D_{4h} holohedral symmetry (if the en bridge is neglected) and could be incorporated in Table 5 as an example of an axially labilized tetragonal complex, and indeed Cl^- equation is correctly predicted. Interestingly the two possible mono-chloro products are formed to almost equal extents. Now applying the first and second stereo rule, we end up with an excited state of a TBP with three different triangular ligands. Following foregoing experience, both the excited and ground state of the TBP can be assumed to be populated and hence once again the observed non-selective product isomer composition is not unexpected.

Overlooking the experimental evidence, it should be clear that the stereo rules proposed here are not intended as empirical generalizations, but they simply express the rationale behind the general methodology. The first stereo rule implies a strict site selectivity which appears to be very well obeyed. Further, the second and third rules apparently do not lead to high stereospecificity if a TBP excited state is involved. In that case some ground state reactivity is observed as well. Finally, the wavelength dependent observation of subsidiary isomers suggests that the photochemical Kasha rule, adopted by Zink as a working hypothesis (see section D (ii)) is only of limited validity.

The orbital model offers an appealing picture of the origins of stereomobility. The excitation consists of in-plane rotation of electron density and the excited system can only successfully restore the ground state in a chemical pathway, if ligand motion involves some kind of counter rotation. In this sense also octahedrons with six equal ligands are expected to react in a stereomobile way. A recent observation of Cimolino and Linck provides interesting information in this respect [140]. They examined the photo aquation of Λ-$[Cr(en)_3]^{3+}$ and found a large fraction of *trans*$[Cr(en)_2(enH)(H_2O)]^{4+}$. This process can be expected to be less influenced by electronic factors than by steric factors and therefore it does not really put the stereo rules to test. However the use of optical activity to study the photochemistry of substituted complexes offers an attractive new perspective.

(v) d^6 Complexes

Returning to the general mechanism in Figs. 3 and 4, we now consider the effect of adding three more *d* electrons [118]. A number of important differences immediately appear. One single triplet curve correlates the photo-

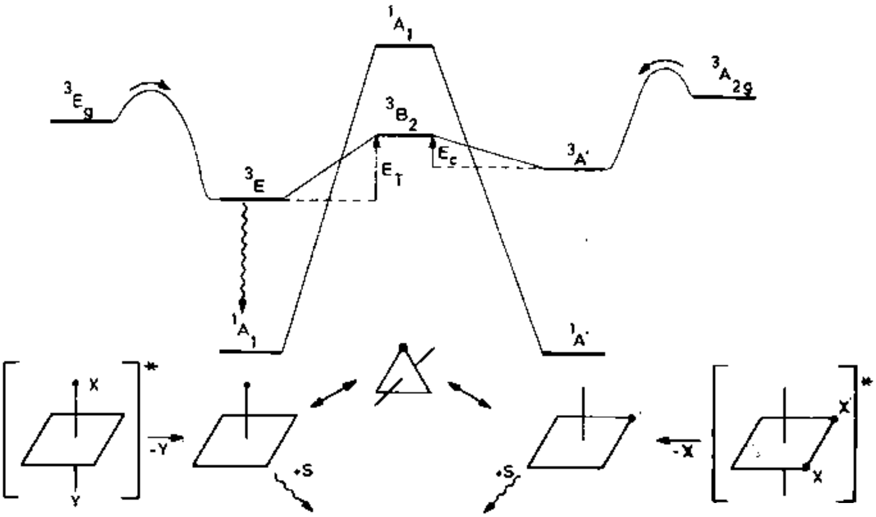


Fig. 9. General excited state reaction scheme for tetragonal d^6 complexes. The photo active states of the hexacoordinated complexes (^3E_g or $^3A_{2g}$) correlate with the lowest excited triplet states of SPY structures. These structures can interconvert through internal rotation along a common triplet curve. The $^3B_2$ (TBP) acts as a transition state, E_T and E_C being respective barrier heights for the rearrangement process. The SPY* ↔ SPY* isomerization will compete with intersystem crossing to the SPY singlet ground states, wherefrom solvent anation spontaneously restores hexacoordination.

active states of both SPY structures. They correspond to local minima around the common TBP transition state. Nowhere in the triplet state, is a vacant orbital available to facilitate nucleophile attack. In fact, the only species able to restore the low-spin ground state of the hexacoordinated products is the singlet SPY ground state, via a vacant orbital on its empty coordination site [141]. This association therefore presupposes triplet → singlet intersystem crossing in the five-coordinated fragment, depending on the detailed features of the excited state curve. It is assumed that the SPY minima act as deactivation funnels. Stereomobility is possible if internal rotation through the TBP barrier occurs within the lifetime of the excited state. In that case the lowest sink collects the excitation and determines the dominant product geometry. The resulting model of d^6 photostereochemistry is represented in Fig. 9.

This remarkably simple model has been very successful in rationalizing

TABLE 8

Strong-field d^6 complexes with stereoretentive axial labilization and stereomobile equatorial modes

---

trans-$\mathrm{Co(CN)_4(SO_3)_2^{5-} + H_2O \xrightarrow{h\nu}}$ *trans*-$\mathrm{Co(CN)_4(SO_3)(H_2O)^{3-} + SO_3^{2-}}$ [145]

cis-$\mathrm{Co(CN)_4(H_2O)_2^-} \underset{kT}{\overset{h\nu}{\rightleftarrows}}$ *trans*-$\mathrm{Co(CN)_4(H_2O)_2^-}$ [a] [39]

$\mathrm{M(NH_3)_5X^{n+} + H_2O \xrightarrow{h\nu}}$ *trans*-$\mathrm{M(NH_3)_4X(H_2O)^{n+} + NH_3}$ [b]

