Excited State Redox Properties of Phthalocyanines: Influence of the Axial Ligand on the Rates of Relaxation and Electron-transfer Quenching of the Lowest $^3\pi\pi^*$ Excited State

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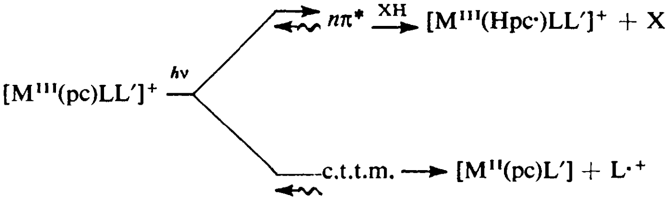
Laser flash excitations at 640 nm have been used to generate the transient spectra of the lowest-lying $^3\pi\pi^*$ state of phthalocyaninatoruthenium(II) complexes. The properties of this excited state such as the positions of the maxima, $\lambda_{max.}$ = 500 ± 30 nm, and lifetimes, $t_{\frac{1}{2}}$ = 70—4 500 ns, exhibit a large dependence on the electron-accepting and electron-withdrawing tendencies of the axial ligands. A similar influence was observed upon the rate of electron-transfer quenching of the $^3\pi\pi^*$ state. Values between 10^6 and 10^7 dm^3 mol^{-1} s^{-1} for the self-exchange rate constant have been obtained, according to Marcus–Hush theoretical treatments, for $[Ru(pc^\cdot)LL']^+/(^3\pi\pi^*)[Ru(pc)LL']$ [L and L' = neutral axial ligands; pc = phthalocyaninate(2−)] and isoelectronic cobalt(III) and rhodium(III) couples. The redox properties of the ground and excited states are correlated with axial ligand-induced perturbations of the electronic structure.

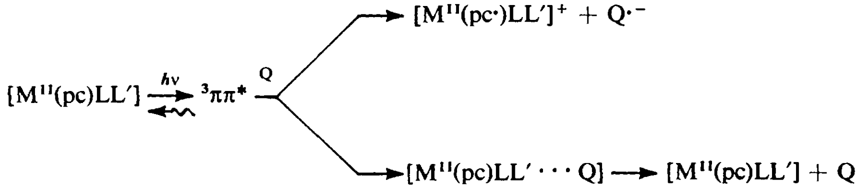
Photochemical studies on phthalocyaninatometal(III) complexes have shown that the u.v. photochemistry of these compounds consists largely of redox processes (such as the abstraction of hydrogen from given donors) which are originated in ligand-centred $n\pi^*$ states.[1-5] Only a few examples (namely with Co^{III} phthalocyaninates [2]) exhibited a charge-transfer photochemistry involving the axially co-ordinated ligand. These photoredox processes are briefly described in equations (1) and (2), where L and L' are neutral axially co-ordinated species [c.t.t.m. = charge transfer to metal; pc = phthalocyaninate(2 −); XH = hydrogen donor].



$$[M^{III}(pc)LL']^+ \xrightarrow{h\nu} n\pi^* \xrightarrow{XH} [M^{III}(Hpc^\cdot)LL']^+ + X^\cdot \qquad (1)$$

$$[M^{III}(pc)LL']^+ \xrightarrow{h\nu} \text{c.t.t.m.} \longrightarrow [M^{II}(pc)L'] + L^{\cdot+} \qquad (2)$$

The excited states populated by excitation in the red, *e.g.* the lowest-lying singlet and triplet $\pi\pi^*$, lack the kind of reactivity described in equations (1) and (2). However, these states are susceptible to quenching by electron transfer, equation (3), and/or exciplex mediated quenching, equation (4) (Q = quencher).[6-12] The results of electron-transfer quenching obtained in previous works were rationalised in terms of the Marcus–Hush theoretical treatments, and the self-exchange rate constants derived by these were close to 10^7 dm^3 mol^{-1} s^{-1} for a series of phthalocyaninatoruthenium(II) complexes.[7] However, the members of this series exhibited small differences between them and little was learned about the influence of various structural features on the excited state properties. Hence we have investigated in this work the effect of the axial ligand on the properties of phthalocyanines with isoelectronic d^6 metal centres: Rh^{III}, Ru^{II}, and Co^{III}.



