

QUENCHING OF TRIPLET STATES OF ORGANIC COMPOUNDS BY COORDINATION COMPLEXES

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ABSTRACT

Recent evidence which establishes that electronic energy transfer is the most common mechanism for quenching of organic triplet states by coordination compounds is discussed. It is pointed out that only when energy transfer produces ligand field excited states is there likely to be markedly different behaviour observed from that expected for a typical organic triplet energy acceptor. Transfer to produce internal ligand and ligand to metal or metal to ligand charge-transfer excited states is not expected to show any differences other than the occurrence of spin statistical factors and these probably only when transfer produces excited charge transfer states. New evidence is presented that triplet state quenching by ferrocene, tris(acetylacetonate) iron(III), $\text{Fe}^{\text{III}}(\text{acac})_3$, and tris(dipivaloylmethanate) iron(III), $\text{Fe}^{\text{III}}(\text{dpm})_3$, is due to electronic energy transfer. For these quenchers a high degree of correlation between their spectroscopically determined energy levels and plots of the quenching rate constants as a function of the energy of the triplet state being quenched is demonstrated. It is suggested that the use of such quenching plots in conjunction with stereochemical and spectroscopic information concerning the excited states which are energetically available to accept electronic excitation energy is likely to allow progress to be made in establishing the determining parameters which govern triplet energy transfer to produce ligand field excited states in coordination compounds.

The mechanism of quenching of electronically excited triplet states of organic compounds by coordination complexes is still imperfectly understood despite the fact that the early pioneering work of Porter¹, Linschitz², Hammond³ and their respective co-workers has been followed by several recent enlightening investigations⁴⁻⁹. It has been established that the observed quenching rate constants show no correlation with magnetic susceptibility¹⁻³ and even that diamagnetic coordination complexes with low-lying electronically excited states can quench very efficiently^{3, 8}. Conversely, it has been shown that when no low-lying electronically excited states of paramagnetic coordination complexes are available no quenching is observed^{5, 7}.

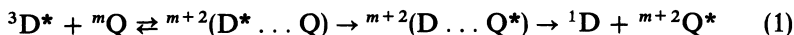
These findings, as well as those few examples where sensitized luminescence of the quenching coordination complexes has been observed^{4, 6}, together with the less direct evidence of observations of several photosensitized reactions of coordination compounds by organic triplet states¹⁰⁻¹², establish

beyond doubt that electronic energy transfer is an important quenching mechanism for coordination complexes.

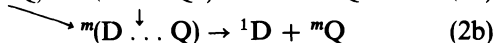
It is important to recognize from the outset that there is no reason why the physical processes of electronic energy transfer and catalysed intersystem crossing¹ should be the only quenching mechanisms for coordination complexes. Thus quenching due to chemical reactions such as electron transfer¹³ or H-atom transfer¹⁴ etc. probably occurs especially when reactive triplet states or coordination compounds are involved. Since few coordination compounds luminesce in fluid media at room temperature and the absorption spectra of electronically excited states of coordination complexes have been characterized as transients in flash experiments in even fewer cases¹⁵, direct demonstration of electronic energy transfer in dilute solution at room temperature is likely to remain a relatively rare event.

Electronic energy transfer can occur as a result of coulombic and exchange interactions¹⁶. Although recent work⁹ has established that in rigid media quenching of phosphorescence by transition metal ions is often due to exchange interaction, quenching by Co^{2+} of the phosphorescence of naphthalene- d_8 and of triphenylene has been shown to be due to spin-forbidden dipole-dipole electrostatic interaction⁹. This mechanism is very unlikely in fluid solutions where lifetimes of triplet states are usually considerably shorter than they are in rigid media. Furthermore the efficiency of transfer by coulombic interaction is directly proportional to the transition probabilities of possible acceptor levels which are generally low since these often involve Laporte-forbidden and/or spin-forbidden transitions. Thus in fluid solution quenching of the triplet state of an organic triplet state donor, $^3\text{D}^*$ is likely to result from exchange interactions in accordance with Wigner's spin rule¹⁷ which may be represented by the following spin-allowed processes for a quencher Q with multiplicity m .