M = Rh, Ir X = Cl, Br, I [49,147,148]

trans-$\mathrm{M(NH_3)_4XY^{n+} + H_2O \xrightarrow{h\nu}}$ *trans*-$\mathrm{M(NH_3)_4X(H_2O)^{m+} + Y}$

M = Rh XY = $\mathrm{Cl_2}$, $\mathrm{Cl(H_2O)}$, $\mathrm{Br_2}$, $\mathrm{Br(H_2O)}$, $\mathrm{I_2}$ [107,147]

M = Ir XY = $\mathrm{Cl_2}$, $\mathrm{Br_2}$ (?), $\mathrm{I_2}$, $\mathrm{I(H_2O)}$ [148]

cis-$\mathrm{Rh(NH_3)_4XY^{n+} + H_2O \xrightarrow{h\nu}}$ *trans*-$\mathrm{Rh(NH_3)_4X(H_2O)^{m+} + Y}$ [c]

XY = $\mathrm{Cl_2}$, $\mathrm{Cl(H_2O)}$, $\mathrm{Br_2}$, $\mathrm{Br(H_2O)}$, $\mathrm{(H_2O)_2}$ [107,149]

trans-$\mathrm{M(en)_2XY^{n+} + H_2O \xrightarrow{h\nu}}$ *trans*-$\mathrm{M(en)_2X(H_2O)^{m+} + Y}$

M = Rh XY = $\mathrm{Cl_2}$, $\mathrm{Br_2}$, $\mathrm{Br(H_2O)}$, $\mathrm{Br(NH_3)}$, $\mathrm{I_2}$, $\mathrm{I(H_2O)}$, $\mathrm{I(NH_3)}$ [108,150,151]

M = Ir XY = $\mathrm{Cl_2}$, $\mathrm{Cl(H_2O)}$, $\mathrm{Br_2}$, $\mathrm{I_2}$ [152,153]

cis-$\mathrm{M(en)_2XY^{n+} + H_2O \xrightarrow{h\nu}}$ *trans*-$\mathrm{M(en)_2X(H_2O)^{m+} + Y}$

M = Rh XY = $\mathrm{Cl_2}$, $\mathrm{Br_2}$, $\mathrm{Br(H_2O)}$, $\mathrm{Br(NH_3)}$, $\mathrm{I_2}$, $\mathrm{I(NH_3)}$ [108,150,151]

M = Ir [d] XY = $\mathrm{I_2}$ [152,154]

---

[a] Originally an alternative intramolecular twist mechanism was proposed, see also ref. 146. However we note the parallellism with isoelectronic complexes, such as *cis*-$\mathrm{Rh(NH_3)_4Cl_2^+}$, where clearly isomerization is concomitant with ligand dissociation. [b] In the chloro complexes $\mathrm{NH_3}$ loss is usually inefficient except for $\mathrm{Rh(NH_3)_5Cl^{2+}}$ in selected solvents DMF, dmso, methanol [123]. [c] The diaquo complex establishes a *cis* ⇋ *trans* photoequilibrium, with preference for the *trans* isomer [149]. [d] The $\mathrm{Cl^-}$ and $\mathrm{Br^-}$ isomers are exceptional in that they show only limited stereomobility (see text).

the experimental data, and several details of the interpretation have been corroborated a posteriori [101], mainly through the efforts of Ford, Petersen and co-workers. Referring to Fig. 9, stereomobility is expected to depend on the activation energies E_T and E_C. In the crudest orbital approximation, one has for a ML_4X fragment

$$E_T = \tfrac{1}{2}\sigma_L - \tfrac{1}{4}\sigma_X$$

$$E_C = \tfrac{1}{2}\sigma_X - \tfrac{1}{4}\sigma_L$$

$$E(^3A') - E(^3E) = E_T - E_C = \tfrac{3}{4}(\sigma_L - \sigma_X) \qquad (23)$$

Several aspects can be commented upon.

(a) Usually X is a weak σ-donor (Cl^-, Br^-, I^-, H_2O) while L is a strong σ-donor (NH_3, CN^-). From eqn. (23), the SPY → TBP path will nearly always be characterized by a positive activation energy, and $E_C < E_T$; therefore efficient *cis* → *trans* stereomobility is expected. For example, LF contributions for E_C and E_T in $[Rh(NH_3)_4Cl]^{2+}$ were estimated at 1160 and 2800 cm^{-1} respectively. This difference explains the pattern in Table 6; abundant experimental evidence is available, as listed in Table 8 [142–154].

(b) If on the contrary X is a stronger σ-donor (CN^-, OH^-) than L, a behavioral cross over is expected and *cis* isomers will be favoured. This was fully confirmed by Skibsted and Ford [155] in the reaction

$$trans\text{-}Rh(NH_3)_4(OH)Cl^+ + OH^- \xrightarrow{h\nu} cis\text{-}Rh(NH_3)_4(OH)_2^+ + Cl^- \qquad (24)$$

and has subsequently been also established for *trans*$[Co(en)_2(CN)Cl]^+$ [101], *cis*- and *trans*$[Rh(NH_3)_4(OH)(H_2O)]^{2+}$, *trans*$[Rh(NH_3)_4(OH)Br]^+$ [149] and even for *cis*- and *trans*$[Ir(en)_2(OH)Cl]^+$ [152]. The experimental proof that the theoretical anticipation was essentially correct lent additional credibility to the assumption that the stereochemical distribution of products is simply determined by the relative value of the relevant ligand-field parameters.