$$[M^{II}(pc)LL'] \xrightarrow{h\nu} {}^3\pi\pi^* \xrightarrow{Q} [M^{II}(pc^\cdot)LL']^+ + Q^{\cdot-} \qquad (3)$$

$$[M^{II}(pc)LL'] \xrightarrow{h\nu} {}^3\pi\pi^* \xrightarrow{Q} [M^{II}(pc)LL' \cdots Q] \longrightarrow [M^{II}(pc)LL'] + Q \qquad (4)$$

Results and Discussion

It has been demonstrated previously in laser flash photolysis of various phthalocyanines that irradiations at wavelengths of the near-i.r. band, namely the *Q* band, produce the low-lying ligand-centred $^3\pi\pi^*$ state.[3,7-15] Studies of the lowest-lying excited states with ruthenium(II) phthalocyanines show that the lifetime of $^3\pi\pi^*$ is largely determined by the nature of the axial ligand, as in Table 1. Although this behaviour of the ($^3\pi\pi^*$) ruthenium(II) phthalocyanines seems to be the same as that exhibited by similar ($^3\pi\pi^*$) rhodium(III) phthalocyanines,[13] there are different reasons (in the Rh^{III} and Ru^{II} derivatives) for such a dependence on the nature of the axial ligand. Contributions from metal–ligand vibrations to Franck–Condon factors, especially those involving the axial ligand, were regarded as the most probable cause of the different $^3\pi\pi^*$ lifetimes measured with members of the aniono(phthalocyanine)rhodium(III) series.† For members of the ruthenium(II) series, the results in Table 1 show that the large differences between triplet lifetimes are as relevant as the differences observed between redox potentials of the couple $[Ru(pc^\cdot)LL']^+/[Ru(pc)LL']$ (L and L' = neutral axial ligands). Indeed, these can be associated largely with those perturba-

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† Note that the rate of relaxation of the $^3\pi\pi^*$ state is mainly determined by the non-radiative path and that the perturbation of the phthalocyanine electronic structure is approximately the same for the series of ligands co-ordinated to Rh^{III}.[15]

Table 1. Dependence of the ground state redox potential and the lifetime of the ($^3\pi\pi^*$) state of ruthenium(II) phthalocyanines on the axial ligand

Complex [a]	$t_{\frac{1}{2}}$/ns [b]	$10^{-6}k$/s^{-1} [c]	$-\varepsilon_{\frac{1}{2}}$/V [d]
[Ru(pc)(4Bu^t-py)$_2$]	79	8.8	1.295
[Ru(pc)(4Me-py)$_2$]	90	7.7	1.276
[Ru(pc)(py)$_2$]	135	5.1	1.24
[Ru(pc)(dmf)$_2$]	146	4.7	1.285
[Ru(pc)(dmso)$_2$]	4 000	0.173	1.359
[Ru(pc)(py)(CO)]	4 200	0.165	1.387
[Ru(pc)(dmf)(CO)]	4 500	0.152	1.397

[a] The complexes are listed in the order of an increasing nephelauxetic series:[16] 4Bu^t-py (4-t-butylpyridine) < 4Me-py (4-methylpyridine) < py (pyridine) < dmf (*NN*-dimethylformamide) < dmso (dimethyl sulphoxide) < CO. This is also the order of the increasing acceptor numbers (see footnote † on this page). [b] Half-lifetimes of the $^3\pi\pi^*$ state were determined in deaerated solutions of the compounds in CH$_2$Cl$_2$ at room temperature. Experimental errors are $\leqslant 5\%$. [c] k = rate constant for decay of $^3\pi\pi^*$. [d] Half-wave potentials of the [Ru(pc$^\cdot$)LL$'$]$^+$/[Ru(pc)LL$'$] couples are expressed *vs.* a normal hydrogen electrode and determined in CH$_2$Cl$_2$ at 25 °C with 0.05 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte.