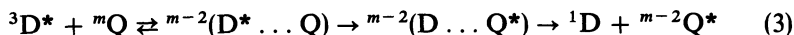
For all values of m



also when $m \geq 2$



and in addition when $m \geq 3$



As was first pointed out by Porter and Wright¹ paramagnetic molecules can quench triplet states by spin-allowed catalysed intersystem crossing, i.e. process (2b). However, if low-lying states of the quencher with multiplicity equal to $m \pm 2$ are available to accept the donor energy then internal conversion within the collision complexes i.e. ${}^{m\pm 2}(\text{D}^* \dots \text{Q}) \rightarrow {}^{m\pm 2}(\text{D} \dots \text{Q}^*)$ is expected to be more efficient than direct internal conversion of the collision complex ${}^m(\text{D}^* \dots \text{Q})$ to the ground state. This increases the likelihood of electronic energy transfer by processes (1) and (3) relative to process (2b). When low-lying excited states of the quencher of multiplicity m are available internal conversion to collision complexes of the type ${}^m(\text{D} \dots \text{Q}^*)$ does not

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necessarily lead to electronic energy transfer since, as shown, this complex may dissociate (process 2a) or internally convert to the ground state resulting in an alternative route for catalysed intersystem crossing which depends on the presence of low-lying excited states of the quencher of multiplicity m which facilitate the conversion of the electronic energy originally on the donor into vibrational energy by allowing the conversion to occur in more than one stage.

When one compares coordination complexes as triplet energy quenchers with typical organic triplet energy acceptors one is struck by the much greater variation in quenching rate constants observed for coordination complexes¹⁻⁸. Thus although some transition metal complexes quench triplet states at room temperature with rate constants approaching those expected for diffusion-controlled reactions^{3, 8} often the quenching rate constants are several orders of magnitude less than this even when low-lying electronic excited states of the coordination compound of the appropriate multiplicity exist for exothermic spin-allowed electronic energy transfer^{1, 6, 7}. Rate constants for triplet quenching by coordination complexes have been found to depend on the donor^{7, 8}, the transition metal¹⁻³, the nature of the ligands^{6, 7}, the charge on the complex⁷, the stereochemistry of the complex⁸ and on the solvent². It is well known that the nature and the position of the electronically excited states of coordination complexes depend on many of these same variables and the question arises whether many of the variations in quenching efficiency observed, when exothermic energy transfer is possible, result from variable electronic energy transfer to coordination compounds depending on the type of electronically excited state which is being produced. Spectroscopic measurements on coordination compounds have established that three main types of transition may be distinguished.

(i) $d \rightarrow d$ or *ligand field transitions*

These transitions which are mainly localized on the metal are markedly dependent on the number of d electrons, the local symmetry around the central metal atom and the field strengths of the coordinating ligands. Ligand field theory can be used to explain the position and type of such transitions which are usually given group theoretical symmetry labels, e.g. the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition in octahedral Cr^{III} complexes (for a review, see ref. 18).

(ii) *Internal ligand transition*

These transitions are mainly localized on the ligand. Thus for example the absorption spectrum of a coordination complex will often contain a $\pi \rightarrow \pi^*$ transition also present in the separate ligand which may be only very slightly affected by complex formation.

(iii) *Charge-transfer transitions*

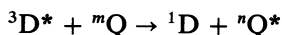
These involve electronic transitions to or from molecular orbitals localized on the metal from or to orbitals on the ligand respectively. These transitions are referred to as ligand to metal or metal to ligand charge-transfer transitions.

Only when electronic energy transfer produces ligand field states, i.e. those centred on the metal and hardly at all on the ligands, is there likely to be any markedly different behaviour between energy transfer to coordination complexes and that observed for electronic energy transfer between organic molecules about which much detailed knowledge has been accumulated¹⁹. The following predictions are therefore made:

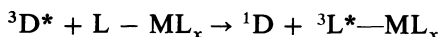
(i) Spin-allowed exothermic electronic energy transfer from or to triplet states of organic molecules which results in the production or quenching of excited internal ligand states or charge-transfer states of coordination compounds should be diffusion-controlled although there may in addition be a spin statistical factor operating (see below).

(ii) Spin-allowed exothermic electronic energy transfer to or from ligand-field states will depend critically on the spatial overlap between the metal localized d orbitals and the π orbitals of the organic donor or acceptor molecules during collisions.