(c) If both σ_X and σ_L are not too large, stereomobility is likely to be less pronounced. A case in point is provided by the photoreactions that involve the $[Co(en)_2Cl]^{2+}$ fragment [87,103] ($E_C = 800$ cm^{-1}, $E_T = 1474$ cm^{-1}), since Co(III) parameters are significantly smaller than Rh(III) analogues.

$$\begin{tikzcd}
trans\text{-}Co(en)_2Cl_2^+ \arrow[dr, "h\nu"] & & \\
& \left\{ \begin{array}{l} 70\%\ trans\text{-}Co(en)_2(H_2O)Cl^{2+} \\ +30\%\ cis\text{-}Co(en)_2(H_2O)Cl^{2+} \end{array} \right. & (25) \\
cis\text{-}Co(en)_2Cl_2^+ \arrow[ur, "h\nu"'] & &
\end{tikzcd}$$

Clearly eqn. (25) strongly suggests that one single excited state mechanism intervenes. The photochemistry of the *cis*- and *trans*-aquochloro product also adheres to this mechanism, since the same $[Co(en)_2Cl]^{2+}$ fragment is being formed.

(d) Petersen and co-workers [101,150] have drawn attention to yet another possibility. If both σ_X and σ_L are moderate to strong (NH_3, en), the barrier might well be too high in any direction. This is also accentuated by reduced configuration interaction as the trigonal symmetry is restored (for $[Rh(NH_3)_5]^{3+}$: $E_C = E_T = 2250\ cm^{-1}$). Stereo inertness was indeed observed in mixed (en)–NH_3 complexes, e.g. [150]

$$cis[Rh(en)_2(NH_3)Cl]^{2+} \rightarrow cis[Rh(en)_2(NH_3)(H_2O)]^{3+} + Cl^- \qquad (26)$$

$$trans[Rh(en)_2(NH_3)Cl]^{2+} \rightarrow trans[Rh(en)_2(NH_3)(H_2O)]^{3+} + Cl^- \qquad (27)$$

Cis$[Rh(en)_2(NH_3)Br]^{2+}$ and *cis*$[Rh(en)_2(NH_3)I]^{2+}$ behave similarly [108]. Again retention upon Cl^- loss in *cis*$[Co(en)_2(NH_3)Cl]^{2+}$ is less pronounced, probably because of a smaller activation barrier [102]. Also the photolysis of $[Rh(en)_3]^{3+}$ can be accommodated in this scheme [156].

$$Rh(en)_3^{3+} + HCl \xrightarrow{h\nu} cis[Rh(en)_2(enH)Cl]^{3+} \qquad (28)$$

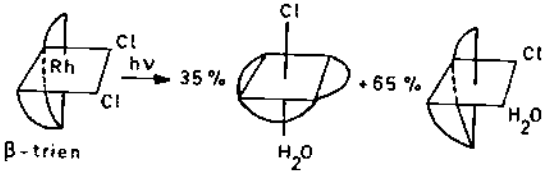
It would be interesting to verify if chiro optical purity is maintained in this reaction.

In view of the large LF parameters in Ir(III) compounds, the limited degree of stereomobility, which is observed in halogenide loss from *cis*$[Ir(en)_2Cl_2]^+$ and *cis*$[Ir(en)_2Br_2]^+$ (10% *trans* product for the chloro compound and 30% for the bromo compound [152]) might also be understood in a similar scheme.

Very recently Clark and Petersen have further substantiated their case by showing that a temperature increase can enhance the degree of photoisomerization in a $[Rh(en)_2(NH_3)]^{3+}$ fragment [157]. Apparently its lifetime is long enough to allow thermal activation.

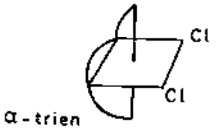
(e) Since both E_T and E_C of eqn. (23) can be presumed to be positive steric factors, that hinder the SPY → TBP ("inverse" Berry-type) rotation are not expected to quench the photo reaction in contrast with the d^3 case; they might block the stereomobility however. This is confirmed in the (stereo retentive) halogenide-loss from *trans*$[Co(cyclam)Cl_2]^+$ [87], *trans*$[Rh(cyclam)X_2]^+$ [129,131] ($X = Cl^-$, Br^-, I^-), *cis*$[Rh(chel)Cl_2]^+$ (chel = cyclam, $(bipy)_2$, $(phen)_2$) [130,132].

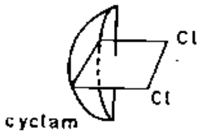
The tren and trien chelates mostly induce comparable effects. *Cis*$[Co(tren)Cl_2]^+$ and *cis*$[Rh(tren)Cl_2]^+$ [142,143] both photoaquate with normal quantum yields, although the formation of *trans* products is impossible for steric reasons.



(29)

The β-isomers *cis*-β-$[M(trien)Cl_2]^+$ (M = Co, Rh) [142,144] are also fairly photo active, with some limited stereomobility (eqn. 29) and indeed in-plane bending is not prohibited. In the Co analog the fraction of *trans* isomer is even predominant. H_2O-loss from the *cis*-β-aquo products also leads to formation of *trans*$[M(trien)(H_2O)Cl]^{2+}$. The puzzling observation however is that the *cis*-α complexes are virtually photoinert, both for Rh(III) and Co(III). No convincing explanation has been offered to date. Admittedly in this case both equatorial nitrogens are "anchored", but so are the nitrogens in the *cis*-cyclam complexes. Even more paradoxically, Sheridan has shown that the analogous Cr(III) complex is easily photolyzed [105]. *Cis*-β-isomers of Cr(III) have not yet been investigated.