tions of the phthalocyanine electronic structure induced by the electron-withdrawing and electron-accepting tendencies of the axial ligand. The nephelauxetic concept[16] or parameters describing the electron-donor and electron-acceptor tendencies of the axial ligand,† Table 1, can be used for a qualitative rationalisation of the trends observed with the excited state lifetime and ground state redox potential. Hence, the increase of the reduction potential in the same direction that increases the ability of the axial ligand to function as an electron acceptor, Table 1, suggests that the ground-state phthalocyanines are stabilised with respect to the corresponding radical cation by the drain of the electron density from the metal centre. One possible reason for this stabilisation is a reduction in the value of the repulsive Coulombic factors that determine in part the energy of the phthalocyanine orbitals.[17,18] Similar electronic contributions are expected to play a significant role in determining the properties of the excited state. For example, we have observed that irradiations at 640 nm of the ruthenium(II) complexes in Table 1 generate the transient spectra of the $^3\pi\pi^*$ state with $\lambda_{\text{max.}} \sim 500$ nm and differences of up to ±30 nm in the position of the maxima. Such minute but significant differences between the spectra of the $^3\pi\pi^*$ state are a clear demonstration of the perturbation of the electronic structure of the phthalocyanine ligand by axially co-ordinated species. Moreover, the increase of the lifetime of the $^3\pi\pi^*$ state with increase of the electron-withdrawing character of the axial ligand, Table 1, must be the synergetic manifestation of changes in the energy gap between excited and ground states and in the vibrational frequencies that determine the rate of the non-radiative relaxation.‡

The observations described above are in agreement with results obtained in the investigation of the properties of the $^3\pi\pi^*$ state by electron-transfer quenching. The procedures that we followed for the study of the quenching processes have been reported elsewhere.[7,19] The value for the self-exchange rate constant, k_{11}, of reaction (5) was obtained by means of its

$$[\mathrm{Ru(pc^\cdot)LL'}]^+ + (^3\pi\pi^*)[\mathrm{Ru(pc)LL'}] \xrightarrow{k_{11}} (^3\pi\pi^*)[\mathrm{Ru(pc)LL'}] + [\mathrm{Ru(pc^\cdot)LL'}]^+ \quad (5)$$

relationship, equation (6), with the rate constant for the self-exchange electron transfer of the quencher, k_{22}, and the rate constant of the cross reaction, k_{12} (abbreviations and labelling of rate constants are as in refs. 7 and 19).[20,21]

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}};\ \log f = \frac{(\log K_{12})^2}{4\log(k_{11}k_{22}/Z^2)} \quad (6)$$

The rate constant k_{12} of the cross reaction was related to the quenching rate constant, k_q, by using the Rehm–Weller mechanism[22] for the description of the quenching process, and the rate constant k_q was derived from the observed quenching rate constant, k_Q, by correcting for diffusional contributions, equation (7).