Triplet quenching rate constants for paramagnetic compounds are subject to spin statistical factors of $(m - 2)/3m$, $\frac{1}{3}$, and $(m + 2)/3m$ for processes (1), (2) and (3) respectively, i.e. if the process is written as



the spin statistical factor is $n/3m$ as has been established for oxygen quenching of triplet states where $m = 3$ and $n = 1$ and the observed factor is close to one ninth²⁰. However, when transfer is to an internal ligand triplet state which is considered to be isolated the factor will be one since the process can be represented as



irrespective of the overall multiplicity of the coordination complex $L - ML_x$. Triplet quenching rate constants by coordination complexes have been measured accurately for very few examples where the internal triplet ligand levels lie at lower energy than the triplet donor but prediction (i) seems to hold⁸, i.e. quenching is close to diffusion-controlled. However, there are not sufficient data available to establish whether or not the spin statistical factor is unity. N.B. It is well known that there is very efficient exothermic energy transfer to internal ligand triplet states from organic triplet state sensitizers in the case of rare-earth chelates²¹.

The nature and position of spin-forbidden charge-transfer transitions in coordination complexes are often not very well characterized and few of the triplet quenching data in the literature can be classified as being examples where energy transfer to charge-transfer states is the most likely quenching mechanism²². However, evidence that charge-transfer states in coordination compounds give similar behaviour to organic excited states comes from recent photosensitization^{23, 24} and phosphorescence quenching studies²⁵ on the triplet charge-transfer state of the tris(2,2'-bipyridine)ruthenium(II) ion, $Ru^{II}(dipy)_3^{2+}$. We have interpreted some of our recent observations of efficient triplet quenching by coordination complexes as involving transfer to charge-transfer states (ref. 26 and see later).

Recent work at low temperatures has conclusively shown that electronic energy transfer to produce ligand field excited states does occur during triplet quenching by several Cr^{III} complexes since under these conditions the sensitized luminescence of the ligand field states is observed^{4, 6}. In these studies the measured rate constants which are often in the range $10^6 - 10^7$ l. mol⁻¹ s⁻¹ are close to being diffusion-controlled. However, quenching by these same coordination complexes is not usually diffusion-controlled at room temperature (see Table 1). Thus the longer lifetimes of encounter pairs in the

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Table I. A selection of rate constants for the quenching of triplet states of organic molecules by coordination compounds

Donor ($E_T, 10^3 \text{ cm}^{-1}$)	Complex (Ground state multiplicity)	Lower energy levels of complex, 10^3 cm^{-1} (multiplicity)	Solvent (Temperature ^a)	$k_q, \text{l. mol}^{-1} \text{ s}^{-1}$	Ref.
Naphthalene (21.2)	Cr(CN) ₆ ³⁻ (4)	12.8 (2)	50% Ethanol 50% water	1.7 × 10 ⁸	7
Chrysenes (19.8)			7% MTHF ^b 60% ethanol		
Benzil (18.8)			33% Water		
Naphthacene (10.0)	Cr(acac) ₃ (4)	26.7 (4)	88% Methanol 12% Water (160 K)	1.9 × 10 ⁶	4
Xanthone (25.8)			30% MTHF ^b , 40% Ethanol 30% water	2 × 10 ⁵ †	7
Benzil (18.8)	Cr(OH) ₆ ³⁻ (4) Cr(C ₂ O ₄) ₃ ³⁻ (4)	12.8, 14.0, 19.3 (2) 17.8, 23.0 (4) 24.4 (CT?)	Benzene	1.0 ± 0.5 × 10 ¹⁰	30
Fluorenone (18.7)			88% Methanol	1.0 × 10 ⁷	4
Acridine (15.8)			12% Water (160 K)	1.1 × 10 ⁹	3 (d)
Acridine (15.8)	Mn(H ₂ O) ₆ ²⁺ (6)	17.2 (4) 14.39 (2), 17.5 (4)	Aqueous NaOH	0 ± 0.1 × 10 ⁷ †	5
Acridine (15.8)			Water	6.1 × 10 ⁸	5
Naphthalene (21.2)	Co(H ₂ O) ₆ ²⁺ (4)	18.9, 23.0, 25.0 (4)	Water	2.8 × 10 ⁷	1 (b)
Acridine (15.8)			Ethylene glycol	1.6 × 10 ⁷	1 (b)
Naphthalene (21.2)	Co(NH ₃) ₆ ²⁺ (4)	8.35, 16.0, 19.8, 21.55 (4)	Water	0 ± 0.1 × 10 ⁷ †	5
Acridine (15.8)			Ethylene glycol	5.0 × 10 ⁷	1 (b)
Acridine (15.8)	Ni(NH ₃) ₆ ²⁺ (3)	9.0, 18.5 (4) 10.75, 17.5 (3) 13.15 (1)	Water	4.4 × 10 ⁷	1 (b)
Acridine (15.8)			Aqueous ammonia	1.0 × 10 ⁷	5
Acridine (15.8)	PtCl ₄ ²⁻ (1)	18.0, 20.6, 24.0 (3) 26.3, 29.8 (1)	Aqueous ammonia	3.6 × 10 ⁸	5
Xanthone (25.8)			Aqueous 1M KCl	3.3 × 10 ⁸	5
Erythrosin (14.6)	Pt(CN) ₄ ²⁻ (1)	about 30.0 (3) 35.92 (1)	Aqueous 1M KCl	4.6 × 10 ⁹	30
Erythrosin (14.6)			Water	1.65 × 10 ⁸ †	30
			Water	7 × 10 ⁶ †	30
			Water	8 × 10 ⁶ †	30