In summary, experimental confirmation of the proposed model is rather convincing. The photochemistry of d^6 complexes is perhaps less diversified than the d^3 case, in that all examples belong to one and the same structural family, involving a common ML_4X fragment, where σ_X is smaller (b), stronger (c) or equal (d) to σ_L. In only one case, is a more complex pattern exhibited. Viaene et al. [38] observed efficient *fac* → *mer* isomerization in a tris-substituted complex

$$fac\text{-}Co(CN)_3(H_2O)_3 \xrightarrow{h\nu} mer\text{-}Co(CN)_3(H_2O)_3 \qquad (30)$$

Upon H_2O-dissociation a $[Co(CN)_3(H_2O)_2]$ fragment is formed, and three SPY isomers as well as three TBP structures are to be considered. Analysis of the excited triplet curves [35] again indicates that the SPY with apical H_2O is characterized by the lowest energy and hence will direct the system to the *mer* product. Irradiation of *cis*$[Rh(NH_3)_4I_2]^+$ could be expected to produce a pattern of similar complexity and potential stereochemical interest. Apparently this complex has not yet been synthesized [158].

A discussion of LF photochemistry in strong-field d^6 complexes would be incomplete without drawing attention to the important class of isoelectronic carbonyl complexes of zerovalent Cr, Mo and W. These compounds indeed exhibit pronounced substitutional photoactivity, which can often be related to LF excitations [159,160]. Although a detailed comparison with the data discussed here is beyond our present scope, the occurrence of common structural features, regarding photolysis mode and stereochemical trends, should be noted [161,162].

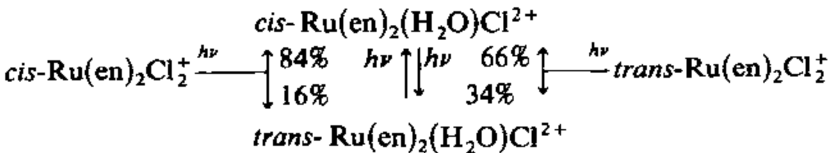
Burdett et al. [163] have modelled a general reaction profile for $Cr(CO)_6$ photolysis, using the AOM and Extended Hückel methods. The same three step mechanism as in Fig. 3 was proposed, the key to the stereochemistry being the Berry-type pseudo rotation SPY ↔ TBP ↔ SPY. However their results led to a strikingly different interpretation. The TBP was situated at a minimum of the excited state surface, in contrast with its role as a transition state in Fig. 9, and with all empirical evidence on substituted Werner complexes. It cannot be excluded however, that in the case of CO-ligands strong π-acceptor interactions might stabilize the TBP geometry [164]. As a consequence, the photostereochemistry of substituted hexacoordinated carbonyl compounds might depend on the interconversion rates from a metastable triplet TBP structure to the singlet ground states of the different SPY isomers. The detailed features of such a profile have not yet been confronted with the observed photostereochemistry of substituted carbonyl compounds.

F. FURTHER OUTLOOK

(i) d^5 Complexes

In recent years considerable efforts have been invested in the use of coordination compounds for solar energy conversion. Quite understandably these studies mainly focus on energy- and charge-transfer processes.

The Ru(III)/(Ru(II) redox couple in its ground and excited states has especially enjoyed increasing popularity. There are some indications that a modest LF photochemistry currently starts gaining interest [165,166]. The Ru(III) complexes present a new outlook as they exemplify a d^5 configuration. The first and only detailed stereochemical analysis of photolysis products at a d^5-center is due to Rerek and Sheridan [167]. Their results are presented in eqn. (31)



$$\begin{tikzcd} & \textit{cis}\text{-}\mathrm{Ru(en)_2(H_2O)Cl^{2+}} \arrow[d, shift left, "h\nu"] & \\ \textit{cis}\text{-}\mathrm{Ru(en)_2Cl_2^+} \arrow[ur, "h\nu\ 84\%"] \arrow[dr, "16\%"'] & & \textit{trans}\text{-}\mathrm{Ru(en)_2Cl_2^+} \arrow[ul, "h\nu\ 66\%"'] \arrow[dl, "34\%"] \\ & \textit{trans}\text{-}\mathrm{Ru(en)_2(H_2O)Cl^{2+}} \arrow[u, shift left, "h\nu"] & \end{tikzcd}$$

(31)

These results are quite interesting in that a new reactivity pattern, different from d^3 or d^6 photochemistry is emerging. Petersen [168] has argued that the general rearrangement model of d^6-photochemistry might still be applicable, since different *cis/trans* product ratios from photodissociation of *cis* and *trans* reagents do not preclude the presence of a common five-coordinate intermediate. While this is certainly true (see e.g. *cis*- and *trans*-$Ir(en)_2Cl_2^+$ [152]) the experimental data then require a *cis* preference, despite the fact that $\sigma(Cl) < \sigma(N)$. From preliminary calculations on the hypothetical $[Ru(en)_2Cl]^{2+}$ fragment, we observe an important difference with the Rh(III) case. It remains true that a common quartet curve, with the same features as the triplet-curve in Fig. 9, connects both SPY isomers, but now several low-spin (doublet) states intersect this curve, probably offering possible alternative rearrangement pathways. A detailed account of these calculations will be presented elsewhere [169]. Certainly much more experimental work will be needed to establish a general model for d^5 photochemistry, which can stand the comparison with what is presently known about d^3 and d^6 systems.

(ii) d^8 Complexes

The photochemistry of Pt(II) compounds has been accounted for in two recent reviews [5,49]. One is forced to conclude that experimental investigation of the photoactivity of Pt(II) complexes has virtually come to an end since 1975. Only two theoretical contributions are in the recent literature [146,170]. More interest has been devoted to Ni(II) compounds of various geometries. A survey of the experimental data and their interpretation in a LF model has been published recently [171].