$$\frac{1}{k_q} = \frac{1}{k_Q} + \frac{1}{k_D} \quad (7)$$

Values of the rate constants k_{12} for various phthalocyanines and quenchers are reported in Table 2. The corresponding values derived for the self-exchange rate constants of the ruthenium(II) phthalocyanines, Table 3, are close to 10^7 dm^3 mol^{-1} s^{-1} when they are determined with nitroaromatic quenchers and close to 10^6 dm^3 mol^{-1} s^{-1} when the quenchers are iron(III) complexes, *e.g.* high-spin [Fe(OH$_2$)$_6$]$^{3+}$ or low-spin [Fe(CN)$_6$]$^{3-}$. These differences between rate constants cannot be accounted only by the non-adiabatic contributions that are introduced by spin restrictions.§ Indeed the introduction of corrections according to spin statistical factors ¶ failed to give a complete explanation of the observed differences between self-exchange rate constants. Hence it is possible that the disparity between self-exchange rate constants derived from quenching with nitroaromatic compounds and Fe$^{\text{III}}$ complexes most probably reflects some intrinsic contributions to the cross reaction activation energy such as differences in electrostatic interactions || and differences in the overlap of the donor–acceptor electronic clouds[24] with neither of these contributions being contemplated in equation (6).

Henceforth the points discussed above make it difficult to

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† See, for example, V. Gutman, *Electrochim. Acta*, 1976, **21**, 661, for the definition of donoticities and acceptor numbers of various molecules.

‡ Note that the largest contribution to the rate of relaxation comes from the non-radiative path. Therefore this rate must principally reflect variations of the non-radiative rate constant within the series of Rh$^{\text{III}}$ compounds and the small Stokes shift (<4 000 cm^{-1}) allows such a non-radiative rate constant to be expressed in terms of the weak coupling mechanism: $k_{\text{n.r.}} = [C^2/\hbar(2\pi\bar{\nu}_M\Delta E)^{\frac{1}{2}}]$-$\exp(-\nu\Delta E/\bar{\nu}_M)$, where ΔE is the energy gap between states, C is the electronic coupling matrix element, and $\bar{\nu}_M$ is the energy of the highest-frequency vibrational modes. See J. P. Byrne, E. F. McCoy, and I. G. Ross, *Aust. J. Chem.*, 1965, **18**, 1589 and refs. therein.

§ Spin restrictions in quenching reactions were treated according to G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, 1959, **27**, 18. According to this treatment the spin statistical factors for the cross reactions are 1 for quenching with nitroaromatic compounds; 1/3 with ($^2T_{2g}$)[Fe(CN)$_6$]$^{3-}$, where the reactants form an encounter complex (six microstates) which transforms in products with an overall doublet spin multiplicity, $^2\{(^3\pi\pi^*)[\mathrm{Ru(pc)LL'}];\ (^2T_{2g})[\mathrm{Fe(CN)_6}]^{3-}\} \longrightarrow {}^2\{(^2A_{2u})[\mathrm{Ru(pc^\cdot)LL'}]^+;\ (^1A_{1g})[\mathrm{Fe(CN)_6}]^{4-}\}$; and 5/9 when the quencher is high-spin ($^6A_{1g}$)[Fe(OH$_2$)$_6$]$^{3+}$.

¶ Equation (6) does not contemplate non-adiabatic contributions. The effect of this contribution has been discussed elsewhere.[23]

|| Differences between contributions to the activation energy from changes in the outer-sphere reorganisation energy were small as expected for solvents with a dielectric constant larger than the optical dielectric constant.[24,25] Equally small were energetic contributions arising from weaker interactions, such as ion-dipole interactions in the cross reaction.[26]

Table 2. Rate constants ($10^{-8}\,k_{12}$/dm^3 mol^{-1} cm^{-1}) [a] for the cross reaction between ($^3\pi\pi^*$) ruthenium(II) phthalocyanines and various quenchers

	Quencher [b]					
Complex	pdnb	mdnb	odnb	dmna	Fe^{3+}	$[Fe(CN)_6]^{3-}$
$[Ru(pc)(4Bu^t\text{-}py)_2]$	42	0.29	0.97	36		
$[Ru(pc)(4Me\text{-}py)_2]$	14	0.17	0.12	27		
$[Ru(pc)(py)_2]$	22	3.8	8.7	12	98	14
$[Ru(pc)(dmf)_2]$	52	0.35	2.6	45	69	20
$[Ru(pc)(dmso)_2]$				59	38	6.9
$[Ru(pc)(py)(CO)]$				59	89	1.3
$[Ru(pc)(dmf)(CO)]$				50	16	0.70
$[Rh(pc)Cl]$ [c]				29		3.9
						4.3 [d]
$Na_3[Co(tspc)]$ [e]				29		3.8
						3.3 [f]