† Uphill energy transfer; (a) room temperature except where stated.

(b) MTHF denotes 2-methyltetrahydrofuran.

solvent cage which allow multi-collisions, are apparently responsible for diffusion-controlled quenching at these reduced temperatures. It is reasonable to suppose that quenching by other coordination complexes, that have similar efficiencies which are considerably less than diffusion-controlled at room temperature, probably also involves electronic energy transfer to produce ligand field excited states when such states are energetically available. The fact that when no low-lying ligand field states are available no triplet quenching is observed (see *Table 1*) suggests that no other general mechanism for quenching of comparable or higher efficiency than energy transfer exists and that catalysed intersystem crossing is usually rather inefficient presumably because of the small Franck-Condon factors involved. We have examined over two hundred rate constants for organic triplet quenching by coordination compounds published in the literature and the vast majority of these are most probably due to electronic energy transfer to produce excited ligand-field states. A representative selection is presented in *Table 1*.

When one is attempting to understand and characterize all the factors which determine the efficiency of energy transfer to ligand field states in fluid solution these are only likely to be revealed by observing the variations in rate constants under conditions where the energy transfer is not diffusion-controlled, e.g. in low viscosity solvents at room temperature where the energy transfer step becomes rate-determining. Unfortunately under such conditions, one cannot usually demonstrate directly that electronic energy transfer is occurring. However, one can obtain strong evidence for its occurrence by observing how the quenching rate constants vary with the energy of the triplet state being quenched and seeing how this correlates with spectroscopic information concerning the energy states of the quencher.

We have already shown the value of this kind of approach in our investigations of quenching by some trans-planar diamagnetic Ni(II) Schiff-base complexes⁸ for which catalysed intersystem crossing is of course spin-forbidden. On the basis of the dependence of the observed quenching rate constants on the triplet donor energy together with a spectroscopic analysis of the electronically excited states of these complexes, quenching was confidently attributed to electronic energy transfer. It was suggested that the very efficient transfer observed even when ligand field states were the energy acceptors was due to the good orbital overlap which is possible with these planar complexes. These speculations were nicely supported by our observation that energy transfer to produce excited ligand field states in tetrahedral and octahedral Schiff-base complexes of Ni(II) was much lower due to steric hindrance⁸. Furthermore a predicted different behaviour for an analogous planar Pd(II) complex which has much higher-lying ligand field triplet states and should therefore be unable to accept energy from low-lying organic triplet donors has been experimentally confirmed²⁶.

Another diamagnetic organometallic compound which is known to quench some triplet states very effectively is ferrocene³. The lowest excited triplet ligand field state of which is reported²⁷ to lie at 14200 cm^{-1} . It follows therefore that if electronic energy transfer is the mechanism of quenching, organic triplet donors with energies which are lower than this should give very little quenching and this is just what is observed in practice (see *Figure 1*).