(iii) Photophysics

Clearly LF models have concentrated on the obvious: stoichiometry and stereochemistry. A logical next step would involve the prediction of quantum yields, but no serious attempt can be made in this respect, unless competing photophysical processes are more closely examined [172,173]. Recent reviews in this Journal [7–9] address themselves to the survey of actual highlights in the rapidly growing field of chromium(III) photophysics. Progress in excited state kinetics of d^6 complexes is reviewed by Ford [6].

Two recent contributions to the present status of the field are particularly relevant from our point of view, and probably hold a promising new outlook. They will be briefly discussed.

(a) Once again the curiosity of LF-methodologists is being solicited through a set of empirical rules, formulated by Walters and Adamson, but now referring to a photophysical process [4,174].

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

Rule 2: If two different kind of ligands are coordinated, the emission lifetime will be relatively short (< 1 μs) if that ligand which is preferentially substituted in the thermal reaction lies on the weak field axis of the complex.

The important difference between the emission rules and the photolysis rules is that the latter are solely based on LF characteristics, while the former also incorporate a non-theoretical piece of information, notably the observed thermal behaviour. Probably it is too early to decide whether or not the rules really have a general empirical foundation. Right from the start the emission rules were interpreted in view of the hypothesis of doublet state reactivity, hereby reopening a decade-long controversy. A major factor in this hypothesis was the suggestion that a vacant t_{2g} orbital in the doublet state [174,175] very likely facilitates bimolecular substitution processes. Most recently we have tried to clarify this point in a detailed analysis of the doublet functions [176]. The half-filled shell configurational origin was shown to be incompatible with a vacant orbital picture. The remarkable spectroscopic properties of the doublet states are also related to this half-filled shell nature and time has come to investigate possible photochemical implications.

(b) The photochemistry of coordination compounds is still commonly regarded in much the same way as a thermally activated process, eventually handicapped by competing photophysical deactivation routes. This classical view has culminated in the concept of a thermally equilibrated excited state (thexi-state) [177] which engenders the photoreaction. A stimulating new proposal [8] recently expressed the view that photoprocesses in molecules at a high level of excitation might approach another limit, referred to as 'Decay on Specific Nuclear Coordinate" (DOSENCO). In this case the reactive deactivation successfully competes with vibrational relaxation to a pseudo-equilibrium thexi-state. It is unknown to what extent transition metal complexes might show Dosenco-behaviour, but evidently such prompt photoprocesses can only lead to the observed selective chemistry if specific vibrational modes are preferentially coupled to the electronic excitation. Unavoidably the cumbersome problems of vibronic structure and intensities of LF excited states need further examination both experimentally and theoretically [178]. A debate on these issues has started already [179], the possible outcome of which might be a new theory of vibronic selectivity. In the end one might hope that a more profound integration of viewpoints in inorganic spectroscopy and photochemistry can be achieved.

ACKNOWLEDGEMENTS

The authors are indebted to the Belgian Government (Programmatie van het Wetenschapsbeleid). One of us (A.C.) thanks the Belgian Science Foundation (N.F.W.O.) for a postdoctoral fellowship.

REFERENCES

1 V. Balzani and V. Carassiti, Photochemistry of Coordination Compounds, Academic Press, London, 1970.
2 A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975.
3 T.J. Kemp, Prog. React. Kinet., 10 (1980) 301.
4 A.W. Adamson, Pure Appl. Chem., 51 (1979) 313.
5 F. Scandola, Org. Chem., 42/3 (1980) 549.
6 P.C. Ford, Coord. Chem. Rev., 44 (1982) 61.
7 M.A. Jamieson, N. Serpone and M.Z. Hoffman, Coord. Chem. Rev., 39 (1981) 121.
8 B.R. Hollebone, C.H. Langford and N. Serpone, Coord. Chem. Rev., 39 (1981) 181.
9 A.D. Kirk, Coord. Chem. Rev., 39 (1981) 225.
10 V. Balzani, F. Bolletta, M.T. Gandolfi and M. Maestri, Topics Curr. Chem., 75 (1978) 1.
11 L. Moggi, A. Juris, D. Sandrini and M.F. Manfrin, Rev. Chem. Intermediates, 4 (1981) 171.
12 J.S. Griffith, Theory of Transition-Metal Ions, Cambridge University Press, Cambridge, 1961.
13 C.J. Ballhausen, Introduction to Ligand Field Theory, McGraw-Hill, New York, 1962.
14 C.K. Jørgensen, Modern Aspects of Ligand Field Theory, North Holland, Amsterdam, 1971.
15 M. Gerloch and R.C. Slade, Ligand Field Parameters, Cambridge University Press, Cambridge, 1973.
16 C.J. Ballhausen, Molecular Electronic Structures of Transition Metal Complexes, McGraw-Hill, New York, 1979.
17 M. Gerloch, J.H. Harding and R.G. Woolley, Struct. Bond., 46 (1981) 1.
18 R.G. Woolley, Mol. Phys., 42 (1981) 703.
19 J.C. Donini, B.R. Hollebone and A.B.P. Lever, Prog. Inorg. Chem., 22 (1977) 225.
20 C.E. Schäffer and C.K. Jørgensen, Mol. Phys., 9 (1965) 401.
21 C.E. Schäffer, Pure Appl. Chem., 24 (1970) 361.
22 H. Yamatera, Bull. Chem. Soc. Jpn., 31 (1958) 95.
23 D.S. McClure, Proc. VI I.C.C.C., MacMillan, New York, 1961, p. 498.
24 M. Gerloch and R.G. Woolley, J. Chem. Soc. Dalton Trans., (1981) 1714.
25 C.E. Schäffer, Theor. Chim. Acta, 34 (1974) 237.
26 M. Keeton, B. Fa Chun Chou and A.B.P. Lever, Can. J. Chem., 49 (1971) 192.
27 L. Dubicki and P. Day, Inorg. Chem., 10 (1971) 2043.
28 W.W. Fee and J.N. MacB. Harrowfield, Aust. J. Chem., 23 (1970) 1049.
29 J. Glerup, O. Mønsted and C.E. Schäffer, Inorg. Chem., 15 (1976) 1399.
30 J.R. Perumareddi, Coord. Chem. Rev., 4 (1969) 73.
31 H.L. Schläfer, H. Gausmann and H. Witzke, J. Chem. Phys., 46 (1967) 1423.
32 L.F. Book, K.Y. Hui, O.W. Lau and Wai-Kee Li, Z. Anorg. Allg. Chem., 426 (1976) 227.
33 R.A.D. Wentworth and T.S. Piper, Inorg. Chem., 4 (1965) 709.
34 M. Linhard, H. Siebert, B. Breitenstein and G. Tremmel, Z. Anorg. Allg. Chem., 389 (1972) 11.
35 D. Beyens, M.Sc. Thesis, Leuven, 1978.
36 B. Loeb and F. Zuloaga, J. Phys. Chem., 81 (1977) 59.
37 V.M. Miskowski and H.B. Gray, Inorg. Chem., 14 (1975) 401.
38 L. Viaene, J. D'Olieslager and S. De Jaegere, J. Inorg. Nucl. Chem., 37 (1975) 2435.
39 L. Viaene, J. D'Olieslager and S. De Jaegere, Inorg. Chem., 14 (1975) 2736.