[a] Experimental errors in the rate constants are $\leqslant 5\%$. [b] Abbreviations pdnb = *p*-dinitrobenzene, mdnb = *m*-dinitrobenzene, odnb = *o*-dinitrobenzene, and dmna = *NN'*-dimethyl-*p*-nitrosoaniline (in deaerated CH_2Cl_2). Fe^{3+} and $[Fe(CN)_6]^{3-}$ were in deaerated H_2O–CH_3CN (1 : 9) with ionic strength $I \sim 0.01$ mol dm^{-3} ($NaClO_4$) unless otherwise indicated. [c] The $^3\pi\pi^*$ state is reduced by $[Fe(CN)_6]^{4-}$ with a rate constant $k_{12} = 1.0 \times 10^7$ dm^3 mol^{-1} s^{-1}. [d] Rate constant determined in H_2O–CH_3CN (1 : 1) with ionic strength $I \sim 0.01$ mol dm^{-3} ($NaClO_4$). [e] tspc = 3,10,17,24-tetrasulphonatophthalocyaninate (6 −). The $^3\pi\pi^*$ state is reduced by $[Fe(CN)_6]^{4-}$ with a rate constant $k_{12} = 8.0 \times 10^7$ dm^3 mol^{-1} s^{-1}. [f] Rate constant determined in H_2O with ionic strength $I \sim 0.01$ mol dm^{-3} ($NaClO_4$).

Table 3. Self-exchange rate constants for ($^3\pi\pi^*$)[Ru(pc)LL′]

Complex	$10^{-7}k_{11}$/dm^3 mol^{-1} s^{-1}	Quencher
$[Ru(pc)(4Bu^t\text{-}py)_2]$	1.33	*a*
$[Ru(pc)(4Me\text{-}py)_2]$	3.65	*a*
$[Ru(pc)(py)_2]$	1.9	*a*
	0.158	Fe^{3+}
	0.282	$[Fe(CN)_6]^{3-}$
$[Ru(pc)(dmf)_2]$	9.58	*a*
	0.164	Fe^{3+}
	0.128	$[Fe(CN)_6]^{3-}$
$[Ru(pc)(dmso)_2]$	0.136	Fe^{3+}
	0.336	$[Fe(CN)_6]^{3-}$
$[Ru(pc)(py)(CO)]$	2.17	Fe^{3+}
	12.4	$[Fe(CN)_6]^{3-}$
$[Rh(pc)(CH_3OH)Cl]$ [b]	0.22	$[Fe(CN)_6]^{3-}$
$Na_3[Co(tspc)]$ [b]	0.30	$[Fe(CN)_6]^{3-}$

[a] Nitromatic compounds pdnb, mdnb, odnb, and dmna (see ref. 7). [b] The $^3\pi\pi^*$ state of these compounds is reduced by $[Fe(CN)_6]^{4-}$. Data from these reactions, Table 2, give the following self-exchange rate constants: $k_{11} = 2.7 \times 10^8$ dm^3 mol^{-1} s^{-1} for ($^3\pi\pi^*$)[Rh(pc)(CH$_3$OH)Cl] and $k_{11} = 5.0 \times 10^6$ dm^3 mol^{-1} s^{-1} for ($^3\pi\pi^*$)[Co(tspc)]$^{3-}$.