The triplet quenching rate constant for most paramagnetic coordination

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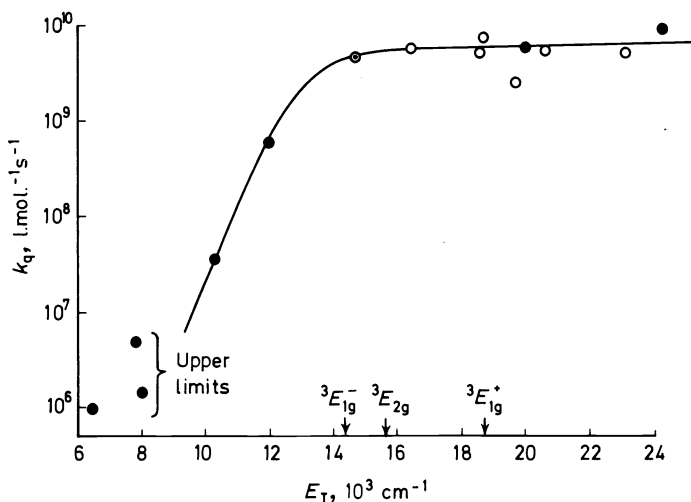


Figure 1. Dependence of the quenching rate constants, k_q , for organic triplet states by ferrocene in benzene solution at 20°C on E_T , the energy of the triplet state being quenched. Arrows indicate the energies of various ferrocene transitions. (○) literature values and (●) values from ref. 28 where full details will be given.)

complexes is in the range 2×10^7 – $5 \times 10^8 \text{ l. mol}^{-1} \text{ s}^{-1}$ although acetylacetonato-complexes have been shown to quench some triplet states with much higher efficiencies⁵. It is interesting to note that there are several studies in the literature where rate constants for the quenching of a single triplet donor by several coordination compounds have been obtained^{1,2,6} and a few where the same workers used several triplet donors^{3,7} but none, apart from our own work^{8,26}, where an extensive systematic study has been made of the variation in the triplet quenching constants as a function of the triplet energy of the organic donor. This is partly due to the fact that few water-soluble well characterized triplet donors are available while few coordination complexes are readily soluble in organic solvents. We have recently carried out such studies using $\text{Fe}^{\text{III}}(\text{acac})_3$ and $\text{Fe}^{\text{III}}(\text{dpm})_3$ which have already been shown to exhibit several interesting features by Hammond and co-workers³. Furthermore these compounds are highly soluble in benzene and thus quenching of a series of well characterized triplet energy donors could be made. The results are summarized in Figure 2 which reveals that the quenching constants show a very marked dependence on the energy of the triplet being quenched. Figure 2 also includes quenching constants for $\text{Al}(\text{acac})_3$ a metal complex where only internal ligand states are available to accept energy. It was not possible to study quenching of any triplet state with a higher energy than xanthone ($E_T = 25800 \text{ cm}^{-1}$) and unfortunately this is slightly less than that reported for the complexed acetylacetonate ligand [$E(^3\text{L}) = 26000 \text{ cm}^{-1}$].

Although full experimental details and a more detailed discussion of Figure 2 will be given elsewhere²⁸, it illustrates several important points of