40 J. Fujita and Y. Shimura, Bull. Chem. Soc. Jpn., 36 (1963) 1281.

41 K. Konya, H. Nishikawa and M. Shibata, Inorg. Chem., 7 (1968) 1165.

42 L.I. Elding and L.F. Olsson, J. Phys. Chem., 82 (1978) 69.

43 E.U. Condon and H. Odabashi, Atomic Structure, Cambridge University Press, Cambridge, 1980.

44 Only in an exceptional case such as D_{4h} square planar complexes, is this relation problematical, since apparently the AOM description has one degree of freedom less than the reference set (see also ref. 45).

45 (a) L.G. Vanquickenborne and A. Ceulemans, Inorg. Chem., 20 (1981) 796.
(b) D.W. Smith, Struct. Bond., 35 (1978) 87.

46 M.A. Bergkamp, J. Brannon, D. Magde, R.J. Watts and P.C. Ford, J. Am. Chem. Soc., 101 (1979) 4549.

47 E.L. Wehry, Quart. Rev. (London), 21 (1967) 213.

48 E. Zinato, in A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, Chap. 4.

49 P.C. Ford, R.E. Hintze and J.D. Petersen, in A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, 1975, Chap. 5.

50 L.E. Orgel, Ligand-Field Theory, Methuen, London, 1960.

51 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd. edn., Wiley, New York, 1967.

52 H.L. Schläfer, J. Phys. Chem., 69 (1965) 2201; only a crude spin-pairing model was used to evaluate electron repulsion effects, so that the energy expression for $^1T_{1g}$ is not entirely correct in Table 3.