arrive at a single value of the self-exchange rate constant for $[M(pc^{\cdot})LL']^+/(^3\pi\pi^*)[M(pc)LL']$ couples, for a given transition metal M. However it seems that for ruthenium(II) phthalocyanines with weak electron-withdrawing ligands in the axial positions, the value of the self-exchange rate constant will be very close to 10^7 dm^3 mol^{-1} s^{-1}.[7] Departures from this value must be expected when the electronic structure of the phthalocyanine ligand is perturbed by the axial ligand and/or when it experiences enough mixing with the electronic density of the metal.† The examples in Table 3 show that, at least for several d^6 metal centres such as Rh^{III}, Co^{III}, and Ru^{II}, the lowest-lying $^3\pi\pi^*$ state does not lose the features of a ligand-centred state by mixing electronic density of the metal, and in consequence the self-exchange rate constant remains close to 10^7 dm^3 mol^{-1} s^{-1}. Moreover, values of 10^7 dm^3 mol^{-1} s^{-1} for the self-exchange rate constant do not support Ohno's assumption [12] of a diffusion-controlled self-exchange rate and support earlier assignments of the electron-donor excited state of Ru^{II} and Rh^{III} phthalocyanines as a $^3\pi\pi^*$ and not a charge transfer state.†

Experimental

Materials.—The Co^{III}, Ru^{II}, and Rh^{III} phthalocyanines were available from previous works.[2,3,7] Nevertheless, the purity of these compounds was routinely investigated by procedures reported elsewhere.[2,3,7] The commercially available nitroaromatic derivatives (see Table 2) and $K_3[Fe(CN)_6]$ were purified by recrystallisation. The viologen salts (4,4′-bipyridinium salts) used as quenchers were prepared following literature procedures,[27] and recrystallised as hexafluorophosphate salts.

Acetonitrile and dichloromethane (Aldrich Gold Label) were distilled in an all-glass distillation apparatus fitted with a '70 theoretical plates' fractionating column.

Photochemical Procedures.—The properties of the $^3\pi\pi^*$ excited state in transition metal phthalocyanines were investigated by laser flash photolysis. The apparatus and procedures used for these studies have been previously described.[3,7] A Quanta Ray Neodymium Yag pumped dye laser with a DCM dye for irradiation of the compounds at 640 nm was used as a source of 12-ns pulses. The signal from the detection system was digitized in a Tektronix R7912 Transient Digitizer and processed in a PDP-11 Digital Computer to obtain spectroscopic information and the evaluation of rate constants. The power of the laser was adjusted to values where ground state depletion or biphotonic processes were not detected. Solutions for the photochemical experiments were deaerated with streams of Ar, and they were replenished after each irradiation.

Electrochemical Procedures.—Half-wave redox potentials, $\varepsilon_{\frac{1}{2}}$, were determined by cyclic voltammetry in an apparatus that has been described elsewhere.[28] Appropriate circuitry changes were introduced in the apparatus in order to add the capability of d.c. cyclic voltammograms. Values of $\varepsilon_{\frac{1}{2}}$ were obtained from cyclic voltammograms by means of the relationship, $\varepsilon_{\frac{1}{2}} = 0.5\,(\varepsilon_p + \varepsilon_{p/2})$, between the potential for the maximum diffusion current, ε_p, and the potential for a half

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† Charge-transfer states, very close in energy to the lowest-lying ligand-centred states, can eventually mix with these ligand states or be populated by internal conversion; then the electron transfer involves charge-transfer states rather than ligand-centred $^3\pi\pi^*$ states. See A. B. P. Lever, S. Licoccia, B. S. Ramaswamy, S. Kandil, and D. V. Stynes, *Inorg. Chim. Acta*, 1981, **51**, 169.

of the maximum diffusion current, $\varepsilon_{p/2}$. The waves obtained in the oxidation of the ruthenium(II) phthalocyanines suggested reversibility in the electrode process in contrast with those obtained by reduction of the complexes. Such reduction waves are strongly irreversible with profiles that exhibit extreme sensitivity to medium conditions, *e.g.* solvent and support electrolyte. This behaviour is not surprising since it has been found in previous studies that the oxidation of Ru^{II} phthalocyanines produces stable products while their reduction gives extremely reactive species.[5,29]

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