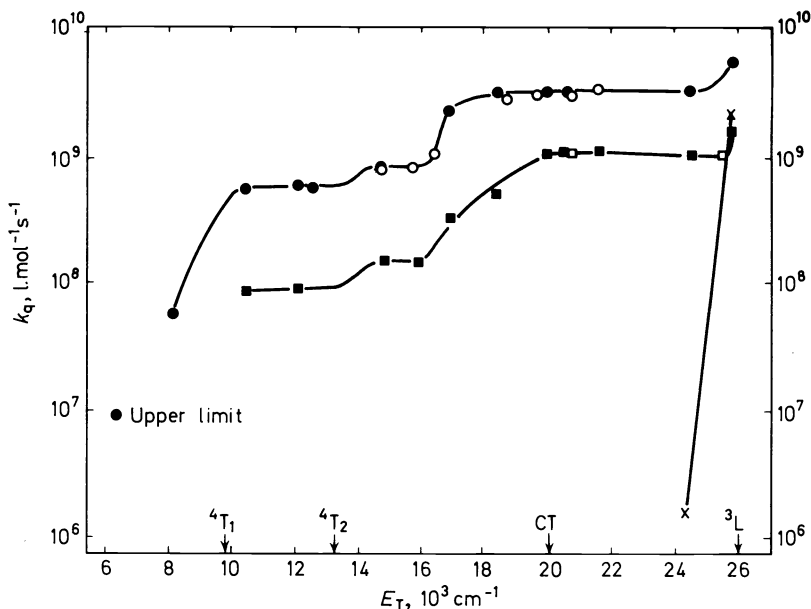


Figure 2. Dependence of the quenching rate constants k_q , for organic triplet states by $\text{Fe}(\text{acac})_3$, \circ , \bullet , $\text{Fe}(\text{dpm})_3$, \square , \blacksquare and $\text{Al}(\text{acac})_3$, \times , in benzene solution at 20°C on E_T , the energy of the triplet state being quenched. Arrows indicate the energies of various transitions within the quenchers. (\circ , \square literature values and \bullet , \blacksquare and \times values from ref. 28 where full details will be given.)

general interest which are discussed here. The form of the triplet energy plots for $\text{Fe}^{\text{III}}(\text{acac})_3$ and $\text{Fe}^{\text{III}}(\text{dpm})_3$ is just what one might expect for quenching by energy transfer to several excited states within the complexes which have variable accepting probabilities. It constitutes the proof for which Hammond and co-workers³ searched in vain that quenching by $\text{Fe}^{\text{III}}(\text{acac})_3$ and $\text{Fe}^{\text{III}}(\text{dpm})_3$ is due to electronic energy transfer. The discontinuities in the curves correlate very well with the spectroscopically determined energy levels which are virtually identical for $\text{Fe}^{\text{III}}(\text{acac})_3$ and $\text{Fe}^{\text{III}}(\text{dpm})_3$. There is some uncertainty concerning the assignment of the transition to the charge-transfer excited state which is almost certainly responsible for the quenching observed for triplet states with energies in the range $18000\text{--}24000\text{ cm}^{-1}$. The quenching plateau in this region of $\sim 3 \times 10^9\text{ l. mol}^{-1}\text{ s}^{-1}$ for $\text{Fe}^{\text{III}}(\text{acac})_3$ could be due to diffusion-controlled energy transfer with a spin statistical factor of $\frac{1}{3}$. As expected transfer to the ligand field states is the least efficient although the rate constants are still high relative to the values observed for quenching due to energy transfer to ligand-field states in other octahedral coordination complexes. The results shown in Figure 2 indicate that different ligand field states within the same complex can have different quenching efficiencies. When the quenching rate constants for $\text{Fe}^{\text{III}}(\text{acac})_3$ and $\text{Fe}^{\text{III}}(\text{dpm})_3$ are compared, the steric effect first observed by Hammond and co-workers³ is shown to be largest for transfer to low-lying ligand field states illustrating

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the more critical overlap requirements for excitation of ligand field states. The fact that the *t*-butyl groups in $\text{Fe}^{\text{III}}(\text{dpm})_3$ also sterically hinder transfer to the internal triplet ligand state and to the charge-transfer state is not so surprising when one considers the stereochemistry of these complexes.

The results presented in *Figures 1* and *2* are further demonstrations of the importance of electronic energy transfer in quenching by coordination complexes. It is also apparent that explanations of the effect of charge⁷, solvation² and even possible 'conductor'² or nephelauxetic⁶ effects of different ligands etc. are unlikely to be forthcoming until full spectroscopic investigations of the number and type of the excited states available to accept energy within each coordination compound are made. Ligand field excited states are often considerably distorted relative to the structure of the ground state, e.g. the difference between the absorption and emission maxima for the lowest spin-allowed ligand field band for the $\text{Cr}^{\text{III}}(\text{CN})_6^{3-}$ ion is reported²⁹ to be $\sim 14000 \text{ cm}^{-1}$. Thus care must be exercised when applying spectroscopic information and where possible quenching rate constant plots as a function of triplet donor energy should be made.

To summarize: Much recent evidence points to electronic energy transfer as the predominant mechanism for quenching by coordination compounds. The accepting probabilities of internal ligand and/or charge-transfer excited states are not expected to (and preliminary results demonstrate that they do not) depart significantly from the behaviour of typical organic triplet state acceptors except that spin statistical factors may often apply. The usefulness of plots of quenching rate constants versus the energy of the triplet state being quenched by the coordination complexes has been stressed and it is suggested that only when stereochemical and full spectroscopic knowledge concerning the number and nature of the energetically accessible ligand field excited states is available, will comparisons which will lead to a full understanding of the determining features for quenching to produce excited ligand field states be likely to be forthcoming.

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