53 M. Wrighton, H.B. Gray and G.S. Hammond, Mol. Photochem., 5 (1973) 165.

54 A.W. Adamson, J. Phys. Chem., 71 (1967) 798.

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

56 G.B. Kauffman, J. Chem. Educ., 54 (1977) 86.

57 C.F.C. Wong and A.D. Kirk, Inorg. Chem., 15 (1976) 1519.

58 E. Zinato, P. Riccieri and A.W. Adamson, J. Am. Chem. Soc., 96 (1974) 375.

59 S.C. Pyke and R.G. Linck, J. Am. Chem. Soc., 93 (1971) 5281.

60 A.D. Kirk and L.A. Frederick, Inorg. Chem., 20 (1981) 60.

61 J.I. Zink, J. Am. Chem. Soc., 94 (1972) 8039.

62 J.I. Zink, Inorg. Chem., 12 (1973) 1018.

63 J.I. Zink, Inorg. Chem., 12 (1973) 1959.

64 M.J. Incorvia and J.I. Zink, Inorg. Chem., 13 (1974) 2489.

65 J.I. Zink, Mol. Photochem., 5 (1973) 151.

66 J.I. Zink, J. Am. Chem. Soc., 96 (1974) 4464.

67 C. Furlani, Theor. Chim. Acta, 34 (1974) 233.

68 A. Goursot and E. Pénigault, Chem. Phys., 61 (1981) 83.

69 T.H. Whitesides, J. Am. Chem. Soc., 91 (1969) 2395.

70 G. Wirth and R.G. Linck, J. Am. Chem. Soc., 95 (1973) 5913.

71 C.F.C. Wong and A.D. Kirk, Inorg. Chem., 16 (1977) 3148.

72 A.D. Kirk, Inorg. Chem., 18 (1979) 2326.

73 L.G. Vanquickenborne and A. Ceulemans, Inorg. Chem., 18 (1979) 897.

74 J.R. Perumareddi, J. Phys. Chem., 71 (1967) 3144, 3155.

75 B.R. Hollebone and J.C. Donini, Theor. Chim. Acta, 39 (1975) 33.

76 L.G. Vanquickenborne and A. Ceulemans, J. Am. Chem. Soc., 99 (1977) 2208.

77 L.G. Vanquickenborne and A. Ceulemans, Inorg. Chem., 20 (1981) 110.

78 S.F.A. Kettle, J. Chem. Soc. A, (1966) 420.

79 J.K. Burdett, Chem. Phys. Lett., 47 (1977) 43.
80 J.K. Burdett, J. Chem., Soc. Faraday Trans. 2, 70 (1974) 1599.
81 J.K. Burdett, Molecular Shapes, Wiley, New York, 1980.
82 E. Zinato, P. Riccieri and M. Prelati, Inorg. Chem., 20 (1981) 1432.
83 P. Riccieri and E. Zinato, Inorg. Chem., 19 (1980) 853, 3279.
84 R.E. Wright and A.W. Adamson, Inorg. Chem., 16 (1977) 3360.
85 P. Riccieri and E. Zinato, Proc. VII IUPAC Symp. Photochem., Leuven University Press, Belgium, 1978, p. 378; Inorg. Chim. Acta, 52 (1981) 133.
86 M.F. Manfrin, L. Moggi and V. Balzani, Inorg. Chem., 10 (1971) 207.
87 R.A. Pribush, C.K. Poon, C.M. Bruce and A.W. Adamson, J. Am. Chem. Soc., 96 (1974) 3027.
88 C.H. Langford and C.P.J. Vuik, J. Am. Chem. Soc., 98 (1976) 5409.
89 M. Wrighton and D. Bredesen, Inorg. Chem., 12 (1973) 1707.
90 G. Ferraudi and J.F. Endicott, J. Chem. Soc. Chem. Commun., (1973) 674.
91 L. Viaene, J. D'Olieslager and S. De Jaegere, Bull. Soc. Chim. Belg., 83 (1974) 31.
92 A.W. Adamson, A. Chiang and E. Zinato, J. Am. Chem. Soc., 91 (1969) 5467.
93 M. Cusumano and C.H. Langford, Inorg. Chem., 17 (1978) 2222.
94 P. Riccieri and E. Zinato, J. Am. Chem. Soc., 97 (1975) 6071.
95 A.D. Kirk and G.B. Porter, Inorg. Chem., 19 (1980) 445.
96 C.F.C. Wong and A.D. Kirk, Can. J. Chem., 54 (1976) 3794.
97 A.D. Kirk and T.L. Kelly, Inorg. Chem., 13 (1974) 1613.
98 M.T. Gandolfi, M.F. Manfrin, A. Juris, L. Moggi and V. Balzani, Inorg. Chem., 13 (1974) 1342.
99 W.J. Rosebush and A.D. Kirk, Can. J. Chem., 54 (1976) 2335.
100 A.D. Kirk, K.C. Moss and J.G. Valentin, Can. J. Chem., 48 (1971) 1524.
101 K.F. Purcell, S.F. Clark and J.D. Petersen, Inorg. Chem., 18 (1980) 2183.
102 R.A. Pribush, R.E. Wright and A.W. Adamson, J. Am. Chem. Soc., 99 (1977) 2495.
103 P.S. Sheridan and A.W. Adamson, J. Am. Chem. Soc., 96 (1974) 3032.
104 E. Zinato, Inorg. Chem., submitted.
105 M.S. Thompson and P.S. Sheridan, Inorg. Chem., 18 (1979) 1580.
106 M.J. Saliby, P.S. Sheridan and S.K. Madan, Inorg. Chem., 19 (1980) 1291.
107 L.H. Skibsted, D. Strauss and P.C. Ford, Inorg. Chem., 18 (1979) 3171.
108 S.F. Clark and J.D. Petersen, Inorg. Chem., 18 (1979) 3394.
109 J.K. Burdett and T.A. Albright, Inorg. Chem., 18 (1979) 2112.
110 A.D. Kirk, J. Am. Chem. Soc., 93 (1971) 283.
111 E. Zinato and P. Riccieri, Inorg. Chem., 12 (1973) 1451.
112 T.W. Swaddle, Coord. Chem. Rev., 14 (1974) 217.
113 A.D. Kirk, Mol. Photochem., 5 (1973) 127.
114 D. Strauss and P.C. Ford, J. Chem. Soc. Chem. Commun., (1977) 194.
115 L.G. Vanquickenborne and A. Ceulemans, EUCHEM Conf. Electronic Struct. of Trans. Met. Comp., Dublin, 1978 (unpublished).
116 A. Ceulemans and L.G. Vanquickenborne, Proc. VII IUPAC Symp. Photochem., Leuven University Press, Belgium, 1978, p. 73.
117 L.G. Vanquickenborne and A. Ceulemans, J. Am. Chem. Soc., 100 (1978) 475.
118 L.G. Vanquickenborne and A. Ceulemans, Inorg. Chem., 17 (1978) 2730.
119 L.G. Vanquickenborne and A. Ceulemans, Inorg. Chem., 18 (1979) 3475.
120 L.G. Vanquickenborne, J. Vranckx and C. Görller-Walrand, J. Am. Chem. Soc., 96 (1974) 4121.
121 O. Mønsted, Acta Chem. Scand. A, 32 (1978) 297.

122 R.B. Woodward and R. Hoffmann, Angew. Chem. Int. Ed. Engl., 8 (1969) 781.
123 M.A. Bergkamp, R.J. Watts and P.C. Ford, J. Am. Chem. Soc., 102 (1980) 2627.
124 H.H. Krause and F. Wasgestian, Inorg. Chim. Acta, 29 (1978) 231; 49 (1981) 231.
125 K. Angermann, R. van Eldik, H. Kelm and F. Wasgestian, Inorg. Chem., 20 (1981) 955.
126 C.H. Langford and J.P.K. Tong, J. Chem. Soc. Chem. Commun., (1977) 138.
127 C. Kutal and A.W. Adamson, J. Am. Chem. Soc., 93 (1971) 5581.
128 C. Kutal and A.W. Adamson, Inorg. Chem., 12 (1973) 1990.
129 C. Kutal and A.W. Adamson, Inorg. Chem., 12 (1973) 1454.
130 M.M. Muir and W.-L. Huang, Inorg. Chem., 12 (1973) 1831.
131 J. Sellan and R. Rumfeldt, Can. J. Chem., 54 (1976) 519.
132 K. Fukui, Topics Curr. Chem., 15 (1970) 1.
133 E. Zinato, C. Furlani, G. Lanna and P. Riccieri, Inorg. Chem., 11 (1972) 1746.
134 P. Riccieri and H.L. Schläfer, Inorg. Chem., 9 (1970) 727.
135 C. Bifano and R.G. Linck, Inorg. Chem., 13 (1974) 609.
136 P. Riccieri and E. Zinato, Inorg. Chim. Acta, 7 (1973) 117.
137 M.F. Manfrin, D. Sandrini, A. Juris and M.T. Gandolfi, Inorg. Chem., 17 (1978) 90.
138 S.C. Pyke and R.G. Linck, Inorg. Chem., 19 (1980) 2468.
139 R.T. Walters and R.G. Linck, Inorg. Chem., 14 (1975) 2098.
140 M.C. Cimolino and R.G. Linck, Inorg. Chem., 20 (1981) 3499.
141 M. Elian and R. Hoffmann, Inorg. Chem., 14 (1975) 1058.
142 P.S. Sheridan and A.W. Adamson, Inorg. Chem., 13 (1974) 2482.
143 E. Martins and P.S. Sheridan, Inorg. Chem., 17 (1978) 2822.
144 E. Martins and P.S. Sheridan, Inorg. Chem., 17 (1978) 3631.
145 M.S. Wrighton, Topics Curr. Chem., 65 (1976) 37.
146 J.K. Burdett, Inorg. Chem., 15 (1976) 212.
147 T.L. Kelly and J.F. Endicott, J. Phys. Chem., 76 (1972) 1937.
148 M. Talebinasab-Sarvari, A.W. Zanella and P.C. Ford, Inorg. Chem., 19 (1980) 1835.
149 L.H. Skibsted and P.C. Ford, Inorg. Chem., 19 (1980) 1828.
150 J.D. Petersen and F.P. Jakse, Inorg. Chem., 18 (1979) 1818.
151 S.F. Clark and J.D. Petersen, Inorg. Chem., 19 (1980) 2917.
152 M. Talebinasab-Sarvari and P.C. Ford, Inorg. Chem., 19 (1980) 2640.
153 M.M. Muir and W.-L. Huang, Inorg. Chem., 12 (1973) 1930.
154 G.S. Kovalenko, I.B. Baranovskii and A.V. Babaeva, Russ. J. Inorg. Chem., 16 (1971) 148.
155 L.H. Skibsted and P.C. Ford, J. Chem. Soc. Chem. Commun., (1979) 853.
156 J.D. Petersen and F.P. Jakse, Inorg. Chem., 16 (1977) 2845.
157 S.F. Clark and J.D. Petersen, Inorg. Chem., 20 (1981) 280.
158 M.P. Hancock, Acta Chem. Scand. A, 29 (1975) 468.
159 J. Nasielski and A. Colas, Inorg. Chem., 17 (1978) 237.
160 A.F. Schreiner, S. Amer, W.M. Duncan, G. Ober, R.M. Dahlgren and J. Zink, J. Am. Chem. Soc., 102 (1980) 6872.
161 R.M. Dahlgren and J.I. Zink, Inorg. Chem., 16 (1977) 3154.
162 D.J. Darensbourg and M.A. Murphy, J. Am. Chem. Soc., 100 (1978) 463.
163 J.K. Burdett, J.M. Grzybowski, R.N. Perutz, M. Poliakôff, J.J. Turner and R.F. Turner, Inorg. Chem., 17 (1978) 147.
164 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.
165 B. Durham, J.L. Walsh, C.L. Carter and T.J. Meyer, Inorg. Chem., 19 (1980) 860.
166 W.M. Wallace and P.E. Hoggard, Inorg. Chem., 19 (1980) 2141.
167 M.E. Rerek and P.S. Sheridan, Inorg. Chem., 19 (1980) 2646.

168 J.D. Petersen, Inorg. Chem., 20 (1981) 3124.

169 L.G. Vanquickenborne, D. Beyens and A. Ceulemans, Inorg. Chem., in press.

170 O.V. Sizova and V.I. Baranowskii, Koord. Khim., 5 (1979) 1692.

171 L.G. Vanquickenborne, A. Ceulemans, D. Beyens and J.J. McGarvey, J. Phys. Chem., 86 (1982) 494.

172 P.C. Ford, Inorg. Chem., 14 (1975) 1440.

173 G.B. Porter, in A.W. Adamson and P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, Chap. 2.

174 R.T. Walters and A.W. Adamson, Acta Chem. Scand. A, 33 (1979) 53.

175 M.A. Jamieson, N. Serpone, M.S. Henry and M.Z. Hoffman, Inorg. Chem., 18 (1979) 214.

176 A. Ceulemans, D. Beyens and L.G. Vanquickenborne, J. Am. Chem. Soc., 104 (1982) 2988.

177 A.W. Adamson, Pure Appl. Chem., 24 (1970) 451.

178 B.R. Hollebone, Theor. Chim. Acta, 56 (1980) 45.

179 P.E. Hoggard and M. Albin, Inorg. Chem., 20 (1981) 4413.